Fundamentals of quantum mechanics, band theory, and first-principles calculation

量子力学、バンド理論の基礎、第一原理計算

神谷利夫

東京工業大学
科学技術創成研究院
フロンティア材料研究所

Fundamental of quantum mechanics
Schrödinger equation and one-electron Schrödinger equation

量子力学の基礎
Schrödinger方程式と一電子Schrödinger方程式

Newtonian equation of motion

$$\mathbf{F} = m\frac{d^2}{dt^2}\mathbf{r}$$

- Mathematical expression may be different for different coordinates other than the **Cartesian coordinate**
- The definition of force includes ambiguity
  => Energy would be more fundamental physics concept

Generalized coordinate $\mathbf{r} = \mathbf{r}(q_1, q_2, \cdots q_n, t)$

Lagrangian $L = T - V$

T: Kinetic energy V: Potential energy

Generalized (Canonical) momentum $$p_r = \frac{\partial L}{\partial \dot{q}_r}$$

Euler-Lagrange equation (equivalent to Newtonian eq) $$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_r} - \frac{\partial L}{\partial q_r} = 0$$

Analytical mechanics: Hamilton equation

Hamiltonian $H(q,p,t) = \sum_r p_r \dot{q}_r - L(q,p,t)$

in Cartesian coord. $H(r,p,t) = \sum_r \frac{1}{2m_i} {p_i}^2 + V(r,p)$

Hamilton's eq of motion $\frac{\partial q_r}{\partial t} = \frac{\partial H}{\partial p_r}$ $\frac{\partial p_r}{\partial t} = -\frac{\partial H}{\partial q_r}$

Poisson bracket (classical commutation relation) $\{A,B\} = \sum_i \left(\frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} - \frac{\partial B}{\partial p_i} \frac{\partial A}{\partial q_i} \right)$

Equation of motion $\dot{A} = \{H,A\} + \frac{\partial A}{\partial t}$

A, B: Physical quantities

If A is independent of time $\dot{A} = \{H,A\}$

Quantization: Heisenberg's uncertainty principle

Derived from quantum commutation relation for conjugate physical qunatities:

$$qp_q - p_q q = [q, p_q] i\hbar$$

Example:

$$\left. \begin{array}{l} \hat{x} = x, \qquad \hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x} \\ \hat{x} = i\hbar \frac{\partial}{\partial p_x}, \hat{p}_x = p_x \end{array} \right\}$$

Both the upper and the bottom combinations satisfy the quantum commutation relation

$$\hat{x}\hat{p}_x - \hat{p}_x\hat{x} = i\hbar$$

⇨ $\Delta x \cdot \Delta p_x \sim h$

Schrödinger equation

Classical Hamiltonian (phys quantities are **C (classical) numbers**)

$$H(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{p}_2,\mathbf{p}_1,\cdots,t)=\sum_r \frac{1}{2m_i}|\mathbf{p_i}|^2+V(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{p}_2,\mathbf{p}_1,\cdots)$$

Regard the physical quantities in H as **Q (quantum) numbers**
and apply **the quantum commutation relations**

Commut. rel. $\hat{x}_i\hat{p}_{x,i}-\hat{p}_{x,i}\hat{x}_i=i\hbar$ ➡ $\hat{x}_i=x_i,\ \hat{p}_{x,i}=\frac{\hbar}{i}\frac{\partial}{\partial x_i}$

$H\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots)=E\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots)$ **Schrödinger equation**

$$\left\{-\frac{1}{2}\sum_l \nabla_l{}^2+V(\mathbf{r}_1,\mathbf{r}_2,\cdots)\right\}\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots)=E\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots)$$

E **is the eigenvalue of the H operator: Total energy**

$\boldsymbol{\Psi}$: $|\boldsymbol{\Psi}|^2$ corresponds to the electron density distribution

- Many number simultaneous partial differential equation (6 x number of electrons)
- Very difficult to solve analytically

One-electron equation

Schrödinger eq **Wave func** **Total energy**

$$H\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots)=E\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots) \quad \Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots) \quad E$$

Separation of variables

$$\Psi(\mathbf{r})=\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N)$$

$$H(\mathbf{r})=\sum h_i(\mathbf{r}_i)$$

$$\boxed{h_i(\mathbf{r}_i)=-\frac{1}{2}\nabla_i{}^2-\sum_m\frac{Z_m}{r_{im}}+\sum_m\int\frac{\phi_m^*(\mathbf{r}_m)\phi_m(\mathbf{r}_m)}{r_{im}}d\mathbf{r}_m}$$

$$h_i\phi(\mathbf{r}_i)=\varepsilon\phi(\mathbf{r}_i)$$

One-electron Schrödinger eq

- ε_i: Eigenvalues of one-e equation
- ϕ_i: Eigenvectors of one-e equation

What are their physical meaning?

Atomic unit (a.u.): Dimensionless equations

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2-\frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r}\right]\psi(\mathbf{r})=E\psi(\mathbf{r}) \qquad r'=ar \qquad E'=bE$$

$$\left[-\frac{\hbar^2}{2m_e a^2}\nabla'^2-\frac{e^2}{4\pi\varepsilon_0 a}\frac{Z}{r'}\right]\psi(a\mathbf{r}')=bE'\psi(a\mathbf{r}')$$

$$\left[-\frac{1}{2}\nabla^2-\frac{Z}{r}\right]\psi(\mathbf{r})=E\psi(\mathbf{r})$$

Atomic unit: a.u.

$$a=\frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}=5.2918\times10^{-11}\,\mathrm{m}$$

Unit of length: boh

Radius of H 1*s* orbital

$$b=\frac{m_e e^4}{2(4\pi\varepsilon_0)^2\hbar^2}=13.6\,\mathrm{eV}$$

Unit of energy #1: Rydberg

Energy level of H 1*s* orbital

$$\left[-\nabla^2-2\frac{Z}{r}\right]\psi(\mathbf{r})=E\psi(\mathbf{r})$$

$$b=\frac{m_e e^4}{(4\pi\varepsilon_0)^2\hbar^2}=27.2\,\mathrm{eV}$$

Unit of energy #2: Hartree

(One-electron) Hartree-Fock equation

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

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

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

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

Band theory from LCAO
(Linear Combination of Atomic Orbitals)

原子基底関数からのバンド理論

Approximation: Linear combination (LC) of basis functions

Complete system of basis set: Any function is expanded to a linear combination of basis functions in a complete system

ex.: Any 3D vector *r* is expressed by independent basis vectors *a*, *b*, *c* as

$$r = C_a a + C_b b + C_c c$$

ex: Fourier transform: Any function $f(x)$ is expressed by basis functions e^{ikx} as $f(x) = \int c(k)\exp(ikx)dk$

note: requires infinite number of basis functions

If the basis functions do not make a complete system, the expansion is just an approximation

=> In actual process, wave function Ψ is approximated by **a linear combination of basis functions (not necessary a complete system) u_n**

$$\Psi = \sum_{n=0}^{N} C_n u_n$$

u_n: Basis functions

Plain Wave (PW)

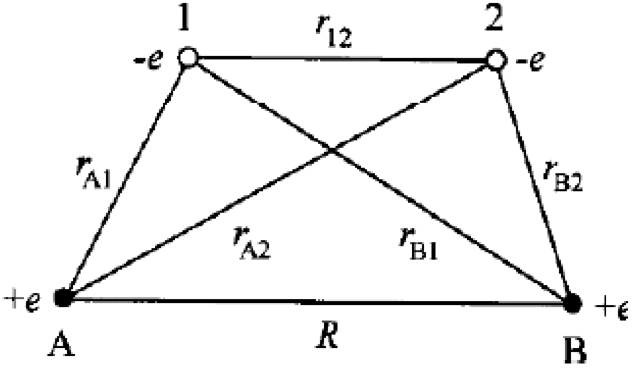
Atomic Orbital (AO)

Gaussian-type Orbital (GTO)

Slater-type (exponential) Orbital (STO)

One-electron wave function etc

Valence bond theory and Molecular orbital theory



H_2 molecule as an example:

H nuclei : A, B

Electrons: 1, 2

One-electron wave functions for A and B:

ϕ_A, ϕ_B

Valence bond theory: LC of total wave function basis set

$$\psi(1,2) = \underbrace{c_{c1}\phi_A(1)\phi_B(2) + c_{c2}\phi_A(2)\phi_B(1)}_{\text{Covalent bond}} + \underbrace{c_{i1}\phi_A(1)\phi_A(2) + c_{c2}\phi_B(1)\phi_B(2)}_{\text{Ionic bond}}$$

$$\psi_{\text{cov}\pm}(1,2) = 2^{-1/2}\left[\phi_A(1)\phi_B(2) \pm \phi_A(2)\phi_B(1)\right] \qquad E_\pm = \frac{H_{11} \pm H_{12}}{1 + S_{12}}$$

Molecular orbital theory: one-electron wave function is first formed by LCAO and then total wave function is formed

$$\psi(1,2) = \varphi_1(1)\varphi_2(2)$$

One-electron wf: $\varphi_i(\mathbf{r}) = c_1\phi_A(\mathbf{r}) + c_2\phi(\mathbf{r})$

$$\psi(1,2) = 2^{-1}[\phi_A(1) + \phi_B(1)][\phi_A(2) + \phi_B(2)]$$

$$= \mathbf{2^{-1}}[\underbrace{\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)}_{\text{Covalent bond}} + \underbrace{\phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2)}_{\text{Ionic bond}}]$$

Problem of molecular orbital theory

For nuclei of the same element *A*, *B*: Consider LCAO of ϕ_A and ϕ_B

$$\phi(\mathbf{r}) = c_A\phi_A(\mathbf{r}) + c_B\phi_B(\mathbf{r})$$

$$\phi_\pm(\mathbf{r}) = 2^{1/2}\left[\phi_A(\mathbf{r}) \pm \phi_B(\mathbf{r})\right]$$

$$\begin{aligned}\psi(1,2) &= 2^{-1}[\phi_A(1)+\phi_B(1)][\phi_A(2)+\phi_B(2)]\\ &= \mathbf{2^{-1}}[\underbrace{\phi_A(1)\phi_B(2)+\phi_B(1)\phi_A(2)}_{\text{Covalent bond}}+\underbrace{\phi_A(1)\phi_A(2)+\phi_B(1)\phi_B(2)}_{\text{Ionic bond}}]\end{aligned}$$

Problem: Even if *A* and *B* will be separated in infinite distance, the contribution of the ionic bond is constant at 50 % (i.e., the two-atom state does not appear)

=> Configuration Interaction (CI) method

$$\psi_\pm(\mathbf{r}_1,\mathbf{r}_2) = c_{\mathrm{cov}\pm}\psi_{\mathrm{cov}\pm}(\mathbf{r}_1,\mathbf{r}_2) + c_{ion_\pm}\psi_{ion\pm}(\mathbf{r}_1,\mathbf{r}_2)$$

Linear combination and variational principle: Roothaan-Hall equation

Ritz's variational principle:

Expectation value of Hamiltonian $\langle E \rangle$ for any wave function ψ is equal to or larger than E_0, that of the ground state

$$\langle E \rangle = \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle \geq E_0$$

ψ is approximated by **linear combination of basis functions u_n**

$$\psi = \sum_{n=0}^{\infty} C_n u_n$$

Based on the variational principle, C_n are obtained by minimizing $\langle E \rangle$

$$< E >= \frac{\sum_m \sum_n C_m^* C_n \langle u_m | H | u_n \rangle}{\sum_n C_n^* C_n \langle u_m | u_n \rangle}$$

$$\sum_m C_m \langle u_n | H | u_m \rangle - E \sum_m C_m \langle u_n | u_m \rangle = 0$$

Many quantum equations will lead to eigenvalue problems

Roothaan-Hall equation

$$\sum_m C_m \langle u_n | H | u_m \rangle - E \sum_m C_m \langle u_n \mid u_m \rangle = 0$$

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

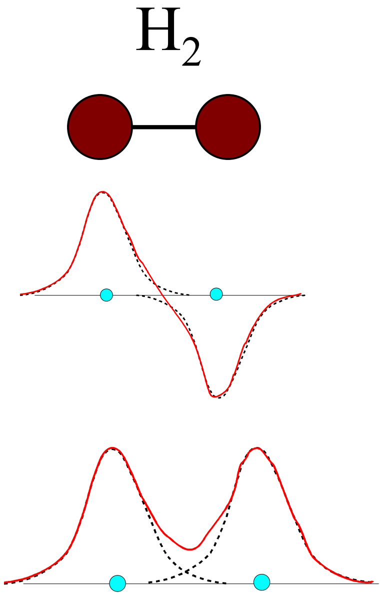
$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{ss} & & H_{2n} - ES_{2n} \\ \vdots & & \ddots & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \cdots & H_{nn} - ES_{nn} \end{vmatrix} = 0$$

Fock matrix
Transfer matrix $H_{nm} = \langle u_n | H | u_m \rangle$

Overlap integral $S_{nm} = \langle u_n \mid u_m \rangle$

H_2 molecule

Ignore overlap integrals $S_{nm} = \delta_{nm}$



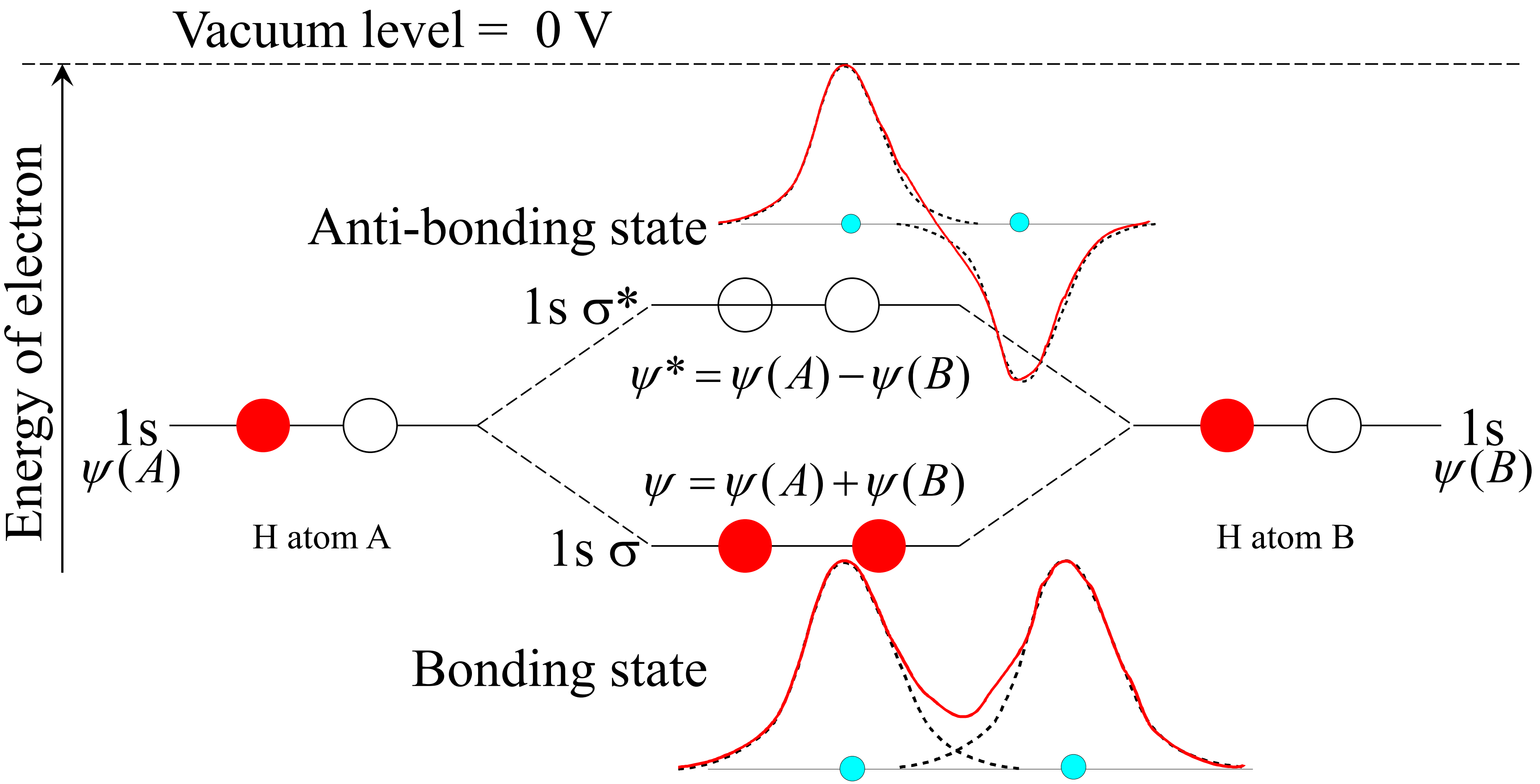
$$H_{1s1s} = \varepsilon_{1s}$$

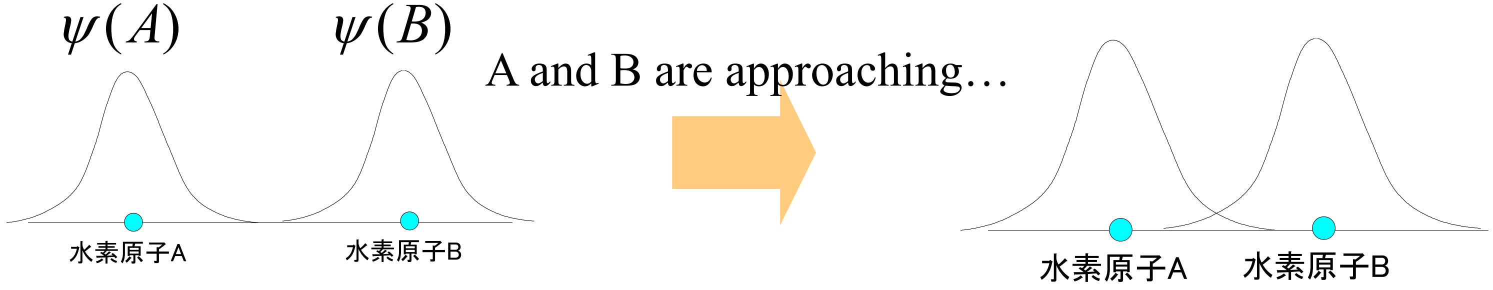
$$\begin{vmatrix} \varepsilon_{1s} - \varepsilon & h_{12} \\ h_{12} & \varepsilon_{1s} - \varepsilon \end{vmatrix} = 0$$

$$\varepsilon = \varepsilon_{1s} \pm h_{12}$$

$$\phi_{\pm} = \frac{1}{\sqrt{2}}\left(\varphi_1 \pm \varphi_2\right)$$

Electronic structure of H_2 molecule

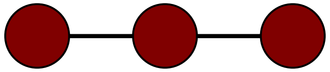




A and B are approaching…

H_3 molecules

H_3



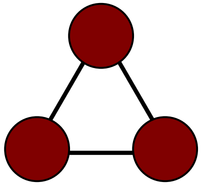
Linear

$$\begin{pmatrix} \varepsilon_{1s} & h_{12} & 0 \\ h_{12} & \varepsilon_{1s} & h_{12} \\ 0 & h_{12} & \varepsilon_{1s} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \varepsilon \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}$$

$$\varepsilon_{\pm} = \varepsilon_{1s} \pm \sqrt{2} h_{12}, \; \varepsilon_{non-bonding} = \varepsilon_{1s}$$

$$\phi_{\pm} = \frac{1}{\sqrt{2}} \left(\varphi_{+} \pm \varphi_2 \right), \; \varphi_{-} = \frac{1}{2} \left(\varphi_1 + \sqrt{2} \varphi_2 + \varphi_3 \right)$$

H_3



Ring

$$\begin{pmatrix} \varepsilon_{1s} & h_{12} & h_{12} \\ h_{12} & \varepsilon_{1s} & h_{12} \\ h_{12} & h_{12} & \varepsilon_{1s} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \varepsilon \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}$$

$$c_i^{(l)} = \exp\left(i k_l x_j \right)$$

$$k_l = \frac{2\pi}{Na} l$$

l are integers from 0 to 2

a is interatomic distance

$$E\left(k_l\right) = \varepsilon_{1s} + 2 h_{12} \cos\left(k_l a\right)$$

Solution for ring H_3 molecule

$$\begin{pmatrix}\varepsilon_{1s} & h_{12} & h_{12}\\ h_{12} & \varepsilon_{1s} & h_{12}\\ h_{12} & h_{12} & \varepsilon_{1s}\end{pmatrix}\begin{pmatrix}c_1\\ c_2\\ c_3\end{pmatrix}=\varepsilon\begin{pmatrix}c_1\\ c_2\\ c_3\end{pmatrix}$$

$$k_l=\frac{2\pi}{Na}l$$

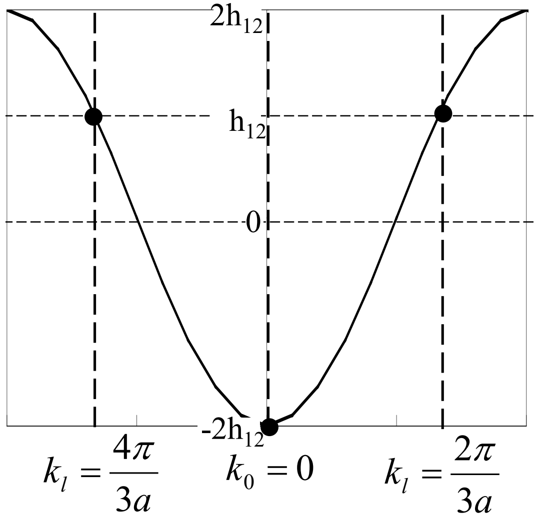
N=3, l=0, 1, 2, · · · , N-1

$$\phi_{kl}=\sum_j \varphi_j \exp(ik_l x_j) \qquad E(k_l)=\varepsilon_{1s}+2h_{12}\cos(k_l a)$$

$$\begin{pmatrix}\varepsilon_{1s} & h_{12} & h_{12}\\ h_{12} & \varepsilon_{1s} & h_{12}\\ h_{12} & h_{12} & \varepsilon_{1s}\end{pmatrix}\begin{pmatrix}1\\ \exp(ik_l a)\\ \exp(i2k_l a)\end{pmatrix}=\begin{pmatrix}\varepsilon_{1s}+h_{12}(\exp(ik_l a)+\exp(i2k_l a))\\ \varepsilon_{1s}\exp(ik_l a)+h_{12}(1+\exp(i2k_l a))\\ \varepsilon_{1s}\exp(i2k_l a)+h_{12}(1+\exp(ik_l a))\end{pmatrix}=[\varepsilon_{1s}+h_{12}(\exp(ik_l a)+\exp(i2k_l a))]\begin{pmatrix}1\\ \exp(ik_l a)\\ \exp(i2k_l a)\end{pmatrix}$$

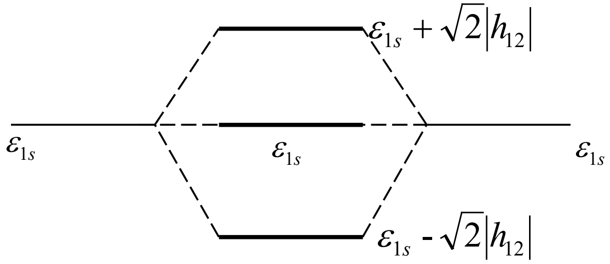
Energy levels of ring H_3

$$\varepsilon_{1s}-2\,|\,h_{12}\,| \qquad \varepsilon_{1s}+|h_{12}| \qquad \varepsilon_{1s}+|h_{12}|$$



Energy levels of linear H_3

$$\varepsilon_{1s}-\sqrt{2}|h_{12}| \qquad \varepsilon_{1s} \qquad \varepsilon_{1s}+\sqrt{2}|h_{12}|$$



If same wave functions align periodically…

The result of the ring H_3 can be extended to ring H_N molecules

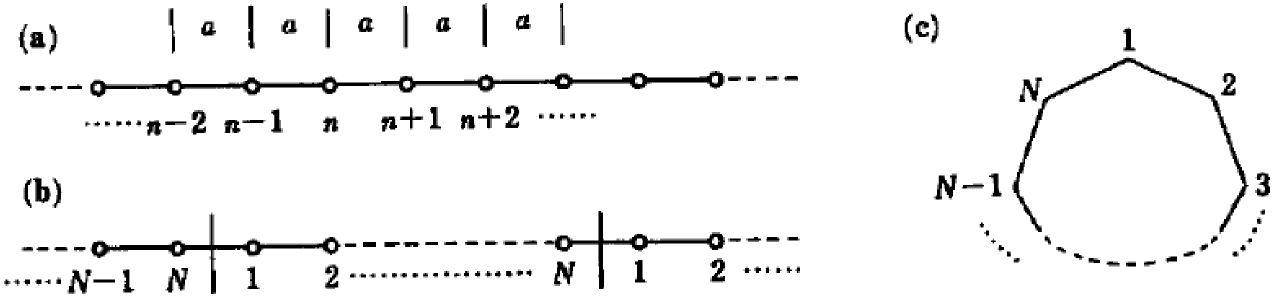
$$\begin{pmatrix} \varepsilon_{1s} & h_{12} & 0 & 0 & h_{12} \\ h_{12} & \varepsilon_{1s} & h_{12} & 0 & 0 \\ 0 & h_{12} & \varepsilon_{1s} & \ddots & \vdots \\ 0 & 0 & \ddots & \ddots & h_{12} \\ h_{12} & 0 & \cdots & h_{12} & \varepsilon_{1s} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix} = \varepsilon \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix}$$

$$k_l = \frac{2\pi}{Na} l \qquad c_i^{(l)} = \exp\left(ik_l x_j\right)$$

$$\phi_{kl} = \sum_j \varphi_j \exp\left(ik_l x_j\right)$$

$$E\left(k_l\right) = \varepsilon_{1s} + 2h_{12}\cos\left(k_l a\right)$$

Solution of ring H_N molecule

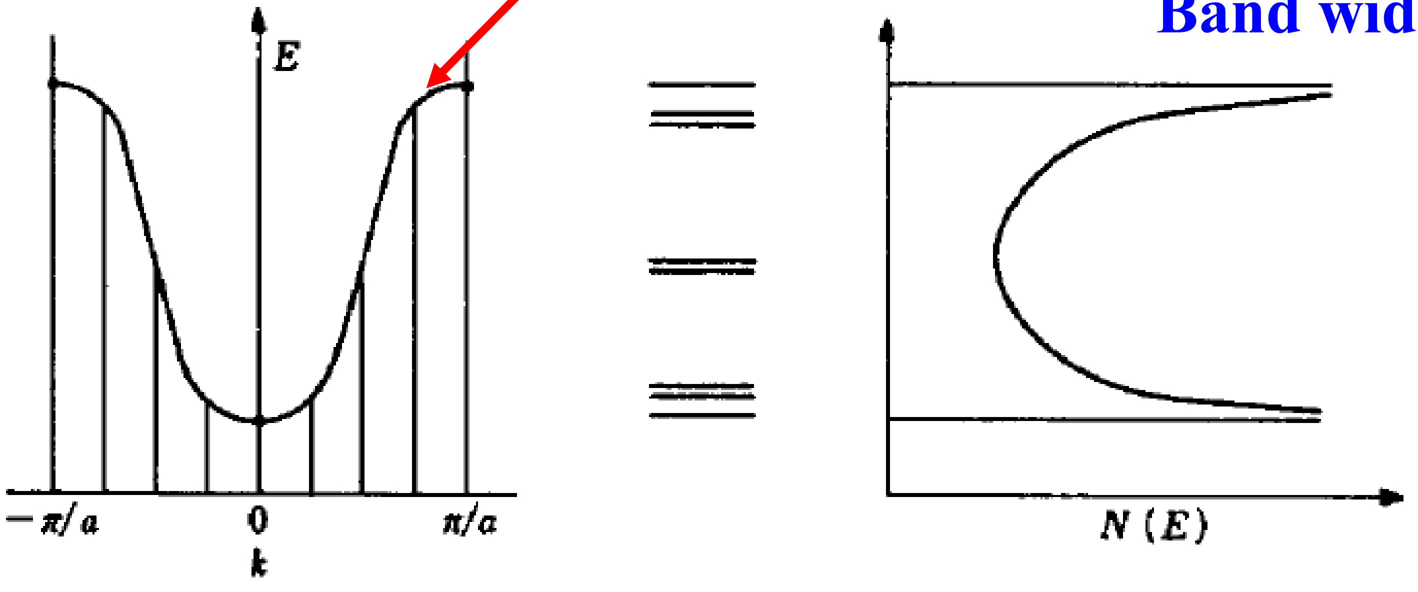


$$\begin{pmatrix} \varepsilon_{1s} & h_{12} & 0 & 0 & h_{12} \\ h_{12} & \varepsilon_{1s} & h_{12} & 0 & 0 \\ 0 & h_{12} & \varepsilon_{1s} & \ddots & \vdots \\ 0 & 0 & \ddots & \ddots & h_{12} \\ h_{12} & 0 & \cdots & h_{12} & \varepsilon_{1s} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix} = \varepsilon \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix}$$

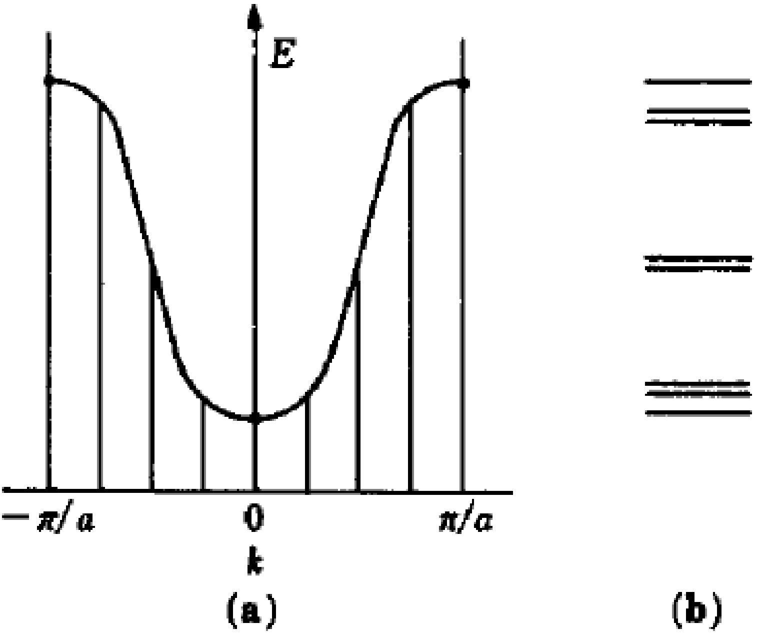
$$\phi_{kl} = \sum_j \varphi_j \exp\left(ik_l x_j\right) \qquad k_l = \frac{2\pi}{Na} l$$

$$\boxed{E\left(k_l\right) = \varepsilon_{1s} + 2h_{12}\cos\left(k_l a\right)}$$

Band width: $4\left|h_{12}\right|$



Wave function of benzene (C_6H_6) and Bloch's theorem

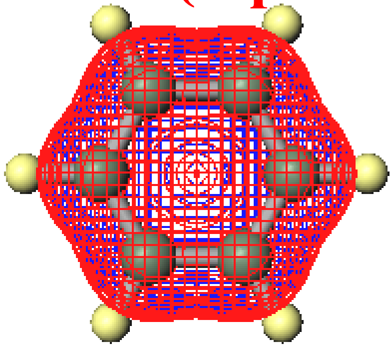


(a)

(b)

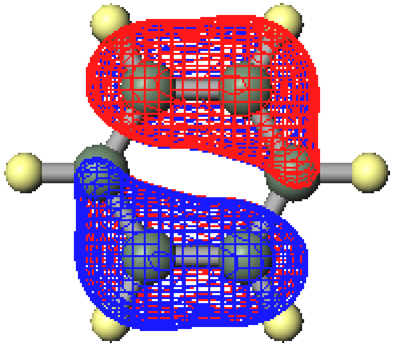
#11 A_{2u} –13.381 eV

***k* = 0 (Γ point)**



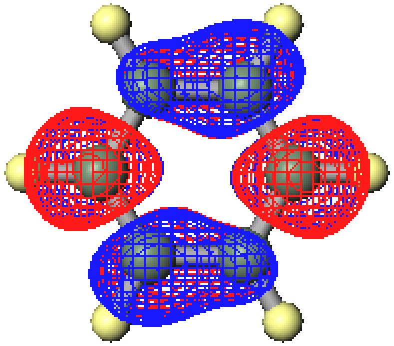
#14,15 E_{1g} –9.653 eV

***k* = 1/(3d)**



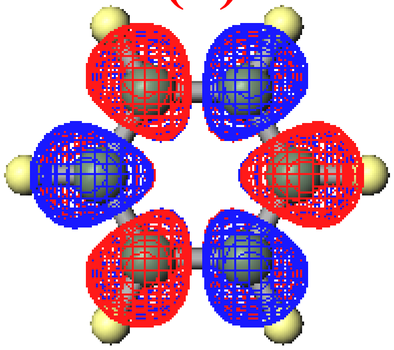
#16,17 E_{2u} 0.555 eV

***k* = 1/(2d)**



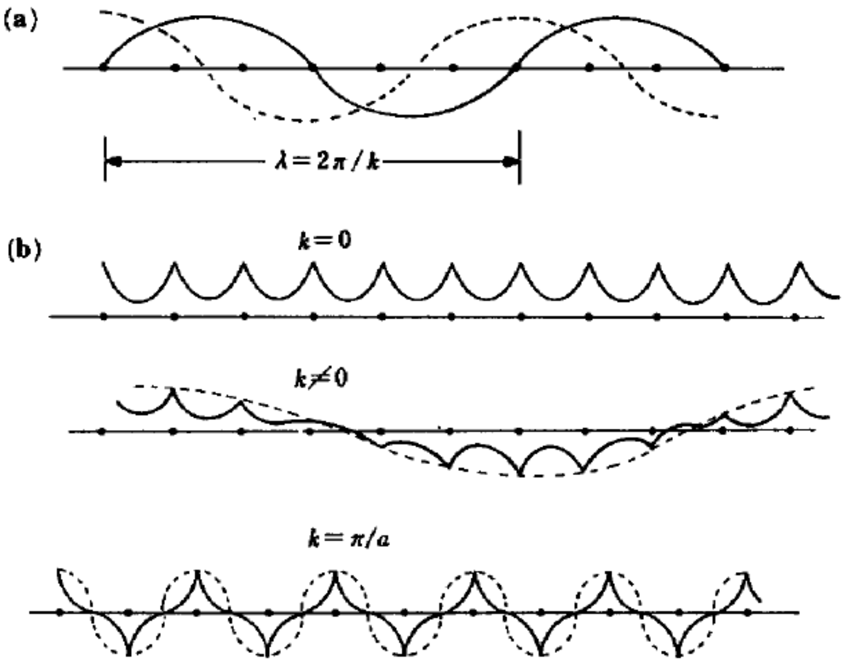
#18 B_{1g} 2.978 eV

***k* = 1/(d)**



Bloch's theorem

$$\begin{pmatrix} \varepsilon_{1s} & h_{12} & 0 & 0 & h_{12} \\ h_{12} & \varepsilon_{1s} & h_{12} & 0 & 0 \\ 0 & h_{12} & \varepsilon_{1s} & \ddots & \vdots \\ 0 & 0 & \ddots & \ddots & h_{12} \\ h_{12} & 0 & \cdots & h_{12} & \varepsilon_{1s} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix} = \varepsilon \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix}$$



$$k_l = \frac{2\pi}{Na} l,\ c_i^{(l)} = \exp(ik_l x_j)$$

$$\varphi_{kl} = \sum\nolimits_j c_i^{(l)} \phi_j = \sum\nolimits_j \underline{\phi_j}\ \underline{\exp(ik_l x_j)}:$$ **Bloch's theorem**

Periodic func Phase factor from Bloch's ***k***

$$E(k_l) = \varepsilon_{1s} + 2h_{12}\cos(k_l a)$$

Equation for band calculation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\Psi_{\boldsymbol{k}}(\mathbf{r}) = E\Psi_{\boldsymbol{k}}(\mathbf{r})$$

$\Psi_{\boldsymbol{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})u(\mathbf{r})$ $u(\mathbf{r})$: Function with the periodicity of crystal

$$\left(\frac{1}{2m}(-i\hbar\nabla + \hbar\mathbf{k})^2 + V(\mathbf{r})\right)u(\mathbf{r}) = H_{\boldsymbol{k}}u(\mathbf{r}) = Eu(\mathbf{r})$$

Expand by basis functions: $u(\mathbf{r}) = \sum_i C_i\phi_i(\mathbf{r})$

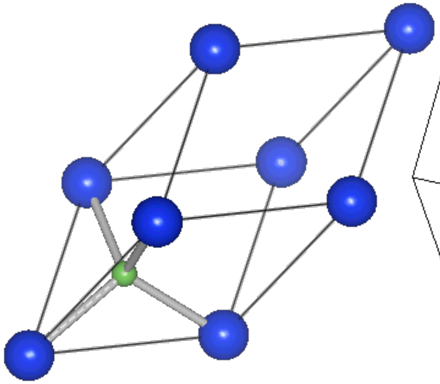
$$\sum_j \langle u_i|H_k|u_j\rangle C_j - E\sum_j\langle u_i|u_j\rangle C_j = 0$$

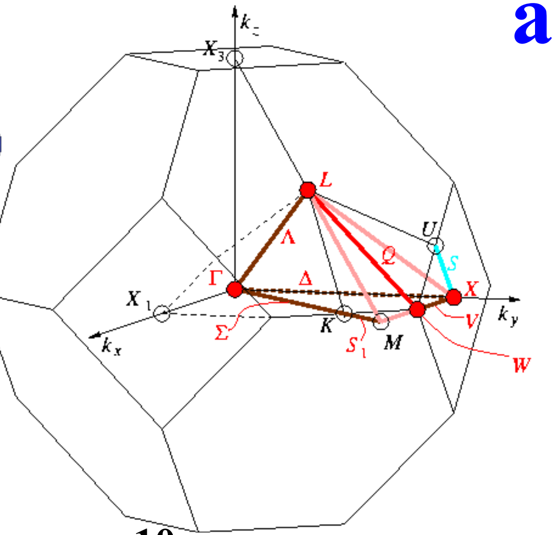
$$\mathbf{H}(\boldsymbol{k})\mathbf{C} = E\mathbf{SC}$$

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

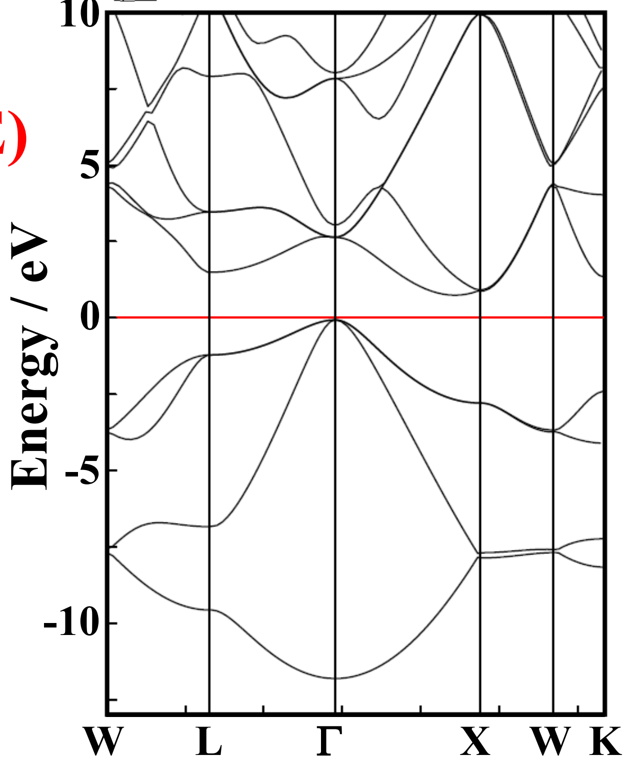
Band structures by DFT and Tight-binding: an example for Si

$N_{Si}=2$

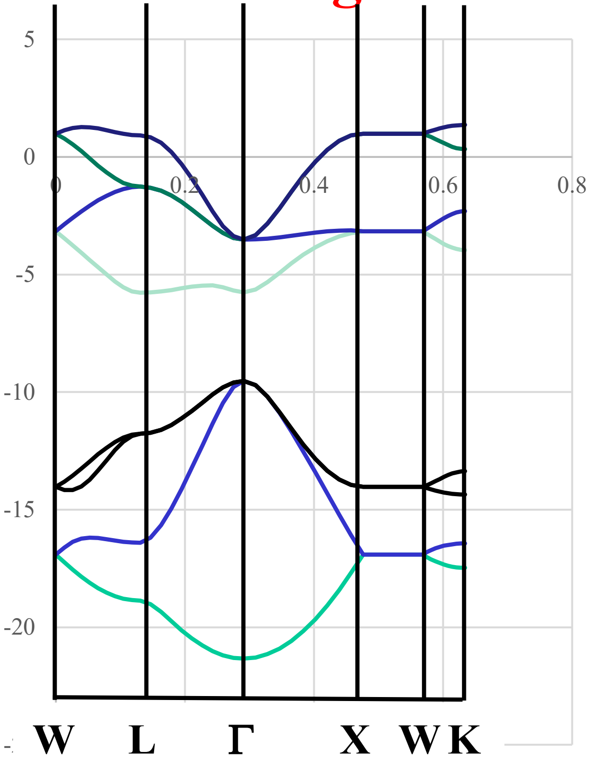




DFT (PBE)



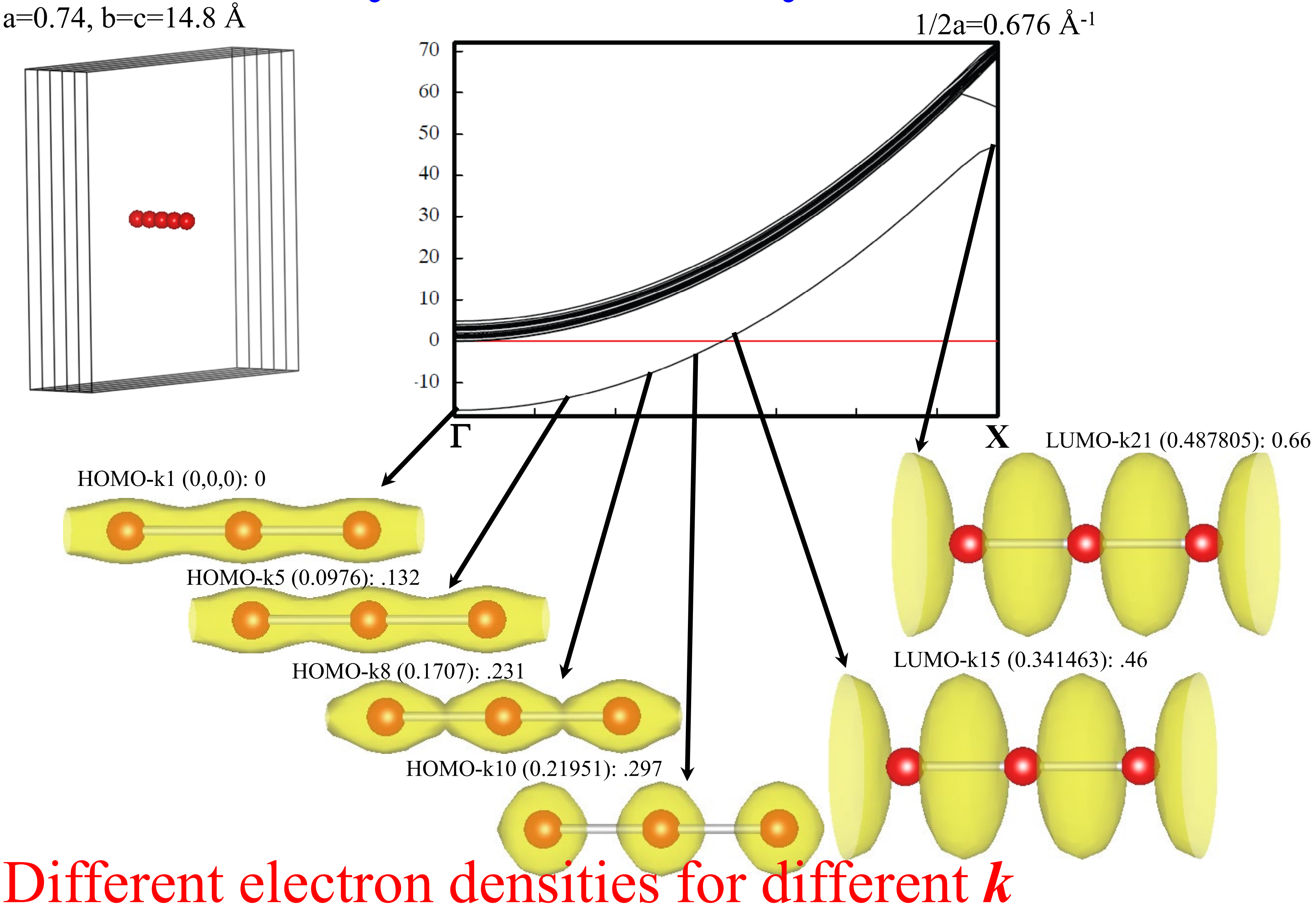
Harrison's tight-binding



Bloch’s wave number, k

Blochの波数ベクトル k

1D H crystal: *k* and crystal orbitals

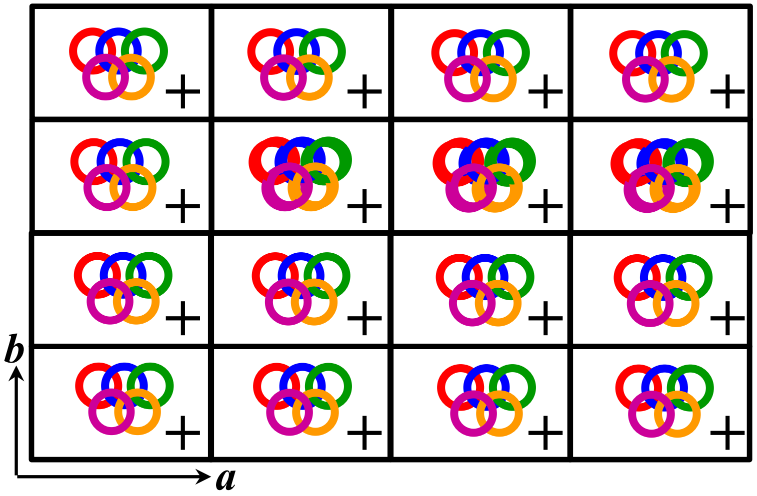


Different electron densities for different ***k***

Illustrative explanation of Bloch's $\boldsymbol{k}$

Γ: $\boldsymbol{k}$ = (0, 0, 0)

$\exp(i\boldsymbol{k}\cdot\boldsymbol{r}) = 1$: Phases are the same for all unit cells

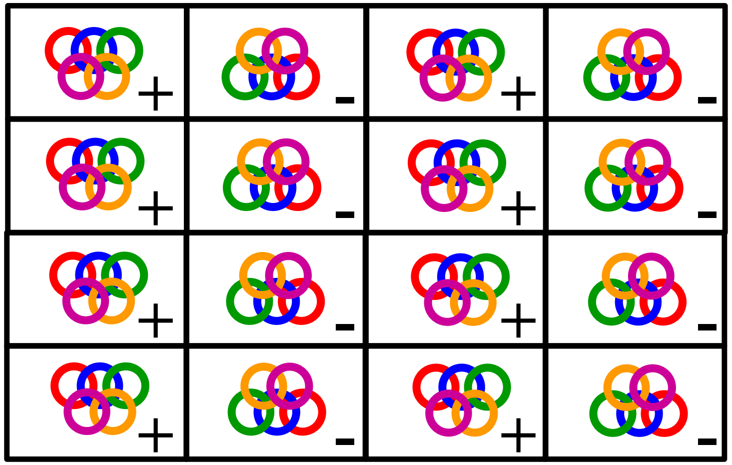


X: $\boldsymbol{k}$ = (π /a, 0, 0) [wave number unit]

(π, 0, 0) [phase unit]

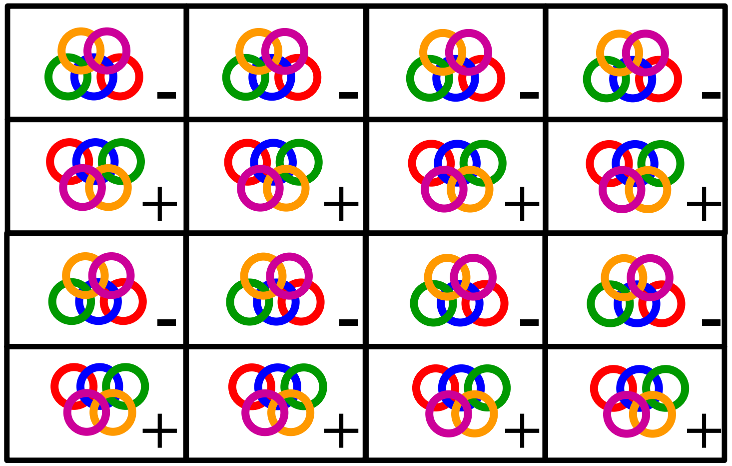
(1/2, 0, 0) [Recip. Lattice param unit, 2π/a]

$\exp(i\boldsymbol{k}\cdot\boldsymbol{r}) = \exp[i\pi(n_x)]$: Sign flip for odd n_x



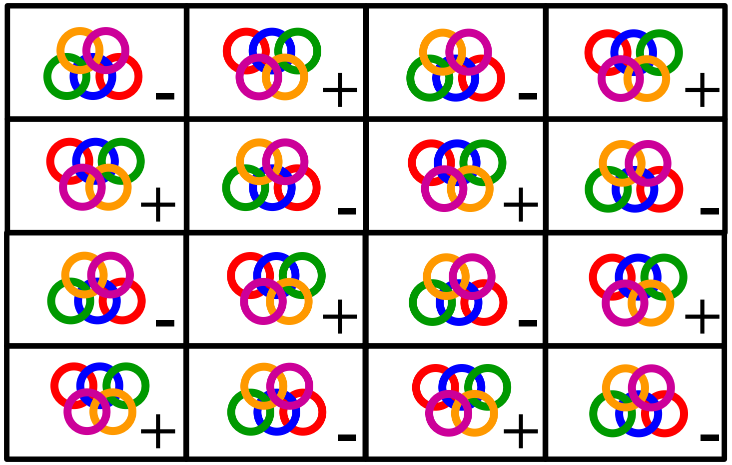
Y: $\boldsymbol{k}$ = (0, 1/2, 0)

$\exp(i\boldsymbol{k}\cdot\boldsymbol{r}) = \exp[i\pi(n_x)]$: Sign flip for odd n_y



M: $\boldsymbol{k}$ = (1/2, 1/2, 0)

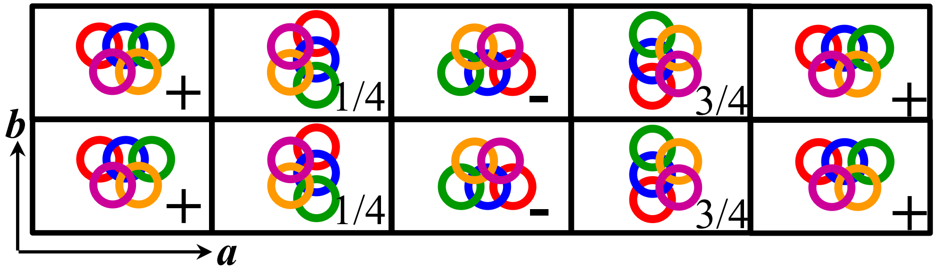
$\exp(i\boldsymbol{k}\cdot\boldsymbol{r}) = \exp[i\pi(n_x+n_y)]$: Sign flip for odd n_x+n_y



Illustrative explanation of Bloch's *k*

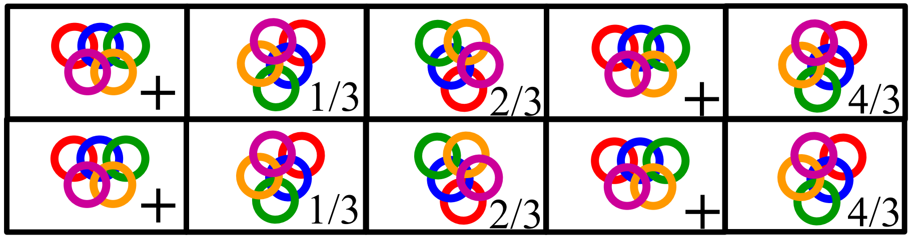
Δ_x : k = (1/4, 0, 0) [in (2π/a, 2π/b, 2π/c)]

exp(i$\boldsymbol{k}\cdot\boldsymbol{r}$) = exp[iπ($n_x$/2)]: Phase returns to zero for every 4 units along the ***a*** axis

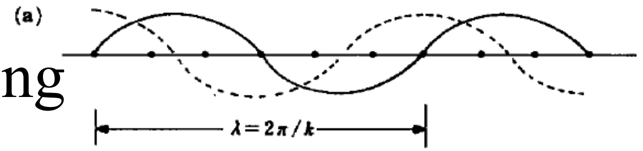


Δ_x : k = (1/3, 0, 0)

exp(i$\boldsymbol{k}\cdot\boldsymbol{r}$) = exp[iπ($n_x$/3)]: Phase returns to zero for every 3 units along the ***a*** axis



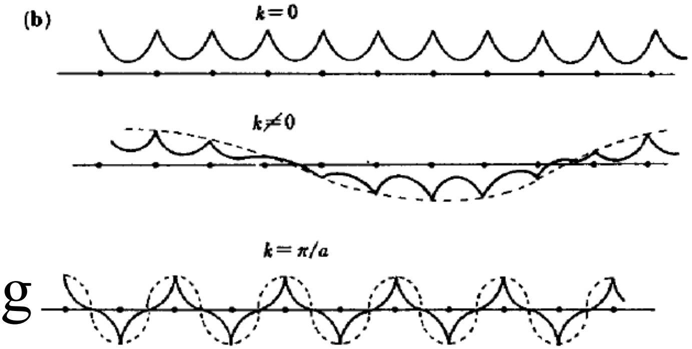
Γ point ($\boldsymbol{k}$ = 0): Bonding



Arbitrary $\boldsymbol{k} \neq 0$:

Many unit cells (2π/*ka*) are incorporated

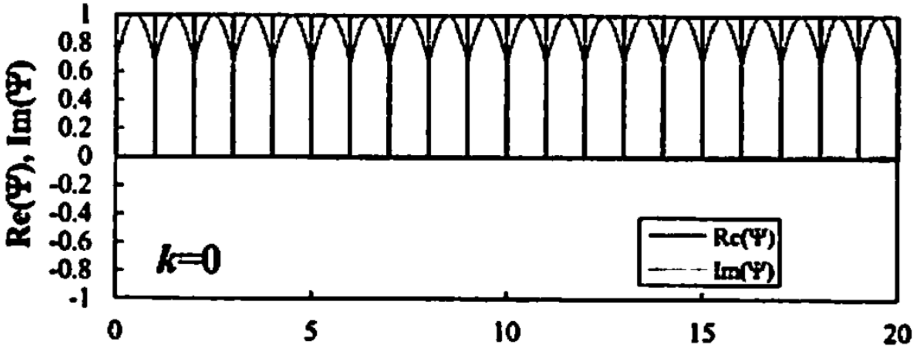
BZ bondary: Anti-bonding



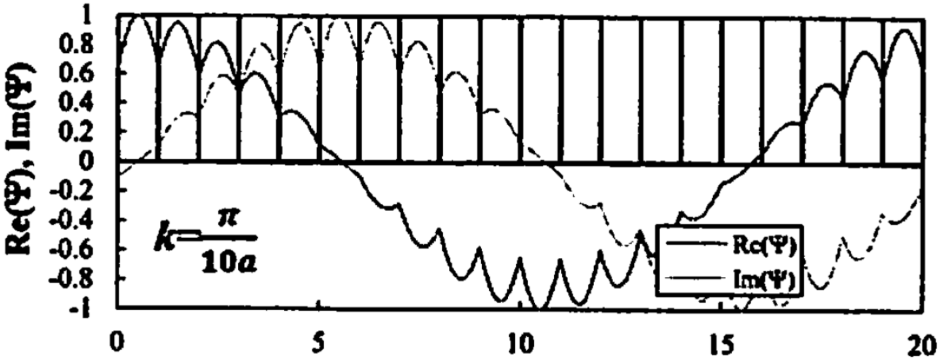
Effect of Bloch's *k*: Kronig-Penney model

杉山、結晶工学スクールテキスト p. 110

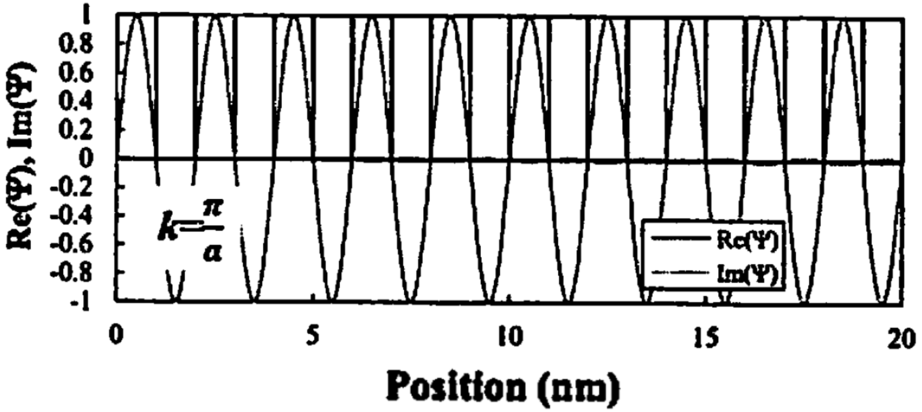
Γ point ($\boldsymbol{k} = 0$) : Bonding



Arbitrary $\boldsymbol{k} \neq 0$:



BZ boundary: Anti-bonding

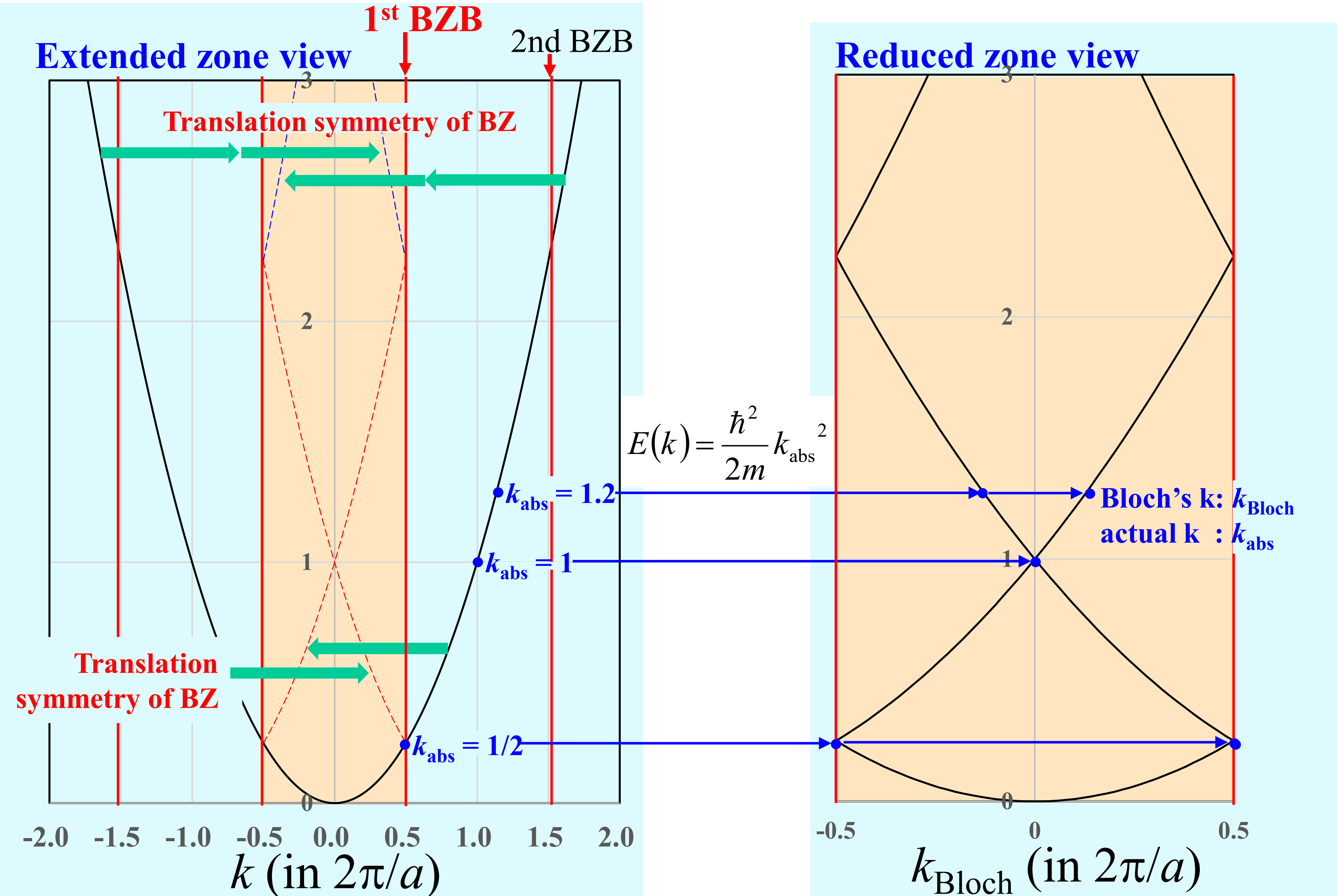


Band theory from free electron (plain wave basis set: PW)

自由電子 (平面波基底関数) からのバンド理論

Free electron (empty lattice) band

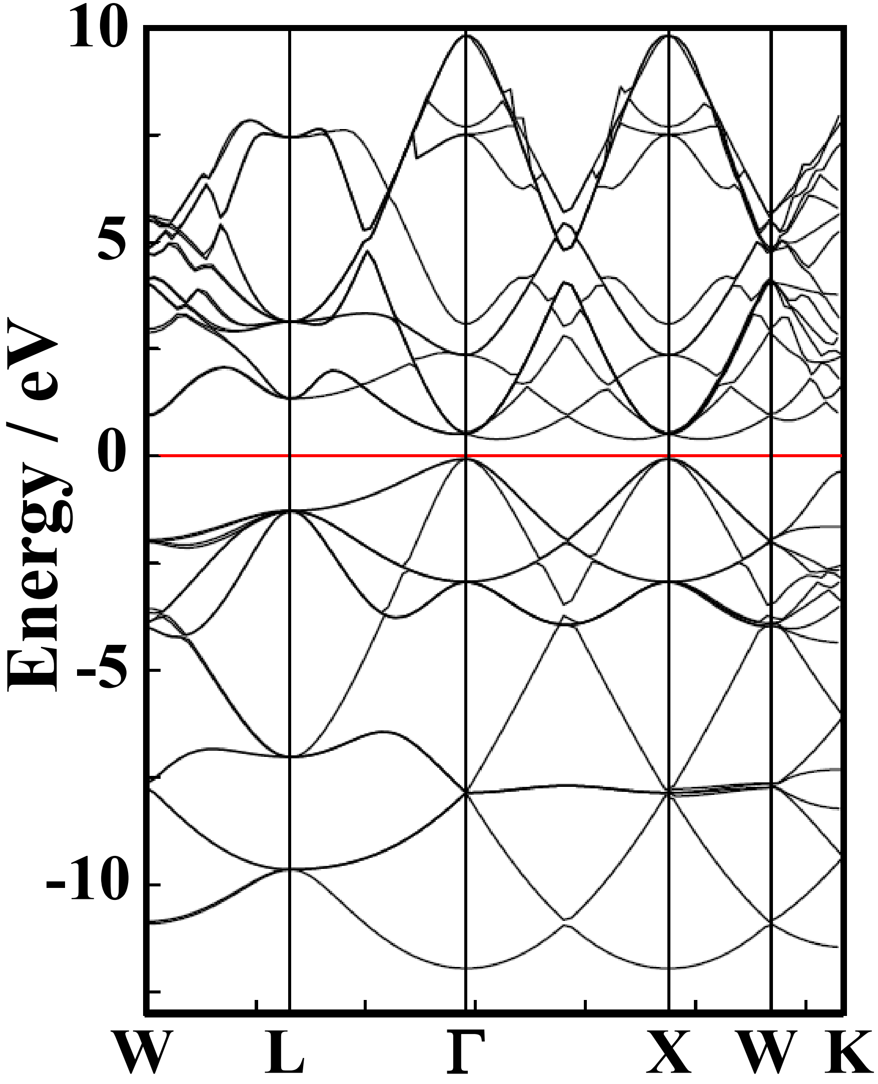
$$\Psi_k(x) = C\exp\left[i(k+G_h)\right] = C\exp\left[i(k+ha^*)\right] \qquad h = \cdots, \text{-2, -1, 0, 1,2,} \cdots$$



$$E(k) = \frac{\hbar^2}{2m} k_{abs}{}^2$$

(Extended) band can be understood as free electron: an example for Si

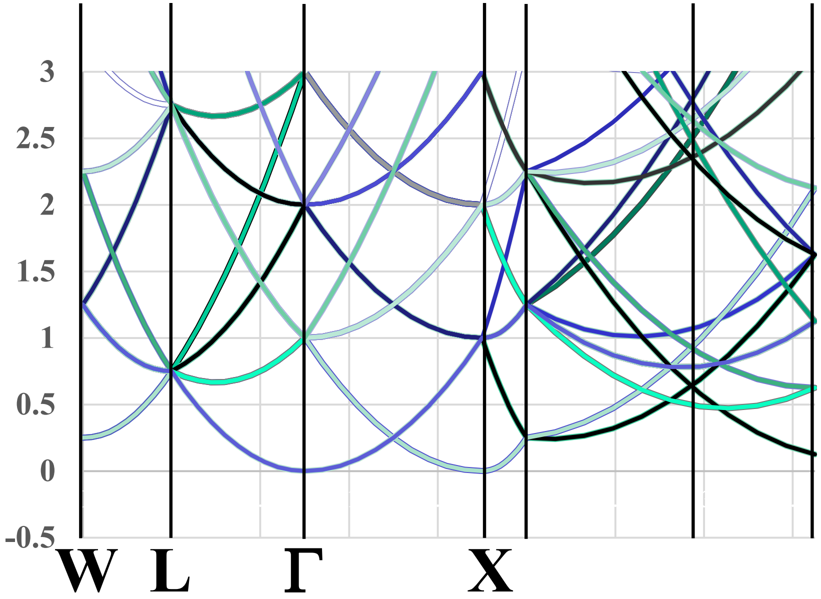
VASP, PBE96, Conventional cell



Free electron model

$$E_{free}(\mathbf{k}) = \frac{\hbar^2}{2m}\mathbf{K}^2 = \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G_{hkl}})^2$$

$$\mathbf{G_{hkl}} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$



Boundary condition of Schrödinger equation

$$\frac{d^2}{dx^2}\psi(x) = 2(V(x) - E)\psi(x)$$

Integrate the both side from $x_0 - h$ to $x_0 + h$

$$\psi'(x_0 + h) - \psi'(x_0 - h) = 2\int_{x_0-h}^{x_0+h}(V(x) - E)\psi(x)dx$$

$$= 2h[(V(x_0 + h) - E)\psi(x_0 + h) - (V(x_0 - h) - E)\psi(x_0 - h)]$$

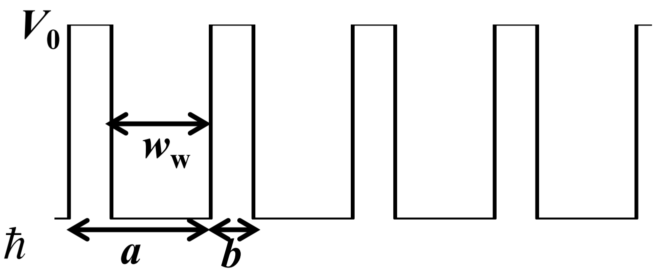
$$\sim 2h[V(x_0 + h) - V(x_0 - h)]\psi(x_0)$$

The last deformation assumes that $\Psi(x)$ is continuous at x_0.

Further, the change of $V(x)$ is smaller than $1/h$ at x_0 ,
the first differential should be continuous, $\Psi'(x+h) = \Psi'(x-h)$

Ex., for a finite well potential, as hV$_0$ => 0 for h => 0,
the first differential should be continuous at x_0 as well.

Band theory: Kronig-Penney model



Solution of $\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right)\phi=E\phi$

In well: $\phi=A\exp(i\alpha x)+B\exp(-i\alpha x)$ $\quad \alpha=\sqrt{2mE}/\hbar$

In barrier $\phi=C\exp(\beta x)+D\exp(-\beta x)$ $\quad \beta=\sqrt{2m\left(V_0-E\right)}/\hbar$

Boundary condition at well/barrier interfaces: ϕ and ϕ' are continuous

Bloch's theorem: ϕ(*x*+*a*) = λϕ(*x*) $\qquad$ **λ = exp(i*ka*)**

$$\begin{pmatrix} 1 & 1 & -1 & -1 \\ i\alpha & -i\alpha & -\beta & \beta \\ \exp(i\alpha w_w) & \exp(-i\alpha w_w) & -\lambda\exp(-\beta b) & -\lambda\exp(-\beta b) \\ i\alpha\exp(i\alpha w_w) & -i\alpha\exp(-i\alpha w_w) & -\beta\lambda\exp(-\beta b) & \beta\lambda\exp(-\beta b) \end{pmatrix}\begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix}=\begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

The left determinant must be zero:

$$2\cos ka=\left(\frac{\beta^2-\alpha^2}{\alpha\beta}\sin\alpha w_w\sin\beta b+2\cos\alpha w_w\cosh\beta b\right)$$

Take the limit b => 0 for constant bV_0:

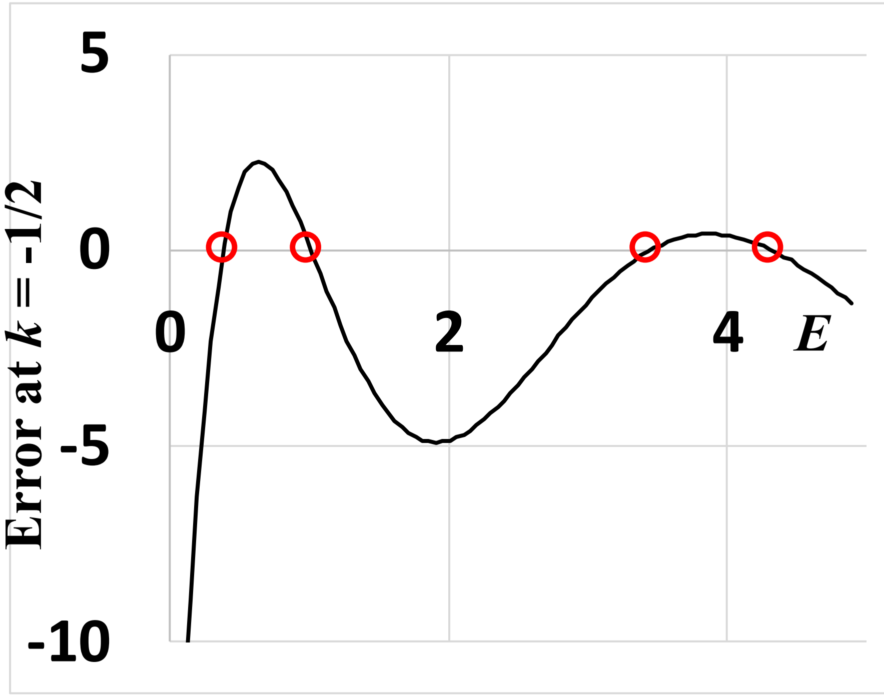
$$2\cos ka=\left(\frac{\beta^2-\alpha^2}{\alpha}b\sin\alpha a+2\cos\alpha a\right)\Longrightarrow\cos ka=\left(\frac{mV_0}{\hbar^2}\frac{b}{\alpha}\sin\alpha a+\cos\alpha a\right)$$

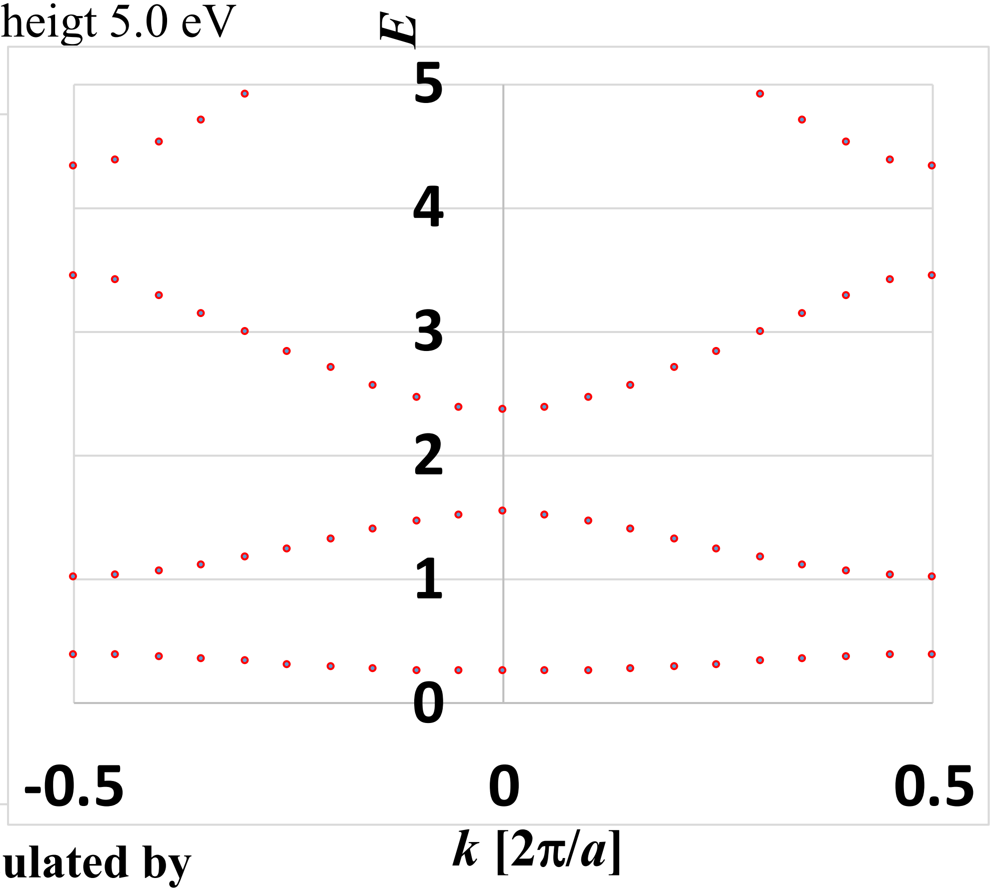
How to solve Kronig-Penney eq

$$\Delta = 2\cos ka - \left(\frac{\beta^2 - \alpha^2}{\alpha} b \sin \alpha a + 2\cos \alpha a \right)$$

Periodicy a = 1 nm, barrier width 0.1 nm, heigt 5.0 eV

Eff. mass m_e, $k = (2\pi/a)[-1/2, 1/2]$





Approximated from the left figure	**Accurately calculated by the Newton-Raphson method (error = 10-^{10})**
0.3675	0.3934
1.0045	1.0244
3.4545	3.4585
4.3365	4.3345

Plain wave approx.: Transfer matrix method

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

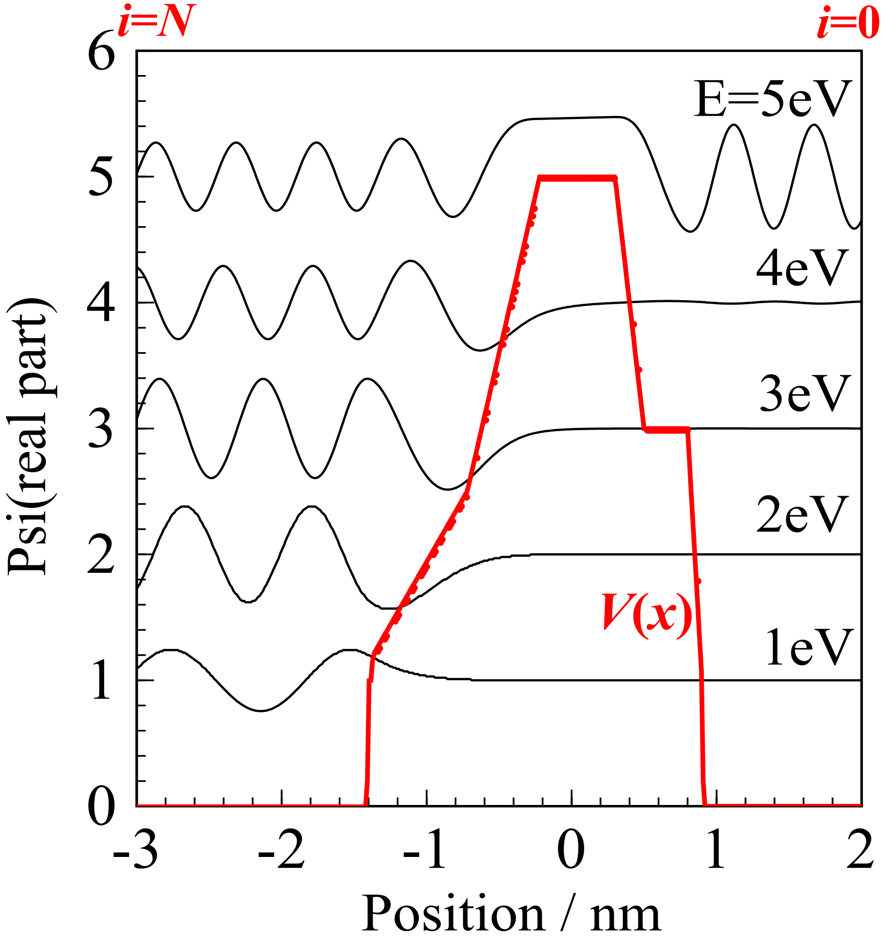
$\Psi_i = A_i \exp(ik_i x) + B_i \exp(-ik_i x)$

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

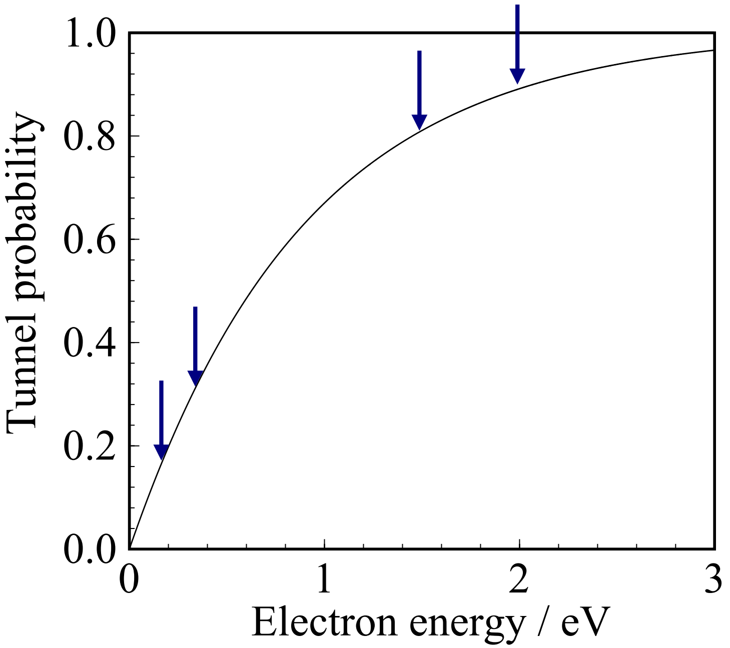
$$\begin{pmatrix} A_N \\ B_N \end{pmatrix} = \begin{pmatrix} \alpha^{+}{}_{N-1} P_{N-1} & \alpha^{-}{}_{N-1} / Q_{N-1} \\ \alpha^{-}{}_{N-1} Q_{N-1} & \alpha^{+}{}_{N-1} / P_{N-1} \end{pmatrix} \begin{pmatrix} A_{N-1} \\ B_{N-1} \end{pmatrix} = T_{N-1} \begin{pmatrix} A_{N-1} \\ B_{N-1} \end{pmatrix} = T_{N-1} T_{N-2} \begin{pmatrix} A_{N-2} \\ B_{N-2} \end{pmatrix} = T \begin{pmatrix} A_0 \\ B_0 \end{pmatrix}$$

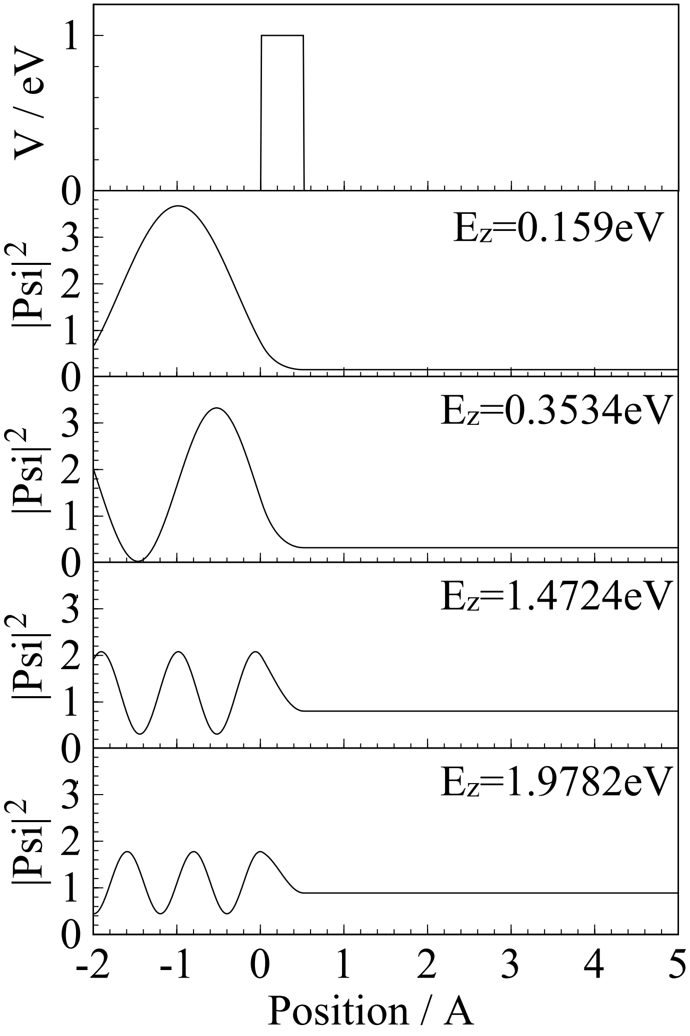
$$T = T_{N-1} T_{N-2} \cdots T_0$$

An example of boundary condition:
Only propagation wave remains
in the transmitted region (*i* = 0)
$A_0 = 1$, $B_0 = 0$



Tunneling in a single barrier

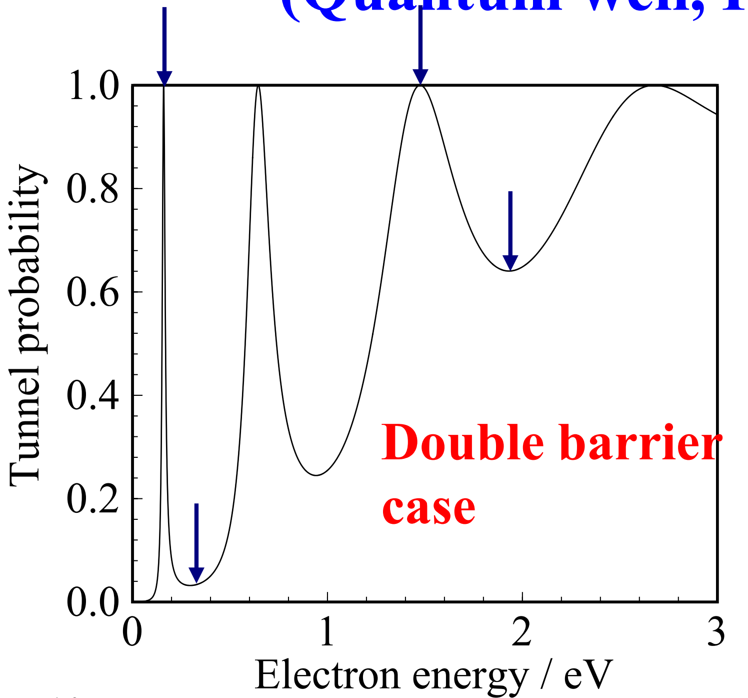




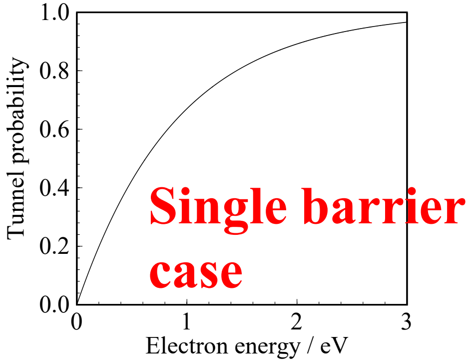
Wave function is scattered by the barrier (atom) and the transmittance must be < 1
=> For crystal with many atom, the total transmittance should be zero?

Tunneling for two barriers

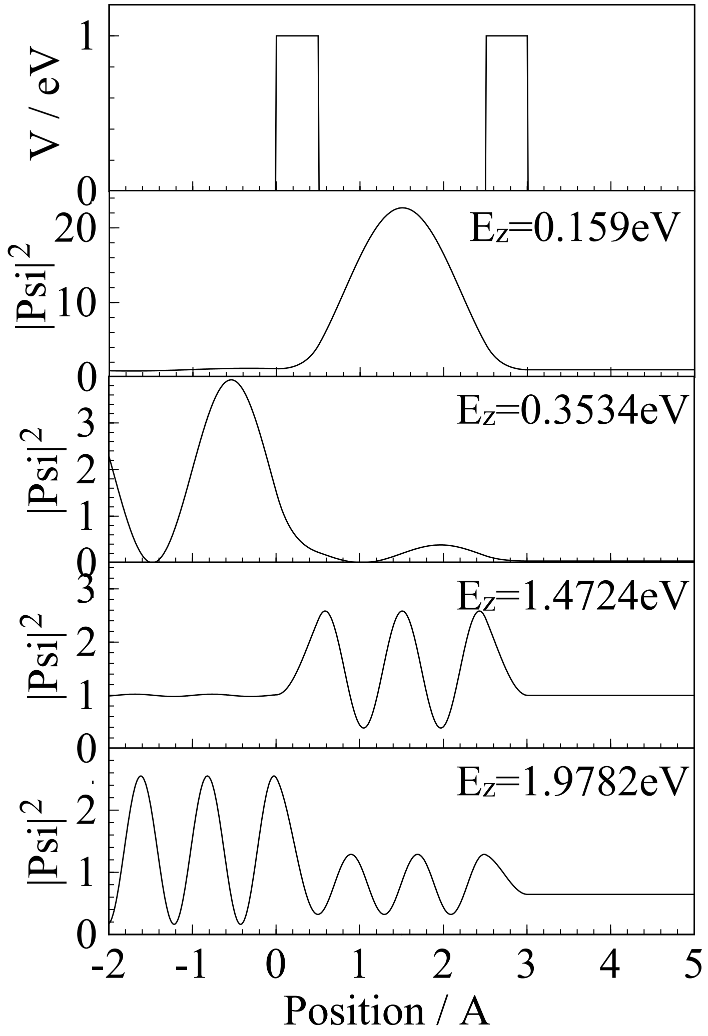
(Quantum well, Resonant tunneling diode)



Double barrier case



Single barrier case

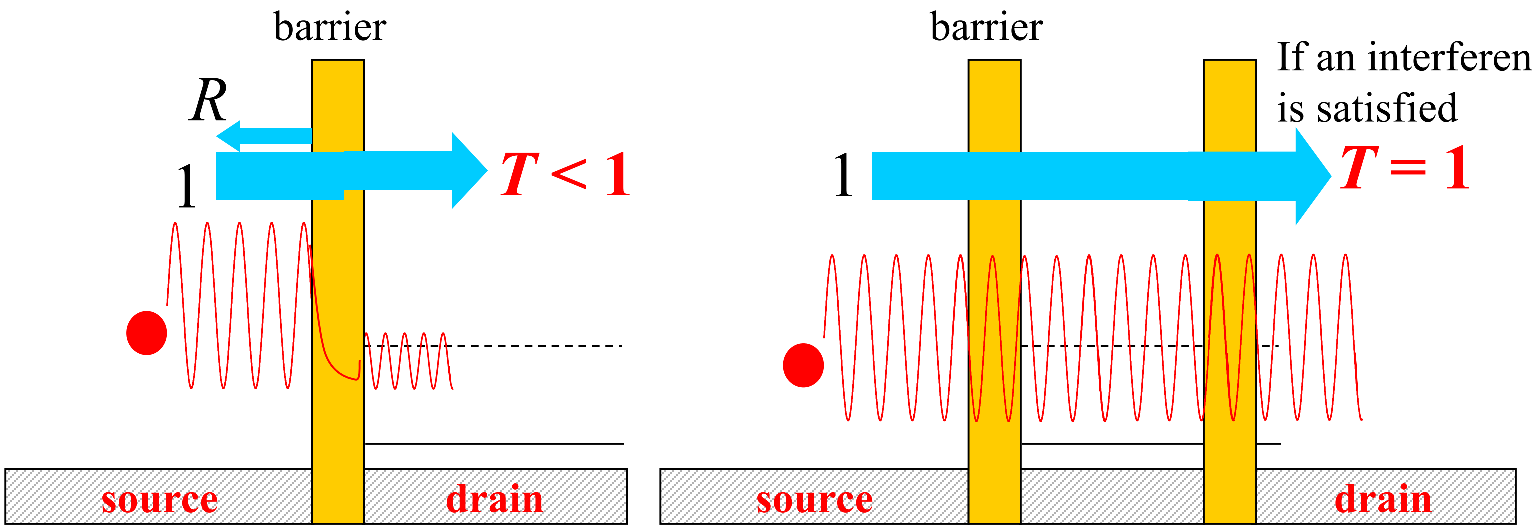


Transmittance *T* will be zero for many atoms?

=> No, for more than two atoms (barriers), *T* can be 100 % at some energies

Similarity: Scattering of electrons and light

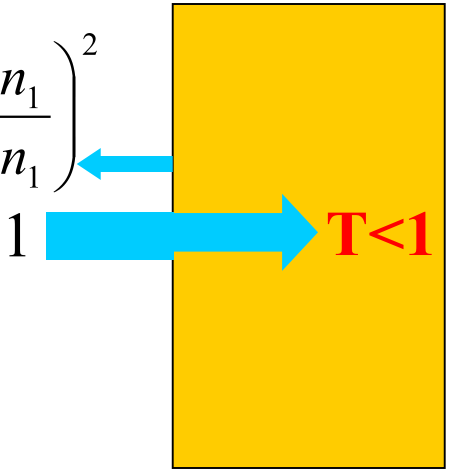
Transmission and reflection of electron



If an interference condition is satisfied

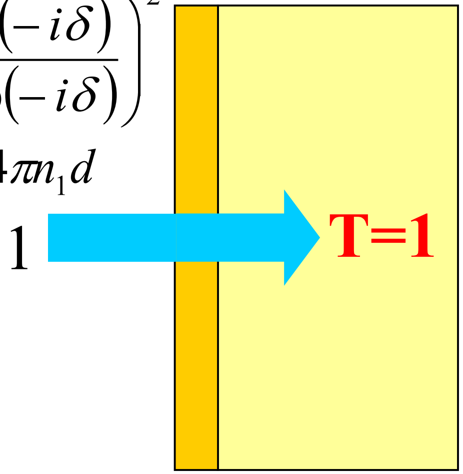
Transmission and reflection of light

$$R = \left(\frac{n_2 - n_1}{n_2 + n_1} \right)^2$$

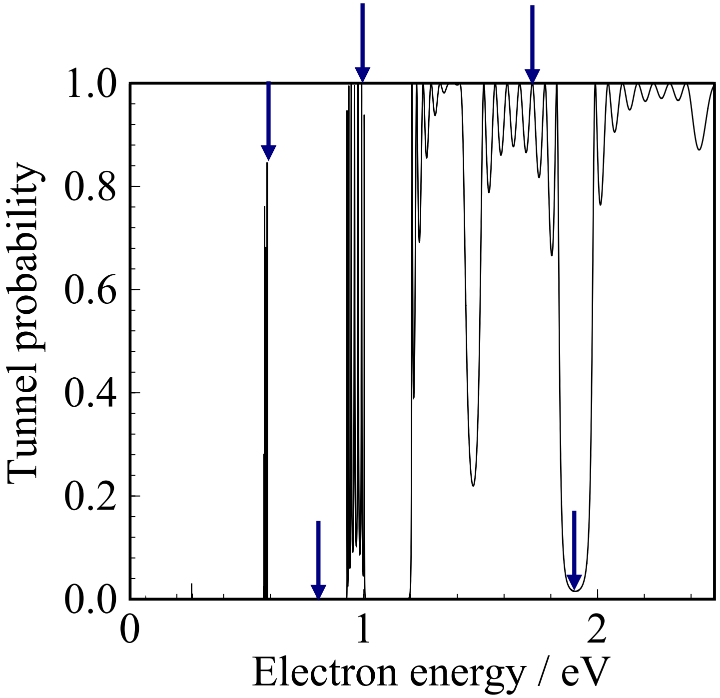


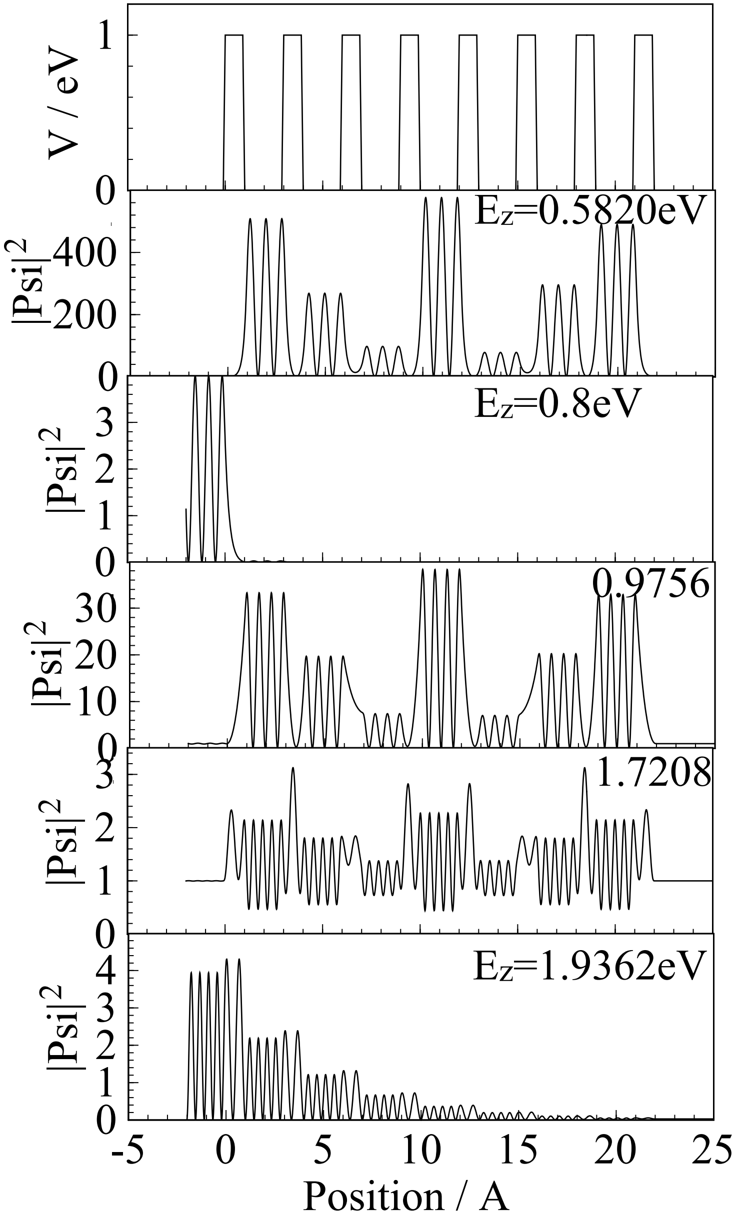
$$R = \left(\frac{r_1 + r_2 \exp(-i\delta)}{1 + r_1 r_2 \exp(-i\delta)} \right)^2$$

$$\delta = 4\pi n_1 d$$



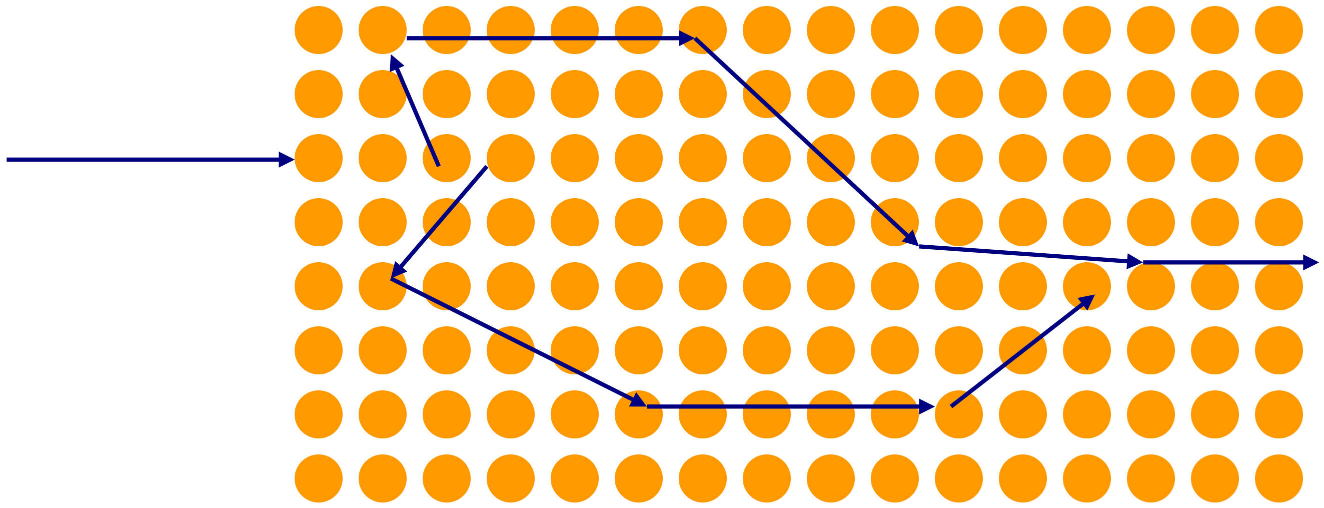
Transmission through multiple quantum well (MQW): band



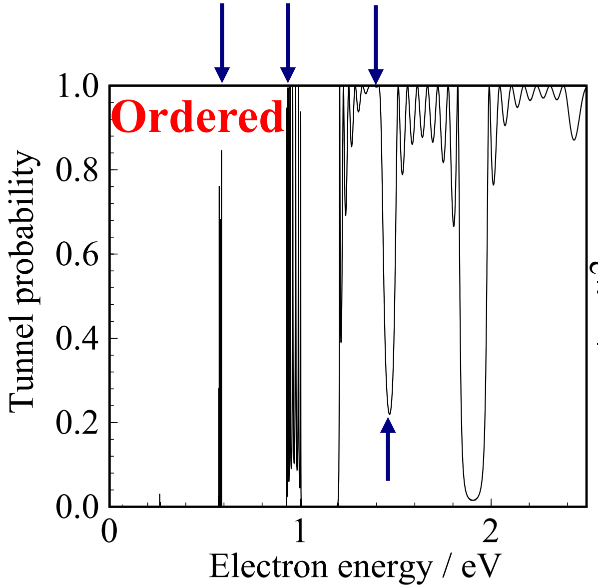


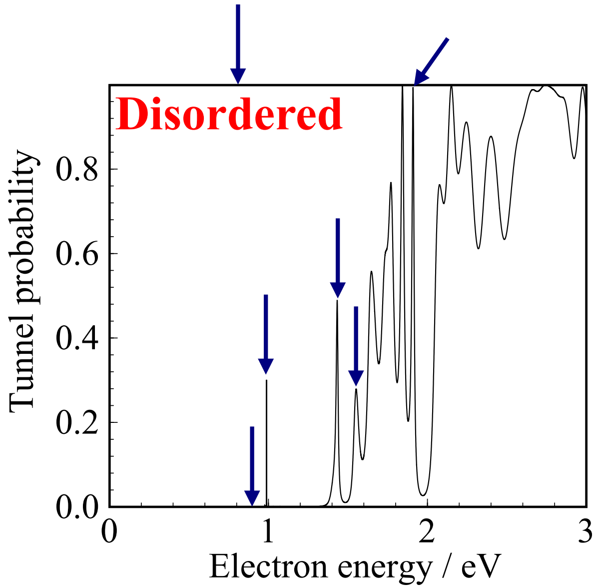
Transmission of e^- through crystal

- e^- can transmit crystal without scattering ($T = 1$) thanks to the interference of wave functions scattered by the 3D-periodically aligned atoms.
- Band structure indicates only the $T = 1$ states
- Electron states exist at any energy even in the bandgap, but those states accompany attenuation (scattering)

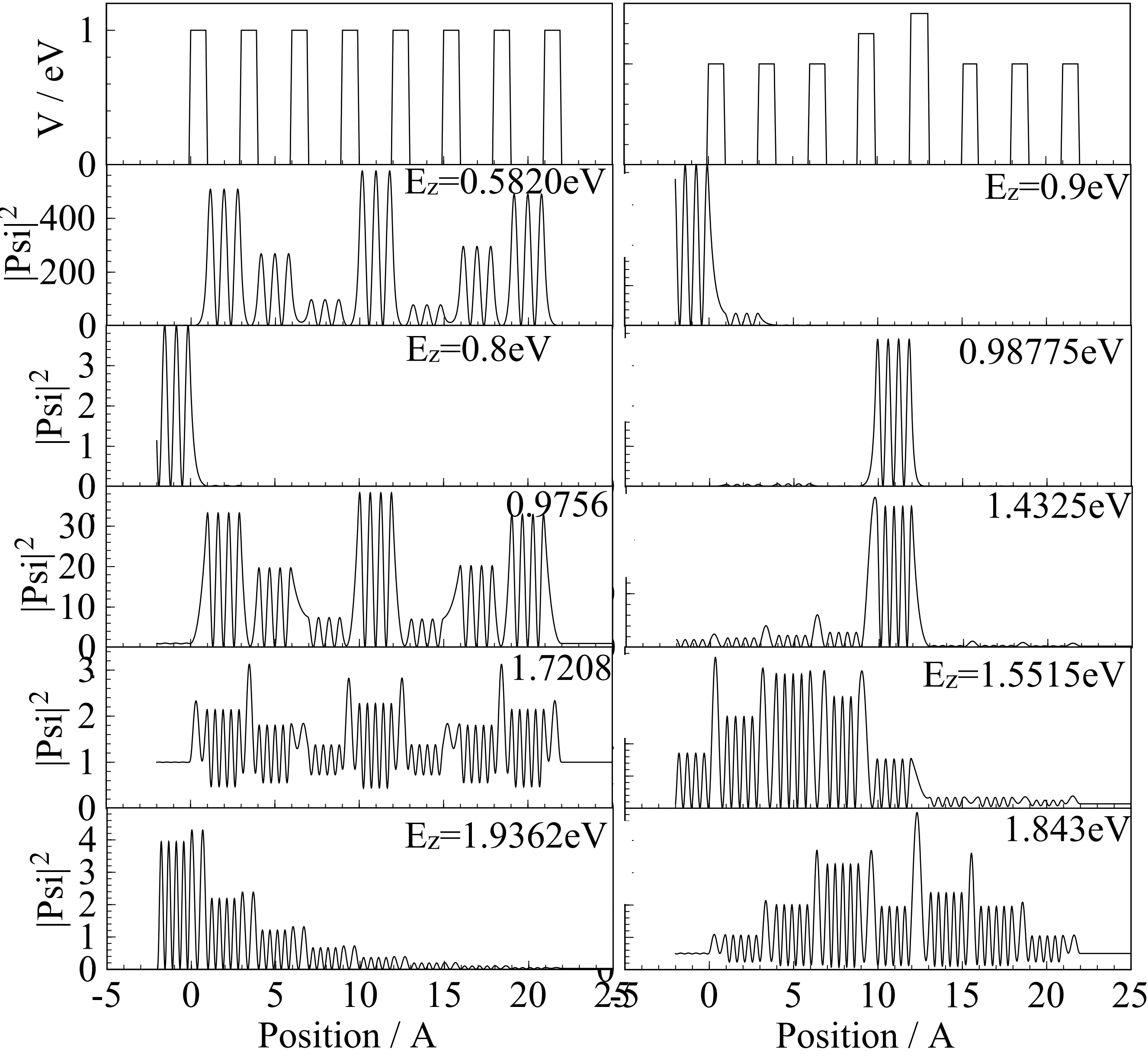


Transmission through disordered MQW

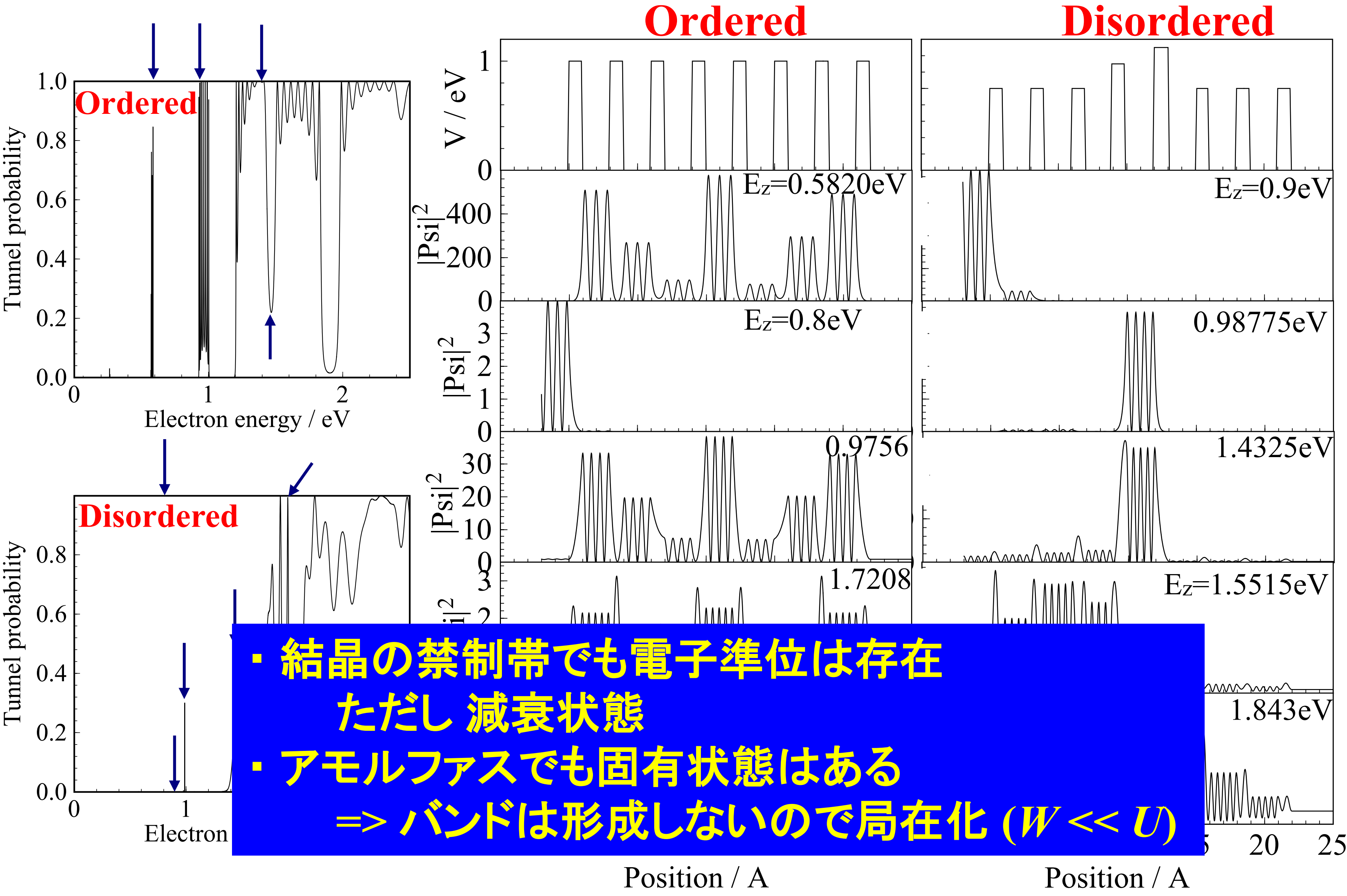




Ordered **Disordered**



Transmission through disordered MQW



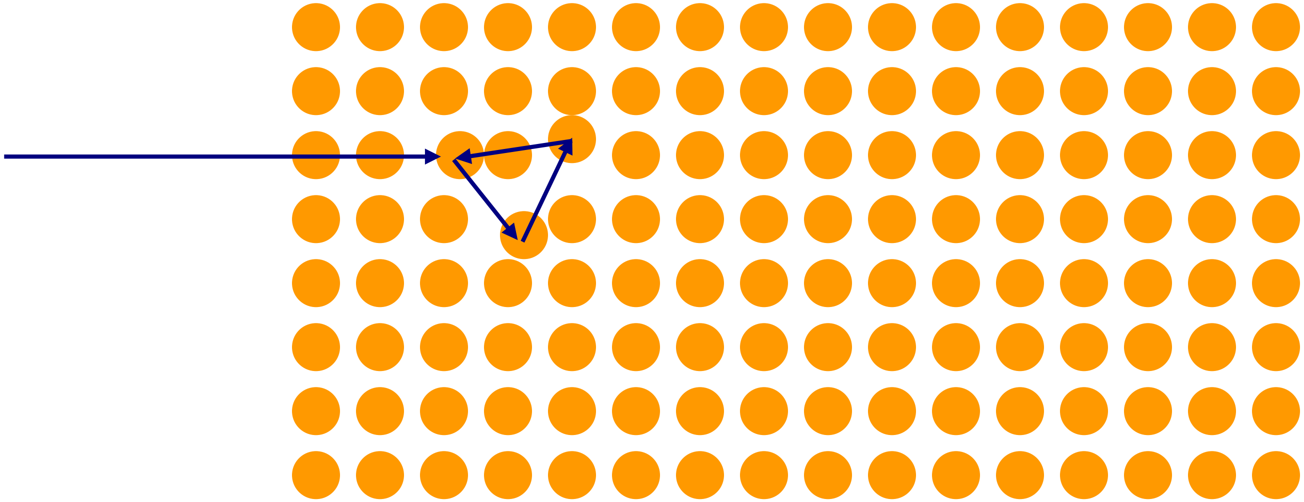
・結晶の禁制帯でも電子準位は存在

　ただし 減衰状態

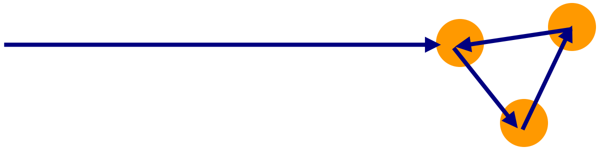
・アモルファスでも固有状態はある

　=> バンドは形成しないので局在化 ($W << U$)

Transmission through disordered crystal



- Back ground periodic atoms contribute only to *e*⁻ transmission: we can consider only the difference from the perfect crystal

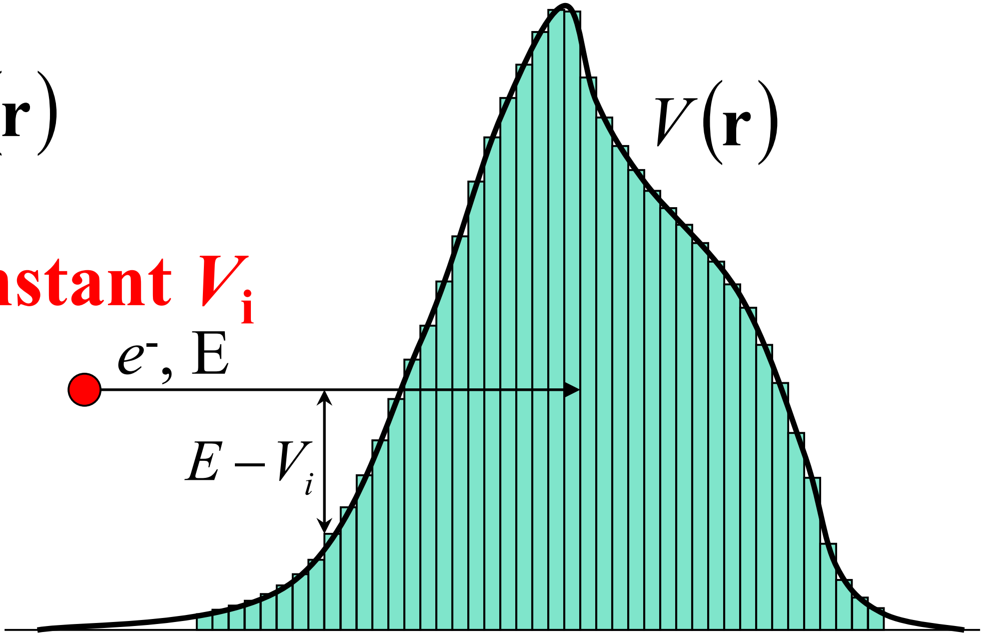


- Due to scattering and interference from the disordered structure, standing wave is formed in a localized region: Anderson localization

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:

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

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

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

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

Plain wave 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

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

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

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

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

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

Plain wave basis

Fourier transform

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

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

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

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_{cut} (or k_{cut}, $|\boldsymbol{G}_{hkl,\text{ut}}|$) limits the accuracy of the basis set

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

Plain wave method

Plain waves are employed as basis functions of LC

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

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 $|G_{\mathrm{hkl}}| < G_{\mathrm{max}}$ ($\hbar\omega < E_{\mathrm{cut}}$**

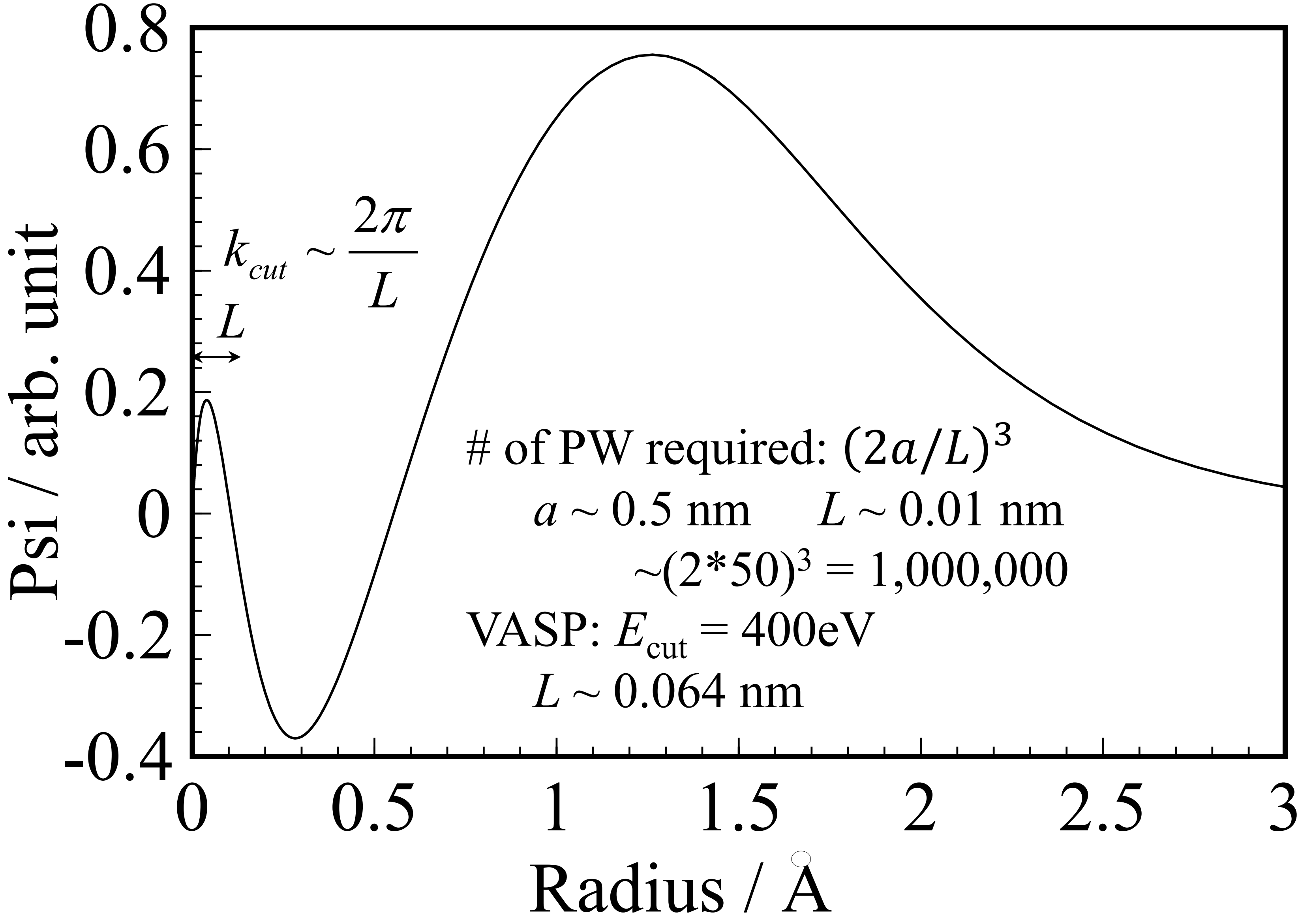
$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & \cdots & H_{1n}-ES_{1n} \\ H_{21}-ES_{21} & H_{22}-ES_{ss} & & H_{2n}-ES_{2n} \\ \vdots & & \ddots & \vdots \\ H_{n1}-ES_{n1} & H_{n2}-ES_{n2} & \cdots & H_{nn}-ES_{nn} \end{vmatrix} = 0$$

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

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

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)



# of PW required: $(2a/L)^3$

$a \sim 0.5$ nm $\quad L \sim 0.01$ nm

$\sim(2*50)^3 = 1{,}000{,}000$

VASP: $E_{\mathrm{cut}} = 400\mathrm{eV}$

$L \sim 0.064$ nm

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):** $e_i(\boldsymbol{k}) = E\left(n_{\boldsymbol{k},i}\right) - E(n_{\boldsymbol{k},i} - 1)$
- **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 σ_{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

$F = U \quad + \quad F_{\text{electron}} \quad + \quad \boldsymbol{F}_{\textbf{phonon}}$

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 $\rho(r)$
   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

Density Function Theory: DFT

Hohenberg-Kohn theorem

1. For interacting electron gas in external potential $V_{\mathrm{ext}}(\boldsymbol{r})$, $V_{\mathrm{ext}}(\boldsymbol{r})$ 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. **3.** (HF) Energy eigen values correspond to ionization potential
  - **DFT:**
    1. Hohenberg-Kohn theorem（Ground state is determined by $\rho(\boldsymbol{r})$)
    2. **Depending only on the coordinate of the space $\boldsymbol{r}$**
    3. Energy eigen values correspond to chemical potential

Physical meaning of 'eigenvalue' ε_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**

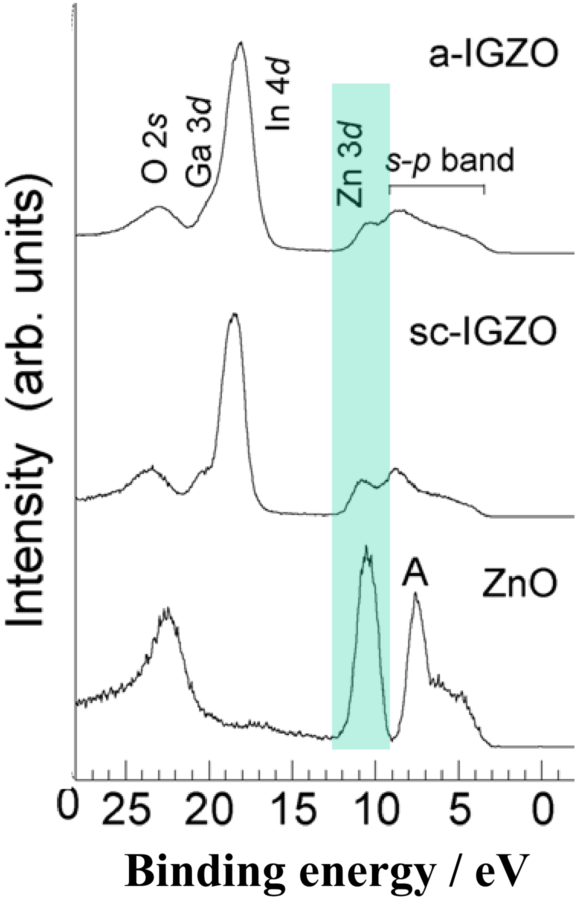
$$\varepsilon_i = \frac{\partial E}{\partial n_i}$$

  Corresponding to chemical potential

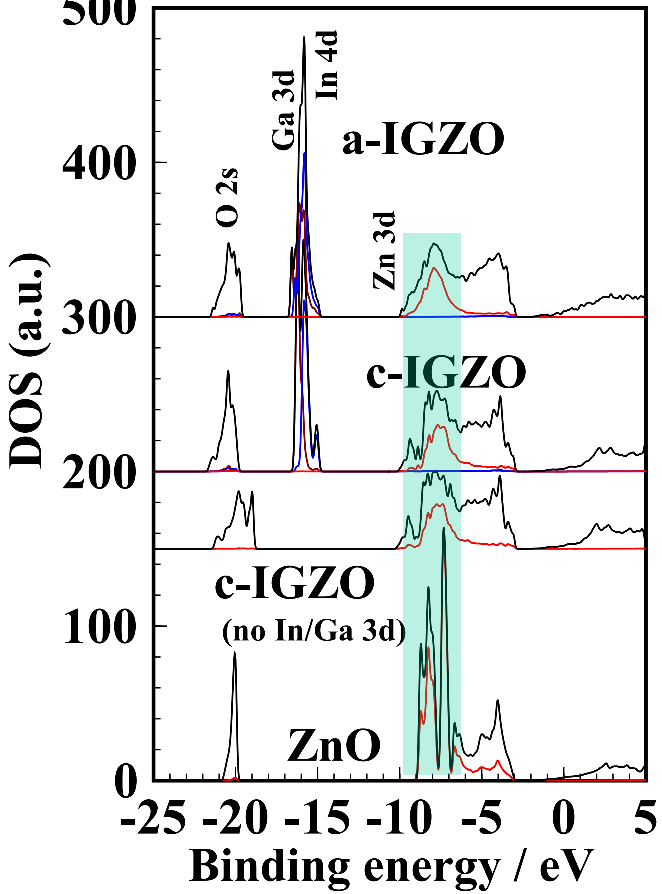
  Underestimated compared to PES binding energy

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

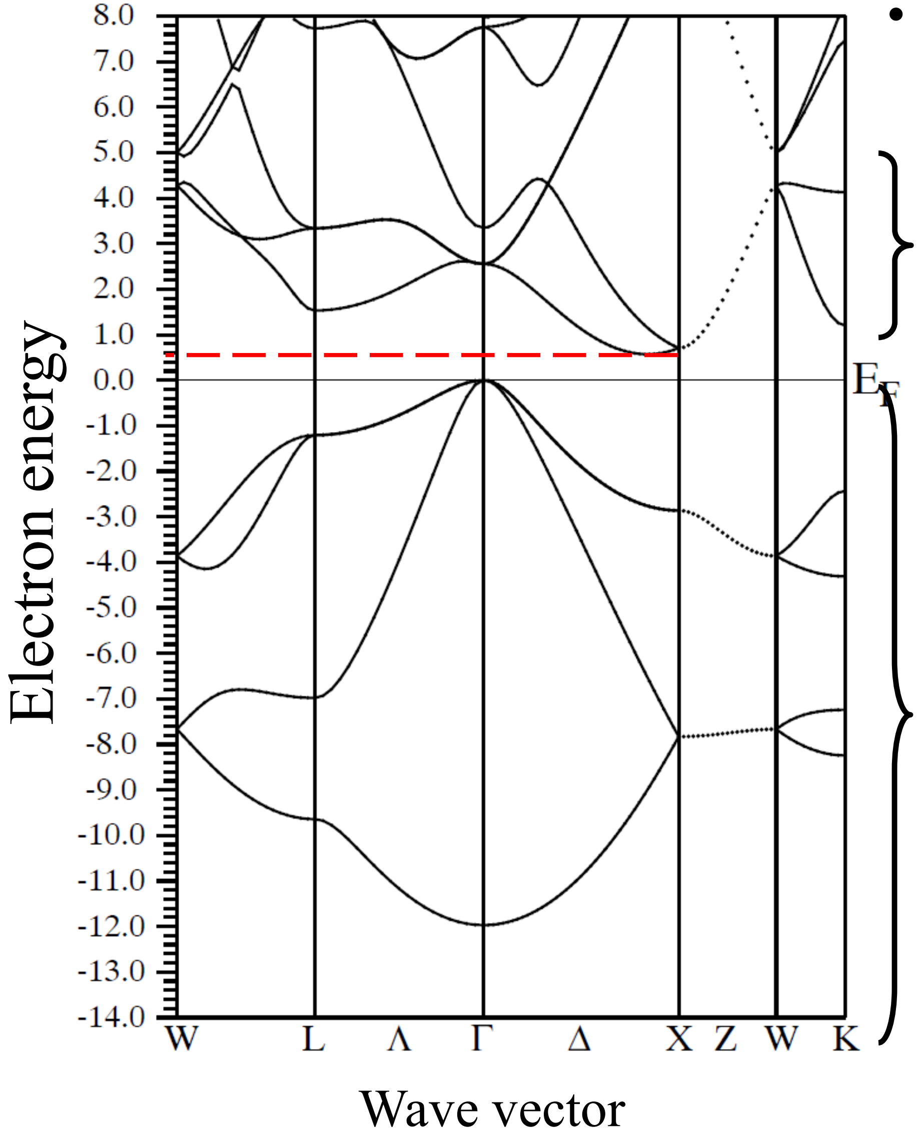
- **Bandgap**
- **Deep levels**
- **Vacuum level**

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

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

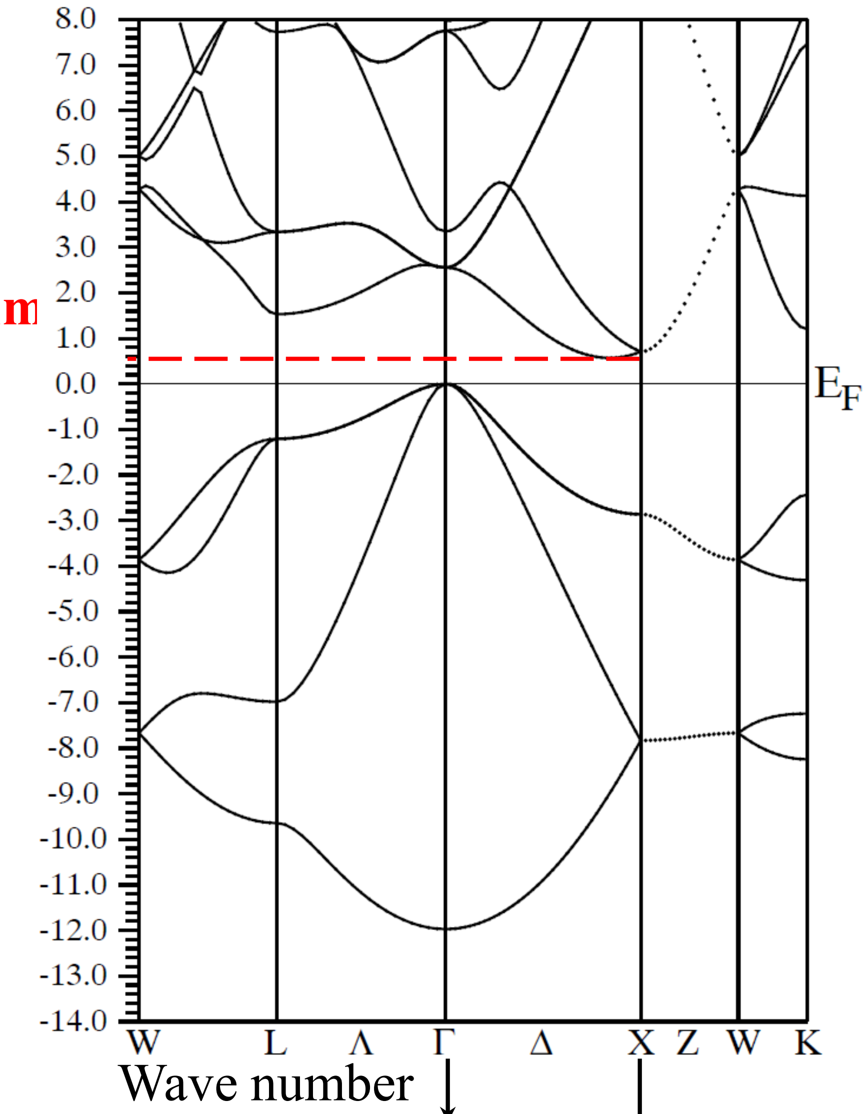
Quant mech: $E = \frac{\hbar^2}{2}k^2 + V$

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
$\hbar \boldsymbol{k}$: Crystal momentum

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



***k* = (0, 0, 0)**

***k* = (1/2, 0, 0)**

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

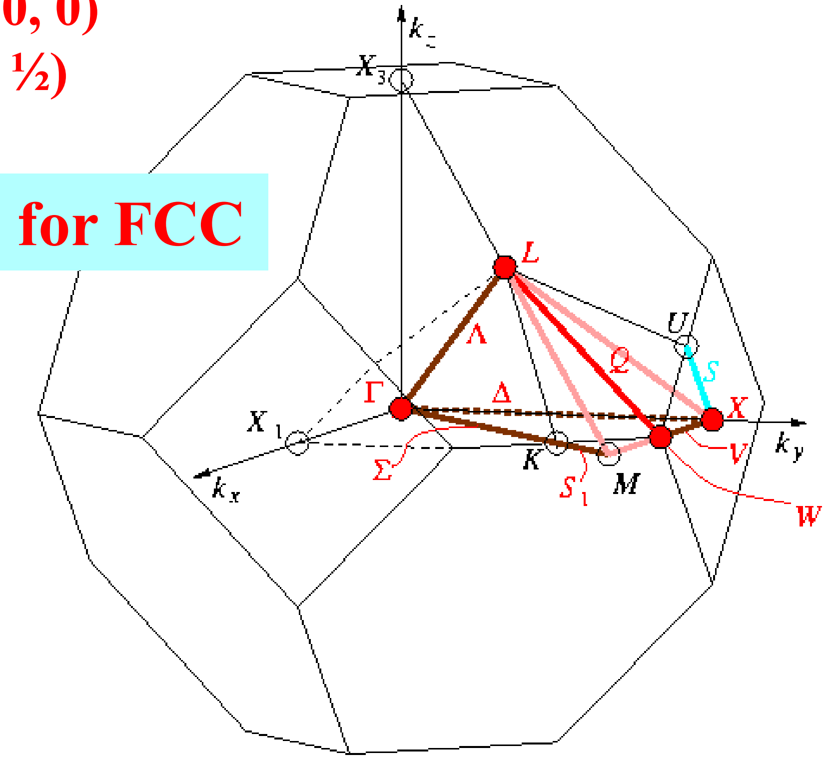
for simple lattice

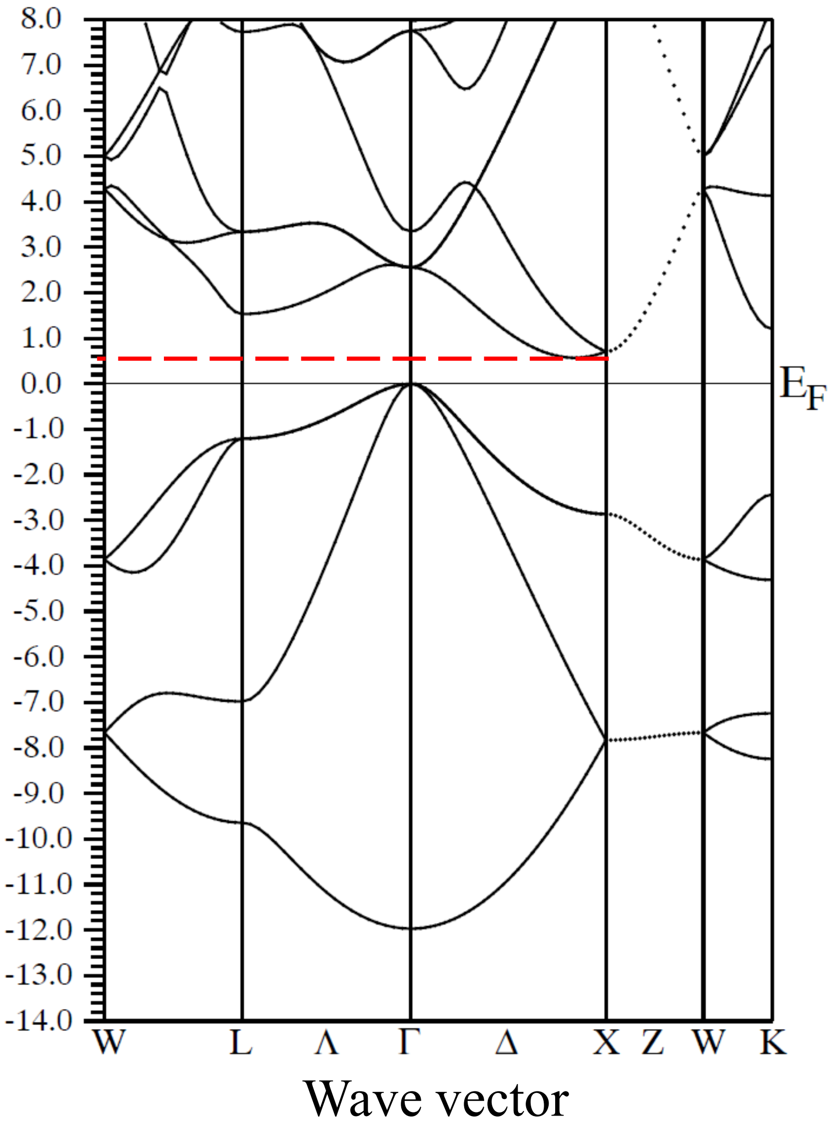
Γ: *k* = (0, 0, 0) (unit may be in e.g. 1/*a*)

X: (1/2, 0, 0)

Z: (0, 0, ½)

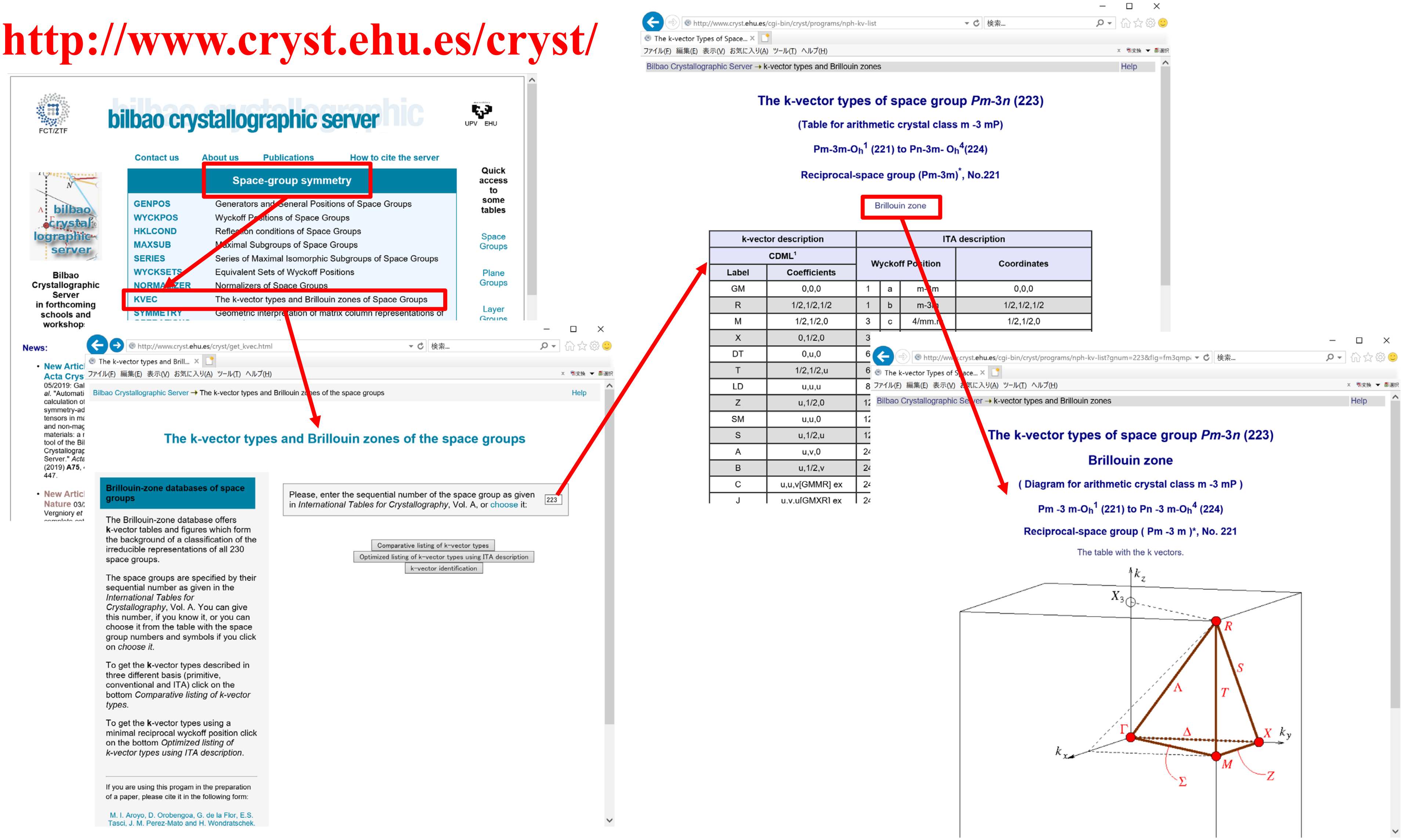
1st BZ for FCC





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

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



Bilbao Crystallographic Server in forthcoming schools and workshops

News:

- **New Articl Acta Crys** 05/2019: Gal *al.* "Automati calculation of symmetry-ad tensors in ma and non-mag materials: a r tool of the Bil Crystallograp Server." *Acta* (2019) **A75**, 447.
- **New Articl Nature** 03/ Vergniory *et*

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

Bilbao Crystallographic Server → The k-vector types and Brillouin zones of the space groups

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

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			

Bilbao Crystallographic Server → k-vector types and Brillouin zones

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)*

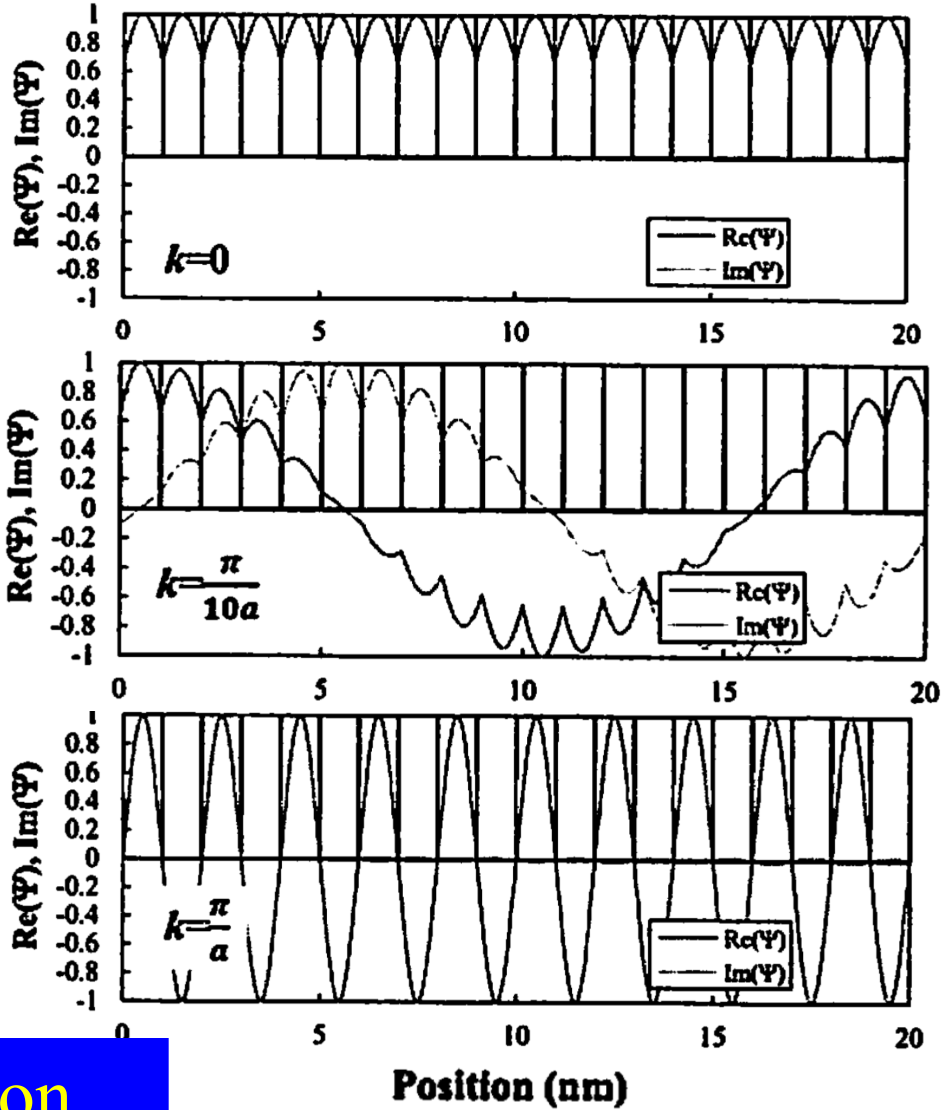
Γ (***k***=0) : Bonding

Arbitrary ***k*** ≠ 0 :

Considering many unit cells

BZ boundary : }

Anti-bonding



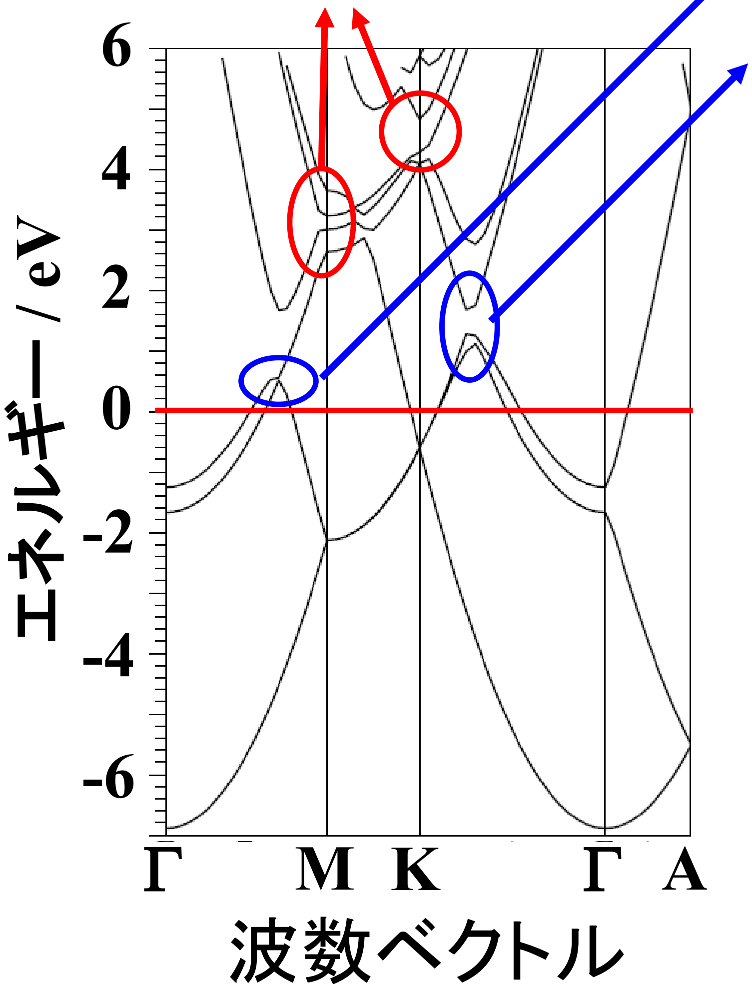
Shape of crystal wave function is very different depending on *k*

Band structure: metal

Mg

E_g by free electron model:

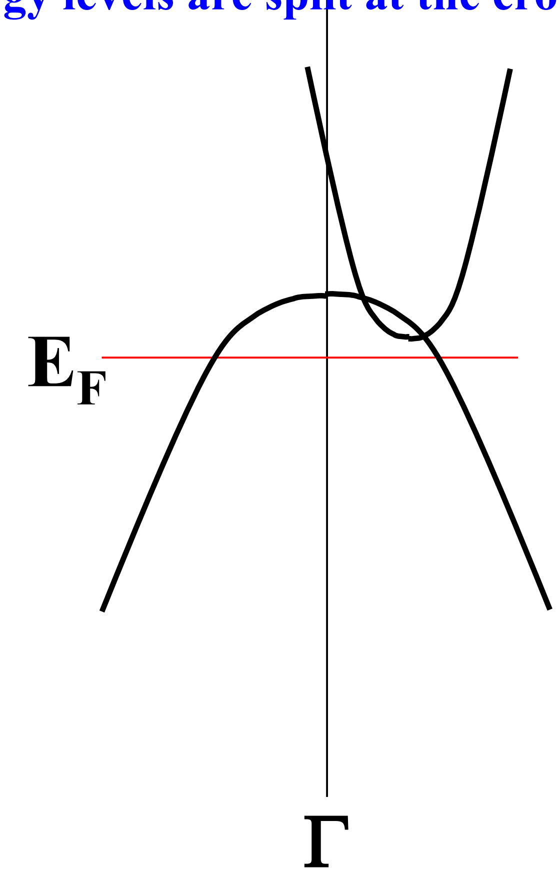
Bragg diffraction



Two bands are crossing

=> Different symmetry

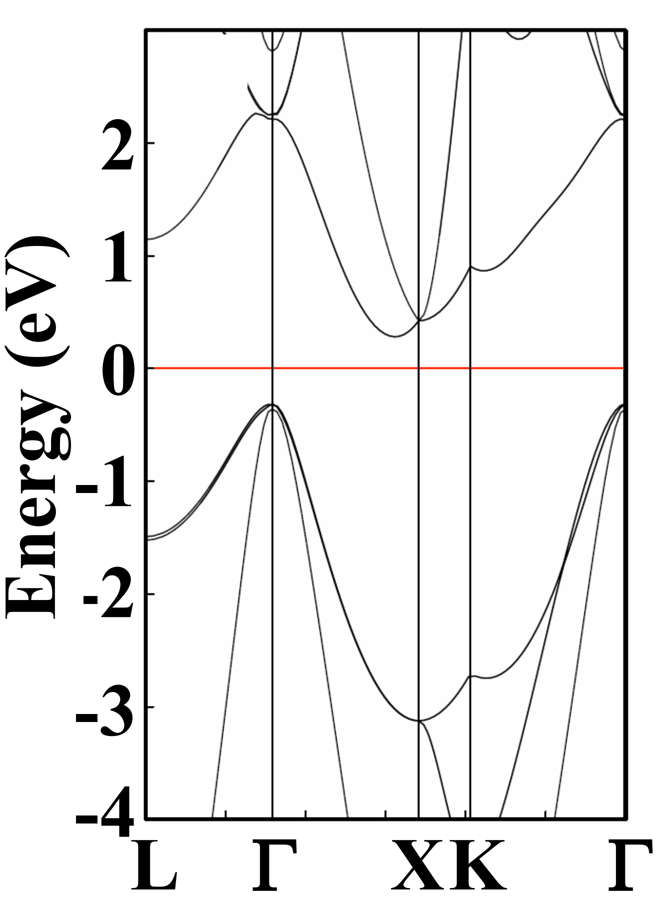
If two wave functions with the same symmetry,
the energy levels are split at the crossing point

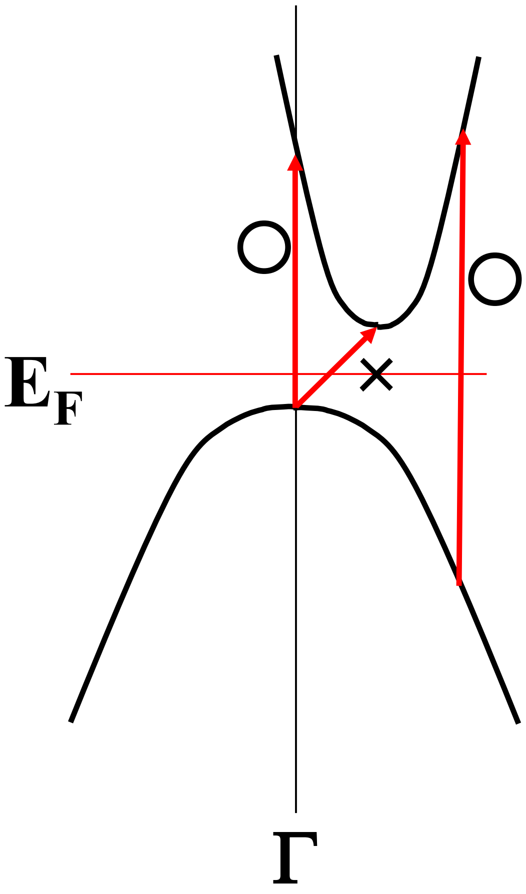


Band structure: Semiconductor

Si Indirect-transition type:

Optical absorption coefficient is very small near the fundamental bandgap





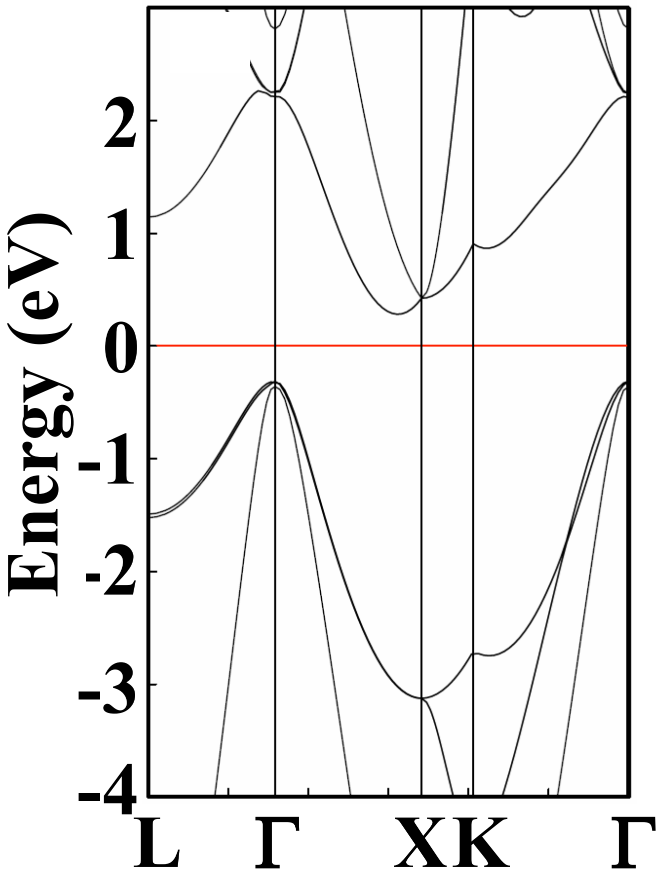
Band structure: Semiconductor

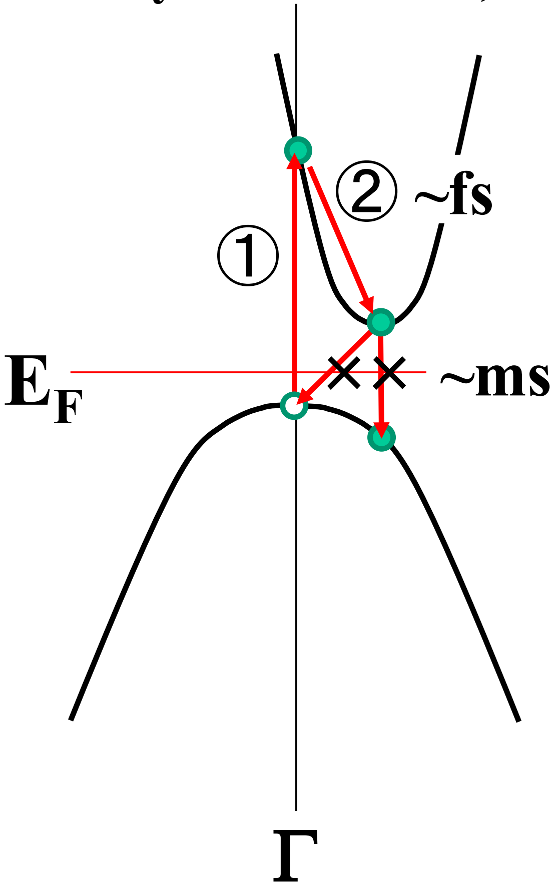
Si Indirect-transition type:

Weak optical absorption, not good for solar cell

Slow recombination, good for solar cell

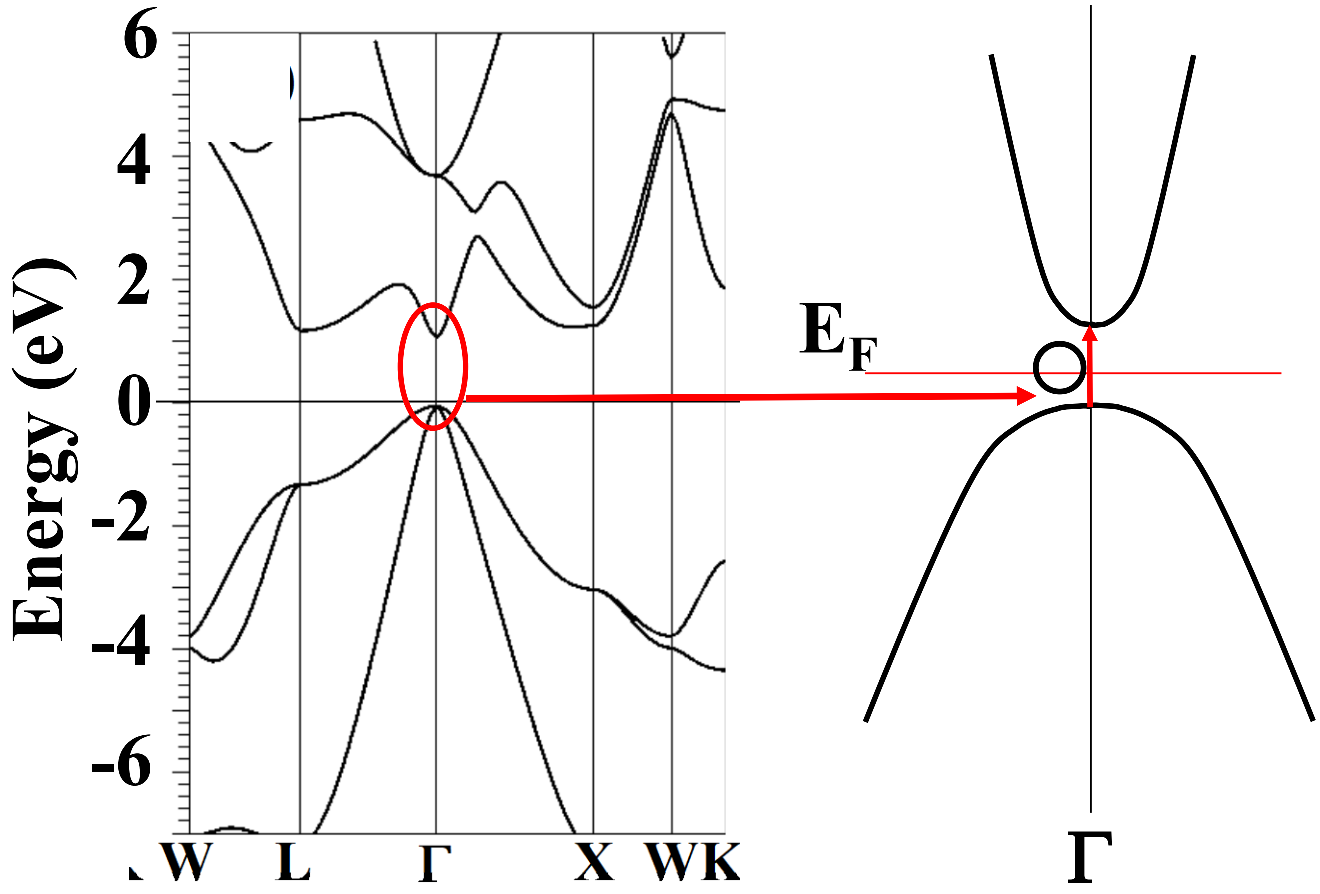
Non-radiation recombination may be dominant, bad for LED





Band structure: Semiconductor

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

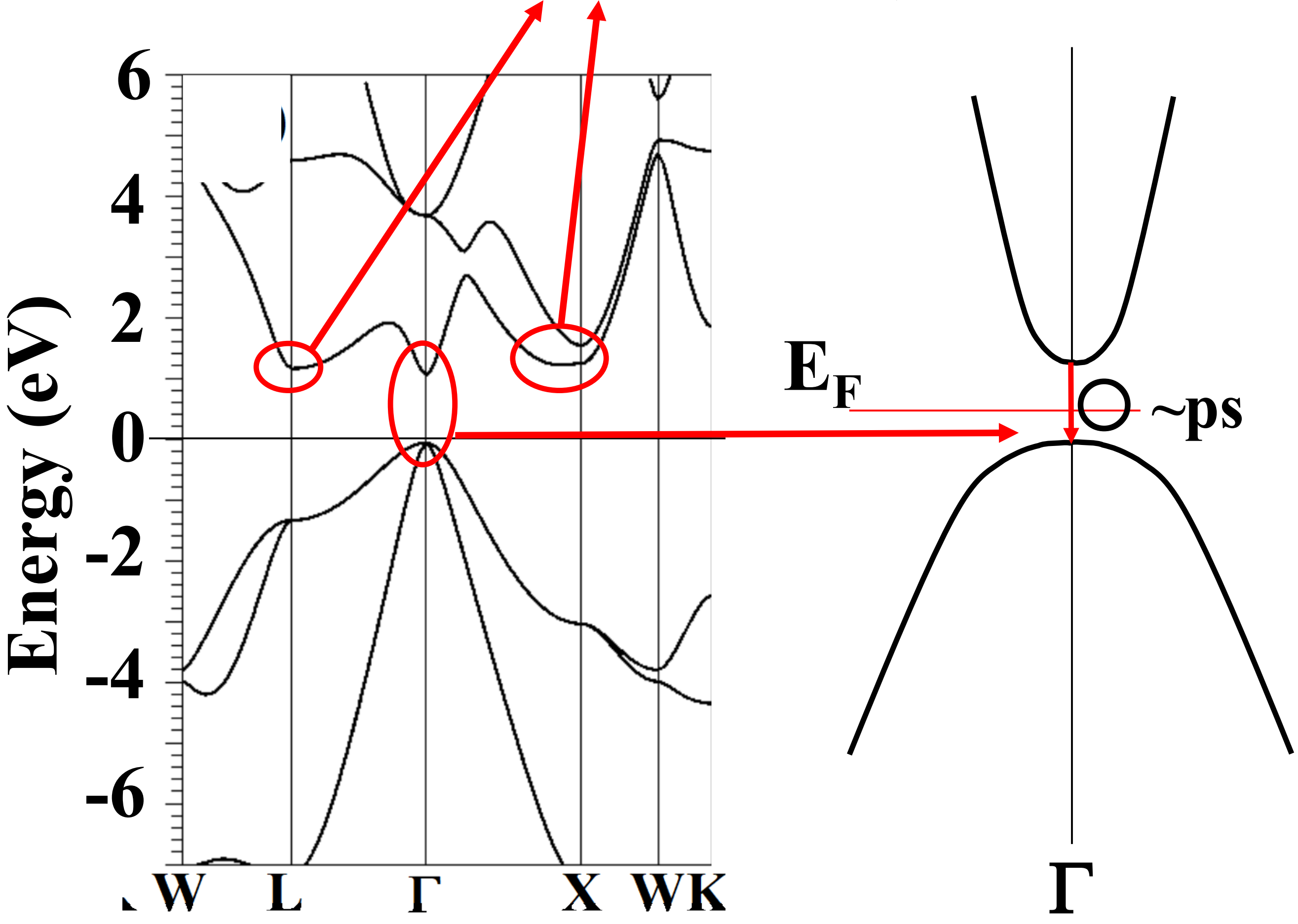


Band structure: Semiconductor

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^*.

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

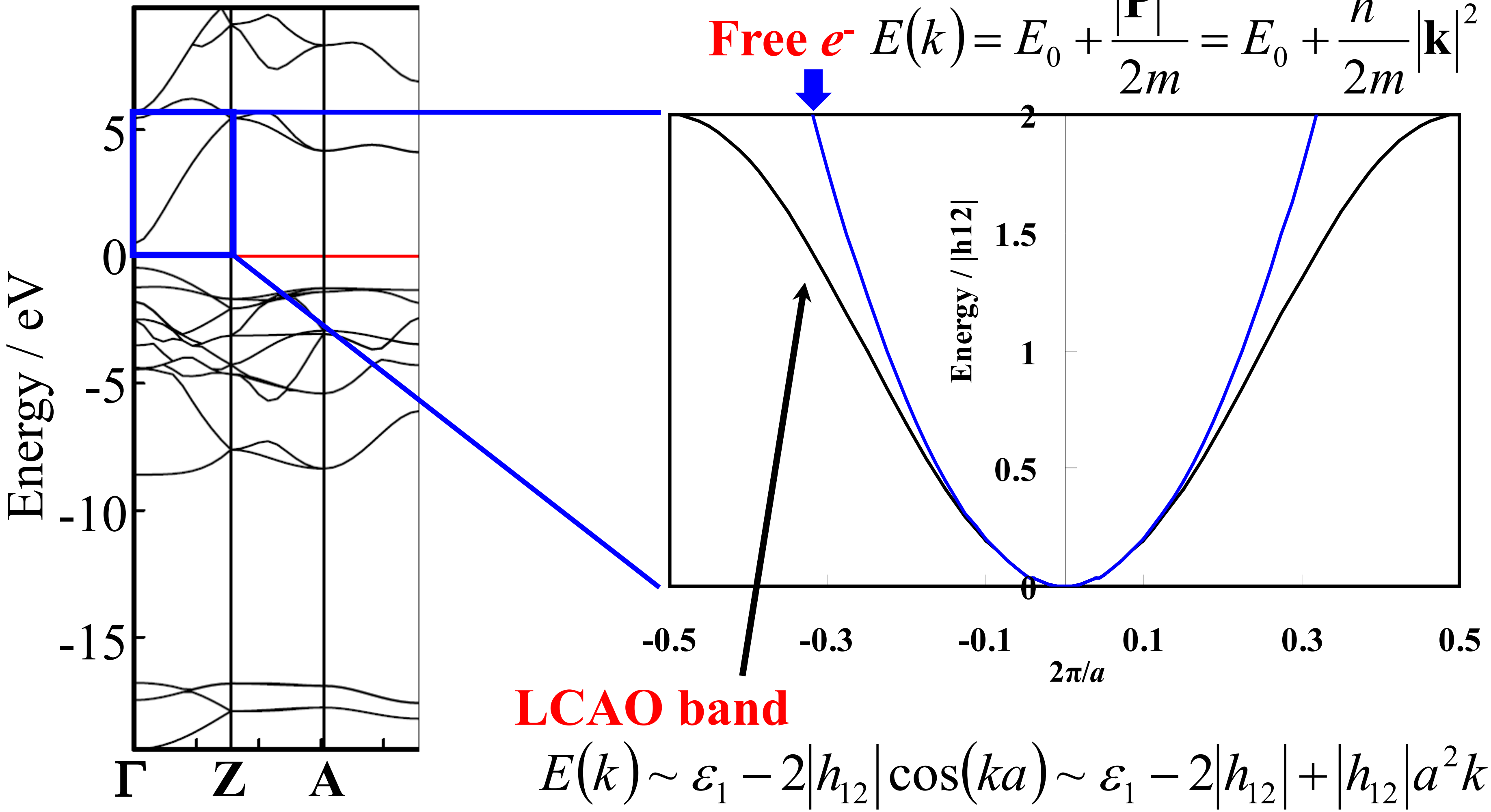
Thermal velocity $\frac{1}{2} m_e^* v_{th}^2 = \frac{3}{2} k_B T$ $v_{th} = \sqrt{3k_B T / m_e^*}$

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

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

Band structure of SnO$_2$



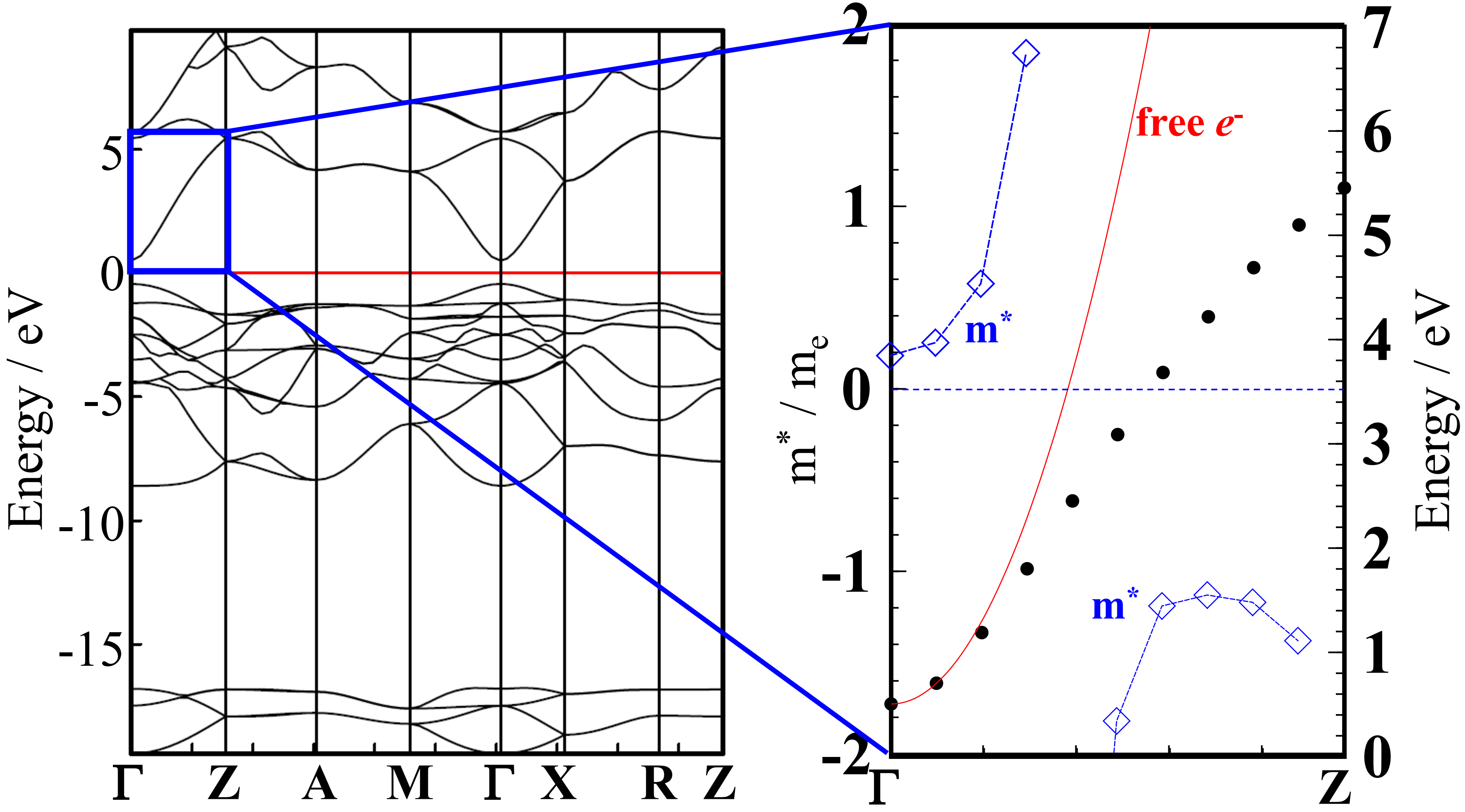
Free e^- $E(k) = E_0 + \frac{|\mathbf{P}|^2}{2m} = E_0 + \frac{\hbar^2}{2m}|\mathbf{k}|^2$

LCAO band

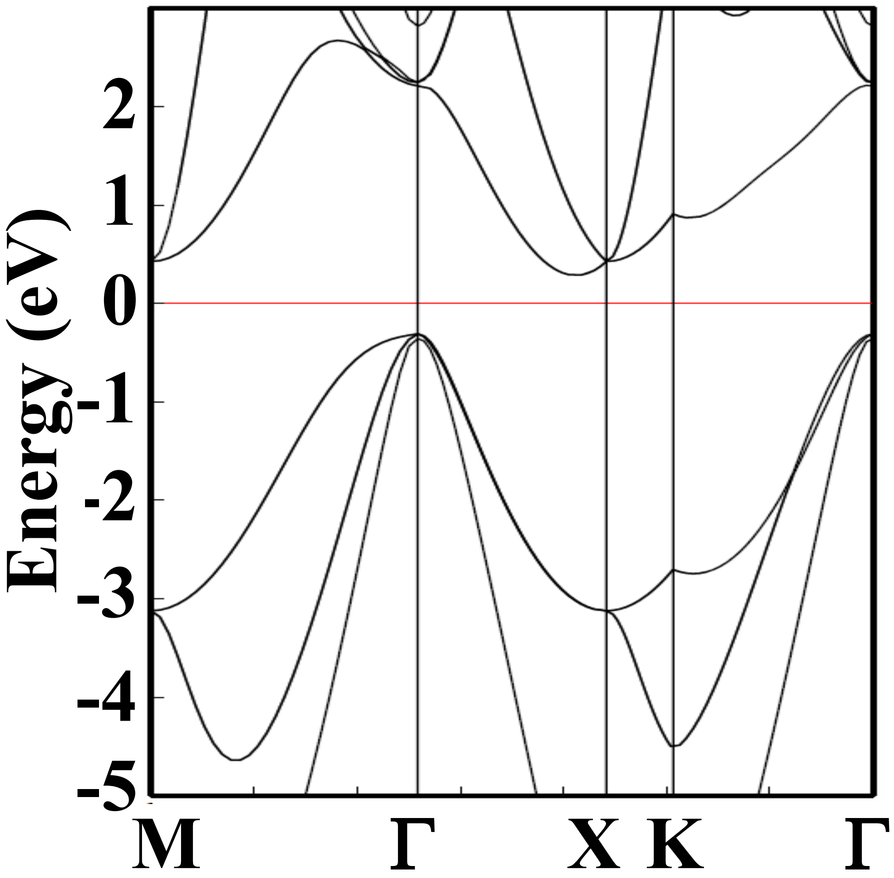
$$E(k) \sim \varepsilon_1 - 2|h_{12}|\cos(ka) \sim \varepsilon_1 - 2|h_{12}| + |h_{12}|a^2k^2$$

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>)**

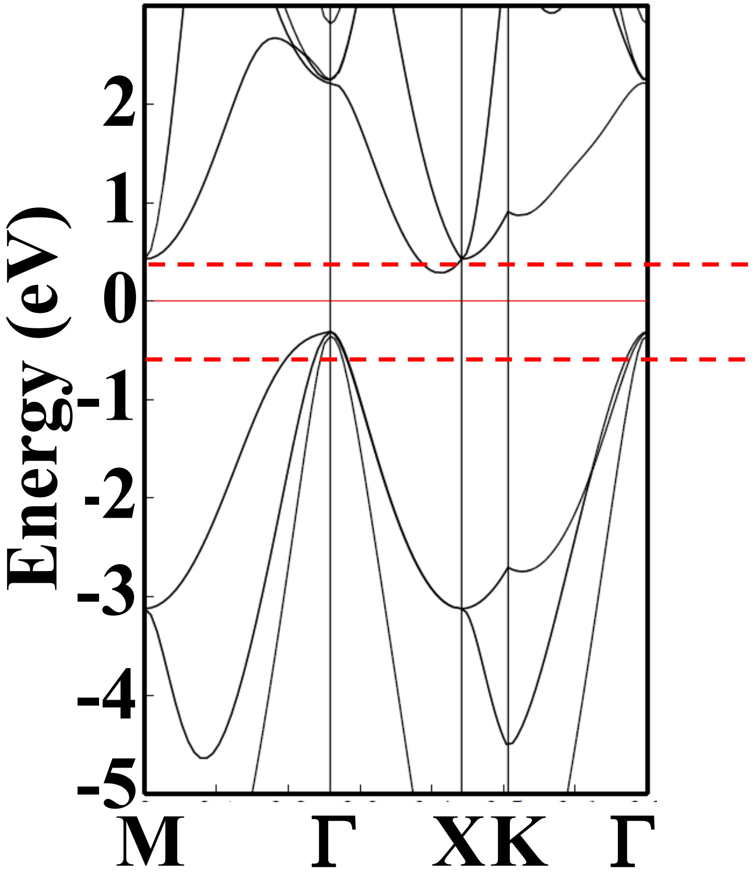
Split off hole band

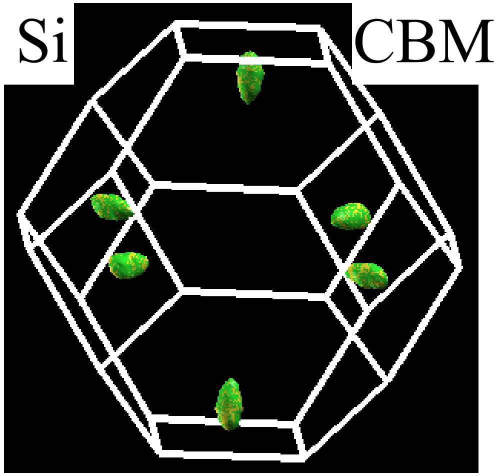
$0.14m_e$ **(<110>)** $0.22m_e$ **(<100>)**

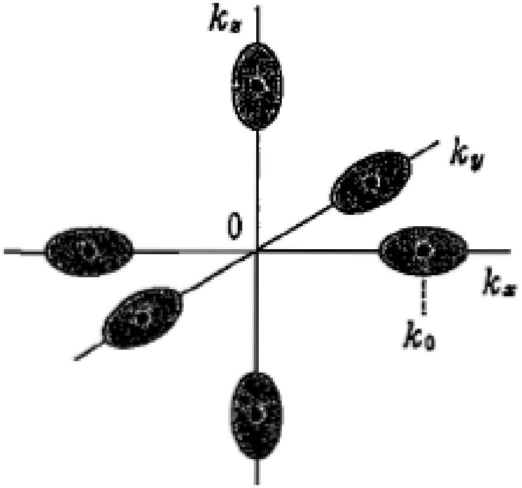
***k·p* perturbation method**

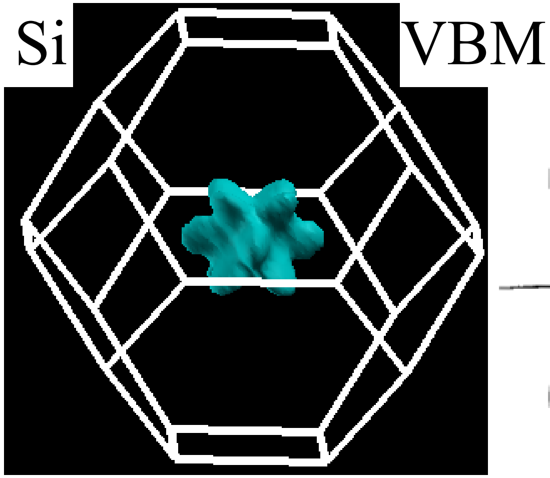
$$m_e^* = \left(1 + 2P^2 / m_e E_g\right)^{-1} m_e$$

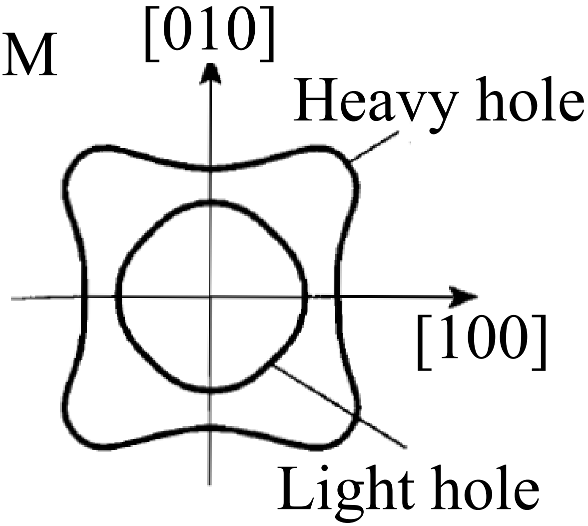
Fermi surface of Si











Widened Fermi surface

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

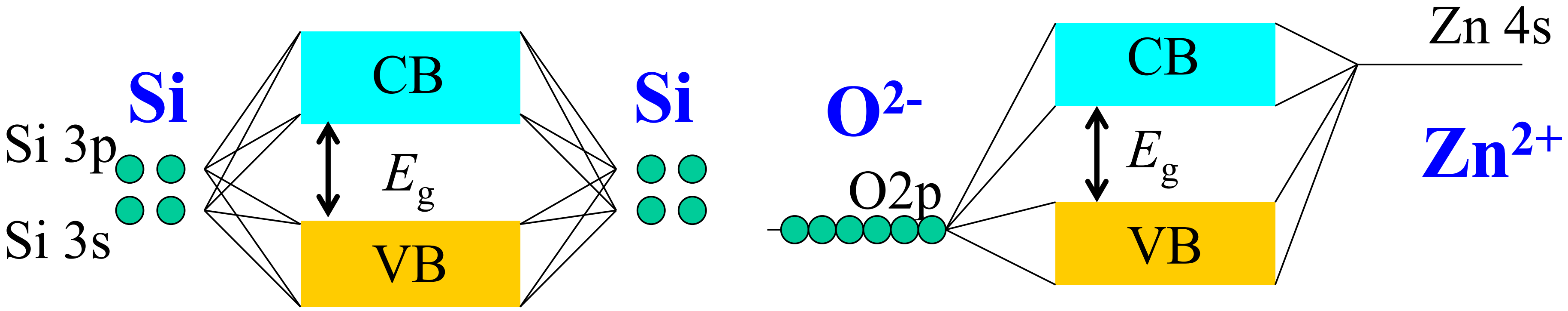
=> Larger effective mass

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

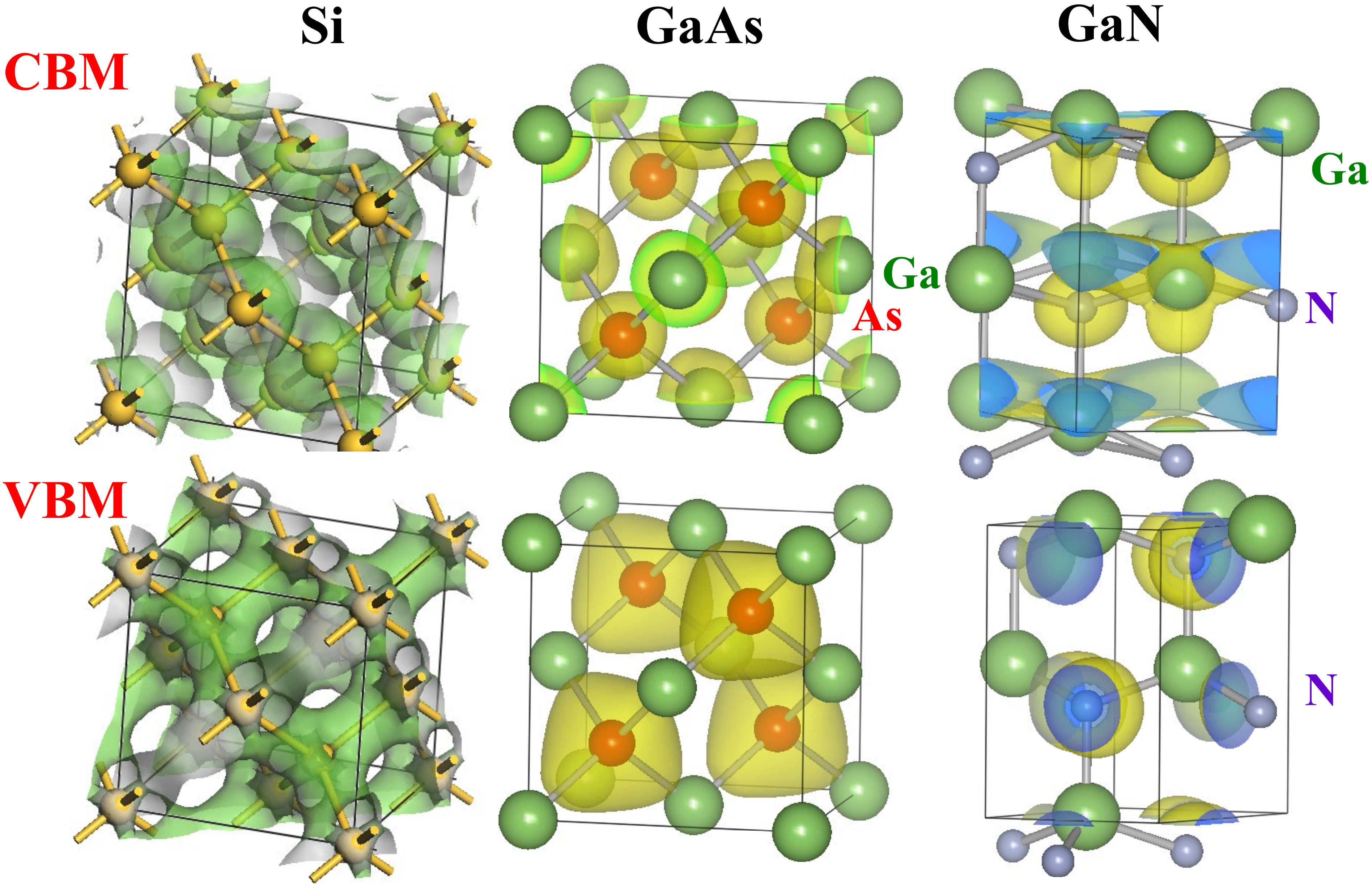
Origins of bandgap

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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   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

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

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

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

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

$$x_\sigma = \boxed{\left|\nabla\rho_\sigma\right|} / \rho_\sigma^{\frac{4}{3}} \qquad E_{XC} = E_{XC}^{LSDA} - b\sum_\sigma \int \rho_\sigma^{\frac{4}{3}} \frac{x_\sigma^{2}}{1 + 6bx_\sigma \sinh^{-1} x_\sigma} dv + E_X^{NL}$$

Exact exchange:

Hartree-Fock exchange potential

Functionals

LDA/LSDA:

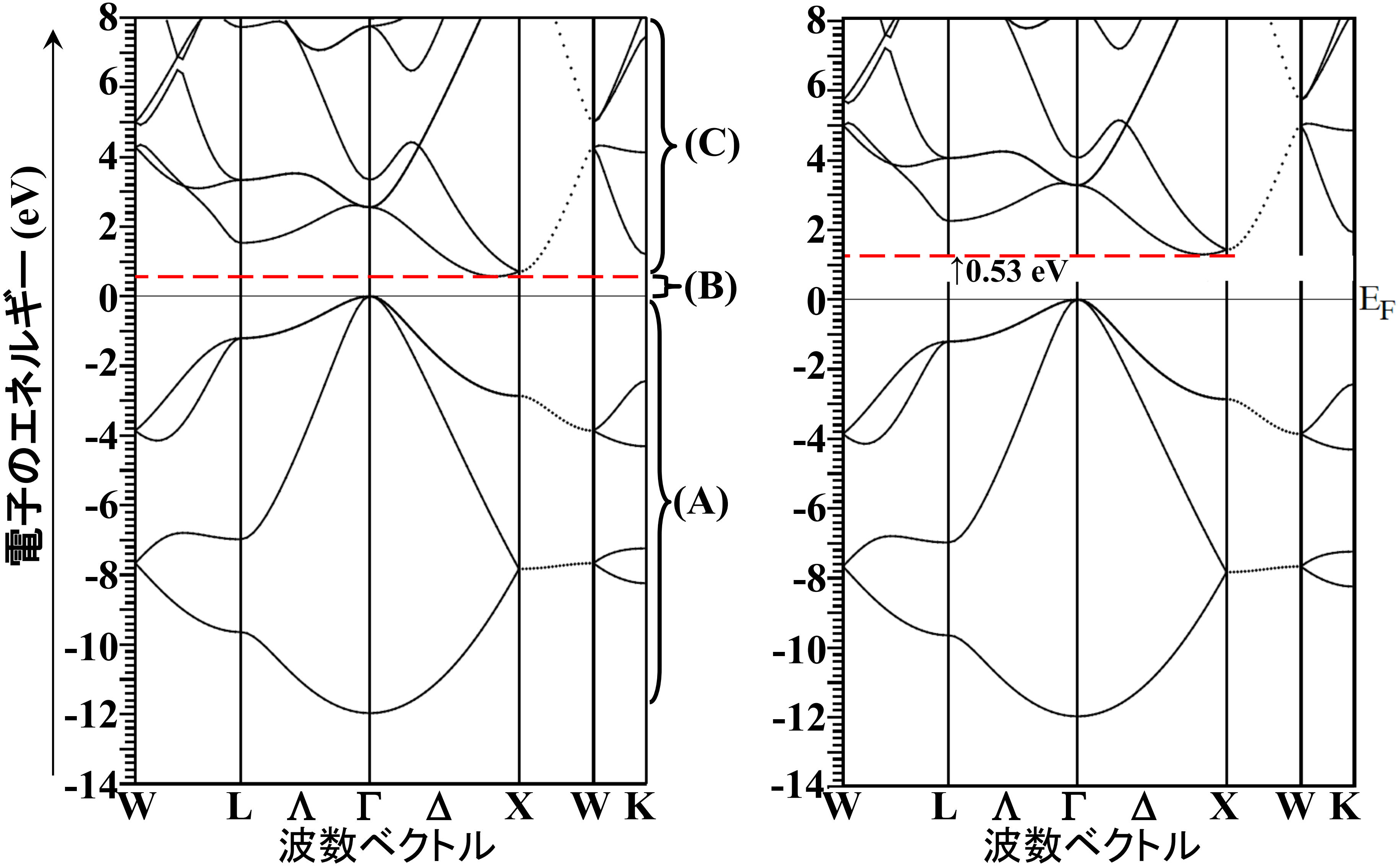
- **CA** (Ceperley-Alder)/PZ (Perdew-Zunger) [Perdew and Zunger, Phys. Rev. B **23** (1981) 5048]
- **PW92** (Perdew-Wang 92) [J.P. Perdew and Y. Wang, Phys. Rev. B **45** (1992) 13244]

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]

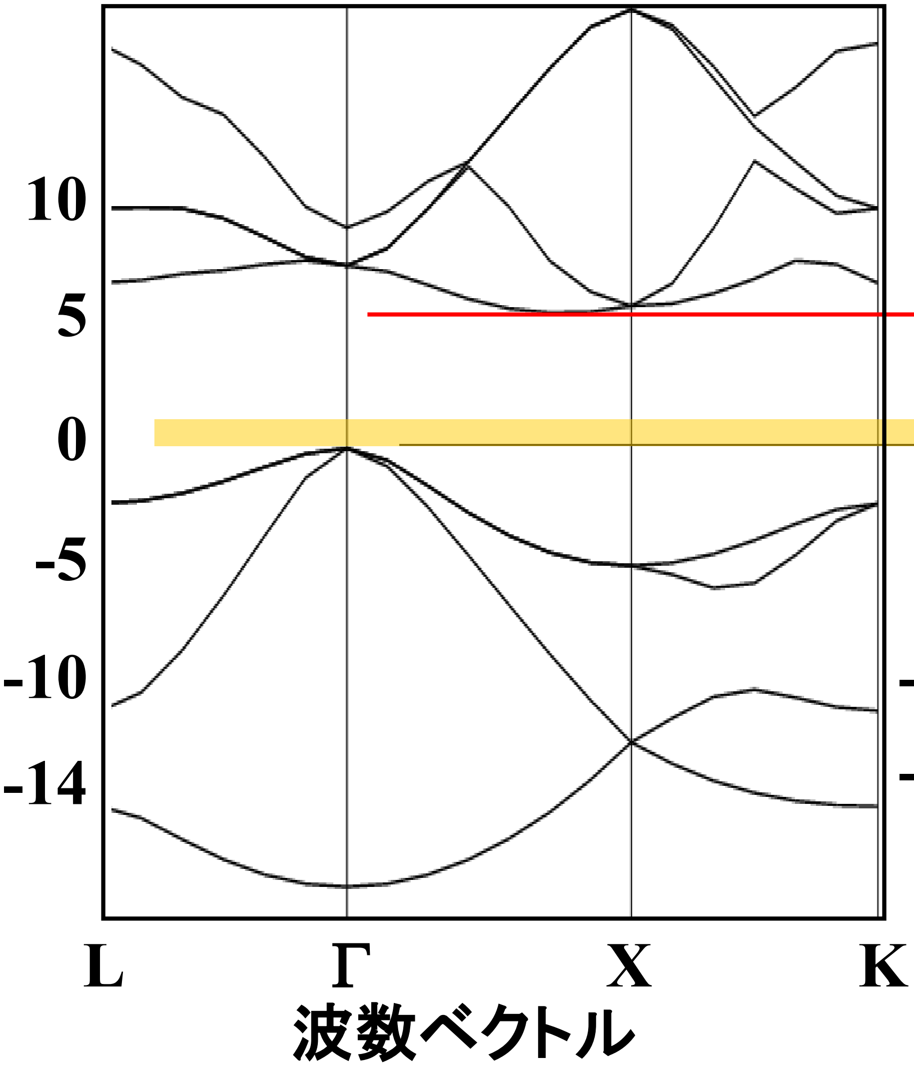
Bandgap problem

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

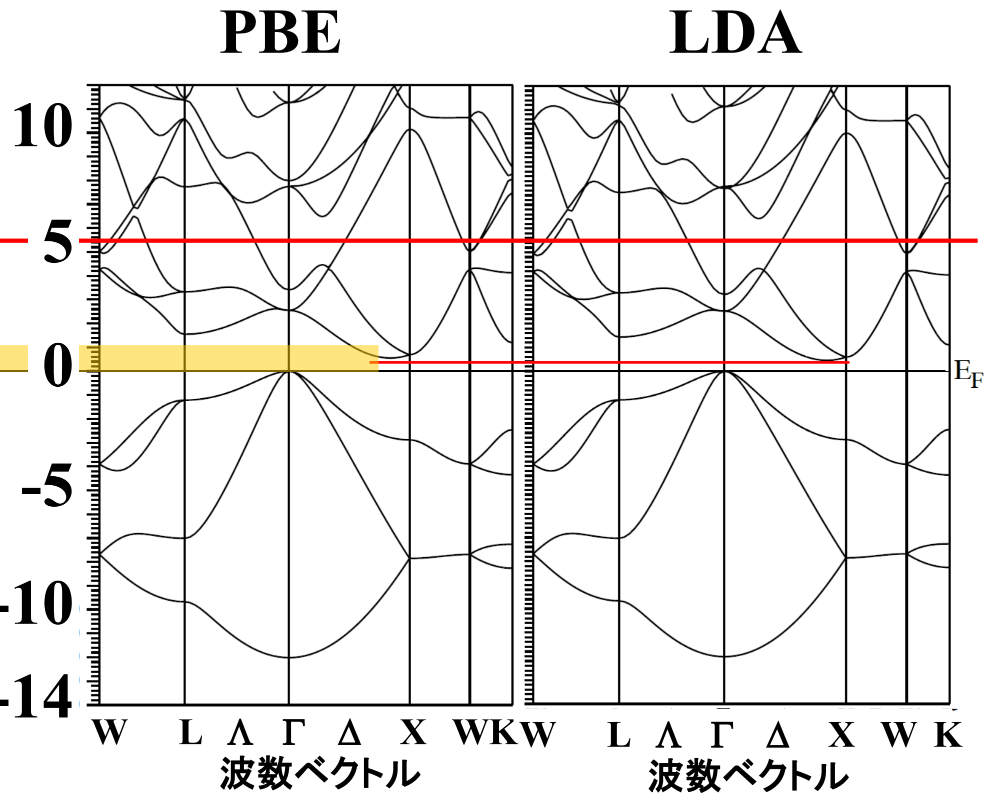


Bandgap problem: HF vs DFT

HF (CRYSTAL06, 3(6)-21G)



DFT (WIEN2k)



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 ω → 0: **PBE0** ω → ∞: **PBE96 (GGA)**

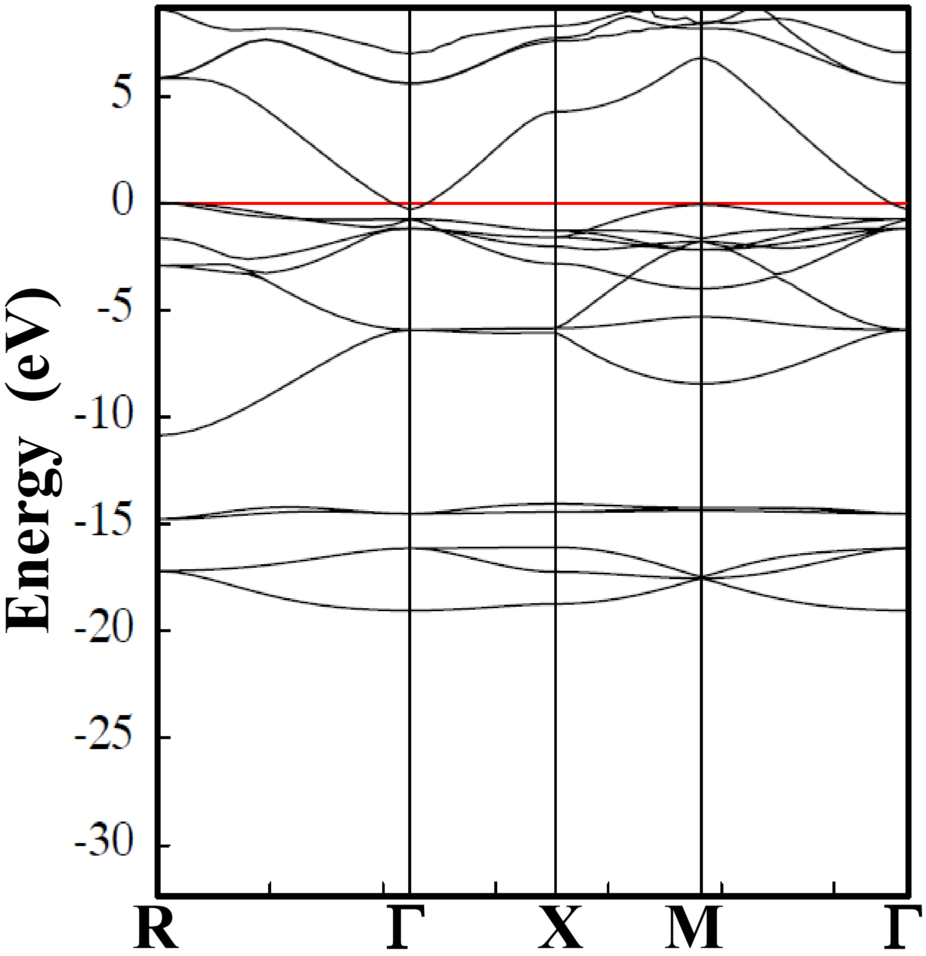
(sometimes adjusted so as to reproduce observed bandgap)

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*

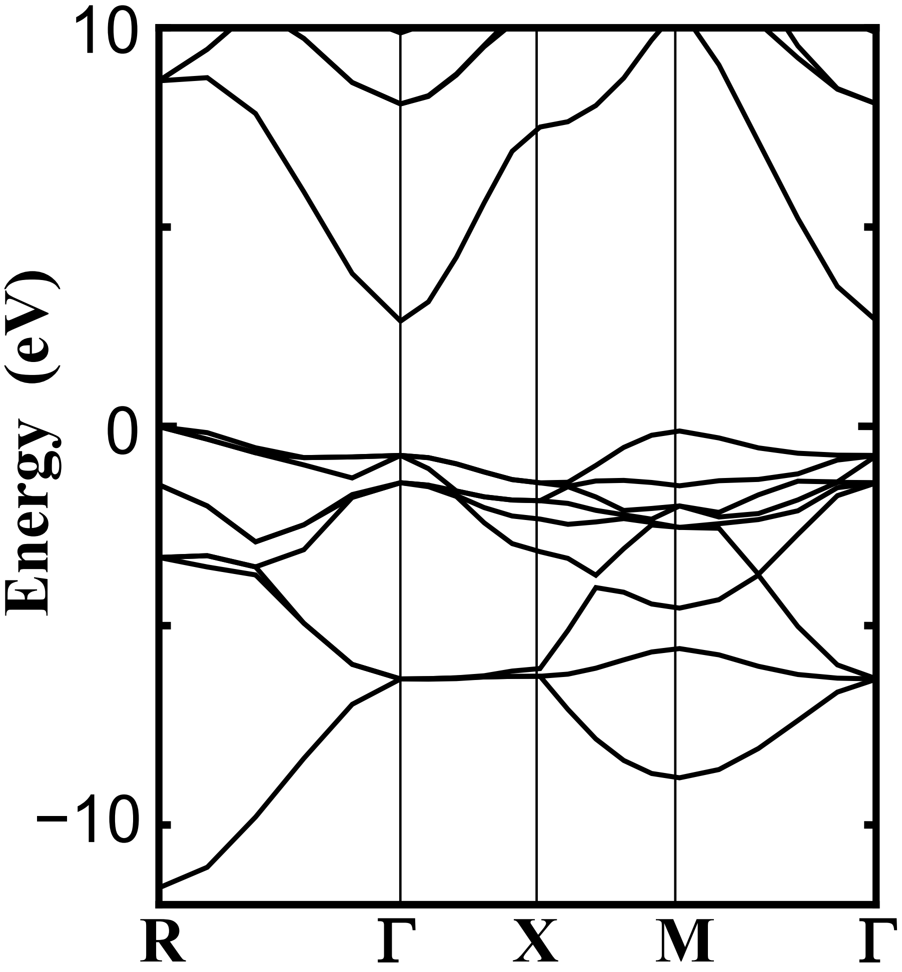
Band structures of cubic SrGeO$_3$

GGA (PBE96)



Negative bandgap !!

PBE0



Exp. $E_g \sim 2.7$ eV

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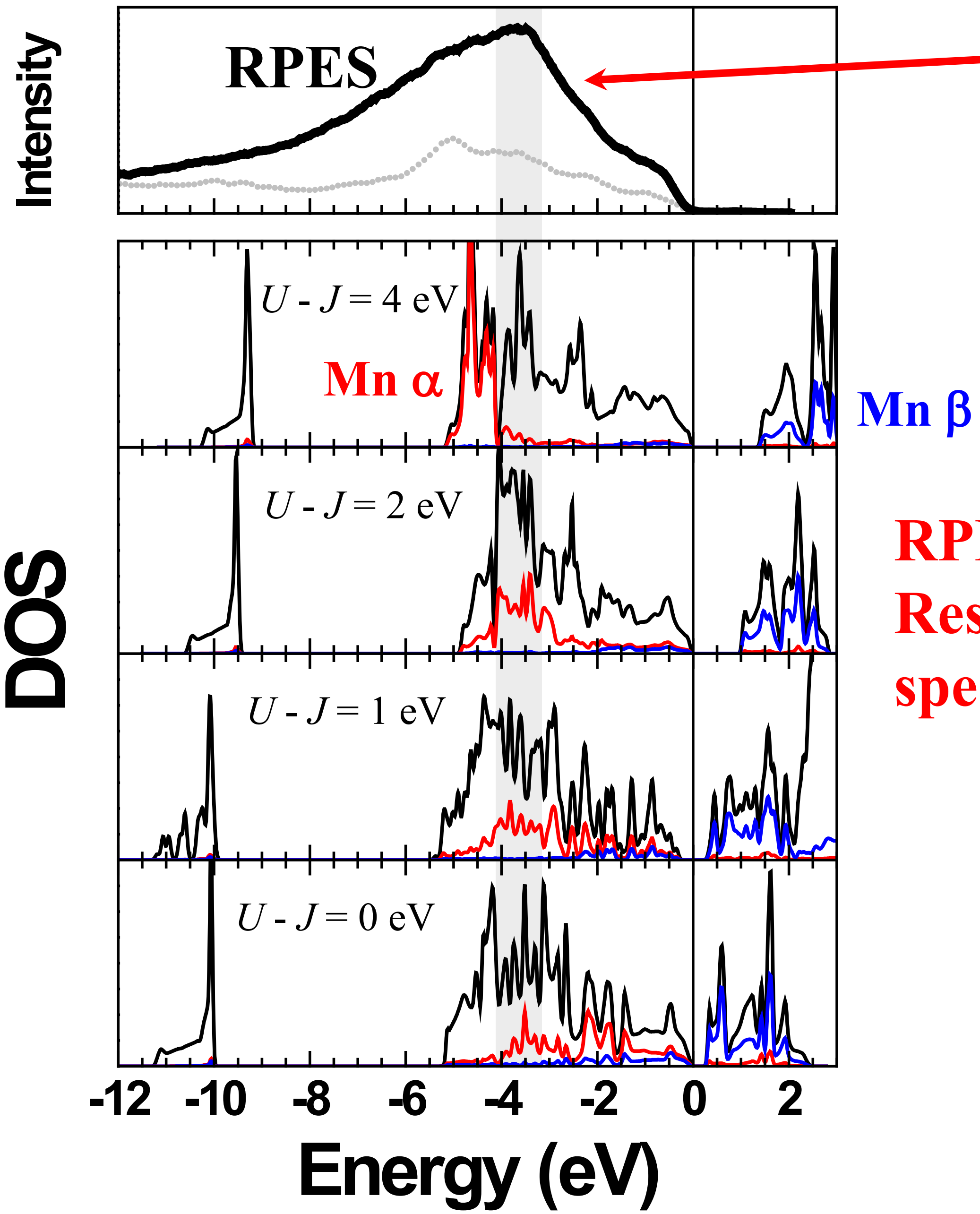
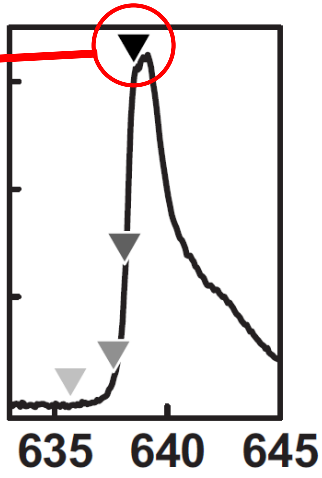
   Important e.g. for Peiels transition
4. Strong **electron correlation** materials
   Eg can not be explained by one-electron mean-field approximation such as DFT.
   Important for d and f electrons systems.
   Can be treated by beyond DFT methods like LDA/GGA+U, GW approximations.

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

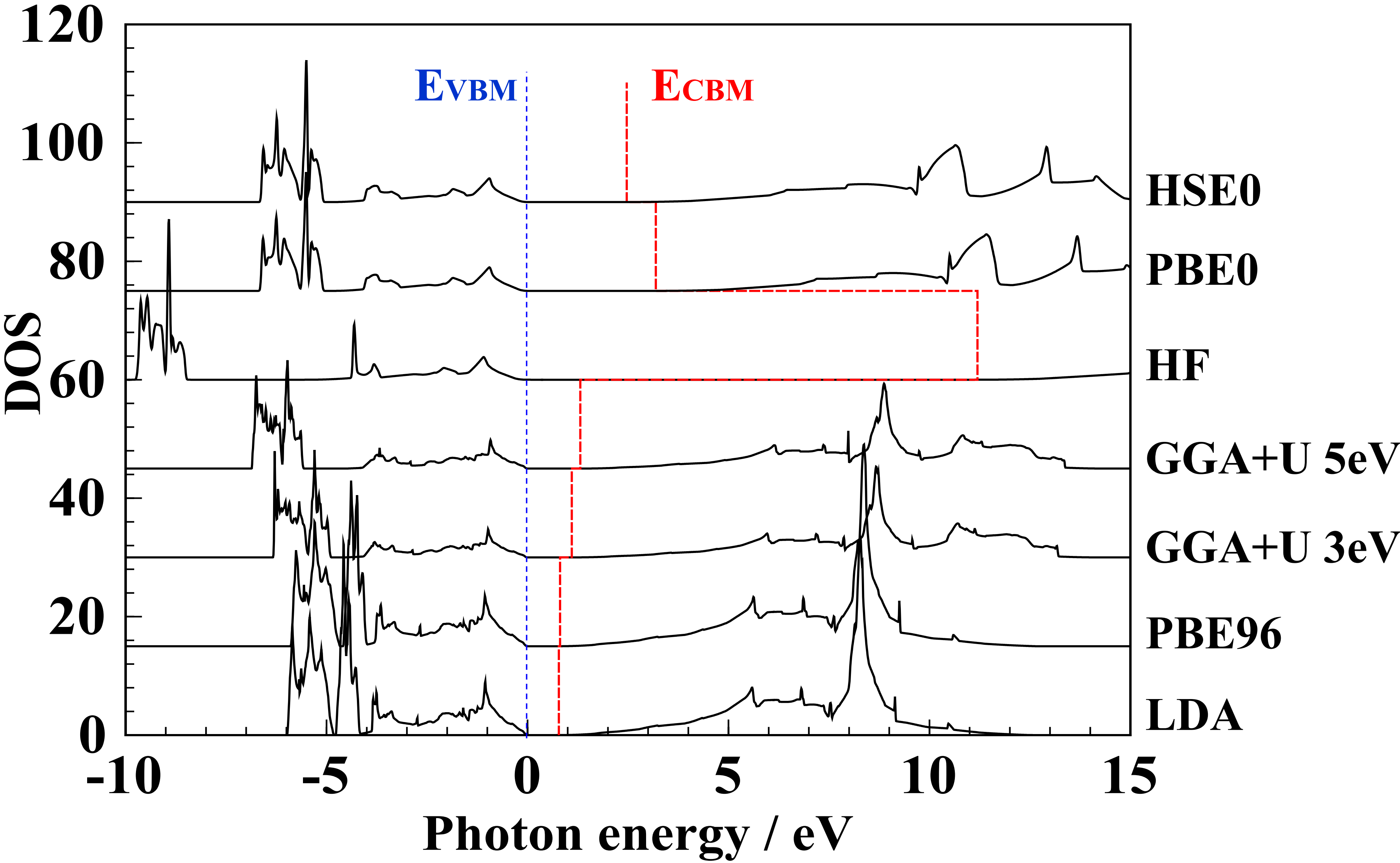




RPES:
Resonant photoemission spectroscopy

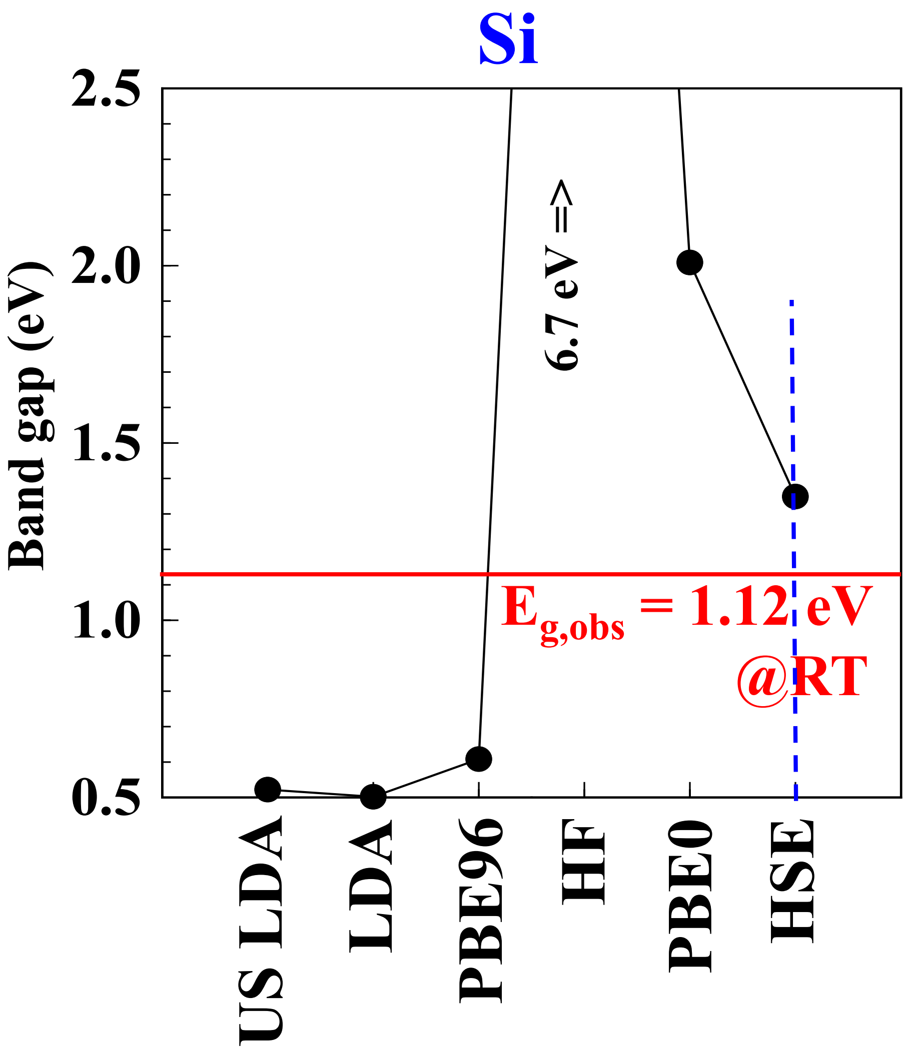
Effects of functional and *U*: ZnO

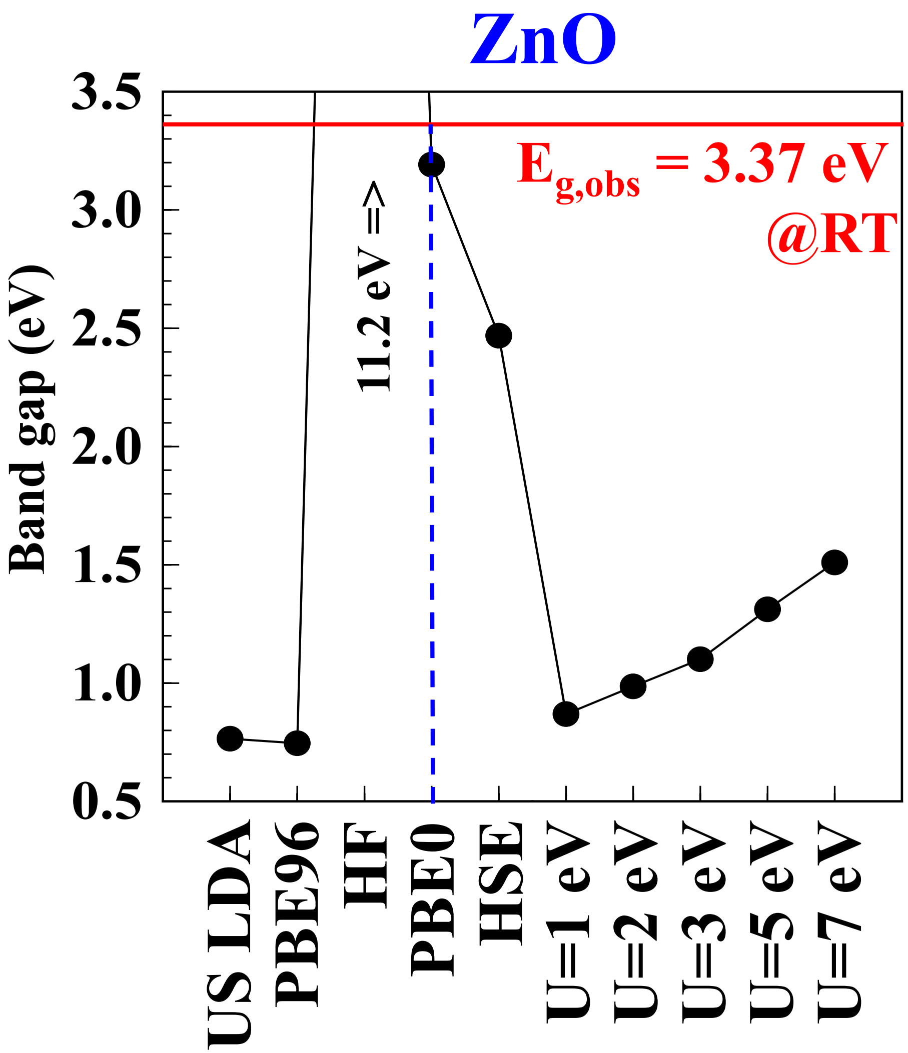
VASP



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)

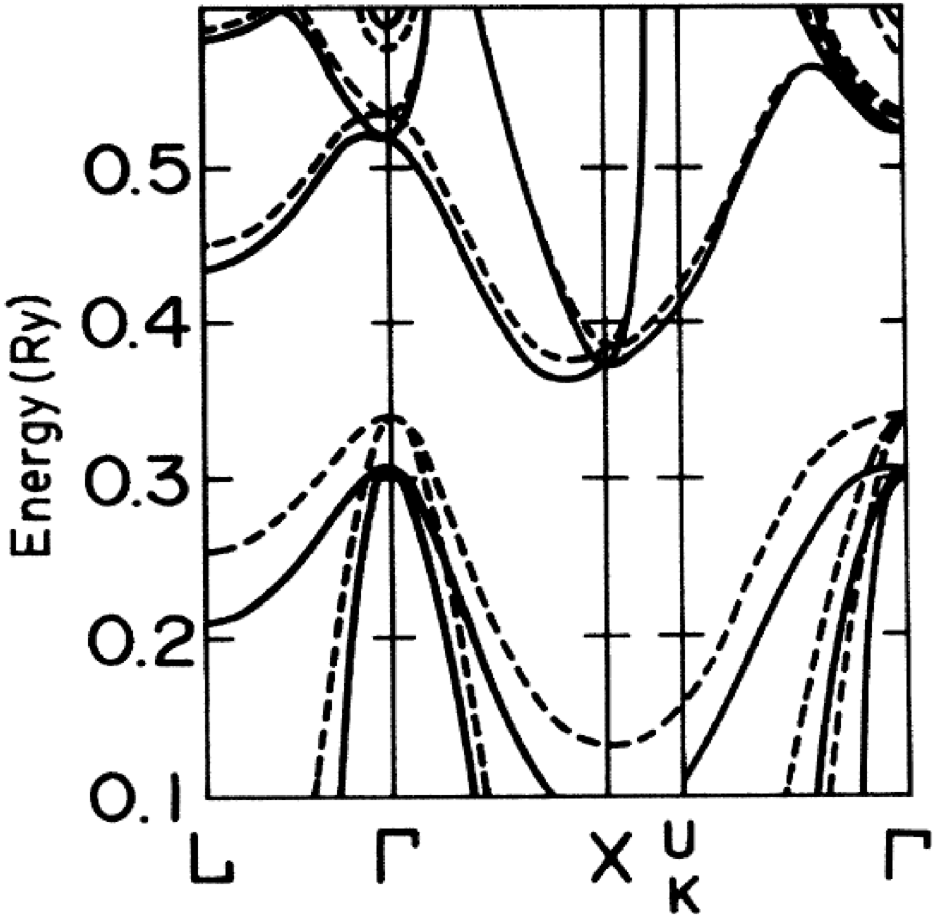
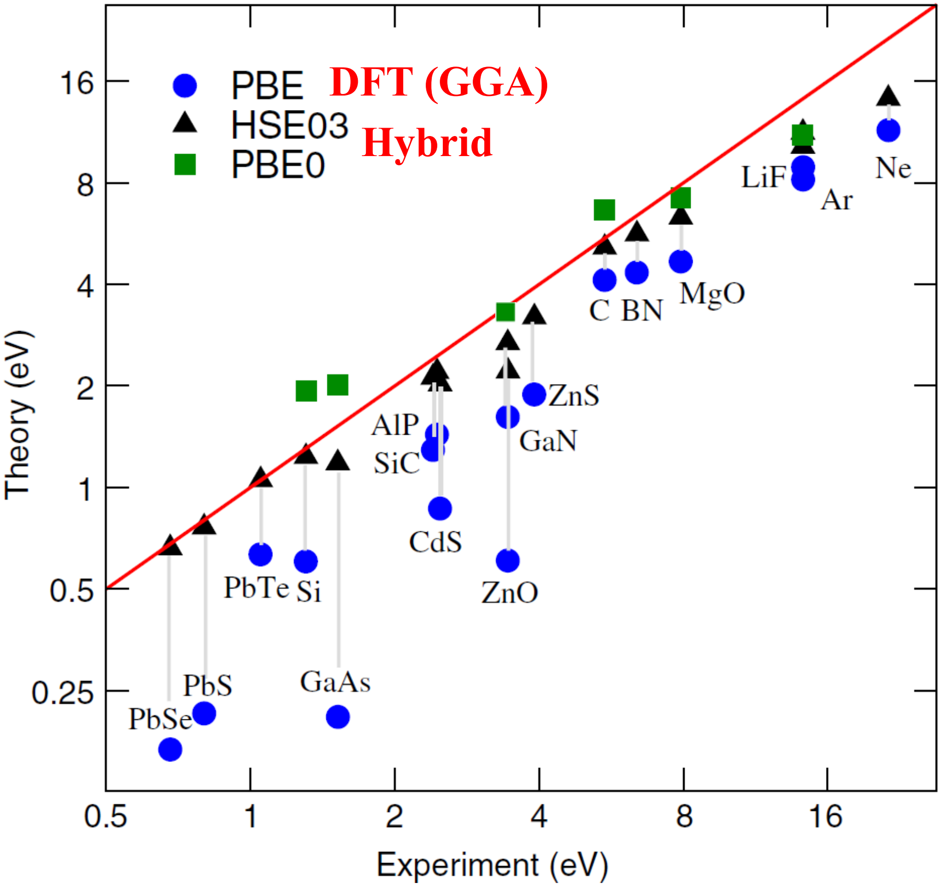


FIG. 1. Energy band structures of Si along high symmetry lines. Solid curves represent the SIC-LDA calculation, and dashed curves the LDA. Fundamental energy band gap is given by the difference between the conduction band minimum near *X* point and the valence band top at Γ point. Note that the energy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

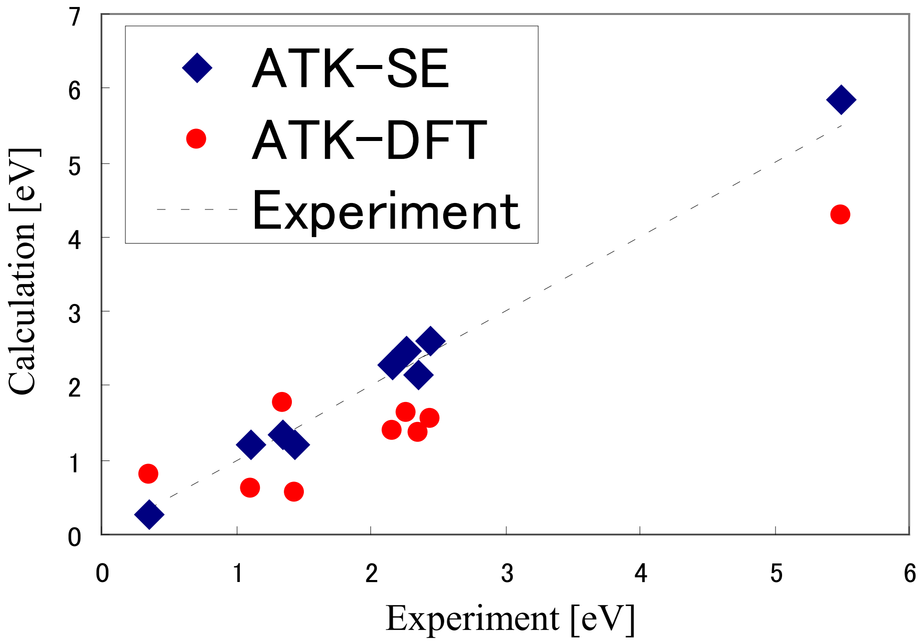
[Japanese] 大橋直樹監修、バンドギャップエンジニアリング －高効率デバイスへの挑戦－
大場史康、*第4章　半導体の物性シミュレーション*(シーエムシー出版)
M. Marsman et al, J. Phys.:Condens. Matter, ***20****, 064201 (2008)*



DFT (GGA)

Hybrid

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)

$$\mathcal{H} = \mathcal{H}_{\mathbf{0}} - \boldsymbol{e}\boldsymbol{r} \cdot \boldsymbol{E}$$

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

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

Kramers-Kronig conversion

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

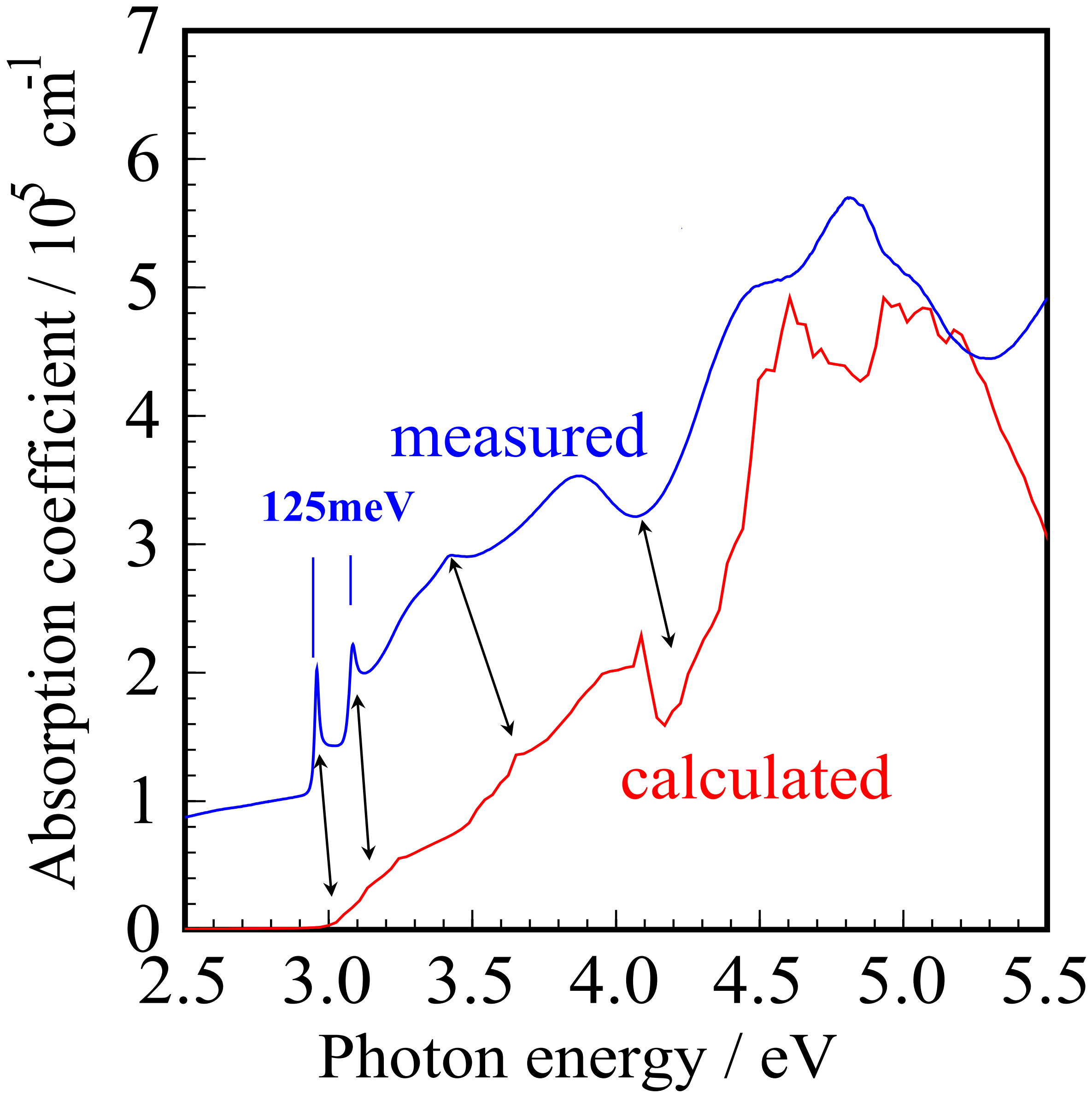
$$= \frac{4\pi N e^2}{m} \sum_j f_j \frac{\pi}{2\omega} \left[\delta\left(\omega - \omega_j\right) + \delta\left(\omega + \omega_j\right)\right]$$

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

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

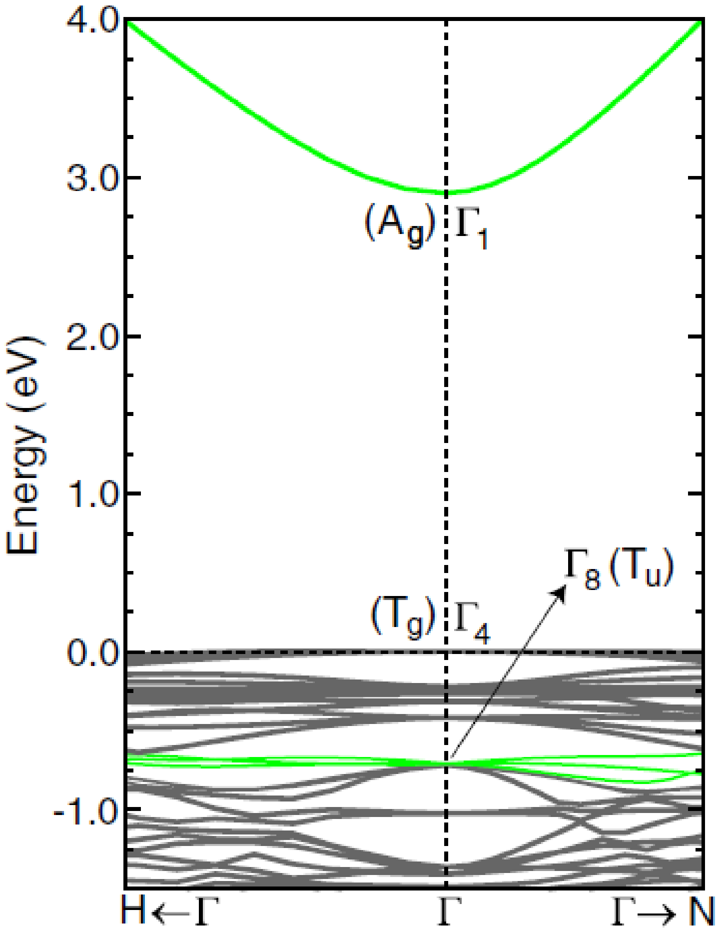
Optical spectra: LaCuOSe

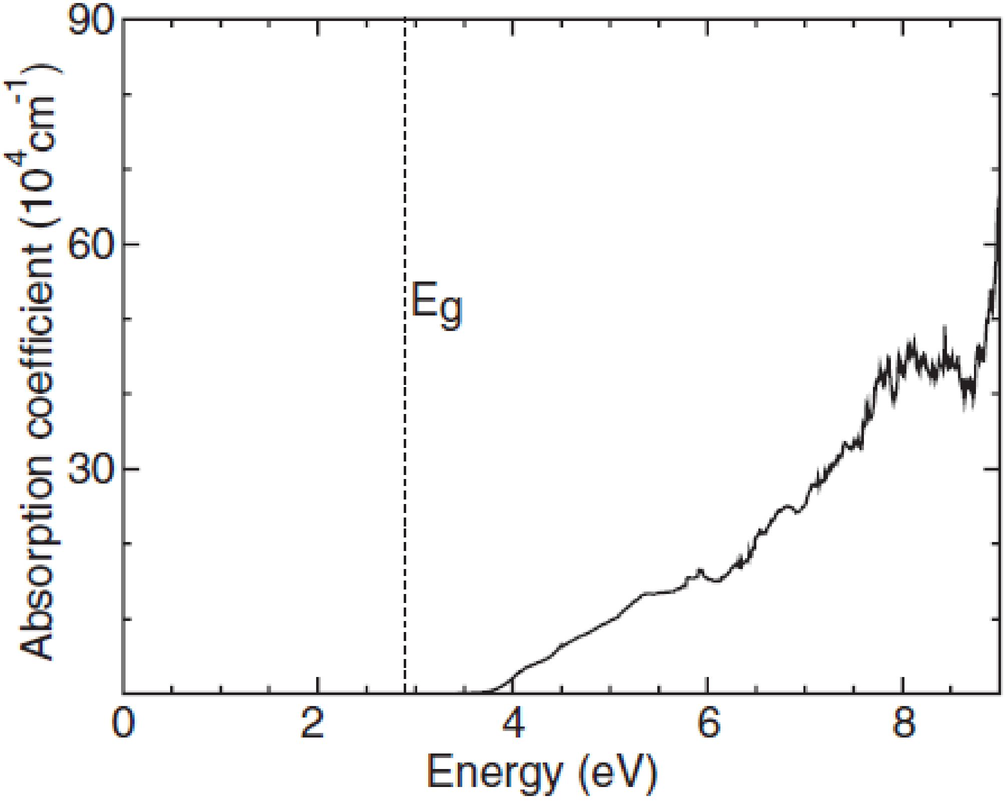
WIEN2k+OPTICS



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

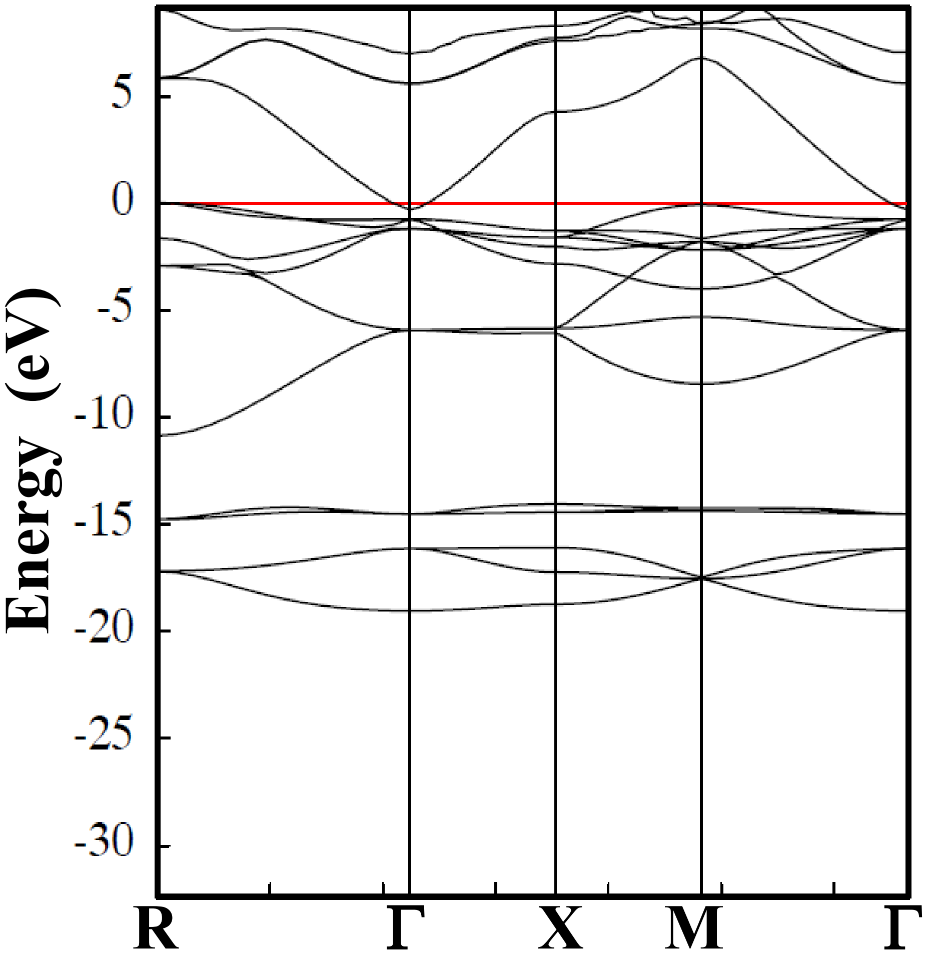




$$E_{ind} = 2.89 \text{ eV}$$
$$E_{dir} = 3.70 \text{ eV}$$

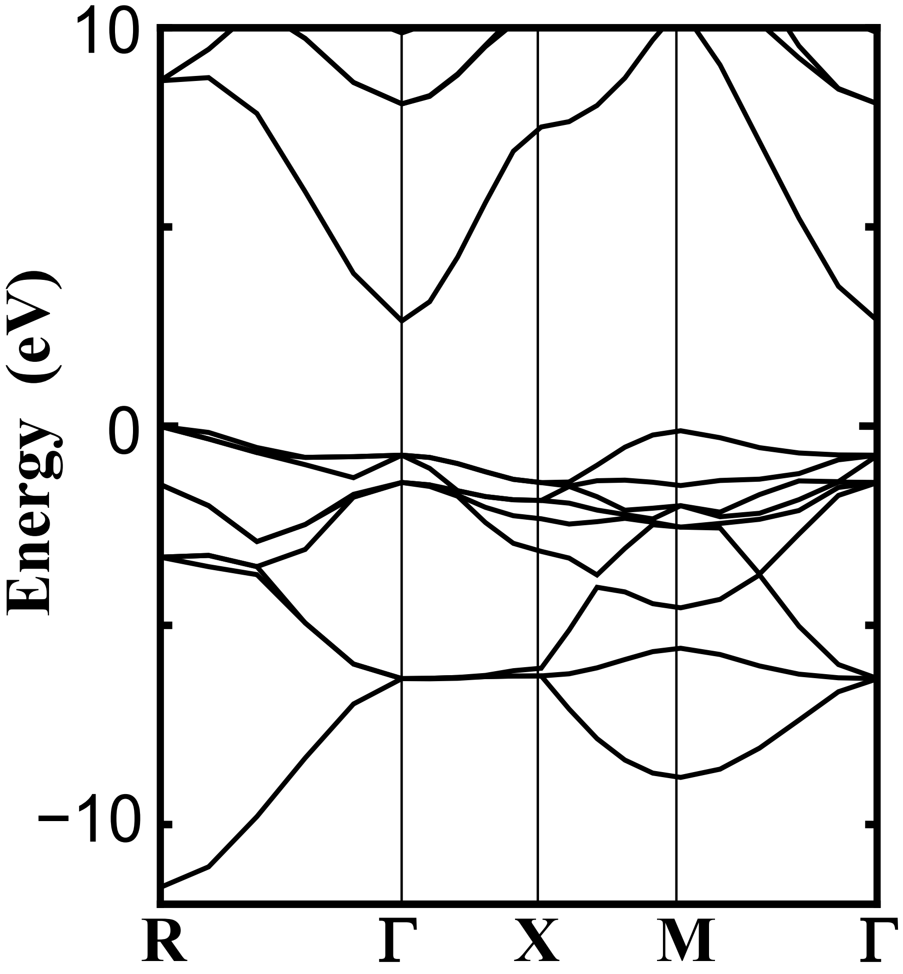
Band structures of cubic $SrGeO_3$

GGA (PBE96)



Negative bandgap !!

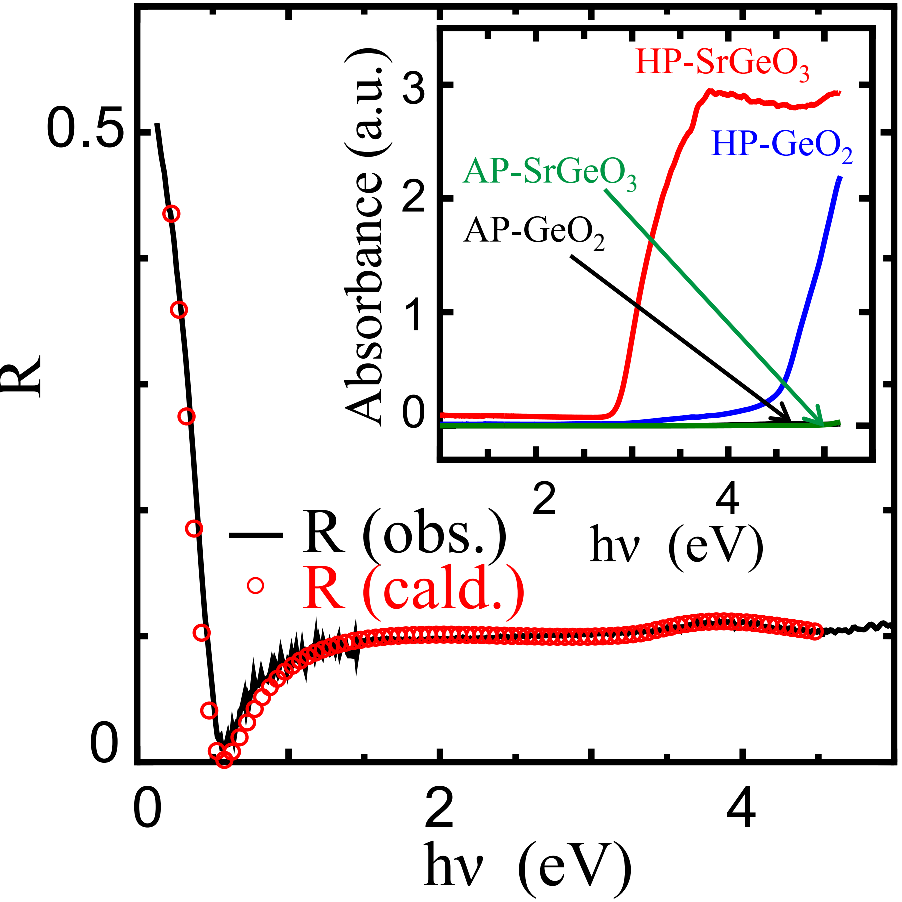
PBE0



Exp. $E_g \sim 2.7$ eV

Optical spectra og Ge-based oxides

Observed



PBE0