

# Optical Properties of Solids: Lecture 7

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Development and Education



# Optical Properties of Solids: Lecture 7+8

## Electronic Band Structure

Direct and indirect band gaps

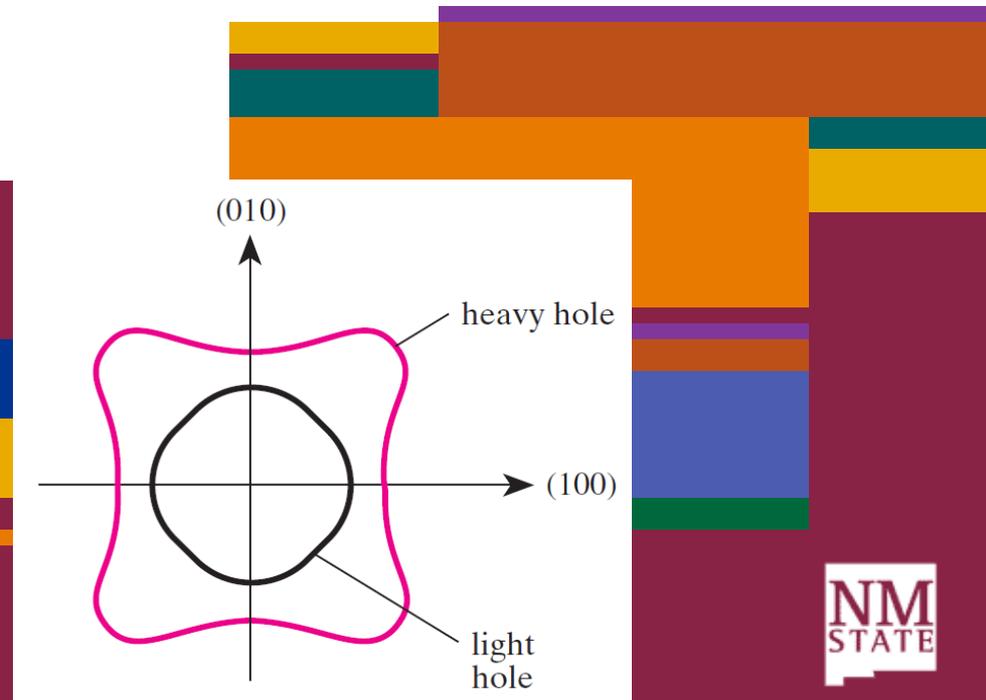
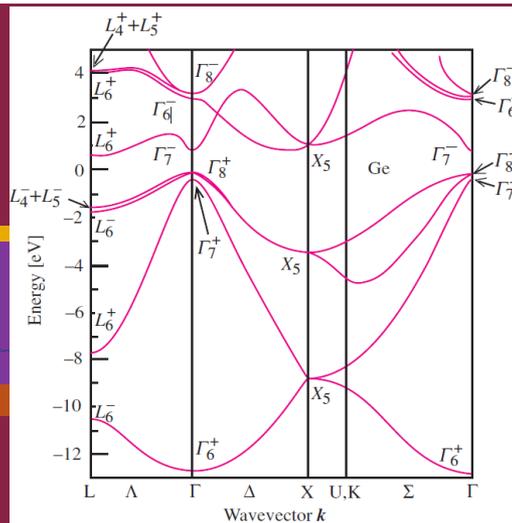
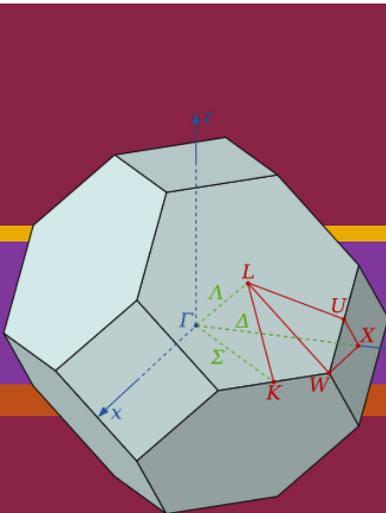
Empty lattice, pseudopotential, k.p band structures

Optical interband transitions, Fermi's Golden Rule

Absorption coefficient for direct and indirect gaps

Tauc plot

Van Hove singularities



# References: Band Structure and Optical Properties

## Solid-State Theory and Semiconductor Band Structures:

- **Mark Fox, *Optical Properties of Solids***
- Ashcroft and Mermin, Solid-State Physics
- **Yu and Cardona, *Fundamentals of Semiconductors***
- Dresselhaus/Dresselhaus/Cronin/Gomes, Solid State Properties
- Cohen and Chelikowsky, Electronic Structure and Optical Properties
- Klingshirn, Semiconductor Optics
- Grundmann, Physics of Semiconductors
- **Ioffe Institute web site: NSM Archive**  
<http://www.ioffe.ru/SVA/NSM/Semicond/index.html>

# Outline

Band structure and Bloch's theorem

Examples: Si, Ge, Al, Cu, SrTiO<sub>3</sub>

Free-electron approximation

Nearly free electron gas

Empirical and ab initio pseudopotential methods

**k.p** theory band structure method

Effective masses, valence band warping, Luttinger parameters

# Band Structure: Where did this come from?

Crystal symmetry: **Translational + point group symmetry.**

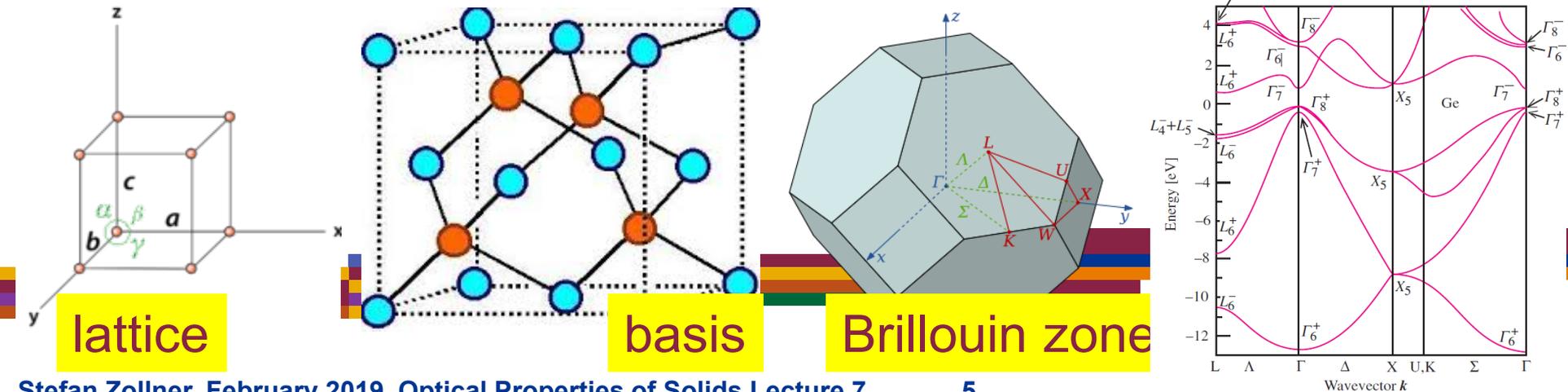
Translational symmetry results in **Bloch's Theorem.**

$$\vec{T}\psi(\vec{r}) = \psi(\vec{r} + \vec{T}) = e^{i\vec{k}\cdot\vec{T}}\psi(\vec{r})$$

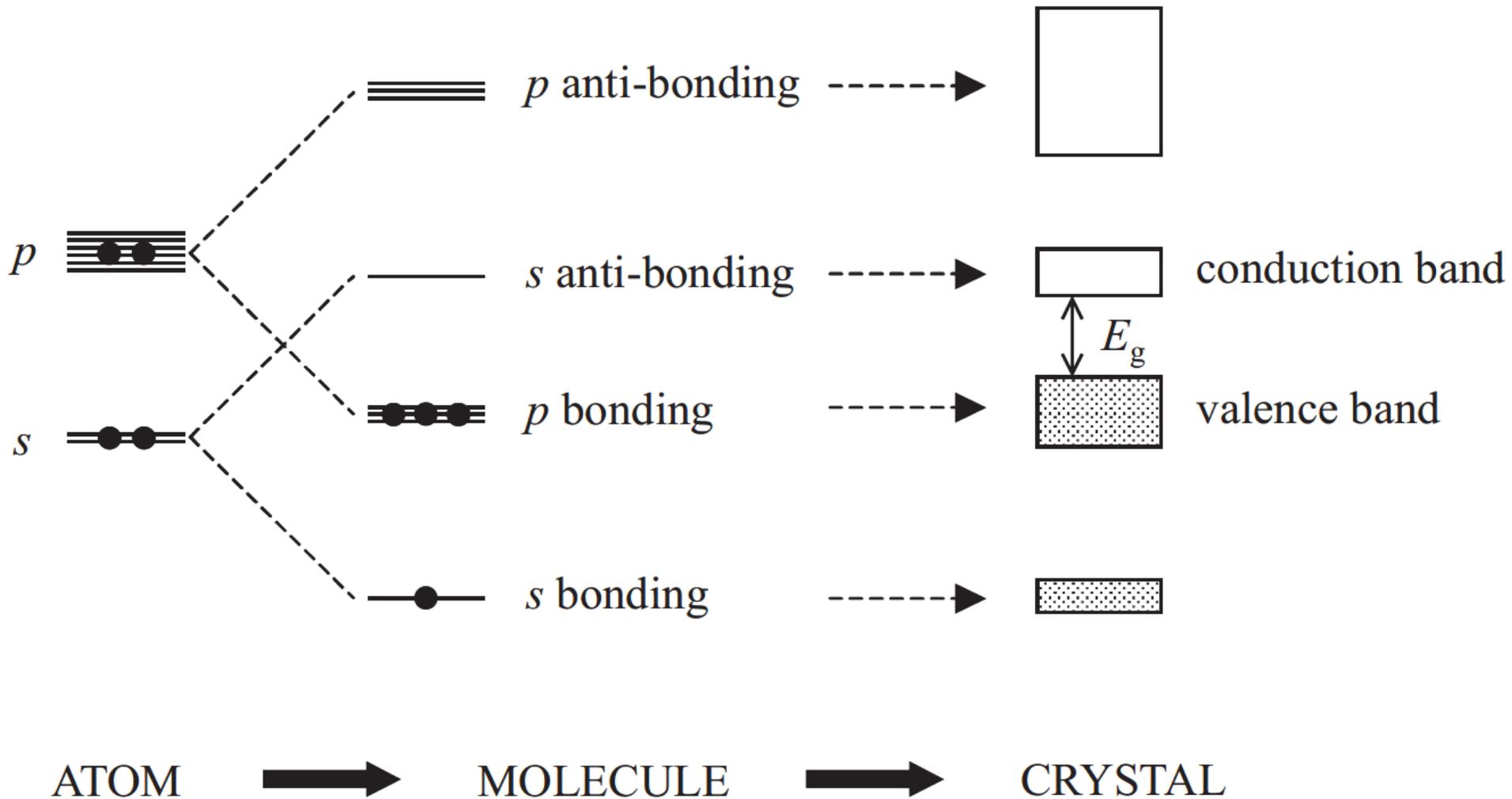
$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{n,\vec{k}}(\vec{r})$$

Representations of cyclic groups are one-dimensional generated by primitive lattice vectors. The characters are the roots of unity.

Energy and wave vector are good quantum numbers. For each  $\mathbf{k}$ , we label the bands from lower to higher energies. This results in band structure  $E_n(\mathbf{k})$ , for  $\mathbf{k}$  in Brillouin zone.

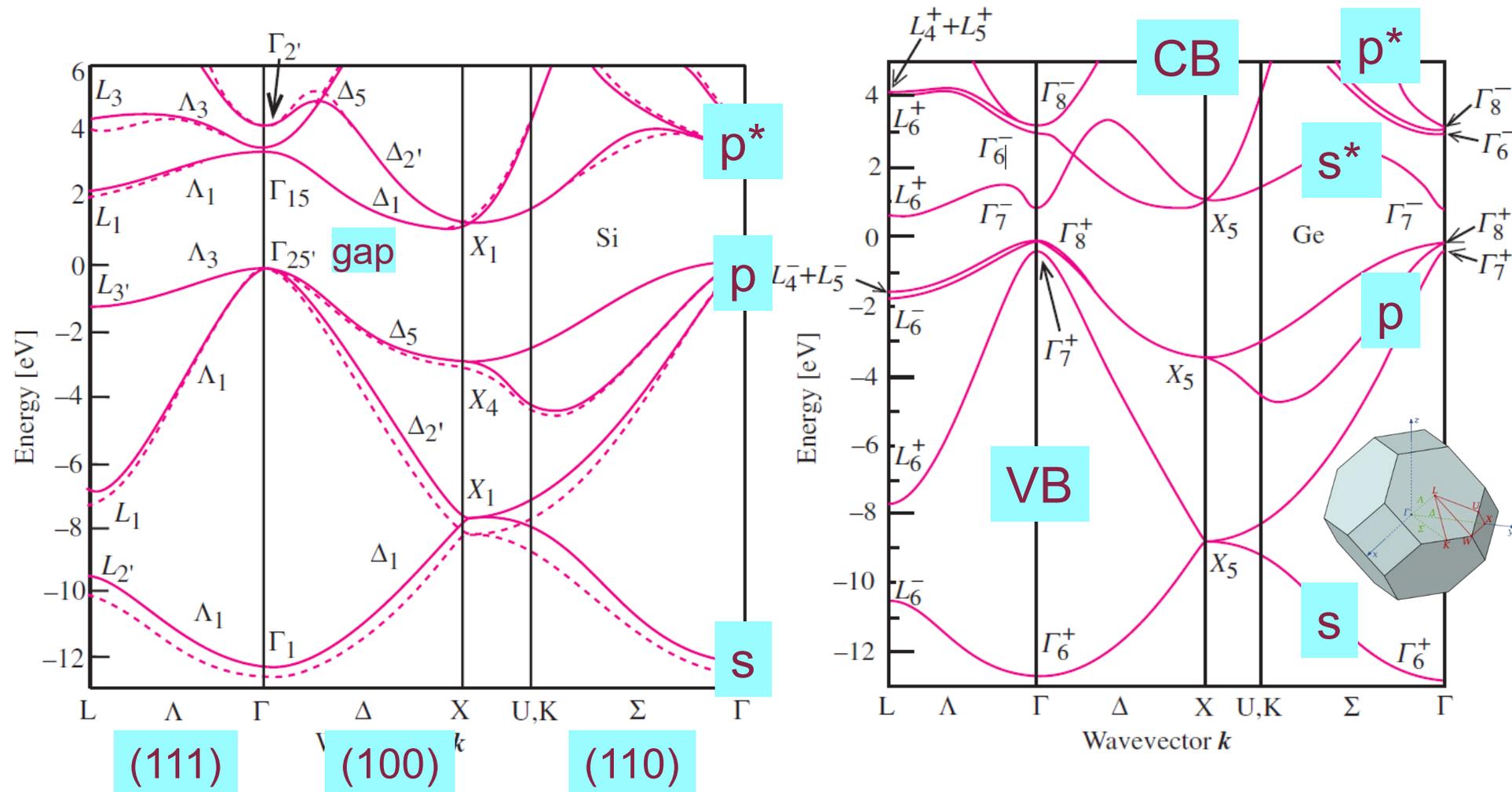


# Band Structure: Where did this come from?



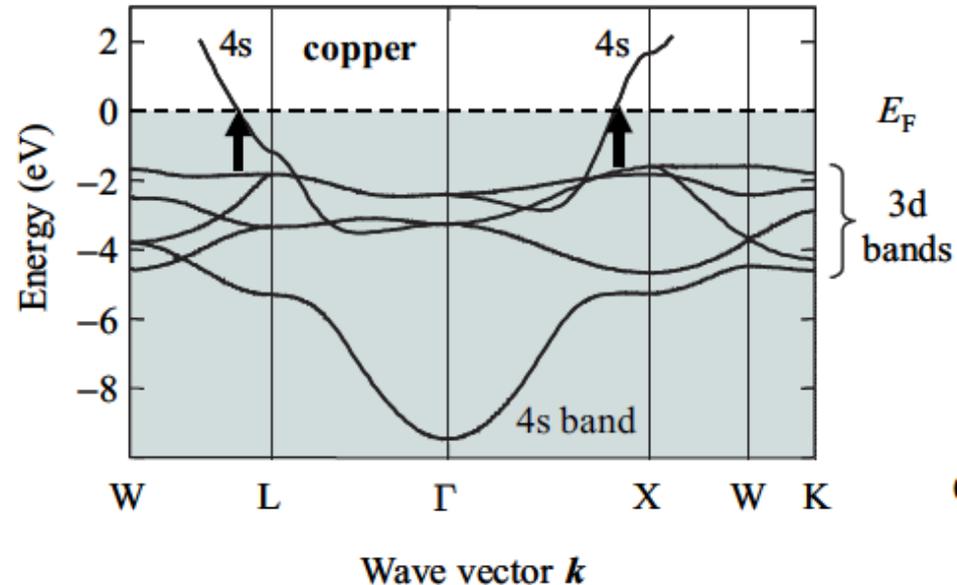
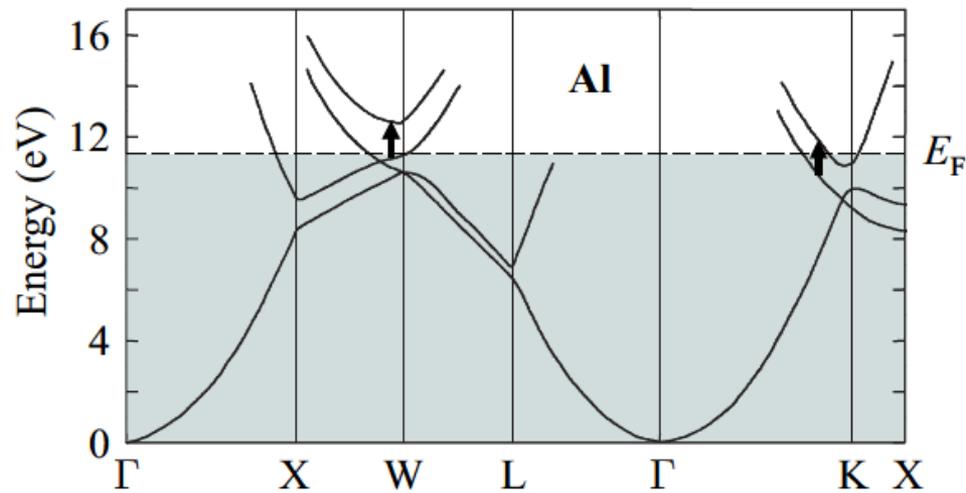
Works well for Ge, GaAs, etc.

# Examples of Band Structures: Si and Ge



Total Energy:  $E=K+V$ ,  $K=\mathbf{p}^2/2m$ ,  $\mathbf{p}=0$  corresponds to  $\Gamma$ -point in BZ.  
 Four valence electrons per atom:  $3s^2, 3p^2$  (8 e<sup>-</sup> per cell)  
 Symmetry labels are representations from the point group.

# Examples of Band Structures: Al and Cu

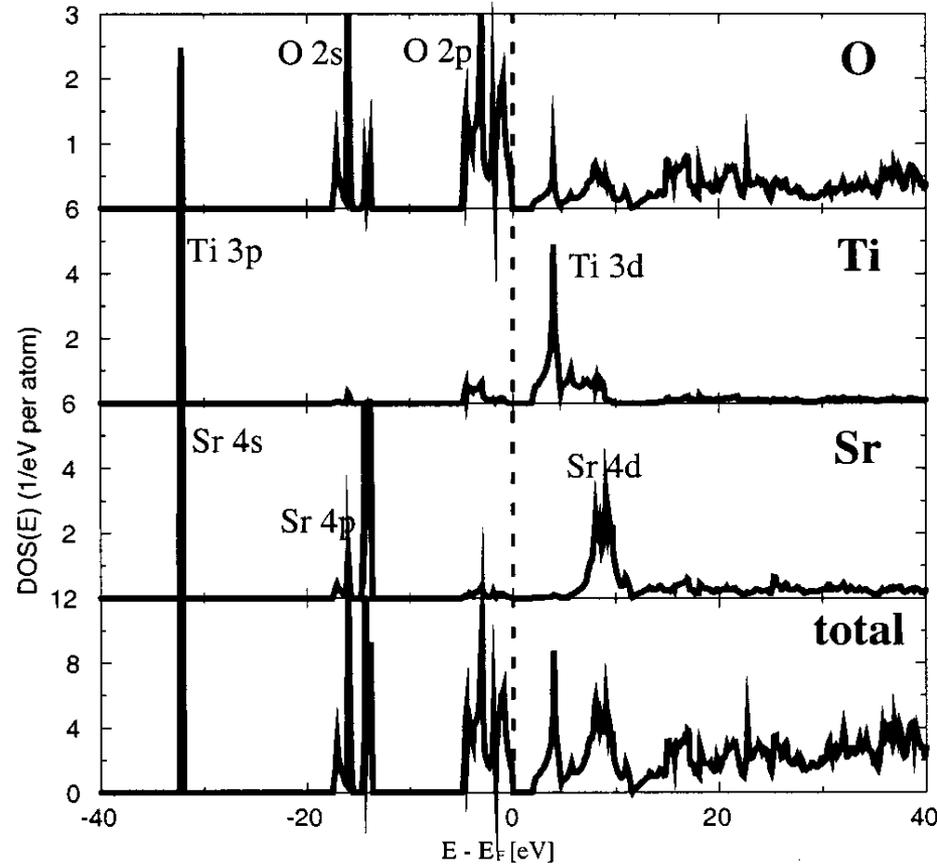
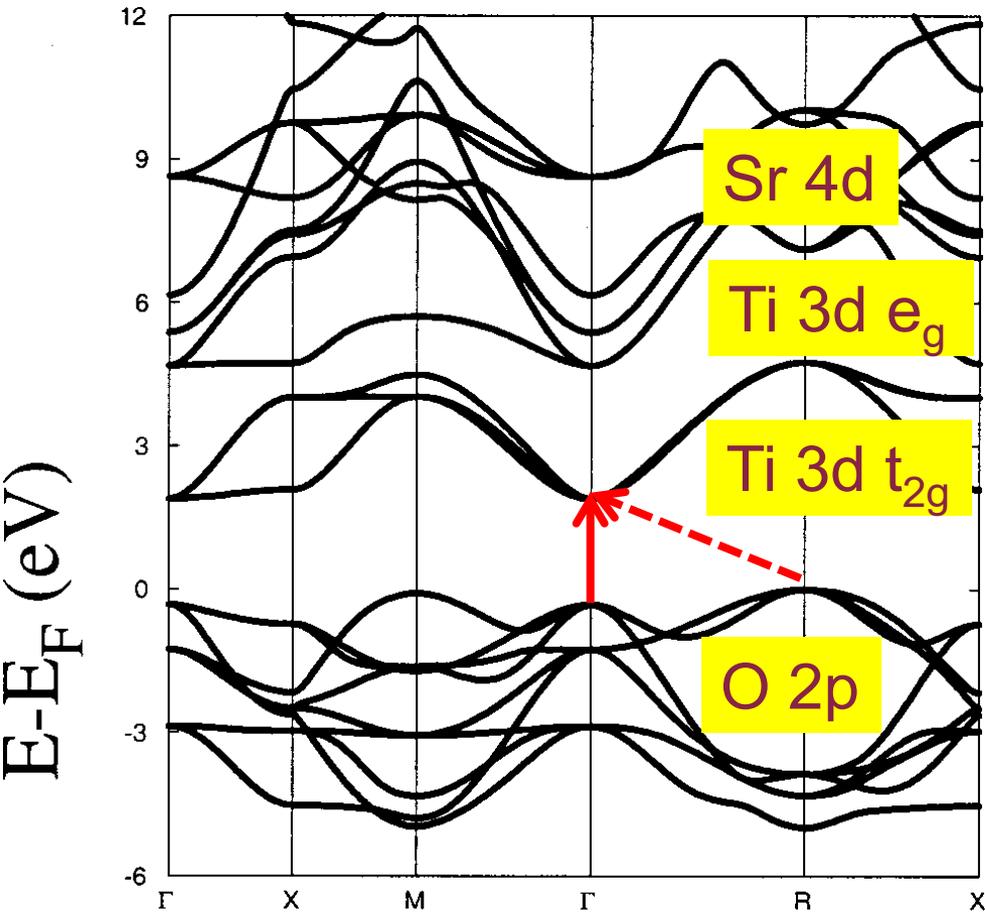


Three valence electrons:  
 $3s^2, 3p^1$   
 No d-electrons.  
 3p band only half full.  
 (This must be a metal).

Noble metal Cu, Ag, Au:  
 s-band half full (metal)  
 d-bands completely full.  
 Not ferromagnetic  
 (paired d-electron spins).



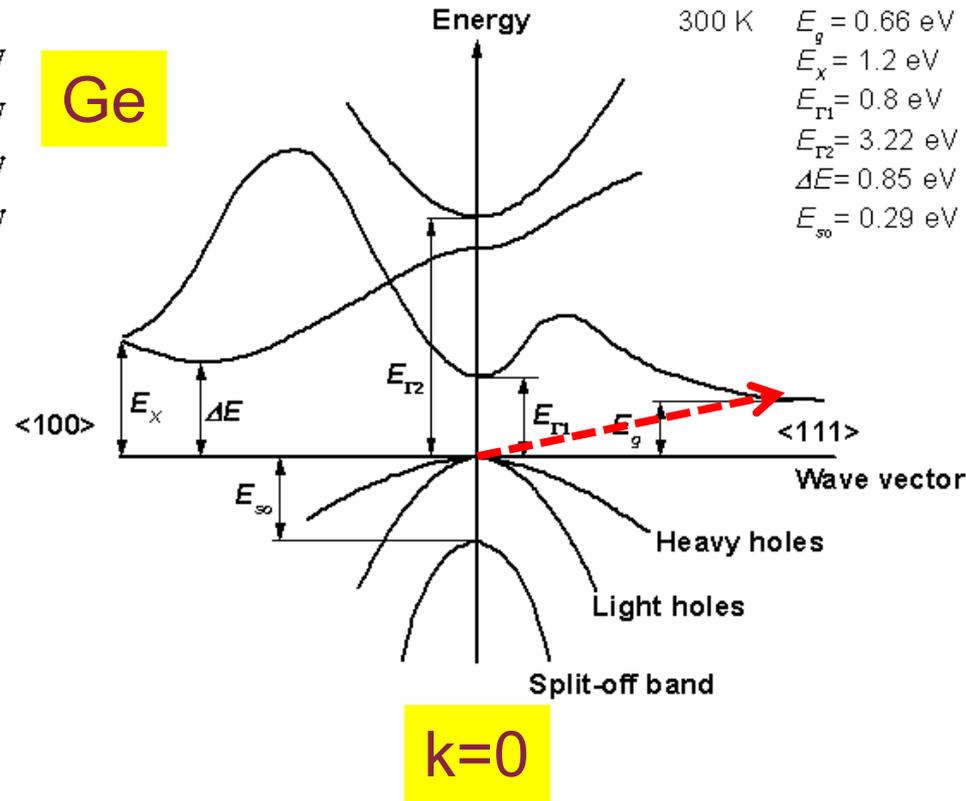
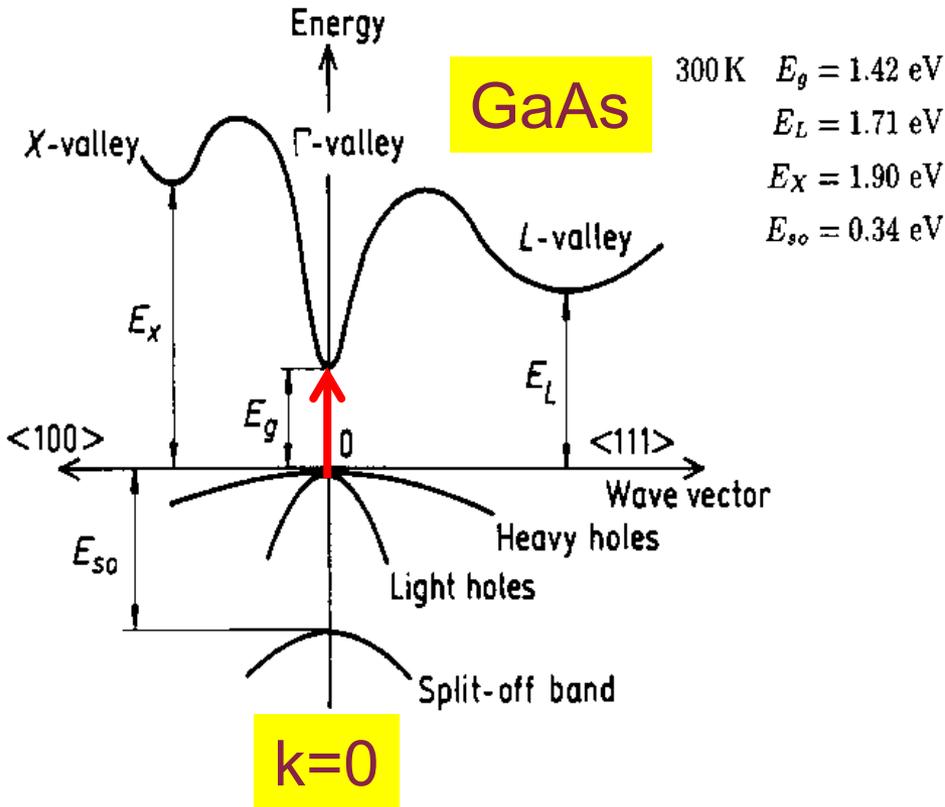
# Examples of Band Structures: SrTiO<sub>3</sub>



LDA underestimates gap (need GW).  
 Hybrid functionals for d-electrons (LDA+U).  
 Direct/indirect transitions.

Projected density of states.

# Direct and indirect transitions



## Direct transition:

Initial and final electron state have **same** wave vector.

## Indirect transition:

Initial and final electron state have **different** wave vector.

# Free-electron approximation (empty lattice: $V=0$ )

$$H = T + U$$

Ignore potential energy ( $U=0$ )

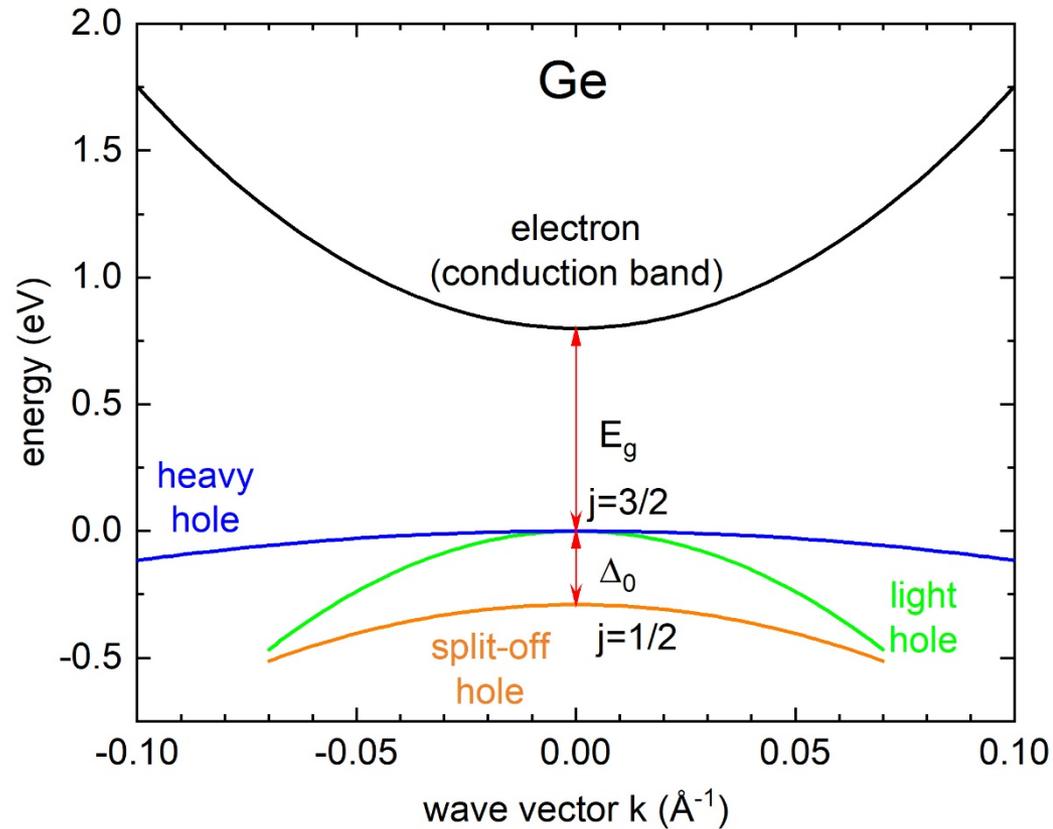
$$H = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 k^2}{2\mathbf{m}^* m_0}$$

$$E_e = E_g + \frac{\hbar^2 k^2}{2\mathbf{m}_e m_0}$$

$$E_{hh} = -\frac{\hbar^2 k^2}{2\mathbf{m}_{hh} m_0}$$

$$E_{lh} = -\frac{\hbar^2 k^2}{2\mathbf{m}_{lh} m_0}$$

$$E_{so} = -\Delta_0 - \frac{\hbar^2 k^2}{2\mathbf{m}_{so} m_0}$$



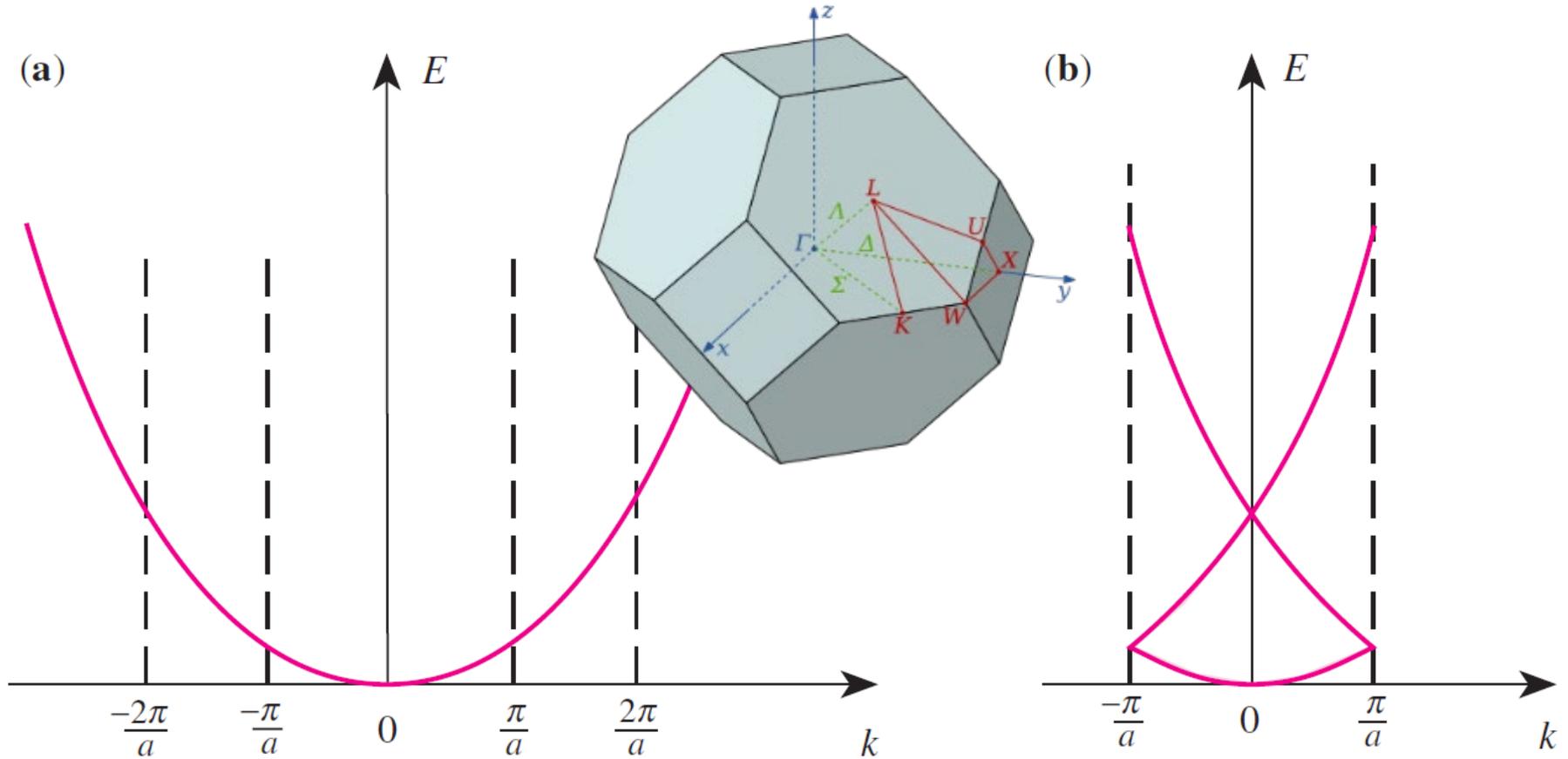
$$(\mathbf{m}_{ij})^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j}$$

Effective mass  $\mathbf{m}^*$

Effective mass tensor

Free particle: Plane wave

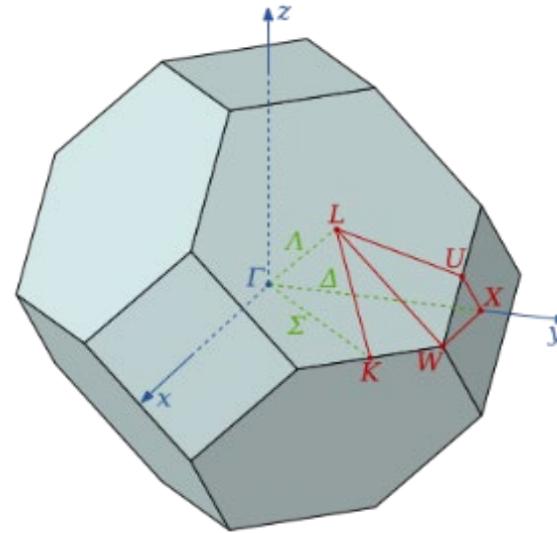
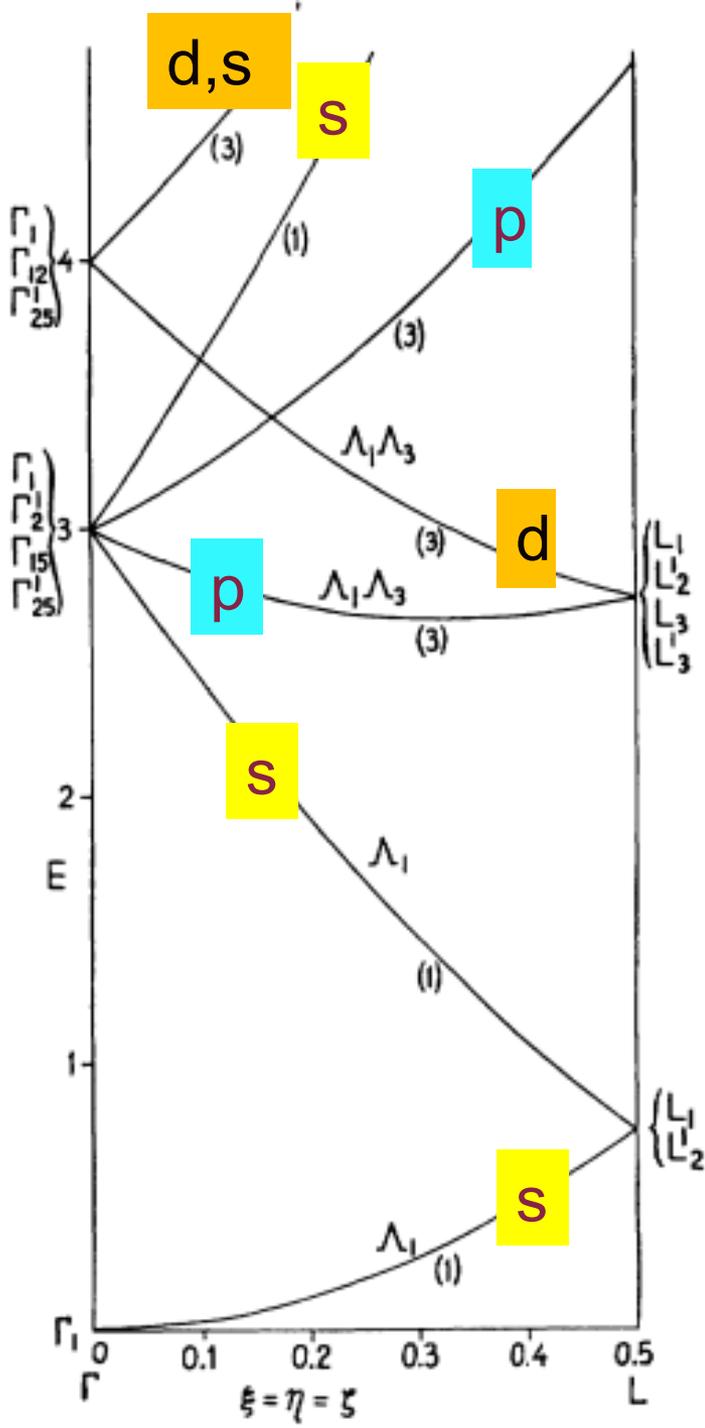
# Free-electron approximation (empty lattice: $V=0$ )



Bands are folded at edges of Brillouin zone.

Yu & Cardona, Fundamentals of Semiconductors  
H. Jones, Theory of Brillouin Zones (1975)

# Free-electron approximation for FCC lattice



Bands are folded at edges of Brillouin zone.

Wave functions are plane waves (calculated matrix elements).

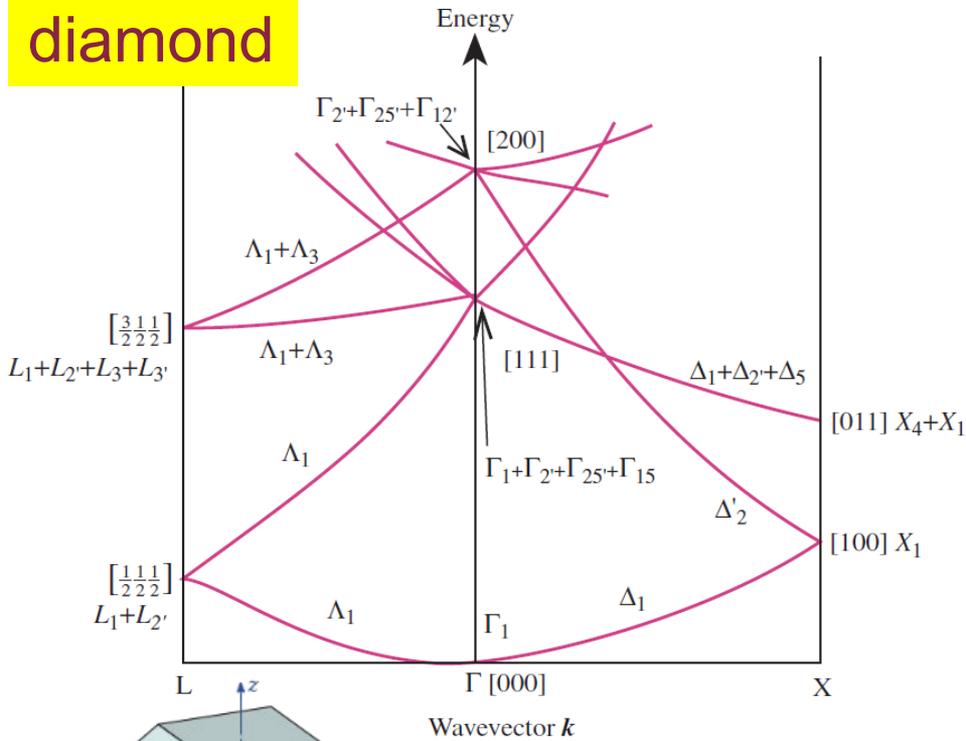
Note point group symmetry notations.

Yu & Cardona, Fundamentals of Semiconductors  
 H. Jones, Theory of Brillouin Zones (1975)

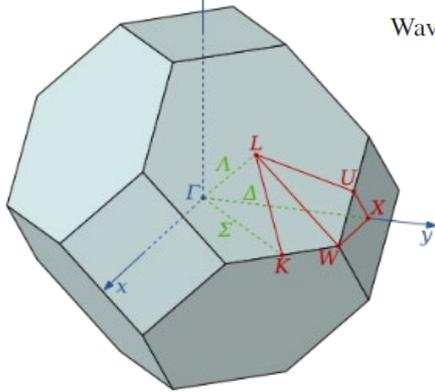
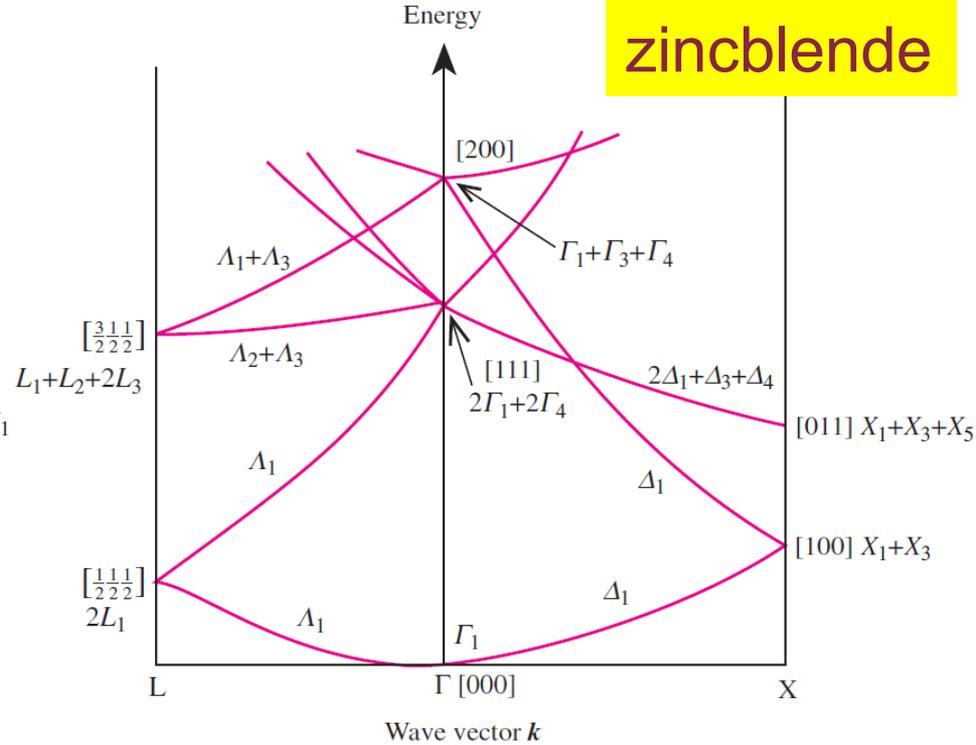


# Free-electron approximation for FCC lattice

diamond



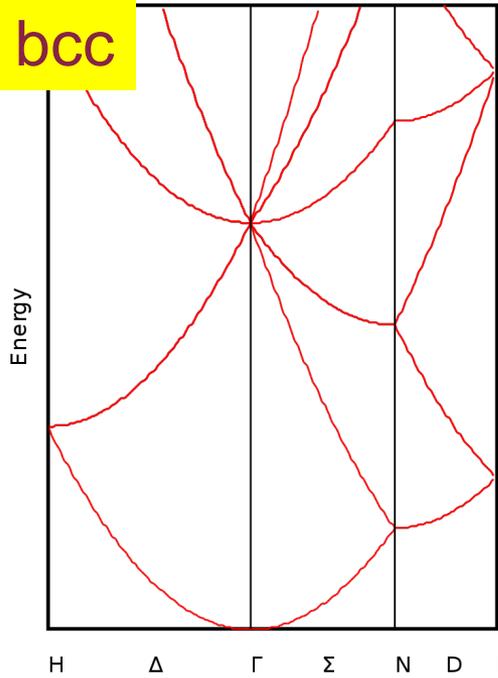
zincblende



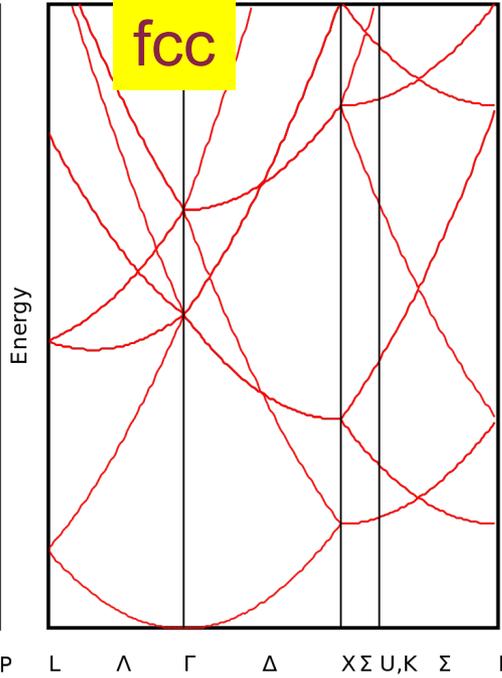
Bands are folded at edges of Brillouin zone.  
 Wave functions are plane waves related to RLV  $\mathbf{K}$   
 (calculate matrix elements).  
 Note point group symmetry notations.  
 No crystal potential: Lots of degeneracies

# Free-electron approximation: bcc, fcc, hcp lattices

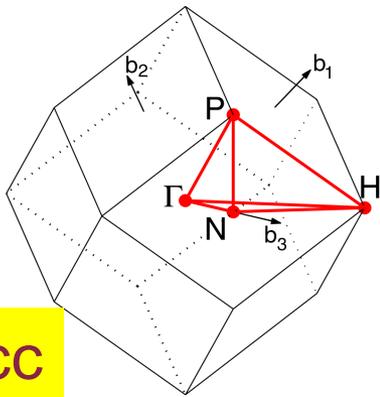
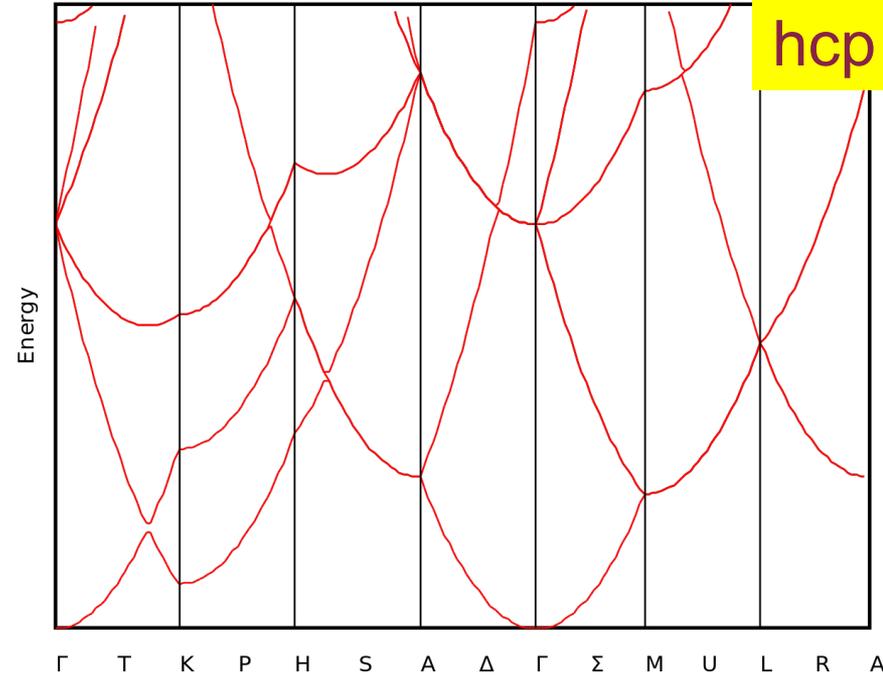
bcc



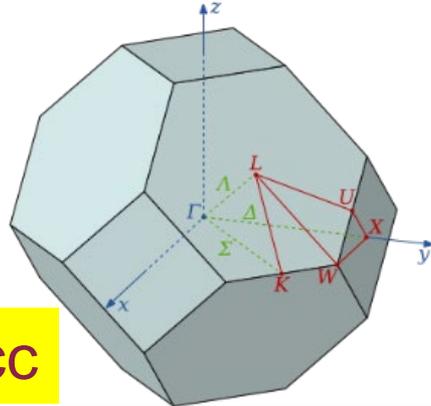
fcc



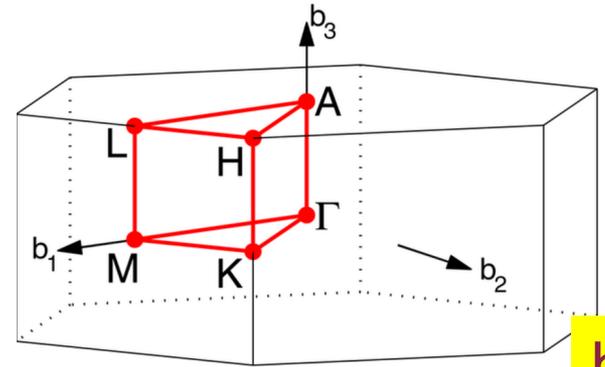
hcp



bcc



fcc



hcp

Wikipedia (empty lattice approximation)



# Nearly free electron gas (weak potential)

$$H = T + U$$

Assume that  $U$  is very small.

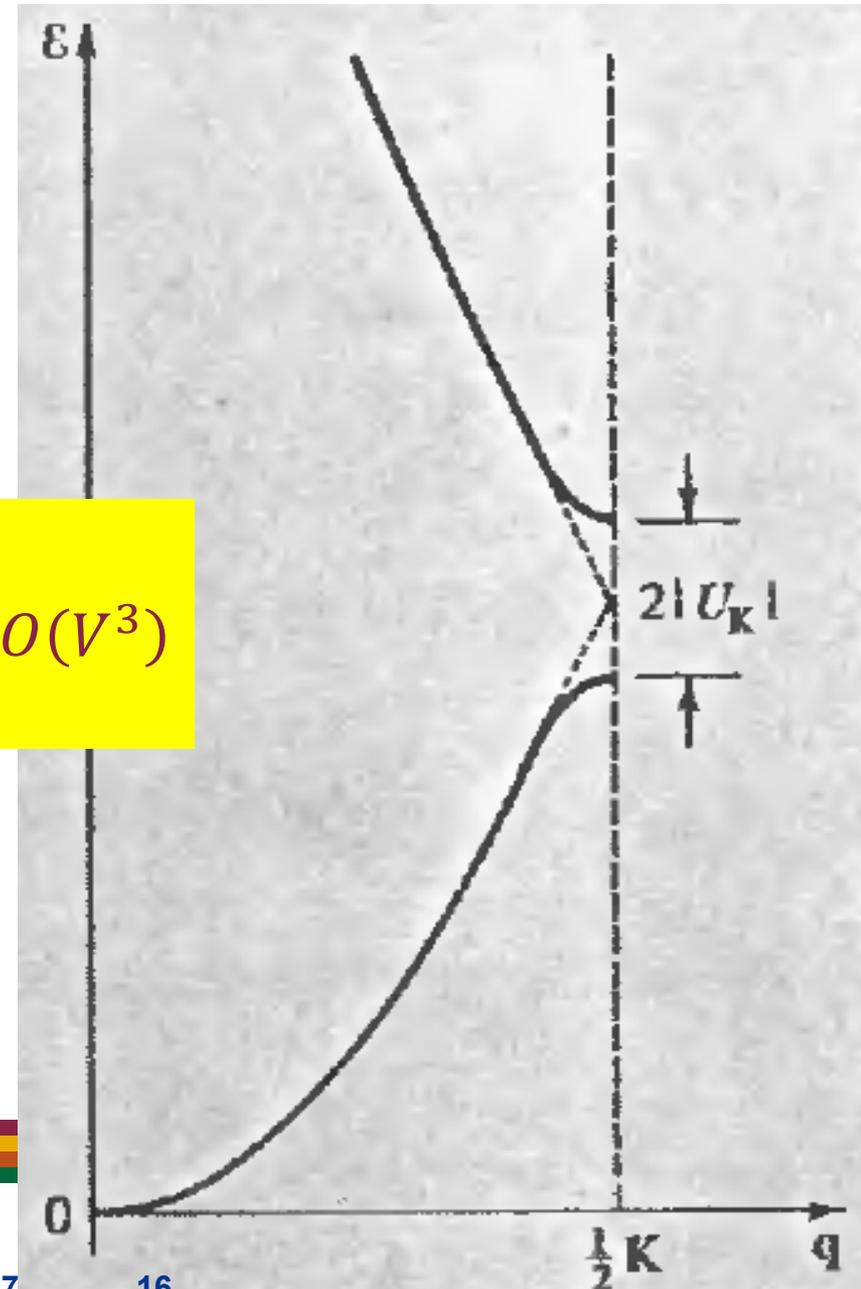
**Non-degenerate states** are not affected much (second order in  $U$ ).

**Bands repel each other.**

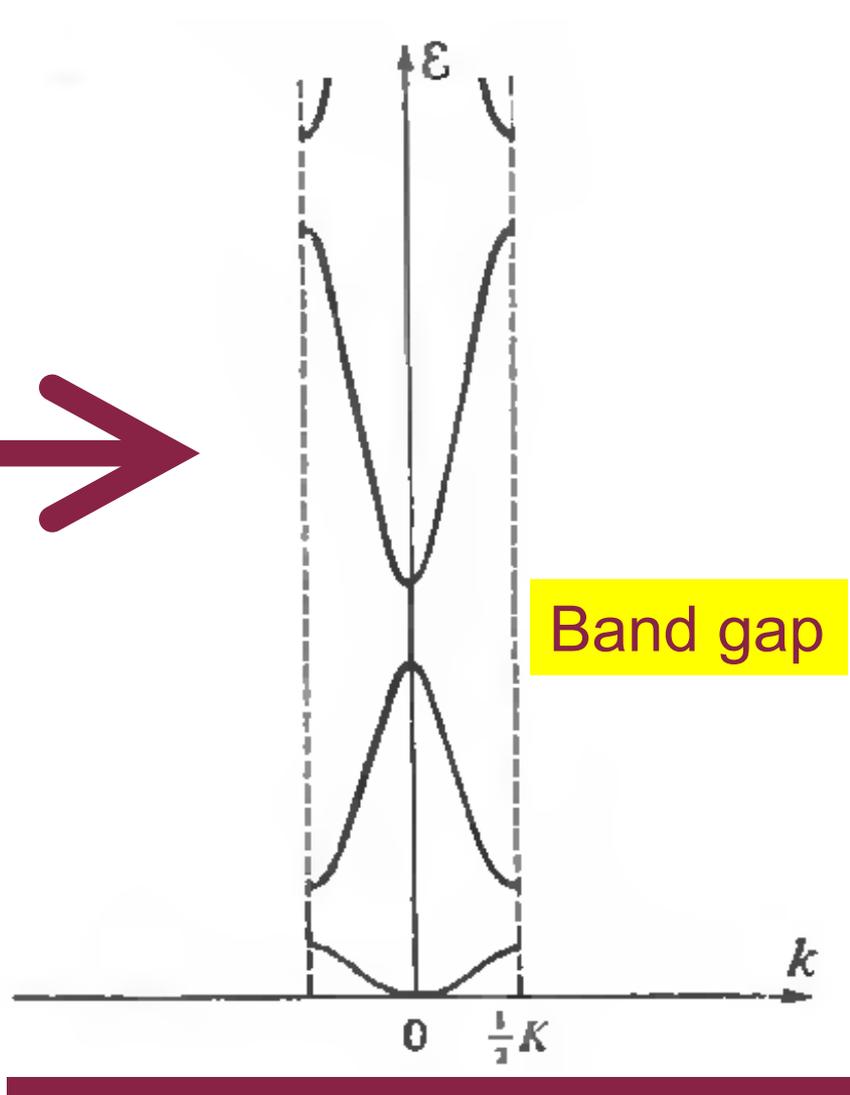
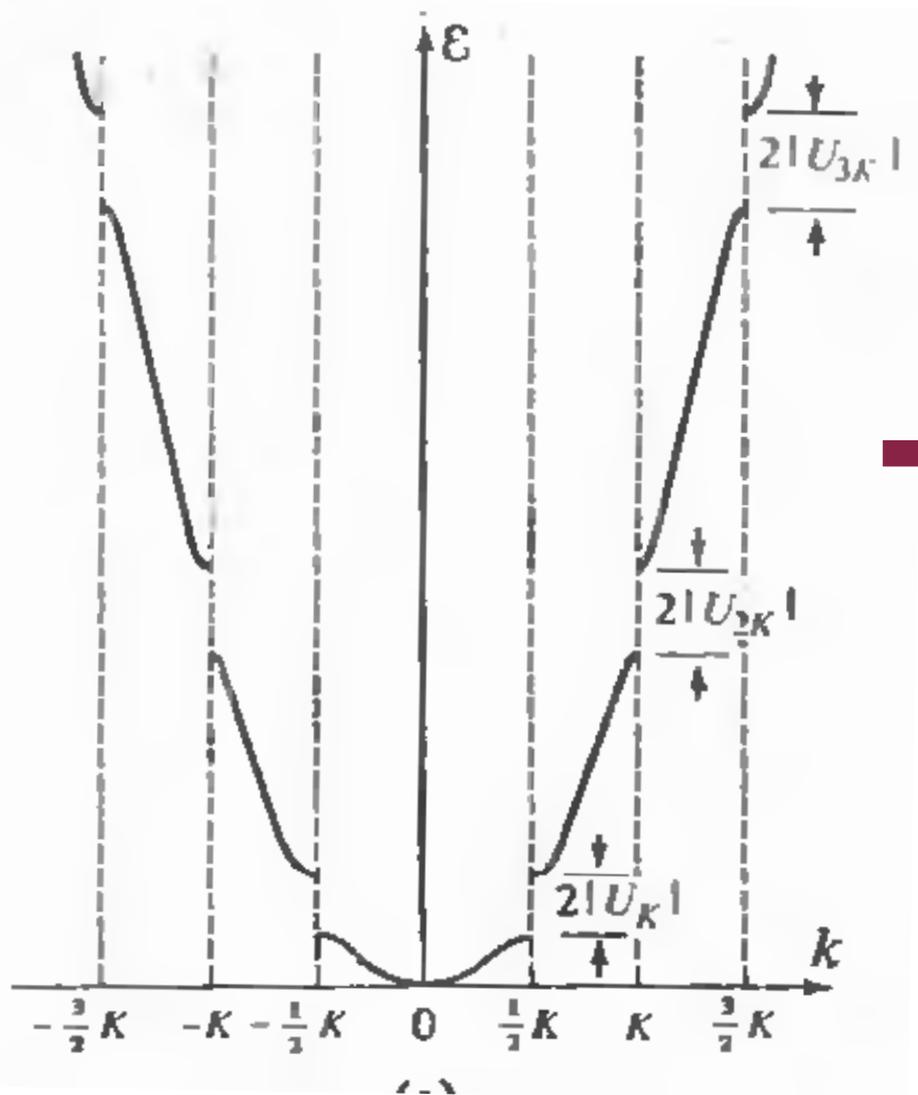
$$E(\vec{k}) = E_{\vec{k}-\vec{K}_1}^0 + \sum_{\vec{K}} \frac{|U_{\vec{K}-\vec{K}_1}|^2}{E_{\vec{k}-\vec{K}_1}^0 - E_{\vec{k}-\vec{K}}^0} + O(V^3)$$

**Degeneracies are lifted.**

Gaps open, especially near the BZ boundary.



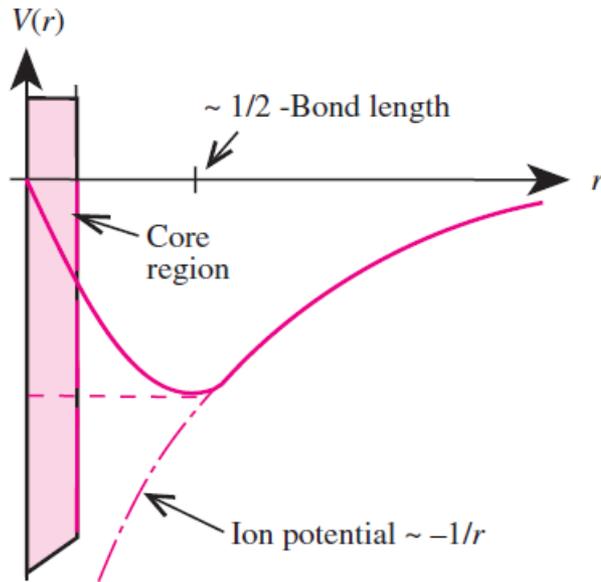
# Nearly free electron gas (weak potential)



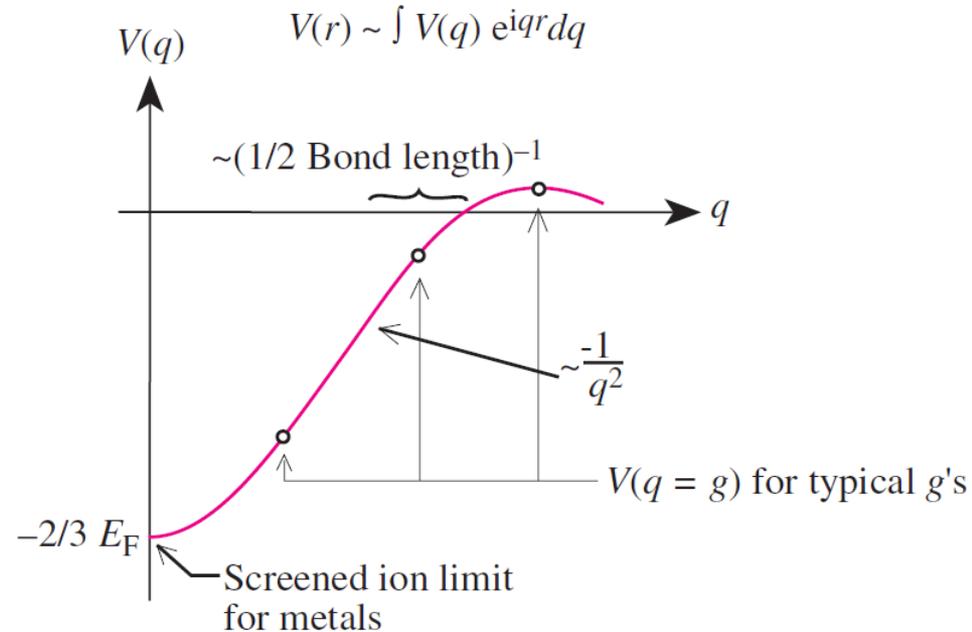
Band gap

# Crystal potential as pseudopotential

## Real-space pseudopotential



## Reciprocal-space pseudopotential



Coulomb potential diverges for  $r=0$ .  
Replace with “soft-core” pseudopotential.

Only need to know  $V(g)$  for a few points.  
Calculate band structure with empirical pseudopotential (EPM) method.  
Requires diagonalization of  $59 \times 59$  matrix.

# Crystal potential as pseudopotential

## Empirical pseudopotential method

$V_g$   
↓  
 $V(\mathbf{r}) = \sum_g V_g \exp(-ig \cdot \mathbf{r})$   
↓  
 $H = (p^2/2m) + V(\mathbf{r})$   
Solve  $H\psi_k(\mathbf{r}) = E_k\psi_k(\mathbf{r})$  to obtain  $\psi_k(\mathbf{r})$  and  $E_k$   
↓  
Calculate reflectivity, density of states, etc., and compare with experiments  
↓  
Alter  $V_g$  if agreement between theory and experiment is not satisfactory.

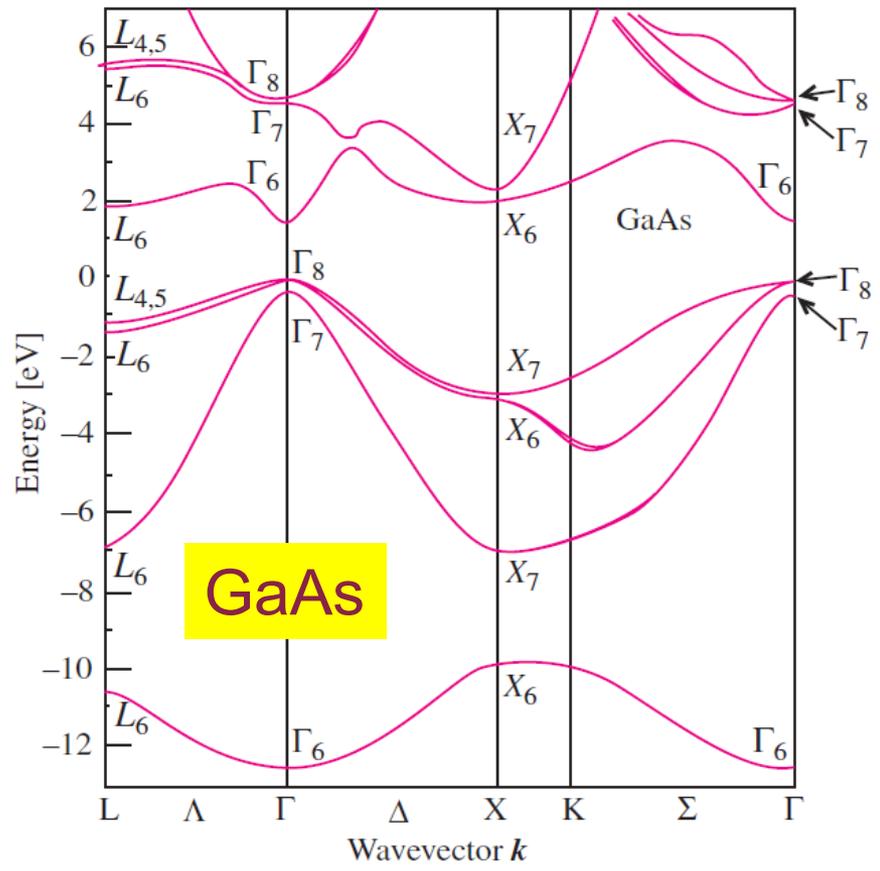
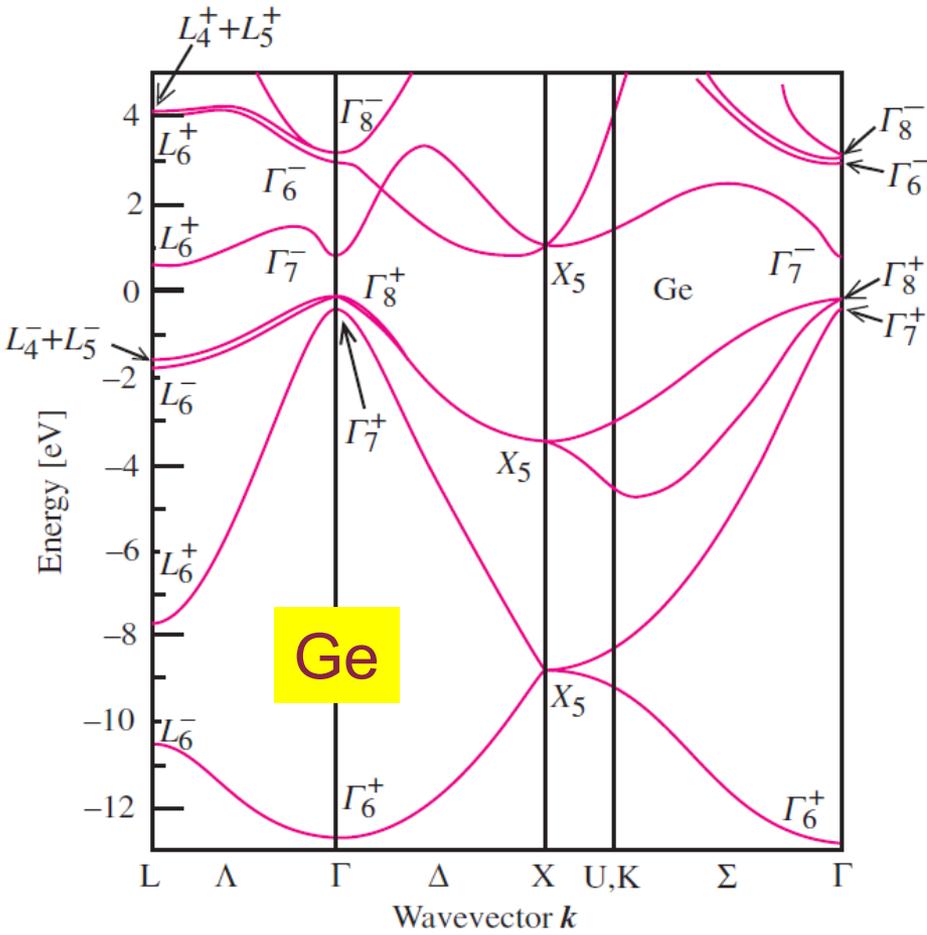
## Self-consistent pseudopotential method

Choose  $V(r)$   
↓  
Solve  $(H + V)\psi = E\psi$   
↓  
Calculate charge density  $\rho = \psi^*\psi$   
↓  
Solve  $\nabla^2 V_{\text{Hartree}} = 4\pi\rho \left(\frac{1}{4\pi\epsilon_0}\right)$   
↓  
Calculate  $V_{\text{xc}} = f[\rho(r)]$   
↓  
 $V_{\text{sc}} = V_{\text{Hartree}} + V_{\text{xc}}$   
↓  
Model structure  $V_{\text{ion}} \rightarrow V = V_{\text{sc}} + V_{\text{ion}}$

Guess  $V(g)$   
Calculate band structure  
Compare with experimental results.  
**Adjust  $V(g)$  until good agreement.**  
Single-electron equation.  
Diagonalization of a matrix works for s- and p-electrons (not d-electrons).

Start with atomic pseudopotential  $V$   
Calculate band structure  
Calculate charge density  $\rho$   
Include many-body effects (LDA)  
**Replace  $V$  and start over.**  
No experimental input needed.

# Pseudopotential (EPM) band structures for Ge, GaAs

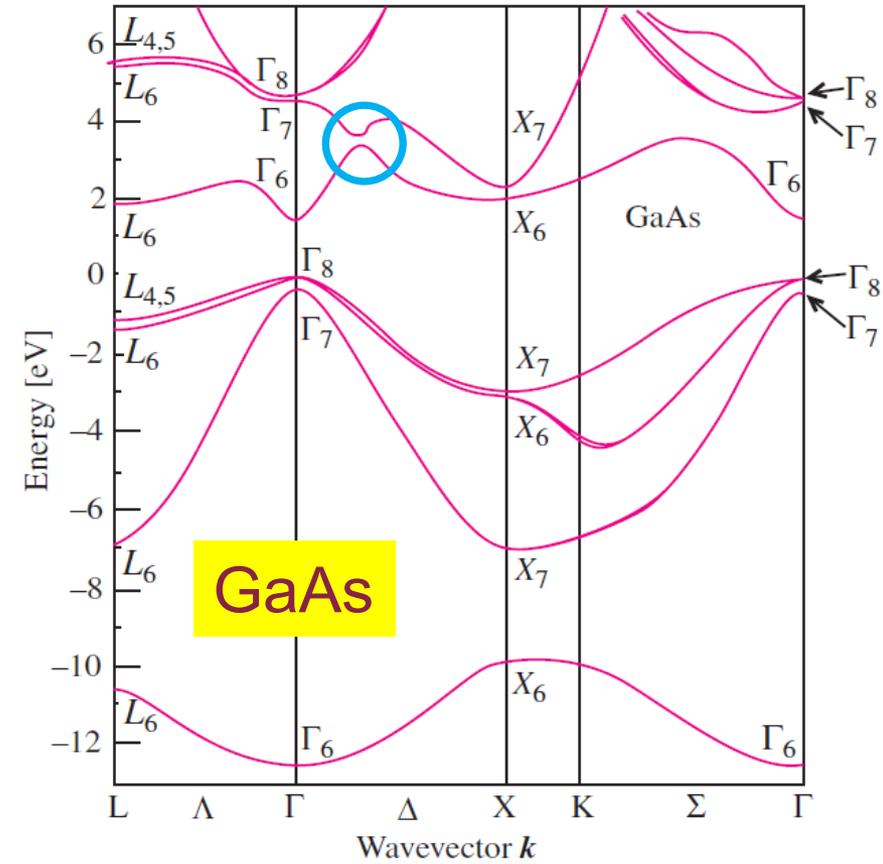
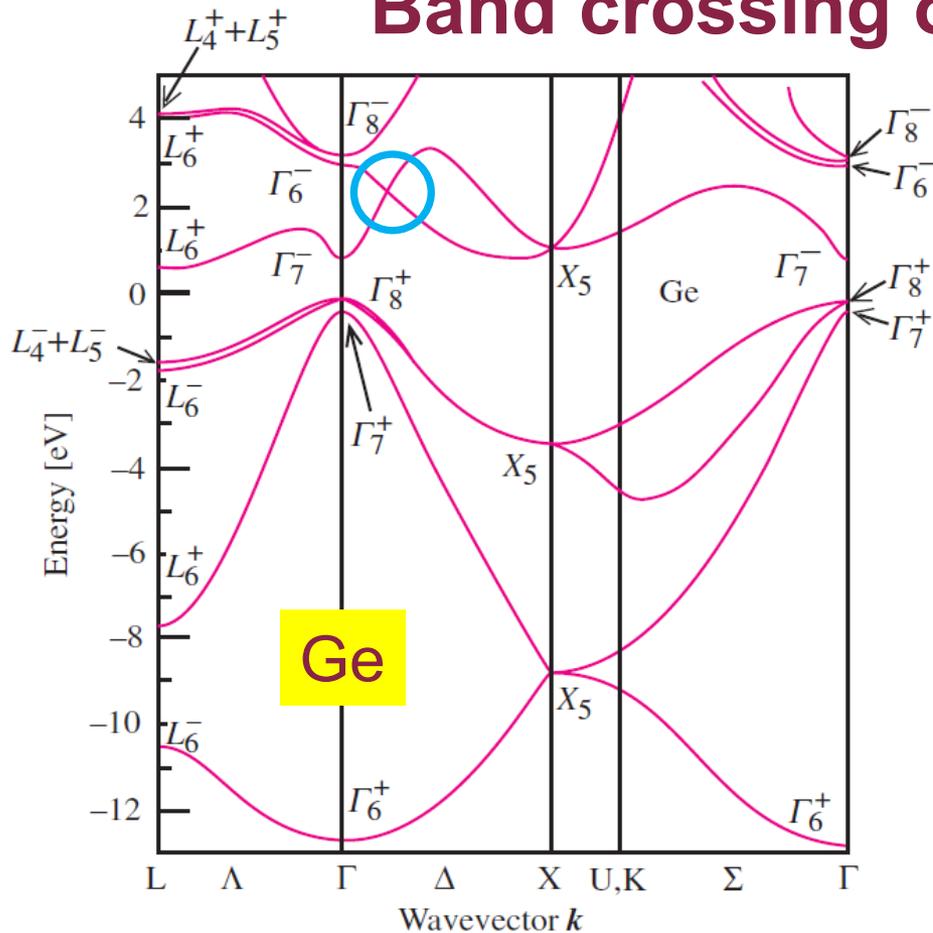


Compare with empty lattice results:  
 Crystal potential opens a band gap.  
 Bands are flat at BZ edges.

Chelikowsky & Cohen, PRB 14 556 (1976)



# Band crossing or anti-crossing



Bands cross: different symmetries.  
 Dirac point: Linear dependence on  $k$   
 Inversion symmetry leads to crossing.

Bands repel: same symmetry.  
 Anti-crossing due to interactions.  
 No degeneracy at the X-point.

# k·p theory (band structure method)

Schrödinger equation

$$H\Phi_{n\vec{k}} = \left( \frac{\vec{p}^2}{2m} + V \right) \Phi_{n\vec{k}} = E_{n\vec{k}} \Phi_{n\vec{k}}$$

Use Bloch's theorem:

$$\Phi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r})$$

Product rule

$$(fg)'' = f''g + 2f'g' + fg''$$

$$\left( \frac{\vec{p}^2}{2m} + \frac{\hbar^2 \vec{k}^2}{2m} + \frac{\hbar \vec{k} \cdot \vec{p}}{m} + V \right) u_{n\vec{k}} = E_{n\vec{k}} u_{n\vec{k}}$$

Solve equation for  $\mathbf{k}=0$ .

**Then treat red terms in perturbation theory.**

Works very well for semiconductors with local  $V(\mathbf{r})$  potentials.

# k·p theory: Effective mass of a non-generate band

$$\left( \frac{\vec{p}^2}{2m} + \frac{\hbar^2 \vec{k}^2}{2m} + \frac{\hbar \vec{k} \cdot \vec{p}}{m} + V \right) u_{n\vec{k}} = E_{n\vec{k}} u_{n\vec{k}}$$

Solve for  $\mathbf{k}=0$  (at  $\Gamma$ ). Linear terms in  $\mathbf{k}$  vanish (extremum).  
Treat **red terms** in perturbation theory (up to second order).

$$u_{n\vec{k}} = u_{n\Gamma} + \frac{\hbar}{m} \sum_{n' \neq n} \frac{\langle u_{n\Gamma} | \vec{k} \cdot \vec{p} | u_{n'\Gamma} \rangle}{E_{n\Gamma} - E_{n'\Gamma}} u_{n'\Gamma}$$

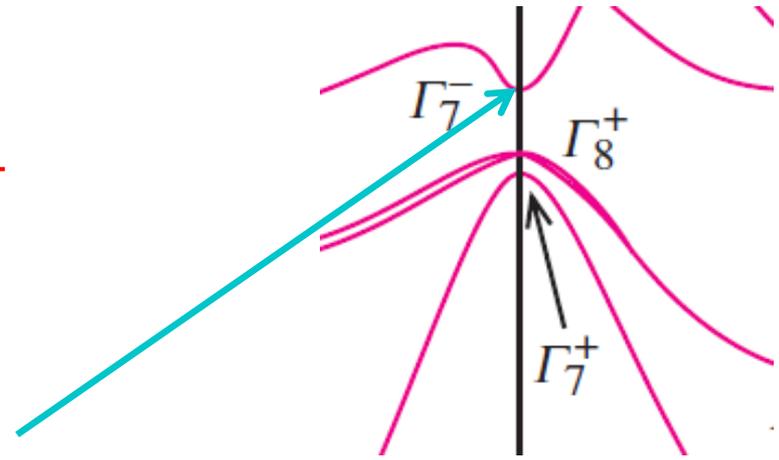
$$E_{n\vec{k}} = E_{n\Gamma} + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{m^2} \sum_{n' \neq n} \frac{|\langle u_{n\Gamma} | \vec{k} \cdot \vec{p} | u_{n'\Gamma} \rangle|^2}{E_{n\Gamma} - E_{n'\Gamma}} = E_{n\Gamma} + \frac{\hbar^2 k^2}{2m^*}$$

$$\frac{1}{m^*} = \frac{1}{m} + \frac{2}{m^2 k^2} \sum_{n' \neq n} \frac{|\langle u_{n\Gamma} | \vec{k} \cdot \vec{p} | u_{n'\Gamma} \rangle|^2}{E_{n\Gamma} - E_{n'\Gamma}}$$

Effective mass comes from band-band interactions.

# k·p theory: Application to electron band at $\Gamma$

$$\frac{1}{m^*} = \frac{1}{m} + \frac{2}{m^2 k^2} \sum_{n' \neq n} \frac{|\langle u_{n\Gamma} | \vec{k} \cdot \vec{p} | u_{n'\Gamma} \rangle|^2}{E_{n\Gamma} - E_{n'\Gamma}}$$



Keep only the largest term:

$$\frac{1}{m_e^*} = \frac{1}{m_0} + \frac{2 |\langle \Gamma_{1c} | \vec{k} \cdot \vec{p} | \Gamma'_{25v} \rangle|^2}{m_0^2 E_0 k^2} = \frac{1}{m_0} + \frac{2P^2}{m_0^2 E_0} \cong \frac{2P^2}{m_0^2 E_0}$$

$$E_P = 2P^2/m_0$$

$$E_P \approx 20 \text{ eV}$$

Momentum matrix element:  $iP = \langle X | p_x | \Gamma_1 \rangle = \langle Y | p_Y | \Gamma_1 \rangle = \langle Z | p_z | \Gamma_1 \rangle$

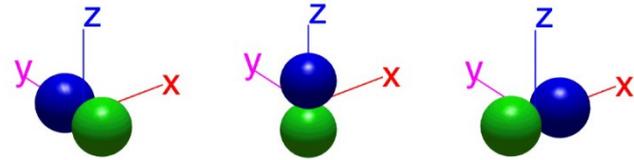
	Ge	GaN	GaAs	GaSb	InP	InAs	ZnS	ZnSe	ZnTe	CdTe
$E_0$ [eV]	0.89	3.44	1.55	0.81	1.34	0.45	3.80	2.82	2.39	1.59
$m_c^*/m$ (exp)	0.041	0.17	0.067	0.047	0.073	0.026	0.20	0.134	0.124	0.093
$m_c^*/m$ ((2.44))	0.04	0.17	0.078	0.04	0.067	0.023	0.16	0.14	0.12	0.08

$$m_e^* \propto E_0$$

# k·p theory: Application to valence bands at $\Gamma$

## Valence band maximum $\Gamma_{25}'$ : Spherical harmonics (L=1)

$$|lm_l\rangle = \begin{cases} |11\rangle = -(X + iY)/\sqrt{2} \\ |10\rangle = Z \\ |1-1\rangle = (X - iY)/\sqrt{2} \end{cases}$$



## Include spin 1/2: $\mathbf{J=L+S}$ , $\mathbf{j=1/2,3/2}$

$$|jm_j\rangle = \begin{cases} |3/2, 3/2\rangle = |1, 1\rangle\alpha \\ |3/2, 1/2\rangle = (1/\sqrt{3})(|1, 1\rangle\beta + \sqrt{2}|1, 0\rangle\alpha) \\ |3/2, -1/2\rangle = (1/\sqrt{3})(|1, -1\rangle\alpha + \sqrt{2}|1, 0\rangle\beta) \\ |3/2, -3/2\rangle = |1, -1\rangle\beta \\ |1/2, 1/2\rangle = (1/\sqrt{3})(|1, 0\rangle\alpha - \sqrt{2}|1, 1\rangle\beta) \\ |1/2, -1/2\rangle = (1/\sqrt{3})(|1, 0\rangle\beta - \sqrt{2}|1, -1\rangle\alpha) \end{cases}$$

Momentum matrix element:  
14 by 14 matrix (p, s\*, p\*)

$$iQ = \langle X | p_y | \Gamma_{15c}(z) \rangle = \langle X | p_z | \Gamma_{15c}(x) \rangle$$

# k·p theory: Application to valence bands at $\Gamma$

Momentum matrix elements:

$$iP = \langle X | p_x | \Gamma_1 \rangle = \langle Y | p_y | \Gamma_1 \rangle = \langle Z | p_z | \Gamma_1 \rangle$$

$$iQ = \langle X | p_y | \Gamma_{15c}(z) \rangle = \langle X | p_z | \Gamma_{15c}(x) \rangle$$

$$\frac{m_0}{m_{so}^*} = 1 - \frac{2}{3} \left[ \frac{P^2}{m_0(E_0 + \Delta_0)} + \frac{2Q^2}{m_0(E'_0 + \Delta_0)} \right]$$

**Inverse effective mass parameters A, B, C:**

$$\frac{2m}{\hbar^2} A = 1 - \frac{2}{3} \left[ \left( \frac{P^2}{mE_0} \right) + \left( \frac{2Q^2}{mE'_0} \right) \right]$$

$$\frac{2m}{\hbar^2} B = \frac{2}{3} \left[ \left( \frac{-P^2}{mE_0} \right) + \left( \frac{Q^2}{mE'_0} \right) \right]$$

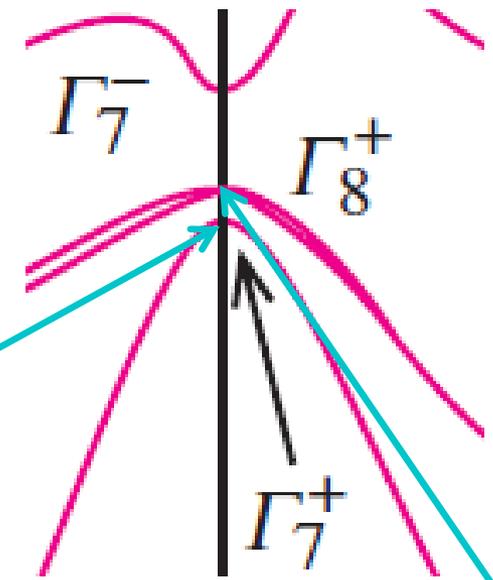
$$\left( \frac{2m}{\hbar^2} C \right)^2 = \frac{16P^2 Q^2}{3mE_0 mE'_0}$$

$$m_{hh, lh}^{-1} = A \pm |B| \sqrt{1 + C^2 / 5B^2}$$

Also **Luttinger parameters**

$$\gamma_1 = -A, \quad \gamma_2 = -B/2,$$

$$\gamma_3 = \sqrt{(B^2/4) + (C^2/12)}$$

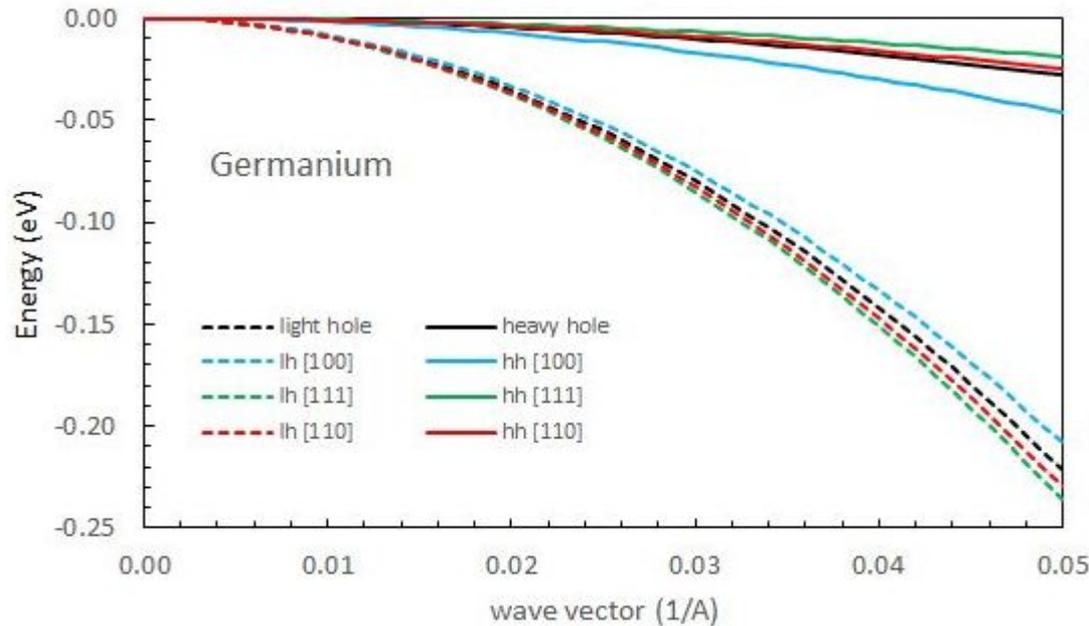


$$E_{lh, hh} = -Ak^2 \pm \sqrt{B^2 k^4 + C^2 (k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)}$$

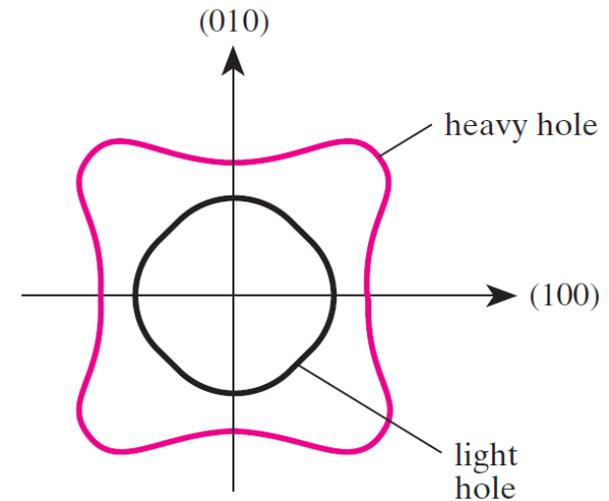
# k·p theory: Application to valence bands at $\Gamma$

	$A$	$B$	$ C ^2$	$\Delta_0$ [eV]	$m_{hh}/m_0$		$m_{lh}/m_0$		$m_{so}/m_0$	
					exp	th	exp	th	exp	th
C <sup>b</sup>	-2.5	0.2	4.6	0.013 <sup>a</sup>		0.66 <sup>e</sup>		0.29 <sup>e</sup>		0.39 <sup>b</sup>
Si <sup>e</sup>	-4.28	-0.68	24	0.044	0.54	0.50	0.15	0.15	0.23	0.24
Ge	-13.38	-8.5	173	0.295	0.34	0.43	0.043	0.041	0.095	0.1
SiC <sup>c</sup>	-2.8	-1.016	5.8	0.014		0.6		0.25		0.36
GaN <sup>d</sup>	-5.05	-1.2	34	0.017		0.5 <sup>e</sup>		0.13 <sup>e</sup>		0.2
GaP <sup>e</sup>	-4.05	-0.98	16	0.08	0.57	0.51	0.18	0.16		0.25
GaAs	-6.9	-4.4	43	0.341	0.53	0.73	0.08	0.08	0.15	0.17
GaSb	-13.3	-8.8	230	0.75	0.8	0.98	0.05	0.04		0.15
InP <sup>e</sup>	-5.15	-1.9	21	0.11	0.58	0.44	0.12	0.11	0.12	0.2
InAs	-20.4	-16.6	167	0.38	0.4	0.4	0.026	0.026	0.14	0.10
InSb	-36.41	-32.5	43	0.81	0.42	0.48	0.016	0.013		0.12
ZnS	-2.54	-1.5		0.07						
ZnSe	-2.75	-1.0	7.5	0.43		1.09		0.145		
ZnTe	-3.8	-1.44	14.0	0.93						
CdTe	-4.14	-2.18	30.3	0.92						

# Valence Band Warping



**Hole effective mass depends on k-direction:**  
 $m_{hh}$  larger along (111)  
 $m_{hh}$  smaller along (100)  
 Reversed for light hole.



$$T = \sum_{i,j} \frac{\hbar^2 k_i k_j}{2m_{ij}m_0}$$

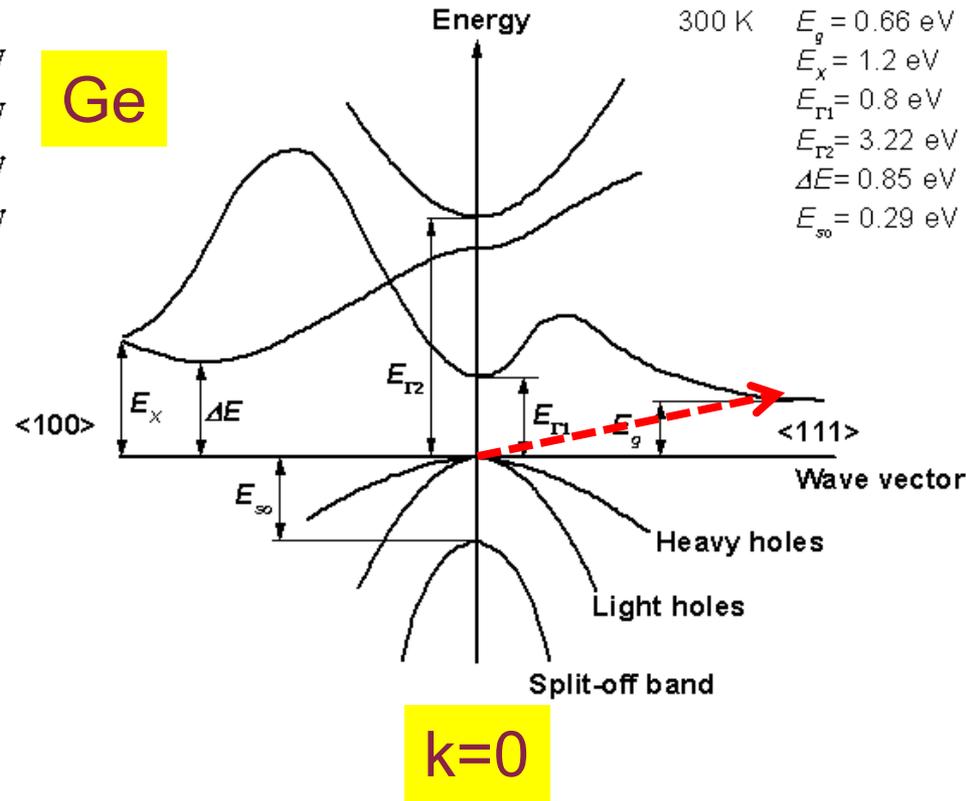
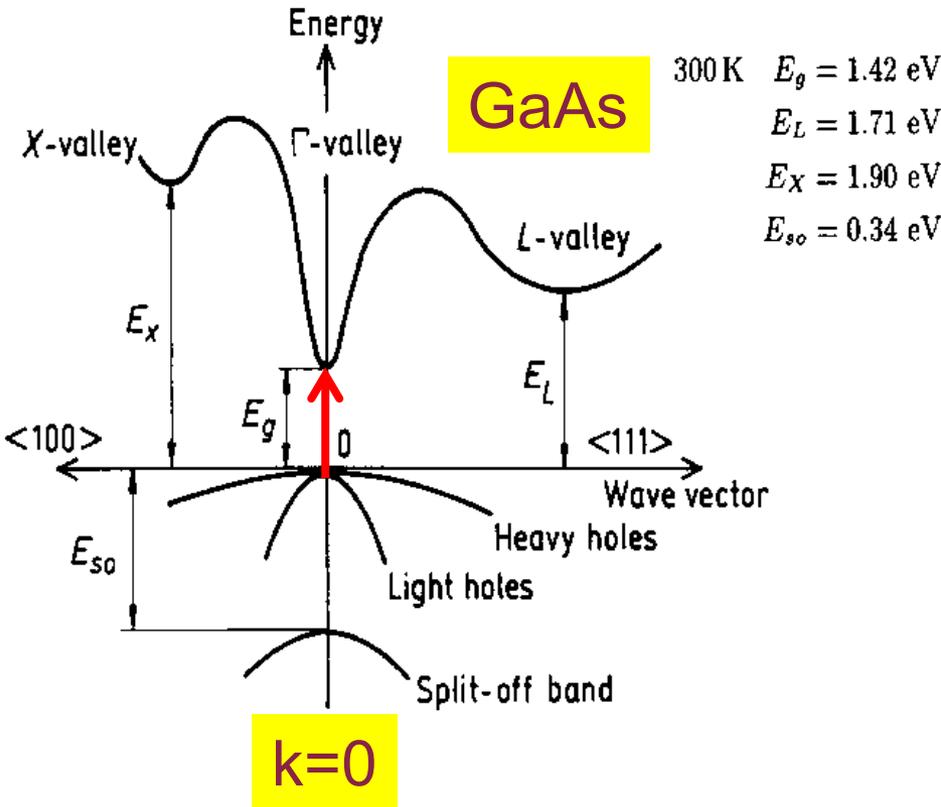
$$(m_{ij})^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j}$$

Effective mass tensor

Constant-energy surfaces

$$E_{lh, hh} = -Ak^2 \pm \sqrt{B^2k^4 + C^2(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2)}$$

# Semiconductor Band Structures



## Direct transition:

Initial and final electron state have **same** wave vector.

## Indirect transition:

Initial and final electron state have **different** wave vector.

# Summary

- Band structure and Bloch's theorem
  - Examples: Si, Ge, Al, Cu, SrTiO<sub>3</sub>
- Free-electron approximation
- Nearly free electron gas
- Empirical and ab initio pseudopotential methods
- **k.p** theory band structure method
- Effective masses, valence band warping, Luttinger parameters