Chap 8 Nearly free and tightly bound electrons

- (<<) Nearly-free electron
  - lattice perturbation
  - empty lattice approximation
  - Fermi surface
- (>>) Tightly bound electron
  - Linear combination of atomic orbitals
  - Wannier function

Special topic:

Geometric phase in crystalline solid

Dept of Phys

M.C. Chang

Nearly-free electron

Lattice perturbation to plane wave

$$\left(\varepsilon^0_{\vec{k}-\vec{G}} - \varepsilon_k\right) C_{\vec{k}}(\vec{G}) + \sum_{\vec{G}'} U_{\vec{G}'-\vec{G}} C_{\vec{k}}(\vec{G}') = 0 \qquad \left(\varepsilon^0_k \equiv \frac{\hbar^2 k^2}{2m} >> U_{\vec{G}}\right)$$

- O-th order:

$$\varepsilon^{(0)}_k = \varepsilon^0_{\vec{k}-\vec{G}_1}\ ; \qquad C^{(0)}_{\vec{k}}(\vec{G}) = \begin{cases} 1 & \text{when } \vec{G} = \vec{G}_1 \\ 0 & \text{when } \vec{G} \neq \vec{G}_1 \end{cases}$$

By iteration,

$$\left(\varepsilon^0_{\vec{k}-\vec{G}} - \varepsilon_k\right) C_{\vec{k}}(\vec{G}) + U_{\vec{G}_1-\vec{G}} C^0_{\vec{k}}(\vec{G}_1) = 0$$

- Let $G=G_1$,

$$\Rightarrow \quad \varepsilon^{(1)}_k = \varepsilon^0_{\vec{k}-\vec{G}_1} + U_0 + O(U^2)$$ ← 1st order energy correction

- Let $G \neq G_1$,

$$\Rightarrow \quad C^{(1)}_{\vec{k}}(\vec{G}) = \frac{U_{\vec{G}_1-\vec{G}}}{\varepsilon^0_{\vec{k}-\vec{G}_1} - \varepsilon^0_{\vec{k}-\vec{G}}}$$ ← 1st order state correction

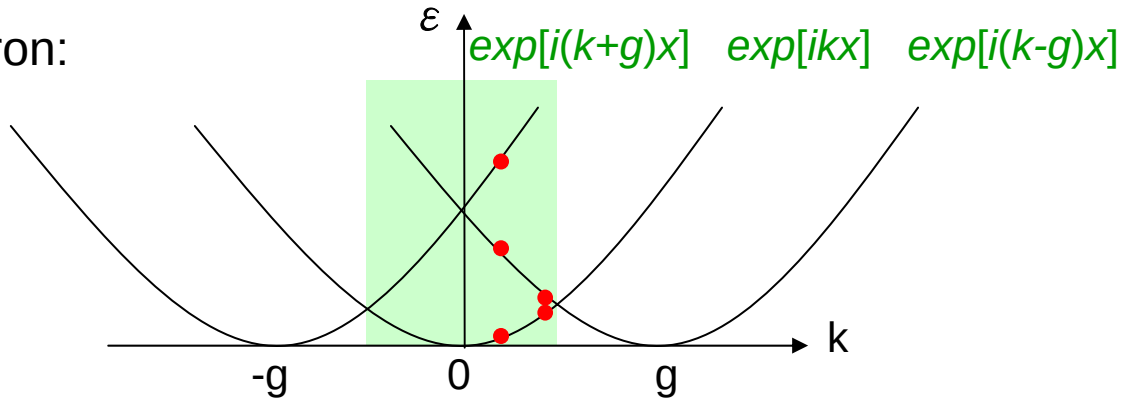
- If, for $G=G_2 \neq G_1$, $\varepsilon^0_{\vec{k}-\vec{G}_2} \cong \varepsilon^0_{\vec{k}-\vec{G}_1}$, then the perturbation above fails.

Nearly-free electron (for illustration, consider 1D)

• The Bloch state $\psi_{nk}(x) = \sum_G C_{nk}(G) e^{i(k-G)x}$

is a superposition of … *exp*[*i*(*k*-*g*)*x*], *exp*[*ikx*], *exp*[*i*(*k*+*g*)*x*] …

Free electron:



Under a weak perturbation:

• If $k \sim 0$, then the most significant component of $\phi_{1k}(x)$ (at low energy) is *exp*[*ikx*] (little superposition from other plane waves)

• If $k \sim g/2$, then the most significant components of $\phi_{1k}(x)$ and $\phi_{2k}(x)$ (at low energy) are *exp*[*i*(*k*-*g*)*x*] *and exp*[*ikx*], others can be neglected.

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Degenerate perturbation

• If $\{G_1, G_2, \ldots G_m\}$ give similar energy $\varepsilon^0_{k\text{-}G}$

(and are away from other energy levels), then

• for $G \neq \{G_1, G_2, \ldots G_m\}$, one has

$$C^{(1)}_{\vec{k}}(\vec{G}) = \frac{\sum_{i=1}^{m} U_{\vec{G}_i - \vec{G}} C^0_k(\vec{G}_i)}{\varepsilon^0_{\vec{k}-\vec{G}_i} - \varepsilon^0_{\vec{k}-\vec{G}}}, \quad \vec{G} \neq \vec{G}_1$$

• for $G = \{G_1, G_2, \ldots G_m\}$, one has

$$\left(\varepsilon^0_{\vec{k}-\vec{G}_i} - \varepsilon_k\right) C_{\vec{k}}(\vec{G}_i) + \sum_{j=1}^{m} U_{\vec{G}_j - \vec{G}_i} C_{\vec{k}}(\vec{G}_j) + \cancel{\sum_{\vec{G}' \neq \vec{G}_i} U_{\vec{G}' - \vec{G}_i} C_{\vec{k}}(\vec{G}')} = 0$$

or

$$\begin{pmatrix} \varepsilon^0_{\vec{k}-\vec{G}_1} - \varepsilon_k & U_{\vec{G}_2-\vec{G}_1} & \cdots & U_{\vec{G}_m-\vec{G}_1} \\ U_{\vec{G}_1-\vec{G}_2} & \ddots & & \vdots \\ \vdots & & \ddots & U_{\vec{G}_m-\vec{G}_{m-1}} \\ U_{\vec{G}_1-\vec{G}_m} & \cdots & U_{\vec{G}_{m-1}-\vec{G}_m} & \varepsilon^0_{\vec{k}-\vec{G}_m} - \varepsilon_k \end{pmatrix} \begin{pmatrix} C_{\vec{k}}(\vec{G}_1) \\ \vdots \\ \vdots \\ C_{\vec{k}}(\vec{G}_m) \end{pmatrix} = 0$$

→ 1st order eigen-energy and 0-th order eigen-states

For example, m=2

near |***k***|=|***k***-***G***|,

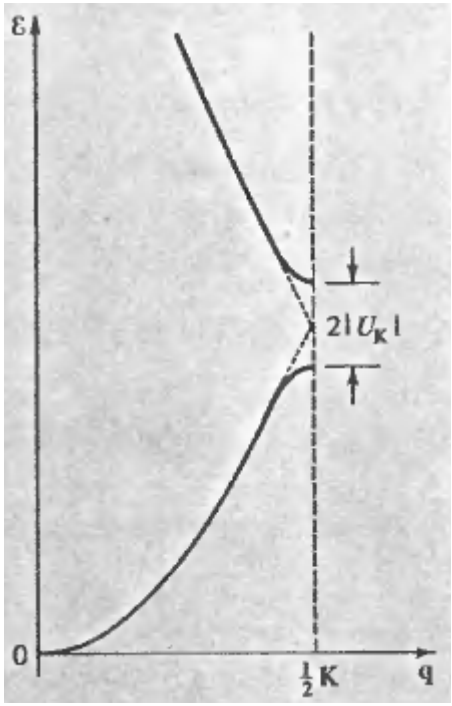
$$\begin{pmatrix} \varepsilon^0_{\vec{k}} - \varepsilon_k & U_{\vec{G}_2} \\ U_{-\vec{G}_2} & \varepsilon^0_{\vec{k}-\vec{G}} - \varepsilon_k \end{pmatrix} \begin{pmatrix} C_{\vec{k}}(0) \\ C_{\vec{k}}(\vec{G}) \end{pmatrix} = 0$$

• Energy eigenvalues

$$\varepsilon^{(1)}_{k\pm} = \frac{\varepsilon^0_{\vec{k}} + \varepsilon^0_{\vec{k}-\vec{G}}}{2} \pm \sqrt{\left(\frac{\varepsilon^0_{\vec{k}} - \varepsilon^0_{\vec{k}-\vec{G}}}{2}\right)^2 + \left|U_{\vec{G}}\right|^2}$$

$$\rightarrow \varepsilon^0_{\vec{k}} = \varepsilon^0_{\vec{k}-\vec{G}} \quad \text{when } \vec{k}\cdot\hat{G} = \frac{G}{2}$$

∴ for a **k** near a Bragg plane, need to use degenerate perturbation and the energy correction is of order U



Back to the example with m=2,

- Bloch states with **q** <u>on</u> the Bragg plane

$$\varepsilon_{k\pm}^{(1)} = \varepsilon_{\vec{k}}^{0} \pm |U_{\vec{G}}|$$

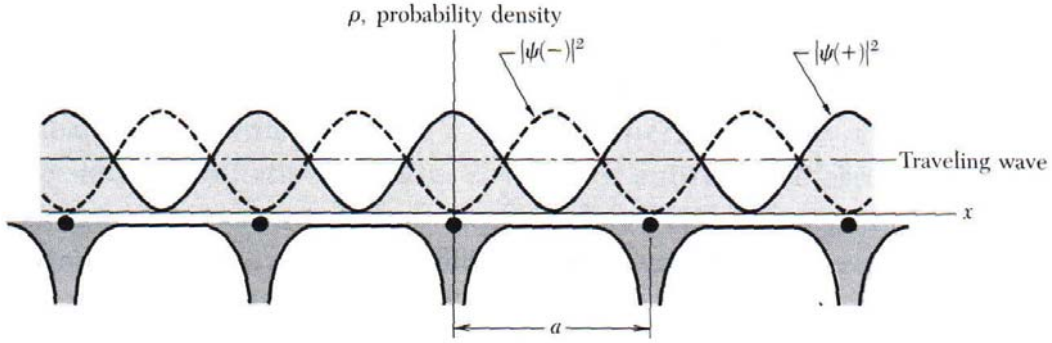
$$\Rightarrow \begin{pmatrix} \mp U_{\vec{G}} & U_{\vec{G}} \\ U_{\vec{G}_2}^{*} & \mp U_{\vec{G}_2} \end{pmatrix} \begin{pmatrix} C_k(0) \\ C_k(\vec{G}) \end{pmatrix} = 0$$

- From inversion symmetry, U_G is real, then

$$\begin{pmatrix} C_k(0) \\ C_k(\vec{G}) \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}$$

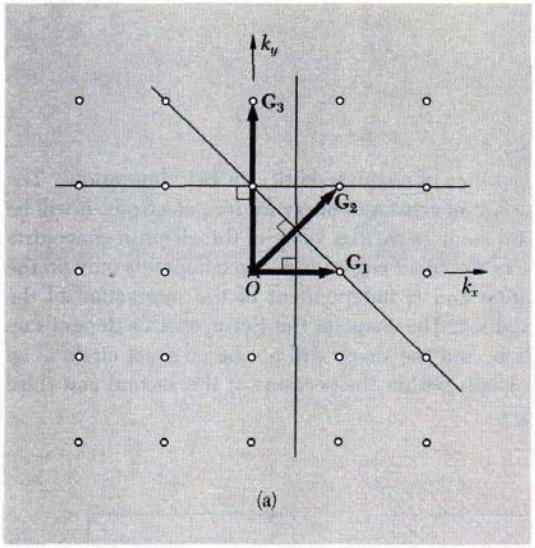
$$\psi_{\vec{k}\pm}^{(0)}(\vec{r}) = C_{\vec{k}\pm}(0) e^{i\vec{k}\cdot\vec{r}} + C_{\vec{k}\pm}(\vec{G}) e^{i(\vec{k}-\vec{G})\cdot\vec{r}}$$

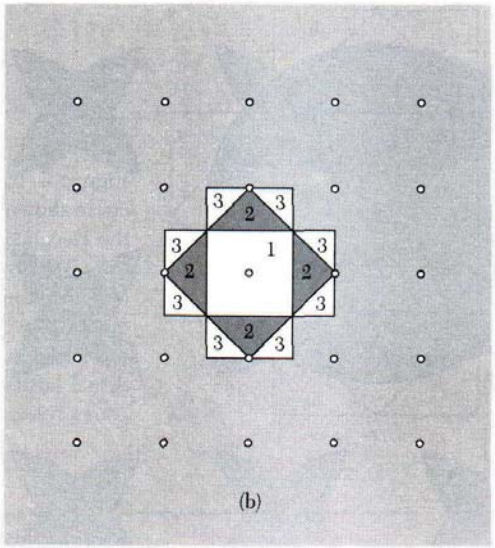
$$\Rightarrow \quad \left|\psi_{\vec{k}\pm}^{(0)}(\vec{r})\right|^2 = \begin{cases} 2\cos^2\left(\dfrac{\vec{G}\cdot\vec{r}}{2}\right) \\ 2\sin^2\left(\dfrac{\vec{G}\cdot\vec{r}}{2}\right) \end{cases},$$



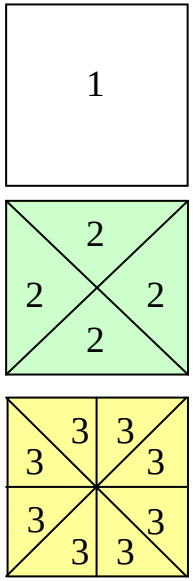
Bragg reflection at BZB forms two standing wave with a finite energy difference (energy gap)

Higher Brillouin zones





Reduced zone scheme

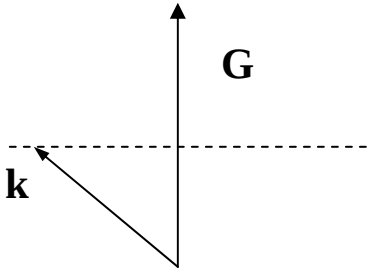


Same area

• At zone boundary, **k** points to the plane bi-secting the **G** vector,

thus satisfying the Laue condition

$$\vec{k} \cdot \hat{G} = \frac{G}{2}$$

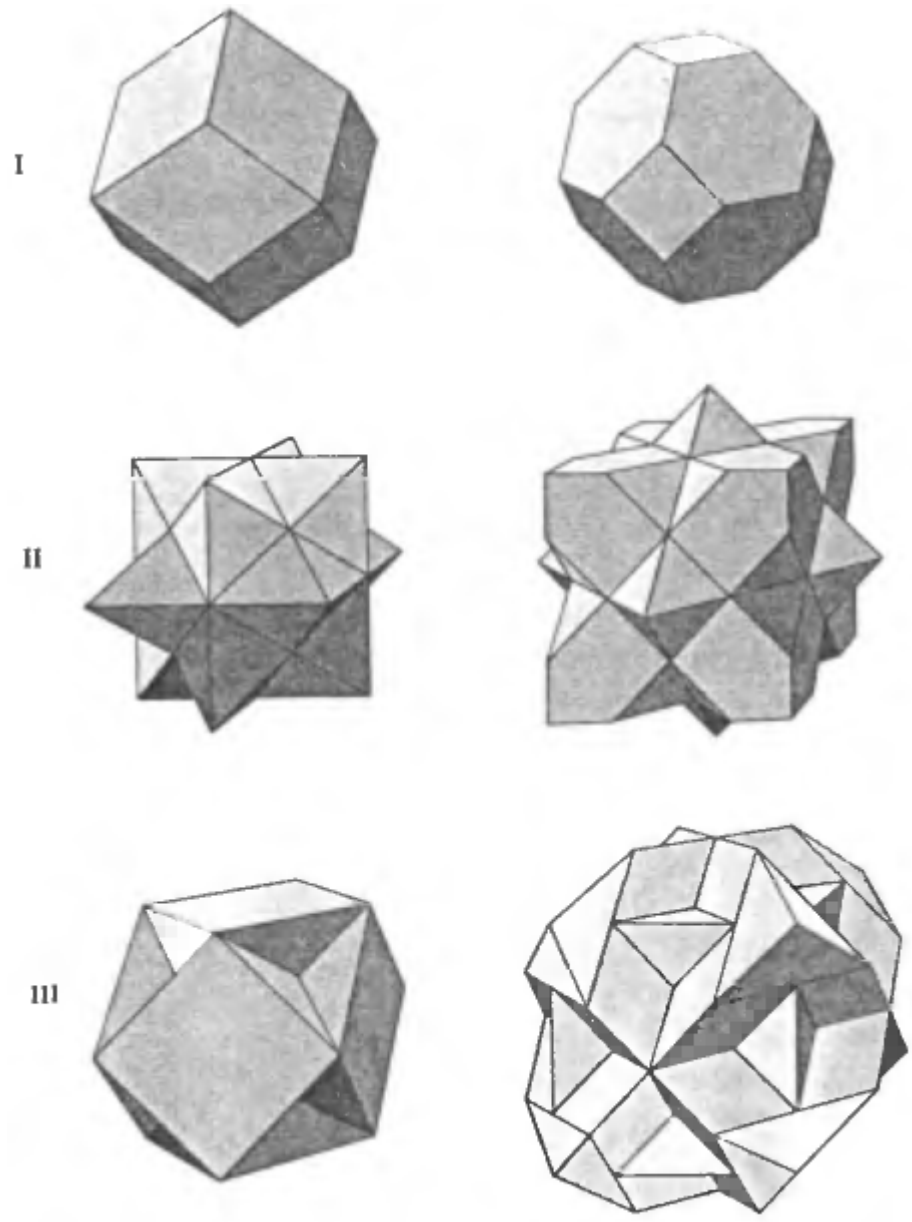


• Bragg reflection at zone boundaries produce energy gaps (Peierls, 1930)

Beyond the 1st Brillouin zone

BCC crystal

FCC crystal



“Empty lattice” in 2D

Free electron in vacuum:

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2 \mathbf{k}^2}{2m}$$

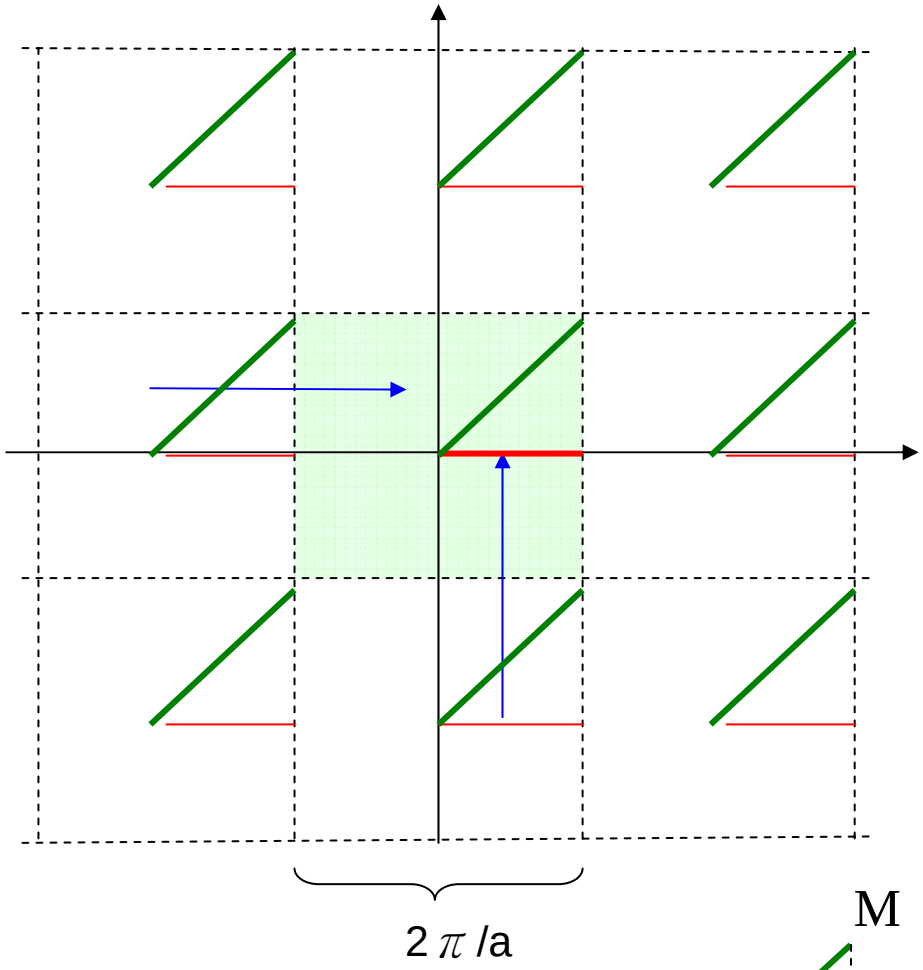
Free electron in empty lattice:

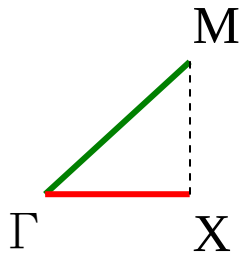
$$\varepsilon_{\mathbf{k}} = \varepsilon_{n\mathbf{k}'} = \frac{\hbar^2 \left(\mathbf{k}' + \mathbf{G}\right)^2}{2m}$$

$$\mathbf{k} = \mathbf{k}' + \mathbf{G}$$

$$\mathbf{k}' \in 1^{st}\, BZ$$

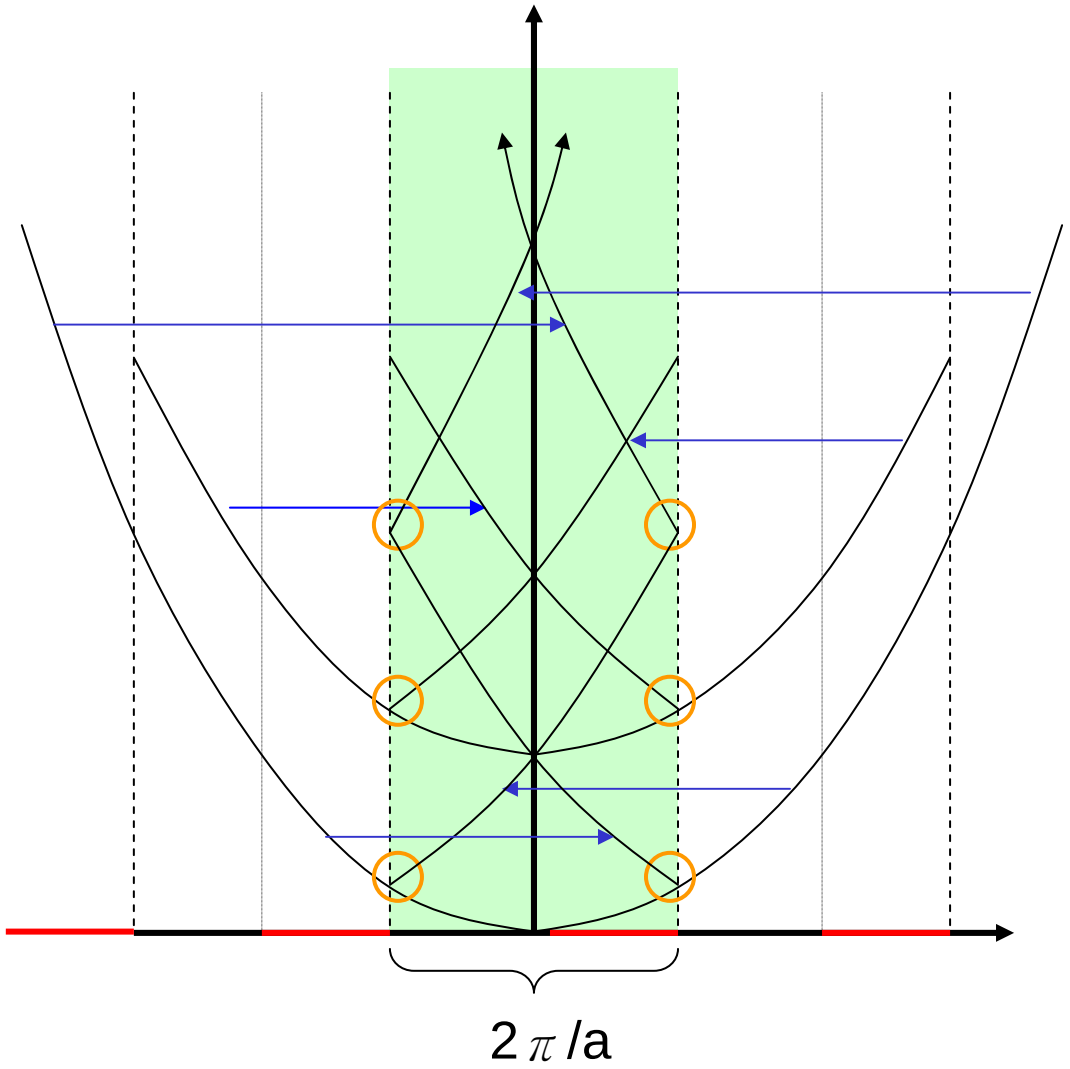
2D square lattice



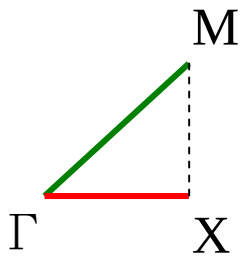


- How to fold a parabolic “surface” back to the first BZ?

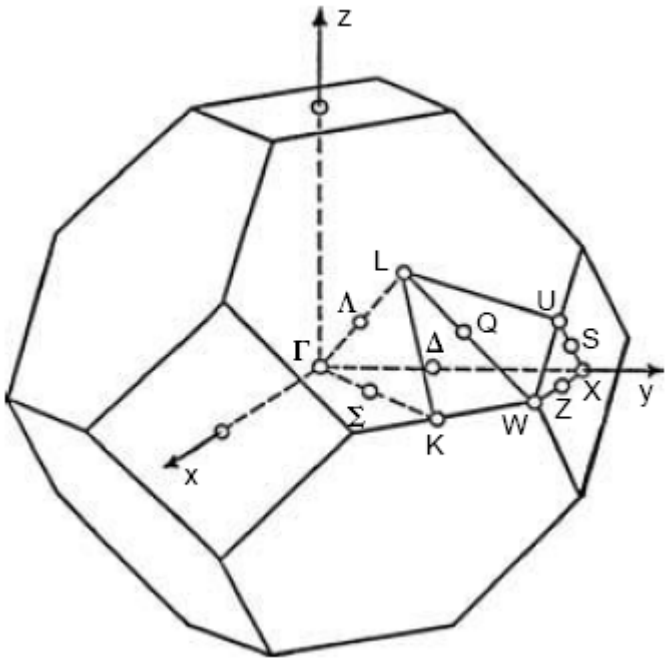
Folded parabola along Γ X (reduced zone scheme)

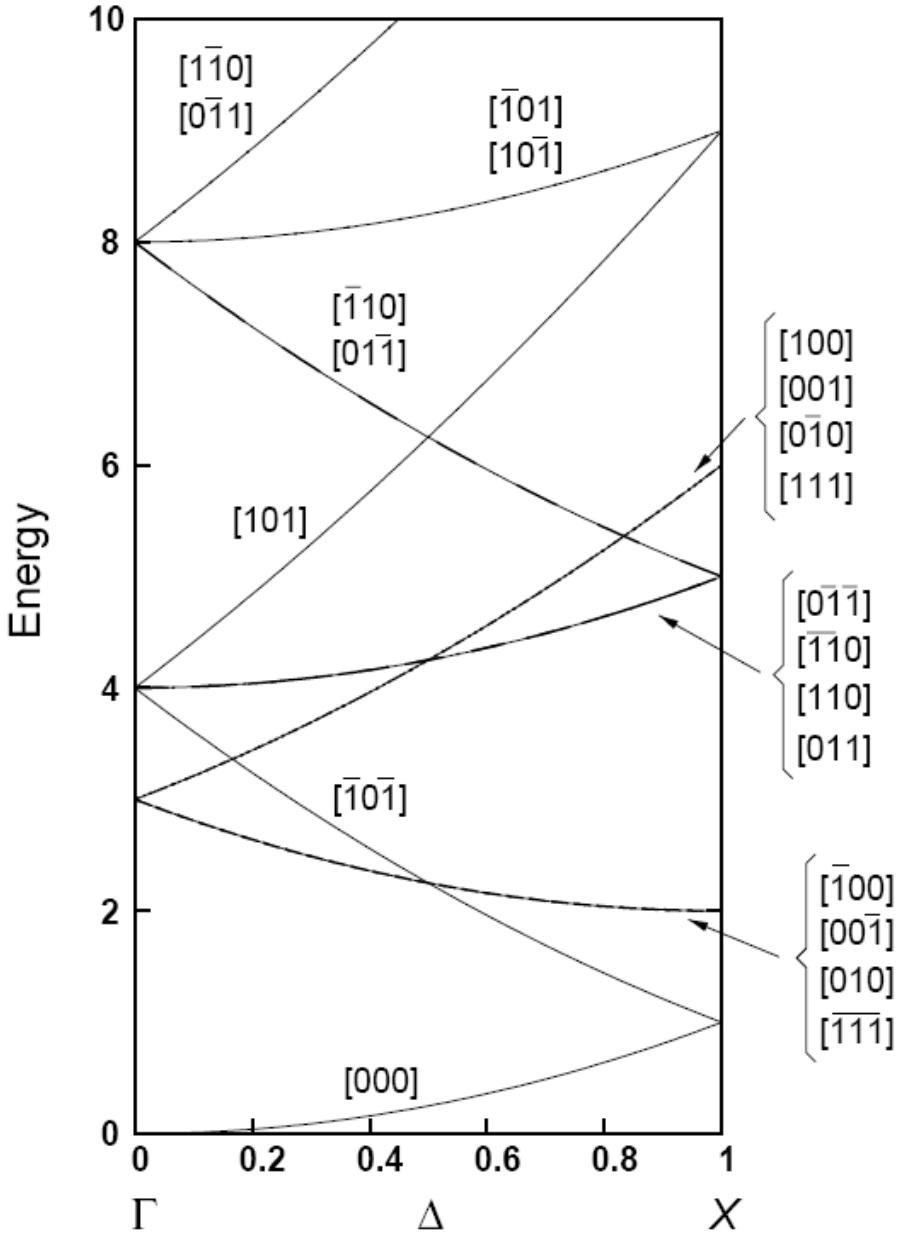


- For U≠0, there are energy gaps at BZ boundaries



Empty FCC lattice



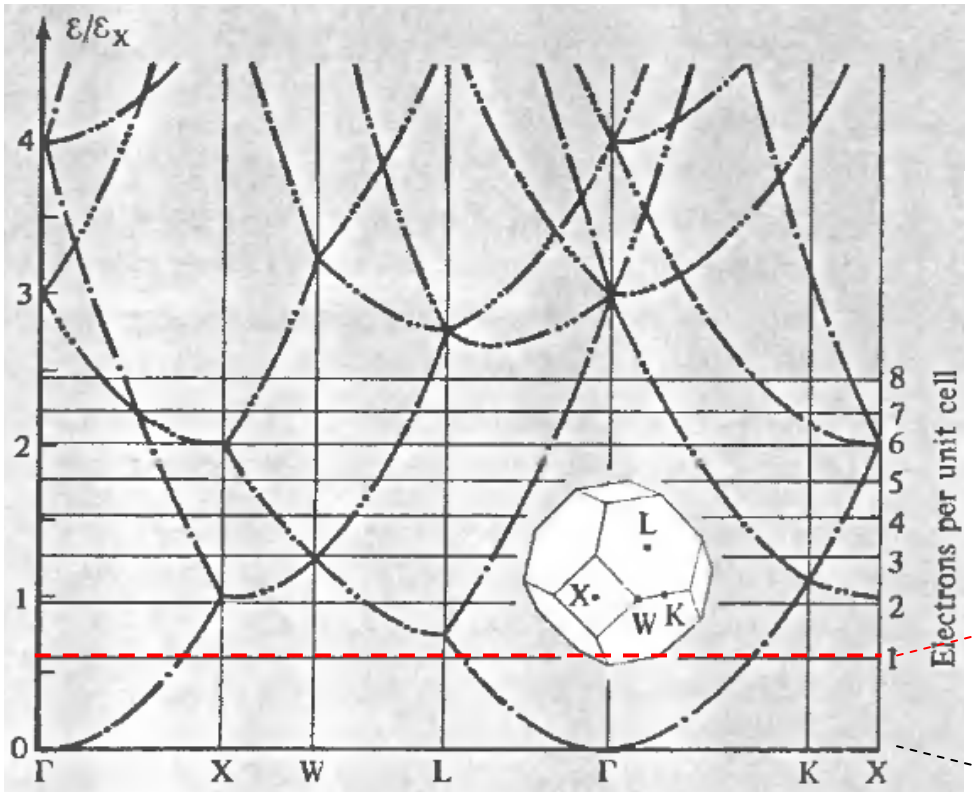


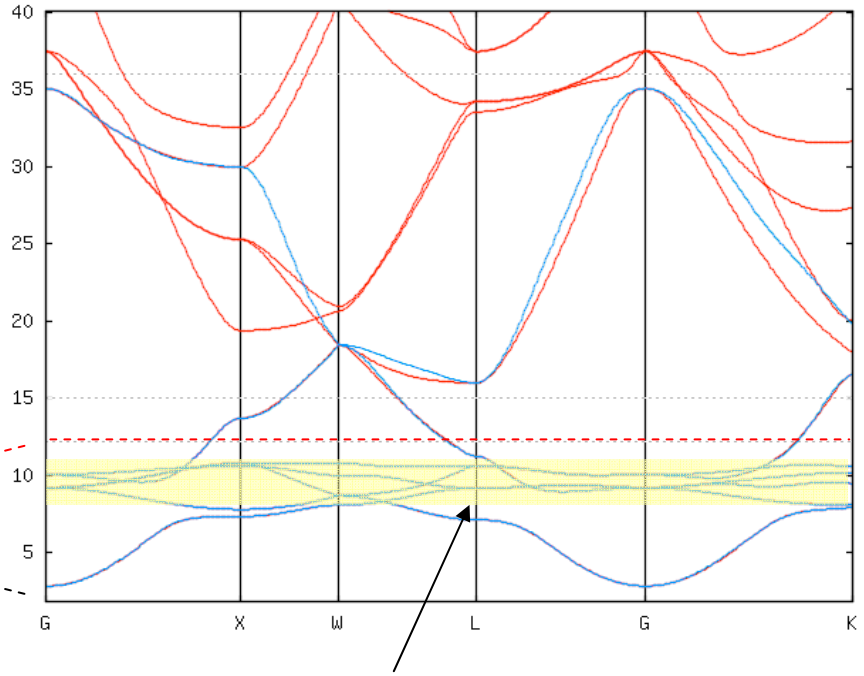
Energy bands for empty FCC lattice along the Γ-*X* direction.

Comparison with real band structure

The energy bands for
"empty" FCC lattice

Actual band structure for
copper (FCC, $3d^{10}4s^{1}$)





d bands

From Dr. J. Yates's ppt

Fermi surface for (2D) empty lattice

For a monovalent element,
the Fermi wave vector

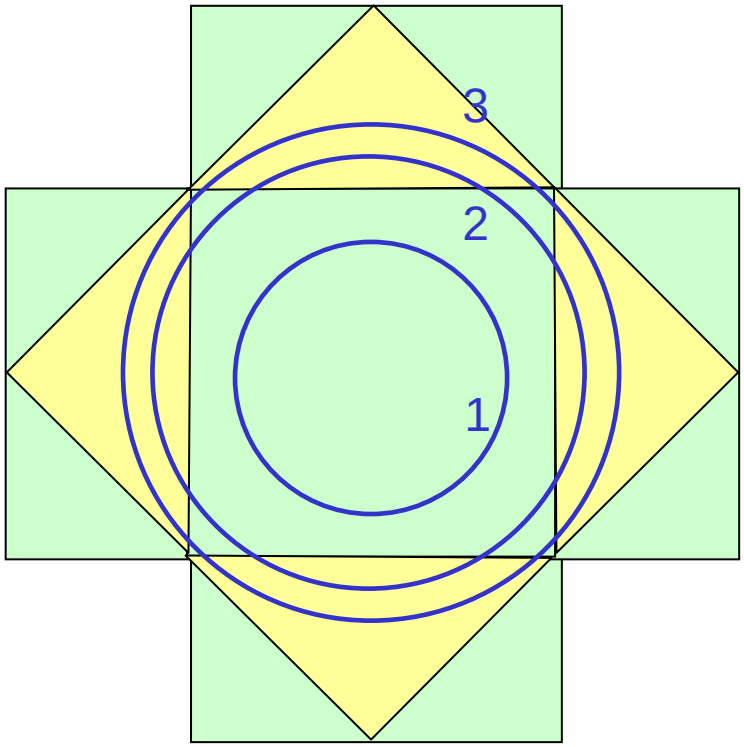
$$k_F = \sqrt{2\pi}/a$$

For a divalent element

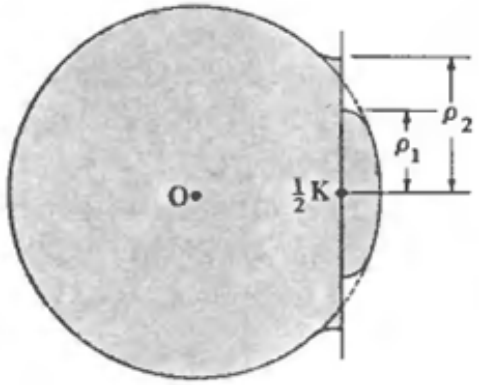
$$k_F = \sqrt{4\pi}/a$$

For a trivalent element

$$k_F = \sqrt{6\pi}/a$$



Distortion due to lattice potential



Fermi surface of alkali metals (monovalent, BCC lattice)

THE MONOVALENT METALS

ALKALI METALS (BODY-CENTERED CUBIC)[a]		NOBLE METALS (FACE-CENTERED CUBIC)	
Li:	$1s^2 2s^1$	—	
Na:	$[Ne]3s^1$	—	
K:	$[Ar]4s^1$	Cu:	$[Ar]3d^{10}4s^1$
Rb:	$[Kr]5s^1$	Ag:	$[Kr]4d^{10}5s^1$
Cs:	$[Xe]6s^1$	Au:	$[Xe]4f^{14}5d^{10}6s^1$

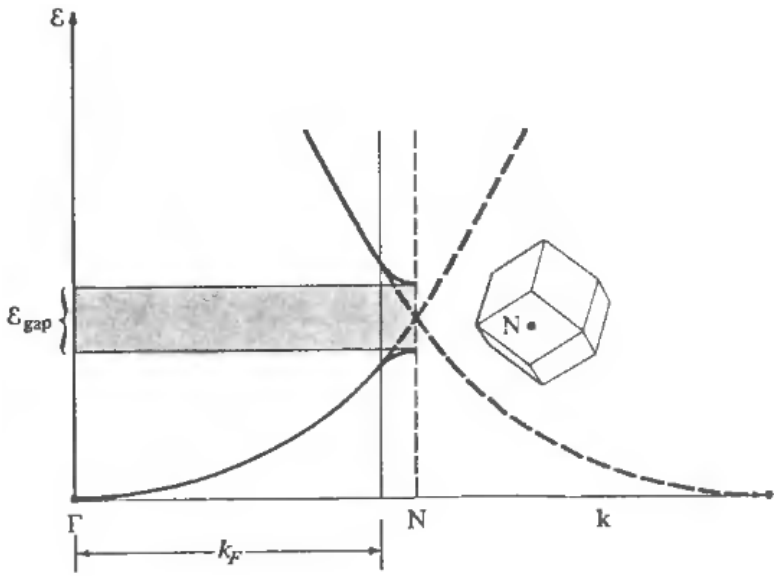
$k_F = (3\pi^2 n)^{1/3}$

$n = 2/a^3$

$\rightarrow k_F = (3/4\pi)^{1/3}(2\pi/a)$

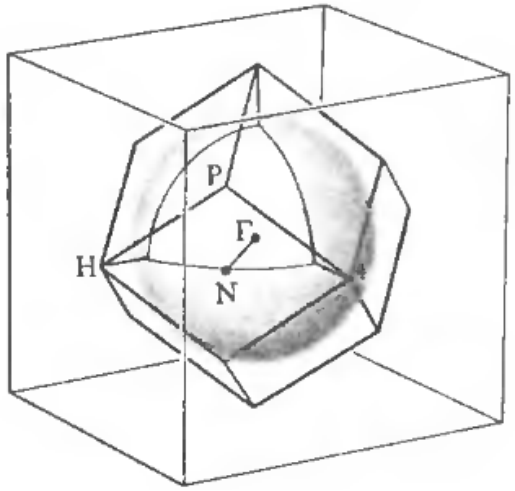
$\Gamma N = (2\pi/a)[(1/2)^2+(1/2)^2]^{1/2}$

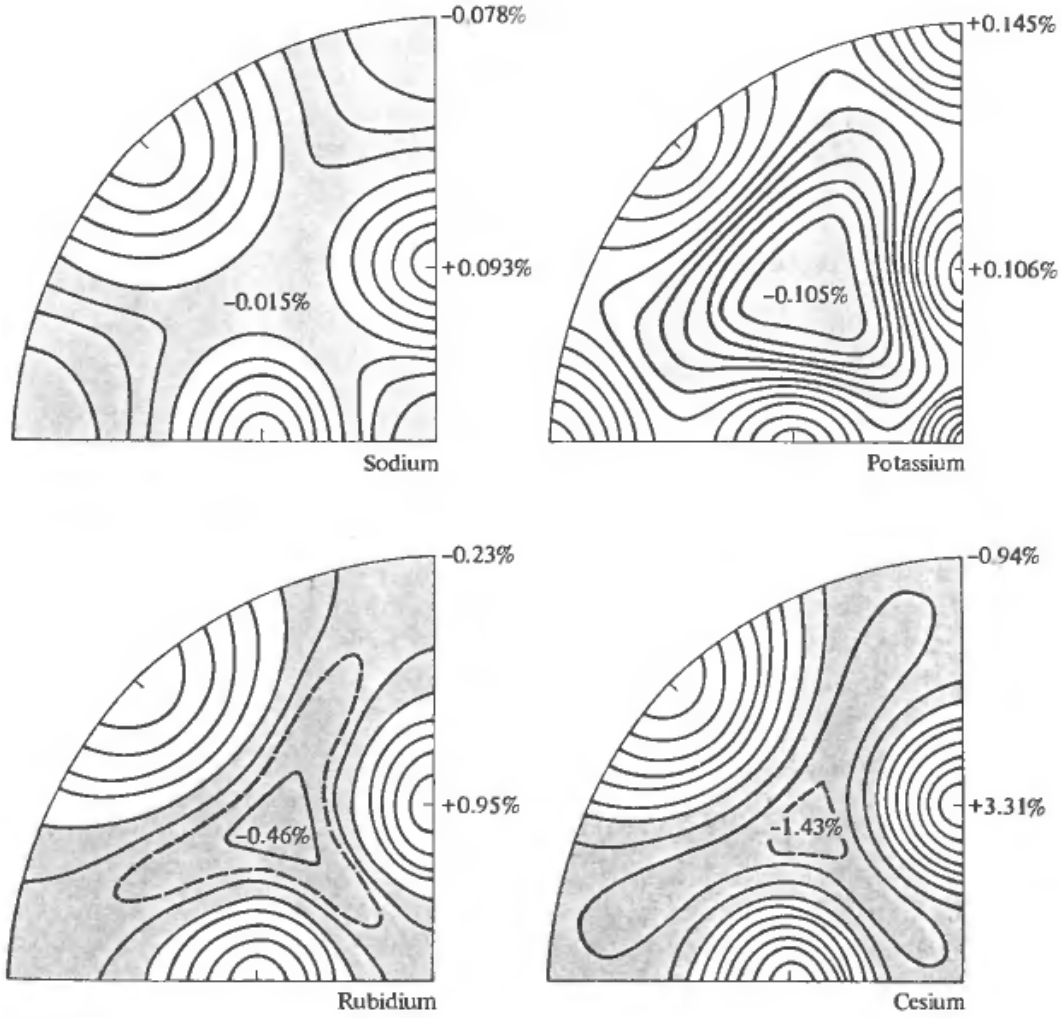
$\therefore k_F = 0.877\ \Gamma N$



Fermi spheres of alkali metals

Percent deviation of k from the free electron value

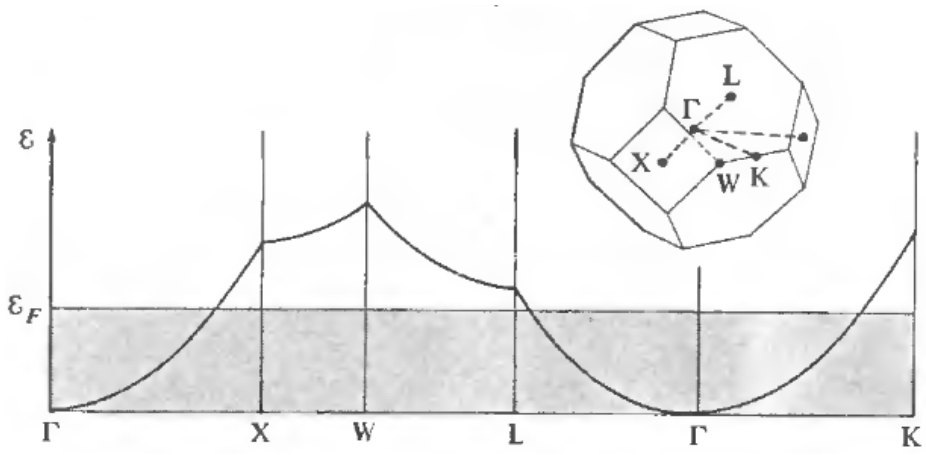




Fermi surface of noble metals (monovalent, FCC lattice)

Band structure

(empty lattice)



$k_F = (3\pi^2 n)^{1/3}$,

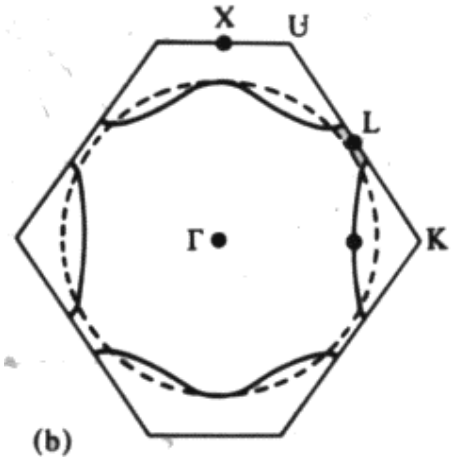
$n = 4/a^3$

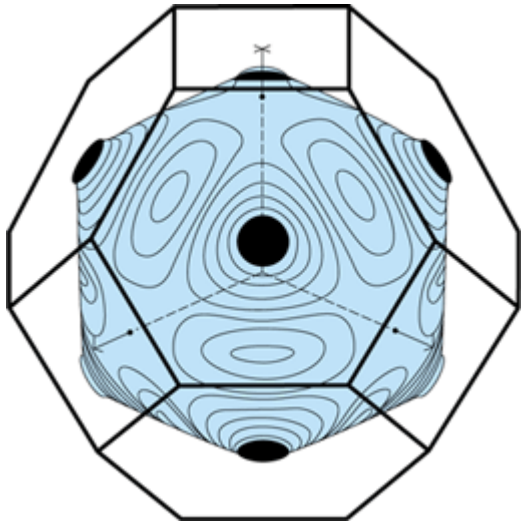
$\rightarrow k_F = (3/2\pi)^{1/3}(2\pi/a)$

$\Gamma L =$ ___

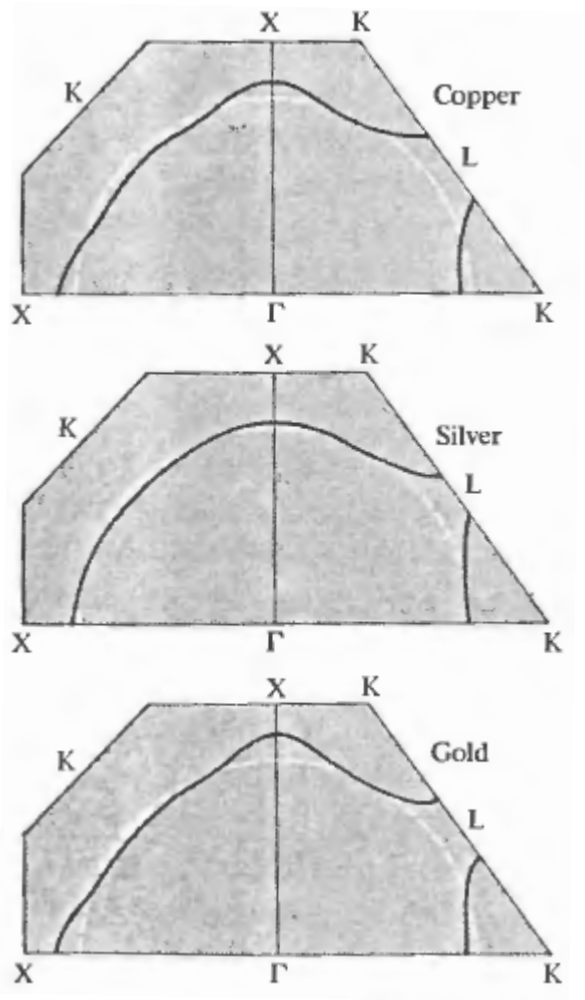
$k_F =$ ___ ΓL

Fermi surface
(a cross-section)

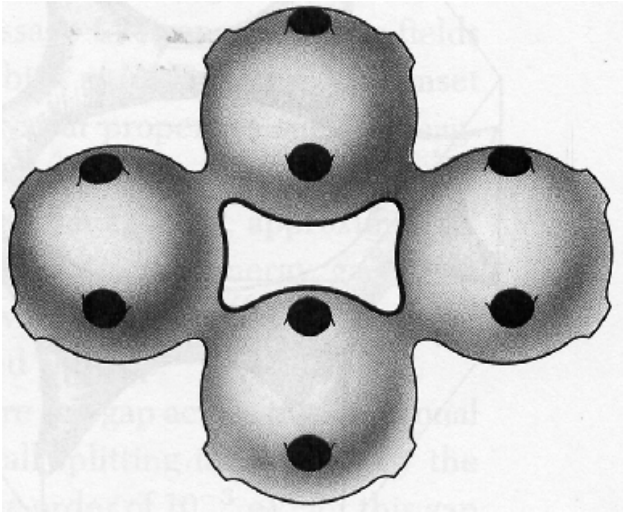




Fermi surfaces of noble metals

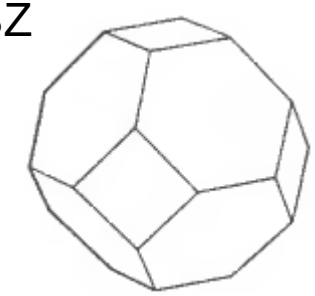


Periodic zone scheme

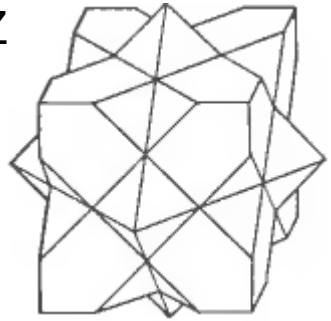


Fermi surface of Al (trivalent, FCC lattice)

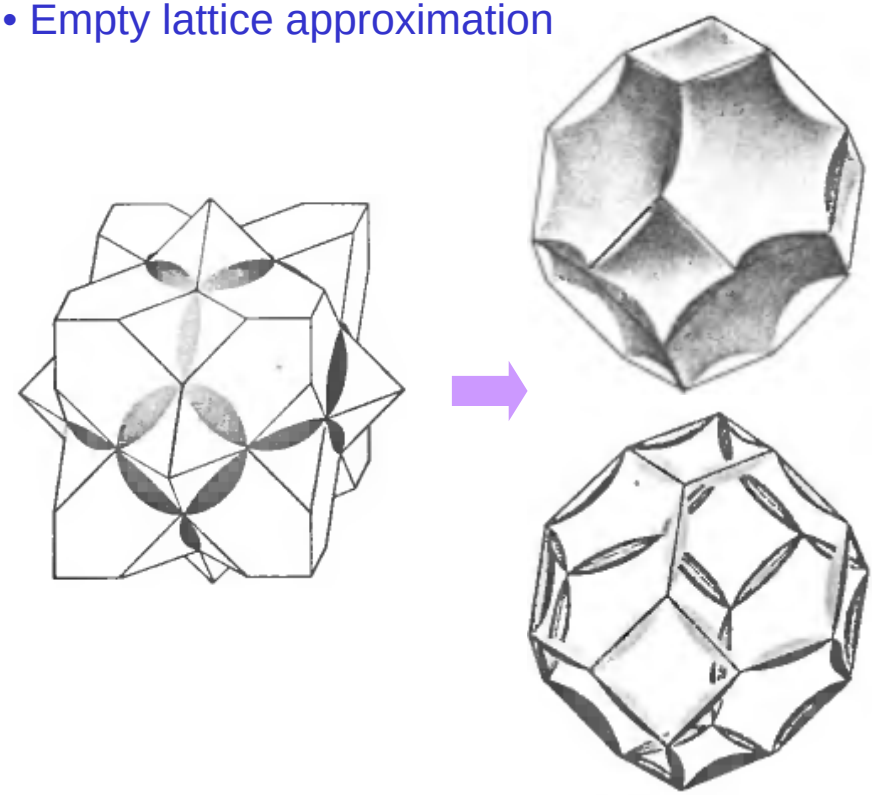
1st BZ



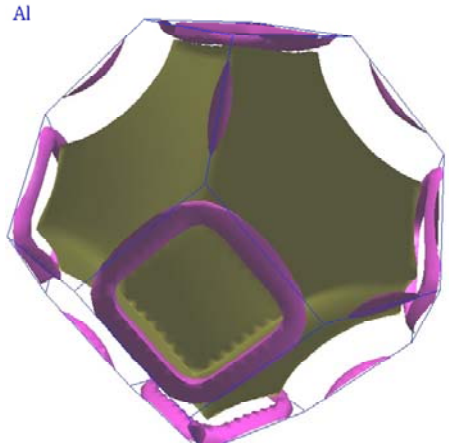
2nd BZ



- Empty lattice approximation



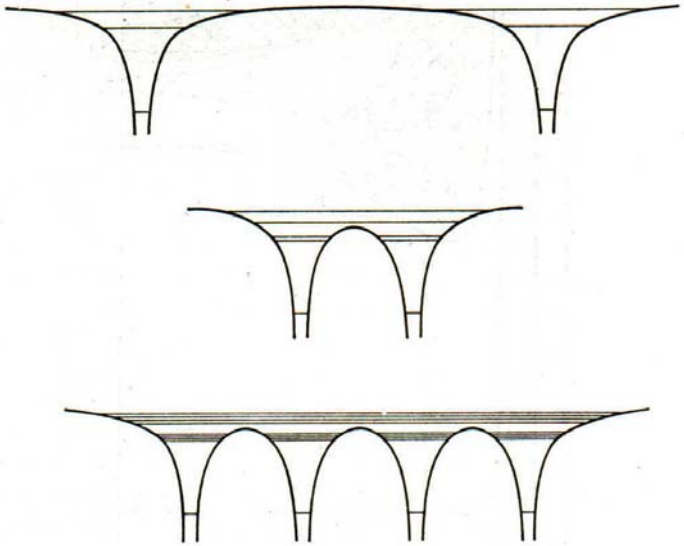
- Actual Fermi surface

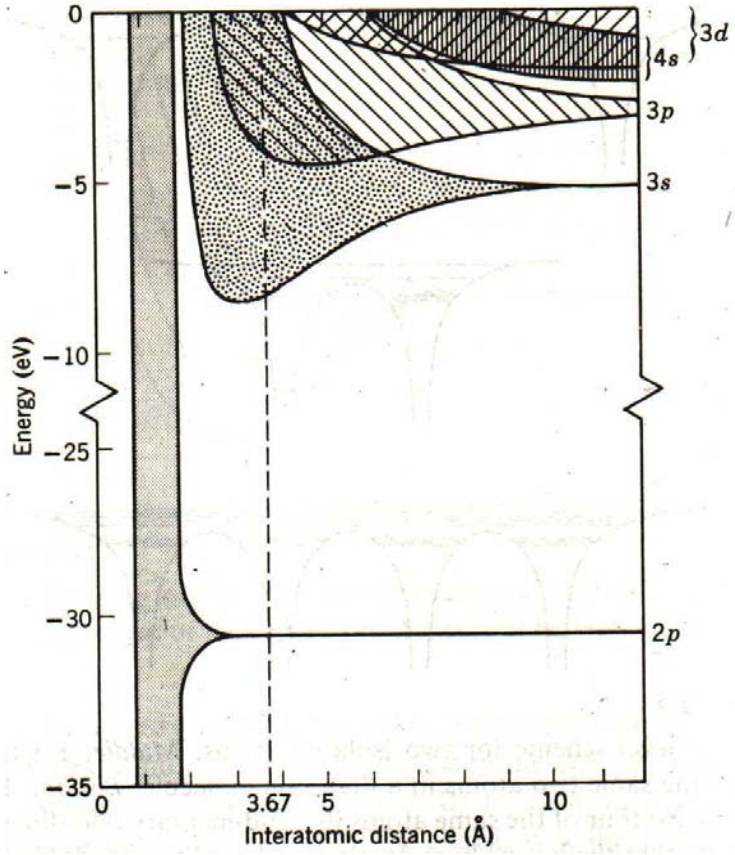


Tightly bound electron

Tight binding model:

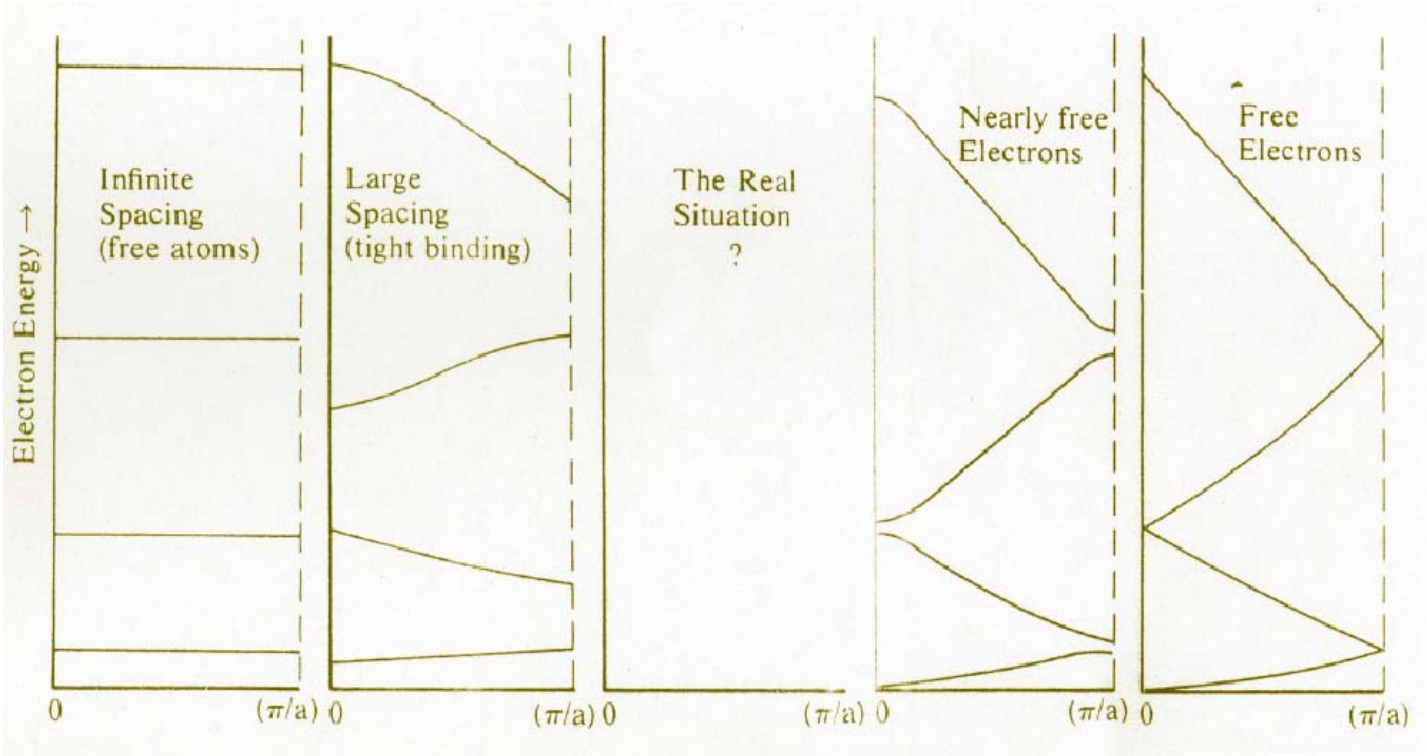
Energy bands as an extension of atomic orbitals





- Covalent solid
- d-electrons in transition metals

- Alkali metal
- noble metal



"We have the rather curious result that not only is it possible to obtain conduction with bound electrons, but it is also possible to obtain non-conduction with free electrons.“ A. Wilson

important

Tight binding method (Bloch, 1928)

Let $a_m(r)$ be the eigenstate of an electron in the potential $U_{at}(r)$ of an isolated atom.

$$H_{at} a_m(r) = \varepsilon_m^{at} a_m(r)$$

atomic orbital

Consider a crystal with N atoms at lattice sites ***R***,

• A wave function with translation symmetry
(but still not an energy eigenstate)

$$\varphi_{m\vec{k}}(\vec{r}) = \sum_{\vec{R}} d_{\vec{k}}(\vec{R}) a_m(\vec{r} - \vec{R})$$

$$= \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} a_m(\vec{r} - \vec{R})$$

Linear combination of atomic orbitals (LCAO)

Check:

$$\varphi_{m\vec{k}}(\vec{r} + \vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}'} e^{i\vec{k}\cdot\vec{R}'} a_m(\vec{r} - (\vec{R}' - \vec{R}))$$

$$= e^{i\vec{k}\cdot\vec{R}} \frac{1}{\sqrt{N}} \sum_{\vec{R}'} e^{i\vec{k}\cdot\vec{R}'} a_m(\vec{r} - \vec{R}') = e^{i\vec{k}\cdot\vec{R}} \varphi_{m\vec{k}}(\vec{r})$$

important

An energy eigenstate (Bloch state)

$$\psi_{n\vec{k}}(\vec{r}) = \sum_m C_m^n \varphi_{m\vec{k}}(\vec{r})$$

Schrödinger equation

$$H = \frac{p^2}{2m} + U(\vec{r})$$

$$H\left|\psi_{n\vec{k}}\right\rangle = \varepsilon_n \left|\psi_{n\vec{k}}\right\rangle$$

$$\left\langle \varphi_{m\vec{k}} \middle| (H - \varepsilon_n) \middle| \psi_{n\vec{k}} \right\rangle = 0$$

$$\Rightarrow$$

$$\sum_{m'} \left\langle \varphi_{m\vec{k}} \middle| (H - \varepsilon_n) \middle| \varphi_{m'\vec{k}} \right\rangle C_{m'}^n = 0$$

define

$$H_{mm'}(\vec{k}) = \left\langle \varphi_{m\vec{k}} \middle| H \middle| \varphi_{m'\vec{k}} \right\rangle$$

$$S_{mm'}(\vec{k}) = \left\langle \varphi_{m\vec{k}} \middle| \varphi_{m'\vec{k}} \right\rangle$$

then

$$\sum_{m'} \left(H_{mm'} - \varepsilon_n S_{mm'}\right) C_{m'}^n = 0$$

- $$H_{mm'} = \frac{1}{N} \sum_{\vec{R},\vec{R}'} \left\langle a_{m\vec{R}} \middle| H \middle| a_{m'\vec{R}'} \right\rangle e^{-i\vec{k}\cdot\left(\vec{R}-\vec{R}'\right)},$$

where $\left\langle \vec{r} \middle| a_{m'\vec{R}'} \right\rangle \equiv a_{m'}(\vec{r} - \vec{R}')$.

- $$S_{mm'} = \frac{1}{N} \sum_{\vec{R},\vec{R}'} \left\langle a_{m\vec{R}} \middle| a_{m'\vec{R}'} \right\rangle e^{-i\vec{k}\cdot\left(\vec{R}-\vec{R}'\right)}$$

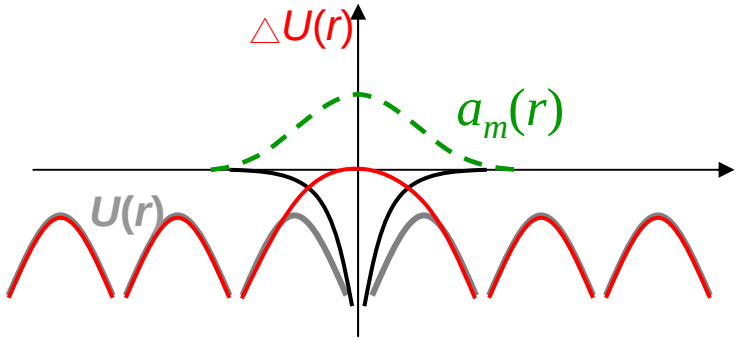
$$= \delta_{mm'} + \sum_{\vec{R}\neq 0} \left\langle a_{m\vec{R}} \middle| a_{m'0} \right\rangle e^{-i\vec{k}\cdot\vec{R}}$$

$$\equiv \alpha_{mm'}(\vec{R})$$

Overlap integral

important

$$H = \frac{p^2}{2m} + U_{at} + (U - U_{at})$$
$$= H_{at} + \Delta U$$



$$H_{mm'} = \frac{1}{N}\sum_{\vec{R},\vec{R}'} \langle a_{m\vec{R}} | H | a_{m'\vec{R}'} \rangle e^{-i\vec{k}\cdot(\vec{R}-\vec{R}')}$$
$$= \langle a_{m0} | H | a_{m'0} \rangle + \sum_{\vec{R}\neq 0} \langle a_{m\vec{R}} | H | a_{m'0} \rangle e^{-i\vec{k}\cdot\vec{R}}$$

- $\langle a_{m0} | H | a_{m'0} \rangle = \langle a_{m0} | H_{at} + \Delta U | a_{m'0} \rangle$
  $= \delta_{mm'}\varepsilon_m^{at} + \langle a_{m0} | \Delta U | a_{m'0} \rangle$
  $\equiv \beta_{mm'}$ ⬅
- $\langle a_{m\vec{R}} | H | a_{m'0} \rangle = \varepsilon_m^{at} \langle a_{m\vec{R}} | a_{m'0} \rangle + \langle a_{m\vec{R}} | \Delta U | a_{m'0} \rangle$
  $= \varepsilon_m^{at} \alpha_{mm'}(\vec{R}) + \gamma_{mm'}(\vec{R})$ ⬅

energy shift due to the potential of neighboring atoms. (U in Marder's)

inter atomic matrix element between nearby atoms. (t in Marder's)

$$\Rightarrow H_{mm'} = \delta_{mm'}\varepsilon_m^{at} + \beta_{mm'} + \varepsilon_m^{at}\alpha_{mm'}(\vec{k}) + \gamma_{mm'}(\vec{k})$$

$$\sum_{m'}\left(H_{mm'}-\varepsilon_n S_{mm'}\right)C^n_{m'}=0 \quad \sim \quad \text{same status as the central eq. in NFE model}$$

$$\Downarrow$$

$$\boxed{\sum_{m'}\left[\varepsilon^{at}_m\left(\delta_{mm'}+\alpha_{mm'}(\vec{k})\right)+\beta_{mm'}+\gamma_{mm'}(\vec{k})\right]C^n_{m'}=\varepsilon_n\sum_{m'}\left(\delta_{mm'}+\alpha_{mm'}(\vec{k})\right)C^n_{m'}}$$

i.e.

$$\mathbf{A}\vec{C}=\varepsilon_n\mathbf{B}\vec{C} \quad \Rightarrow \quad \left(\mathbf{B}^{-1}\mathbf{A}\right)\vec{C}=\varepsilon_n\vec{C} \quad : \text{an eigenvalue problem}$$

- so far no approximation has been used!

Approximation 1:

The ranks of A, B depend on the number of atomic orbitals a_m

- s-orbital, m=1
- p-orbital, m=1…3
- d-orbital, m=1…5
- s-p mixing, m=1…4 etc

Approximation 2:

Keep only a few overlap integrals (e.g. for NN and NNN)

$$\alpha_{mm'}(\vec{R})=\left\langle a_{m\vec{R}}\middle|a_{m'0}\right\rangle$$

$$\gamma_{mm'}(\vec{R})=\left\langle a_{m\vec{R}}\middle|\Delta U\middle|a_{m'0}\right\rangle$$

$$\beta_{mm'}=\left\langle a_{m0}\middle|\Delta U\middle|a_{m'0}\right\rangle$$

(no R-dependence)

Example: s-band from the s-orbital (m=1)

$$\left[\varepsilon_s^{at}\left(1+\alpha(\vec{k})\right)+\beta+\gamma(\vec{k})\right]C^n=\varepsilon_n\left(1+\alpha(\vec{k})\right)C^n$$

$$\Rightarrow\quad \varepsilon_n=\varepsilon_s^{at}+\frac{\beta+\gamma(\vec{k})}{1+\alpha(\vec{k})}$$

$$\alpha(\vec{k})=\sum_{\vec{R}\neq 0}\alpha(\vec{R})e^{-i\vec{k}\cdot\vec{R}};\quad \alpha(\vec{R})=\int d^3r\, a_s^*(\vec{r}-\vec{R})a_s(\vec{r})$$

$$\beta=\int d^3r\, a_s^*(\vec{r})\Delta U a_s(\vec{r})$$

$$\gamma(\vec{k})=\sum_{\vec{R}\neq 0}\gamma(\vec{R})e^{-i\vec{k}\cdot\vec{R}};\quad \gamma(\vec{R})=\int d^3r\, a_s^*(\vec{r}-\vec{R})\Delta U a_s(\vec{r})$$

- If we keep only the NN integrals, then

$$\left(\alpha(-\vec{R})=\alpha(-\vec{R});\ \gamma(-\vec{R})=\gamma(-\vec{R})\ \text{have been used}\right)$$

$$\alpha(\vec{k})=2\sum_{\text{half of } NN}\alpha_0\cos\left(\vec{k}\cdot\vec{R}\right),\quad \alpha_0=\alpha(\vec{R}_{NN})$$

$$\gamma(\vec{k})=2\sum_{\text{half of } NN}\gamma_0\cos\left(\vec{k}\cdot\vec{R}\right),\quad \gamma_0=\gamma(\vec{R}_{NN})$$

Square lattice

- 3D $\varepsilon_n \simeq \varepsilon_s^{at} + \beta + \gamma(\vec{k})$

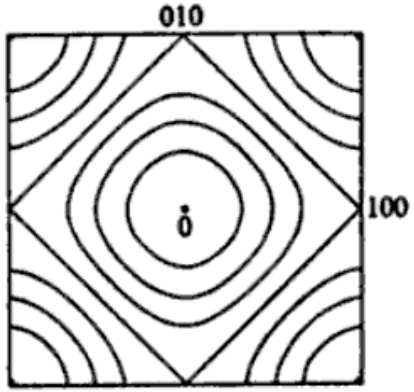
$$= 2 \sum_{\text{half of } NN} \gamma_0 \cos\left(\vec{k}\cdot\vec{R}\right) + \text{const.}$$

$$= 2\gamma_0 \left(\cos k_x a + \cos k_y a + \cos k_z a\right)$$

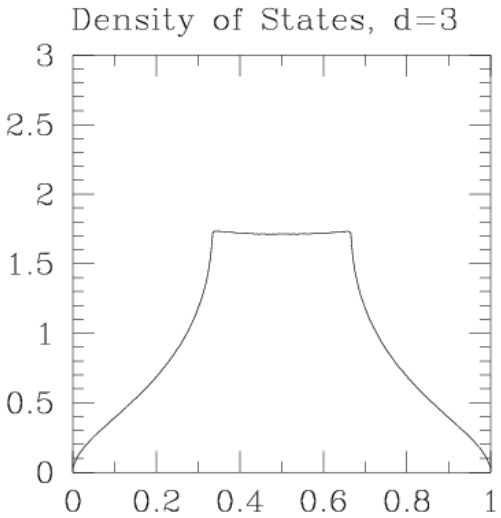
- 2D $\varepsilon_n = 2\gamma_0 \left(\cos k_x a + \cos k_y a\right)$

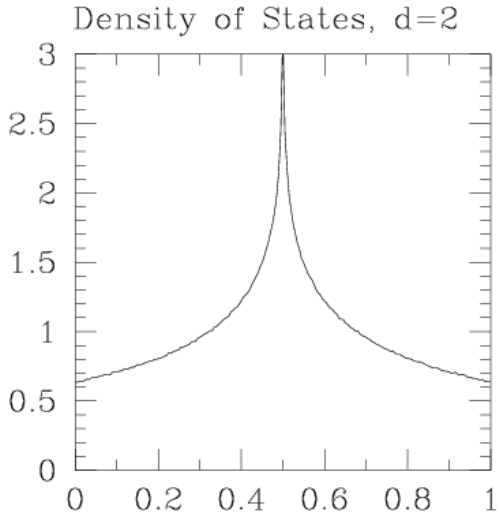
- 1D $\varepsilon_n = 2\gamma_0 \cos ka$

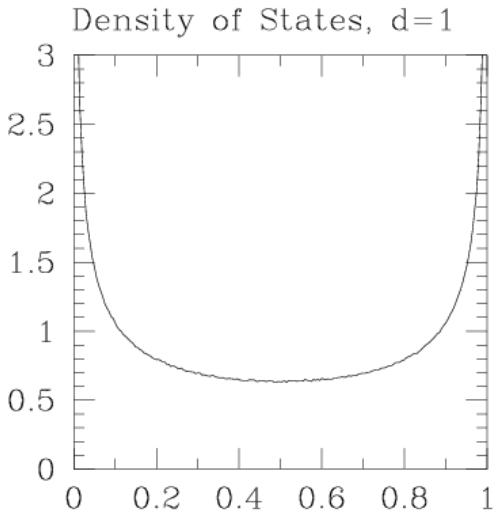
Energy contours



Density of states







From Dr. P. Young's at UCSC

Wannier function (1937)

- $\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} \sum_{m} e^{i\vec{k}\cdot\vec{R}} C_m^n a_m(\vec{r} - \vec{R})$

let $w_n(\vec{r} - \vec{R}) = \sum_m C_m^n a_m(\vec{r} - \vec{R})$

i.e. $\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} w_n(\vec{r} - \vec{R})$

$\Leftrightarrow \quad w_n(\vec{r} - \vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{k} \in 1st\ BZ} e^{-i\vec{k}\cdot\vec{R}} \psi_{n\vec{k}}(\vec{r})$ (localized)

$\left\langle \psi_{n\vec{k}} \middle| \psi_{n'\vec{k}'} \right\rangle = \delta_{nn'}\delta_{\vec{k},\vec{k}'} \quad \Leftrightarrow \quad \left\langle w_{n\vec{R}} \middle| w_{n'\vec{R}'} \right\rangle = \delta_{nn'}\delta_{\vec{R},\vec{R}'}$ An orthonormal set

Comparison

Bloch state	Wannier function	
• Energy eigenstate	not an energy eigenstate	
• $T_{\vec{R}}\psi_{n\vec{k}} = e^{i\vec{k}\cdot\vec{R}}\psi_{n\vec{k}}$	$\left(P_n \vec{r} P_n\right) w_{n\vec{R}} = \vec{R} w_{n\vec{R}}$	Kivelson, PRB, '82 (for 1D)
• Extended function	localized function	
• orthonormal basis	orthonormal basis	

Wannier function for the Kronig-Penny model

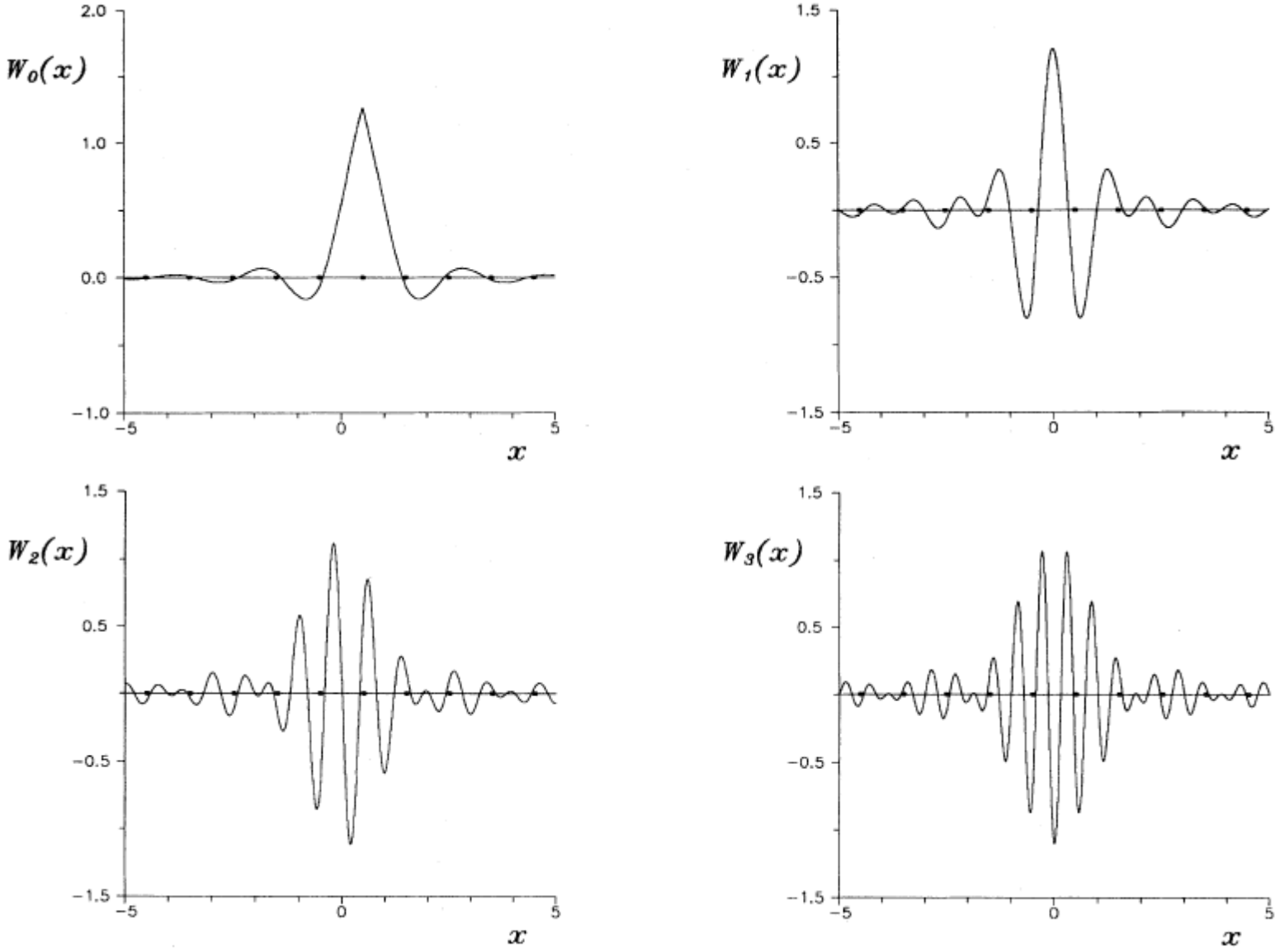


FIG. 5. Wannier-Kohn functions for the four lowest bands for weak potentials, $\alpha = 1$.

Pedersen et al, PRB 1991

Tight-binding model (TBM)

• As a basis, Wannier functions are better than atomic orbitals:

$$\left\langle w_{n\vec{R}} \middle| w_{n'\vec{R}'} \right\rangle = \delta_{nn'}\delta_{\vec{R},\vec{R}'}$$

$$\left\langle a_{m\vec{R}} \middle| a_{m'\vec{R}'} \right\rangle \neq \delta_{mm'}\delta_{\vec{R},\vec{R}'}$$

$$H = \sum_{nR,n'R'} \left|w_{n\vec{R}}\right\rangle \left\langle w_{n\vec{R}} \middle| H \middle| w_{n'\vec{R}'} \right\rangle \left\langle w_{n'\vec{R}'}\right|, \quad H = \frac{p^2}{2m} + U(\vec{r})$$

• One-band approx. (omit *n*)

$$H_{TB} = \sum_{R,R'} \left|w_{\vec{R}}\right\rangle H_{R,R'} \left\langle w_{\vec{R}'}\right|, \quad H_{R,R'} \equiv \left\langle w_{n\vec{R}} \middle| H \middle| w_{n\vec{R}'} \right\rangle$$

$$\approx \sum_{R} U_R \left|w_{\vec{R}}\right\rangle \left\langle w_{\vec{R}}\right| + \sum_{R,\delta} t_{R,\delta} \left|w_{\vec{R}}\right\rangle \left\langle w_{\vec{R}+\vec{\delta}}\right|, \; U_R \equiv H_{R,R}\,; \quad t_{R,\delta} = H_{R,R+\delta}$$

Hopping amplitude

On-site energy

(usually are treated as parameters)

• For a uniform system, *U*, *t* are indep of *R*, then by

$$\left|w_{\vec{R}}\right\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{k}\in 1st\ BZ} e^{-i\vec{k}\cdot\vec{R}} \left|\psi_{\vec{k}}\right\rangle$$

$$\Rightarrow \quad H_{TB} = \sum_{\vec{k}} \varepsilon_{\vec{k}} \left|\psi_{\vec{k}}\right\rangle \left\langle \psi_{\vec{k}}\right|, \qquad \varepsilon_{\vec{k}} = U + t\sum_{\delta} e^{i\vec{k}\cdot\vec{\delta}}$$

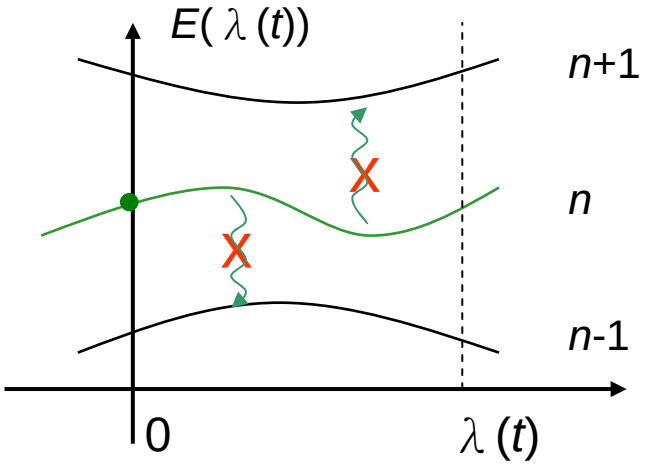
Cf: spectrum from LCAO

Geometric phase
(aka Berry phase)

Brief introduction of the Berry phase

Adiabatic evolution of a quantum system $H(\vec{r}, \vec{p}; \vec{\lambda})$

- Energy spectrum:



- After a *cyclic* evolution

$$\vec{\lambda}(T) = \vec{\lambda}(0)$$

$$\psi_{n,\vec{\lambda}(T)} = e^{-\frac{i}{\hbar}\int_0^T dt' E_n(t')} \psi_{n,\vec{\lambda}(0)}$$

Dynamical phase

- Phases of the snapshot states at different λ's are independent and can be arbitrarily assigned

$$\psi_{n,\vec{\lambda}(t)} \rightarrow e^{i\gamma_n(\vec{\lambda})} \psi_{n,\vec{\lambda}(t)}$$

- Do we need to worry about this phase?

No!

- Fock, Z. Phys 1928
- Schiff, Quantum Mechanics (3rd ed.) p.290

Pf : Consider the *n*-th level,

$$\Psi_{\vec{\lambda}}(t) = e^{i\gamma_n(\vec{\lambda})} e^{-\frac{i}{\hbar}\int_0^t dt' E_n(t')} \psi_{n,\vec{\lambda}}$$

Stationary, snapshot state

$$H\psi_{n,\vec{\lambda}} = E_n \psi_{n,\vec{\lambda}}$$

$$H\Psi_{\vec{\lambda}}(t) = i\hbar \frac{\partial}{\partial t} \Psi_{\vec{\lambda}}(t)$$

$$\Rightarrow \quad \dot{\gamma}_n = i\left\langle \psi_{n,\vec{\lambda}} \middle| \frac{\partial}{\partial \vec{\lambda}} \middle| \psi_{n,\vec{\lambda}} \right\rangle \cdot \dot{\vec{\lambda}} \neq 0$$

$$\equiv \mathbf{A}_n(\lambda)$$

- Redefine the phase, (gauge transformation)

$$\psi'_{n,\vec{\lambda}} = e^{i\phi_n(\vec{\lambda})} \psi_{n,\vec{\lambda}}$$

$$\Rightarrow \quad \mathbf{A}_n'(\lambda) = \mathbf{A}_n(\lambda) - \frac{\partial \phi_n}{\partial \vec{\lambda}}$$

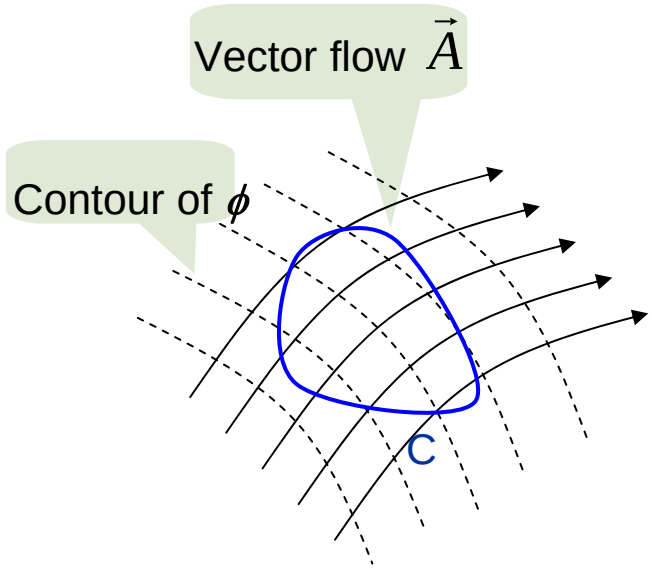
- Choose a $\phi(\lambda)$ such that,

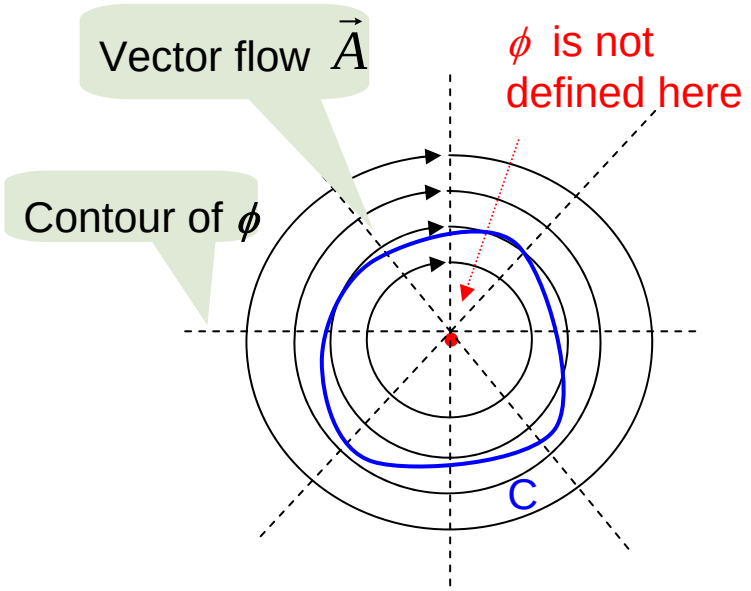
$\mathbf{A}_n'(\lambda)=0$ Thus removing the extra phase.

One problem:

$$\nabla_{\vec{\lambda}}\phi = \vec{A}(\vec{\lambda})$$

does not always have a well-defined (global) solution

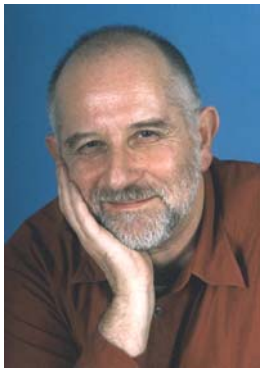




$$\gamma(T) - \gamma(0) = \oint_C \vec{A} \cdot d\vec{\lambda} = 0$$

$$\oint_C \vec{A} \cdot d\vec{\lambda} \neq 0$$

M. Berry, 1984 :
Parameter-dependent phase NOT always removable!



$$\psi_{\vec{\lambda}(T)} = e^{i\gamma_C} e^{-\frac{i}{\hbar}\int_0^T dt' E(t')} \psi_{\vec{\lambda}(0)}$$

Index *n* neglected

- Berry phase (gauge independent, path dependent)

$$\gamma_C = \oint_C \vec{A}(\vec{\lambda}) \cdot d\vec{\lambda}$$

- Berry connection (or Berry potential)

$$\vec{A}(\vec{\lambda}) \equiv i \left\langle \psi_{\vec{\lambda}} \middle| \nabla_\lambda \middle| \psi_{\vec{\lambda}} \right\rangle$$

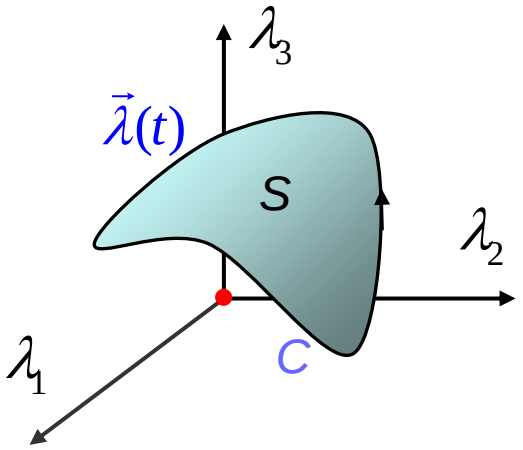
("*R*" in Marder's)

- Berry curvature (or Berry field)

$$\vec{\Omega}(\vec{\lambda}) \equiv \nabla_\lambda \times \vec{A}(\vec{\lambda}) = i \left\langle \nabla_\lambda \psi_{\vec{\lambda}} \middle| \times \middle| \nabla_\lambda \psi_{\vec{\lambda}} \right\rangle$$

- Stokes theorem (3-dim here, can be higher)

$$\gamma_C = \oint_C \vec{A} \cdot d\vec{\lambda} = \int_S \vec{\Omega} \cdot d\vec{a}$$



Berry phase in crystalline solid (for the *n*-th band)

$$\tilde{H}(\vec{k})u_{n\vec{k}} = \varepsilon_{n\vec{k}}u_{n\vec{k}} \quad \text{where } \tilde{H}(\vec{k}) = \frac{\hbar^2}{2m}\left(\frac{\nabla}{i} + \vec{k}\right)^2 + U(\vec{r})$$

- Berry phase

$$\gamma_n = \oint_C \left\langle u_{n\vec{k}} \middle| i\frac{\partial}{\partial \vec{k}} \middle| u_{n\vec{k}} \right\rangle \cdot d\vec{k}$$

- Berry connection

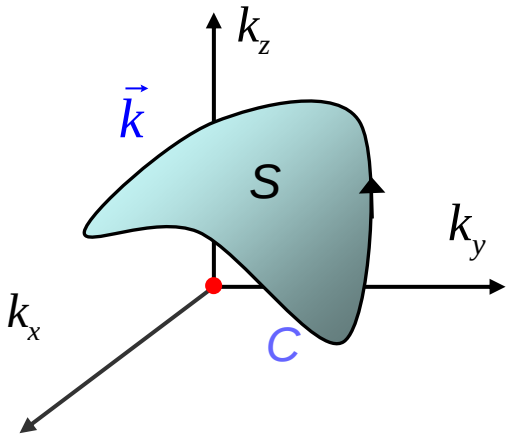
$$\vec{A}_n(\vec{k}) = \left\langle u_{n\vec{k}} \middle| i\nabla_{\vec{k}} \middle| u_{n\vec{k}} \right\rangle$$

- Berry curvature

$$\vec{\Omega}_n(\vec{k}) = \nabla_{\vec{k}} \times \vec{A}_n(\vec{k}) = i\left\langle \nabla_{\vec{k}} u_{n\vec{k}} \middle| \times \middle| \nabla_{\vec{k}} u_{n\vec{k}} \right\rangle$$

- Stokes theorem

$$\gamma_n = \oint_C \vec{A}_n \cdot d\vec{k} = \int_S \nabla_{\vec{k}} \times \vec{A}_n \cdot d^2k$$



◆ Symmetry and Berry curvature

For *non*-degenerate band:

- Space inversion symmetry: $\vec{\Omega}_n(-\vec{k}) = \vec{\Omega}_n(\vec{k})$
- Time reversal symmetry: $\vec{\Omega}_n(-\vec{k}) = -\vec{\Omega}_n(\vec{k})$

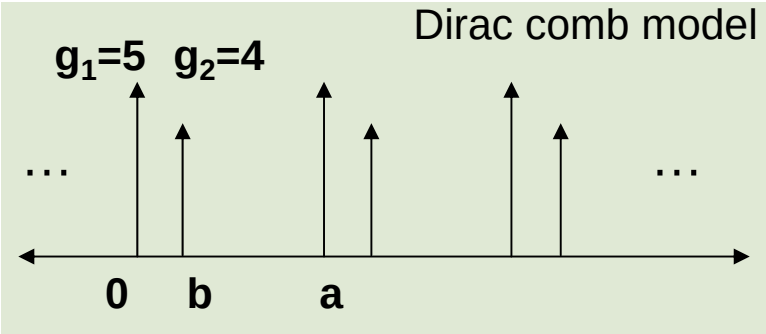
} both symmetries $\Rightarrow$ $\vec{\Omega}_n(\vec{k}) = 0, \ \forall \vec{k}$

◆ When could we see nonzero Berry curvature? $\vec{\Omega}_n(\vec{k}) \neq 0$

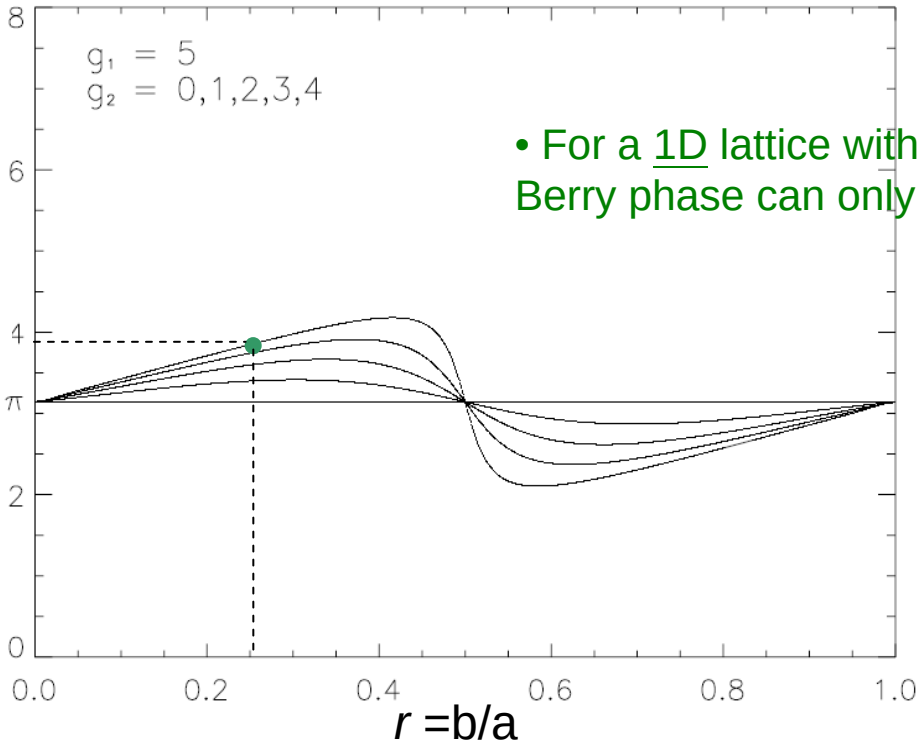
- SI symmetry is broken ← electric polarization
- TR symmetry is broken ← QHE
- band crossing ← “monopole”

For more, see Xiao D. et al, Rev Mod Phys 2010

Berry phase (crossing the BZ) in one dimension



Lowest energy band: γ_1



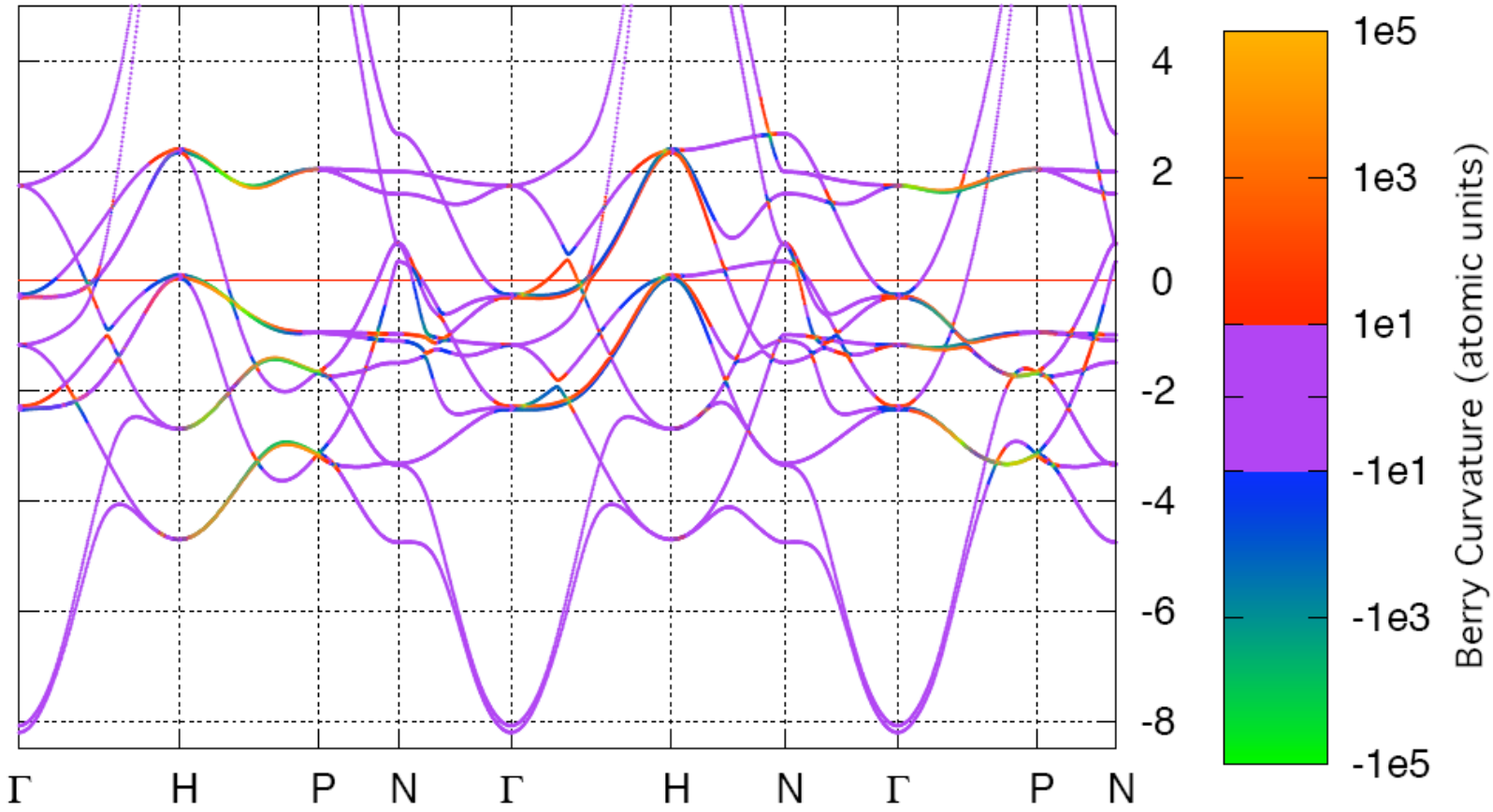
• For a 1D lattice with inversion symm, Berry phase can only be 0 or π

← g_2=0

$\gamma_1 = \pi$

Rave and Kerr, EPJ B 2005

Realistic Berry curvature for BCC Fe



From Dr. J. Yates's ppt

→ (intrinsic) anomalous Hall effect
(Karplus and Luttinger, 1954)

- In addition to $\varepsilon_n(k)$, there is a 2nd fundamental quantity $\Omega_n(k)$