2. Quantum Theory of Solids

2A. Free Electron Model
2B. Periodic Potential and Band Structure
2C. Lattice Vibration

While the free electron model is highly successful in explaining many observations for metals, it fails dramatically for certain properties, most notably the existence of positively charged hole carriers.

To explain this, we explicitly consider the **periodic potential** experienced by the electrons, and the resulting energy structures are termed as the **band structure**. The band theory is the most widely used model for explaining the electronic properties of solid materials.

2B. Periodic Potential and Band Structure (Bube Ch. 7)

The free-electron model in the previous section is certainly very useful in explaining key features in metals. Even though simple, the theory is based on the two quantum mechanical principles - **quantization of energy states and Fermi-Dirac distribution**, which are essential for correct theory of solids.

Nevertheless, it cannot explain several phenomena. Notable examples are as follows:
i) Existence of hole carrier (instead of electron carrier) in some metals.
ii) Boron is an insulator while its vertical neighbor aluminum is an excellent metal.
iii) Why materials like silicon does not show metallic character?

So, what is missing in the free-electron theory? Foremost, the potential by ions were completely ignored. In crystals, the atoms form a periodic structure. Therefore, **the potential is also periodic**. In this chapter, we will explore solutions of the Schrödinger equation when the potential is periodic.

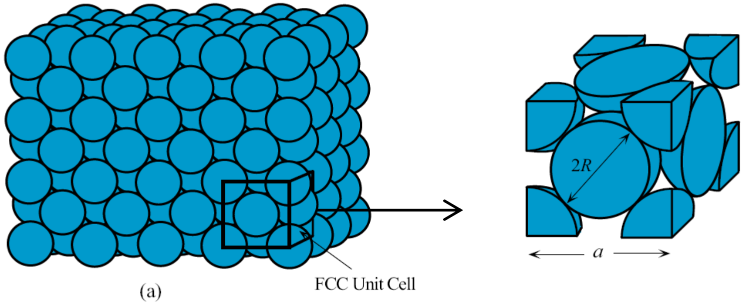
2B.1. Overview on the Crystalline Structure

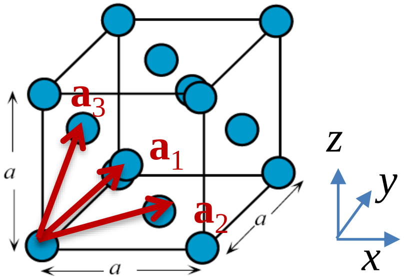
Basic definitions

Conventional Unit Cell & Primitive Unit Cell

As you have learned in Crystallography, the crystal is just a three-dimensional repetition of atoms. That is to say, the system is periodic and invariant under translation of $\boldsymbol{R} = n_1\boldsymbol{a}_1+n_2\boldsymbol{a}_2+n_3\boldsymbol{a}_3$ (n_1,n_2, and n_3 are any integers). We call $\mathbf{a}_1$,$\mathbf{a}_2$, and $\mathbf{a}_3$ lattice vectors. The minium periodic unit of the crystal is called the unit cell and it contains basis atoms. In other words, you can make a crystalline structure by repeating basis atoms infinitely with lattice vectors. Bravais lattice is the lattice points expanded by $\boldsymbol{a}_1$,$\boldsymbol{a}_2$, and $\boldsymbol{a}_3$ (just one basis atom).

Ex) FCC structure





FCC (primitive) unit cell

a: lattice parameter

Lattice vectors in cartesian coordinates:

$\mathbf{a}_1 = a/2(1,0,1) = a/2(\hat{x} + \hat{z})$.

$\mathbf{a}_2 = a/2(1,1,0) = a/2(\hat{x} + \hat{y})$.

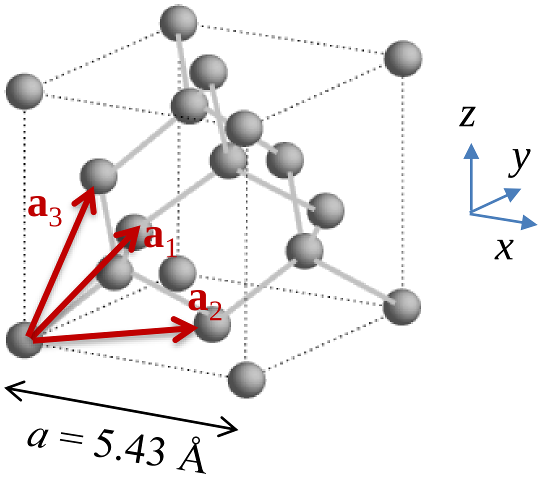
$\mathbf{a}_3 = a/2(0,1,1) = a/2(\hat{y} + \hat{z})$.

$\hat{x}$, $\hat{y}$, and $\hat{z}$ are the Cartesian unit vectors.

Basis atom: (0,0,0)

Ex) **Silicon (Diamond Structure)**

GaN



Lattice vectors:

$\mathbf{a}_1 = a/2(1,0,1)$

$\mathbf{a}_2 = a/2(1,1,0)$

$\mathbf{a}_3 = a/2(0,1,1)$

Basis atoms:

(0,0,0)

(¼, ¼, ¼)

The position of basis atoms are usually referenced to lattice vectors. That is to say, (¼, ¼, ¼) = ¼ $\mathbf{a}_1$+ ¼ $\mathbf{a}_2$+ ¼ $\mathbf{a}_3$. Lattice vectors are in cartesian coordinates: $\mathbf{a}_1 = a/2(1,0,1) = a/2(\hat{x} + \hat{z})$.

Ex) **BCC Fe**

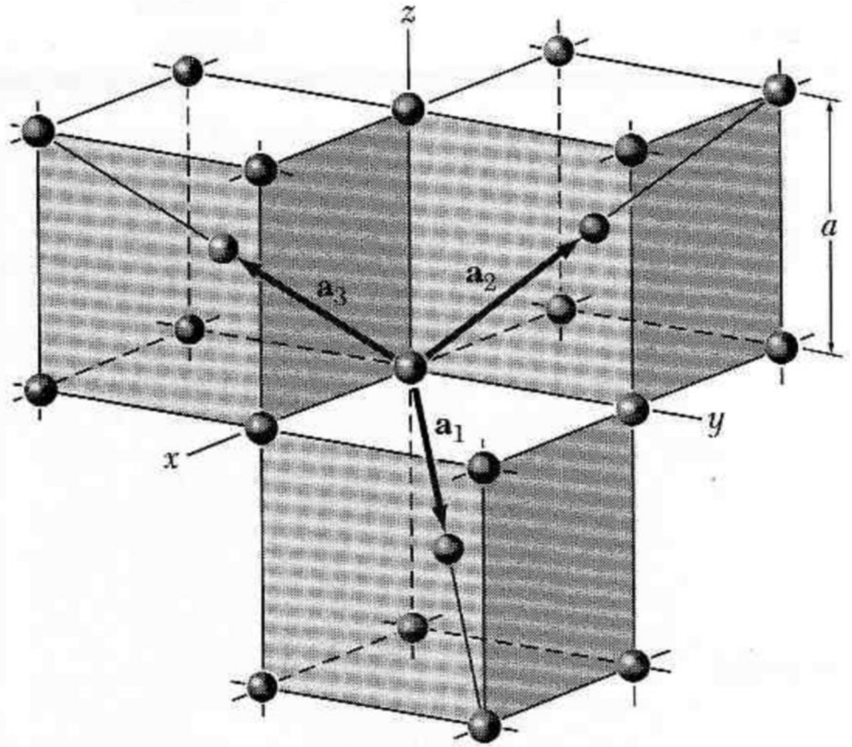


Figure 10 Primitive translation vectors of the body-centered cubic lattice; these vectors connect the lattice point at the origin to lattice points at the body centers. The primitive cell is obtained on completing the rhombohedron. In terms of the cube edge a, the primitive translation vectors are

$$\mathbf{a}_1 = \tfrac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) \; ; \qquad \mathbf{a}_2 = \tfrac{1}{2}a(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \; ;$$

$$\mathbf{a}_3 = \tfrac{1}{2}a(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}) \; .$$

Reciprocal Lattice

For lattice vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, and $\boldsymbol{a}_3$, reciprocal lattice vectors $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ are defined as follows:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

Note that the denominator is the volume of the unit cell. The Bravais lattice **G** expanded by these vectors, i.e., $\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$ (m_1,m_2, and m_3 are any integers) are called the reciprocal lattice. The space in which $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ lie is called the reciprocal space or **k**-space, which contrasts with the real space or **r**-space. Keep in mid that reciprocal space is an imaginary space that is mathematically constructed. It is completely different from the real space. It is straightforward to show that $\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$. This in turn means that $\exp i\mathbf{G} \cdot \mathbf{R} = 1$ for any **G** and **R**.

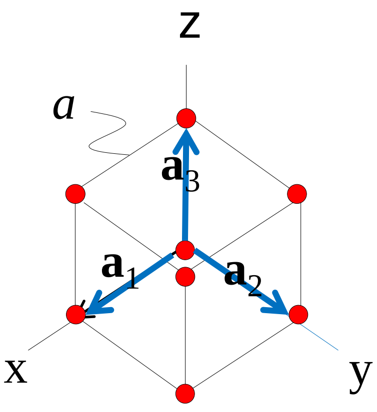
r **space vs.** ***k*** **space**

Band Structure
Diffraction

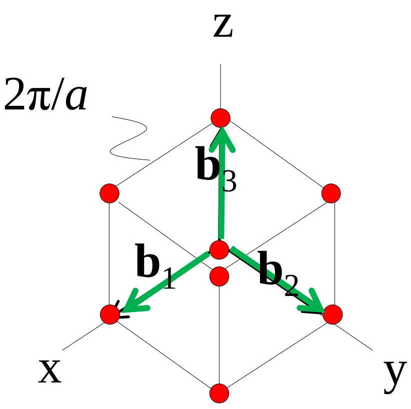
Examples)

Cubic ⟷ Cubic

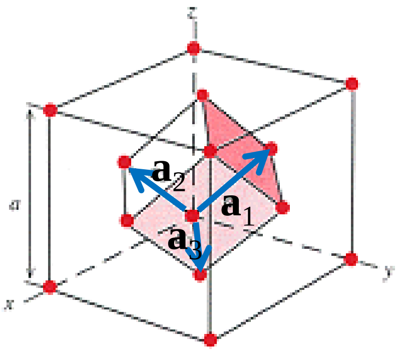
FCC ⟷ BCC



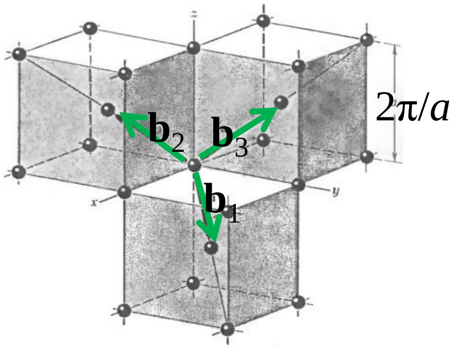
Real space



Reciprocal space



Real space



Reciprocal space

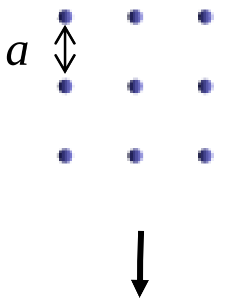
The lattice parameters in real and reciprocal spaces are inversely proportional.
If the real lattice is BCC, the reciprocal lattice is FCC.

One can also define the reciprocal lattice for low dimensional systems. In this case, we can ignore periodicity in the unused dimensions by simply equating the lattice vectors with the unit vector along the direction.

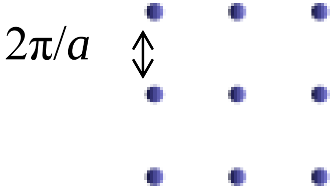
Ex) 2-d system in the *xy* plane → $\mathbf{a}_3 = \hat{z}$

Square lattice

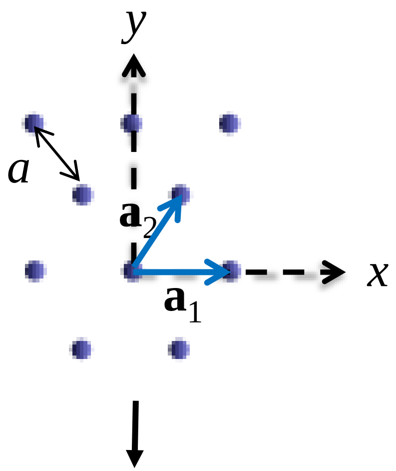
***r* space**



***k* space**



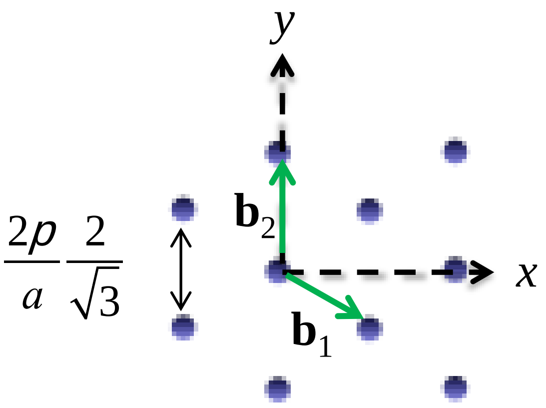
Hexagonal lattice (ex. graphene)



$$\mathbf{a}_1 = a\hat{x}$$

$$\mathbf{a}_2 = \frac{a}{2}\hat{x} + \frac{\sqrt{3}}{2}a\hat{y}$$

$$(\mathbf{a}_3 = \hat{z})$$



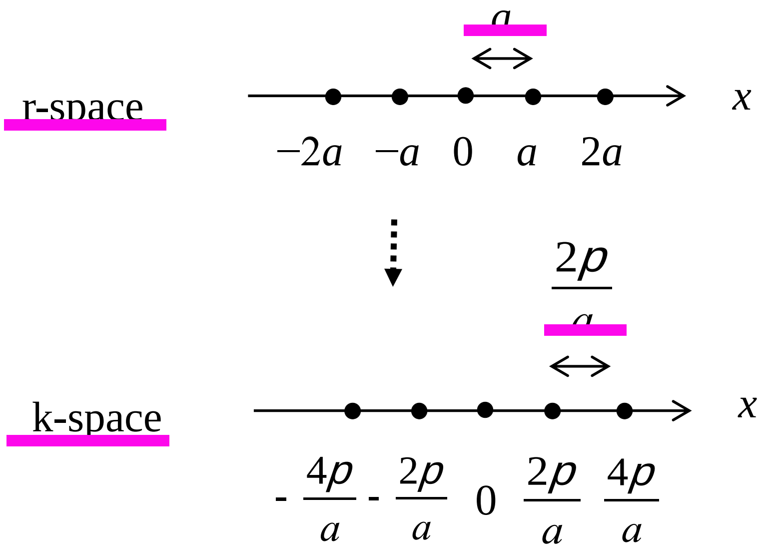
$$\mathbf{b}_1 = \frac{2p}{a}\left(\hat{x} - \frac{\hat{y}}{\sqrt{3}}\right)$$

$$\mathbf{b}_2 = \frac{2p}{a}\frac{2}{\sqrt{3}}\hat{y}$$

$$(\mathbf{b}_3 = 2p\hat{z})$$

30° rotated hexagonal lattice

Ex) **1D** system along the x-axis → $\mathbf{a}_2 = \hat{y}$, $\mathbf{a}_3 = \hat{z}$

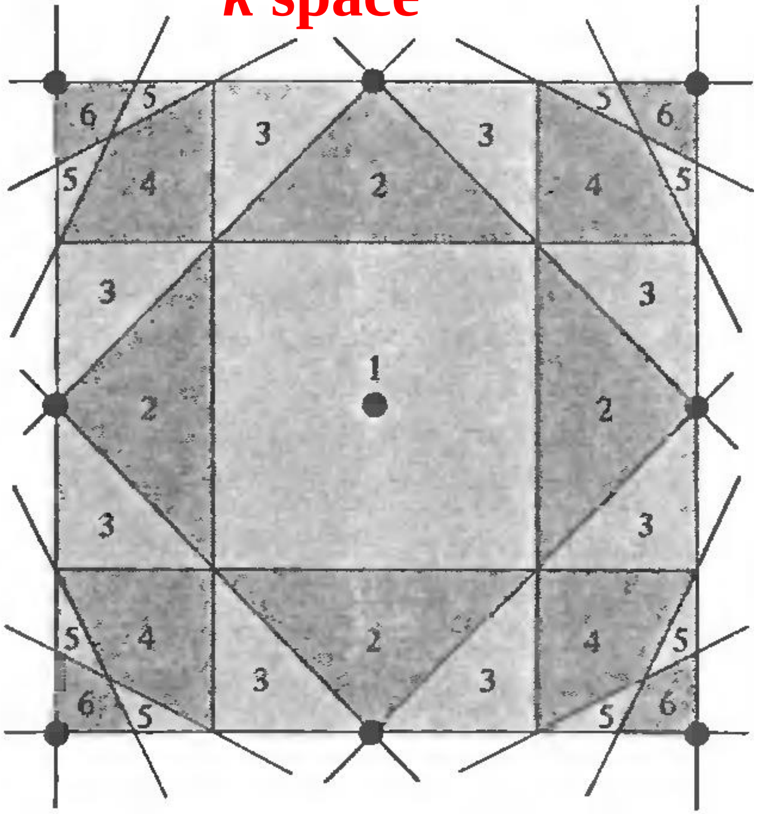


Brillouin Zone

Definition) A primitive cell in the reciprocal space whose boundaries are set by intersecting planes (lines in 2-d and points in 1-d) connecting points in the reciprocal space

Ex) 2D square Bravais lattice

***k* space**



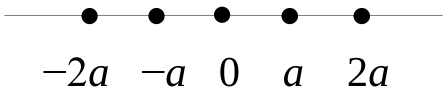
The number *i* in each zone indicates that points in the zone relate to the central point as the *i*th nearest neighbor. Each zone is named as *i*th Brillouin zone (BZ). Every *i*th BZ expands the whole **k** space when added over lattice points. **1st BZ is a unit cell of the reciprocal lattice**, which is called the **Wigner-Seitz cell**.

- Examples of 1st BZ.

1D

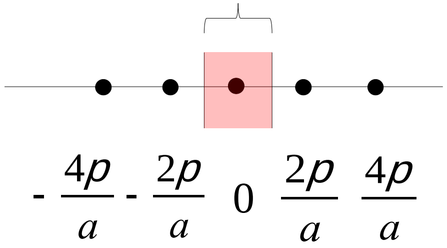
2D

r-space



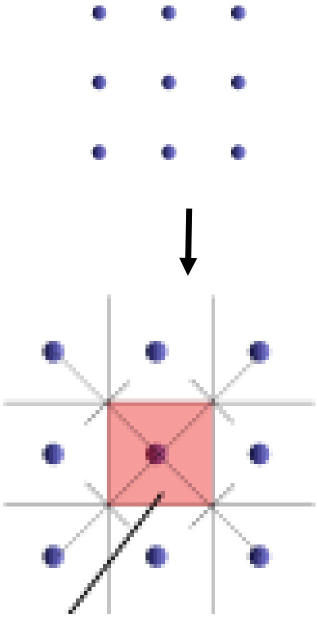
1st BZ :

k-space



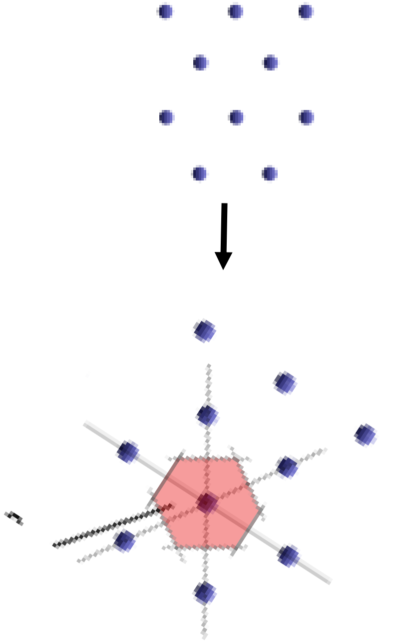
$$-\frac{p}{a} < k £ \frac{p}{a}$$

Square lattice



1st BZ

Hexagonal lattice



1st BZ

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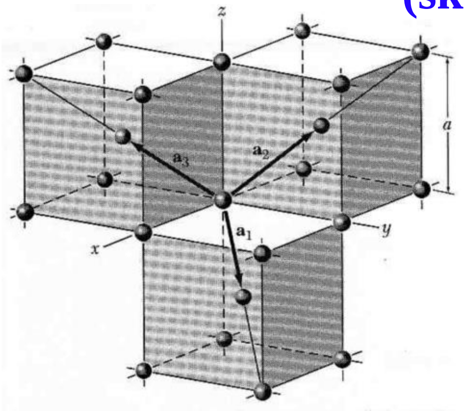
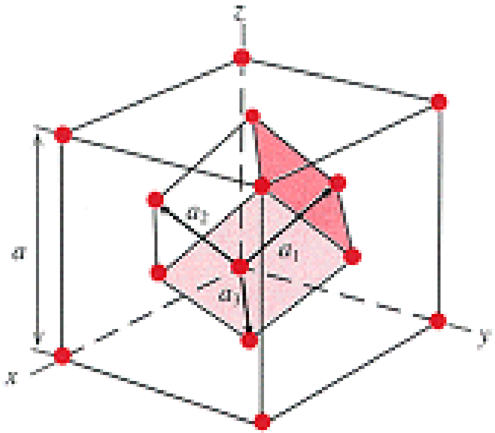
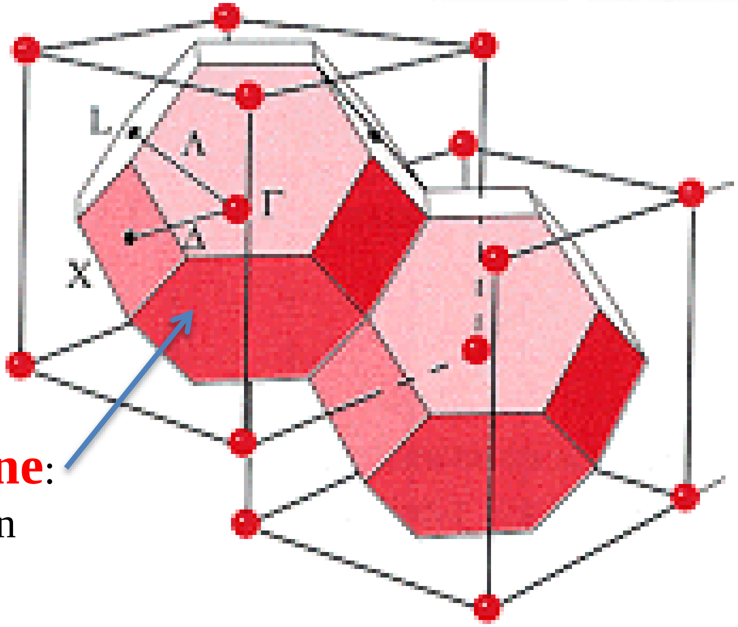
3D

k-space: BCC



r-space: FCC





1st Brillouin zone: truncated octahedron

In the 1st BZ, points with high symmetry are called the special points and given specific names. The name depends on the crystal system but some names are commonly used. For example, Γ point always means the origin when certain lattice point is assigned to the origin. X point is the intersection between the *x*-axis and boundary of 1st BZ. In the above example, there are 6 points that are equivalent to X if the crystal has the full symmetry of FCC.

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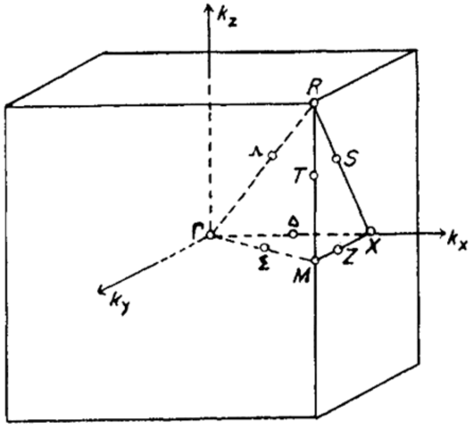
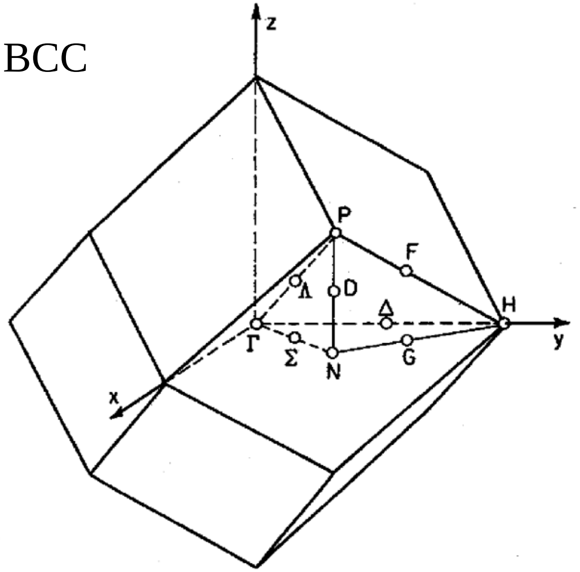
Repeating the truncated octahedron fills the whole space without leaving any void.

1st BZ of other structures.

Simple cubic



BCC



2B.2. Bloch Theorem

Because of translational symmetry of atoms in crystals,
the potential experienced by electrons is also periodic in crystals.

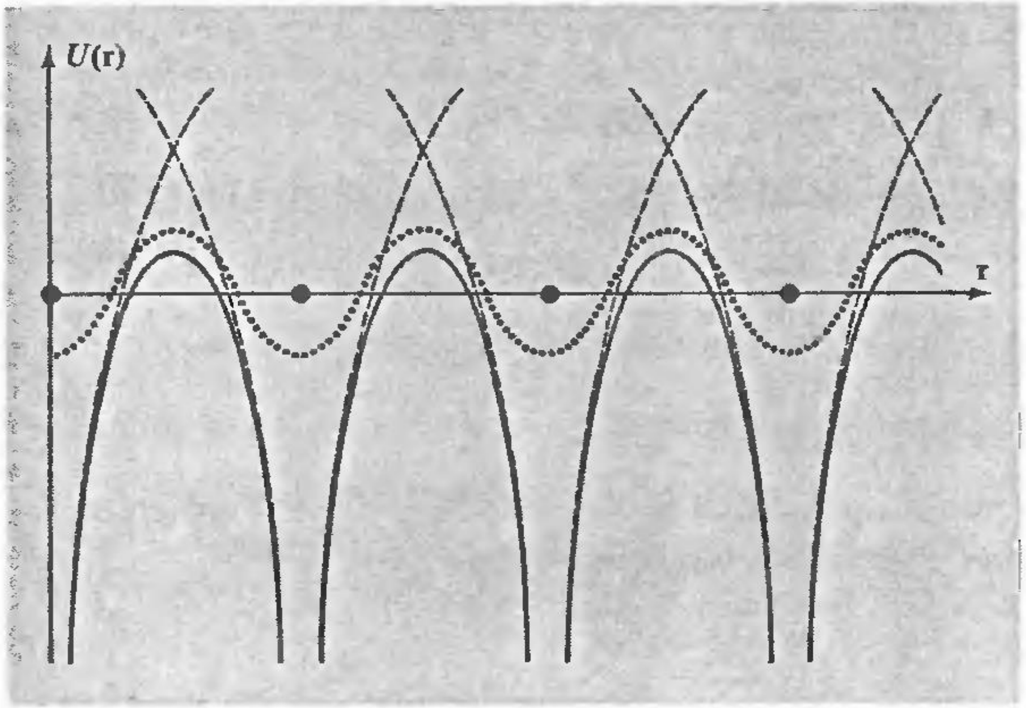


Figure 8.1
A typical crystalline periodic potential, plotted along a line of ions and along a line midway between a plane of ions. (Closed circles are the equilibrium ion sites; the solid curves give the potential along the line of ions; the dotted curves give the potential along a line between planes of ions; the dashed curves give the potential of single isolated ions.)

Mathematically, $V(\boldsymbol{r} + \boldsymbol{R}) = V(\boldsymbol{r})$ for any lattice vector $\boldsymbol{R}$. What is the solution of Schrödinger equation under this potential?

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

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2B.2. Bloch Theorem

There is a theorem that applies to any energy eigenstate under periodic potential. It starts with the question that whether the eigenstate is also periodic. That is to say, **$\psi(\mathbf{r}+\mathbf{R}) = \psi(\mathbf{r})$?.** This may sound plausible but it is **incorrect**. It is true that every physical quantity that we measure should be periodic but we cannot measure the wave function itself. Instead, we can measure **the electron density** or $|\psi(\mathbf{r})|^2$. That is to say, **$|\psi(\mathbf{r}+\mathbf{R})|^2 = |\psi(\mathbf{r})|^2$**. The mathematical condition compatible with this was found by Bloch, who proved that the eigenstate under the periodic potential can be expressed as:

$$\underline{\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r})}$$

where ~~k can be any vector in the 1st BZ~~ and $\underline{u(\mathbf{r}) = u(\mathbf{r}+\mathbf{R})}$, i.e, lattice periodic.

(For a proof, refer to A&M pp 133.)

This is called the Bloch theorem, and ***k*** is named as Bloch vector. The function in this form is called Bloch function. According to this theorem,

any lattice vector *R*

$$\psi(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{R})}u(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r})$$

Therefore, $\left|\psi(\mathbf{r}+\mathbf{R})\right|^2 = \left|\psi(\mathbf{r})\right|^2$.

Momentum (*p* = *mv*) vs. crystal momentum?

The dynamic significance of the wave vector *k* can only be acquired when one considers the response of Bloch electrons to externally applied electromagnetic fields (**by electron dynamics**). Refer to Aschcroft/Mermin pp. 133.

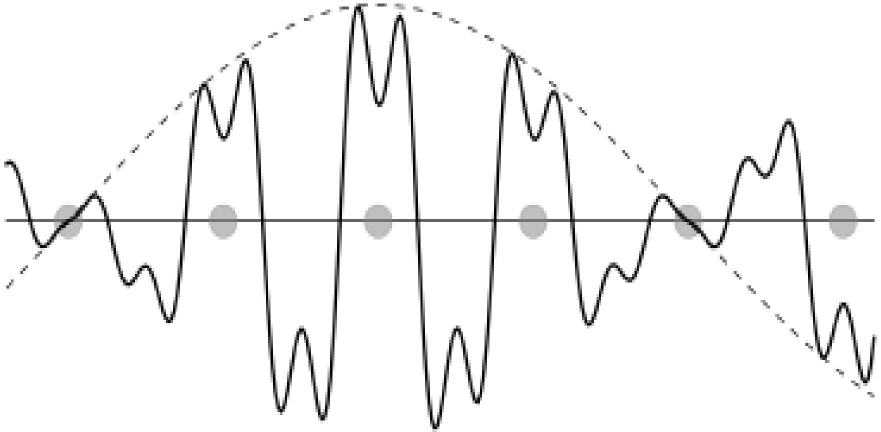
Bloch Wave

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\, u(\mathbf{r})$$

$u(\mathbf{r}+\mathbf{R}) = u(\mathbf{r})$

$\mathbf{k}$ in the 1st BZ

any lattice vector $\mathbf{R}$



Solid line: a schematic of a typical Bloch wave in 1D. (The actual wave is complex; this is the real part.)

The dotted line is **from the $e^{i\mathbf{k}\cdot\mathbf{r}}$ factor**. The light circles represent atoms.

from Wikipidea

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When we put this form into the Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r})\right]\psi(\mathbf{r})=E\psi(\mathbf{r})\rightarrow\left[-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r})\right]e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r})=Ee^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r})$$

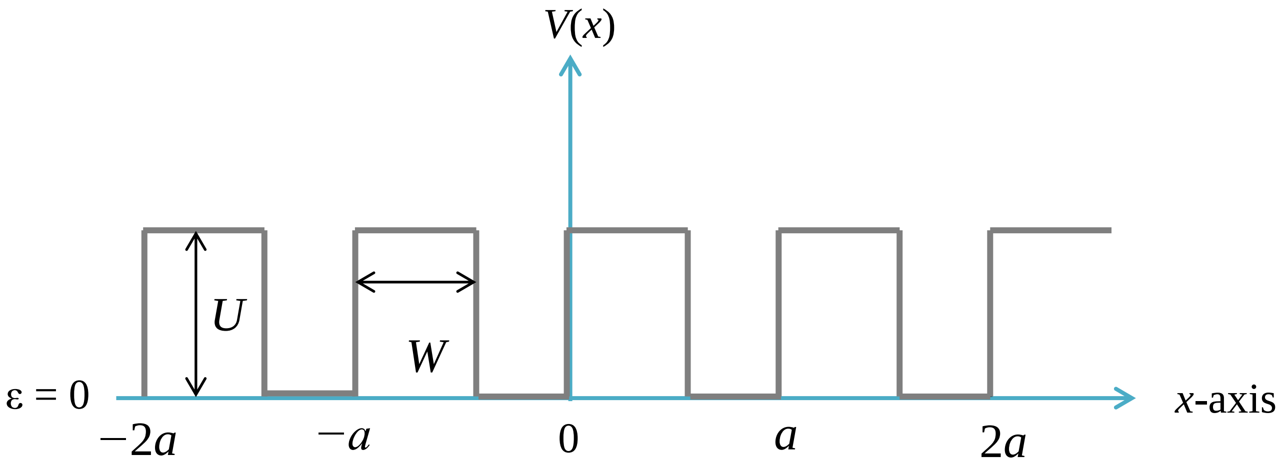
$$\rightarrow-\frac{\hbar^2}{2m}e^{i\mathbf{k}\cdot\mathbf{r}}\left(-|\mathbf{k}|^2+2i\mathbf{k}\cdot\nabla+\nabla^2\right)u(\mathbf{r})+V(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r})=Ee^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r})$$

$$\rightarrow-\frac{\hbar^2}{2m}\left(-|\mathbf{k}|^2+2i\mathbf{k}\cdot\nabla+\nabla^2\right)u(\mathbf{r})+V(\mathbf{r})u(\mathbf{r})=Eu(\mathbf{r})\qquad\text{with}\quad u(\mathbf{r})=u(\mathbf{r}+\mathbf{R})$$

Therefore, for each **k**, we solve different Schrödinger equations. In the next section, we will first solve this equation for the simple 1D system.

2B.3. Kronig-Penney Model

Kronig-Penney model is the simplest 1D periodic model. Nevertheless, it exhibits many essential features of periodic system. In many textbooks, the analytic approach is discussed but we first investigate the numerical solutions.



a: lattice parameter
W: barrier width.
U: barrier height

When the Bloch theorem is applied on 1D system, $\underline{\psi(x) = e^{ikx}u(x)}$, $\underline{-\frac{\pi}{a} < k \le \frac{\pi}{a}}$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = \varepsilon\psi(x)$$

$$\rightarrow -\frac{\hbar^2}{2m}\left(-k^2 + 2ik\frac{d}{dx} + \frac{d^2}{dx^2}\right)u(x) + V(x)u(x) = \varepsilon u(x)$$

(skip)

Since $u_k(x)$ and $V(x)$ are periodic ($u(x+a)=u(x)$, $V(x+a)=V(x)$), one can expand them using Fourier series,

$$u(x)=\sum_{n=-\infty}^{\infty} c_n e^{i\frac{2\pi n}{a}x}=\sum_{n=-\infty}^{\infty} c_n e^{iG_n x}$$

$$c_m=\frac{1}{a}\int_0^a u(x)e^{-i\frac{2\pi m}{a}x}dx$$

$$V(x)=\sum_{n=-\infty}^{\infty} V_n e^{i\frac{2\pi n}{a}x}$$

$$V_m=\frac{1}{a}\int_0^a V(x)e^{-i\frac{2\pi m}{a}x}dx$$

By inserting $u(x)$ into the equation in the previous page,

$$\sum_{n=-\infty}^{\infty}\left[\frac{\hbar^2\left(k+G_n\right)^2}{2m}+V(x)\right]c_n e^{iG_n x}=\varepsilon\sum_{n=-\infty}^{\infty}c_n e^{iG_n x}$$

Then multiply $e^{-iG_\ell x}$ on both sides, integrate with x from 0 to a, and use the relation $\int_0^a e^{i(G_n-G_\ell)x}dx=a\delta_{n,\ell}$.

$$\sum_{n=-\infty}^{\infty}\left[\frac{\hbar^2\left(k+G_n\right)^2}{2m}\delta_{n,\ell}+V_{\ell-n}\right]c_n=\varepsilon c_\ell$$

This is equivalent to the matrix eigenvalue problem. In practice, the matrix is cut into a finite size (10×10 is enough). From the eigenvalue problem, a series of quantized energy levels are obtained and they can be labelled by (n,**k**), in which n = 1, 2, 3,… indexing the energy level in the increasing order. 'n' is called the band index. This means that (n,**k**) is the quantum number in the crystal and the energy and eigenstates can be labelled as $\varepsilon_{n\mathbf{k}}$ and $\psi_{n\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}$.

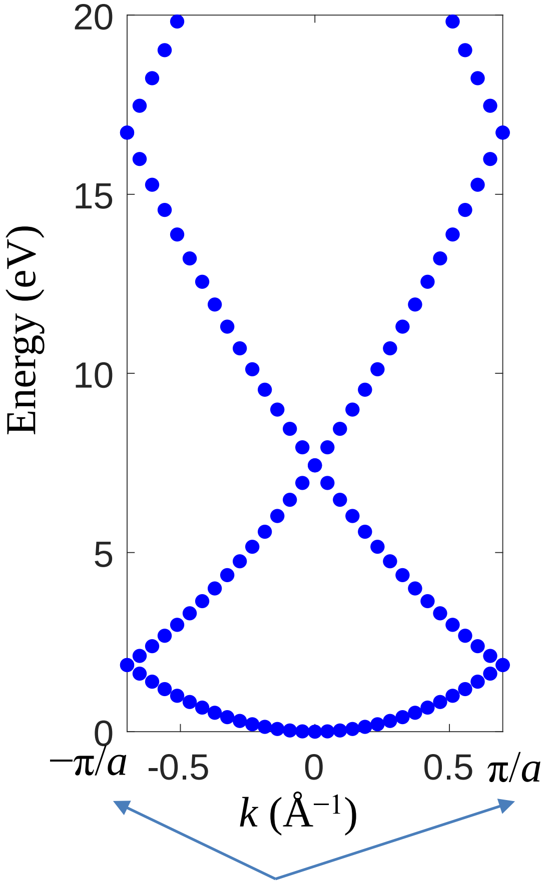
$$\begin{pmatrix}\ddots & & & \\ & \frac{\hbar^2\left(k-\frac{2\pi}{a}\right)^2}{2m}+V_0 & V_{-1} & V_{-2} \\ & V_1 & \frac{\hbar^2k^2}{2m}+V_0 & V_{-1} \\ & V_2 & V_1 & \frac{\hbar^2\left(k+\frac{2\pi}{a}\right)^2}{2m}+V_0 \\ & & & & \ddots\end{pmatrix}\begin{pmatrix}\vdots\\ c_{-1}\\ c_0\\ c_1\\ \vdots\end{pmatrix}=\varepsilon\begin{pmatrix}\vdots\\ c_{-1}\\ c_0\\ c_1\\ \vdots\end{pmatrix}$$

k = pi/a 에서 sinusoidal potential을 가정하고 2x2 형렬을 직접풀어보면?

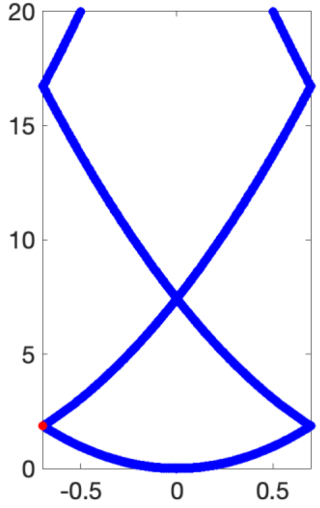
Free Particle or **Empty-Lattice** **Approximation** (with a = 4.5 Å, $U = 0$)

Band Structure (collection of Energies ε_{nk})

The results were produced by KPmodel.m



Zone boundary



Note that k points can be any real number within 1st BZ. Here we uniformly sampled k points with an equal spacing. In reality, the band structures consist of continuous lines.

Free Particle vs. Empty-Lattice Calculation

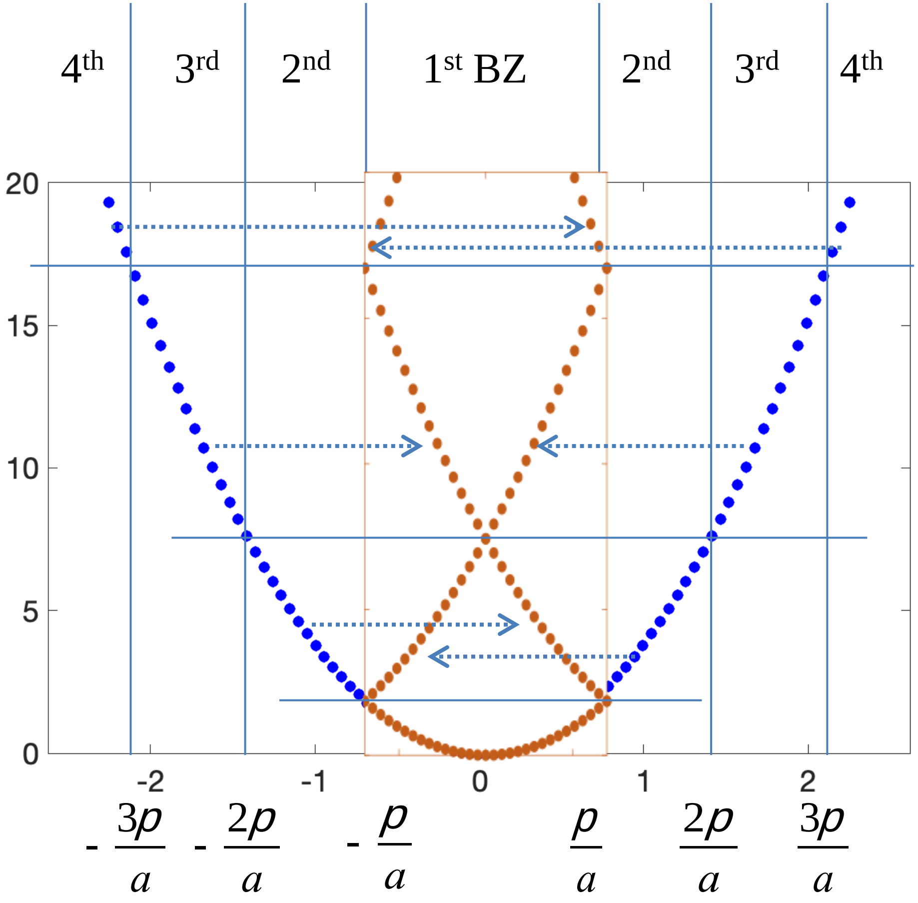
However, we already have the solution for the free particle state:

$$\psi(x) = Ae^{ikx} \ \& \ E = \frac{\hbar^2 k^2}{2m}$$

→

$$e^{ikx} = e^{i(k+\frac{2pN}{a})x} e^{-i\frac{2pN}{a}x} \qquad (\,N \text{ is an integer})$$

$$= e^{i(k+\frac{2pN}{a})x} u(x)$$



$$(u(x) = e^{-i\frac{2pN}{a}x};$$

$$u(x+a) = e^{-i\frac{2pN}{a}(x+a)} =$$

$$e^{-i\frac{2pN}{a}x} e^{-i2pN} = e^{-i\frac{2pN}{a}x} = u(x))$$

$\boldsymbol{\varepsilon_{nk}}$ $\quad$ $\boldsymbol{\psi(r) = e^{ik\cdot r}\, u(r)}$

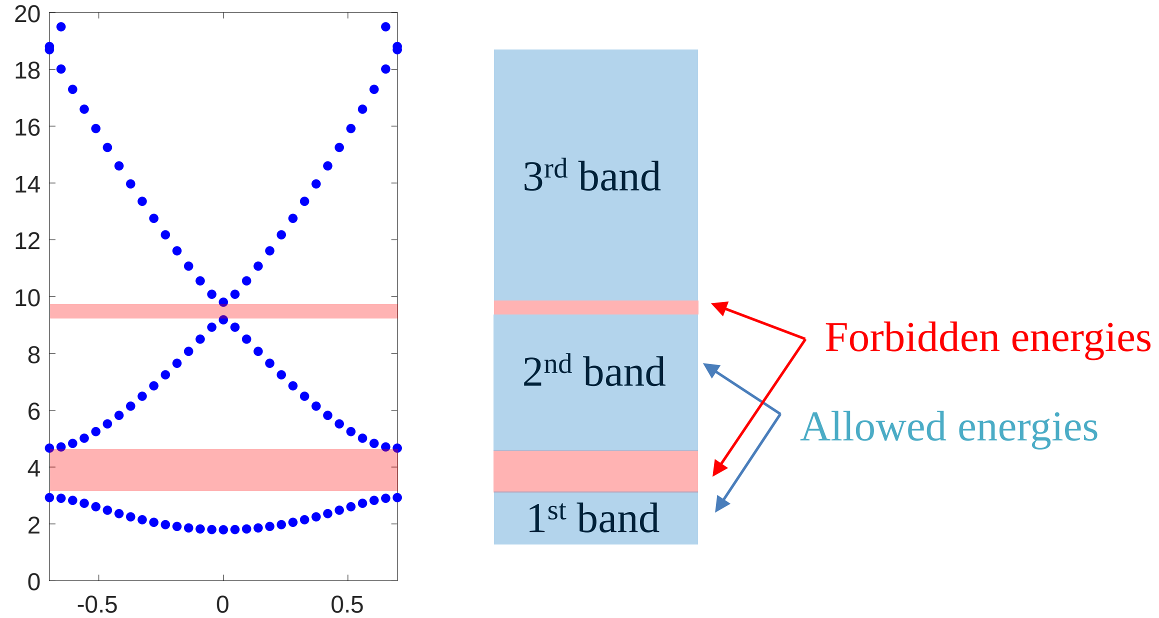
***u*(*r*+*R*) = *u*(*r*)**

***k* in the 1st BZ**

Weak Potential

$a = 4.5$ Å, $W = 3$ Å, $U = 3$ eV

When U is relatively small, the band structure is similar to the free-electron band structure.



However, one clear difference is that there exist forbidden energy regions that electrons cannot have. As a result, the allowed energies form ”energy bands” that are separated by the **bandgap energy**. Note that there is no such energy gaps in the free electrons.

To emphasize, the band structure or ε-k relation dictates the electrical and optical properties.

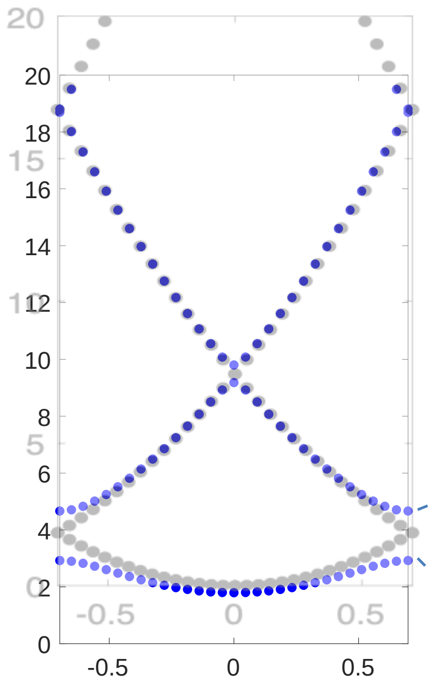
What is the Origin of the Bandgap?

***U* = 3 eV**

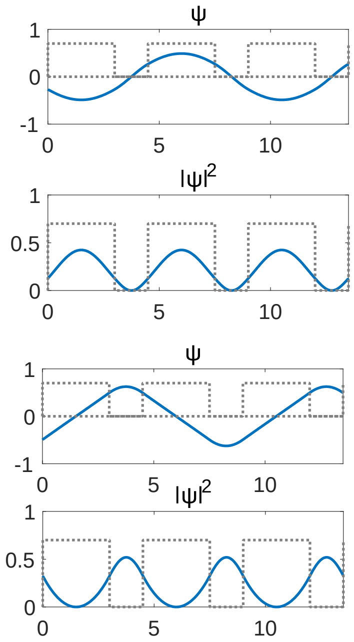
When superimposed with the free-electron band structure, it is found that the bandgap is caused by the energy change near the zone boundary.

At the zone boundary ***k* = π/*a* (λ = 2*a*)**, the free electron states are:

$$e^{i\frac{\pi}{a}x},\; e^{-i\frac{\pi}{a}x} \quad \text{or} \quad \sin\frac{\pi}{a}x,\; \cos\frac{\pi}{a}x \qquad \text{(doubly degenerate)}$$



(Gray: free-electron band structure shifted upward)



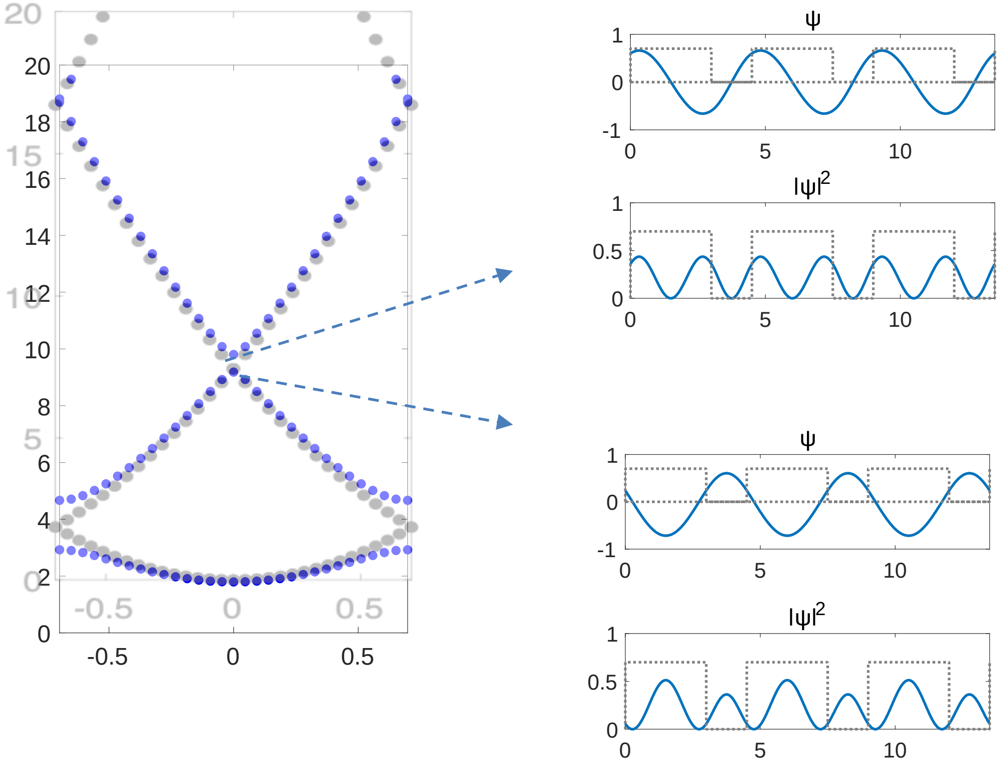
→ $\sim \sin\frac{\pi}{a}x$ (If x = 0 is set to the well center.)

These two states are degenerate when *U* = 0.

→ $\sim \cos\frac{\pi}{a}x$ (If x = 0 is set to the well center.)

The two degenerate states are split (lifted) into **two states with maximum and minimum exposure to the barrier**, creating the energy gap between them. This also explains why the maximum splitting occurs at the zone boundaries where linear combination of degenerate states produce states that are maximally or minimally exposed to the periodic potential.

$\lambda = a$ or $k = 0$



$$\sim \sin \frac{2p}{a} x$$

$$\psi(x) = e^{ik \cdot x}\, u(x)$$

$$u(x+R) = u(x)$$

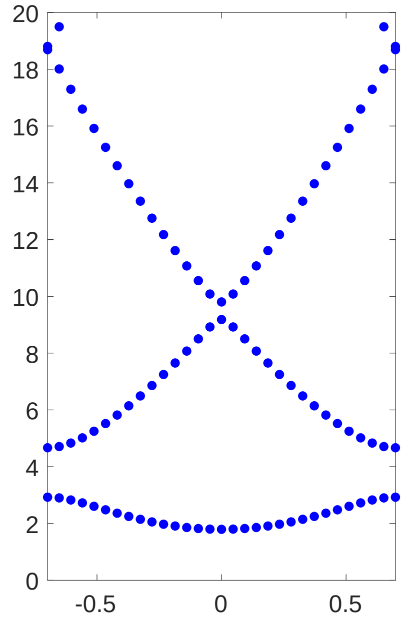
k in the 1st BZ

$$\sim \cos \frac{2p}{a} x$$

Since the two states could not fully avoid or face up to the barrier, the energy splitting is smaller.

The band structures drawn within the 1st BZ is called the reduced zone scheme. Below is the extended scheme. The *n*th band shift into the *n*th BZ.

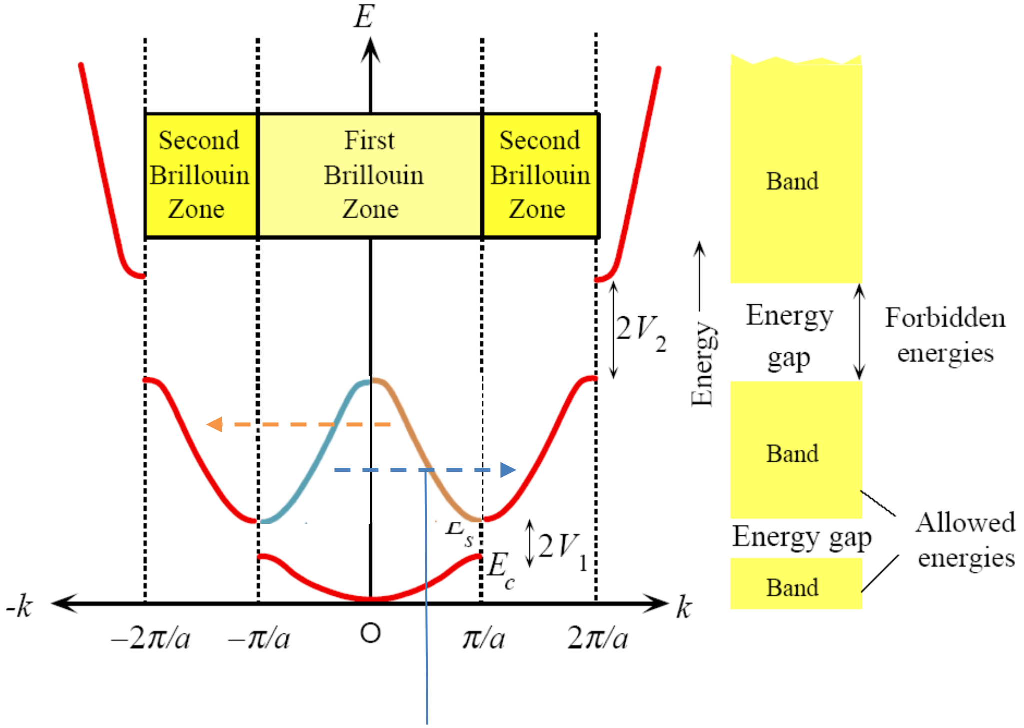
Reduced Zone Scheme



$$\psi(x) = e^{ik\cdot x}\,u(x)$$

$$u(x+R) = u(x)$$

Extended Zone Scheme (red)



$$e^{ikx}u(x) = e^{i(k+\frac{2\pi}{a})x}\,\underline{e^{-i\frac{2\pi}{a}x}u(x)} = e^{i(k+\frac{2\pi}{a})x}\,\underline{u'(x)}$$

In the extended zone scheme, the energy splitting occurs between zone boundaries.

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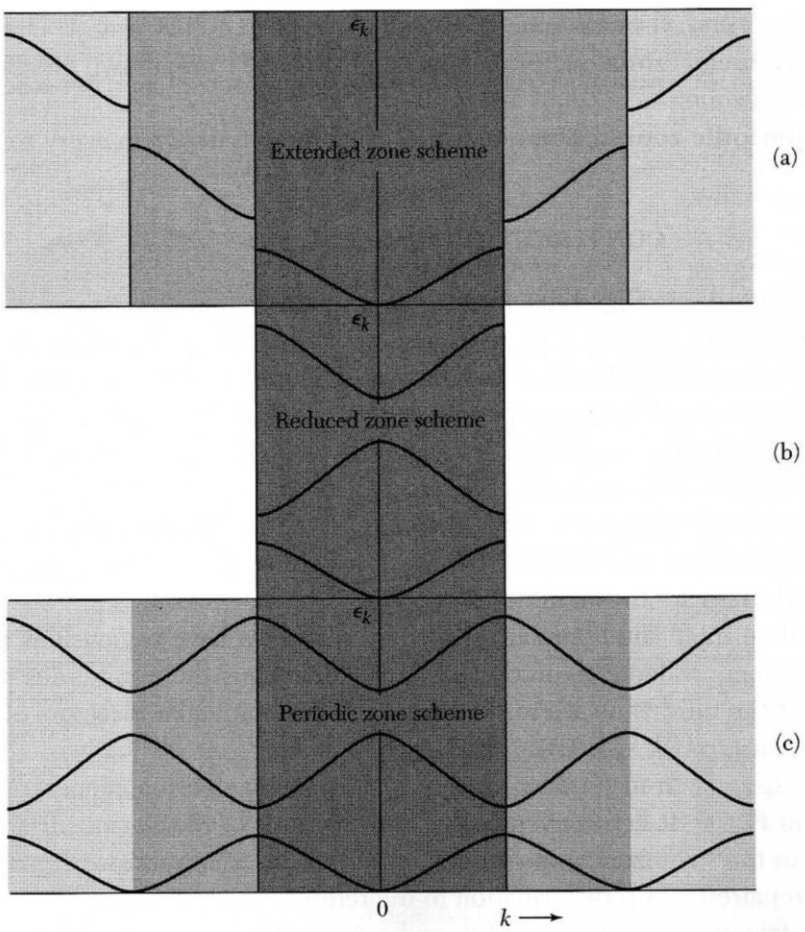
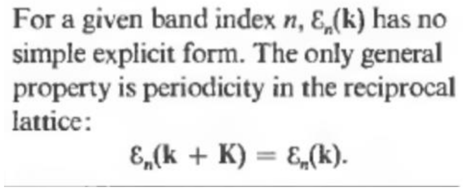


Figure 4 Three energy bands of a linear lattice plotted in (a) the extended (Brillouin), (b) reduced, and (c) periodic zone schemes.

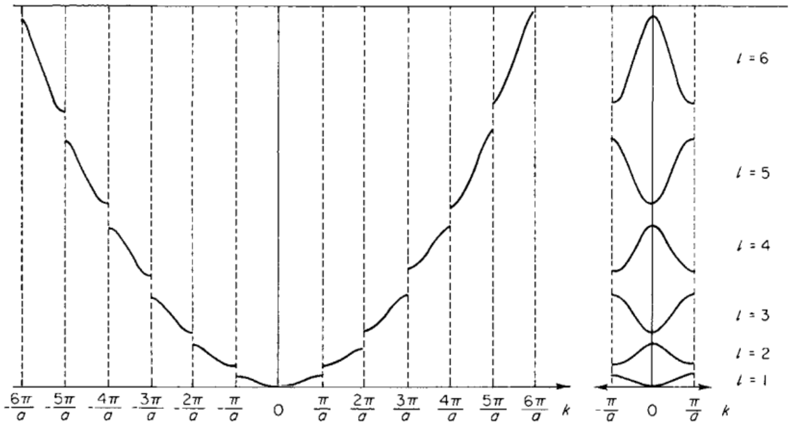
Periodic zone scheme is just for representational convenience.



For a given band index n, $\mathcal{E}_n(\mathbf{k})$ has no simple explicit form. The only general property is periodicity in the reciprocal lattice:

$$\mathcal{E}_n(\mathbf{k} + \mathbf{K}) = \mathcal{E}_n(\mathbf{k}).$$

Bube Fig. 7.4



Bloch Theorem

$$\boldsymbol{\psi(r) = e^{ik\cdot r}\, u(r)}$$

Group Velocity
Bube pp. 124-125

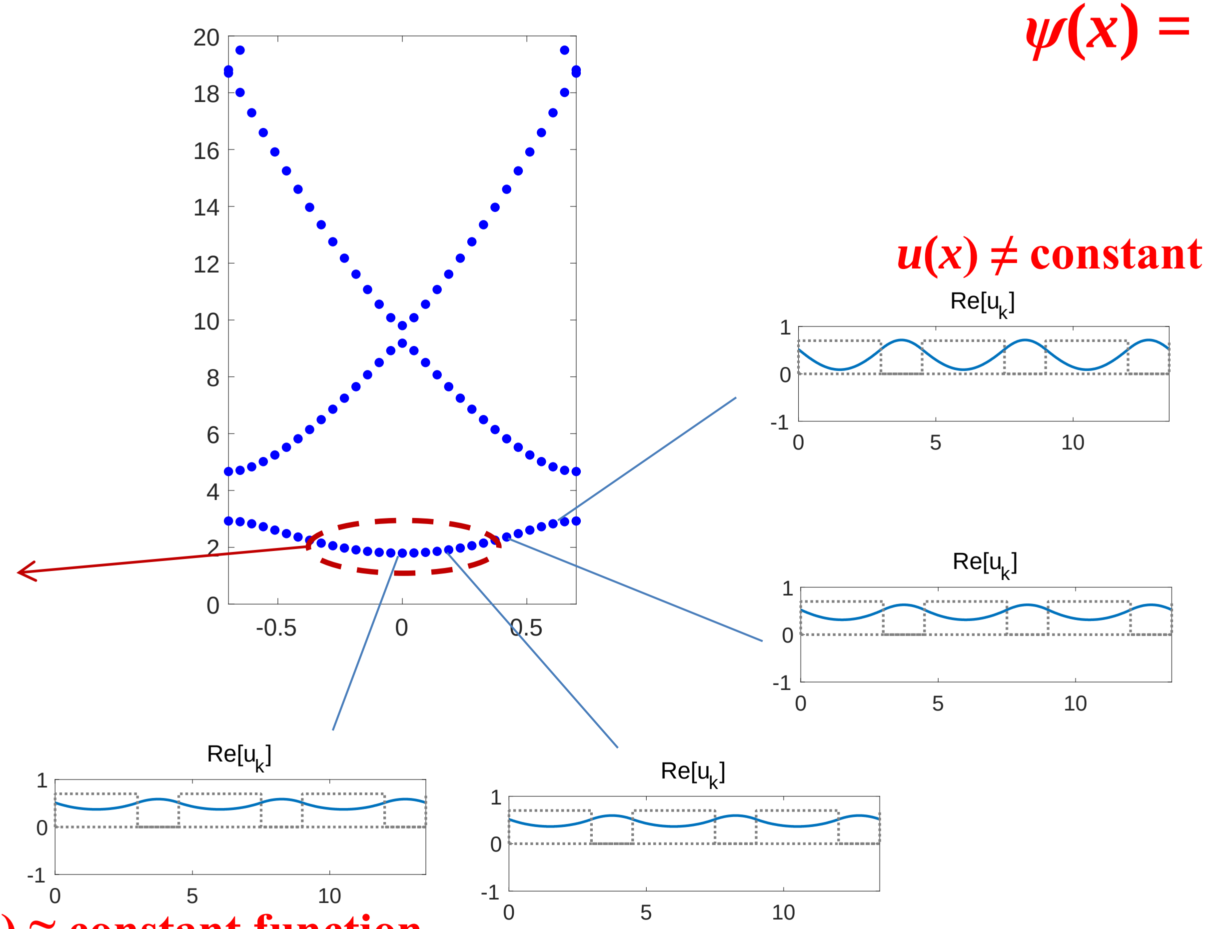
The extended zone scheme is useful in understanding the band structure when the potential is weak and electrons are free-electron like. One can simply start with the free-electron band structure and split the energy at zone boundaries. By folding the band structure into the 1st BZ, one may obtain the approximate form of band structure in the 1st BZ. This is particularly useful in 2D or 3D.

Important:

In the free electron model, ***k*** relates to the particle momentum or velocity ($\boldsymbol{p} = \hbar\boldsymbol{k}$). However, in the periodic system, ***k*** is the Bloch vector and $\hbar\boldsymbol{k}$ is called the **crystal momentum**, which *can* be very different from the **real momentum** especially near the zone boundary. We will learn more about its meaning in the next chapter.

How similar are the **Bloch function $e^{ikx}u(x)$** to the **free electron wave function e^{ikx}** ? This can be examined by plotting the periodic $u(x)$. If it is close to a constant function, the Bloch state is similar to the free-electron state.

$$\psi(x) = e^{ik\cdot x}\, u(x)$$



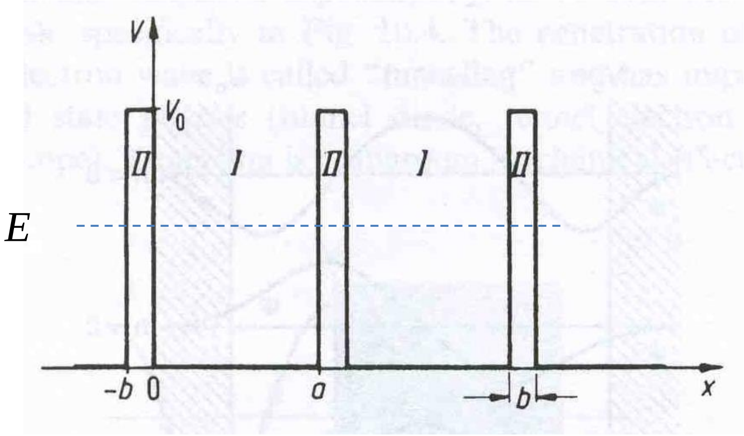
$u(x) \neq$ **constant function**

Free-electron like behavior

$u(x) \approx$ **constant function**

(skip---)

Analytical approach



(I) $$\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}E\psi=0,$$

(II) $$\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}(E-V_0)\psi=0.$$

$$\alpha^2=\frac{2m}{\hbar^2}E, \qquad \gamma^2=\frac{2m}{\hbar^2}(V_0-E).$$

$$\psi(x)=u(x)\cdot e^{ikx}$$ **(Bloch function)**

$$\frac{d^2\psi}{dx^2}=\left(\frac{d^2u}{dx^2}+\frac{du}{dx}2ik-k^2u\right)e^{ikx}.$$

➡ **Put it to equation (I) , (II) then**

(I) $$\frac{d^2u}{dx^2} + 2ik\frac{du}{dx} - (k^2 - \alpha^2)u = 0,$$

(II) $$\frac{d^2u}{dx^2} + 2ik\frac{du}{dx} - (k^2 + \gamma^2)u = 0.$$

(I) $$u = e^{-ikx}(Ae^{iax} + Be^{-iax}),$$

(II) $$u = e^{-ikx}(Ce^{-\gamma x} + De^{\gamma x}).$$

Boundary condition

➡ $$\psi_{\mathrm{I}} = \psi_{\mathrm{II}}$$

$$\left(d\psi / dx\right)_{\mathrm{I}} = \left(d\psi / dx\right)_{\mathrm{II}}$$

(1) At x=0

$$A + B = C + D.$$

$$A(i\alpha - ik) + B(-i\alpha - ik) = C(-\gamma - ik) + D(\gamma - ik).$$

(2) From periodicity , Eq I = Eq II (at x=0,x=a+b)

$$Ae^{(i\alpha - ik)a} + Be^{(-i\alpha - ik)a} = Ce^{(ik+\gamma)b} + De^{(ik-\gamma)b}.$$

$$Ai(\alpha - k)e^{ia(\alpha - k)} - Bi(\alpha + k)e^{-ia(\alpha + k)}$$
$$= -C(\gamma + ik)e^{(ik+\gamma)b} + D(\gamma - ik)e^{(ik-\gamma)b}.$$

➡ **From this 4 equations we can determine unknowns A,B,C,D and the conditions which tells us where solutions to the Schrödinger equations exist.**

$$\therefore \ \frac{\gamma^2-\alpha^2}{2\alpha\gamma}\sinh(\gamma b)\cdot\sin(\alpha a)+\cos(\gamma b)\cos(\alpha a)=\cos k(a+b).$$

$$\gamma=\sqrt{\frac{2m}{h^2}}\sqrt{V_0}\,,\quad \gamma b=\sqrt{\frac{2m}{h^2}}\sqrt{(V_0 b)b}.$$

Krong-Penney approximation:

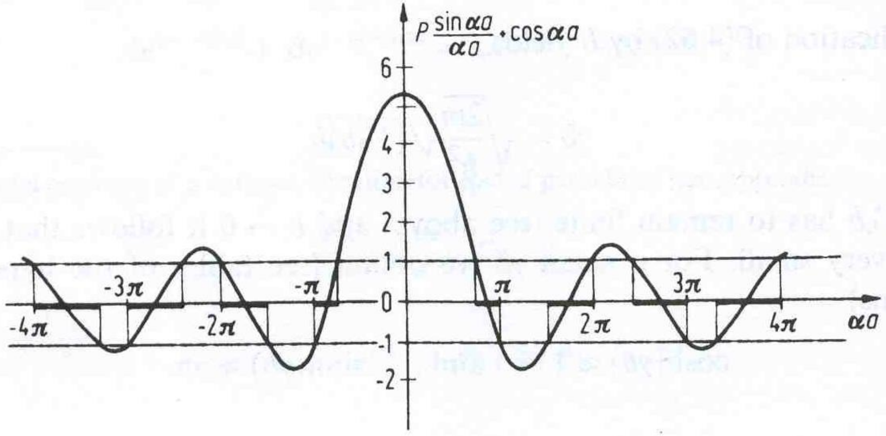
$b\to 0$ but $V_0 b$ (potential barrier strength) is finite

(That is to say, the potential is a delta function.)

$$\cosh(\gamma b)\approx 1 \quad \text{and} \quad \sinh(\gamma b)\approx \gamma b.$$

$$\frac{m}{\alpha h^2}V_0 b\sin\alpha a+\cos\alpha a=\cos ka.$$

$$\boxed{P\frac{\sin\alpha a}{\alpha a}+\cos\alpha a=\cos ka.}$$



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Because of $-1 \leq \cos ka \leq 1$

$P\dfrac{\sin \alpha a}{\alpha a} + \cos \alpha a$ **are allowed at specific region of** αa

It means that Energy of electron is forbidden at specific regions

Because of $\alpha^2 = \dfrac{2m}{h^2}E,$ **this forbidden regions are called by "Energy band gap".**

2B.4. Density of States

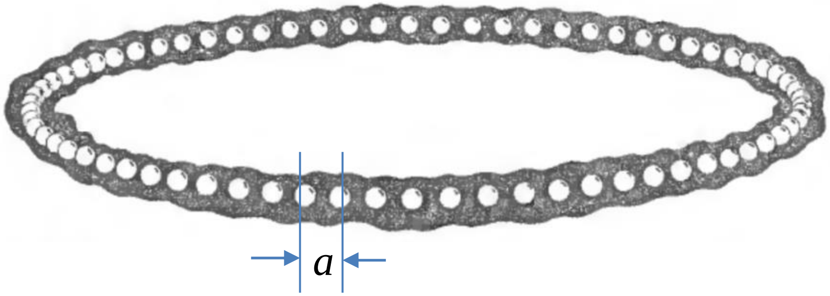
According to the Bloch theorem, there are infinite number of states because ***k* is continuous**. This is unphysical because any system is finite. Let's check how the finiteness can limit ***k*** values. Suppose that *N* unit cells (*N* around the Avogadro number) are connected in a macroscopic circular ring with a regular spacing of *a* (periodic boundary condition or Born-von Karman boundary condition). This boundary condition is compatible with the translational symmetry of crystal, i.e., $V(x+a) = V(x)$.

$$\psi(x) = e^{ikx}u(x) \quad (u(x+a) = u(x))$$

$$\psi(x+Na) = \psi(x)$$

$$\rightarrow e^{ik(x+Na)}u(x+Na) = e^{ik(x+Na)}u(x) = e^{ikx}u(x)$$

$$\rightarrow \underline{e^{ikNa} = 1} \leftrightarrow kNa = 2m\pi \quad (m \in Z) \rightarrow k = \frac{2m\pi}{Na}$$



Therefore, **Bloch vectors *k* are not truly continuous** and they are separated by a constant **Δ*k* = 2π/*Na***, which is a extremely small number because *N* is on the order of Avogadro number. Since *k* is confined with the 1st BZ,

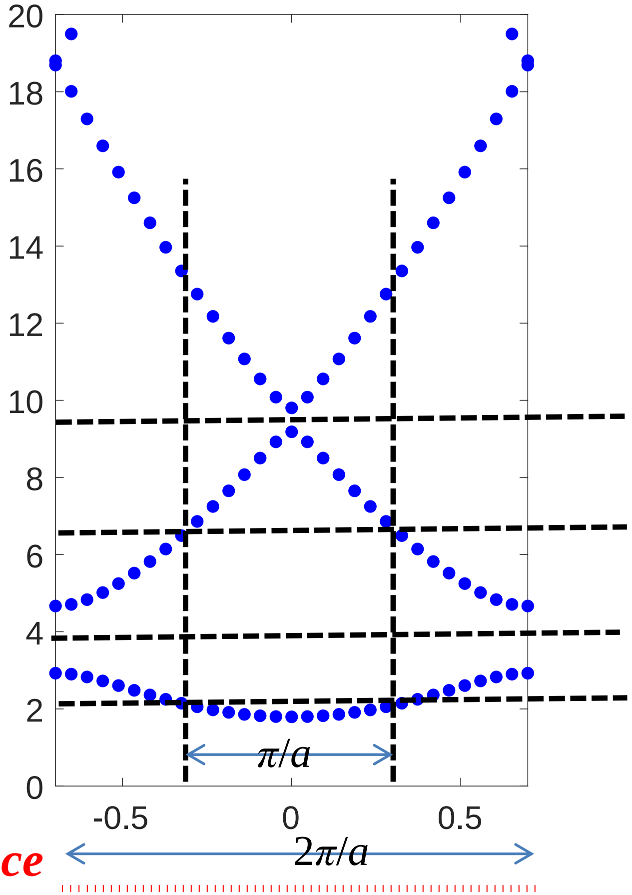
$$-\frac{\pi}{a} < k \leq \frac{\pi}{a} \rightarrow -\frac{\pi}{a} < \frac{2m\pi}{Na} \leq \frac{\pi}{a} \leftrightarrow -\frac{N}{2} < m \leq \frac{N}{2}$$

Free Electron
k* = π*n*/*L
potential well

Thus, the number of possible *m* is exactly *N*. If there are *N* cells in the whole system, each band has *N* discrete points within 1st BZ. Since each Bloch state can be filled with two electrons (spin up and down), **one band can house up to 2*N* electrons, i.e., 2 electrons per unit cell**.

-Tue/9/15/20

At 0 K, electrons are filled up to the Fermi level (E_F). If there is only one electron per primitive unit cell, half of the bands are occupied. To be specific, E_F is increased up to the point where the projected line on the *k*-axis is the half of the total length of 1st BZ. N_e = number of electrons per primitive unit cell.



E_F when $N_e = 4$

E_F when $N_e = 3$

E_F when $N_e = 2$

E_F when $N_e = 1$

quantized k space

The Fermi level can lie at any point within the bandgap at 0 K. (At finite *T*, E_F is close to the middle of the bandgap as will be discussed later.)

The bandgap or energy gap (E_g) of the material is the difference between the energies of highest occupied (**HOMO**) and lowest unoccupied states (**LUMO**). If E_g is zero, it is metal. If E_g is finite but small (**~1-3 eV**), it is semiconductor. Otherwise, the material is an insulator. (The boundary between insulator and semiconductor is not clear-cut.)

The above 1D material is metallic if electrons per unit cell are odd numbers. When the number is 2 and 4, E_g exits.

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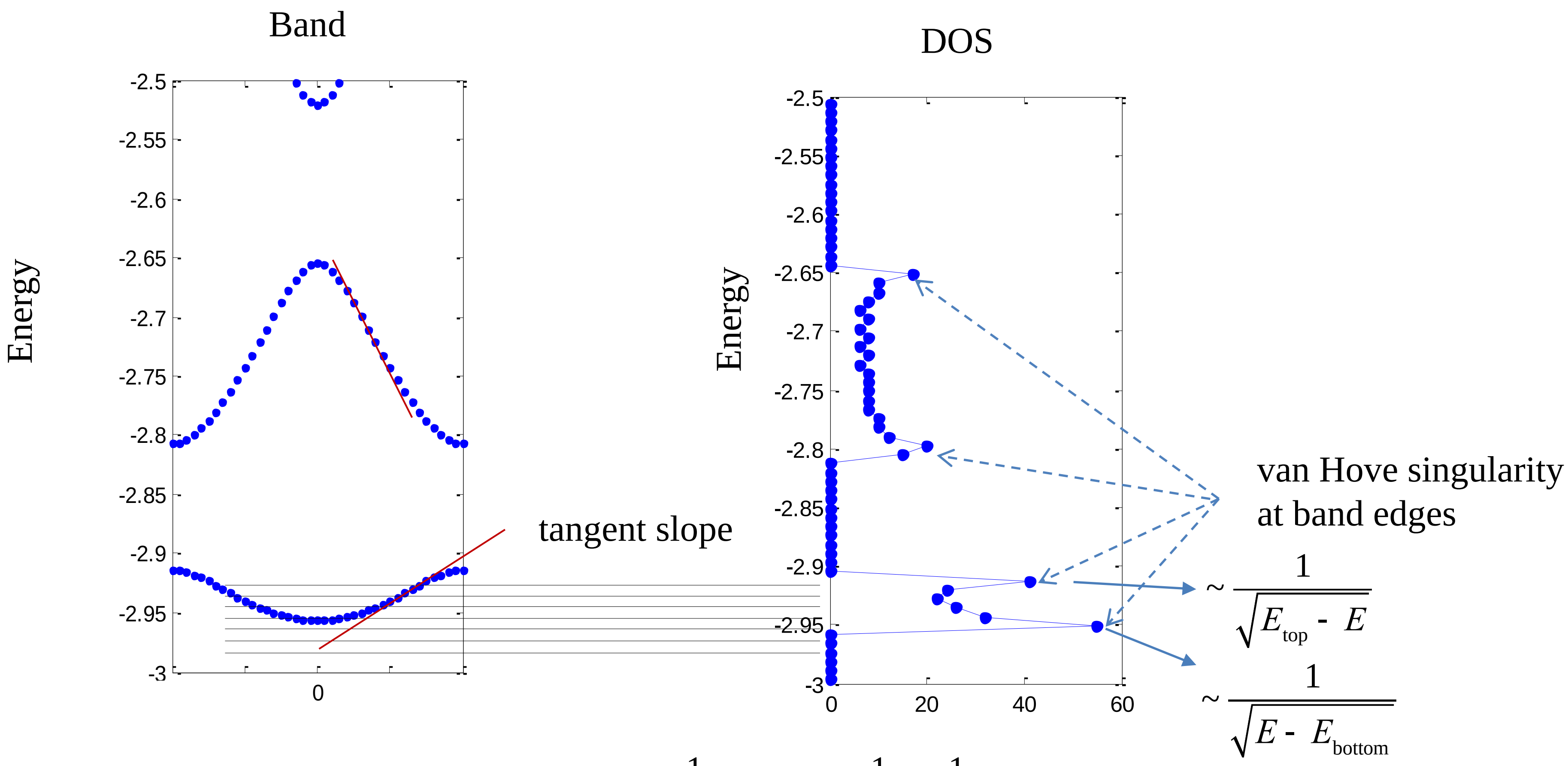
The density of states can be obtained by applying the definition to the band structure. That is to say, $D(E)dE$ = number of states in $[E, E+dE]$



$$\sim \frac{1}{\sqrt{E_{\text{top}} - E}}$$

$$\sim \frac{1}{\sqrt{E - E_{\text{bottom}}}}$$

$$D(E) \propto \frac{1}{[\text{tangent slope at } E]} \propto \frac{1}{k} \propto \frac{1}{\sqrt{E}}$$

1D

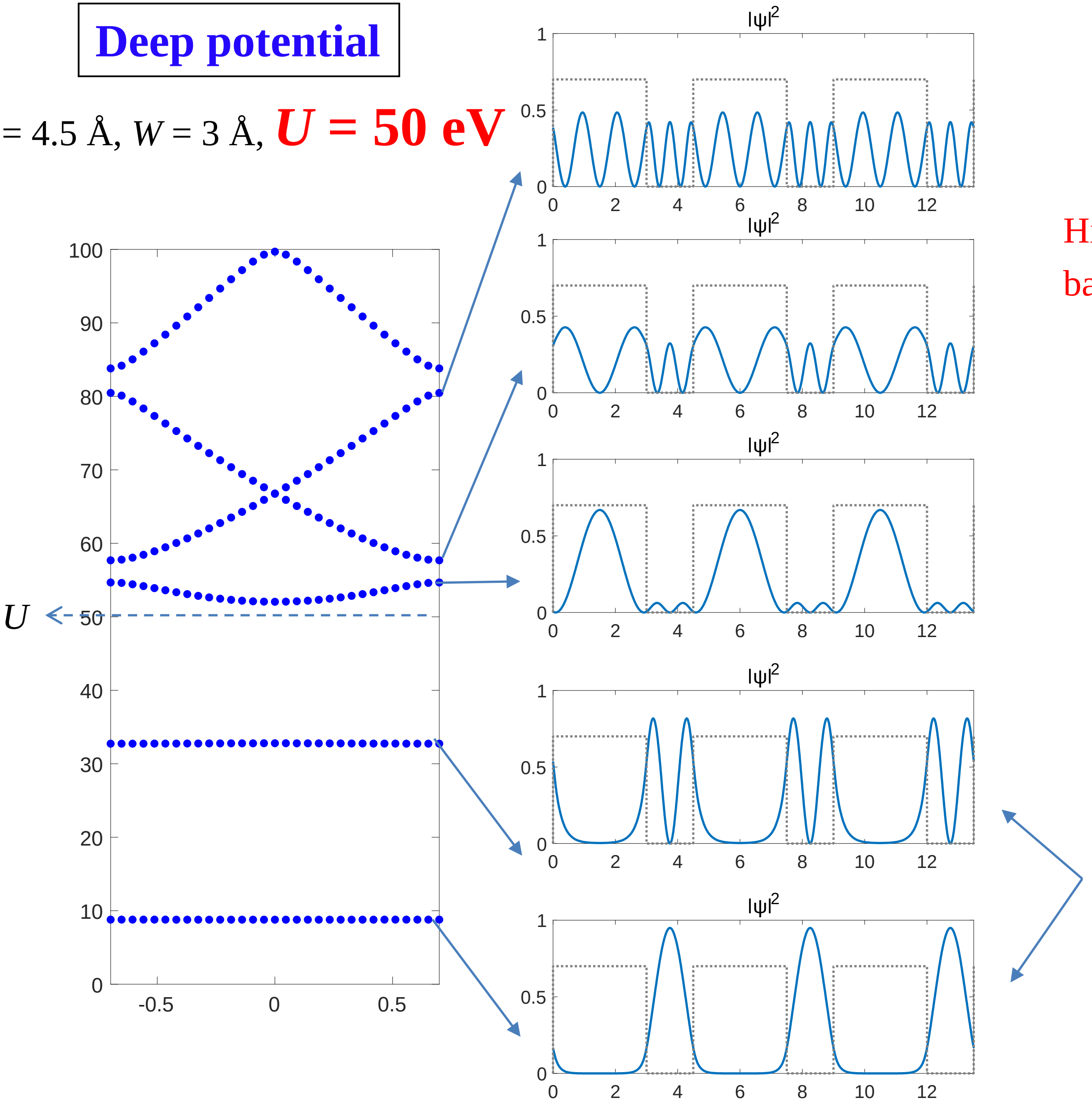
Since the band shape near the top and bottom of each band is similar to that of 1D free electron system, DOS is also similar to the free-electron form (D(E) ~ $E^{-0.5}$).

2B.5. Tight-Binding Approach

Deep potential

a = 4.5 Å, W = 3 Å, U = 50 eV

$$\psi(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\, u(\boldsymbol{r})$$



High energy states resemble band structures of free electrons.

These originate from the ground and 1st excited state of the quantum well.

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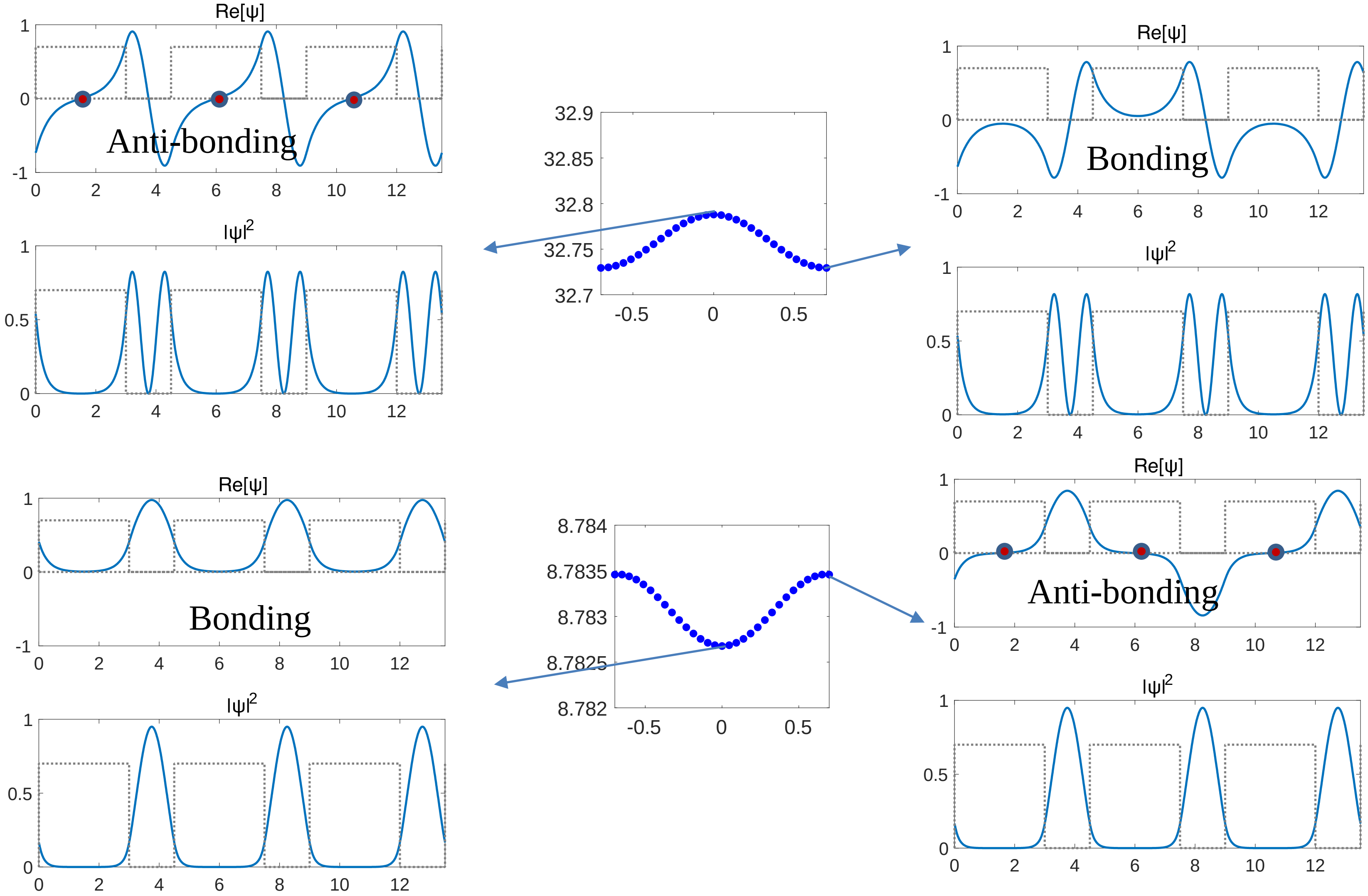

These bands originate from the eigenstates in the quantum well. Nodal points (●) between orbitals are signature of anti-bonding character.

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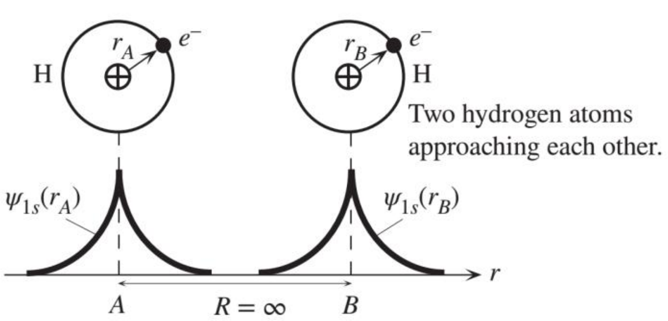
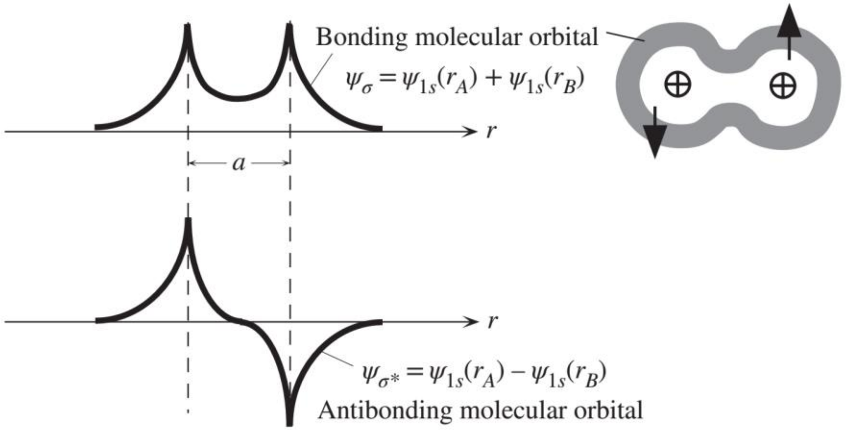
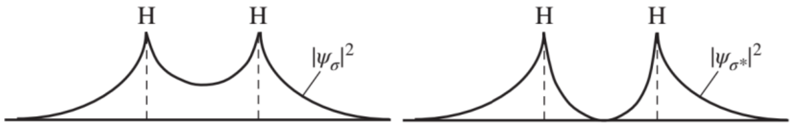
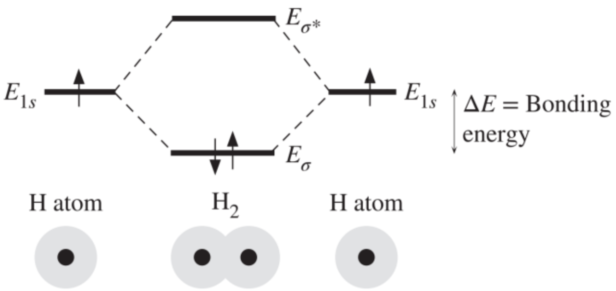
Cf. Bonding and antibonding in H_2 molecule.

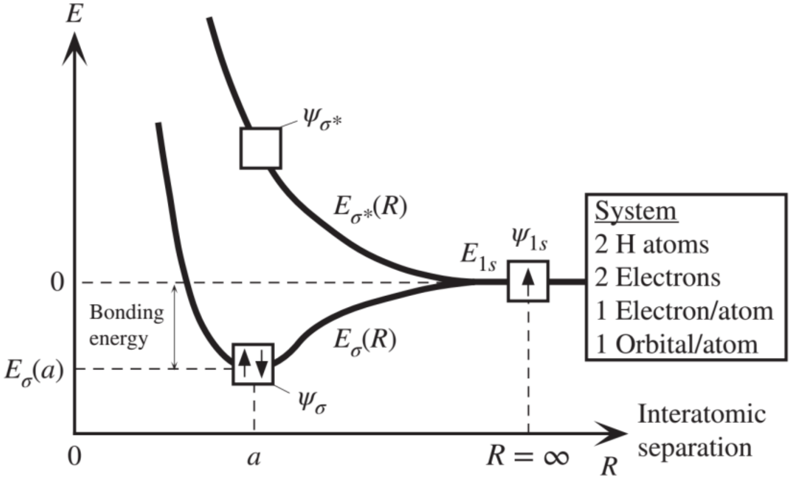






(a) Electron probability distributions for bonding and antibonding orbitals, ψ_σ and $\psi_{\sigma*}$.





(a) Energy of ψ_σ and $\psi_{\sigma*}$ vs. the interatomic separation *R*.

How the phase relation is determined?

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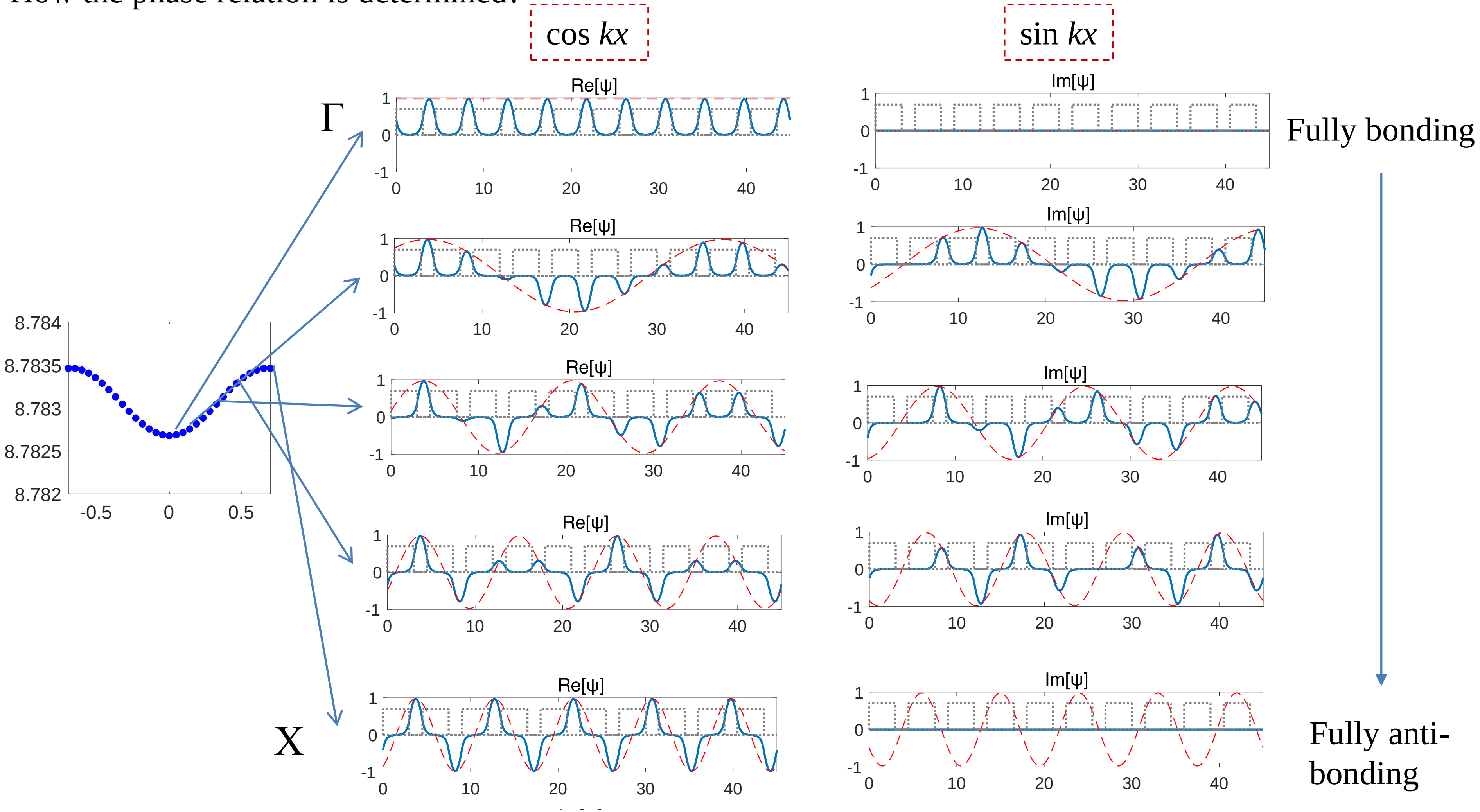

It is seen that the phase relation between orbitals is determined by the phase factor of e^{ikx}.

$$\psi_k(x) = \cdots + e^{-2ika}\phi(x+2a) + e^{-ika}\phi(x+a) + e^{0}\phi(x) + e^{ika}\phi(x-a) + e^{2ika}\phi(x-2a) + \cdots$$

where ϕ is the ground-state wave function in the isolated quantum well. This is called the tight-binding approach or tight-biding approximation.

Tight-binding approach works when orbitals at different atomic sites are well separated. This is a good approximation for most states in real solids except for conduction electrons in metals for which free electron picture is more appropriate. When $\phi(x)$ is a localized function that is an eigenstate of the isolated potential, the eigenstate of the periodic potential is approximated as follows:

(skip)

$$\psi(x) \simeq \sum_{n=-\infty}^{\infty} e^{inka}\phi(x-na)$$

In chemistry, this is known as the linear combination of atomic orbitals (LCAO)

This approximation is consistent with the Bloch theorem:

$$\psi(x) = \sum_{n=-\infty}^{\infty} e^{inka}\phi(x-na) = e^{ikx}\sum_{n=-\infty}^{\infty} e^{-ik(x-na)}\phi(x-na) = e^{ikx}u(x)$$

The energy of this state is obtained by the Schrödinger equation.

$$\psi = \sum_{n=-\infty}^{\infty} e^{inka}\phi(x-na) = \sum_{n=-\infty}^{\infty} e^{inka}\phi_n \to H\psi = \varepsilon\psi \qquad \left(H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \right)$$

$$\sum_{n=-\infty}^{\infty} e^{inka} H\phi_n = \varepsilon \sum_{n=-\infty}^{\infty} e^{inka}\phi_n$$

$$\sum_{n=-\infty}^{\infty} e^{inka}\int \phi_m H\phi_n = \varepsilon \sum_{n=-\infty}^{\infty} e^{inka}\int \phi_m\phi_n \simeq \varepsilon \sum_{n=-\infty}^{\infty} e^{inka}\delta_{m,n} = \varepsilon e^{imka}$$

$$\int \phi_m H\phi_n = \begin{cases} \varepsilon_0 & m = n \ \text{(on-site energy)} \\ t & m = n \pm 1 \end{cases}$$

$$e^{ikma}\varepsilon_0 + t(e^{ik(m+1)a} + e^{ik(m-1)a}) = \varepsilon e^{ikma}$$

$$\to \varepsilon = \varepsilon_0 + 2t\cos ka$$

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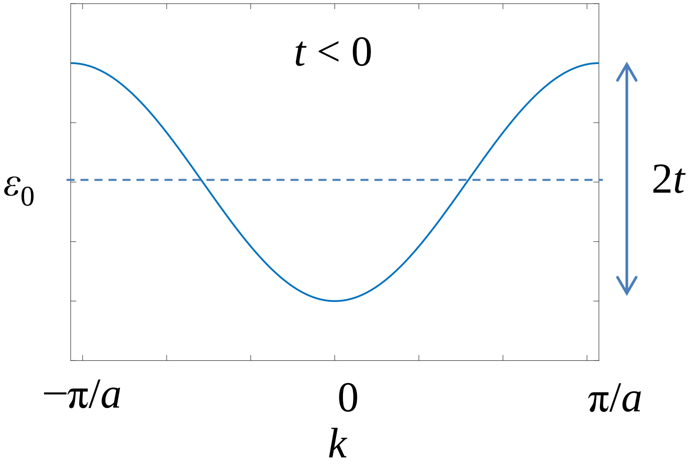
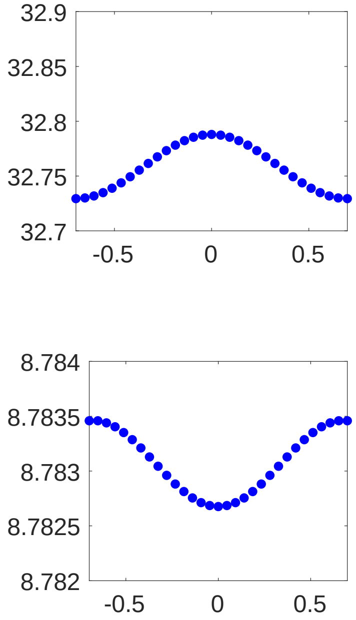
$$\varepsilon = \varepsilon_0 + 2t\cos ka$$





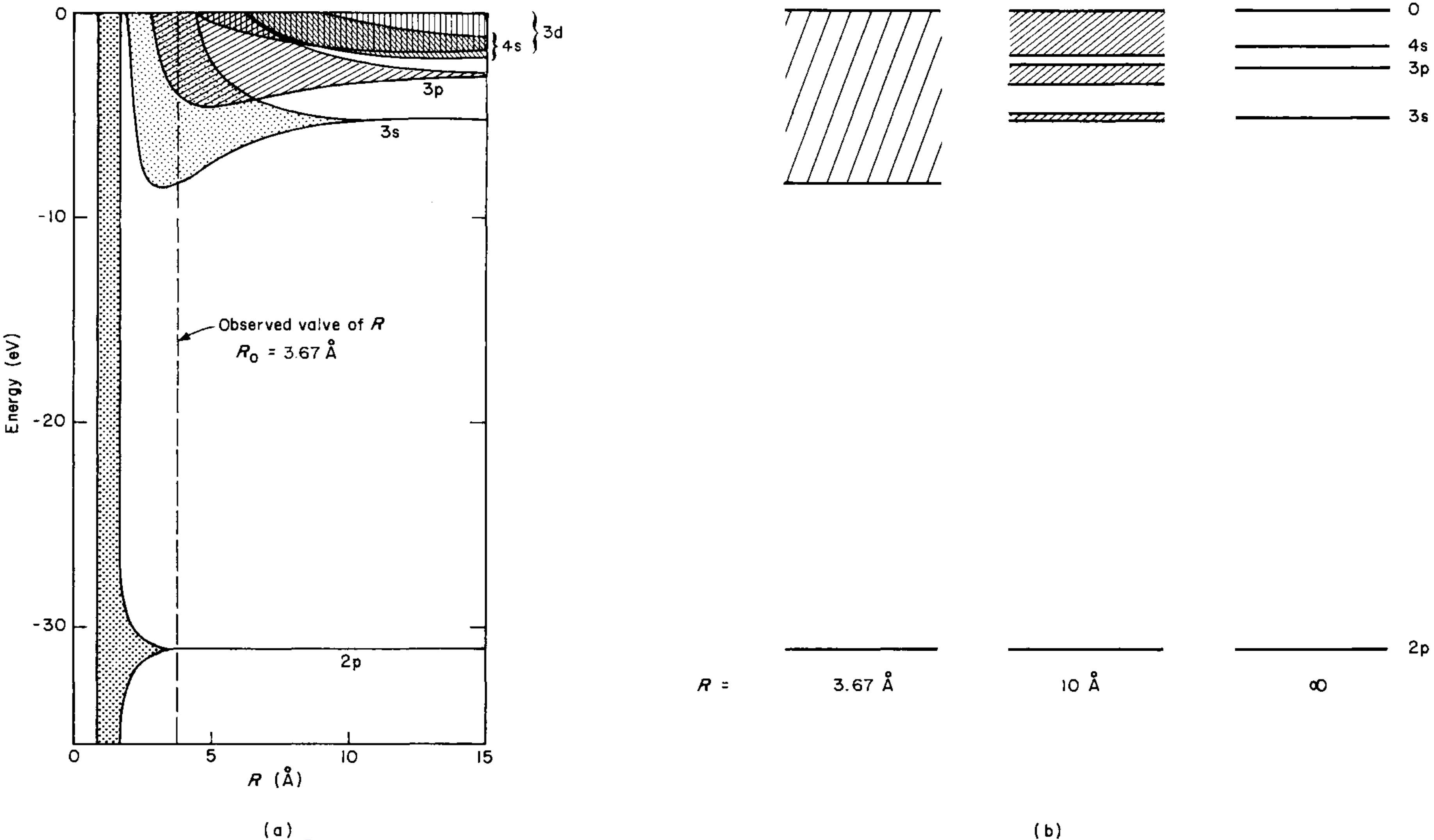
t is called the transfer integral and its magnitude mainly depends on how much two neighboring orbitals overlap. When wave functions overlap with the same phase, this value is usually negative. The 1st and 2nd bands of the deep potential is well approximated by this energy form.

The band width ($2t$) of the second band is larger than for the first band. This is because the orbital forming the second band is more extended so the neighboring orbitals overlap more than the first band. (Recall the tunneling effect for the finite quantum well.)

Energy Bands vs. Distance

Na: $1s^2\,2s^2\,2p^6\,3s^1$

Cohesive Energy vs. Distance

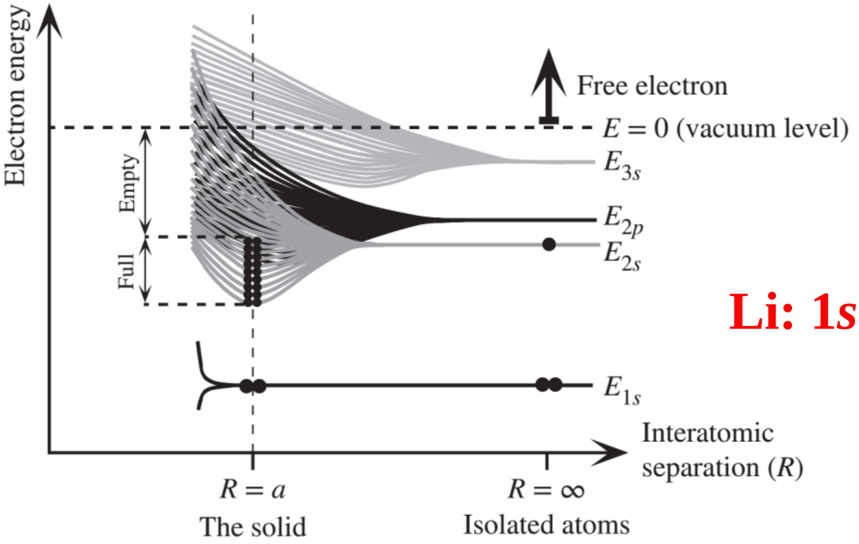


Bube **FIG. 7.3** (a) Energy bands developing in metallic sodium as a function of the interatomic distance *R*. (From J. C. Slater, *Phys. Rev.* **45,** 794 (1934).) (b) Specific energy-band formation for three values of *R*.

4.6 eV for *c*-Si

Cohesive Energy = *Energy required to form separated neutral atoms in their ground state from the solid at 0 K at 1 atm*

When bands from different orbitals overlap, they are intermixed (no pure $2s$ or $2p$ bands).



Li: $1s^2\,2s^1$

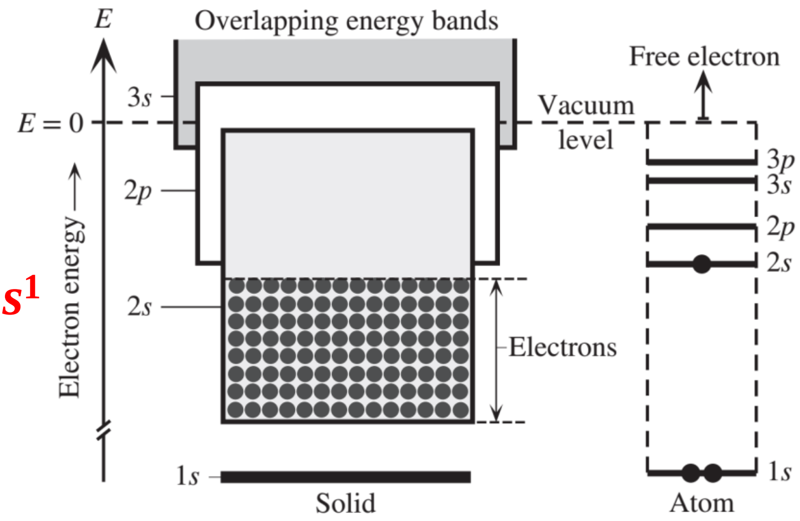


Figure 4.9 As Li atoms are brought together from infinity, the atomic orbitals overlap and give rise to bands (Schematic only.)

Outer orbitals overlap first. The 3*s* orbitals give rise to the 3*s* band, 2*p* orbitals to the 2*p* band, and so on. The various bands overlap to produce a single band in which the energy is nearly continuous.

Figure 4.10 In a metal, the various energy bands overlap to give a single energy band that is only partially full of electrons.

There are states with energies up to the vacuum level, where the electron is free.

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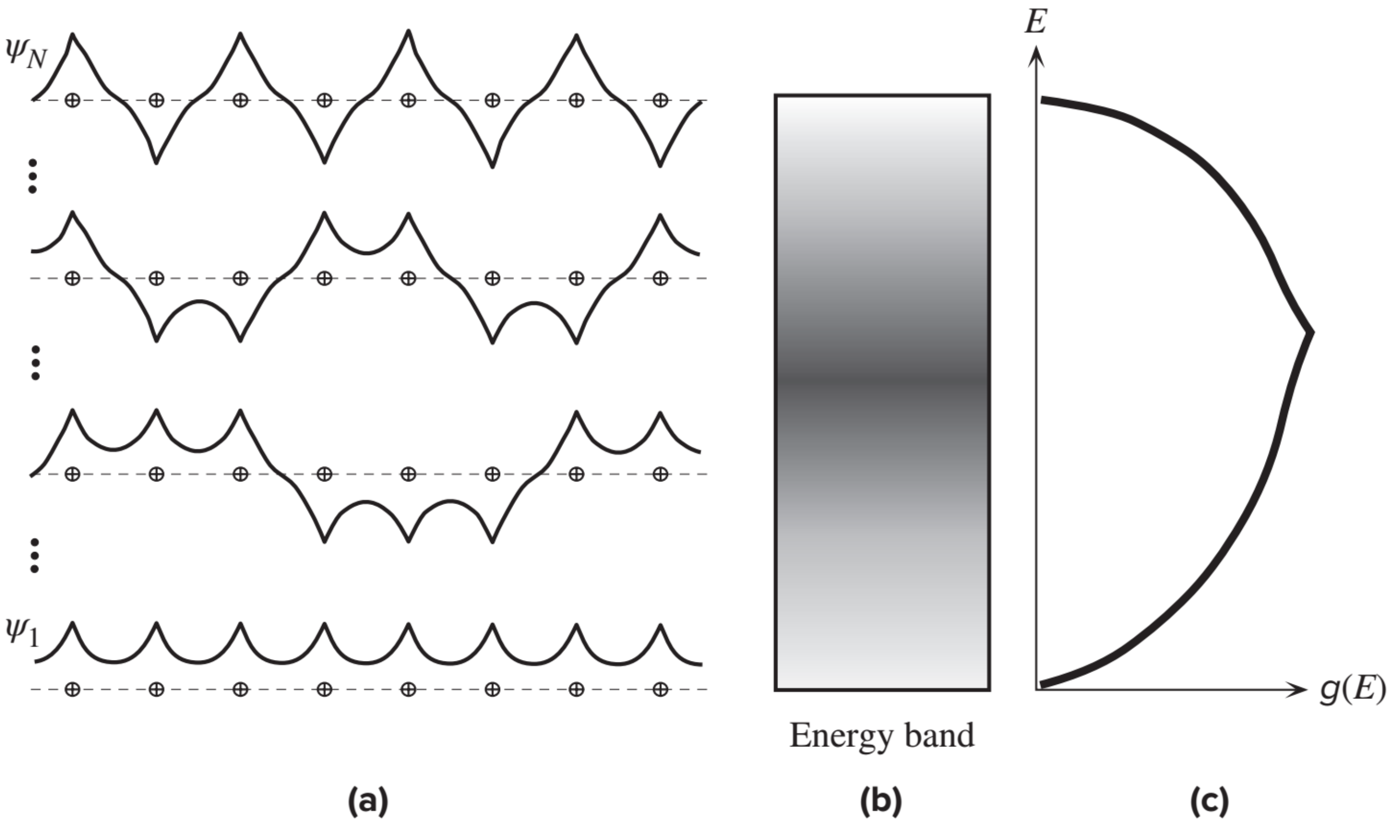

Figure 4.23 (a) In the solid there are N atoms and N extended electron wavefunctions from ψ_1 all the way to ψ_N. There are many wavefunctions, states, that have energies that fall in the central regions of the energy band. Note that although only eight atoms are shown, these are eight sequential atoms among N atoms, and N is very large. Overall, the wavefunctions for N atoms must be symmetric or antisymmetric. (b) The distribution of states in the energy band; darker regions have a higher number of states. (c) Schematic representation of the density of states $g(E)$ versus energy E.

Free Electron Limit → **Band Structure** ← Isolated atom

Weak Periodic Potential		**Tight-Binding Approach**
Weak	Potential	Strong
Momentum	***k***	Bonding-antibonding
Vacuum	**Materials Science** **Inorganic Chemistry**	Chemistry

$$e^{i\mathbf{k}\cdot\mathbf{r}} \longrightarrow e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r}) \longleftarrow u(\mathbf{r})$$

The bands in real solids have both free-electron and tight-binding natures. Depending on the situation, one of them provide better interpretation. Since the valence bands are low in energy, they are well described by the tight-binding approach in most cases.

2B.6. Band structures in 2*d*

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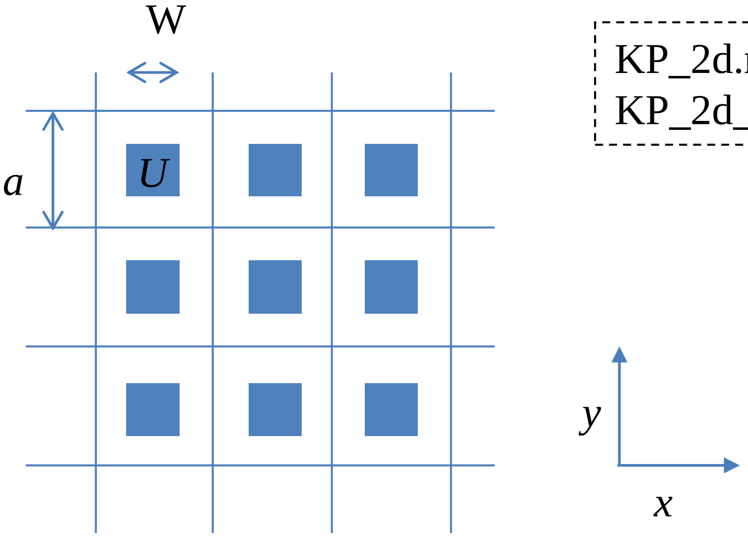
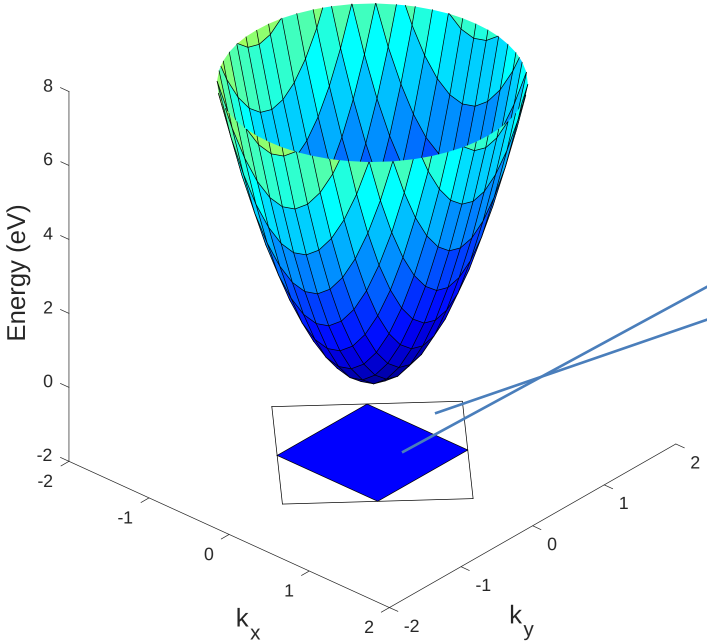
KP_2d.m
KP_2d_line.m

2d square lattice



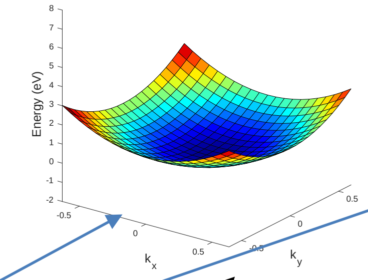
Free electron (a = 5 Å, W = 3 Å, U = 0)

$$E = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2\right)$$

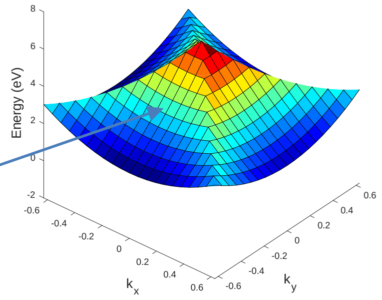


Shift into 1st BZ

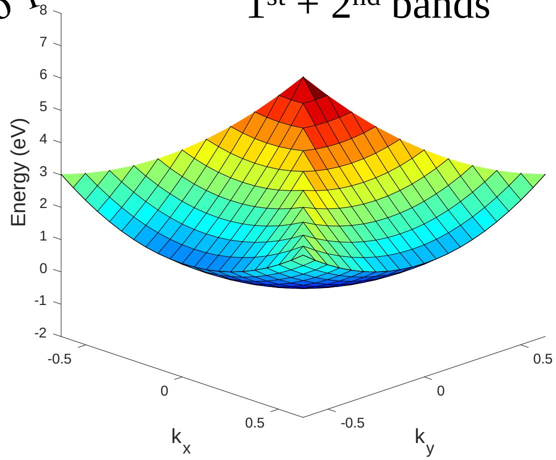
1st band



2nd band

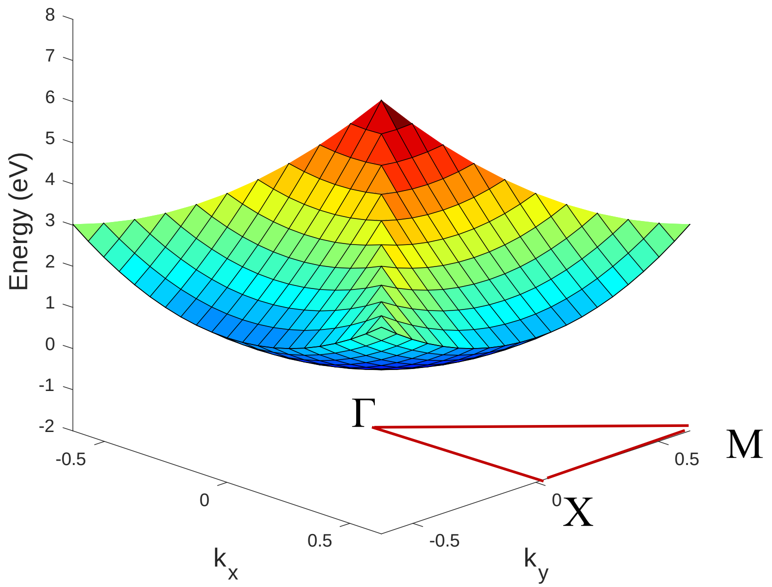


1st + 2nd bands

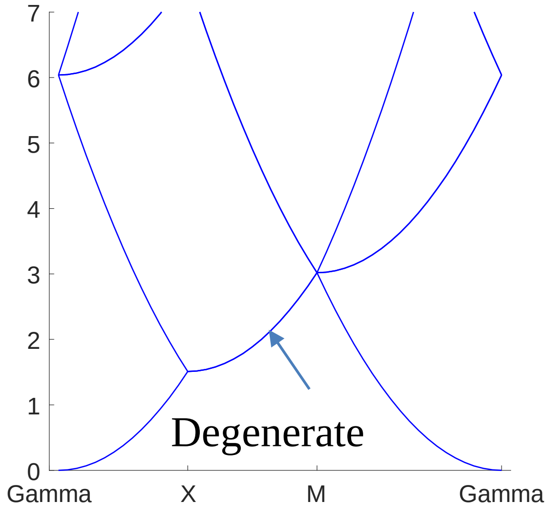


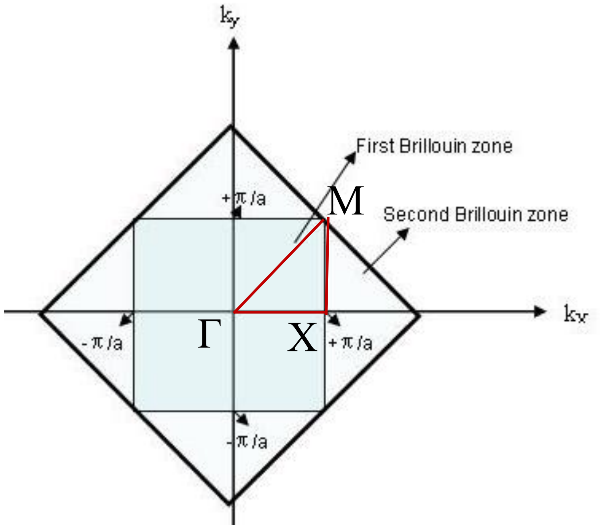
(skip)

The full 3-d band structure is beautiful but it is difficult to capture the whole aspect in one shot. In addition, the band structure of 3d materials cannot be visualized in this way. Therefore, one usually plot the band structure along the lines connecting high-symmetry points.



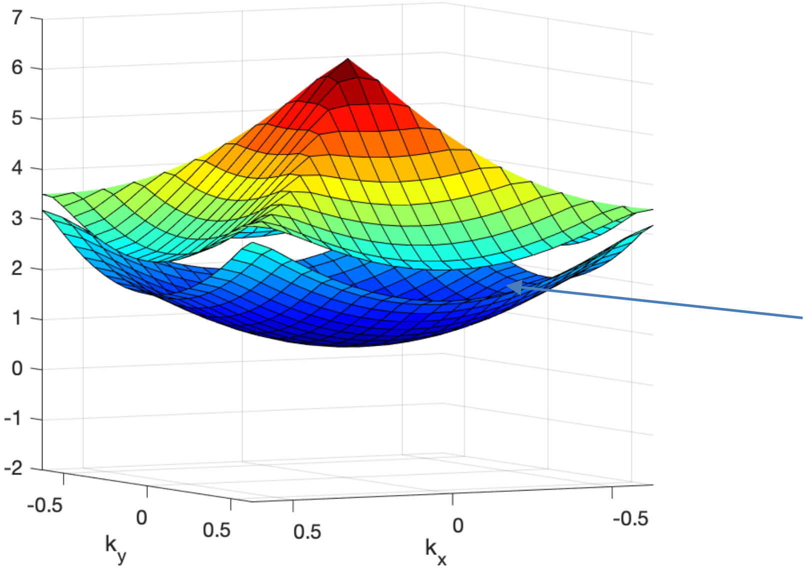
Line plot

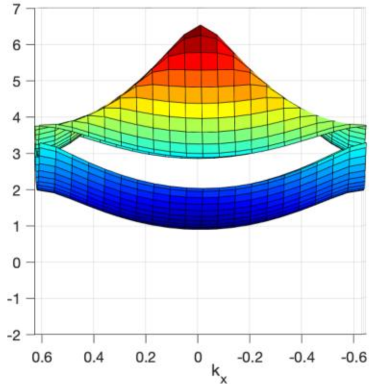




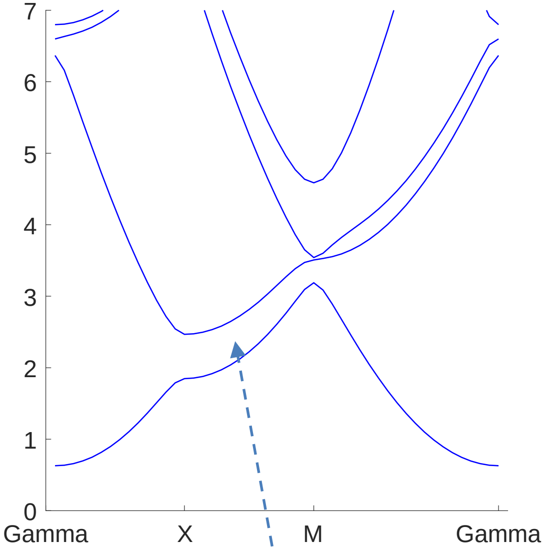
(skip)

Weak potential (a = 5 Å, W = 3 Å, U = 3 eV)





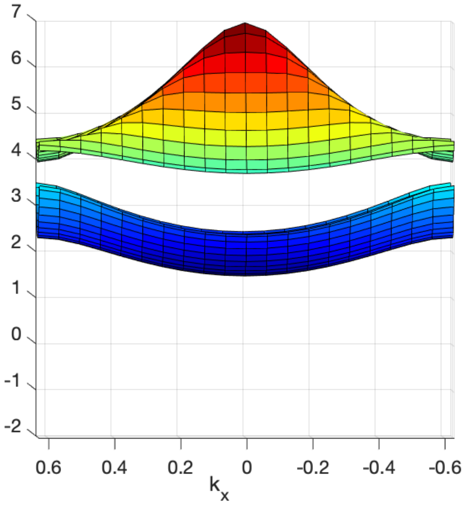
Energy splitting at zone boundaries! Unlike 1d, this does not result in the gap opening. In 1d, the periodic potential is unavoidable, which is not the case in 2d.



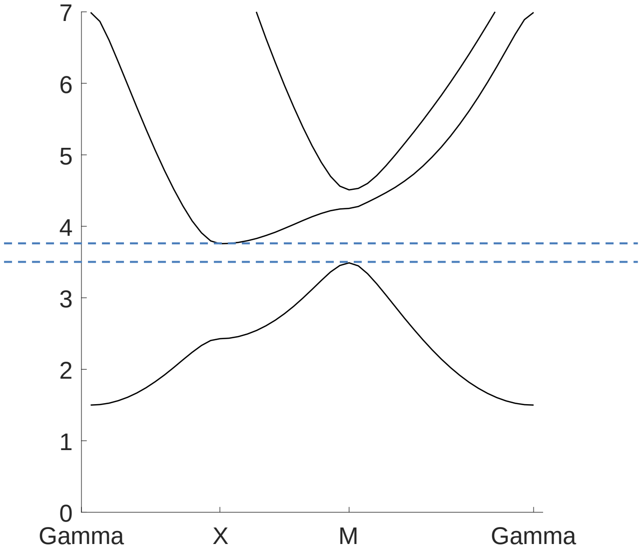
Degeneracy is lifted because of the periodic potential. This is similar to the 1-d case.

(skip)

Strong potential (a = 5 Å, W = 3 Å, U = 6 eV)



Gap opens!



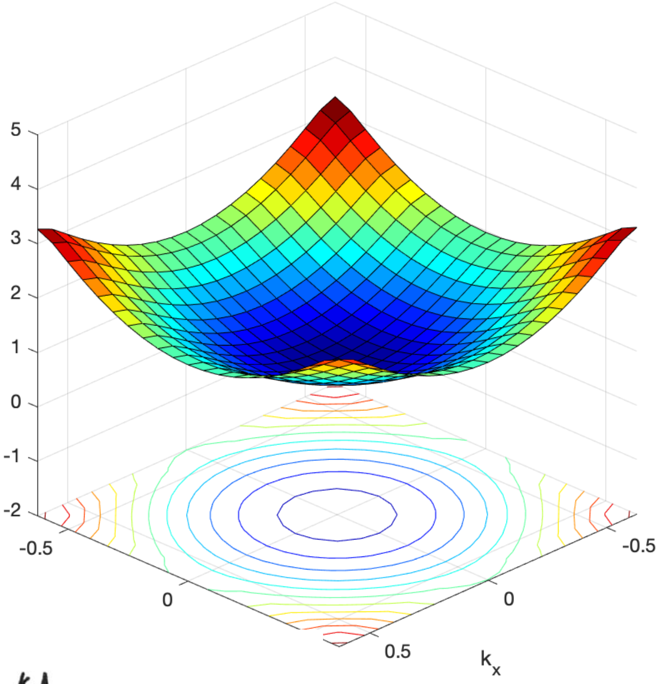
However, recall that this line plot is along the high-symmetry points. Therefore, the appearance of band gap in the line plot does not necessarily indicate the finite band gap, which should be checked over the entire 1st BZ as in the left figure. Nevertheless, in most materials, the band extrema (maximum or minimum) usually appear on or between high-symmetry points, so it is enough to check the band gap in the line plot.

(skip)

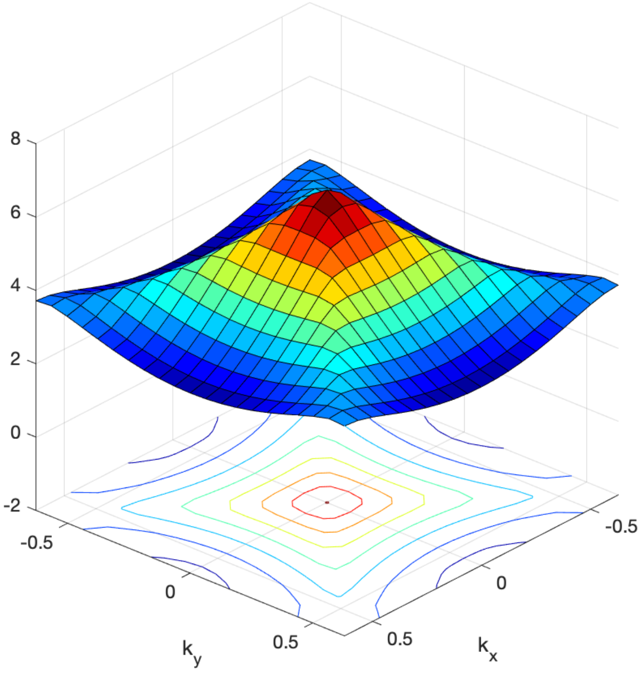
Constant energy line (surface in 3d)

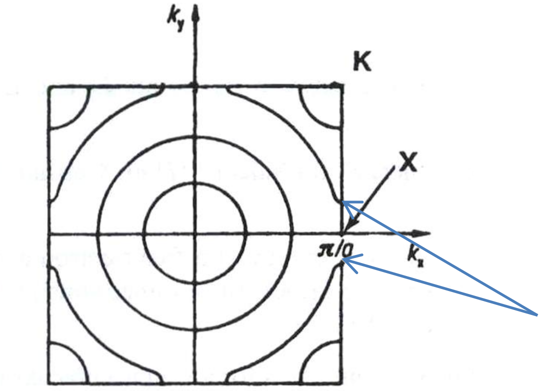
Weak potential (*a* = 5 Å, W = 3 Å, *U* = 3 eV)

1^{st} band



2^{nd} band





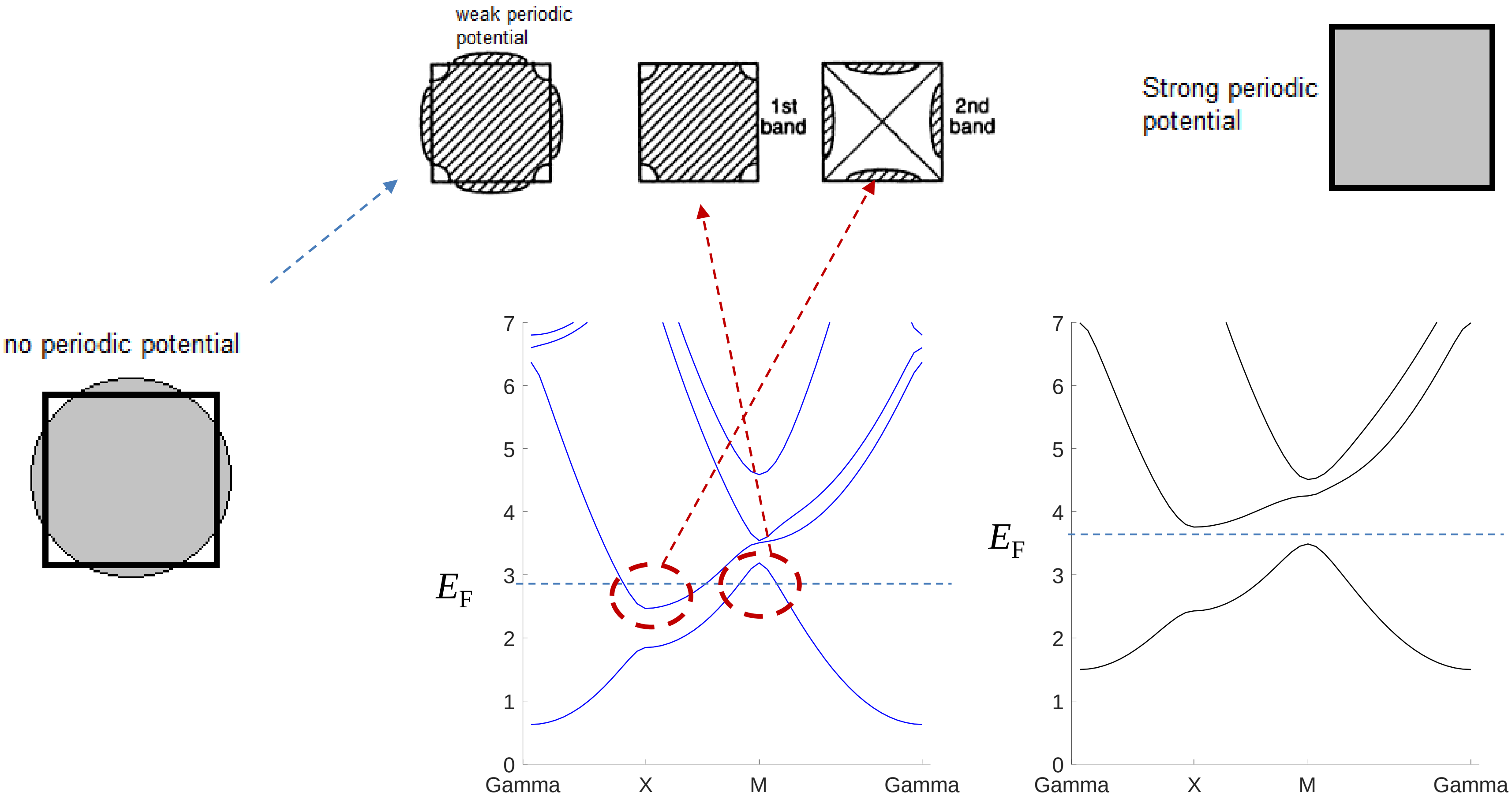
Curves of equal energy inserted into the first Brillouin zone for 2-D square lattice

It can be proved that the constant energy line always perpendicular to the zone boundary.

(skip)

Electron occupation

Like in 1d system, each state is separated in the regular mesh in k_x-k_y plane with the total number in the BZ equal to the number of whole cells. Therefore, each band can house up to 2 electrons per cell. In the below, occupied states are marked in shade when $N_e = 2$.



(skip)

Fermi surface in 2d

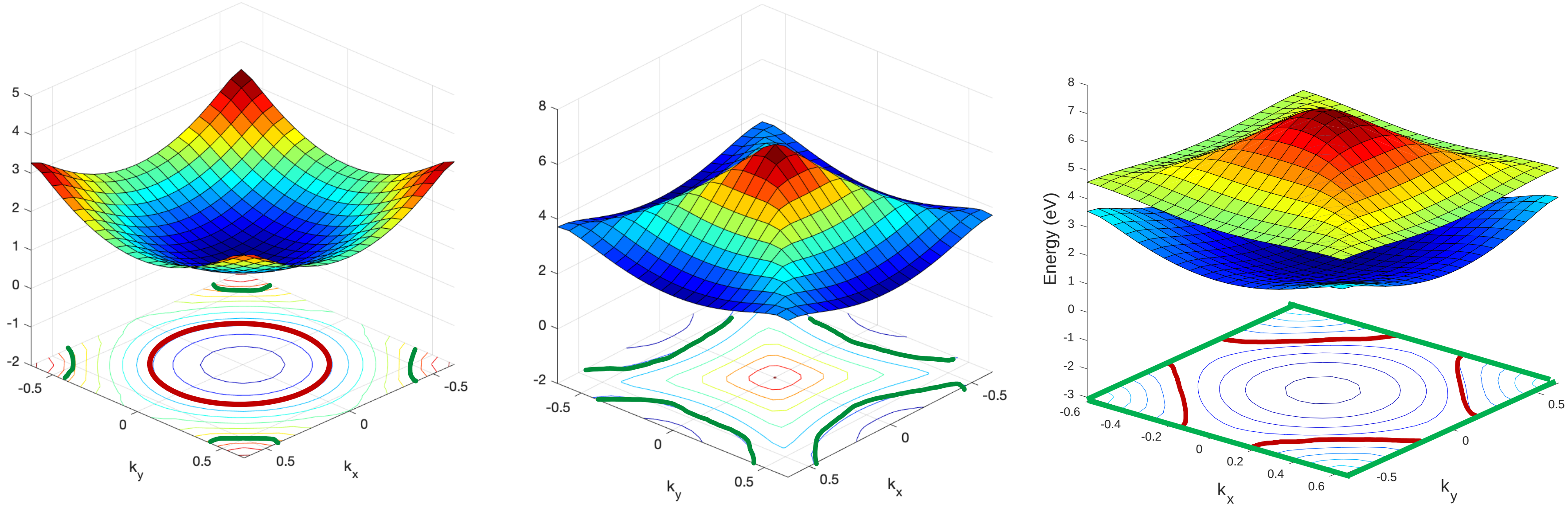
Collection of **k** points crossing the Fermi level in 3d is called Fermi surface. That is to say, equal energy surfaces for the Fermi energy. All **k** points inside the Fermi surface are occupied. For free electrons, the constant energy surface is always spherical. Here “inside” means the direction to which the energy decreases.

Weak potential

Strong potential

1st band

2nd band



🟥 Fermi surface (line) when $N_e = 1$

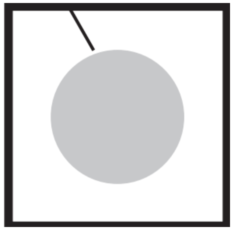
🟩 Fermi surface (line) when $N_e = 2$

(skip)

Fermi surface repeated in the periodic zone scheme. Fermi surfaces of real materials (see later) can be understood schematically using 2d models.

Weak potential

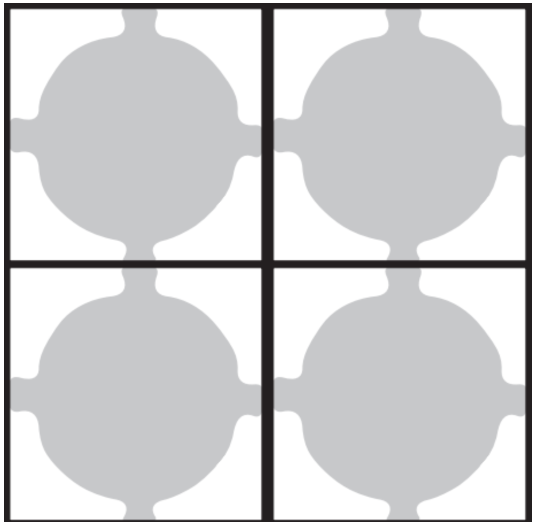
$N_e = 1$



Li, Na, or K

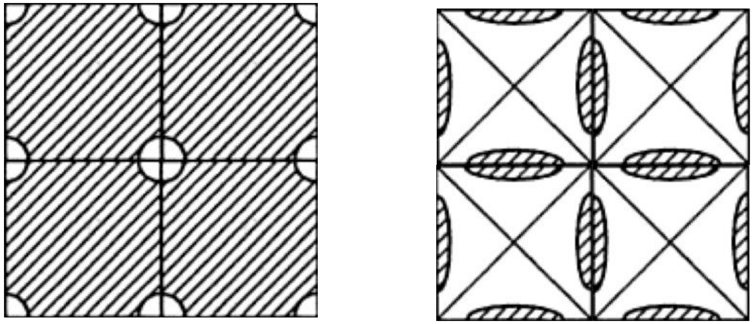
Strong potential

$N_e = 1$



Cu, Ag, or Au

$N_e = 2$

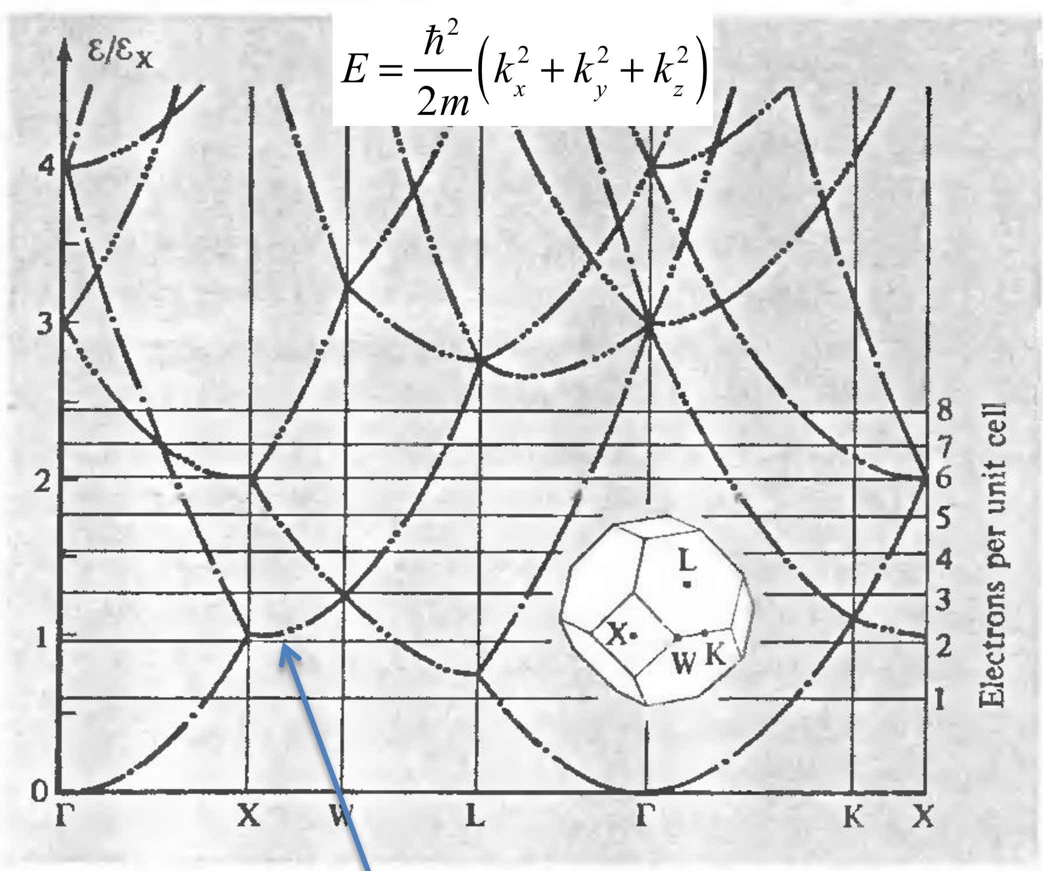


Be, Cd, or Zn

2B.7. Band structures in 3*d*

Band structure of free electrons on FCC (empty) lattice

(skip)



$$E=\frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right)$$

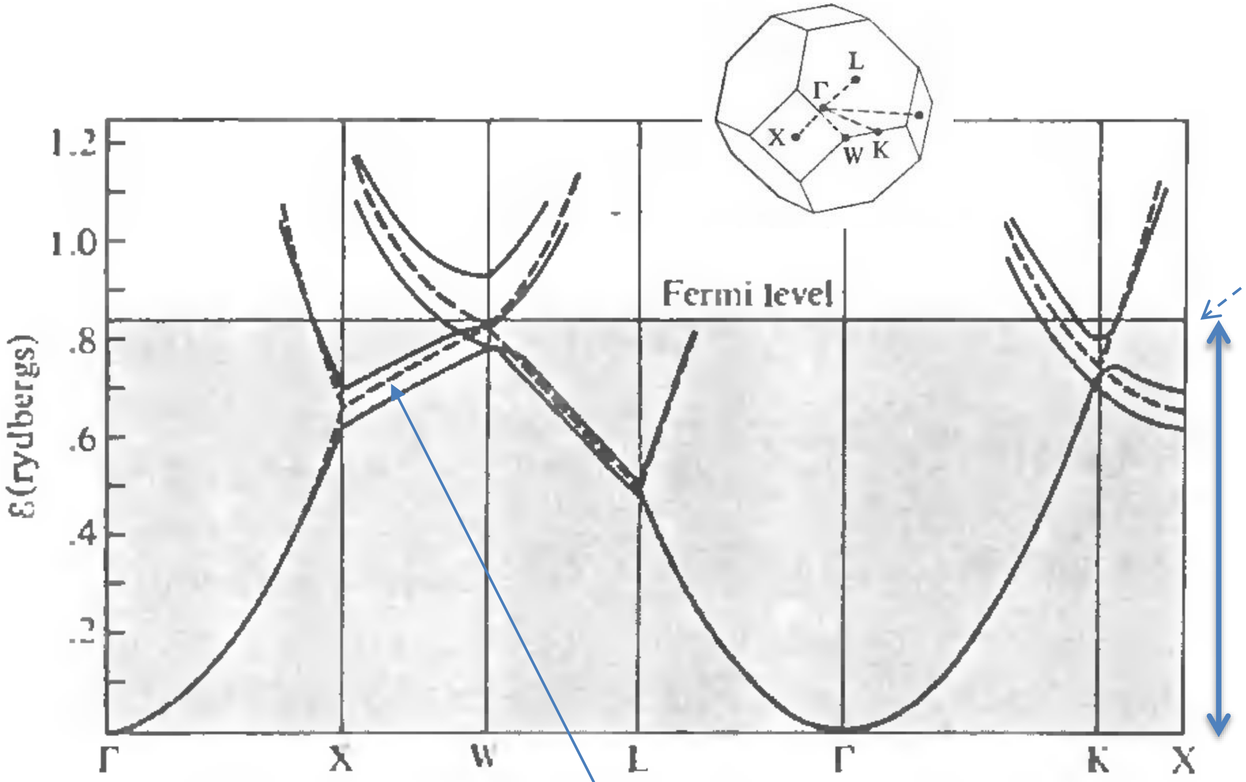
Figure 9.5

Free electron energy levels for an fcc Bravais lattice. The energies are plotted along lines in the first Brillouin zone joining the points Γ(k = 0), K, L, W, and X. ε_x is the energy at point X ($[\hbar^2/2m][2\pi/a]^2$). The horizontal lines give Fermi energies for the indicated numbers of electrons per primitive cell. The number of dots on a curve specifies the number of degenerate free electron levels represented by the curve. (From F. Herman, in *An Atomistic Approach to the Nature and Properties of Materials*, J. A. Pask, ed., Wiley, New York, 1967.)

Some of the lines are degenerate.

Like 1d&2d, the number of states constituting each band is equal to the number of unit cells in the macroscopic material.

For real materials, the band structure can be calculated quite accurately using the computational approach based on the **density functional theory**. The following is the calculated band structure of **Al (=[Ne]3$s^2$3p^1)** for valence electrons.



There are three valence electrons per cell.

= 11.4 eV (11.7 eV from free-electron model)

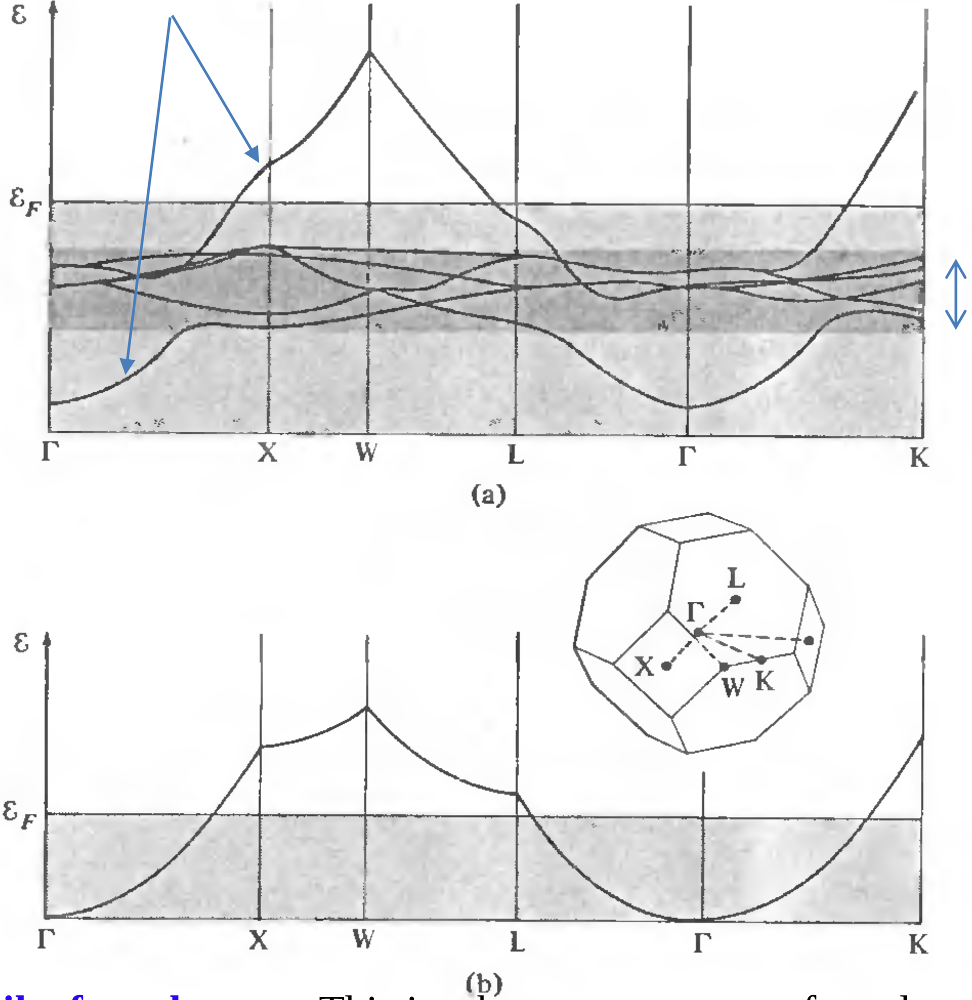
1 Rydberg = 13.6 eV

Degeneracy along the high-symmetry line is lifted by the periodic potential.

The band structure is similar to the free-electron model, except that degeneracy is lifted by weak potential by ions. For metals belonging to group I, II, III, and IV, *s* and *p* electrons experience only weak ionic potential, because potentials are largely screened by free electrons and valence electrons are relatively away from the ion. These elements are called “nearly free-electron metals”. The band structure explains why the free-electron model worked so well for these metals.

Band structure of **Cu ([Ar]$3d^{10}4s^1$)**

One can know the orbital character of the band by inspecting the wave function shape.



s-band (close to the free-electron band)

d-band (localized and so well described by tight-binding approach)

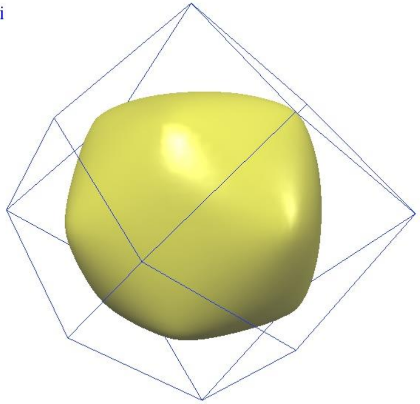
Figure 15.4
(a) Calculated energy bands in copper. (After G. A. Burdick, *Phys. Rev.* 129, 138 (1963).) The ε vs. *k* curves are shown along several lines in the interior and on the surface of the first zone. (The point Γ is at the center of the zone.) The *d*-bands occupy the darkest region of the figure, whose width is about 3.5 eV. (b) The lowest-lying free electron energies along the same lines as in (a). (The energy scales in (a) and (b) are not the same.)

Only 4*s* states behave like free electron. This is why we assume one free electron for Cu. The *d* electrons are more localized than s electrons and so they are better described by the tight-binding approach and develop flat bands. Even though ***d* electrons contribute to chemical bonding and belong to the valence band, they do not behave like free electrons**.

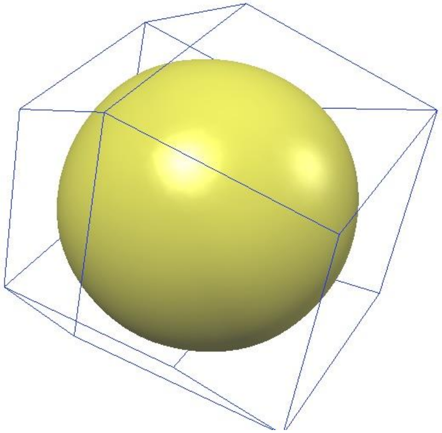
Fermi Surface of Some Metals

Collection of ***k* points crossing the Fermi level** in 3d is called Fermi surface. That is to say, equal energy surfaces for the Fermi energy. All ***k*** points inside the Fermi surface are occupied. For free electrons, the constant energy surface is always spherical. Here “inside” means the direction to which the energy decreases.

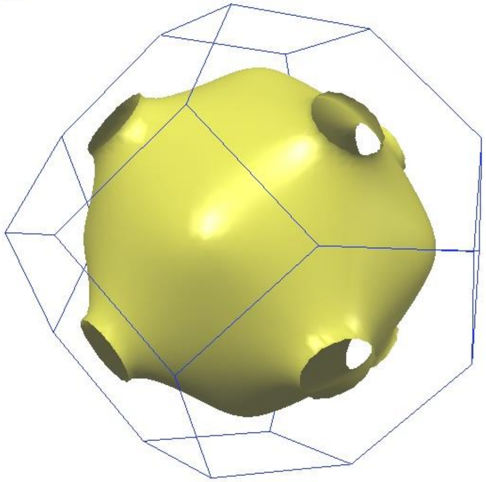
Li



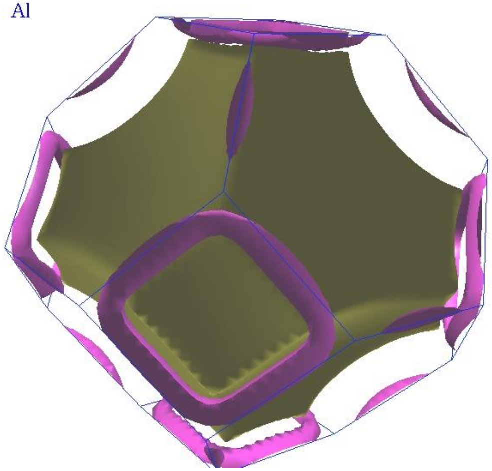
K



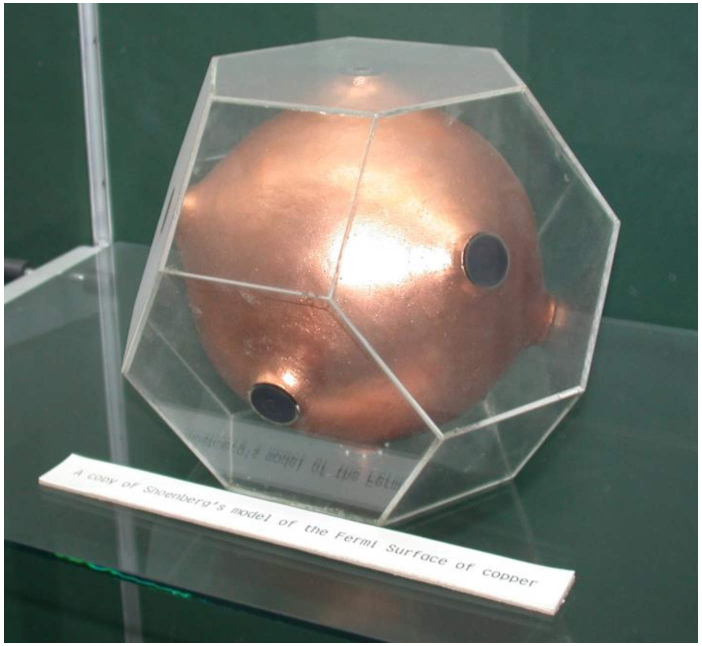
Cu

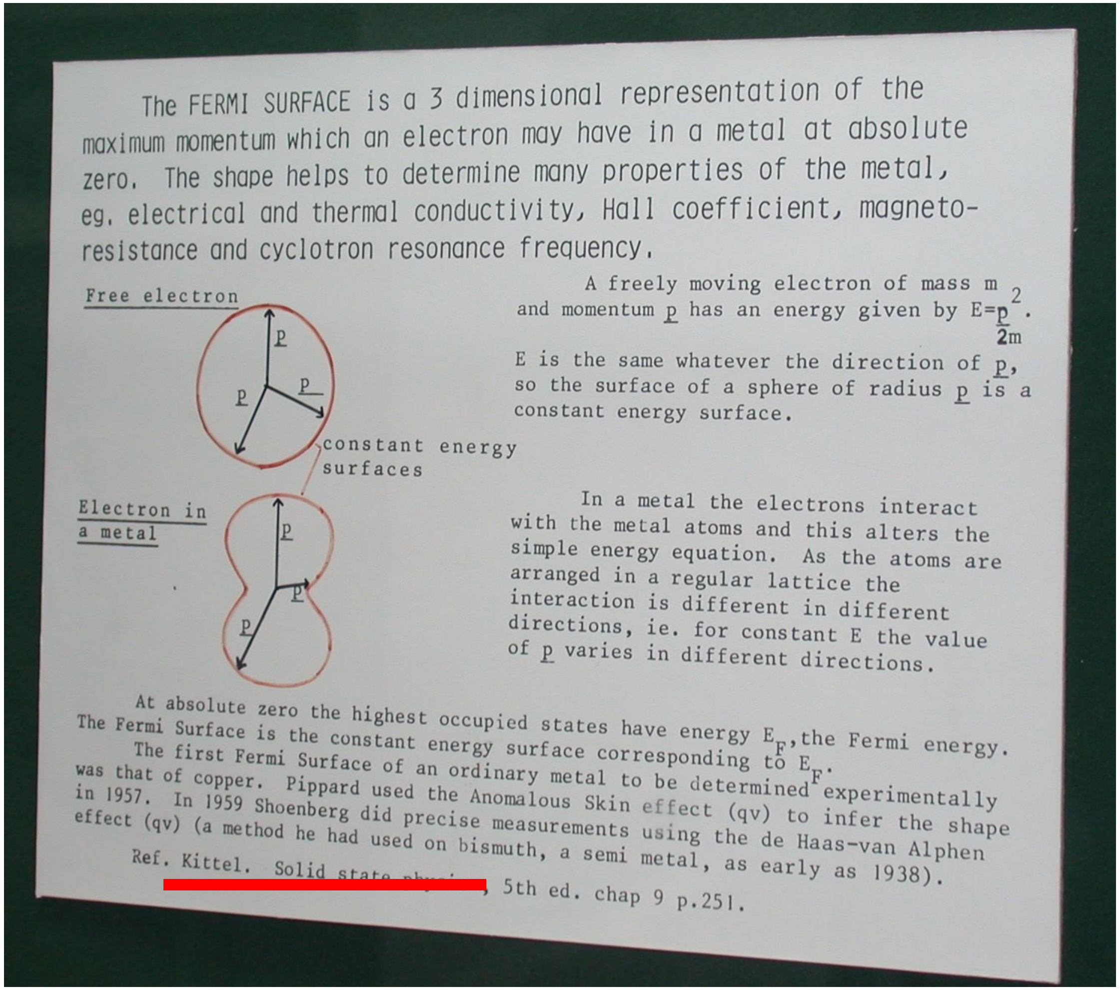


Al



Museum at Cambridge University





The FERMI SURFACE is a 3 dimensional representation of the maximum momentum which an electron may have in a metal at absolute zero. The shape helps to determine many properties of the metal, eg. electrical and thermal conductivity, Hall coefficient, magneto-resistance and cyclotron resonance frequency.

Free electron

A freely moving electron of mass m and momentum p has an energy given by $E=\frac{p^2}{2m}$.

E is the same whatever the direction of p, so the surface of a sphere of radius p is a constant energy surface.

constant energy surfaces

Electron in a metal

In a metal the electrons interact with the metal atoms and this alters the simple energy equation. As the atoms are arranged in a regular lattice the interaction is different in different directions, ie. for constant E the value of p varies in different directions.

At absolute zero the highest occupied states have energy E_F, the Fermi energy. The Fermi Surface is the constant energy surface corresponding to E_F.

The first Fermi Surface of an ordinary metal to be determined experimentally was that of copper. Pippard used the Anomalous Skin effect (qv) to infer the shape in 1957. In 1959 Shoenberg did precise measurements using the de Haas-van Alphen effect (qv) (a method he had used on bismuth, a semi metal, as early as 1938).

Ref. Kittel. Solid state [redacted], 5th ed. chap 9 p.251.

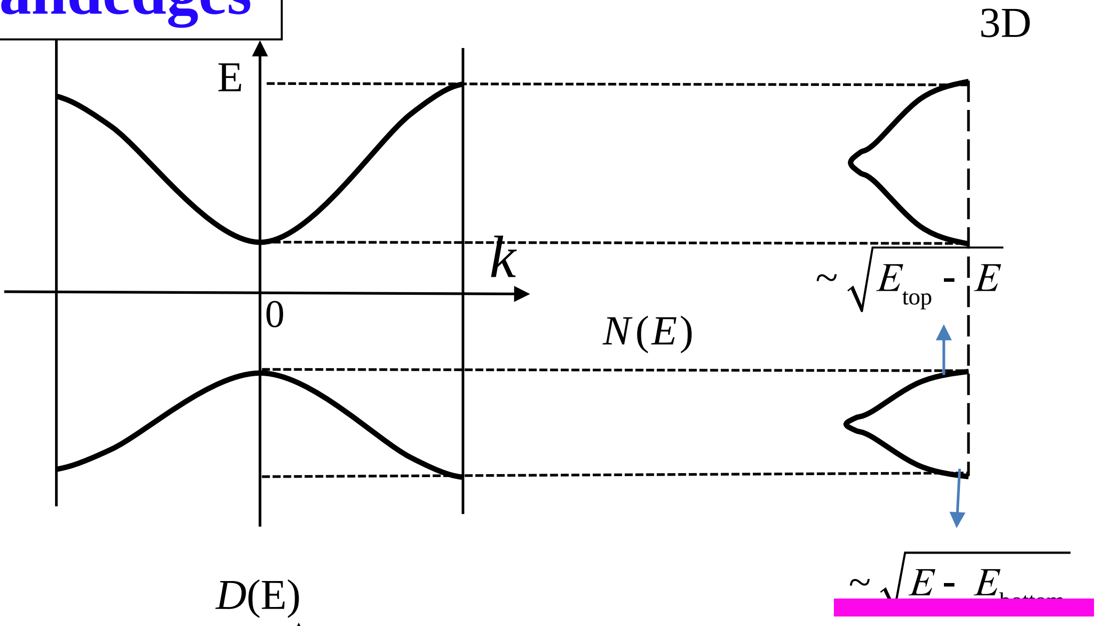
Density of States Near the Bandedges

Near the band edges, $E = \pm \frac{\hbar^2}{2m}|\mathbf{k} - \mathbf{k_0}|^2$.

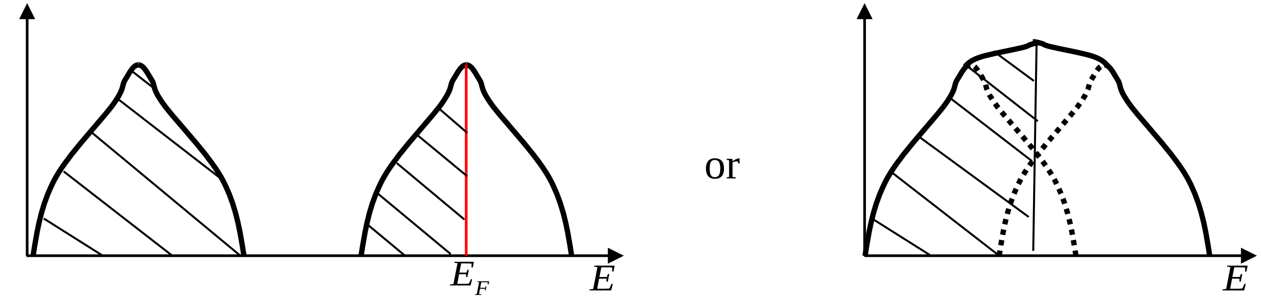
Therefore, DOS is proportional ~~to $\sqrt{E}$~~ as was calculated in the free-electron model.

$$D(E) = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E}$$

Free Electron Model
ppt 2A-8



Metals

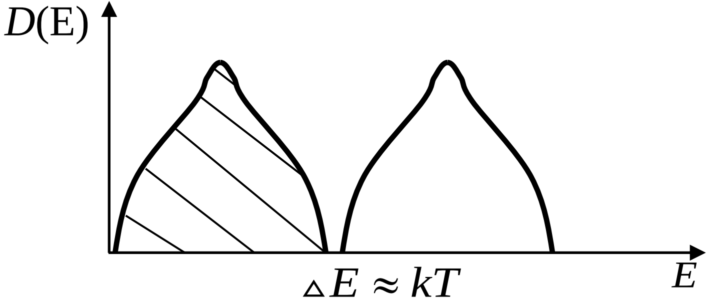


Partially occupied

Bands overlap

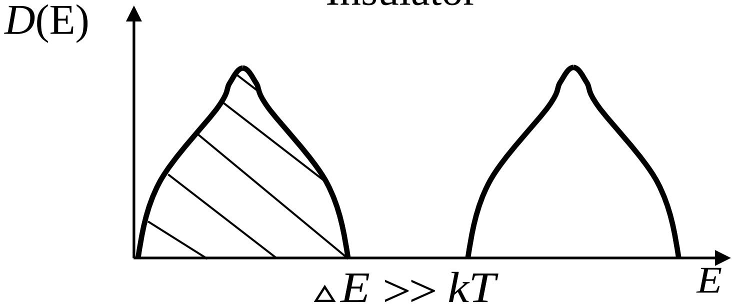
Bube Chap. 7
pp. 120-124
Figs. 7-7 & 7-8

Semiconductor



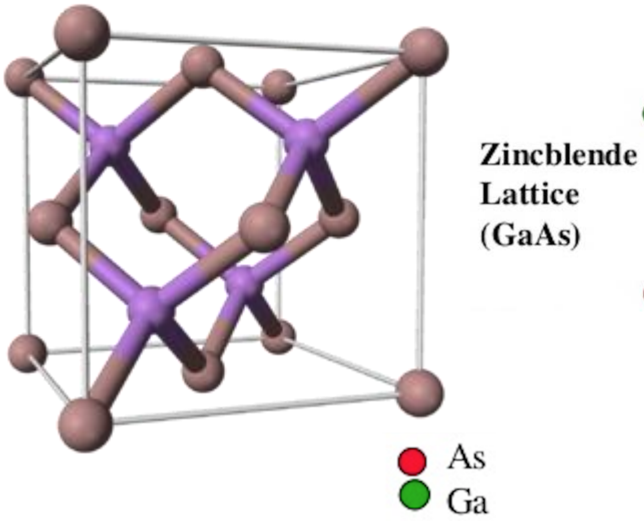
$\Delta E \approx kT$

Insulator

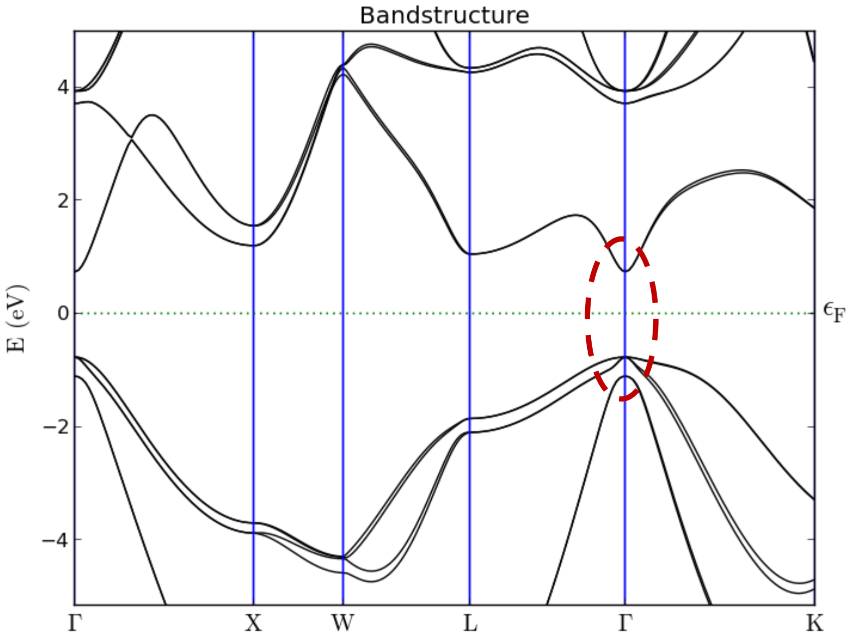


$\Delta E >> kT$

Band Structure of GaAs



Zincblende Lattice (GaAs)

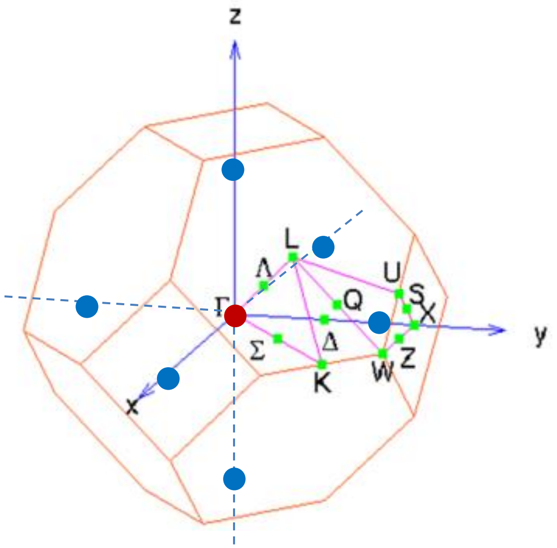


Direct bandgap

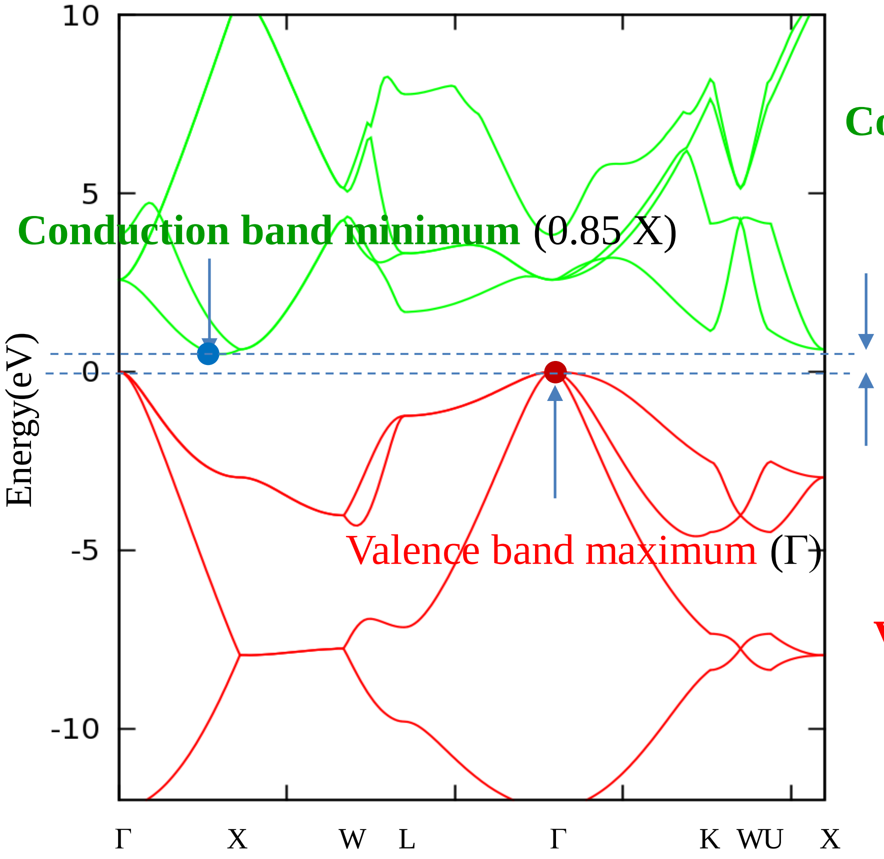
Band Structure of Si ([Ne]$3s^2 3p^2$)

Valence electrons from 3*s* and 3*p* orbitals form the bands around the band gap.

6 “valleys”



1st BZ of FCC



Conduction Bands

Conduction band minimum (0.85 X)

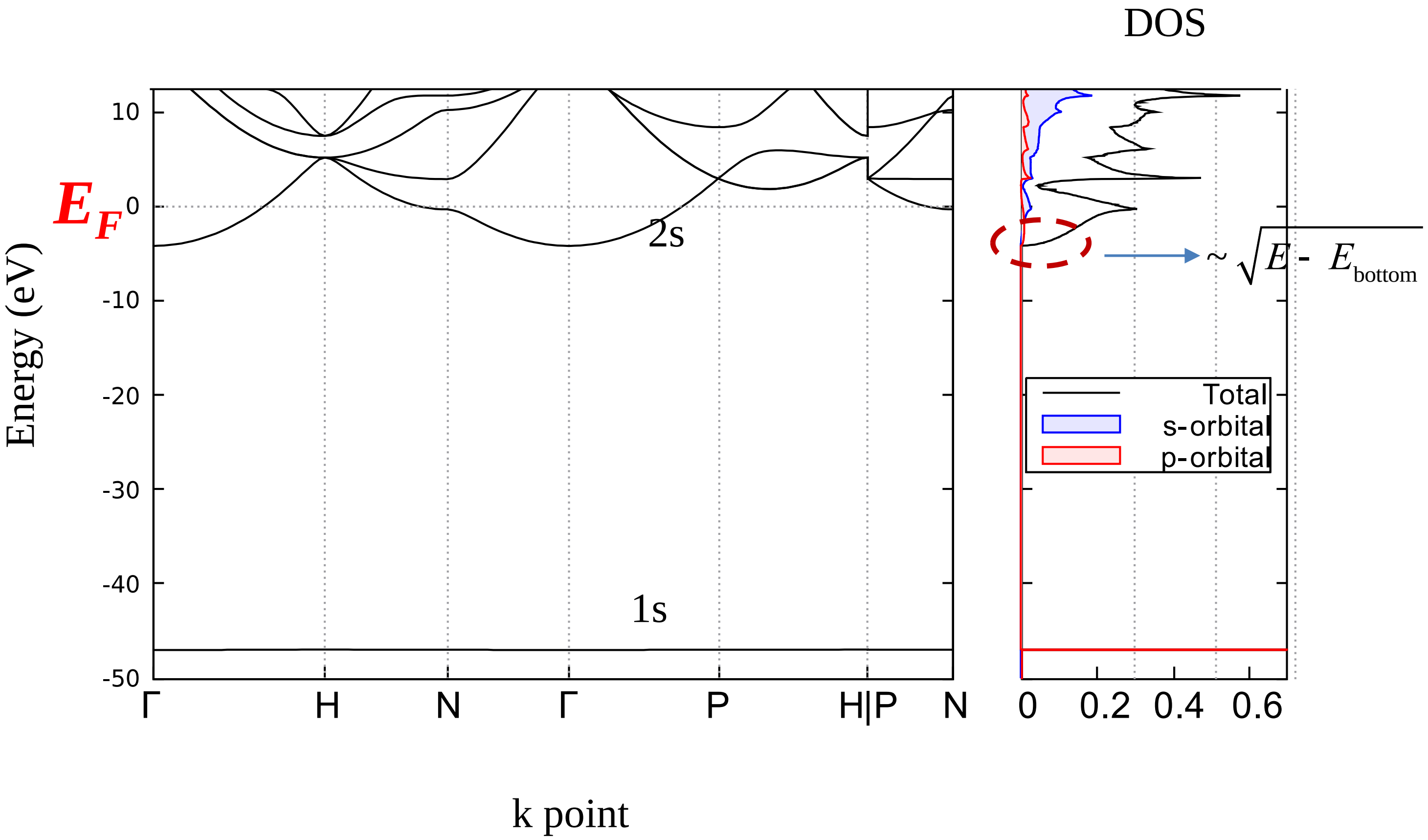
1.14 eV

Valence band maximum (Γ)

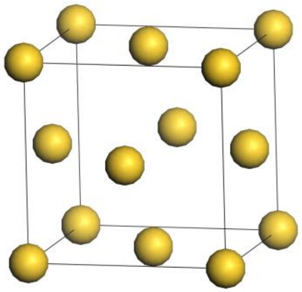
Valence Bands

In the band structure, the conduction band minimum appears at a point close to X along the Γ-X line (around 0.85 X). Because of full symmetry of the diamond structure, this means that there are six **k** points in BZ (●) that correspond to the conduction band minimum. When conduction band minimum and valence band maximum appears **at the (approximately) same *k* points**, it is called the **direct bandgap**. Otherwise, it is called the **indirect bandgap**. This distinction is very important for the **optical properties**.

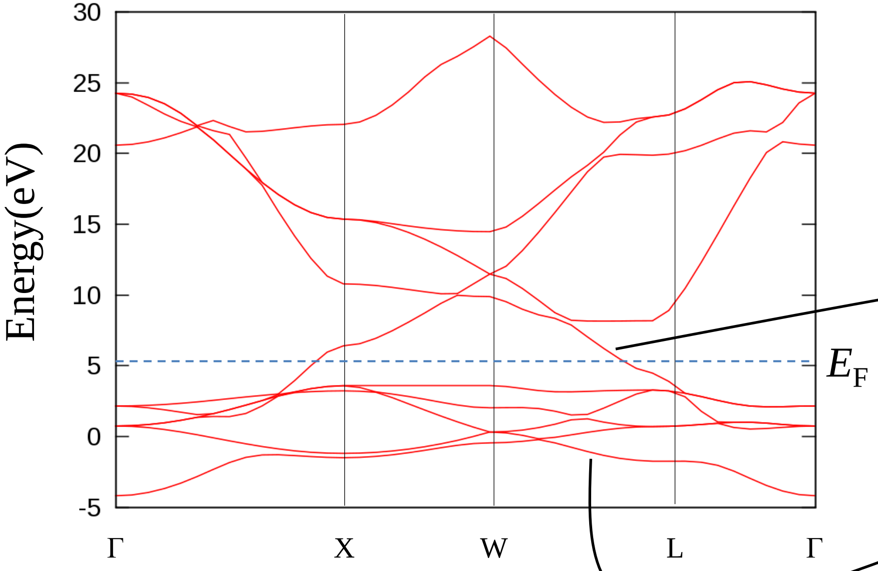
Band structure and DOS of Li ($1s^2 2s^1$)

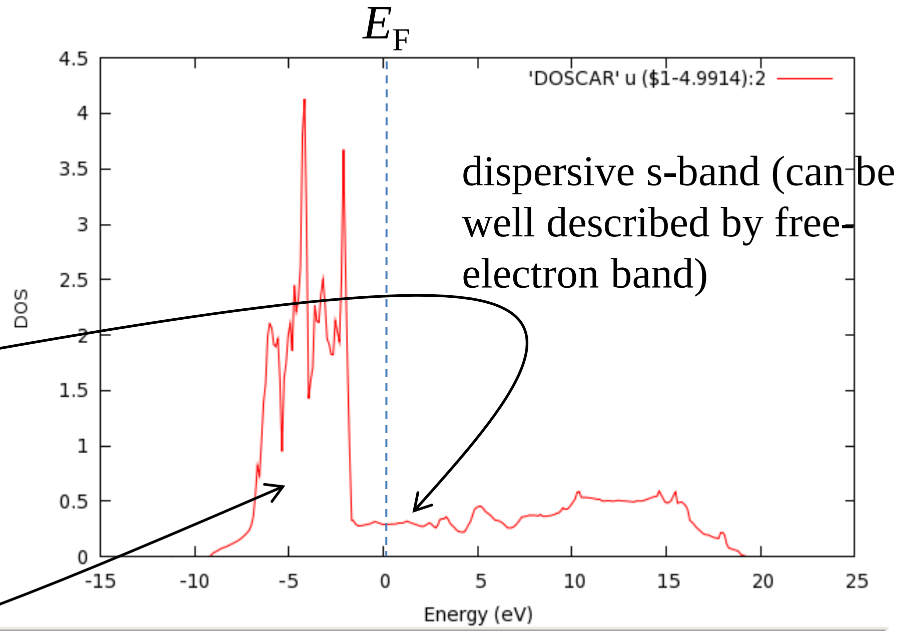


Band structure and DOS for Au ([Xe]$4f^{14}5d^{10}6s^{1}$)



Density of states





dispersive s-band (can be well described by free-electron band)

flat *d*-band (can be well described by tight-binding approach)