Fundamentals of Solid State Physics

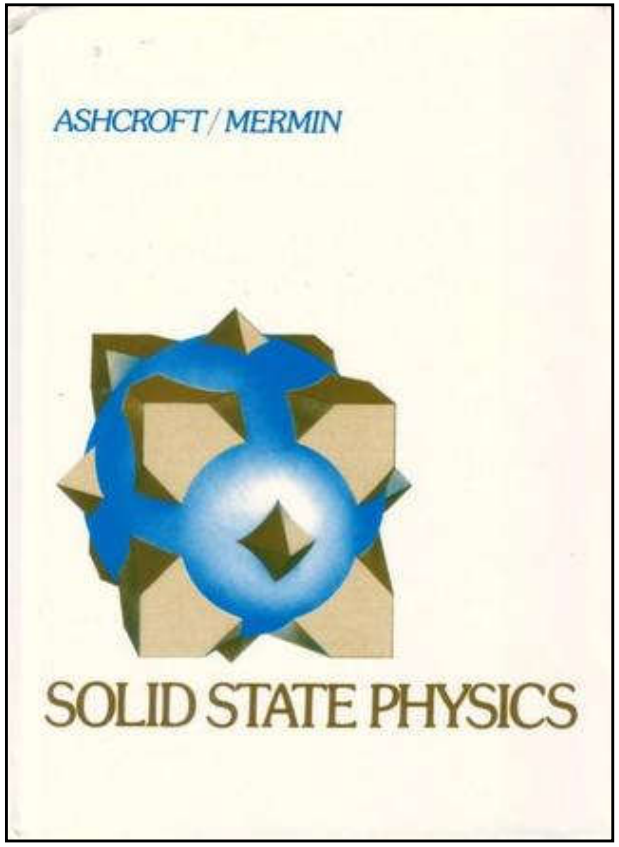
Electrons in a Periodic Potential

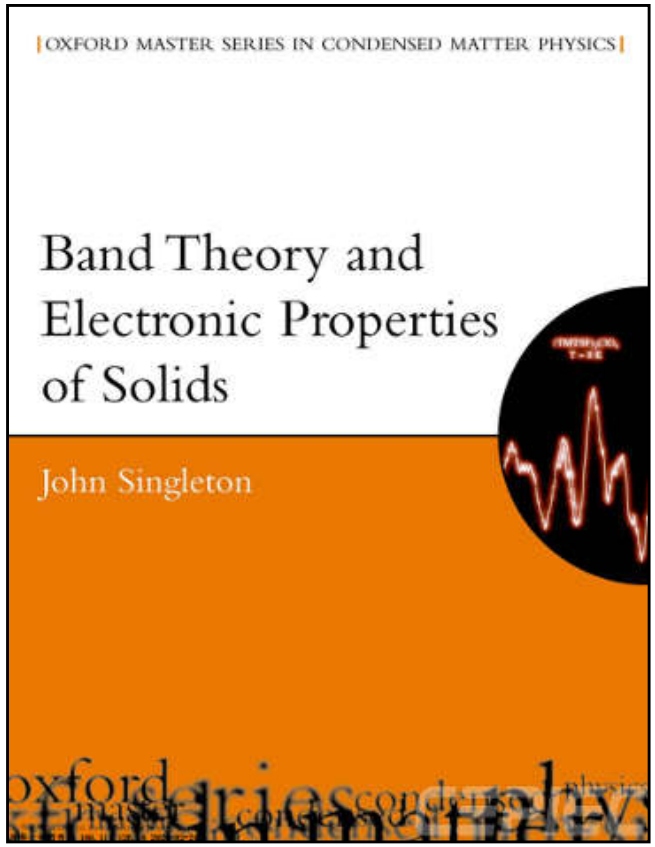
Xing Sheng 盛 兴

Department of Electronic Engineering
Tsinghua University
xingsheng@tsinghua.edu.cn

Further Reading

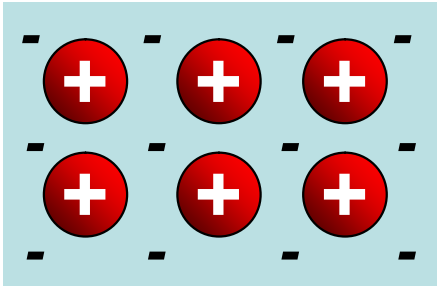
- **Ashcroft & Mermin, Chapter 8**
- **Singleton, Chapter 2**





The Drude Model 德魯德模型

Free electron 'gas'



positive ions
+
electron cloud

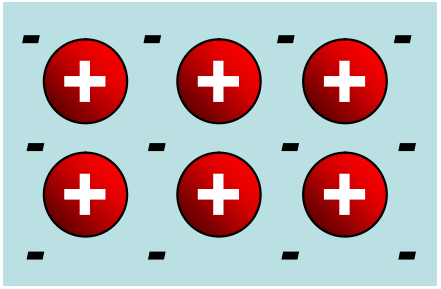
- Independent
  - electrons do not interact with each other
- Free
  - electrons do not interact with ions, except collision
- Collision (Origin of the resistance)
  - electrons are scattered by the ions instantaneously
- Relaxation time τ
  - average time between two collisions
  - electron mean free path $l = v^*\tau$
- Maxwell–Boltzmann distribution
  - average kinetic energy

$$\frac{1}{2}mv^2 = \frac{3}{2}k_B T$$

P. Drude
1863–1906

The Sommerfeld Model 索末菲模型

Free electron 'Fermi gas'



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- Relaxation time τ
  - average time between two collisions
  - electron mean free path $l = v^*\tau$
- Fermi–Dirac distribution
  - quantum mechanics

A. Sommerfeld
1868–1951

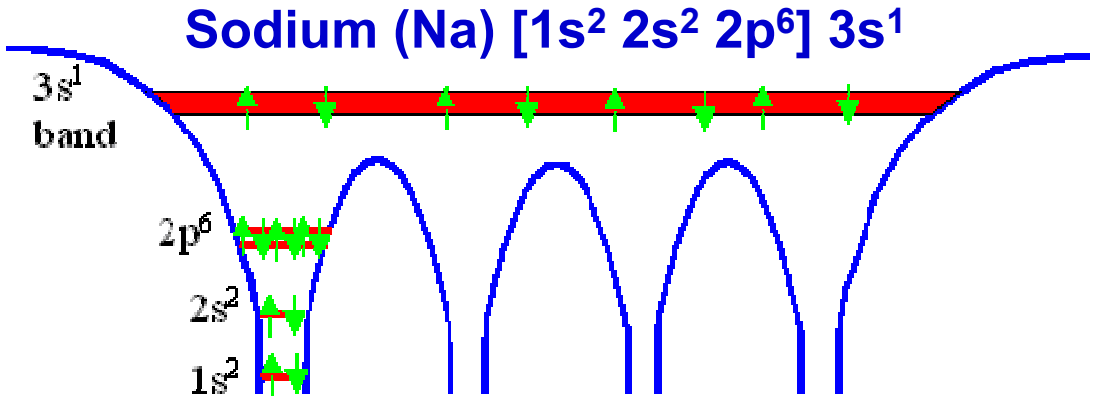
The Drude and Sommerfeld Models

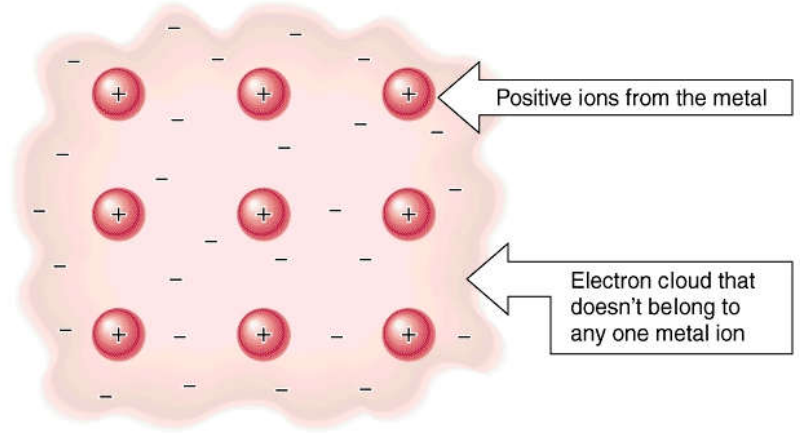
- Success for some metals
- Failure for semiconductors

- They omitted:
  - Material and atom structures
  - Potentials of positive ions
  - Localized eletrons
  - ...

P. Drude
1863–1906

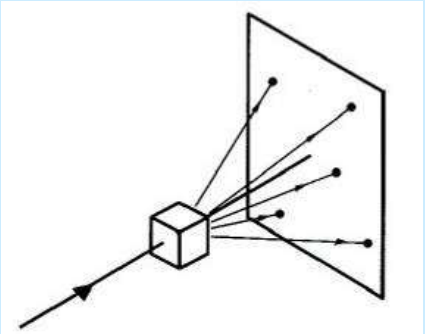
A. Sommerfeld
1868–1951

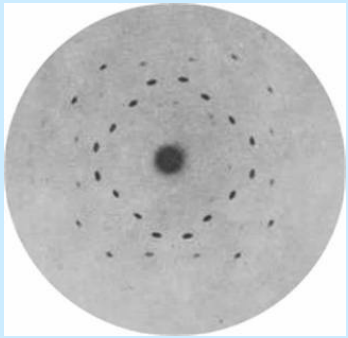




Crystal Structures

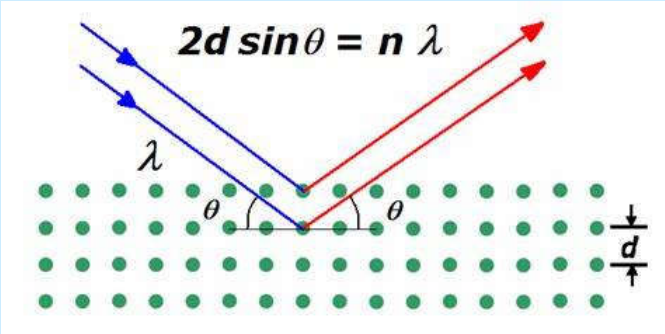
X-ray diffraction of crystals





M. von Laue (劳厄)
Nobel Prize in 1914

Bragg's law

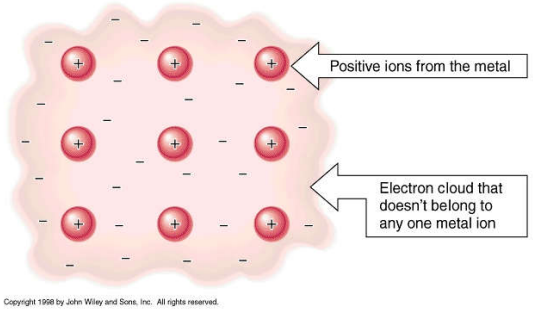


Bragg & Bragg
(布拉格父子)
Nobel Prize in 1915

Many solids have crystal structures:
***Periodic* atomic arrays -> *Periodic* potentials**

Bloch Electrons

- Electrons are *not free*, but *in a periodic potential* formed by the atomic lattice



- Born-Oppenheimer Approximation
  - The behaviors of electrons and nuclei can be calculated separately.

- Independent Electron Approximation
  - We still assume electrons are independent and do not interact with each other

Born-Oppenheimer Approximation

- **Adiabatic Approximation 绝热近似**
- **Static Approximation 定核近似**
  - **The behaviors of electrons and nuclei can be calculated separately.**

$$\Psi_{\text{total}} = \Psi_{\text{electron}} * \Psi_{\text{nuclear}}$$

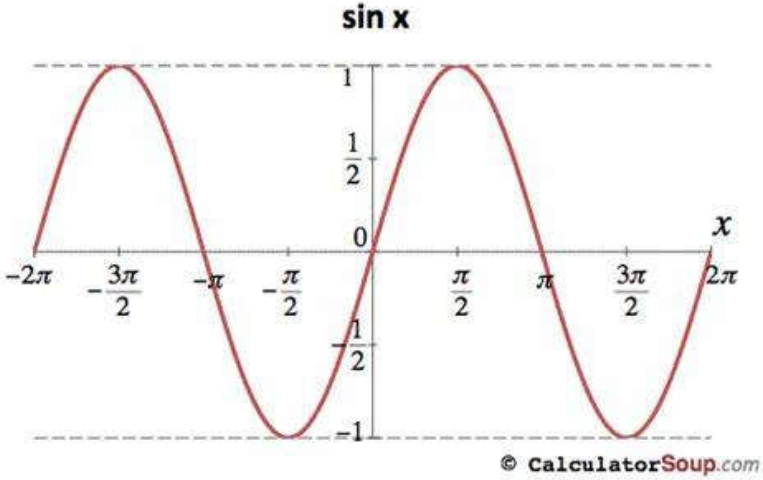
  - **Electrons move much faster than nuclei**
  - **When we consider the electronic behaviors, we assume the atomic lattice is static.**

Fourier Series

- **Periodic wave functions**

$$f(x+na)=f(x)$$

$$n=0,\pm1,\pm2,\ldots$$



- **We can have**

$$f(x)=\sum_n A_n \cos(nkx)$$

$$n=0,\pm1,\pm2,\ldots$$

- **or complex solutions**

$$f(x)=\sum_n A_n \exp(inkx)$$

$$k=\frac{2\pi}{a}$$

***A* - amplitude**

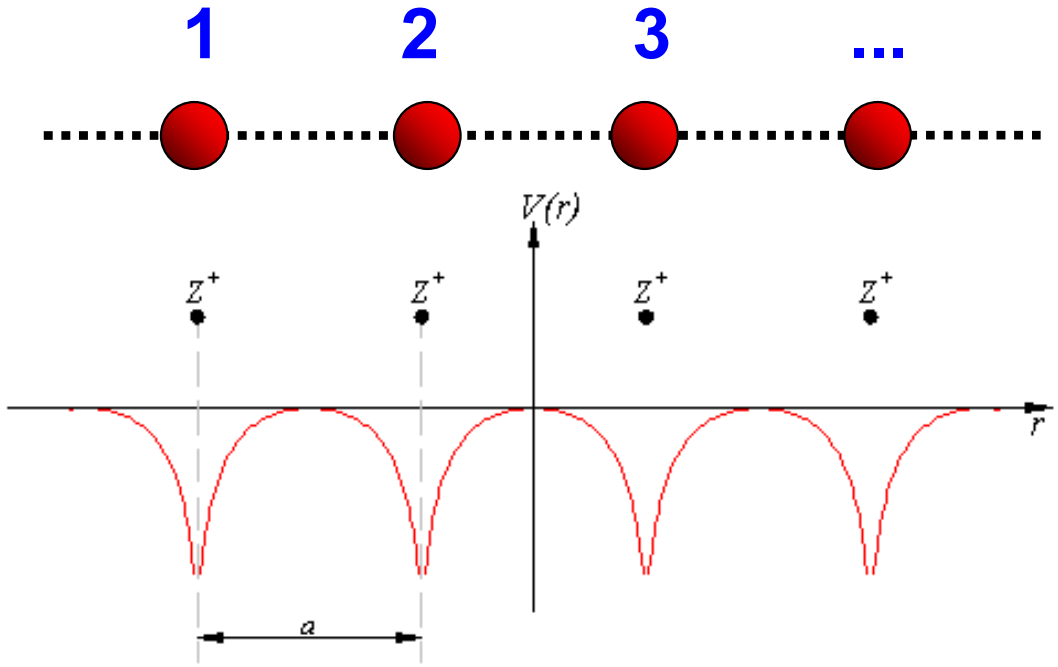
***k* - wavenumber**

Periodic Potentials

For a Bravais lattice

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

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



$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r})$$

a Fourier series

$$\exp(i\mathbf{G}\cdot\mathbf{R}) = 1$$

Reciprocal Lattice 倒易点阵

$$\exp(i\mathbf{G}\cdot\mathbf{R}) = 1$$

- For a Bravais lattice

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

n_1, n_2, n_3 are integers

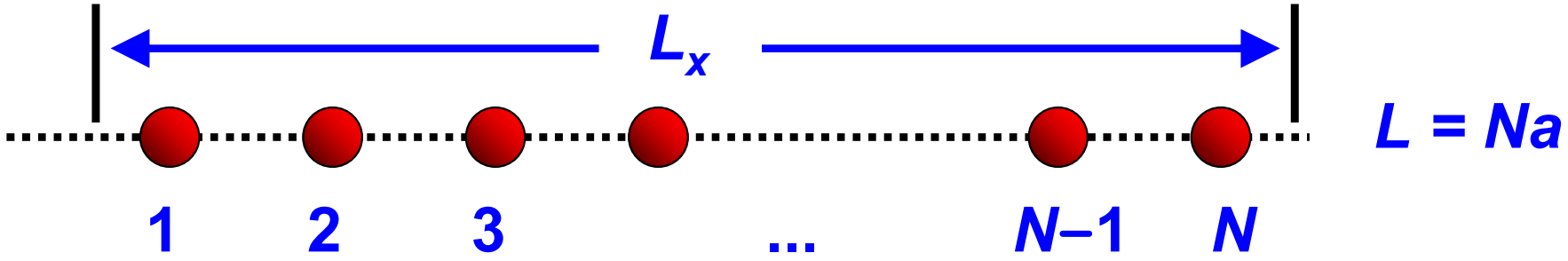
- We define vector G as

$$\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$$

m_1, m_2, m_3 are integers

(b_1, b_2, b_3) forms reciprocal lattice (倒易点阵 / 倒格子)
G is in the reciprocal space (倒易空间 / 倒空间)

Electrons in a Periodic Potential

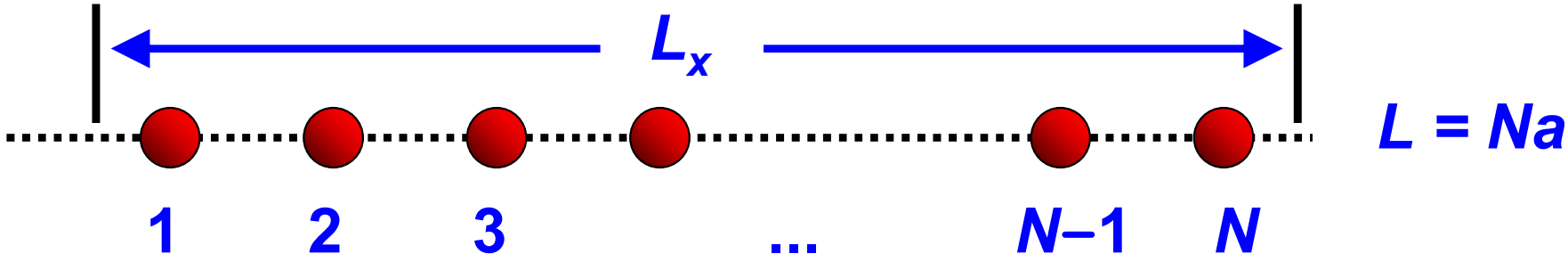


atom 1 = atom N, when N is large ~ 10^{23}

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r})+V(\mathbf{r})\cdot\psi(\mathbf{r})=E\psi(\mathbf{r})$$

→ $\psi(\mathbf{r}) = ???$

Born-von Karman *periodic* boundary condition



atom 1 = atom *N*, when *N* is large ~ 10^{23}

$$\psi(x) = \psi(x + L_x) \rightarrow \psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r}) \qquad \exp(ik_x L_x) = 1$$

$$\rightarrow \quad k_x = \frac{2\pi n_x}{L_x}, k_y = \frac{2\pi n_y}{L_y}, k_z = \frac{2\pi n_z}{L_z}$$

quasi-continuous

$$\rightarrow \quad \mathbf{k} = \frac{n_1}{N_1}\mathbf{b}_1 + \frac{n_2}{N_2}\mathbf{b}_2 + \frac{n_3}{N_3}\mathbf{b}_3$$

$$n = 0, \pm 1, \pm 2, \ldots$$

r, R, k, G

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r})$$

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r})$$

- R: position of lattice point in real space
- r: vector in real space

3D $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ 1D $R = 0, \pm a, \pm 2a, \ldots$

- G: position of lattice point in reciprocal space
- k: wave vector in reciprocal space

3D $\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$ 1D $G = 0, \pm\frac{2\pi}{a}, \pm\frac{4\pi}{a}, \ldots$

Electrons in a Periodic Potential

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r})+V(\mathbf{r})\cdot\psi(\mathbf{r})=E\psi(\mathbf{r})$$

$$\psi(\mathbf{r})=\sum_{\mathbf{k}}C_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r})$$

$$V(\mathbf{r})=\sum_{\mathbf{G}}V_{\mathbf{G}}\exp(i\mathbf{G}\cdot\mathbf{r})$$

→

$$\left(\frac{\hbar^2k^2}{2m}-E\right)C_{\mathbf{k}}+\sum_{\mathbf{G}}V_{\mathbf{G}}C_{\mathbf{k}-\mathbf{G}}=0$$

The Central Equation

If we know *V(r)* → $C_{\mathbf{k}}, C_{\mathbf{k}\pm\mathbf{G}}, C_{\mathbf{k}\pm2\mathbf{G}}\cdots$ $E_1, E_2, E_3\cdots$

The Central Equation

We only need to solve it in the first Brillouin zone

$$\begin{pmatrix} \ddots & \cdots & \cdots & \cdots & \ddots \\ \cdots & \frac{\hbar^2}{2m}(k-g)^2 - E + V_0 & V_{-g} & V_{-2g} & \cdots \\ \cdots & V_g & \frac{\hbar^2}{2m}k^2 - E + V_0 & V_{-g} & \cdots \\ \cdots & V_{2g} & V_g & \frac{\hbar^2}{2m}(k+g)^2 - E + V_0 & \cdots \\ \ddots & \cdots & \cdots & \cdots & \ddots \end{pmatrix} \begin{pmatrix} \vdots \\ C_{k-g} \\ C_k \\ C_{k-g} \\ \vdots \end{pmatrix} = 0$$

$$g = \frac{2\pi}{a}$$

The Central Equation

We only need to solve it in the first Brillouin zone

$$\begin{pmatrix} \ddots & \cdots & \cdots & \cdots & \ddots \\ \cdots & \frac{\hbar^2}{2m}(k-g)^2 - E & V_{-g} & V_{-2g} & \cdots \\ \cdots & V_g & \frac{\hbar^2}{2m}k^2 - E & V_{-g} & \cdots \\ \cdots & V_{2g} & V_g & \frac{\hbar^2}{2m}(k+g)^2 - E & \cdots \\ \ddots & \cdots & \cdots & \cdots & \ddots \end{pmatrix} \begin{pmatrix} \vdots \\ C_{k-g} \\ C_k \\ C_{k-g} \\ \vdots \end{pmatrix} = 0$$

$V_{G=0}$ is a constant (the ground level energy)
here we set $V_{G=0} = 0$

$$g = \frac{2\pi}{a}$$

The Central Equation

We only need to solve it in the first Brillouin zone

$$\det\begin{pmatrix} \ddots & \cdots & \cdots & \cdots & \ddots \\ \cdots & \frac{\hbar^2}{2m}(k-g)^2 - E & V_{-g} & V_{-2g} & \cdots \\ \cdots & V_g & \frac{\hbar^2}{2m}k^2 - E & V_{-g} & \cdots \\ \cdots & V_{2g} & V_g & \frac{\hbar^2}{2m}(k+g)^2 - E & \cdots \\ \ddots & \cdots & \cdots & \cdots & \ddots \end{pmatrix} = 0$$

$$g = \frac{2\pi}{a}$$

If we know *V(r)* → $E_1(k), E_2(k), E_3(k), \ldots$

Free Electron, $V = 0$

$$\det\begin{pmatrix} \ddots & \cdots & \cdots & \cdots & \ddots \\ \cdots & \frac{\hbar^2}{2m}(k-g)^2 - E & 0 & 0 & \cdots \\ \cdots & 0 & \frac{\hbar^2}{2m}k^2 - E & 0 & \cdots \\ \cdots & 0 & 0 & \frac{\hbar^2}{2m}(k+g)^2 - E & \cdots \\ \ddots & \cdots & \cdots & \cdots & \ddots \end{pmatrix} = 0$$

$$g = \frac{2\pi}{a}$$

$$E = \frac{\hbar^2}{2m}k^2 \quad E = \frac{\hbar^2}{2m}(k-g)^2 \quad E = \frac{\hbar^2}{2m}(k+g)^2 \quad \cdots$$

$$\psi \sim \exp[ikx] \quad \psi \sim \exp[i(k-g)x] \quad \psi \sim \exp[i(k+g)x] \quad \cdots$$

Free Electron, $V = 0$

$$\det\begin{pmatrix} \ddots & \cdots & \cdots & \cdots & \ddots \\ \cdots & \frac{\hbar^2}{2m}(k-g)^2 - E & 0 & 0 & \cdots \\ \cdots & 0 & \frac{\hbar^2}{2m}k^2 - E & 0 & \cdots \\ \cdots & 0 & 0 & \frac{\hbar^2}{2m}(k+g)^2 - E & \cdots \\ \ddots & \cdots & \cdots & \cdots & \ddots \end{pmatrix} = 0$$

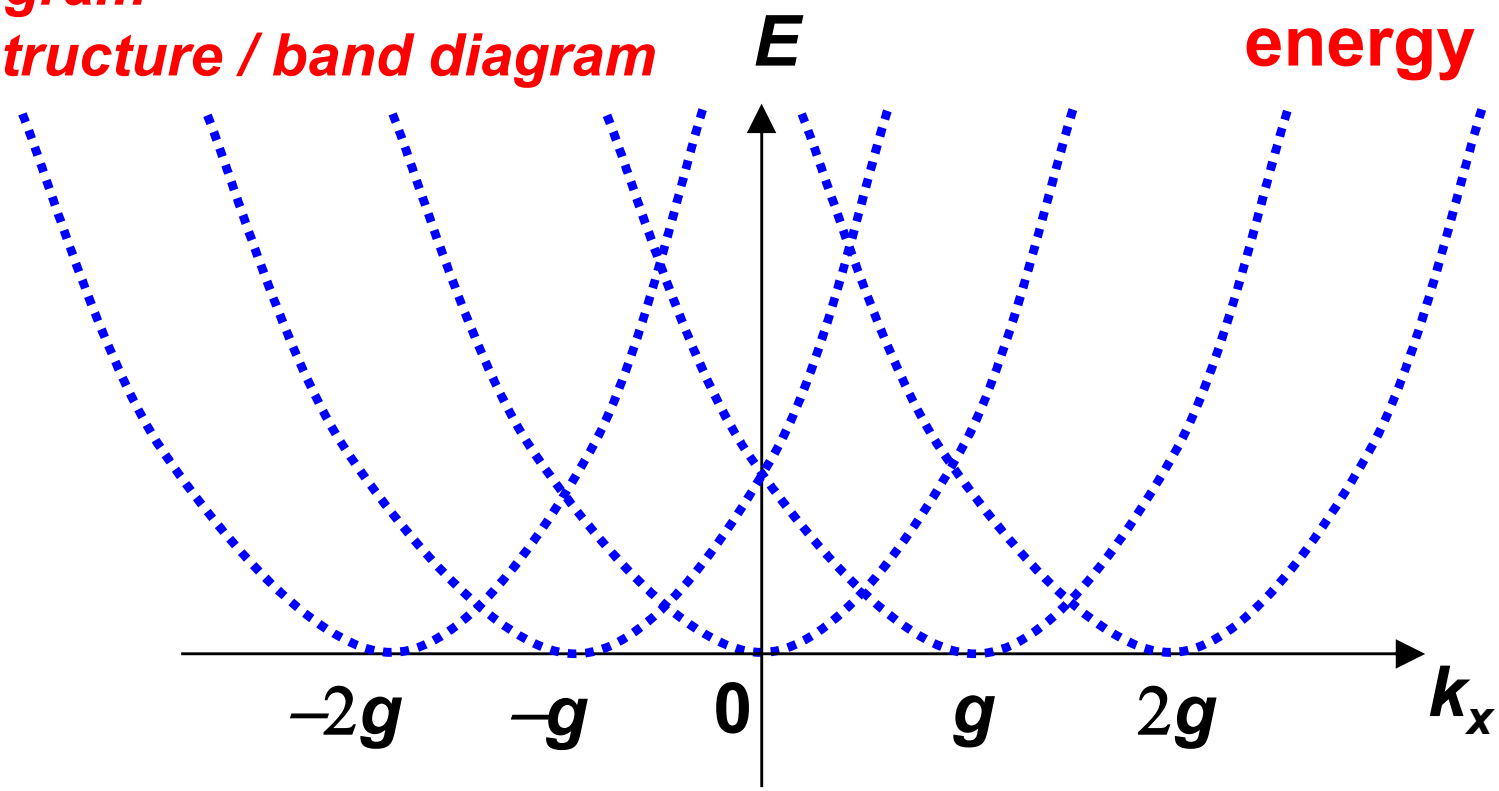
$$g = \frac{2\pi}{a}$$

plane wave for free electrons

$$\psi \sim \exp[ikx] \qquad \psi \sim \exp[i(k-g)x] \qquad \psi \sim \exp[i(k+g)x] \qquad \cdots$$

Free Electron

E-k diagram
band structure / band diagram
能带图



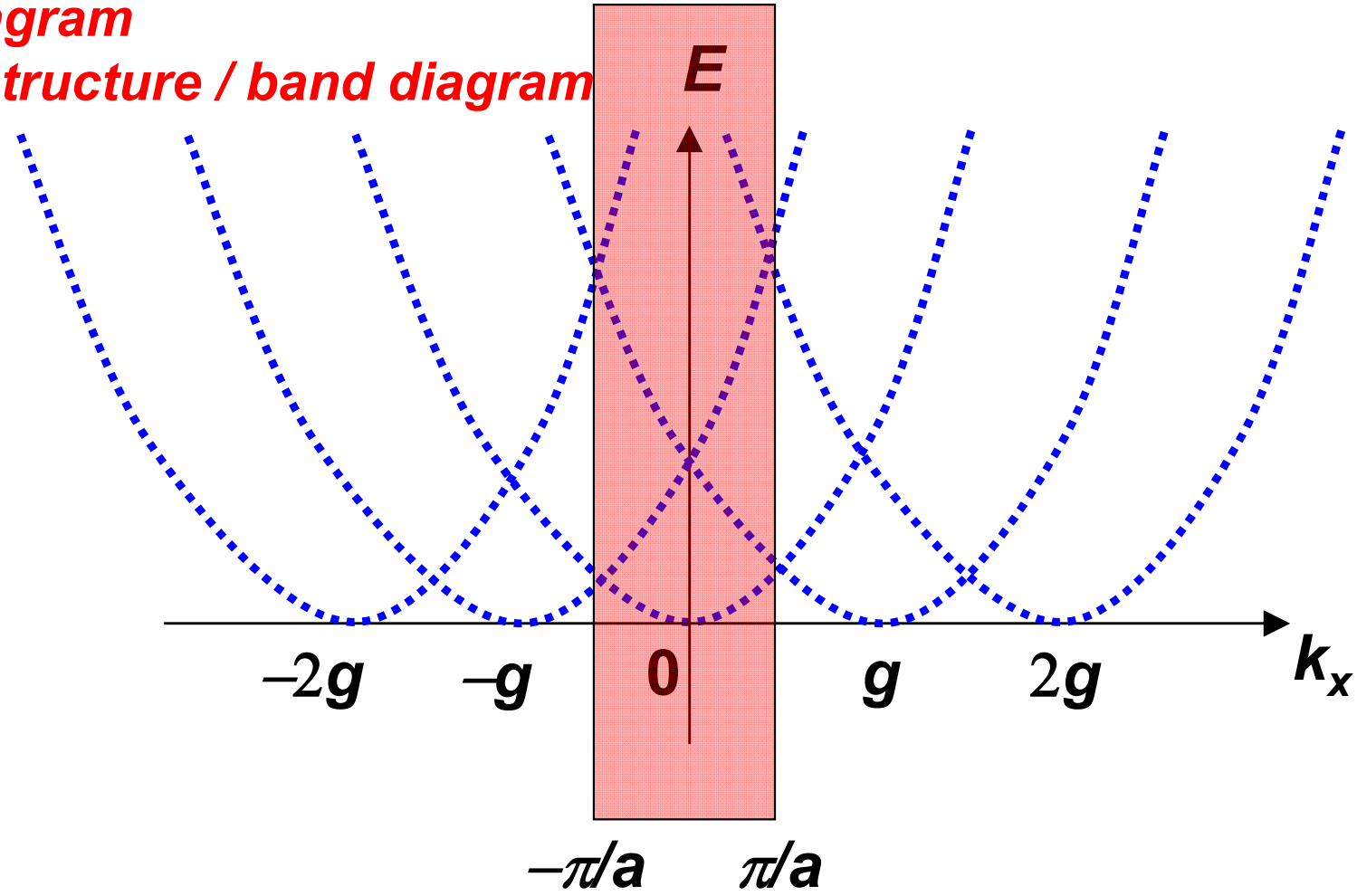
$$g = \frac{2\pi}{a}$$

$$E = \frac{\hbar^2}{2m}k^2 \qquad E = \frac{\hbar^2}{2m}(k-g)^2 \qquad E = \frac{\hbar^2}{2m}(k+g)^2 \qquad \cdots$$

$$k = 2\pi n / L$$ **quasi-continuous**

Free Electron

E-k diagram
band structure / band diagram
能带图

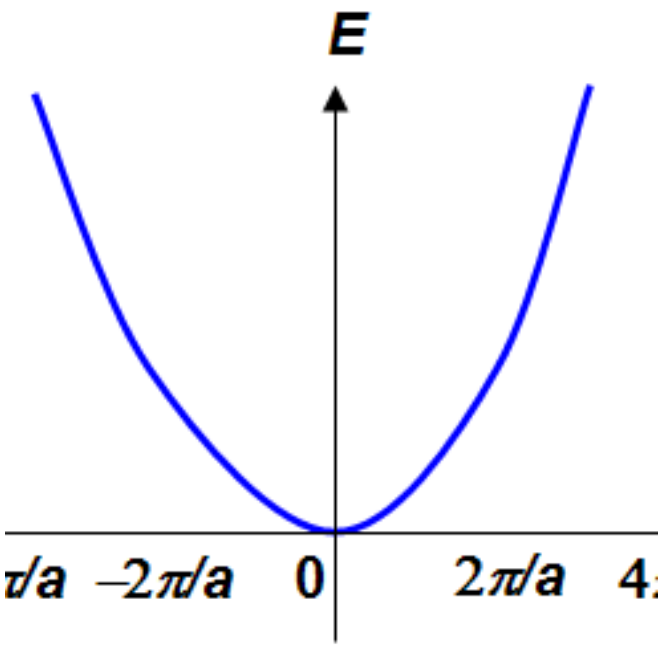


$$g = \frac{2\pi}{a}$$

The first Brillouin zone contains all the useful information

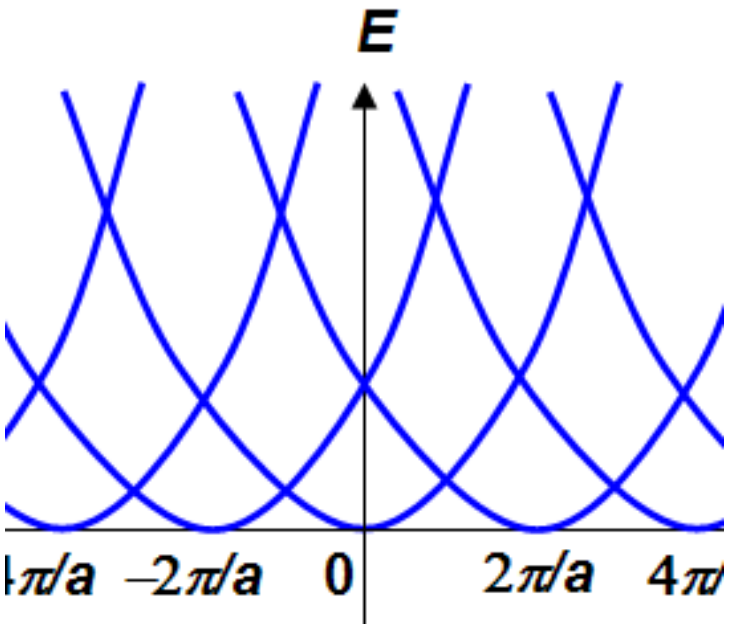
Band Structure / Diagram

Sommerfeld Model

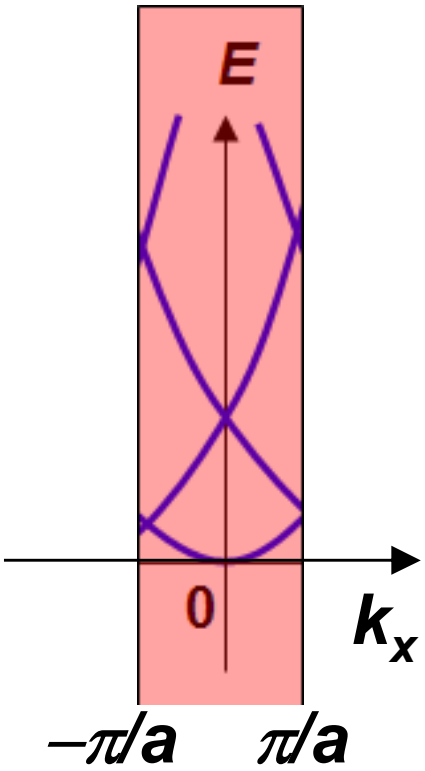


extended zone / band structure
扩展布里渊区

+ Periodic Potentials



repeated zone / band structure
周期性布里渊区



reduced zone / band structure
简约布里渊区

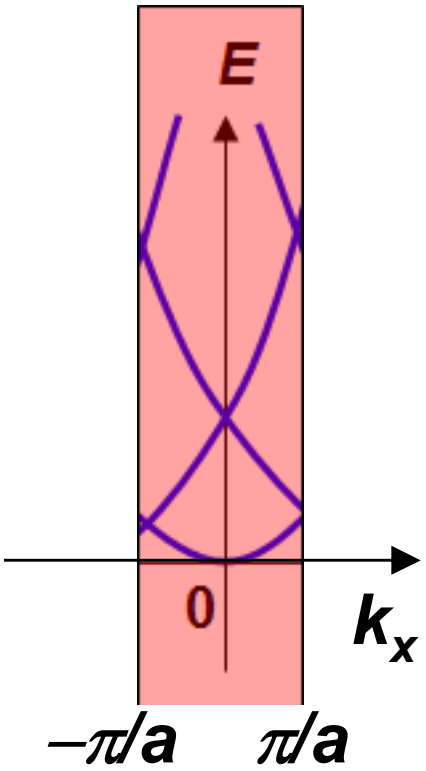
Brillouin Zones 布里渊区

- The *First Brillouin Zone (FBZ)*
  - the Wigner-Seitz cell of the reciprocal lattice
  - the volume of FBZ is a primitive cell

$$V_{\mathrm{G}} = \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)$$

- Values of *k*

$$\mathbf{k} = \frac{n_1}{N_1}\mathbf{b}_1 + \frac{n_2}{N_2}\mathbf{b}_2 + \frac{n_3}{N_3}\mathbf{b}_3$$



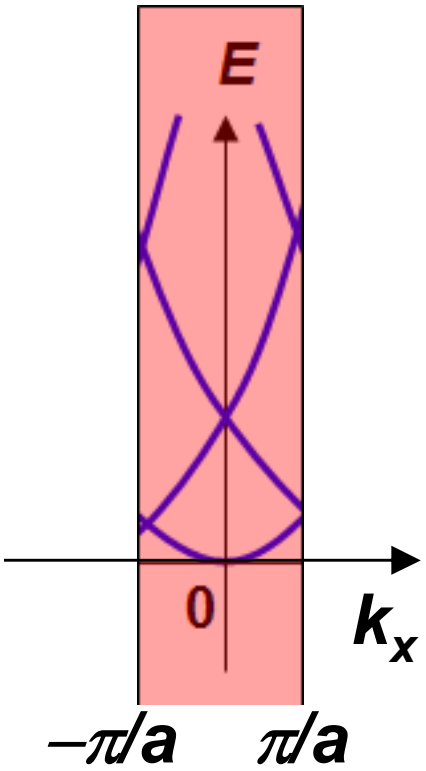
Brillouin Zones 布里渊区

- The *First Brillouin Zone (FBZ)*
  - the Wigner-Seitz cell of the reciprocal lattice
  - the volume of FBZ is a primitive cell

$$V_{\mathrm{G}} = \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)$$

- The volume of a *k*-state

$$V_{\mathrm{k}} = \frac{\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)}{N_1 N_2 N_3} = \frac{1}{N} V_{\mathrm{G}}$$



The first Brillouin zone has N k-states, thus contains all the useful information
(*N* - number of primitive unit cells)

Electrons in a Periodic Potential

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r})+V(\mathbf{r})\cdot\psi(\mathbf{r})=E\psi(\mathbf{r})$$

$$\psi(\mathbf{r})=\sum_{\mathbf{k}}C_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r})$$

$$V(\mathbf{r})=\sum_{\mathbf{G}}V_{\mathbf{G}}\exp(i\mathbf{G}\cdot\mathbf{r})$$

→

$$\left(\frac{\hbar^2k^2}{2m}-E\right)C_{\mathbf{k}}+\sum_{\mathbf{G}}V_{\mathbf{G}}C_{\mathbf{k}-\mathbf{G}}=0$$

The Central Equation

If we know *V(r)* → $C_{\mathbf{k}}, C_{\mathbf{k}\pm\mathbf{G}}, C_{\mathbf{k}\pm2\mathbf{G}}\cdots$ $E_1, E_2, E_3\cdots$

Bloch's Theorem

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r})$$

Ashcroft & Mermin
p.137-p.139

$$\psi(\mathbf{r}+\mathbf{R}) = \exp(i\mathbf{k}\cdot\mathbf{R})\cdot\psi(\mathbf{r}) \quad \Longleftrightarrow \quad \psi(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})\cdot u_{\mathbf{k}}(\mathbf{r})$$

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

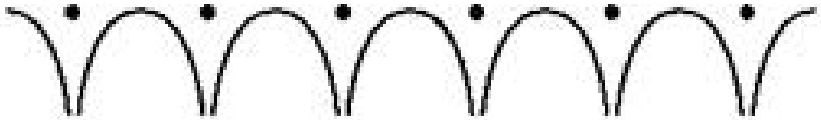
$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}+\mathbf{R})$$

The wave function can be expressed as *a plane wave* times *a periodic function*

$\exp(i\mathbf{k}\cdot\mathbf{r})$ $u_{\mathbf{k}}(\mathbf{r})$

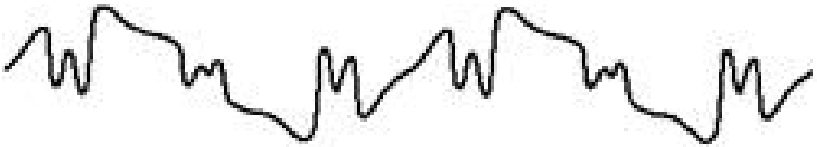
Bloch Wave

$V(\mathbf{r})$



potential

$\psi(\mathbf{r})$

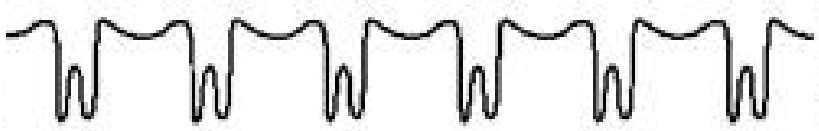


wave function

$$\psi(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})\cdot u_{\mathbf{k}}(\mathbf{r})$$

Bloch wave

plane wave (free electron)



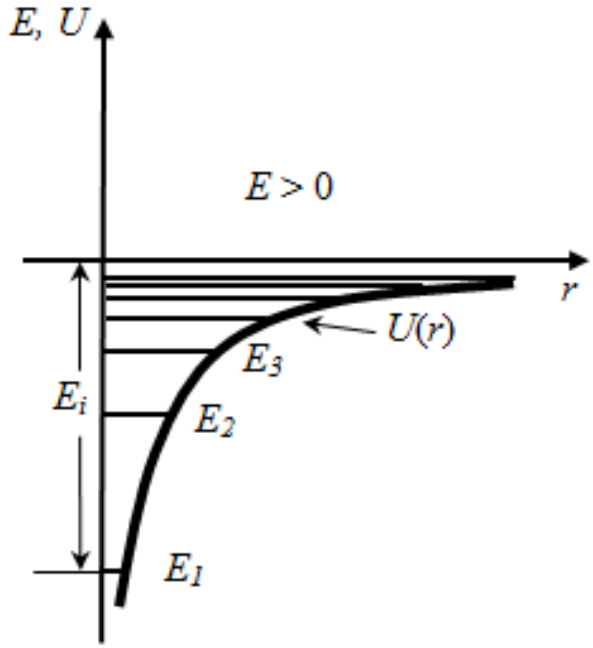
periodic function

https://thiscondensedlife.wordpress.com/tag/education/

Ideal Electrons

$$V(\mathbf{r}) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{\mathbf{r}}$$

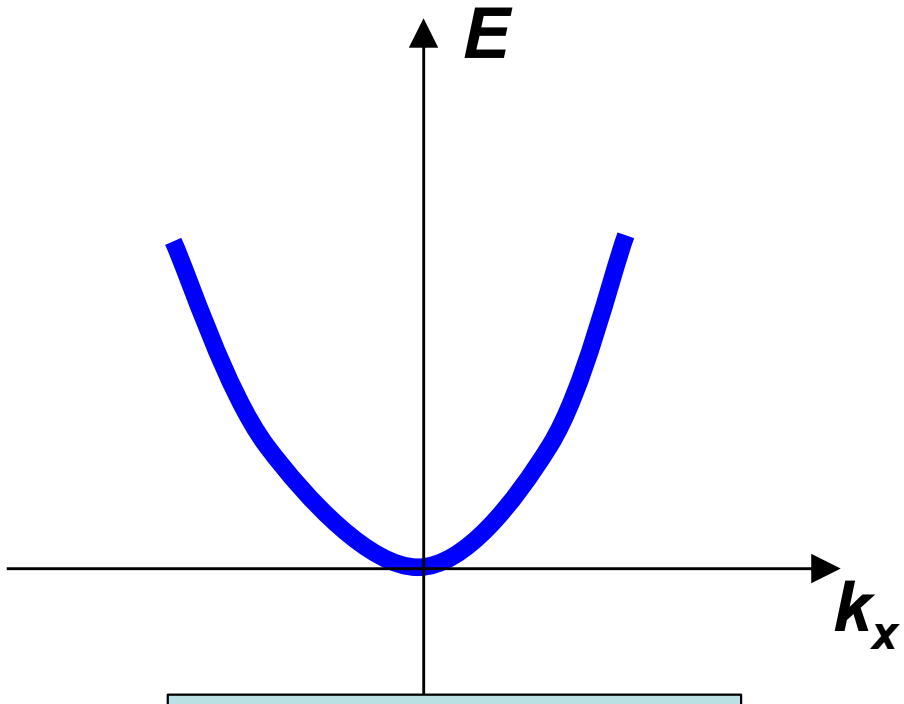
hydrogen atom



$$\psi(r,\theta,\varphi) = R_{nl}(r)\cdot Y_{lm}(\theta,\varphi)$$

purely localized

$$V(\mathbf{r}) = 0$$



$$\psi(\mathbf{r}) \sim \exp(i\mathbf{k}\cdot\mathbf{r})$$

purely delocalized 'free'

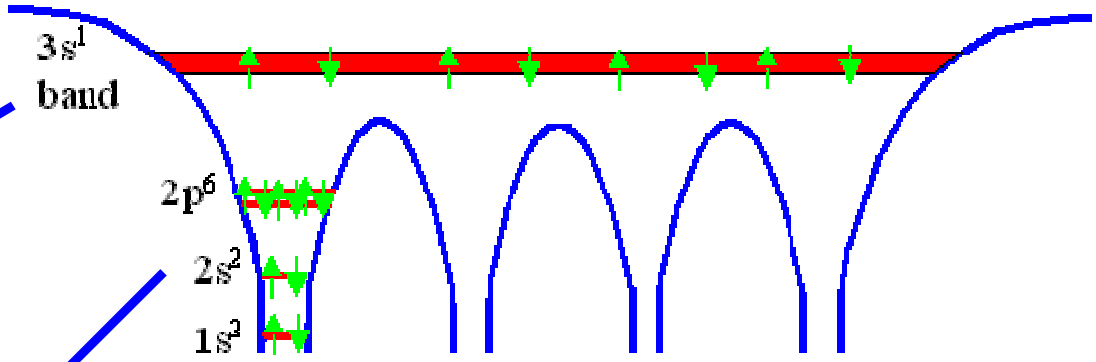
Real Electrons in Solids

Electrons are in *periodic* potentials

→ **Bloch Wave**

$$\psi(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})\cdot u_{\mathbf{k}}(\mathbf{r})$$

Nearly Free Electron Model
"近自由"近似



Sodium (Na) [$1s^2$ $2s^2$ $2p^6$] $3s^1$

Tight Binding Model
"紧束缚"近似

Thank you for your attention