Chapter 7 Energy Bands

7.1 Basic Assumption of Energy Band Theory

7.2 Bloch Theorem and Bloch Wave

7.3 Nearly Free Electron Approximation

7.4 Tight-binding Approximation & Wannier Function

Energy band theory, also called single electron theory

Main theoretical framework for studying the electronic structure/motion in solids.

Progress in Solids State Theory

Computational Techniques Improves rapidly

Energy Band Calculation becomes a hot research field in modern solid state/condensed matter physics

“Approximation theory” for many-electron system

7.1 Basic Assumptions of Energy Band Theory

In a solid (with volume $V = L^3$) there exists N positively charged ion Ze, with NZ valence electrons. $\vec{r}_i$ and $\vec{R}_n$ are position vector. The *total Hamiltonian* can be written:

$$\hat{H} = -\sum_{i=1}^{NZ} \frac{\hbar^2}{2m}\nabla_i^2 + \frac{1}{2}\sum_{i,j}{}' \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

$$-\sum_{n=1}^{N} \frac{\hbar^2}{2M}\nabla_n^2 + \frac{1}{2}\sum_{n,m}{}' \frac{1}{4\pi\varepsilon_0}\frac{(Ze)^2}{|\vec{R}_n - \vec{R}_m|}$$

$$-\sum_{i=1}^{NZ}\sum_{n=1}^{N} \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{|\vec{r}_i - \vec{R}_n|}$$

The Theory of Everything!

7.1 Basic Assumptions of Energy Band Theory

$$= \hat{T}_e + V_{ee}\left(\vec{r}_i, \vec{r}_j\right) + \hat{T}_n + V_{nm}\left(\vec{R}_n, \vec{R}_m\right) + V_{en}\left(\vec{r}_i, \vec{R}_n\right)$$

1st, 2nd terms: kinetic & Culomb interaction of *NZ* electrons;

3rd & 4th terms: kinetic & Culomb interaction of *N* ions;

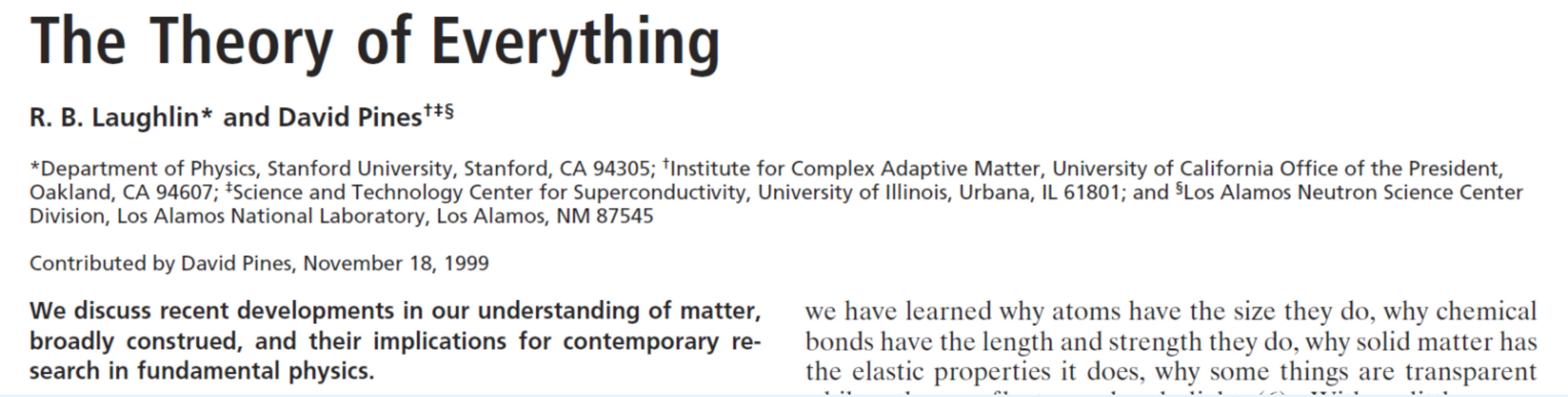
5th term: Culomb interactions between electrons and ions.

$\sum_{i,j}{}'$ **means partial summation** $i \neq j$

Schrödinger's equation:

$$\hat{H}\Psi\left(\vec{r}, \vec{R}\right) = \varepsilon\Psi\left(\vec{r}, \vec{R}\right)$$

7.1 Basic Assumptions of Energy Band Theory



The Theory of Everything

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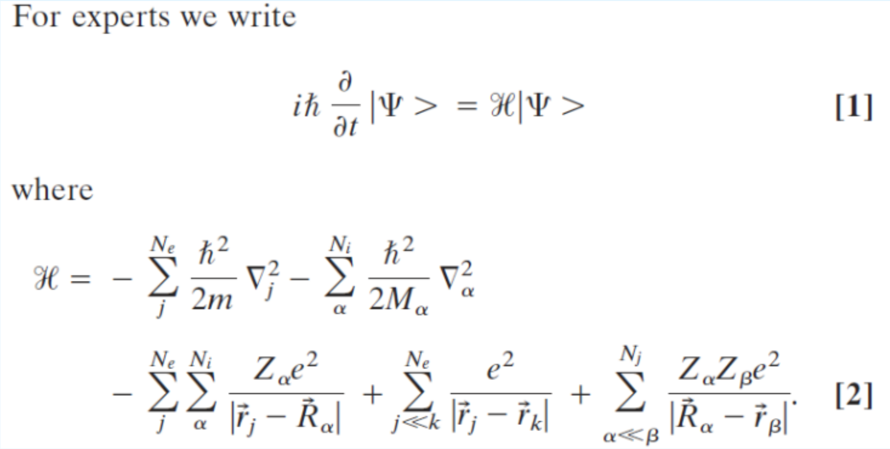
Contributed by David Pines, November 18, 1999

We discuss recent developments in our understanding of matter, broadly construed, and their implications for contemporary research in fundamental physics.

we have learned why atoms have the size they do, why chemical bonds have the length and strength they do, why solid matter has the elastic properties it does, why some things are transparent



For experts we write

$$i\hbar \frac{\partial}{\partial t}|\Psi > \; = \mathcal{H}|\Psi > \qquad [1]$$

where

$$\mathcal{H} = -\sum_{j}^{N_e} \frac{\hbar^2}{2m}\nabla_j^2 - \sum_{\alpha}^{N_i} \frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 - \sum_{j}^{N_e}\sum_{\alpha}^{N_i} \frac{Z_\alpha e^2}{|\vec{r}_j - \vec{R}_\alpha|} + \sum_{j\ll k}^{N_e} \frac{e^2}{|\vec{r}_j - \vec{r}_k|} + \sum_{\alpha\ll\beta}^{N_j} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{r}_\beta|}. \qquad [2]$$

Except for light, which is easily included, and possibly gravity, these missing parts are irrelevant to people scale phenomena. **Eqs. 1 and 2 are, for all practical purposes, the *Theory of Everything* for our everyday world.**

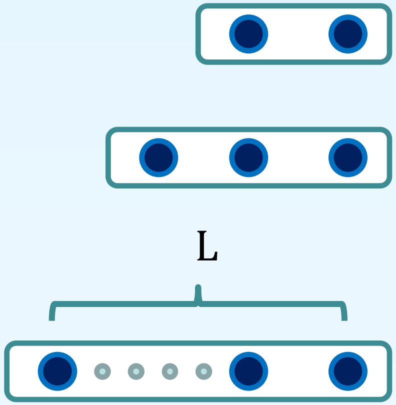
However, it cannot be solved accurately when the number of particles exceeds about 10. **No computer existing, or that will ever exist, can break this barrier** because it is a ***catastrophe of dimension***.

7.1 Basic Assumptions of Energy Band Theory

精确对角化的指数墙困难

Exponential Wall!
NP-hard

Site number ***Dimension of Hilbert Space***



$D = d^2$

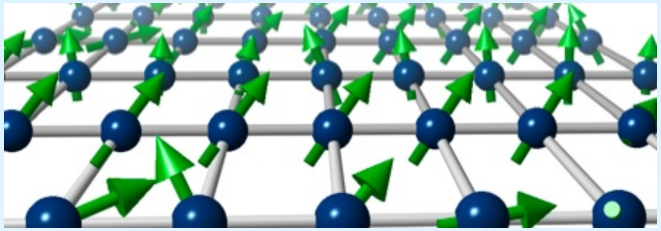
$D = d^3$

⋮

$D = d^L$

自旋 S=1/2 d=2

电子 d=4



Heisenberg Model

$$H = \sum_{\langle i,j \rangle} J\, \boldsymbol{S}_i \boldsymbol{S}_j$$

I. Adiabatic Approximation

Divide solids into electronic and ionic subsystems:

$$m \ll M$$

Born-Oppenheimer Approx.: assume that the motion of atomic nuclei and electrons in a molecule can be separated.

Consider only the motion of electrons, and ions fixed at its instantaneous position.

$$\hat{H} = \hat{T}_e + V_{ee}\left(\vec{r}_i, \vec{r}_j\right) + V_{en}\left(\vec{r}_i, \vec{R}_n\right)$$

At intermediate temperatures, ignore the effects of crystal vibration, take $\vec{R}_n$ as its equilibrium position.

II. Single Electron Approximation (self consistent field)

Utilize Hatree-Fock method to reduce a many-electron problem to a single electron problem.

Use mean field to replace V_{ee} , and assume every electron "feels" exactly the same potential.

$$\hat{H}_e = \sum_{i=1}^{N}\left[-\frac{\hbar^2}{2m}\nabla_i^2 + v_{eff}\left(\vec{r}_i\right) - \sum_{R_n}\frac{1}{4\pi\varepsilon_0}\frac{e^2}{\left|\vec{r}_i - \vec{R}_n\right|}\right]$$

7.1 Basic Assumptions of Energy Band Theory

$$\hat{H}_i = -\frac{\hbar^2}{2m}\nabla_i^2 + v_e(\vec{r}_i) - \sum_{R_n}\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{|\vec{r}_i - \vec{R}_n|}$$

total $\hat{H}_e$ is the sum of N single electron Hamiltonians.

$$\hat{H}_e = \sum_i \hat{H}_i$$

Schrödinger Equation:

$$\hat{H}_e \Psi(\vec{r}, \vec{R}) = \varepsilon \Psi(\vec{r}, \vec{R})$$

Hatree-Fock Equation

According to variational principle $\Psi(\vec{r}_1, \cdots, \vec{r}_i \cdots) = \prod_i \psi_i(\vec{r}_i)$

$$\varepsilon = \sum_i \varepsilon_i$$

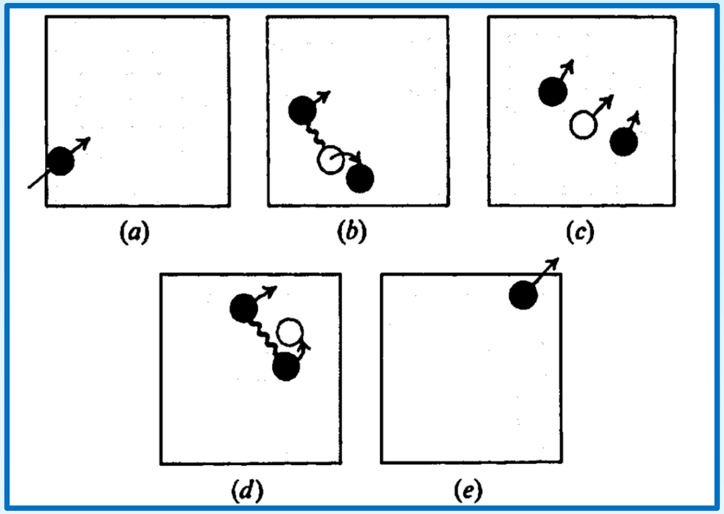
$$H_i \psi_i(\vec{r}_i) = \varepsilon_i \psi_i(\vec{r}_i)$$

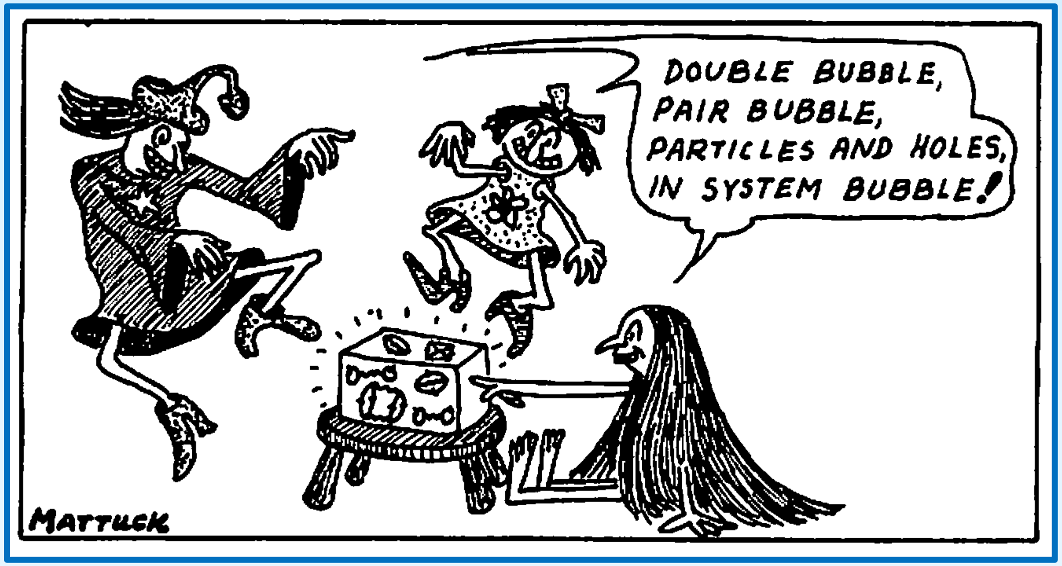
many electron ⇒ single electron problem

7.1 Basic Assumptions of Energy Band Theory

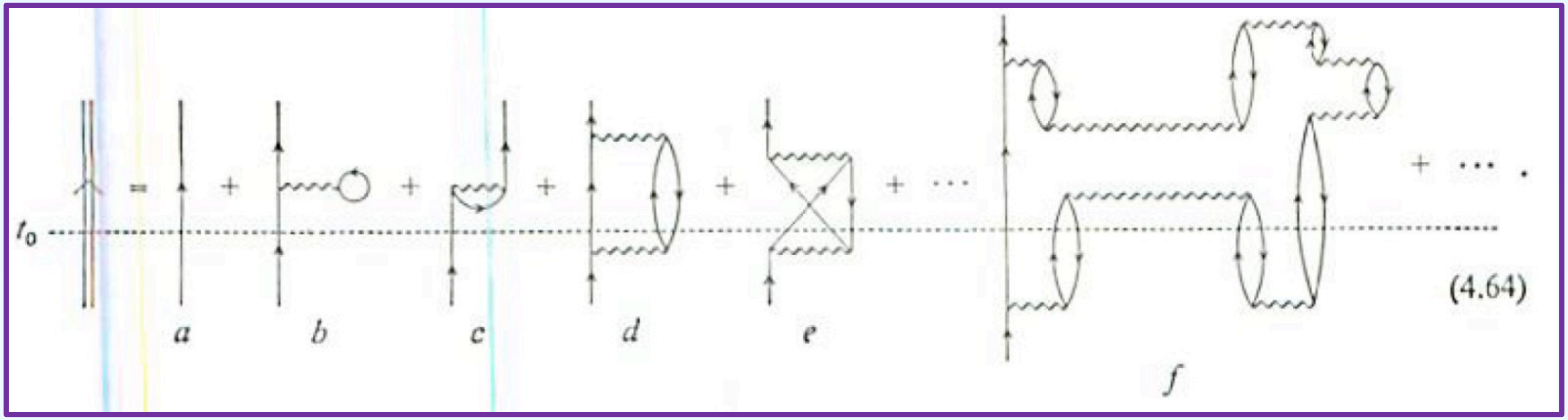
Feynman Diagrams

R.D. Mattuck, 1976

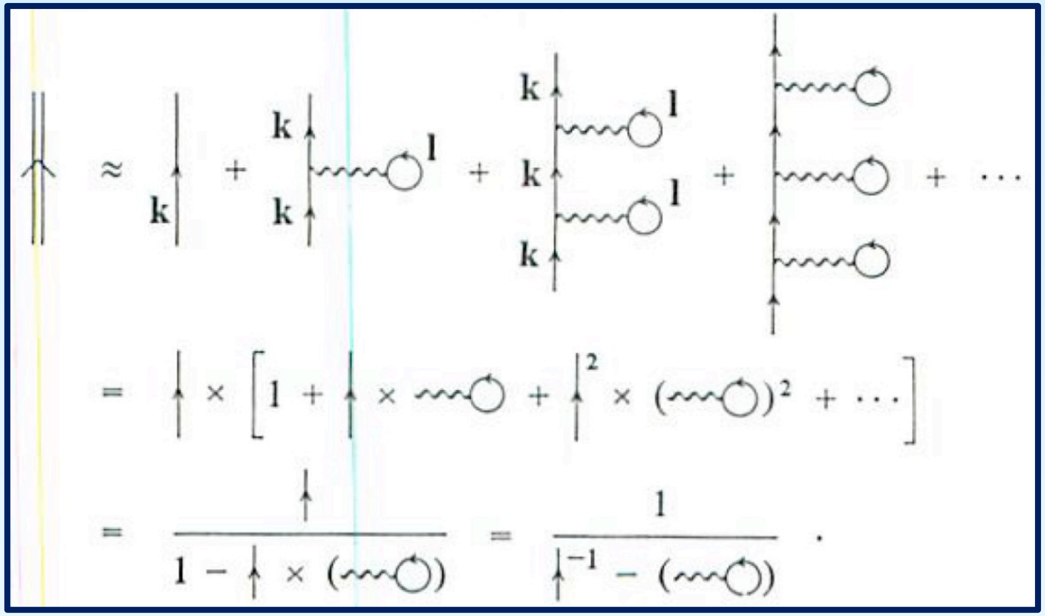




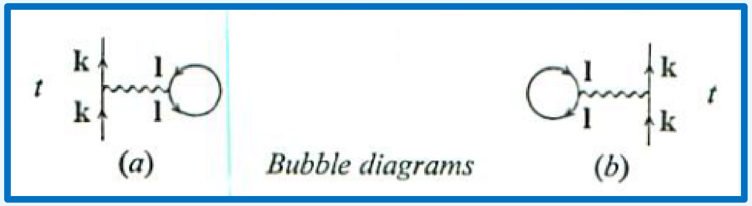
Single particle approximation: **Bare electron churns the Fermi sea.**



Hatree-Fock Approximation in Feynmann Diagrams



Feynman Diagrams in the Amazon Jungle



Bubble diagrams

“Forward Scattering”

The bubble processes can be physically interpreted as follows: a *particle* enters in **k**, knocks a particle out of state **l** ($|\mathbf{l}| < k_F$) at time *t*, then knocks the particle instantaneously back into **l** at time *t*, then continues freely in state **k**.

III. Periodic Potential Approximation

Suppose *total* single electron potential:

$$V(\vec{r}) = v_e(\vec{r}) - \sum_{R_n} \frac{1}{4\pi\varepsilon_0} \frac{e^2}{|\vec{r} - \vec{R}_n|}$$

has exactly the same periodicity as the lattice:

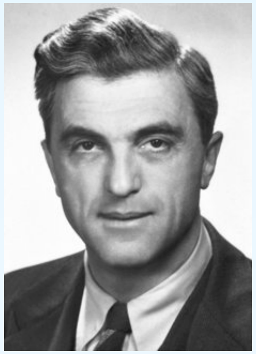
$$V(\vec{r} + \vec{R}_n) = V(\vec{r})$$

Many Electron Problem ⇒ Single Electron Problem in Periodic Potential $V(\vec{r})$

$$\boxed{\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = \varepsilon\psi(\vec{r})}$$

7.2 Bloch Wave

When I started to think about it, I felt that the main problem was to explain ***how the electrons could sneak by all the ions in a metal***. . . . By straight Fourier analysis I found to my delight that the ***wave differed from the plane wave of free electrons only by a periodic modulation***.



F. Bloch

7.2 Bloch Wave

Single-electron potential has a lattice translation symmetry, so the single-electron wave function has the form of Bloch wave.

I. Bloch theorem

In the single electron approximation, for periodic potential, i.e.,

$$V\left(\vec{r}+\vec{R}_n\right)=V\left(\vec{r}\right)$$

$V\left(\vec{r}\right)$ **includes all electron-electron and electron-ion interactions for a specific electron.**

7.2 Bloch Wave

Single electron Schrödinger equation:

$$H\psi(\vec{r})=\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\psi(\vec{r})=\varepsilon\psi(\vec{r})$$

Eigen function $\psi(\vec{r})$ modulated plane wave according to the Bravais lattice:

in which:

$$\boxed{\begin{gathered}\psi_{\vec{k}}(\vec{r})=e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r})\\ u_{\vec{k}}(\vec{r}+\vec{R}_n)=u_{\vec{k}}(\vec{r})\end{gathered}}$$

wavefunction in such form is called the Bloch wave.

7.2 Bloch Wave

Proof: suppose a translation operator $\hat{T}$

$$\hat{T}f(\vec{r})=f(\vec{r}+\vec{R}_n)$$

potential energy term has a periodicity:

$$\hat{T}V(\vec{r})=V(\vec{r}+\vec{R}_n)=V(\vec{r})$$

$\hat{H}$ is translational invariant:

$$\boxed{\hat{H}(\vec{r}+\vec{R}_n)=\hat{H}(\vec{r})}$$

apply $\hat{T}$ to $\hat{H}$

$$\hat{T}\hat{H}\psi(\vec{r})=\hat{H}(\vec{r}+\vec{R}_n)\psi(\vec{r}+\vec{R}_n)$$

$$=\hat{H}(\vec{r})\psi(\vec{r}+\vec{R}_n)=\hat{H}\hat{T}\psi(\vec{r})$$

$\hat{T}$ commutes with $\hat{H}$, thus share the same eigenfunctions

7.2 Bloch Wave

Suppose the eigen state and values are $\psi(\vec{r})$ and $\lambda(\vec{R}_n)$, respectively.

$$\hat{T}(\vec{R}_n)\psi(\vec{r}) = \lambda(\vec{R}_n)\psi(\vec{r})$$

$$\hat{T}\psi(\vec{r}) = \psi(\vec{r} + \vec{R}_n)$$

$$\psi(\vec{r} + \vec{R}_n) = \lambda(\vec{R}_n)\psi(\vec{r})$$

Normalize the wave function:

$$\int |\psi(\vec{r})|^2 \mathrm{d}\vec{r} = \int |\psi(\vec{r} + \vec{R}_n)|^2 \mathrm{d}\vec{r} = 1$$

$$\boxed{\therefore |\lambda(\vec{R}_n)|^2 = 1}$$

7.2 Bloch Wave

By applying two tanslation operators:

$$\hat{T}(\vec{R}_n)\hat{T}(\vec{R}_m)\psi(\vec{r}) = \hat{T}(\vec{R}_n)\lambda(\vec{R}_m)\psi(\vec{r})$$
$$= \lambda(\vec{R}_n)\lambda(\vec{R}_m)\psi(\vec{r})$$

Two successive translations is equal to one composition one $\vec{R}_n + \vec{R}_m$

$$\hat{T}(\vec{R}_n)\hat{T}(\vec{R}_m)\psi(\vec{r}) = \hat{T}(\vec{R}_n + \vec{R}_m)\psi(\vec{r})$$
$$= \lambda(\vec{R}_n + \vec{R}_m)\psi(\vec{r})$$

the eigenvalues satisfy:

$$\lambda(\vec{R}_n + \vec{R}_m) = \lambda(\vec{R}_n)\lambda(\vec{R}_m)$$

$$\Rightarrow \boxed{\lambda(\vec{R}_n) = e^{i\vec{k}\cdot\vec{R}_n}}$$

7.2 Bloch Wave

$$\psi\left(\vec{r}+\vec{R}_n\right)=\lambda\left(\vec{R}_n\right)\psi\left(\vec{r}\right)=e^{i\vec{k}\cdot\vec{R}_n}\psi\left(\vec{r}\right)$$

$\therefore$ **the wave function can be written as:**

$$\boxed{\begin{aligned}&\psi_{\vec{k}}\left(\vec{r}\right)=e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}\left(\vec{r}\right)\\&u_{\vec{k}}\left(\vec{r}+\vec{R}_n\right)=u_{\vec{k}}\left(\vec{r}\right)\end{aligned}}$$

which satisfies:

$$\hat{T}\psi\left(\vec{r}\right)=\psi\left(\vec{r}+\vec{R}_n\right)=e^{i\vec{k}\cdot\left(\vec{r}+\vec{R}_n\right)}u_{\vec{k}}\left(\vec{r}+\vec{R}_n\right)$$

$$=e^{i\vec{k}\cdot\vec{r}}e^{i\vec{k}\cdot\vec{R}_n}u_{\vec{k}}\left(\vec{r}\right)$$

$$=e^{i\vec{k}\cdot\vec{R}_n}\psi\left(\vec{r}\right)$$

II. General Properties of the Bloch wave

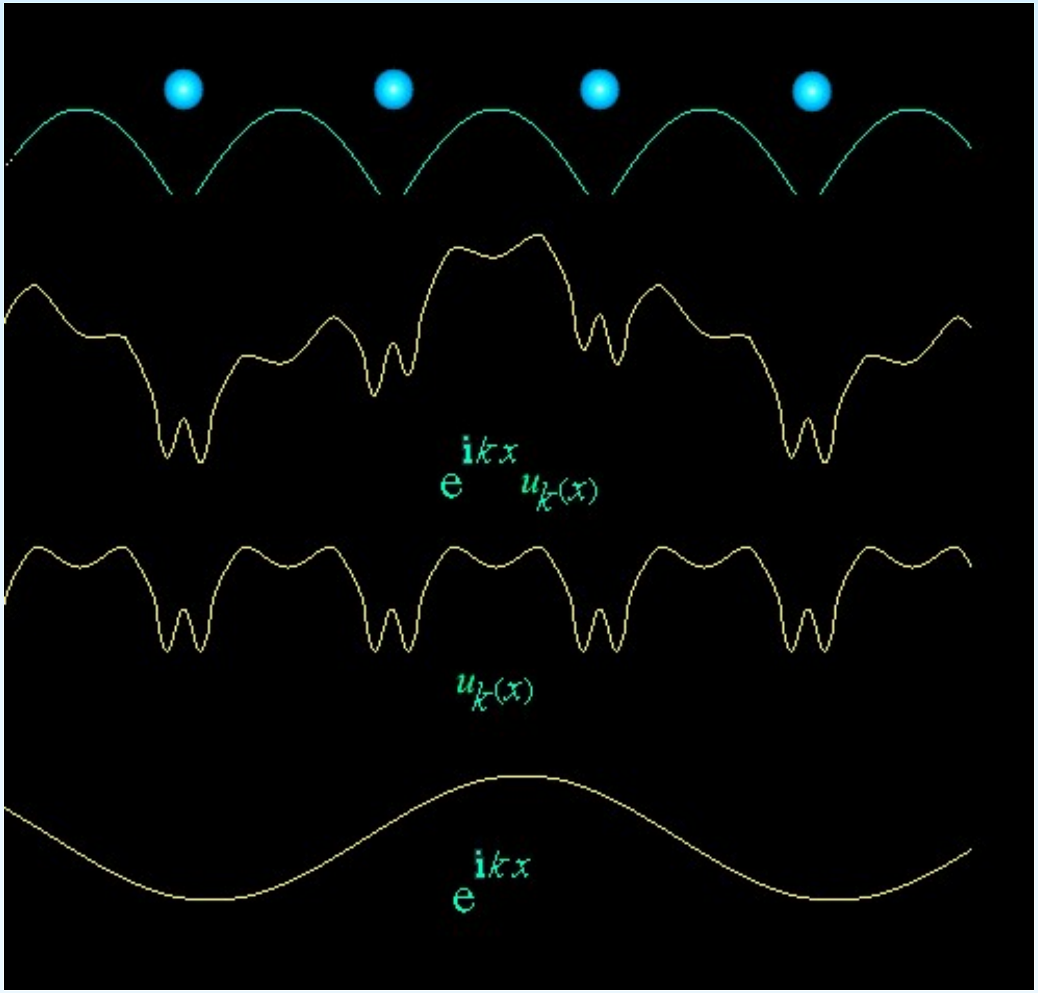
1. periodically modulated plane wave

$e^{i\vec{k}\cdot\vec{r}}$ suggests that electron waves propagates as a plane wave, i.e., *like a free particle*. $u_{\vec{k}}(\vec{r})$ *modulates* the vibration amplitude, making a periodic oscillation from one unit cell to another.

- ✓ **$e^{i\vec{k}\cdot\vec{r}}$ plain wave factor: *communal* electron motion between unit cells**
- ✓ **$u_{\vec{k}}(\vec{r})$ describes the electron motion within the unit cell. Due to the lattice periodicity, electrons have equal probabilities to be found in equivalent points of each unit cell.**

$$\boxed{\left|\psi_{\vec{k}}\left(\vec{r}+\vec{R}_n\right)\right|^2=\left|\psi_{\vec{k}}\left(\vec{r}\right)\right|^2=\left|u_{\vec{k}}\left(\vec{r}\right)\right|^2}$$

7.2 Bloch Wave



2. electron wave vector and crystal momentum

Wave vector $\vec{k}$ labels the electron state, like a quantum number.

$$\hat{T}(\vec{R}_n)\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{R}_n}\psi_{\vec{k}}(\vec{r})$$

$$\begin{aligned}\hat{T}(\vec{R}_n)\psi_{\vec{k}+\vec{G}_h}(\vec{r}) &= e^{i(\vec{k}+\vec{G}_h)\cdot\vec{R}_n}\psi_{\vec{k}+\vec{G}_h}(\vec{r}) \\ &= e^{i\vec{k}\cdot\vec{R}_n}\psi_{\vec{k}+\vec{G}_h}(\vec{r})\end{aligned}$$

$\vec{k}$ and $\vec{k}+\vec{G}_h$ corresponds to exactly the same state, therefore, we can restrict $\vec{k}$ within the first B.Z.

$\hbar\vec{k}$ quasi-momentum or crystal momentum, has the same physical dimension as momentum, but *not* ture momentum of Bloch electrons.

7.2 Bloch Wave

In study of the motion of cyrstal electron under external fields, and the interaction process with phonon and photons, $\hbar\vec{k}$ is formally momentum.

3. Bloch wave is the crystal orbit of electrons, an extended state in the whole crystal, not a localized state trapped in the vicinity of any specific atom.

III. periodic boundary condition and $\vec{k}$ values

Due to PBC: $\psi\left(\vec{r}+N_i\vec{a}_i\right)=\psi\left(\vec{r}\right)$

$\vec{a}_i\left(i=1,2,3\right)$ **--lattice primitive vector**

$N=N_1\cdot N_2\cdot N_3$ **--total number of sites**

7.2 Bloch Wave

Apply the Bloch theorem:

$$\psi\left(\vec{r}+N_i\vec{a}_i\right)=e^{iN_i\vec{k}\cdot\vec{a}_i}\psi\left(\vec{r}\right)$$

$$e^{iN_i\vec{k}\cdot\vec{a}_i}=1 \qquad iN_i\vec{k}\cdot\vec{a}_i=2\pi l_i$$

l_i **is integer**

$$\vec{k}=k_1\vec{b}_1+k_2\vec{b}_2+k_3\vec{b}_3 \qquad \vec{b}_i\left(i=1,2,3\right)$$

reciprocal lattice vector

⇨ $$\vec{k}=\frac{l_1}{N_1}\vec{b}_1+\frac{l_2}{N_2}\vec{b}_2+\frac{l_3}{N_3}\vec{b}_3$$

every $\vec{k}$ point occupies volume (in *k*-space):

$$\Delta\vec{k}=\frac{\vec{b}_1}{N_1}\cdot\left(\frac{\vec{b}_2}{N_2}\times\frac{\vec{b}_3}{N_3}\right)=\frac{1}{N}\vec{b}_1\cdot\left(\vec{b}_2\times\vec{b}_3\right)=\frac{\left(2\pi\right)^3}{N\Omega_d}=\frac{\left(2\pi\right)^3}{V}$$

7.2 Bloch Wave

$\vec{k}$ space density of states: $\dfrac{V}{(2\pi)^3}$

restrict $\vec{k}$ within the 1st B.Z.

$$-\frac{\vec{b}_i}{2} < \vec{k}_i \le \frac{\vec{b}_i}{2} \qquad\qquad -\frac{N_i}{2} < l_i \le \frac{N_i}{2}$$

number of *k*-points: $N = N_1 \cdot N_2 \cdot N_3$

IV. Energy Band

1. formation of energy bands

Substitute the Bloch wavefunction into single electron Shrödinger eq., eliminate $e^{i\vec{k}\cdot\vec{r}}$

$$\left[-\frac{\hbar^2}{2m}\left(\nabla + i\vec{k}\right)^2 + V(\vec{r})\right]u_{\vec{k}}(\vec{r}) = \varepsilon_{\vec{k}}u_{\vec{k}}(\vec{r})$$

7.2 Bloch Wave

wave eqation of $u_{\vec{k}}(\vec{r})$

eigenfunction and values are related to $\vec{k}$

for each wave eq. of specific $\vec{k}$, there is a infinite series of solutions $\varepsilon_1(\vec{k}), \varepsilon_2(\vec{k}), \cdots, \varepsilon_n(\vec{k}), \cdots$

Bloch electron state are denoted by two quantum number $\vec{k}$ and n, with corresponding energy and wave function:

$$\varepsilon_n(\vec{k}) \qquad \psi_{n\vec{k}}(\vec{r})$$

7.2 Bloch Wave

For $\vec{k}$ and $\vec{k}+\vec{G}_h$

$$\psi_{n,\vec{k}+\vec{G}_h}(\vec{r})=\psi_{n,\vec{k}}(\vec{r})$$

$$\varepsilon_n(\vec{k}+\vec{G}_h)=\varepsilon_n(\vec{k})$$

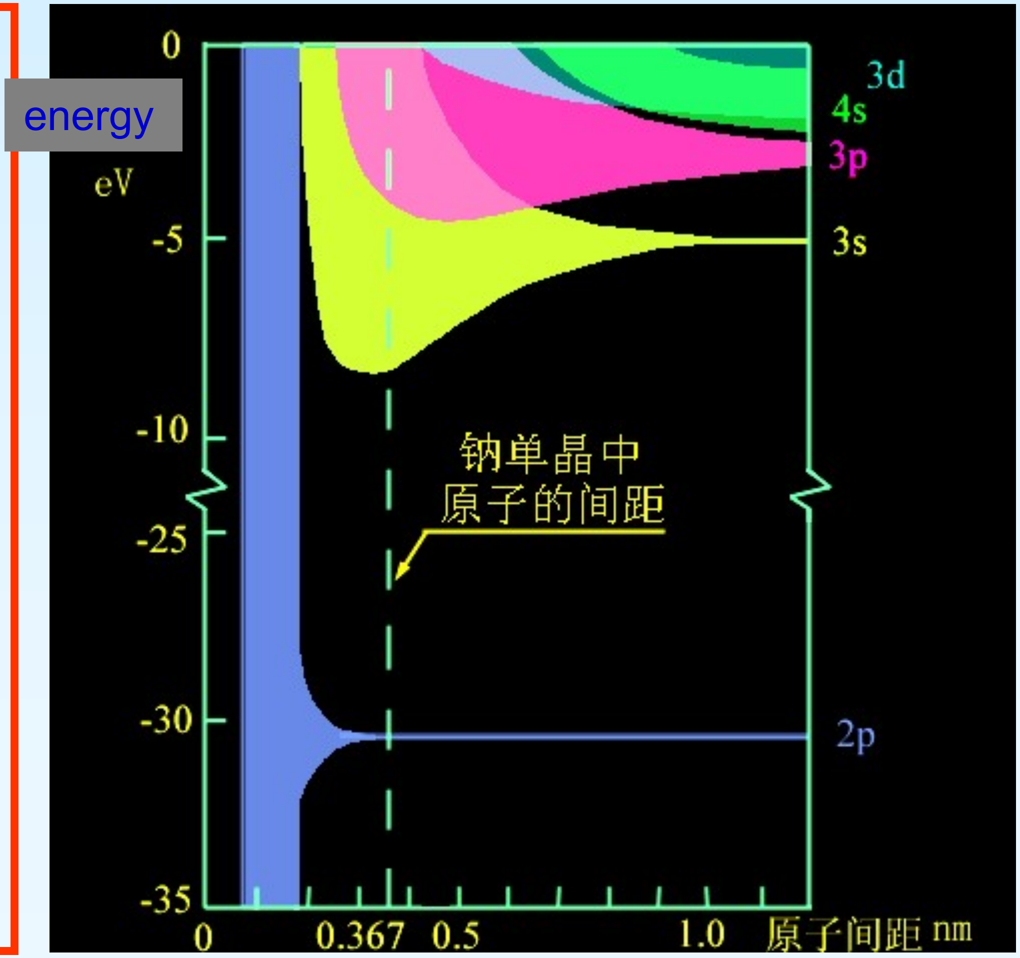
for a specific *n*, $\varepsilon_n(\vec{k})$ is a periodic function of $\vec{k}$, can change within a range, and has energy upper and lower bound, forms the so called ***energy band***. Different *n* represents different band, *n* is the band index. Two neigboring bands can have a gap or some overlap.

$\varepsilon_n(\vec{k})$ (dispersion relation for Bloch electrons) is called band structure of crystal.

7.2 Bloch Wave

Number of wave vectors $\vec{k}$ in the 1st B.Z. = lattice site number N

Every single band contains N electronic state ($2N$ for spin-1/2 electrons)



2.properties of energy bands

(1) periodicity $\boxed{\varepsilon_n(\vec{k})=\varepsilon_n(\vec{k}+\vec{G}_h)}$

$\varepsilon_n(\vec{k})$ **is a periodic function of *k*, with periodicity equal to reciprocal lattice vector. In *k*-space, two points with distance equal to any reciprocal lattice vector have exactly the same energy.**

(2) inversion symmetry

$$\boxed{\varepsilon_n(\vec{k})=\varepsilon_n(-\vec{k})} \qquad \boxed{\psi^*_{n,\vec{k}}(\vec{r})=\psi_{n,-\vec{k}}(\vec{r})}$$

Energy band has inversion symmetry with respect to $\vec{k}=0$ **point.**

$$\left[-\frac{\hbar^2}{2m}(\nabla+i\vec{k})^2+V(\vec{r})\right]u_{\vec{k}}(\vec{r})=\varepsilon_{\vec{k}}u_{\vec{k}}(\vec{r})$$

7.2 Bloch Wave

$-\vec{k}$ point corresponds to a Schrodinger eq. complex congugate to that for $\vec{k}$ point, so

$$\varepsilon_n\left(-\vec{k}\right)=\varepsilon_n^*\left(\vec{k}\right)$$

energy is real

$$\boxed{\varepsilon_n\left(-\vec{k}\right)=\varepsilon_n\left(\vec{k}\right)}$$

(3) energy bands have the *same rotational symmetry* as real-space crystal

Apply to the real space lattice a symmetric operation, potential $V(\vec{r})$ is intact. So the new state function has the same energy as the old one. These new states corresponds to rotational operation in *k*-space.

3. Diagrammatic representation of energtgy bands

Extended zone scheme:

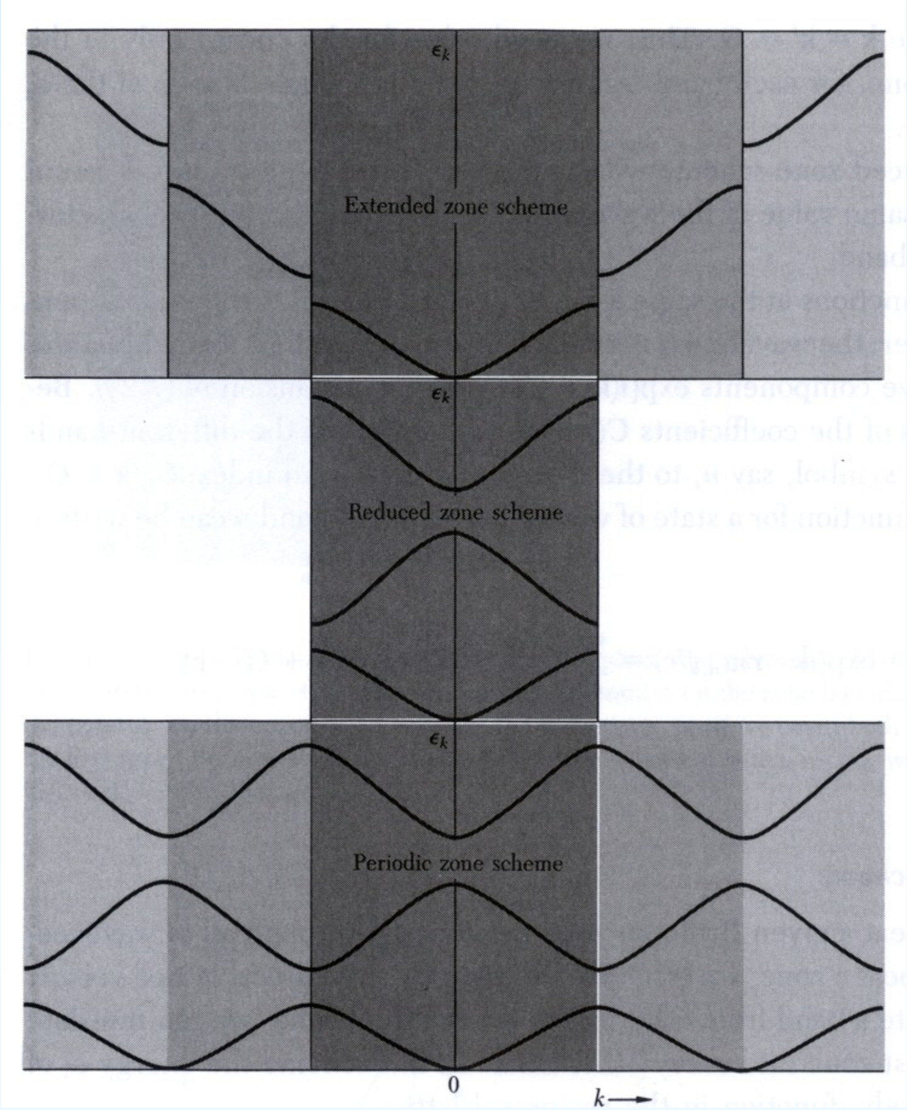
Plot different energy bands in various Brillouin zone of *k*-space.

Reduced zone scheme:

Plot all energy bands in the first B.Z.

Repeated zone scheme:

All $\vec{k}$ points in the whole *k*-space.



7.3 Nearly Free Electron Model

Periodic potential → general properties of electron eigen energy/wavefunction

Now: weak periodic potential → effect of periodic potential to free electrons, a good approximation for *s & p* electrons in metals.

Use perturbation theory to solve the Schrödinger eqs of the electrons in periodic potential——*H* can be devided into two Hermitian parts, $H' \ll H^0$.

- ✓ **Weak periodic potential is regarded as pertubation, and can be treated with standard perturbation theory of quantum mechanics.**

7.3 Nearly Free Electron Model

I. 1 dimensional case

1. perturbation method & nearly free electron approx.

1D: a crystal of length *L*=*Na*, i.e., *N* primitive cells of length *a*.

$$\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}+V(x)\right]\psi(x)=\varepsilon\psi(x)$$

Expand the potential $V(x)$ as superpostion of plane waves

(Fourier Trans.)

$$V(x)=\sum_n V_n e^{i\frac{2\pi}{a}nx}=V_0+\sum_n{}' V_n e^{i\frac{2\pi}{a}nx}$$

where, ′ means the partial summation (*n* = 0 term excluded),
***a* is the lattice constant.**

7.3 Nearly Free Electron Model

$$V_0 = \frac{1}{L}\int_0^L V(x)\mathrm{d}x = \bar{V}$$ ——mean potential energy

$$V_n = \frac{1}{L}\int_0^L V(x)e^{-i\frac{2\pi}{a}nx}\mathrm{d}x \qquad V_n = V_n^* \qquad V_n = V_{-n}$$

According to the perturbation theory, single electron Hamiltonian:

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

where $$\hat{H}_0 = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V_0$$

$$\hat{H}' = \sum_n{}' V_n e^{i\frac{2\pi}{a}nx}$$ **-- deviation of potential energy from mean value**

7.3 Nearly Free Electron Model

Compute the modified wavefunction & eigen energy

$$\boxed{\begin{aligned}&\psi_k(x)=\psi_k^{(0)}(x)+\psi_k^{(1)}(x)+\psi_k^{(2)}(x)+\cdots\\&\varepsilon_k=\varepsilon_k^{(0)}+\varepsilon_k^{(1)}+\varepsilon_k^{(2)}+\cdots\end{aligned}}$$

- zeroth order: select a proper potential gauge, such that $V_0=0$

$$H_0\psi_k^0=\varepsilon_k^0\psi_k^0$$

i.e. $$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi_k^{(0)}=\varepsilon_k^{(0)}\psi_k^{(0)}$$

eigenvalue & normalized wavefunction:

$$\boxed{\varepsilon_k^0=\frac{\hbar^2k^2}{2m}\qquad\psi_k^0=\frac{1}{\sqrt{L}}e^{ikx}}$$

7.3 Nearly Free Electron Model

- **1st order perturbation:**

$$\varepsilon_k^{(1)} = H'_{kk} = \int_0^L \psi_k^{0*}(x)\left(\sum_n{}' V_n e^{i\frac{2\pi}{a}nx}\right)\psi_k^0(x)\mathrm{d}x$$

$$= \frac{1}{L}\int_0^L e^{-ikx}V(x)e^{ikx}\mathrm{d}x$$

$$= \overline{V} = V_0 = 0$$

- **2nd order perturbation:**

$$\varepsilon_k^{(2)} = \sum_{k'}{}' \frac{\left|H'_{kk'}\right|^2}{E_k^0 - E_{k'}^0}$$

7.3 Nearly Free Electron Model

in which: $$H'_{kk'} = \int_0^L \psi_k^{0*} H' \psi_{k'}^0 \mathrm{d}x$$

$$= \frac{1}{L}\int_0^L \sum_n{}' V_n e^{i\left(k'-k+\frac{2\pi}{a}n\right)x}\mathrm{d}x$$

$$\begin{cases} = V_n, \quad \text{if} \quad k-k' = \dfrac{2\pi}{a}n = G \\ = 0, \quad \text{if} \quad k-k' \neq G \end{cases}$$

electron energy up to *2nd order* perturbation modification

$$\boxed{\varepsilon_k = \frac{\hbar^2 k^2}{2m} + \sum_n{}' \frac{2m\left|V_n\right|^2}{\hbar^2 k^2 - \hbar^2\left(k - 2\pi\dfrac{n}{a}\right)^2}}$$

7.3 Nearly Free Electron Model

■1st order perturbation in wavefunction：

$$\psi_k^{(1)}(x)=\sum_{k'}{}'\frac{H'_{kk'}}{E_k^0-E_{k'}^0}\psi_{k'}^0(x)$$

$$=\sum_{n}{}'\frac{2mV_n}{\hbar^2k^2-\hbar^2\left(k-\frac{2\pi n}{a}\right)^2}\frac{1}{\sqrt{L}}e^{ikx}\cdot e^{-i\frac{2\pi}{a}nx}$$

electron wavefunction in 1st order perturbation：

$$\psi_k(x)=\psi_k^0(x)+\sum_{k'}{}'\frac{H'_{kk'}}{E_k^0-E_{k'}^0}\psi_{k'}^0(x)$$

$$=\frac{1}{\sqrt{L}}e^{ikx}u_k(x)$$

7.3 Nearly Free Electron Model

where

$$\boxed{u_k(x) = 1 + \sum_n{}' \frac{2mV_n e^{-i\frac{2\pi}{a}nx}}{\hbar^2 k^2 - \hbar^2\left(k - \frac{2\pi n}{a}\right)^2}}$$

one can verify:

$$u_k(x) = u_k(x + na)$$

$u_k(x)$ is a lattice periodic function, the modified wavefunction obtained from perturbation theory obeys Bloch's theorem.

In the 1st-order approximated wavefunction

1st part: plane wave with wave vector *k*, *i.e.*, $\frac{1}{\sqrt{L}}e^{ikx}$

2nd part: scattering of plane wave on periodic potentials

7.3 Nearly Free Electron Model

scattering amplitude:
$$\frac{2mV_n}{\hbar^2 k^2 - \hbar^2\left(k - \frac{2\pi n}{a}\right)^2}$$

when $k^2 \neq \left(k - \frac{2\pi n}{a}\right)^2$ **sacttering amplitudes are *small* and *perturbation theory works***

when $k^2 = \left(k - \frac{2\pi n}{a}\right)^2$

i.e. $$\frac{\hbar^2 k^2}{2m} - \frac{\hbar^2}{2m}\left(k - \frac{2\pi n}{a}\right)^2 = 0 \qquad \varepsilon_k^0 = \varepsilon_{k'}^0$$

Scattering amplitudes *diverge*, preceding perturbation calculations break down, and one should resort to degenerate perturbation method.

7.3 Nearly Free Electron Model

when $k = \frac{n\pi}{a}$ $\lambda = \frac{2a}{n}$

——corresponding to Bragg reflection.

2. degenerate perturbation — strong scattering case

$$k = \frac{n\pi}{a} \text{ and } k' = k - \frac{2n\pi}{a} = -\frac{n\pi}{a}$$

two states with equal energy (degenerate).

zeroth-order wavefucntion is linear superposition as:

$$\boxed{\psi = A\psi_k^0 + B\psi_{k'}^0}$$

7.3 Nearly Free Electron Model

in which, $\psi_k^0 = \frac{1}{\sqrt{L}} e^{ikx}$ **——forward plane wave,**

$$\psi_{k'}^0 = \frac{1}{\sqrt{L}} e^{ik'x}$$ **——Bragg reflection**

***A*,*B* are coefficients of linear superposition.**

Substitute into Schrödinger's Eq

$$\left(\hat{H}_0 + \hat{H}'\right)\psi(x) = \varepsilon\psi(x)$$

Left multiply ψ_k^{0*} or $\psi_{k'}^{0*}$, and take integral over dx , we arrive at

$$\begin{cases} \left(\varepsilon_k^0 - \varepsilon\right)A + V_n B = 0 \\ V_n A + \left(\varepsilon_{k'}^0 - \varepsilon\right)B = 0 \end{cases}$$

7.3 Nearly Free Electron Model

Nontrivial Solution:

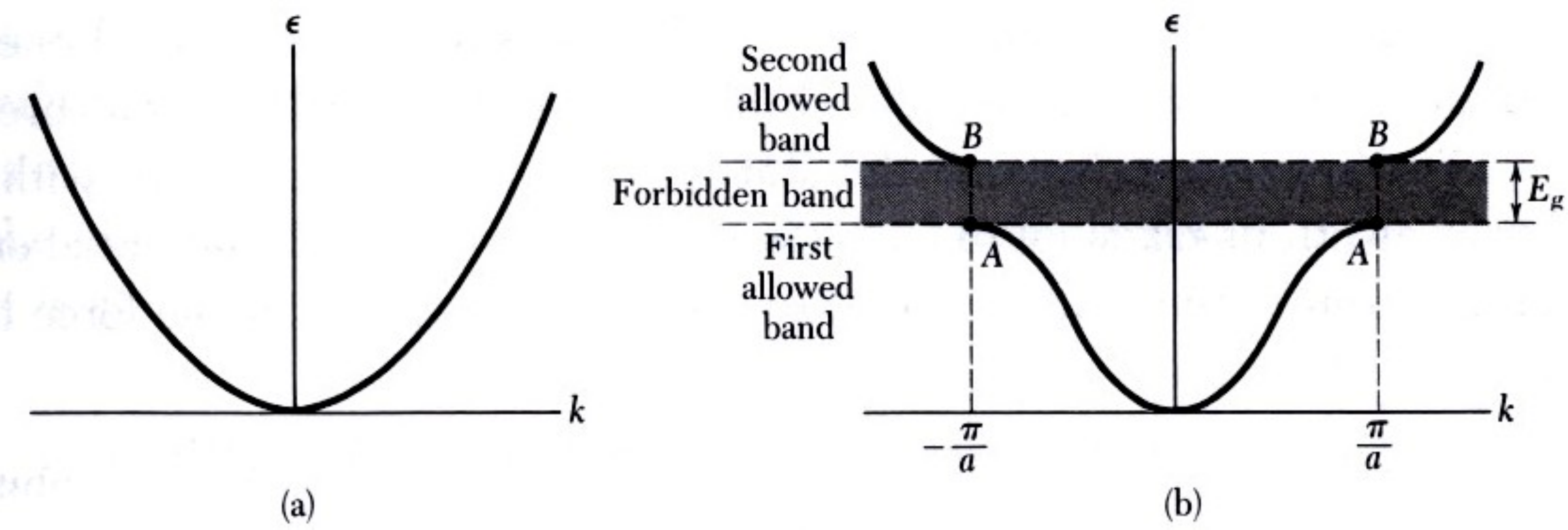
$$\begin{vmatrix} \varepsilon_k^0 - \varepsilon & V_n \\ V_n & \varepsilon_{k'}^0 - \varepsilon \end{vmatrix} = 0$$

Consider $k = \dfrac{n\pi}{a}$ & $k' - \dfrac{n\pi}{a}$

Two states with the same energy now split into

$$\boxed{\varepsilon_\pm = \varepsilon_k^{(0)} \pm |V_n| = \frac{\hbar^2 k^2}{2m} \pm |V_n|}$$

7.3 Nearly Free Electron Model



- **Gap width (forbidden band):** $\varepsilon_g = \varepsilon_+ - \varepsilon_- = 2|V_n|$

within gap ε_g, there exists no allowed electron state

- **energy gap & Bragg reflection**

gaps appear at $k = \frac{n\pi}{a}$ **&** $k' = -\frac{n\pi}{a}$

7.3 Nearly Free Electron Model

$k = \pm \frac{n\pi}{a}$ **are BZ boundary of 1D lattice of constant *a*.**

electrons in weak periodic potential change energy abruptly near BZ boundary, and energy gaps show up.

$$\psi_k^0 = \frac{1}{\sqrt{L}} e^{i\frac{n\pi}{a}x}$$ **——right moving wave**

$$\psi_{k'}^0 = \frac{1}{\sqrt{L}} e^{-i\frac{n\pi}{a}x}$$ **——left moving wave**

At BZ boundary, *k* and *k'* states propagates in opposite directions, and have the same amplitude and frequency, whose superposition results in a standing wave.

7.3 Nearly Free Electron Model

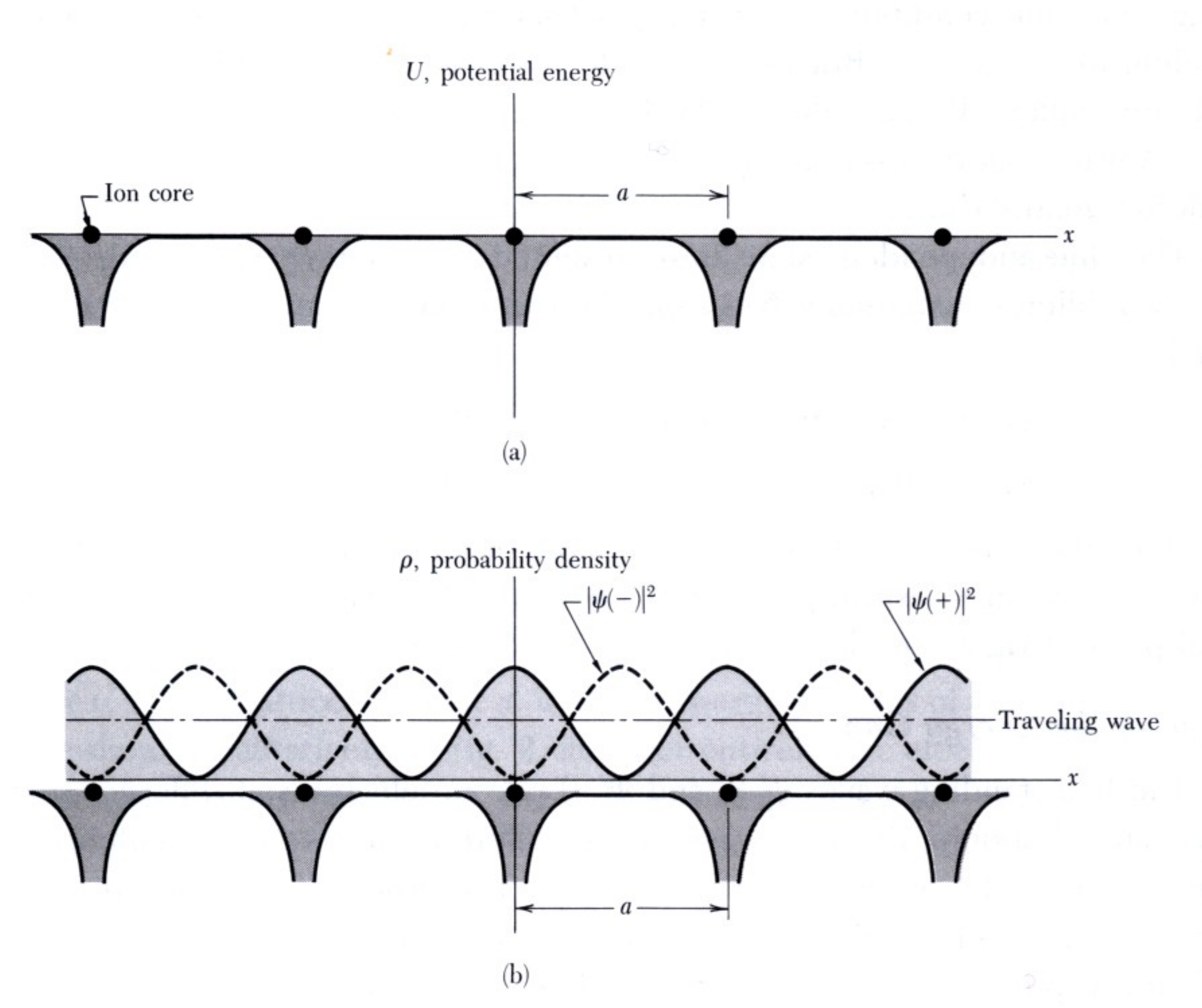
$$\psi_{\pm} = \frac{1}{\sqrt{2}}\left(\psi_k^0 + \psi_{k'}^0\right) = \frac{1}{\sqrt{2L}}\left(e^{i\frac{n\pi}{a}x} \pm e^{-i\frac{n\pi}{a}x}\right)$$

distribution probability of electrons:

$$\left|\psi_+(x)\right|^2 \propto \cos^2\left(\frac{n\pi}{a}x\right)$$

$$\left|\psi_-(x)\right|^2 \propto \sin^2\left(\frac{n\pi}{a}x\right)$$

7.3 Nearly Free Electron Model



7.3 Nearly Free Electron Model

for $k = \frac{n\pi}{a}$ & $\lambda = \frac{2a}{n}$

$$2d\sin\theta = n\lambda$$

$$d = a, \quad \sin\theta = 1$$

$$n\lambda = 2a$$

Electrons with wave vector at BZ boundary undergo a Bragg reflection, and the energy jumps at the BZ boundary, resulting in an energy gap (forbidden band).

7.3 Nearly Free Electron Model

(2) close to the BZ boundary

When the wave vector almost satifies Bragg reflection condition, the diffracted wave is very strong.

set $k=\frac{n\pi}{a}(1+\Delta)$, $k'=-\frac{n\pi}{a}(1-\Delta)$, **then we have**

$$\boxed{\varepsilon_{\pm}=T_n\left(1+\Delta^2\right)\pm\sqrt{\left|V_n\right|^2+4T_n^2\Delta^2}}$$

In which, $T_n=\frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2$

——kinetic energy of fee electron near $k=\frac{n\pi}{a}$

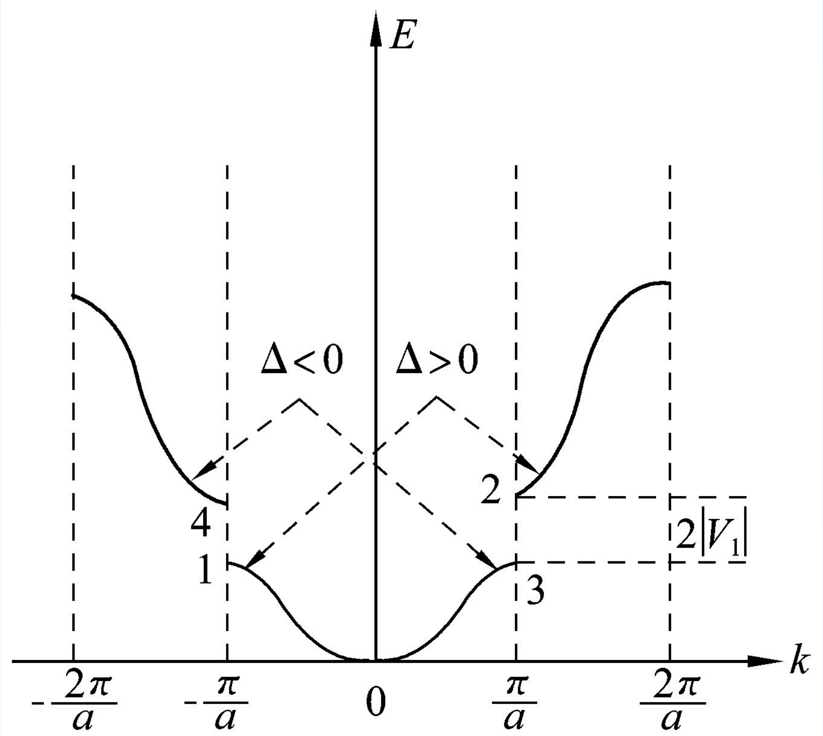
7.3 Nearly Free Electron Model

if $\Delta \ll 1,\ T_n\Delta \ll |V_n| < T_n$

expand it up to Δ^2 term

$$\varepsilon_+ = T_n + |V_n| + T_n\left(1 + \frac{2T_n}{|V_n|}\right)\Delta^2$$

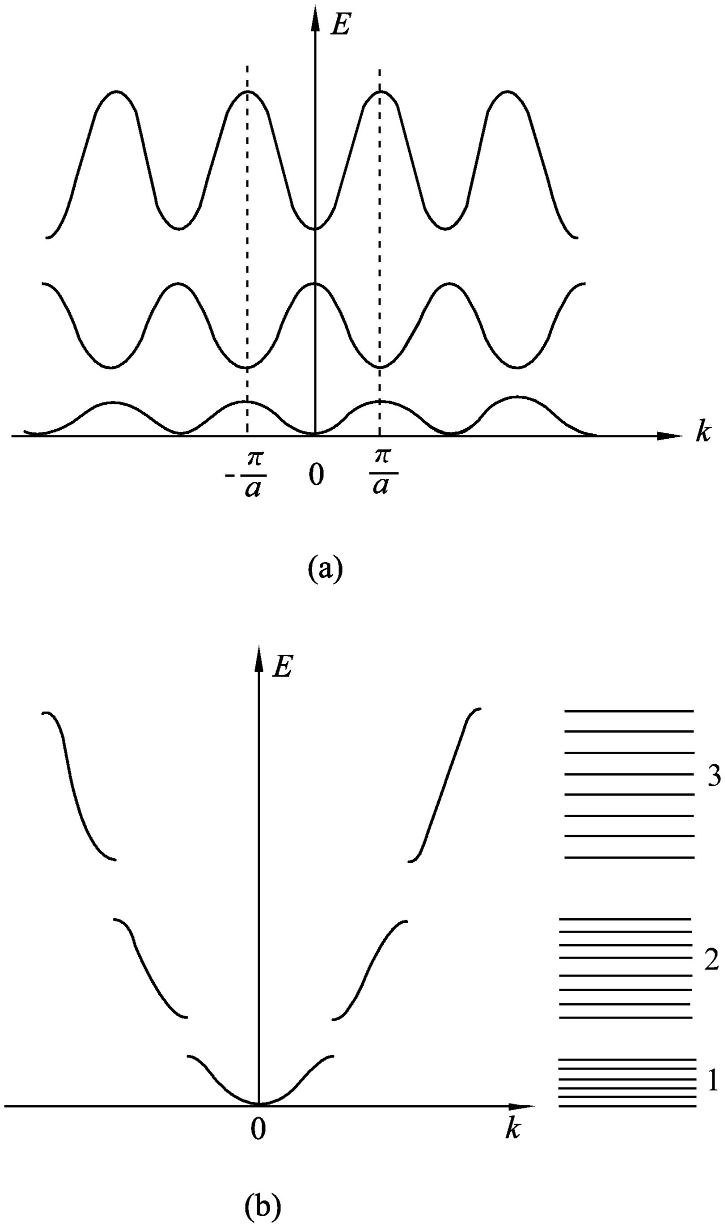
$$\varepsilon_- = T_n - |V_n| - T_n\left(\frac{2T_n}{|V_n|} - 1\right)\Delta^2$$



when k approaches BZ boundary, i.e., $\Delta\rightarrow 0$, ε_+ & ε_- approach

$T_n + |V_n|$ and $T_n - |V_n|$ in a *parabolic* way, from both sides.

7.3 Nearly Free Electron Model



(a)

(b)

7.3 Nearly Free Electron Model

- ✓ The perturbation strategy (for lattice systems in *any* spatial dimensions)

1. zeroth order wave function & eigen energy

eigen energy
$$\boxed{\varepsilon_{\vec{k}}^{0}=\frac{\hbar^{2}k^{2}}{2m}}$$

normalized wavefunction
$$\boxed{\psi_{\vec{k}}^{0}=\frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{r}}}$$

V—volume of crystal

2. Perturbation Calculations

1st order modification of energy

$$\langle\vec{k}|H'|\vec{k}\rangle=0$$

7.3 Nearly Free Electron Model

2nd order correction to energy:

$$\varepsilon_{\vec{k}}^{(2)} = \sum_{\vec{k}'}{}' \frac{\left| H'_{\vec{k}\vec{k}'} \right|^2}{E_{\vec{k}}^0 - E_{\vec{k}'}^0}$$

1st order correction to wavefunction:

$$\psi_{\vec{k}}^{(1)}(\vec{r}) = \sum_{\vec{k}'}{}' \frac{H'_{\vec{k}\vec{k}'}}{E_{\vec{k}}^0 - E_{\vec{k}'}^0} \psi_{\vec{k}'}^0(\vec{r})$$

when $\vec{k}'^2 = \left(\vec{k} - \vec{G}_h\right)^2$, ordinary perturbation calculations diverge.

since $\varepsilon_{\vec{k}}^0 = \varepsilon_{\vec{k}'}^0$ one should resort to degenerate perturbation theory.

7.3 Nearly Free Electron Model

3. degeneracy

- ✓ Take linear combination of $\vec{k}$ & $\vec{k}'$ states and get zeroth order wavefunction.
- ✓ Under the condition of $k'^2 = (\vec{k} - \vec{G}_h)^2$, one always get:

$$\boxed{\varepsilon_{\pm} = \varepsilon_{\vec{k}}^{0} \pm |V_n|}$$

V_n ——*Fourier components* of the periodic potential

- ✓ Eigen energy of Bloch wave undergoes a jump at $k'^2 = (\vec{k} - \vec{G}_h)^2$; which possibly leads to a forbidden band of width $2|V_n|$.
- ✓ This condition is the same as the Laue's equation, and be satisfied at BZ boundary (where Bragg reflection occurs).

II. Three-Dimensional (3D) case

Energy levels of quantum states form quasi-continuous spetra, constitutes a series of energy bands, energy gap between bands is called the forbidden band.

- ✓ **3D crystal band has periodicity and inversion symmetry.**
- ✓ **# of quantum states contained in each band is equal to *N*, and can be increased as 2*N* if electronic spin is taken into consideration.**

Main difference: 3D cases, different energy bands are not necessarily separated by a gap, but could share some overlap.

7.4 Tight-binding Approximation

- ✓ Free atoms has strong binding potential to its electrons.
- ✓ When atoms approach each other, treat the interatomic interaction as perturbation, what will happen?
- ✓ Suitable for 3d electrons in transition metals & inner electrons in solids.

I. Wavefunction in tight-binding model (linear combination of atomic orbits)

Position vector of m-*th* atom is $\vec{R}_m$, regard this atom as an isolated one, and the electrons moving around is in a bound state (an atomic orbit):

$$\varphi_i(\vec{r}-\vec{R}_m)$$

7.4 Tight-binding Approximation

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V_{\text{at}}\left(\vec{r}-\vec{R}_m\right)\right]\varphi_i\left(\vec{r}-\vec{R}_m\right)=\varepsilon_i\varphi_i\left(\vec{r}-\vec{R}_m\right)$$

$V_{\text{at}}\left(\vec{r}-\vec{R}_m\right)$: atomic potential for m-*th* atom.

ε_i, $\varphi_i\left(\vec{r}-\vec{R}_m\right)$ are electronic energy level & wavefunction.

In a crystal consists of *N* atoms, there exist *N* different atomic orbits $\varphi_i\left(\vec{r}-\vec{R}_m\right)$ with energy of ε_i .

These atomic orbits constitute a *N*-fold degenerate system:

N-fold degeneracy of energy level ε_i : $\varphi_i\left(\vec{r}-\vec{R}_m\right)\quad m=1,2,\cdots,N$

7.4 Tight-binding Approximation

Tight-binding Approximation: Single electron wavefunction in the crystal can be regarded as linear combination of N degenerate atomic wavefunction, i.e.,

Approximately:

$$\boxed{\begin{gathered}\psi_{\vec{k}}(\vec{r})=\sum_{m=1}^{N}a_m\varphi_i(\vec{r}-\vec{R}_m)\\ \int\varphi_i^*(\vec{r}-\vec{R}_n)\varphi_i(\vec{r}-\vec{R}_m)\mathrm{d}\vec{r}=\delta_{nm}\end{gathered}}$$

φ_i is *normalized* at any lattice site.

φ_i has little overlap with that on a different lattice site => approximately *orthogonal* to each other.

7.4 Tight-binding Approximation

In the vicinity of every lattice site, the atomic orbit is $\psi_{\vec{k}}(\vec{r})$

--Linear Combination of Atomic Orbitals *(LCAO)*, i.e., the communal orbit all through the crystal is a linear combination of atomic orbits $\varphi_i(\vec{r}-\vec{R}_m)$

$\psi_{\vec{k}}(\vec{r})$ obeys Bloch's theorem:

$$\boxed{\begin{aligned} a_m &= \frac{1}{\sqrt{N}} e^{i\vec{k}\cdot\vec{R}_m} \\ \psi_{\vec{k}}(\vec{r}) &= \frac{1}{\sqrt{N}} \sum_{m=1}^{N} e^{i\vec{k}\cdot\vec{R}_m} \varphi_i(\vec{r}-\vec{R}_m) \end{aligned}}$$

7.4 Tight-binding Approximation

check it

$$\psi_{\vec{k}}\left(\vec{r}+\vec{R}_n\right)=\frac{1}{\sqrt{N}}\sum_{m=1}^{N}e^{i\vec{k}\cdot\vec{R}_m}\varphi_i\left(\vec{r}-\vec{R}_m+\vec{R}_n\right)$$

$$=\frac{1}{\sqrt{N}}e^{i\vec{k}\cdot\vec{R}_n}\sum_{m=1}^{N}e^{i\vec{k}\cdot(\vec{R}_m-\vec{R}_n)}\varphi_i\left(\vec{r}-(\vec{R}_m-\vec{R}_n)\right)$$

$$=\frac{1}{\sqrt{N}}e^{i\vec{k}\cdot\vec{R}_n}\sum_{\vec{R}_l}e^{i\vec{k}\cdot\vec{R}_l}\varphi_i\left(\vec{r}-\vec{R}_l\right) \qquad \vec{R}_l=\vec{R}_m-\vec{R}_n$$

$$=e^{i\vec{k}\cdot\vec{R}_n}\psi_{\vec{k}}\left(\vec{r}\right)$$

——satisfy Bloch's theorem

II. Energy Calculation & Formation of Energy Bands

Single electron Schrödinger eq in a crystal:

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\psi(\vec{r})=\varepsilon\psi(\vec{r})$$

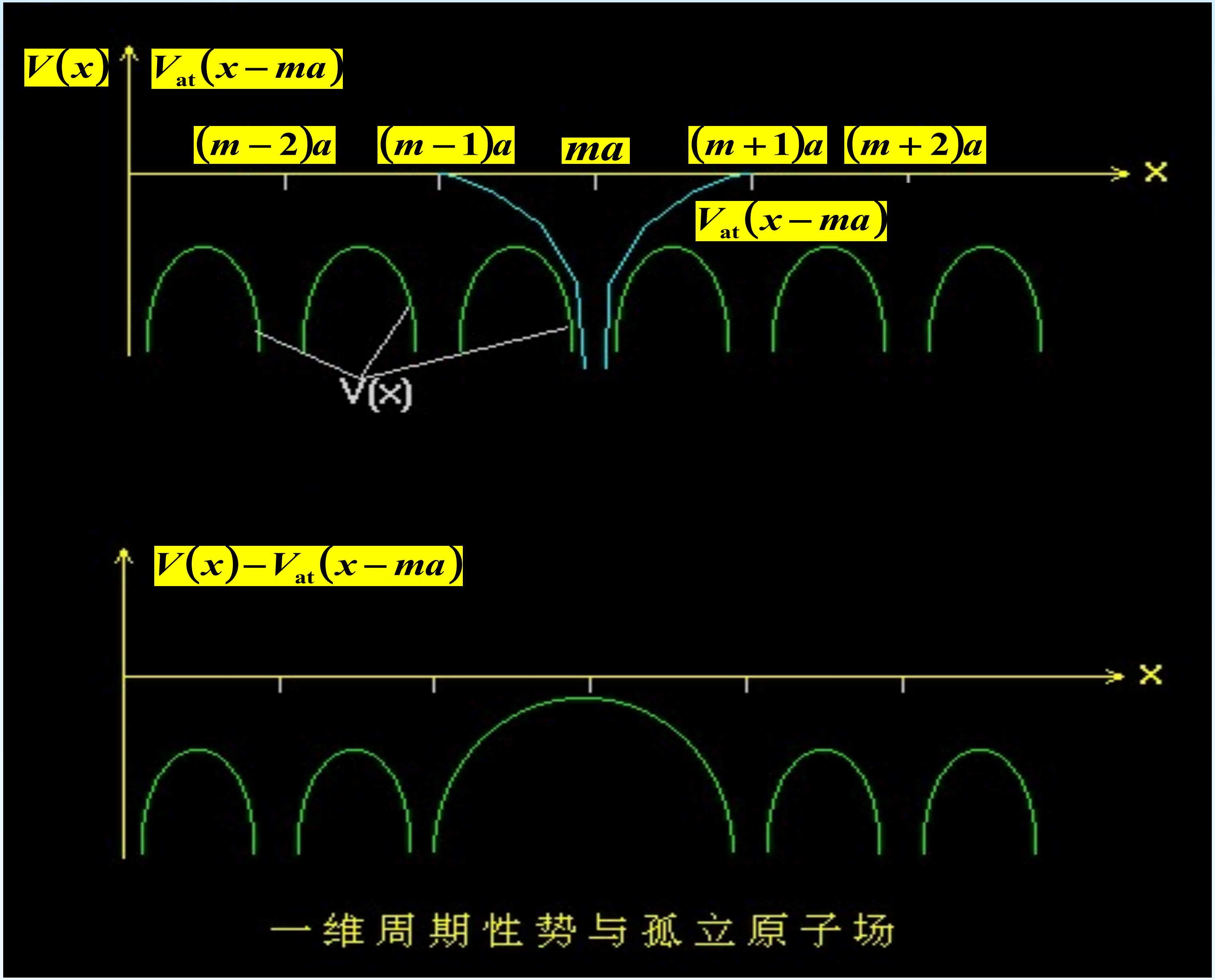
$V(\vec{r})$ **——lattice peroidic potential:**

$$V(\vec{r})=\sum_{m=1}^{N}V_{\text{at}}(\vec{r}-\vec{R}_m)$$

set $\Delta V(\vec{r},\vec{R}_m)=V(\vec{r})-V_{\text{at}}(\vec{r}-\vec{R}_m)$

Difference btw latt. potential and atomic potential of position $\vec{R}_m$ **.**

7.4 Tight-binding Approximation



7.4 Tight-binding Approximation

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V_{\text{at}}\left(\vec r-\vec R_m\right)+\Delta V\left(\vec r,\vec R_m\right)\right]\psi\left(\vec r\right)=\varepsilon\psi\left(\vec r\right)$$

substitute $\psi_{\vec k}\left(\vec r\right)=\frac{1}{\sqrt N}\sum_{m=1}^{N}e^{i\vec k\cdot\vec R_m}\varphi_i\left(\vec r-\vec R_m\right)$

$$\frac{1}{\sqrt N}\sum_{\vec R_m}e^{i\vec k\cdot\vec R_m}\left[\underline{-\frac{\hbar^2}{2m}\nabla^2+V_{\text{at}}\left(\vec r-\vec R_m\right)}+\Delta V\left(\vec r,\vec R_m\right)-\varepsilon\right]\varphi_i\left(\vec r-\vec R_m\right)=0$$

$$\Rightarrow\quad\sum_{\vec R_m}e^{i\vec k\cdot\vec R_m}\left[\varepsilon_i-\varepsilon+\Delta V\left(\vec r,\vec R_m\right)\right]\varphi_i\left(\vec r-\vec R_m\right)=0$$

left multiply $\varphi_i^*\left(\vec r\right)$ and take integration, $\varphi_i(\vec r-\vec R_m)$'s are orthonormal to each other.

7.4 Tight-binding Approximation

$$\varepsilon-\varepsilon_i+\int\varphi_i^*(\vec{r},0)\Delta V(\vec{r},0)\varphi_i(\vec{r},0)d\vec{r}$$

$$+\sum_{R_m}\int\boldsymbol{\varphi_i^*(\vec{r},0)\Delta V(\vec{r},\vec{R}_m)\,\varphi(\vec{r},\vec{R}_m)e^{i\vec{k}\,\vec{R}_m}\,d\vec{r}=0}$$

let: $$J(0)=-\int\varphi_i^*(\vec{r},0)\Delta V(\vec{r},0)\varphi_i(\vec{r},0)\mathrm{d}\vec{r}$$

$$J_m=-\int\varphi_i^*(\vec{r})\Delta V(\vec{r},\vec{R}_m)\varphi_i(\vec{r}-\vec{R}_m)\mathrm{d}\vec{r}$$

—— overlap integral.

It is nonzero when atomic orbits with distance $\vec{R}_m$ have overlap.

$$\boxed{\varepsilon=\varepsilon_i-J(0)-\sum_{\vec{R}_m}J_m e^{i\vec{k}\cdot\vec{R}_m}}$$

7.4 Tight-binding Approximation

In the tight-binding approximation, consider only the N.N. overlap:

$$\boxed{\varepsilon(\vec{k}) = \varepsilon_i - J(0) - \sum_{n,n} J_m e^{i\vec{k}\cdot\vec{R}_m}}$$

1D case: $\varepsilon(\vec{k}) = \varepsilon_i - J(0) - 2J_1 \cos ka$

Energy levels expand to a band of width $4J_1$

Simple Cubic: NN sites are $(\pm a,0,0)$ $(0,\pm a,0)$ $(0,0,\pm a)$

$$\varepsilon(\vec{k}) = \varepsilon_i - J_0 - J_m \sum_{n,n} e^{i\vec{k}\cdot\vec{R}_m}$$

$$= \varepsilon_i - J_0 - J_1\Big[\left(e^{ik_xa} + e^{-ik_xa}\right) + \left(e^{ik_ya} + e^{-ik_ya}\right) + \left(e^{ik_za} + e^{-ik_za}\right)\Big]$$

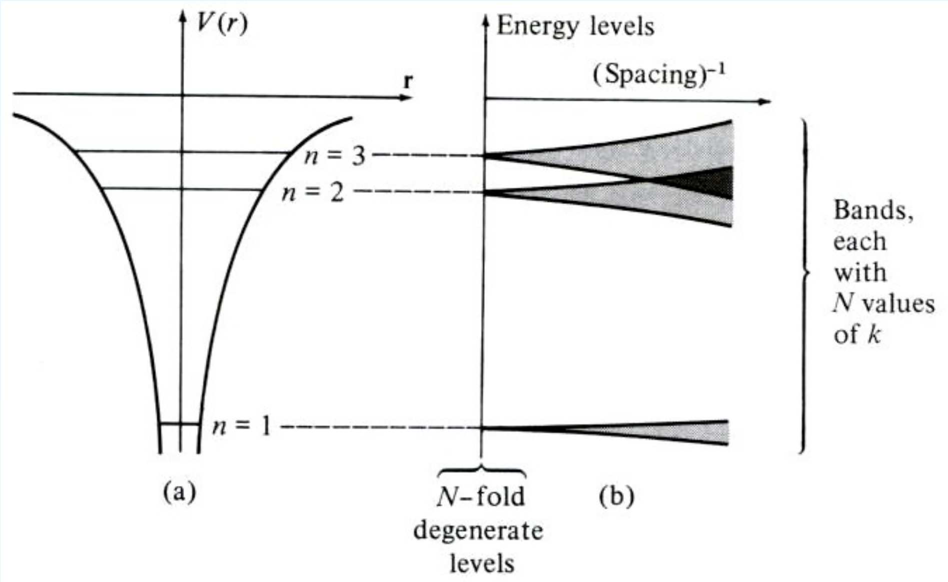
$$= \varepsilon_i - J_0 - 2J_1\left(\cos k_xa + \cos k_ya + \cos k_za\right)$$

Energy level expands as energy band of width $\varepsilon_{\max} - \varepsilon_{\min}$

7.4 Tight-binding Approximation

✓ *N* identical atoms (when are far apart) have their own energy level ε_i and $\varphi_\mathrm{i}(\vec{r})$, 1-electron states are *N*-fold degenerate.

✓ When the atoms approach each other and the electron obits start to develop some ***overlap***, *N*-fold degeneracy is ***removed*** and a energy band is formed which contains *N* inequivalent extensive states (***labelled* by *k***).



III. Wannier function

Nearly free electron approximation:

modulated plane wave ⇒ Bloch wave

Tight-binding approximation:

linear combination of free atomic orbits ⇒ Bloch wave

The wavefunction reflects local properties—Wannier function

Bloch wave is a periodic function in *k* space, which can be expanded by F.T. in direct space:

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

***n* is band index, and $a_n(\vec{r} - \vec{R}_m)$ is Wannier function.**

7.4 Tight-binding Approximation

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

1. locality

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

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

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

$u_{n\vec{k}}(\vec{r})$ is a lattice periodic function, $a_n(\vec{r}-\vec{R}_m)$ is only dependent on $(\vec{r}-\vec{R}_m)$.

7.4 Tight-binding Approximation

Change to integrate over $\vec{k}$, set $\vec{r} = \vec{R}_l$, then

$$a_n\left(\vec{R}_l-\vec{R}_m\right)=\frac{1}{\sqrt{N}}\frac{V}{(2\pi)^3}\int \mathrm{d}^3\vec{k}e^{i\vec{k}\cdot(\vec{R}_l-\vec{R}_m)}u_{n\vec{k}}\left(\vec{R}_l\right)$$

Quanlitatively: **when $\left|\vec{R}_l-\vec{R}_m\right|$ is large, exponential function oscillates strongly and the integration becomes small, showing that Wannier function is centered at $\vec{R}_m$, and decay with distances.**

2. orthogonality

Bloch waves with different *n* or *k* are orthogonal:

$$\int \psi^*_{n\vec{k}}\left(\vec{r}\right)\psi_{m\vec{k}'}\left(\vec{r}\right)\mathrm{d}\vec{r}=\delta_{nm}\delta_{\vec{k}\vec{k}'}$$

7.4 Tight-binding Approximation

$$\int a_n^*(\vec{r}-\vec{R}_m)a_{n'}(\vec{r}-\vec{R}_l)\mathrm{d}\vec{r}$$

$$=\frac{1}{N}\sum_{\vec{k}}\sum_{\vec{k}'}e^{i(\vec{k}\cdot\vec{R}_m-\vec{k}'\cdot\vec{R}_l)}\int\psi_{n\vec{k}}^*(\vec{r})\psi_{n'\vec{k}'}(\vec{r})\mathrm{d}\vec{r}$$

$$=\frac{1}{N}\sum_{\vec{k}}e^{i\vec{k}\cdot(\vec{R}_m-\vec{R}_l)}\delta_{nn'}$$

$$=\delta_{nn'}\delta_{m,l}$$

Wannier functions in *different bands* or *centered at different sites* are orthogonal to each other.