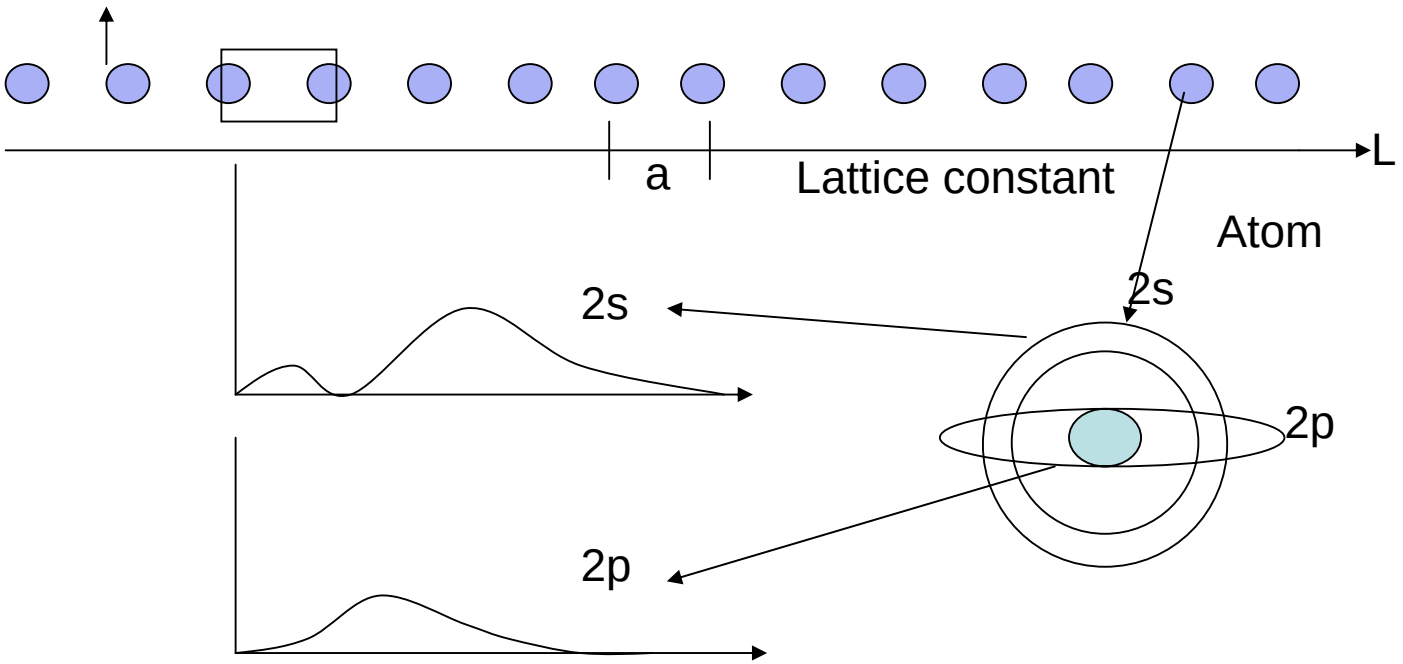
Electronic States

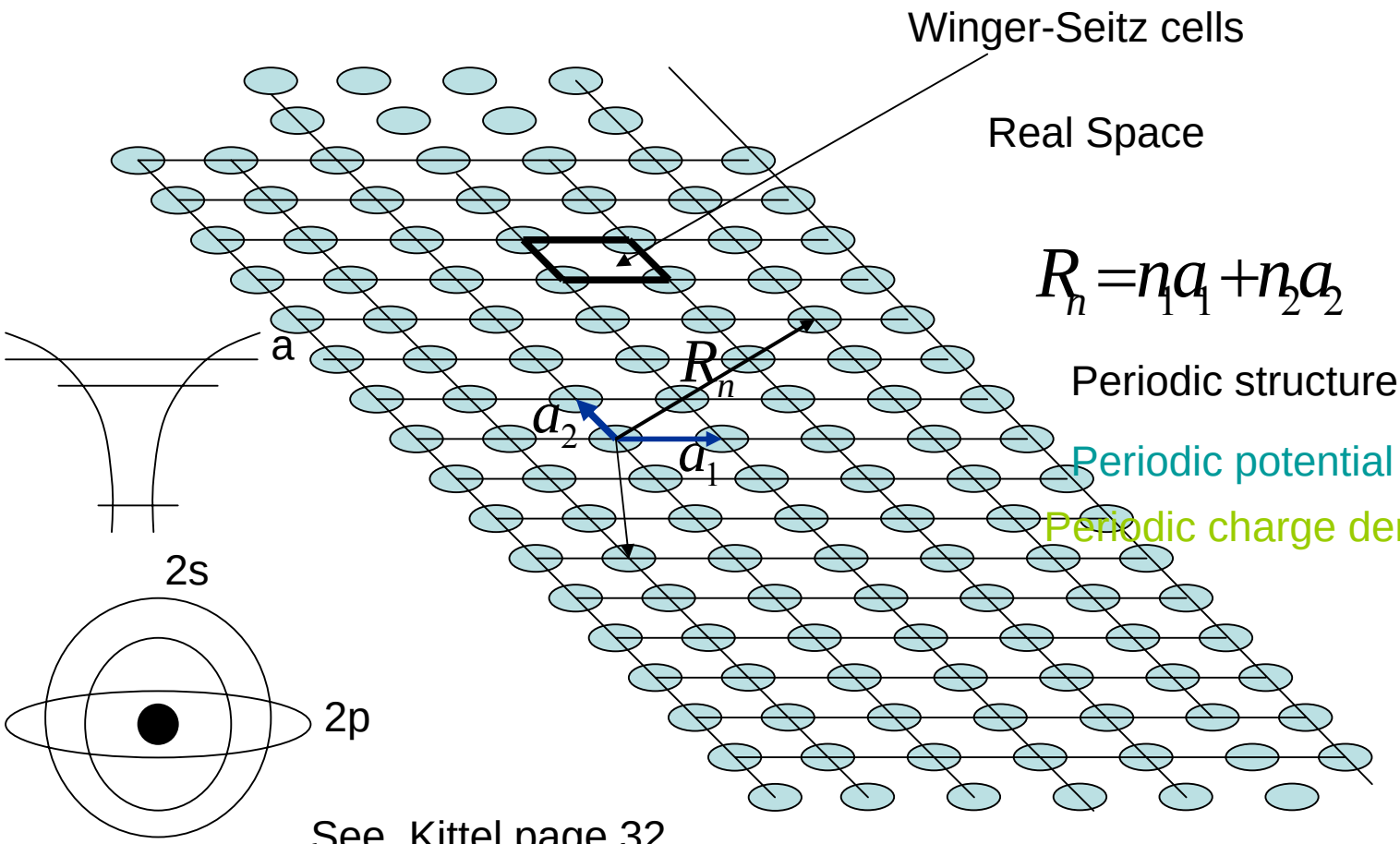
1. Bloch Theorem
2. Nearly free-electron model
3. Kronig-Penny Model
4. Plane-wave expansion (pseudopotential method)
5. Tight-binding approximation
6. $\mathbf{k}\cdot\mathbf{p}$ theory

HW assignment: Ch. 7, Problems 4, 5, and 7.

Bloch Theorem



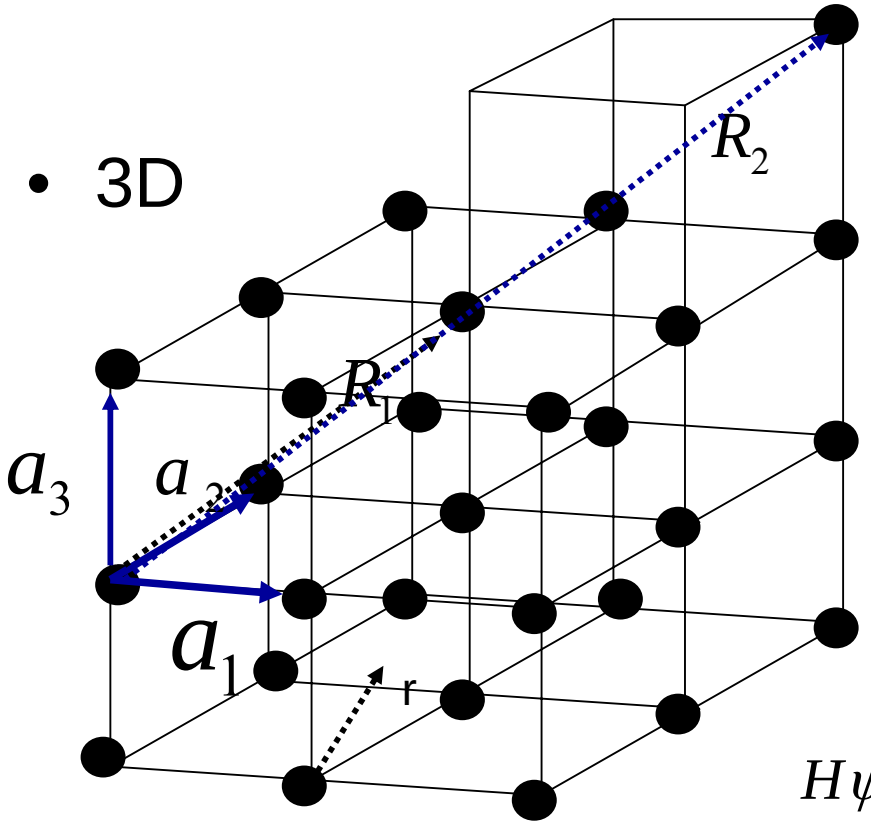
Periodic potential



See, Kittel page 32

Three dimensional lattice

- 3D



$$R_n = \sum_i n_i a_i$$

$$V_0(r) = V_0(r + R_n)$$

$$T_n \psi(r) = \psi(r + R_n) = t_n \psi(r)$$

$$[H, T_n] = 0$$

$$H\psi_\lambda(k,r) = E_\lambda \psi_\lambda(k,r)$$

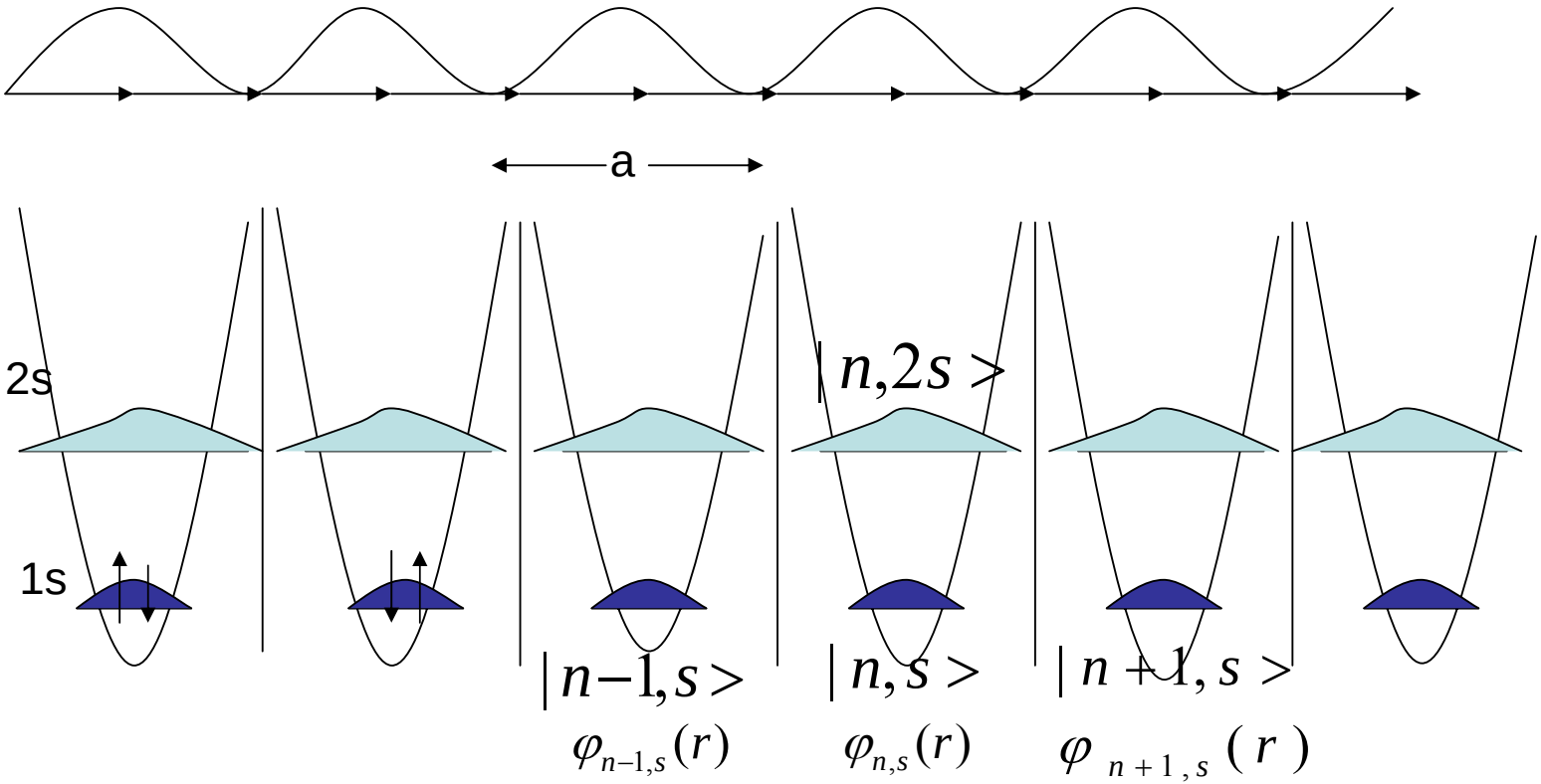
and

$$T_n \psi_\lambda(k,r) = \psi_\lambda(k, r + R_n) = t_n \psi_\lambda(k,r)$$

r is a continuous variable
R is a discrete variable

Translational symmetry

- Lattice translation as a discrete symmetry operation



Proof of Bloch Theorem

Eigenstates of an electron in a 3D periodic system (solid) takes the form $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot r}u_{\mathbf{k}}(\mathbf{r})$, where $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}+\mathbf{R})$ for any lattice vector $\mathbf{R}$.

(Pf) Since the system is invariant under a translation by $\mathbf{R}$, we must have

$$\psi(\mathbf{r}+\mathbf{R}) = C(\mathbf{R})\psi(\mathbf{r}),$$

where $C(\mathbf{R})$ is a phase factor depending on $\mathbf{R}$.

Similarly, $\psi(\mathbf{r}+\mathbf{R}') = C(\mathbf{R}')\psi(\mathbf{r})$

and $\psi(\mathbf{r}+\mathbf{R}+\mathbf{R}') = C(\mathbf{R}+\mathbf{R}')\psi(\mathbf{r}) = C(\mathbf{R}')\psi(\mathbf{r}+\mathbf{R}) = C(\mathbf{R})C(\mathbf{R}')\psi(\mathbf{r})$

$\Rightarrow C(\mathbf{R}+\mathbf{R}') = C(\mathbf{R})C(\mathbf{R}')$.

In 1D: $C(R+R') = C(R)C(R')$ with $|C(R)| = |C(R')| = 1$,

which implies $C(R) = e^{ikR}$ with $k =$ some real number.

In 3D: We have $C(\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}$ with any choice of $\mathbf{k}$ which becomes a label of the state. $\mathbf{k}$ is the crystal wave vector and $\mathbf{k}$ & $\mathbf{k}+\mathbf{G}$ are equivalent, so we restrict $\mathbf{k}$ in the first Brillouin zone.

Born von Karmon Boundary Condition

$$\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{L}) = \psi_{\mathbf{k}}(\mathbf{L})$$

where $\mathbf{L} = L\mathbf{a}_1 + M\mathbf{a}_2 + N\mathbf{a}_3 \Rightarrow e^{i\mathbf{k}\cdot\mathbf{L}} = 1$ or

$$Lk_x a_1 = l \cdot 2\pi \Rightarrow k_x = l(2\pi/La_1)$$

$$Mk_y a_2 = m \cdot 2\pi \Rightarrow k_y = m(2\pi/Ma_2)$$

$$Nk_z a_3 = n \cdot 2\pi \Rightarrow k_z = n(2\pi/Na_3).$$

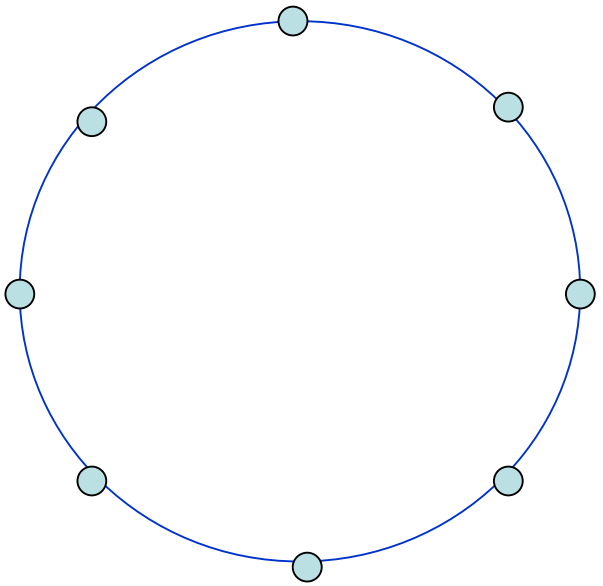
In the limit, $L, M, N \to \infty, \mathbf{k}$ is any value in 3D space.

Properties of Translation operator

- Unitary
-
- Not Hermitian

$$T_n^+(na)T_n(na) = e^{ip_x(na)}e^{-ip_x(na)} = 1$$

$$e^{-ip_x(na)} \neq e^{ip_x(na)}$$



N=8

Cyclic Group of order N:

Character: $\chi_n = w^n = e^{i\Phi n}$

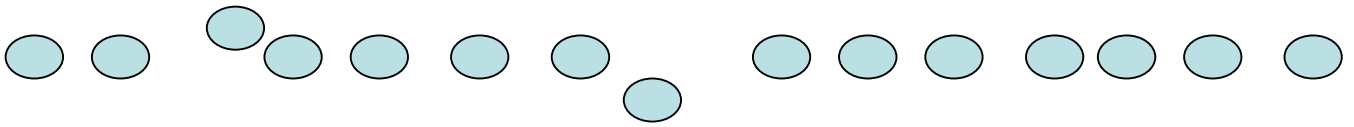
$W^N = 1$

$\Phi = s(2\pi/N)$

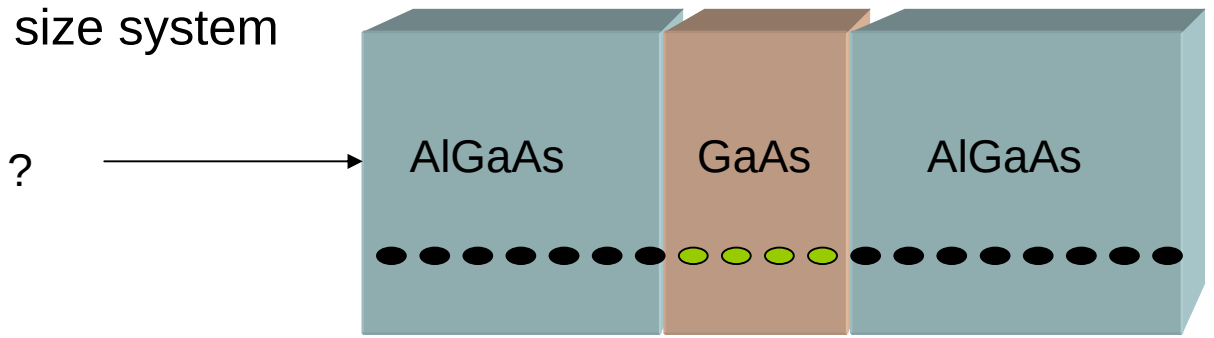
Symmetry of crystal

- Bloch theorem $\longrightarrow \psi_s(r+a) = e^{i\theta}\psi_s(r)$
- To describe electron in a symmetry crystal, not in local atom

- Dislocation



Finite size system



Lattice constant; b a

Summary

- Lattice vector $R_n = \sum_i n_i a_i$
- Primitive vectors a_i
- Periodic potential $V_0(r) = V_0(r + R_n)$
- Electron wave function $\psi(r)$
- Translation operator T_n
- Hamiltonian (1d case) $H(x) = \frac{-\hbar^2}{2m^*}\frac{d^2}{dx^2} + V(x)$
- Compatible observables $[H, T_n] = HT_n - T_n H$

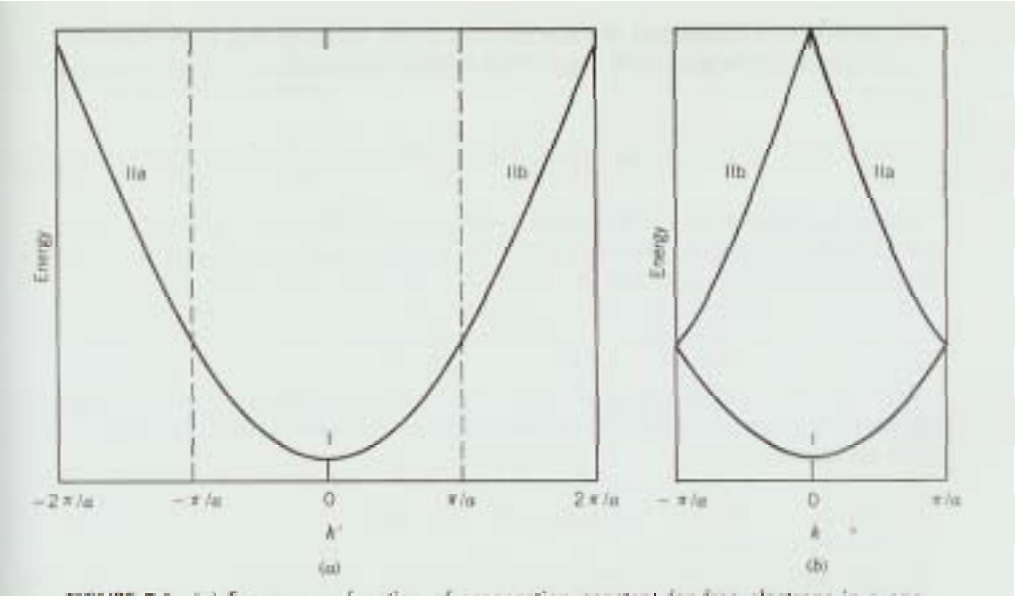
$$(H(x)T_n - T_n H(x))\psi(x) = 0\psi(x)$$

- T_n not a Hermitian operator, the eigenvalue is complex

$$T_n(na) = e^{-ip_x(na)}$$

$$T_n(a)\psi(x) = \psi(x + a)$$

Empty lattice band structure



$$U(r) = 0,\ \epsilon_n(k) = \frac{\hbar^2(k - G_n)^2}{2m}$$

Example: simple cubic lattice

$$\mathbf{G}_n = (n_1, n_2, n_3)(\frac{2\pi}{a}),\ \ \mathbf{k} = (\lambda_1, \lambda_2, \lambda_3)(\frac{2\pi}{a}),\ \ (|\lambda_i| \leq 0.5)$$

$$\Rightarrow \epsilon_n(\mathbf{k}) = \frac{\hbar^2}{2m}(\frac{2\pi}{a})^2[(\lambda_1 + n_1)^2 + (\lambda_2 + n_2)^2 + (\lambda_3 + n_3)^2].$$

Extend zone & Reduced zone

$\star$ Extended zone scheme:

For any $\mathbf{k}$ in 3D space, we have a Bloch state $\psi_{\mathbf{k}}(\mathbf{r})$ with energy $\epsilon = \epsilon(\mathbf{k})$. There is a one-to-one correspondence between free particle solution $(e^{i\mathbf{k}\cdot\mathbf{r}})$ and the Bloch state $(\psi_{\mathbf{k}}(\mathbf{r}))$.

$\star$ Reduced zone scheme:

Since the phase factor $e^{i\mathbf{k}\cdot\mathbf{R}}$ and $e^{i(\mathbf{k}+\mathbf{G}_n)} \cdot \mathbf{R}$ for any reciprocal lattice vector $\mathbf{G}_n$ are the same, we can rename the Bloch state with $(\mathbf{k} + \mathbf{G}_n)$, $\psi_{\mathbf{k}+\mathbf{G}_n}(\mathbf{r})$ by $\psi_{n\mathbf{k}}(\mathbf{r})$ and the corresponding energy $\epsilon(\mathbf{k}+\mathbf{G}_n)$ by $\epsilon_n(\mathbf{k}), \mathbf{k}$ is restricted in the 1st BZ.

Nearly free electron model

Consider a 1D solid with weak periodic potential $U(x)$ Write the Hamiltonian of the electron as $H = H_0 + U(x)$.

$H_0 = -\frac{\hbar^2}{2m}(\frac{\partial}{\partial x})^2$ with eigenfunctions $\psi_k(x) = e^{jkx}/\sqrt{L}$.

(normalized over sample length L) The free travelling electrons scatter from the periodic potential $U(x)$ in the same way as the Xray scattering. Thus, Bragg reflection occurs when $k - k' = G$ with $|k| = |k'| = k$. In 1D, this happens only when $k = G/2 = \frac{1}{2}(n \cdot \frac{2\pi}{a}) = n|\frac{\pi}{a}|$. This leads to two standing waves with wave functions

$$\psi^{(+)} = (e^{ikx} + e^{-ikx})/\sqrt{2L} = \sqrt{\frac{2}{L}}\cos(n\pi x/a);$$

$$\psi^{(-)} = (e^{ikx} - e^{-ikx})/\sqrt{2L} = \sqrt{\frac{2}{L}}i\sin(n\pi x/a).$$

Thus, the charge density $|\psi(x)|^2$ is either peaked at the atomic site or the interstitial site. An energy gap exists between these two states, since they

experience different effects from the periodic potential.

$$E_g = \Delta < U >= \int |\psi^{(+)}(x)|^2 U(x)dx - \int |\psi^{(-)}(x)|^2 U(x)dx.$$

Assume $U(x)$ takes the form

$$U(x) = U_0 \cos(2\pi x/a) \Rightarrow E_g = \frac{2N}{L}\int_0^a dx U_0 \cos(2\pi x/a)(\cos^2(\pi x/a) - \sin^2(\pi x/a))$$

$$= \frac{2}{a}\int_0^a dx U_0 \cos(2\pi x/a)\cos(2\pi x/a) = U_0$$

$\star$ A more rigorous treatment is to use the degenerate perturbation theory. Since states $|k>$ and $|-k>$ have the same energy $E(k) = \frac{\hbar^2 k^2}{2m}$, and they are coupled by the potential $U(x)$ with matrix elements

$$< k|U|k >=< -k|U|-k >= \frac{1}{a}\int_0^a dx U(x) = 0$$

and $< k|U|-k >= \frac{1}{a}\int_0^a dx U(x)e^{-2ikx} = \frac{1}{2a}\int_0^a dx U_0[e^{i\frac{2\pi x}{a}} + e^{-i\frac{2\pi x}{a}}]e^{-2ikx}$

$$= \frac{1}{2}[\delta_{k,\pi/a} + \delta_{k,-\pi/a}]U_0$$

$$\Rightarrow \begin{pmatrix} E(k) & \frac{1}{2}U_0 \\ \frac{1}{2}U_0 & E(k) \end{pmatrix}\begin{pmatrix} C_+ \\ C_- \end{pmatrix} = \epsilon \begin{pmatrix} C_+ \\ C_- \end{pmatrix}$$

or $(E(k) - \epsilon)^2 - \frac{1}{4}U_0^2 = 0 \Rightarrow \epsilon_\pm = E(k) \pm \frac{1}{2}U_0 \Rightarrow E_g = \epsilon_+ - \epsilon_- = U_0.$

Kronig-Penny Model

Consider a piecewise constant periodic potential $U(x) = U(x + nd)$, $d =$ period. For x in the period $(0, d)$

$$U(x) = \begin{cases} 0 \text{ if } 0 < x < a \\ U_0 \text{ if } a < x < a + b = d \end{cases}$$

We want to solve the 1D Schrödinger equation

$$[-\frac{\hbar^2}{2m}(\frac{\partial}{\partial x})^2 + U(x)]\psi(x) = \epsilon\psi(x).$$

In the well region $(0 < x < a)$: $\psi(x) = A\cos Kx + B\sin Kx$ with $K = \sqrt{2m\epsilon}/\hbar$. In the barrier region $(a < x < d)$: $\psi(x) = C\cosh[Q(x-a)] + D\sinh[Q(x-a)]$ with $Q = \sqrt{2m(U_0 - \epsilon)}/\hbar$

Boundary condition (B.C.) at $x = a$:

$\psi(x)$ continuous: $A\cos Ka + B\sin Ka = C$

$\psi'(x)$ continuous: $K(-A\sin Ka + B\cos Ka) = QD$.

In the next well region $(d < x < d + a)$:

$\psi(x) = A'\cos[K(x-d)] + B'\sin[K(x-d)]$ with $A' = e^{ikd}A, B' = e^{ikd}B$

B.C. at $x = d$: $\psi(x)$ continuous:

$C\cosh Qb + D\sinh Qb = A'$ and $Q(C\sinh Qb + D\cosh Qb) = KB'$

Using 1st B.C., we obtain

$$\begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} \cos Ka & \sin Ka \\ -\frac{K}{Q}\sin Ka & \frac{K}{Q}\cos Ka \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix}.$$

Similarly,

$$e^{ikd}\begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} \cosh Qb & \sinh Qb \\ \frac{Q}{K}\sinh Qb & \frac{Q}{K}\cosh Qb \end{pmatrix} \begin{pmatrix} C \\ D \end{pmatrix} \equiv T \begin{pmatrix} A \\ B \end{pmatrix}.$$

$$T = \begin{pmatrix} \cosh Qb\cos Ka - \frac{K}{Q}\sinh Qb\sin Ka & -- \\ -- & \frac{Q}{K}\sinh Qb\sin Ka + \cosh Qb\cos Ka \end{pmatrix}.$$

T has two eigenvalues e^{ikd} and e^{-ikd}

$$\Rightarrow Tr(T) = 2\cos kd = 2\cosh Qb\cos Ka + (\frac{Q}{K} - \frac{K}{Q})\sinh Qb\sin Ka.$$

Plane-wave expansion

Let $\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}}(\mathbf{G}) e^{j(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}}; U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$,

where $\mathbf{G}$'s are reciprocal lattice vectors. Substituting into the Schrödinger equation

$$\Rightarrow \frac{\hbar^2}{2m}|\mathbf{k}-\mathbf{G}|^2 C_{\mathbf{k}}(\mathbf{G}) + \sum_{\mathbf{G}'} U_{\mathbf{G}'} \int e^{-i(\mathbf{k}-\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} \psi_{\mathbf{k}}(r) d^3r = \epsilon C_{\mathbf{k}}(\mathbf{G})$$

$$\Rightarrow \frac{\hbar^2}{2m}|\mathbf{k}-\mathbf{G}|^2 C_k(\mathbf{G}) + \sum_{\mathbf{G}'} U_{\mathbf{G}'} C_{\mathbf{k}}(\mathbf{G}-\mathbf{G}') = \epsilon C_{\mathbf{k}}(\mathbf{G}).$$

In 1D case, we have

$$\lambda_G C_k(G) + \sum_{G''} U_{G-G''} C(G'') = \epsilon C_k(G),$$

where $\lambda_G = \frac{\hbar^2}{2m}(k-G)^2$, Let $\epsilon' = \epsilon - U_0$. Assume $G = -2g, -g, 0, g, 2g$ (truncated basis)

$$\begin{vmatrix} \lambda_{-2g}-\epsilon' & U_{-g} & U_{2g} & 0 & 0 \\ U_g & \lambda_{-g}-\epsilon' & U_{-g} & U_{2g} & 0 \\ U_{2g} & U_g & \lambda_0-\epsilon' & U_{-g} & U_{2g} \\ 0 & U_{2g} & U_g & \lambda_g-\epsilon' & U_{-g} \\ 0 & 0 & U_{2g} & U_g & \lambda_{2g}-\epsilon' \end{vmatrix} = 0.$$

KP Model with plane-wave expansion

Let $U(x) = Aa\sum_s \delta(x - sa) = \sum_G U_G e^{jGx}$

$\Rightarrow U_G = \frac{1}{a}\int_{-a/2}^{a/2} dx U(x) e^{-iGx} dx = A$ for any G

$\lambda_G C_k(G) + A\sum_{G''} C_k(G'') = \epsilon C_k(G) \Rightarrow C_k(G) = \frac{A}{\epsilon - \lambda_G}\sum_{G''} C_k(G'')$

$\Rightarrow f_k \equiv \sum_G C_k(G) = \sum_G (\frac{A}{\epsilon - \lambda_G}) f_k$

or $1 = A\sum_G \frac{1}{\epsilon - \lambda_G} = A\sum_n \frac{1}{\epsilon - \frac{\hbar^2}{2m}(k - \frac{n2\pi}{a})^2}$ (Let $\epsilon = \frac{\hbar^2 K^2}{2m}$)

$= (\frac{2m}{\hbar^2})A\sum_n \frac{1}{K^2 - (k - \frac{n2\pi}{a})^2} = \frac{1}{2K}(\frac{2m}{\hbar^2})A\sum_n [\frac{1}{K - (k - \frac{n2\pi}{a})} + \frac{1}{K + (k - \frac{n2\pi}{a})}]$

$= \frac{mA}{\hbar^2 K}(\frac{a}{2})(\cot[(K - k)a/2)] + \cot[(K + k)a/2])$ (Note: $\cot x = \sum_n \frac{1}{n\pi + x}$)

$= (\frac{mA}{\hbar^2 K})(\frac{a}{2})\frac{\sin(ka)}{\sin[(K - k)\frac{a}{2}]\sin[(K + k)\frac{a}{2}]} = (\frac{mAa}{\hbar^2 K})\frac{\sin(ka)}{\cos ka - \cos Ka}$

$\Rightarrow \cos ka = \cos Ka + \frac{mAa}{\hbar^2 K}\sin Ka = \cos Ka + (P/Ka)\sin Ka.$

Empirical Pseudopotential method

Use plane-wave expansion

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum C(\mathbf{k}-\mathbf{G}) e^{j\mathbf{G}\cdot\mathbf{r}} \quad \text{... periodic function}$$

$$\Rightarrow [\frac{\hbar^2}{2m}(\mathbf{k}-\mathbf{G})^2 - \epsilon] C(\mathbf{k}-\mathbf{G}) + \sum_{\mathbf{G}'} U(\mathbf{G}'-\mathbf{G}) C(\mathbf{k}-\mathbf{G}) = 0$$

[just like in the nearly-free electron model]

•Assumptions:

$$(i) C(\mathbf{k}-\mathbf{G}) = 0 \text{ for } |\mathbf{G}| > k_C \text{ ... cutoff value .}$$

$$(ii) U(\mathbf{G}) = \frac{1}{V}\int e^{i\mathbf{G}\cdot\mathbf{r}} U(\mathbf{r}) d^3r = \frac{1}{V_c}\int_{cell} e^{i\mathbf{G}\cdot\mathbf{r}} U(\mathbf{r}) d^3r$$

$$= \frac{1}{V_c}\int_{cell} e^{j\mathbf{G}\cdot\mathbf{r}} [\sum_i u_i(\mathbf{r}-\vec{\tau}_i)] d^3r = \sum_i v_i(\mathbf{G}) e^{i\mathbf{G}\cdot\vec{\tau}_i}$$

Assume $v_i(\mathbf{G}) = v_i(|\mathbf{G}|)$ ... spherical approximation

(iii) $v_i(|\mathbf{G}|)$ = nonzero only for small values of $|\mathbf{G}|$, implying a smooth potential $v_i(\mathbf{r})$. This is valid only if $v_i(\mathbf{r})$ here is the "pseudo potential", instead of the real potential.

For zincblende materials

[Ref: Cohen and Bergstasser, Phys. Rev. **141**, 789(1966)]

$$U(\mathbf{G}) = v_a(\mathbf{G})e^{i\mathbf{G}\cdot\vec{\tau}_a} + v_b(\mathbf{G})e^{i\mathbf{G}\cdot\vec{\tau}_b}$$

If we choose the origin of $\mathbf{r}$ to be at $(\frac{1}{8},\frac{1}{8},\frac{1}{8})a$, [half way between the two atoms in a unit cell] then $\tau_a = -\tau_b = (\frac{1}{8},\frac{1}{8},\frac{1}{8})a = \tau$, and

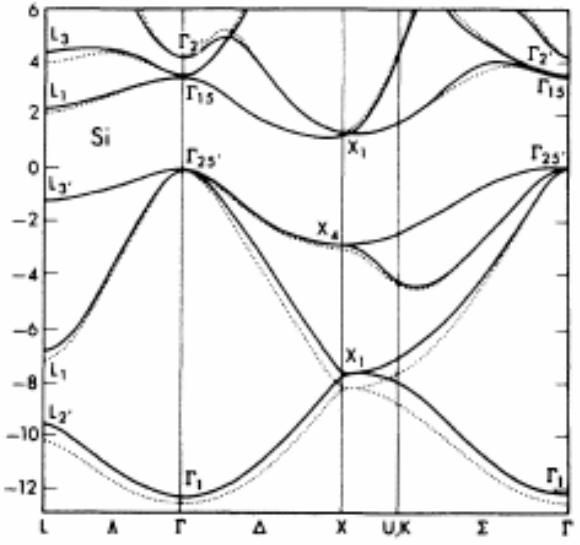
$$U(\mathbf{G}) = v_S(\mathbf{G})\cos\mathbf{G}\cdot\vec{\tau} + iv_A(\mathbf{G})\sin\mathbf{G}\cdot\vec{\tau}$$

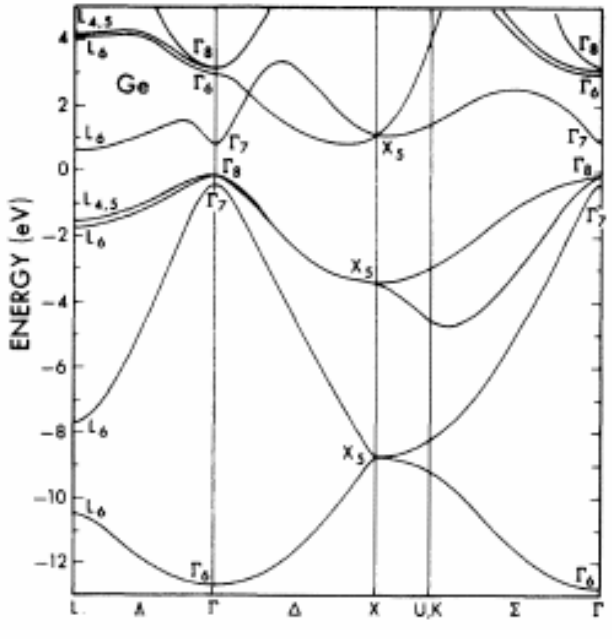
$$v_S(|\mathbf{G}|) = v_a(|G|) + v_b(|\mathbf{G}|),\ v_A(|\mathbf{G}|) = v_a(|\mathbf{G}|) - v_b(|\mathbf{G}|)$$

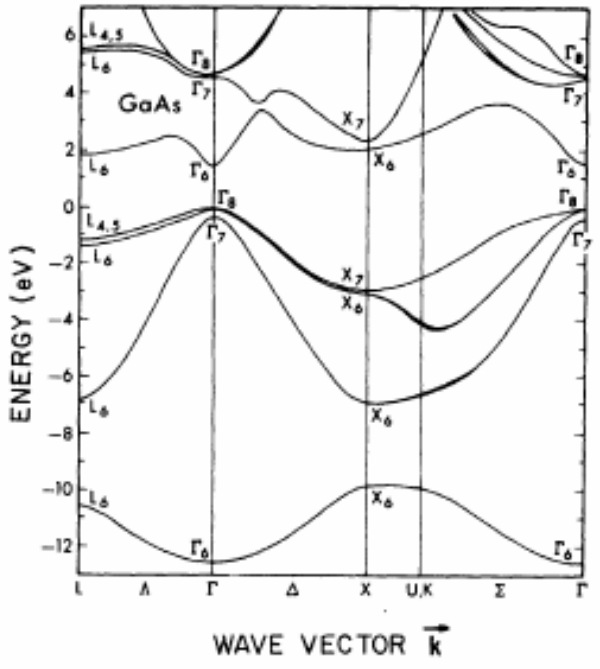
$v_S(|\mathbf{G}|)$ and $v_a(|\mathbf{G}|)$ are called symmetric and antisymmetric pseudopotential form factors.

Note: $v_A(|\mathbf{G}|) = 0$ for dimond structures

$\star$ Example: choose $|\mathbf{G}|^2 = 3,4,8,11(\frac{2\pi}{a})^2$ [for $(111),(200),(220),(311)$ shells]. [Set $U(0) = 0$ ... arbitrary energy shift] $v_S(4)$ has no contribution, since $cos(\mathbf{G}\cdot\vec{\tau}) = cos(\pi/2) = 0$. $v_A(8)$ has no contribution, since $sin(\mathbf{G}\cdot\vec{\tau}) = sin(\pi) = 0$. Thus, we only need 6 (3) parameters for zincblende(dimond structures)[in units of rydbergs = 13.6 eV] :





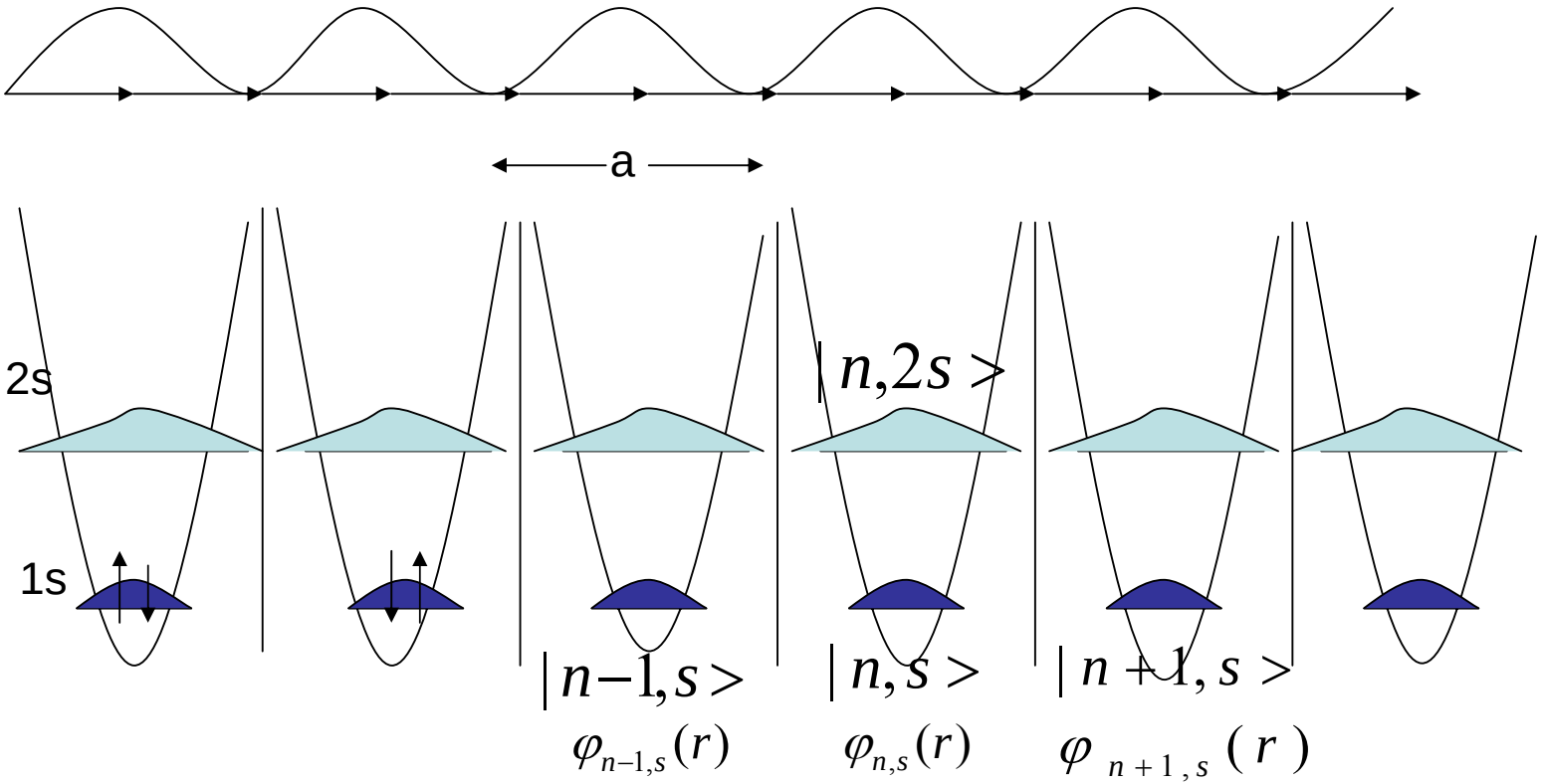


J. R. Chelikowsky and M. L. Cohen, *Nonlocal pseudopotential calculations for the electronic structure of eleven diamond and zinc-blende semiconductors*, Phys. Rev. B 14, 556 (1976)

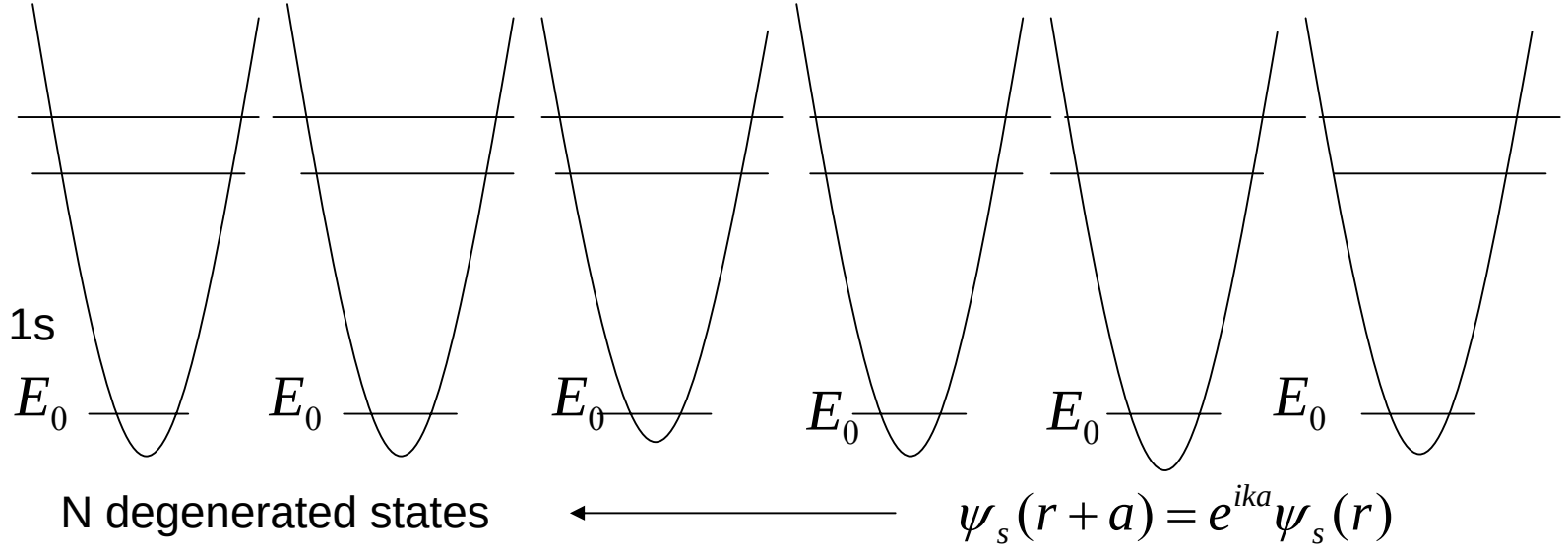
parameters [in units of rydbergs = 13.6 eV] :

	$v_S(3)$	$v_S(8)$	$v_S(11)$	$v_A(3)$	$v_A(4)$	$v_A(11)$
Si	-0.21	0.04	0.08	0	0	0
Ge	-0.23	0.01	0.06	0	0	0
GaAs	-0.23	0.01	0.06	0.07	0.05	0.01

Tight-binding model



Core orbitals vs. valence orbitals



$$< n',1s \mid H \mid n,1s >= 0, \qquad n' \neq n$$

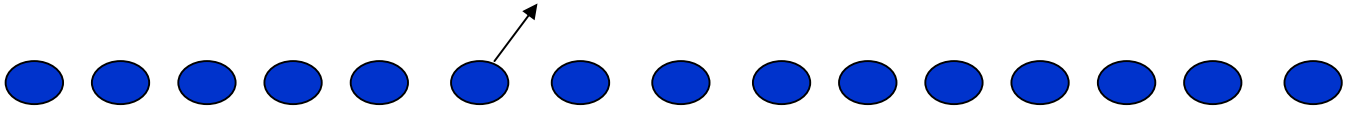
$$\int dr\, \varphi_{n',1s}(r) H(r) \varphi_{n,1s}(r) = 0, \qquad n' \neq n$$

Coupling between neighboring orbitals

- 2s-orbital

$$H_0\varphi_{2s}(r-R_l)=E_{2s}\varphi_{2s}(r-R_l)$$

$$[\frac{-\hbar^2\nabla^2}{2m_0}+V_0(r-R_l)]\varphi_{2s}(r-R_l)=E_{2s}\varphi_{2s}(r-R_l)$$



$$[\frac{-\hbar^2\nabla^2}{2m_0}+\sum_l V_0(r-R_l)-E_{2s}]\psi_{2s}(r)=0$$

$$E_{2s}=\frac{\int dr\ \psi^*_{2s}(r)H\psi_{2s}(r)}{\int dr\ \psi^*_{2s}(r)\psi_{2s}(r)}=\frac{N}{D}$$

$$N=\sum_{n,m}e^{i\theta(n-m)}\int d^3r\varphi^*_{2s}(r-R_m)H\varphi_{2s}(r-R_n)$$

$$=\sum_{n,m}e^{i\theta(n-m)}L_{2s,nm}$$

$$L_{2s,nm}=\int d^3r\varphi^*_{2s}(r-R_m)[\frac{-\hbar^2\nabla^2}{2m_0}+\sum_l V\ (r-R_l)]\varphi_{2s}(r-R_n)$$

Energy level versus k

- Renormalized atomic energy level $E_{2s}^{'}$
- Overlap integral B_{2s}

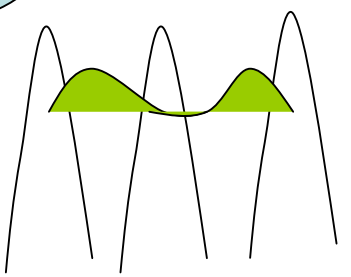
$$L_{2s,nm} = \int d^3 r \varphi_{2s}^*(r - R_m)[\frac{-\hbar^2 \nabla^2}{2m_0} + \sum_l V_0(r - R_l)]\varphi_{2s}(r - R_n)$$

$$= \delta_{nm}[\sum_l \delta_{l,n} E_{2s} + \sum_{l \neq n} \int d^3 r \varphi_{2s}(r - R_n) V_0(r - R_l) \varphi_{2s}(r - R_n)]$$

$$+ \delta_{n\pm1,m} \sum_l \int d^3 r \varphi_{2s}^*(r + R_{n\pm1}) V_0(r - R_l) \varphi_{2s}(r + R_n)$$

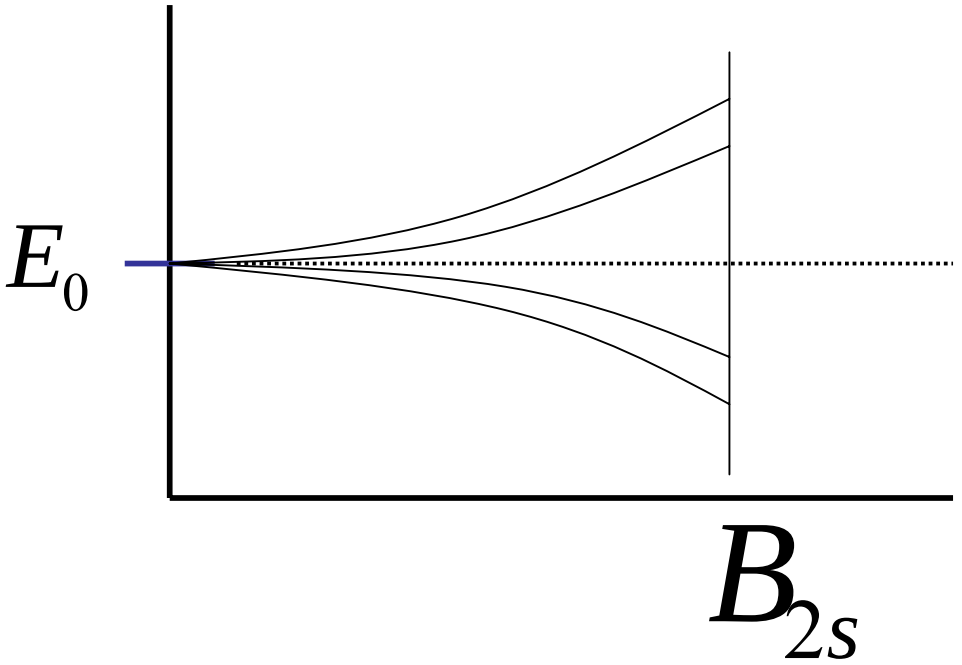
$$= \delta_{n,m} E_{2s}^{'} + \delta_{n\pm1,m} B_{2s} + \ldots.$$

$$E_{2s} = E_{2s}^{'} - B_{2s} \cos(\vec{k} \bullet \vec{a})$$



Band formation in solids

Energy levels form a continuous energy band as the overlap integral increasea from zero



Tight-binding method

Linear combination of atomic orbitals (LCAO):

[J.C. Slater and G.F Koster, Phys. Rev. **94**, 1498(1954)]:

1. construct Bloch sum of atomic orbitals

$$\Psi_{\alpha,i}(\mathbf{k};\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_\alpha(\mathbf{r} - \mathbf{R} - \vec{\tau}_i)$$

where $\phi_\alpha(\mathbf{r})$ is an atomic orbital of symmetry type $\alpha(\alpha = s, x, y, z, \text{ ... etc.})$.

Note: $\Psi_{\alpha_i}(\mathbf{k};\mathbf{r}+\mathbf{R}') = \frac{1}{\sqrt{N}} \Sigma_{\mathbf{R}}\, e^{i\mathbf{k}\cdot\mathbf{R}} \phi_\alpha(\mathbf{r}+\mathbf{R}' - \mathbf{R} - \vec{\tau}_i)$

$= \frac{1}{\sqrt{N}} \Sigma_{\mathbf{R}"}\, e^{i\mathbf{k}\cdot(\mathbf{R}"+\mathbf{R}')} \phi_\alpha(\mathbf{r} - \mathbf{R}" - \vec{\tau}_i) = e^{i\mathbf{k}\cdot\mathbf{R}'} \Psi_\alpha(\mathbf{k};\mathbf{r})$. It satisfies the Bloch theorem. We expect that any linear combinations of $\Psi_\alpha(\mathbf{k};\mathbf{r})$ will also satisfy the Bloch theorem.

2. Expand $\Psi_{\mathbf{k}}(\mathbf{r})$ in terms of $\Psi_\alpha(\mathbf{k};\mathbf{r})$.

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\alpha_i} C_{\alpha i}(\mathbf{k}) \Psi_{\alpha i}(\mathbf{k};\mathbf{r}).$$

3. Substitute expansion (2) into the Schrödinger equation. We obtain a generalized eigenvalue problem.

$$\sum_{\alpha' i'} < \Psi_{\alpha i}(\mathbf{k}) | H | \Psi_{\alpha' i'}(\mathbf{k}) > C_{\alpha' i'}(\mathbf{k}) = \mathcal{E} \sum_{\alpha' i'} | \Psi_{\alpha' i'}(\mathbf{k}) > C_{\alpha i}(\mathbf{k}).$$

4. $\phi_\alpha(\mathbf{r})$ can be chosen to be slightly different from the atomic orbitals

with $\int \Psi_{\alpha i}(\mathbf{k};\mathbf{r})\Psi_{\alpha' i'}(\mathbf{k};\mathbf{r}) = \delta_{\alpha\alpha'}\delta_{ii}$

and we have an eigen-value problem

$$\sum_{\alpha' i'} < \Psi_{\alpha i}(\mathbf{k})|H|\Psi_{\alpha' i'}(\mathbf{k}) > C_{\alpha' i'}(\mathbf{k}) = \mathcal{E}_{\alpha i}(\mathbf{k}).$$

5. The matrix element

$$< \Psi_{\alpha i}(\mathbf{k})|H|\Psi_{\alpha' i'}(\mathbf{k}) >= \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} < \phi_\alpha(\mathbf{r}-\vec{\tau}_i)|H|\phi_{\alpha'}(\mathbf{r}-\mathbf{R}-\vec{\tau}_{i'}) >$$

$$= \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} E^{(ii')}_{\alpha\alpha'}(\mathbf{R}).$$

$E^{(ii')}_{\alpha\alpha'}(\mathbf{R})$ are empirical parameters to be adjusted to fit the band structure obtained by other methods requiring less fitting parameters (e.g. the empirical pseudo-potential method).

6. To minimize the number of independent parameters, symmetry is used, and $\mathbf{R}$ is truncated at a short distance (typically less than 3rd nearest neighbor). For example, in a nearest neighbor sp^3 model for zincblende structures, the only independent parameters are (assuming two atoms per unit cell):

$E^{(aa)}_{ss}(000), E^{(aa)}_{pp}(000), E^{(bb)}_{ss}(000), E^{(bb)}_{pp}(000),$

$E^{(ab)}_{ss}(111), E^{(ab)}_{sx}(111), E^{(ab)}_{xx}(111), E^{(ab)}_{xy}(111), E^{(ab)}_{xs}(111).$

Comments

- Tight-binding model is the most efficient of all realistic band theories. The computation involves a diagonalization of the Hamiltonian Matrix $H_{\alpha i,\alpha' i'} = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} E^{(ii')}_{\alpha\alpha'}(\mathbf{R})$, whose dimension is equal to the number of atomic orbitals used per unit cell. For example, in an sp^3 model, for two atoms per unit cell, the dimension is 8.
- If nearest-neighbor truncation is used, the result is analytic along special directions (100), (111), (110) etc.
- Good band structures can be obtained if sufficient number of parameters are used. The fit, however, is often non-unique and one has to be aware of this fact.
- very helpful in understanding the symmetry of Bloch states at various points in the Brillouin zone.
- Spin-orbit interaction can be easily incorporated. When this is done, the size of the Hamiltonian matrix will be doubled.

One-band TB model

Consider an fcc lattice with one atom per unit cell. Use one s-like atomic orbital per atom.

$$E(\mathbf{k}) = < \Psi_s(\mathbf{R})|H|\Psi_s(\mathbf{k}) > = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} < \phi_s(\mathbf{r})|H||\phi_s(\mathbf{r}-\mathbf{R}) > \; E_{ss}(000)$$

$$+E_{ss}(110)\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} + ...$$

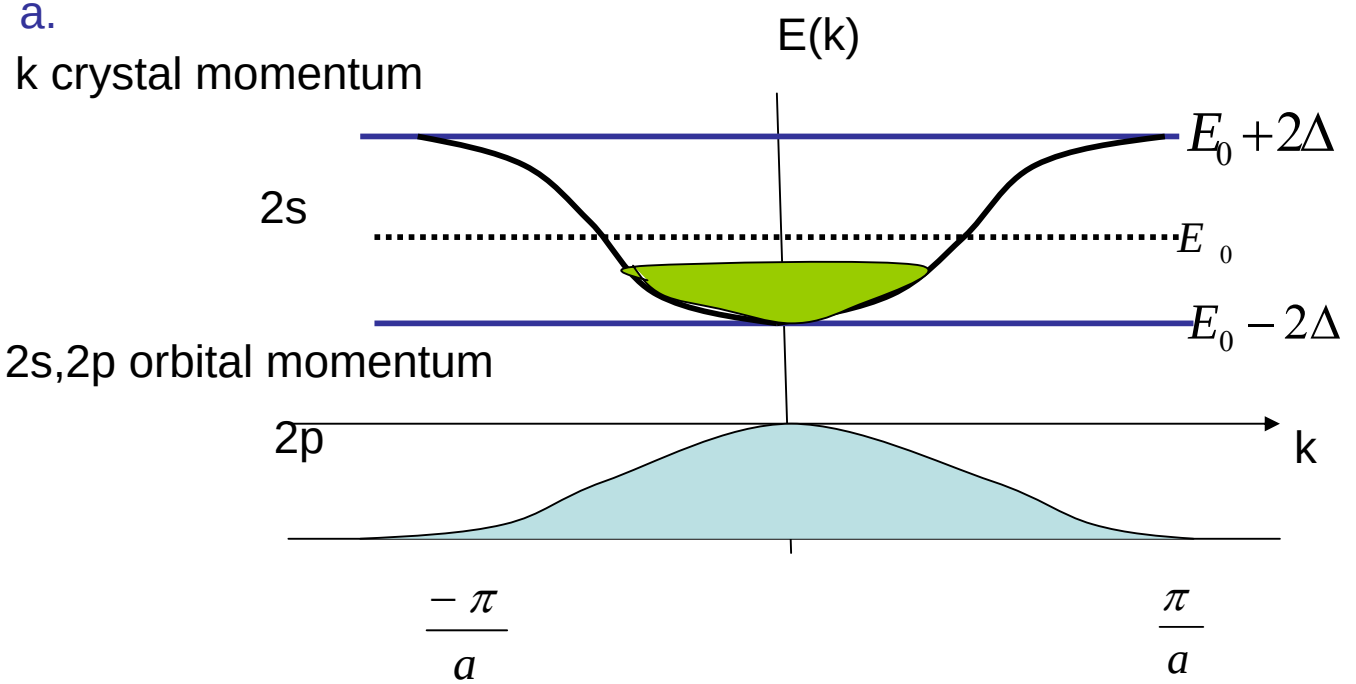
$$= E_0 + 4\gamma[cos(k_x a')cos(k_y a') + cos(k_x a')cos(k_z a') + cos(k_y a')cos(k_z a')] \; [a' = \frac{a}{2}]$$

Along [100] ($k_y = k_z = 0$): $E(\mathbf{k}) = E_0 + 4\gamma[2cos(k_x a') + 1]$.

Along [111] ($k_x = k_y = k_z = k$): $E(\mathbf{k}) = E_0 + 12\gamma cos^2(ka') = E_0 + 6\gamma[1 + cos(zka')]$.

Bloch's function

The wave function $|\theta>$,which is an eigenket of $T(a)$, can be written as a plane wave e^{ikx} times a periodic function with periodicity a.



Filling of Bands

orbitals in a band = #k points in 1st BZ = # primitive cell in a solid. Each orbital can be occupied by two electrons due to spin degeneracy. At zero T, electrons fill the bands up to the Fermi level, or the highest level below ϵ_F.

(1) If each primitive cell has (2ν) valence electrons (even integer), then the lowest ν bands (valence bands) are completely filled and if there is a gap between the filled band and the unfilled band (conduction band) then, we have a semiconductor or insulator.

(2) If each primitive cell has $(2\nu + 1)$ valence electrons (odd integer), the lowest $(\nu - 1)$ bands are filled and the ν-th band is half filled, and we have a metal.

(3) If there is an overlap of ν-th band and $(\nu + 1)$-th band, then we have a semimetal.

Important aspects

- The discrete atomic energy levels become quasi-continuous energy resgions, called energy bands, with certain band width.
- There may be energy gaps between different bands.
- Bands may have positive or negative curvature around the band extrema.

- In the vicinity of the band extrema one can often makes a parabolic approximation

$$E_{2,l}(k) = E_{2,0} + \frac{\hbar^2 k^2}{2m_{eff,2l}}, \qquad m_{eff,2l} = \frac{\hbar^2}{\frac{\partial^2 E_{2l}(k)}{\partial k^2}|_{k=0}}$$

$$m_{eff,2l} = \frac{\hbar^2}{\Delta a^2}$$

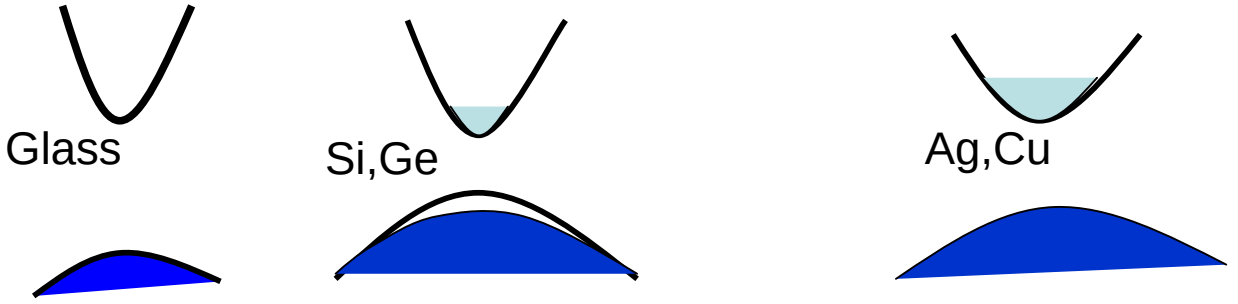
- The states in the bands are filled according to the Pauli principle, beginning with the lowest states. The last completely filled band is called valence band. The next higher band is the conduction band.

Insulator, semiconductor, and metal

(a) The conduction band is empty and separated by a large band gap from the valence band. This defines an insulator. The electrons can not be accelerated in an electric field since no empty states with slightly different E(k) are avarilable. Therefore we have no electrical conductivity.

(b) An insulator with a relatively small band gap is called semiconductor.The definition of small band gap is somewhat arbitrary, but a good operational definition is to say that the band gap should be on the order of or less than an optical photon energy. In semiconductors electrons can be moved relatively easily from the valence band into the conduction band,e.g., by absorption of visible or infrared light.

(c) If the conduction band is partly filled, we have a finite electrical conductivity and hence a metal.



Fermi surface of metals

- Fermi surface: Constant energy surface for $\epsilon = \epsilon_F$.

Symmetry of band structure: $E_n(\mathbf{k}+\mathbf{G}) = \epsilon_n(\mathbf{k})$ ... periodic in reciprocal space.

(repeated zone scheme versus extended zone scheme)

$E_n(-\mathbf{k}) = E_n(\mathbf{k})$ ... time-reversal symmetry

- Group velocity vanishes at zone boundaries for non-degenerate bands

(Pf)For $\mathbf{k} = \frac{\mathbf{G}}{2}(1+\delta)$, $\mathcal{E}(\mathbf{k}) = \mathcal{E}(-\mathbf{k}) = \mathcal{E}(-\mathbf{k}+\mathbf{G})$

$\Rightarrow \mathcal{E}[\frac{\mathbf{G}}{2}(1+\delta)] = \mathcal{E}[\frac{\mathbf{G}}{2}(1-\delta)]$

$\Rightarrow \delta\mathcal{E}/\delta\mathbf{G} = 0$ or $\frac{d\mathcal{E}}{dk} = \hbar v_g(\mathbf{k}) = 0.$

- Construction of Fermi surface:

1. Draw a sphere with volume $\nu\Omega_{BZ}$,

where ν = valency and Ω_{BZ} = volume of BZ.

2. Distort the sphere according to properties of band structure.

(i.e. smooth the edges)

Schrödinger equation for periodic part

$$e^{i\vec{k}\cdot\vec{R_n}}\psi_b(r)=\psi_b(r+R_n)$$

Bloch theorem

Band index

$$\psi_b(k,r) = e^{ikr}\, u_b(k,r)$$

Bloch function

The Schrödinger equation for the crystal electron

$$[\frac{p^2}{2m^*} + V_0(r)]\psi_b(k,r) = E_b\psi_b(k,r)$$

Crystal momentum

$$[\frac{-\hbar^2}{2m^*}\nabla^2 + \frac{\hbar}{m^*}\vec{k}\cdot\vec{p} + V_0(r)]u_b(k,r) = [E_b(k) - \frac{\hbar^2k^2}{2m^*}]u_b(k,r)$$

Orbital momentum

k·p theory

$$[-\frac{\hbar^2\nabla^2}{2m}+U(\mathbf{r})]\psi_{n\mathbf{k}}(\mathbf{r})=\mathcal{E}_n(\mathbf{k})\psi_{n\mathbf{k}}(\mathbf{r}),\ \psi_{nk}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$$

$$H_k u_{n\mathbf{k}}(\mathbf{r})=\mathcal{E}_n(\mathbf{k})u_{n\mathbf{k}}(\mathbf{r}),$$

$$\text{where } H_{\mathbf{k}}=\frac{\hbar^2}{2m}(-i\nabla+\mathbf{k})^2+U(\mathbf{r})=\frac{1}{2m}(p^2+2\hbar\mathbf{k}\cdot\mathbf{p}+k^2)+U(\mathbf{r})$$

$$\Rightarrow[-\frac{\hbar^2\nabla^2}{2m}+U(\mathbf{r})+\frac{\hbar}{m}(\mathbf{k}\cdot\mathbf{p})]u_{n\mathbf{k}}(\mathbf{r})=[\mathcal{E}_n(k)-\frac{\hbar^2k^2}{2m}]u_{n\mathbf{k}}(\mathbf{r})$$

$$\Rightarrow[H_0+\frac{\hbar}{m}(\mathbf{k}\cdot\mathbf{p})]u_{n\mathbf{k}}(\mathbf{r})=\mathcal{E'}_n(\mathbf{k})u_{n\mathbf{k}}(\mathbf{r})$$

$\frac{\hbar}{m}(\mathbf{k}\cdot\mathbf{p})$ is treated as a perturbation.

⋆ Zeroth-order solutions are: $u_{no}(r)$ with energies $\mathcal{E}_n(0)$.

$$\text{Expansion: } u_{n\mathbf{k}}(\mathbf{r})=\sum_{n'}C^n_{n'}(\mathbf{k})u_{n'o}(\mathbf{r})$$

$$\Rightarrow\sum_{n'}\{[\mathcal{E}_n(0)-\mathcal{E}'_n(\mathbf{k})]\delta_{nn'}+<u_{no}|\frac{\hbar}{m}(\mathbf{k}\cdot\mathbf{p})|u_{n'o}>\}C^n_{n'}(\mathbf{k})=0.$$

Full zone k·p theory

[Cardona & Pollak, Phys. Rev. **142** ,530 (1966)]

Keep sufficiently large number of u_{no} [e.g. lowest 15 states corresponding to $k = (000)$, 8(111)'s, and 6(200)'s].

• Comments:

Solutions obtained are good for **k** throughtout the entire Brillouin zone.

Matrix elements $< u_{n0}|\mathbf{p}|u_{n0} >$ can be computed from pseudopotential method or taken from experimental data (cyclotron resonance).

When the group theory (symmetry) is used, only the independent matrix elements need to be determined for covalent material (Si,Ge,α-Sn,etc.).

For III-V materials, one needs additional six parameters. The band structures do not have correct periodicity (not valid in repeated zone scheme)

Most accurate near the zone center, predicting best effective masses among all the models. Near the zone-center, band structures can be calculated by second-order perturbation theory.

[E. O. Kane, J. Phys. Chem. Sol. 1, (1960)]:

A. Non-degenerate case: [e.g. conduction band of most semiconductors (s-like band)]

$$E_n(\mathbf{k}) = E_n(0) + \frac{\hbar^2 k^2}{2m} + < u_{n0}|\frac{\hbar}{m}(\mathbf{k}\cdot\mathbf{p})|u_{n0} > + \sum_{n'\neq n} \frac{|< u_{n0}|\frac{\hbar}{m}\mathbf{k}\cdot\mathbf{p}|u_{n'0}>|^2}{E_n(0) - E_{n'}(0)}$$

[NOTE: $< u_{n0}|\frac{\hbar}{m}\mathbf{k}\cdot\mathbf{p}|u_{n0} >= 0$ by symmetry]

$$= E_n(0) + \frac{\hbar^2 k^2}{2} \sum_{ij} (1/m^*)_{ij} k_i k_j$$

$$\text{where } (\frac{1}{m^*})_{ij} = \frac{1}{m}\delta_{ij} + \frac{1}{m^2} \sum_{n'\neq n} \frac{p_i^{n,n'} p_j^{n,n'} + p_j^{n,n'} p_i^{n,n'}}{E_n(0) - E_{n'}(0)}$$

is called the effective-mass tensor.

$$p_i^{n,n'} \equiv < u_{n0}|p_i|u_{n'0} > .$$

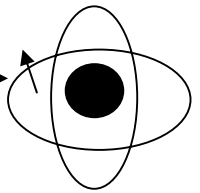
For cublic crystals (including sc, bcc, fcc, diamond, and zincblende), we have

$$E_n(\mathbf{k}) = E_n(0) + \frac{\hbar^2 k^2}{2m^*}.$$

Here the effective mass tensor is reduced to a scalar.

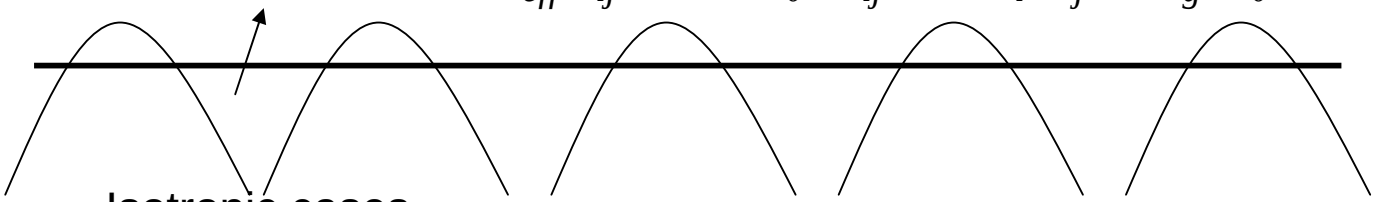
Meaning of the effective mass

- Bare electron mass m_0



- Effective mass

$$(1/m_{eff})_{ij} = 1/m_0(\delta_{ij} \pm 2p_i p_j/(E_g m_0))$$



Isotropic cases

- For electrons in conduction band +
- For electrons in valence band –
- Effective mass can be measured by cycltron resonance experiment

$$(m_{c,v})_{eff} = \frac{m_0}{1 \pm \frac{2 < c \mid p \mid v >^2}{m_0 E_g}}$$

Band with degenerated states

- Isolated atom Si $3s^2 3p^2$
- Semiconductor $3sp^3$
- In the presence of spin – orbital interaction only the total angular
- Momentum,i.e. the sum of the orbital and spin angular momentum,
- is a conserved quantity.

$$[H=\frac{p^2}{2m_0}+V_0(r)+\frac{\hbar}{4m_0^2c^2}\sigma\cdot\nabla V(r)\times\vec{p}]\psi_b(k,r)=E_b(k)\psi_b(k,r)$$

$$\{\frac{p^2}{2m_0}+V(r)+\frac{\hbar}{m_0}\vec{k}\cdot\vec{p}+\frac{\hbar}{4m_0^2c^2}[\nabla V(r)\times(\vec{p}+\vec{k})]\cdot\sigma\}u_b(k,r)=$$

$$(E_b(k)-\hbar^2k^2/2m_0)u_b(k,r)$$ ← Time reversal symmetry

B. Degenerate case: [e.g. valence bands of semiconudctors]

Let $|u_\nu(0)>$ denote the J-fold degenerate states at the zone center (Γ point). Ignore the interactions among $|u_\nu(0)>$'s first. The first-order correction to the perturbed state due coupling to other states is given by

$$|u_\nu(\mathbf{k})>=|u_\nu(0)>+\sum_{n'\neq J}\frac{<u_\nu(0)|\frac{\hbar}{m}\mathbf{k}\cdot\mathbf{p}|u_{n'}(0)>}{E_\nu(0)-E_{n'}(0)}|u_{n'}(0)>.$$

Thus, the first-order correction to the energy for states $|u_\nu>$'s are given by diagonalizing the perturbed matrix within the J-fold basis (degenerate perturbation theory)

$$H^{(1)}_{\nu,\nu'}\equiv E_\nu(0)\delta_{\nu,\nu'}+\sum_{n'\neq J}\frac{<u_\nu(0)|\frac{\hbar}{m}\mathbf{k}\cdot\mathbf{p}|u_{n'}(0)><u_{n'}(0)|\frac{\hbar}{m}\mathbf{k}\cdot\mathbf{p}|u_{\nu'}(0)>}{E_\nu(0)-E_{n'}(0)}.$$

For cubic crystals with p-like valence bands (e.g. Si, Ge, GaAs, InAs,...), we have

$$H^{(1)}=\begin{pmatrix} Ak_x^2+B(k_y^2+k_z^2) & Ck_xk_y & Ck_xk_z \\ - & Ak_y^2+B(k_x^2+k_z^2) & Ck_xk_z \\ - & - & Ak_z^2+B(k_y^2+k_x^2) \end{pmatrix},$$

where A, B, C are three band parameters, which are determined experimentally (typically via cyclotron resonance measurements).

The valence bands become 6-fold, since $J = 1 \oplus 1/2 = 1/2, 3/2$. The top four valence bands are given by $|3/2, 3/2 >= -\frac{1}{\sqrt{2}}(|x > +i|y >) \uparrow, |3/2, 1/2 >= -\frac{1}{\sqrt{6}}(|x > +i|y >) \downarrow -2|z > \uparrow$, $|3/2, -1/2 >= \frac{1}{\sqrt{6}}(|x > -i|y >) \uparrow +2|z > \downarrow$, $|3/2, -3/2 >= \frac{1}{\sqrt{2}}(|x > -i|y >) \downarrow$.

$$H^{(off)} = \frac{\hbar^2}{2m} \begin{pmatrix} A_+ & L & M & 0 \\ L^* & A_- & 0 & M \\ M^* & 0 & A_- & -L \\ 0 & M^* & -L^* & A_+ \end{pmatrix},$$

where

$$A_\pm \equiv (\gamma_1 \pm \gamma_2)(k_x^2 + k_y^2) + (\gamma_1 \mp 2\gamma_2)k_z^2,$$

$$L = -2i\sqrt{3}\gamma_3 K^- k_z,$$

$$M = -\sqrt{3}\bar{\gamma} K^{-2} + (\gamma_2 - \gamma_3)k_x k_y$$

$$K^\pm \equiv (k_x \pm i k_y),$$

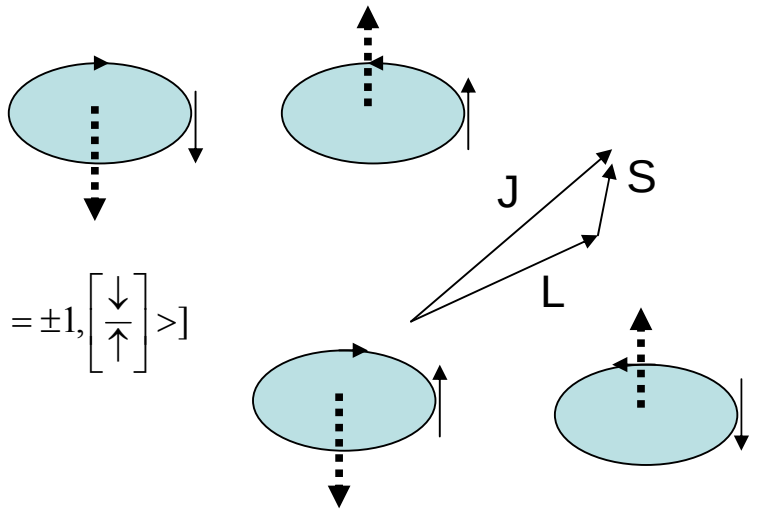
$\gamma_1, \gamma_2, \gamma_3$ are called "Luttinger parameters" and they are related to A, B, C by $\gamma_1 = \frac{1}{3}(A + B), \gamma_2 = \frac{1}{6}(A - B)$, and $\gamma_3 = \frac{1}{6}C$.

Degenerate Valence bands

- J=3/2

$$|3/2,\pm 3/2> = |m_L = \pm 1, \left[\begin{matrix}\uparrow\\ \downarrow\end{matrix}\right]>$$

$$|3/2,\pm 1/2> = \frac{1}{\sqrt{3}}[\sqrt{2}\,|m_L = 0, \left[\begin{matrix}\uparrow\\ \downarrow\end{matrix}\right]> + |m_L = \pm 1, \left[\begin{matrix}\downarrow\\ \uparrow\end{matrix}\right]>]$$

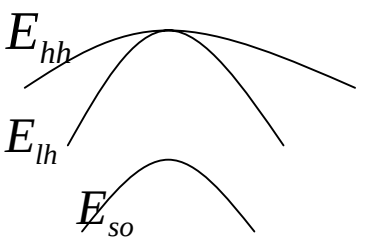


- J=1/2

$$|1/2,\pm 1/2> = \frac{1}{\sqrt{3}}[-|m_L = 0, \left[\begin{matrix}\uparrow\\ \downarrow\end{matrix}\right]> + \sqrt{2}\,|m_L = \pm 1, \left[\begin{matrix}\downarrow\\ \uparrow\end{matrix}\right]>]$$

Kane's model ×

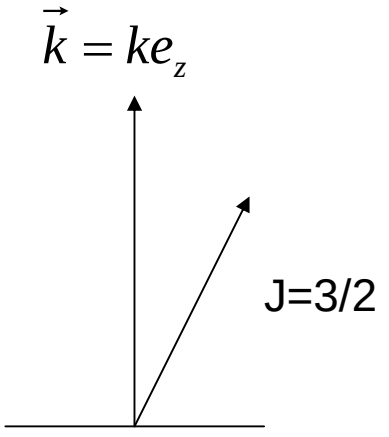
Luttinger-Kohn's model ✓



Littinger Model

Hamiltonian for heavy and light hole bands in spherical approximation

$$H_V = \frac{\hbar^2}{2m_0}\left[\left[\gamma_1 + \frac{5}{2}\gamma_2\right]k^2 - 2\gamma_2(\vec{k}\cdot\vec{J})^2\right]$$



For $m_J = \pm\frac{3}{2}$ $\quad E_{hh} = (\gamma_1 - 2\gamma_2)\frac{\hbar^2 k^2}{2m_0}$

For $m_J = \pm\frac{1}{2}$ $\quad E_{lh} = (\gamma_1 + 2\gamma_2)\frac{\hbar^2 k^2}{2m_0}$

$$\frac{1}{m_{hh}} = \frac{1}{m_0}(\gamma_1 - 2\gamma_2) \longrightarrow (1) \qquad \frac{1}{m_{lh}} = \frac{1}{m_0}(\gamma_1 + 2\gamma_2) \longrightarrow (2)$$