STEFANO
CURTAROLO

- BLOCK THEORY
- SCHRODINGER IN MOM. SPACE
- BANDS
- GROUP VELOCITIES
- EFFECTIVE MASSES
- DENSITIES OF LEVELS
- BRILLOUIN ZONES ....

QMPS 1 - QMPS 2

BG 1 - BG 20

BLOCK THEOREM.

$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$ $\qquad V(r+R) = V(r)$ $\forall R \in$ Bravais $\forall r \in$ coordinates = direct space

$\Rightarrow$ $\boxed{\psi_{nk}(r) = e^{ikr} \cdot u_{nk}(r)}$ $\qquad u_{nk}(r) = u_{nk}(r+R)$ BLOCK FUNCTION.

AND/OR

$\boxed{\psi_{nk}(r+R) = e^{ik\cdot R}\psi_{nk}(r)}$

Proof.

pick function $f(r)$ $\Rightarrow$

define Translation operator (R) $\hat{T}_R$

$\hat{T}_R(f(r)) = f(r+R)$ $\qquad r \to r+R$

$\hat{H}$ is periodic: $\hat{H}(r)\psi(r) =$

$\hat{T}_R\,\hat{H}(r)\psi(r) = \hat{H}(r+R)\psi(r+R) = \hat{H}(r)\,\hat{T}_R\,\psi(r)$

$\Rightarrow$ $\hat{T}_R\hat{H} = \hat{H}\hat{T}_R \Rightarrow$

$H\cdot T_R - T_R H \equiv [H, T_R] = 0$

commutator $\forall R \in$ Bravais

PHYSICS: they can be measured at the same time

COMPATIBLE OPERATORS

QM. properties:

- if 2 operator (matrices) commute $(AB = BA)$
- then it is possible to find a basis of ~~eigen~~vectors which are eigenvectors of both operator at the same time.

$\Rightarrow$ basis $\Rightarrow$ elements $\{\psi_n\}$

$\Rightarrow$ $\hat{H}\psi_n = E_n\psi_n$ $\qquad \psi_n$ eigenvectors (functions) of $\hat{H}, \hat{T}_R$

$\hat{T}_R\psi_n = C(R)\psi_n$

$$\hat{T}_{R'}\hat{T}_R\,\psi_n(r) = \hat{T}_{R'}\,C(R)\,\psi_n(r) = C(R')\,C(R)\,\psi_n(r)$$

($\hat{T}_R\psi_n(r) = C(R)\psi_n(r)$)

$$r \to r+R \to r+R+R' \Rightarrow \quad \hat{T}_{R'}\hat{T}_R = \hat{T}_{R+R'}$$

↑ group — operators form a group

$$\hat{T}_{R'}\hat{T}_R\,\psi_n(r) = C(R'+R)\,\psi_n(r)$$

$$\Rightarrow \quad C(R'+R) = C(R')\,C(R)$$

$\forall R, R' \in$ Bravais lattice.

~~$R = n\bar{a}_1$~~ multiple vectors ~~$\Rightarrow$~~

~~$R' = n'\bar{a}_1$~~

~~$C(n\bar{a}_1 + n'\bar{a}_1) = C(n'\bar{a}_1)\,C(n\bar{a}_1)$~~

~~$\Rightarrow C(n\bar{a}_1) = e^{i 2\pi n a_1}$~~ ~~exponential~~

$C(0) = 1$

$C(-R) = C(R)^{-1}$

~~$\frac{1}{C(R)} = -C(R)$~~

$= \perp$

$C(0) = 0$

exponential

$C(R) = e^{iK\cdot\bar{R}}$

$R \in$ Bravais lattice

$K \in$ generic vector in momentum space (continuous, not Reciprocal)

$$T_R\,\psi_n(r) = \boxed{\psi_{nK}(r+R) = e^{iK\cdot\bar{R}}\,\psi_{nK}(r)}$$

I write $\forall r \in$ D.S.

$$\psi_{nK}(r) \equiv e^{iK\cdot r}\,u_{nK}(r)$$ dependence on n

$$\psi_{nK}(r+R) = e^{iKr}e^{iKR}\,u_{nK}(r+R)$$

$$= e^{iK\cdot\bar{R}}\,e^{iKr}\,u_{nK}(r)$$

$u_{nK}(r+R) \equiv u_{nK}(r)$ PERIODIC.

SCHRÖDINGER IN MOMENTUM SPACE

TRUE HAMILTONIAN

$$\hat{H}\phi = \left[\sum_{i \in \text{electrons}} \hat{T}_i + \sum_{j \in \text{ions}} \hat{T}_j + \sum_{\substack{ii' \\ \text{electrons}}} V_{ee}(r_i - r_{i'}) + \sum_{\substack{i \in \text{electrons} \\ j \in \text{ions}}} V_{eI}(r_i - R_j) + \sum_{\substack{jj' \\ \text{IONS}}} V_{II}(R_j - R_{j'}) \right] \phi$$

$$= +i\hbar \frac{\partial}{\partial t} \phi(r_1, r_2, r_3 \ldots R_1 R_2 R_3 \ldots t)$$

IONS are heavy and slow $v_{T\,\text{ROOM}}$ $\Rightarrow$ CLASSICAL (not e/proton) MECHANICS & FEEL CLOUD OF electrons around

$$\left[\sum_{j \in \text{IONS}} \hat{T}_j + \sum_{jj'} V_{II} + \sum_{ij} V_{eI} \right]$$

$\Rightarrow$ POSITIONS & DYNAMICS

$\Rightarrow$ (FROZEN IONS APPROX = BORN OPPENHEIMER)

$\Rightarrow$ given ions position, electron follow immediately $v_{T\,\text{Fermi}} \sim 500\,\text{Km/s}$

$$\Rightarrow \left[\sum_i \hat{T}_i + \sum_{ii} V_{ee}(r_i - r_{i'}) + \sum_{ij} V_{eI}(r_i - R_j) \right] \psi(\ ) = +i\hbar \partial_t \psi$$

APPROX independent electrons $\Rightarrow$ ONLY SPIN $\uparrow\downarrow$ for every state $\Rightarrow$ neglect all correlations

all electrons

Wrong but acceptable

$$\left[\sum_i \hat{T}_i + \sum_{ij} V_{eI}(r_i - R_j) \right] \psi(r_1, r_2, r_3 \ldots t)$$

$P(r_1, r_2 \ldots) = P(r_1) P(r_2) \ldots$

AFTER SPIN APPROX, the electrons are decoupled independent

$\Rightarrow \psi = \psi_1(r_1, t)\, \psi_2(r_2, t) \ldots$ all equal

$\Rightarrow$ we can solve only ONE

$$\left[\hat{T}_i + \sum_j V_{eI}(r_i - R_j) \right] \psi = +i\hbar \partial_t \psi$$

$\Rightarrow$ end up with SINGLE ELECTRON SCHROEDINGER EQUATION

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + \sum_j V(r-R_j)\right]\psi = +i\hbar\frac{\partial}{\partial t}\psi(r,t)$$

Stationary $\Rightarrow = E\psi(r)$

V is periodic $\quad V(r+R) = V(r)$

$r \in DS$

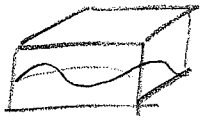
$R \in BL$

BLOCK SOLUTIONS (periodic)

$$\psi_{nk}(r) = e^{ik\cdot r}u_{nk}(r)$$

$$\psi_{nk}(r+R) = e^{ik\cdot R}\psi_{nk}(r)$$

HOW WE DID? $\rightarrow$ 1 solution every $k = n\frac{2\pi}{L}$ ... ect....



BORN-VON KARMAN PERIODIC SOLID (CUBE) $L \to \infty$ macroscopic

$\psi(r+L) = \psi(r) \Rightarrow \psi$ periodic in L $\Rightarrow$ FOURIER ! ($L = Na$)

$$\psi(r) = \sum_{k\in KS} c_k e^{ik\cdot r}$$

$k \in$ M.Space = k-space

$$k \in \left\{\left(n_1\frac{2\pi}{L}, n_2\frac{2\pi}{L}, n_3\frac{2\pi}{L}\right)\right\}_{L\to\infty}$$

$V(r+R) = V(r) \Rightarrow V$ periodic in BL $\Rightarrow$ FOURIER

$G \in$ R. Lattice (K-space)

$$V(r) = \sum_{G\in RL} V_G e^{iG\cdot r}$$

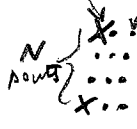
$$G \in \left\{\left(n_1 b_1, n_2 b_2, n_3 b_3\right)\right\}$$

$\downarrow$ cubic

$$= \left\{\left(n_1\frac{2\pi}{a}, n_2\frac{2\pi}{a}, n_3\frac{2\pi}{a}\right)\right\}$$

$$V_G \equiv \frac{1}{N_{cell}}\int_{N_{cell}} d^3r\, V(r) e^{-iG\cdot r}$$

RL NS $L = Na \Rightarrow$ G grid is much coarser than k-space



BG 2.

PROPERTIES V real $\xrightarrow{\mathcal{F}}$ $V_{-G} = V_G^*$

KINETIC

$$\hat{T}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi = \sum_{K\in KS} -\frac{\hbar^2}{2m} c_K (iK)^2 e^{iK\cdot r} = \sum_{K\in KS} \frac{\hbar^2 K^2}{2m} c_K e^{iK\cdot r}$$

POTENTIAL

$$V(r)\psi(r) = \left(\sum_{G\in RL} V_G e^{iG\cdot r}\right)\left(\sum_{K\in KS} c_K e^{iK\cdot r}\right) =$$

$$= \sum_{\substack{G\in RL \\ K\in KS}} V_G\, c_K\, e^{i(K+G)\cdot r}$$

↑ sum over all k-space, $K+G$ is still a sum over all space because $G \in RL$, $K \in KS$

$$\Rightarrow \quad K+G \longrightarrow K' = K+G \in KS$$

$$K = K' - G$$

$$= \sum_{\substack{G\in RL \\ K'\in KS}} V_G\, c_{K'-G}\, e^{iK'\cdot r} \quad \Rightarrow \quad K' \Longleftrightarrow K \text{ change name}$$

$$= \sum_{\substack{G\in RL \\ K\in KS}} V_G\, c_{K-G}\, e^{iK\cdot r}$$

$\Rightarrow$

SCHROEDINGER: $\hat{T}\psi + V\psi = E\psi$

$\Rightarrow$

$$\sum_{K\in KS} e^{iK\cdot r}\left[\frac{\hbar^2 K^2}{2m} c_K + \sum_{G\in RL} V_G\, c_{K-G}\right] = \sum_{K\in KS} E c_K e^{iK\cdot r}$$

MORE COMPACT FORM.

$$\sum_{K\in KS} e^{iKr}\left[\left(\frac{\hbar^2K^2}{2m}-E\right)C_K+\sum_{G\in RL}V_G C_{K-G}\right]=0$$

PLANE WAVES ~~are~~ Free particles → solution of free particles H operator ⇒ orthogonal set

$$\Rightarrow \sum_{K\in KS} e^{iKr}[\ \ ]=0 \iff [\ \ ]=0 \quad \forall K\in KS$$

$$\boxed{\left(\frac{\hbar^2K^2}{2m}-E\right)C_K+\sum_{G\in RL}V_G C_{K-G}=0 \qquad \forall K\in KS}$$

Change of variable $K\in KS$

$K_{NEW} \to K_{OLD} - Q$ where Q is vector that brings K in 1st Brillouin zone

$\Rightarrow K_{OLD} = K_{NEW} - Q$

$$\left(\frac{\hbar^2}{2m}\underbrace{(K_{NEW}-Q)}_{B.Z}{}^2-E\right)C_{K-Q}+\sum_{G\in RL}V_G C_{K-Q-G}=0$$

$\forall K\in$ BRILLOUN
$\forall Q\in R.L$

$G_{NEW} = G_{OLD} + Q$

$\sum_{G_{OLD}} = \sum_{G_{NEW}}$ because spans all R.L

$G_{OLD} = G_{NEW} - Q$

$$\boxed{\left(\frac{\hbar^2}{2m}(K-Q)^2-E\right)C_{K-Q}+\sum_{G\in R.L}V_{G-Q}C_{K-G}=0}$$

$\forall K\in$ BRILLOUN
$\forall Q\in R.L$

SCHROEDINGER IN MOMENTUM SPACE

HOW MANY?

$\forall k$ BRILLOUIN: choose one k.

N = number of unit cells in MACROSCOPIC SOLID

$$(\quad) c_{k-q} + \sum_{G \in} V_{G-q}\, c_{k-G} = 0$$

LINEAR COUPLING

$$V_{-q}\, c_k + c_{k-G'} V_{G'-q} + c_{k-G''} V_{G''-q} \cdots$$

$$\begin{pmatrix} (\quad)+V_0 & V_{G-q} & V_{G'-q} \\ V_{G-q} & (\quad)+V_0 & V_{G-q} \\ V_{G-q} & V_{G-q} & (\quad)+V_0 \end{pmatrix} \begin{pmatrix} c_{k-G''-q} \\ c_k \\ c_{k-G'+q} \end{pmatrix} \#RL = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

↑ all the R.L.

1 Hard mode

$\Rightarrow$ N linear equations between $c_k, c_{k-q}, c_{k-2q} \ldots$

all the c with index that differ of points in R.L

$\forall k$ in B.L $\Rightarrow$ get N linear equations between c_k, c_{k+q} $\forall q$ in R.L

$\Downarrow$

NOW we need to use BLOCH

EQUATION

$$\left(\frac{\hbar^2}{2m}(k-Q)^2 - E\right) c_{k-Q} + \sum_{G \in R.L} V_{G-Q}\, c_{k-G} = 0$$

pick one → $\forall k \in BZ$ } $(k-Q)^2$ is repeated!
span rows of matrix → $\forall Q \in R.L.$ }

SOLUTIONS ARE CONTINUOUS in $k \in BZ$ but not at the borders

System of equations in $\{c_\kappa,\ c_{\kappa+G},\ c_{\kappa+2G}\ldots\}$
↑ ↑
when matrix differ of R.L.

$$\Rightarrow \psi(r) = \sum_{k \in ks} c_k e^{ik\cdot r} = \sum_{\substack{G \in RL \\ k \in BZ}} c_{k-G}\, e^{i(\kappa-G)r} = \Sigma \psi_\kappa$$

$$\Rightarrow \psi_k(r) = \sum_{G \in RL} c_{k-G}\, e^{i(k-G)r}$$

$$= e^{ikr} \sum_{G \in RL} c_{k-G}\, e^{-iGr}$$

Remember the Bloch $\psi_{nk}(r) = e^{ikr} u_{nk}(r)$
↑
index of solution

$$\psi_k(r) = e^{ikr} \underbrace{\sum_{G \in RL} c_{k-G}\, e^{-iGr}}_{u_{nk}(r)}$$

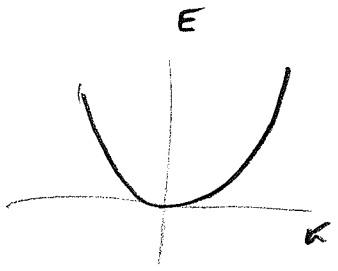
$$\Rightarrow u_{nk}(r) = \sum_{G \in RL} c_{k-G}\, e^{-iGr} = \text{Bloch}$$

↑ energy levels → (more than 1 solution)

FREE ELECTRONS

$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi \Rightarrow \psi = e^{ikr}$

$E = \frac{\hbar^2 k^2}{2m}$



$\hat{p} = -i\hbar\nabla \Rightarrow \quad p = \hbar k$ [p ∝ k]

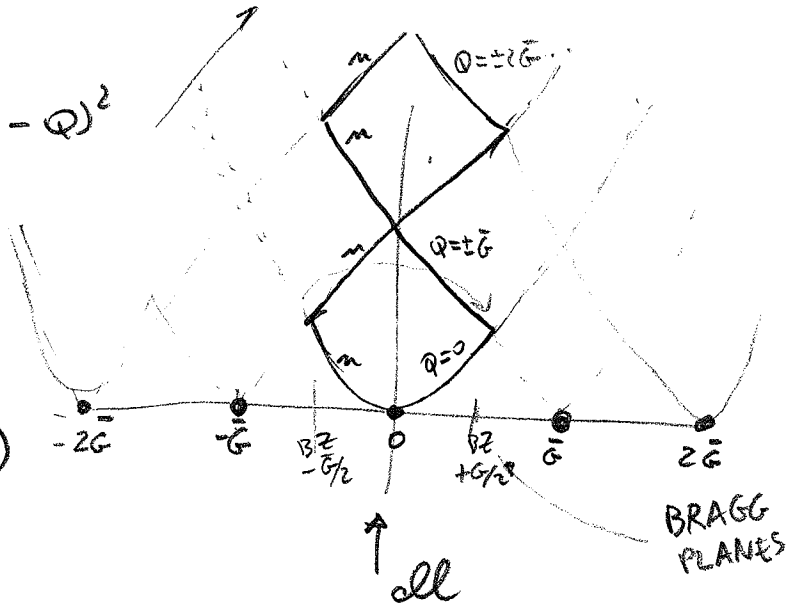
wave vector = momentum

FREE ELECTRON IN SOMETHING PERIODIC $\Rightarrow V_G = 0 \ \forall G \in RL$

$\left(\frac{\hbar^2}{2m}(k-Q)^2 - E\right) c_{k-Q} = 0$ $\quad \forall k \in BZ$, $\forall Q \in R.L$

$\Rightarrow$

$E = \frac{\hbar^2}{2m}(k-Q)^2$



Solutions ψ_{nk}

periodic in R.L. { eigenvalues $\Rightarrow E_n(k+G) = E_n(k)$

{ eigenfunctions $\psi_{n,k+G}(R) = \psi_{nk}(r)$

all information is in B.Z.

$\hat{p} = -i\hbar\nabla \Rightarrow$

$-i\hbar\nabla\psi_{nk} = -i\hbar\nabla e^{ikr}u_{nk}(r)$

$= \hbar k\psi_{nr} - i\hbar e^{ikr}\nabla u_{nk}(r)$

$\Rightarrow$ p ~~∝~~ k NO! MORE

$= \hbar k\, e^{ikr}u_{nk} - i\hbar e^{ikr}\nabla u_{nk}$

$= e^{ikr}(\hbar k - i\hbar\nabla)u_{nk}$

p = momentum

k = crystal momentum which is not a "traslational momentum"

$\Rightarrow$ SCH. EQ for u is similar to ψ but with $\hbar(k - i\nabla)$ instead of $-i\hbar\nabla$

$\Rightarrow \left[\frac{\hbar^2}{2m}(k-i\nabla)^2 + V(r)\right] u_k(r) = E\,u_k(r)$

$\Rightarrow$ n solutions!!

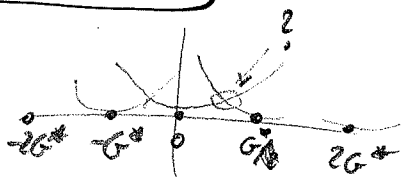
NON FREE ELECTRONS IN SOMETHING PERIODIC (NEARLY FREE)

$$\left(\frac{\hbar^2}{2m}(k-q)^2 - E\right) c_{k-q} + \sum_G V_{G-q}\, c_{k-q-G} = 0$$

$k \in BZ$, $q \in R.L$

$$\boxed{\left(\frac{\hbar^2}{2m}k^2 - E\right) c_k + \sum_{G \in R.L.} V_G\, c_{k-G} = 0 \quad \forall k \in ks}$$

1D → near border B.Z. $\pm \frac{G^*}{2}$



2 parabola highting, the are starting from 0 ($E(k)$) and the other starting from $G^* \Rightarrow E(G^*_{-k})$ which is the one translated from $(-k)$

NEARLY FREE = weak potential V_G rapidly decaying.

$$\Rightarrow V_{G+K} << V_G \qquad \left(V \sim \frac{1}{2} \quad V_G \sim \frac{1}{G^2}\right)$$

$E(k)$ against $E(-k)$ around B.Z

$k \approx G^*/2 \qquad -k^* \approx -G^*/2$

V_0 not necessary

$$\begin{cases} \left(\frac{\hbar^2}{2m}\left(\frac{G}{2}\right)^{*2} - \epsilon\right) c_{G^*/2} + V_{G^*}\, c_{\left(\frac{G^*}{2} - G^*\right)} = 0 \\ \left(\frac{\hbar^2}{2m}\left(\frac{-G^*}{2}\right)^2 - \epsilon\right) * c_{-G^*/2} + V_{-G^*}\, c_{-\frac{G^*}{2}+G^*} = 0 \end{cases}$$

$\left(-\frac{G^*}{2} + G^* = +G^*/2\right)$

$E\left(\pm\frac{G^*}{2}\right) = \frac{\hbar^2}{2m}\left(\pm\frac{G^*}{2}\right)^2 \qquad V_{-G^*} = V_{G^*}^*$ because V real

V_G centrosimetric

$\Rightarrow$ separate in plane wave and $\forall k \in BZ$
$\forall Q \in R.L.$

$\Rightarrow$ SOLUTION ARE continuous and Periodic $\forall k \in B.Z.$

—○—

Non vanishing mean velocity

$$\boxed{v_n(k) = \frac{1}{\hbar} \nabla_k E_n(k)}$$

$$\boxed{\left(\frac{\hbar^2}{m}\right)_{ij} = \frac{\partial^2 E_{n,k}}{\partial k_i \partial k_j}}$$

MEAN
electrons move
forever in a direction
without degradation!
(ghost DRUDE)

Effective mass $\Rightarrow$

small mass $\Rightarrow$ fast

big mass $\Rightarrow$ slow

$$\Rightarrow \begin{cases} (E_{G^*/2} - E)\, C_{G^*/2} + V_{G^*}\, C_{-G^*/2} = 0 \\ (E_{-G^*/2} - E)\, C_{-G^*/2} + V_{-G^*}\, C_{G^*/2} = 0 \end{cases}$$

$$V_{-G^*} = V_{G^*}^*$$

$$= \begin{pmatrix} E_{G^*/2} - E & V_{G^*} \\ V_{G^*}^* & E_{-G^*/2} - E \end{pmatrix} \begin{pmatrix} C_{G^*/2} \\ C_{-G^*/2} \end{pmatrix} = 0$$

$$\downarrow$$

$$\begin{pmatrix} E_{G^*/2} & V_{G^*} \\ V_{G^*}^* & E_{-G^*/2} \end{pmatrix} \begin{pmatrix} C_{G^*/2} \\ C_{-G^*/2} \end{pmatrix} = E \begin{pmatrix} C_{G^*/2} \\ C_{-G^*/2} \end{pmatrix}$$

↑ are Hermitian $\Rightarrow$ real solutions!

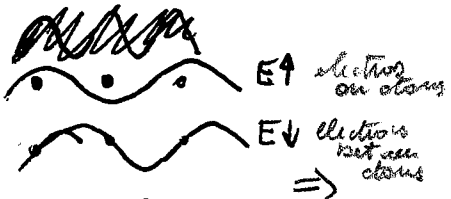
$\text{Det}[\ ] = 0$

$$E = \frac{E_{G^*/2} + E_{-G^*/2}}{2} \pm \sqrt{\left(\frac{E_{G^*/2} - E_{-G^*/2}}{2}\right)^2 + V_{G^*}^* V_{G^*}}$$

$$V_{G^*}^* V_{G^*} = |V_G|^2$$

↓ semi Sum

↓ semi difference



$\Rightarrow$

AT BRAGG PLANE $E_{G^*/2} = E_{-G^*/2}$

$\Rightarrow E = E_{G^*/2} \pm V_{G^*} \Rightarrow 2V_G =$ BAND GAP

near band edge $E_{G^*/2} \pm V_G = \frac{\hbar^2}{2m} \Delta k \Delta k$

SOLUTIONS

$C_{G^*} = \pm C_{G^*/2}$

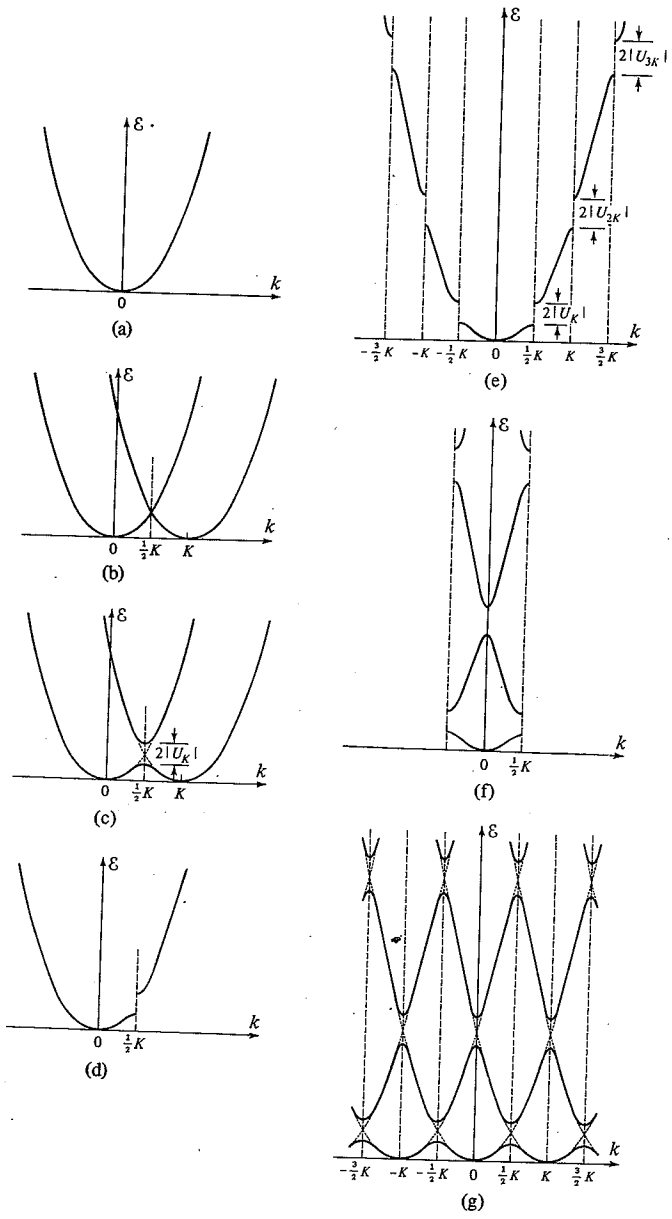


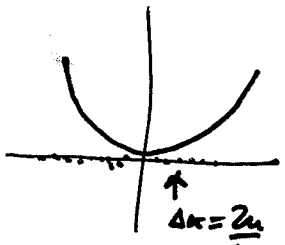
Figure 9.4
(a) The free electron ε vs. k parabola in one dimension. (b) Step 1 in the construction to determine the distortion in the free electron parabola in the neighborhood of a Bragg "plane," due to a weak periodic potential. If the Bragg "plane" is that determined by K, a second free electron parabola is drawn, centered on K. (c) Step 2 in the construction to determine the distortion in the free electron parabola in the neighborhood of a Bragg "plane." The degeneracy of the two parabolas at $K/2$ is split. (d) Those portions of part (c) corresponding to the original free electron parabola given in (a). (e) Effect of all additional Bragg "planes" on the free electron parabola. This particular way of displaying the electronic levels in a periodic potential is known as the *extended-zone scheme.* (f) The levels of (e), displayed in a *reduced-zone scheme.* (g) Free electron levels of (e) or (f) in a *repeated-zone scheme.*

One can also emphasize the periodicity of the labeling in k-space by periodically extending Figure 9.4f throughout all of k-space to arrive at Figure 9.4g, which emphasizes that a particular level at k can be described by any wave vector differing from k by a reciprocal lattice vector. This representation is the *repeated-zone scheme* (see page 142). The reduced-zone scheme indexes each level with a k lying in the first zone, while the extended-zone scheme uses a labeling emphasizing continuity with the free electron levels. The repeated-zone scheme is the most general representation,

BG 10b

DENSITY OF LEVELS

→ FREE ELECTRONS



$k = \left\{ n_1\left(\frac{2\pi}{L}\right), n_2\left(\frac{2\pi}{L}\right), n_3\left(\frac{2\pi}{L}\right) \right\}$ BORN-VON KARMAN

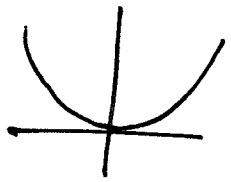
need a quantity

$Q \Rightarrow \langle Q \rangle$ = average over all states

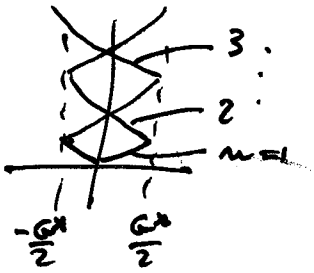
$$Q = \underbrace{2}_{\text{Spin}} \sum_{k \in K.Space} Q(k) \xrightarrow[V\to\infty]{} \underbrace{\frac{Q}{V}}_{\text{per unit volume}} = 2\int_{K.Space} \frac{d^3k}{(2\pi)^3} Q(k) \xrightarrow[\varepsilon]{\text{if } Q(|k|)} \int g(\varepsilon) Q(\varepsilon) d\varepsilon$$

$g(\varepsilon)$: density of electrons

→ IN PERIODIC POTENTIAL



$\Rightarrow$



$$\Rightarrow Q = \langle Q \rangle = 2 \sum_{n,\, k \in BZ} Q(k) \xrightarrow[V\to\infty]{} 2\int_{BZ} \frac{d^3k}{(2\pi)^3} \sum_n Q_n(k)$$

$$\xrightarrow[\varepsilon]{} 2\int g(\varepsilon) Q(\varepsilon) d\varepsilon$$

$$g(\varepsilon) = \sum_n g_n(\varepsilon)$$

$g_n(\varepsilon)$: extract all the cases in which $\varepsilon_n(k)$ is identical to ε

$$g_n(\varepsilon) \equiv \int_{BZ} 2\frac{d^3k}{(2\pi)^3} \delta(\varepsilon_n - \varepsilon(k))$$

BETTER WAY (PHYSICS)

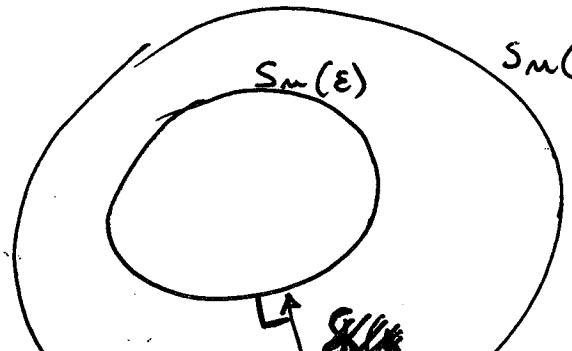
$$g_n(\varepsilon)\,d\varepsilon = \frac{2}{V}\cdot\left\{\begin{array}{l}\#\text{ of allowed wave vector}\\ \text{in the } n\text{th band in energy}\\ \text{range } \varepsilon \to \varepsilon+d\varepsilon\end{array}\right\}$$

per unit volume

$\Rightarrow$ Volume of k-space between $\varepsilon, \varepsilon+d\varepsilon$ (all k so that $\varepsilon \le \varepsilon(k) \le \varepsilon+d\varepsilon$) divided by the volume for each point $(\Delta k)^3 = \frac{(2\pi)^3}{V}$

$$\Rightarrow g_n(\varepsilon)\,d\varepsilon = \frac{2}{(2\pi)^3}\int \frac{d^3k}{(2\pi)^3}\cdot\left\{\begin{array}{l}1 \text{ if } \varepsilon(k)\in[\varepsilon,\varepsilon+d\varepsilon]\\ 0 \text{ otherwise}\end{array}\right\}$$

$d\varepsilon \to 0 \Rightarrow$ volume becomes surface times $d\varepsilon$



$$\Rightarrow g_n(\varepsilon) = \frac{2}{(2\pi)^3}\int_{\text{volume}}^{d\varepsilon} = \frac{2}{(2\pi)^3}\int_{S_n} dS\cdot\delta k(\bar{k})$$

$\delta k \perp dS \Rightarrow S = S(\varepsilon = \text{constant})$

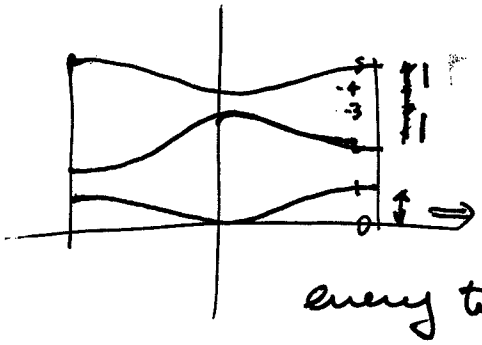
$\Rightarrow \nabla_k \varepsilon =$ vector $\perp$ to S with magnitude equal to rate of change $d\varepsilon$ along $\perp$ direction with magnitude $dk \Rightarrow$

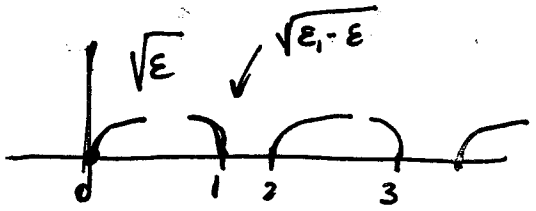
BG 12 $\quad \varepsilon + d\varepsilon = \varepsilon + |\nabla_k \varepsilon_n(k)|\,\delta k(\bar{k}) \Rightarrow \delta k = \dfrac{d\varepsilon}{|\nabla_k \varepsilon_n(k)|} \Rightarrow$

$$g_n(\varepsilon) \overset{d\varepsilon}{=} \int \frac{ds}{(4\pi)^2} \frac{d\varepsilon}{|\nabla_k \varepsilon_n|}$$

$$\Rightarrow \boxed{g_n(\varepsilon) = 2\int \frac{ds}{(2\pi)^3} \frac{1}{|\nabla_k \varepsilon_n(k)|}}$$

~~troubles when~~ $\nabla_k \varepsilon = 0$
but still integrable.





every time a band starts/dies we get a $\sqrt{\varepsilon}$, with right & "direction" and right "magnitude"

$$g(\varepsilon) = \frac{m}{\hbar^2 \pi^2} \sqrt{\frac{2m\varepsilon}{\hbar^2}} \qquad \varepsilon > 0$$

$|\nabla_k \varepsilon| = 0$ van Hove singularities

Equation (8.63) and the analysis leading to it will be applied in subsequent chapters.[27] Here we only note the following quite general property of the density of levels:

Because $\varepsilon_n(\mathbf{k})$ is periodic in the reciprocal lattice, bounded above and below for each n, and, in general, everywhere differentiable, there must be values of $\mathbf{k}$ in each primitive cell at which $|\nabla\varepsilon| = 0$. For example, the gradient of a differentiable function vanishes at local maxima and minima, but the boundedness and periodicity of each $\varepsilon_n(\mathbf{k})$ insure that for each n there will be at least one maximum and minimum in each primitive cell.[28]

When the gradient of ε_n vanishes, the integrand in the density of levels (8.63) diverges. It can be shown that in three dimensions[29] such singularities are integrable, yielding finite values for g_n. However, they do result in divergences of the slope, $dg_n/d\varepsilon$. These are known as *van Hove singularities.*[30] They occur at values of ε for which the constant energy surface $S_n(\varepsilon)$ contains points at which $\nabla\varepsilon_n(\mathbf{k})$ vanishes. Since derivatives of the density of levels at the Fermi energy enter into all terms but the first in the Sommerfeld expansion,[31] one must be on guard for anomalies in low-temperature behavior if there are points of vanishing $\nabla\varepsilon_n(\mathbf{k})$ on the Fermi surface.

Typical van Hove singularities are shown in Figure 8.3 and are examined in Problem 2, Chapter 9.

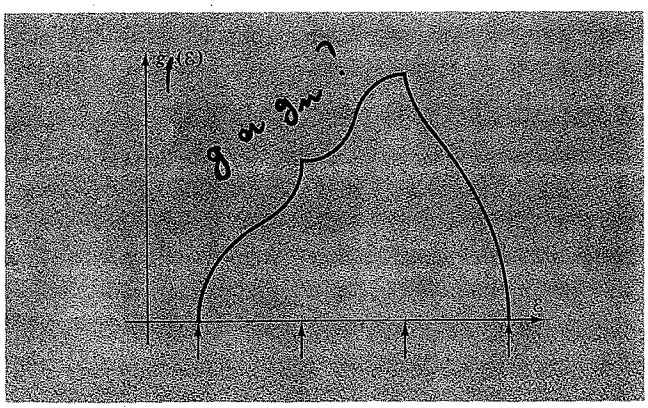


Figure 8.3
Characteristic van Hove singularities in the density of levels, indicated by arrows at right angles to the ε-axis.

This concludes our discussion of the general features of one-electron levels in a periodic potential.[32] In the following two chapters we consider two very important, but quite different, limiting cases, which provide concrete illustrations of the rather abstract discussions in this chapter.

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[27] See also Problem 2.

[28] A very general analysis of how many points of vanishing gradient must occur is fairly complex. See, for example, G. Weinreich, *Solids*, Wiley, New York, 1965, pp. 73–79.

[29] In one dimension $g_n(\varepsilon)$ itself will be infinite at a van Hove singularity.

[30] Essentially the same singularities occur in the theory of lattice vibrations. See Chapter 23.

[31] See, for example, Problem 2f, Chapter 2.

[32] Problem 1 pursues the general analysis somewhat further in the tractable but somewhat misleading case of a one-dimensional periodic potential.

but is highly redundant, since the same level is shown many times, for all equivalent wave vectors k, $k \pm K$, $k \pm 2K$, ...

ENERGY-WAVE-VECTOR CURVES IN THREE DIMENSIONS

In three dimensions the structure of the energy bands is sometimes displayed by plotting $\mathcal{E}$ vs. $\mathbf{k}$ along particular straight lines in k-space. Such curves are generally shown in a reduced-zone scheme, since for general directions in k-space they are not periodic. Even in the completely free electron approximation these curves are surprisingly complex. An example is shown in Figure 9.5, which was constructed by plotting, as $\mathbf{k}$ varied along the particular lines shown, the values of $\mathcal{E}^0_{\mathbf{k}-\mathbf{K}} = \hbar^2(\mathbf{k} - \mathbf{K})^2/2m$ for all reciprocal lattice vectors $\mathbf{K}$ close enough to the origin to lead to energies lower than the top of the vertical scale.

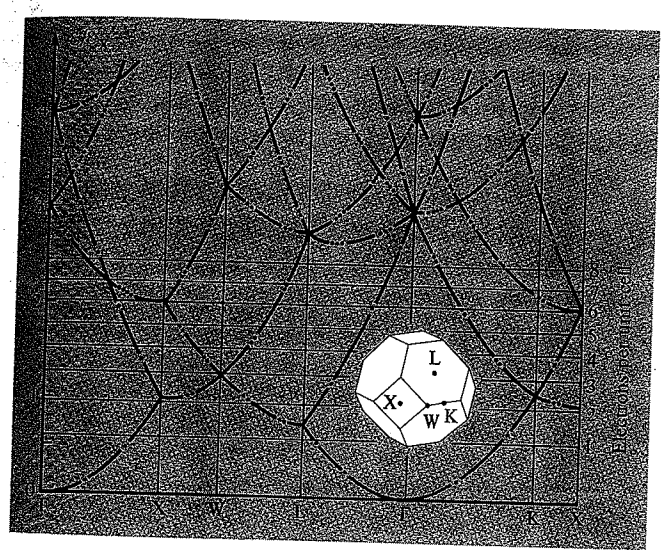

Figure 9.5
Free electron energy levels for an fcc Bravais lattice. The energies are plotted along lines in the first Brillouin zone joining the points $\Gamma(\mathbf{k} = \mathbf{0})$, K, L, W, and X. $\mathcal{E}_X$ is the energy at point X ($[\hbar^2/2m][2\pi/a]^2$). The horizontal lines give Fermi energies for the indicated numbers of electrons per primitive cell. The number of dots on a curve specifies the number of degenerate free electron levels represented by the curve. (From F. Herman, in *An Atomistic Approach to the Nature and Properties of Materials*, J. A. Pask, ed., Wiley, New York, 1967.)

Note that most of the curves are highly degenerate. This is because the directions along which the energy has been plotted are all lines of fairly high symmetry, so points along them are likely to be as far from several other reciprocal lattice vectors as they are from any given one. The addition of a weak periodic potential will in general remove some, but not necessarily all, of this degeneracy. The mathematical theory of groups is often used to determine how such degeneracies will be split.

THE ENERGY GAP

Quite generally, a weak periodic potential introduces an "energy gap" at Bragg planes. By this we mean the following:

Figure 9.4
(a) The free electron $\mathcal{E}$ vs. k parabola in one dimension. (b) Step 1 in the construction to determine the distortion in the free electron parabola in the neighborhood of a Bragg "plane," due to a weak periodic potential. If the Bragg "plane" is that determined by K, a second free electron parabola is drawn, centered on K. (c) Step 2 in the construction to determine the distortion in the free electron parabola in the neighborhood of a Bragg "plane." The degeneracy of the two parabolas at $K/2$ is split. (d) Those portions of part (c) corresponding to the original free electron parabola given in (a). (e) Effect of all additional Bragg "planes" on the free electron parabola. This particular way of displaying the electronic levels in a periodic potential is known as the *extended-zone scheme*. (f) The levels of (e), displayed in a *reduced-zone scheme*. (g) Free electron levels of (e) or (f) in a *repeated-zone scheme*.

ıg in k-space by periodically
/e at Figure 9.4g, which em-
ıy any wave vector differing
ı is the *repeated-zone scheme*
:vel with a k lying in the first
:mphasizing continuity with
most general representation,

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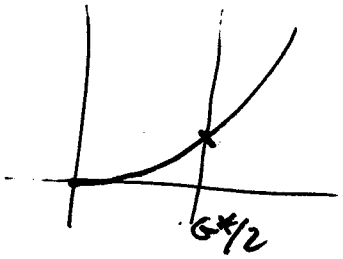
BANDS & EXCITATIONS

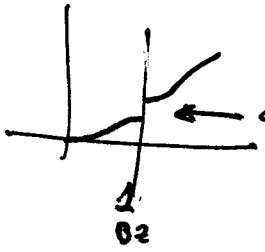
1) SHOW FREE ELECTRON FOR FCC.

EFFECT of weak potential



- no potential ⇒ free electron curve (in function of k) is discontinuous

- potential



← discontinuity in k and in ε ⇒

every time an electron crosses BZ (BRAGG plane) gets a discontinuity.

⇒ DEFINE Further BZ

- (n+1) BZ is the set of points not in the (n-1) BZ that can be reached from the nBZ crossing 1 Bragg Plan
- nBZ = set of points reachable crossing n-1 Bragg planes

Show Pics.

When $U_{\mathbf{K}} = 0$, as $\mathbf{k}$ crosses a Bragg plane the energy changes continuously from the lower root of (9.26) to the upper, as illustrated in Figure 9.4b. When $U_{\mathbf{K}} \neq 0$, this is no longer so. The energy only changes continuously with $\mathbf{k}$, as the Bragg plane is crossed, if one stays with the lower (or upper) root, as illustrated in Figure 9.4c. To change branches as $\mathbf{k}$ varies continuously it is now necessary for the energy to change *discontinuously* by at least $2|U_{\mathbf{K}}|$.

We shall see in Chapter 12 that this mathematical separation of the two bands is reflected in a physical separation: When the action of an external field changes an electron's wave vector, the presence of the energy gap requires that upon crossing the Bragg plane, the electron must emerge in a level whose energy remains in the original branch of $\mathcal{E}(\mathbf{k})$. It is this property that makes the energy gap of fundamental importance in electronic transport properties.

BRILLOUIN ZONES

Using the theory of electrons in a weak periodic potential to determine the complete band structure of a three-dimensional crystal leads to geometrical constructions of great complexity. It is often most important to determine the Fermi surface (page 141) and the behavior of the $\mathcal{E}_n(\mathbf{k})$ in its immediate vicinity.

In doing this for weak potentials, the procedure is first to draw the free electron Fermi sphere centered at $\mathbf{k} = \mathbf{0}$. Next, one notes that the sphere will be deformed in a manner of which Figure 9.6 is characteristic[11] when it crosses a Bragg plane and in a correspondingly more complex way when it passes near several Bragg planes. When the effects of all Bragg planes are inserted, this leads to a representation of the Fermi surface as a fractured sphere in the extended-zone scheme. To construct the portions of the Fermi surface lying in the various bands in the repeated-zone scheme one can make a similar construction, starting with free electron spheres centered about all reciprocal lattice points. To construct the Fermi surface in the reduced-zone scheme, one can translate all the pieces of the single fractured sphere back into the first zone through reciprocal lattice vectors. This procedure is made systematic through the geometrical notion of the higher Brillouin zones.

Recall that the first Brillouin zone is the Wigner-Seitz primitive cell of the reciprocal lattice (pages 73 and 89), i.e. the set of points lying closer to $\mathbf{K} = \mathbf{0}$ than to any other

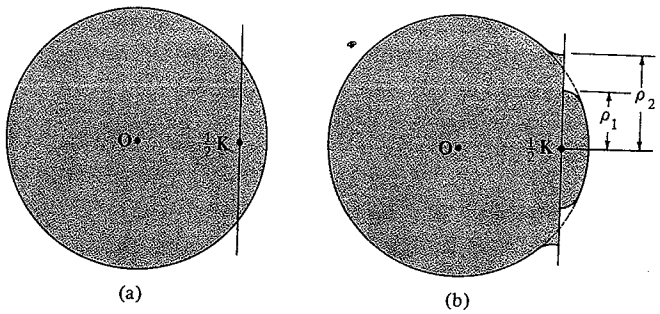


Figure 9.6
(a) Free electron sphere cutting Bragg plane located at $\frac{1}{2}\mathbf{K}$ from the origin ($U_{\mathbf{K}} = 0$). (b) Deformation of the free electron sphere near the Bragg plane when $U_{\mathbf{K}} \neq 0$. The constant-energy surface intersects the plane in two circles, whose radii are calculated in Problem 1.

[11] This follows from the demonstration on page 159 that a constant-energy surface is perpendicular to a Bragg plane when they intersect, in the nearly free electron approximation.

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reciprocal lattice point. Since Bragg planes bisect the lines joining the origin to points of the reciprocal lattice, one can equally well define the first zone as the set of points that can be reached from the origin without crossing any Bragg planes.[12]

Higher Brillouin zones are simply other regions bounded by the Bragg planes, defined as follows:

The *first Brillouin zone* is the set of points in k-space that can be reached from the origin without crossing *any* Bragg plane. The *second Brillouin zone* is the set of points that can be reached from the first zone by crossing only one Bragg plane. The $(n + 1)$*th Brillouin zone* is the set of points not in the $(n - 1)$th zone that can be reached from the nth zone by crossing only one Bragg plane.

Alternatively, the *nth Brillouin zone* can be defined as the set of points that can be reached from the origin by crossing $n - 1$ Bragg planes, but no fewer.

These definitions are illustrated in two dimensions in Figure 9.7. The surface of the first three zones for the fcc and bcc lattices are shown in Figure 9.8. Both definitions emphasize the physically important fact that the zones are bounded by Bragg planes. Thus they are regions at whose surfaces the effects of a weak periodic potential are important (i.e., first order), but in whose interior the free electron energy levels are only perturbed in second order.

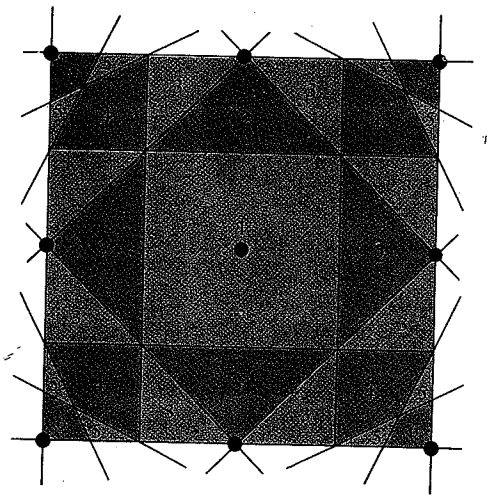

Figure 9.7
Illustration of the definition of the Brillouin zones for a two-dimensional square Bravais lattice. The reciprocal lattice is also a square lattice of side b. The figure shows all Bragg planes (lines, in two dimensions) that lie within the square of side $2b$ centered on the origin. These Bragg planes divide that square into regions belonging to zones 1 to 6. (Only zones 1, 2, and 3 are entirely contained within the square, however.)

It is very important to note that each Brillouin zone is a primitive cell of the reciprocal lattice. This is because the nth Brillouin zone is simply the set of points that have the origin as the nth nearest reciprocal lattice point (a reciprocal lattice point $\mathbf{K}$ is nearer to a point $\mathbf{k}$ than $\mathbf{k}$ is to the origin if and only if $\mathbf{k}$ is separated from the origin by the Bragg plane determined by $\mathbf{K}$). Given this, the proof that the nth Brillouin zone is a primitive cell is identical to the proof on page 73 that the Wigner-Seitz cell (i.e., the first Brillouin zone) is primitive, provided that the phrase "nth nearest neighbor" is substituted for "nearest neighbor" throughout the argument.

[12] We exclude from consideration points lying *on* Bragg planes, which turn out to be points common to the surface of two or more zones. We define the zones in terms of their interior points.

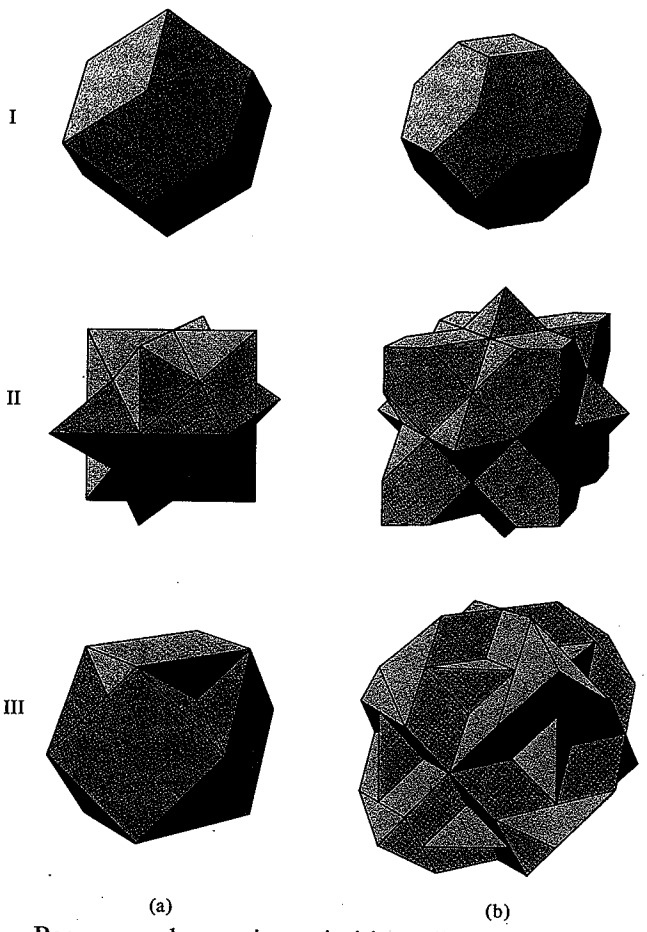

Figure 9.8
Surfaces of the first, second, and third Brillouin zones for (a) body-centered cubic and (b) face-centered cubic crystals. (Only the *exterior* surfaces are shown. It follows from the definition on page 163 that the *interior* surface of the nth zone is identical to the exterior surface of the $(n-1)$th zone.) Evidently the surfaces bounding the zones become increasingly complex as the zone number increases. In practice it is often simplest to construct free electron Fermi surfaces by procedures (such as those described in Problem 4) that avoid making use of the explicit form of the Brillouin zones. (After R. Lück, doctoral dissertation, Technische Hochschule, Stuttgart, 1965.)

Because each zone is a primitive cell, there is a simple algorithm for constructing the branches of the Fermi surface in the repeated-zone scheme[13]:

1. Draw the free electron Fermi sphere.
2. Deform it slightly (as illustrated in Figure 9.6) in the immediate vicinity of every Bragg plane. (In the limit of exceedingly weak potentials this step is sometimes ignored to a first approximation.)
3. Take that portion of the surface of the free electron sphere lying within the nth Brillouin zone, and translate it through all reciprocal lattice vectors. The resulting surface is the branch of the Fermi surface (conventionally assigned to the nth band) in the repeated-zone scheme.[14]

[13] The representation of the Fermi surface in the repeated-zone scheme is the most general. After surveying each branch in its full periodic splendor, one can pick that primitive cell which most lucidly represents the topological structure of the whole (which is often, but by no means always, the first Brillouin zone).

[14] An alternative procedure is to translate the pieces of the Fermi surface in the nth zone through those reciprocal lattice vectors that take the pieces of the nth zone in which they are contained, into the first zone. (Such translations exist because the nth zone is a primitive cell.) This is illustrated in Figure 9.9. The Fermi surface in the repeated-zone scheme is then constructed by translating the resulting first zone structures through all reciprocal lattice vectors.

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Figure 9.8
Surfaces of the first, second, and third Brillouin zones for (a) body-centered cubic and (b) face-centered cubic crystals. (Only the *exterior* surfaces are shown. It follows from the definition on page 163 that the *interior* surface of the nth zone is identical to the exterior surface of the $(n-1)$th zone.) Evidently the surfaces bounding the zones become increasingly complex as the zone number increases. In practice it is often simplest to construct free electron Fermi surfaces by procedures (such as those described in Problem 4) that avoid making use of the explicit form of the Brillouin zones. (After R. Lück, doctoral dissertation, Technische Hochschule, Stuttgart, 1965.)

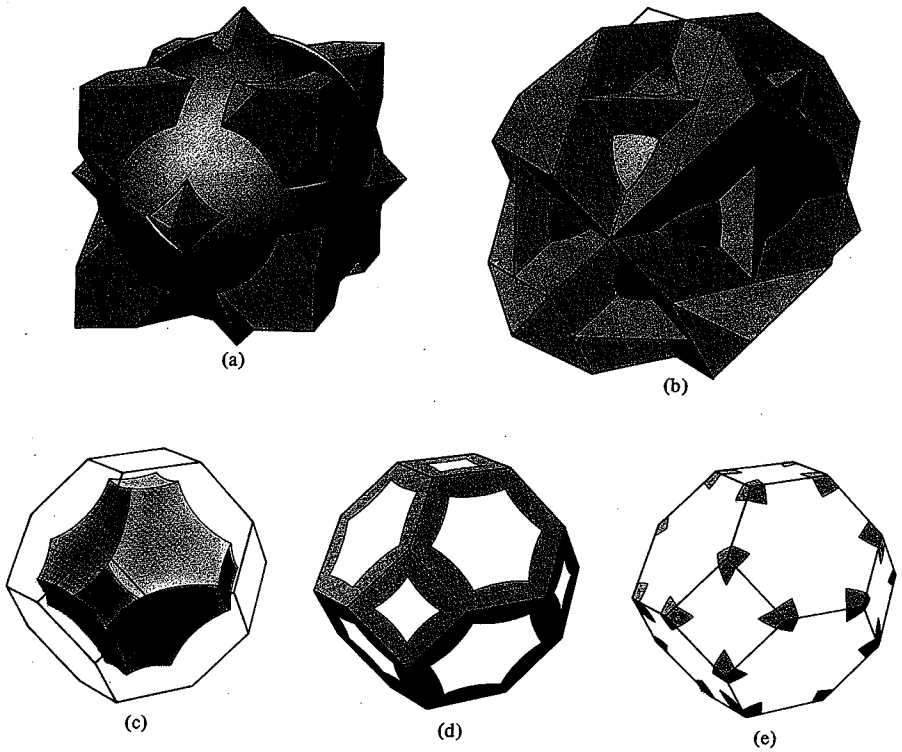

Figure 9.9
The free electron Fermi sphere for a face-centered cubic metal of valence 4. The first zone lies entirely within the interior of the sphere, and the sphere does not extend beyond the fourth zone. Thus the only zone surfaces intersected by the surface of the sphere are the (exterior) surfaces of the second and third zones (cf. Figure 9.8b). The second-zone Fermi surface consists of those parts of the surface of the sphere lying entirely within the polyhedron bounding the second zone (i.e., all of the sphere except the parts extending beyond the polyhedron in (a)). When translated through reciprocal lattice vectors into the first zone, the pieces of the second-zone surface give the simply connected figure shown in (c). (It is known as a "hole surface"; the levels it encloses have higher energies than those outside). The third-zone Fermi surface consists of those parts of the surface of the sphere lying outside of the second zone (i.e., the parts extending beyond the polyhedron in (a)) that do not lie outside the third zone (i.e., that are contained within the polyhedron shown in (b)). When translated through reciprocal lattice vectors into the first zone, these pieces of sphere give the multiply connected structure shown in (d). The fourth-zone Fermi surface consists of the remaining parts of the surface of the sphere that lie outside the third zone (as shown in (b)). When translated through reciprocal lattice vectors into the first zone they form the "pockets of electrons" shown in (e). For clarity (d) and (e) show only the intersection of the third and fourth zone Fermi surfaces with the surface of the first zone. (From R. Lück, *op. cit.*)

algorithm for constructing
cheme[13]:

mmediate vicinity of every
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sphere lying within the nth
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ranslating the resulting first zone

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