

PHYS 342/555

Condensed Matter in a Nutshell

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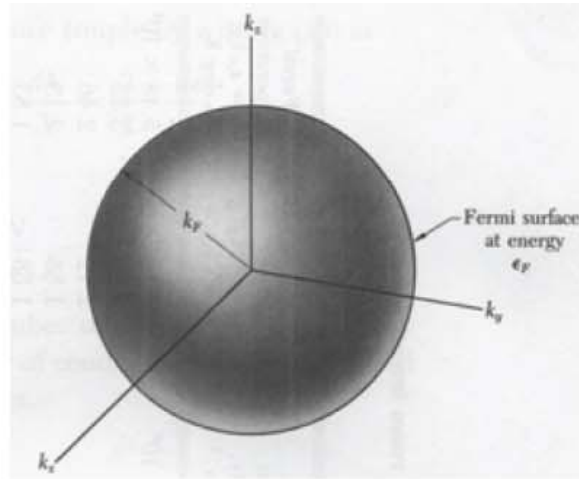
Chapter 8: Fermi surfaces and metals

Lecture in pdf format will be available at:

<http://www.phys.utk.edu>

Fermi surfaces and metals

The Fermi surface is the surface of constant energy ε_F in \vec{k} space. The electrical properties of the metal are determined by the shape of the Fermi surface.



Since the energy of a one-electron level is directly proportional to k^2 , when N is enormous the occupied region will be indistinguishable from a sphere. The radius of this sphere is called k_F (F for Fermi), and its volume Ω is $4\pi k_F^3 / 3$. The # of allowed \vec{k} within the sphere is:

$$\left(\frac{4\pi k_F^3}{3}\right)\left(\frac{V}{8\pi^3}\right) = \frac{k_F^3}{6\pi^2} V. \text{ Since each allowed } k\text{-value leads to two}$$

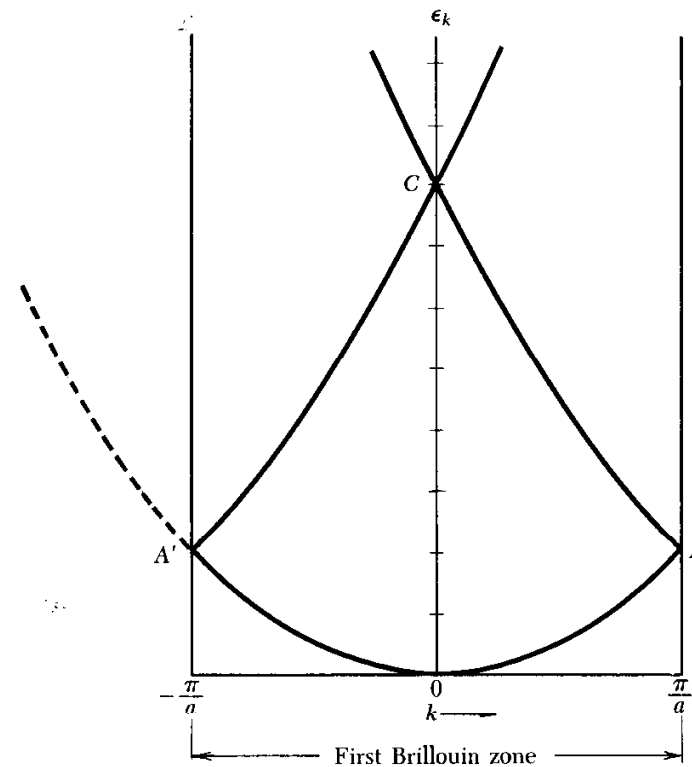
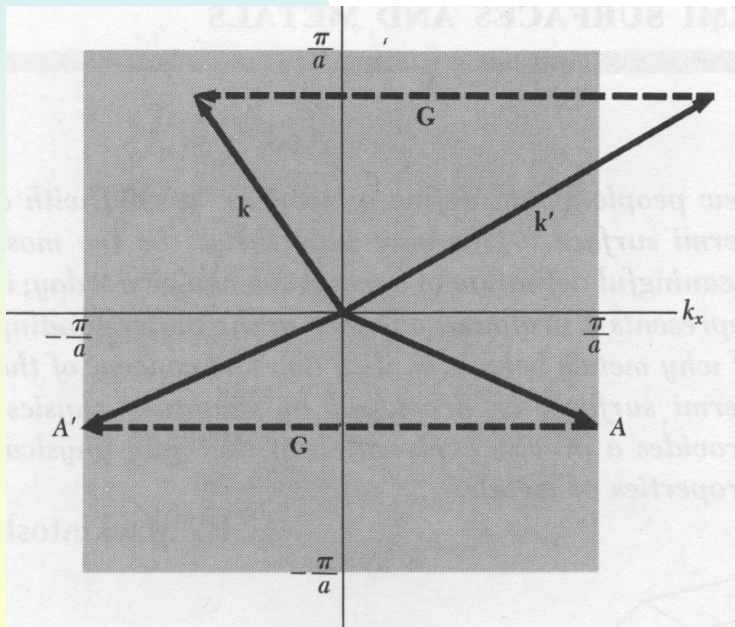
one-electron levels, we must have $N = 2 \frac{k_F^3}{6\pi^2} V = \frac{k_F^3}{3\pi^2} V$.

If electron density is $n = N/V$, then we have $n = k_F^3 / 3\pi^2$.

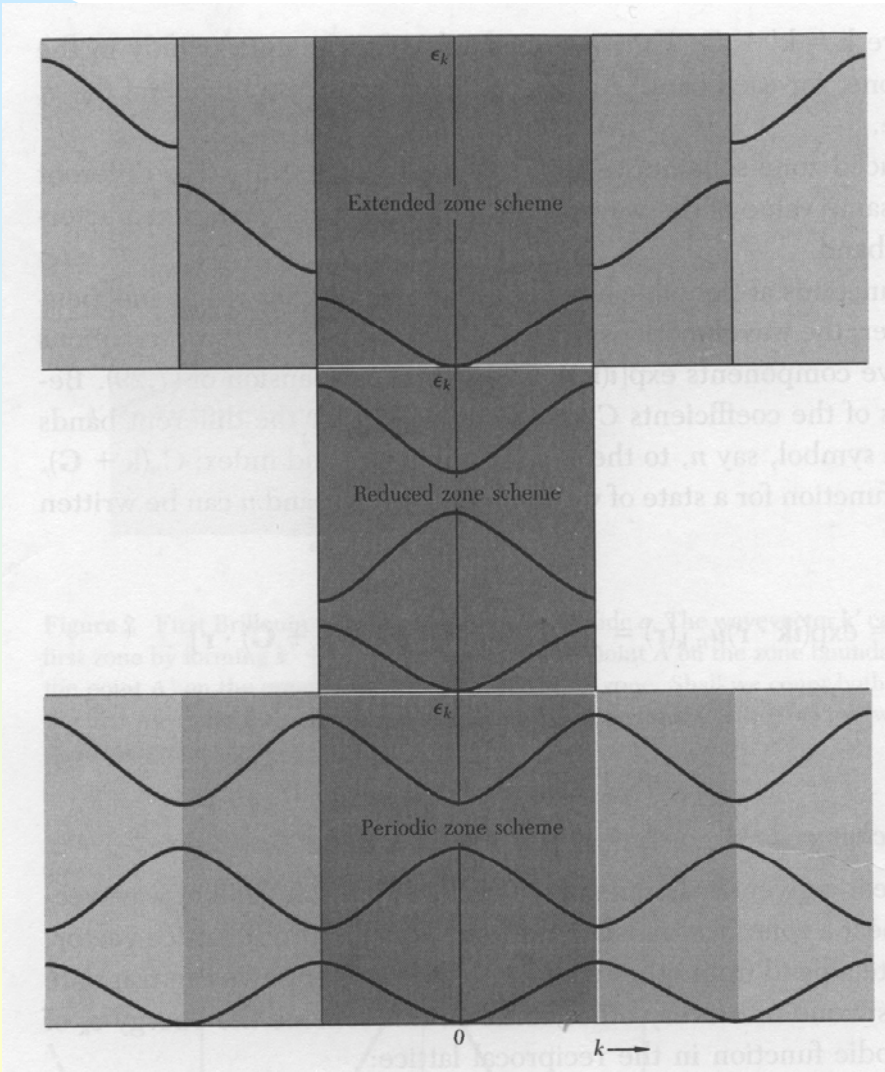
Reduced zone scheme

For a Bloch function written as $\psi_{\vec{k}'}(\vec{r}) = e^{i\vec{k}' \cdot \vec{r}} u_{\vec{k}'}(\vec{r})$, with \vec{k}' outside the first Brillouin zone, we have $\vec{k} = \vec{k}' + \vec{G}$.

$$\psi_{\vec{k}'}(\vec{r}) = e^{i\vec{k}' \cdot \vec{r}} u_{\vec{k}'}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \left(e^{-i\vec{G} \cdot \vec{r}} u_{\vec{k}'}(\vec{r}) \right) \equiv e^{i\vec{k} \cdot \vec{r}} u_{\vec{k}}(\vec{r}) = \psi_{\vec{k}}(\vec{r})$$



Periodic zone scheme



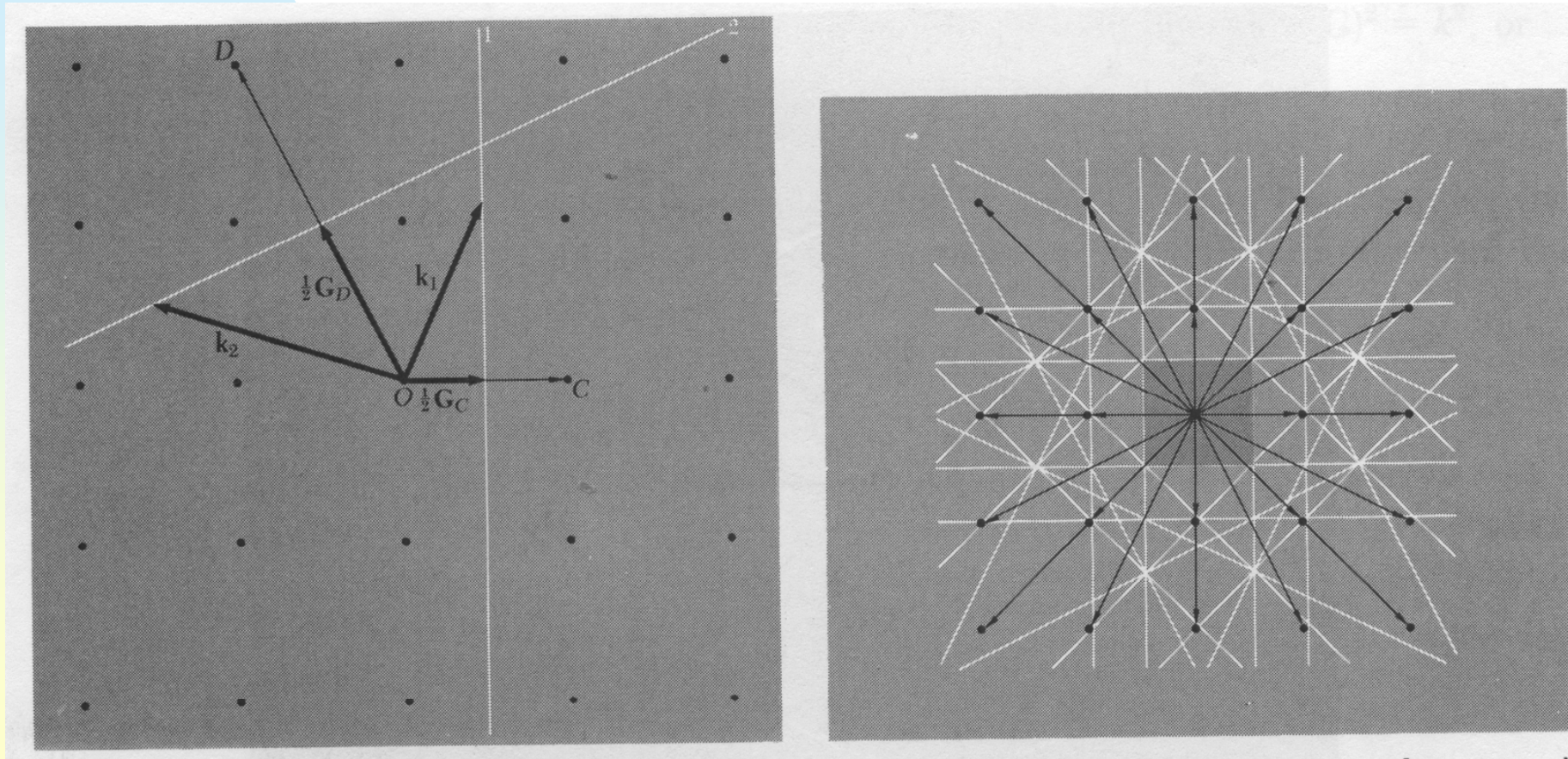
The energy $\epsilon_{\vec{k}}$ of a band is periodic function in reciprocal lattice: $\epsilon_{\vec{k}} = \epsilon_{\vec{k} + \vec{G}}$. This is known as the periodic zone scheme.

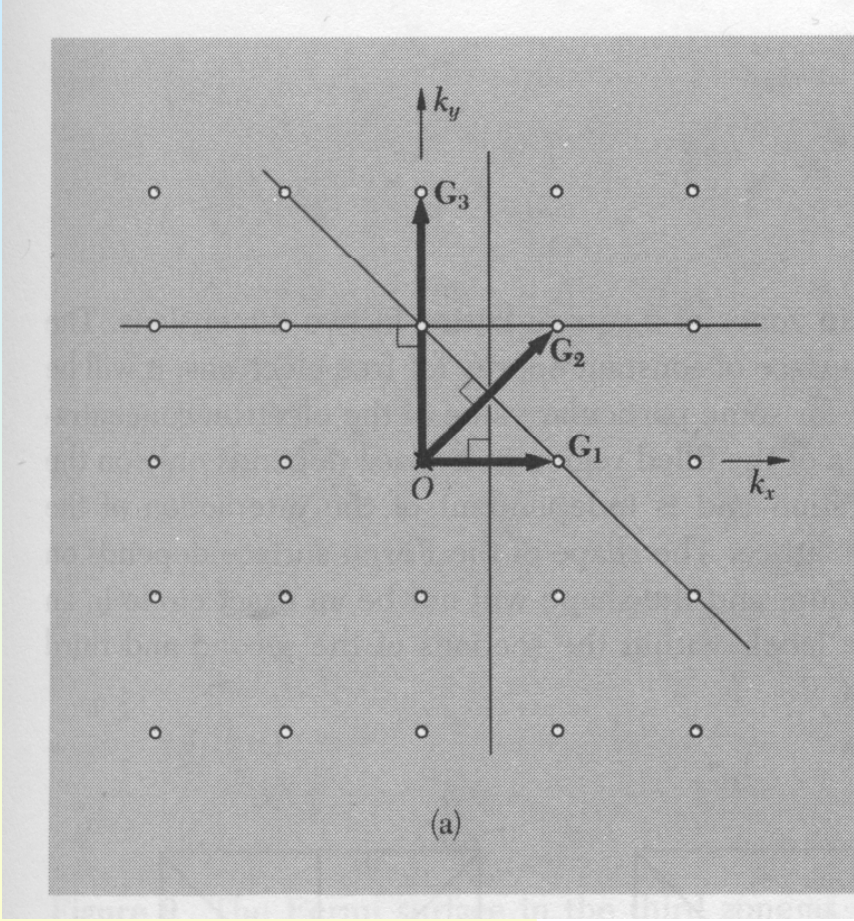
In a simple cubic lattice, the dispersion has form:

$$\epsilon_{\vec{k}} = -\alpha - 2\gamma(\cos k_x a + \cos k_y a + \cos k_z a).$$

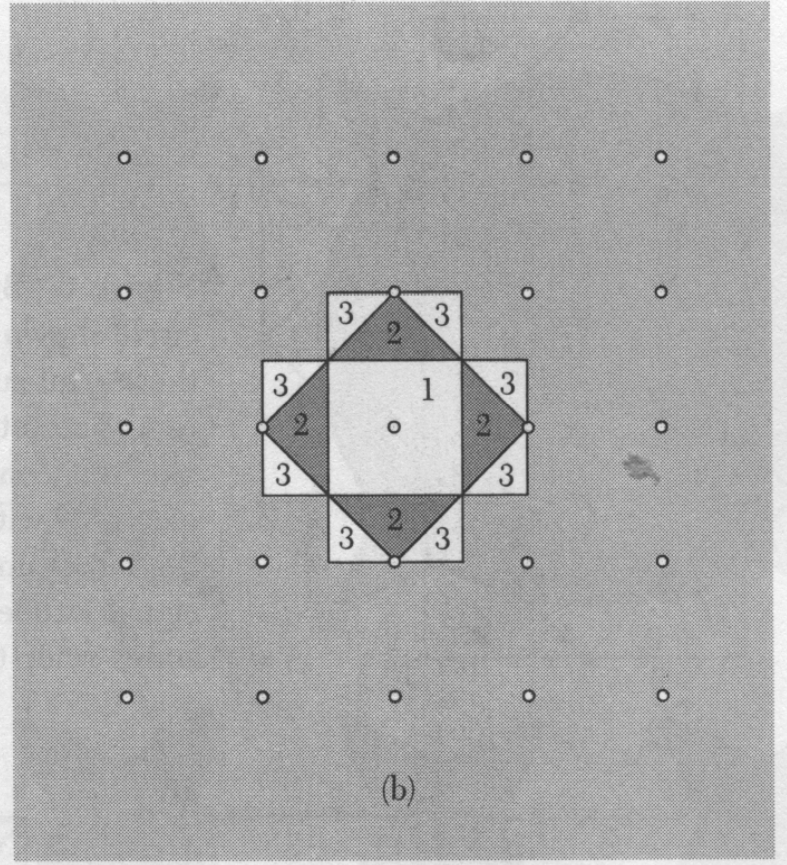
Construction of Fermi surfaces

The equation of the zone boundaries is $2\vec{k} \cdot \vec{G} + G^2 = 0$ and is satisfied if \vec{k} terminates on the plane normal to \vec{G} at the midpoint of \vec{G} .

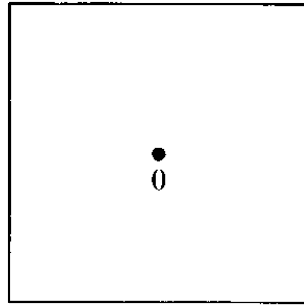
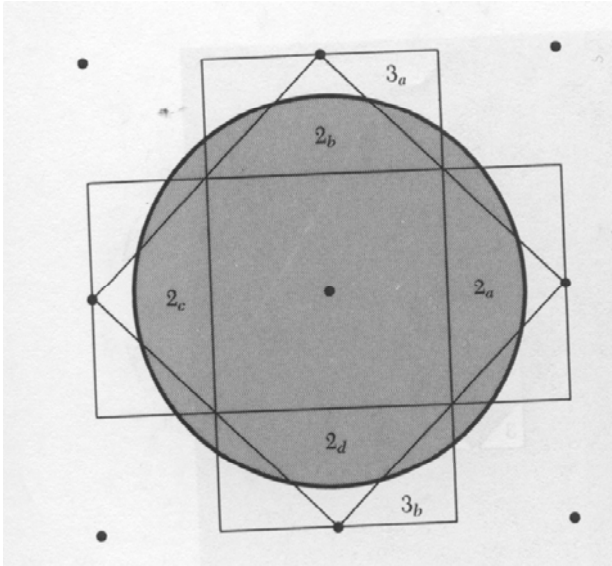




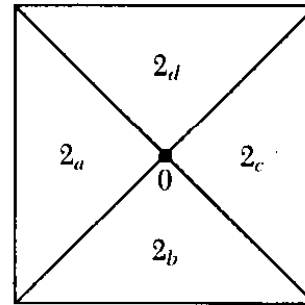
(a)



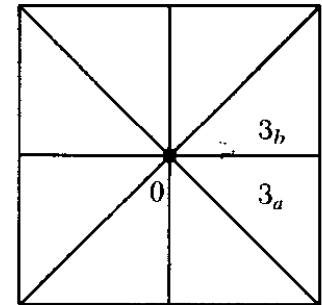
(b)



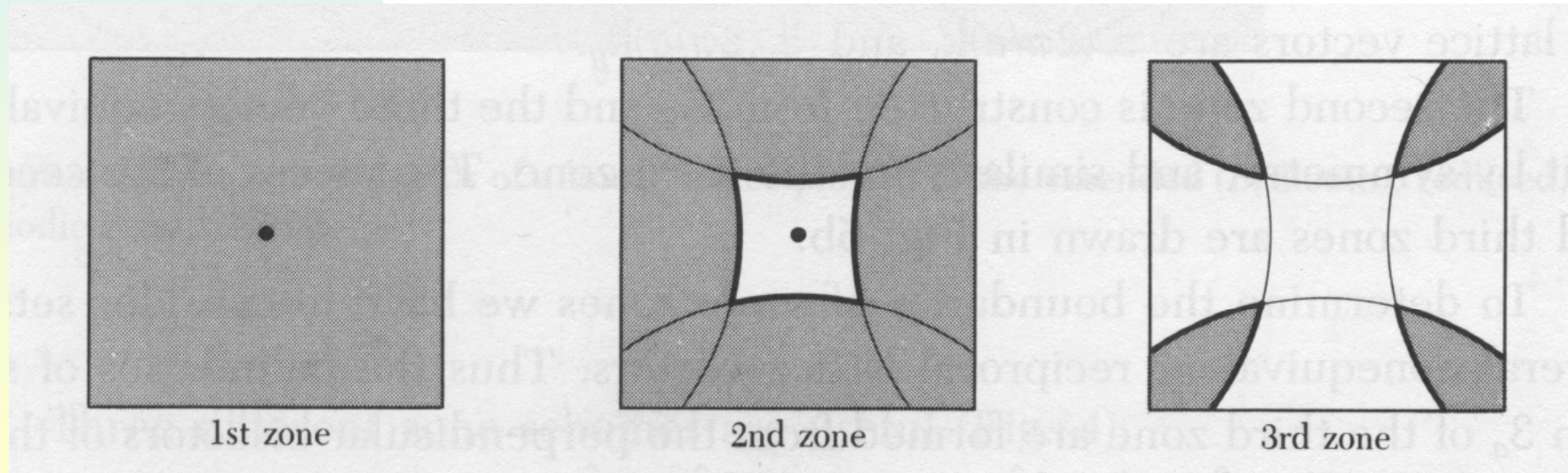
1st zone



2nd zone



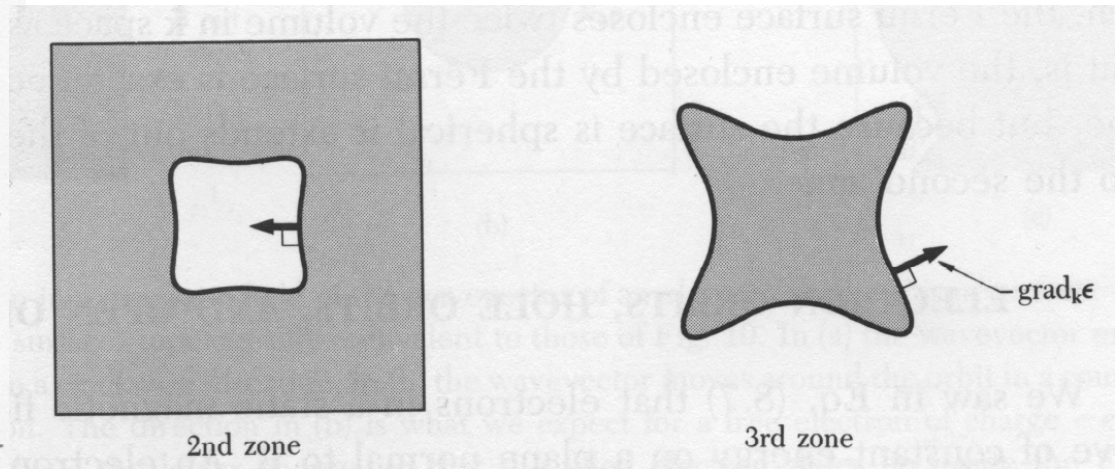
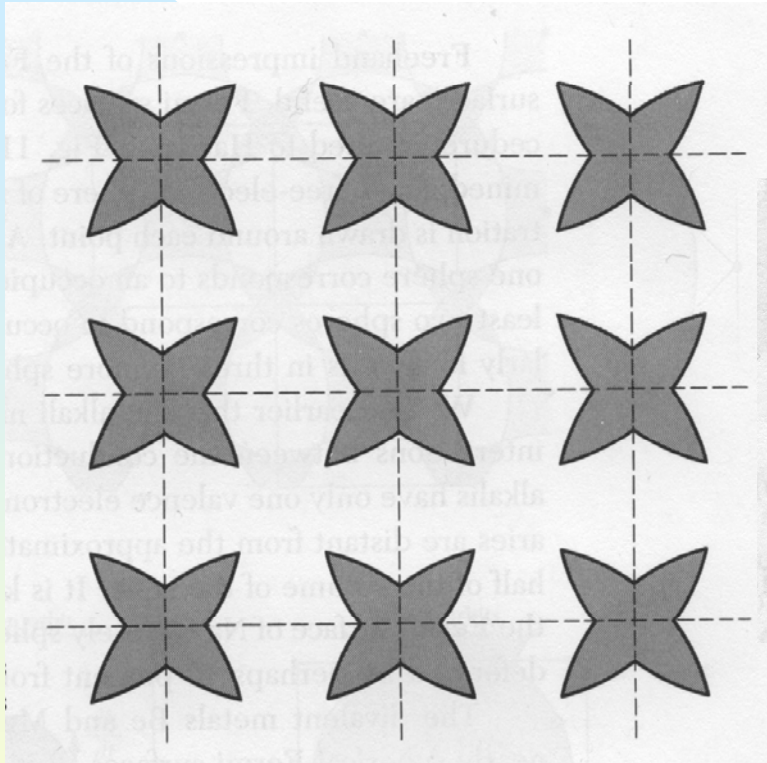
3rd zone



1st zone

2nd zone

3rd zone



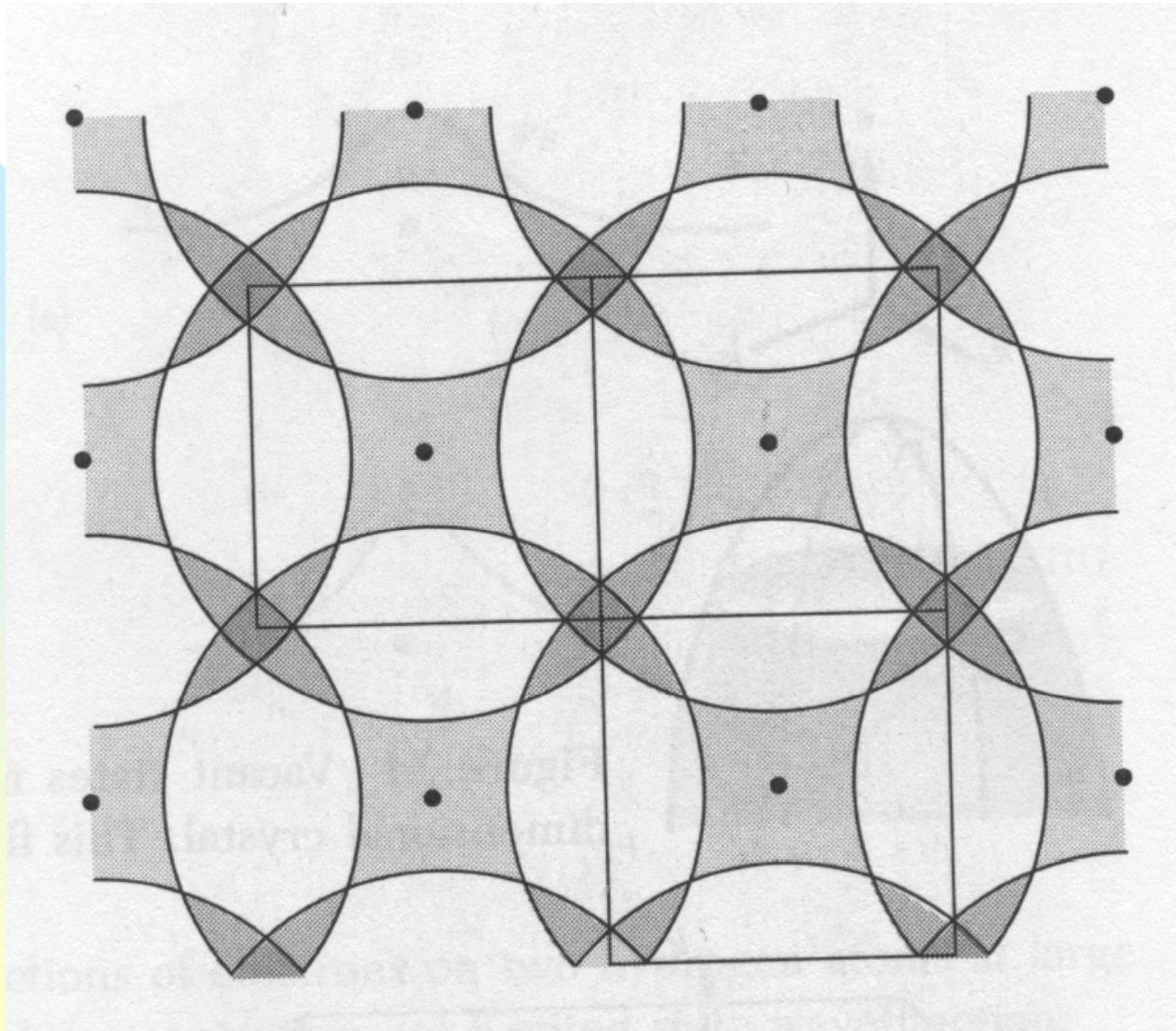
Nearly Free electrons

The interaction of the electron with the periodic potential of the crystal causes energy gaps at the zone boundaries.

Almost always the Fermi surface will intersect zone boundaries perpendicularly.

The crystal potential will round out sharp corners in the Fermi surfaces.

The total volume enclosed by the Fermi surface depends only on the electron concentration.

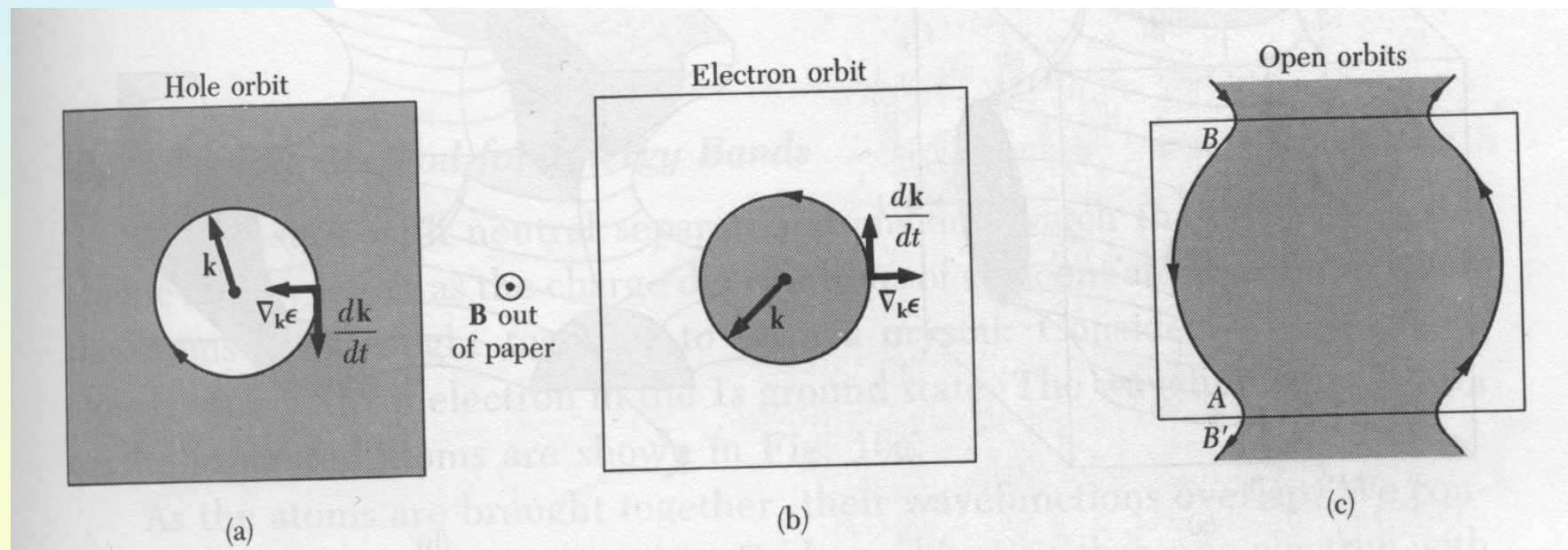





Make a plot of the first two Brillouin zones of a primitive rectangular two-dimensional lattice with axes, $a, b = 3a$.

Electron orbits, hole orbits, and open orbits

An electron on the Fermi surface will move in a curve on the Fermi surface, because it is a surface of constant energy.

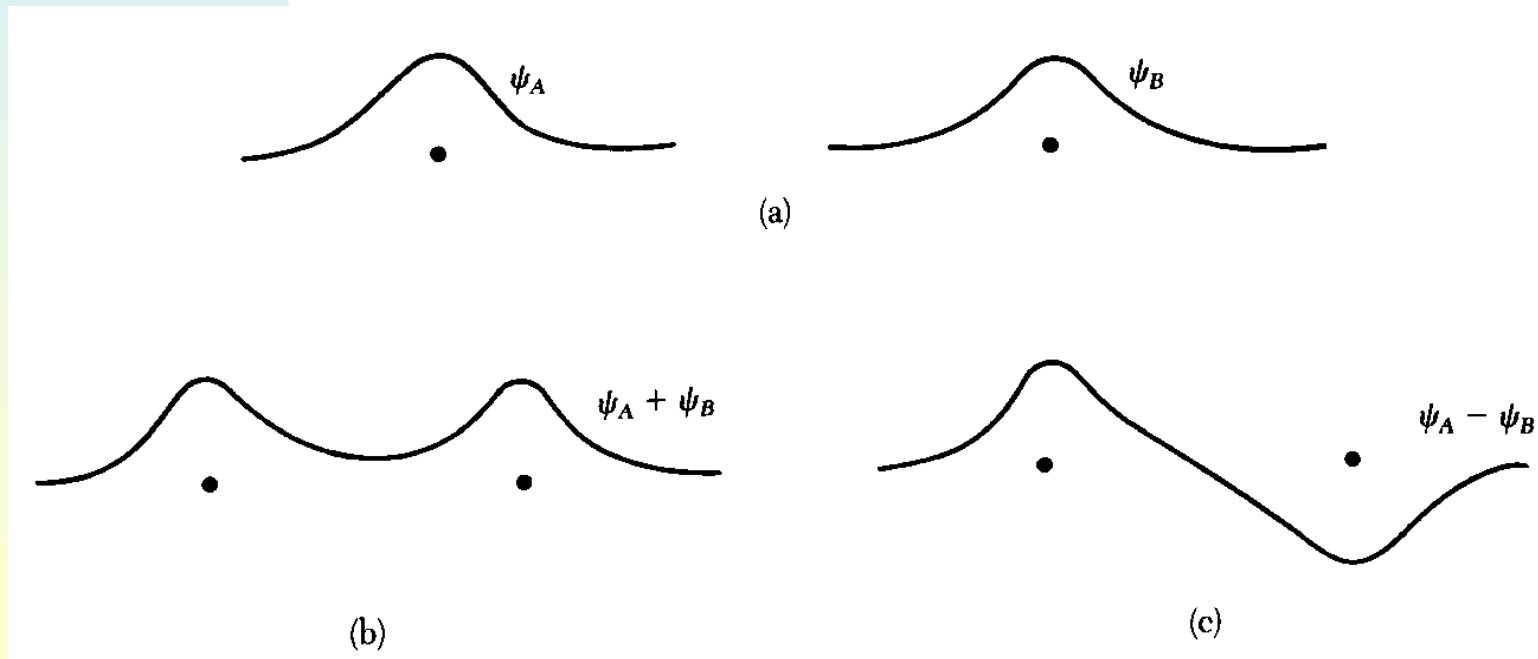




Brillouin zones of two-dimensional divalent metal. A two-dimensional metal in the form of a square lattice has two conduction electrons per atom. In the almost free electron approximation, sketch carefully the electron and hole energy surfaces. For the electrons choose a zone scheme such that the Fermi surface is shown as closed.

Tight banding method for energy bands

Tight banding approximation deals with the case in which the overlap of atomic wave functions is enough to require corrections to the picture of isolated atoms, but not so much as to render the atomic description irrelevant.



Assuming that in the vicinity of each lattice point the full Hamiltonian H can be approximated by H_{at} of a single atom located at the lattice point. If ψ_n is a bound level of H_{at} for an atom at the origin, $H_{at}\psi_n = E_n\psi_n$. $\psi_n(\vec{r})$ will be very small when \vec{r} exceeds a distance of the order of the lattice constant.

To calculate the extreme case in which the crystal H differs from H_{at} , $H = H_{at} + \Delta U(\vec{r})$, where $\Delta U(\vec{r})$ contains all corrections to the atomic potential of the crystal. If ψ_n satisfies $H_{at}\psi_n = E_n\psi_n$, then it will also satisfy the crystal Schrodinger equation if $\Delta U(\vec{r})$ vanishes wherever $\psi_n(\vec{r})$ does not. To preserve Bloch condition, we must have

Each atomic level $\psi_n(\vec{r})$ would yield N levels in the periodic potential, with wave function $\psi_n(\vec{r} - \vec{R})$, for each of the N sites \vec{R} in the lattice.

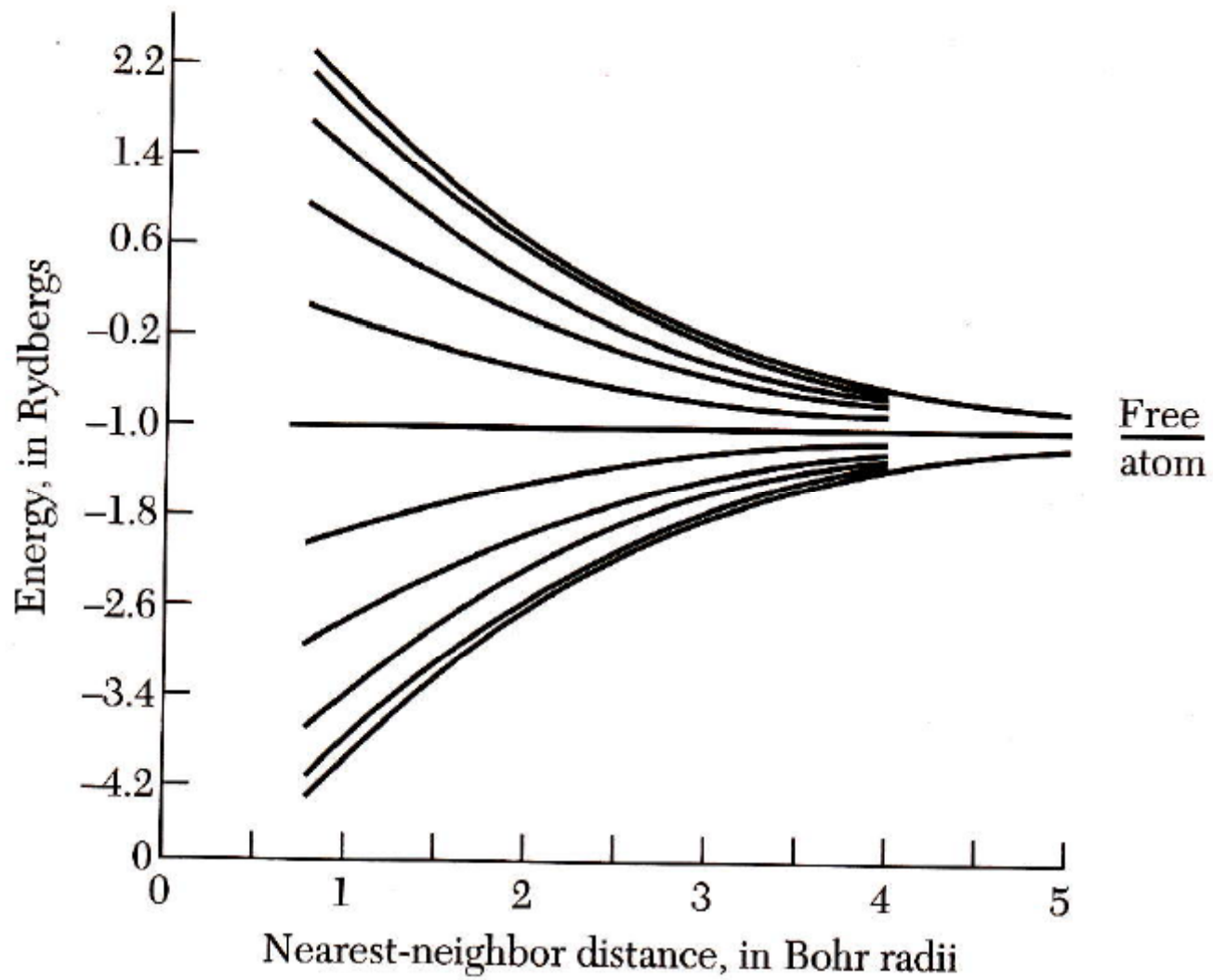
$$\psi_n(\vec{r}) = \sum_R e^{i\vec{k} \cdot \vec{R}} \psi_n(\vec{r} - \vec{R}),$$

The Bloch condition is satisfied $\psi(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi(\vec{r})$.

The energy bands have no difference from the energy of the atomic level, E_n , regardless of the value of \vec{k} .

Consider the general form of the wave function:

$$\psi(\vec{r}) = \sum_R e^{i\vec{k} \cdot \vec{R}} \phi(\vec{r} - \vec{R}).$$



If $\Delta U(\vec{r})\psi_n(\vec{r})$ is nonzero but small,

$\phi(\vec{r})$ should be quite close to the atomic wave function $\psi_n(\vec{r})$.

$\phi(\vec{r}) = \sum_n b_n \psi_n(\vec{r})$. Then we have crystal Schrodinger equation

$$H\psi(\vec{r}) = (H_{at} + \Delta U(\vec{r}))\psi(\vec{r}) = \varepsilon(\vec{k})\psi(\vec{r})$$

Multiply by the atomic wave function $\psi_m^*(\vec{r})$, integrate over all \vec{r} , consider

$$\int \psi_m^*(\vec{r})H_{at}\psi(\vec{r})d\vec{r} = \int (H_{at}\psi_m(\vec{r}))^*\psi(\vec{r})d\vec{r} = E_m \int \psi_m^*(\vec{r})\psi(\vec{r})d\vec{r},$$
$$\left(\varepsilon(\vec{k}) - E_m\right) \int \psi_m^*(\vec{r})\psi(\vec{r})d\vec{r} = \int \psi_m^*(\vec{r})\Delta U(\vec{r})\psi(\vec{r})d\vec{r}.$$

Considering the orthonormality of the atomic wave function,

$$\int \psi_m^*(\vec{r})\psi_n(\vec{r})d\vec{r} = \delta_{nm}$$

We arrive at an eigenvalue equation that determines the coefficients $b_n(\vec{k})$ and the Bloch energies $\varepsilon(\vec{k})$:

$$\begin{aligned} (\varepsilon(\vec{k}) - E_m) b_m &= -(\varepsilon(\vec{k}) - E_m) \sum_n \left(\sum_{\vec{R} \neq 0} \int \psi_m^*(\vec{r}) \psi_n(\vec{r} - \vec{R}) e^{i\vec{k} \cdot \vec{R}} d\vec{r} \right) b_n \\ &+ \sum_n \left(\int \psi_m^*(\vec{r}) \Delta U(\vec{r}) \psi_n(\vec{r}) d\vec{r} \right) b_n \\ &+ \sum_n \left(\sum_{\vec{R} \neq 0} \int \psi_m^*(\vec{r}) \Delta U(\vec{r}) \psi_n(\vec{r} - \vec{R}) e^{i\vec{k} \cdot \vec{R}} d\vec{r} \right) b_n. \end{aligned}$$

The first term contains integral of the form

$$\int \psi_m^*(\vec{r}) \psi_n(\vec{r} - \vec{R}) d\vec{r}$$

Our assumption of well-localized atomic levels mean that the above term is small compared to unity.

We assume that the integral in the third term is small, since they also contain the product of two atomic wave functions centered at different sites. Finally, we assume that the second term on the right is small because we expect the atomic wave functions to become small at distances large enough for the periodic potential to deviate appreciably from the atomic one.

Therefore, $\varepsilon(k) \approx E_0$ if b_m is not small or vice versa.

Application to an s-band arising from a single atomic s-level

If all the coefficient b are zero that for a single atomic s-level,

$$\varepsilon(\vec{k}) = E_s - \frac{\beta + \sum \gamma(\vec{R}) e^{i\vec{k} \cdot \vec{R}}}{1 + \sum \alpha(\vec{R}) e^{i\vec{k} \cdot \vec{R}}}, \text{ where } E_s \text{ is the energy of the}$$

atomic s-level and

$$\beta = -\int \Delta U(\vec{r}) |\phi(\vec{r})| d\vec{r}, \alpha(\vec{R}) = \int \phi^*(\vec{r}) \phi(\vec{r} - \vec{R}) d\vec{r},$$

$$\gamma(\vec{R}) = -\int \phi^*(\vec{r}) \Delta U(\vec{r}) \phi(\vec{r} - \vec{R}) d\vec{r}.$$

Since ϕ is an s-level, $\phi(\vec{r})$ only depends on magnitude of r and $\alpha(-\vec{R}) = \alpha(\vec{R})$. Since $U(\vec{r}) = U(-\vec{r})$, $\gamma(\vec{R}) = \gamma(-\vec{R})$.

If we assume that only nearest-neighbor separations give appreciable overlap integrals, we have

$$\varepsilon(\vec{k}) = E_s - \beta + \sum_{n,n} \gamma(\vec{R}) \cos \vec{k} \cdot \vec{R}$$

$$E(k) = E_v - \beta - \gamma \sum_{j=-1}^1 e^{ikX_j}, \quad (5.41)$$

which may thus be written as

$$E(k) = E_v - \beta - 2\gamma \cos ka. \quad (5.42)$$

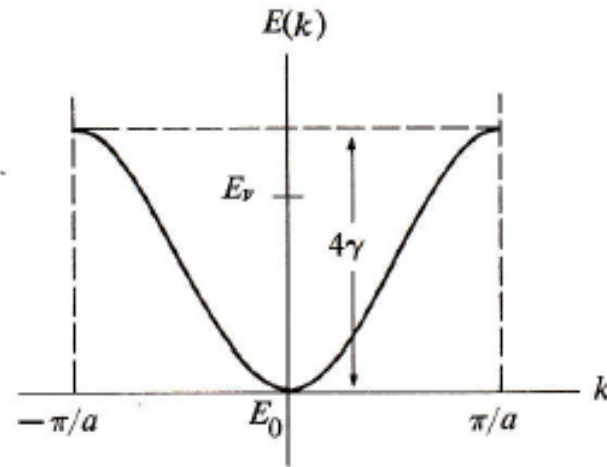
This is the expression we have been seeking. It gives band energy as a function of k in terms of well-defined parameters which we can evaluate from our knowledge of atomic energy and atomic orbitals.

Equation (5.42) may be rewritten more conveniently as

$$E(k) = E_0 + 4\gamma \sin^2 \left(\frac{ka}{2} \right), \quad (5.43)$$

where

$$E_0 = E_v - \beta - 2\gamma. \quad (5.44)$$



Note also that the bandwidth, 4γ , is proportional to the overlap integral. This is reasonable, because, as we saw in Section 5.2, the greater the overlap the stronger the interaction, and consequently the wider the band.

When the electron is near the bottom of the band, where k is small, one may make the approximation $\sin(ka/2) \sim ka/2$, and hence

$$E(k) - E_0 = \gamma a^2 k^2, \quad (5.45)$$

which is of the same form as the dispersion relation of a free electron. An electron in that region of k -space behaves like a free electron with an effective mass

$$m^* = \frac{\hbar^2}{2a^2} \frac{1}{\gamma}. \quad (5.46)$$

Note, however, that an electron near the top of the band shows unusual behavior. If we define $k' = \pi/a - k$, and expand the energy $E(k)$ near the

maximum point, using (5.43), we arrive at

$$E(k') - E_{\max} = -\frac{a^2}{2}\gamma k'^2, \quad (5.47)$$

which shows that the electron behaves like a particle of *negative* effective mass

$$m^* = -\frac{\hbar^2}{a^2\gamma}. \quad (5.48)$$

This, you recall, is in agreement with the results obtained on the basis of the NFE model.

The above treatment can be extended to three dimensions in a straightforward manner. Thus for a sc lattice, the band energy is given by

$$E(k) = E'_0 + 4\gamma \left[\sin^2\left(\frac{k_x a}{2}\right) + \sin^2\left(\frac{k_y a}{2}\right) + \sin^2\left(\frac{k_z a}{2}\right) \right]. \quad (5.49)$$

where E'_0 is the energy at the bottom of the band. The energy contours for this band, in the $k_x - k_y$ plane, are shown in Fig. 5.17(a), and the dispersion curves along the [100] and [111] directions are shown in Fig. 5.17(b). The bottom of the band is at the origin $k = 0$, and the electron there behaves as a free particle with an effective mass given by (5.46). The top of the band is located at the corner of the zone along the [111] direction, that is, at $[\pi/a, \pi/a, \pi/a]$; the electron there has a negative effective mass given by (5.48). The width of the band is equal to 12γ .

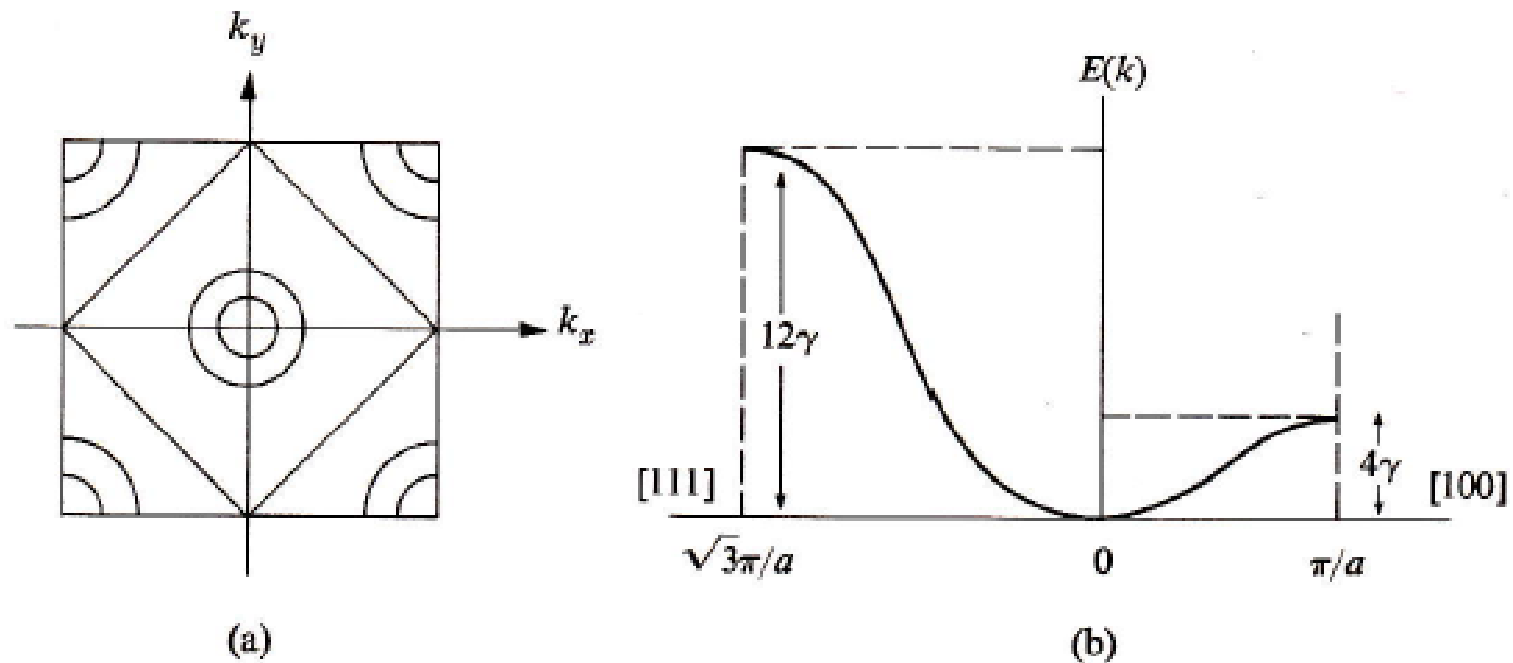
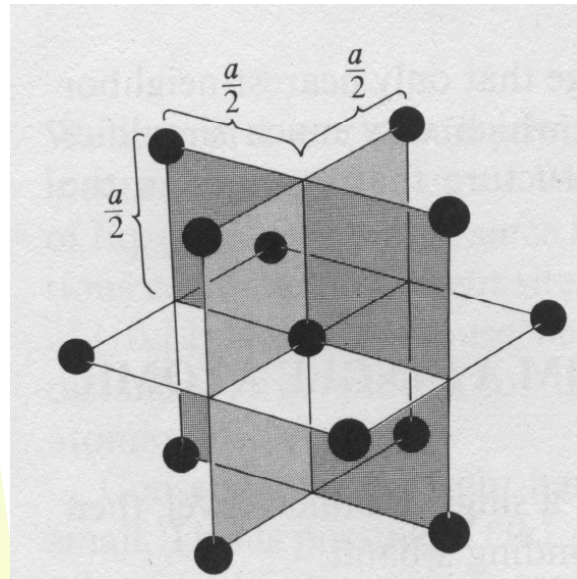


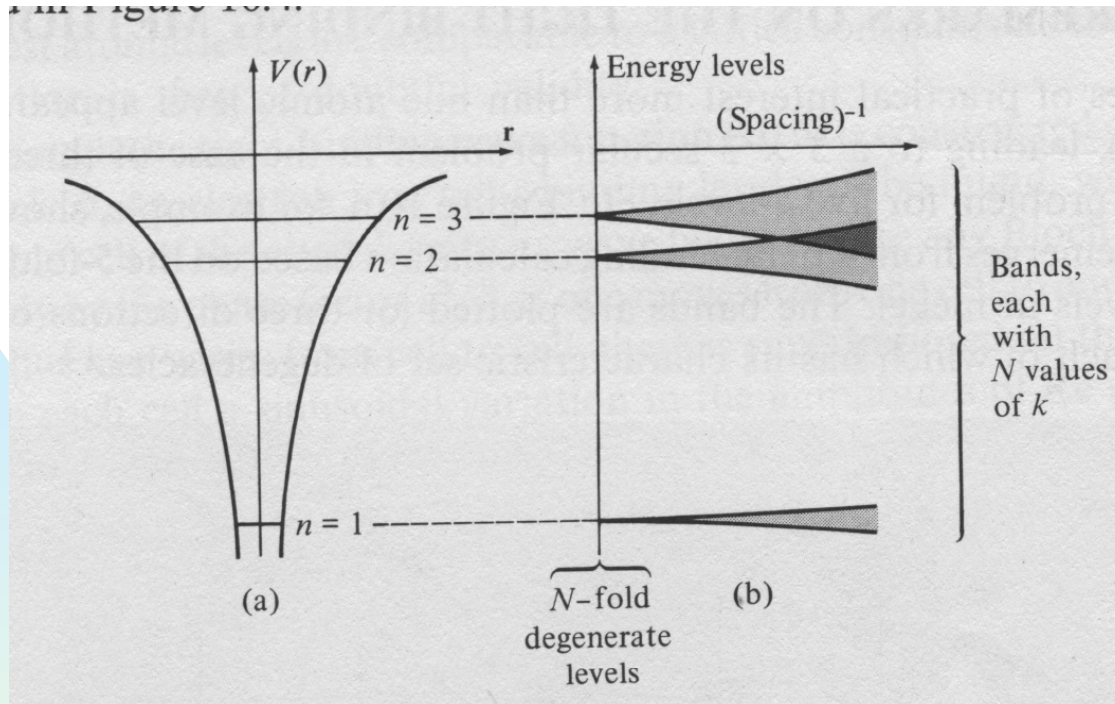
Fig. 5.17 (a) Energy contours for an sc lattice in the tight-binding model. (b) Dispersion curves along the $[100]$ and $[111]$ directions for an sc lattice in the TB model.

For FCC crystal, the 12 nearest neighbors of the origin are

$$\vec{R} = \frac{a}{2}(\pm 1, \pm 1, 0), \frac{a}{2}(\pm 1, 0, \pm 1), \frac{a}{2}(0, \pm 1, \pm 1).$$

For $\vec{k} = (k_x, k_y, k_z)$, $\vec{k} \cdot \vec{R} = \frac{a}{2}(\pm k_i, \pm k_j), i, j = x, y; y, z; z, x.$





Consider $\Delta U(\vec{r}) = \Delta U(x, y, z)$ has full cubic symmetry,
 $\gamma(\vec{R})$ is the same constant for all 12 of the vectors.

$$\begin{aligned} \varepsilon(\vec{k}) = E_s - \beta - 4\gamma & \left(\cos \frac{1}{2} k_x a \cos \frac{1}{2} k_y a + \cos \frac{1}{2} k_y a \cos \frac{1}{2} k_z a \right. \\ & \left. + \cos \frac{1}{2} k_z a \cos \frac{1}{2} k_x a \right), \end{aligned}$$

$$\gamma(\vec{R}) = - \int \phi^*(x, y, z) \Delta U(x, y, z) \phi\left(x - \frac{1}{2}a, y - \frac{1}{2}a, z\right) d\vec{r}.$$

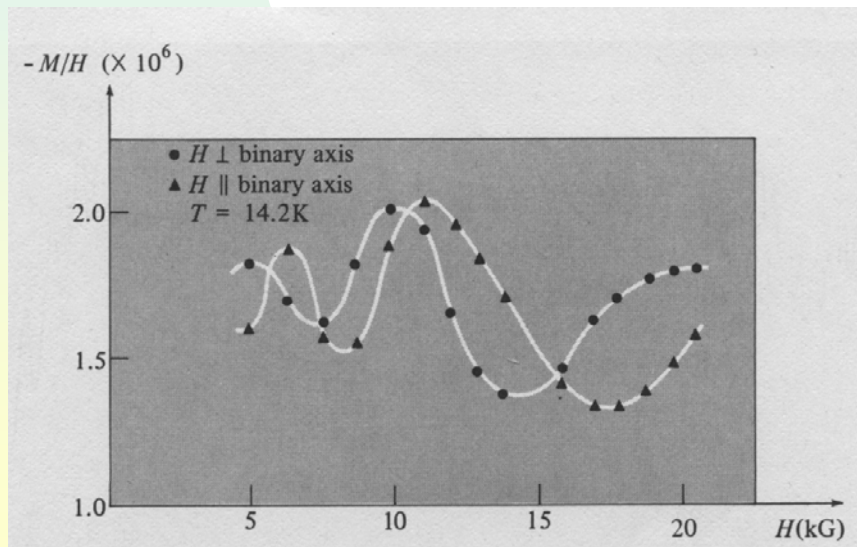


5. **Open orbits.** An open orbit in a monovalent tetragonal metal connects opposite faces of the boundary of a Brillouin zone. The faces are separated by $G = 2 \times 10^8 \text{ cm}^{-1}$. A magnetic field $B = 10^3 \text{ gauss} = 10^{-1} \text{ tesla}$ is normal to the plane of the open orbit. (a) What is the order of magnitude of the period of the motion in \mathbf{k} space? Take $v \approx 10^8 \text{ cm/sec}$. (b) Describe in real space the motion of an electron on this orbit in the presence of the magnetic field.



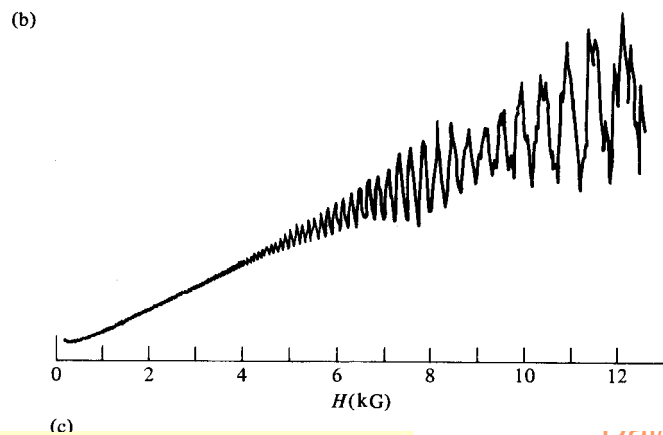
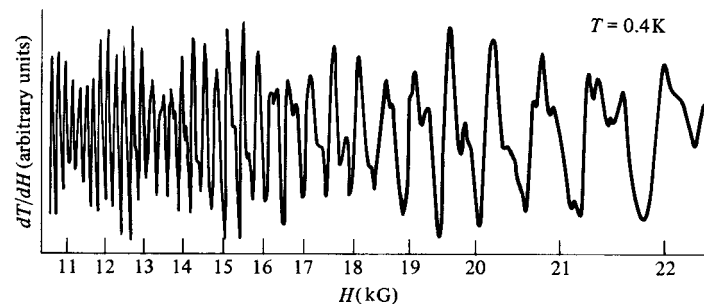
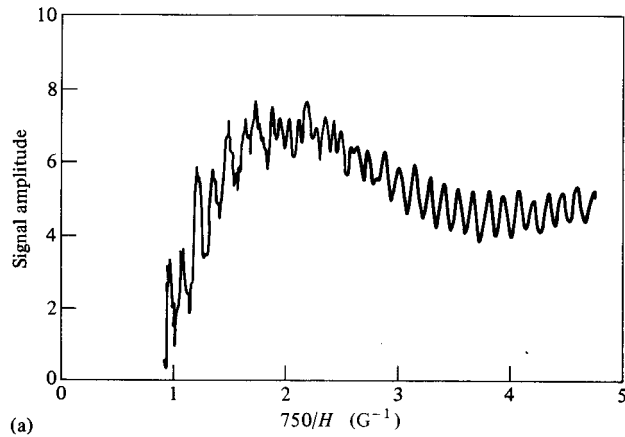
Measuring the Fermi surface

Fermi surface measurements require pure single crystal at low temperatures and is frequently performed in very strong magnetic fields. The shape of the Fermi surface is intimately involved in the transport coefficients of a metal as well as in the equilibrium and optical properties. The most powerful method to deduce the Fermi surface geometry is the de Haas-van Alphen effect.



$$\chi = dM / dH,$$

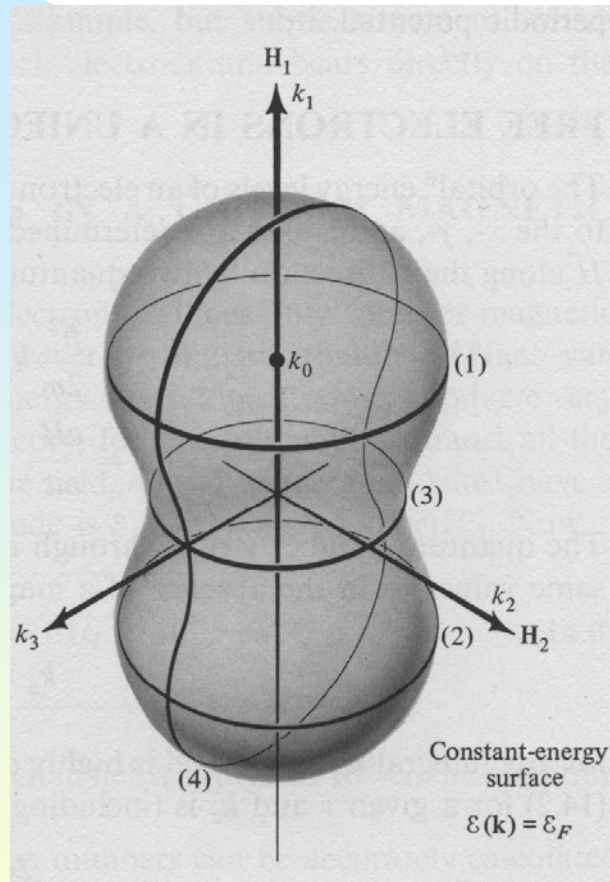
Landau accounted the oscillations in free electron theory.



The change in $1/H$ through a single period of oscillation, $\Delta(1/H)$, was determined by:

$$\Delta\left(\frac{1}{H}\right) = \frac{2\pi e}{\hbar c} \frac{1}{A_e}$$

where A_e is any extremal cross-section area of the Fermi surface in a plane normal to the magnetic field.



The de Haas-van Alphen effect is an indication of the failure of the semiclassical model. The failure arises whenever the semiclassical theory predicts closed orbits for the electron motion projected on a plane perpendicular to the field. When this happens, the energies of motion perpendicular to H are quantized.

Free electrons in a uniform magnetic field

The orbital energy levels of an electron in a cubic box with sides of length L parallel to the x -, y -, and z -axes are determined in the presence of a uniform magnetic field H along the z -direction by two quantum numbers, ν and k_z :

$$\varepsilon_\nu(k_z) = \frac{\hbar^2}{2m} k_z^2 + \left(\nu + \frac{1}{2}\right) \hbar \omega_c, \quad \omega_c = \frac{eH}{mc}.$$

ν runs through all nonmagnetic integers, and k_z takes on the same values as in the absence of a magnetic field:

$$k_z = 2\pi n_z / L \text{ for any integral } n_z.$$

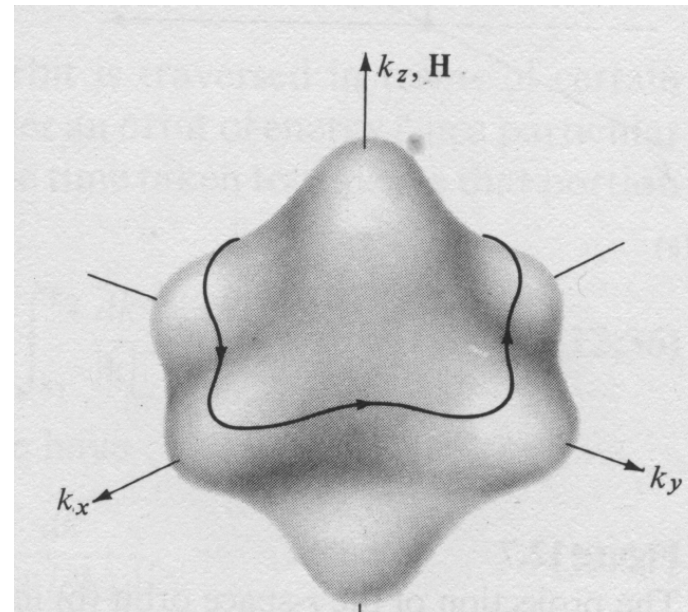
The energy of motion perpendicular to the field, which would be $\hbar^2(k_x^2 + k_y^2) / 2m$ if no field were present, is quantized in steps of $\hbar\omega_c$ ($\omega_c = eH / mc$). This is orbit quantization.

Semi-classical motion in a uniform magnetic field

In the semiclassical equation of motion:

$$\vec{v}(\vec{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon(\vec{k})}{\partial \vec{k}}, \quad \frac{d(\hbar \vec{k})}{dt} = (-e) \frac{1}{c} \vec{v}(\vec{k}) \times \vec{H}.$$

Electrons move along curves given by the intersection of surfaces of constant energy with planes perpendicular to the magnetic field.

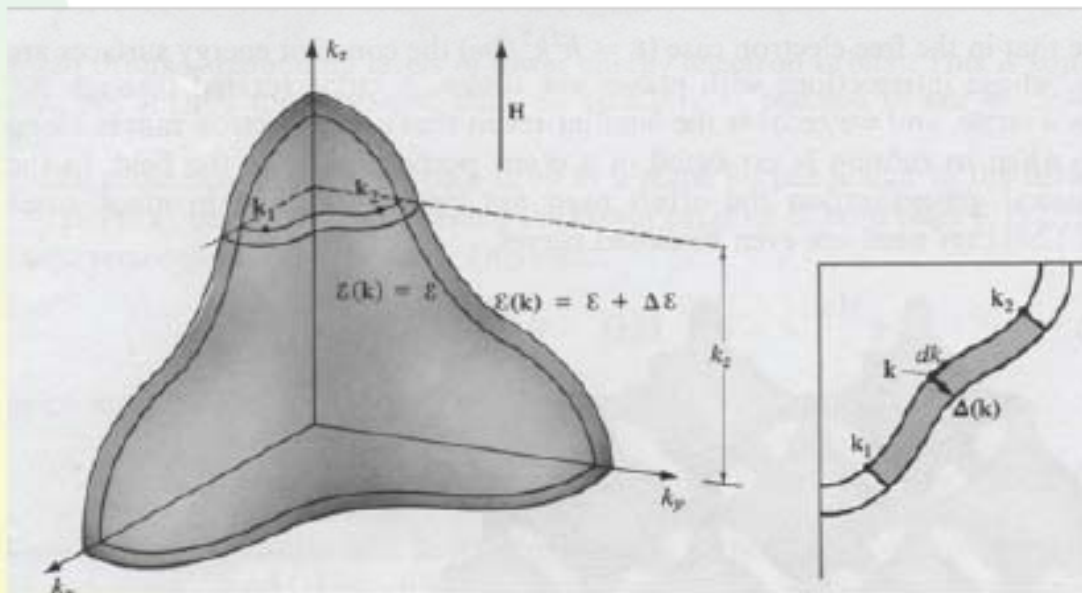


The time taken to traverse the orbit between \vec{k}_1 and \vec{k}_2 is:

$$t_2 - t_1 = \int_{t_1}^{t_2} dt = \int_{k_1}^{k_2} \frac{dk}{|\dot{\vec{k}}|} = \frac{\hbar^2 c}{eH} \int_{k_1}^{k_2} \frac{dk}{\left| \left(\frac{\partial \varepsilon}{\partial \vec{k}} \right)_\perp \right|} = \frac{\hbar^2 c}{eH} \frac{1}{\Delta \varepsilon} \int_{k_1}^{k_2} \Delta(\vec{k}) dk$$

$$= \frac{\hbar^2 c}{eH} \left(\frac{\partial A_{1,2}}{\partial \varepsilon} \right) = \frac{\hbar^2 c}{eH} \left(\frac{\partial A(\varepsilon, k_z)}{\partial \varepsilon} \right)$$

$$\Delta \varepsilon = \frac{\partial \varepsilon}{\partial \vec{k}} \cdot \Delta(\vec{k}) = \left(\frac{\partial \varepsilon}{\partial \vec{k}} \right)_\perp \cdot \Delta(\vec{k}) = \left| \left(\frac{\partial \varepsilon}{\partial \vec{k}} \right)_\perp \right| \Delta(\vec{k})$$



Levels of Bloch electrons in a uniform magnetic field

In free electron theory, a level of ε_F must have a quantum number ν whose order of magnitude is $\varepsilon_F / \hbar\omega_c = \varepsilon_F / [(e\hbar / mc)H]$.

$e\hbar / mc = 1.16 \times 10^{-8}$ eV/G. Typically, ε_F is several eV, so quantum number ν will be of order 10^4 .

Energies at two adjacent levels is determined by $h\nu$. Let $\varepsilon_\nu(k_z)$ be the energy of the ν th allowed level at a given k_z .

$$(\varepsilon_{\nu+1}(k_z) - \varepsilon_\nu(k_z)) = h\nu = h / T(\varepsilon_\nu(k_z), k_z),$$

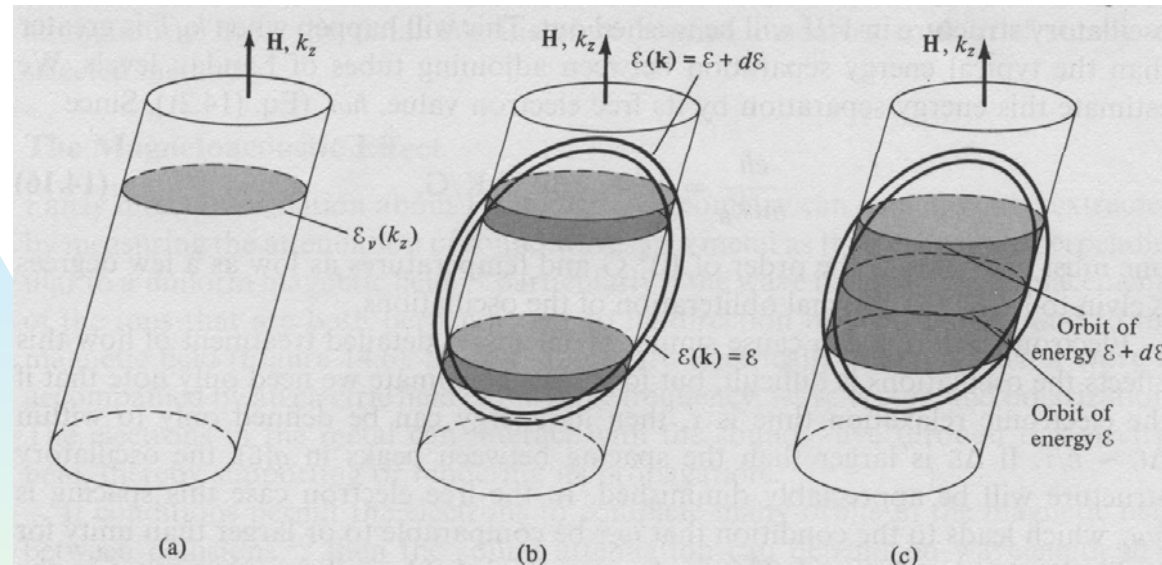
$$(\varepsilon_{\nu+1}(k_z) - \varepsilon_\nu(k_z)) \frac{\partial A(\varepsilon_\nu)}{\partial \varepsilon} = \frac{2\pi eH}{\hbar c}.$$

Because we are interested in ε_ν of order ε_F , $\varepsilon_{\nu+1}(k_z) - \varepsilon_\nu(k_z) \ll \varepsilon_F$.

$$A(\varepsilon_{\nu+1}) - A(\varepsilon_\nu) = 2\pi eH / \hbar c = \Delta A$$

$$A(\varepsilon_\nu(k_z), k_z) = (\nu + \lambda)\Delta A, \text{ where } \lambda \text{ is independent of } \nu.$$

Origin of the oscillatory phenomena



Most electronic properties of metals depend on the density of levels at the Fermi energy, $g(\varepsilon_F)$. It follows that $g(\varepsilon_F)$ will be singular whenever the value of H causes an extramal orbit on the Fermi surface to satisfy the quantization condition $(\nu + \lambda)\Delta A = A_e(\varepsilon_F)$.

$$\Delta\left(\frac{1}{H}\right) = \frac{2\pi e}{\hbar c} \frac{1}{A_e(\varepsilon_F)}. \quad \frac{e\hbar}{mck_B} = 1.34 \times 10^{-4} K/G.$$

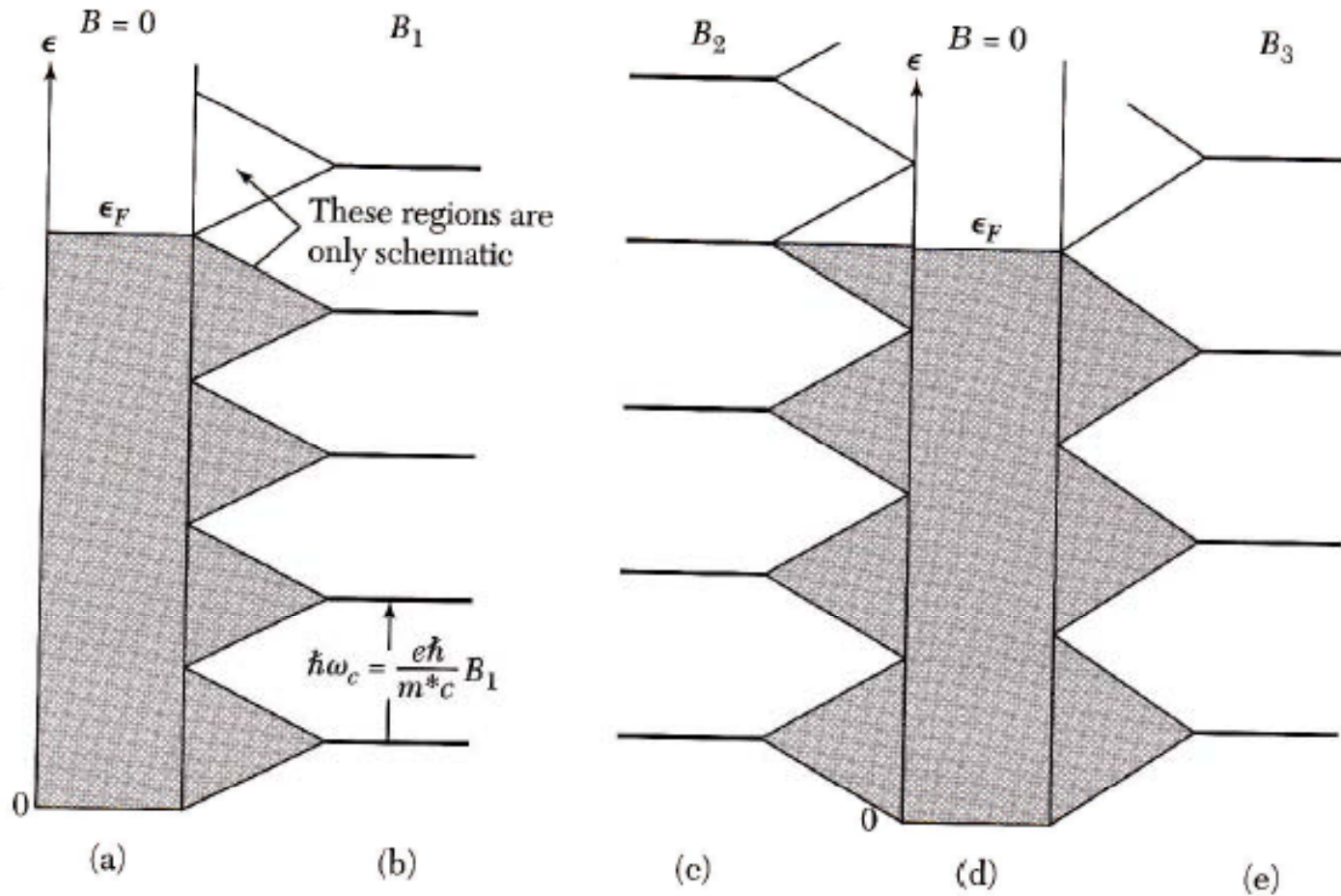
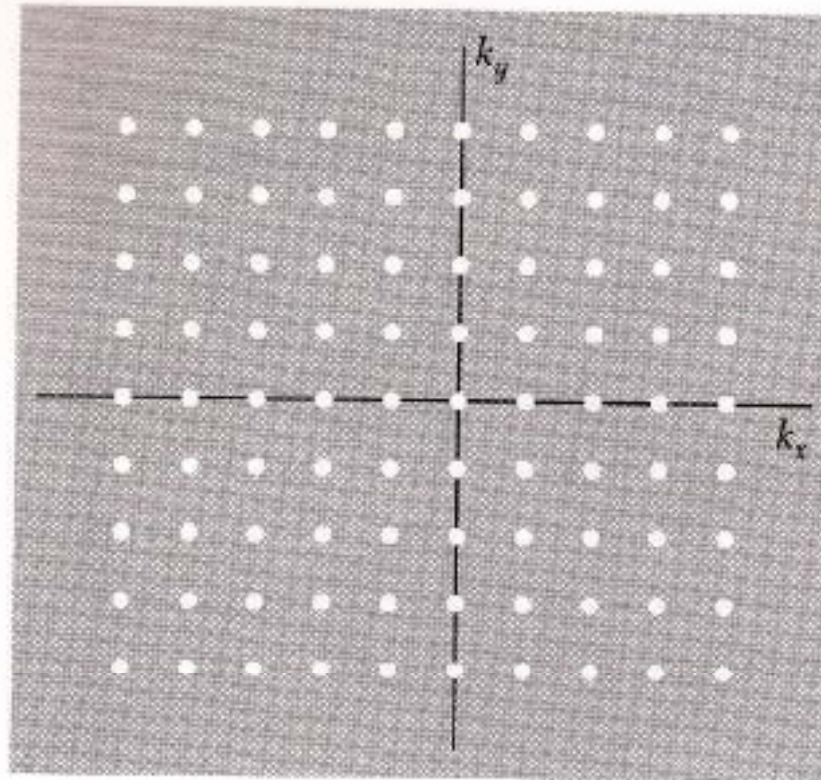
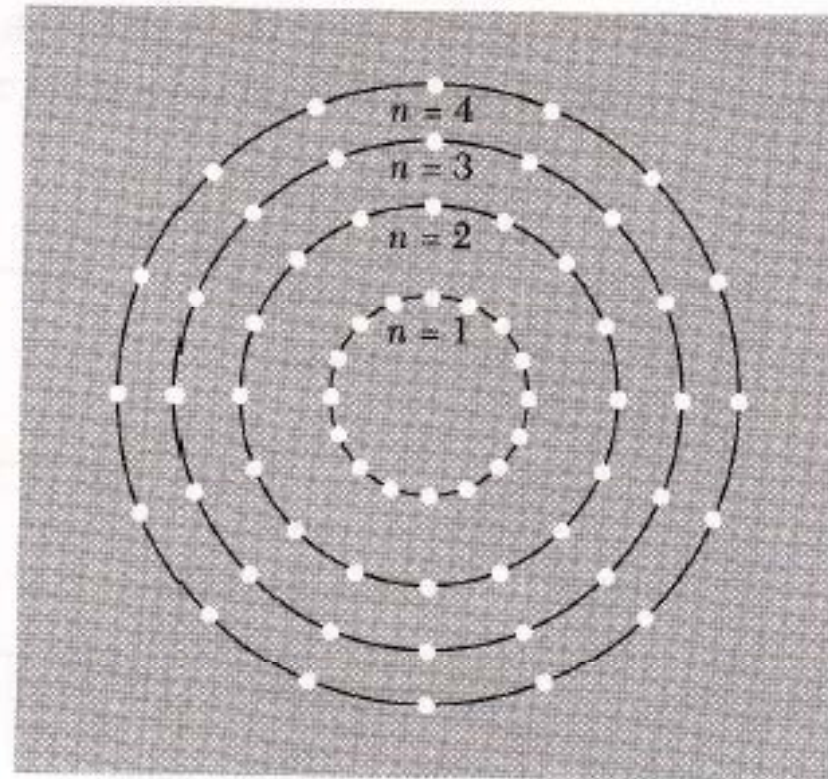


Figure 23 Explanation of the de Haas-van Alphen effect for a free electron gas in two dimensions in a magnetic field. The filled orbitals of the Fermi sea in the absence of a magnetic field are shaded in *a* and *d*. The energy levels in a magnetic field are shown in *b*, *c*, and *e*. In *b* the field has a value B_1 such that the total energy of the electrons is the same as in the absence of a magnetic field: as many electrons have their energy raised as lowered by the orbital quantization in the magnetic field B_1 . When we increase the field to B_2 the total electron energy is increased, because the uppermost electrons have their energy raised. In *e* for field B_3 the energy is again equal to that for the field $B = 0$. The total energy is a minimum at points such as B_1, B_3, B_5, \dots , and a maximum near points such as B_2, B_4, \dots .



(a)



(b)

Figure 24 (a) Allowed electron orbitals in two dimensions in absence of a magnetic field. (b) In a magnetic field the points which represent the orbitals of free electrons may be viewed as restricted to circles in the former $k_x k_y$ plane. The successive circles correspond to successive values of the quantum number n in the energy $(n - \frac{1}{2})\hbar\omega_c$. The area between successive circles is

$$\text{(CGS)} \quad \pi\Delta(k^2) = 2\pi k(\Delta k) = (2\pi m/\hbar^2) \Delta\epsilon = 2\pi m\omega_c/\hbar = 2\pi eB/\hbar c .$$

The angular position of the points has no significance. The number of orbitals on a circle is constant and is equal to the area between successive circles times the number of orbitals per unit area in (a), or $(2\pi eB/\hbar c)(L/2\pi)^2 = L^2 eB/2\pi\hbar c$, neglecting electron spin.

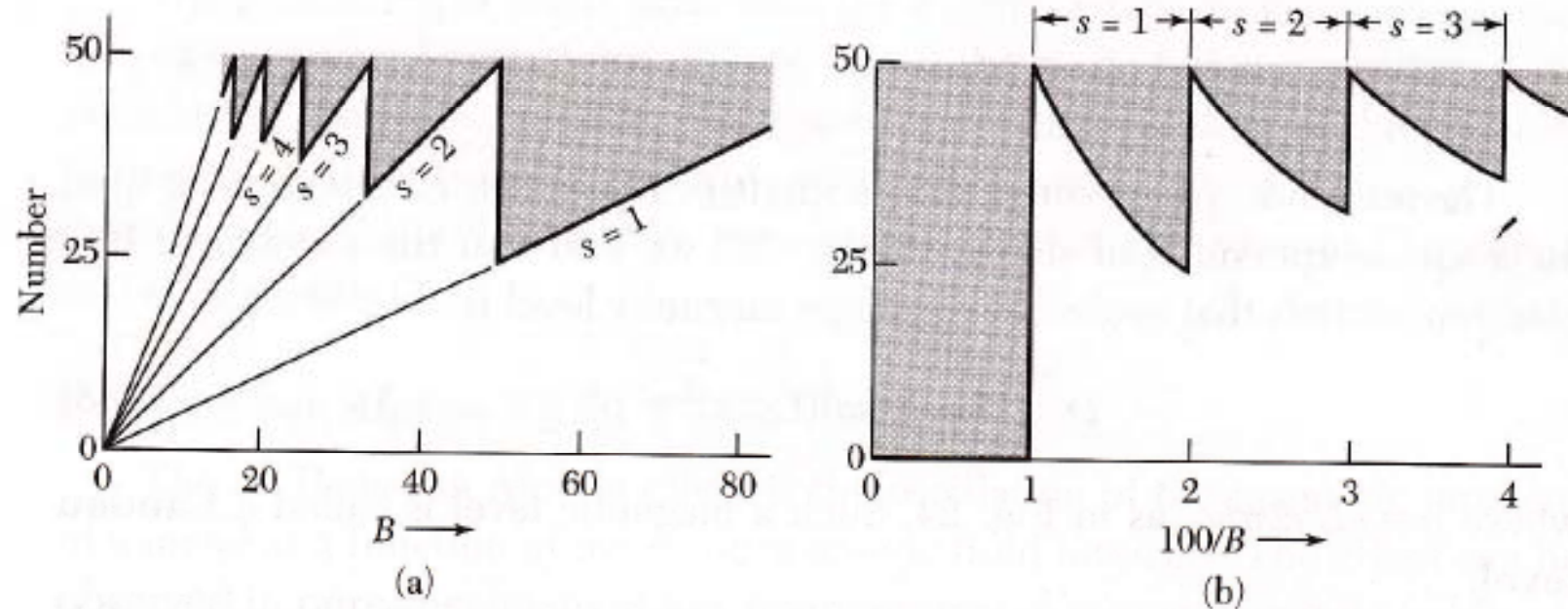


Figure 25 (a) The heavy line gives the number of particles in levels which are completely occupied in a magnetic field B , for a two-dimensional system with $N = 50$ and $\rho = 0.50$. The shaded area gives the number of particles in levels partially occupied. The value of s denotes the quantum number of the highest level which is completely filled. Thus at $B = 40$ we have $s = 2$; the levels $n = 1$ and $n = 2$ are filled and there are 10 particles in the level $n = 3$. At $B = 50$ the level $n = 3$ is empty. (b) The periodicity in $1/B$ is evident when the same points are plotted against $1/B$.

Fermi Surface of Copper. The Fermi surface of copper (Fig. 29) is distinctly nonspherical: eight necks make contact with the hexagonal faces of the first Brillouin zone of the fcc lattice. The electron concentration in a monovalent metal with an fcc structure is $n = 4/a^3$; there are four electrons in a cube of volume a^3 . The radius of a free electron Fermi sphere is

$$k_F = (3\pi^2 n)^{1/3} = (12\pi^2/a^3)^{1/3} \cong (4.90/a) , \quad (38)$$

and the diameter is $9.80/a$.

The shortest distance across the Brillouin zone (the distance between hexagonal faces) is $(2\pi/a)(3)^{1/2} = 10.88/a$, somewhat larger than the diameter of the free electron sphere. The sphere does not touch the zone boundary, but we know that the presence of a zone boundary tends to lower the band energy near the boundary. Thus it is plausible that the Fermi surface should neck out to meet the closest (hexagonal) faces of the zone (Figs. 18 and 29).

The square faces of the zone are more distant, with separation $12.57/a$, and the Fermi surface does not neck out to meet these faces.

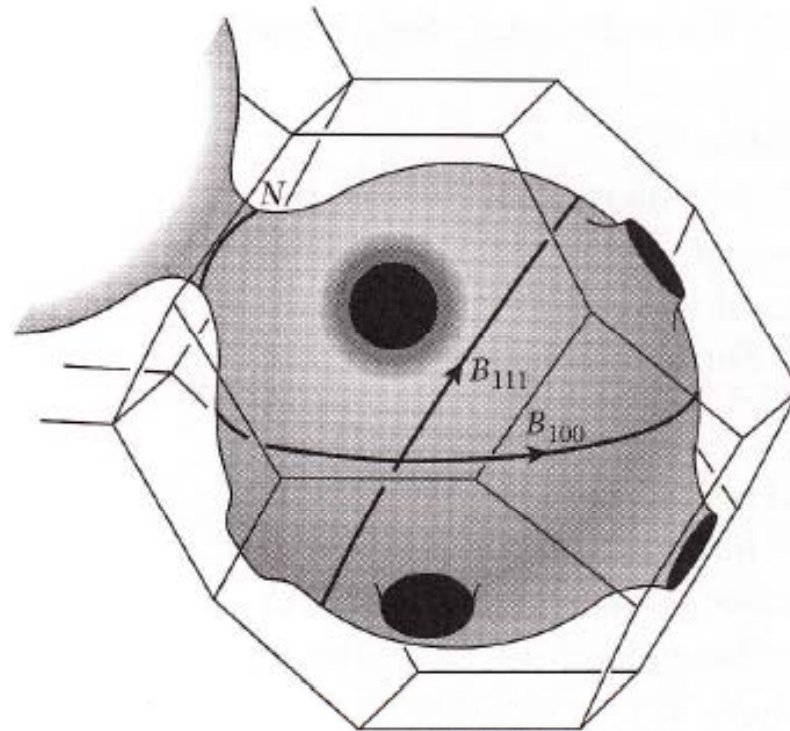


Figure 29 Fermi surface of copper, after Pippard. The Brillouin zone of the fcc structure is the truncated octahedron derived in Chapter 2. The Fermi surface makes contact with the boundary at the center of the hexagonal faces of the zone, in the $[111]$ directions in \mathbf{k} space. Two "belly" extremal orbits are shown, denoted by B ; the extremal "neck" orbit is denoted by N .

Figure 28 The orbits in the section AA' are extremal orbits: the cyclotron period is roughly constant over a reasonable section of the Fermi surface. Other sections such as BB' have orbits that vary in period along the section.

