Calculation of Energy Bands

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B. Tight Binding Method
C. Wigner Seitz (Cellular) Method
D. Density Functional Theory
E. Fermi Surfaces
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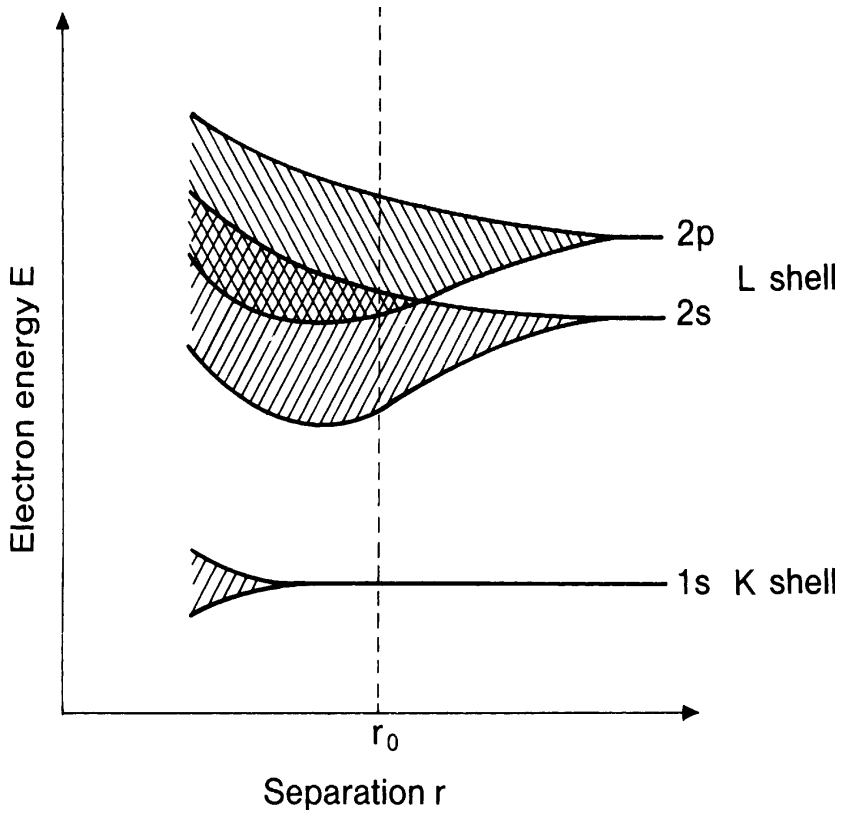
G. Photoemission Spectroscopy

From Bonds to Bands



If a very large number of atoms are involved, as in the case of a real solid, then the energy levels will lie on a quasi- continuous scale and one therefore speaks of energy bands. The broadening of the band depends on the overlap of the wavefunctions concerned. Thus for the deep lying levels the broadening is small, and these ``core levels'' retain their atomic shell-like character even in the solid. For the highest occupied levels, on the other hand, the broadening is so large that the s-, p- and where present, d-levels merge into a single band.

Hydrogen Molecule

Consider two hydrogen atoms to form into a molecule, each with an electron in the 1*s* ground state, their wavefunctions are ψ_A and ψ_B, respectively.

As the atoms are brought together, their wavefunctions overlap. We consider the two combinations $\psi_A \pm \psi_B$. Each combination shares an electron with the two protons, but an electron in the state $\psi_A + \psi_B$ will have a somewhat lower energy than in the state $\psi_A - \psi_B$.

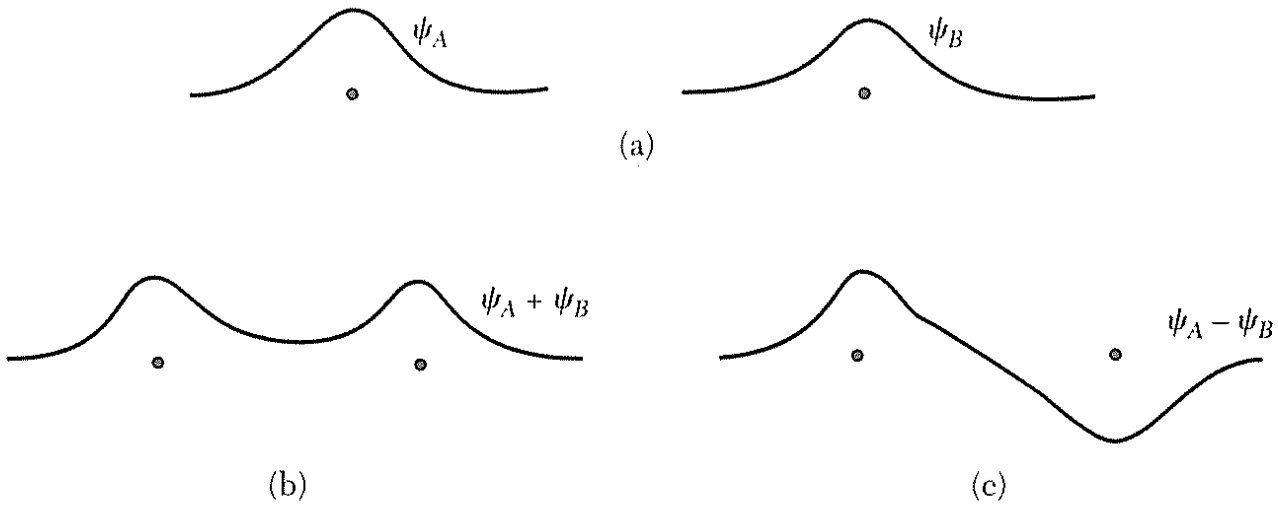
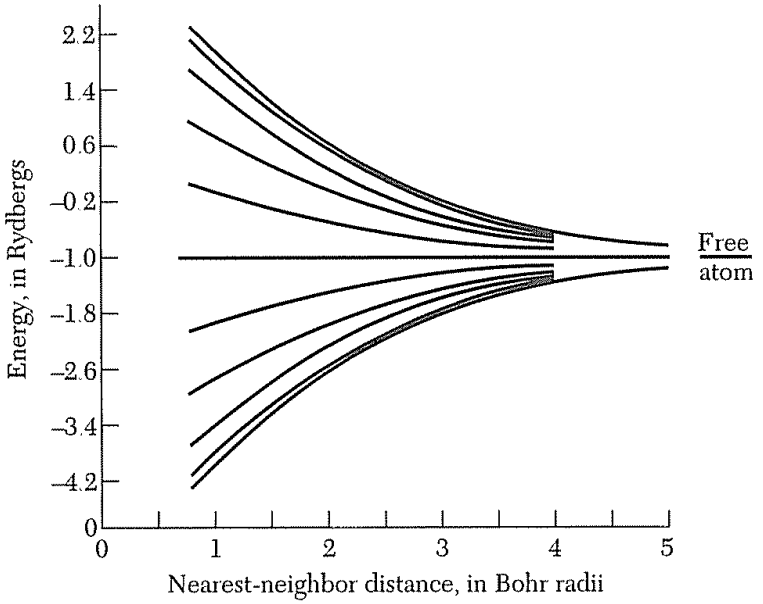


Figure 16 (a) Schematic drawing of wavefunctions of electrons on two hydrogen atoms at large separation. (b) Ground state wavefunction at closer separation. (c) Excited state wavefunction.

As free atoms are brought together, the coulomb interaction between the atom cores and the electron splits the energy levels, spreading them into bands. Each state of given quantum number of the free atom is spread in the crystal into a band of energies. The width of the band is proportional to the strength of the overlap interaction between neighboring atoms.

There will also be bands formed from p, d, . . . states ($l = 1, 2, \ldots$) of the free atoms. States degenerate in the free atom will form different bands. Each will not have the same energy as any other band over any substantial range of the wavevector. Bands may coincide in energy at certain values of $\mathbf{k}$ in the Brillouin zone.

The 1*s* band of a ring of 20 hydrogen atoms calculated by the tight-binding method



Tight Binding Method

The tight binding approximation is also called the linear combination of atomic orbital (LCAO) approximation in which the one electron wavefunction $\psi_{\mathbf{k}}(\mathbf{r})$ is built from the electron wavefunction of an isolated atom, $\varphi(\mathbf{r})$.

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_j C_{\mathbf{k}j}\varphi(\mathbf{r} - \mathbf{r}_j)$$

where the sum is over all lattice points.

This function of the Bloch form if $C_{\mathbf{k}j} = N^{-1/2}\, e^{i\mathbf{k}\cdot\mathbf{r}}$, for a crystal of N atoms:

$$\psi_{\mathbf{k}}(\mathbf{r}) = N^{-1/2} \sum_j \exp(i\mathbf{k}\cdot\mathbf{r}_j)\varphi(\mathbf{r} - \mathbf{r}_j)$$

We find the first-order energy by calculating the diagonal matrix elements of the hamiltonian of the crystal:

$$\langle \mathbf{k}|H|\mathbf{k}\rangle = N^{-1}\sum_j \sum_m \exp[i\mathbf{k}\cdot(\mathbf{r}_j - \mathbf{r}_m)]\, \langle \varphi_m|H|\varphi_j\rangle \quad ,$$

where $\varphi_m \equiv \varphi(\mathbf{r} - \mathbf{r}_m)$. Writing $\boldsymbol{\rho}_m = \mathbf{r}_m - \mathbf{r}_j$,

$$\langle \mathbf{k}|H|\mathbf{k}\rangle = \sum_m \exp(-i\mathbf{k}\cdot\boldsymbol{\rho}_m) \int dV\, \varphi^*(\mathbf{r} - \boldsymbol{\rho}_m) H \varphi(\mathbf{r}) \quad .$$

We consider the integrals over the same atom and the nearest neighbor atoms only, then

$$\int dV\, \varphi^*(\mathbf{r}) H \varphi(\mathbf{r}) = -\alpha \;; \quad \int dV\, \varphi^*(\mathbf{r}-\boldsymbol{\rho}) H \varphi(\mathbf{r}) = -\gamma \;;$$

and we have the first-order energy, provided $\langle \mathbf{k}|\mathbf{k}\rangle = 1$:

$$\langle \mathbf{k}|H|\mathbf{k}\rangle = -\alpha - \gamma \sum_m \exp(-i\mathbf{k}\cdot\boldsymbol{\rho}_m) = \epsilon_{\mathbf{k}} \,.$$

For a simple cubic structure the nearest-neighbor atoms are at

$$\boldsymbol{\rho}_m = (\pm a,0,0) \;; \quad (0,\pm a,0) \;; \quad (0,0,\pm a) \;,$$

we have $$\epsilon_{\mathbf{k}} = -\alpha - 2\gamma(\cos k_x a + \cos k_y a + \cos k_z a)$$

Thus the energies are confined to a band of width 12γ. The weaker the overlap, the narrower is the energy band.

If $ka \ll 1$, $\epsilon_k \simeq -\alpha - 6\gamma + \gamma k^2 a^2$, the effective mass $m^* = \hbar^2/2\gamma a^2$

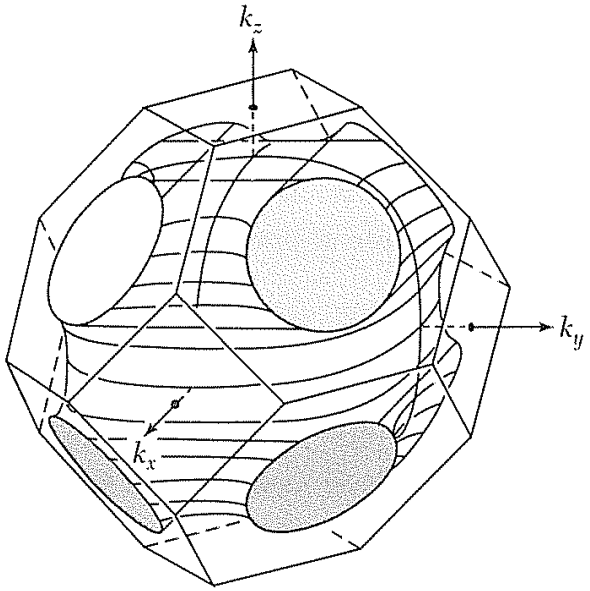
When the overlap integral γ is small, the band is narrow and the effective mass is high.

For the bcc structure with eight nearest neighbors,

$$\epsilon_{\mathbf{k}} = -\alpha - 8\gamma \cos \tfrac{1}{2} k_x a \cos \tfrac{1}{2} k_y a \cos \tfrac{1}{2} k_z a$$

For the fcc structure with twelve nearest neighbors,

$$\epsilon_{\mathbf{k}} = -\alpha - 4\gamma(\cos \tfrac{1}{2} k_y a \cos \tfrac{1}{2} k_z a + \cos \tfrac{1}{2} k_z a \cos \tfrac{1}{2} k_x a + \cos \tfrac{1}{2} k_x a \cos \tfrac{1}{2} k_y a)$$



A constant energy surface of an fcc crystal structure in the nearest neighbor tight-binding approximation. The surface shown has $\epsilon = -\alpha + 2|\gamma|$.

The tight-binding (or LCAO) approximation is quite good for inner electrons of atoms, but it is not often good description for the conduction electrons. It is used to describe approximately the *d* bands of transition metals and the valence bands of diamondlike and inert gas crystals.

Wigner Seitz Method

A Bloch function satisfies the wave equation

$$\left(\frac{1}{2m}\mathbf{p}^2 + U(\mathbf{r})\right) e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}}\, e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

With $\mathbf{P} = -i\hbar\boldsymbol{\nabla}$, we have

$$\mathbf{p}\, e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) = \hbar\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) + e^{i\mathbf{k}\cdot\mathbf{r}}\, \mathbf{p} u_{\mathbf{k}}(\mathbf{r}) \ ;$$

$$\mathbf{p}^2 e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) = (\hbar k)^2 e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) + e^{i\mathbf{k}\cdot\mathbf{r}} (2\hbar\mathbf{k}\cdot\mathbf{p}) u_{\mathbf{k}}(\mathbf{r}) + e^{i\mathbf{k}\cdot\mathbf{r}}\, \mathbf{p}^2 u_{\mathbf{k}}(\mathbf{r}) \ ;$$

So,

$$\left(\frac{1}{2m}(\mathbf{p} + \hbar\mathbf{k})^2 + U(\mathbf{r})\right) u_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r}) \ .$$

At $\mathbf{k} = 0$ we have $\psi_0 = u_0(\mathbf{r})$, where $u_0(\mathbf{r})$ has the periodicity of the lattice, sees the ion cores, and near them will look like the wavefunction of the free atom.

We then approximate the exact wavefunction $\psi_{\mathbf{k}}$ with $u_0(\mathrm{r})$,

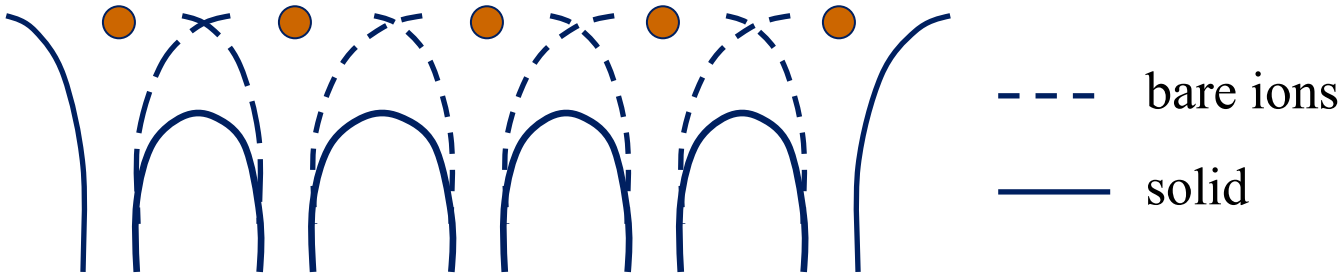
for $\mathbf{k} \neq 0$, $\psi_{\mathbf{k}} = \exp(i\mathbf{k} \cdot \mathbf{r}) u_0(r)$

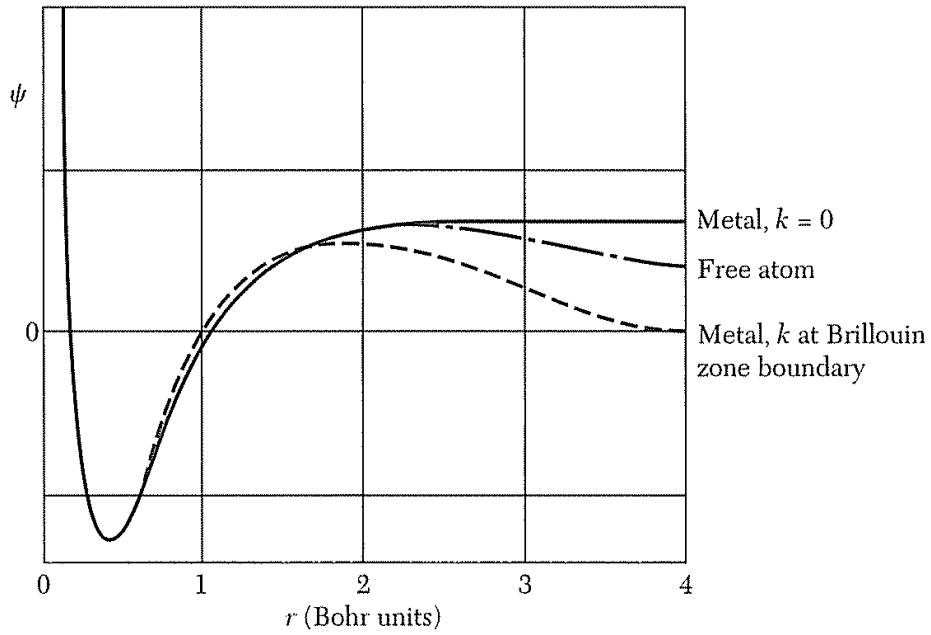
$$\left(\frac{1}{2m}\mathbf{p}^2 + U(\mathbf{r})\right) u_0(\mathbf{r}) = \epsilon_0 u_0(\mathbf{r}) \quad , \quad \epsilon_{\mathbf{k}} = \epsilon_0 + (\hbar^2 k^2 / 2m)$$

In a spherical approximation to the shape of the smallest Wigner-Seitz cell we use the Wigner-Seitz boundary condition

$$(d\psi/dr)_{r_0} = 0$$

where r_0 is the radius of a sphere equal in volume to a primitive cell





The stability of the simple metals with respect to free atoms is caused by the lowering of the energy of the Bloch orbital with k = 0 in the crystal.

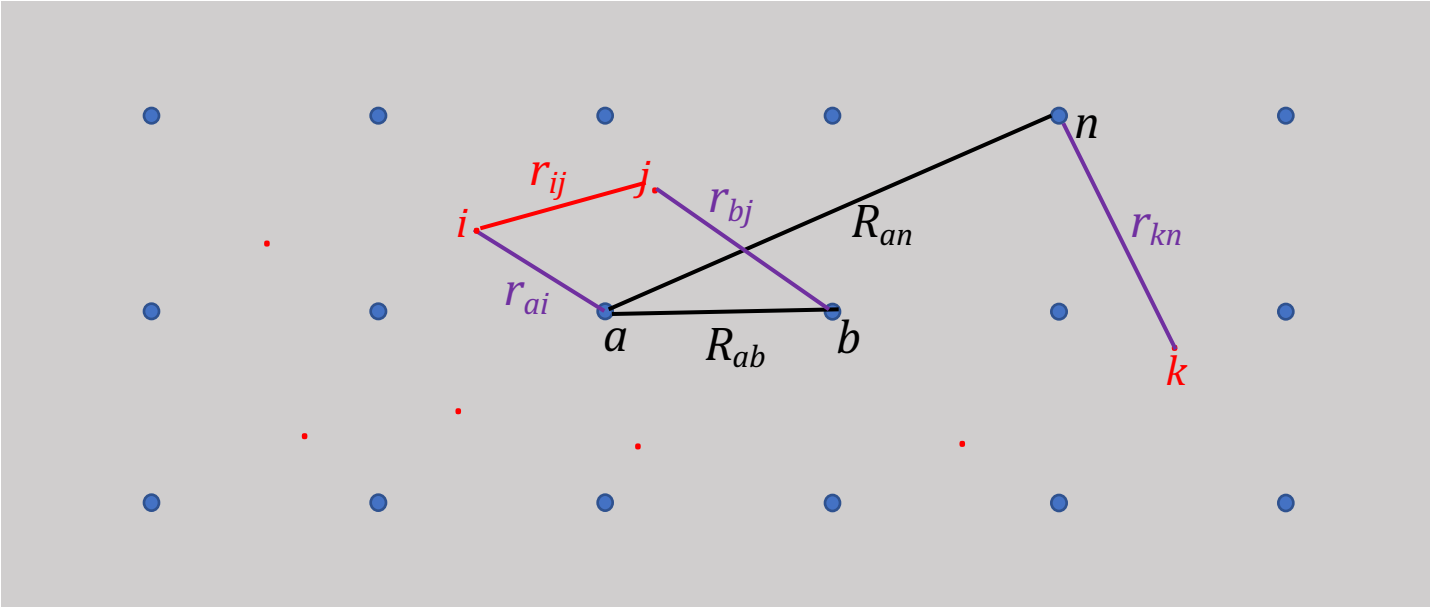
Figure 19 Radial wavefunctions for the 3*s* orbital of free sodium atom and for the 3*s* conduction band in sodium metal. The wavefunctions, which are not normalized here, are found by integrating the Schrödinger equation for an electron in the potential well of an Na^+ ion core. For the free atom the wavefunction is integrated subject to the usual Schrödinger boundary condition $\psi(r) \rightarrow 0$ as $r \rightarrow \infty$; the energy eigenvalue is -5.15 eV. The wavefunction for wavevector $k = 0$ in the metal is subject to the Wigner-Seitz boundary condition that $d\psi/dr = 0$ when r is midway between neighboring atoms; the energy of this orbital is -8.2 eV, considerably lower than for the free atom. The orbitals at the zone boundary are not filled in sodium; their energy is $+2.7$ eV. (After E. Wigner and F. Seitz.)

Many-electron Hamiltonian

For a solid, the many-electron Hamiltonian whose Schrödinger wave equation must be solved is

$$\mathcal{H} = -\frac{\hbar^2}{2m}\sum_{i\,(\text{electrons})}\nabla_i^2 - \sum_{\substack{a\,(\text{nuclei})\\ i\,(\text{electrons})}}\frac{e^2}{4\pi\varepsilon_0 r_{ai}}$$

$$+\frac{1}{2}{\sum_{a,b\,(\text{nuclei})}}'\frac{Z_a Z_b e^2}{4\pi\varepsilon_0 R_{ab}} + \frac{1}{2}{\sum_{i,j\,(\text{electron})}}'\frac{e^2}{4\pi\varepsilon_0 r_{ij}}.$$



The many-electron Hamiltonian:

$$\mathcal{H} = -\frac{\hbar^2}{2m}\sum_{i\,(\text{electrons})}\nabla_i^2 - \sum_{\substack{a\,(\text{nuclei})\\ i\,(\text{electrons})}}\frac{e^2}{4\pi\varepsilon_0 r_{ai}}$$
$$+\frac{1}{2}\sum_{a,b\,(\text{nuclei})}{}'\frac{Z_a Z_b e^2}{4\pi\varepsilon_0 R_{ab}} + \frac{1}{2}\sum_{i,j\,(\text{electron})}{}'\frac{e^2}{4\pi\varepsilon_0 r_{ij}}.$$

1. The first term in the Hamiltonian is the operator representing the kinetic energy of all the electrons. Each different *i* corresponds to a different electron.
2. The second term is the potential energy of interaction of all of the electrons with all of the nuclei, and r_{ai} is the distance from the *a*th nucleus of Z_a to the *i*th electron.
3. The third term is the Coulomb potential energy of interaction between the nuclei. R_{ab} is the distance between nucleus *a* and nucleus *b*. The prime on the sum as usual means omission of those terms for which $a = b$.
4. The fourth term is the Coulomb potential energy of interaction between the electrons, and r_{ij} is the distance between the *i*th and *j*th electrons.

$$\mathcal{H} = -\frac{\hbar^2}{2m}\sum_{i\,(\text{electrons})}\nabla_i^2 - \sum_{\substack{a\,(\text{nuclei})\\ i\,(\text{electrons})}}\frac{e^2}{4\pi\varepsilon_0 r_{ai}}$$

$$+\frac{1}{2}{\sum_{a,b\,(\text{nuclei})}}'\frac{Z_a Z_b e^2}{4\pi\varepsilon_0 R_{ab}} + \frac{1}{2}{\sum_{i,j\,(\text{electron})}}'\frac{e^2}{4\pi\varepsilon_0 r_{ij}}.$$

This N-electron Hamiltonian is unnecessarily cumbersome. It is more convenient to write it in the more abstract form

$$\mathcal{H}(x_1 \cdots x_n) = \sum_{i=1}^{N}\mathcal{H}(i) + \frac{1}{2}{\sum_{i,j}}'V(ij)$$

$$\mathcal{H}(i) = (-\hbar^2/2m)\nabla_i^2 - \sum_{\substack{a\,(\text{nuclei})\\ i\,(\text{electrons})}}\frac{e^2}{4\pi\varepsilon_0 r_{ai}}$$

$$V(ij) = V(ji) = \frac{1}{2}{\sum_{i,j\,(\text{electron})}}'\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

Density Functional Theory

A N-electron state described by a wavefunction $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ satisfies the many-electron time-independent Schrödinger equation

$$\hat{H}\Psi = \left[\hat{T} + \hat{V} + \hat{U}\right]\Psi = \left[\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m_i}\nabla_i^2\right) + \sum_{i=1}^{N} V(\mathbf{r}_i) + \sum_{i<j}^{N} U(\mathbf{r}_i, \mathbf{r}_j)\right]\Psi = E\Psi,$$

The ground-state properties of a many-electron system are uniquely determined by an electron density that depends on only three spatial coordinates. It set down the groundwork for reducing the many-body problem of N electrons with $3N$ spatial coordinates to three spatial coordinates, through the use of functionals of the electron density $n(\mathbf{r})$, so that the ground state wavefunction Ψ_0 is a unique functional of the ground state density $n_0(\mathbf{r})$.

$$n(\mathbf{r}) = N \int \mathrm{d}^3\mathbf{r}_2 \cdots \int \mathrm{d}^3\mathbf{r}_N \, \Psi^*(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N).$$

$$\Psi_0 = \Psi[n_0]$$

So, the ground-state energy E_0 is a functional of n_0:

$$E_0 = E[n_0] = \left\langle \Psi[n_0] \middle| \hat{T} + \hat{V} + \hat{U} \middle| \Psi[n_0] \right\rangle,$$

More generally, the contribution of the external potential $\left\langle \Psi \middle| \hat{V} \middle| \Psi \right\rangle$ can be written explicitly in terms of the density n:

$$V[n] = \int V(\mathbf{r}) n(\mathbf{r}) \, \mathrm{d}^3\mathbf{r}.$$

The effective single-particle potential can be written as

$$V_\mathrm{s}(\mathbf{r}) = V(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}^3\mathbf{r}' + V_\mathrm{XC}[n(\mathbf{r})],$$

where $V(\mathbf{r})$ is the external potential, the second term is the Hartree term describing the electron–electron Coulomb repulsion, and the last term V_XC is the exchange–correlation potential. Here, V_XC includes all the many-particle interactions.

Kohn–Sham equations of this auxiliary noninteracting system can be derived:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{\mathrm{s}}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r}),$$

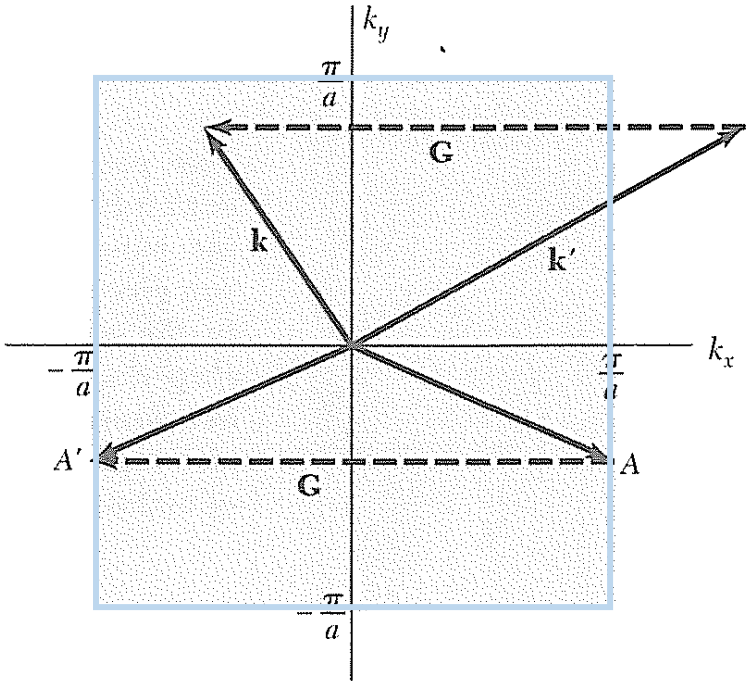
which yields the orbitals φ_i that reproduce the density $n(\mathbf{r})$ of the original many-body system

$$n(\mathbf{r}) = \sum_{i=1}^{N} \left|\varphi_i(\mathbf{r})\right|^2.$$

Usually one starts with an initial guess for $n(\mathbf{r})$, then calculates the corresponding V_s and solves the Kohn–Sham equations for the φ_i. From these one calculates a new density and starts again. This procedure is then repeated until convergence is reached.

Fermi Surfaces and Zone Schemes

The Fermi surface is the surface of constant energy ϵ_F in $\mathbf{k}$ space. The Fermi surface separates the unfilled orbitals from the filled orbitals, at absolute zero. The electrical properties of the metal are determined by the volume and shape of the Fermi surface, because the current is due to changes in the occupancy of states near the Fermi surface.



For any **k**' outside of the first Brillouin zone, we can always find a reciprocal lattice vector G so that **k** = **k**' + **G** and **k** lies in the first Brillouin zone.

$$\psi_{\mathbf{k}'}(\mathbf{r}) = e^{i\mathbf{k}'\cdot\mathbf{r}} u_{\mathbf{k}'}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} (e^{-i\mathbf{G}\cdot\mathbf{r}} u_{\mathbf{k}'}(\mathbf{r}))$$
$$= e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r})$$

Reduced, Extended and Periodic Zone Schemes

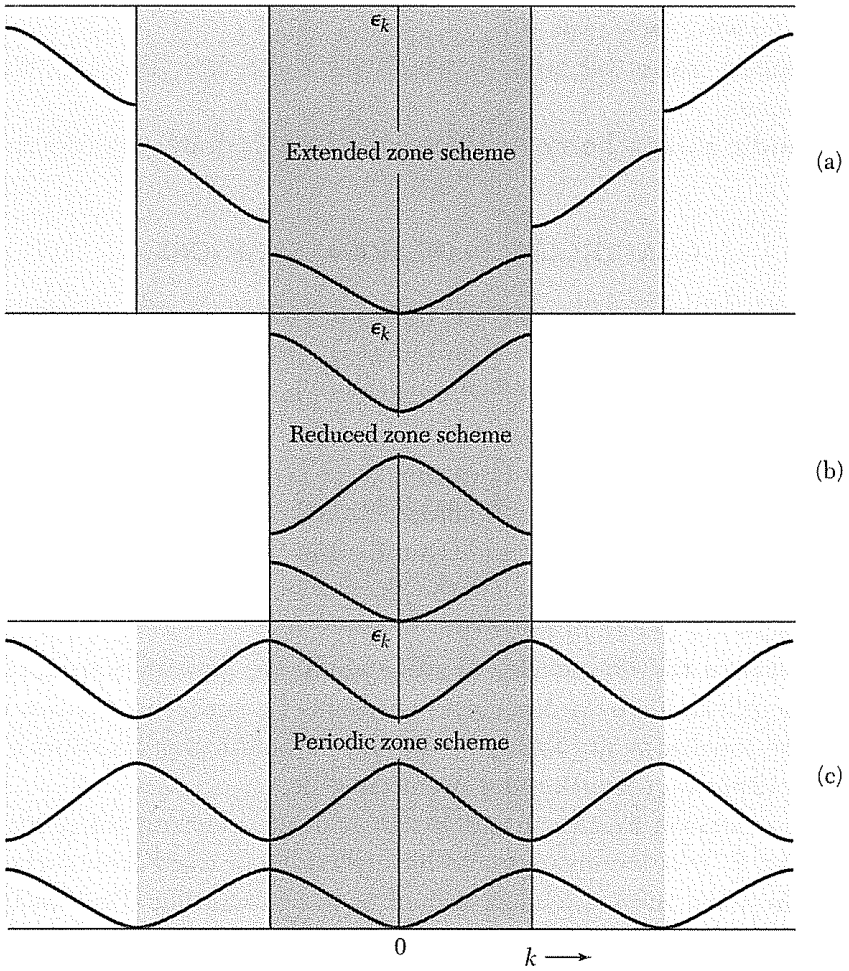
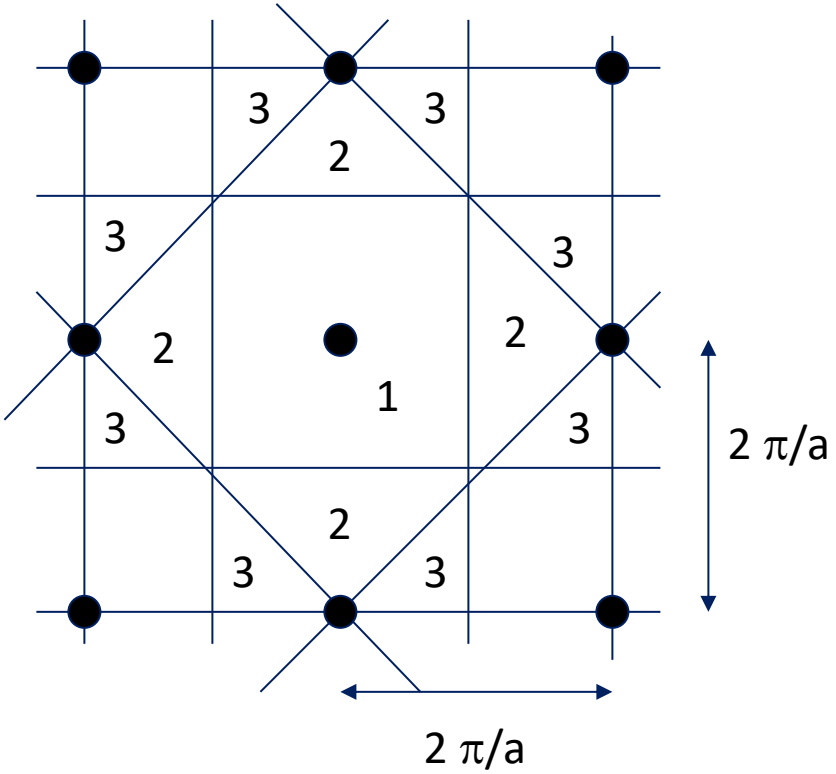
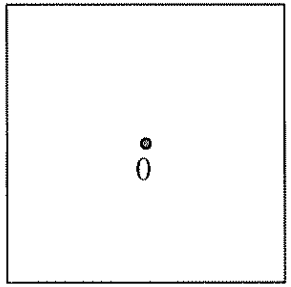


Figure 4 Three energy bands of a linear lattice plotted in (a) the extended (Brillouin), (b) reduced, and (c) periodic zone schemes.

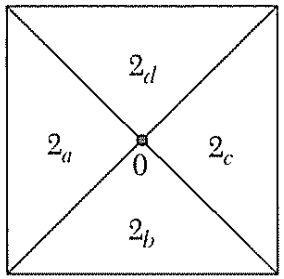
Brillouin Zones of Square Lattice

For a simple square lattice of atoms with interatomic distance a. Its reciprocal lattice will also be square, with reciprocal lattice base vector of length $2\pi/a$.

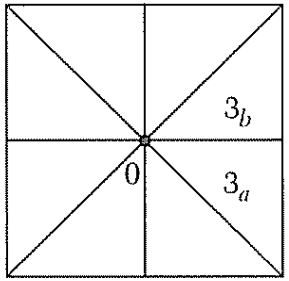




1st zone

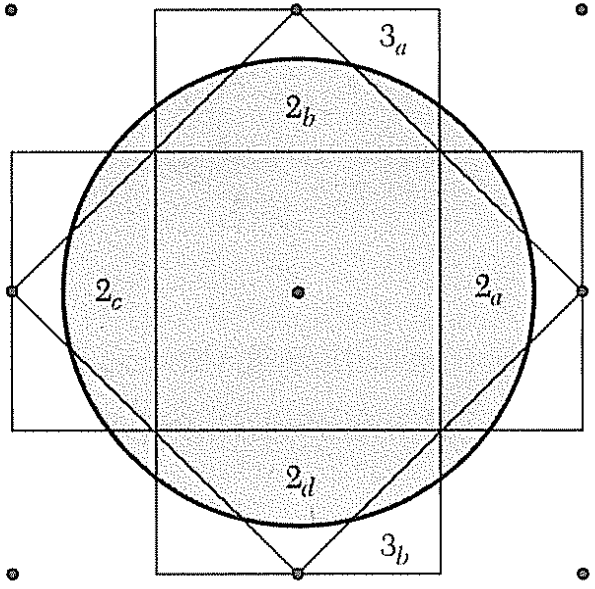


2nd zone

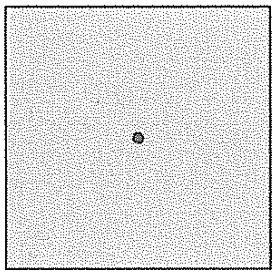


3rd zone

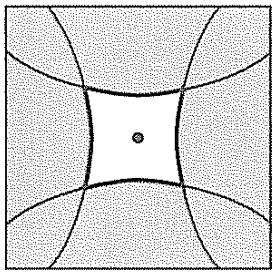
Construction of Fermi Surfaces for Free Electrons



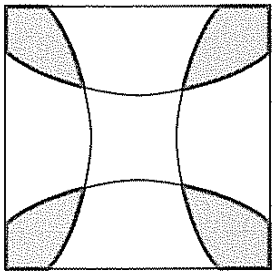
Brillouin zones of a square lattice in two dimensions. The circle shown is a surface of constant energy for free electrons; it will be the Fermi surface for some particular value of the electron concentration. The total area of the filled region in **k** space depends only on the electron concentration and is independent of the interaction of the electrons with the lattice. The shape of the Fermi surface depends on the lattice interaction, and the shape will not be an exact circle in an actual lattice.



1st zone



2nd zone



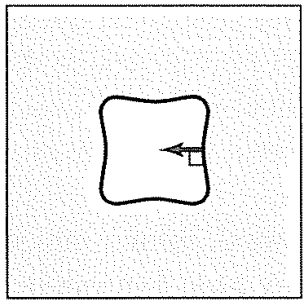
3rd zone

Fermi circle viewed in the reduced zone scheme

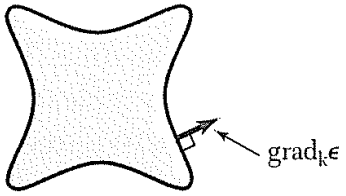
Nearly Free Electrons Fermi Surfaces

From free electrons Fermi surfaces to nearly free electrons Fermi surfaces:

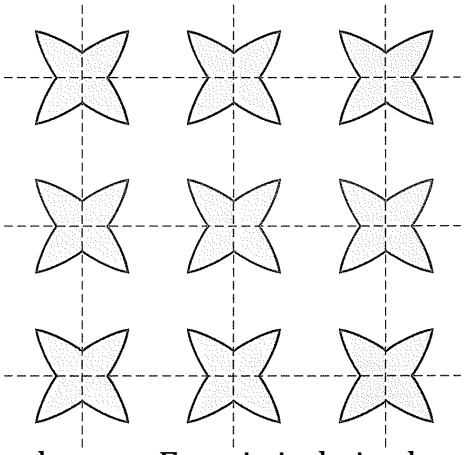
- The interaction of the electron with the periodic potential of the crystal creates energy gaps at the zone boundaries.
- Almost always the Fermi surface will intersect zone boundaries perpendicularly.
- The crystal potential will round out sharp corners in the Fermi surfaces.
- The total volume enclosed by the Fermi surface depends only on the electron concentration and is independent of the details of the lattice interaction.



2nd zone



3rd zone

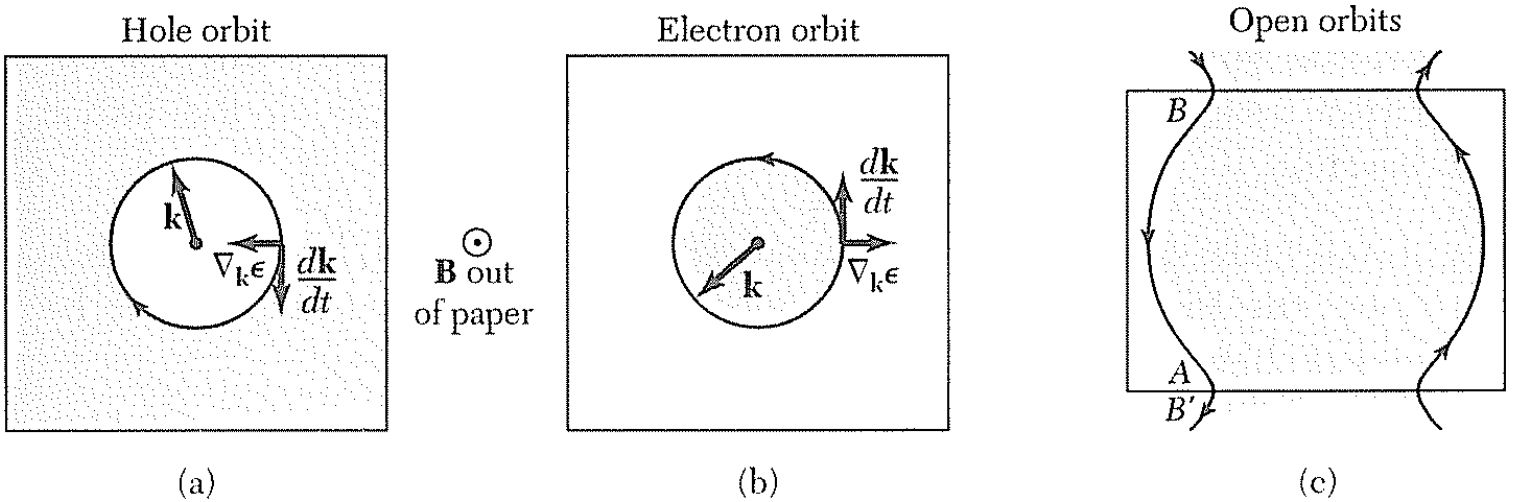


Free electron Fermi circle in the third zone drawn in the periodic zone scheme

Three Types of Orbits in Magnetic Field

Lorentz force on the electron:

$$\hbar\frac{d\mathbf{k}}{dt} = -\frac{e}{c}\mathbf{v}\times\mathbf{B} \longrightarrow \frac{d\mathbf{k}}{dt} = -\frac{e}{\hbar^2 c}\nabla_{\mathbf{k}}\epsilon\times\mathbf{B} \qquad \mathbf{v} = \hbar^{-1}\nabla_{\mathbf{k}}\epsilon$$



Motion in a magnetic field of the wavevector of an electron on the Fermi surface.

Orbits that enclose filled states are electron orbits. Orbits that enclose empty states are hole orbits. Orbits that move from zone to zone without closing are open orbits.

Schematic Shape of a 3-D Fermi Surface

In 3D crystals the periodic potential distorts the shape of a Fermi sphere in the vicinity of the BZ boundary. A schematic example for a simple cubic lattice and a crude model E(k) function is shown here:

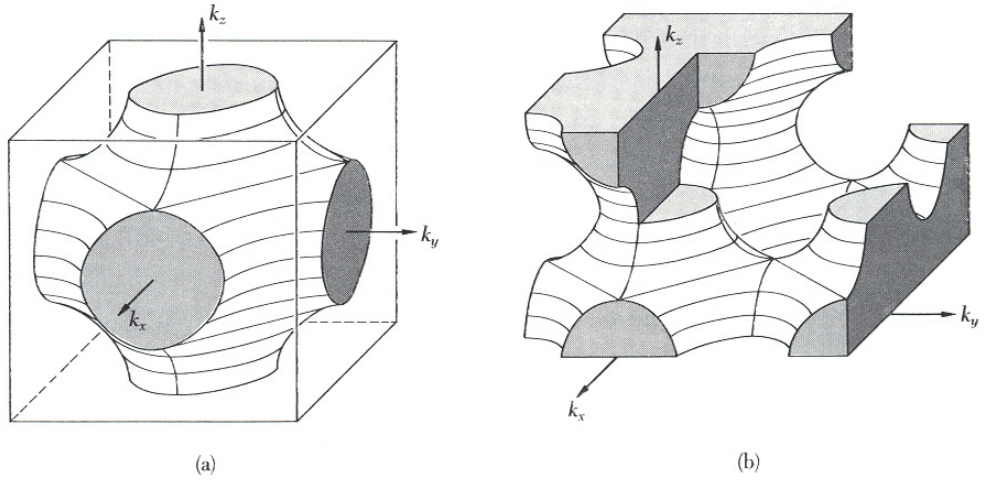


Figure 15 Constant energy surface in the Brillouin zone of a simple cubic lattice, for the assumed energy band $\epsilon_k = -\alpha - 2\gamma(\cos k_x a + \cos k_y a + \cos k_z a)$. (a) Constant energy surface $\epsilon = -\alpha$. The filled volume contains one electron per primitive cell. (b) The same surface exhibited in the periodic zone scheme. The connectivity of the orbits is clearly shown. Can you find electron, hole, and open orbits for motion in a magnetic field $B\hat{z}$? (A. Sommerfeld and H. A. Bethe.)

Note: the Fermi circle does not completely fill the 1st BZ but makes contact with the 1st BZ boundary along the [100] directions.

Shape of 3-D Energy Bands in a Real Metal

In 3D the energy bands are plotted along the major symmetry directions in the 1st BZ. Many of the high symmetry points on the 1st BZ boundary are labeled by letters.

The gamma point (Γ) is always the zone center, where k = 0.

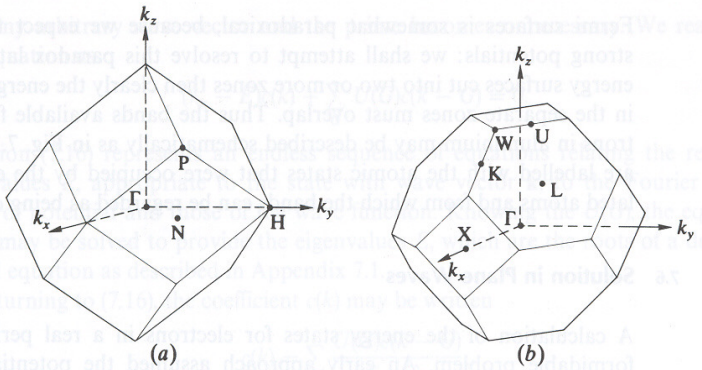
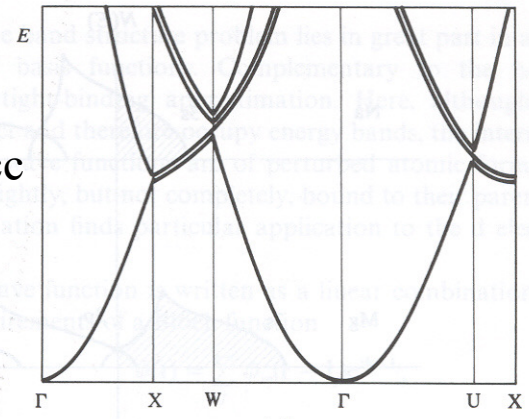


Figure 7.15 The first Brillouin zone for the bcc (a) and fcc (b) lattices.

Free-electron bands in an fcc crystal



Electron bands in Al

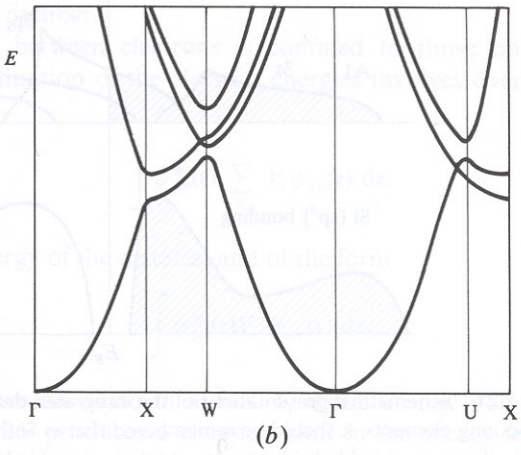


Figure 7.20 A comparison of the empty-lattice energy bands (a) and detailed calculations for Al (b). Again the nearly free electron character of Al is confirmed. (Harrison, W., *Pseudopotentials in the Theory of Metals*, 1966, Addison-Wesley Publishing Co., Reading, Massachusetts. Figures 3.19 and 3.20. Reprinted with permission.)

Quantization of Orbits in Magnetic Field

The momentum $\mathbf{p}$ of a particle in a magnetic field $\mathbf{B}$ is the sum of two parts:

$$\mathbf{p} = \mathbf{p}_{\text{kin}} + \mathbf{p}_{\text{field}} = \hbar\mathbf{k} + q\mathbf{A}/c \quad \text{and} \quad \mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$$

the orbits in a magnetic field are quantized by the Bohr-Sommerfeld relation

$$\oint \mathbf{p} \cdot d\mathbf{r} = (n + \gamma)2\pi h \quad , \quad \text{when } n \text{ is an integer and } \gamma \text{ is a phase correction}$$

The equation of motion of a particle of charge q in a magnetic field is

$$\hbar \frac{d\mathbf{k}}{dt} = \frac{q}{c} \frac{d\mathbf{r}}{dt} \times \mathbf{B} \quad \Rightarrow \quad \hbar\mathbf{k} = \frac{q}{c} \mathbf{r} \times \mathbf{B}$$

Thus,

$$\begin{aligned} \oint \mathbf{p} \cdot d\mathbf{r} &= \oint \hbar\mathbf{k} \cdot d\mathbf{r} + \frac{q}{c} \oint \mathbf{A} \cdot d\mathbf{r} \\ &= \frac{q}{c} \oint \mathbf{r} \times \mathbf{B} \cdot d\mathbf{r} + \frac{q}{c} \int \mathbf{curl}\, \mathbf{A} \cdot d\boldsymbol{\sigma} \\ &= -\frac{q}{c} \mathbf{B} \cdot \oint \mathbf{r} \times d\mathbf{r} + \frac{q}{c} \int \mathbf{B} \cdot d\boldsymbol{\sigma} \\ &= -\frac{2q}{c} \Phi + \frac{q}{c} \Phi = -\frac{q}{c} \Phi = (n + \gamma)2\pi\hbar \end{aligned}$$

It follows that the orbit of an electron is quantized in such a way that the flux through it is

$$\Phi_n = (n + \gamma)(2\pi\hbar c/e) \quad .$$

The flux unit $2\pi\hbar c/e = 4.14 \times 10^{-7}$ gauss cm^2 or T m^2.

$\because$ $\hbar\mathbf{k} = \frac{q}{c}\mathbf{r} \times \mathbb{B}$, a line element Δr in the plane normal to $\mathbb{B}$ is

$\Delta r = (\hbar c/eB)\Delta k$, so that the area S_n in $\mathbf{k}$ space is related to the area A_n of the orbit in $\mathbf{r}$ space by

$$A_n = (\hbar c/eB)^2 S_n$$

Thus,

$$\Phi_n = BA_r = \left(\frac{\hbar c}{e}\right)^2 \frac{1}{B} S_n = (n + \gamma)\frac{2\pi\hbar c}{e}$$

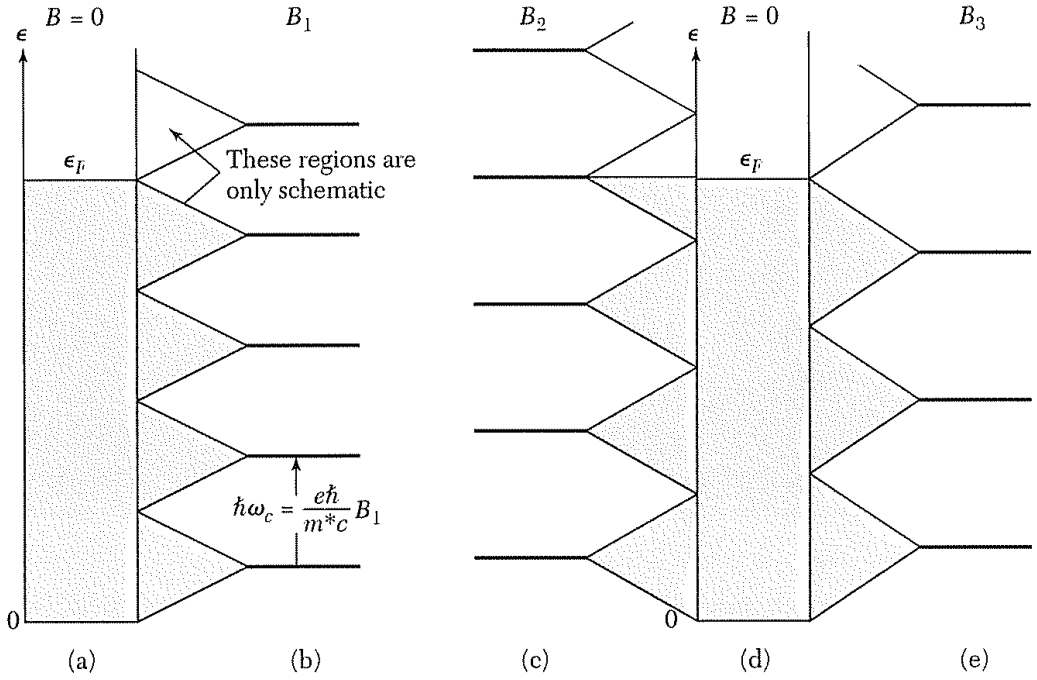
$$\Rightarrow \quad \boxed{S_n = (n + \gamma)\frac{2\pi e}{\hbar c} B}$$

De Haas-van Alphen Effect

The de Haas-van Alphen effect is the oscillation of the magnetic moment of a metal as a function of the static magnetic field intensity. The effect can be observed in pure specimens at low temperatures in strong magnetic fields:

Assume the magnetic field is applied along the z axis, the area of an orbit in k_x, k_y plane is quantized and the area between successive orbits is

$$\Delta S = S_n - S_{n-1} = 2\pi eB/\hbar c$$



The number of free electron orbits collapsed into a **Landau level** is

Degeneracy of Orbits in Magnetic Field

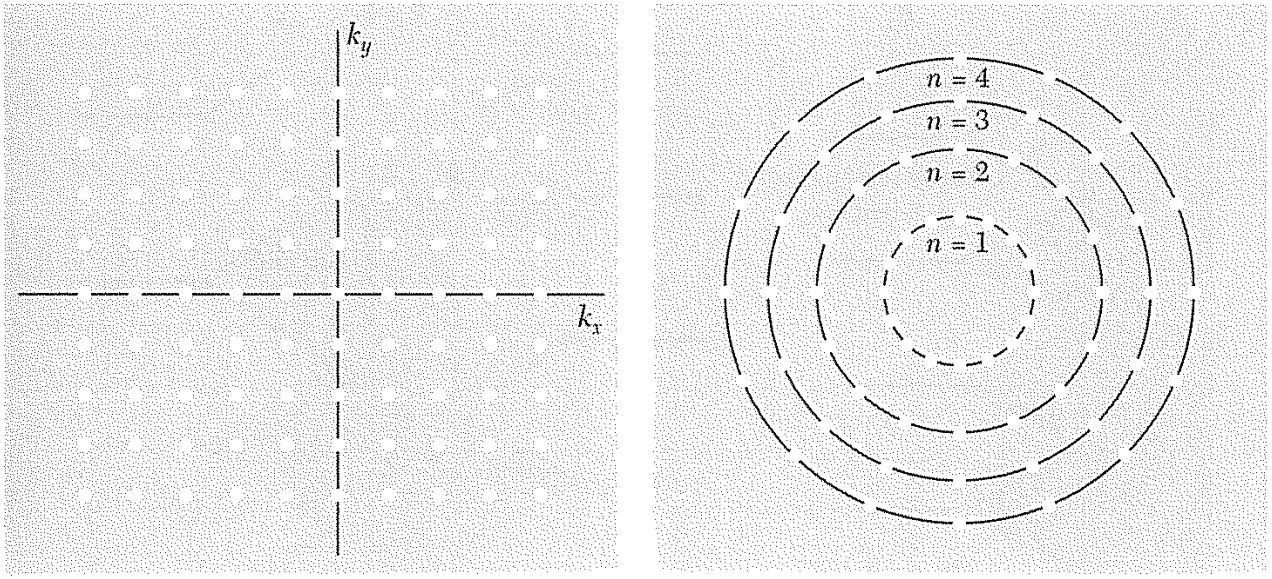


Figure 24 (a) Allowed electron orbitals in two dimensions in absence of a magnetic field. (b) In a magnetic field the points which represent the orbitals of free electrons may be viewed as restricted to circles in the former $k_x k_y$ plane.

The area between successive circles is

$$\pi\Delta(k^2) = 2\pi k(\Delta k) = (2\pi m/\hbar^2)\,\Delta\epsilon = 2\pi m\omega_c/\hbar - 2\pi eB/\hbar c$$

The number of free electron orbits collapsed into a **Landau level** is

$$D = (2\pi eB/\hbar c)(L/2\pi)^2 = \rho B \qquad \text{where } \rho = eL^2/2\pi\hbar c,$$

Orbital Degeneracy Increases with *B*

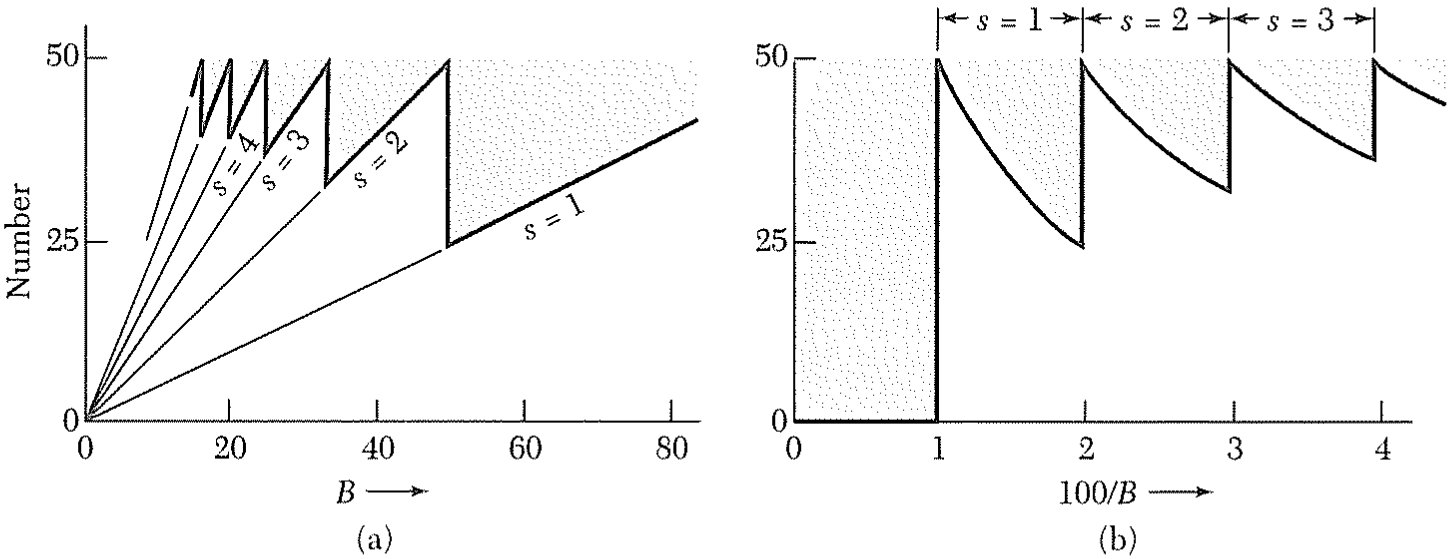
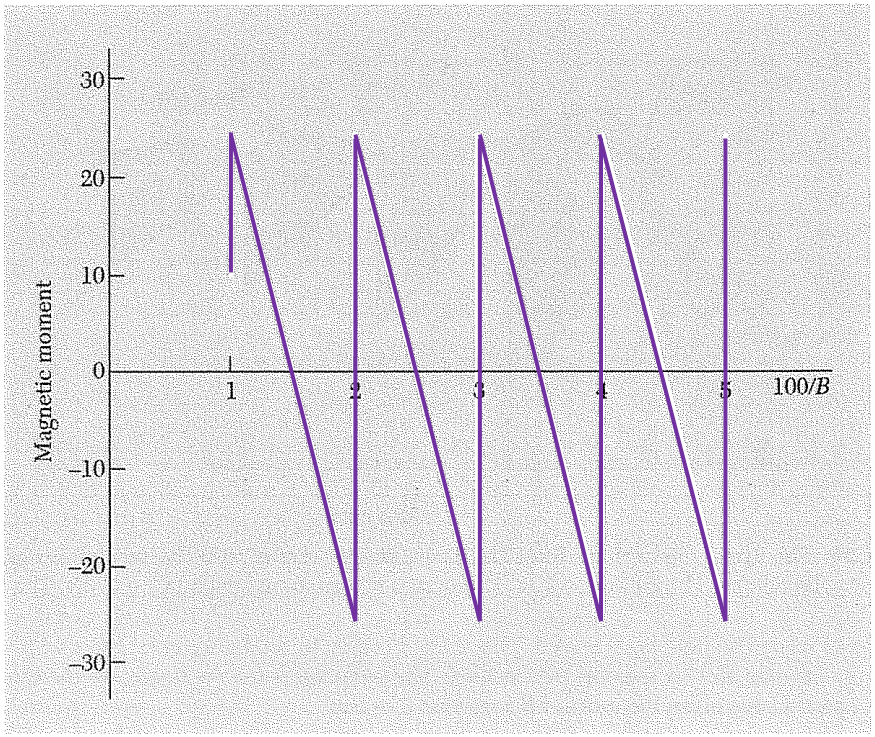


Figure 25 (a) The heavy line gives the number of particles in levels which are completely occupied in a magnetic field B, for a two-dimensional system with $N = 50$ and $\rho = 0.50$. The shaded area gives the number of particles in levels partially occupied. The value of s denotes the quantum number 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 $1/B$.

dHvA Oscillation

The magnetic moment μ of a system at absolute zero is given by $\mu = -\partial U/\partial B$. The moment here is an oscillatory function of $1/B$, Fig. 27. This oscillatory magnetic moment of the Fermi gas at low temperatures is the de Haas-van Alphen effect.



The oscillations occur at equal interval of $1/B$ so that

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

where S is the extremal area of the Fermi surface normal to the direction of $\boldsymbol{B}$.

Extremal Orbits in Magnetic Field

For a Fermi surface of general shape the sections at different values of k_B will have different periods. Here k_B is the component of k along the direction of the magnetic field. The response will be the sum of contributions from all sections or all orbits. *But the dominant response of the system comes from orbits whose periods are stationary with respect to small changes in* k_B. Such orbits are called **extremal orbits**. Thus, in Fig. 28 the section AA' dominates the observed cyclotron period.

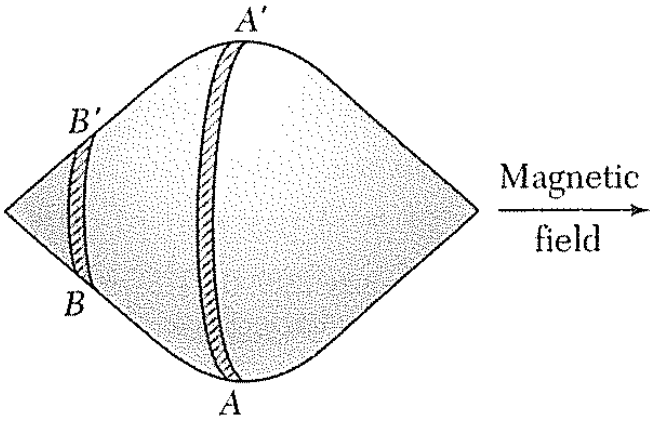


Figure 28 The orbits in the section AA' are extremal orbits: the cyclotron period is roughly constant over a reasonable section of the Fermi surface. Other sections such as BB' have orbits that vary in period along the section.

Fermi Surface of Copper

Even if the free-electron Fermi sphere does not intersect a BZ boundary, its shape can still be affected at points close to the boundary where the energy bands begin to deviate from the free-electron parabolic shape. This is the case with Cu.

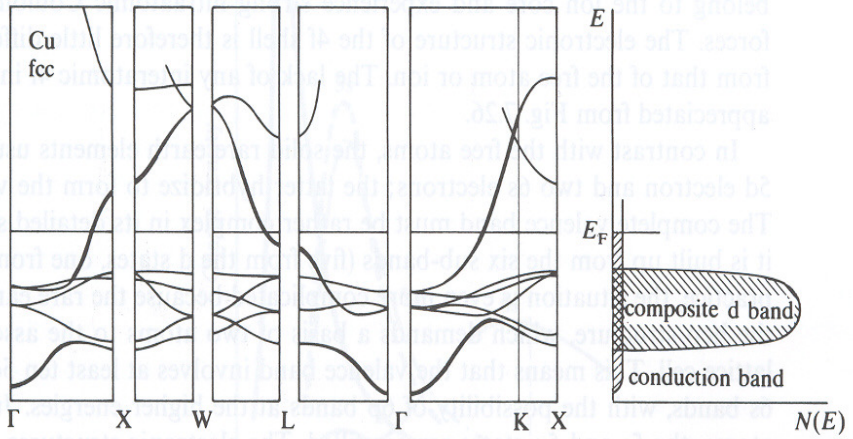


Figure 7.25 The complete band structure diagram for Cu along the major symmetry directions (compare with the Brillouin zone of Fig. 7.15*b*). The diagram to the right is a simple schematic representation of the integrated density of levels and is convenient as a basis for the discussion of many physical properties of the later 'd' metals. We shall soon find that the sp valence electrons are responsible for the electrical conductivity of these metals; one therefore speaks of the 'conduction band'. (After Segall 1962.)

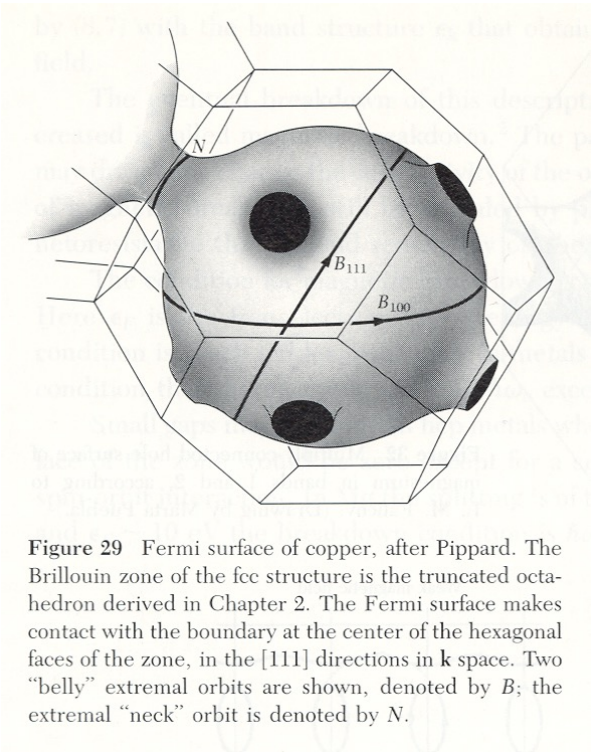


Figure 29 Fermi surface of copper, after Pippard. The Brillouin zone of the fcc structure is the truncated octahedron derived in Chapter 2. The Fermi surface makes contact with the boundary at the center of the hexagonal faces of the zone, in the [111] directions in **k** space. Two "belly" extremal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

Just a slightly perturbed free-electron sphere!

Fermi Surface of Gold

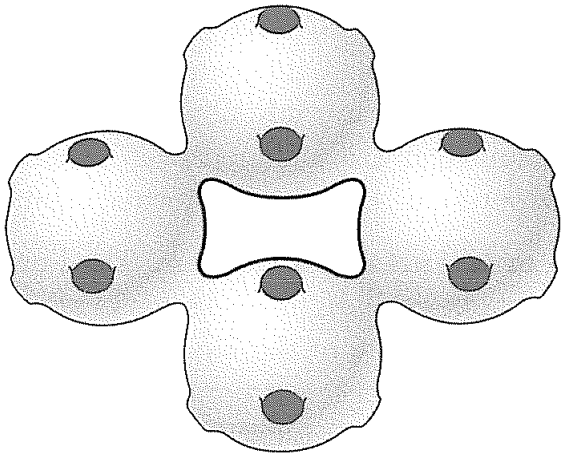


Figure 30 Dog's bone orbit of an electron on the Fermi surface of copper or gold in a magnetic field This orbit is classified as holelike because the energy increases toward the interior of the orbit

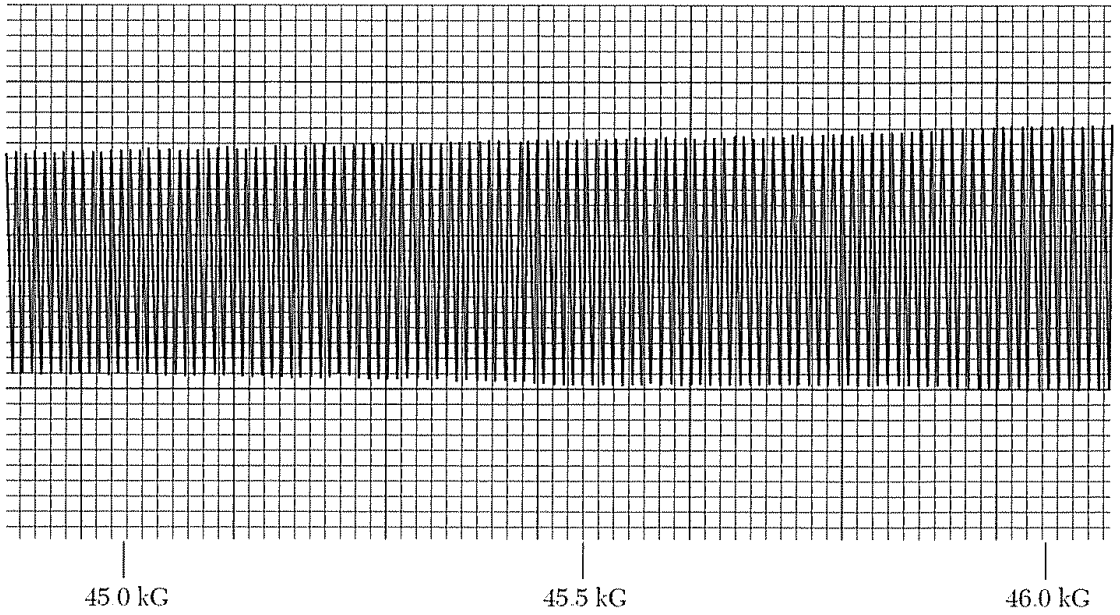
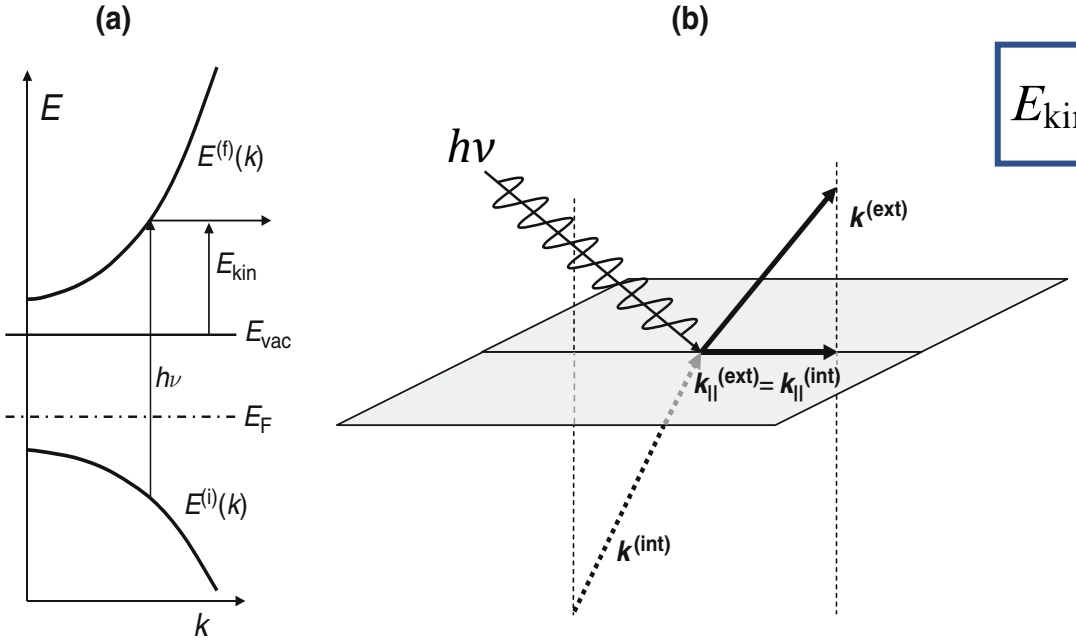


Figure 31 De Haas-van Alphen effect in gold with **B** || [110] The oscillation is from the dog's bone orbit of Fig. 30 The signal is related to the second derivative of the magnetic moment with respect to field. The results were obtained by a field modulation technique in a high-homogeneity superconducting solenoid at about 1.2 K. (Courtesy of I. M. Templeton.)

Photoemission Process

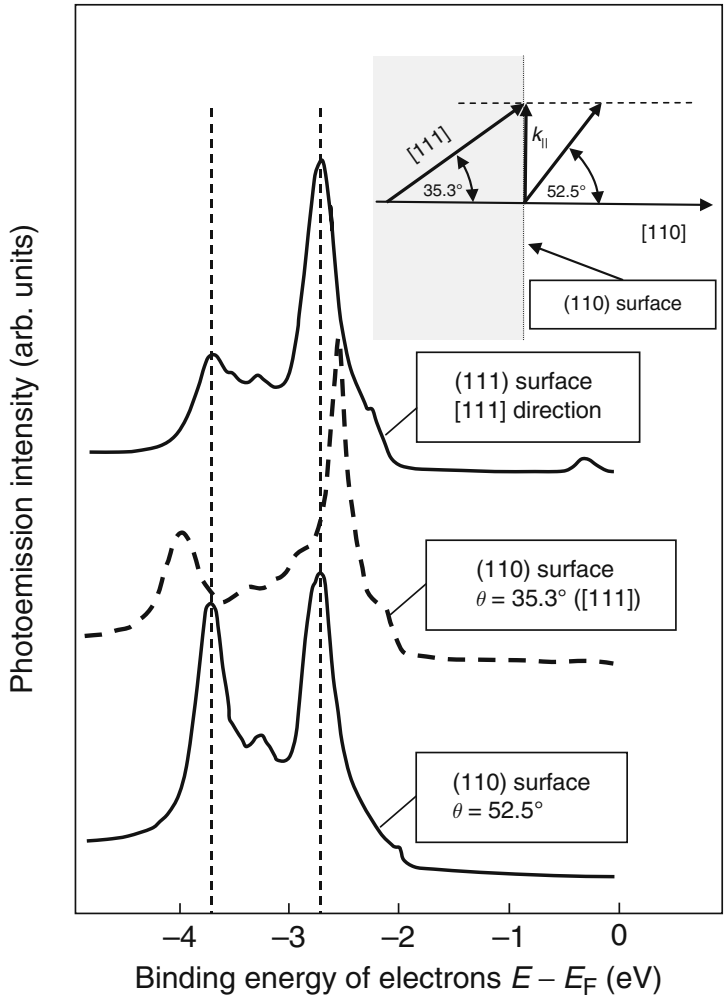
$$I_{\mathrm{ph}}(\boldsymbol{k}_{||}^{(\mathrm{el})}, E_{\mathrm{kin}}) \propto \sum_{i,j} \sum_{k_z} \left| \left\langle j, \boldsymbol{k}_{||}, k_z | \boldsymbol{x} | i, \boldsymbol{k}_{||}, k_z \right\rangle \right|^2 \times \delta(E_{\mathrm{kin}} + E_{\mathrm{vac}} - E^{(\mathrm{i})}(\boldsymbol{k}_{||}, k_z) - h\nu)\delta(\boldsymbol{k}_{||} - \boldsymbol{k}_{||}^{(\mathrm{el})})$$



$$E_{\mathrm{kin}} = -E_{\mathrm{vac}} + E^{(\mathrm{i})}(\boldsymbol{k}_{||}, k_z) + h\nu$$

Here, i, j denote the initial and final bands, $\boldsymbol{k}_{||}$, k_z are the components of the wave vector in the initial and the final state, and $E^{(\mathrm{i})}$, E_{vac} are the energies of the initial state and the vacuum level.

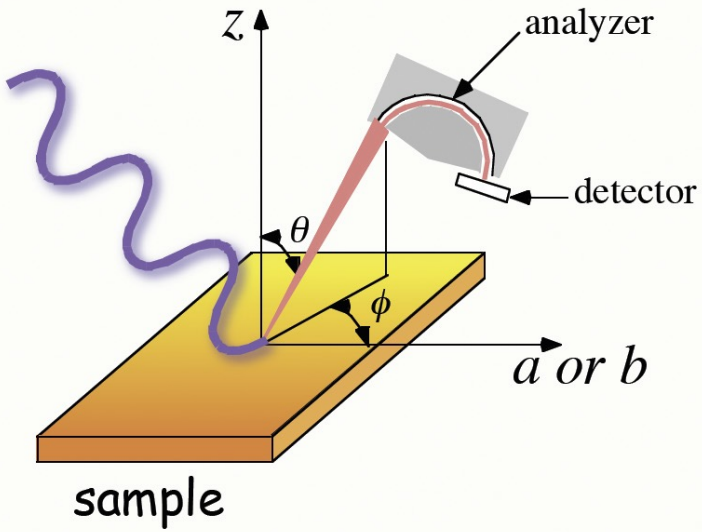
Photoemission Spectra of Cu(111) and Cu(110)



Photoemission spectra of Cu(111) and Cu(110) surfaces serving to establish the wave vector k_{111} for bulk electronic states: the two prominent peaks appearing in the spectra along [111] on Cu(111) are found at an angle of θ = 52.5° in the [110] zone on Cu(110). The magnitude of k_{111} is determined by considering $\boldsymbol{k}_{||}$ conservation.

$$k_{||}^{(\mathrm{int})} = k_{||}^{(\mathrm{ext})} \Rightarrow k_{111}^{(\mathrm{int})} \sin 35^\circ = k^{(\mathrm{ext})} \sin 52.5^\circ$$

Angle-resolved photoemission spectroscopy (ARPES)



We need:

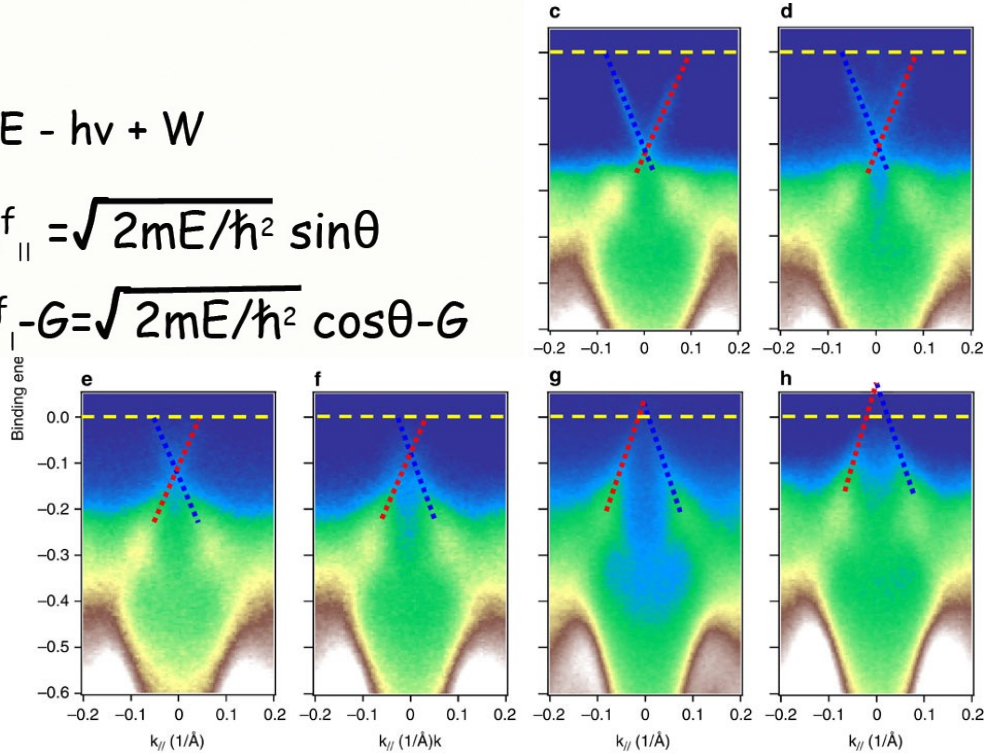
binding energy - E_b

initial momentum - k^i

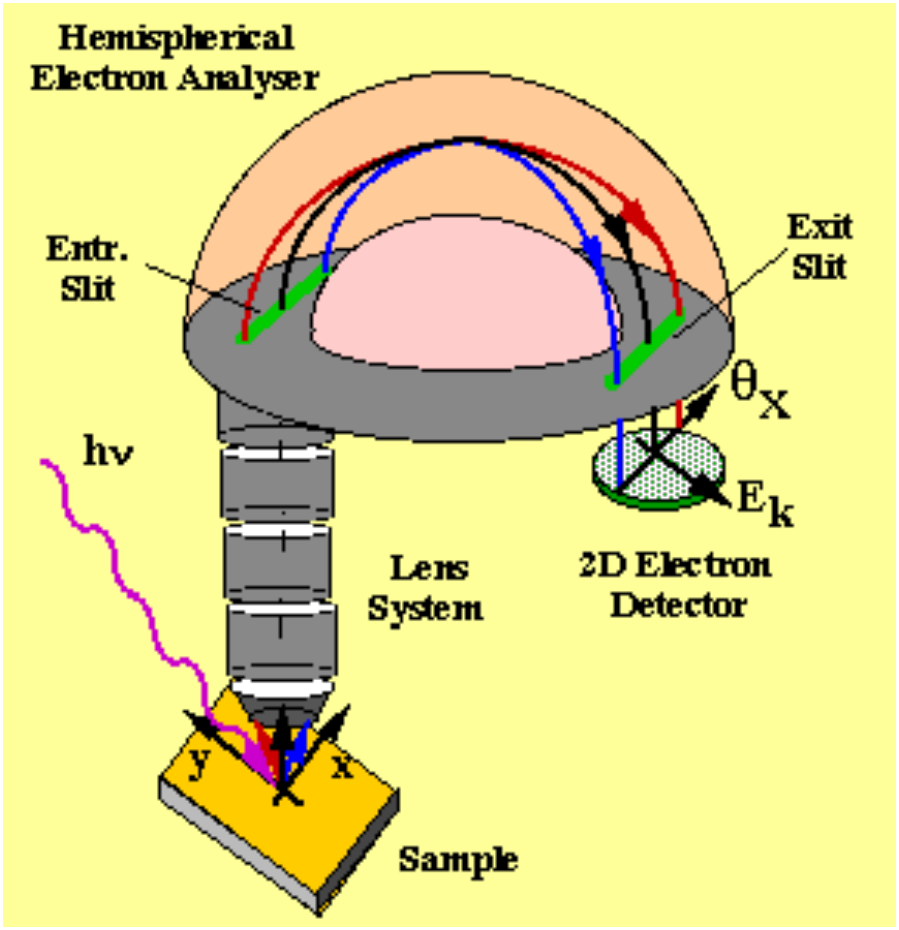
$$E_b = E - h\nu + W$$

$$k^i_{||} = k^f_{||} = \sqrt{2mE/\hbar^2}\sin\theta$$

$$k^i_{\perp} = k^f_{\perp} - G = \sqrt{2mE/\hbar^2}\cos\theta - G$$



Concentric Hemispherical Analyzer (CHA)



$\Delta E/E_0 = s/ R_0$

s: mean slit width; R_0: mean radius

Problems

1. ***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.

2. ***De Haas-van Alphen period of potassium.*** (a) Calculate the period $\Delta(1/B)$ expected for potassium on the free electron model. (b) What is the area in real space of the extremal orbit, for $B = 10$ kG $= 1$ T? The same period applies to oscillations in the electrical resistivity, known as the Shubnikow-de Haas effect.

Problems

3. ***Landau levels.*** The vector potential of a uniform magnetic field $B\hat{\mathbf{z}}$ is $\mathbf{A} = -By\hat{\mathbf{x}}$ in the Landau gauge. The hamiltonian of a free electron without spin is

$$H = -(\hbar^2/2m)(\partial^2/\partial y^2 + \partial^2/\partial z^2) + (1/2m)[-i\hbar\partial/\partial x - eyB/c]^2 \ .$$

We will look for an eigenfunction of the wave equation $H\psi = \epsilon\psi$ in the form

$$\psi = \chi(y)\exp[i(k_x x + k_z z)] \ .$$

(a) Show that $\chi(y)$ satisfies the equation

$$(\hbar^2/2m)d^2\chi/dy^2 + [\epsilon - (\hbar^2 k_z^2/2m) - \tfrac{1}{2}m\omega_c^2(y - y_0)^2]\chi = 0 \ ,$$

where $\omega_c = eB/mc$ and $y_0 = c\hbar k_x/eB$. (b) Show that this is the wave equation of a harmonic oscillator with frequency ω_c, where

$$\epsilon_n = (n + \tfrac{1}{2})\hbar\omega_c + \hbar^2 k_z^2/2m \ .$$