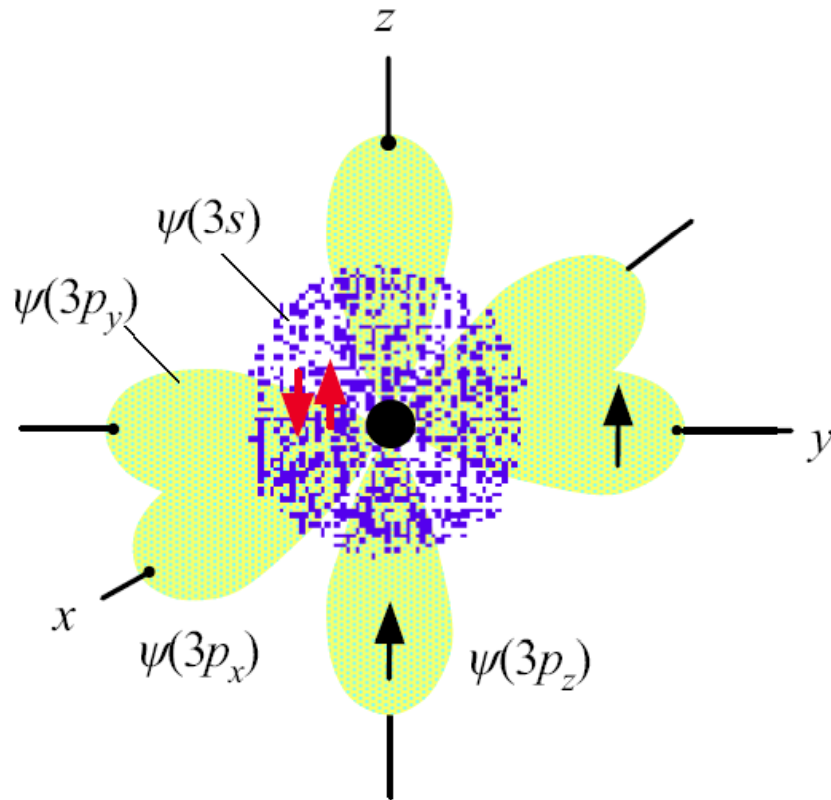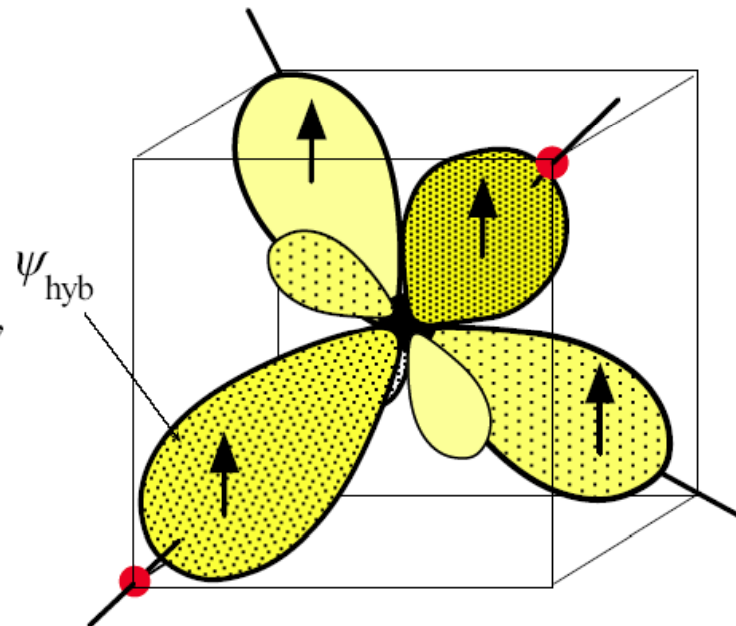# Lecture 16

Band structure & Energy levels in Metals & Semiconductors
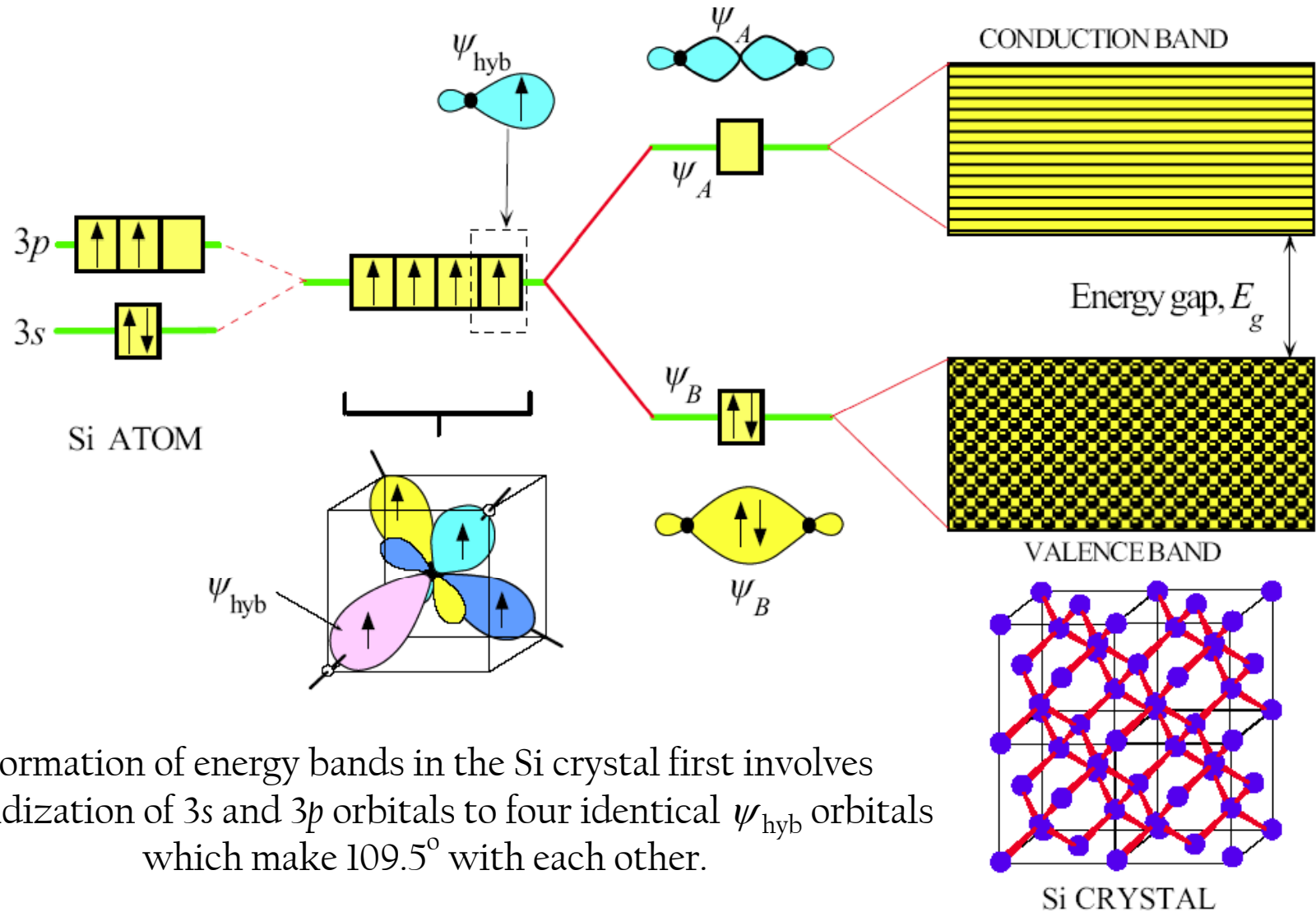
Hybridization of Si orbitals

(a) Isolated Si

(b) Si preparing to bond

When Si is about to bond, the one 3s orbital and the three 3p orbitals become perturbed and mixed to form four hybridized orbitals, ψ_{hyb}, called sp^3 orbitals, which are directed toward the corners of a tetrahedron. The ψ_{hyb} orbital has a large major lobe and a small back lobe. Each ψ_{hyb} orbital takes one of the four valence electrons.

Hybridization of Si orbitals

Formation of energy bands in the Si crystal first involves hybridization of 3s and 3p orbitals to four identical ψ_{hyb} orbitals which make 109.5° with each other.

ψ_{hyb} orbitals on two neighboring Si atoms can overlap to form ψ_B or ψ_A. The first is a bonding orbital (full) and the second is an antibonding orbital (empty). In the crystal ψ_B overlap to give the valence band (full) and ψ_A overlap to give the conduction band (empty).

Energy bands arise from bonding & antibonding wavefunctions
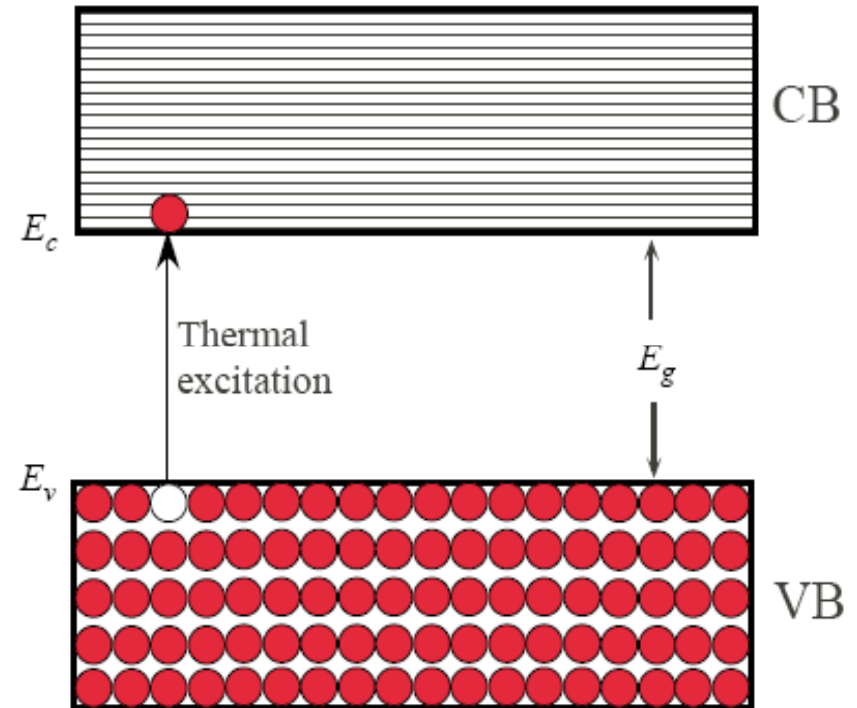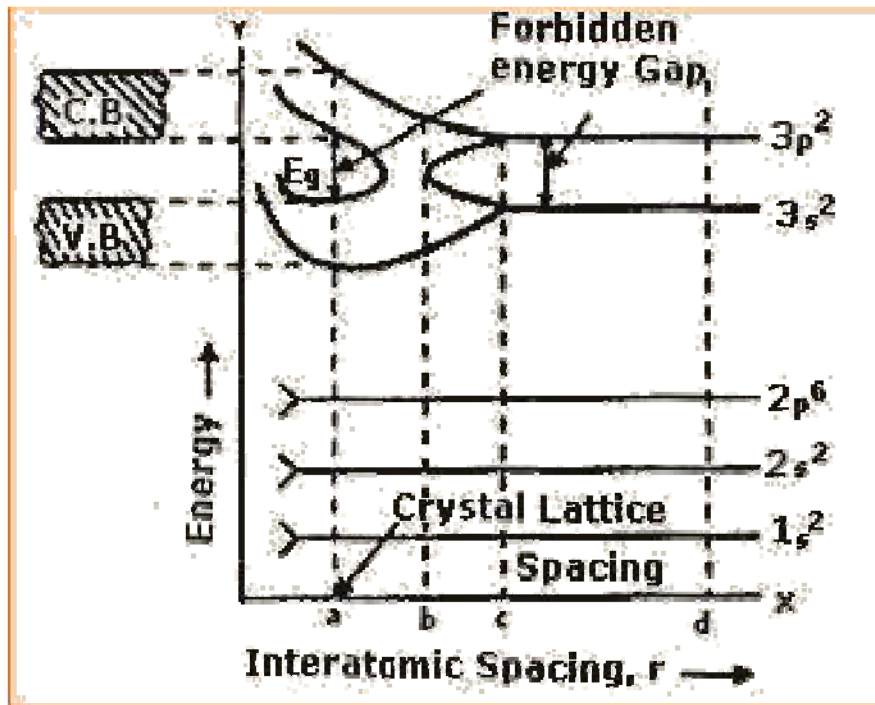
Left: potential energy versis atomic separation. At the equilibrium distance for Si, a bandgap is formed.
Right: Simple energy band diagram of a semiconductor. CB is the conduction band and VB is the valence band. AT 0 K, the VB is full with all the valence electrons.

Determining the number of electrons in a band, n

Why? n → conductivity

Analogy: Calculate the population of San Francisco

1.Find the density of houses in the city (# houses/area): g(A)
2.Multiply g(A) by the probability of finding a person in the house: f(A)
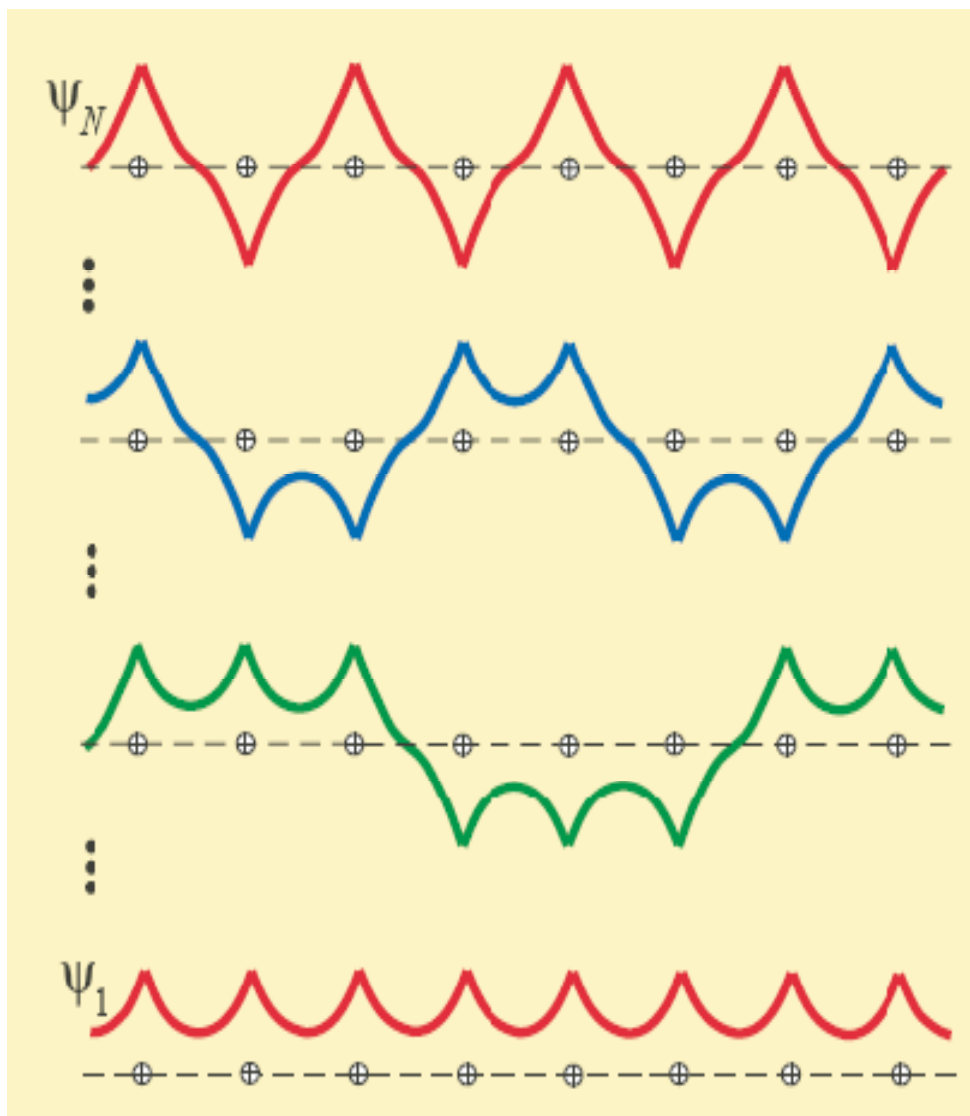3.Integrate over the area of the city

Distribution function $n = \int_{band} f(E)g(E)dE$ Density of states

Density of States, g(E)

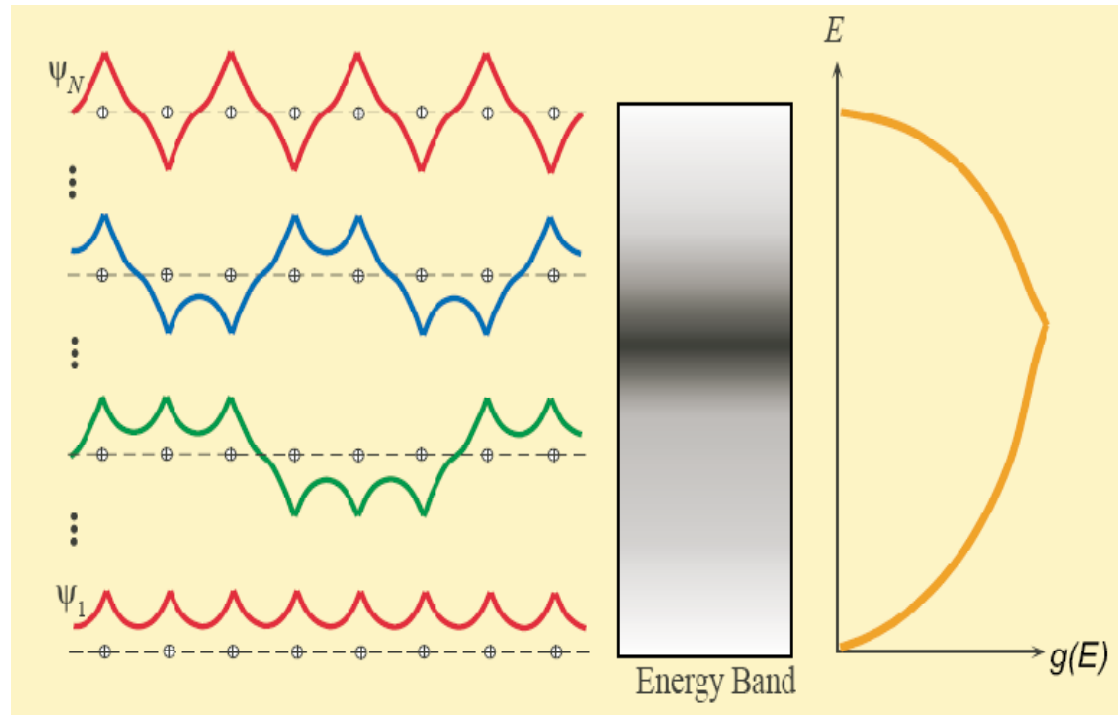How are the energies of the electrons distributed in a band?

1 state with the highest energy

Many states with comparable intermediate energies (given by the # of nodes)

1 state with the lowest energy

Density of States, g(E)

g(E) is the number of states (wavefunctions) in the energy interval E to (E+dE) per unit volume of the sample. It is crucial for determining the electron concentration per unit energy in a sample.

The total number of states per unit volume up to some energy E' is:

$$S_V(E) = \int_0^{E'} g(E)dE$$

Deriving the density of states in 2D -- metal

Let's consider the electrons in the solid to be in a 3D potential well of volume V, with sides L. The energy of the electrons is:

$$E_{n_1 n_2 n_3} = \frac{h^2}{8mL^2}\left(n_1^2 + n_2^2 + n_3^2\right)$$

In 2D, we only have n_1 and n_2.

Each state, or electron wavefunctions in the crystal, can be represented by a box at n_1, n_2.

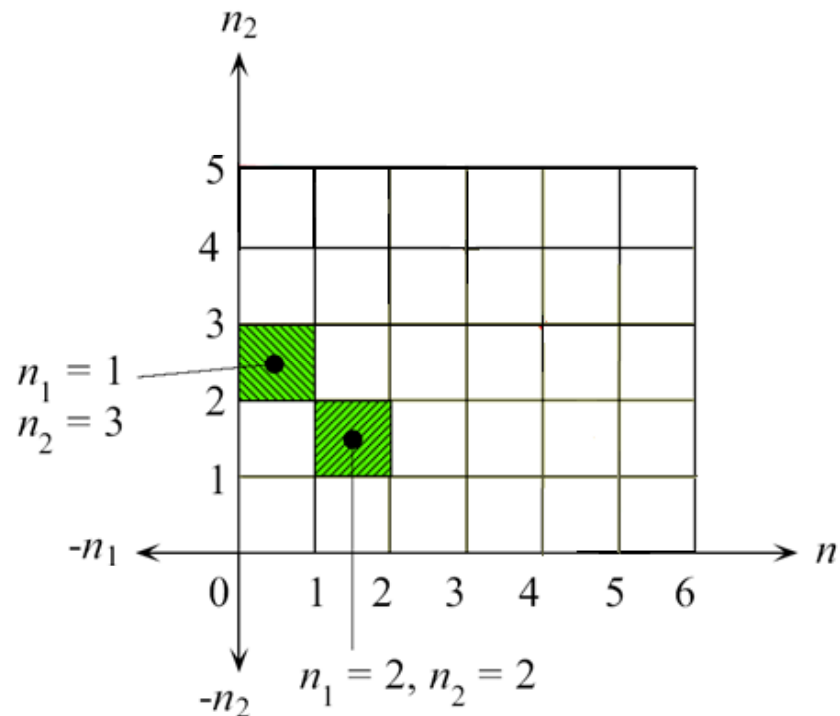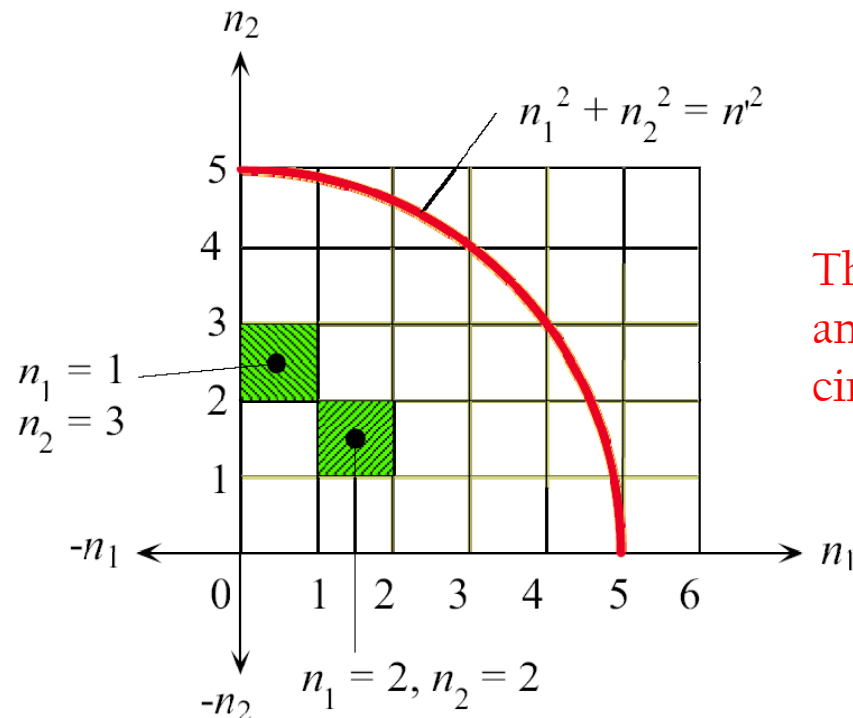How many combinations of n_1 and n_2 have an energy less than E'?

Deriving the density of states in 2D -- metal

Let's consider the electrons in the solid to be in a 3D potential well of volume V, with sides L. The energy of the electrons is:

$$E_{n_1 n_2 n_3} = \frac{h^2}{8mL^2}\left(n_1^2 + n_2^2 + n_3^2\right)$$

In 2D, we only have n_1 and n_2.

Each state, or electron wavefunctions in the crystal, can be represented by a box at n_1, n_2.

The area contained by n_1 and n_2 approximates a circle with area $\tfrac{1}{4}(\pi n'^2)$

Deriving the density of states in 3D -- metal

In three dimensions, the volume defined by a sphere of radius n' and the positive axes n_1, n_2, and n_3, contains all the possible combinations of positive n_1, n_2, and n_3 values that satisfy $n_1^2 + n_2^2 + n_3^2 \leq n'^2$

In here $n_1^2 + n_2^2 + n_3^2 \leq n'^2$

Vol. $= \frac{1}{8}(\frac{4}{3} \pi n'^3)$
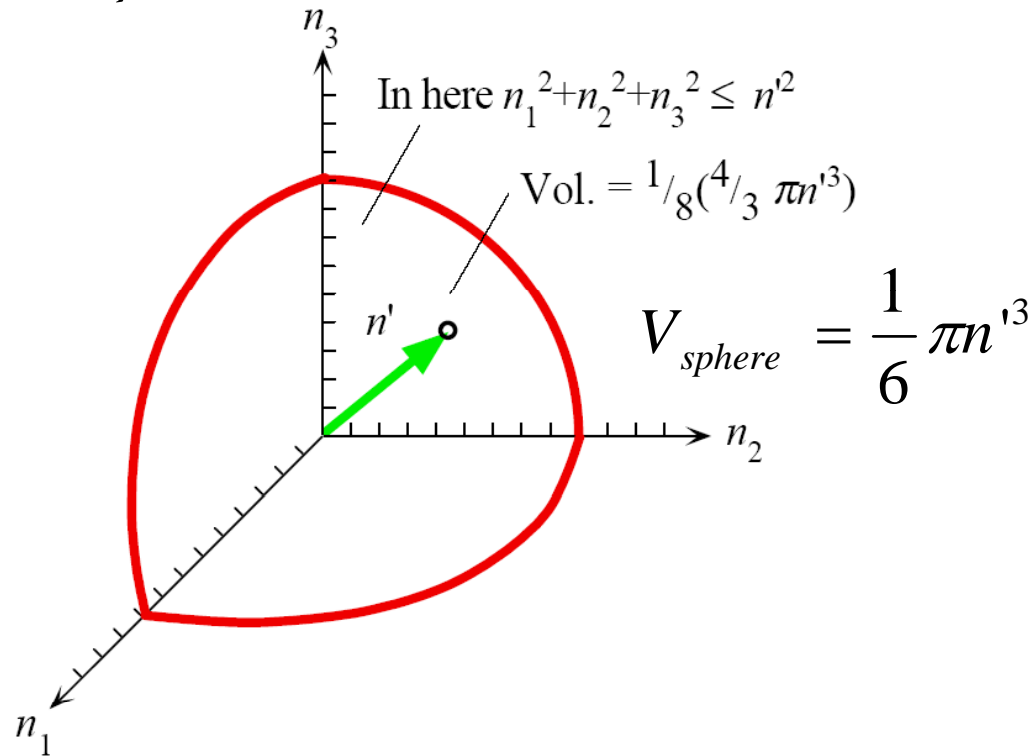
$$V_{sphere} = \frac{1}{6} \pi n'^3$$

Each orbital can hold two electrons, so the total number of states up to some quantum number n' is:

$$S(n) = 2V_{sphere} = \frac{1}{3} \pi n'^3$$

Deriving the density of states in 3D -- metal

$$S(n) = 2V_{sphere} = \frac{1}{3}\pi n'^3$$

$$E_{n_1 n_2 n_3} = \frac{h^2}{8mL^2}\left(n_1^2 + n_2^2 + n_3^2\right) = \frac{h^2 n^2}{8mL^2} \longrightarrow n'^2 = \frac{8mL^2 E'}{h^2}$$
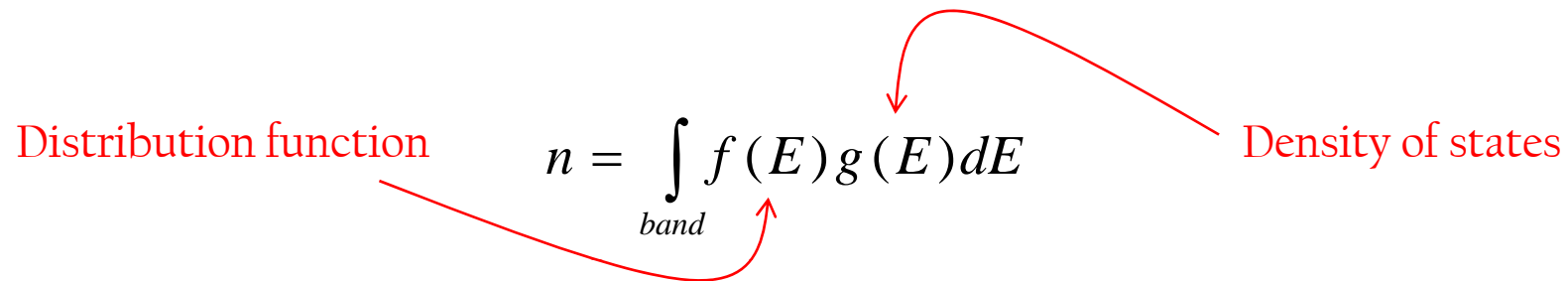
$$S(E') = \frac{\pi L^3 \left(8mE'\right)^{3/2}}{3h^3}$$

Since L^3 is the volume of the solid, the total number of states per unit volume is:

$$S_V(E') = \frac{\pi \left(8mE'\right)^{3/2}}{3h^3}$$

$$g(E) = \frac{dS_V}{dE} = \left(8\pi 2^{1/2}\right)\left(\frac{m_e}{h^2}\right)^{3/2} E^{1/2}$$

Determining the number of electrons in a band, n

Distribution function

$$n = \int_{band} f(E)\, g(E)\, dE$$

Density of states

Knowing how are the energies of the electrons are distributed in a band (g(E)), we seek the probability of finding a particle with an energy E (i.e., the "distribution function," f(E)).

# The Distribution Function f(E) & Particle Statistics

The probability of finding a particle with a given energy will depend on whether or not multiple particles can occupy the same energy state.

Formally, particles are called "bosons" if they can occupy the same energy state or "fermions" if they cannot.

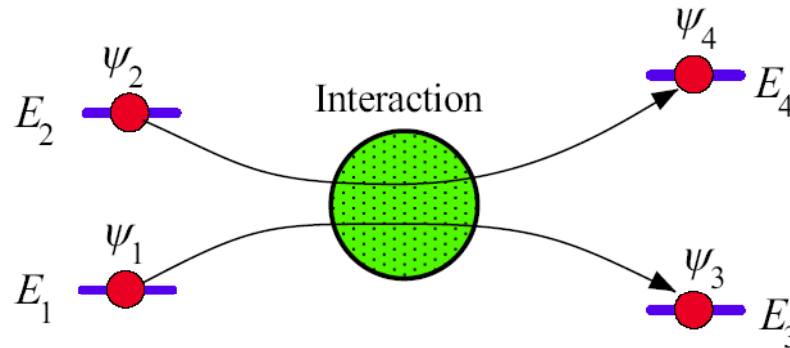Ex: Bose-Einstein Condensation (Nobel Prize, 2001)

Rubidium gas
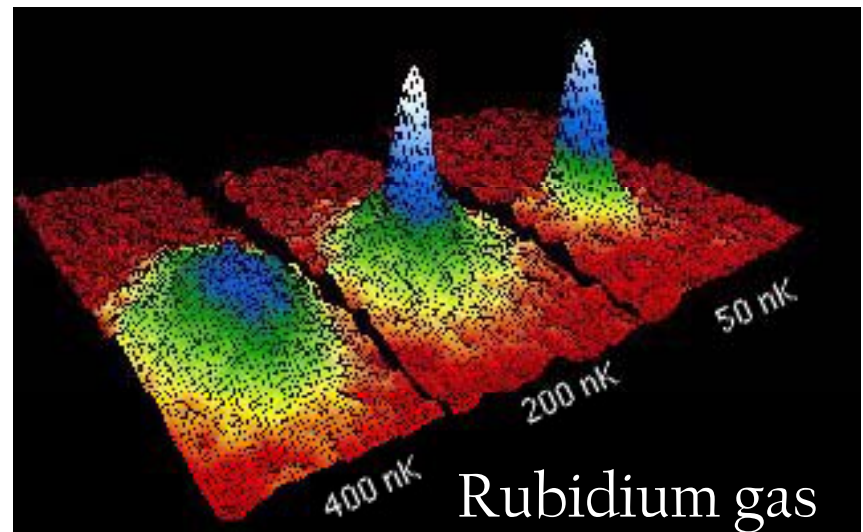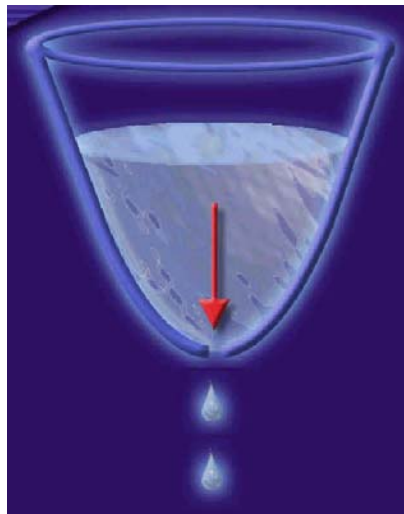
Boltzmann Statistics
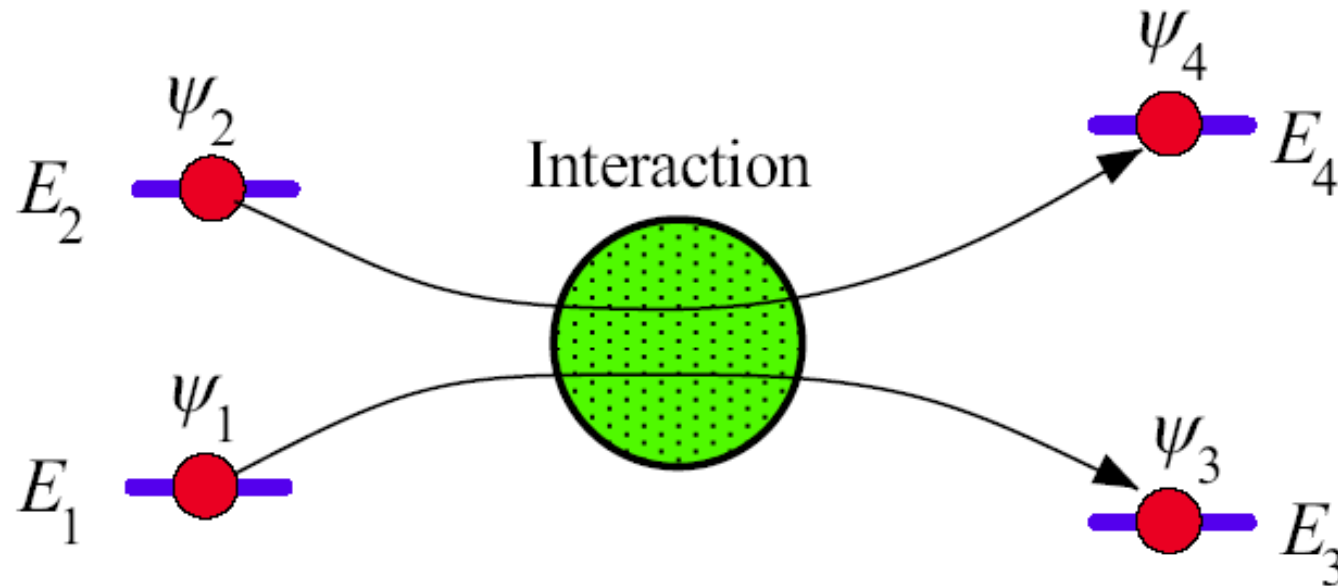
Two particles with initial wavefunctions ψ_1 and ψ_2 at E_1 and E_2 interact and end up at different energies E_3 and E_4. Their corresponding wavefunctions are ψ_3 and ψ_4.

Here, let's assume it doesn't matter if E_3 and E_4 are already occupied by other particles.

Boltzmann Statistics

P(E)=probability of an particle having energy E

The probability of an particle with energy E_1 interacting with an particle of energy E_2 is: $P(E_1)P(E_2)$

The probability of the reverse process is $P(E_3)P(E_4)$

In thermal equilibrium, the forward process will be just as likely as the reverse process:
$$P(E_1)P(E_2)=P(E_3)P(E_4)$$

Also: $E_1+E_2=E_3+E_4$ (conservation of energy)

Boltzmann Statistics
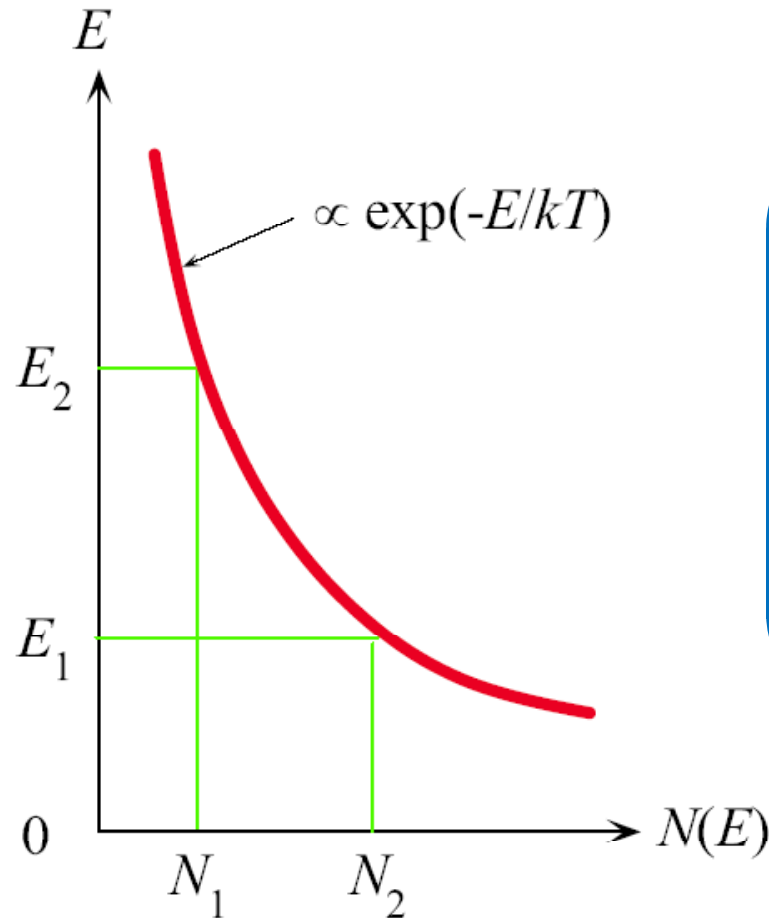
The only function that satisfies:

$$P(E_1)P(E_2) = P(E_3)P(E_4)$$

$$E_1 + E_2 = E_3 + E_4$$

Is the Boltzmann function:

$$P(E) = A \exp\left(-\frac{E}{kT}\right)$$

Boltzmann Distribution

$\propto \exp(-E/kT)$

### Boltzmann Statistics for two energy levels

$$\frac{N_2}{N_1} = \exp\left(-\frac{E_2 - E_1}{kT}\right)$$

as T increases, N_2/N_1 increases

The Boltzmann energy distribution describes the statistics of boson particles, which are not restricted by how many particles can occupy an energy level.

The distribution also holds for electrons (fermions) when there are many more available states than the number of particles.

Fermi-Dirac Statistics
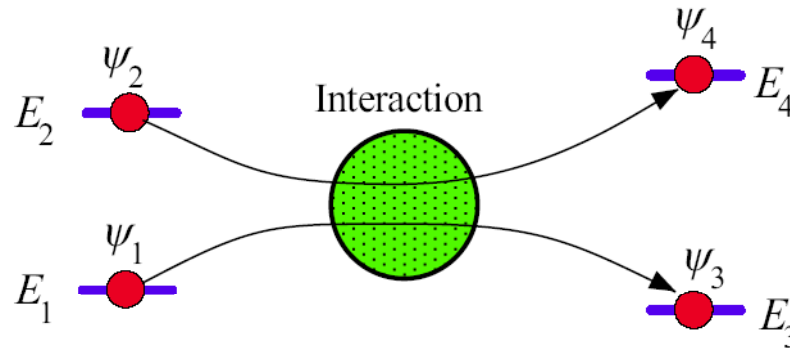
Now, consider particles that cannot occupy identical energy levels (i.e., electrons obeying the Pauli exclusion principle)

When particles 1 and 2 interact, they can only enter new energy levels that are not already occupied

The probability of interaction between particles 1 and 2 to yield energies 3 and 4 is: $P(E_1)P(E_2)[1-P(E_3)][1-P(E_4)]$

In thermal equilibrium, the forward process will be just as likely as the reverse process:

Also: $E_1+E_2=E_3+E_4$ (conservation of energy)

Fermi-Dirac Statistics

The only function that satisfies:

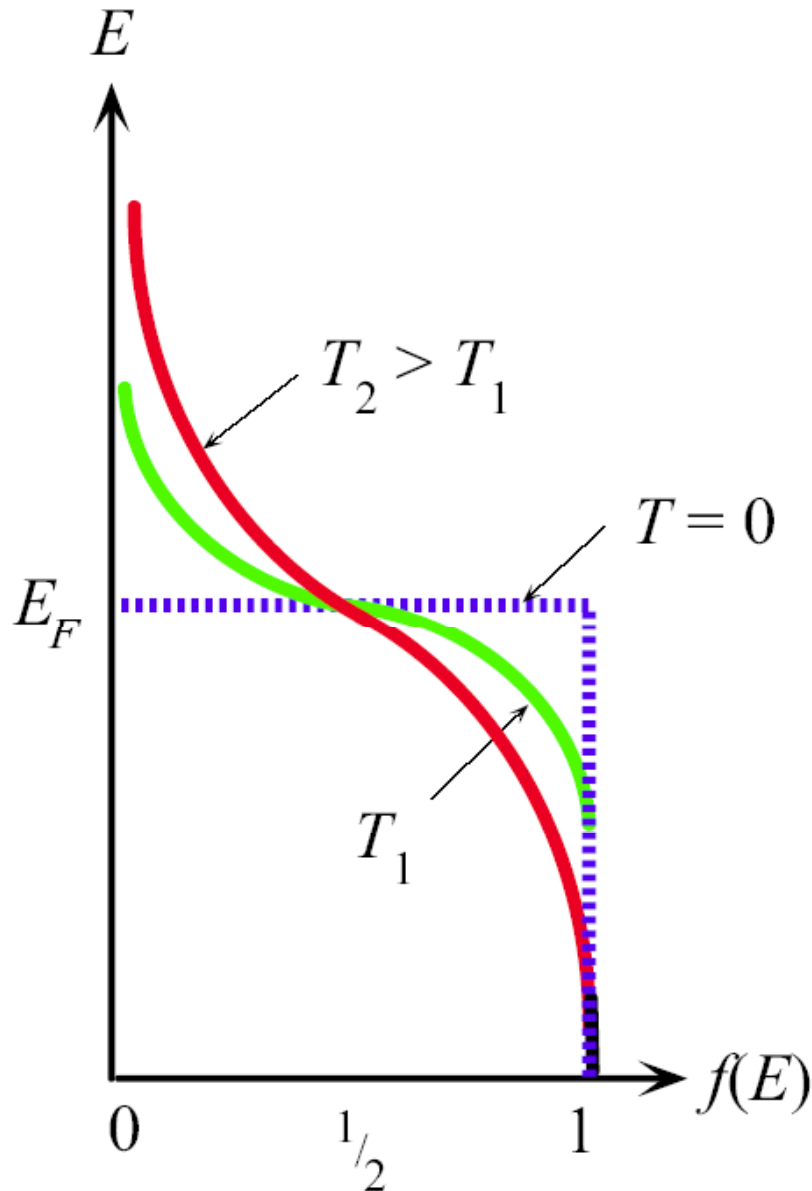$$P(E_1)P(E_2)[1-P(E_3)][1-P(E_4)] = P(E_3)P(E_4)[1-P(E_1)][1-P(E_2)]$$

$$E_1+E_2=E_3+E_4$$

Is the Fermi-Dirac function:

$$P(E) = \frac{1}{1+\exp\left(\dfrac{E-E_F}{kT}\right)}$$

where E_F is the **Fermi energy**.

$P(E)$ = the probability of finding an electron in a state with energy E

Fermi-Dirac Distribution

The Fermi-Dirac distribution $f(E)$ describes the statistics of electrons in a solid. The electrons interact with each other and the environment, obeying the Pauli exclusion principle.

Above E_F, for temperatures of a few kT, f(E) resembles the Boltzmann distribution, $\exp[-(E-E_F)/kT]$.

Metals -- Electrons in a Band
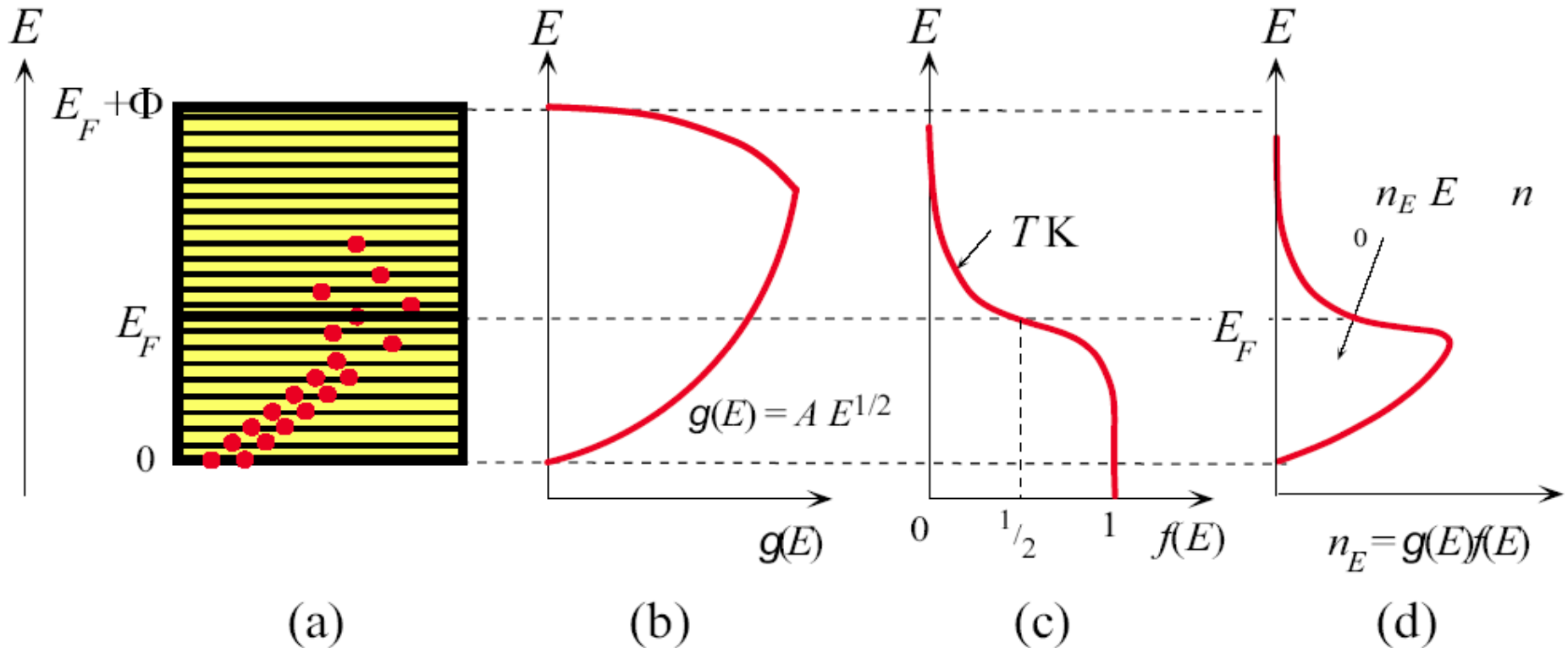
(a) Above 0K, due to thermal excitation, some of the electrons are at energies above EF.
(b) The density of states, $g(E)$ versus E in the band.
(c) The probability of occupancy of a state at an energy E is $f(E)$.
(d) The product of $g(E) f(E)$ is the number of electrons per unit energy per unit volume, or the electron concentration per unit energy. The area under the curve on the energy axis is the concentration of electrons in the band.