A photograph of a natural rock archway in a desert canyon. The arch is made of layered sandstone and is illuminated by warm sunlight, creating a strong contrast between the lit and shadowed areas. The sky is a clear, bright blue. The text "Semiconductor Statistics and Density of States Function" is overlaid in the center of the image in a bold, yellow font.

**Semiconductor Statistics
and
Density of States Function**

Metals, Insulators, and Semiconductors

- * Fermi-Dirac distribution

 - *Quantum statistics—getting there!

- * Broadening of the distribution with temperature

- * Density of states

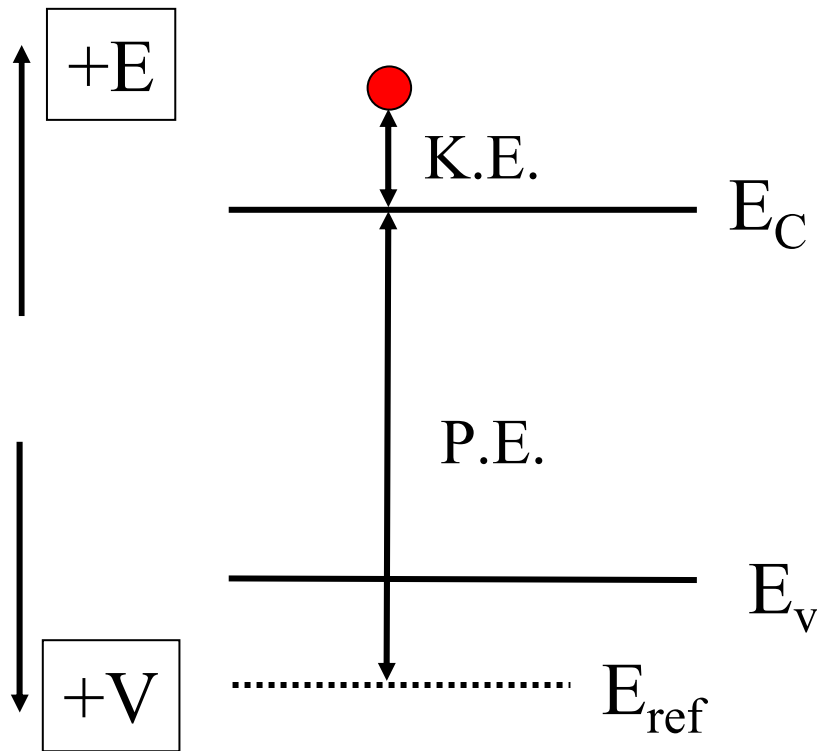


Enrico Fermi
Nobel prize in Physics, 1938
“for discovery of neutron
irradiation and slow
neutrons”



Paul A. M. Dirac
Nobel prize in Physics, 1933
“for discovery of new forms
of atomic radiation”
(positrons and the Dirac
equation)

Basic Notation



Kinetic energy:

$$K.E. = E - E_C$$

Potential Energy:

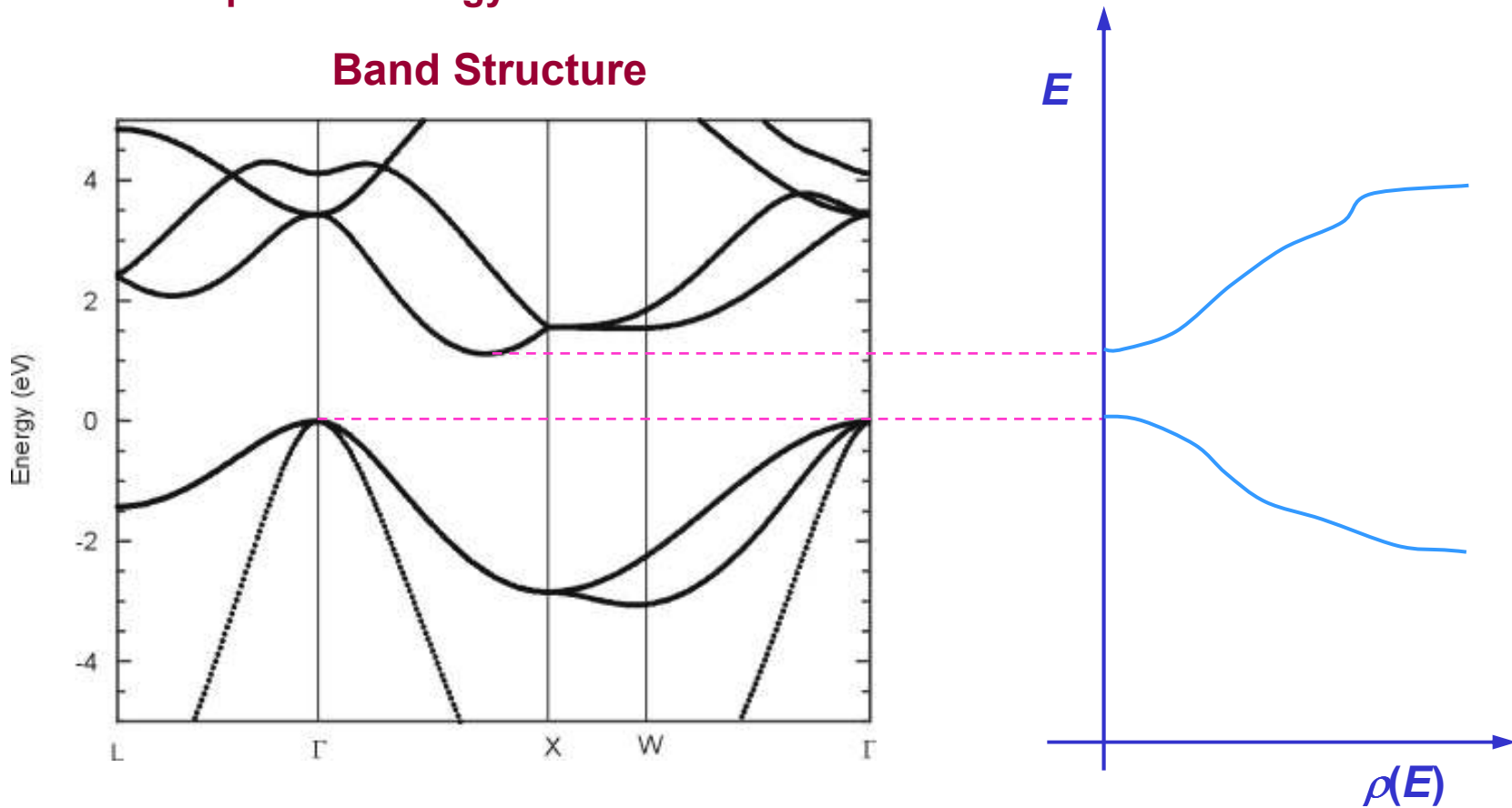
$$P.E. = -qV = E_C - E_{ref}$$

$$V = -\frac{1}{q}(E_C - E_{ref})$$

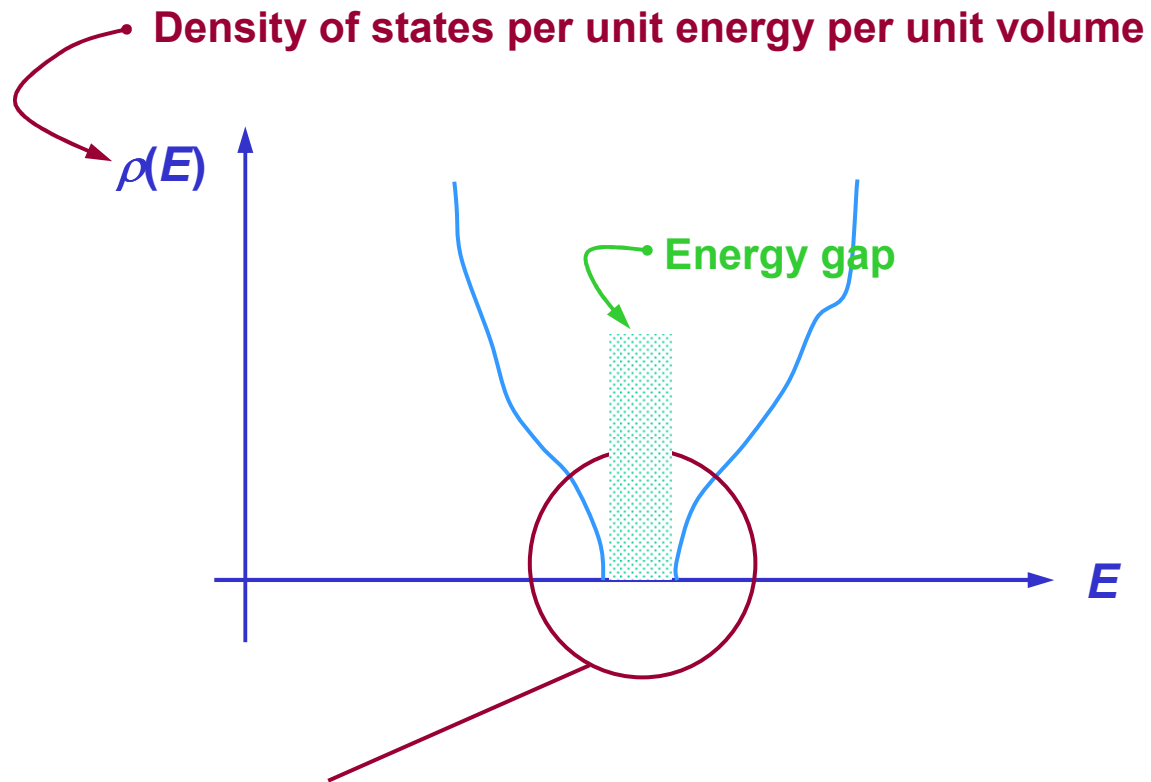
Electric field: $\boldsymbol{\varepsilon} = -\nabla V$, or in 1D $\boldsymbol{\varepsilon} = -\frac{dV}{dx} = \frac{1}{q} \frac{dE_C}{dx}$

While this is the Si band structure, it could be any material for the purposes of the present argument. We want to discuss the “number of states per unit energy”...

Band Structure



$$n = \int \rho(E) f(E) dE$$



How many of these available states are filled?

What is the probability that any one state is filled?

- ❖ We need a **QUANTUM MECHANICAL** distribution function that gives the probability of electrons **OCCUPYING** certain energy states
 - ⇒ **AT FINITE** temperatures
 - ⇒ and with the electrons satisfying the **Pauli exclusion principle**
- ❖ This function is known as the **FERMI-DIRAC** distribution function $f(E)$:

$$f(E) = \frac{1}{\exp[(E - E_F)/k_B T] + 1}$$

- ❖ $f(E)$ IS THE **FERMI-DIRAC DISTRIBUTION FUNCTION** AND DESCRIBES THE **OCCUPATION OF ELECTRON STATES AT FINITE TEMPERATURES**
- ❖ **MORE PRECISELY** $f(E)$ IS THE **PROBABILITY** THAT ANY STATE AT ENERGY E WILL BE **OCCUPIED** BY AN ELECTRON AT AN ARBITRARY TEMPERATURE T AND FOR A GIVEN FERMİ ENERGY E_F
- ❖ THE FUNCTION $f(E)$ THEREFORE TAKES VALUES RANGING FROM **ZERO TO ONE**
- ❖ THE PROBABILITY OF THE STATE **NOT** BEING OCCUPIED AT THE SAME TEMPERATURE MAY THEN EASILY BE WRITTEN AS $1 - f(E)$

How do we determine this function?

Fermi-Dirac Distribution

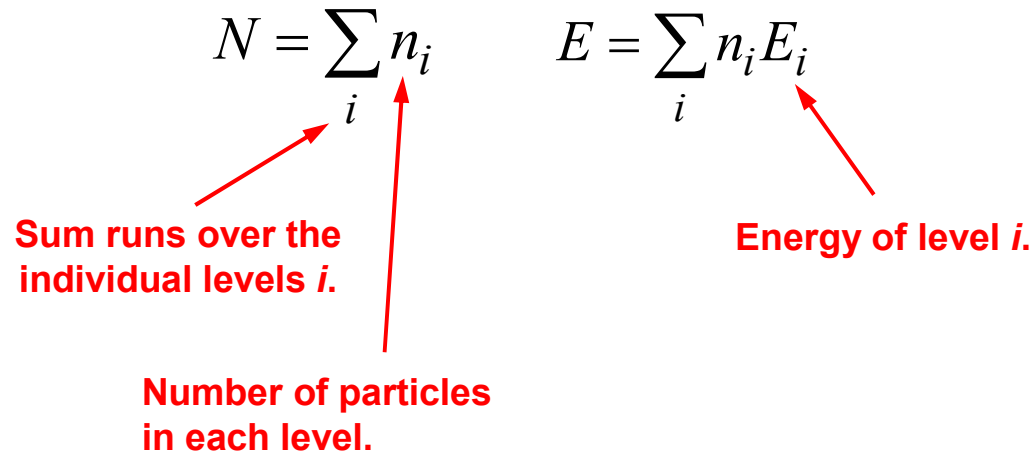
We have two *constraints* on the problem: conservation of particles and energy

$$N = \sum_i n_i \qquad E = \sum_i n_i E_i$$

Sum runs over the individual levels i .

Number of particles in each level.

Energy of level i .

The diagram shows two equations side-by-side. The first equation is N = sum over i of n_i. A red arrow points from the text 'Sum runs over the individual levels i.' to the index 'i' in the denominator of the sum. Another red arrow points from the text 'Number of particles in each level.' to the variable 'n_i'. The second equation is E = sum over i of n_i E_i. A red arrow points from the text 'Energy of level i.' to the variable 'E_i'.



Consider that we have N_i particles to distribute into S_i quantum states of level i . The number of ways to do this is:

$$W_i = \frac{S_i!}{N_i!(S_i - N_i)!}$$

Fermi-Dirac Distribution

How do we get this probability? Well, the probability of a particle being in box j is:

$$P_{j1} = \frac{N_i}{S_i}$$

 **Number of balls**
 **Number of boxes**

The probability of a second ball is:

$$P_{j2} = \frac{N_i - 1}{S_i - 1}$$

Finally, for N_i balls in box j :

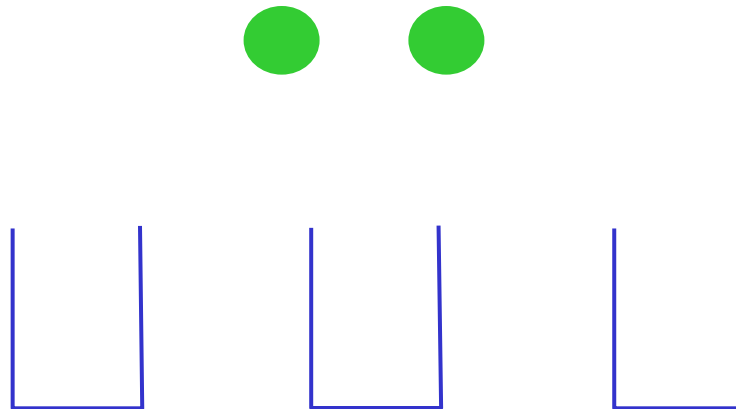
$$\begin{aligned} P_j &= P_{j1} P_{j2} \cdots P_{jN_i} = \frac{N_i}{S_i} \frac{N_i - 1}{S_i - 1} \cdots \frac{1}{S_i - N_i + 1} \\ &= \frac{N_i}{S_i} \frac{N_i - 1}{S_i - 1} \cdots \frac{1}{S_i - N_i + 1} \bullet \left[\frac{S_i - N_i}{S_i - N_i} \cdot \frac{S_i - N_i - 1}{S_i - N_i - 1} \cdots \frac{1}{1} \right] \end{aligned}$$

Fermi-Dirac Distribution

$$P_j = \frac{N_i}{S_i} \frac{N_i - 1}{S_i - 1} \dots \frac{1}{S_i - N_i + 1} \bullet \left[\frac{S_i - N_i}{S_i - N_i} \cdot \frac{S_i - N_i - 1}{S_i - N_i - 1} \dots \frac{1}{1} \right]$$
$$= \frac{N_i!(S_i - N_i)!}{S_i!} \equiv \frac{1}{W_i}$$

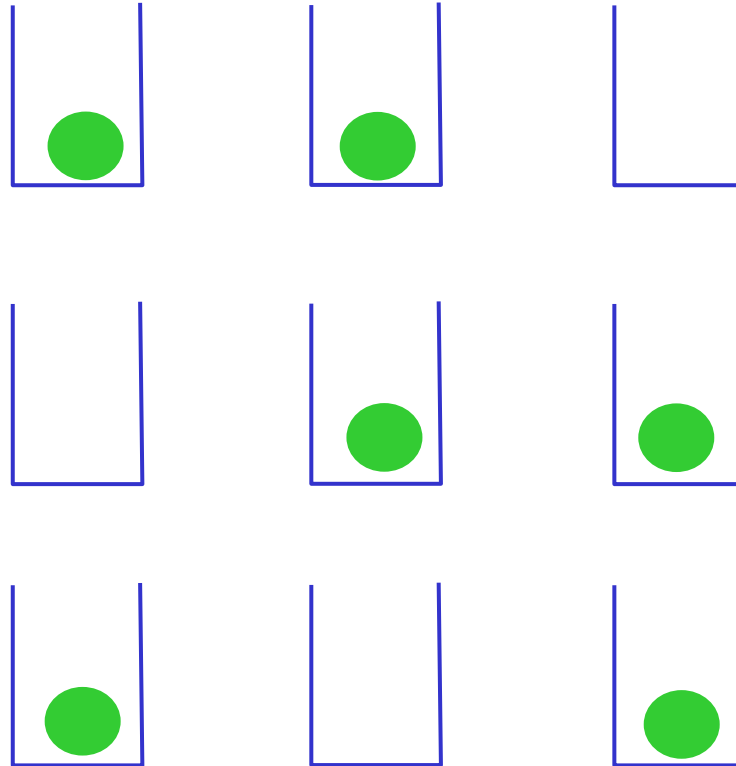
Number of ways the balls can be distributed in the boxes

Consider an example with 3 buckets and 2 balls (with each bucket containing at most 1 ball):



Fermi-Dirac Distribution

There are three possible ways in which the balls can be put into the buckets:



$$\frac{S!}{N!(S-N)!} = \frac{3!}{2!(3-2)!} = \frac{(3 \cdot 2 \cdot 1)}{(2 \cdot 1)(1)} = 3$$

Fermi-Dirac Distribution

The number of ways to arrange **ALL** of the electrons is then

$$\begin{aligned} W &= W_1 W_2 \cdots W_n \\ &= \frac{S_1!}{N_1!(S_1 - N_1)!} \frac{S_2!}{N_2!(S_2 - N_2)!} \cdots \frac{S_n!}{N_n!(S_n - N_n)!} \end{aligned}$$

This is *messy*, but

$$\ln W = \sum_i \ln \frac{S_i!}{N_i!(S_i - N_i)!}$$

We use an approximation (Sterling's approximation):

$$\ln x! = \ln x + \ln(x-1) + \dots + \ln(1)$$

$$\approx \left(x + \frac{1}{2}\right) \ln x - x$$

Fermi-Dirac Distribution

We wish to MINIMIZE the number of ways of distributing the electrons, so we will take the differential $d \ln W$. For example,

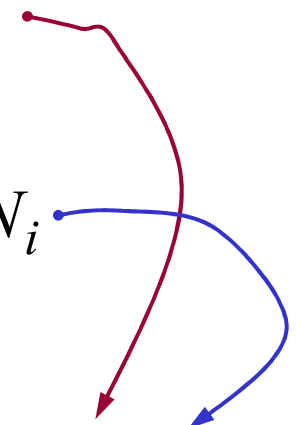
$$\begin{aligned}d \ln N_i! &= d \left[(N_i + 1/2) \ln N_i - N_i \right] && \text{Sterling's approximation} \\ &= dN_i \ln N_i + \frac{N_i + 1/2}{N_i} dN_i - dN_i \\ &\approx dN_i \ln N_i\end{aligned}$$

Then,

$$\begin{aligned}d \ln W &= \sum_i \left[-\ln N_i + \ln(S_i - N_i) \right] dN_i \\ &= \sum_i \ln \left(\frac{S_i - N_i}{N_i} \right) dN_i\end{aligned}$$

Fermi-Dirac Distribution

We now want to build in our constraints:

$$\begin{aligned}dN = 0 &= \sum_i dN_i \\dE = 0 &= \sum_i E_i dN_i \\d \ln W &= \sum_i \ln \left(\frac{S_i - N_i}{N_i} \right) dN_i - 0 - 0 \\&= \sum_i \left[\ln \left(\frac{S_i - N_i}{N_i} \right) - \alpha - \beta E_i \right] dN_i\end{aligned}$$
A diagram consisting of two curved arrows. A red arrow starts from the right side of the first equation, $dN = 0 = \sum_i dN_i$, and points to the -0 term in the third equation, $d \ln W = \sum_i \ln \left(\frac{S_i - N_i}{N_i} \right) dN_i - 0 - 0$. A blue arrow starts from the right side of the second equation, $dE = 0 = \sum_i E_i dN_i$, and points to the second -0 term in the same third equation.

We now achieve our minimized configuration by $d \ln W = 0$, or by setting this bracket = 0.

Fermi-Dirac Distribution

$$\ln\left(\frac{S_i - N_i}{N_i}\right) - \alpha - \beta E_i = 0$$

$$P_i = \frac{N_i}{S_i} = \frac{1}{1 + e^{\alpha + \beta E_i}}$$

If we define the Fermi energy as that value at which the probability is $\frac{1}{2}$, then

$$\alpha = -\beta E_F$$

By connection with classical physics, for $E \gg E_F$, we must recover the Maxwell-Boltzmann distribution, and this leads to

$$\beta = \frac{1}{k_B T}$$

Fermi-Dirac Distribution

- ❖ We now have a **QUANTUM MECHANICAL** distribution function that tells the probability of electrons **OCCUPYING** certain energy states

⇒ AT **FINITE** temperatures

- ❖ This function is known as the **FERMI-DIRAC** distribution function $f(E)$ and takes the form shown below:

$$f(E) = \frac{1}{\exp[(E - E_F)/k_B T] + 1}$$

- $f(E)$ IS THE **FERMI-DIRAC DISTRIBUTION FUNCTION** AND DESCRIBES THE **OCCUPATION** OF ELECTRON STATES AT **FINITE TEMPERATURES**
- MORE PRECISELY $f(E)$ IS THE **PROBABILITY** THAT ANY STATE AT ENERGY E WILL BE **OCCUPIED** BY AN ELECTRON AT AN ARBITRARY TEMPERATURE T AND FOR A GIVEN FERMİ ENERGY E_F
- THE FUNCTION $f(E)$ THEREFORE TAKES VALUES RANGING FROM **ZERO** TO **ONE**
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[web]

<http://www.benfold.com/sse/fd.html>

Quantum Electron Gas at Zero Temperatures

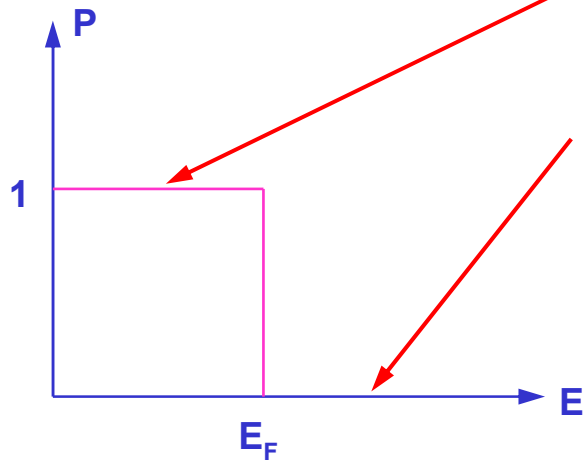
- **EXAMPLE**

* At absolute zero what is the probability of a state being occupied above and below the Fermi energy?

$$f(E) = \frac{1}{\exp[(E - E_F)/k_B T] + 1}$$

$$T = 0, E < E_F : \exp[(E - E_F)/k_B T] = 0 \quad \therefore f(E) = 1$$

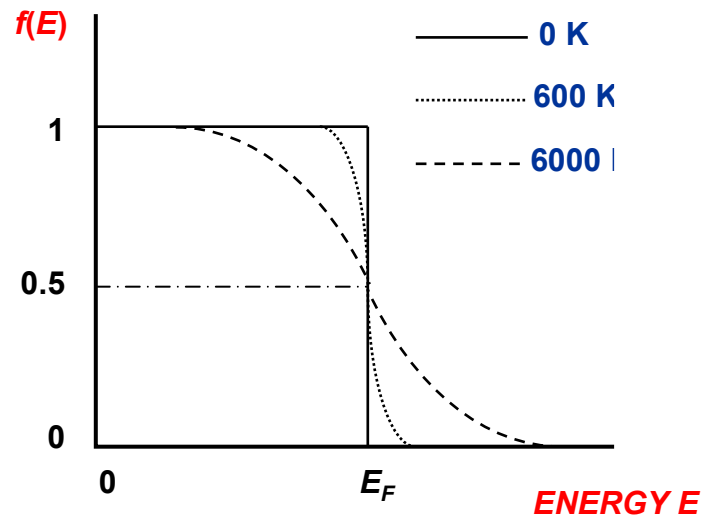
$$T = 0, E > E_F : \exp[(E - E_F)/k_B T] = \infty \quad \therefore f(E) = 0$$



IN OTHER WORDS ALL STATES E_F ARE FILLED AND ALL STATES ABOVE E_F ARE EMPTY AT ABSOLUTE ZERO. THIS IS EXACTLY WHAT WE ARGUED PREVIOUSLY!

Quantum Electron Gas at Finite Temperatures

- At finite temperatures the kinetic energy of the electron gas **INCREASES**
- Some energy states that were empty at absolute zero become **FILLED**
While others that were filled now **EMPTY**
- This process is **ALSO** described by the Fermi-Dirac distribution function



- *AS THE TEMPERATURE IS INCREASED THE PROBABILITY OF OCCUPYING STATES JUST ABOVE THE FERMİ SURFACE **INCREASES** WHILE THE PROBABILITY OF OCCUPATION JUST **BELOW** THE FERMİ SURFACE **DECREASES***
- *THIS TENDENCY INDICATES THE FACT THAT AS TEMPERATURE IS INCREASED ELECTRONS TEND TO MOVE TO OCCUPY **HIGHER** ENERGY STATES*

Quantum Electron Gas at Finite Temperatures

- **EXAMPLE**

* In a metal with a Fermi energy of 8 eV what is the probability that an electron will occupy a state with $E = 8.1$ eV at 0 K, 300 K and 600 K?

$$f(8.1 \text{ eV}, 0 \text{ K}) = 0 \text{ since } 8.1 \text{ eV} > E_F$$

$$f(8.1 \text{ eV}, 300 \text{ K}) = \frac{1}{\exp[(8.1 - 8.0) \times 1.6 \times 10^{-19} / (1.38 \times 10^{-23} \times 300)] + 1} \approx 0.02$$

$$f(8.1 \text{ eV}, 600 \text{ K}) = \frac{1}{\exp[(8.1 - 8.0) \times 1.6 \times 10^{-19} / (1.38 \times 10^{-23} \times 600)] + 1} \approx 0.13$$

NOTE HOW DOUBLING THE TEMPERATURE FROM 300 K TO 600 K INCREASES THE PROBABILITY OF OCCUPATION BY A FACTOR OF SIX THIS IS A CONSEQUENCE OF THE EXPONENTIAL DEPENDENCE OF OCCUPATION ON TEMPERATURE

Quantum Electron Gas at Finite Temperatures

- The Fermi-Dirac function thus shows that the main effect of finite temperature is to change the occupation of levels over an energy **WINDOW** of width $k_B T$ that is **CENTERED** on the Fermi energy

$$f(E) = \frac{1}{\exp[(E - E_F)/k_B T] + 1}$$

$$f(E = E_F + k_B T) = \frac{1}{e^1 + 1} \approx 27\%$$

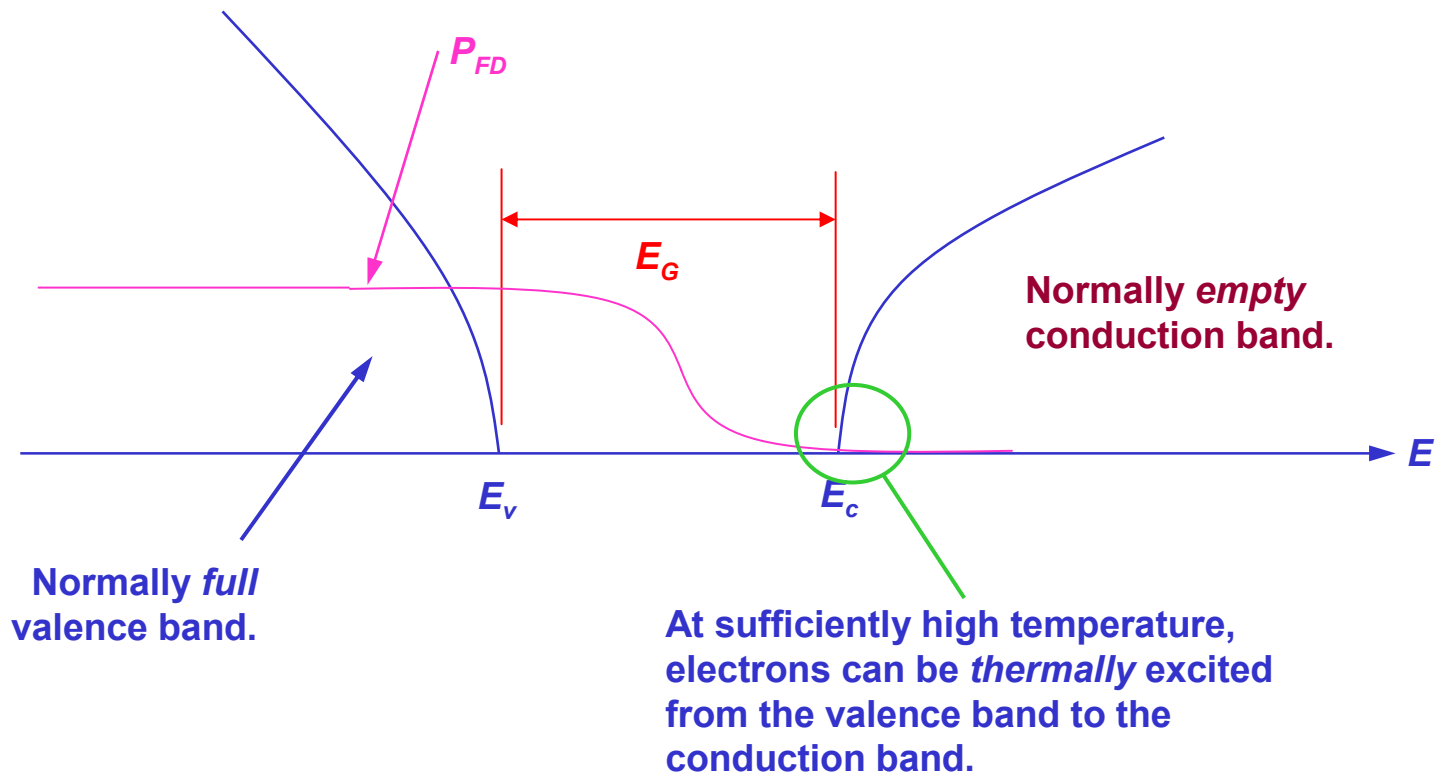
$$f(E = E_F + 3k_B T) = \frac{1}{e^3 + 1} \approx 5\%$$

$$f(E = E_F + 5k_B T) = \frac{1}{e^5 + 1} < 1\%$$

THE MAIN EFFECT OF FINITE TEMPERATURE IS TO MODIFY THE FILLING OF STATES WITHIN A FEW $k_B T$ OF THE FERMI SURFACE

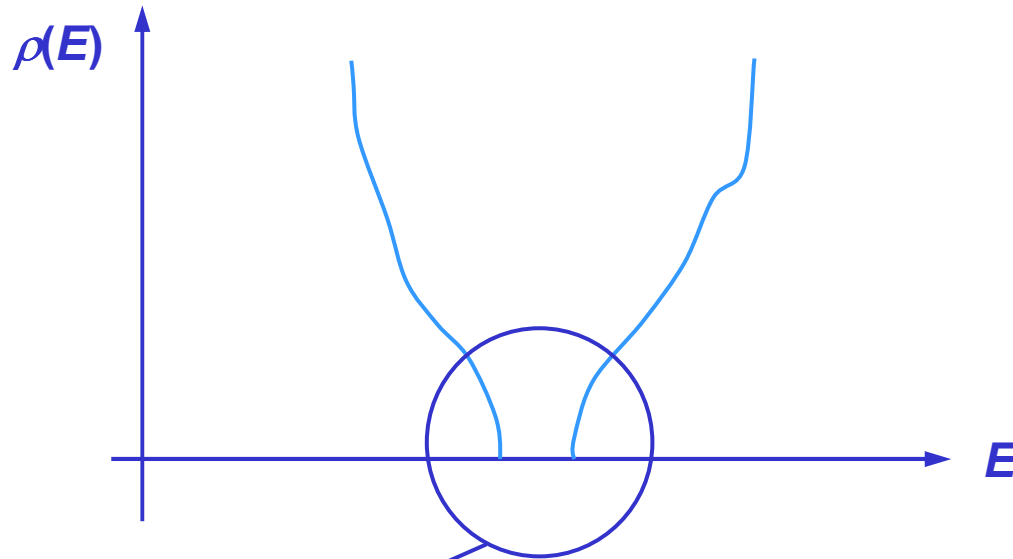
Quantum Electron Gas at Finite Temperatures

What does the Fermi function spread mean for semiconductors such as Si?



At 300 K in silicon, $n_i \sim 10^{10} \text{ cm}^{-3}$

Quantum Electron Gas at Zero Temperatures



How many of these available states are filled?

What is the probability that any one state is filled?

Now, we know the answer to the *second* of these questions.

The next question is: “How many electrons and holes are present at a temperature T ?”

DOS: Free Electrons

→ Definition: $E = \frac{p^2}{2m_0}$, $m_0 =$ free electron mass

→ de Broglie hypothesis:

$$p = \frac{h}{\lambda} = \frac{h}{2\pi} k = \hbar k \quad \longrightarrow \quad E = \frac{\hbar^2 k^2}{2m_0}$$

- Energy-wavevector relation for electrons in a crystal is obtained by solving the Schrödinger wave equation:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \phi_{\mathbf{k}}(\mathbf{r}) = E_k \phi_{\mathbf{k}}(\mathbf{r})$$

DOS: Bloch Theorem

- If the potential energy $V(\mathbf{r})$ is periodic, then the solutions of the SWE are of the form:

$$\phi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u_n(\mathbf{k}, \mathbf{r})$$

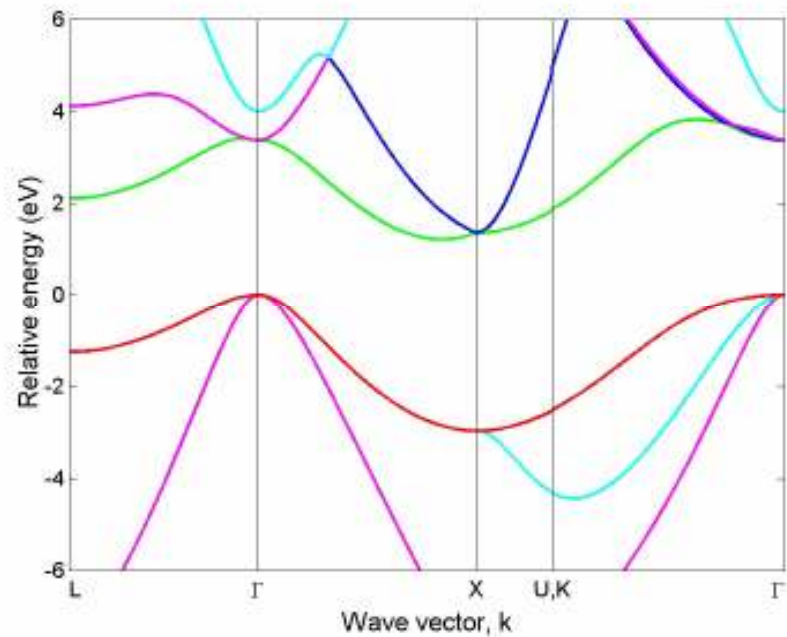
where $u_n(\mathbf{k}, \mathbf{r})$ is periodic in \mathbf{r} with the periodicity of the direct lattice and n is the band index.

- **Methods used to calculate the energy band structure:**
 - Tight-binding method
 - Orthogonal plane-wave method
 - Pseudopotential method
 - $\mathbf{k} \cdot \mathbf{p}$ method
 - Density functional technique (DFT)

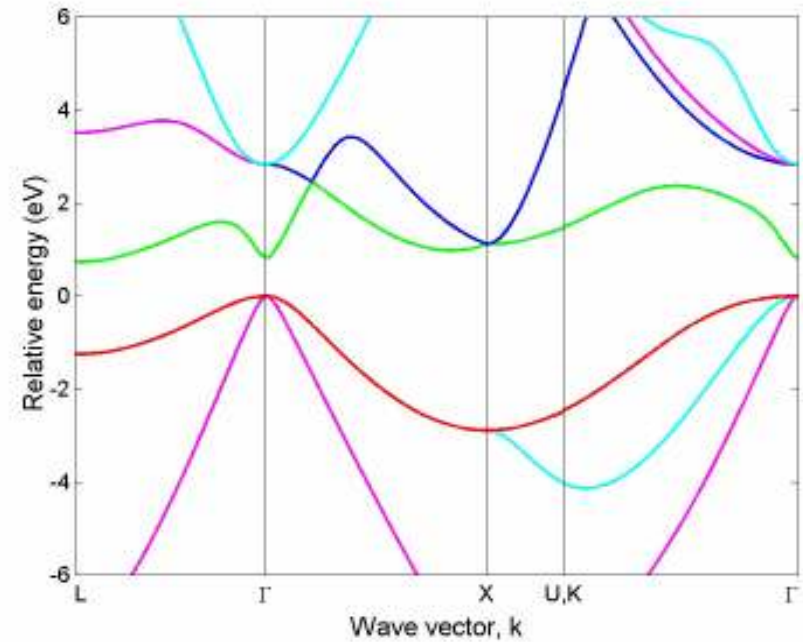
Covalent Crystals

- Typically semiconductors have an average of 4 valence electrons per atom composed of partially-filled s- and p-type orbitals that contribute to tetrahedral bonds that form through sp^3 hybridization.
- The symmetry properties of these atomic orbitals are apparent from consideration of their angular components:

Empirical Pseudopotential Method

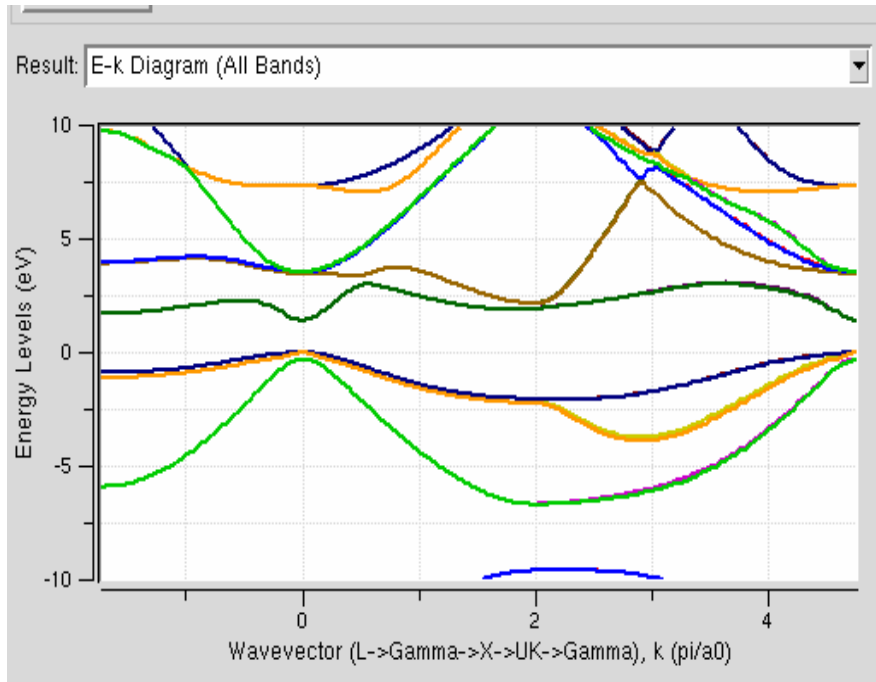


Silicon

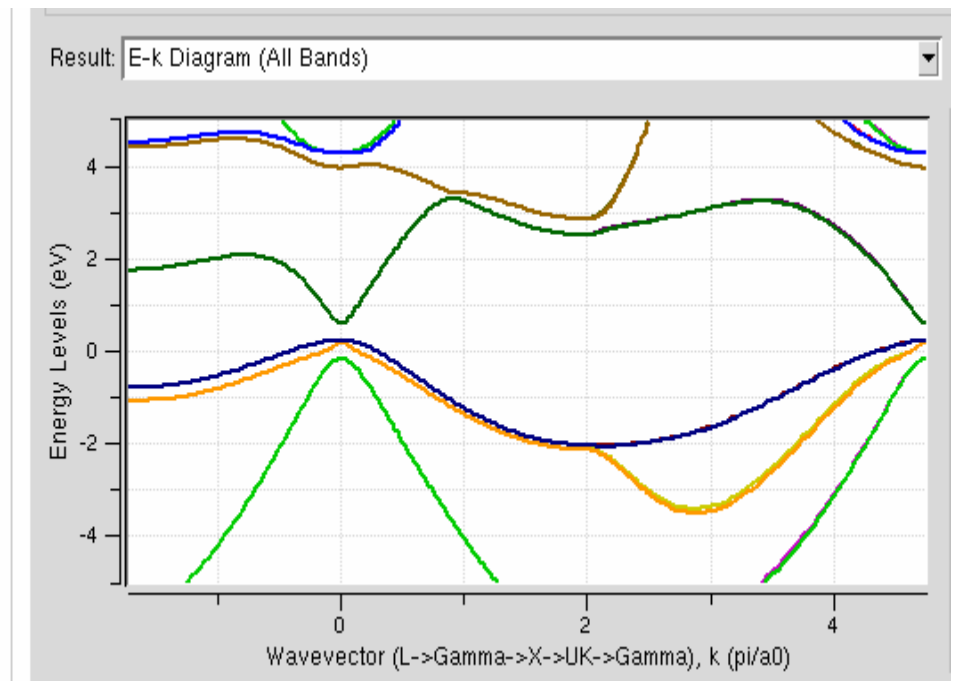


Germanium

Empirical Pseudopotential Method



GaAs



InAs

Density of States Within a Band

Now, we remember that our solid has a length L . We impose periodic boundary conditions, so that

$$\begin{aligned}\psi(L) &= \psi(0) \\ \frac{d\psi(L)}{dx} &= \frac{d\psi(0)}{dx}\end{aligned}$$

This means that our Bloch wave function has to have the exponential behave as

$$\begin{aligned}e^{ikL} &= e^{ik0} = 1 \\ kL &= 2n\pi \\ k &= \frac{2n\pi}{L} \rightarrow n = 1, 2, \dots, N\end{aligned}$$

Density of States Within a Band

Hence, there are N values of k in the overall “length” (in reciprocal space). Each value of k occupies a “length”

$$\Delta k = \frac{2\pi}{L}$$

And, therefore, the amount of *real space per value of k* is given by

$$\left(\frac{2\pi}{L}\right)^{-1} = \frac{L}{2\pi}$$

Thus, since the total number of values of k is N , we must have

$$\sum_{i=1}^N \text{index} = N$$

On the other hand, if we integrate over k , we must include the volume per k point as

$$N = \int_0^{k_{\max}} dk \frac{L}{2\pi}$$

Density of States Within a Band

In 3 dimensions, this becomes

$$N(E) = 2 \int_0^{k_{x,\max}} dk_x \int_0^{k_{y,\max}} dk_y \int_0^{k_{z,\max}} dk_z \frac{V}{(2\pi)^3}$$

subject to the constraint

Density of states
in k-space

$$k_{x,\max}^2 + k_{y,\max}^2 + k_{z,\max}^2 = E$$

It is easier if we convert to spherical coordinates:

$$\begin{aligned} N(E) &= 2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin \theta d\theta \int_0^{k_{\max}} k^2 dk \frac{V}{(2\pi)^3} \\ &= \frac{V}{\pi^2} \int_0^{k_{\max}} k^2 dk \end{aligned}$$

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

Now,

$$kdk = \frac{m_d}{\hbar^2} dE \quad , \quad k = \sqrt{\frac{2m_d E}{\hbar^2}}$$

so that

$$N(E) = \frac{V}{\pi^2} \int_0^{k_{\max}} k^2 dk = \frac{V}{\pi^2} \int_0^E \frac{1}{2} \left(\frac{2m_d}{\hbar^2} \right)^{3/2} E^{1/2} dE$$

and the density of states per unit volume is

$$\rho(E) = n(E) = \frac{1}{V} \frac{dN(E)}{dE} = \frac{1}{2\pi^2} \left(\frac{2m_d}{\hbar^2} \right)^{3/2} E^{1/2}$$

NOTE: minimum energy is taken as zero. We need to take it as E_c

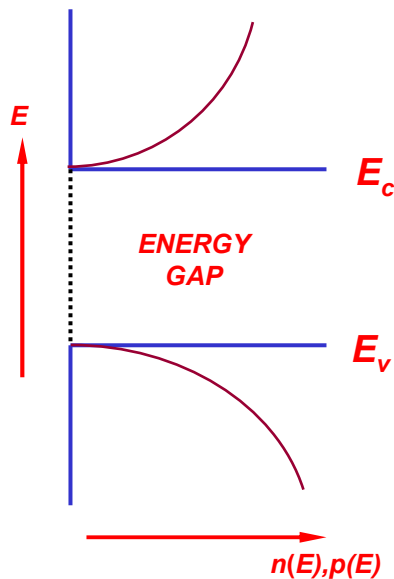
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This is for each valley. There are six valleys in Silicon, so this must be multiplied by 6. However, this factor is usually incorporated in the mass, so that we have

$$m_d = 6^{2/3} m_{d0} \rightarrow 6^{2/3} \times 0.32m_0 = 1.06m_0$$

Density of States Within a Band

- ❖ **NEAR** the gap we assume that the density of states takes the form we derived earlier Remembering too that **INCREASING** hole energy corresponds
⇒ To moving **DOWN** the valence band
- ❖ We can then compute the **EFFECTIVE** number of electrons and holes available as a function of **TEMPERATURE**



THE ELECTRON AND HOLE DENSITY OF STATES
ARE DEFINED
IN THE FOLLOWING MANNER:

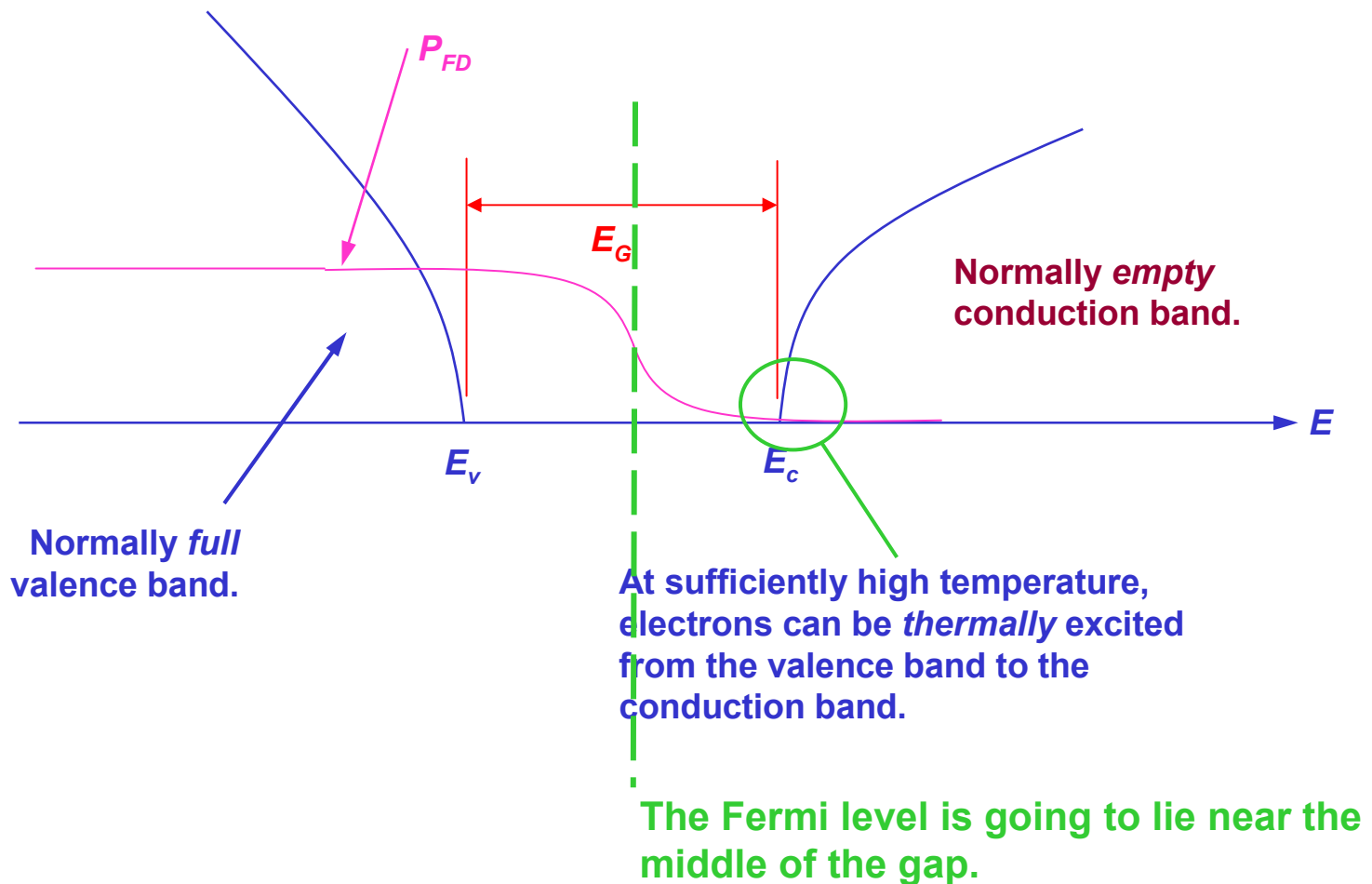
$$\text{Electrons : } n(E) = \frac{1}{2\pi^2} \left[\frac{2m_e^*}{\hbar^2} \right]^{3/2} [E - E_c]^{1/2}$$

$$\text{Holes : } p(E) = \frac{1}{2\pi^2} \left[\frac{2m_h^*}{\hbar^2} \right]^{3/2} [E_v - E]^{1/2}$$

$$E_c - E_v = E_G$$

Quantum Electron Gas at Finite Temperatures

What does the Fermi function spread mean for semiconductors such as Si?



Density of States Within a Band

So, we ask the question: What is the probability that there is an electron in the upper (conduction) band?

$$p = \frac{1}{1 + \exp\left(\frac{E_c - E_F}{k_B T}\right)}$$

Now, with the Fermi energy at the middle of the gap,

$$E_c - E_F = \frac{E_G}{2}$$

and

$$p = \frac{1}{1 + \exp\left(\frac{E_G}{2k_B T}\right)}$$

Density of States Within a Band

If, as is the case for Si, at 300 K

$$E_G = 1.0eV$$

$$p = \frac{1}{1 + \exp\left(\frac{0.5}{0.026}\right)} \sim 4.5 \times 10^{-9}$$

This is not so small (there are 10^{23} electrons per cc in the valence band), so at higher temperatures (~ 400 C), we will get conduction.

On the other hand, if, as is the case for SiO_2 ,

$$E_G = 9.0eV$$

$$p = \frac{1}{1 + \exp\left(\frac{4.5}{0.026}\right)} \sim 6.8 \times 10^{-76}$$

it is unlikely that an electron will appear, and this is an *insulator*. (Even at 1000 K, the probability is only 10^{-23}).

Effective Masses

- Curvature of the band determines the effective mass of the carriers in a crystal, which is different from the free electron mass.

Smaller curvature → heavier mass

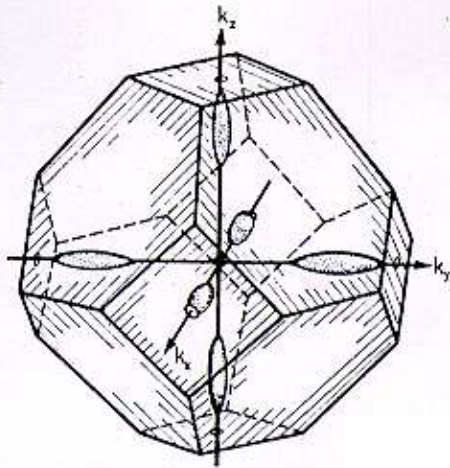
Larger curvature → lighter mass

- For parabolic bands, the components of the effective mass tensor are calculated according to:

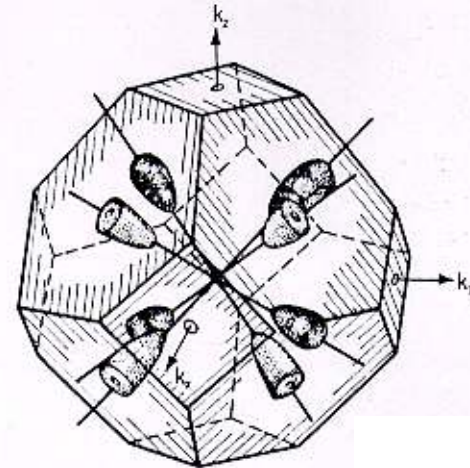
$$\frac{1}{m_{ij}^*} = \frac{1}{\hbar^2} \cdot \frac{\partial^2 E}{\partial k_i \partial k_j} \quad \xrightarrow{\text{Si}} \quad \frac{1}{m^*} = \begin{bmatrix} \frac{1}{m_{xx}^*} & 0 & 0 \\ 0 & \frac{1}{m_{yy}^*} & 0 \\ 0 & 0 & \frac{1}{m_{zz}^*} \end{bmatrix}$$

Constant Energy Surfaces - Electrons

Si



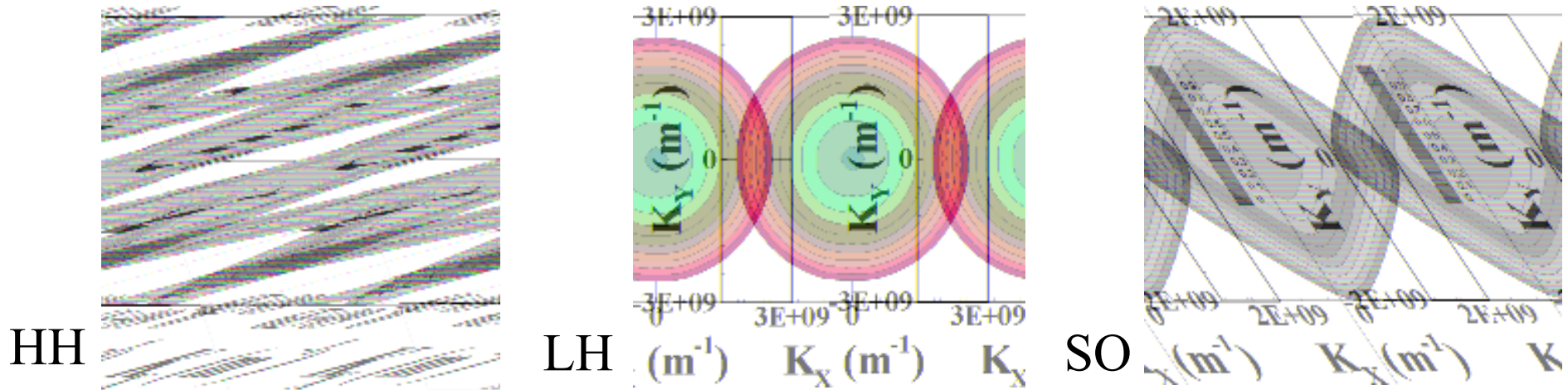
Ge



$$(E - E_C)_i = \frac{\hbar^2}{2} \left(\frac{k_x^2}{m_{xi}^*} + \frac{k_y^2}{m_{yi}^*} + \frac{k_z^2}{m_{zi}^*} \right)$$

- Note: The electron effective mass in GaAs is isotropic, which leads to spherically symmetric constant energy surfaces.

Constant Energy Surfaces - Holes



$$E(k) = -\frac{\hbar^2}{2m} \left\{ Ak^2 \pm \left[B^2 k^4 + C^2 (k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2) \right]^{1/2} \right\}$$

$$m_{hh}^* = \frac{m_o}{A - \sqrt{B^2 + C^2/6}}, \quad m_{lh}^* = \frac{m_o}{A + \sqrt{B^2 + C^2/6}}, \quad m_{so}^* = \frac{m_o}{A}$$

Use of Different Masses

- In transport calculations there are two different masses in use:
 - **Density of States effective mass** – used in DOS calculations

$$m_{e,dos}^* = M_C^{2/3} (m_l m_t m_t)^{1/3}$$

- **Conductivity effective mass** – used in conductivity calculations

$$m_{e,cond}^* = \frac{3}{\frac{1}{m_l} + \frac{1}{m_t} + \frac{1}{m_t}}$$

Some Parameters

Name	Symbol	Germanium	Silicon	Gallium Arsenide
Smallest energy bandgap at 300 K	E_g (eV)	0.66	1.12	1.424
Effective mass for density of states calculations				
Electrons	$m_{e,dos}^*/m_0$	0.56	1.08	0.067
Holes	$m_{h,dos}^*/m_0$	0.29	0.57/0.8	0.47
Effective mass for conductivity calculations				
Electrons	$m_{e,cond}^*/m_0$	0.12	0.26	0.067
Holes	$m_{h,cond}^*/m_0$	0.21	0.36/0.38	0.34

Simplified Band-Structure Models

- **Parabolic Band Model**

$$E(\mathbf{k}) = \frac{\hbar^2 |\mathbf{k}|^2}{2m_0^*} \quad \mathbf{v} = \frac{1}{\hbar} \nabla_{\mathbf{k}} E(\mathbf{k}) = \frac{\hbar \mathbf{k}}{m_0^*}$$

- **Non-Parabolic Band Model**

$$E(\mathbf{k})(1 + \alpha E(\mathbf{k})) = \frac{\hbar^2 |\mathbf{k}|^2}{2m_0^*} \quad E(k) = \frac{\sqrt{1 + \frac{4\alpha \hbar^2 |\mathbf{k}|^2}{2m_0^*}} - 1}{2\alpha}$$

$$\mathbf{v} = \frac{1}{\hbar} \nabla_{\mathbf{k}} E(\mathbf{k}) = \frac{\hbar \mathbf{k}}{m_0^*} \left(1 + 4\alpha \frac{\hbar^2 |\mathbf{k}|^2}{2m_0^*} \right)^{-1/2}$$