

Lecture Notes # 3

- Understanding Density of States
 - Solve 1-D Schrödinger equation for particle-in-a-box
 - Extend to 3-D
 - Invoke periodicity requirement
 - Solve for density of states

Review of Quantum Mechanics

$$H\psi = \varepsilon\psi$$

H = Hamiltonian operator

ψ = Mathematic wavefunction depicting
nature of electron in space/time

ε = Energy or allowable quantized energies
of that electron

- Often times you do not know ψ or ε , but you have boundary conditions and want to solve for possible values of ε and a functional form of ψ

Review of Quantum Mechanics

- Most general case: Time independent

$$H = \underbrace{\frac{-\hbar^2}{2m} \nabla^2}_{\text{Kinetic E.}} + \underbrace{U(x, y, z)}_{\text{Potential E.}}$$

- How do we know first part is K.E?

$$KE = \frac{1}{2}mv^2 \text{ classically}$$

$$\frac{1}{2}mv^2 = \frac{p^2}{2m}$$

$\hat{p} = -i\hbar\nabla$ is quantum momentum operator

$$\text{So, } \frac{1}{2}mv^2 = \frac{-\hbar^2}{2m} \nabla^2$$

Review of Quantum Mechanics

$$\text{For } \psi(r) = \exp(ik \cdot r)$$

$$\hat{p}\psi = a\psi$$

Momentum operator Eigenvalue

$$\hat{p}\psi = -i\hbar\nabla\psi(r) = -i\hbar\frac{\partial}{\partial r}\psi(r) = -i\hbar(ik)\psi(r) = \underbrace{\hbar k}\psi(r)$$

$a = \hbar k$ = Momentum Eigenvalue

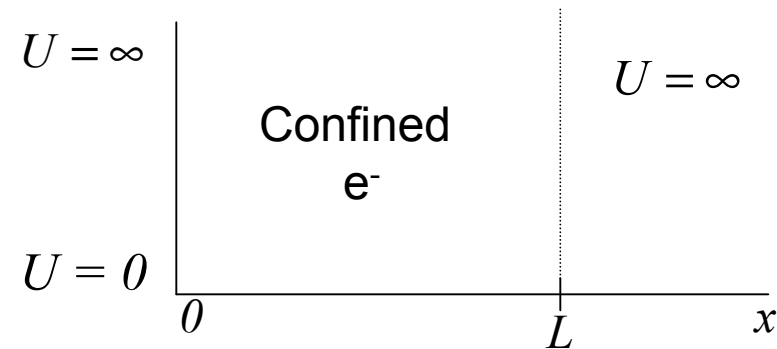
$$p = mv = \hbar k$$

$$v = \frac{\hbar k}{m} = \text{velocity of particle}$$

Particle in a 1-D Box

- Free electron floating around in vacuum
- Let's impose some boundary – confine it to a region of space, a box or a unit cell in 1-D

Confine it by setting $U = \infty$ outside the box and $U = 0$ inside the box



- Since $U(x) = 0$ for $0 < x < L$, we can drop $U(x)$ out of the Hamiltonian, which becomes

$$H = \frac{-\hbar^2}{2m} \nabla^2$$

Particle in a 1-D Box

- Because $U = \infty$ outside the box, we know the e- CANNOT be there, so we get the boundary condition:

$$\psi(x=0) = \psi(x=L) = 0$$

Because the Hamiltonian must give

back an eigenvalue, we must pick

$$\psi = f(x) \text{ where } f''(x) = Af(x)$$

$$\text{and } f(0) = f(L) = 0$$

- We do not care what happens between 0 and L, so the simplest solution is just:

$$\psi = A \sin\left(\frac{n\pi}{L}x\right), \quad n = 1, 2, 3, 4, \dots$$

$$\text{for } x = 0, \sin(0) = 0 \quad \text{OK}$$

$$\text{for } x = L, \sin(nL) = 0 \quad \text{OK}$$

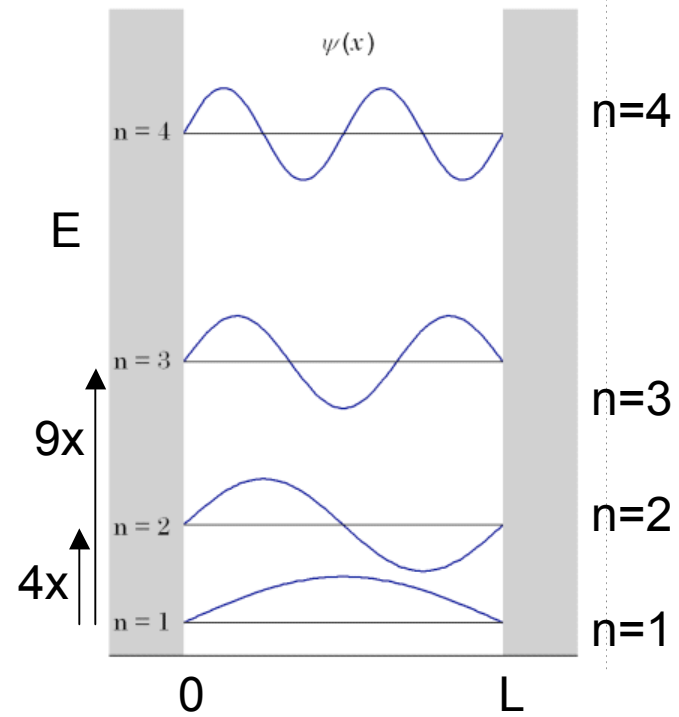
Particle in a 1-D Box

- Plug ψ into the Schrödinger equation to make sure $H\psi = E\psi$

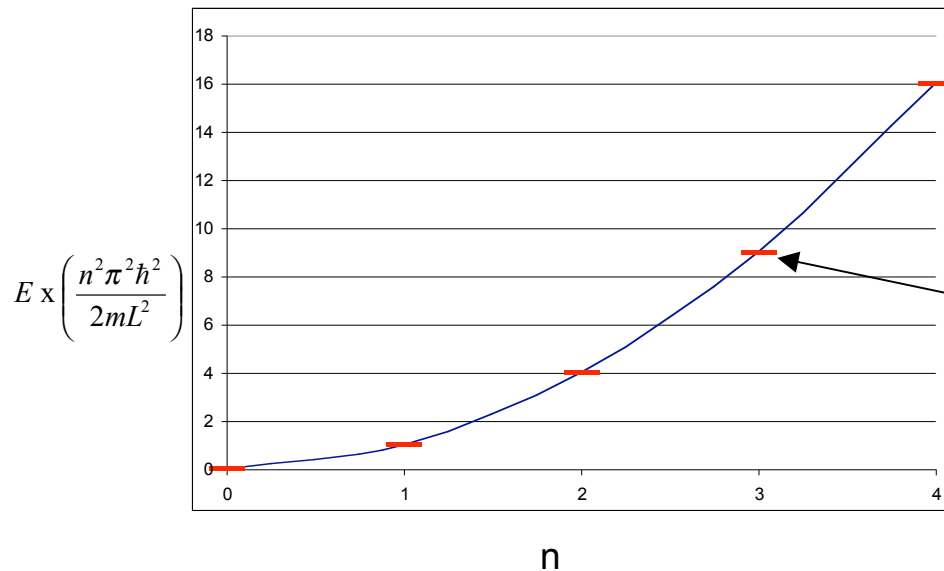
$$\begin{aligned} & \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \left(A \sin\left(\frac{n\pi}{L} x\right) \right) = \\ & \frac{-\hbar^2}{2m} \frac{d}{dx} \left[\frac{n\pi}{L} A \cos\left(\frac{n\pi}{L} x\right) \right] = \\ & \frac{-\hbar^2}{2m} \left[-\frac{n^2 \pi^2}{L^2} A \sin\left(\frac{n\pi}{L} x\right) \right] = \\ & \underbrace{\frac{1}{2m} \left(\frac{\hbar n \pi}{L} \right)^2}_{\text{Energy, } E} \underbrace{A \sin\left(\frac{n\pi}{L} x\right)}_{\psi} \end{aligned}$$

Particle in a 1-D Box

- Energy values are quantized since n is an integer
- $n=1$ is lowest energy state, $n=2$ has higher energy, etc.

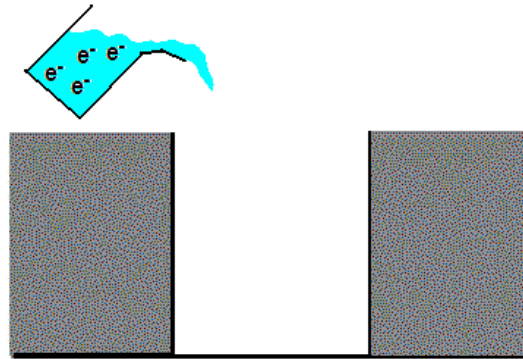


- We can map out $\psi(x,n)$ vs. E
- Allowed energy states



Particle in a 1-D Box

- Now let's fill up the states with electrons. Suppose we have N e^- we want to pour into our 1-D box.

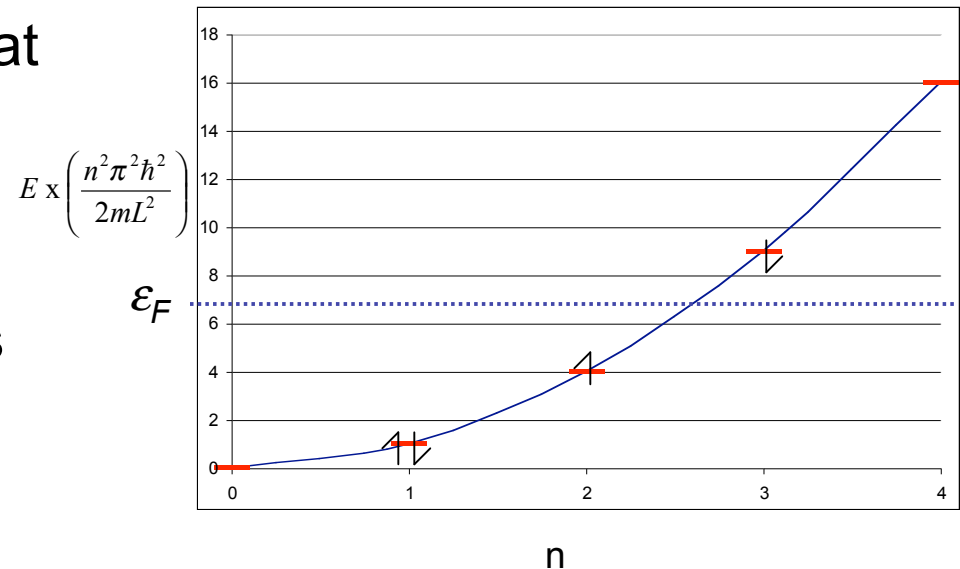


- For N e^- you can calculate the energies since we know we can have $2e^-/n$ states (two spins).
- So N electrons fills $n_F = N/2$ states.
- The highest energy state, n_F , gives ϵ_F , the Fermi energy.

$$\epsilon_F = \frac{\hbar^2}{2m} \left(\frac{n_F \pi}{L} \right)$$

Fermi-Dirac Distribution

- Fermi energy is well defined at $T = 0$ K because there is no thermal promotion
- At high T , there is thermalization, so ε_F is not as clear



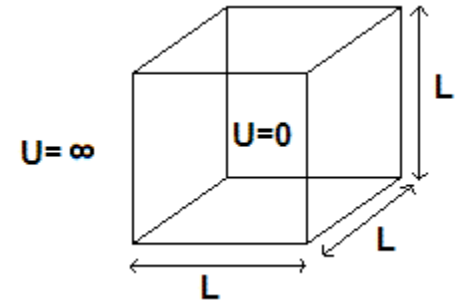
- Officially defined as the energy where the probability of finding an electron is $1/2$
- This definition comes from the Fermi-Dirac Distribution:

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

- This is the probability that an orbital (at a given energy) will be filled with an e^- at a given temperature
- At $T=0$, $\mu = \varepsilon_F$ and $\varepsilon = \varepsilon_F$, so $f(\varepsilon_F) = 1/2$

Particle in a 3-D Box

- Let's confine e^- now to a 3-D box
- Similar to a unit cell, but e^- is confined inside by $U = \infty$ outside the box
- Schrödinger's equation is now



$$\frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) = \epsilon \psi(x, y, z)$$

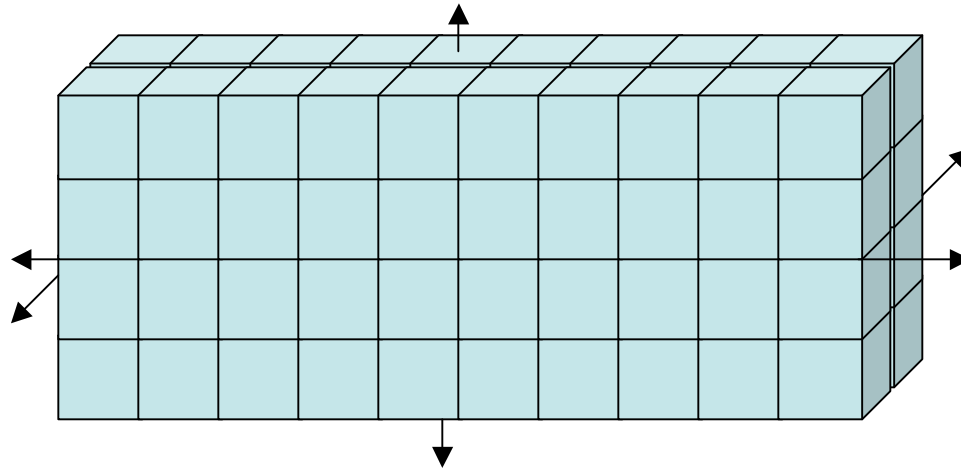
- You can show that the answer is:

$$\psi_n(x, y, z) = A \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right)$$

- We now have 3 quantum numbers n_x , n_y , and n_z that are totally independent
- (1,2,1) is energetically degenerate with (2,1,1) and (1,1,2)

Particle in a 3-D Box

- Now let's repeat this box infinitely in each direction to get a repeated "unit cell"



- What's different about this situation?
 - $U(x,y,z)=0$
 - No region where $U = \text{infinity}$
- So, there's really no reason that $\psi(x=0)=\psi(x=L)=0$
since $U(x=0)=U(x=L)\neq \infty$
- We don't need those boundary conditions anymore

Periodic Boundary Condition

- For now, we don't need such a strict boundary condition
- Make sure ψ is periodic with L , which would make each 3-D box identical
- Because of this, we'll have a periodic boundary condition such that

$$\psi(x + L, y, z) = \psi(x, y, z)$$

- Wave functions that satisfy this periodic B.C. and are solutions to the Schrödinger equation are TRAVELING WAVES (not a standing wave anymore)

Periodic Boundary Condition

- Bloch function

$$\psi_k(\vec{r}) = \exp(i\vec{k} \cdot \vec{r})$$

- Wave vector k satisfies

$$\vec{k}_x = 0; \pm \frac{2\pi}{L}; \pm \frac{4\pi}{L}; \dots$$

- Etc. for k_y and k_z
- Quantum numbers are components of k of the form $2n\pi/L$ where $n=+$ or $-$ integer

$$\begin{aligned} \exp[ik_x(x+L)] &= \exp[i2\pi n(x+L)/L] \\ &= \exp[i2\pi nx/L] \exp[i2\pi n] \\ &= \exp[i2\pi nx/L] \\ &= \exp[ik_x x] \end{aligned}$$

- Periodicity satisfied

Back to Schrödinger Equation

- Substitute $\psi_k(\vec{r}) = \exp(i\vec{k} \cdot \vec{r})$

into

$$\frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_k(\vec{r}) = \varepsilon_k \psi_k(\vec{r})$$

gives

$$\varepsilon_k = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

- Important that k_x can equal k_y can equal k_z or NOT
- The linear momentum operator $\hat{p} = -i\hbar\nabla$

for $\psi_k(\vec{r}) = \exp[i\vec{k} \cdot \vec{r}]$

$$\hat{p}\psi_k(\vec{r}) = -i\hbar\nabla\psi_k(\vec{r}) = \hbar k\psi_k(\vec{r})$$

so the plane wave $\psi_k(\vec{r})$ is an eigenfunction of linear momentum with an eigenvalue of $\hbar k$, and the particle velocity in orbital k is

$$v = \frac{\hbar k}{m}$$

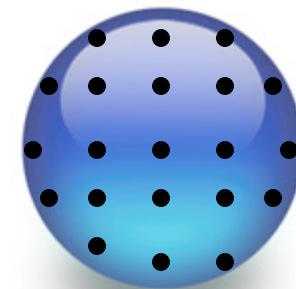
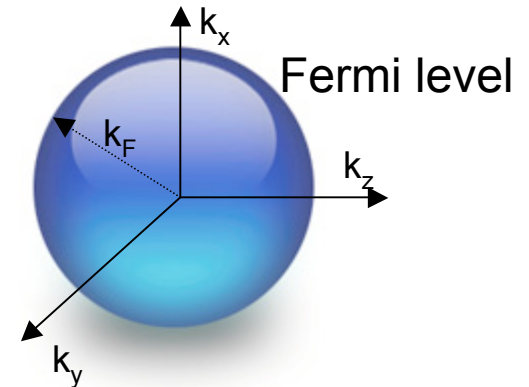
Fermi Level in 3-D

- Similarly, can calculate a Fermi level

$$\epsilon_F = \frac{\hbar^2}{2m} k_F^2 \leftarrow \text{Vector in 3-D space}$$

- Inside sphere $k < k_F$, so orbitals are filled. $k > k_F$, orbitals are empty
- Quantization of k in each direction leads to discrete states within the sphere
- Satisfy the periodic boundary conditions at $\pm 2\pi/L$ along one direction
- There is 1 allowed wave vector k , with distinct k_x , k_y , k_z quantum #s for the volume element $(2\pi/L)^3$ in k -space
- So, sphere has a k -space volume of

$$V = \frac{4}{3} \pi k_F^3$$



NOTE: This is a sphere only if $k_x = k_y = k_z$. Otherwise, we have an ellipsoid and have to recalculate everything. That can be a mess.

Sphere: GaAs (CB&VB), Si (VB)

Ellipsoid: Si (CB)

Number of Quantum States

- Number of quantum states is $\frac{\text{total volume}}{\text{volume of 1 allowed quantized state}} = \frac{\frac{4}{3} \pi k_F^3}{\left(\frac{2\pi}{L}\right)^3}$
- Since there are 2 e⁻ per quantum state

$$N = 2 \left(\frac{\frac{4}{3} \pi k_F^3}{\left(\frac{2\pi}{L}\right)^3} \right) = \frac{L^3}{3\pi^2} k_F^3$$

$$N = \frac{V}{3\pi^2} k_F^3$$

Solve for k_F ,

$$k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3}$$

- Depends on e⁻ concentration

Density of States

- Plug k_F into

$$\epsilon_F = \frac{\hbar^2}{2m} \bar{k}^2$$

$$\epsilon_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

- Relates Fermi energy to electron concentration
- Total number of electrons, N:

$$N = \frac{V}{3\pi^2} \left(\frac{2m\epsilon}{\hbar^2} \right)^{3/2}$$

- Density of states is the number of orbitals per unit energy

$$D(\epsilon) \equiv \underbrace{\frac{dN}{d\epsilon}} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2}$$

← Relate to the surface of the sphere. For the next incremental growth in the sphere, how many states are in that additional space?

Density of States

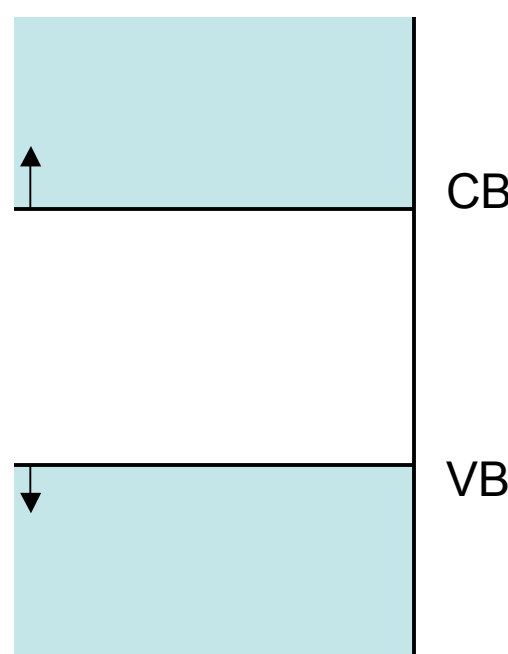
- Divide by V to get N/V which is electron density ($\#/cm^3$)
- Volume density of orbitals/unit energy for free electron gas in periodic potential

$$D(\varepsilon) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2}$$

Effective mass of e^-

$$D(\varepsilon) = \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} (E - E_{CB})^{1/2}$$

Starting point energy



Effective mass of h^+

$$D(\varepsilon) = \frac{1}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{3/2} (E_{VB} - E)^{1/2}$$

Start from VB and go down

Concentration of Electrons

$$n = \int_{E_C}^{\infty} D_e(E) f_e(E) dE = \text{fun}$$

$$n = 2 \left(\frac{m_e^* kT}{2\pi\hbar^2} \right)^{3/2} \exp[(\mu - E_C) / kT]$$

“ E_F ”

$$N_C = 2 \left(\frac{m_e^* kT}{2\pi\hbar^2} \right)^{3/2} \quad \text{Effective density of states in CB}$$

$$n = N_C \exp[-(E_C - E_F) / kT]$$

Writing it with a minus sign indicates that as E difference between E_C and E_F gets bigger, probability gets lower

Concentration of Holes

$$p = \int_{-\infty}^{E_V} D_h(E) f_h(E) dE \quad f_h = 1 - f_e$$

$$p = 2 \left(\frac{m_h^* kT}{2\pi\hbar^2} \right)^{3/2} \exp[(E_V - \mu) / kT]$$

$$N_V = 2 \left(\frac{m_h^* kT}{2\pi\hbar^2} \right)^{3/2} \quad \text{Effective density of states in VB}$$

$$p = N_V \exp[-(E_F - E_V) / kT]$$

Intrinsic Carrier Concentration

$$n \cdot p = N_C N_V \exp\left[\frac{-(E_C - E_F) - (E_F - E_V)}{kT}\right]$$

$$n \cdot p = N_C N_V \exp\left[\frac{-(E_C - E_V)}{kT}\right]$$

$E_C - E_V = E_G$, the band gap

$$n \cdot p = N_C N_V \exp[-E_G / kT]$$

Entropy term Enthalpy term

$$n \cdot p = n_i^2$$

n_i = intrinsic carrier concentration

Constant for a given temperature.

Intrinsic = undoped

Intrinsic Carrier Concentration

$$n_i = \sqrt{N_C N_V} \exp\left(\frac{-E_G}{2kT}\right)$$

n_i = constant for a given T means that
 $n \cdot p$ is constant, too, which holds under
equilibrium and away from it

n_i
Ge: $2.4 \times 10^{13} \text{ cm}^{-3}$
Si: $1.05 \times 10^{10} \text{ cm}^{-3}$
GaAs: $2 \times 10^6 \text{ cm}^{-3}$
At 300 K

- At temperature T, $n = p$ by conservation
- Add a field and $np = \text{constant}$, but n does not equal p
- As n increases, p decreases, and vice versa
- Useful to define E_i , which is $E_i = E_F$ when it is an intrinsic semiconductor (undoped), so $n = p = n_i$

$$n_i = N_C \exp\left(\frac{-(E_C - E_i)}{kT}\right) = N_V \exp\left(\frac{-(E_i - E_V)}{kT}\right)$$

Intrinsic Fermi Level

$$n_i = N_C \exp\left(\frac{-(E_C - E_i)}{kT}\right) = N_V \exp\left(\frac{-(E_i - E_V)}{kT}\right)$$

$$\left(\frac{-(E_C - E_i)}{kT}\right) = \left(\frac{-(E_i - E_V)}{kT}\right) + \ln\left(\frac{N_V}{N_C}\right)$$

$$E_i - E_C = E_V - E_i + kT \ln\left(\frac{N_V}{N_C}\right)$$

$$2E_i = E_V + E_C + kT \ln\left(\frac{N_V}{N_C}\right)$$

$$2(E_i - E_V) = E_C - E_V + kT \ln\left(\frac{N_V}{N_C}\right)$$

$$\boxed{(E_i - E_V) = \frac{E_G}{2} + \frac{kT}{2} \ln\left(\frac{N_V}{N_C}\right)}$$

Intrinsic Fermi Level

$$(E_i - E_V) = \frac{E_G}{2} + \frac{kT}{2} \ln\left(\frac{N_V}{N_C}\right)$$

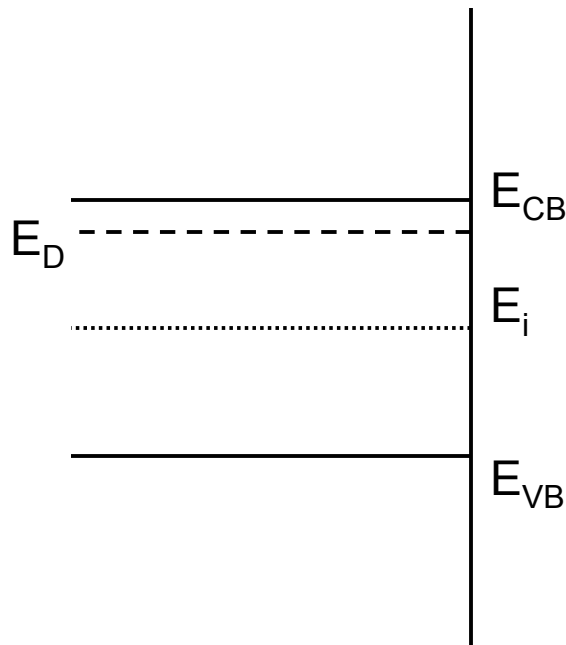
- This says that the intrinsic Fermi level (relative to the valence band) is about mid-gap \pm the $(kT/2)\ln(N_V/N_C)$ scaling factor

$\frac{kT}{2} \ln\left(\frac{N_V}{N_C}\right)$	E_G (eV)
-13 meV for Si	1.12
35 meV for GaAs	1.42
-7 meV for Ge	0.67

- So E_i for Si and Ge is slightly below mid-gap. E_i for GaAs is slightly above. It is minor compared to E_G , but just so you know
- All of this has been intrinsic with no dopants

Dopants

- Let's consider adding dopants



n-type

$$\text{carriers } n = n_i + N_D^+$$

Depends
on E_G , T

Depends on ϵ_D , T ,
and dopant density

$$\epsilon_D = E_{CB} - E_D$$

At $T=0$, all donor states are filled. Hence, $n = 0$.
But at room temperature in P doped Si, 99.96%
of donor states are ionized.

At mid temperature, if $N_D^+ \gg n_i$, then $n \approx N_D^+$

At high temperature, such that $n_i \gg N_D$, then $n \approx n_i$

Dopants

$n \cdot p = n_i^2$ still holds, just substitute

$$n = n_i + N_D^+$$

$p = \frac{n_i^2}{n_i + N_D}$ at room temperature, $n \approx N_D$ for typical dopant densities

Say $N_D = 10^{16} \text{ cm}^{-3} \longrightarrow N_D^+ = 10^{16} \text{ cm}^{-3} \longrightarrow n \cong 10^{16} \text{ cm}^{-3}$

$$n = N_C \exp[-(E_C - E_F)/kT]$$

$$\frac{n}{N_C} = \frac{10^{16} \text{ cm}^{-3}}{10^{19} \text{ cm}^{-3}} = \exp[-(E_C - E_F)/kT] \quad \text{about 60 mV/decade}$$

3 decades x 60 mV = 180 mV = 180 meV down