Department of Electrical and Computer Engineering

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ECE 745 – Solid State Electronics

Fall 2004, Lecture Notes

Part I: Introduction to Quantum Mechanics

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Classical vs. quantum: An Introduction

Classical "particle" – a baseball

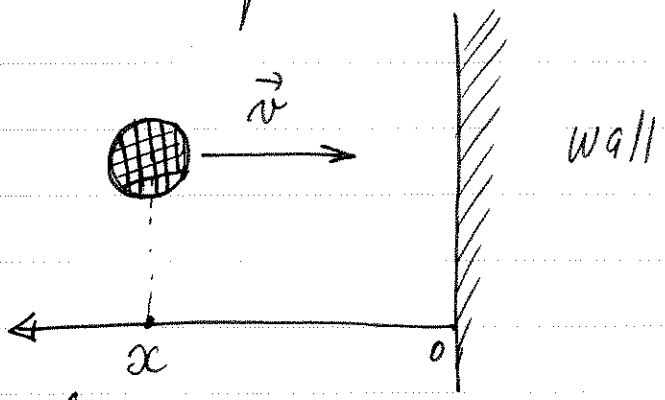


Fig. 1

What makes it classical:

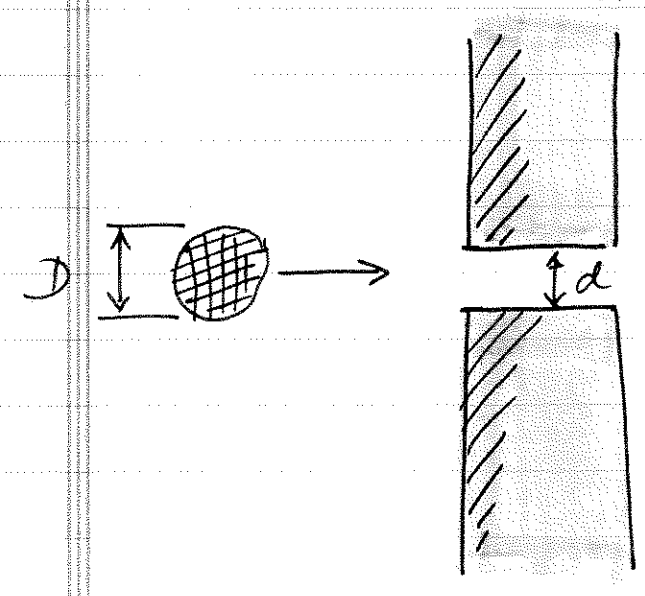
1) we can say at any point in time where the ball is, and also what its momentum is

2) Its equation of motion is the 2nd Newton's Law

$$m\ddot{\vec{r}} = \vec{F}$$

(more correctly

$$\frac{d\vec{p}}{dt} = \vec{F}.)$$



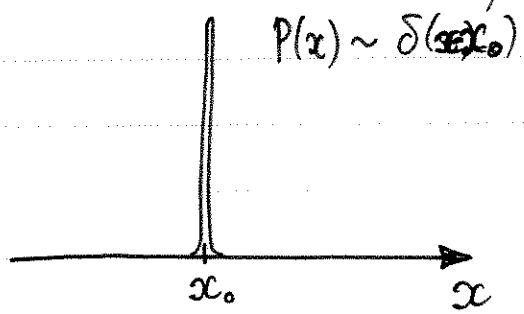
3) If there is a wall at $x=0$, there is no way the ball will be found at $x \leq 0$ (Fig. 1)

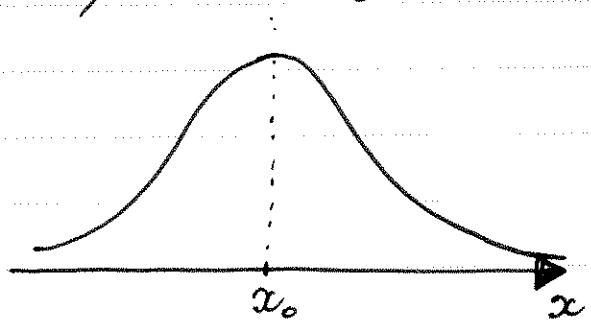
4) If there is a hole in the wall, the ball goes through if and only if $d > D$. Otherwise, reflection.

A quantum particle – e.g. an electron

1) One cannot simultaneously say what the position & the momentum are, due to the Heisenberg uncertainty principle

2) A quantum particle is "smeared", you can speak of probability to find it around a certain point – there is a probability density to capture it at a certain point $P(x)$, so that $\int P(x)dx = 1$

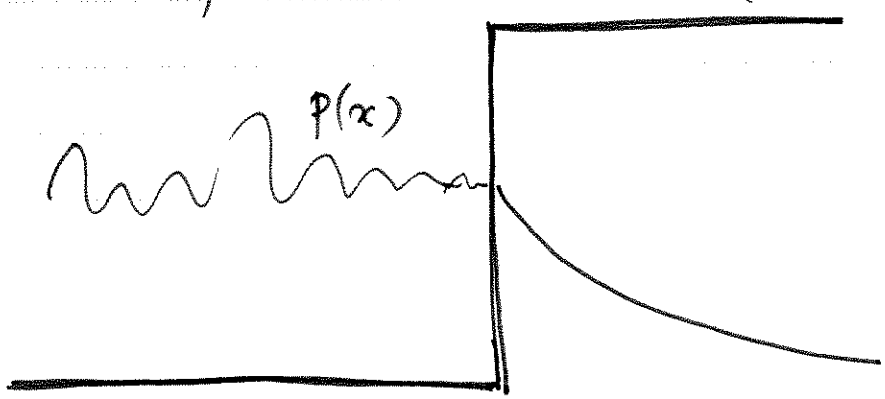




Classical particle –
– we always know where it is

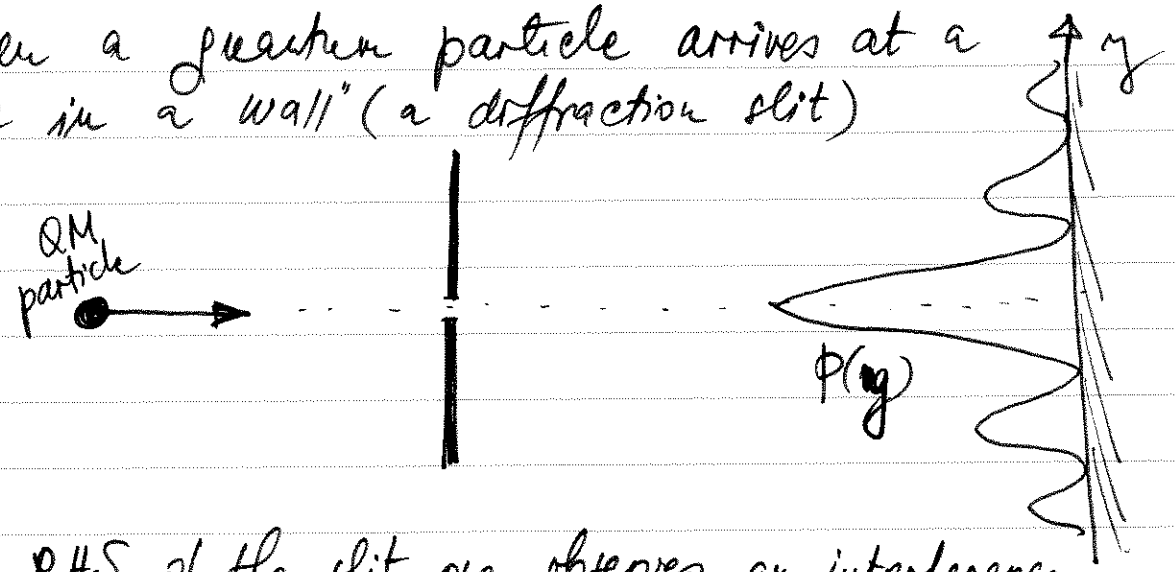
Quantum-mechanical (QM) particle: the probability to find it at x_0 is not a δ-function, it is typically more smeared

3) When a QM particle hits a wall, that does not mean ~~so pro~~ the probability of finding it on the side of the wall is zero (unless "wall" infinite)



far from the barrier prob. will become small but not zero right away

4) When a quantum particle arrives at a "hole in a wall" (a diffraction slit)



on the RHS of the slit, one observes an interference pattern, just like one does with waves! (EM or mechanical)

QM particle can be described by a WAVEFUNCTION, a quantity capable of capturing its wave-like behavior in many experiments.

$$\psi(\vec{r},t)$$

Probability density to find an electron (or a general QM particle, actually) is given by

$$P(\vec{r},t) = \psi^*(\vec{r},t)\psi(\vec{r},t)$$

probability density

position $\vec{r}$

time t

$$P(\vec{r},t) = |\psi(\vec{r},t)|^2$$

$\boxed{\text{Wavefunction itself cannot be measured, BUT PROBABILITIES CAN!}}$

Probability to capture a particle between points A and B

$$P_{AB}(t) = \int_A^B dx\, P(x,t) \quad (\text{case of 1D})$$

Probability to capture a particle (in 3D) around a point A, within a tiny volume ΔV

$$P_{\Delta V}(t) = \int_{\Delta V} d^3\vec{r}\, P(\vec{r},t)$$

YOU CANNOT SPEAK OF PROBABILITY TO FIND A PARTICLE AT A CERTAIN POINT

$$\boxed{P_{\Delta V \to 0} = 0}$$

IT IS ALWAYS ZERO

THE SAME WAY YOU CANNOT SAY THAT AN ELECTROMAGNETIC WAVE IS PRECISELY AT A CERTAIN POINT.

What can we measure? What is the meaning of a statement such as

1) Where is the particle? Its position is $x = \ldots$
2) The particle's energy is 5 meV.
3) The particle's momentum is $p = \ldots$

Where in classical physics we had classical variables that we measured (position, momentum, ...) in quantum mechanics we have OPERATORS associated with classical variables, and what we measure are EXPECTATION (AVERAGE) VALUES of these operators.

Classical variable		Operator in QM
x	$\longrightarrow$	x
p_x	$\longrightarrow$	$-i\hbar\frac{\partial}{\partial x}$
E_k	$\longrightarrow$	$\frac{\hat{\vec{p}}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2$
$\vec{L}$	$\longrightarrow$	$\vec{r}\times\vec{p} = -i\hbar(\vec{r}\times\vec{\nabla})$

What is measured

$$\langle x\rangle = \int dx\, \psi^*(x,t)\, x\, \psi(x,t) \qquad \text{(in 1D)}$$

over all available x's (from $-\infty$ to ∞, unless some boundary constraints present)

expectation value of position

$$\langle p_x\rangle = \int_{\text{all } x\text{'s}} dx\, \psi^*(x,t)\, \underbrace{\hat{p}_x}_{\text{operator}}\, \psi(x,t) =$$

$$= \int_{\text{all } x} dx\, \psi^*(x,t) \left[-i\hbar\frac{\partial}{\partial x}\right]\psi(x,t)$$

Current (carried by an electron of charge $-e$, $e>0$)

$$\vec{J} = -e\langle\vec{v}\rangle = -e\cdot\frac{1}{m}\,\mathrm{Re}\,\langle\hat{\vec{p}}\rangle =$$

$$= -\frac{e}{2m}\left\{\int_{\text{all } x} dx\ \psi^*(x,t)\left[-i\hbar\frac{\partial}{\partial x}\right]\psi(x,t) + \int_{\text{all } x} dx\ \psi(x,t)\left[i\hbar\frac{\partial}{\partial x}\right]\psi^*(x,t)\right]$$

- <u>Normalization</u>: the wavefunction must be normalized to 1, i.e. the probability to find a QM particle from $-\infty$ to $+\infty$ has to be exactly 1

$$\boxed{1 = \int_{-\infty}^{\infty} dx\ \psi^*(x,t)\,\psi(x,t)} \quad \text{1D}$$

$$\boxed{1 = \int_{\text{all space}} d^3\vec{r}\ \psi^*(\vec{r},t)\,\psi(\vec{r},t)} \quad \underline{\underline{\text{3D}}}$$

If a classical particle obeyed the 2nd Newton's Law

$$\frac{d\vec{p}}{dt} = \vec{F}$$

which yielded $\vec{x}, \vec{p}$ as functions of time, what is the law of motion for a quantum particle?

The Schrödinger Equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

$\hat{H}$ – the energy operator (it is called "the Hamiltonian").

It contains the <u>kinetic energy part</u>

$$\hat{T} = \frac{\hat{p}^2}{2m} = \frac{1}{2m}(-i\hbar\vec{\nabla})^2$$
$$= -\frac{\hbar^2}{2m}\vec{\nabla}^2 = -\frac{\hbar^2}{2m}\Delta$$

Kinetic energy operator

and the <u>potential operator</u>

$$\hat{V} = V(\vec{r})$$

potential energy operator acts on the wavefunction by multiplying it

$$\boxed{\hat{H} = \hat{T} + \hat{V}}$$

Total energy operator consists of the kinetic energy operator and the potential energy operator

How does $\hat{H}$ act on the wavefunction $\Psi(\vec{r},t)$?

$$\hat{H}\Psi(\vec{r},t) = -\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r},t) + V(\vec{r})\Psi(\vec{r},t)$$

Example 1: Can a wavefunction of the form

$$\psi(x,t) = A\, e^{ikx - i\omega t}$$

describe a free particle? What is the relationship between k and ω?

Solution: Free particle = no potential energy contribution. The Hamiltonian is equal to the kinetic energy operator

$$\hat{H} = \hat{T} = -\frac{\hbar^2}{2m}\nabla^2 \quad \left(\text{in 1D } \nabla^2 = \frac{\partial^2}{\partial x^2}\right)$$

The Schrödinger equation

$$i\hbar \frac{\partial \psi(x,t)}{\partial x} = \hat{H}\psi(x,t)$$

We have to see if it holds for the free-particle Hamiltonian, and the test wavefunction given above

$$i\hbar \frac{\partial \psi(x,t)}{\partial x} = i\hbar(-i\omega)\psi = \hbar\omega\psi$$

$$\hat{H}\psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) = -\frac{\hbar^2}{2m}(ik)^2\psi = \frac{\hbar^2 k^2}{2m}\psi$$

These two lines are equal if it holds

$$\boxed{\hbar\omega = \frac{\hbar^2 k^2}{2m}}$$

Time-independent Schrödinger equation

When the potential $\hat{V}$ doesn't depend on time, then in the Schrödinger equation we can perform separation of variables, i.e., assume that the solution $\psi(x,t)$ is of the following form

$$\psi(x,t) = \Phi(x)\Theta(t)$$

$$i\hbar\frac{\partial}{\partial t}\left(\Phi(x)\Theta(t)\right) = \hat{H}(x)\,\Phi(x)\Theta(t)$$

$$\cancel{\Phi(x)} \quad \phi(x)\, i\hbar\frac{d\Theta(t)}{dt} = \hat{H}(x)\phi(x)\,\Theta(t)$$

$$\boxed{\frac{1}{\Theta(t)}\, i\hbar\frac{d\Theta(t)}{dt} = \frac{1}{\phi(x)}\hat{H}(x)\phi(x)}$$

The two sides of this equation depend on different variables, yet they are equal! This can only happen if the value of each side of the equation is a constant

$$\frac{1}{\Theta(t)}\, i\hbar\frac{d\Theta}{dt} = \text{const} \equiv \mathcal{E} \qquad (1)$$

$$\frac{1}{\phi(x)}\hat{H}(x)\phi(x) = \text{const.} \qquad (2)$$

$$\cancel{i\hbar\, d\Theta} \quad \frac{1}{\Theta(t)}\frac{d\Theta}{dt} = -i\,\mathcal{E}/\hbar$$

$$\cancel{\Theta(t) = \Theta} \quad \boxed{\ln\Theta(t) = e^{-\frac{i\mathcal{E}t}{\hbar}} + \text{const}}$$

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$$\boxed{\Theta(t) = \Theta(0)\, e^{-i\mathcal{E}t/\hbar}}$$ Temporal evolution

$$(2) \Rightarrow \quad \boxed{\hat{H}(x)\,\phi(x) = \mathcal{E}\,\phi(x)}$$

Hamiltonian $\hat{H}$ acts on ϕ ~~and~~ as a ~~mult~~ constant: THIS MEANS ϕ IS AN EIGENFUNCTION (A.K.A. EIGENVECTOR) OF OPERATOR $\hat{H}$, ASSOCIATED WITH EIGENVALUE $\mathcal{E}$

Such solutions ϕ are so-called stationary solutions of the Schrödinger equations.

They form an orthonormal basis: ϕ's associated with different $\mathcal{E}$'s are necessarily orthogonal

$$\int_{\substack{\text{available}\\ x}} dx\; \phi^*_{\mathcal{E}_1}(x)\,\phi_{\mathcal{E}_2}(x) = 0 \qquad \mathcal{E}_1 \neq \mathcal{E}_2$$

It can happen that multiple mutually orthogonal wavefunctions correspond to the same energy $\mathcal{E}$ (the eigenvalue of the Hamiltonian). In that case, we say that the energy $\mathcal{E}$ is DEGENERATE.

~~Example~~

Lecture 2
9/8/2005

Eigenproblem of a toy 3x3 Hamiltonian

Let us start from a Hermitian 3x3 matrix that represents a toy Hamiltonian $\hat{H}$.
(A matrix is said to be Hermitian if it is the same as its adjoint = transpose + complex conjugate. Adjoint matrix (a.k.a. Hermitian conjugate) is denoted often by a dagger superscript.

So, a Hermitian matrix A satisfies

$$A = A^{\dagger} \quad , \text{where } A^{\dagger} = (A^T)^* = (A^*)^T)$$

Let us take our toy Hamiltonian $\hat{H}$ to be

$$\hat{H} = \begin{bmatrix} 1 & i & 0 \\ -i & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \times \text{energy unit (e.g., eV)}$$

Let us solve this matrix eigenproblem, i.e. find its eigenvalues E (there will be 3 of them, not necessarily different) and corresponding ~~eigenvalues~~ vectors ϕ (they are columns in this case). So we are looking for

$$\hat{H}\phi = E\phi \qquad \phi \equiv \begin{bmatrix} \phi^1 \\ \phi^2 \\ \phi^3 \end{bmatrix}$$

or, equivalently,

$$(\hat{H} - E\hat{I})\phi = 0$$

unit operator (unit matrix)

For the equation $(\hat{H} - E\hat{I})\phi = 0$ to have a nontrivial solution (i.e., a solution other than $\phi = 0$) it must hold

$$\det(\hat{H} - E\hat{I}) = 0$$

This equation is a polynomial equation in E, i.e.,

$$\det \begin{vmatrix} 1-E & i & 0 \\ -i & -E & 0 \\ 0 & 0 & -1-E \end{vmatrix} = 0$$

$$-(1+E)\left[-E(1-E) - 1\right] = 0$$

$$(1+E)\left[E^2 - E - 1\right] = 0$$

<u>Eigenvalues</u> $E_3 = -1$ $\qquad$ $E_{1,2} = \dfrac{1 \pm \sqrt{1+4}}{2} = \dfrac{1 \pm \sqrt{5}}{2}$

There are 3 solutions, ~~two~~ and they are all different — nondegenerate. If one energy appears as a solution multiple times, then the number of times it occurs is called <u>degeneracy</u> (e.g., you can say that the energy is two-fold degenerate, or that the degeneracy equals 2).

<u>Eigenvectors</u> Among the eigenvalues, pick one, and then use it to solve for the eigenvector.
For a chosen energy, the number of independent equations (rank of the system of linear equations) is 3-degeneracy (this is 2 in our case for all 3 energies.)

put here whatever the dimension of the matrix is

$$\begin{bmatrix} 1-E_n & i & 0 \\ -i & -E_n & 0 \\ 0 & 0 & -1-E_n \end{bmatrix} \begin{bmatrix} \phi_n^1 \\ \phi_n^2 \\ \phi_n^3 \end{bmatrix} = 0 \qquad (n=1,..,3)$$

$$(1-E_n)\phi_n^1 + i\phi_n^2 = 0$$
$$-i\phi_n^1 - E_n\phi_n^2 = 0$$
$$(1+E_n)\phi_n^3 = 0$$

- Let's start from $E_3 = -1$. For this energy, the third equation is OK, and ϕ_3^3 can be anything $\phi_3^3 = c$ (free param.)

From the 1st & 2nd Eqn we get (

$$\Big[\underbrace{(1-E_n)\cancel{\phi_n}\, i E_n + i}\Big]\phi_n^2 = 0$$

when $E_n = -1$, not zero, so $\underline{\phi_n^2 = 0}$, and also $\underline{\phi_n^1 = 0}$

Therefore, $\boxed{E_3 = -1 \qquad \phi_3 = \begin{bmatrix} 0 \\ 0 \\ c \end{bmatrix}}$, $c \in \mathbb{C}$ (any complex number)

- $E_1 = \frac{1+\sqrt{5}}{2}$ $\qquad \underbrace{(1+E_1)}_{\neq 0} \phi_1^3 = 0 \implies \phi_1^3 = 0$ fixed

For the remaining 2 equations, ~~are bound~~ they will prove to be one and the same (prove this on your own, like we did in class!), so we can pick $\phi_1^1 = c$, and from either eqn 1 or 2 we will get $\phi_1^2 = -i(1-E_1)\phi_1^1$

$$\phi_1^2 = -i(1-E_1)c = -ic\left(1 - \frac{1+\sqrt{5}}{2}\right) = -\frac{ic}{2}(1-\sqrt{5})$$

$$\boxed{E_1 = \frac{1+\sqrt{5}}{2} \qquad \phi_1 = \begin{bmatrix} c \\ -i\frac{c}{2}(1-\sqrt{5}) \\ 0 \end{bmatrix}}$$

- $E_2 = \frac{1-\sqrt{5}}{2}$, analogy to E_1 ...

$$\boxed{E_2 = \frac{1-\sqrt{5}}{2} \qquad \phi_2 = \begin{bmatrix} c \\ -i\frac{c}{2}(1+\sqrt{5}) \\ 0 \end{bmatrix}}$$

Example 2

Find the eigenvalues and the eigenvectors of the free-particle Hamiltonian, in 1D.

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, \qquad \hat{H}\phi(x) = \mathcal{E}\phi(x)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\phi(x)}{dx^2} = \mathcal{E}\phi(x)$$

$$\boxed{\frac{d^2\phi}{dx^2} + \frac{2m\mathcal{E}}{\hbar^2}\phi(x) = 0}$$

$\underline{\mathcal{E}>0}$ $\quad \frac{2m\mathcal{E}}{\hbar^2} \equiv k^2 \qquad \frac{d^2\phi}{dx^2} + k^2\phi(x) = 0$

Solutions are e^{ikx}, e^{-ikx}, and they are linearly independent (we'll prove later that they are also orthogonal).

<u>For any $k \in \mathbb{R}_0^+$</u> (positive real numbers & zero)

- eigenvectors e^{ikx}, e^{-ikx} (& <u>any linear comb. thereof</u>)
- eigenvalue $\mathcal{E}(k) = \frac{\hbar^2 k^2}{2m}$

<u>Interesting property of $e^{\pm ikx}$</u>

$$\boxed{\hat{p}\, e^{i(\pm k)x} = -i\hbar\frac{\partial}{\partial x}e^{\pm ikx} = (\pm\hbar k)\, e^{\pm ikx}}$$

Plane waves $e^{\pm ikx}$ are also eigenvectors of the momentum operator, corresponding to eigenvalues $\pm\hbar k$.

Plane wave	Momentum	Energy
$e^{\pm ikx}$	$\pm\hbar k$	$\mathcal{E}(k)=\frac{\hbar^2 k^2}{2m}$

Total (x + time) wavefunctions

$$\psi(x,t) \sim \underbrace{e^{\pm ikx - i\frac{\hbar k^2}{2m}t}}_{\text{real wave}}$$

Wavelength $\lambda = \frac{2\pi}{|k|}$

Magnitude of momentum $|p| = \hbar k$

$$\lambda = \frac{2\pi\hbar}{|p|} = h$$

$$\boxed{\lambda = \frac{h}{|p|}}$$

de Broglie relationship

Relates a particle quality (momentum) with a wavelike quality (wave length).

<u>Bottom line</u>: Plane waves, the eigenfunctions of the momentum operator and the free-particle Hamiltonian, are great because any wavefunction can be written as a linear combination of them.

However, a real free particle cannot be described by a single plane wave, because plane waves are not SQUARE INTEGRABLE, i.e. for them it does not hold $\int d^3\vec{r}\, \psi^*_{\vec{k}}(\vec{r},t)\psi_{\vec{k}}(\vec{r},t) < \infty$.

<u>Orthogonality of plane waves</u>: $\phi_{\vec{k}}(\vec{r}) = A e^{i\vec{k}\vec{r}}$

$$\int d^3\vec{r}\, \phi^*_{\vec{k}}(\vec{r})\, \phi_{\vec{k}'}(\vec{r}) =$$

$$= \int d^3\vec{r}\, e^{-i\vec{k}\vec{r}} \cdot e^{i\vec{k}'\vec{r}} \cdot |A|^2 =$$

$$= |A|^2 \underbrace{\int d^3\vec{r}\, e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}}}_{(2\pi)^3\,\delta(\vec{k}-\vec{k}')} \qquad \text{when } \vec{k}=\vec{k}' \text{ diverges}$$

~~Plane waves can then~~ $|A|$ is chosen so that

$$\int d^3\vec{r}\, \phi^*_{\vec{k}}(\vec{r})\, \phi_{\vec{k}'}(\vec{r}) = \delta(\vec{k}-\vec{k}')$$

therefore $|A| = 1/(2\pi)^{3/2}$.

(In 1D $|A| = 1/\sqrt{2\pi}$, in 2D $|A| = 1/2\pi$, i.e., for d-dim $|A| = \dfrac{1}{(2\pi)^{d/2}}$)

Although a plane wave cannot describe a particle alone, we like them because

1) They are eigenfunctions of momentum –
   – we can speak of definite momentum and wavevector of a plane wave
2) They are eigenfunctions of the free-particle Hamiltonian
   – we can speak of definite energy of a plane wave

DISPERSION RELATION FOR FREE PARTICLE:

$$\mathcal{E}(k) = \frac{\hbar^2 k^2}{2m}$$

3) Plane waves constitute an orthonormal basis; ~~so~~ any wavefunction of any particle in any potential, and at any given fixed point in time, can be written in terms of plane waves

<u>Example 3</u> Describe temporal evolution of a free particle that was, at $t=0$, ~~given by~~ described by the wavefunction

$$\psi(x, t=0) = B e^{-\alpha x^2}$$

At $t=0$, $\psi(x,0) = \int_{-\infty}^{\infty} dk\, A(k) \frac{e^{ikx}}{\sqrt{2\pi}} = \phi_k(x)$

At t, since every plane wave will evolve according to its own $\mathcal{E}(k)$, we will obtain

$$\psi(x,t) = \int_{-\infty}^{\infty} dk\, A(k)\, \phi_k(x)\, e^{-i\frac{\mathcal{E}(k)t}{\hbar}}.$$

Therefore, what needs to be found are the coefficients in the linear combination, $A(k)$, and that we find using the normalization condition

$$\int_{-\infty}^{\infty} dx\, \phi_k^*(x)\, \phi_{k'}(x) = \delta(k-k')$$

and the given form for $\psi(x,0)$

$$\int_{-\infty}^{\infty} dx\, \phi_{k'}^*(x)\, \psi(x,0) = \int_{-\infty}^{\infty} dx\, \phi_{k'}^*(x) \int_{-\infty}^{\infty} dk\, A(k)\, \underline{\phi_k(x)}$$

$$= \int_{-\infty}^{\infty} dk\, A(k)\, \delta(k-k') = A(k')$$

$$A(k') = \int_{-\infty}^{\infty} dx\, \frac{e^{-ik'x}}{\sqrt{2\pi}} \cdot B e^{-\alpha x^2} =$$

$$= \frac{B}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, e^{-\alpha\left(x^2 + \frac{ik'x}{\alpha}\right)} =$$

$$= \frac{B}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, e^{-\alpha\left(x + \frac{ik'}{2\alpha}\right)^2} e^{-\alpha \frac{k'^2}{4\alpha^2}}$$

$$= \frac{B}{\sqrt{2\pi}} \cdot e^{-k'^2/4\alpha} \cdot \sqrt{\frac{\pi}{\alpha}}$$

We forgot to normalize $\psi(x,0)$.

$$\int_{-\infty}^{\infty} dx\, \psi^*(x,0)\psi(x,0) = |B|^2 \int_{-\infty}^{\infty} dx\, e^{-2\alpha x^2} = |B|^2 \sqrt{\frac{\pi}{2\alpha}}$$

$$\boxed{|B| = \left(\frac{2\alpha}{\pi}\right)^{1/4}}$$

$$A(k') = \left[\frac{\cancel{2\alpha}}{\pi} \cdot \frac{1}{(2\cancel{\pi})^{\cancel{2}}} \cdot \frac{\pi^{\cancel{2}}}{\alpha^{\cancel{2}}}\right]^{1/4} \cdot e^{-k'^2/4\alpha} = \frac{1}{(2\pi\alpha)^{1/4}} e^{-k'^2/4\alpha}$$

$$\psi(x,t) = \int_{-\infty}^{\infty} \frac{dk}{\sqrt{2\pi}} \cdot \frac{1}{(2\pi\alpha)^{1/4}}\, e^{-k^2/4\alpha} e^{ikx} e^{-i\frac{\hbar k^2}{2m}t}$$

$$-k^2\left(\frac{1}{4\alpha} + \frac{i\hbar t}{2m}\right) + ikx =$$

$$= -\left(\frac{1}{4\alpha} + \frac{i\hbar t}{2m}\right)\left[k^2 - k\,\frac{ix \cdot 4\alpha m}{m + 2i\hbar t\alpha}\right]$$

$$= -\left(\frac{m + 2i\hbar t\alpha}{4\alpha m}\right)\left[\left(k - \frac{ix \cdot 2\alpha m}{m + 2i\hbar t\alpha}\right)^2 + \frac{4\alpha^2 x^2 m^2}{(m + 2i\hbar t\alpha)^2}\right]$$

$$\psi(x,t) = \frac{1}{(2\pi)^{3/4}\alpha^{1/4}} \cdot \cancel{e^{-\left(\frac{m+2i\hbar t\alpha}{4\alpha m}\right)}} \cdot$$

$$\cdot\, e^{-\frac{\cancel{m+2i\hbar t\alpha}}{\cancel{4\alpha m}} \cdot \frac{\cancel{4}\alpha^{\cancel{2}} x^2 m^{\cancel{2}}}{(m+2i\hbar t\alpha)^{\cancel{2}}}} \underbrace{\boxed{\int_{-\infty}^{\infty} dk\, e^{-\alpha'(k-\varkappa)^2}}}$$

$$\alpha' = \frac{m + 2i\hbar t\alpha}{4\alpha m}$$

$$\varkappa' = \frac{i \cdot 2\alpha m x}{m + 2i\hbar t\alpha}$$

$$\sqrt{\frac{\pi}{\alpha'}} \quad \mathrm{Re}\,\alpha' > 0$$

$$\psi(x,t) = \frac{1}{(2\pi)^{3/4}\alpha^{1/4}} e^{-\frac{\alpha x^2}{1+i\frac{2\hbar t\alpha}{m}}} \cdot \sqrt{\frac{4\sqrt{\pi}\alpha}{1+i\frac{2\hbar t\alpha}{m}}}$$

$$= \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\frac{\alpha x^2}{1+i\frac{2\hbar t\alpha}{m}}} \Big/ \sqrt{1+2i\frac{\hbar t\alpha}{m}}$$

$$\boxed{|\psi(x,t)|^2 = \left(\frac{2\alpha}{\pi}\right)^{1/2} e^{-\frac{2\alpha x^2}{1+\frac{4\hbar^2 t^2\alpha^2}{m^2}}} \cdot \left(1+\frac{4\hbar^2 t^2\alpha^2}{m^2}\right)^{-1/2}}$$

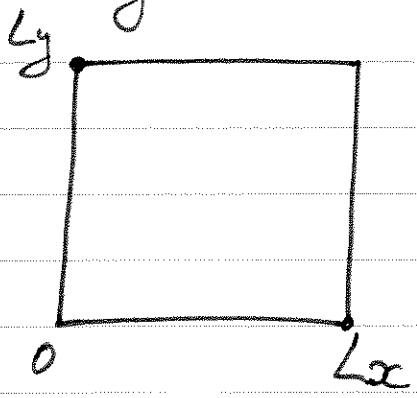
Born-von Karman periodic boundary conditions

Although unable to fully ~~re~~ describe real particles that move freely in unbound space, plane waves are immensely useful, ~~as the~~ especially when describing free electrons in a real-world system, such as a metal, where

- there are multiple electrons; they occupy single-particle states according to the Pauli principle; as a result, it is very important to work with states that are ~~eigenvalu~~ the eigenstates of the single-particle Hamiltonian
- We are interested in phenomena that involve transport of charge, spin, etc., so we want eigenstates of the free-particle Hamiltonian, which are propagating

[$e^{\pm ikx}$ propagate, unlike $\sin(kx)$ and $\cos(kx)$ standing waves]

Instead of infinite available volume, we take large available volume V, and in order to disregard the influence of ~~cont~~ surfaces, we put



$$\phi_x(0) = \phi_x(L_x)$$

$$e^{ik_x L_x} = 1 \Rightarrow k_x L_x = 2\pi \cdot n_x$$

$$\boxed{k_x = \frac{2\pi}{L_x} n_x}$$

B-vK periodic bound. condition

$$k_y = \frac{2\pi}{L_y} n_y, \quad k_z = \frac{2\pi}{L_z} n_z$$

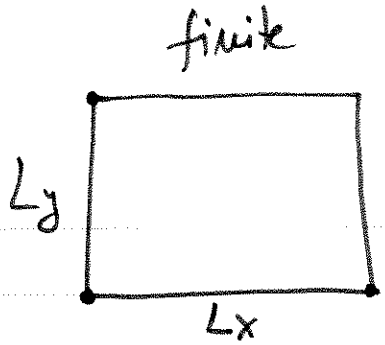
Born-von Karman boundary conditions induce <u>discretization</u> among k's: they are no longer infinitely close together, but spaced by

$$\Delta k_x = k_x(n_x+1) - k_x(n_x) = \frac{2\pi}{L_x}$$

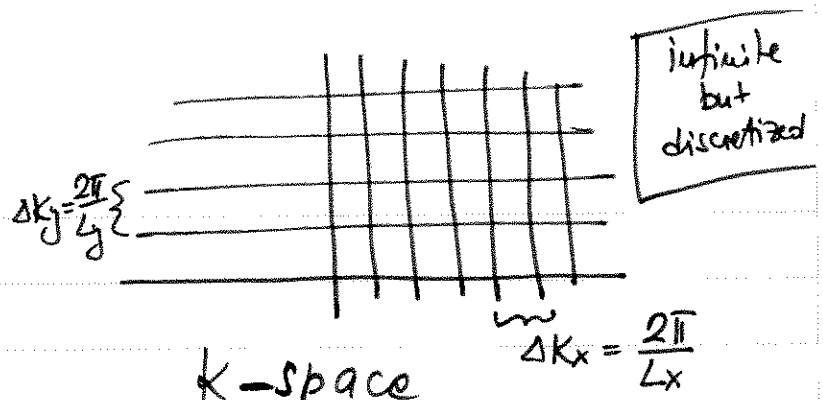
Available "volume" (in 1D) is L_x, which agrees with the Heisenberg uncertainty relationship

$$\boxed{\Delta k_x \cdot \Delta x = \frac{2\pi}{L_x} \cdot L_x = 2\pi}$$

(as $\Delta p_x \cdot \Delta x = (\hbar \Delta k_x) \cdot \Delta x = \hbar \cdot 2\pi = h$)



Real space



k-space

Normalization in a finite box

(1D) We want $\phi(k)$ & $\phi(k')$ to be orthogonal unless $k = k'$

$$\phi(k_x) = A e^{ik_x x}, \quad \phi(k_x') = A e^{ik_x' x}, \quad k_x' k = \frac{2\pi}{L_x} n', n$$

$$\int_0^{L_x} |A|^2 e^{-ik_x x} e^{ik_x' x} = |A|^2 \int_0^{L_x} e^{-i\frac{2\pi x}{L_x}(n_x - n_x')} dx$$

$$= |A|^2 \begin{cases} \text{if } n_x' = n_x, \text{ the integral is } L_x \\ \text{if } n_x' \neq n_x, \text{ the integral is } \dfrac{e^{-i\frac{2\pi \cancel{L_x}}{\cancel{L_x}}(n_x - n_x')} - 1}{\frac{2\pi(n_x' - n_x)}{L_x}} = 0 \end{cases}$$

$$\int_0^{L_x} |A|^2 e^{-ik_x x} e^{ik_x' x} = \underbrace{|A|^2 \cdot L_x}_{\text{We need it to be } 1} \cdot \delta_{k_x, k_x'}$$

$$|A| = \frac{1}{\sqrt{L_x}}$$

$$\boxed{\begin{array}{l} \text{Plane waves in a box of side } L_x \\ \phi(k_x) = \dfrac{1}{\sqrt{L_x}} e^{ik_x x} \end{array}}$$

Department of Electrical and Computer Engineering

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ECE 745 – Solid State Electronics

Fall 2004, Lecture Notes

Part II: Electronic Structure of Semiconductors

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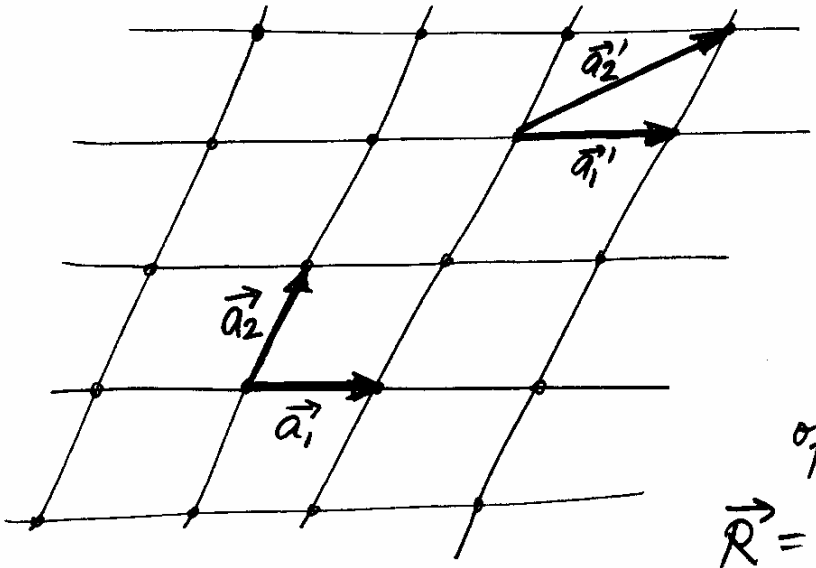
Crystal Lattices

- Recommended reading:
  Ashcroft & Mermin, "Solid State Physics," Ch. 4

Bravais lattice

An infinite array of discrete points, with an arrangement such that from whichever point the lattice is viewed, it looks exactly the same.

In 3D, one can always find 3 non-coplanar vectors such that a Bravais lattice can be obtained as all linear combinations of these vectors, so that the coefficients in the linear combination are integers.

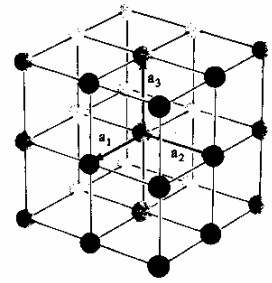


In 2D, an example of a Bravais lattice.
All the points in the lattice correspond to integer linear combinat. of vectors $\vec{a}_1$ and $\vec{a}_2$

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2$$

Vectors $\vec{a}_1$ and $\vec{a}_2$ are <u>primitive vectors</u>. However, their choice is not unique. For instance, vectors $\vec{a}_1'$ and $\vec{a}_2'$ are also good candidates to span the Bravais lattice.

One of the most familiar Bravais lattices – simple cubic. One set of primitive vectors can be chosen to be three mutually orthogonal (perpendicular) vectors, all of the same magnitude.



Finite crystals

The Bravais lattice is infinite, but a physical crystal is finite. However, many physical phenomena in crystals are unaffected by the boundaries.

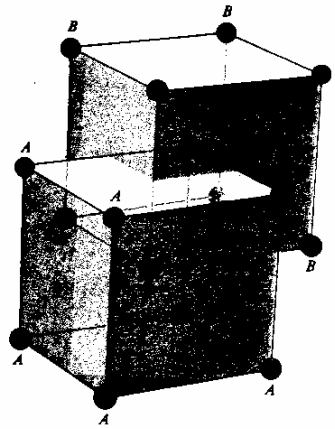
Therefore, one picks a ~~not~~ finite subset of the Bravais lattice; if a set of primitive vectors is given, then we limit ourselves to $N = N_1 N_2 N_3$ sites, corresponding to

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

where $0 \leq n_1 < N_1$, $0 \leq n_2 < N_2$, $0 \leq n_3 < N_3$.

Although a finite volume is chosen (we will later relate it to Born-von Karman periodic boundary conditions), we retain ~~some~~ many of the notions inherent to the infinite Bravais lattice: invariance to (virtually) any ~~not~~ translation, etc.

Example: <u>Body-centered cubic lattice</u> (<u>bcc</u>)



Formed by adding another point to the center of each cube. Can be viewed as two interpenetrating simple cubic lattices, shifted by $\frac{1}{2}(\vec{a}_1+\vec{a}_2+\vec{a}_3)$

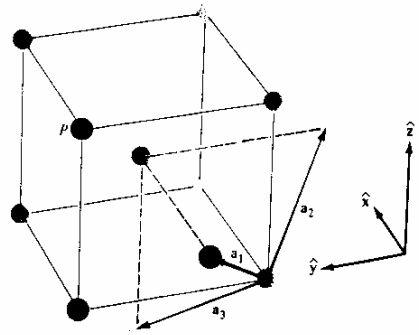
Original simple cubic lattice

$$\vec{a}_1 = \vec{e}_x a, \quad \vec{a}_2 = a\vec{e}_y, \quad \vec{a}_3 = a\vec{e}_z$$

<u>Bcc</u>

$$\vec{a}_1 = a\vec{e}_x, \quad \vec{a}_2 = a\vec{e}_y, \quad \vec{a}_3 = \frac{a}{2}(\vec{e}_x+\vec{e}_y+\vec{e}_z)$$

a possible set.



More commonly used:
a symmetrized set

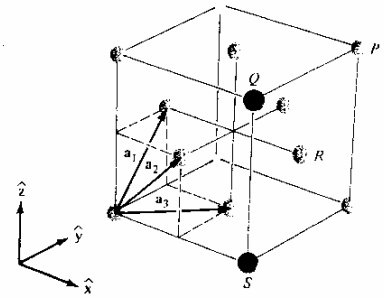
$$\vec{a}_3 = \frac{a}{2}(\vec{e}_x + \vec{e}_y - \vec{e}_z)$$

$$\vec{a}_1 = \frac{a}{2}(\vec{e}_y + \vec{e}_z - \vec{e}_x)$$

$$\vec{a}_2 = \frac{a}{2}(\vec{e}_z + \vec{e}_x - \vec{e}_y)$$

Example: <u>Face-centered cubic lattice</u>

Starting from a simple cubic lattice, add a lattice point in the center of each face of the cube. The most symmetric set of primitive vectors are



$$\vec{a}_1 = \frac{a}{2}(\vec{e}_y + \vec{e}_z) \quad \vec{a}_2 = \frac{a}{2}(\vec{e}_z + \vec{e}_x) \quad \vec{a}_3 = \frac{a}{2}(\vec{e}_x + \vec{e}_y)$$

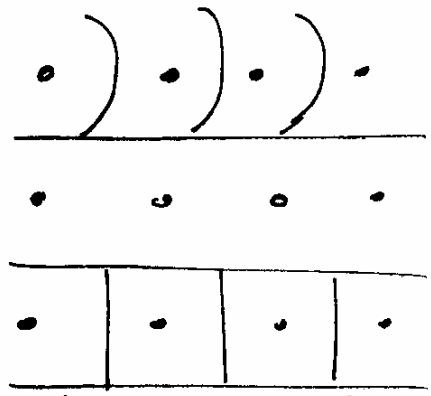
<u>Note</u>: Fcc & Bcc are extremely important in studying semiconductors. For instance, fcc is the underlying Bravais lattice for both Si and GaAs (however, more to follow.)

<u>Primitive unit cell</u>

A volume of space such that, when translated through the Bravais lattice, fills the space without overlapping itself or leaving voids.

A primitive cell contains precisely one lattice point, therefore its volume is given by

$$v = V/N$$



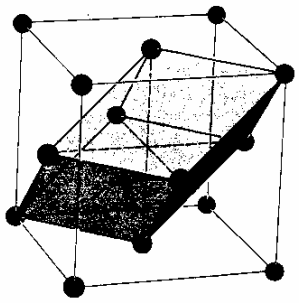
Different types of primitive unit cells

V - volume of the crystal

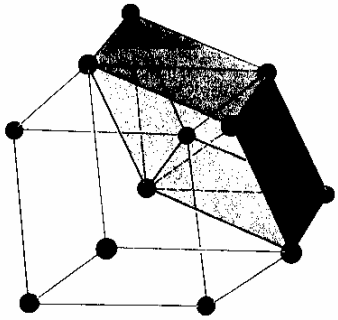
$N = N_1 N_2 N_3$ total # of lattice pts.

Volume of the primitive cell independent of shape! You can cut one & get the other one, after rearranging the pieces.

However, the primitive cells often do not have the full symmetry of the Bravais lattice. Often, a ~~the~~ (conventional) unit cell is chosen, such that it has the Bravais lattice full symmetry, and generally larger volume than the primitive cell.



Primitive and conventional unit cells for the face-centered cubic Bravais lattice. The conventional cell is the large cube. The primitive cell is the figure with six parallelogram faces. It has one quarter the volume of the cube, and rather less symmetry.



Primitive and conventional unit cells for the body-centered cubic Bravais lattice. The primitive cell (shaded) has half the volume of the conventional cubic cell.

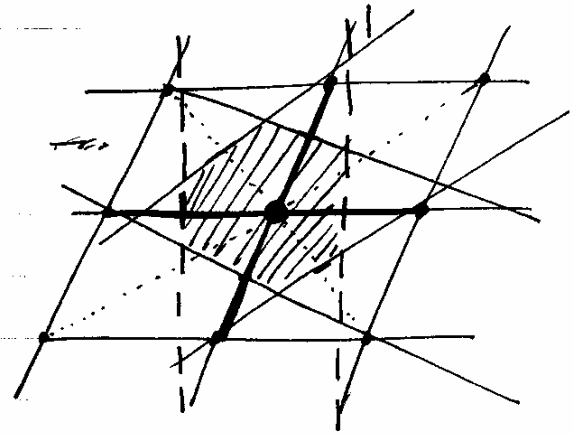
For instance, for both fcc and bcc, the (simple) cubic unit cell is chosen as the unit cell.

Wigner-Seitz primitive cell

It is a particular type of primitive cell, which retains full symmetry of the Bravais lattice.

Construction of the Wigner-Seitz cell.
Pick a lattice point, connect it to all the nearest neighbors in all directions, and then bisect each of the lines with a plane, and take the smallest polyhedron bound by the planes.

Construction of the Wigner-Seitz primitive cell for a 2D lattice. →



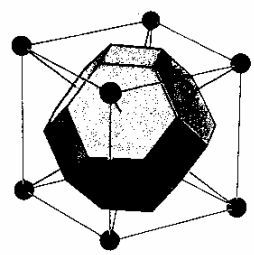


Figure 4.15
The Wigner-Seitz cell for the body-centered cubic Bravais lattice (a "truncated octahedron"). The surrounding cube is a conventional body-centered cubic cell with a lattice point at its center and on each vertex. The hexagonal faces bisect the lines joining the central point to the points on the vertices (drawn as solid lines). The square faces bisect the lines joining the central point to the central points in each of the six neighboring cubic cells (not drawn). The hexagons are regular (see Problem 4d).

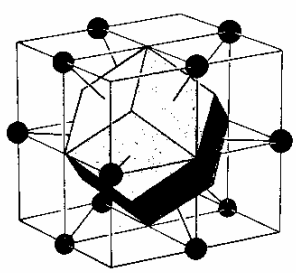


Figure 4.16
Wigner-Seitz cell for the face-centered cubic Bravais lattice (a "rhombic dodecahedron"). The surrounding cube is *not* the conventional cubic cell of Figure 4.12, but one in which lattice points are at the center of the cube and at the center of the 12 edges. Each of the 12 (congruent) faces is perpendicular to a line joining the central point to a point on the center of an edge.

Lattice with a basis

To make a jump from an abstract, empty Bravais lattice to a real crystal, we need to know what the arrangement of atoms is within a primitive cell. Lattice + basis = crystal structure.

The two most important crystal structures in semiconductor physics are

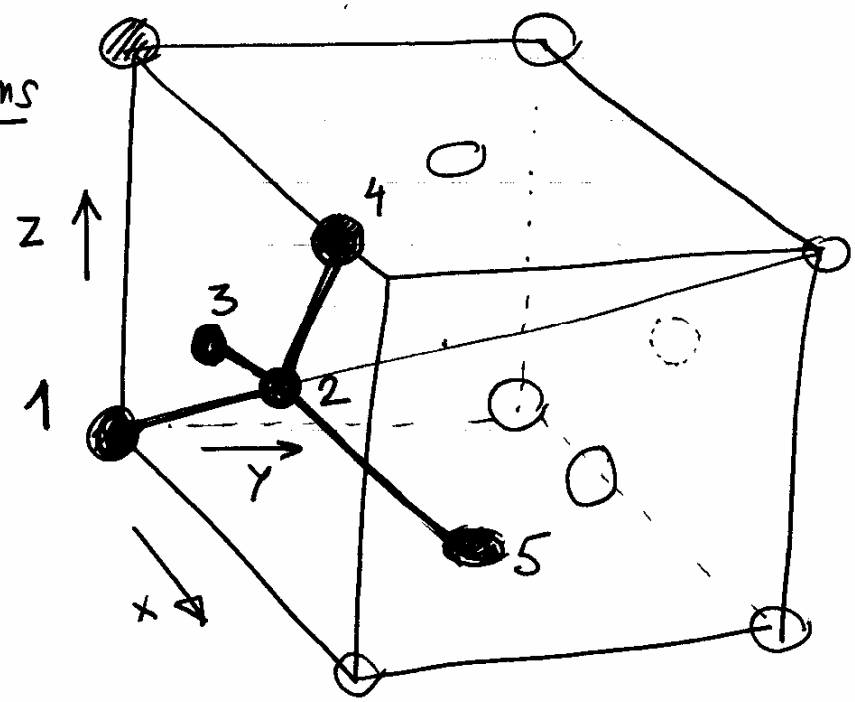
ZINCBLENDE < Si (diamond), GaAs

WURTZITE < SiC, GaN

Underlying Bravais lattices:

- Zincblende – face centered cubic with two basis atoms

Basis atoms 1 & 2



Atom coordinates

1: $(0,0,0)$

2: $a(\frac{1}{4},\frac{1}{4},\frac{1}{4})$

3: $a(\frac{1}{2},0,\frac{1}{2})$

4: $a(0,\frac{1}{2},\frac{1}{2})$

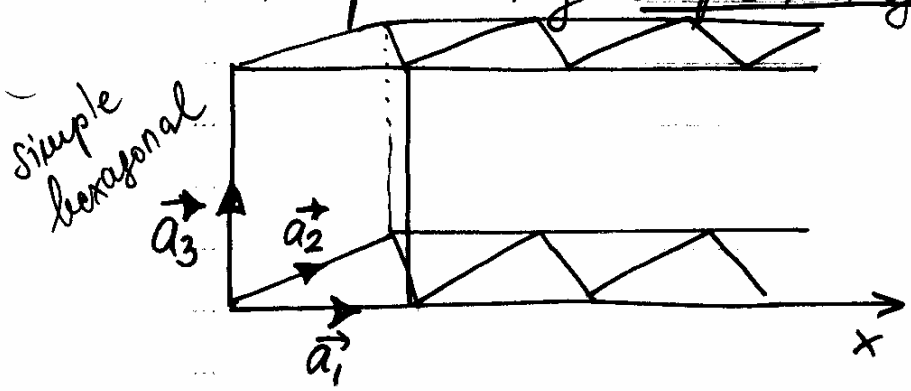
5: $a(\frac{1}{2},\frac{1}{2},0)$

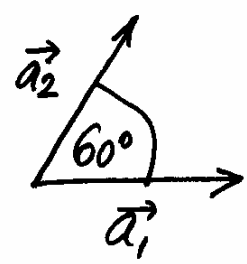
If the nearest neighbors are of the opposite kind, we call it <u>zincblende</u> (like III-V's, except nitrides.) If the nearest neighbors are the same as the atoms under consideration, then the structure is called <u>diamond</u> (Si, C, Ge).

- <u>Wurtzite</u> (GaN equil. configuration, ZnS (also can be ZB) ...)

Underlying ~~Bravais lattice~~ structure is <u>hexagonal close packed</u> (hcp)

Hexagonal close packed structure consists of two interpenetrating <u>simple hexagonal lattices</u>:



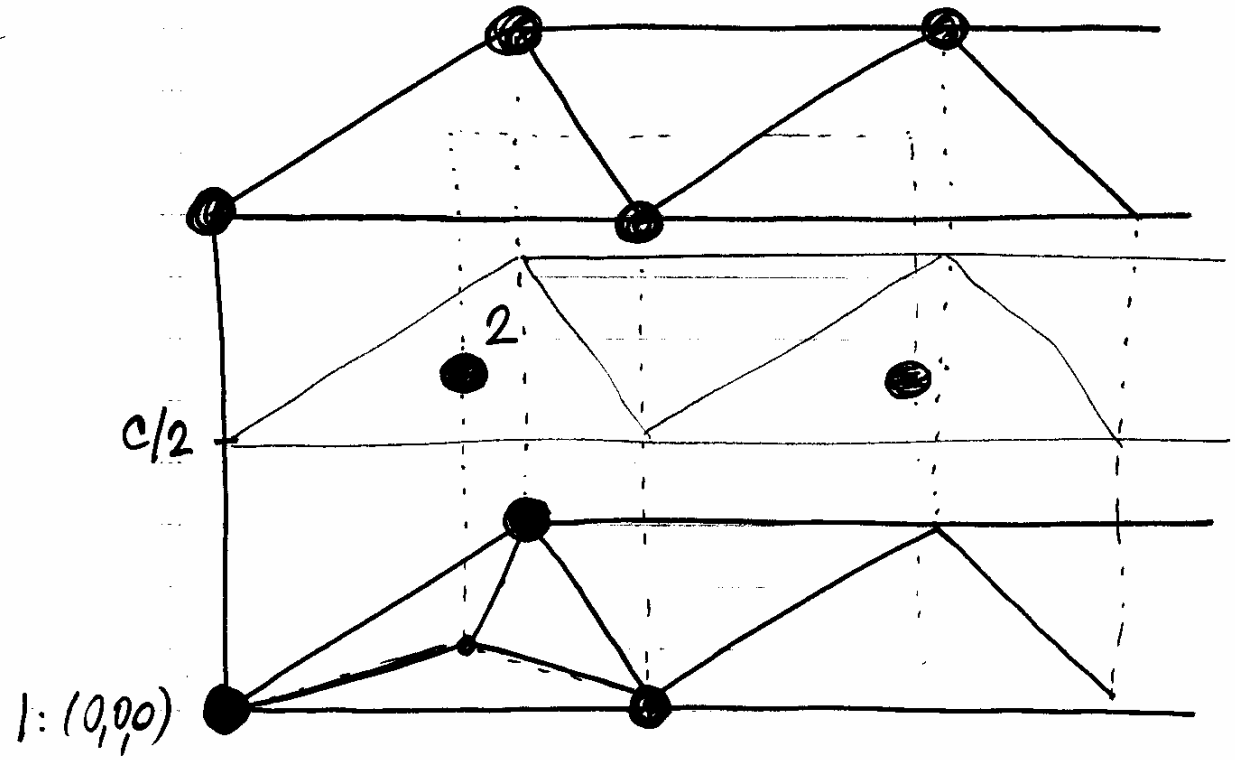


$|\vec{a}_1| = |\vec{a}_2|$

Distance between two hexagonal layers stacked above one another is c (the "3" axis is referred to as the c-axis).

$$\boxed{\vec{a}_1 = a\vec{e}_x \quad \vec{a}_2 = \frac{a}{2}\vec{e}_x + \frac{a\sqrt{3}}{2}\vec{e}_y \quad \vec{a}_3 = c\vec{e}_z}$$

conventional primitive vectors for simple hexagonal 3D lattice



Hcp structure obtained by adding another simple hexagonal lattice, such that ~~the~~ it is displaced by c/2 along the c-axis.

The ratio of c/a is structure-dependent.

GaN $c = 5.16\,\text{Å}$ $a = 3.175\,\text{Å}$

InN $c = 8.7\,\text{Å}$ $a = 3.54\,\text{Å}$

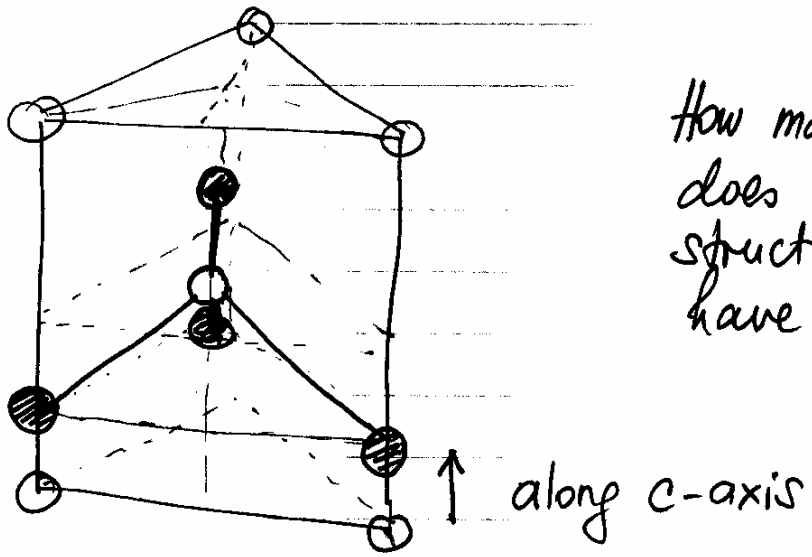
The two atoms in the basis are

1: (0,0,0)

2: $\left(\frac{a}{3}, \frac{a}{3}, \frac{c}{2}\right)$

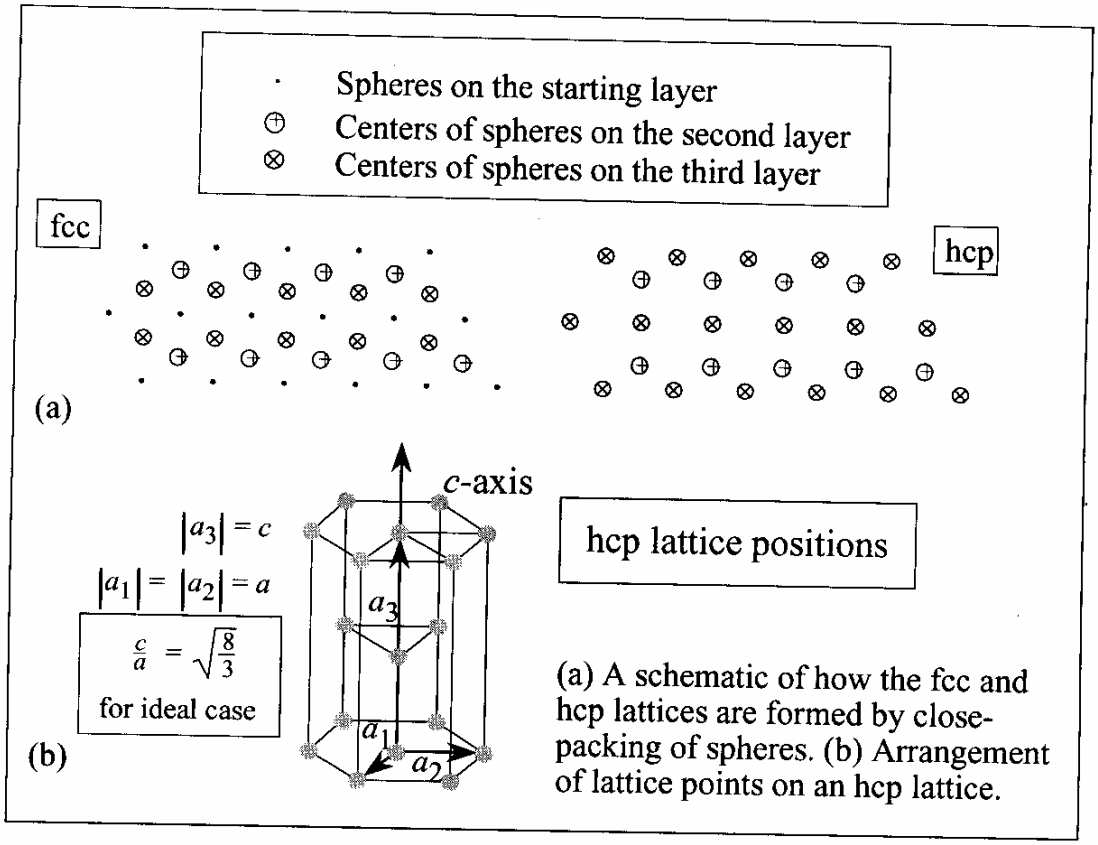
However, this is still not wurtzite.

The hcp structure is formed by one species of atoms. Now imagine dressing each atom in the hcp lattice by 4 neighboring atoms of different species

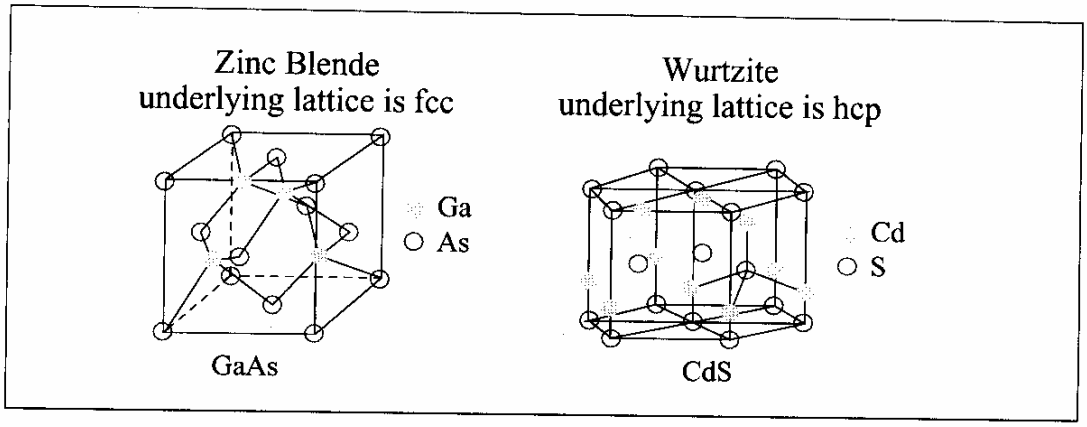


How many basis atoms does a wurtzite structure finally have?

FCC and HCP STRUCTURES



(a) A schematic of how the fcc and hcp lattices are formed by close-packing of spheres. (b) Arrangement of lattice points on an hcp lattice.



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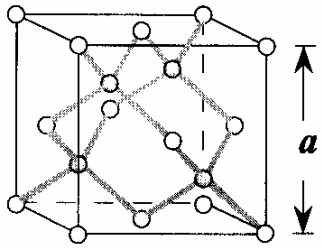
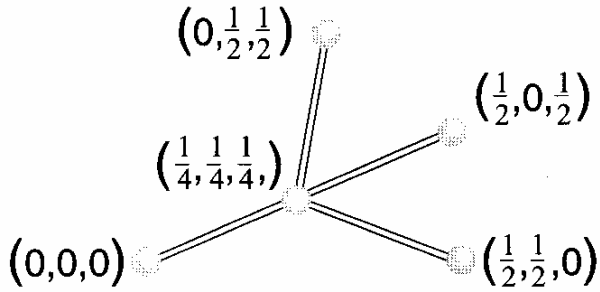
DIAMOND AND ZINC BLENDE STRUCTURES



The zinc blende crystal structure. The structure consists of the interpenetrating fcc lattices, one displaced from the other by a vector $\left(\frac{a}{4},\frac{a}{4},\frac{a}{4}\right)$ along the body diagonal. The underlying Bravais lattice is fcc with a two-atom basis. The positions of the two atoms is (000) and $\left(\frac{a}{4},\frac{a}{4},\frac{a}{4}\right)$.

Positions of the atoms

$$\begin{aligned}\mathbf{A} = &(n_1,n_2,n_3),\ (n_1+\tfrac{1}{4},n_2+\tfrac{1}{4},n_3+\tfrac{1}{4}),\\ &(n_1+\tfrac{1}{2},n_2+\tfrac{1}{2},n_3),(n_1+\tfrac{3}{4},n_2+\tfrac{3}{4},n_3+\tfrac{1}{4}),\\ &(n_1+\tfrac{1}{2},n_2,n_3+\tfrac{1}{2}),(n_1+\tfrac{3}{4},n_2+\tfrac{1}{4},n_3+\tfrac{3}{4}),\\ &(n_1,n_2+\tfrac{1}{2},n_3+\tfrac{1}{2}),(n_1+\tfrac{1}{4},n_2+\tfrac{3}{4},n_3+\tfrac{3}{4})\end{aligned}$$



Tetrahedral bonding

Nature of chemical bonds in a diamond or zinc blende structure

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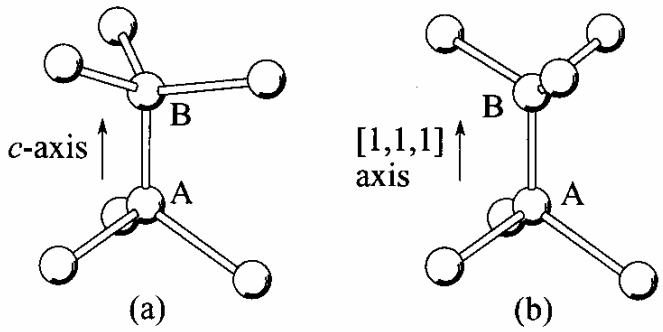
Zinc Blende and Wurtzite



Orientations of adjacent atomic tetrahedra in wurtzite (a) and zinc blende (b). The A and B refer to the two different species of atom.

Semiconductors

Elements commonly found in semiconductor compounds

I	II	III	IV	V	VI	VII
	Be	B	C	N	O	F
	Mg	Al	Si	P	S	Cl
Cu	Zn	Ga	Ge	As	Se	Br
Ag	Cd	In	Sn	Sb	Te	I
	Hg	Tl	Pb	Bi		

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Zinc Blende and Wurtzite

Material	Crystal Structure	Bandgap (eV)	Static Dielectric Constant	Lattice Constant (Å)	Density (gm-cm^{-3})
C	DI	5.50, I	5.570	3.56683	3.51525
Si	DI	1.1242, I	11.9	5.431073	2.329002
SiC	ZB	2.416, I	9.72	4.3596	3.166
Ge	DI	0.664, I	16.2	5.6579060	5.3234
BN	HEX	5.2, I	$\varepsilon_{\parallel} = 5.06$	$a = 6.6612$	2.18
			$\varepsilon_{\perp} = 6.85$	$c = 2.5040$	
BN	ZB	6.4, I	7.1	3.6157	3.4870
BP	ZB	2.4, I	11.	4.5383	2.97
BAs	ZB	—	—	4.777	5.22
AlN	W	6.2,D	$\bar{\varepsilon} = 9.14$	$a = 3.111$	3.255
				$c = 4.981$	
AlP	ZB	2.45,I	9.8	5.4635	2.401
AlAs	ZB	2.153,I	10.06	5.660	3.760
AlSb	ZB	1.615,I	12.04	6.1355	4.26
GaN	W	3.44,D	$\varepsilon_{\parallel}=10.4$	$a = 3.175$	6.095
			$\varepsilon_{\perp}= 9.5$	$c = 5.158$	
GaP	ZB	2.272,I	11.11	5.4505	4.138
GaAs	ZB	1.4241,D	13.18	5.65325	5.3176
GaSb	ZB	0.75,D	15.69	6.09593	5.6137
InN	W	1.89,D		$a = 3.5446$	6.81
				$c = 8.7034$	
InP	ZB	1.344,D	12.56	5.8687	4.81
InAs	ZB	0.354,D	15.15	6.0583	5.667
InSb	ZB	0.230,D	16.8	6.47937	5.7747
ZnO	W	3.44,D	$\varepsilon_{\parallel}= 8.75$	$a = 3.253$	5.67526
			$\varepsilon_{\perp}= 7.8$	$c = 5.213$	
ZnS	ZB	3.68,D	8.9	5.4102	4.079
ZnS	W	3.9107,D	$\bar{\varepsilon} = 9.6$	$a = 3.8226$	4.084
				$c = 6.2605$	
ZnSe	ZB	2.8215,D	9.1	5.6676	5.266
ZnTe	ZB	2.3941,D	8.7	6.1037	5.636
CdO	R	0.84,I	21.9	4.689	8.15
CdS	W	2.501,D	$\bar{\varepsilon} = 9.83$	$a = 4.1362$	4.82
				$c = 6.714$	
CdS	ZB	2.50,D	—	5.818	—
CdSe	W	1.751,D	$\varepsilon_{\parallel}=10.16$	$a = 4.2999$	5.81
			$\varepsilon_{\perp}= 9.29$	$c = 7.0109$	
CdSe	ZB	—	—	6.052	—
CdTe	ZB	1.475,D	10.2	6.482	5.87
PbS	R	0.41,D*	169.	5.936	7.597
PbSe	R	0.278,D*	210.	6.117	8.26
PbTe	R	0.310,D*	414.	6.462	8.219

Data are given at room temperature values (300 K).
Key: DI: diamond; HEX: hexagonal; R: rocksalt; W: wurtzite; ZB: zinc blende;
*: gap at L point; D: direct; I: indirect $\varepsilon_{\parallel}$: parallel to c-axis; $\varepsilon_{\perp}$: perpendicular to c-axis

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Bandgaps (in eV) of some semiconductors

TETRAHEDRALLY BONDED MATERIALS

V	C	Si	Ge	α-Sn
C	5.5i,D			
Si	2.6i,Z/W	1.1i,D	0.7-1.1i	
Ge		0.7-1.1	0.74i,D	
α-Sn				0.09,D
III-V	**N**	**P**	**As**	**Sb**
B	3.8,W	2.0i,Z	1.5i,Z	
Al	5.9,W	2.5,Z	2.2,Z	1.7,Z
Ga	3.5,W	2.4i,Z	1.5,Z	0.81,Z
In	0.9,W	1.4,Z	0.41,Z	0.24,Z
II-VI	**O**	**S**	**Se**	**Te**
Zn	3.4,W	3.6,Z/W	2.8,Z/W	2.4,Z
Cd	1.3i,R	2.5,Z/W	1.8,Z/W	1.6,Z
Hg	2.2,O/Rh	2.3,T	–.06,Z	–.3,Z
I-VII	**F**	**Cl**	**Br**	**I**
Cu		3.4,Z	3.1,Z	3.1,Z
Ag	2.8i,R	3.2i,R	2.7i,R	3.0,W

i: Indirect gap
D: Diamond
Z: Zinc Blende
W: Wurtzite
R: Rocksalt
O: Orthorhombic
Rh: Rhombohedral
T: Trigonal
OR: Orthorhombic distorted rocksalt
M: Monoclinic

NON-TETRAHEDRAL BONDED MATERIALS

IV-VI compounds

IV-VI	O	S	Se	Te
Ge		1.7,OR	1.1,OR	0.15,R
Sn		1.1,OR	0.9,OR	2.1,R
Pb	2.0,i	0.29,R	0.15,R	0.19,R

Group VI elements

VI	S	Se	Te
	3.6,O	1.9i,T 2.5,M	0.33,T

Group V elements

V	P	As	Sb	Bi
	.33,O	.17,Rh	.10	.015

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Reciprocal Lattice (A&M, Ch. 5 & 6)

For a given Bravais Lattice the set of all $\vec{K}$'s that give plane waves with the periodicity of the Bravais lattice is called the **RECIPROCAL LATTICE.**

$\forall \vec{r}; \forall \vec{R}$ from Bravais lattice

$$e^{i\vec{K}(\vec{r}+\vec{R})} = e^{i\vec{K}\cdot\vec{r}}$$

$$e^{i\vec{K}\cdot\vec{R}} = 1 \Rightarrow \vec{K}\cdot\vec{R} = 2\pi \cdot \text{integer}$$

If $\vec{R}$ from the **DIRECT** Bravais lattice is given by

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3,$$

where $\vec{a}_1, \vec{a}_2, \vec{a}_3$ is a set of primitive vectors, then one can show that ~~a basis~~ in the reciprocal lattice a set of primitive vectors is given by

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}$$

$\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3) = v$ volume of the primitive cell

It can be shown that the primitive vectors of the direct lattice, $\vec{a}_i$, and the primitive vectors of the reciprocal lattice, $\vec{b}_i$, satisfy

$$\vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij}, \quad \delta_{ij} = \begin{cases} 1, & i=j \\ 0, & i \neq j \end{cases}$$

the Kronecker delta symbol

Any vector $\vec{K}$ of the reciprocal lattice can be written as a linear combination of $\vec{b}_i$, with integer coefficients, i.e.,

$$\vec{K} = k_1 \vec{b}_1 + k_2 \vec{b}_2 + k_3 \vec{b}_3, \quad k_i \text{: integers}$$

It is therefore satisfied

$$\vec{K} \cdot \vec{R} = 2\pi (n_1 k_1 + n_2 k_2 + n_3 k_3) = 2\pi \cdot \text{integer}$$

<u>Simple cubic lattice</u>

$$\vec{a}_1 = a\vec{e}_x, \ \vec{a}_2 = a\vec{e}_y, \ \vec{a}_3 = a\vec{e}_z$$

$$\vec{b}_1 = \frac{2\pi}{a}\vec{e}_x, \ \vec{b}_2 = \frac{2\pi}{a}\vec{e}_y, \ \vec{b}_3 = \frac{2\pi}{a}\vec{e}_z$$

Reciprocal lattice of a simple cubic lattice is also a simple cubic lattice, with lattice constant $2\pi/a$.

$$v = a^3 \longrightarrow v_{\text{reciprocal}} = \frac{(2\pi)^3}{a^3}$$

Face-centered cubic lattice

Primitive vectors of the direct lattice

$$\vec{a}_1 = \frac{a}{2}(\vec{e}_y + \vec{e}_z),\ \vec{a}_2 = \frac{a}{2}(\vec{e}_z + \vec{e}_x),\ \vec{a}_3 = \frac{a}{2}(\vec{e}_x + \vec{e}_y)$$

Primitive vectors of the reciprocal lattice

$$\vec{b}_1 = \frac{4\pi}{a}\cdot\frac{1}{2}(\vec{e}_y + \vec{e}_z - \vec{e}_x)$$

$$\vec{b}_2 = \frac{4\pi}{a}\cdot\frac{1}{2}(\vec{e}_z + \vec{e}_x - \vec{e}_x)$$

$$\vec{b}_3 = \frac{4\pi}{a}\cdot\frac{1}{2}(\vec{e}_x + \vec{e}_y - \vec{e}_z)$$

primitive vectors of a bcc lattice with constant $4\pi/a$

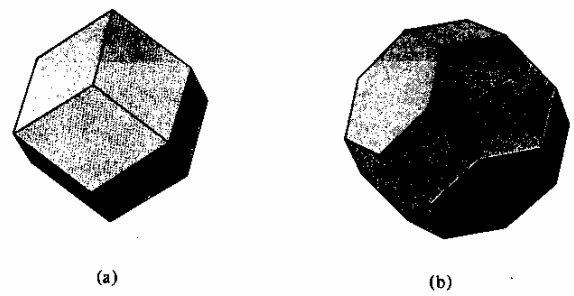
<u>Reciprocal lattice of fcc is a bcc lattice.</u> And vice-versa, reciprocal lattice of a bcc lattice is an fcc lattice formed starting from a cubic lattice with constant $4\pi/a$.

IF v IS THE VOLUME OF A PRIMITIVE CELL OF THE DIRECT LATTICE, THEN THE RECIPROCAL LATTICE HAS A PRIMITIVE CELL OF VOLUME $(2\pi)^3/v$.

First Brillouin Zone

The Wigner-Seitz cell of the reciprocal lattice is called THE FIRST BRILLOUIN ZONE. It is of TREMENDOUS IMPORTANCE in understanding electronic phenomena.

Figure 5.2
(a) The first Brillouin zone for the body-centered cubic lattice.
(b) The first Brillouin zone for the face-centered cubic lattice.



The first Brillouin zone of the fcc lattice is the Wigner-Seitz cell of the bcc lattice. The characteristic shape with hexagons & squares is where much of the information regarding the bandstructure of our semiconductors (Si, Ge, GaAs, etc.) will lie.

Lattice Planes and Miller Indices

A lattice plane in a Bravais lattice contains at least 3 noncolinear points of the Bravais lattice. (Actually, any lattice plane contains infinitely many lattice points, which form a two-dimensional Bravais lattice.)

The full 3D Bravais lattice can be alternatively viewed as a <u>family of lattice planes</u>, which are all parallel and equally spaced. (The selection of a family is not unique, as seen in the Figure.)

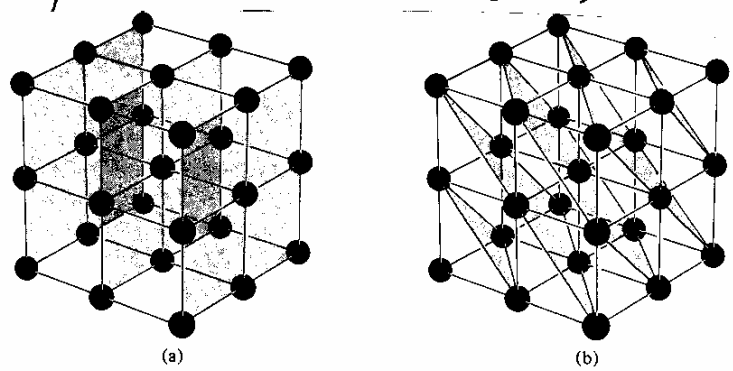


Figure 5.3
Some lattice planes (shaded) in a simple cubic Bravais lattice; (a) and (b) show two different ways of representing the lattice as a family of lattice planes.

For any family of lattice planes separated by a distance d, there are reciprocal lattice vectors perpendicular to the planes, and the shortest among them has length $2\pi/a$. Conversely, FOR ANY RECIPROCAL LATTICE VECTOR $\vec{K}$, THERE IS A FAMILY OF LATTICE PLANES NORMAL TO $\vec{K}$ AND SEPARATED BY d, WHERE $2\pi/d$ IS THE LENGTH OF THE SHORTEST RECIPROCAL LATTICE VECTOR PARALLEL TO $\vec{K}$.

$\Updownarrow$

Directions in reciprocal lattice

$\Updownarrow$

Families of planes in direct lattice

Miller indices of the (crystalographic) lattice plane are the coordinates of the shortest reciprocal lattice vector normal to that plane

$$\vec{K} = h\vec{b_1} + k\vec{b_2} + l\vec{b_3}$$

Plane given by Miller indices $(h\,k\,l)$.
(They can have no common factor if $\vec{K}$ is indeed the shortest among vectors perpendicular to the plane.)

Simple cubic, fcc, bcc

For all 3, we rely on the notation for sc, since any lattice plane in fcc or bcc is also a lattice plane in sc.
(Miller indices important as defined above in noncubic crystals.)

If $h=4$, $k=-2$, $l=1$

Miller indices in parentheses $(h\,k\,l) = (4\,\bar{2}\,1)$

specifies plane

Directions in the direct lattice in square brackets

$$[n_1\, n_2\, n_3]$$

There are families of lattice planes mutually equivalent because of a point group symmetry of the crystal (rotation or a reflection). E.g., in a cubic crystal, planes (100), (010), and (001) are all equivalent, so one denotes them collectively as

$$\{1\,0\,0\} \quad \text{(curly brackets).}$$

Generally, you use curly brackets and Miller indices of one set of planes to denote the collection of symmetry-equivalent lattice families.

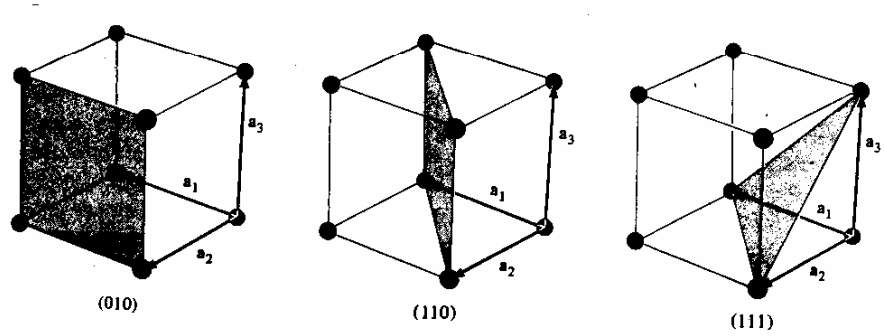
$$\{h\,k\,l\}$$

In a similar fashion, equivalent directions in the direct lattice are denoted by

$$\langle n_1\, n_2\, n_3 \rangle,$$

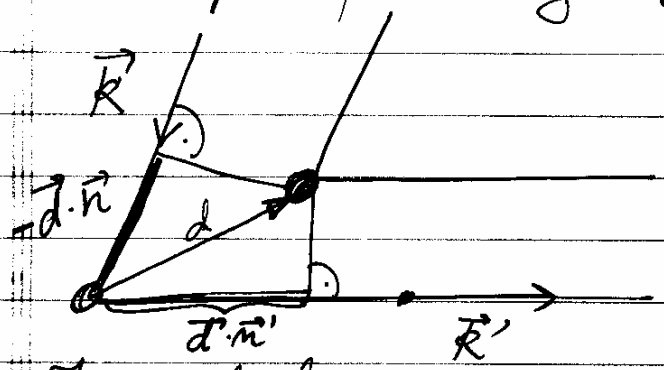
E.g., in a cubic crystal, [100], [$\bar{1}$00], [010], [0$\bar{1}$0], [001], and [00$\bar{1}$] are denoted collectively as

$$\langle 1\,0\,0 \rangle \text{ directions.}$$



Reciprocal lattice vectors & von Laue diffraction

Constructive interference by a set of periodically distributed objects (Bravais lattice) can be read as a map. If incoming light has wavevector



$$\vec{k} = \frac{2\pi}{\lambda}\cdot\vec{n}$$

and the scattered light

$$\vec{k}' = \frac{2\pi}{\lambda}\vec{n}'$$

In order to have constructive interference, the difference of between optical paths ~~for~~ has to be an integer multiple of the wavelength

$$\vec{d}\cdot(\vec{n}'-\vec{n}) = m\lambda$$

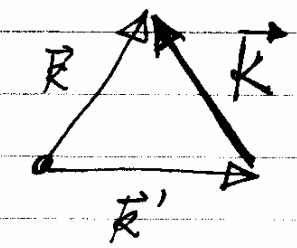
$$\vec{d}\cdot(\vec{k}'-\vec{k}) = m\lambda\cdot\frac{2\pi}{\lambda} = 2\pi m$$

Since $\vec{d}$ is from the Bravais lattice, if constructive interference peak is observed, it means that for all $\vec{d} = \vec{R}$ from the Bravais lattice

$$\vec{R}\cdot(\vec{k}'-\vec{k}) = 2\pi m$$

Therefore $\vec{k}'-\vec{k}$ has to be a RECIPROCAL LATTICE VECTOR

$$\vec{k}-\vec{k}' = \vec{K}$$



Electrons in a Periodic Potential (A&M, Ch8)

The problem of electrons in a crystal is a many-body problem, since one needs to take into account not only the electron – nuclei interaction, but electron-electron interaction as well.

However, for many solid-state phenomena, the "single electron approximation" is sufficient. Within it, you think about independent electrons: an electron moves in an effective one-electron potential.

(How to obtain the potential is not trivial; however, if we are dealing with a perfect crystal, then the effective potential must be periodic, with the periodicity of the underlying Bravais lattice:

$(\forall \vec{R} \in \text{Bravais lat.})$ $$U(\vec{r}+\vec{R}) = U(\vec{r})$$

eff. potential

any point within crystal (not necessarily a lattice pt.)

Therefore, we are going to examine the properties of the single-electron time-independent Schrödinger eqn.

$$\hat{H}\phi = \left(-\frac{\hbar^2}{2m}\vec{\nabla}^2 + U(\vec{r})\right)\phi = \varepsilon\phi$$

periodic potential

Independent electrons moving in a periodic potential are known as <u>Bloch electrons</u>. (free electrons are a special species of Bloch electrons, for $\mathcal{U}(\vec{r})=0$)

<u>General remark regarding motion in a periodic potential</u>
Since the potential is periodic, we should expect that any measurable quantity around a point $\vec{r}$ should have the same value as around $\vec{r}+\vec{R}$. Since in the expectation value for any operator $\hat{A}$ we have

$$\langle \hat{A} \rangle = \int d^3\vec{r}\, \psi^*(\vec{r},t)\, \hat{A}\, \psi(\vec{r},t)$$

we see that the quantity which should be insensitive to translation by $\vec{R}$ is the probability density $|\psi(\vec{r},t)|^2$, namely, for any $\vec{R}$ from the crystal's underlying Bravais lattice, it should hold

$$|\psi(\vec{r},t)|^2 = |\psi(\vec{r}+\vec{R},t)|^2$$

For the Bloch electrons described by solutions to the time-independent Schrödinger equation with the periodic potential, we should have

$$|\phi(\vec{r})|^2 = |\phi(\vec{r}+\vec{R})|^2$$

When two complex numbers have the same magnitude, we conclude that they can differ only by a phase factor, i.e.,

$$\boxed{\phi(\vec{r}+\vec{R}) = \phi(\vec{r})\, e^{i\underbrace{\varphi(\vec{R})}_{\text{phase}}}}$$

Similarly, $\phi(\vec{r}+2\vec{R}) = e^{i\varphi(\vec{R})}\phi(\vec{r}+\vec{R}) = e^{i2\varphi(\vec{R})}\phi(\vec{r})$,
and in general
$$\phi(\vec{r}+n\vec{R}) = e^{in\varphi(\vec{R})}\phi(\vec{r})$$
So we see that the effect of spatial translations on the wavefunction is manifested through a phase factor, such that ~~#~~ the phase "accumulates" the information about repeated translations as

$$\vec{r} \longrightarrow \vec{r} + n\vec{R}$$
$$\phi \longrightarrow \phi \cdot \exp(\underbrace{in\varphi(\vec{R})}_{n \text{ times the phase of translation by } \vec{R}})$$

How exactly ϕ's look in a periodic crystal is given by

Bloch's theorem

The eigenstates ϕ of the one-electron Hamiltonian
$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r}),$$
where $U(\vec{r}+\vec{R}) = U(\vec{r})$ for all $\vec{R}$ in a Bravais lattice, can be chosen to have the form of a plane wave times a function with the periodicity of the Bravais lattice

$$\phi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, u_{n\vec{k}}(\vec{r}),$$

where $u_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r}+\vec{R})$ is the periodic function (n is for now ~~the~~ a generic, unknown quantum number, which we will learn to associate with the band index.)

Let us first see if this form agrees with our criteria:

$$\phi_{n\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot(\vec{r}+\vec{R})} u_{n\vec{k}}(\vec{r}+\vec{R})$$

$$= e^{i\vec{k}\cdot\vec{R}} \left[e^{i\vec{k}\vec{r}} u_{n\vec{k}}(\vec{r}) \right]$$

$$= e^{i\vec{k}\cdot\vec{R}} \phi_{n\vec{k}}(\vec{r})$$

indeed depends only on $\vec{R}$ (not $\vec{r}$)

$$\phi_{n\vec{k}}(\vec{r}+N\vec{R}) = e^{i\vec{k}\cdot\vec{R}\cdot N} \phi_{n\vec{k}}(\vec{r})$$ behaves properly with repeated translations

Are there any restrictions on $\vec{k}$?

Any $\vec{k}$ one can think of can be written as

$$\vec{k} = \vec{k}_{IBZ} + \vec{K}$$

where $\vec{k}_{IBZ}$ belongs to the first Brillouin zone, and $\vec{K}$ is a vector of the reciprocal lattice. Therefore

$$\phi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}} u_{n\vec{k}}(\vec{r})$$

$$\phi_{n\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}(\vec{r}+\vec{R})} u_{n\vec{k}}(\vec{r}+\vec{R})$$ periodic

$$= e^{i\vec{k}\vec{r}} \cdot e^{i(\vec{k}'+\vec{K})\vec{R}} u_{n\vec{k}}(\vec{r})$$

$$= \cancel{e^{i\vec{k}'\vec{r}}} \; \cancel{e^{i\vec{K}\vec{r}}} \; \cancel{e^{i\vec{K}\vec{R}}}$$

$$= e^{i\vec{k}'(\vec{r}+\vec{R})} \underbrace{e^{i\vec{K}(\vec{r}+\vec{R})}}_{\text{since } \vec{K}\cdot\vec{R} = 2\pi\cdot n \quad e^{i\vec{K}\vec{R}} = 1} u_{n\vec{k}}(\vec{r})$$

$$= e^{i\vec{k}'(\vec{r}+\vec{R})} \underbrace{\left[e^{i\vec{K}\vec{r}} u_{n\vec{k}}(\vec{r}) \right]}_{\text{a modified periodic fn}}$$

So we see that there will be a distinction between $\vec{k}$'s from the first Brillouin zone, and all the others.

Towards the proof of the Bloch theorem

- Born–von Karman periodic boundary conditions revisited

We used to pick a box with sides L_x, L_y & L_z and impose that the wavefunction be the same on opposite sides of the cube (we did so for a free electron).

In a crystal with primitive vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$, it makes more sense to specify the number of lattice points along each of the primitive vector directions: N_1, N_2, N_3, and require

$$\phi(\vec{r}+N_i\cdot\vec{a}_i)=\phi(\vec{r}), \quad i=1,2,3$$

When we apply Bloch's theorem, we obtain

$$\phi_{n\vec{k}}(\vec{r}+N_i\vec{a}_i)=e^{iN_i\vec{k}\cdot\vec{a}_i}\phi_{n\vec{k}}(\vec{r})$$

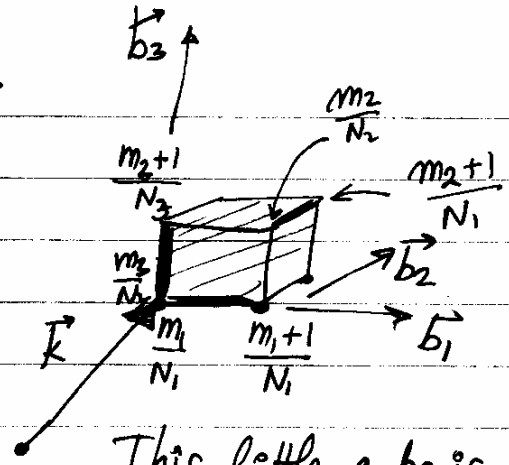
$$\boxed{e^{iN_i\vec{k}\cdot\vec{a}_i}=1}$$

If ~~$\vec{k}=k_1\vec{b}_1+k_2$~~ $\vec{k}=x_1\vec{b}_1+x_2\vec{b}_2+x_3\vec{b}_3$
(these coefficients do not have to be integers, as $\vec{k}$ is not from the reciprocal lattice exclusively!)

$$N_i \vec{K}\cdot\vec{a}_i = N_i \cdot 2\pi x_i = 2\pi m_i$$

$$\boxed{x_i = \frac{m_i}{N_i}}$$

$$\boxed{\vec{K} = \sum_{i=1}^{3} \frac{m_i}{N_i}\vec{b}_i} \quad (*)$$



This little cube is the volume that you can attribute to a given $\vec{k}$

Per $\vec{K}$, you have a tiny $\vec{k}$-space volume of

$$\Delta\vec{k} = \underbrace{\frac{1}{N_1N_2N_3}}_{N}\ \underbrace{\vec{b}_1\cdot(\vec{b}_2\times\vec{b}_3)}_{\frac{(2\pi)^3}{v}} = \frac{(2\pi)^3}{\underbrace{Nv}_{\text{total volume of crystal}}} = \frac{(2\pi)^3}{V}$$

same as for free electron

Now take any function that satisfies the Born-von Karman condition. It can be written as

$$\phi(\vec{r}) = \sum_{\vec{q}} \phi(\vec{q})\, e^{i\vec{q}\cdot\vec{r}} \qquad \vec{q} - \text{those given by } (*)$$

For a periodic potential U, however, its plane wave expansion contains <u>only</u> those plane waves given by reciprocal lattice vectors

$$U(\vec{r}) = \sum_{\vec{K}} U(\vec{K})\, e^{i\vec{K}\cdot\vec{r}}$$

capital $\vec{K}$'s will always denote reciprocal lattice vectors

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right]\phi(\vec{r}) = \varepsilon\phi(\vec{r})$$

- $$-\frac{\hbar^2}{2m}\nabla^2 \sum_{\vec{q}} \phi(\vec{q}) e^{i\vec{q}\cdot\vec{r}} = \sum_{\vec{q}} \frac{\hbar^2 q^2}{2m}\phi(\vec{q}) e^{i\vec{q}\cdot\vec{r}}$$
- $$U(\vec{r})\phi(\vec{r}) = \sum_{\vec{K}} U(\vec{K}) e^{i\vec{K}\cdot\vec{r}} \sum_{\vec{q}} \phi(\vec{q}) e^{i\vec{q}\cdot\vec{r}} =$$

$$= \sum_{\vec{K},\vec{q}} U(\vec{K})\phi_{\vec{q}}\, e^{i(\vec{q}+\vec{K})\vec{r}}$$

rename: $\vec{q}+\vec{K} \to \vec{q}$ $$= \sum_{\vec{K},\vec{q}} U(\vec{K})\phi_{\vec{q}-\vec{K}}\, e^{i\vec{q}\cdot\vec{r}}$$

Now the time-independent Schrödinger eqn. can be written as

$$\sum_{\vec{q}} \left[\left(\frac{\hbar^2 q^2}{2m} - \varepsilon\right)\phi(\vec{q}) + \sum_{\vec{K}} U(\vec{K})\phi(\vec{q}-\vec{K})\right] e^{i\vec{q}\vec{r}} = 0$$

Since all $e^{i\vec{q}\cdot\vec{r}}$ are mutually orthogonal,

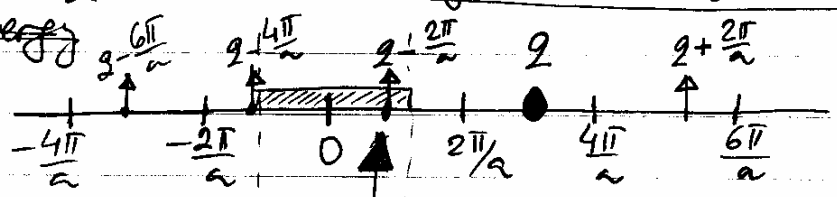
$$\boxed{(\forall \vec{q}) \quad \left(\frac{\hbar^2 q^2}{2m} - \varepsilon\right)\phi(\vec{q}) + \sum_{\vec{K}} U(\vec{K})\phi(\vec{q}-\vec{K}) = 0}$$

We see that for any $\vec{q}$ that we choose, it is coupled with all other $\vec{q}-\vec{K}$'s. Basically, for a given $\vec{q}$, there is a set of equations that all involve $\vec{q}$ and all other $\vec{q}-\vec{K}$'s. An energy corresponds to basically all of them (namely, this is a set of N algebraic equations, and it is a homogeneous one; the energies are found by annulling the system determinant).

Therefore, for any energy $\mathcal{E}$ that annulls the determinant of the above linear system, we will have generally nonzero $\phi_{\vec{q}}$ and all other $\phi_{(\vec{q}-\vec{K})}$'s that contribute to $\phi(\vec{r})$.

Should we attribute label $\vec{q}$ to the energy? Yes, as a given energy will be associated with the set of wavevectors generated by $\vec{q}$ & all the reciprocal lattice vectors $\vec{K}$. Should we label it $\vec{q}$ + some $\vec{K}$ then?

Since a given energy belongs as much to $\vec{q}$ as to any other $\vec{q}-\vec{K}$, we should choose one among all them to label the energy. That wavevector will be taken ~~to~~ as that $\vec{q}-\vec{K}$ that belongs to the first Brillouin zone. ~~Since energy~~



For this sequence $\left(q, q\pm\frac{2\pi}{a}, q\pm\frac{4\pi}{a}, \text{etc.}\right)$ the $\vec{q}_{IBZ}$ will be taken as representative

$$\mathcal{E} \equiv \mathcal{E}_{\vec{q}_{IBZ}} = \mathcal{E}_{\vec{q}_{IBZ}+\vec{K}} \text{ for any } \vec{K}$$

Also, for a given energy, one or more particular linear combinations of $\phi_{\vec{q}}$'s are in order; again, we choose to numerate the sum by $\vec{q}_{IBZ}$, ~~and~~

~~Th~~ Generally, for one $\vec{q}_{IBZ}$ there will be as many energies as there are ~~vect~~ wavevectors of

the reciprocal lattice. The index that counts these solutions is often called the band index, n.

So basically we have energies $\mathcal{E}_{\vec{q}_{IBZ}}$, and for every such energy there exists (at least one, since energies can be degenerate) solution $\phi_{\vec{q}_{IBZ}}(\vec{r})$, which is a combination of $\phi(\vec{q}_{IBZ}+\vec{K})\, e^{i(\vec{q}_{IBZ}+\vec{K})\cdot\vec{r}}$

$$\phi(\vec{r}) \equiv \phi_{\vec{q}_{IBZ}}(\vec{r}) = \sum_{\vec{K}} \phi(\vec{q}_{IBZ}+\vec{K})\, e^{i(\vec{q}_{IBZ}+\vec{K})\cdot\vec{r}}$$

$$= e^{i\vec{q}_{IBZ}\cdot\vec{r}} \underbrace{\sum_{\vec{K}} \phi(\vec{q}_{IBZ}+\vec{K})\, e^{i\vec{K}\cdot\vec{r}}}_{\text{periodic with the periodicity of the Bravais lattice}}$$

Therefore, we see

$$\phi_{\vec{q}_{IBZ}}(\vec{r}) = e^{i\vec{q}_{IBZ}\cdot\vec{r}}\, u_{\vec{q}_{IBZ}}(\vec{r})$$

which is of the Bloch form.

Some considerations regarding Bloch electrons

- Unlike a free particle, a Bloch electron does not have a well defined momentum. Namely

free electron: $\phi = \frac{1}{\sqrt{V}} e^{i\vec{q}\cdot\vec{r}}$, $\vec{q}$ unrestricted, except by periodic bound. cond

$$\hat{p}\phi = -i\hbar\vec{\nabla}\phi = \hbar\vec{q}\,\phi$$

Bloch electron: $\phi_{\vec{q}_{IBZ}}(\vec{r}) = e^{i\vec{q}_{IBZ}\cdot\vec{r}}\, u_{\vec{q}_{IBZ}}(\vec{r})$

$$\hat{p}\,\phi_{\vec{q}_{IBZ}} = -i\hbar\vec{\nabla}\phi_{\vec{q}_{IBZ}} = \Big[\hbar\vec{q}_{IBZ}\,\phi_{\vec{q}_{IBZ}} + \left(-i\hbar\, e^{i\vec{q}_{IBZ}\cdot\vec{r}}\right)\vec{\nabla}u_{\vec{q}_{IBZ}}(\vec{r})\Big]$$

$\hbar\vec{q}_{IBZ}$ is not exactly the momentum of a Bloch electron, because a crystal does not have full translational symmetry, required for momentum to be a good quantum number.

- For one $\vec{q}_{IBZ}$ and one energy $\mathcal{E}_{\vec{q}_{IBZ}}$ there is a particular form of $u_{\vec{q}_{IBZ}}$. However, different energy solutions & consequently different $\mathcal{E}$'s for one $\vec{q}$ $\rightarrow$ they give <u>different bands</u>.

Basically, the time-independent Schrödinger eqn can be rewritten as

$$\left[\frac{\hbar^2}{2m}\left(\vec{q}_{IBZ} - i\vec{\nabla}\right)^2 + U(\vec{r})\right]u_{\vec{q}_{IBZ}}(\vec{r}) = \mathcal{E}_{\vec{q}_{IBZ}}\, u_{\vec{q}_{IBZ}}(\vec{r})$$

Different $\mathcal{E}$'s correspond to different bands. These solutions are going to be <u>discrete</u>.

$$\mathcal{E}_{\vec{q}_{IBZ}} \longrightarrow \mathcal{E}_{\vec{q}_{IBZ},\, n}$$

band index

(Discreteness because periodity of the potential, the above eqn. can be solved within a single primitive cell, and finite volume $\leftrightarrow$ discrete states.)

Electrons in a Weak Periodic Potential; Opening of the Gap

(Reading: Ashcroft & Mermin, Ch. 9)

We have shown that a wavefunction of the Bloch form is given by

$$\phi_{\vec{q}}(\vec{r}) = \sum_{\vec{K}} \phi(\vec{q}+\vec{K})\, e^{i(\vec{q}+\vec{K})\vec{r}}$$

Such solution corresponds as much to $\vec{q}$ as to any other $\vec{q}+\vec{K}$, so one usually chooses the member of the family that belongs to the first Brillouin zone; however, this is not a must.

The coefficients $\phi(\vec{q}+\vec{K})$ were given by the set of equations

$$0 = \left(\frac{\hbar^2}{2m}(\vec{q}+\vec{K})^2 - \mathcal{E}\right)\phi(\vec{q}+\vec{K}) + \sum_{\vec{K}'} U(\vec{K}')\,\phi(\vec{q}+\vec{K}-\vec{K}')$$

If we assume that the periodic potential vanishes, the equations become uncoupled, and we obtain:

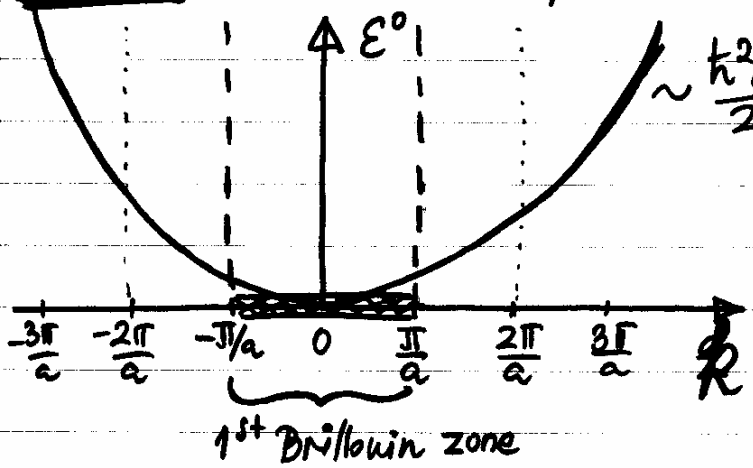
$$\boxed{(\mathcal{E}^{0}_{\vec{q}+\vec{K}} - \mathcal{E})\,\phi(\vec{q}+\vec{K}) = 0}$$

$$\boxed{\mathcal{E}^{0}_{\vec{q}+\vec{K}} = \frac{\hbar^2(\vec{q}+\vec{K})^2}{2m}}$$

$$\boxed{\begin{aligned} \mathcal{E}_{\vec{q}} &= \mathcal{E}^{0}_{\vec{q}+\vec{K}} \\ \phi_{\vec{q}} &\sim e^{i(\vec{q}+\vec{K})\vec{r}} \end{aligned}}$$

If there are two (or more) $\vec{q}+\vec{K}$ that have the same $\mathcal{E}^0_{\vec{q}+\vec{K}}$, then $\phi_{\vec{q}}$ corresponding to that energy can be a linear combination of the plane waves.

• **Example** 1D lattice of constant a.



$\sim \frac{\hbar^2 k^2}{2m} = \mathcal{E}^0_k$, any k allowed by periodic bound. conditions

The function $\mathcal{E}^0_{\vec{q}} = \frac{\hbar^2 q^2}{2m}$ is a parabola. However, let's look what happens in a crystal. We are solving to find energies $\mathcal{E}$, which will be associated with a $\vec{q}_{IBZ}$ and all its clones $\vec{q}_{IBZ}+\vec{K}$.

When we let $U \to 0$, we obtain

$$\boxed{\mathcal{E}_{\vec{q}_{IBZ}} = \mathcal{E}^0_{\vec{q}_{IBZ}+\vec{K}}, \quad \phi_{\vec{q}_{IBZ}} \sim e^{i(\vec{q}_{IBZ}+\vec{K})\vec{r}}}$$

This is true unless for some $\vec{q}_{IBZ}$ there are two or more $\vec{K}$'s that produce the same $\mathcal{E}^0$.

An example: $q_{IBZ} = -\frac{\pi}{a}$ $\quad K_1 = 0, \; K_2 = \frac{2\pi}{a}$

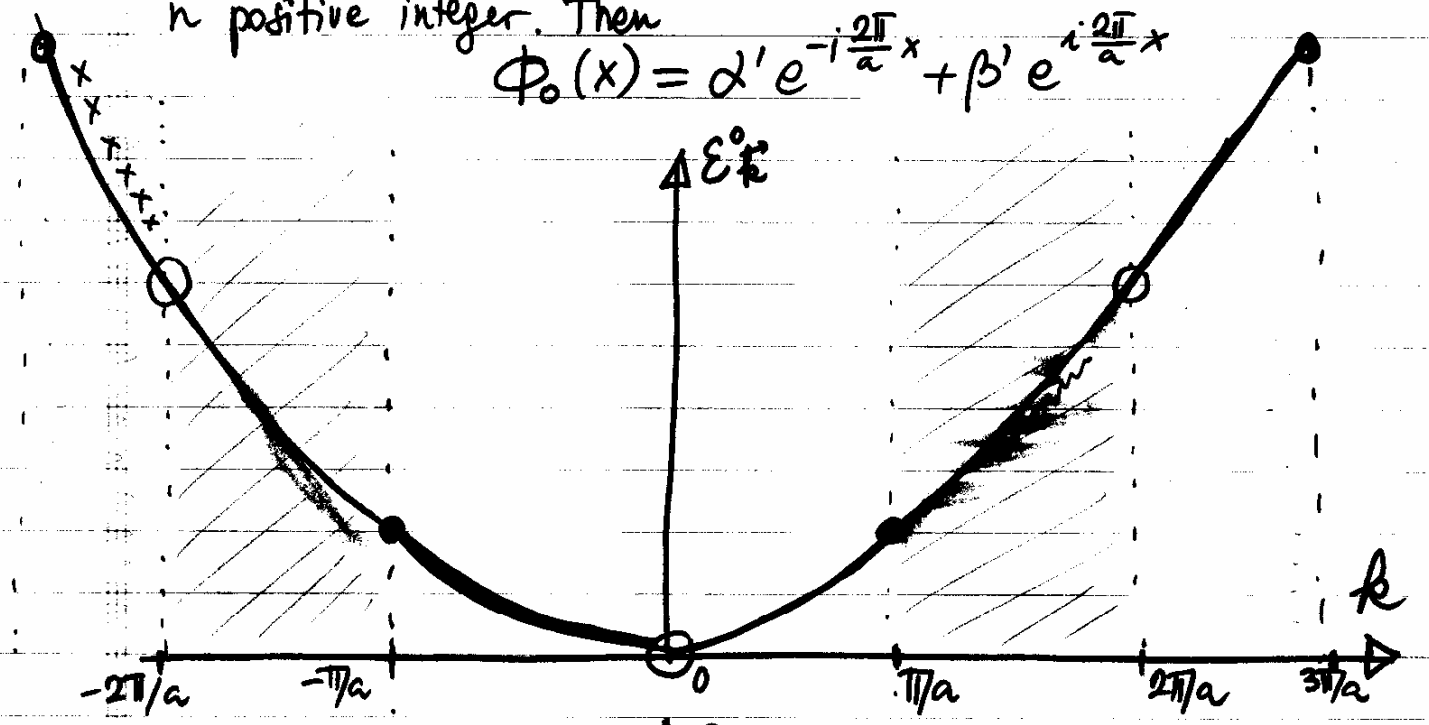
$$\boxed{\mathcal{E}^0_{q_{IBZ}} = \mathcal{E}^0_{q_{IBZ}+\frac{2\pi}{a}}} \leftarrow \text{edges of the } 1^{st}\text{BZ}$$

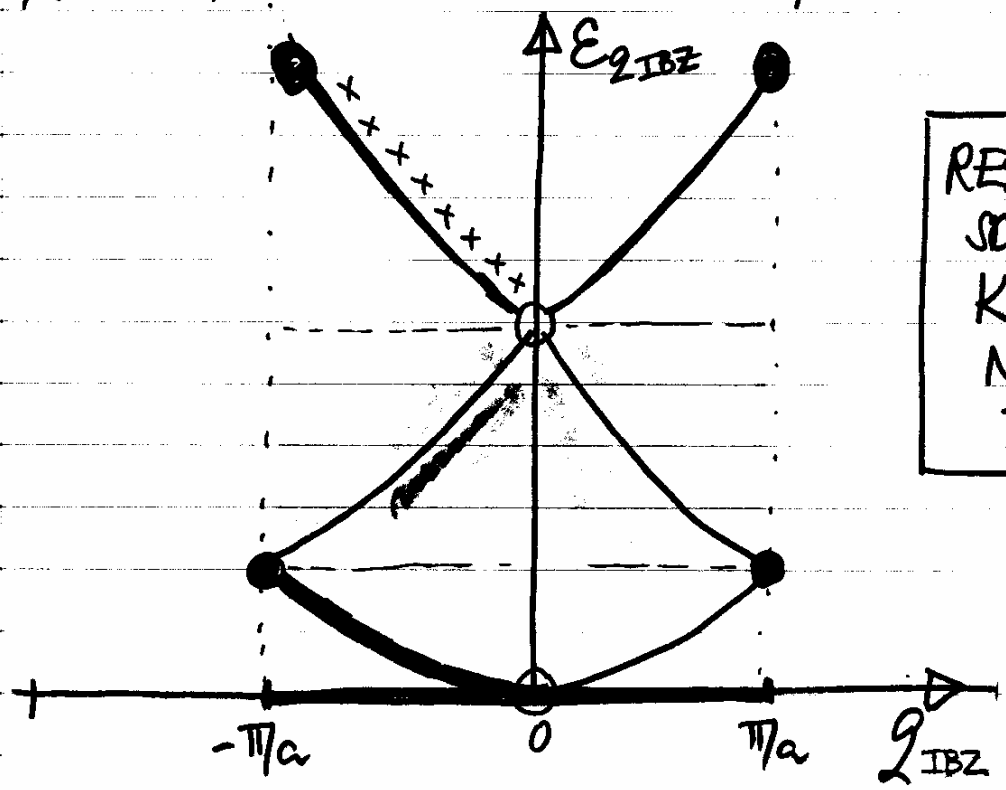
Then the Bloch function for $q_{IBZ} = -\pi/a$ is a linear combination

$$\Phi_{-\pi/a}(x) = \alpha e^{-i\frac{\pi}{a}x} + \beta e^{i\frac{\pi}{a}x}$$

Another example is $q_{IBZ} = 0$, $K_1 = -\frac{2\pi}{a} \cdot n$, $K_2 = +\frac{2\pi}{a} n$, n positive integer. Then

$$\Phi_0(x) = \alpha' e^{-i\frac{2\pi}{a}x} + \beta' e^{i\frac{2\pi}{a}x}$$





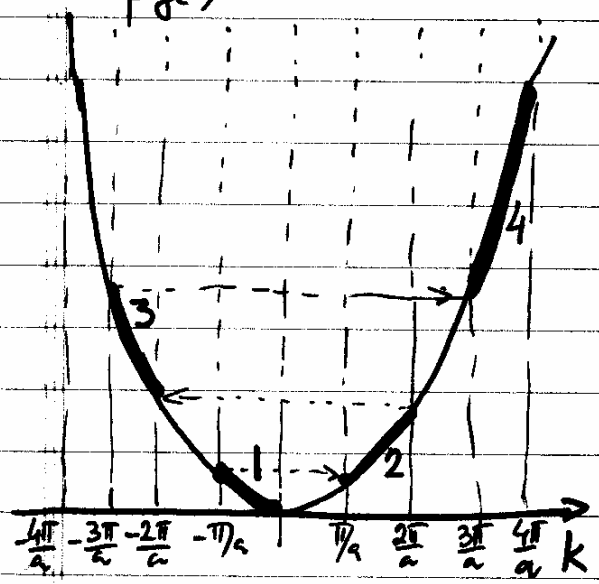
REDUCED ZONE SCHEME
K's NUMERATE ZONES

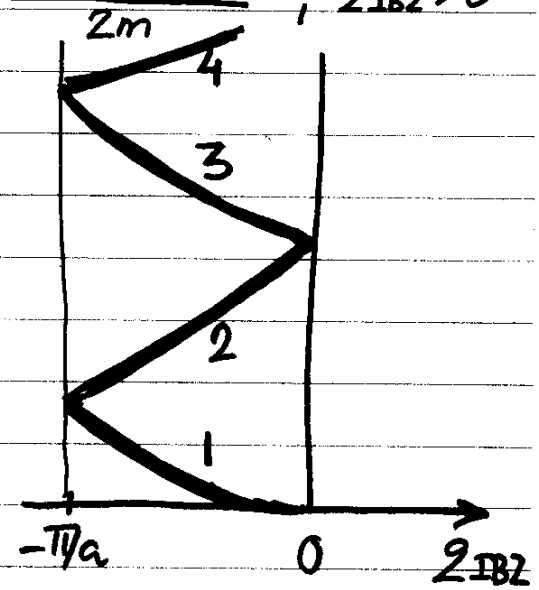
It is clear that $\vec{K}$'s numerates the bands!

1st band $\quad \mathcal{E}_{q_{IBZ},n=1} = \dfrac{\hbar^2 q_{IBZ}^2}{2m}$

2nd band (see Figure on last page)

$$\mathcal{E}_{q_{IBZ},n=2} = \begin{cases} \dfrac{\hbar^2\left(q_{IBZ}+\frac{2\pi}{a}\right)^2}{2m}, & q_{IBZ}<0 \\ \dfrac{\hbar^2\left(q_{IBZ}-\frac{2\pi}{a}\right)^2}{2m}, & q_{IBZ}>0 \end{cases}$$





- Now what happens when we do allow for the periodic potential to be appreciable?

Let us consider $\vec{q}_{IBZ}+\vec{K}_1$ for which there are no other $\vec{K}$'s that would yield an energy $\mathcal{E}^{\circ}_{\vec{q}_{IBZ}+\vec{K}} \approx \mathcal{E}^{\circ}_{\vec{q}+\vec{K}_1}$.
For this situation

$$\Phi(\vec{q}_{IBZ}+\vec{K})$$

has to be peaked around $\vec{q}_{IBZ}+\vec{K}_1$, i.e, when $U\to 0$, this is the only term that survives.

$$\left(\mathcal{E} - \frac{\hbar^2(\vec{q}_{IBZ}+\vec{K})^2}{2m}\right)\phi(\vec{q}_{IBZ}+\vec{K}) = \sum_{\vec{K}'}{}' \underbrace{U_{\vec{K}'}}_{U} \phi(\vec{q}_{IBZ}+\underbrace{\vec{K}-\vec{K}'}_{\text{call this } \vec{K}'})$$

$$= \sum_{\vec{K}'}{}' U_{\vec{K}-\vec{K}'}\, \phi(\vec{q}_{IBZ}+\vec{K}')$$

When we put $\vec{K}=\vec{K}_1$ (remember $\mathcal{E}^0_{(\vec{q}+\vec{K}_1)}$ is nondegenerate), and choose $U_0=0$ (we can shift the potential by an arbitrary constant), we see that on the RHS there are <u>only terms different from $\vec{K}_1$</u>, i.e.

$$\boxed{\left[\mathcal{E} - \frac{\hbar^2(\vec{q}_{IBZ}+\vec{K}_1)^2}{2m}\right]\phi(\vec{q}_{IBZ}+\vec{K}_1) = \sum_{\vec{K}'\neq\vec{K}_1} U_{\vec{K}_1-\vec{K}'}\, \phi(\vec{q}_{IBZ}+\vec{K}')}$$

Since all the other $\phi(\vec{q}_{IBZ}+\vec{K}')$, $\vec{K}'\neq\vec{K}_1$, ~~tend to~~ go to zero as $U\to 0$, we see that the RHS is going to be <u>at least of second order in U</u> ($\phi(\vec{q}+\vec{K}')$ are at least of first order in U, to provide $\phi\to 0$ as $U\to 0$).

On the other hand, for $\vec{K}\neq\vec{K}_1$ & that same energy $\mathcal{E}$

$$\left[\mathcal{E} - \frac{\hbar^2(\vec{q}_{IBZ}+\vec{K})^2}{2m}\right]\phi(\vec{q}_{IBZ}+\vec{K}) =$$

$$= U_{\vec{K}-\vec{K}_1}\,\phi(\vec{q}_{IBZ}+\vec{K}_1) + \sum_{\vec{K}'\neq\vec{K}_1} U_{\vec{K}-\vec{K}'}\,\phi(\vec{q}_{IBZ}+\vec{K}')$$

$$\phi(\vec{q}_{IBZ}+\vec{K}) = \frac{U_{\vec{K}-\vec{K}_1}\,\phi(\vec{q}_{IBZ}+\vec{K}_1)}{\mathcal{E}-\mathcal{E}^0_{\vec{q}+\vec{K}}} + \sum_{\vec{K}'\neq\vec{K}_1} \frac{U_{\vec{K}-\vec{K}'}\,\phi(\vec{q}_{IBZ}+\vec{K}')}{\mathcal{E}-\mathcal{E}^0_{\vec{q}+\vec{K}}}$$

$$\vec{K}\neq\vec{K}_1 \quad \phi(\vec{q}_{IBZ}+\vec{K}) = \frac{U_{\vec{K}-\vec{K}_1}\,\phi(\vec{q}_{IBZ}+\vec{K}_1)}{\mathcal{E}-\mathcal{E}^{\circ}_{\vec{q}+\vec{K}}} + O(U^2)$$

Going back to equation for $\phi(\vec{q}_{IBZ}+\vec{K})$

$$\boxed{(\mathcal{E}-\mathcal{E}^{\circ}_{\vec{q}+\vec{K}_1})\,\phi(\vec{q}+\vec{K}_1) = \sum_{\vec{K}'\neq\vec{K}_1} \frac{U_{\vec{K}_1-\vec{K}'}\,U_{\vec{K}'-\vec{K}_1}}{\mathcal{E}-\mathcal{E}^{\circ}_{\vec{q}+\vec{K}'}}\,\phi(\vec{q}+\vec{K}_1) + O(U^3)}$$

(From now on, unless explicitely said differently, $\vec{q}$ will belong to the 1st Brillouin zone.)

We see that the energy levels with a weak periodic potential differ from the unperturbed levels by a factor of order U^2

$$\mathcal{E} \approx \mathcal{E}^{\circ}_{\vec{q}+\vec{K}_1} + \sum_{\vec{K}'\neq\vec{K}_1}{}' \frac{|U_{\vec{K}'-\vec{K}_1}|^2}{(\mathcal{E}^{\circ}_{\vec{q}+\vec{K}_1}-\mathcal{E}^{\circ}_{\vec{q}+\vec{K}'})} + O(U^3)$$

This is how one can correct the energy level that was $\mathcal{E}^{\circ}_{\vec{q}+\vec{K}_1}$ without the periodic potential.

For nondegenerate $\mathcal{E}_{\vec{q}+\vec{K}_1}$, it holds, once periodic U is applied:

- The correction is quadratic in U.
- Nondegenerate bands repel: all $\mathcal{E}_{\vec{q}+\vec{K}'} < \mathcal{E}_{\vec{q}+\vec{K}_1}$ give a positive contribution, $\mathcal{E}_{\vec{q}+\vec{K}'} > \mathcal{E}_{\vec{q}+\vec{K}_1}$ give a negative contribution.

Correction of a degenerate energy level

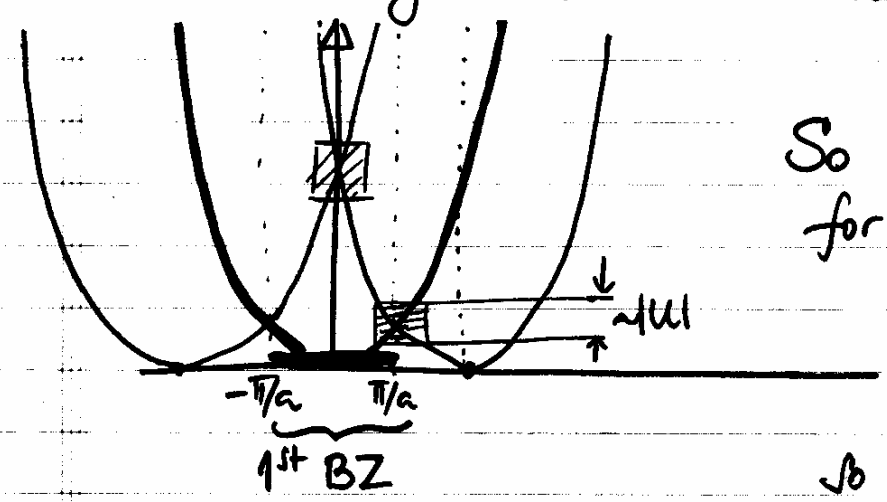
Suppose we have a value of $\vec{q}_{IBZ}$, such that for reciprocal lattice vectors $\vec{K}_1, \dots, \vec{K}_m$, the free particle energies $\mathcal{E}^0_{\vec{q}+\vec{K}_i}$ are within U of each other, i.e.,

$$|\mathcal{E}^0_{\vec{q}+\vec{K}_i} - \mathcal{E}^0_{\vec{q}+\vec{K}_j}| \approx U \qquad i,j = 1,\dots,m$$

but they are far from all the other $\mathcal{E}^0_{\vec{q}+\vec{K}}$, i.e.,

$$\forall \vec{K} \neq \vec{K}_1, \dots \vec{K}_m \qquad |\mathcal{E}^0_{\vec{q}+\vec{K}} - \mathcal{E}^0_{\vec{q}+\vec{K}_i}| \gg U \qquad i = 1,\dots,m.$$

Example: (In 1D, m cannot exceed 2, but can be large in 3D.) Let's see where those $\vec{q}$'s are in 1D: the best way to look is the extended zone scheme



So we see that for $q = -\pi/a$,

$$\mathcal{E}^0_q = \mathcal{E}^0_{q+2\pi/a},$$

so q's around $q = -\pi/a$ are degenerate.

(The same holds for $q = \pi/a$, $\mathcal{E}^0_q = \mathcal{E}^0_{q-2\pi/a}$).

Also, for $q = 0$ $\mathcal{E}^0_{q-\frac{2\pi}{a}} = \mathcal{E}^0_{q+\frac{2\pi}{a}}$, so q's around zero are also degenerate.

$$(\mathcal{E}-\mathcal{E}^{\circ}_{\vec{q}+\vec{K}_i})\phi(\vec{q}+\vec{K}_i)=\sum_{\text{all }\vec{K}} U_{\vec{K}_i\vec{K}}\phi(\vec{q}+\vec{K})$$

Let us separate this sum into $\vec{K}$'s that coincide with one of $\vec{K}_i$'s, and those which don't

$$(\mathcal{E}-\mathcal{E}^{\circ}_{\vec{q}+\vec{K}_i})\phi(\vec{q}+\vec{K}_i)=\sum_{j=1}^{m} U_{\vec{K}_i-\vec{K}_j}\phi(\vec{q}+\vec{K}_j)$$
$$+\sum_{\vec{K}\neq\vec{K}_1,\dots,\vec{K}_m}{}' U_{\vec{K}_i-\vec{K}}\phi(\vec{q}+\vec{K})$$

A similar equation holds for $\vec{K}\neq\vec{K}_1,\dots,\vec{K}_m$

$$\underbrace{(\mathcal{E}-\mathcal{E}^{\circ}_{\vec{q}+\vec{K}})}_{\gg|U|}\phi(\vec{q}+\vec{K})=\sum_{j=1}^{m} U_{\vec{K}-\vec{K}_j}\phi(\vec{q}+\vec{K}_j)$$
$$+\underbrace{\sum_{\vec{K}\neq\vec{K}_1,\dots,\vec{K}_m} U_{\vec{K}-\vec{K}'}\phi(\vec{q}+\vec{K}')}_{O(U^2)}$$

Therefore, we can approximate

$$\phi(\vec{q}+\vec{K})\simeq\frac{1}{\mathcal{E}-\mathcal{E}^{\circ}_{\vec{q}+\vec{K}}}\sum_{j=1}^{m} U_{\vec{K}-\vec{K}_j}\phi(\vec{q}+\vec{K}_j)+O(U^2)$$

Going back into the equation for $\phi(\vec{q}+\vec{K}_i)$

$$(\mathcal{E}-\mathcal{E}^{\circ}_{\vec{q}+\vec{K}_i})\phi(\vec{q}+\vec{K}_i)=\sum_{j=1}^{m} U_{\vec{K}_i-\vec{K}_j}\phi(\vec{q}+\vec{K}_j)$$ leading terms!
$$+\sum_{\vec{K}\neq\vec{K}_1,\dots,\vec{K}_m}\sum_{j=1}^{m}{}' \frac{U_{\vec{K}_i-\vec{K}}U_{\vec{K}-\vec{K}_j}}{\mathcal{E}-\mathcal{E}^{\circ}_{\vec{q}+\vec{K}}}\phi(\vec{q}+\vec{K}_j)+O(U^3)$$

$$\boxed{\left(\mathcal{E}-\mathcal{E}^{\circ}_{\vec{q}+\vec{K}_i}\right)\phi(\vec{q}+\vec{K}_i)=\sum_{j=1}^{m}{}' U_{\vec{K}_i-\vec{K}_j}\,\phi(\vec{q}+\vec{K}_j)}$$

This is a homogeneous algebraic system of m equations. Annulling the system determinant yields Energies:

$$\det\begin{bmatrix} \mathcal{E}-\mathcal{E}^{\circ}_{\vec{q}+\vec{K}_1} & -U_{\vec{K}_1-\vec{K}_2} & \dots & -U_{\vec{K}_1-\vec{K}_m} \\ -U_{\vec{K}_2-\vec{K}_1} & \mathcal{E}-\mathcal{E}^{\circ}_{\vec{q}+\vec{K}_2} & \dots & -U_{\vec{K}_2-\vec{K}_m} \\ \vdots & & & \vdots \\ -U_{\vec{K}_m-\vec{K}_1} & \dots & & \mathcal{E}-\mathcal{E}^{\circ}_{\vec{q}+\vec{K}_m} \end{bmatrix}=0 \longrightarrow \text{ENERGIES}$$

(We have used $U_0=0$. Also, $U(\vec{r})$ is real, which implies $U^*_{\vec{K}}=U_{-\vec{K}}$, so the above matrix is hermitian.)

<u>Example</u> 1D, near $q=-\pi/a$; [$q+\frac{2\pi}{a}$ is degenerate with $q=-\pi/a$].

$$\det\begin{vmatrix} \mathcal{E}-\mathcal{E}^{\circ}_{q} & -\overbrace{U_{-2\pi/a}}^{U^*_{2\pi/a}} \\ -U_{2\pi/a} & \mathcal{E}-\mathcal{E}^{\circ}_{2\pi/a+q} \end{vmatrix}=0$$

$$(\mathcal{E}-\mathcal{E}^{\circ}_{q})\left(\mathcal{E}-\mathcal{E}^{\circ}_{q+\frac{2\pi}{a}}\right)-|U_{2\pi/a}|^2=0$$

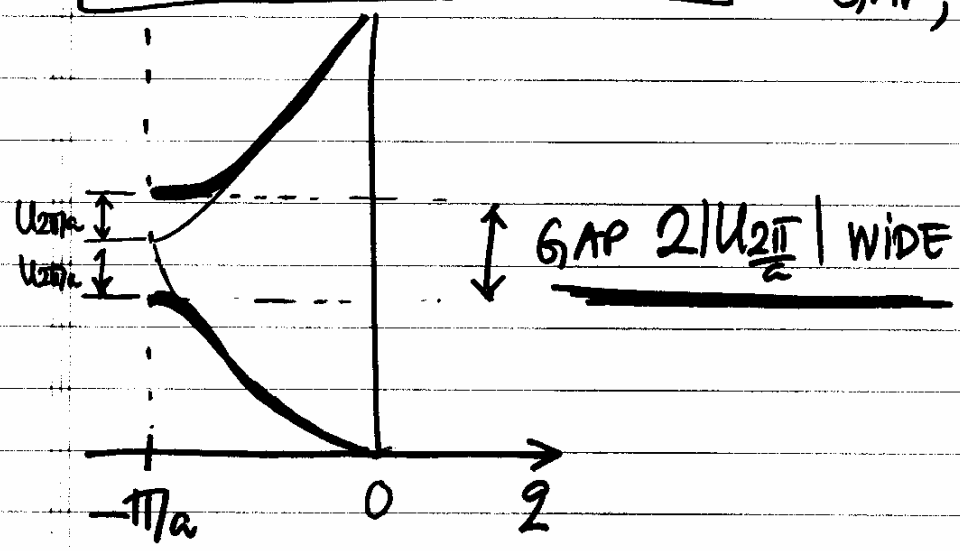
$$\mathcal{E}^2-\mathcal{E}\left(\mathcal{E}^{\circ}_{q}+\mathcal{E}^{\circ}_{q+\frac{2\pi}{a}}\right)+\left[\mathcal{E}^{\circ}_{q}\mathcal{E}^{\circ}_{q+\frac{2\pi}{a}}-|U_{\frac{2\pi}{a}}|^2\right]=0$$

$$\boxed{\mathcal{E} = \frac{1}{2}\left(\mathcal{E}^{\circ}_{q} + \mathcal{E}^{\circ}_{q+\frac{2\pi}{a}}\right) \pm \frac{1}{2}\sqrt{\left(\mathcal{E}^{\circ}_{q} - \mathcal{E}^{\circ}_{q+\frac{2\pi}{a}}\right)^2 - 4\left|U_{\frac{2\pi}{a}}\right|^2}}$$

Exactly for $q = -\pi/a$

$$\boxed{\mathcal{E}_{q=-\pi/a} = \mathcal{E}^{\circ}_{-\pi/a} \pm |U_{2\pi/a}|}$$

OPENING OF THE GAP, $2|U_{\frac{2\pi}{a}}|$ WIDE



Another look at level degeneracy in a crystal

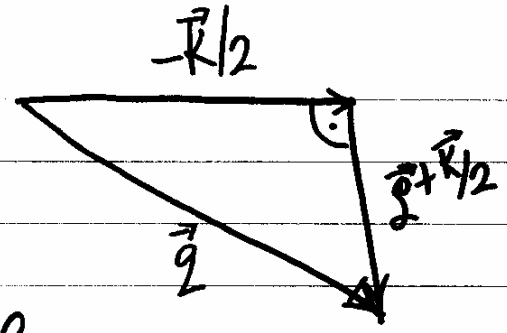
$$\mathcal{E}^{\circ}_{\vec{q}} \sim \mathcal{E}^{\circ}_{\vec{q}+\vec{K}} \text{ for some } \vec{K}$$

$$\downarrow$$

$$\cancel{\vec{q}^{\,2}} \approx (\vec{q}+\vec{K})^2 = \cancel{\vec{q}^{\,2}} + \vec{K}(2\vec{q}+\vec{K})$$

$$\vec{K}\cdot(2\vec{q}+\vec{K}) = 0$$

$$\vec{K}\cdot\left(\vec{q}+\frac{1}{2}\vec{K}\right) = 0$$



$\vec{q}+\frac{\vec{K}}{2}$ must be in the Bragg plane determined by $\vec{K}$!

The weak periodic potential has most impact on the wavevectors close to ones at which Bragg reflection.

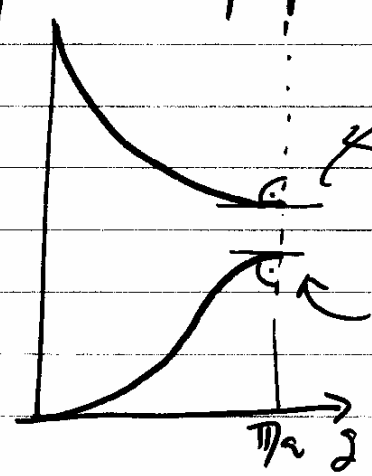
Another view:

From

$$\varepsilon = \frac{1}{2}\left[\varepsilon^0_{\vec{q}} + \varepsilon^0_{\vec{q}+\vec{K}}\right] \pm \sqrt{\frac{\left(\varepsilon^0_{\vec{q}} - \varepsilon^0_{\vec{q}+\vec{K}}\right)^2}{4} + |U_{\vec{K}}|^2}$$

$$\left.\frac{\partial \varepsilon}{\partial \vec{q}}\right|_{\varepsilon^0_{\vec{q}} \approx \varepsilon^0_{\vec{q}+\vec{K}}} = \frac{\hbar^2}{2m}\left(\vec{q} + \vec{q}+\vec{K}\right) = \frac{\hbar^2}{m}\left(\vec{q} + \frac{1}{2}\vec{K}\right)$$

This is the gradient (normal to isoenergy surface). (Therefore, the constant energy surfaces at the Bragg plane are perpendicular to the plane!)

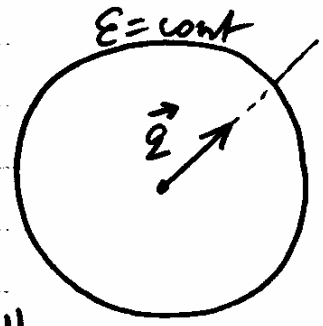


$\phi(\vec{r}) \sim \cos\left(\frac{1}{2}\vec{K}\cdot\vec{r}\right)$, $U_{\vec{K}} > 0$

$\phi(\vec{r}) \sim \sin\left(\frac{1}{2}\vec{K}\vec{r}\right)$, $U_{\vec{K}} < 0$

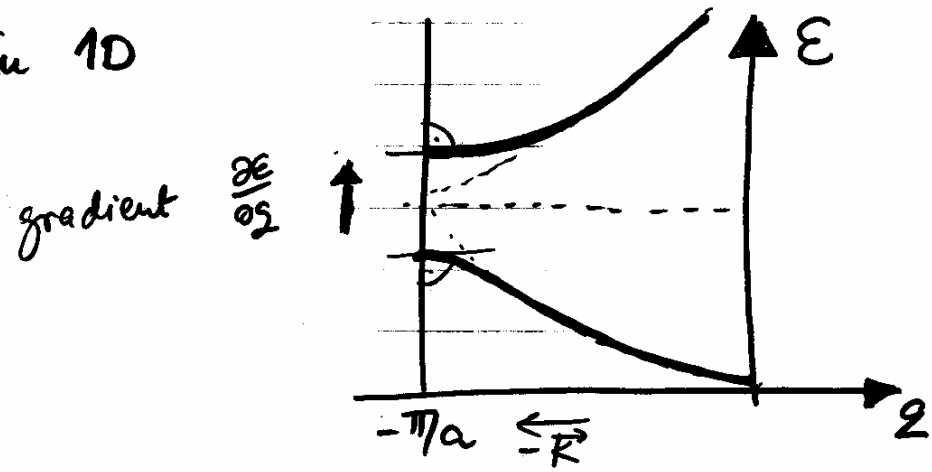
(In general $\frac{\partial \mathcal{E}}{\partial \vec{q}}$ is normal to the isoenergy surfaces $\mathcal{E}(\vec{q})$. An example is $\mathcal{E}_{\vec{q}}$ in 3D

$\mathcal{E}$ = const. on a sphere, so the gradient is expected to be colinear with $\vec{q}$. Indeed



$$\frac{\partial \mathcal{E}}{\partial \vec{q}} = \frac{\hbar^2}{m} \cdot \vec{q}$$ it is in the radial direction.

In 1D

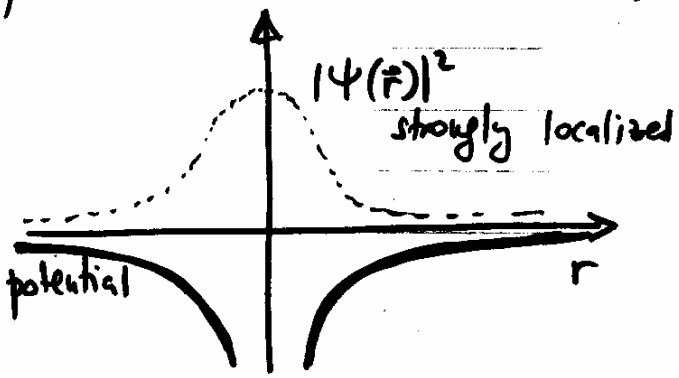


Application of the Band Structure on the Classification of Crystals Transport Prop.

A crystal structure has an underlying Bravais lattice and a certain number of basis atoms per primitive cell. Depending on the number of electrons participating in crystalline bonds, the bands vary in occupation. Inherent transport properties, i.e., whether an elements is a metal, a semiconductor or an insulator,

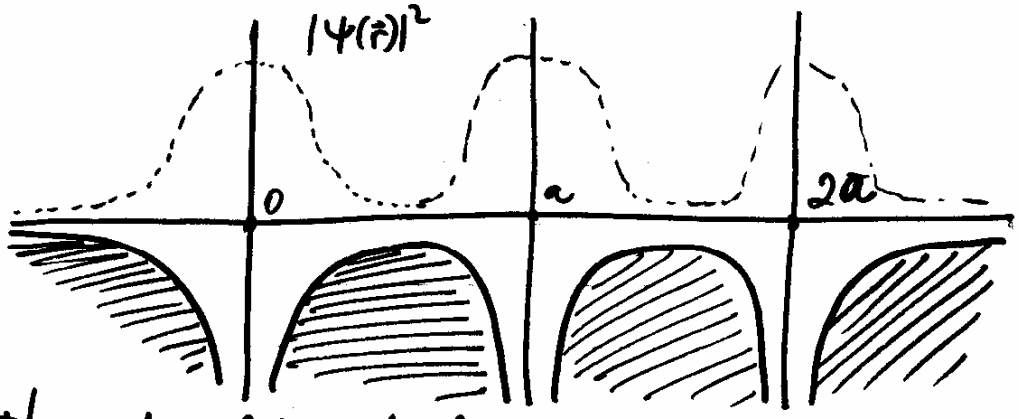
can be deduced by analyzing the crystalline bonding.

1) First of all, when a crystal is formed, formally all of the atomic levels form bands. However, those atomic levels that <u>do not</u> take part in bonding end up forming bands ~~which~~ with states strongly localized around atoms, so that if an electron originally belonged to an atom, it is very likely going to remain in the vicinity of that atom even if the crystal is formed. For transport analyses, these bands (from non-valent electrons) are not very interesting.



One atom

Many such atoms



The probability of finding an electron between atomic sites is small for bands originating from non-valent ~~[illegible]~~ atomic states.

2) Valent electrons end up residing in bands that are much less localized (because these electrons take part in bonding, so they will naturally "belong" to more than one atom).

Say we are given a crystal structure, and an underlying Bravais lattice, and the number of atoms in a basis. Also, we know that there is N primitive cells in the crystal, so mN atoms total, where m is the number of atoms in the basis.

Every band contains N wavevectors (N different $\vec{q}$'s that satisfy Born-von Karman periodic boundary conditions).

Quantum numbers of electrons in a crystal are

$$\underset{\text{band index}}{n}, \underset{\text{wavevector in } 1^{st} BZ}{\vec{q}}, \underset{\text{spin } (\pm 1/2)}{s}$$

$$\boxed{\text{So any given band can accomodate at most } \underset{\text{due to spin}}{2}N \text{ electrons.}}$$

So let us assume that the temperature is close to zero, so that the electrons will fill lower energy

levels until they are full completely before going to higher energy levels.

- **Valence 1**
  - Alkali metals: Li, Na, K, Rb, ...
    Crystalize in bcc
  - Noble metals: Cu, Au, Ag
    Crystalize in fcc

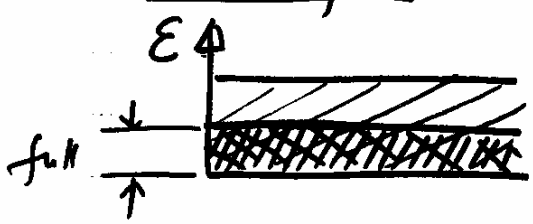
These typically have 1 atom/cell (primitive cell), and each contributes with 1 el/atom

$$1\,\text{atom/cell} \times 1\,\text{el/atom} = 1\,\text{el/cell}$$

$$\downarrow$$

N electrons in the crystals

Since a band can accomodate 2N, all of the N electrons are in one band that is <u>half-full</u> $\Longrightarrow$



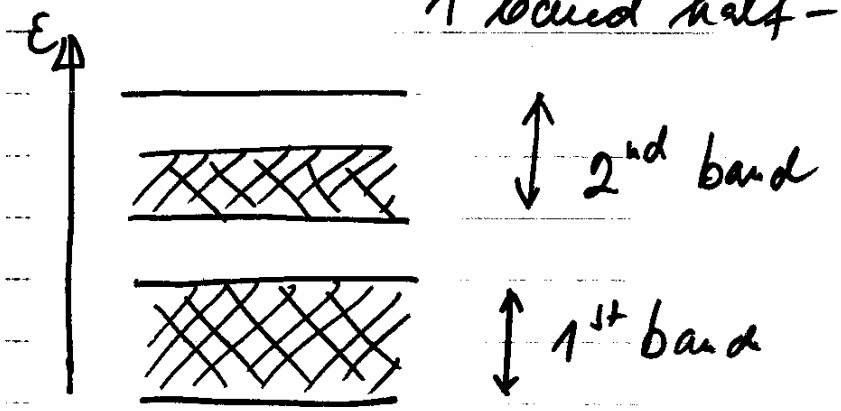
available levels in band

the last full level is where the Fermi level is. For metals it is inside ~~a band~~ an allowed band, which is then referred to as the conduction band.

• **Valence 3** Al, Ga, In, ... crystalize in fcc
1 atom/primitive cell

$3\,el/atom \times 1\,\frac{atom}{cell} = 3\,\frac{el}{cell}$

$3/2 \rightarrow$ 1 full band
1 band half-full $\rightarrow$ (metal again)

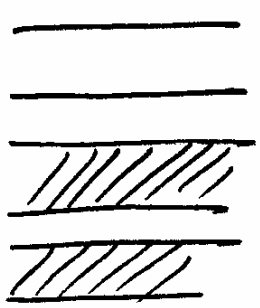


• **Valence 2** Be, Mg, Zn, Cd crystalize in hcp

hcp $\rightarrow$ simple hexagonal with 2 atoms in the basis

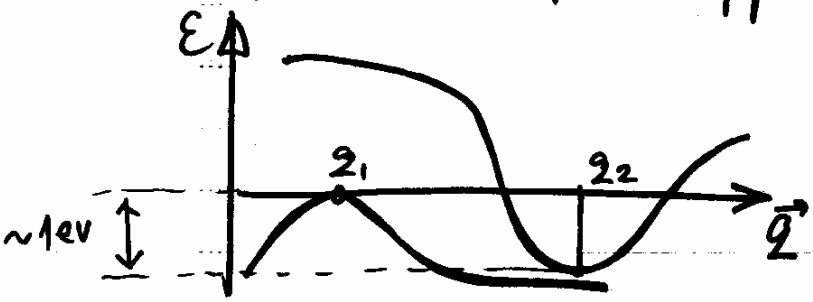
$$2\,\frac{atoms}{cell} \times 2\,\frac{el}{atom} = 4\,\frac{\cancel{atoms}\,el}{cell}$$

Since there is an even number of electrons/cell $4/2 = 2$, the bands are going to be either completely full or completely empty (first two bands are full, others empty), so we



would expect these ~~atom~~ elements to be semiconductors or insulators. However, due to BAND OVERLAP they are not, they are metals.

Band overlap – happens in more than 1D. Very typical of hexagonal lattices



(Min (for q_2) is below max (for q_1).)

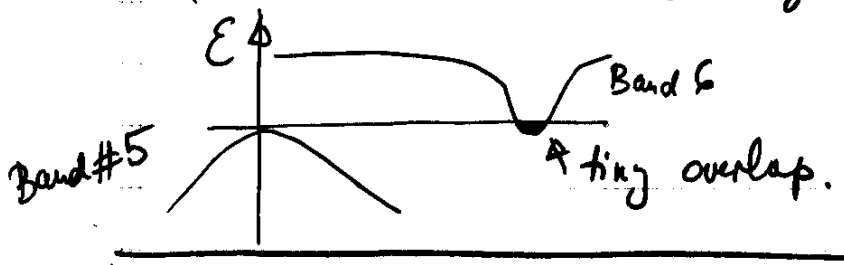
When overlap is strong, like it is with group 2 metals (~1eV), then the material behaves as metal.

- **Group 5** As, Bi, Sb, ...
  ↓ $4s^2 4p^3$

Crystalize in distorted fcc → rhombohedral
2 atoms / primitive cell

$$2\frac{\text{atoms}}{\text{cell}} \times 5\frac{\text{els}}{\text{atom}} \rightarrow 10\frac{\text{els}}{\text{cell}}$$

You would expect 10/2 = 5 full bands, but again, due to slight overlap, these are semi-metals (have small carrier density ~$10^{17}/\text{cm}^3$).



- **Valence 4** Si, Ge fcc, $2\frac{\text{atoms}}{\text{cell}}$ (diamond)

$$2\frac{\text{atoms}}{\text{cell}} \times 4\frac{\text{els}}{\text{atom}} = 8\frac{\text{els}}{\text{cell}}$$

4 full bands → semiconductors

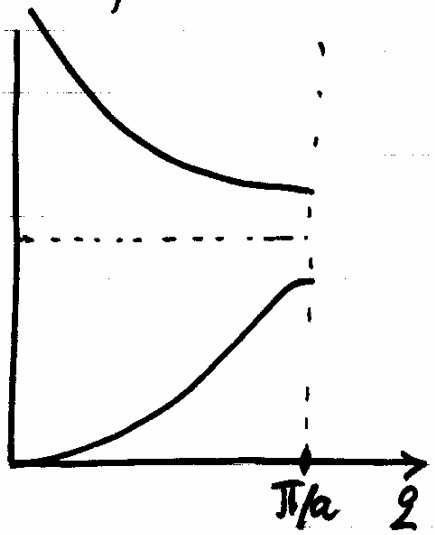
TYPE	$\rho(\Omega cm)$	OCCUPANCY OF LAST BAND	E_g
metal	10^{-6}	1/2 full	none
insulator	$10^{14} - 10^{22}$	full	large
semiconductor	$10^{2} - 10^{9}$	full	small
semimetal	10^{-3}	almost full	overlap

Among compounds, GaAs & other III-V's are of much interest to us.

GaAs : fcc, $\frac{2 \text{ atoms}}{\text{prim cell}}$ $\left.\begin{array}{l} Ga \rightarrow 3 el \\ As \rightarrow 5 el \end{array}\right\} 8 \frac{el}{cell}$

Just like Si and Ge, these are ~~two~~ semiconductors, with 4 bands full.

Effective mass



Without the weak periodic potential, $\mathcal{E}^{\circ}_{\pi/a}$ is doubly degenerate

$$\mathcal{E}^{\circ}_{\pi/a} = \mathcal{E}^{\circ}_{-\pi/a} = \mathcal{E}^{\circ}_{(\pi/a - \frac{2\pi}{a})}$$

With the application of the weak potential, the gap opens. Let us examine what happens near $q = \pi/a \equiv q_G$ ← denotes gap opens there

$$q = q_G - \delta, \quad q_G = \pi/a$$

$$\mathcal{E}_q = \frac{\mathcal{E}^{\circ}_q + \mathcal{E}^{\circ}_{q+K}}{2} \pm \sqrt{\left[\frac{\mathcal{E}^{\circ}_q - \mathcal{E}^{\circ}_{q+K}}{2}\right]^2 + |U_K|^2}, \quad K = -\frac{2\pi}{a}$$

$$\mathcal{E}^{\circ}_q = \frac{\hbar^2}{2m}(q_G - \delta)^2 = \frac{\hbar^2}{2m}(q_G^2 - 2q_G\delta + \delta^2)$$

$$\mathcal{E}^{\circ}_{q+K} = \frac{\hbar^2}{2m}(\underbrace{q_G + K}_{-q_G} - \delta)^2 = \frac{\hbar^2}{2m}(q_G^2 + 2\delta q_G + \delta^2)$$

$$\mathcal{E}_q = \underbrace{\frac{\hbar^2}{2m} q_G^2}_{\mathcal{E}^{\circ}_{q_G}} + \frac{\hbar^2\delta^2}{2m} \pm \sqrt{\underbrace{\left(\frac{\hbar^2}{2m} \cdot 2\delta q_G\right)^2}_{4\mathcal{E}^{\circ}_{q_G} \cdot \frac{\hbar^2\delta^2}{2m}} + |U_K|^2}$$

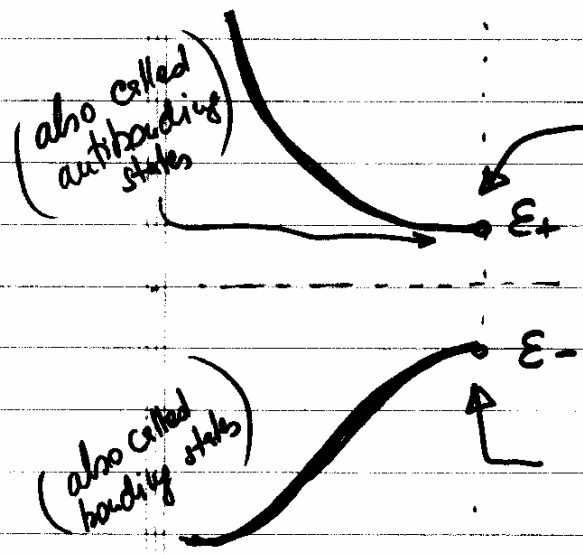
If $\mathcal{E}^{\circ}_{q_G} \frac{\hbar^2\delta^2}{2m} \ll |U_K|^2$ (we are VERY close to q_G)

$$\mathcal{E}_2 = \mathcal{E}_{2G}^{\circ} + \frac{\hbar^2\delta^2}{2m} \pm |U_K|^2 \left(1 + 2\frac{\mathcal{E}_{2G}^{\circ}}{|U_K|^2} \cdot \frac{\hbar^2\delta^2}{2m}\right)$$

$$\boxed{\mathcal{E}_2 = \mathcal{E}_{2G}^{\circ} \pm |U_K|^2 \pm \frac{\hbar^2\delta^2}{2m}\left(2\frac{\mathcal{E}_{2G}^{\circ}}{|U_K|} \pm 1\right)}$$

Upper sign: $\mathcal{E}_{2+} = \mathcal{E}_+ + \frac{\hbar^2\delta^2}{2m}\left(2\frac{\mathcal{E}_{2G}^{\circ}}{|U_K|} + 1\right)$

Lower sign: $\mathcal{E}_{2-} = \mathcal{E}_- - \frac{\hbar^2\delta^2}{2m}\left(2\frac{\mathcal{E}_{2G}^{\circ}}{|U_K|} - 1\right)$



$$\mathcal{E}_{2+} - \mathcal{E}_+ = \frac{\hbar^2\delta^2}{2m} \cdot \frac{1}{\left[\frac{2\mathcal{E}_{2G}^{\circ}}{|U_K|} + 1\right]^{-1}} \quad (1)$$

$$\mathcal{E}_{2-} - \mathcal{E}_- = -\frac{\hbar^2\delta^2}{2m} \cdot \frac{1}{\left[2\frac{\mathcal{E}_{2G}^{\circ}}{|U_K|} - 1\right]^{-1}} \quad (2)$$

(1) Near the band minimum, $\mathcal{E}$ behaves quadratically with the wavevector, so we can identify the effective mass

$$m_+ = m\left[\frac{2\mathcal{E}_{2G}^{\circ}}{|U_K|} + 1\right]^{-1}$$

This is the effective mass of the antibonding states near the gap.

(2) In the bottom band, the energy decreases as one moves away from the band maximum. The effective mass (so-called bonding effective mass) is negative:

$$m_- = m\left(1 - \frac{2\mathcal{E}^0_{2G}}{|U_K|}\right)^{-1} < 0$$

In magnitude $|m_-| > |m_+|$ (bonding mass slightly larger).

The negative mass indicates HOLES, and this negative mass can be often compensated by the change of sign of the charge. Negative mass is a signature of band behavior near a maximum.

When δ is not so small, we need to keep the full square root. If we measure energies with respect to the bottom of the upper ("antibonding") band

measured with respect to antibond. band bottom

$$\tilde{\mathcal{E}}_2 = \mathcal{E}_2 - (\mathcal{E}^0_{2G} + |U_K|) =$$

$$\approx \cancel{\mathcal{E}^0_2} \pm |U_K|\left(1 + \frac{4\mathcal{E}^0_{2G}}{|U_K|^2}\cdot\frac{\hbar^2\delta^2}{2m}\right)^{1/2} - \cancel{\mathcal{E}^0_{2G}} - |U_K|$$

When we take into account $\mathcal{E}_{GAP} = 2|U_K|$

$$\tilde{\mathcal{E}}_2 = \tilde{\mathcal{E}}_{2G-\delta} = -\frac{\mathcal{E}_{GAP}}{2} \pm \frac{\mathcal{E}_{GAP}}{2}\left(1 + \frac{2\mathcal{E}^0_{2G}\cdot\hbar^2\delta^2}{|U_K|^2\cdot m}\right)^{1/2}$$

We have noted that

$$m_+ = \frac{m}{\left[\frac{2\mathcal{E}^\circ_{2G}}{|U_K|}+1\right]} \overset{\text{small } u}{\approx} \frac{m|U_K|}{2\mathcal{E}^\circ_{2G}} = \frac{m\,\mathcal{E}_{GAP}}{4\mathcal{E}^\circ_{2G}}$$

is the antibonding band mass at the bottom of the band. We can write

$$\boxed{\tilde{\mathcal{E}}_{2G-\delta} = -\frac{\mathcal{E}_{GAP}}{2} \pm \frac{\mathcal{E}_{GAP}}{2}\left(1+\frac{2\hbar^2\delta^2}{m_+\mathcal{E}_{GAP}}\right)^{1/2}}$$

This is the equation for <u>hyperbolic bands</u>, very typical of semiconductors.

Why is it "hyperbolic"? It can be rewritten as

$$(\tilde{\mathcal{E}} - \text{const}\#1)^2 - \text{const}_2 \cdot \delta^2 = \text{const}_3$$

which is a hyperbola.

Only if $\frac{\hbar^2\delta^2}{m_+\mathcal{E}_{GAP}} \ll 1$ can the above variation be reduced to parabolic behavior & constant effective mass. Otherwise, the band energy contains higher order terms in δ, and we can speak of an <u>effective mass that depends on the wavevector</u>.

We have already noted, near a ~~cond~~ band minimum (actually, extremum), the energy behaves as

$$\mathbf{q} = \mathbf{q}_{min/max} + \delta\mathbf{q}$$

$$\mathcal{E}(\mathbf{q}) = \mathcal{E}_{min/max} + \sum_{\alpha=1}^{3} \cancel{\left(\frac{\partial \mathcal{E}}{\partial q_\alpha}\right)_{q_{min/max}}}^{\,0 \text{ since extremum}} \cdot \delta q_\alpha + \frac{1}{2} \sum_{\alpha,\beta} \left(\frac{\partial^2 \mathcal{E}}{\partial q_\alpha \partial q_\beta}\right)\Bigg|_{q_{min/max}} \times \delta q_\alpha \delta q_\beta + \delta \ldots$$

The second-order term is the basis for defining the <u>EFFECTIVE MASS TENSOR</u>

$$\boxed{\left(\frac{1}{m^*}\right)^{\alpha\beta} = \frac{1}{\hbar^2} \cdot \frac{\partial^2 \mathcal{E}(\mathbf{q})}{\partial q_\alpha \partial q_\beta}}$$

SYMMETRIC TENSOR; WHEN DIAGONALIZED, GIVES PRINCIPAL EFF. MASSES

Indeed, if $\mathcal{E} = \frac{\hbar^2 \mathbf{p}^2}{2m}$ $\quad \frac{\partial \mathcal{E}}{\partial q_i} = \frac{\hbar^2 q_i}{m}$ $\quad \frac{\partial^2 \mathcal{E}}{\partial q_i \partial q_j} = \frac{\hbar^2}{m} \cdot \delta_{ij}$,

so $\left(\frac{1}{m^*}\right)^{ij} = \frac{1}{\hbar^2} \cdot \left(\frac{\hbar^2}{m}\right) \delta_{ij} = \frac{1}{m} \delta_{ij} \rightarrow$ diagonal tensor $\quad \left(\overleftrightarrow{\frac{1}{m^*}}\right) = \frac{1}{m} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

- However, some caution is in order. We must not forget that the above definition of the effective mass tensor is based on the assumption that we are <u>close to a band extremum</u> (minimum → → positive mass, electrons; maximum → negative mass, holes).

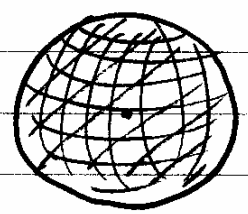
When we are far from an extremum, how "inert" a particle is can no longer be described by a constant mass.

Bond-Orbital Model for Tetrahedrally Coordinated Semiconductors

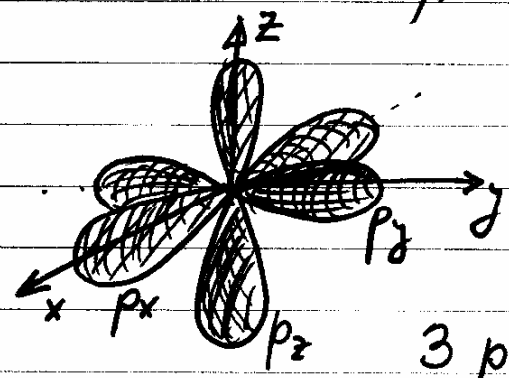
In Si, the bonds are composed of 3s and 3p levels, while in GaAs the levels involved are 4s and 4p.

$$Si: \ldots 3s^2 3p^2$$
$$Ga: \ldots 4s^2 4p^1$$
$$As: \ldots 4s^2 4p^3$$

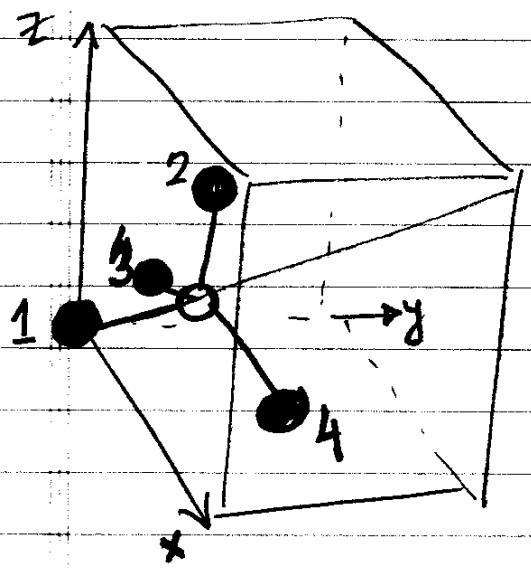
The s and p levels form <u>hybrids</u> that enable tetrahedral bonding; in an atom, the probability densities of s & p orbitals look as follows:



s orbital –
– radially symmetric



3 p-orbitals, directed along different axes



Hybrid orbitals, in sync with tetrahedral bonding

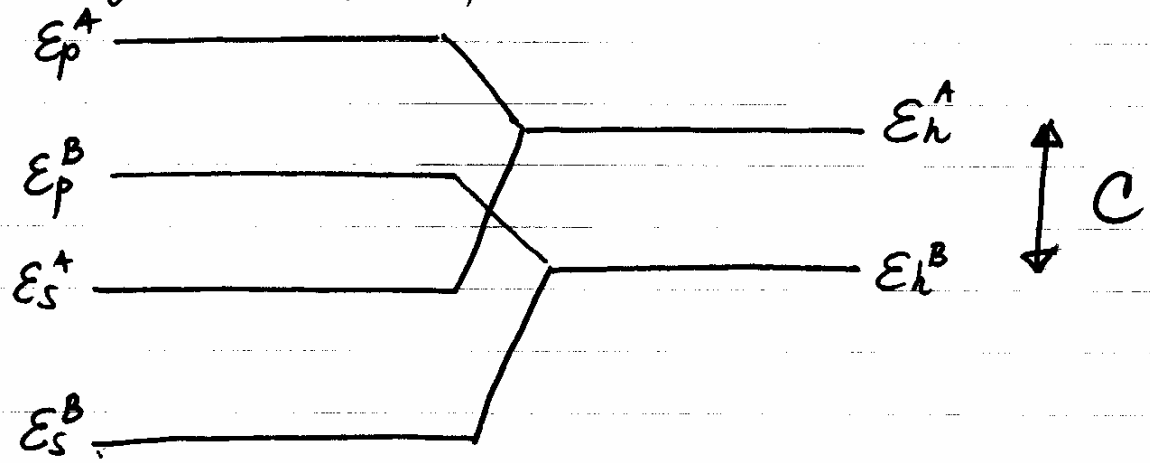
$$|h_1\rangle = \frac{1}{2}\left[|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle\right]$$
$$|h_2\rangle = \frac{1}{2}\left[|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle\right]$$
$$|h_3\rangle = \frac{1}{2}\left[|s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle\right]$$
$$|h_4\rangle = \frac{1}{2}\left[|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle\right]$$

Each atom has a certain energy $\mathcal{E}_s$ associated with s orbitals, and $\mathcal{E}_p$ associated with p orbitals. In heteropolar compounds, like GaAs, each of the atoms will have different $\mathcal{E}_s$ and $\mathcal{E}_p$; so in general for AB compound, the levels will be $\mathcal{E}_s^A, \mathcal{E}_p^A, \mathcal{E}_s^B$, and $\mathcal{E}_p^B$ respectively.

The <u>hybrid energies</u> will be given by

$$\mathcal{E}_h^{A,B} = \frac{1}{4}\left(\mathcal{E}_s^{A,B} + 3\mathcal{E}_p^{A,B}\right)$$

and can be derived from the atomic Hamiltonians and the formulas for hybrids. Generally $\mathcal{E}_{s,p}^A > \mathcal{E}_{s,p}^B$, and the hybrid energies formation can be depicted as follows



Heteropolar energy (a.k.a. hybrid polar energy) C measures the ionic transfer of charge a compound, and is given by

$$C = \mathcal{E}_h^A - \mathcal{E}_h^B = \frac{1}{4}\left(\mathcal{E}_s^A + 3\mathcal{E}_p^A\right) - \frac{1}{4}\left(\mathcal{E}_s^B + 3\mathcal{E}_p^B\right)$$

For homopolar semiconductors, like Si & Ge, $C = 0$.

Hybrid energies & the heteropolar energy have been derived just from the details of atom Hamiltonians and atomic orbitals. Remember, however, that we have constructed the hybrids with tetrahedral bonding in mind, and in a crystal we expect them to eventually yield proper Bloch states. However, the hybrids are not eigenstates of the atomic Hamiltonian, i.e.,

$$\langle h_i | H_{atom} | h_j \rangle = \frac{1}{4}(\varepsilon_s - \varepsilon_p) \equiv -V_1$$

V_1 is the so-called <u>metallic energy</u>, and it measures overlap between various hybrids <u>on one atom</u>.

What about overlap of hybrids on neighboring atoms that actually participate in bonding? This overlap depends (approximately) <u>only on bond length</u>, and is given by the <u>homopolar energy</u> (same for hetero and homopolar bonds, as long as bond length is the same).

Homopolar energy $E_h = 2V_2$, where

$$V_2 \approx 4.37 \frac{\hbar^2}{md^2}$$

The <u>bonding orbitals</u> will be composed of hybrid orbitals <u>belonging to</u> atoms at each end of the bond.

$$|\Phi_{bo}\rangle = u_1 |h^A\rangle + u_2 |h^B\rangle$$

Energy of an electron in the bonding orbital will be given by

$$\mathcal{E} = \frac{\langle \phi_{bo} | H | \phi_{bo} \rangle}{\langle \phi_{bo} | \phi_{bo} \rangle} \qquad (*)$$

where $H = H^A + H^B + H_{interaction}$, and $\langle \phi | \phi' \rangle = \int d^3\vec{r}\, \phi^*(\vec{r}) \phi'(\vec{r})$,
and $\langle \phi | H | \phi' \rangle = \int d^3\vec{r}\, \phi^*(\vec{r})\, H \phi'(\vec{r})$
(the $\langle \ldots \rangle$ is from <u>the Dirac notation</u>).

$$\langle \phi_{bo} | H | \phi_{bo} \rangle = \left(u_1^* \langle h^A | + u_2^* \langle h^B | \right) H \left(u_1 | h^A \rangle + u_2 | h^B \rangle \right)$$

$$= |u_1|^2 \underbrace{\langle h^A | H | h^A \rangle}_{\approx \mathcal{E}_h^A} + u_1^* u_2 \underbrace{\langle h^A | H | h^B \rangle}_{-V_2} + u_1 u_2^* \underbrace{\langle h^B | H | h^A \rangle}_{-V_2}$$

$$+ |u_2|^2 \underbrace{\langle h^B | H | h^B \rangle}_{\approx \mathcal{E}_h^B}$$

$$\langle \phi_{bo} | \phi_{bo} \rangle = |u_1|^2 \langle h^A | h^A \rangle + |u_2|^2 \langle h^B | h^B \rangle$$

$$+ u_1^* u_2 \underbrace{\langle h_A | h_B \rangle}_{\substack{\approx 0 \\ \text{overlap much} \\ \text{smaller than} \\ \text{the first two terms}}} + u_1 u_2^* \underbrace{\langle h_B | h_A \rangle}_{\substack{\approx 0 \\ \text{(same as} \\ \text{previous term)}}}$$

If we assume u_1, u_2 are real, then we get, from (*)

$$\boxed{\mathcal{E}\left(u_1^2 + u_2^2\right) = u_1^2 \mathcal{E}_h^A + u_2^2 \mathcal{E}_h^B - 2 u_1 u_2 V_2}$$

This is a function of variables u_1 and u_2, and to

get bonding, we need to minimize $\mathcal{E}$ with respect to u_1, u_2. From the requirement that the partial derivatives be zero, we obtain

$$2u_1 \mathcal{E} = 2u_1 \mathcal{E}_h^A - 2u_2 V_2$$
$$2u_2 \mathcal{E} = 2u_2 \mathcal{E}_h^B - 2u_1 V_2$$

$$\Downarrow$$

$$u_1 (\mathcal{E} - \mathcal{E}_h^A) + u_2 V_2 = 0$$
$$u_1 V_2 + u_2 (\mathcal{E} - \mathcal{E}_h^B) = 0$$

Introduce $\mathcal{E}_0 = (\mathcal{E}_h^A + \mathcal{E}_h^B)/2$, so $\mathcal{E}_h^A = \mathcal{E}_0 + \frac{c}{2}$; $\mathcal{E}_h^B = \mathcal{E}_0 - \frac{c}{2}$

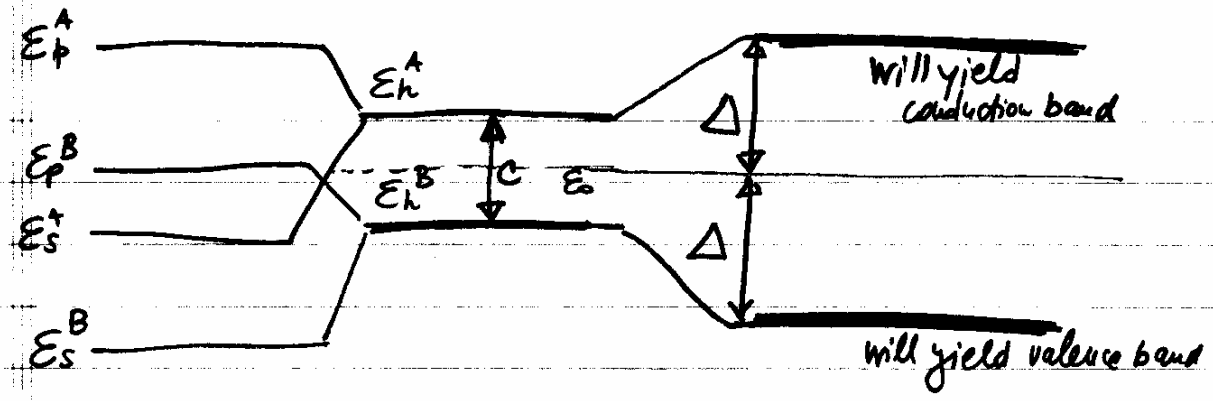
$$\boxed{\begin{aligned} u_1 \left(\mathcal{E} - \mathcal{E}_0 - \frac{c}{2}\right) + u_2 V_2 &= 0 \\ u_1 V_2 + u_2 \left(\mathcal{E} - \mathcal{E}_0 + \frac{c}{2}\right) &= 0 \end{aligned}}$$

$$\Downarrow$$

$$\det \begin{bmatrix} \mathcal{E} - \mathcal{E}_0 - \frac{c}{2} & V_2 \\ V_2 & \mathcal{E} - \mathcal{E}_0 + \frac{c}{2} \end{bmatrix} = 0$$

$$(\mathcal{E} - \mathcal{E}_0)^2 - \frac{c^2}{4} - V_2^2 = 0 \implies \boxed{\mathcal{E} = \mathcal{E}_0 \pm \frac{1}{2}\sqrt{c^2 + 4V_2^2}}$$

This symmetry around $\mathcal{E}_0$ somewhat unexpected in heteropolar materials!



What about u_1 & u_2? If we set $u_1^2 + u_2^2 = 1$, which is actually the normalization condition, we can put

$$u_1 = \sqrt{\frac{1+x}{2}} \quad , \quad u_2 = \sqrt{\frac{1-x}{2}}$$

From the second equation (**) from the last page,

$$u_1 = -\frac{u_2}{V_2}\left(\varepsilon - \varepsilon_0 + \frac{c}{2}\right)$$

$$\frac{1+x}{\cancel{2}} = \frac{(1-x)}{\cancel{2}}\left[\frac{\varepsilon - \varepsilon_0 + c/2}{V_2}\right]^2 = \frac{(1-x)}{\cancel{2}}\left[\frac{\pm\Delta + c/2}{V_2}\right]^2$$

$$x\left[1 + \left[\frac{\frac{c}{2} \pm \Delta}{V_2}\right]^2\right] = \left(\frac{\frac{c}{2} \pm \Delta}{V_2}\right)^2 - 1$$

$$x = \frac{\left(\frac{c}{2} \pm \Delta\right)^2 - V_2^2}{V_2^2 + \left(\frac{c}{2} \pm \Delta\right)^2} = \frac{\frac{c^2}{4} + \cancel{V_2^2} \pm c\Delta - \cancel{V_2^2}}{V_2^2 + \frac{c^2}{4} + \frac{c^2}{4} + V_2^2 \pm c\Delta}$$

$$\boxed{x = C\,\frac{\frac{c}{2} \pm \Delta}{V_2^2 + \left(\frac{c}{2} \pm \Delta\right)^2}} \longrightarrow 0 \text{ in } \begin{matrix} Si \\ Ge \end{matrix}$$

It is important to note that in homopolar materials, where $C = 0$, $x = 0$, so $u_1 = u_2$ (hybrids symmetrically mixed in a bond orbital). Otherwise, we have more or less of one of the atom's hybrid orbitals.

Tight-Binding Method

(a.k.a. LCAO - Linear Combination of Atomic Orbitals)

Starting from free electrons, and then adding on that picture a weak periodic potential, works well for the description of conduction electrons in a metal.

However, this picture does not work well for the cases when electrons remain fairly well localized around atoms. Fairly well localized $\longleftrightarrow$ overlap among wavefunctions of neighboring atoms not large (like it would be in case of atomic orbitals that yield conduction electrons in metals)

Semiconductors } overlap of atomic wavefunctions
Insulators } of neighboring atoms small, but enough to yield a correction in energy to the atomic levels

One-atom basis

Say we have a reason to believe that the overlap between wavefunctions ϕ_m that belong to different atoms is not large enough for us to believe the electrons are completely delocalized (like in a metal), but is large enough for us to believe that it will yield Bloch-electron energies somewhat different than atomic energies.

Start with atomic wavefunction $\phi_m(\vec{r})$, m is the quantum number that came out from solving the one-atom Schrödinger equation. How to make a Bloch function from an atomic function?

atom $\longrightarrow$ crystal

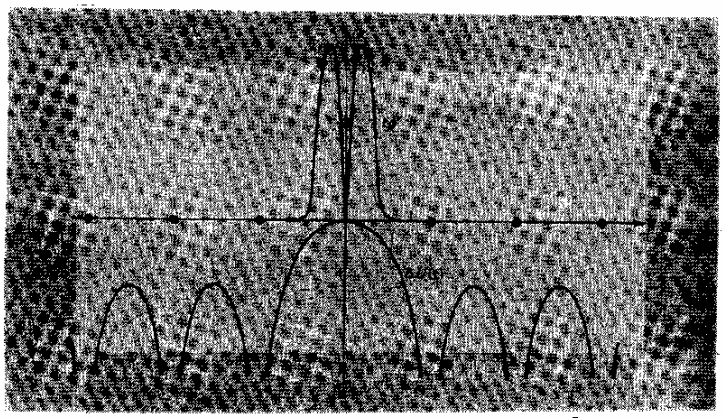
$$\phi_m(\vec{r}) \qquad\qquad \sum_{\vec{R}} e^{i\vec{q}\vec{R}} \underbrace{\phi_m(\vec{r}-\vec{R})}_{\text{these centered around atoms placed at } \vec{R}}$$

As a rule, if ϕ_m's from different atoms overlap a bit, there are usually a few other ϕ_n's that belong to the neighboring atoms, that will also overlap with our test-atom's ϕ_m. So, instead of just m, for one atom we allow a few different additional ϕ_n's to tag along

atom $\longrightarrow$ crystal

$$\phi(\vec{r}) = \sum_n b_n \phi_n(\vec{r}) \qquad\qquad \phi_{\vec{q}}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{q}\cdot\vec{R}} \underbrace{\phi(\vec{r}-\vec{R})}_{\text{atomic, centered around atoms at } \vec{R}}$$

Total crystal Hamiltonian is, of course, such that it contains a periodic potential. However, in the vicinity of an atomic site the crystal Hamiltonian looks basically like that atom's Hamiltonian, plus a "little" correction due to the potential from neighboring atoms.



So we can write

$$\hat{H} = \hat{H}_{atom} + \Delta U(\vec{r})$$

where $\hat{H}_{atom} = \hat{H}_{atom}(\vec{r})$ for the atom centered at $\vec{R}=0$.

$\Delta U(\vec{r}\to 0) = 0$ (that's where potential is atomic.)

$$\boxed{\hat{H}\,\phi_{\vec{q}}(\vec{r}) = \left[\hat{H}_{atom} + \Delta U(\vec{r})\right]\phi_{\vec{q}}(\vec{r}) = \mathcal{E}_{\vec{q}}\,\phi_{\vec{q}}(\vec{r})}$$

Multiply from the left by $\phi_m^*(\vec{r})$, and integrate over all $\vec{r}$'s

$$\int d^3\vec{r}\;\phi_m^*(\vec{r})\left[\hat{H}_{atom} + \Delta U(\vec{r})\right]\phi_{\vec{q}}(\vec{r}) =$$

$$= \underbrace{\int d^3\vec{r}\;\phi_m^*(\vec{r})\,\hat{H}_{atom}\,\phi_{\vec{q}}(\vec{r})} + \int d^3\vec{r}\;\phi_m^*(\vec{r})\,\Delta U(\vec{r})\,\phi_{\vec{q}}(\vec{r})$$

It can be shown that

$$\int d^3\vec{r}\;\phi_m^*\left[\hat{H}_{atom}\,\phi_{\vec{q}}(\vec{r})\right] = \int d^3\vec{r}\;\underbrace{\left[\hat{H}_{atom}\,\phi_m^*(\vec{r})\right]}_{\mathcal{E}_m\phi_m^*(\vec{r})}\phi_{\vec{q}}(\vec{r})$$

$$= \mathcal{E}_m \int d^3\vec{r}\;\phi_m^*(\vec{r})\,\phi_{\vec{q}}(\vec{r})$$

The above is due to HERMITICITY of the Hamiltonian.

Just a note on the Dirac notation:

$$\int d^3\vec{r}\, \phi_1^*(\vec{r})\, \phi_2(\vec{r}) \equiv \langle \underbrace{\phi_1}_{\text{bra}} | \underbrace{\phi_2}_{\text{ket}} \rangle$$

$$\int d^3\vec{r}\, \phi_1^*(\vec{r})\, \hat{A}\, \phi_2(\vec{r}) \equiv \underbrace{\langle \phi_1}_{\text{bra}} | \hat{A} | \underbrace{\phi_2 \rangle}_{\text{ket}}$$

For Hermitian operators (and most of those we will deal with are Hermitian) it holds

$$\langle \phi_1 | \hat{A} \phi_2 \rangle = \langle \hat{A} \phi_1 | \phi_2 \rangle \equiv \langle \phi_1 | \hat{A} | \phi_2 \rangle$$

(because it doesn't matter if $\hat{A}$ acts on the function on the left or the right, we get the "sandwich" $\langle \phi_1 | \hat{A} | \phi_2 \rangle$)

Eqn.(1) $$\boxed{[\mathcal{E}_{\vec{q}} - \mathcal{E}_m] \langle \phi_m | \phi_{\vec{q}} \rangle = \langle \phi_m | \Delta U | \phi_{\vec{q}} \rangle}$$ Compact Dirac form

$$\langle \phi_m | \phi_{\vec{q}} \rangle = \int d^3\vec{r}\, \phi_m^*(\vec{r})\, \phi_{\vec{q}}(\vec{r})$$

$$= \int d^3\vec{r}\, \phi_m^*(\vec{r}) \sum_{\vec{R},n} e^{i\vec{q}\cdot\vec{R}} \phi_n(\vec{r}-\vec{R})\, b_n$$

$$= \sum_n \underbrace{\int d^3\vec{r}\, \phi_m^*(\vec{r})\, \phi_n(\vec{r})}_{\text{different atomic wavefunc. on the same atom are orthogonal}} b_n + \sum_{\vec{R}\neq 0,n} \int d^3\vec{r}\, \phi_m^*(\vec{r})\, \overset{b_n e^{i\vec{q}\vec{R}}}{\phi_n(\vec{r}-\vec{R})}$$

$$\langle \phi_m | \phi_n \rangle \equiv \int d^3\vec{r}\, \phi_m^*(\vec{r}) \phi_n(\vec{r}) = \delta_{mn}$$

So the first term from above is $\sum_n \langle \phi_m | \phi_n \rangle = \sum_n \delta_{mn} b_n = b_m$

$$\langle \phi_m | \phi_{\vec{q}} \rangle = b_m + \sum_{n,\vec{R}\neq 0} \underbrace{\left[\int d^3\vec{r}\, \phi_m^*(\vec{r})\, \phi_n(\vec{r}-\vec{R}) \right]}_{\text{overlap between } \phi_m \text{ centered around } 0\text{, and } \phi_n \text{ centered around } \vec{R}\text{; this overlap is generally nonzero only for the few nearest or second-nearest neighbors.}} b_n e^{i\vec{q}\vec{R}}$$

Eqn. (2)

$$\boxed{\langle \phi_m | \phi_{\vec{q}} \rangle = b_m + \sum_{n,\vec{R}\neq 0} \langle \phi_m | \phi_{n,\vec{R}} \rangle b_n e^{i\vec{q}\vec{R}}}$$

$\phi_{n,\vec{R}}$ ← denotes it is centered at $\vec{R}$

On the other hand

Eqn. (3)

$$\boxed{\begin{aligned} \langle \phi_m | \Delta U | \phi_{\vec{q}} \rangle &= \int d^3\vec{r}\, \phi_m^*(\vec{r})\, \Delta U(\vec{r}) \sum_{\vec{R},n} b_n \phi_n(\vec{r}-\vec{R}) e^{i\vec{q}\vec{R}} \\ &= \sum_n \left[\int d^3\vec{r}\, \phi_m^*(\vec{r})\, \Delta U(\vec{r})\, \phi_n(\vec{r}) \right] \cdot b_n \\ &+ \sum_{\vec{R}\neq 0,n} \underbrace{\left[\int d^3\vec{r}\, \phi_m^*(\vec{r})\, \Delta U(\vec{r})\, \phi_n(\vec{r}-\vec{R}) \right]}_{\langle \phi_m | \Delta U | \phi_{n,\vec{R}} \rangle} e^{i\vec{q}\vec{R}} \cdot b_n \end{aligned}}$$

So we obtain, from Eqns. (1), (2), and (3)

(*)

$$\boxed{\begin{aligned} [\mathcal{E}_{\vec{q}} - \mathcal{E}_m]\, b_m &= -[\mathcal{E}_{\vec{q}} - \mathcal{E}_m] \sum_{n,\vec{R}\neq 0} \underbrace{\langle \phi_m | \phi_{n,\vec{R}} \rangle}_{\alpha_{mn}(\vec{R})} e^{i\vec{q}\vec{R}} b_n \\ &+ \sum_n b_n \underbrace{\langle \phi_m | \Delta U | \phi_n \rangle}_{-\beta_{mn}} \\ &+ \sum_{\vec{R}\neq 0,n} b_n e^{i\vec{q}\vec{R}} \underbrace{\langle \phi_m | \Delta U | \phi_{n,\vec{R}} \rangle}_{-\gamma_{mn}(\vec{R})} \end{aligned}}$$

All the overlap integrals on the RHS of (*) are small, so that means that $(\mathcal{E}_{\vec{q}} - \mathcal{E}_m) b_m$ is small, meaning that $\mathcal{E}_{\vec{q}}$ should be, as expected, close to $\mathcal{E}_m$ in energy.

Equation (*) is written for the correction to a single level $\mathcal{E}_m$. However, the sum over n should go over all ~~energies~~ ~~for~~ orbitals that are close to ϕ_m in energy, and for every such ϕ_n equation (*) can be written. Therefore, we again end up with a system of equations in terms of b_n's, and its determinant will give us the energies:

For all m's close in energy

$$\boxed{\left[\mathcal{E}_{\vec{q}} - \mathcal{E}_m\right]\left[b_m + \sum_{n,\vec{R}\neq 0} \alpha_{mn}(\vec{R})\, e^{i\vec{q}\vec{R}}\, b_n\right] + \\ + \sum_n b_n \beta_{mn} + \sum_{n,\vec{R}\neq 0} \gamma_{mn}(\vec{R})\, e^{i\vec{q}\vec{R}}\, b_n = 0}$$

- So one first estimates up to which neighbors one is going to assume α's, β's and γ's to be appreciable. That fixes over which $\vec{R}$'s the sum is supposed to go. Also, one sees which energy levels & corresponding orbitals are to be included (if energy levels are very close).

Example: For an atomic s-level, which is generally nondegenerate, we obtain the "s-band", and there is only one n in the summation. Therefore we get

$$(\mathcal{E}_{\vec{q}} - \mathcal{E}_s)\left(1 + \sum_{\vec{R}\neq 0} e^{i\vec{q}\vec{r}}\alpha(\vec{R})\right) +$$

$$+ \beta + \sum_{\vec{R}\neq 0} \gamma(\vec{R})\, e^{i\vec{q}\vec{r}} = 0 \qquad /\text{b's cancel out}$$

$$\boxed{\mathcal{E}_{\vec{q}} = \underset{\substack{\uparrow \\ \text{atomic s-level} \\ \text{energ}}}{\mathcal{E}_s} - \frac{\beta + \sum_{\vec{R}\neq 0} \gamma(\vec{R}) e^{i\vec{q}\vec{R}}}{1 + \sum_{\vec{R}\neq 0} \alpha(\vec{R}) e^{i\vec{q}\vec{R}}}}$$

α-terms in the denominator can be generally in the case of one band neglected, as they are much smaller than 1.

$$\boxed{\mathcal{E}_{\vec{q}} = \mathcal{E}_s - \beta - \sum_{\vec{R}\neq 0} \gamma(\vec{R}) e^{i\vec{q}\vec{R}}}$$

For an fcc lattice, with one atom in the basis, and under the assumption that $\gamma(\vec{R})$ is appreciable only with nearest neighbors

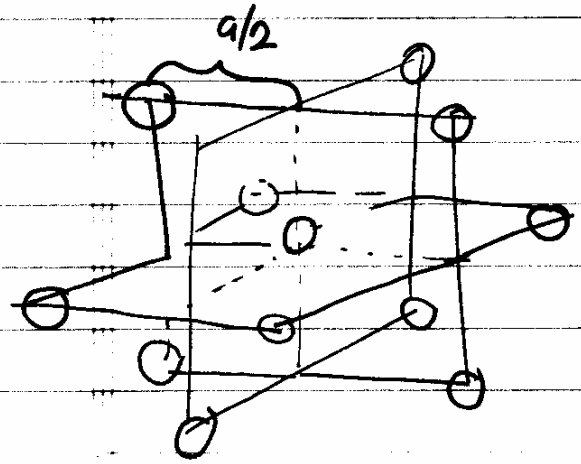
$$\mathcal{E}_{\vec{q}} = \mathcal{E}_s - \beta - \sum_{n.n.} \gamma(\vec{R}) e^{i\vec{q}\vec{R}}$$

Nearest neighbors are located on the faces, so there is 12 of them. Also, due to inversion symmetry of cubic crystals, $\gamma(\vec{R}) = \gamma(-\vec{R})$. Actually, the overlap integral among s-orbitals, since they do not have a preferred direction, should only depend on the distance

between atoms, and it is the same for all nearest neighbors, so

$$\forall \vec{R} \text{ nearest neighbor} \quad \gamma(\vec{R}) \equiv \gamma^{\mu}$$

$$\mathcal{E}_{\vec{q}} = \mathcal{E}_s - \beta - \gamma^{\mu} \sum_{n.n.} e^{i\vec{q}\cdot\vec{R}}$$



Nearest neighbors are at

$$\frac{a}{2}(\pm 1, \pm 1, 0)$$
$$\frac{a}{2}(\pm 1, 0, \pm 1)$$
$$\frac{a}{2}(0, \pm 1, \pm 1)$$

(a – constant of the underlying cubic lattice)

$$\vec{q}\cdot\vec{R} = \frac{a}{2}\begin{cases} \pm q_x \pm q_y \\ \pm q_x \pm q_z \\ \pm q_y \pm q_z \end{cases}$$

$$\mathcal{E}_{\vec{q}} = \mathcal{E}_s - \beta - 2\gamma^{\mu}\left\{\cos\frac{(q_x+q_y)a}{2} + \cos\frac{(q_x-q_y)a}{2} + \cos\frac{(q_x+q_z)a}{2} + \cos\frac{(q_x-q_z)a}{2} + \cos\frac{(q_y+q_z)a}{2} + \cos\frac{(q_y-q_z)a}{2}\right\}$$

$$\boxed{\mathcal{E}_{\vec{q}} = \mathcal{E}_s - \beta - 4\gamma^{\mu}\left\{\cos\frac{q_x a}{2}\cos\frac{q_y a}{2} + \cos\frac{q_x a}{2}\cos\frac{q_z a}{2} + \cos\frac{q_y a}{2}\cos\frac{q_z a}{2}\right\}}$$

$\vec{q}$ from the 1st BZ!!!

In the vicinity of the Γ-point ($\vec{q}=0$)

$$\mathcal{E}_{\vec{q}} = \mathcal{E}_s - \beta - 2\gamma\left(1 - \frac{1}{2}\frac{(q_x+q_y)^2a^2}{4} + 1 - \frac{1}{2}\frac{(q_x-q_y)^2a^2}{4} + \ldots\right)$$

$$= \mathcal{E}_s - \beta - 2\gamma\left[6 - \frac{1}{8}\cdot a^2\underbrace{(4q_x^2+4q_y^2+4q_z^2)}_{4q^2}\right]$$

$$\boxed{\mathcal{E}_{\vec{q}} = \mathcal{E}_s - \beta - 12\gamma + \gamma q^2 a^2}$$ ← spherical isoenergy surface (will hold for cubic crystals)

How wide is the band? Width given by γ (see last eqn on the previous page), so TIGHT-BINDING BANDS ARE NARROW BANDS (the smaller the overlap, the narrower the bands).

Lattice with a basis: Zinc-Blende/Diamond

We want to investigate how the bandstructure of Zinc-blende / diamond looks, having in mind that there are two atoms in a basis, and the underlying Bravais lattice is fcc. The atomic wavefunctions we should be using are s and p_x, p_y, p_z, one quartet for atom A (e.g. Ga) and another for atom B (e.g., As). So it is going to be an $\underline{\underline{8\times 8}}$ matrix that will give us the bands (8 of them, to be exact.)

$$\phi_{\vec{q}}(\vec{r}) = \phi^{(A)}_{\vec{q}}(\vec{r}) + \phi^{(B)}_{\vec{q}}(\vec{r}-\vec{d})\, e^{i\vec{q}\cdot\vec{d}}$$

$\vec{d}$ - displacement of the 2nd basis atom with respect to the 1st

$$\hat{H}|\phi_{\vec{q}}\rangle = \mathcal{E}_{\vec{q}}\,|\phi_{\vec{q}}\rangle$$

$n=1$	s
$n=2$	p_x
$n=3$	p_y
$n=4$	p_z

$$\phi_{\vec{q}}(\vec{r}) = \sum_{n=1}^{4}\sum_{\vec{R}} \left[b_n^{(A)} \phi_n^{(A)}(\vec{r}-\vec{R}) + b_n^{(B)} \phi_n^{(B)}(\vec{r}-\vec{R}-\vec{d})\, e^{i\vec{q}\cdot\vec{d}} \right] e^{i\vec{q}\vec{R}}$$

$$\langle \phi_m^{(A,B)} | \hat{H} | \phi_{\vec{q}} \rangle = \langle \phi_m^{(A,B)} | \underbrace{\hat{H}^{(A,B)}_{atom}}_{\text{centered at } 0 \text{, for (A) or at } \vec{d} \text{ for (B)}} | \phi_{\vec{q}} \rangle + \langle \phi_m^{(A,B)} | \Delta U^{(1,2)} | \phi_{\vec{q}} \rangle$$

$$\langle \phi_m^{(A,B)} | H^{(A,B)}_{atom} | \phi_{\vec{q}} \rangle = \underbrace{\mathcal{E}_m^{(A,B)}}_{\text{this is } \mathcal{E}_s \text{ or } \mathcal{E}_p \text{ of atom A or B}} \langle \phi_m^{(A,B)} | \phi_{\vec{q}} \rangle$$

$$\boxed{\left[\mathcal{E}_{\vec{q}} - \mathcal{E}_m^{(A,B)}\right] \langle \phi_m^{(A,B)} | \phi_{\vec{q}} \rangle = \langle \phi_m^{(A,B)} | \Delta U^{(A,B)} | \phi_{\vec{q}} \rangle}$$

We see there are going to be 8 equations (4 m's for each of the two atoms)

$$\langle \phi_m^{(A,B)} | \phi_{\vec{q}} \rangle = \langle \phi_m^{(A,B)} | \phi_{\vec{q}}^{(A)} + \phi_{\vec{q}}^{(B)} e^{i\vec{q}\vec{d}} \rangle$$

(We neglect the contribution from any overlap among different sites

$$\langle \phi_m^{(A)} | \phi_{\vec{q}} \rangle \approx b_m^{(A)} \qquad \langle \phi_m^{(B)} | \phi_{\vec{q}} \rangle \approx b_m^{(B)} e^{i\vec{q}\vec{d}}$$

$\langle \phi_m^{(A,B)} | \Delta U | \phi_{\vec{q}} \rangle \rightarrow$ we calculate it only in the <u>nearest neighbor approximation</u>

so $\phi_m^{(A,B)}$ will overlap only with $\phi_n^{(B,A)}$ from 4 tetrahedrally bonded neighbors

$$\langle \phi_m^{(A)} | \Delta U | \phi_{\vec{q}} \rangle = \int d^3\vec{r} \sum_{n=1}^{4} \sum_{\vec{R}} e^{i\vec{q}\vec{R}} \times$$

$$\times\ \phi_m^{(A)*}(\vec{r})\, \Delta U(\vec{r}) \left[\phi_n^{(A)}(\vec{r})\, b_n^{(A)} + b_n^{(B)} \phi_n^{(B)}(\vec{r}-\vec{d}-\vec{R})\, e^{i\vec{q}\vec{d}} \right]$$

In the nearest neighbor approximation, only overlap with $\phi_n^{(B)}$'s will be important, and those which are at

Neighbors of atom A:

$$\vec{r}_1 = \frac{a}{2}(\vec{e}_x + \vec{e}_y + \vec{e}_z) \equiv \vec{d}$$

$$\vec{r}_2 = \frac{a}{2}(\vec{e}_x - \vec{e}_y - \vec{e}_z)$$

$$\vec{r}_3 = \frac{a}{2}(-\vec{e}_x + \vec{e}_y - \vec{e}_z)$$

$$\vec{r}_4 = \frac{a}{2}(-\vec{e}_x - \vec{e}_y + \vec{e}_z)$$

$\boxed{\text{a is the period of the fcc lattice (2a is the period of the underlying cubic lattice)}}$

$$\langle \phi_m^{(A)} | \Delta U | \phi_{\vec{q}} \rangle \overset{n.n.}{=} \sum_{n=1}^{4} \sum_{\vec{R}\,n.n.} e^{i\vec{q}(\vec{R}+\vec{d})} \times b_n^{(B)}$$

$$\times \underbrace{\left(\int d^3\vec{r}\ \phi_m^{(A)*}(\vec{r})\, \Delta U\, \phi_n^{(B)}(\vec{r}-\vec{d}-\vec{R}) \right)}$$

when $m=1$ (s orbital) and $n=1$ (s orbital) this overlap is the same for all neighbors and is denoted in Ferry's book by $\mathcal{E}_{ss}$

$$\mathcal{E}_{ss} \equiv \langle s^{(A)} | \Delta U | s^{(B)} \rangle$$

the sum over $\vec{R}_{n.n.}$ basically reduces to

$$\sum_{i=1}^{n} e^{i\vec{q}\cdot\vec{r}_i} = e^{i\frac{a}{2}(q_x+q_y+q_z)} + e^{i\frac{a}{2}(q_x-q_y-q_z)} +$$

$$+ e^{i\frac{a}{2}(-q_x+q_y-q_z)} + e^{i\frac{a}{2}(-q_x-q_y+q_z)} =$$

$$= e^{i\frac{a}{2}q_x} \cdot 2\cos\left(\frac{q_y+q_z}{2}\right)a + e^{-i\frac{a}{2}q_x} \cdot 2\cos\left(\frac{q_y-q_z}{2}\right)a$$

$$= e^{i\frac{a}{2}q_x} 2\left(\cos\frac{q_y a}{2}\cos\frac{q_z a}{2} - \sin\frac{q_y a}{2}\sin\frac{q_z a}{2}\right)$$

$$+ e^{-i\frac{a}{2}q_x} 2\left(\cos\frac{q_y a}{2}\cos\frac{q_z a}{2} + \sin\frac{q_y a}{2}\sin\frac{q_z a}{2}\right)$$

$$\cancel{= \left(\cos\frac{q_x a}{2} + i\sin\frac{q_x a}{2}\right) 2\left(\cos 2\right.}$$

$$= 2\cos\frac{q_y a}{2}\cos\frac{q_z a}{2} \cdot 2\cos\frac{q_x a}{2}$$

$$- 2\sin\frac{q_y a}{2}\cos\frac{q_z a}{2} \cdot 2i\sin\frac{q_x a}{2} =$$

$$= 4\left(\cos\frac{q_x a}{2}\cos\frac{q_y a}{2}\cos\frac{q_z a}{2} - i\sin\frac{q_x a}{2}\sin\frac{q_y a}{2}\sin\frac{q_z a}{2}\right) = B_0(\vec{q})$$

This term, times ε_{ss}, multiplies $b_{1}^{(2)} \equiv b_s^{(2)}$

As for overlap between s from atom A and p's from atom B, the magnitude is the same, ε_{sp}, but it can be positive or negative depending on which neighbor and which orbital:

From neighbor 1 → all orbitals point <u>AWAY</u> from atom A, there will be $+1 \times \varepsilon_{sp}$ from that neighbor

From neighbor 2 → p_x AWAY, p_y and p_z towards

$+1$ $\quad$ 1 $\quad$ 1

Etc...

$$\boxed{\begin{aligned}\langle \phi_1^{(A)} | \Delta U | \phi_{\vec{q}} \rangle &\equiv \langle s^{(A)} | \Delta U | \phi_{\vec{q}} \rangle = \\ &= b_s^{(B)} \cdot E_{ss} \cdot B_0(\vec{q}) + b_{p_x}^{(B)} \mathcal{E}_{sp} B_1(\vec{q}) + \\ &+ b_{p_y}^{(B)} \mathcal{E}_{sp} B_2(\vec{q}) + b_{p_z}^{(B)} \mathcal{E}_{sp} B_3(\vec{q})\end{aligned}}$$

$$B_1(\vec{q}) = e^{i\vec{q}\vec{r}_1} + e^{i\vec{q}\vec{r}_2} - e^{i\vec{q}\cdot\vec{r}_3} - e^{i\vec{q}\cdot\vec{r}_4}$$

$$= 4\left(-\cos\frac{q_x a}{2}\sin\frac{q_y a}{2}\sin\frac{q_z a}{2} + i\sin\frac{q_x a}{2}\cos\frac{q_y a}{2}\cos\frac{q_z a}{2}\right)$$

$$B_2(\vec{q}) = e^{i\vec{q}\cdot\vec{r}_1} - e^{i\vec{q}\vec{r}_2} + e^{i\vec{q}\cdot\vec{r}_3} - e^{i\vec{q}\vec{r}_4}$$

$$= 4\left(-\sin\frac{q_x a}{2}\cos\frac{q_y a}{2}\sin\frac{q_z a}{2} + i\cos\frac{q_x a}{2}\sin\frac{q_y a}{2}\cos\frac{q_z a}{2}\right)$$

$$B_3(\vec{q}) = e^{i\vec{q}\cdot\vec{r}_1} - e^{i\vec{q}\vec{r}_2} - e^{i\vec{q}\vec{r}_3} + e^{i\vec{q}\cdot\vec{r}_4}$$

$$= 4\left(-\sin\frac{q_x a}{2}\sin\frac{q_y a}{2}\cos\frac{q_z a}{2} + i\cos\frac{q_x a}{2}\cos\frac{q_y a}{2}\sin\frac{q_z a}{2}\right)$$

Similarly, one can show that

$$\langle p_x^{(A)} | \Delta U | \phi_{\vec{q}} \rangle = -b_s^{(B)} \mathcal{E}_{sp} B_1(\vec{q}) + b_{p_x}^{(B)} \mathcal{E}_{xx} B_0(\vec{q})$$
$$+ b_{p_y}^{(B)} \mathcal{E}_{xy} B_3(\vec{q}) + b_{p_z}^{(B)} \mathcal{E}_{xz} B_1(\vec{q})$$

Analogously for the other two axes.

The same procedure is followed by replacing $\langle \phi_m^{(A)} |$ with $\langle \phi_m^{(B)} |$, and ~~after everything~~ also multiplying by $e^{-i\vec{q}\cdot\vec{a}}$. These additional 4 equations complete the set of 8 expected equations in terms of constants $b_n^{(A)}, b_n^{(B)}$.

So when 4+4 equations

$$\left[\mathcal{E}_{\vec{q}} - \mathcal{E}_m^{(A)}\right] b_m^{(A)} - \underbrace{\langle \phi_m^{(A)} | \Delta U | \phi_{\vec{q}} \rangle}_{\text{this has sum over all } b_m^{(B)}} = 0$$

$$\left[\mathcal{E}_{\vec{q}} - \mathcal{E}_m^{(B)}\right] b_m^{(B)} - \underbrace{\langle \phi_m^{(B)} | \Delta U | \phi_{\vec{q}} \rangle}_{\text{this will have sum over all } b_m^{(A)}} e^{-i\vec{q}\vec{d}} = 0$$

are written out, we obtain $\mathcal{E}_{\vec{q}}$ by annulling the determinant of the system

$$\det\left\{ \mathcal{E}_{\vec{q}} \underbrace{\hat{I}_{8\times 8}}_{8\times 8 \text{ unit matrix}} - \begin{bmatrix} [\mathcal{E}^A] & [AB] \\ [BA] & [\mathcal{E}^B] \end{bmatrix} \right\} = 0$$

this is what you need to solve numerically in your HW

$$[\mathcal{E}^{A,B}] = \mathrm{diag}\left(\mathcal{E}_s^{A,B}, \mathcal{E}_p^{A,B}, \mathcal{E}_p^{A,B}, \mathcal{E}_p^{A,B}\right)$$

$$[AB] = \begin{bmatrix} \mathcal{E}_{ss} B_0 & \mathcal{E}_{sp}^{AB} B_1 & \mathcal{E}_{sp}^{AB} B_2 & \mathcal{E}_{sp}^{AB} B_3 \\ -\mathcal{E}_{sp}^{BA} B_1 & \mathcal{E}_{xx} B_0 & \mathcal{E}_{xy} B_3 & \mathcal{E}_{xy} B_2 \\ -\mathcal{E}_{sp}^{BA} B_2 & \mathcal{E}_{xy} B_3 & \mathcal{E}_{xx} B_0 & \mathcal{E}_{xy} B_1 \\ -\mathcal{E}_{sp}^{BA} B_3 & \mathcal{E}_{xy} B_2 & \mathcal{E}_{xy} B_1 & \mathcal{E}_{xx} B_0 \end{bmatrix}$$

and $[BA] = [AB]^{+}$ Hermitian adjoint = transposed + + complex. conj.

$$\left([BA]_{ij} = [AB]_{ji}^{*} \right)$$

$\boxed{\text{HW: Plot along } L - \Gamma - X - U - \Gamma !}$

Zones near the Γ-point

Γ-point ($\vec{q}=0$) makes all B's except B_0 vanish so our 8x8 matrix can be reduced to 4 2x2 matrices (where s^A & s^B overlap, p_x^A and p_x^B, etc.) $B_0(0)=4$

$$\det\begin{vmatrix} \mathcal{E}_{\vec{q}\approx 0}-\mathcal{E}_s^A & 4\mathcal{E}_{ss} \\ 4\mathcal{E}_{ss} & \mathcal{E}_{\vec{q}\approx 0}-\mathcal{E}_s^B \end{vmatrix}=0$$

$$\det\begin{vmatrix} \mathcal{E}_{\vec{q}\approx 0}-\mathcal{E}_p^A & 4\mathcal{E}_{xx} \\ 4\mathcal{E}_{xx} & \mathcal{E}_{\vec{q}\approx 0}-\mathcal{E}_p^B \end{vmatrix}=0$$

$$\mathcal{E}_{\vec{q}\approx 0}=\frac{\mathcal{E}_s^A+\mathcal{E}_s^B}{2}\pm\sqrt{\left(\frac{\mathcal{E}_s^A-\mathcal{E}_s^B}{2}\right)^2+16\,\mathcal{E}_{ss}^2}$$

$$\mathcal{E}_{\vec{q}\approx 0}=\frac{\mathcal{E}_p^A+\mathcal{E}_p^B}{2}\pm\sqrt{\frac{(\mathcal{E}_p^A-\mathcal{E}_p^B)^2}{2}+16\,\mathcal{E}_{xx}^2}\quad\Big\}\ \text{THREEFOLD DEGENERATE}$$

Four valence bands (from the solutions corresponding to the minus sign)

increasing energy ↓

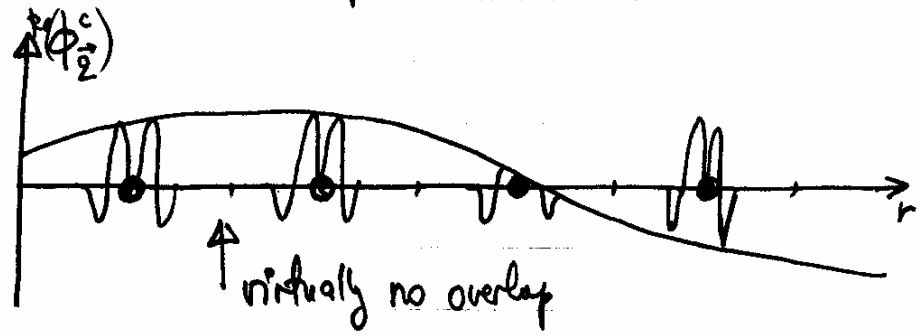
Lowest: "−", from s-level
Next 3: "−", from p-levels → TOP OF THE VALENCE BAND p-like

GAP

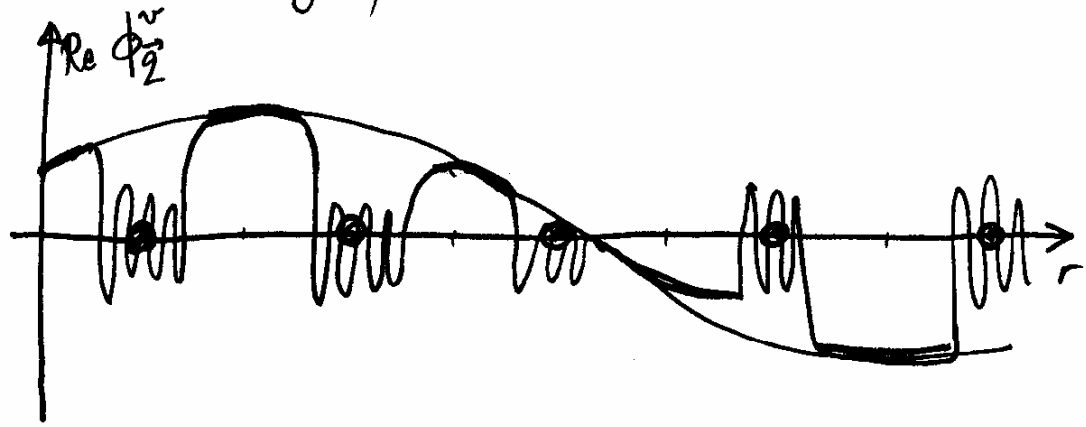
Lowest cond. band
"+", from s-level → BOTTOM OF COND BAND (IN GaAs) s-like
Next 3: "+", from p-level

The Pseudopotential Method

The Bloch functions corresponding to CORE ATOMIC STATES are weakly spatially dependent, except near the atomic sites. They are well-described by tight binding, with negligible inter-atomic overlaps



However, for the Bloch functions corresponding to VALENT ATOMIC LEVELS (those participating in the bonding) we expect more considerable overlap between different atoms, but still the most dynamic spatial variation is in the vicinity of the atoms



So the idea of the pseudopotential method is that if we could somehow take out the atomic potential near the atoms (or at least a part of it), that we

should be able to use a small number of plane waves to describe the behavior of valent electrons.
So the valence band wavefunction ("valence" means coming from atomic levels contributing to bonding, <u>not</u> what it usually means in the semiconductor field) is assumed in the form

$$\boxed{\phi^v_{\vec{q}}(\vec{r}) = \tilde{\phi}^v_{\vec{q}}(\vec{r}) - \sum_{\substack{\text{core}\\ \text{levels}}} \left[\int d^3r' \, \phi^{*c}_{\vec{q}}(\vec{r}\,')\, \tilde{\phi}^v_{\vec{q}}(\vec{r})\right] \phi^c_{\vec{q}}(\vec{r})} \quad (*)$$

$\tilde{\phi}^v_{\vec{q}}(\vec{r})$ — the pseudowavefunction
smooth around the atoms
can be expanded in a "small" number of plane waves

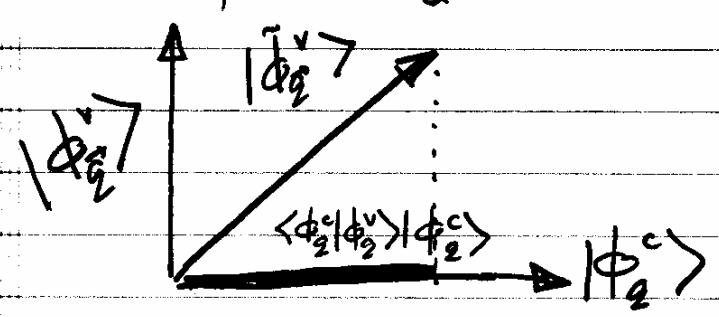
$$\tilde{\phi}^v_{\vec{q}}(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{K}} \alpha_{\vec{K}}\, e^{i(\vec{q}+\vec{K})\vec{r}}$$

Ω: primitive cell volume. N = crystal volume

In the Dirac notation, $(*)$ is written as

$$\boxed{|\phi^v_{\vec{q}}\rangle = |\tilde{\phi}^v_{\vec{q}}\rangle - \sum_c \langle \phi^c_{\vec{q}} | \tilde{\phi}^v_{\vec{q}} \rangle |\phi^c_{\vec{q}}\rangle}$$

Think of this equation as holding for vectors.



We get the valence function from the pseudofunction by subtracting its portion that belongs to the core states.

The valence band wavefunction is an eigenfunction of the Hamiltonian, for energy $\mathcal{E}^v_{\vec{q}}$, i.e.,

$$\hat{H}|\phi^v_{\vec{q}}\rangle = \mathcal{E}^v_{\vec{q}}|\phi^v_{\vec{q}}\rangle$$

By substituting ⊕, we obtain

$$\hat{H}|\tilde{\phi}^v_{\vec{q}}\rangle - \sum_c \langle\phi^c_{\vec{q}}|\tilde{\phi}^v_{\vec{q}}\rangle \hat{H}|\phi^c_{\vec{q}}\rangle =$$

$$= \mathcal{E}^v_{\vec{q}}\left(|\phi^v_{\vec{q}}\rangle - \sum_c \langle\phi^c_{\vec{q}}|\tilde{\phi}^v_{\vec{q}}\rangle|\phi^c_{\vec{q}}\rangle\right)$$

Since core functions are also eigenfunctions for eigenvalues $\mathcal{E}^c_{\vec{q}}$ (these are not much different from the atomic core energies), we obtain

$$\boxed{(\hat{H}+V^R)|\tilde{\phi}^v_{\vec{q}}\rangle = \mathcal{E}^v_{\vec{q}}|\phi^v_{\vec{q}}\rangle}$$

where $V^R = \sum_c (\mathcal{E}^v_{\vec{q}} - \mathcal{E}^c_{\vec{q}})|\phi^c_{\vec{q}}\rangle\langle\phi^c_{\vec{q}}|$ (the scary tensor!)

or, in other words,

$$V^R|\phi\rangle = \sum_c (\mathcal{E}^v_{\vec{q}} - \mathcal{E}^c_{\vec{q}}) \underbrace{\langle\phi^c_{\vec{q}}|\phi\rangle}_{\int d^3\vec{r}'\,\phi^{c*}_{\vec{q}}(\vec{r}')\phi(\vec{r}')} |\phi^c_{\vec{q}}\rangle$$

We speak of the PSEUDOPOTENTIAL

$$\hat{H}+V^R = -\frac{\hbar^2}{2m}\nabla^2 + \underbrace{(V_{crystal} + V^R)}_{V^{pseudo}}$$

So, the <u>pseudowavefunction</u> is the eigenfunction of the Hamiltonian with the <u>pseudopotential</u> in it (instead of the real crystal potential), but for the REAL CRYSTAL ENERGY $\mathcal{E}_{\vec{q}}^{v}$!

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V^{pseudo}\right)|\tilde{\Phi}_{\vec{q}}^{v}\rangle = \mathcal{E}_{\vec{q}}^{v}|\tilde{\Phi}_{\vec{q}}^{v}\rangle$$

- Pseudopotential is <u>nonlocal</u>! (It does not depend only on one $\vec{r}$
- The pseudowavefunction is <u>smooth around atomic sites</u>.

The trick is how to determine V^{pseudo}!
- ab initio → from atomistic calculations
- empirical → using experimental data

<u>Empirical pseudopotential method</u>

Assume V^{pseudo} is local and periodic

$$V^{pseudo}(\vec{r}) = \sum_{\vec{R},\alpha,\vec{\tau}_\alpha} V_\alpha(\vec{r}-\vec{R}-\underbrace{\vec{\tau}_\alpha}_{\text{atom } \alpha \text{, } \vec{\tau}_\alpha \text{ its position in the basis}})$$

$$V^{pseudo}(\vec{r}) = \sum_{\vec{K}} V(\vec{K})e^{i\vec{K}\vec{r}}$$

$$V(\vec{K}) = \sum_{\alpha} S_\alpha(\vec{K})V_\alpha(\vec{K})$$

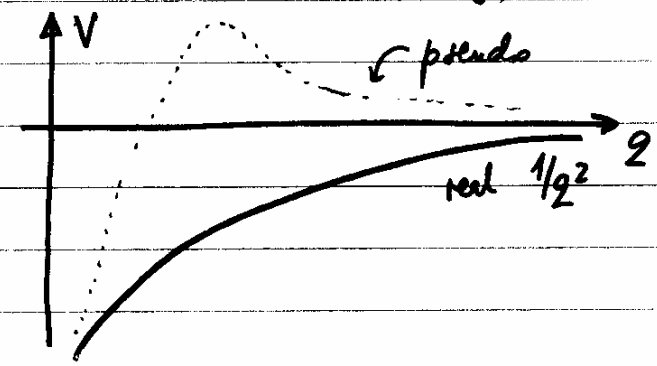
where $S_\alpha(\vec{K}) = \frac{1}{N_{basis}}\sum_{\vec{\tau}_\alpha} e^{-i\vec{K}\cdot\vec{\tau}_\alpha}$ ← structure factor

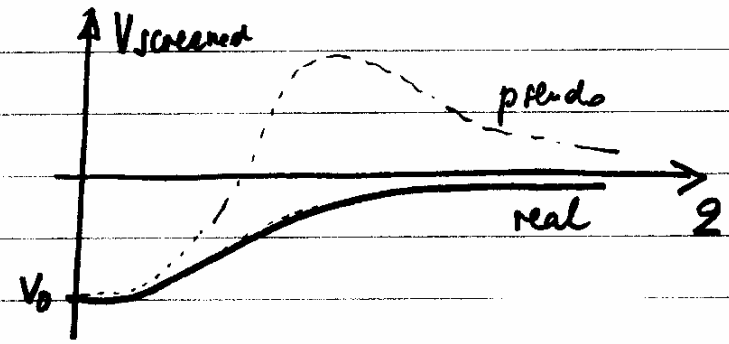
$$V_\alpha(\vec{K}) = \frac{1}{\Omega_\alpha} \int d^3\vec{r}\, e^{-i\vec{K}\cdot\vec{r}}\, \overbrace{V_\alpha(\vec{r})}^{\text{assumed spherically symmetric}} = \underbrace{V_\alpha(|\vec{K}|)}_{\text{atomic form factor depends on } |\vec{K}|}$$

volume per atom $= \dfrac{\text{prim. cell volume}}{N_{basis}}$

How does the pseudopotential look?

No electron-electron interaction (screening)

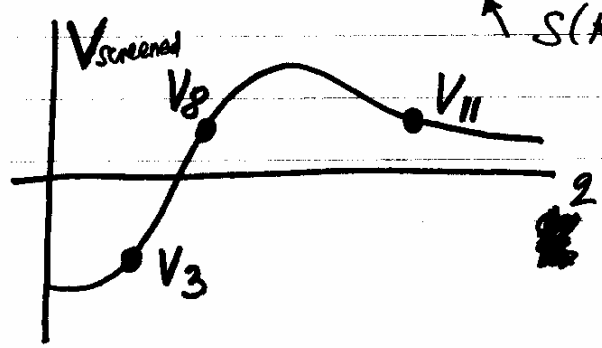




For instance, for Si and Ge, the form factors that are contributing to the pseudopotential are

$$K^2\left[\left(\frac{2\pi}{a}\right)^2\right]: \cancel{0},\ 3,\ \cancel{4},\ 8,\ 11,\ \cancel{12},\ \ldots \rightarrow \left.\begin{matrix} V_3 \\ V_8 \\ V_{11} \end{matrix}\right\} \text{from experiment}$$

$S(K)=0$



Department of Electrical and Computer Engineering

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ECE 745 – Solid State Electronics

Fall 2004, Lecture Notes

Part III: Introduction to Transport. Phonons. Scattering in Semiconductors

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Semiconductor Transport

What does transport theory study? Response of a material or device to external bias → → it studies charge transport, but also transport of energy, information, etc.

Goal: describe how your device structure responds to external bias (DC or AC) → obtain experimentally verifiable transport quantities: charge & current density, conductivity, mobility, thermoelectric coefficient...

Most of the semiconductor transport theory is based on a single-electron transport equation, which has, until recently, usually been the <u>Boltzmann transport equation</u> (does not work well for so-called "quantum transport"). The Boltzmann transport equation is what we will solve in most of the rest of this course. But before we turn on the voltage and start studying transport, let us remind ourselves of what goes on at zero bias, i.e., in semiconductors in equilibrium

Equilibrium Electron Statistics. Density of States

Consider bulk semiconductor, with n being the carrier density at any spatial point (homogeneous semiconductor). We can say that in such a semiconductor, the probability of an ~~elect energy~~ electronic state with energy $\mathcal{E}$ to be occupied is given by

$$f_0(\mathcal{E}) = \frac{1}{1 + e^{\frac{\mathcal{E} - \mathcal{E}_F}{kT}}}$$

where $\mathcal{E}_F$ is the Fermi level. $\mathcal{E}_F$ is determined from the relationship

$$n = \int_{\mathcal{E}_c}^{\infty} d\mathcal{E}\, f_0(\mathcal{E})\, g(\mathcal{E})$$

What is $g(\mathcal{E})$? Number of states having energy $\mathcal{E}$. How do you "count" states?

First, remember those bandstructure calculations. We realized that an electronic state is characterized by

$$\underset{\text{band index}}{n_b}, \quad \underset{\substack{\text{wavevector} \\ \text{in } 1^{st} BZ}}{\vec{k}}, \quad \underset{\text{spin}}{s}$$

Most of transport occurs (electronic transport)

near the bottom of the conduction band. Where is it?

- GaAs — Γ point $[\vec{q} = (0,0,0)]$
- Si — 85% of the way to X (100)
  6 equivalent X points = 6 equiv valleys
- Ge — L point $[\vec{q} = \frac{\pi}{2a}(1,1,1)]$
  8 x 1/2 valley

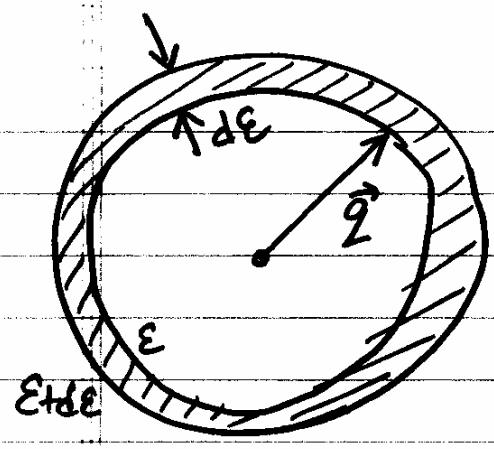
So for most transport calculations near the bottom of the band, the band index n_b will be fixed (unless we consider intervalley processes, and we will specify if we do).

So say the material is GaAs, so the bottom of the c. band is at the Γ point. The states are then characterized by $\vec{q}$ (from the 1st BZ) and spin ($\pm 1/2$). So how many states do we have per tiny energy interval $d\mathcal{E}$? Let us count

$d\mathcal{E} \rightarrow$ all those $\vec{q}$'s giving the energy between $\mathcal{E}$ and $\mathcal{E} + d\mathcal{E}$

Near the bottom of the band, and for isotropic effective mass like in GaAs

$$\mathcal{E}(\vec{q}) = \frac{\hbar^2 q^2}{2m^*} + \underbrace{\mathcal{E}_c}_{\text{bottom of cond band}}, \quad m^*_{GaAs} = 0.067 m_0$$



All the $\vec{q}$'s on the sphere have the same energy.

How many different states is that?

First, only one band (if we will be near the Γ point in GaAs)

Secondly, since the energy does not depend on spin, we know that if we count the $\vec{q}$'s, we put 2 electrons of opposite spins in the Bloch wavefunction with that $\vec{q}$.

Let us count:

$$\underbrace{g(\varepsilon)\cdot d\varepsilon}_{\substack{\#\text{ of available}\\ \text{states between}\\ \varepsilon\ \&\ \varepsilon+d\varepsilon}} = \sum_{\substack{\text{all quantum \#'s,}\\ \text{so that } \varepsilon(\text{quantum numbers})\\ \text{falls between } \varepsilon\ \&\ \varepsilon+d\varepsilon}} 1 = \left(\begin{array}{c}\text{just one band}\\ \text{2 opposite spins}\end{array}\right)$$

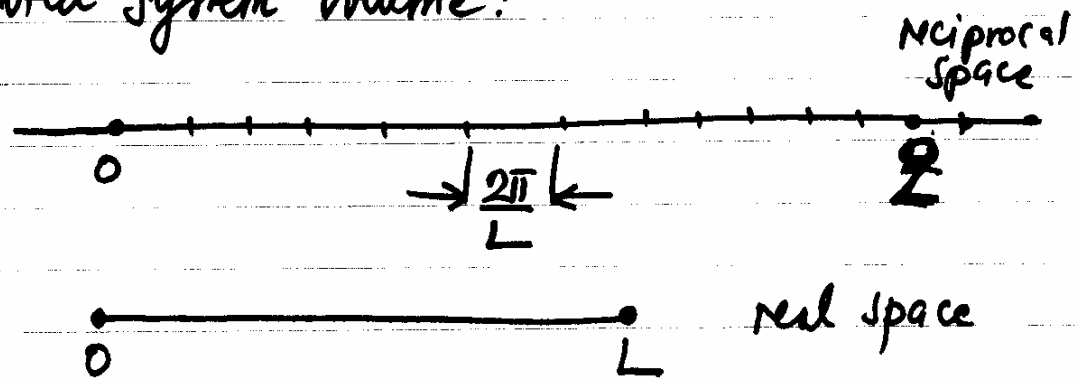
from this you define the density of states

$$= \underset{\substack{\uparrow\\ \text{spin}}}{2} \sum_{\substack{\vec{q},\ \text{so that}\\ \varepsilon(\vec{q})\in[\varepsilon,\varepsilon+d\varepsilon]}} 1$$

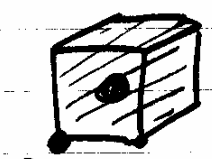
So how many such different $\vec{q}$'s are there in the shaded area on the fig. above?

Let us remember the periodic boundary conditions, that showed us that adjacent allowed $\vec{q}$'s are not infinitely close, but have spacing related to the total system volume:

(1D)



(3D)



The volume corresponding to one $\vec{q}$ is $\frac{2\pi}{L_x} \cdot \frac{2\pi}{L_x} \cdot \frac{2\pi}{L_y}$

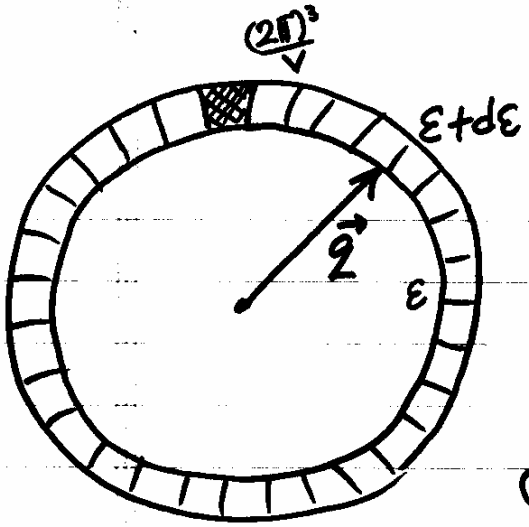
$$\boxed{\Delta^3 \vec{q} = \frac{(2\pi)^3}{V}}$$

Basically, this is the "smallest" volume in reciprocal space. So when we need to perform a sum over available $\vec{q}$'s in some region

$$\sum_{\vec{q}} \text{function}(\vec{q}) = \int \frac{d^3\vec{q}}{\underbrace{\text{Volume per one } \vec{q}}_{= \frac{(2\pi)^3}{V}}} \cdot \text{function}(\vec{q})$$

$$= \boxed{\frac{V}{(2\pi)^3} \int d^3\vec{q} \cdot \text{function}(\vec{q})}$$

This rule, "sum to integral" is often used in physics.



So basically we'll count how many little cubes of tiny volume $\frac{(2\pi)^3}{V}$ there are in the shell.

$$g(\varepsilon)\cdot d\varepsilon = \underset{\text{spin}}{2}\cdot\frac{V}{(2\pi)^3}\oint_{\substack{\text{shell}\\ (\varepsilon(\vec{q})\in[\varepsilon,\varepsilon+d\varepsilon])}} d^3\vec{q}\cdot 1$$

Because $\varepsilon(\vec{q})$ depends only on the magnitude of $\vec{q}$, it is better to write $d^3\vec{q}$ in spherical coordinates

$$d^3\vec{q} = q^2 dq \underbrace{d\varphi_{\vec{q}}\sin\theta_{\vec{q}}\, d\theta_{\vec{q}}}_{d\Omega_{\vec{q}}}$$

and note that

$$\varepsilon(\vec{q}) = \frac{\hbar^2\vec{q}^{\,2}}{2m^*}+\varepsilon_c\,;\quad d\varepsilon = \frac{\hbar^2}{m^*}\,q\,dq$$

($d\varepsilon$ can be written through q, dq)

$$g(\varepsilon)\,d\varepsilon = 2\cdot\frac{V}{(2\pi)^3}\cdot\oint_{\varepsilon(\vec{q})\in[\varepsilon,\varepsilon+d\varepsilon]} q^2 dq\, d\Omega_{\vec{q}}$$

(integrate over the shell → → over all $\Omega_{\vec{q}}$)

$$= 2\cdot\frac{V}{(2\pi)^3}\cdot\underbrace{4\pi}_{\text{all }\Omega_{\vec{q}}}\cdot q^2 dq$$

$$= \frac{V}{\pi^2}\,q^2 dq$$

$$g(\varepsilon) = \frac{V}{\pi^2}\left(q^2\frac{dq}{d\varepsilon}\right)_{\text{write in terms of }\varepsilon}$$

$$q^2 = (\mathcal{E}-\mathcal{E}_c)\cdot\frac{2m^*}{\hbar^2} \qquad \frac{dq}{d\mathcal{E}} = \frac{m^*}{\hbar^2}\cdot\frac{1}{q} = \frac{m^*}{\hbar^2}\left(\frac{\hbar^2}{2m^*(\mathcal{E}-\mathcal{E}_c)}\right)^{1/2}$$

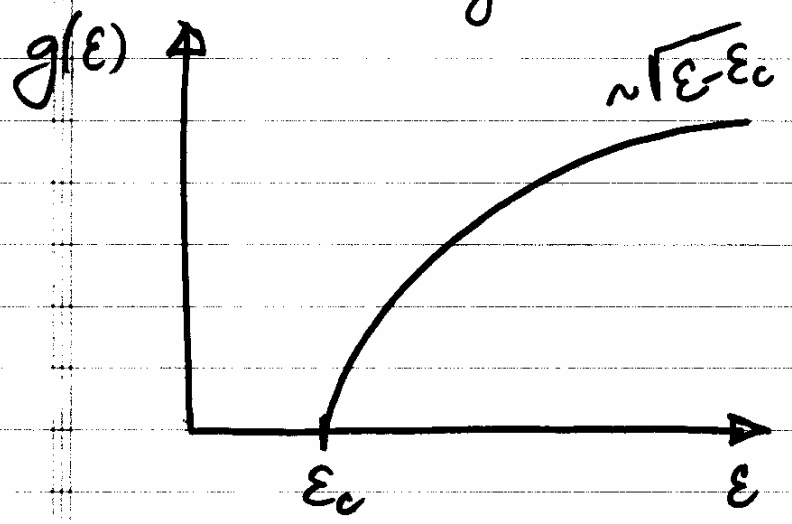
$$g(\mathcal{E}) = \frac{V}{\pi^2}\cdot\frac{2m^*}{\hbar^2}\cdot\mathcal{E}-\mathcal{E}_c\cdot\frac{m^*}{\hbar^2}\cdot\left(\frac{\hbar^2}{2m^*}\right)^{1/2}\cdot\frac{1}{(\mathcal{E}-\mathcal{E}_c)^{1/2}}$$

$$= \boxed{\frac{V}{2\pi^2}\cdot\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\cdot(\mathcal{E}-\mathcal{E}_c)^{1/2}}$$

One usually works with the density of states per unit volume $g(\mathcal{E})/V$, so we will use

$$\boxed{g(\mathcal{E}) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}(\mathcal{E}-\mathcal{E}_c)^{1/2}}$$

This would be the density of states near the bottom of the conduction band for a semiconductor with one valley.



The $\sqrt{\mathcal{E}-\mathcal{E}_c}$ is a signature of three-dimensionality.

$$n = \int_{\varepsilon_c}^{\infty} d\varepsilon\, g(\varepsilon) f_0(\varepsilon) = \frac{1}{2\pi^2}\cdot\left(\frac{2m^*}{\hbar^2}\right)^{3/2} \int_{\varepsilon_c}^{\infty} \frac{\sqrt{\varepsilon-\varepsilon_c}\, d\varepsilon}{1+e^{\frac{\varepsilon-\varepsilon_F}{kT}}}$$

Introduce $\varepsilon' = \varepsilon - \varepsilon_c$

$$n = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2} \int_0^{\infty} \frac{\varepsilon' d\varepsilon'}{1+e^{\frac{\varepsilon'+\varepsilon_c-\varepsilon_F}{k_BT}}}$$

$$= \frac{1}{2\pi^2}\cdot\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\cdot(k_BT)^{3/2} \int_0^{\infty} \frac{\left(\frac{\varepsilon'}{k_BT}\right) d\left(\frac{\varepsilon'}{k_BT}\right)}{1+\frac{\varepsilon'}{k_BT}-\frac{\varepsilon_F-\varepsilon_c}{k_BT}}$$

Integrals of the above type are among the so-called Fermi-Dirac integrals, defined as

$$F_n(x) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} \frac{y^n\, dy}{1+e^{y-x}}, \text{ so}$$

$$n = \frac{1}{2\pi^2}\cdot\left(\frac{2m^* k_BT}{\hbar^2}\right)^{3/2}\cdot\frac{\sqrt{\pi}}{2}\cdot F_{1/2}\left(\frac{\varepsilon_F-\varepsilon_c}{k_BT}\right)$$

$$\boxed{n = \frac{1}{4}\cdot\left(\frac{2m^* k_BT}{\hbar^2\pi}\right)^{3/2} F_{1/2}\left(\frac{\varepsilon_F-\varepsilon_c}{k_BT}\right)}$$

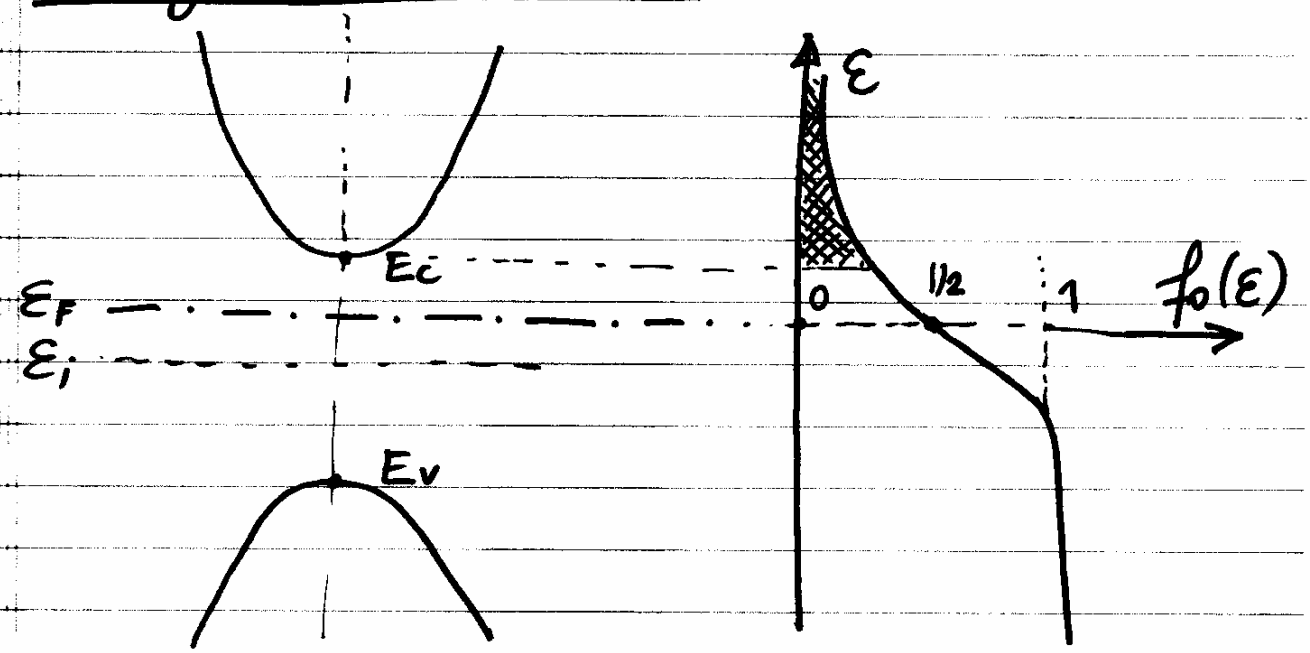
N_c

Relationship between equilibrium carrier density n and Fermi level ε_F

$$N_c = \frac{1}{4}\left(\frac{2m^* k_B T}{\hbar^2 \pi}\right)^{3/2}$$

The "effective conduction band density of states".

Nondegenerate semiconductor



If $\varepsilon_c - \varepsilon_F > 3.5 k_B T$, we can say that we are dealing just with the "tail" of the distribution function

$$\varepsilon' > \varepsilon_c \quad f_0(\varepsilon') = \frac{1}{1+e^{\frac{\varepsilon-\varepsilon_F}{k_B T}}} \qquad \frac{\varepsilon-\varepsilon_F}{k_B T} \gtrsim 3.5$$

$$\approx e^{-\left(\frac{\varepsilon-\varepsilon_F}{k_B T}\right)}$$

Maxwell–Boltzmann!

Works for nondegenerate semiconductors !!!

$$n = N_c \underbrace{\int_0^\infty y^{1/2} e^{-\left(y - \frac{\varepsilon_F - \varepsilon_c}{k_B T}\right)} dy}_{\Gamma(3/2) = \frac{\sqrt{\pi}}{2}} \cdot \frac{2}{\sqrt{\pi}}$$

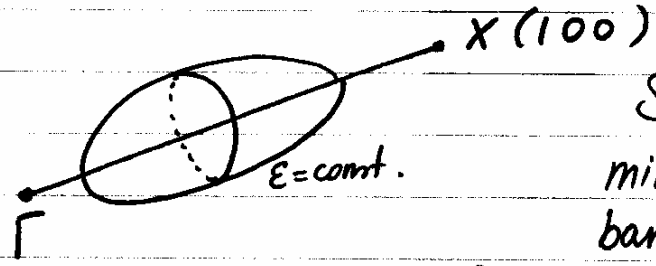
$$\boxed{n = N_c \cdot e^{\frac{\varepsilon_F - \varepsilon_c}{k_B T}}}$$ Nondegenerate case, equilibrium

$\varepsilon_c - \varepsilon_F > 3.5\, k_B T$

For holes

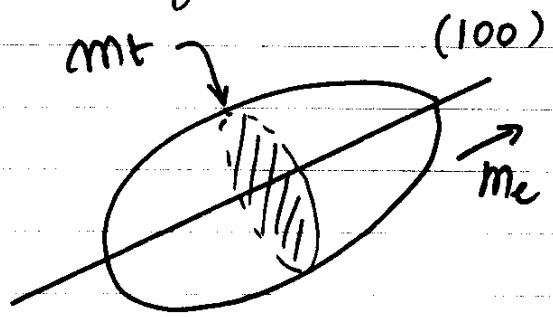
$$\boxed{p = N_v\, e^{\frac{\varepsilon_v - \varepsilon_F}{k_B T}}}$$ Again, $\varepsilon_F - \varepsilon_v > 3.5\, k_B T$

Multi-valley semiconductor + Anisotropic effective mass tensor (Si)



Si has 6 equivalent minima of the conduction band, located on the 6 equivalent $\Gamma \to X$ directions ($\{100\}$ directions)

Near a minimum, the effective mass tensor is anisotropic, i.e., its eigenvalues are not all the same



Along (100) related to a particular minimum, i.e. valley $\boxed{m_e = 0.91\, m_0}$

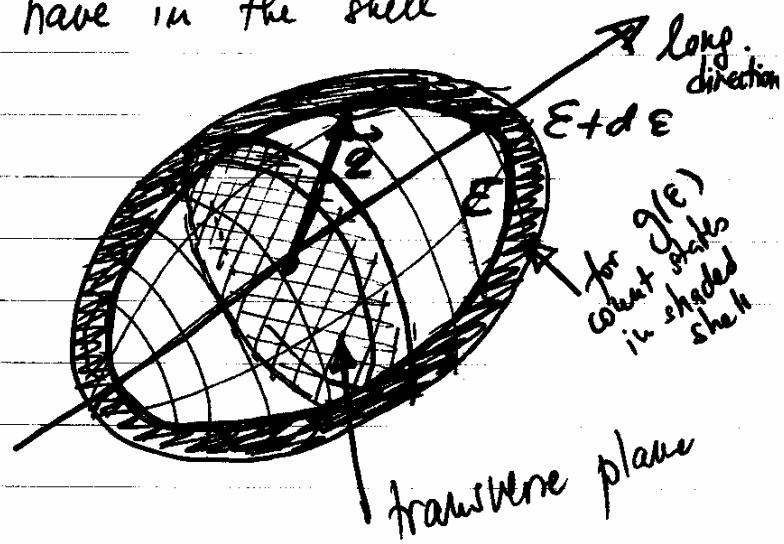
In the perpendicular plane $\boxed{m_t = m_0 \cdot 0.19}$

Let us find the density of states per unit volume

$$g(\varepsilon)d\varepsilon = \underset{\substack{\uparrow \\ \text{6 equivalent valleys}}}{6} \cdot \underset{\substack{\uparrow \\ \text{spin}}}{2} \cdot \underset{\substack{\uparrow \\ \text{from } \frac{V}{(2\pi)^3} \text{ per available } \vec{q}}}{\frac{1}{(2\pi)^3}} \oint d^3\vec{q} \cdot 1$$

$$\oint_{\varepsilon(\vec{q})\in[\varepsilon,\varepsilon+d\varepsilon]} d^3\vec{q} = ?$$

How many $d^3\vec{q}$ "cubes" do we have in the shell



Anisotropic mass:

$$\varepsilon(\vec{q}) = \frac{\hbar^2}{2}\left(\frac{q_\ell^2}{m_\ell} + \frac{q_t^2}{m_t}\right)$$

$$\vec{q}_t = (q_{t_1}, q_{t_2})$$

← The two components in the transverse plane

(We're using "longitudinal" & "transverse", because they change for each valley.)

$$\varepsilon(\vec{q}) = \frac{\hbar^2}{2}\left(\frac{q_\ell^2}{m_\ell} + \frac{q_{t_1}^2}{m_t} + \frac{q_{t_2}^2}{m_t}\right) + \varepsilon_c$$

This equation will yield the above elipsoid.

However, to relate $d\varepsilon$ & $d^3\vec{q}$ is difficult on an elipsoid. So we introduce three new coordinates:

$$x_\ell = q_\ell/\sqrt{m_\ell}$$

$$x_{t_1} = q_{t_1}/\sqrt{m_t}, \quad x_{t_2} = q_{t_2}/\sqrt{m_t}$$

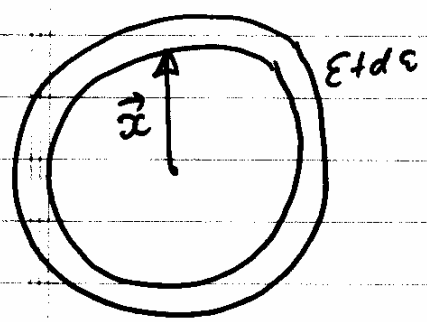
In terms of $\vec{x} = (x_\ell, x_{t_1}, x_{t_2})$

$$\boxed{\mathcal{E}(\vec{x}) = \mathcal{E}_c + \frac{\hbar^2}{2} \cdot x^2} \qquad \left(x = \sqrt{x_\ell^2 + x_{t_1}^2 + x_{t_2}^2} \right)$$

It is now easy to see that $d\mathcal{E}$ depends only on dx, not on the spatial variables

$$\boxed{d\mathcal{E} = \hbar^2 x\, dx}$$

Now let's integrate over that ellipsoid. In terms of $\vec{x}$, constant energy surface is a sphere.



$$\oint_{\mathcal{E}(\vec{q}) \in [\mathcal{E}, \mathcal{E}+d\mathcal{E}]} d^3\vec{q} \ldots = \int_{\mathcal{E}(\vec{x}) \in [\mathcal{E}, \mathcal{E}+d\mathcal{E}]} d^3\vec{x}\, \underbrace{J(\vec{q}, \vec{x})}_{\text{the Jacobian}} \ldots$$

$$J(\vec{q}, \vec{x}) \equiv \frac{\partial(q_\ell, \ldots)}{\partial(x_\ell, x_{t_1}, x_{t_2})} = \begin{vmatrix} \frac{\partial q_\ell}{\partial x_\ell} & \frac{\partial q_\ell}{\partial x_{t_1}} & \frac{\partial q_\ell}{\partial x_{t_2}} \\ \frac{\partial q_{t_1}}{\partial x_\ell} & \ddots & \\ \frac{\partial q_{t_2}}{\partial x_\ell} & & \ddots \end{vmatrix}$$

$$= \begin{vmatrix} \sqrt{m_\ell} & 0 & 0 \\ 0 & \sqrt{m_t} & 0 \\ 0 & 0 & \sqrt{m_t} \end{vmatrix} = \sqrt{m_\ell m_t^2}$$

Now, that integral over all $\vec{q}$'s in the ellipsoidal shell can be calculated as

$$\underbrace{\oint d^3\vec{q}}_{\text{ellipsoidal shell}} = \underbrace{\int d^3\vec{x}}_{\text{spherical shell}} \sqrt{m_\ell m_t^2} = \underbrace{4\pi}_{\text{radial angle}} \sqrt{m_\ell m_t^2} \cdot x^2 dx$$

$$g(\varepsilon)\,d\varepsilon = 6\cdot 2\cdot \frac{1}{(2\pi)^3}\cdot 4\pi\sqrt{m_\ell m_t^2}\; x^2 dx$$

$$g(\varepsilon) = \frac{6}{\pi^2}\cdot\sqrt{m_\ell m_t^2}\cdot\left(x^2\frac{dx}{d\varepsilon}\right)\Big|_{\text{written in terms of } \varepsilon}$$

$$x^2\frac{dx}{d\varepsilon} = x^{\cancel{2}}\cdot\frac{1}{\hbar^2\cancel{x}} = \frac{x}{\hbar^2} = \frac{1}{\hbar^2}\left(\frac{2}{\hbar^2}\right)^{1/2}(\varepsilon-\varepsilon_c)^{1/2}$$

$$= \frac{1}{2}\left(\frac{2}{\hbar^2}\right)^{3/2}\cdot(\varepsilon-\varepsilon_c)^{1/2}$$

$$\boxed{g(\varepsilon) = \frac{1}{2\pi^2}\cdot\left[6\sqrt{m_\ell m_t^2}\right]\left(\frac{2}{\hbar^2}\right)^{3/2}(\varepsilon-\varepsilon_c)^{1/2}}$$

By comparing with the expression for a single-valley semiconductor, with isotropic mass, we see that

$$6\sqrt{m_\ell m_t^2}$$

plays the role of some type of effective mass (to the power 3/2).

This is how we obtain the so-called DENSITY OF STATES EFFECTIVE MASS

$$m_{DOS}^{*\,3/2} = 6\sqrt{m_\ell m_t^2}$$

$$\boxed{m_{DOS}^* = 6^{2/3}\left(m_\ell m_t^2\right)^{1/3}}$$

In experiment, m_{DOS}^* is one of the measurable scalar masses. Another one is the so-called <u>cyclotron effective mass</u> (we'll mention it later.)

Which quantity do we use to describe transport?
In the first half of the course, we tried to find available states for electrons to occupy (bandstructure).
Now we have to see how those states are occupied, i.e., according to what rules.

The quantity of interest is the so-called
DISTRIBUTION FUNCTION

$$f(\vec{r}, \vec{p}, t)$$

that describes how many particles at time t are found in a tiny volume $d^3\vec{r}$ around $\vec{r}$, and have momentum within $d^3\vec{p}$ from $\vec{p}$.

The distribution function is an object borrowed from classical physics, in that it assumes that a particles momentum and position can be determined simultaneously, which we know is not true in quantum mechanics (remember Heisenberg uncertainty principle).

However, for relatively large semiconductor devices (100 nm or more), with potentials that do not vary rapidly, using this SEMICLASSICAL DISTRIBUTION FUNCTION is OK.

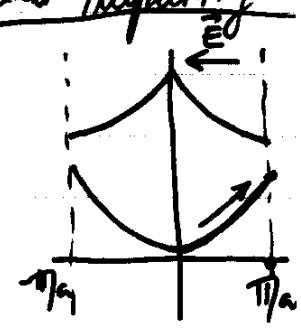
100 nm

The questions we will try to answer are:
* Why does $f(\vec{r},\vec{p},t)$ change in time?
* How does — " — ?
* How do we compute measurable quantities from f? (Current, conductance, etc.)

* <u>Why does $f(\vec{r},\vec{p},t)$ change in time?</u>

- external fields (electric, magnetic)
- scattering
  a) phonons (dominant at room temp.)
  b) ionized impurity scattering (Coulomb scat.)
  c) ~~rute~~ surface roughness scattering
  d) alloy scattering
  e) electron-electron scattering ...

In devices operating at <u>room temperature</u>, phonons are the dominant bulk scattering mechanism. They mask quite a bit (details of carrier-carrier scattering, much of ionized impurity scattering, etc.)



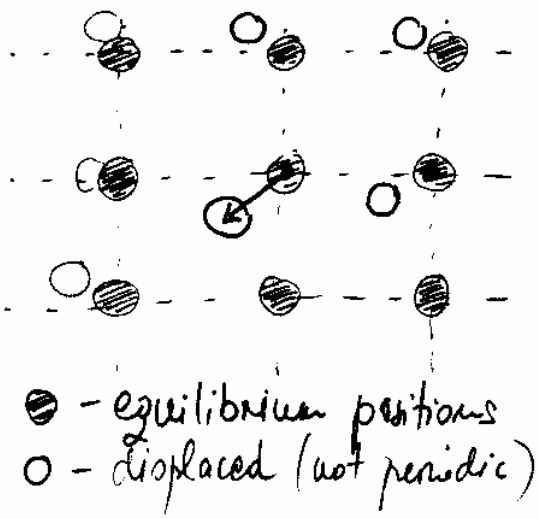
It is important to note that

<u>no scattering → no current</u>

In a perfect crystal, with no scattering, an electron's velocity under $\vec{E}$ increases, when it hits $\hbar\pi/a$ it gets reflected, becomes $-\hbar\pi/a$! Average velocity in perfect crystal is zero!

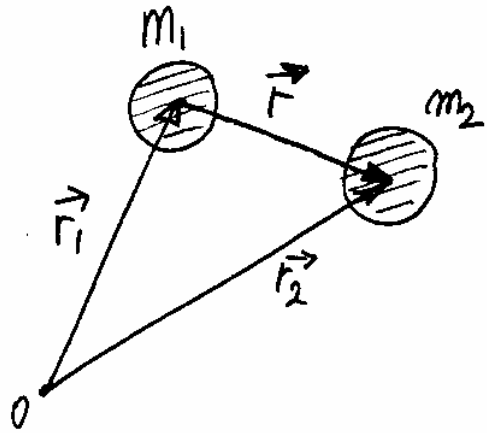
Phonons

Phonons are quanta of mechanical lattice waves. Ions in a lattice are not still, on the contrary: they constantly move about their equilibrium positions. If the ions were still, then they would indeed form a perfectly periodic lattice; an electron described by a Bloch wave would then move through such a perfectly periodic lattice WITHOUT SCATTERING.

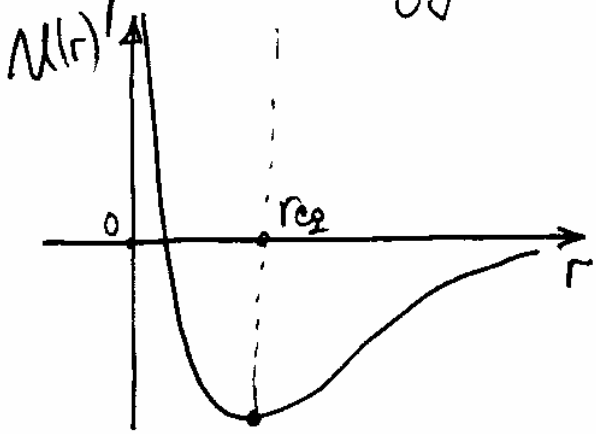


However, ions constantly perform <u>oscillations</u> around their equilibrium configuration. Once one of the ions is displaced, due to the bonding among ions, the displacement transfers to the neighboring atoms, and eventually due to the displacement of that first ion, every other ion in the lattice will be displaced $\rightarrow$ MECHANICAL WAVE.

How do we know that once an atom is displaced, it will indeed oscillate around its equilibrium position?



Consider, for simplicity, a two-atom molecule. In terms of $\vec{r} = \vec{r}_2 - \vec{r}_1$, which is the relative ~~coord~~ position of 2 with respect to 1, a typical shape of the potential energy due to bonding is given by ($\mathcal{U}$ is a function of $r = |\vec{r}|$ only.)



If we displace atoms with respect to one another $\vec{r}_{eq} \to \vec{r}_{eq} + \underbrace{\vec{u}}_{\text{small displacem.}}$

according to 2nd Newton's law

$$m_1 \frac{d^2\vec{r}_1}{dt^2} = -\frac{\partial \mathcal{U}(r)}{\partial \vec{r}_1} = \vec{F}_1 \quad \text{(the force on the 1st atom)}$$

$$m_2 \frac{d^2\vec{r}_2}{dt^2} = -\frac{\partial \mathcal{U}(r)}{\partial \vec{r}_2} = \vec{F}_2$$

$\vec{r} = \vec{r}_2 - \vec{r}_1$

$$\frac{\partial \mathcal{U}(r)}{\partial \vec{r}_1} = \frac{d\mathcal{U}}{d\vec{r}} \cdot (-1) = \frac{d\mathcal{U}}{dr} \cdot (-\vec{e}_r) \qquad \frac{\partial \mathcal{U}}{\partial \vec{r}_2} = \frac{d\mathcal{U}}{d\vec{r}}(+1) = \frac{d\mathcal{U}}{dr} \cdot \vec{e}_r$$

$$\left(\vec{e}_r = \frac{\vec{r}}{|\vec{r}|} = \frac{\vec{r}}{r}\right.$$

$$\left.\begin{aligned} m_1 \frac{d^2\vec{r}_1}{dt^2} &= +\frac{d\mathcal{U}}{dr}\vec{e}_r \\ m_2 \frac{d^2\vec{r}_2}{dt^2} &= -\frac{d\mathcal{U}}{dr}\vec{e}_r \end{aligned}\right\}$$

One thing we see is that

$$m_1 \frac{d^2\vec{r}_1}{dt^2} + m_2 \frac{d^2\vec{r}_2}{dt^2} = 0$$

Total momentum $m_1 \vec{v}_1 + m_2 \vec{v}_2 = \text{const}$

$$\frac{d^2\vec{r}_1}{dt^2} = \frac{1}{m_1}\frac{dU}{dr}\vec{e}_r, \quad \frac{d^2\vec{r}_2}{dt^2} = \frac{-1}{m_2}\frac{dU}{dr}\vec{e}_r$$

$$\vec{r}_2 - \vec{r}_1 = \vec{r} \qquad \boxed{\frac{d^2\vec{r}}{dt^2} = -\left[\frac{1}{m_1} + \frac{1}{m_2}\right]\frac{dU}{dr}\vec{e}_r}$$

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$ REDUCED MASS of a diatomic molecule

$$\boxed{\mu\frac{d^2\vec{r}}{dt^2} = -\frac{dU}{dr}\vec{e}_r}$$

Near r_{eq}, $U(r)$ can be expanded as

$$U(r) = U(r_{eq}) + \underbrace{\cancel{\left(\frac{dU}{dr}\right)_{r_{eq}}}}_{0}(r - r_{eq}) + \frac{1}{2}\left(\frac{d^2U}{dr^2}\right)_{r_{eq}}(r - r_{eq})^2 + O((r-r_{eq})^3)$$

minimum
(see figure on prev. page)

$$U(r) \approx U(r_{eq}) + \frac{1}{2}\underbrace{\left(\frac{d^2U}{dr^2}\right)_{r_{eq}}}_{>0,\ \text{since } r_{eq} \text{ minimum}} \cdot (r - r_{eq})^2$$

$$\frac{dU}{dr} \approx \left(\frac{d^2U}{dr^2}\right)_{r_{eq}}(r - r_{eq})$$

$$\mu\frac{d^2r}{dt^2} = -\frac{dU}{dr} = -\left(\frac{d^2U}{dr^2}\right)_{r_{eq}} \cdot \overbrace{(r - r_{eq})}^{u \text{ (small displacement)}}$$

$$\parallel$$

$$\mu\frac{d^2u}{dt^2} = -\underbrace{\left(\frac{d^2U}{dr^2}\right)}_{>0} u \leftarrow \text{displacement}$$

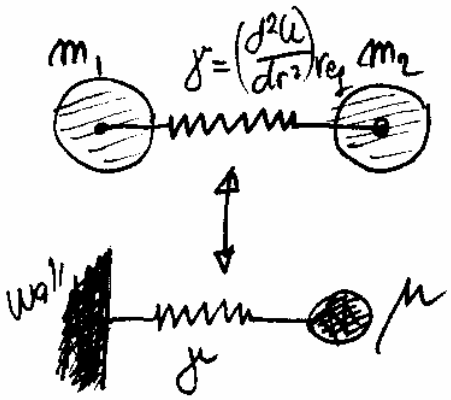
$$\frac{d^2u}{dt^2} + \left[\frac{1}{\mu}\left(\frac{d^2U}{dr^2}\right)_{r_e}\right] u = 0$$

This is an equation for a linear harmonic oscillator with frequency ω, given by

$$\boxed{\omega = \sqrt{\frac{1}{\mu}\left(\frac{d^2U}{dr^2}\right)_{r_e}}}$$

The relative distance in a diatomic molecule oscillates with frequency ω; you can think of a diatomic molecule as one particle of relative mass μ on a spring of spring constant

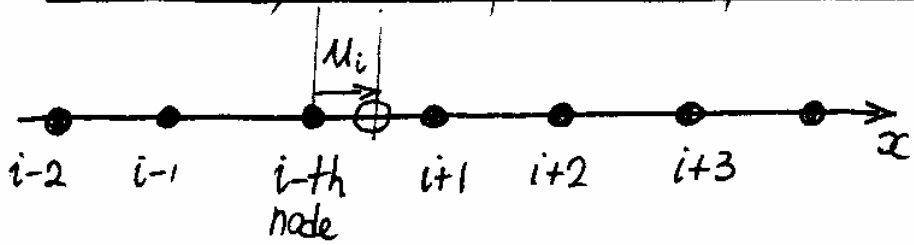
$$\boxed{\gamma = \left(\frac{d^2U}{dr^2}\right)_{r_e}}$$



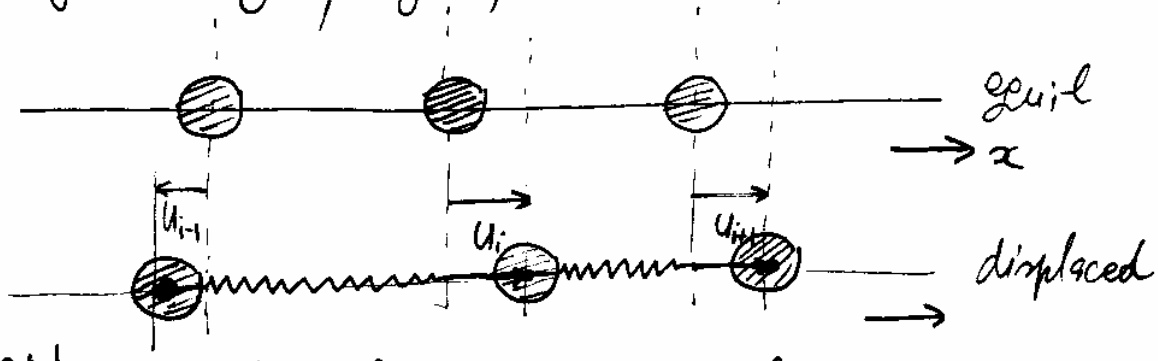
Generally, relative motion of particles with respect to one another can often viewed as motion of one particle of relative mass μ.

Now let us see what happens in a simple crystal.

• 1D lattice, atoms of mass M, 1 atom /primitive cell



u_i – displacement of the i-th atom from its equil. position
Imagine all ~~nodes~~ atoms are connected to their nearest neighbors by springs of constant γ



2nd Newton's law for particle at i-th site

$$M\frac{d^2u_i}{dt^2} = \gamma(u_{i+1}-u_i) - \gamma(u_i-u_{i-1})$$

If $u_{i+1}-u_i$, then the spring

is extended, which means that, in trying to shrink, it will draw the i-th atom to the right.
Similarly, if $u_i-u_{i-1}>0$, the spring from i-1 to i is extended, meaning it will draw the i-th ~~atom~~ atom to the left.

Hence the signs $+\gamma(u_{i+1}-u_i)$ and $-\gamma(u_i-u_{i-1})$

$$\boxed{M\frac{d^2u_i}{dt^2} = \gamma u_{i-1} - 2\gamma u_i + \gamma u_{i+1}}$$

If we assume a wave is propagating (similar to ~~the~~ a Bloch wave) it holds

$$u_{i+1}(t) = e^{iQa}\, u_i(t), \quad \text{and} \quad u_i(t) = e^{i\omega t}\, u_i(0)$$

Q, just like for electrons, is from the 1st Brillouin zone (any particle confined to a crystal will have ~~wave~~ wavevectors confined to the 1st BZ, with that equivalence $\vec{Q} + \vec{K} \longrightarrow$ equiv. to $\vec{Q}$

reciprocal latt. vector

$$-M\omega^2 u_i(t) = \gamma e^{-iQa} u_i(t) - 2\gamma u_i(t) + \gamma e^{iQa} u_i(t)$$

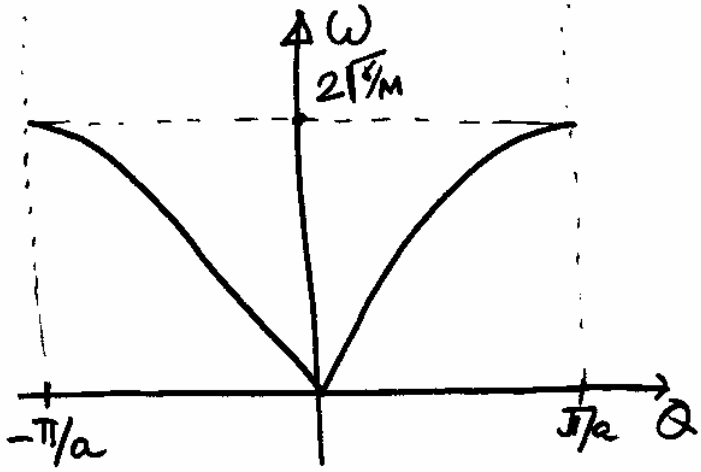
$$\left\{M\omega^2 - 2\gamma\left[1-\cos(Qa)\right]\right\} u_i(t) = 0$$

$$\boxed{\omega^2 = \frac{2\gamma}{M}\left[1-\cos(Qa)\right]}$$

Phonon dispersion relation for a lattice with monoatomic basis, with atoms of mass M.
Spring constant determined from details of inter-atomic interaction potential U.

$$\omega^2 = \frac{2\gamma}{M}\left[1-\cos(Qa)\right]$$
$$= \frac{4\gamma}{M}\sin^2\left(\frac{Qa}{2}\right)$$

$$\omega = 2\sqrt{\frac{\gamma}{M}}\left|\sin\left(\frac{Qa}{2}\right)\right|$$



When $Q \mapsto 0$ $\quad \omega(Q) \approx \cancel{2}\sqrt{\frac{\gamma}{M}} \cdot \frac{|Q|a}{\cancel{2}} = a\sqrt{\frac{\gamma}{M}}|Q|$

<u>Linear behavior</u> of ω with Q for small Q is characteristic for the so-called <u>ACOUSTIC MODES</u>. They are related to inherent materials ~~properties~~ elasticity properties

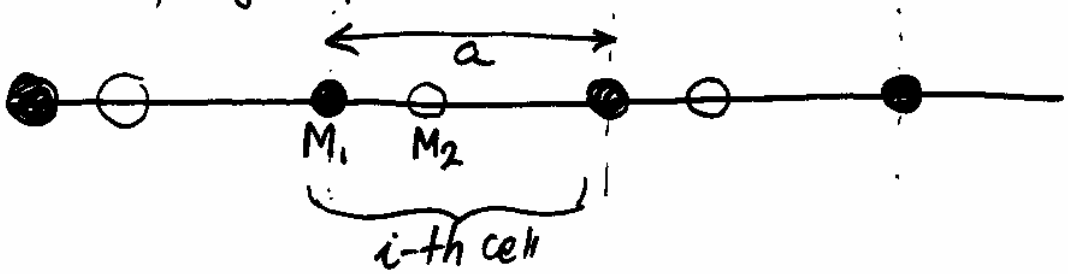
Namely, $\boxed{\lim_{Q\to 0^+} \frac{\omega(Q)}{Q} \equiv v_s}$ — THE SOUND VELOCITY

In this case, $\boxed{v_s = a\sqrt{\frac{\gamma}{M}}}$ ← Sound velocity depends on lattice spacing, bonding interaction ($\gamma \sim \kappa$) and mass

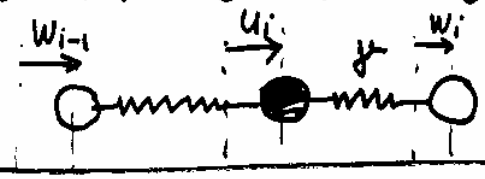
When $Q \to \pm\frac{\pi}{a}$, $\omega(Q) \to 2\sqrt{\frac{\gamma}{M}}$.

When there is <u>one atom in the basis</u>, no matter if the crystal is 1D, 2D, or 3D, there are only $\underbrace{\text{ACOUSTIC MODES}}_{\text{PHONON}}$ in that crystal.

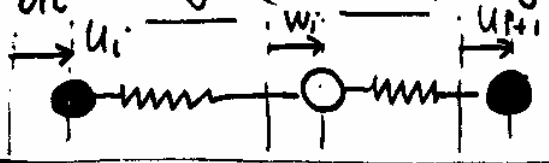
- 1D lattice, 2 atoms/prim. cell, masses M_1 and M_2 all springs of constant γ



Displacement of atom 1 in i-th cell denoted by u_i; of atom 2 in cell i → denoted by w_i.



$$\boxed{M_1 \frac{d^2 u_i}{dt^2} = \gamma (w_i - u_i) - \gamma (u_i - w_{i-1})}$$



$$\boxed{M_2 \frac{d^2 w_i}{dt^2} = \gamma (u_{i+1} - w_i) - \gamma (w_i - u_i)}$$

When putting
$$u_{i+1}(t) = e^{iQa} u_i(t)$$
$$w_{i+1}(t) = e^{iQa} w_i(t)$$
$$u_i(t) = u_i(0) e^{i\omega t}$$
$$w_i(t) = w_i(0) e^{i\omega t}$$

$$\boxed{\begin{aligned} &M_1 \omega^2 u_i(t) + \gamma w_i(t) + \gamma w_i(t) e^{-iQa} - 2\gamma u_i(t) = 0 \\ &M_2 \omega^2 w_i(t) + \gamma u_i(t) e^{iQa} + \gamma u_i(t) - 2\gamma w_i(t) = 0 \end{aligned}}$$

These form a linear, homogeneous system of algebraic equations for $u_i(t), w_i(t)$

$$\begin{bmatrix} M_1\omega^2 - 2\gamma & \gamma(1+e^{-iQa}) \\ \gamma(1+e^{iQa}) & M_2\omega^2 - 2\gamma \end{bmatrix} \begin{bmatrix} u_i \\ w_i \end{bmatrix} = 0$$

$$(M_1\omega^2 - 2\gamma)(M_2\omega^2 - 2\gamma) - \gamma^2(1+e^{iQa})(1+e^{-iQa}) = 0$$

$$\omega^4 \cdot M_1M_2 - 2\gamma\omega^2(M_1+M_2) + \underbrace{4\gamma^2 - \gamma^2[2+2\cos(Qa)]}_{+2\gamma^2(1-\cos(Qa))} = 0$$

$$\omega^4 M_1M_2 - 2\gamma\omega^2(M_1+M_2)$$

$$\omega^2 = \frac{1}{M_1M_2}\left\{\gamma(M_1+M_2) \pm \sqrt{(M_1+M_2)^2\gamma^2 - M_1M_2 \cdot 2\gamma^2[1-\cos(Qa)]}\right\}$$

$$= \gamma\left(\frac{M_1+M_2}{M_1M_2}\right)\left\{1 \pm \sqrt{1 - 2\,\frac{[1-\cos(Qa)]M_1M_2}{(M_1+M_2)^2}}\right\}$$

There are obviously two modes (due to 2 atoms in the basis)

Let's investigate behavior near $|Q| \to 0$, and near $|Q| \to \pi/a$.

$$|Q| \to 0 \quad 1-\cos(Qa) \approx 1 - \left(1 - \frac{1}{2}(Qa)^2 + o((Qa)^4)\right)$$
$$= \frac{1}{2}(Qa)^2 + o((Qa)^4)$$

$$\sqrt{1 - 2\frac{(1-\cos(Qa))\,M_1M_2}{(M_1+M_2)^2}} = \sqrt{1 - \frac{(Qa)^2 M_1 M_2}{(M_1+M_2)^2}} \approx 1 - \frac{1}{2}(Qa)^2\frac{M_1M_2}{(M_1+M_2)^2}$$

$$\omega^2 = \gamma\frac{M_1+M_2}{M_1M_2}\left\{1 \pm \left(1 - \frac{1}{2}(Qa)^2\frac{M_1M_2}{(M_1+M_2)^2}\right)\right\}$$

$$\omega_-^2 = \gamma\frac{\cancel{M_1+M_2}}{\cancel{M_1M_2}}\cdot\frac{1}{2}(Qa)^2\frac{\cancel{M_1M_2}}{(M_1+M_2)^{\cancel{2}}} = \frac{1}{2}\gamma\frac{(Qa)^2}{M_1+M_2}$$

$$\boxed{\omega_- = |Q|\,a\sqrt{\frac{\gamma}{2(M_1+M_2)}}}$$

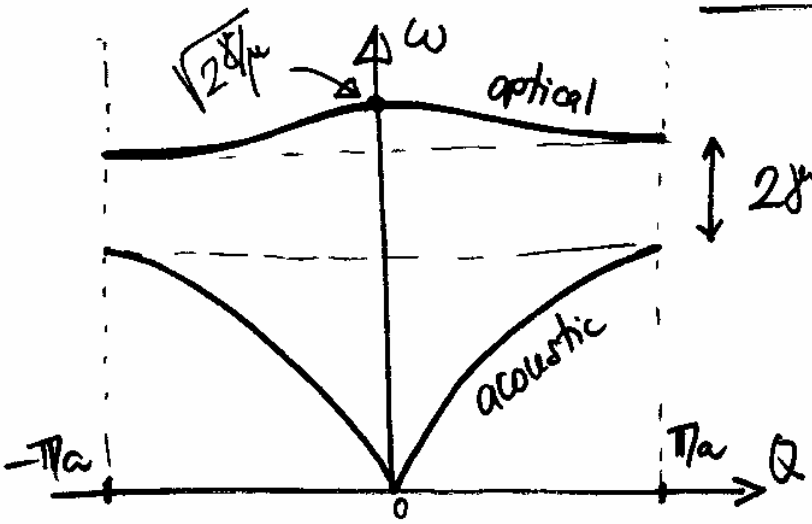
This is obviously an acoustic mode, with $v_s = a\sqrt{\frac{\gamma}{2(M_1+M_2)}}$

The other solution is given by

$$\boxed{\omega_+^2 = 2\gamma\frac{M_1+M_2}{M_1M_2} - \frac{1}{2}\gamma\frac{(Qa)^2}{(M_1+M_2)^2}}$$

when $Q \to 0$ $\quad \omega_+^2 \to 2\gamma\frac{M_1+M_2}{M_1M_2} = 2\frac{\gamma}{\mu}$

So this is a so-called <u>OPTICAL PHONON MODE</u>.



$\omega_-(\pi/a)$

$$2\gamma\frac{M_1+M_2}{M_1M_2}\cdot\sqrt{1 - 4\frac{M_1M_2}{(M_1+M_2)^2}}$$

Important things to remember:

- In 1D, both acoustic & optical phonons can only be longitudinal. In ~~m~~ 2D and 3D, they can be both longitudinal and transverse.

In general, for a D-dimensional crystal, with Nb basis atoms per primitive cell, the <u>total number</u> of phonon modes is

$$D \cdot Nb$$

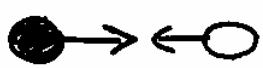
Out of these, D are acoustic : 1 longitudinal, (LA)
D−1 transverse (TA)

~~Out of the re~~ The remaining $D(Nb-1)$ are transverse phonon modes; $Nb-1$ are longitudinal (LO), and $(D-1)(Nb-1)$ are transverse (TO).

- Note how for electrons we had <u>bands</u>, and for phonons we have <u>modes</u>. The number of different modes is determined by the structure of the lattice only: dimensionality and # of basis atoms.

- In a lattice with 2 atoms in the basis, the 2 atoms move

<u>in phase</u> for <u>acoustic modes</u>



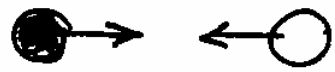
<u>out of phase</u> for <u>optical modes</u>

One can deduce this directly by taking the solutions for $\omega_\pm$, and solving for $u_i(t)$ and $w_i(t)$

acoustic : $w_i = u_i \times$ positive # ; optical : $w_i = u_i \times$ neg. #

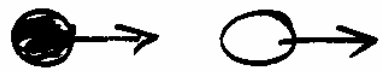
One can see this also by noting that in ω_+, which describes optical phonons, the mass present is the REDUCED MASS, which is associated with relative motion of ions, one with respect to the other

$$\omega_+(0) = \sqrt{\frac{2\gamma}{\mu}}$$



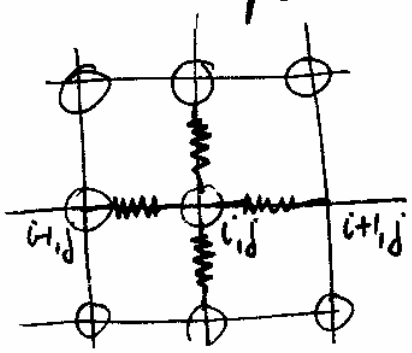
For ~~optical~~ acoustic phonons, however

$$Q \to 0 \quad \omega_-(Q) = |Q|\, a \sqrt{\frac{\gamma}{2(M_1+M_2)}}$$



Mass $M_1+M_2 = M_{tot}$ is associated with the motion of the center of mass of the two ions, i.e., with the motion of them as one particle of mass M_{tot}.

- In multiple dimensions, there would be $N_b \cdot D$ equations to solve: each atom's $\vec{u}_i$ has D components!



If unsure how to determine the force on a certain atom, simply consider the terms in the potential energy due to that atom (e.g. for a square lattice in the Figure)

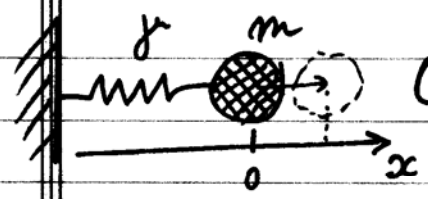
$$\mathcal{U}_{tot} = \ldots + \frac{\gamma}{2}(\vec{u}_{i+1,j} - \vec{u}_{i,j})^2 + \frac{\gamma}{2}(\vec{u}_{i-1,j} - \vec{u}_{i,j})^2 + \gamma/2\,(\vec{u}_{i,j+1} - \vec{u}_{i,j})^2 + \frac{\gamma}{2}(\vec{u}_{i,j-1} - \vec{u}_{i,j})^2 + \ldots \text{ other lattice nodes}$$

Force on i-th atom

$$\vec{F}_i = -\frac{\partial \mathcal{U}}{\partial \vec{u}_i} = -\vec{e}_x \frac{\partial \mathcal{U}}{\partial u_{x,i}} - \vec{e}_y \frac{\partial \mathcal{U}}{\partial u_{y,i}}$$

Nov. 2006

Quantization of one harmonic oscillator



Classically: $m\ddot{x} = -\gamma x$

$$\ddot{x} + \frac{\gamma}{m} x = 0$$

Oscillations w/ frequency ω: $\boxed{\omega^2 = \gamma/m}$

<u>Quantum-mechanically</u> First write the total energy, and then quantize it to get the Hamilton operator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{\gamma x^2}{2} \leftarrow \text{potential energy of the spring}$$

Solve the eigenproblem of this Hamiltonian — — one can find it in any textbook on quantum mechanics.

Here, we will use a shortcut to obtain the energies in a way that will also reveal the concept of phonons later on.

Let us first rewrite $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2 x^2}{2}$

Introduce auxiliary ~~qu~~ operators $\tilde{p}$ & $\tilde{x}$ so that in terms of them

$$\hat{H} = \hbar\omega(\tilde{p}^2 + \tilde{x}^2) \qquad \tilde{p} = \hat{p} \cdot \frac{1}{\sqrt{2m\hbar\omega}}$$

$$\tilde{x} = x\sqrt{\frac{m\omega}{2\hbar}} \qquad (1)$$

Then introduce two more auxiliary operators

$$b = \tilde{x} + i\tilde{p} \; ; \; b^{+} = \tilde{x} - i\tilde{p}$$

Commutator of two operators or matrices

$$[A,B] = AB - BA$$

Clearly $[A,A] = 0$, also $[A,B] = -[B,A]$

b, b^{+} are not Hermitian.

$$[b, b^{+}] = -i\,[\tilde{x}, \tilde{p}] + i\,[\tilde{p}, \tilde{x}]$$

$$= +2i\,[\tilde{p}, \tilde{x}] = +2i \frac{1}{\sqrt{2m\hbar\omega}} \cdot \sqrt{\frac{m\omega}{2\hbar}}\,[\hat{p}, x]$$

$$= \frac{i}{\hbar}[\hat{p}, x]$$

Commutator of $[\hat{p}, x]$ is one of the fundamental relations in quantum mechanics. It can be computed by having it act on a wavefunction

$$[\hat{p}, x]\psi = \hat{p}x\psi - x\hat{p}\psi = \left(-i\hbar\frac{\partial}{\partial x}(x\psi) - x\left(-i\hbar\frac{\partial\psi}{\partial x}\right)\right)$$

$$= -i\hbar\psi \implies \boxed{[\hat{p}, x] = -i\hbar}$$

$$[b, b^{+}] = \frac{i}{\hbar} \cdot -i\hbar = 1$$

$$\boxed{[b, b^{+}] = 1}$$

~~then op~~

$[b, b^+] = 1$ This commutation relation denotes that b and b^+ destroy & create, respectively, a particle that is a <u>boson</u>.

$b^+ b = \hat{n}$ is the ~~[illegible]~~ boson number operator. It is an operator whose eigenvalues are $0, 1, 2, 3, \ldots$

If we try to rewrite the Hamiltonian in terms of b and b^+

$$\tilde{p} = \frac{b - b^+}{2i}, \quad \tilde{x} = \frac{b + b^+}{2}$$

$$\hat{H} = \hbar\omega(\tilde{p}^2 + \tilde{x}^2) = \hbar\omega\left[\frac{(b-b^+)^2}{-4} + \frac{(b+b^+)^2}{4}\right]$$

(Be careful about the square, as $bb^+ \neq b^+ b$!)

$$\hat{H} = \hbar\omega\left[\frac{b^2 + b^{+2} - bb^+ - b^+ b}{-4} + \frac{b^2 + b^{+2} + bb^+ + b^+ b}{4}\right]$$

$$= \frac{\hbar\omega}{2}(bb^+ + b^+ b)$$

from $[b, b^+] = bb^+ - b^+ b = 1$

$bb^+ = 1 + b^+ b$

$$= \frac{\hbar\omega}{2}(2b^+ b + 1) = \hbar\omega(b^+ b + 1/2)$$

$$\boxed{\hat{H} = \hbar\omega(b^+ b + 1/2) = \hbar\omega(\hat{n} + 1/2)}$$

So the eigenvectors of $\hat{H}$ are the same as the eigenvectors of $\hat{n}$ (see the next page), and so are the eigenvalues:

$$\hat{H} = \hbar\omega(\hat{n} + 1/2) \rightarrow \mathcal{E}_n = \hbar\omega(n + 1/2), \quad n = 0, 1, 2, \ldots$$

Ground state has the energy $\mathcal{E}_0 = \hbar\omega/2$.

You can think of a harmonic oscillator as a mass on a spring (equivalently, a real particle in a <u>parabolic</u> potential)

Alternatively, you can think of it as a collection of particles, which are bosons and have the energy $\hbar\omega$.

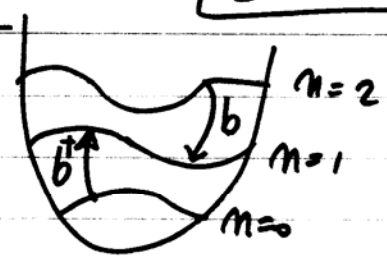
Absence of particles $(n=0)$ $\quad \mathcal{E}_0 =$

n particles present $\quad \mathcal{E}_n = \hbar\omega(n + 1/2)$
Corresponds to eigenvector $|n\rangle$

Creation / destruction operators create / destroy these particles

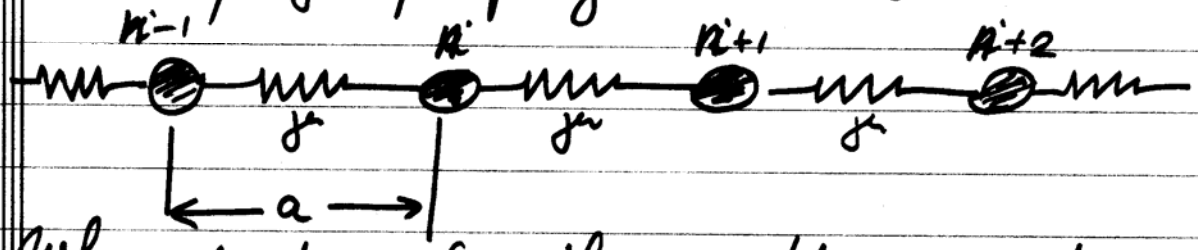
$$\boxed{b|n\rangle = \sqrt{n}\,|n-1\rangle} \qquad \boxed{b^+|n\rangle = \sqrt{n+1}\,|n+1\rangle}$$

$(b|0\rangle = 0)$

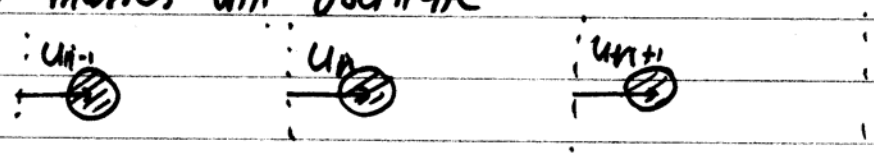


Quantization of a chain of oscillators : Phonons

Let's assume you have N atoms connected with springs of spring constant γ



When displaced from their equilibrium positions, these masses will oscillate



The Hamiltonian of this chain of <u>coupled</u> oscillators can be written as

$$\hat{H} = \sum_{n=1}^{N} \frac{\hat{p}_n^2}{2M} + \sum_{n=1}^{N-1} \frac{\gamma (u_n - u_{n+1})^2}{2}$$

Instead of speaking of displacements and momenta associated with individual atoms, we can introduce displacements and momenta associated with waves (lattice waves) of a given wavevector k

$$\hat{p}_n = \frac{1}{\sqrt{N}} \sum_k e^{ikna} \hat{p}_k$$

$$u_n = \frac{1}{\sqrt{N}} \sum_k e^{ikna} u_k$$

The Hamiltonian can be rewritten as

$$\hat{H} = \frac{1}{2M} \sum_k \hat{P}_k \hat{P}_{-k} + \frac{M}{2} \sum_k \omega_k^2 u_k u_{-k}$$

where ω_k^2 can be found by using the so-called dynamical matrix, or, equivalently, the way we did in class.

Furthermore, if we introduce auxiliary ~~quant~~ unitless operators $\tilde{p}_k$ and $\tilde{u}_k$ as

$$\tilde{p}_k = p_k \frac{1}{\sqrt{2M\hbar\omega_k}}, \quad \tilde{u}_k = u_k \sqrt{\frac{M\omega_k}{2\hbar}}$$

the Hamiltonian can be further rewritten as

$$\hat{H} = \sum_k \hbar\omega_k \left(\tilde{p}_k \tilde{p}_{-k} + \tilde{u}_k \tilde{u}_{-k} \right)$$

We can introduce the operators of creation & destruction of a lattice wave w/ wavevector k:

creation: $b_k^+ = (\tilde{u}_{-k} - i\tilde{p}_k)$ for all k

destruction: $b_k = (\tilde{u}_k + i\tilde{p}_{-k})$

These satisfy $[b_k, b_{k'}^+] = \delta_{kk'}$

which ~~denotes~~ ~~the~~ manifests ~~itself~~ the fact that the waves of different k's are <u>normal</u> — mutually independent excitations.

So the Hamiltonian of N coupled oscillators can be actually rewritten as

$$\hat{H} = \sum_k \hbar\omega_k \left(\underbrace{b_k^+ b_k}_{\hat{n}_k} + 1/2 \right)$$

$\hat{n}_k$ – the number operator for the mode with wavevector k

Lattice ~~wit~~ waves with different wavevectors are the <u>normal modes</u> of the system.

* What is a phonon? A phonon is a quantum of lattice vibrations. A phonon can have momentum k from the 1st Brillouin zone & it has the energy $\underline{\underline{\hbar\omega_k}}$. Phonons are bosons of spin 0.

* How much energy is associated with a lattice wave of wavevector k? In the phonon picture, the energy depends on how many phonons you have. A state $|n_k\rangle$ has n_k phonons & therefore the energy $\hbar\omega_k(n_k + 1/2)$; $n_k = 0, 1, 2, 3, \ldots$

* If you keep your lattice at temperature T, what is the average number of phonons w/ wavevector k? It is given by the Bose–Einstein distribution

$$\langle n_k \rangle = \frac{1}{e^{\hbar\omega_k/k_BT} - 1}$$

average number of phonons in mode k.

Additional useful relationships:

Creation operator creates a phonon:

$$b_k^+ |n_k\rangle = \sqrt{n_k+1}\, |n_k+1\rangle \quad \left(\begin{matrix}\text{from } |n_k\rangle \\ \text{to } |n_k+1\rangle\end{matrix}\right)$$

Destruction operator destroys a phonon:

$$b_k |n_k\rangle = \sqrt{n_k}\, |n_k-1\rangle \quad \left(\begin{matrix}\text{from } |n_k\rangle \\ \text{to } |n_k-1\rangle\end{matrix}\right)$$

* The displacement operator associated w/ a mode of wavevector k actually changes with time:

$$u_k(t) = \frac{1}{2}\left(\frac{2\hbar}{M\omega_k}\right)^{1/2}\left(b_k e^{-i\omega_k t} + b_{-k}^+ e^{i\omega_k t}\right)$$

From it, one can find how an atom's displacement changes w/ time

$$u_n(t) = \sum_k \left(\frac{\hbar}{2MN\omega_k}\right)^{1/2}\left(b_k e^{-i\omega_k t} + b_{-k} e^{i\omega_k t}\right) e^{ikna}$$

One can even go as far as to talk about a displacement field

$$u(x,t) = \sum_k \left(\frac{\hbar}{2\rho V\omega_k}\right)^{1/2}\left(b_k e^{-i\omega_k t} + b_{-k} e^{i\omega_k t}\right) e^{ikx}$$

which is the form we will use to create the models for scattering w/ different types of phonons.

- Further reading: Philip Phillips, "Advanced Solid State Physics", Chapter 10

Scattering in Semiconductors

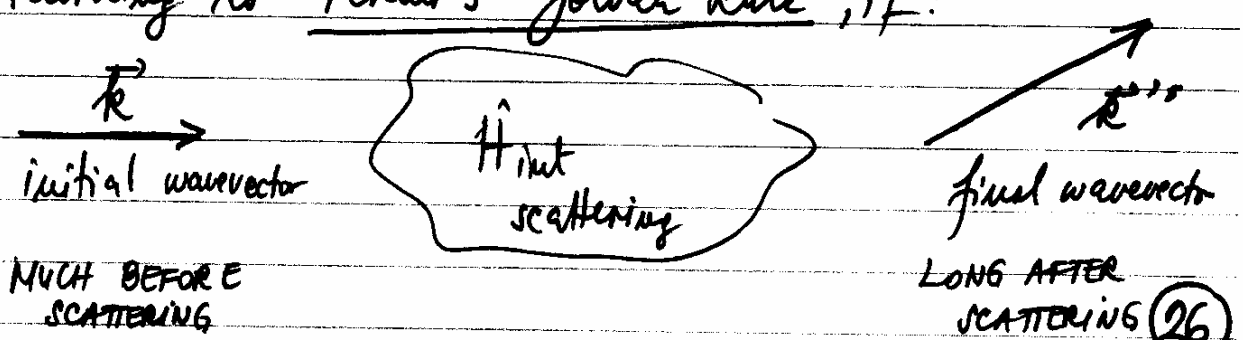
Whenever an electron scatters, that happens due to another particle or a collection of particles, with which the electron interacts. One can generally describe this interaction through an extra term in the electron Hamiltonian, and this term is in general time-dependent (if scattering is inelastic).

Since most of the "action" for an electron in a semiconductor under bias (low bias, that is) occurs near the bottom of the conduction band, where an electron behaves as though it is virtually free (with an effective mass, though), i.e., we don't see the effects from Brillouin zone boundaries, we can just write

$$\phi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, u_{\vec{k}}(\vec{r})$$

$$\mathcal{E}(\vec{k}) = \frac{\hbar^2}{2m^*}k^2$$ (remember that m^* can incorporate information about anisotropy of the effective mass tensor and valley degeneracy)

According to <u>Fermi's Golden Rule</u>, if:



Transition Rates from Fermi's Golden Rule

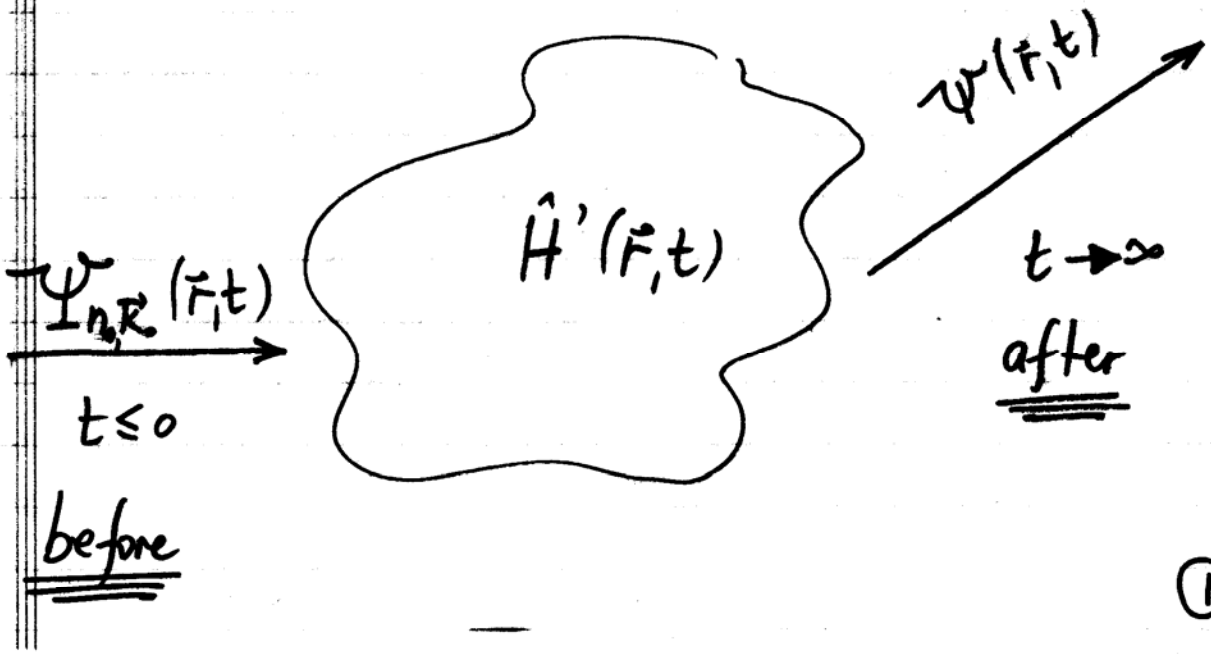
Without scattering centers – phonons, impurities, interfaces, an electron is described by the Bloch wave fn

$$\Psi_{n,\vec{k}_0}(\vec{r},t) = \phi_{n,\vec{k}_0}(\vec{r})\, e^{-iE_{n,\vec{k}_0}t/\hbar} \qquad \text{at } t \le 0$$

that is the eigensolution to the crystalline Hamiltonian

$$\hat{H}_0 |\phi_{n,\vec{k}_0}\rangle = \varepsilon_{n,\vec{k}_0} |\phi_{n,\vec{k}_0}\rangle$$

Now imagine that such an electron comes across a scattering center, described by a generally time-dependent scattering potential $\hat{H}'(\vec{r},t)$. What is the wavefunction of the scattered electron a long time after the scattering?



Let's write the wavefunction $\Psi(\vec{r},t)$ at $t>0$ as a ~~functio~~ linear combination of Bloch waves, which we can do because they constitute a basis

$$\Psi(\vec{r},t) = \sum_{n,\vec{k}} C_{n,\vec{k}}(t)\, \Psi_{n,\vec{k}}(\vec{r},t)$$

where, at $t=0$ $\quad C_{n_0,\vec{k}_0}(0) = 1$

$C_{n,\vec{k}}(0) = 0$ if $n \neq n_0$ or $\vec{k} \neq \vec{k}_0$

The probability of finding the particle in state $\Psi_{n,\vec{k}}$ at time $t>0$ is just $|C_{n,\vec{k}}(t)|^2$.

<u>Transition rate</u> is the increase in this probability per unit time a long time after the collision

$$S(\underbrace{n_0\vec{k}_0}_{\text{initial}};\underbrace{n\vec{k}}_{\text{final}}) = \lim_{t\to\infty} \frac{|C_{n,\vec{k}}(t)|^2}{t}$$

This is the transition rate to go from $n_0,\vec{k}_0$ to $n,\vec{k}$.

So how does $C_{n,\vec{k}}(t)$ change in time? Schrödinger equation describes this evolution:

$$\left[\hat{H}_0 + \hat{H}'(t)\right]\Psi(\vec{r},t) = i\hbar \frac{\partial \Psi(\vec{r},t)}{\partial t}$$

$$\hat{H}_0 \sum_{n,\vec{k}} \cancel{C_{n,\vec{k}}(t)\, \Psi_{n,\vec{k}}(t)} + \hat{H}'(t) \sum_{n,\vec{k}} C_{n,\vec{k}}(t)\, \Psi_{n,\vec{k}}(\vec{r},t) =$$

$$= \sum_{n,\vec{k}} \left(\cancel{\mathcal{E}_{n,\vec{k}} C_{n,\vec{k}}(t)} \Psi_{n,\vec{k}}(t) + i\hbar \frac{\partial C_{n,\vec{k}}(t)}{\partial t} \Psi_{n,\vec{k}}(t) \right)$$

$$\sum_{n,\vec{k}} C_{n,\vec{k}}(t) \; \hat{H}'(t) \Psi_{n,\vec{k}}(\vec{r},t) = \sum_{n,\vec{k}} i\hbar \frac{\partial C_{n,\vec{k}}(t)}{\partial t} \Psi_{n,\vec{k}}(t)$$

Pick $n', \vec{k}'$, multiply both sides by $\Psi^*_{n',\vec{k}'}(\vec{r},t)$ and integrate over all $\vec{r}$'s.

$$\sum_{n,\vec{k}} C_{n,\vec{k}}(t) \int d^3\vec{r} \, \Psi^*_{n',\vec{k}'}(\vec{r},t) \hat{H}'(t) \Psi_{n,\vec{k}}(\vec{r},t)$$

$$= \sum_{n,\vec{k}} i\hbar \frac{\partial C_{n,\vec{k}}(t)}{\partial t} \underbrace{\int d^3\vec{r} \, \Psi^*_{n',\vec{k}'}(\vec{r},t) \Psi_{n,\vec{k}}(\vec{r},t)}_{\text{this is } \langle \Psi_{n',\vec{k}'} | \Psi_{n,\vec{k}} \rangle = \delta_{nn'} \delta_{\vec{k}\vec{k}'}}$$

$$i\hbar \frac{\partial C_{n',\vec{k}'}(t)}{\partial t} = \sum_{n,\vec{k}} C_{n,\vec{k}}(t) \underbrace{\langle \Psi_{n',\vec{k}'} | \hat{H}'(t) | \Psi_{n,\vec{k}} \rangle}_{\text{the matrix element of the scattering potential between } n,\vec{k} \text{ \& } n',\vec{k}'}$$

All C's start as very small, except $C_{n_0,\vec{k}_0} = 1$ at $t=0$. This coefficient will remain dominant even after the scattering, so in the sum on the RHS we basically can just retain the term with $n_0, \vec{k}_0$:

$$i\hbar \frac{\partial C_{n,\vec{k}}(t)}{\partial t} = \langle \Psi_{n,\vec{k}} | \hat{H}'(t) | \Psi_{n_0,\vec{k}_0} \rangle$$

(I've removed the primes from $n, \vec{k}$, as there is no more sum in which they were dummy arguments.)

$$C_{n,\vec{k}}(t) = \cancel{C_{n,\vec{k}}(0)}^{\,0} - \frac{i}{\hbar}\int_0^t \langle \phi_{n,\vec{k}} | \hat{H}'(t) | \phi_{n_0\vec{k}_0} \rangle \times$$

$$\times\, e^{-\frac{i}{\hbar}(\mathcal{E}_{n_0,\vec{k}_0} - \mathcal{E}_{n,\vec{k}})t}\, dt$$

Now assume $\hat{H}' = \hat{H}'^{a,e}(\vec{r})\, e^{\mp i\omega t}$

$$\langle \phi_{n,\vec{k}} | \hat{H}'(t) | \phi_{n,\vec{k}_0} \rangle =$$

$$= \underbrace{\langle \phi_{n,\vec{k}} | \hat{H}'^{a,e} | \phi_{n_0,\vec{k}_0} \rangle}_{\int d^3\vec{r}\, \phi^*_{n,\vec{k}}(\vec{r})\, \hat{H}^{a,e}(\vec{r})\, \phi_{n_0,\vec{k}_0}(\vec{r})}\, e^{\mp i\omega t}$$

this is the relevant matrix element we'll denote as

$$H'^{a,e}_{\underbrace{n,\vec{k}}_{\text{final}};\underbrace{\vec{n}_0,\vec{k}_0}_{\text{initial}}}$$

$$C_{n,\vec{k}}(t) = -\frac{i}{\hbar}\int_0^t H'^{a,e}_{n,\vec{k};n_0,\vec{k}_0}\, e^{-\frac{i}{\hbar}(\mathcal{E}_{n_0,\vec{k}_0} \pm \hbar\omega - \mathcal{E}_{n,\vec{k}})t}\, dt$$

$$= -\cancel{\frac{i}{\hbar}}\, H'^{a,e}_{n,\vec{k};n_0,\vec{k}_0}\, \frac{e^{-\frac{i}{\hbar}(\mathcal{E}_{n_0,\vec{k}_0} \pm \hbar\omega - \mathcal{E}_{n,\vec{k}})t} - 1}{-\cancel{\frac{i}{\hbar}}(\mathcal{E}_{n_0,\vec{k}_0} \pm \hbar\omega - \mathcal{E}_{n,\vec{k}})}$$

$$= H'^{a,e}_{n,\vec{k};n_0,\vec{k}_0}\, \frac{e^{\frac{i}{2\hbar}(\mathcal{E}_{n,\vec{k}} - \mathcal{E}_{n_0,\vec{k}_0} \mp \hbar\omega)t}\, 2i\sin\left[\left(\frac{\mathcal{E}_{n,\vec{k}} - \mathcal{E}_{n_0,\vec{k}_0} \mp \hbar\omega}{2\hbar}\right)t\right]}{-(\mathcal{E}_{n,\vec{k}} - \mathcal{E}_{n_0,\vec{k}_0} \mp \hbar\omega)}$$

$$= \frac{1}{i\hbar} H'^{a,e}_{n\vec{k};n_0\vec{k}_0}\, e^{i\frac{\lambda t}{2}}\, \frac{\sin(\lambda t/2)}{\lambda t/2} \cdot t, \quad \text{where } \lambda = \frac{\mathcal{E}_{n,\vec{k}} - \mathcal{E}_{n_0\vec{k}_0} \mp \hbar\omega}{\hbar}$$

$$S(\underbrace{n_0\vec{k}_0}_{\text{initial}};\underbrace{n\vec{k}}_{\text{final}}) = \lim_{t\to\infty} \frac{|C_{n,\vec{k}}(t)|^2}{t}$$

$$= \frac{1}{\hbar^2} \left| H'^{a,e}_{n\vec{k};n_0\vec{k}_0} \right|^2 \underbrace{\lim_{t\to\infty} \frac{\sin^2(\lambda t/2)}{\left(\frac{\lambda}{2}\right)^2 t}}_{\text{this behaves as } \pi\delta(\lambda/2) = 2\pi\delta(\lambda)}$$

$$= 2\pi\hbar\,\delta(\mathcal{E}_{n,\vec{k}} - \mathcal{E}_{n_0,\vec{k}_0} \mp \hbar\omega)$$

$$\boxed{S(n_0,\vec{k}_0;n,\vec{k}) = \frac{2\pi}{\hbar} \underbrace{\left| H'^{a,e}_{n_0,\vec{k}_0;n_0\vec{k}_0} \right|^2}_{\text{matrix element}} \delta(\mathcal{E}_{n,\vec{k}} - \mathcal{E}_{n_0,\vec{k}_0} \mp \hbar\omega)}$$

different scattering mechanisms differ in this term

Transition rate from $\phi_{\vec{k}}$ to $\phi_{\vec{k}'}$, under the time-dependent interaction Hamiltonian

$$\boxed{\hat{H}'(\vec{r},t) = \hat{H}_{int}(\vec{r})\, e^{-i\omega t}}$$

is given by

$$\mathcal{S}(\vec{k},\vec{k}') = \frac{2\pi}{\hbar} \left|\hat{H}_{int\,\vec{k}',\vec{k}}\right|^2 \delta(\varepsilon(\vec{k}') - \varepsilon(\vec{k}) - \hbar\omega)$$

Ferry calls it P initial final

where $\hat{H}_{int\,\vec{k}',\vec{k}} = \langle \phi_{\vec{k}'} | \hat{H}_{int} | \phi_{\vec{k}} \rangle$

final time-indep. part of $\hat{H}'$ initial

For Bloch functions

$$\hat{H}_{int\,\vec{k}',\vec{k}} = \frac{1}{V}\int d^3\vec{r}\; e^{-i\vec{k}'\cdot\vec{r}}\, u^*_{\vec{k}'}(\vec{r})\, \hat{H}_{int}(\vec{r})\, u_{\vec{k}}(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}$$

$$= \frac{1}{V}\sum_{\vec{R}} \int_{\Omega} d^3\vec{r}'\, u^*_{\vec{k}'}(\vec{r}')\, H_{int}(\vec{r}')\, u_{\vec{k}}(\vec{r}')\, e^{-i(\vec{k}'-\vec{k})\cdot\vec{r}'} \times e^{-i(\vec{k}'-\vec{k})\cdot\vec{R}}$$

one cell

Potential $\vec{H}_{int}$ does not have to be periodic, on the contrary, because it in general isn't periodic is that we have scattering of Bloch electrons to begin with.

$$H_{int}(\vec{r}) = \sum_{\vec{Q}} \tilde{H}_{int}(\vec{Q})\, e^{i\vec{Q}\cdot\vec{r}}$$

$$\hat{H}_{int\,\vec{k}'\vec{k}} = \frac{1}{V}\sum_{\vec{R},\vec{Q}} \int d^3\vec{r}'\, e^{-i(\vec{k}'-\vec{k}-\vec{Q})\vec{r}'}\, u^*_{\vec{k}'}(\vec{r}')\, u_{\vec{k}}(\vec{r}') \times$$
$$\times\ \tilde{H}_{int}(\vec{Q})\ e^{-i(\vec{k}'-\vec{k}-\vec{Q})\vec{R}}$$

$\vec{Q}$ is in general $\vec{q}$ from the 1st B.Z. + a reciprocal lattice vector $\vec{K}$; we will consider $\vec{K}=0$ processes here

$$\sum_{\vec{R}} e^{-i(\vec{k}'-\vec{k}-\vec{Q})\cdot\vec{R}} = N\cdot \delta_{\vec{k}'-\vec{k}-\vec{Q}} \quad \text{(Kronecker delta)}$$

$$\hat{H}_{int\,\vec{k}',\vec{k}} = \frac{1}{V}\cdot N \cdot \int d^3\vec{r}'\, u^*_{\vec{k}'}(\vec{r}')\, u_{\vec{k}}(\vec{r}') \times \tilde{H}_{int}(\vec{k}'-\vec{k})$$

For parabolic bands, the so-called overlap integral

$$\int d^3\vec{r}'\, u^*_{\vec{k}'}(\vec{r}')\, u_{\vec{k}}(\vec{r}') \approx \underset{\text{unit cell volume}}{\Omega}\, \delta_{\vec{k}',\vec{k}}$$

$$\underbrace{\hat{H}_{int\,\vec{k}',\vec{k}}}_{\text{from sandwich with Bloch functions}} = \underbrace{\tilde{H}_{int}(\vec{k}'-\vec{k})}_{\text{this from Fourier series}} = \underbrace{\frac{1}{V}\int d^3\vec{r}\, e^{-i(\vec{k}'-\vec{k})\vec{r}}\, \hat{H}_{int}(\vec{r})}_{\text{often denoted by } M(\vec{k},\vec{k}')}$$

It is important that we have related the matrix element for Bloch waves + parabolic bands with that for a free electron (it will significantly simplify calculation)!

Therefore, as far as scattering rates go, we can think of Bloch electrons as truly free electrons $\psi_{\vec{k}}(\vec{r}) = \frac{e^{i\vec{k}\vec{r}}}{\sqrt{V}}$

Phonon Scattering in Non-Polar Semiconductors

- <u>Acoustic phonon scattering</u>
  (a.k.a. deformation potential scattering)

We have seen that acoustic modes are related to the motion of the crystal as "a whole", so what scatters electrons are the displacement variations between atoms. A model interaction Hamiltonian that describes interaction of an electron with acoustic phonons

$$\hat{H}' = \Xi_1 \cdot \left[\vec{\nabla} \cdot \hat{\vec{u}}(\vec{r},t)\right]$$

where Ξ_1 is the DEFORMATION POTENTIAL, and $\hat{\vec{u}}(\vec{r},t)$ is the DISPLACEMENT OPERATOR (obtained by quantization of classical displacement). The displacement operator is related to creation & destruction of phonons with different $\vec{Q}$'s:

$$\boxed{\hat{\vec{u}}(\vec{r},t) = \left(\frac{\hbar}{2\rho V}\right)^{1/2} \sum_{\vec{Q}} \left[\frac{1}{\omega_{\vec{Q}}}\right]^{1/2} \left\{ \hat{a}_{\vec{Q}}\, e^{i\vec{Q}\vec{r} - i\omega_{\vec{Q}} t} + \hat{a}^{+}_{\vec{Q}}\, e^{-i\vec{Q}\vec{r} + i\omega_{\vec{Q}} t} \right\} \vec{e}_{\vec{Q}}}$$

$\hat{a}_{\vec{Q}}$ – destruction operator of a phonon with wavevector $\vec{Q}$ after destruction (i.e., after the electron has absorbed the phonon), the electron gains wavevector $\vec{Q}$ and energy $\hbar\omega_{\vec{Q}}$

$\hat{a}^+_{\vec{Q}}$ – creation operator of a phonon with wavevector $\vec{Q}$
creation of a phonon (emission of a phonon by an electron) is accompanied by the electron losing momentum $\hbar\vec{Q}$ and energy $\hbar\omega_{\vec{Q}}$, hence the phase factor $\exp(-i\vec{Q}\vec{r} + i\omega_{\vec{Q}}t)$

So the interaction Hamiltonian is given by

$$\hat{H}' = \Xi_1 \cdot \sum_{\vec{Q}}{}' \left(\frac{\hbar}{2\rho V \omega_{\vec{Q}}}\right)^{1/2} (i\vec{Q}\cdot\vec{e}_{\vec{Q}}) \left\{ \hat{a}_{\vec{Q}}\, e^{i\vec{Q}\vec{r} - i\omega_{\vec{Q}}t} - \hat{a}^+_{\vec{Q}}\, e^{-i\vec{Q}\vec{r} + i\omega_{\vec{Q}}t} \right\}$$

We see that only for longitudinal polarization $\vec{e}_{\vec{Q}} \parallel \vec{Q}$ we get non-zero contribution (the model described works well for longitudinal phonons; for transverse acoustic phonons the [acoustic] situation is different.

- A notable feature is that we can definitely pinpoint phonon absorption & phonon emission as two different scattering processes.

$$\hat{H}' = \hat{H}'_{abs} + \hat{H}'_{emission}$$

- What is the electron scattering from? A "bath" of phonons. How many of them do we have with wavevector $\vec{Q}$? $N_{\vec{Q}}$, given by the Bose-Einstein distribution function

$$\boxed{N_{\vec{Q}} = \frac{1}{e^{\frac{\hbar\omega_{\vec{Q}}}{k_B T}} - 1}}$$

k_B – the Boltzmann constant

Absorption: electron: $\vec{k} \longrightarrow \vec{k}+\vec{Q}$
phonon #: $N_{\vec{Q}} \rightarrow N_{\vec{Q}} - 1$

Emission: electron: $\vec{k} \rightarrow \vec{k} - \vec{Q}$
phonon #: $N_{\vec{Q}} \rightarrow N_{\vec{Q}} + 1$

So consider the total electron + phonon bath state before scattering

$$|\Psi_i\rangle = |\vec{k}, N_{\vec{Q}}\rangle$$

Final: $$|\Psi_f\rangle_{\substack{ab\\em}} = |\vec{k} \pm \vec{Q}, N_{\vec{Q}} \mp 1\rangle$$

The creation & destruction ~~of~~ operator act on the initial state as

$$\hat{a}_{\vec{Q}} |\ldots, N_{\vec{Q}}\rangle = \sqrt{N_{\vec{Q}}}\ |\ldots, N_{\vec{Q}} - 1\rangle$$
$$\hat{a}^{+}_{\vec{Q}} |\ldots, N_{\vec{Q}}\rangle = \sqrt{N_{\vec{Q}}+1}\ |\ldots, N_{\vec{Q}} + 1\rangle$$

Therefore
$$\tilde{H}_{abs}(\vec{Q}) = \Xi_1 \left(\frac{\hbar}{2\rho V \omega_{\vec{Q}}}\right)^{1/2} (iQ) \sqrt{N_{\vec{Q}}}$$
$$\tilde{H}_{em}(\vec{Q}) = \Xi_1 \left(\frac{\hbar}{2\rho V \omega_{\vec{Q}}}\right)^{1/2} (-iQ) \sqrt{N_{\vec{Q}}+1}$$

$$\boxed{S(\vec{k}, \vec{k}')_{\substack{ab\\em}} = \frac{2\pi}{\hbar} \left(\frac{\hbar \Xi_1^2}{2\rho V \omega_{\vec{k}'-\vec{k}}}\right) (\vec{k}'-\vec{k}) \begin{cases} N_{\vec{k}'-\vec{k}}, & \text{abs} \\ N_{\vec{k}'-\vec{k}}+1, & \text{emis} \end{cases}}$$

Scattering rate: total number of scattering events per unit time. Inverse of the scattering rate is the relaxation time

$$\underset{\text{relax time}}{\frac{1}{\tau(\vec{k})}} = \underset{\text{scatt. rate}}{\Gamma(\vec{k})} = \sum_{\vec{k}'} \underbrace{S(\vec{k},\vec{k}')}_{\text{transition rate}} \underbrace{\left(1 - f(\vec{k}')\right)}_{\text{occupation of final state}}$$

For nondegenerate semiconductors $f(\vec{k}') \ll 1$, so basically

$$\boxed{\frac{1}{\tau(\vec{k})} = \Gamma(\vec{k}) = \underbrace{\sum_{\vec{k}'}}_{\text{sum over all final states}} S(\vec{k},\vec{k}')}$$

Similarly, there are MOMENTUM RELAXATION RATE & ENERGY RELAXATION RATE, that measure how many momentum-altering scattering events and how many energy-altering scattering events, respectively, the particle undergoes per unit time.

momentum relaxation time

$$\frac{1}{\tau_m(\vec{k})} \equiv \Gamma_m(\vec{k}) = \sum_{\vec{k}'} S(\vec{k},\vec{k}')\left(1 - \frac{\vec{k}'\cdot\vec{k}}{k^2}\right)$$

$$\frac{1}{\tau_E(\vec{k})} \equiv \Gamma_E(\vec{k}) = \sum_{\vec{k}'} S(\vec{k},\vec{k}')\left[1 - \frac{E(\vec{k}')}{E(\vec{k})}\right]$$

(obviously, elastic scattering implies $\tau_E \to \infty$)

What is the total scattering rate for acoustic phonon scattering?

$$\frac{1}{\tau_{tot}(\vec{k})} = \Gamma_{tot}(\vec{k}) = \Gamma_{ab}(\vec{k}) + \Gamma_{em}(\vec{k})$$

$$\Gamma_{\substack{ab\\em}}(\vec{k}) = \sum_{\vec{k}'} S(\vec{k},\vec{k}') =$$

$$= \frac{2\pi}{\hbar}\sum_{\vec{k}'}\left[\frac{\hbar \Xi_1^2 Q^2}{2\rho V \omega_{\vec{k}'-\vec{k}}}\right]\left\{\begin{matrix} N_{\vec{Q}} \\ N_{\vec{Q}}+1\end{matrix}\right\}\delta\left(\varepsilon(\vec{k}')-\varepsilon(\vec{k}) \mp \hbar\omega_{\vec{k}'-\vec{k}}\right)$$

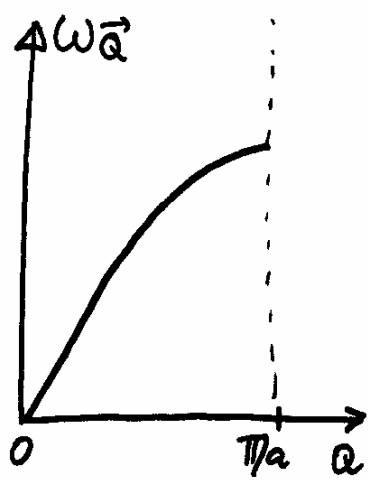
(ab / em)

Summing over $\vec{k}'$ or over $\vec{Q} = \vec{k}' - \vec{k}$ is the same thing (if we allow all $\vec{Q}$'s, at least formally).

$$\Gamma_{\substack{ab\\em}}(\vec{k}) = \frac{2\pi}{\hbar}\frac{V}{(2\pi)^3}\int d^3\vec{Q}\,\frac{\hbar \Xi_1^2 Q^2}{2\rho V \omega_{\vec{Q}}}\left(N_{\vec{Q}} + \frac{1}{2} \mp \frac{1}{2}\right)$$

$$\times\,\delta\left(\varepsilon(\vec{k}+\vec{Q}) - \varepsilon(\vec{k}) \mp \hbar\omega_{\vec{Q}}\right)$$

Let us note first how many acoustic phonons we have with wavevector $\vec{Q}$ at temperature T



$$N_{\vec{Q}} = \frac{1}{e^{\frac{\hbar\omega_{\vec{Q}}}{k_B T}} - 1} \qquad \omega_{\vec{Q}} \uparrow \quad N_{\vec{Q}} \downarrow$$

~~The~~ Most phonons thus occupy low-lying energy states, where $\omega_{\vec{Q}} \approx v_s |\vec{Q}|$. Also, at $T \sim 300K$, there are many phonons ($\hbar\omega_{\vec{Q}} \ll k_B T$, so

$$N_{\vec{Q}} \approx \frac{1}{\left(1 + \frac{\hbar\omega_{\vec{Q}}}{k_B T} - 1\right)} \approx \frac{k_B T}{\hbar\omega_{\vec{Q}}}$$

(pretty big number)

Therefore, the matrix element $|\tilde{H}_{int}(\vec{Q})|^2$ [also denoted as $|M(\vec{k},\vec{Q})|^2$ can be approximated as

$$\frac{\cancel{\hbar}\,\Xi_1^2 \cancel{Q^2}}{2\rho V v_s \cancel{Q}} \cdot \frac{k_B T}{\cancel{\hbar} v_s \cancel{Q}} = \frac{\Xi_1^2 k_B T}{2\rho V v_s^2}$$

you can put this both for $N_{\vec{Q}}$ and for $N_{\vec{Q}}+1$, as they are both very large (so-called <u>equipartition approximation</u>)

Note that the matrix element does not depend on $\vec{Q}$ ($\vec{Q} = \vec{k}' - \vec{k}$)

$$\Gamma^{ab}_{em}(\vec{k}) = \frac{2\pi}{\hbar} \cdot \frac{V^5}{(2\pi)^3} \cdot \frac{\Xi_1^2 k_B T}{2\rho V v_s^2} \cdot \int d^3\vec{Q}\, \delta(\varepsilon(\vec{k}+\vec{Q}) - \varepsilon(\vec{k}) \mp \hbar v_s \vec{Q})$$

Since $\hbar v_s Q \ll \varepsilon(\vec{k})$ for most electrons of interest (those moving with velocity close to thermal velocity) we may approximate, for the argument of δ-function

instead of $\varepsilon(\vec{k}+\vec{Q}) - \varepsilon(\vec{k}) \mp \hbar v_s Q$

we put $\varepsilon(\vec{k}+\vec{Q}) - \varepsilon(\vec{k})$ (elastic scattering approx.)

It holds

$$\sum_{\vec{Q}} \delta(\varepsilon(\vec{k}+\vec{Q}) - \varepsilon(\vec{k})) = \sum_{\vec{k}'} \delta(\varepsilon(\vec{k}') - \varepsilon(\vec{k})) =$$

$$= \frac{V}{2} g(\varepsilon(\vec{k})) \leftarrow \text{the density of states per unit volume}$$

Total scattering rate for acoustic phonons

$$\frac{1}{\tau(\vec{k})} = \Gamma_{tot}(\vec{k}) = \Gamma_{ab} + \Gamma_{em} = 2\Gamma_{ab}$$

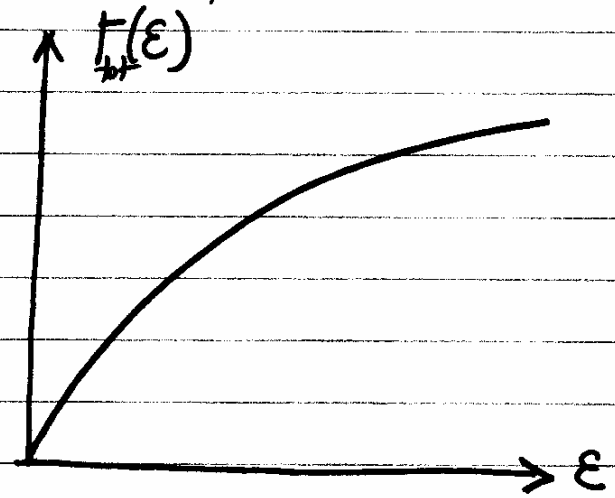
$$= \frac{\cancel{2\pi}}{\hbar} \cdot \frac{\Xi_1^2 k_B T}{\rho \cdot v_s^2 \cancel{V}} \cdot \frac{\cancel{V}}{\cancel{2}} \cdot \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} \mathcal{E}(\vec{k})^{1/2}$$

$$= \boxed{\frac{\Xi_1^2 k_B T}{(2\pi)\hbar \rho v_s^2} \cdot \left(\frac{2m^*}{\hbar^2}\right)^{3/2} \mathcal{E}(\vec{k})^{1/2}}$$

Total scattering rate for acoustic phonon scattering depends on $\vec{k}$ as a linear function $\sqrt{\mathcal{E}} \sim k$. It is usually depicted as a function of energy

$$\frac{1}{\tau(\mathcal{E})} = \Gamma_{tot}(\mathcal{E}) \sim \sqrt{\mathcal{E}}$$

$$\Gamma_{ab} = \Gamma_{em} = \frac{1}{2}\Gamma_{tot}$$

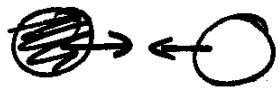


Since $M(\vec{k},\vec{Q})$ does not depend on $\vec{Q}$, scattering is isotropic $\rightarrow$ $\tau_m = \tau$!

Also, in the elastic approximation, $\tau_E \rightarrow \infty$!

Optical Phonon Scattering (Non-Polar)

Optical phonon modes are typical of crystals with more than 1 atom / primitive cell. The two atoms in the cell of zinc-blende semiconductor will move OUT OF PHASE in case of optical excitations, so



what scatters electrons is the jump in displacement from one atom to another.

Good model interaction Hamiltonian for electrons & optical phonons ([redacted] longitudinal again

$$\hat{H}' = D_0 [\hat{u}(\vec{r})_{\parallel}] \qquad D_0 - \text{optical deformation potential}$$

$$\hat{u}_{\parallel}(\vec{r}) = \sum_{Q} \left(\frac{\hbar}{2\rho V \omega_{\vec{Q}}}\right)^{1/2} \left[\hat{a}_{\vec{Q}} e^{i\vec{Q}\vec{r} - i\omega_{\vec{Q}} t} + \hat{a}^{+}_{\vec{Q}} e^{-i\vec{Q}\cdot\vec{r} + i\omega_{\vec{Q}} t} \right]$$

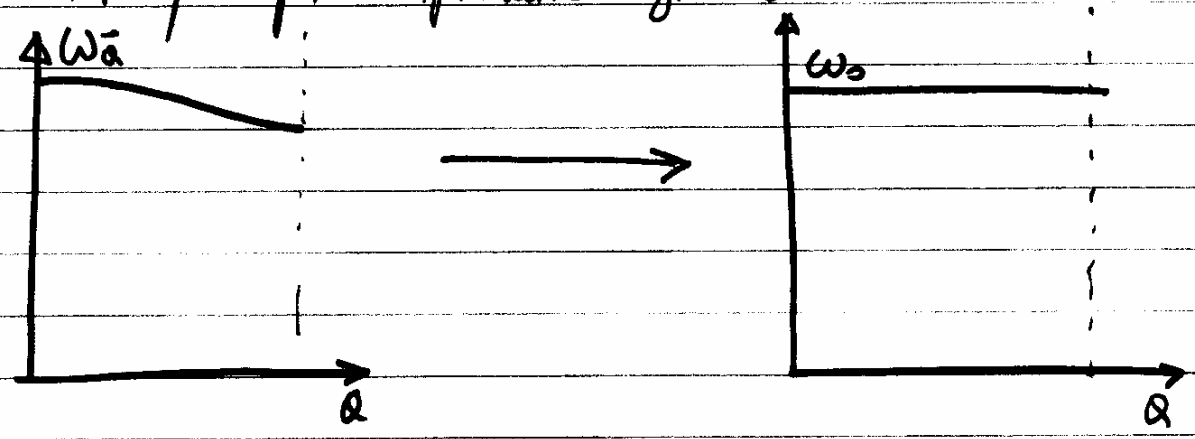
$\parallel$, for longitudinal

Again, $\hat{a}_{\vec{Q}}$ will produce $\sqrt{N_{\vec{Q}}}$, $\hat{a}^{+}_{\vec{Q}} \rightarrow \sqrt{N_{\vec{Q}}+1}$

$$|M(\vec{k},\vec{Q})|^2_{\substack{ab\\em}} = \frac{\hbar D_0^2}{2\rho V \omega_{\vec{Q}}} \cdot \left(N_{\vec{Q}} + \frac{1}{2} \mp \frac{1}{2}\right)$$

Optical phonons have generally appreciable energies, so we cannot make the approx that $\hbar\omega \ll k_B T$. However, remember that the dispersion

relation for optical phonons is given by



REAL DISPERSIONLESS

Because $\omega_{\vec{Q}}$ varies only slightly in the whole range of Q's, a common approximation is to consider optical phonons as DISPERSIONLESS

$$(\forall \vec{Q})\ \omega_{\vec{Q}} \approx \omega_0$$

Then we get

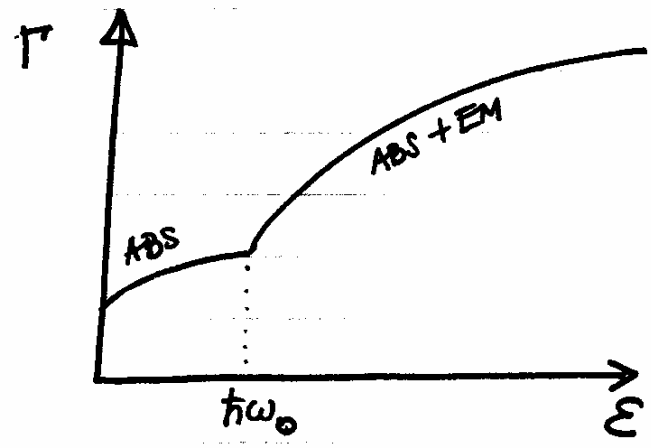
$$|M(\vec{k},\vec{Q})|^2_{\substack{ab\\em}} = \frac{\hbar D_0^2}{2\rho V \omega_0^2}\left(N_0 + \frac{1}{2} \mp \frac{1}{2}\right)$$

We see that the matrix element is independent of $\vec{Q}$, so for the total scattering rate we obtain

$$\Gamma(\vec{k}) = \frac{2\pi}{\hbar}\frac{\hbar D_0^2}{2\rho V \omega_0}\cdot\frac{V}{2}\cdot$$

$$\cdot\Big\{\underbrace{N_0\, g_{3D}(E(\vec{k}) + \hbar\omega_0)}_{\text{absorption}} + (N_0+1)\underbrace{g_{3D}(\mathcal{E}(\vec{k}) - \hbar\omega_0)}_{\text{this is zero if } \mathcal{E}(\vec{k}) < \hbar\omega_0}\Big\}$$

$$\Gamma(\vec{k}) = \frac{\pi D_0^2}{2\rho\omega_0}\left\{N_0\, g_{3D}[\mathcal{E}(\vec{k})+\hbar\omega_0] + (N_0+1)\, g_{3D}[\mathcal{E}(\vec{k})-\hbar\omega_0]\right\}$$



Emission forbidden for energies lower than $\hbar\omega_0$!
Since $|M(\vec{k},\vec{Q})|^2$ does not depend on $\vec{Q}$, the total scattering rate & the momentum relaxation rate are the same!

A note on calculating the integrals over $\vec{Q}$:

in general, when calculating the scattering rates we need to evaluate sums of the form

$$\Gamma(\vec{k}) = \frac{2\pi}{\hbar}\sum_{\vec{Q}} |M(\vec{k},\vec{Q})|^2\, \delta\big(\mathcal{E}(\vec{k}+\vec{Q}) - \mathcal{E}(\vec{k}) \underbrace{\mp \hbar\omega_{\vec{Q}}}_{\text{in general } \hbar\omega_{\vec{Q}} \text{ here can be + or −, depending if it is absorption or emission}}\big)$$

First, we do the "sum to integral" substitution

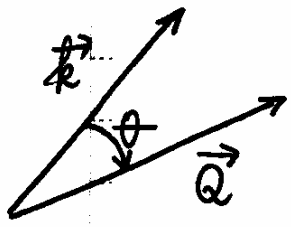
$$\sum_{\vec{Q}} |M(\vec{k},\vec{Q})|^2\, \delta(\dots) = \frac{V}{(2\pi)^3}\int d^3\vec{Q}\, |M(\vec{k},\vec{Q})|^2\, \delta(\dots)$$

Among all the $\vec{Q}$'s, only those that satisfy the δ-function will contribute

$$\mathcal{E}(\vec{k}+\vec{Q}) - \mathcal{E}(\vec{k}) \mp \hbar\omega_{\vec{Q}} = 0$$

Since we're assuming the electron remains near the bottom of the band

$$\frac{\hbar^2(\vec{k}+\vec{Q})^2}{2m^*} - \frac{\hbar^2 k^2}{2m^*} \mp \hbar\omega_{\vec{Q}} = 0$$



(The z-axis chosen along $\vec{k}$):

$$\frac{\hbar^2}{2m^*}\left(2kQ\cos\theta + Q^2\right) \mp \hbar\omega_{\vec{Q}} = 0$$

In case $\omega_{\vec{Q}}$ DOES NOT DEPEND ON $\vec{Q}$ $\boxed{\omega_{\vec{Q}} = \omega}$, like we had for acoustic phonons ($\omega_{\vec{Q}} \approx 0$) and optical phonons ($\omega_{\vec{Q}} = \omega_0$), we have

$$\cos\theta = \left[\pm \hbar\omega \cdot \frac{2m^*}{\hbar^2} - Q^2\right] \cdot \frac{1}{2kQ}$$

Introduce $K_{ph}^2 = \hbar\omega \cdot \frac{2m^*}{\hbar^2}$ ← this is the wavevector (squared) that an electron would have if it possessed the energy of the phonon $\hbar\omega$

$$-1 \leq \cos\theta = \left[\pm K_{ph}^2 - Q^2\right] \cdot \frac{1}{2kQ} \leq 1$$

$$-2kQ \leq \left[\pm K_{ph}^2 - Q^2\right] \leq 2kQ$$

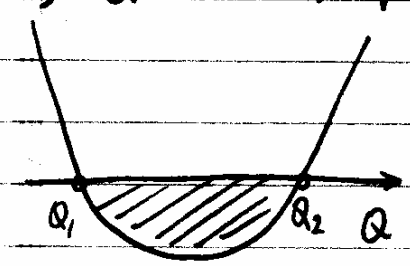
upper sign – abs.
lower sign – emis.

1) $Q^2 - 2kQ \mp K_{ph}^2 \leq 0$

ABS: $Q_{1/2} = k \pm \sqrt{k^2 + K_{ph}^2}$

since $Q \geq 0$

$$\boxed{Q \in \left[0,\ k + \sqrt{k^2 + K_{ph}^2}\right]}$$ ABS condit. 1)

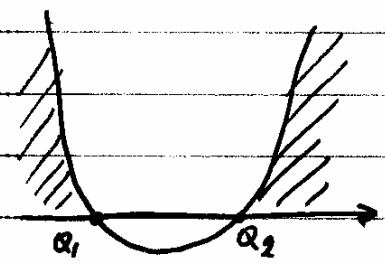


EMISSION: $Q_{1/2} = k \pm \sqrt{k^2 - K_{ph}^2}$

If $k^2 < K_{ph}^2$ no solutions

If $k^2 > K_{ph}^2$ $Q \in [k - \sqrt{k^2 - K_{ph}^2},\ k + \sqrt{k^2 - K_{ph}^2}]$

2) $Q^2 + 2kQ \mp K_{ph}^2 \geq 0$



ABS $Q_{1,2} = -k \pm \sqrt{k^2 + K_{ph}^2}$

$Q \in [-k + \sqrt{k^2 + K_{ph}^2},\ \infty]$

EMIS $Q_{1/2} = -k \pm \sqrt{k^2 - K_{ph}^2}$

If $k^2 < K_{ph}^2$, all Q's are OK

If $k^2 > K_{ph}^2$, $Q \in [-k + \sqrt{k^2 - K_{ph}^2},\ \infty]$

all Q's OK

Conditions 1+2 combined

ABSORPTION

$$\boxed{Q_{abs} \in [-k + \sqrt{k^2 + K_{ph}^2},\ k + \sqrt{k^2 + K_{ph}^2}]}$$

EMISSION If $k^2 < K_{ph}^2$, no Q's allowed

If $k^2 > K_{ph}^2$ $\boxed{Q_{em} \in [k - \sqrt{k^2 - K_{ph}^2},\ k + \sqrt{k^2 - K_{ph}^2}]}$

So the absorption & emission process have their own minimum and maximum allowed Q

$Q_{abs}^{\pm}$ ($+ \leftarrow$ max, $- \leftarrow$ min), $Q_{em}^{\pm}$ ($+ \leftarrow$ max, $- \leftarrow$ min)

Therefore

$$\Gamma(\vec{k}) = \frac{2\pi}{\hbar} \cdot \frac{V}{(2\pi)^3} \cdot \int d^3\vec{Q}\, |M(\vec{k},\vec{Q})|^2 \delta(\mathcal{E}(\vec{k}+\vec{Q}) - \mathcal{E}(\vec{k}) \mp \hbar\omega)$$

$$= \frac{2\pi}{\hbar} \cdot \frac{V}{(2\pi)^3} \int_0^\infty Q^2 dQ \int_{-1}^{1} d(\cos\theta) \int_0^{2\pi} d\varphi \; |M(\vec{k},\vec{Q})|^2 \cdot$$

$$\cdot \; \delta\left(\frac{\hbar^2}{2m^*}(2kQ\cos\theta + Q^2) \mp \hbar\omega\right)$$

So if we cut-off the Q's that are not allowed, and also take into account

$$\delta\left(\frac{\hbar^2}{2m^*}(2kQ\cos\theta + Q^2) \mp \hbar\omega\right) = \frac{1}{\frac{\hbar^2 kQ}{m^*}} \delta\left(\cos\theta - \frac{1}{2kQ}\left[\pm K_{th}^2 - Q^2\right]\right)$$

Because $\delta(ax) = \frac{1}{|a|}\delta(x)$

$$\boxed{\Gamma_{\substack{ab\\em}}(\vec{k}) = \frac{2\pi}{\hbar} \cdot \frac{V}{(2\pi)^3} \cdot \int_{Q^-_{\substack{ab\\em}}}^{Q^+_{\substack{ab\\em}}} Q^2 dQ \cdot \frac{1}{\frac{\hbar^2 kQ}{m^*}} \cdot \int_{-1}^{1} d(\cos\theta)\, \delta(\cos\theta - \ldots) \times \int_0^{2\pi} d\varphi \; |M(\vec{k},\vec{Q})|^2_{\substack{ab\\em}}}$$

If $|M(\vec{k},\vec{Q})|^2$ does not depend on $\vec{Q}$, like in the last two examples (acoustic phonons & optical phonons)

$$\Gamma_{\substack{ab\\em}} = \frac{\cancel{2\pi}}{\hbar} \cdot \frac{V}{(2\pi)^{\cancel{3}}} \cdot |M|^2_{\substack{ab\\em}} \cdot \frac{m^*}{\hbar^2 k} \cdot \cancel{2\pi} \cdot \int_{Q^-_{\substack{ab\\em}}}^{Q^+_{\substack{ab\\em}}} Q\, dQ$$

$$= \frac{V}{2\pi} \cdot \frac{m^*}{\hbar^3 k} |M|^2_{\substack{ab\\em}} \left.\frac{Q^2}{2}\right|_{Q^-_{\substack{ab\\em}}}^{Q^+_{\substack{ab\\em}}}$$

$$\Gamma_{\substack{ab\\em}}(\vec{k}) = \frac{V}{2\pi}\cdot\frac{m^*}{\hbar^3 k}|M|^2_{\substack{ab\\em}}\cdot\frac{1}{2}\left(Q^+_{\substack{ab\\em}} - Q^-_{\substack{ab\\em}}\right)\left(Q^+_{\substack{ab\\em}} + Q^-_{\substack{ab\\em}}\right)$$

absorption: $Q^+_{ab} + Q^-_{ab} = 2\sqrt{k^2+K_{ph}^2}$

$Q^+_{ab} - Q^-_{ab} = 2k$

emission: $Q^+_{em} + Q^-_{em} = 2k$

$Q^+_{em} - Q^-_{em} = 2\sqrt{k^2-K_{ph}^2}$ $\Big\}$ if $k^2 > K_{ph}^2$

Therefore $\Gamma_{\substack{ab\\em}}(\vec{k}) = \frac{V}{2\pi}\cdot\frac{m^*}{\hbar^3 k}|M|^2_{\substack{ab\\em}}\cdot 2k\sqrt{k^2 \pm K_{ph}^2}\times$

× Heaviside fn $(k^2-K_{ph}^2)$ for emission

$$\Gamma_{\substack{ab\\em}} = |M|^2_{\substack{ab\\em}}\cdot\frac{Vm^*}{\hbar^3\pi}\cdot\left(\frac{2m^*}{\hbar^2}\right)^{1/2}\underbrace{\sqrt{\mathcal{E}(\vec{k})\pm\hbar\omega}}$$

$$= |M|^2_{\substack{ab\\em}}\cdot\frac{V}{\hbar\cdot 2\pi}\cdot\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{\mathcal{E}(\vec{k})\pm\hbar\omega}$$

we see the dependence on final energy

$$= \frac{2\pi}{\hbar}\cdot|M|^2_{ab}\cdot\frac{V}{2}\cdot\underbrace{\frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{\mathcal{E}(\vec{k})\pm\hbar\omega}}_{g_{3D}(\mathcal{E}(\vec{k})\pm\hbar\omega)}$$

$\frac{1}{2}$ because per spin

$g_{3D}(\mathcal{E}(\vec{k})\pm\hbar\omega)$ density of final states per unit volume (2 spin orientations included)

$$\boxed{\Gamma_{\substack{ab\\em}} = \frac{2\pi}{\hbar}|M|^2_{ab}\cdot\frac{V}{2}\cdot g_{3D}(\mathcal{E}\pm\hbar\omega)}$$

$$|M|^2_{\substack{ab\\em}} = \frac{\Xi_1^2 k_B T}{2\rho V v_s^2} \quad \text{acoustic ph.; } \omega_{\vec{Q}}=0$$

$$\text{optical } |M|^2_{\substack{ab\\em}} = \frac{\hbar D_0^2}{2\rho V\omega_0}\cdot\left(N_0 + \frac{1}{2} \mp \frac{1}{2}\right)$$

AGAIN, THIS HOLDS FOR

- $\omega_{\vec{Q}} = \text{const.}$
- $|M(\vec{k},\vec{Q})|^2$ does not depend on $\vec{Q}$

(this also implies $\Gamma_m = \Gamma$)

Intervalley Scattering

- In silicon, the bottom of the conduction band is 6-fold degenerate, so an electron can scatter into any of the other valleys via either acoustic or optical phonons (as not too much energy is needed), but the appropriate phonon wavevector must be supplied

  g-process from a valley to the one on the opposite end of the same axis

  f-process from a valley to one of the valleys on the other axes

The phonon wavevectors needed are pretty large, near the Brillouin zone edge: for instance, for a g-process,

change in electron momentum for g & f processes

$$\begin{cases} \Delta\vec{k}_g \approx 2\cdot 0.85\frac{\pi}{a}(1,0,0) = 1.7\frac{\pi}{a}(1,0,0) \rightarrow \text{equiv.} \\ \Delta\vec{k}_f = 0.85\frac{\pi}{a}[(1,0,0)-(0,1,0)] = 0.85\frac{\pi}{a}(1,-1,0) \end{cases}$$

$1.7-2=-0.3$

$$|\Delta\vec{k}_f| = 0.85\frac{\pi}{a}\cdot\sqrt{2} = 1.2\pi/a$$

For large $\vec{Q}$'s, for both acoustic & optical phonons ω's are more or less comparable, and somewhat less than the optical phonon frequency ω_0.

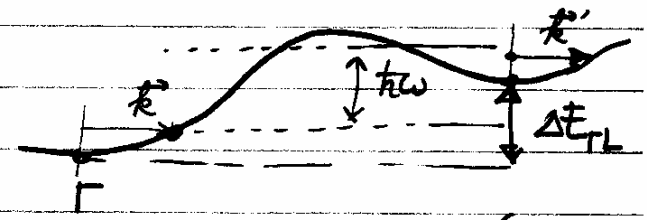
- For GaAs, scattering between Γ-valley and one of the 4 $(1/2\times 8)$ L-valleys becomes pretty prominent, but since there is an energy difference of about 0.3eV between Γ & L, only optical phonons will do that.

Bottom line: intervalley scattering is modeled similar to (non-polar) optical phonons

$$\hat{H}_{int} = D_{if}\, u_{\parallel}(\vec{r},t)$$

initial final

The electron needs to gain at least ΔE_{if}



Before: $\mathcal{E}(\vec{k})$

After: $\mathcal{E}(\vec{k}') + \Delta E_{if}$ (GaAs)

$$\mathcal{E}(\vec{k}') + \Delta E_{if} - (\mathcal{E}(\vec{k}) \pm \hbar\omega_{if}) = 0$$

$$\mathcal{E}(\vec{k}') = \mathcal{E}(\vec{k}) \pm \hbar\omega_{if} - \Delta E_{if}$$

$E_{final\ valley} - E_{initial\ valley}$

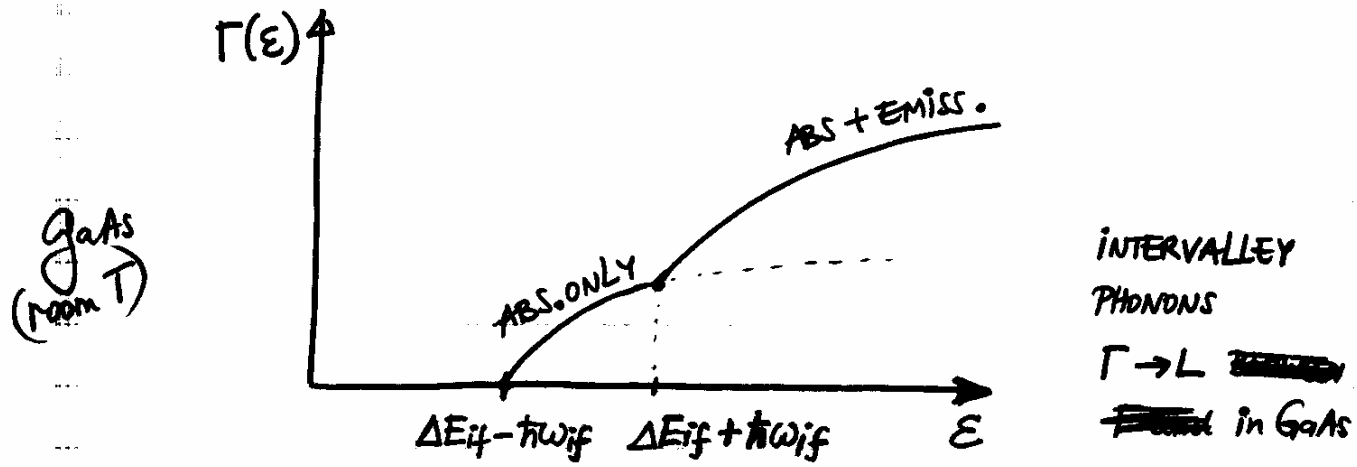
We will obtain a similar expression to what we derived for intravalley phonons, only the difference is that the more final valleys you have – the more scattering into them as a whole

$$\boxed{\frac{1}{\tau(\vec{k})} = \Gamma_{\substack{ab\\em}}(\vec{k}) = \frac{\pi D_{if}^2 Z_f}{2\rho\omega_{if}}\left(N_{if} + \frac{1}{2} \mp \frac{1}{2}\right) \times g_{3D}\left(\mathcal{E}(\vec{k}) \pm \hbar\omega_{if} - \Delta E_{if}\right)}$$

$\boxed{Z_f - \#\text{ of final valleys}}$

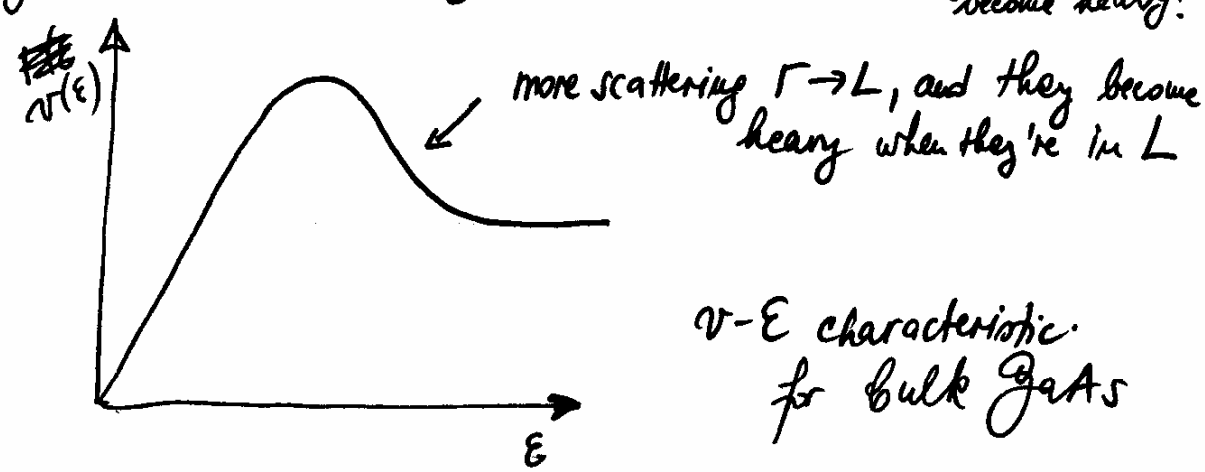
$\Delta E_{if} = 0$ for equivalent valley scattering in Si

N_{if} – number of phonons with energy $\hbar\omega_{if}$



Also note that the dependence is on the density of FINAL STATES, meaning that the <u>effective mass of the FINAL VALLEY is important</u>.

That is why in GaAs scattering from $\Gamma \to L$ is quite efficient, since $m^*_L > m^*_\Gamma$, while the other way around not so much (+ there's 4 L valleys and only 1 Γ valley). That's why electrons that have got to the L-valley <u>don't come back</u>, they stay in L and become heavy!

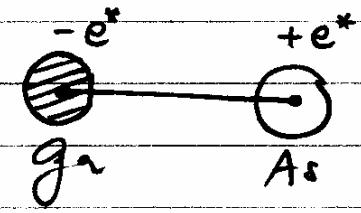


v-ε characteristic for bulk GaAs

Polar-Optical Phonon (POP) Scattering

Due to the polar nature of the bonds, displacement of atoms in a polar semiconductor, like GaAs, induces <u>polarization</u>, proportional to the displacement.

What the electron scatter from are <u>little dipoles</u> induced by displacement, so <u>polar optical phonon scattering is Coulomb in nature</u>, and very strong in GaAs at room T. (polar acoustic phonon scattering is called piezoelectric scattering, and is generally important in very ~~clean~~ pure samples, and at low temperatures).



e^* - effective charge of the dipole

The longitudinal optical phonon-related displacement perturbs the dipole moment as

$$\delta p = e^* u_{\parallel}$$

which leads to a perturbation in polarization

$$\delta P = \frac{1}{V_{pc}} \cdot \delta p \quad , \quad V_{pc} \text{ - volume of primitive cell}$$

$\vec{D} = \varepsilon_0 \vec{E} + \delta \vec{P}$ $\quad \vec{\nabla} \cdot \vec{D} = 0$ (no external charge)

If we're propagating a wave with wavevector $\vec{Q}$

$\vec{D} \cdot \vec{Q} = 0$, and since the perturbation is due to longitudinal phonons $\delta \vec{P} \parallel \vec{u} \parallel \vec{Q} \Rightarrow D = 0$

$$E = E_{\parallel} = -\frac{1}{\varepsilon_0} \frac{e^* u_{\parallel}}{V_{pc}} \Rightarrow \hat{H}_{int} = -e\varphi, \quad \varphi = -\int_{\text{fixed pt.}}^{\vec{r}} \vec{E} \cdot d\vec{r}'$$

Because of the integral

$$M(\vec{k},\vec{Q}) = -e\,\varphi(\vec{Q}) \qquad \varphi(\vec{Q}) = -\frac{E(\vec{Q})}{iQ} \quad \text{(for long. excitations)}$$

$$= \frac{+e}{iQ}\cdot\left(-\frac{1}{\varepsilon_0}\,\frac{e^*\,u_{\parallel}(\vec{Q})}{V_{pc}}\right)$$

$$u_{\parallel}(\vec{Q}) = \begin{cases} \text{absorption: } \left(\dfrac{\hbar}{2\rho V\omega_0}\right)^{1/2}\cdot\sqrt{N_0} \\ \text{emission: } \left(\dfrac{\hbar}{2\rho V\omega_0}\right)^{1/2}\cdot\sqrt{N_0+1} \end{cases}$$

$$|M(\vec{k},\vec{Q})|^2_{\substack{ab\\em}} = \left(\frac{e e^*}{\varepsilon_0 V_{pc} Q}\right)^2\cdot\frac{\hbar}{2\rho V\omega_0}\cdot\left(N_0+\frac{1}{2}\mp\frac{1}{2}\right)$$

$$= \frac{e^2}{\varepsilon_0^2 Q^2}\cdot\left(\frac{e^*}{V_{pc}}\right)^2\cdot\frac{\hbar}{2\rho V\omega_0}\left(N_0+\frac{1}{2}\mp\frac{1}{2}\right)$$

- Note that the matrix element will depend on Q! The $\frac{1}{Q^2}$ dependence is the signature of Coulomb nature!

$$\omega_0 = \omega_{LO}$$

- $$\left(\frac{e^*}{V_{pc}}\right)^2 = \frac{\varepsilon_0\rho\omega_0^2}{\varepsilon_r(0)}\left(\frac{\varepsilon_r(0)}{\varepsilon_r(\infty)}-1\right)$$

these are relative diel. const.

$$|M(\vec{k},\vec{Q})|^2_{\substack{ab\\em}} = \frac{e^2}{Q^2\varepsilon_0^{\cancel{2}}}\cdot\frac{\cancel{\varepsilon_0}\cancel{\rho}\omega_0^{\cancel{2}}}{\varepsilon_r(0)}\cdot\left(\frac{\varepsilon_r(0)}{\varepsilon_r(\infty)}-1\right)\cdot\frac{\hbar}{2\cancel{\rho}V\cancel{\omega_0}}\left(N_0+\frac{1}{2}\mp\frac{1}{2}\right)$$

$$= \frac{\hbar e^2\omega_0}{2Q^2V}\left[\frac{1}{\varepsilon(\infty)}-\frac{1}{\varepsilon(0)}\right]\cdot\left(N_0+\frac{1}{2}\mp\frac{1}{2}\right)$$

these are absolute

Total scattering rate

$$\Gamma(\vec{k})_{\substack{ab\\em}} = \frac{\cancel{2}\pi}{\cancel{\hbar}} \cdot \frac{\cancel{\hbar} e^2 \omega_0}{\cancel{2} \cancel{V}} \left[\frac{1}{\varepsilon(\infty)} - \frac{1}{\varepsilon(0)} \right] \left(N_0 + \frac{1}{2} \mp \frac{1}{2} \right)$$

$$\cdot \frac{\cancel{V}}{(2\pi)^3} \cdot \underbrace{\int d^3\vec{Q} \, \frac{1}{Q^2} \, \delta\left(\varepsilon(\vec{k}+\vec{Q}) - \varepsilon(\vec{k}) \mp \hbar\omega_0\right)}$$

This ~~spatial~~ integral can be rewritten as (since there is no azimuthal-angle dependence)

$$2\pi \int_{Q^-_{\substack{ab\\em}}}^{Q^+_{\substack{ab\\em}}} \cancel{Q^2} dQ \, \frac{1}{\cancel{Q^2}} \int_{-1}^{1} d(\cos\theta) \, \frac{\delta(\cos\theta - (\ldots\ldots))}{\frac{\hbar^2 k Q}{m^*}}$$

$$= 2\pi \cdot \frac{m^*}{\hbar^2 k} \int_{Q^-_{\substack{ab\\em}}}^{Q^+_{\substack{ab\\em}}} dQ \cdot \frac{1}{Q}$$

$$= 2\pi \, \frac{m^*}{\hbar^2 k} \cdot \ln\left(Q^+_{\substack{ab\\em}} / Q^-_{\substack{ab\\em}} \right)$$

$$\Gamma(\vec{k})_{\substack{ab\\em}} = \frac{\pi e^2 \omega_0}{(2\pi)^2} \cdot \frac{m^*}{\hbar^2} \cdot \left[\frac{1}{\varepsilon(\infty)} - \frac{1}{\varepsilon(0)} \right] \cdot \left[N_0 + \frac{1}{2} \mp \frac{1}{2} \right] \cdot$$

$$\cdot \left(\frac{1}{k} \ln\left(\frac{Q^+_{ab/em}}{Q^-_{ab/em}} \right) \right)$$

$$k = \sqrt{\frac{2m^* \varepsilon}{\hbar^2}}$$

Here is your ε-dependence

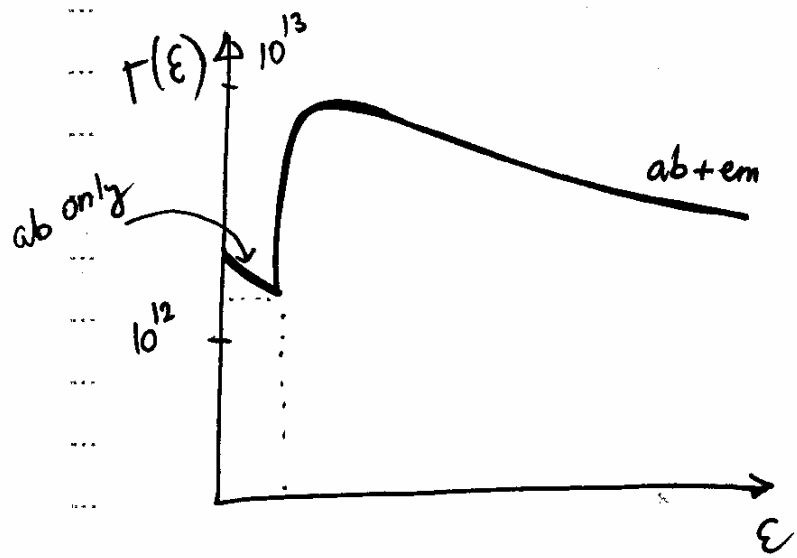
$$\Gamma(\varepsilon)_{\substack{ab\\em}} = \frac{e^2\omega_0}{4\pi}\cdot\frac{m^*}{\hbar^2}\left[\frac{1}{\varepsilon(\infty)}-\frac{1}{\varepsilon(0)}\right]\cdot\left[N_0+\frac{1}{2}\mp\frac{1}{2}\right]$$

$$\times\sqrt{\frac{\hbar^2}{2m^*}}\cdot\frac{1}{\sqrt{\varepsilon}}\ \ln\ldots$$

$$\Gamma(\varepsilon)_{\substack{ab\\em}} = \frac{e^2\omega_0}{8\pi}\left(\frac{2m^*}{\hbar^2}\right)^{1/2}\cdot\frac{1}{\sqrt{\varepsilon}}\ \ln\ldots$$

$$\boxed{\Gamma(\varepsilon)_{tot} = \frac{e^2\omega_0}{8\pi}\cdot\left(\frac{2m^*}{\hbar^2}\right)^{1/2}\cdot\left[\frac{1}{\varepsilon(\infty)}-\frac{1}{\varepsilon(0)}\right]\cdot \cdot\frac{1}{\sqrt{\varepsilon}}\cdot\left\{N_0\ln\left|\frac{1+\sqrt{1+\frac{\hbar\omega_0}{\varepsilon}}}{-1+\sqrt{1+\frac{\hbar\omega_0}{\varepsilon}}}\right|+(N_0+1)\ln\left|\frac{1+\sqrt{1-\frac{\hbar\omega_0}{\varepsilon}}}{1-\sqrt{1-\frac{\hbar\omega_0}{\varepsilon}}}\right|\right\}}$$

this term present only for $\varepsilon > \hbar\omega_0$.



Scattering by Ionized Impurities

An unscreened ionized impurity, with charge $\pm Ze$, would yield the interaction potential energy

$$\hat{H}_{int}^{unscr.} = \frac{\mp Ze^2}{4\pi\varepsilon_0 \varepsilon_s} \cdot \frac{1}{r}$$

↑ relative dielectric const.

However, an impurity in a semiconductor is surrounded by a cloud of mobile charges, so one effectively speaks of a SCREENED POTENTIAL.

In the vicinity of an impurity in an n-type semiconductor (the impurity can be one of the donors, but needn't be; it can be some external metal atom, present due to processing imperfections, etc.)

$$\vec{\nabla}^2 \varphi(\vec{r}) = \frac{(\mp Ze\,\delta(\vec{r}) + ne - N_D e)}{\varepsilon_0 \varepsilon_s}$$

For $r>0$, the δ-function doesn't do much, so we can write

$$\underset{r>0}{\vec{\nabla}^2 \varphi(\vec{r})} = \frac{e}{\varepsilon_0 \varepsilon_s}(n - N_D)$$

On the macro-scale, average n should equal some equilibrium n_0 (in this case, $n_0 = N_D$). However, on the microscopic scale

$$n(\vec{r}) = n_0 + \delta n(\vec{r})$$

Since no current is flowing, we can use the equilibrium expression for n

$$n(\vec{r}) = N_c \exp\left(\frac{1}{k_B T}\left(\varepsilon_F - \varepsilon_c(\vec{r})\right)\right),$$

and $\quad \varepsilon_c(\vec{r}) = \text{const.} - e\,\varphi(\vec{r})$

$$\varphi(\vec{r}) = \underbrace{\varphi_0}_{\text{average}} + \delta\varphi(\vec{r}).$$

We obtain that δn and $\delta\varphi$, which are microscopic deviations of the density and electrostatic potential, respectively, satisfy

$$\frac{\delta n}{\delta\varphi} = n \cdot \frac{e}{k_B T} \approx n_0 \frac{e}{k_B T}$$

Going back to the Poisson equation

$$\nabla^2 \varphi(\vec{r}) = \nabla^2 \delta\varphi(\vec{r}) = \frac{e}{\varepsilon_0 \varepsilon_s}\,\delta n(\vec{r})$$

$$= \frac{e}{\varepsilon_0 \varepsilon_s} \cdot \left(\frac{\delta n}{\delta\varphi}\right) \delta\varphi(\vec{r})$$

$$= \frac{e^2 n_0}{k_B T\, \varepsilon_0 \varepsilon_s}\,\delta\varphi(\vec{r})$$

$$\boxed{\nabla^2 \delta\varphi(\vec{r}) = \frac{e^2 n_0}{k_B T\, \varepsilon_0 \varepsilon_s}\,\delta\varphi(\vec{r})}$$

We can define THE DEBYE LENGTH as

$$\boxed{\frac{1}{L_D^2} = \frac{e^2 n_0}{k_B T\, \varepsilon_0 \varepsilon_s}}$$

In the vicinity of an impurity, if it were bare (unscreened) $\delta\varphi$ would have central symmetry (a.k.a. spherical symmetry). So we can expect the same even for a screened impurity, i.e.,

$$\delta\varphi(\vec{r}) = \delta\varphi(r)$$

which leads to $\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\delta\varphi}{dr}\right) = \frac{1}{L_D^2}\delta\varphi$

By assuming $\delta\varphi = f/r$; $\frac{d(\delta\varphi)}{dr} = -\frac{1}{r^2}f + \frac{f'}{r}$

$$\frac{d}{dr}\left(r^2\frac{d}{dr}\delta\varphi\right) = \frac{d}{dr}\left(-f + f'r\right) = \cancel{-f'} + f''r + \cancel{f'}$$

$$\frac{f''}{\cancel{r}} = \frac{1}{L_D^2}\frac{f}{\cancel{r}}$$

$$\boxed{f'' - \frac{1}{L_D^2}f = 0} \Rightarrow \boxed{f = \alpha e^{-r/L_D} + \beta e^{r/L_D}}$$

Since solutions that blow up are unphysical (there is no reason for the potential far from the impurity to be very large), so $\beta = 0$.

Therefore, $r > 0$ $\boxed{\delta\varphi(r) = \alpha \frac{e^{-r/L_D}}{r}}$

We know that as $r \to 0$ $\delta\varphi$ should behave as that for a bare impurity, so

$$\alpha = \frac{\pm Ze}{4\pi\varepsilon_0 \varepsilon_s}$$

Therefore, the interaction energy between a screened impurity and an electron is

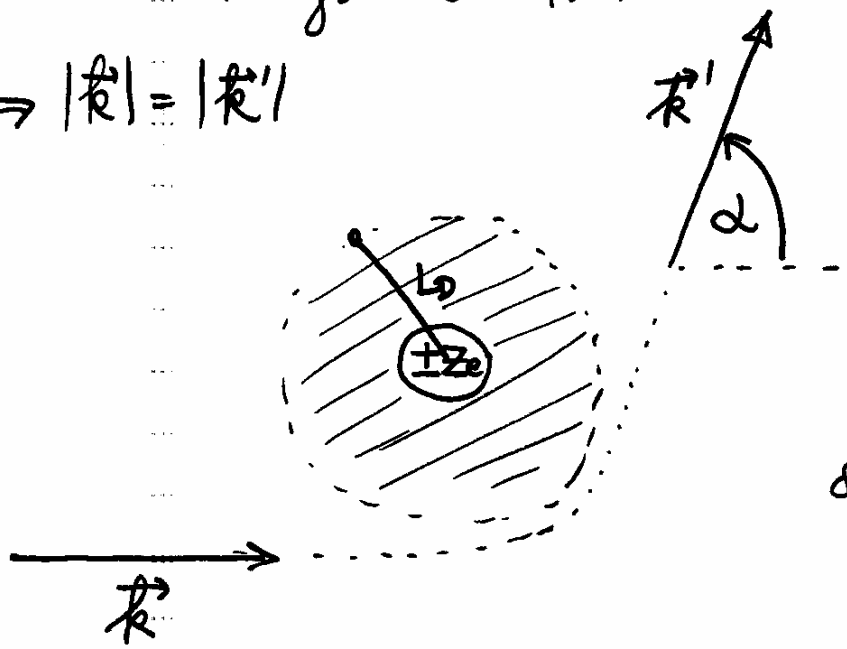
$$\mathcal{E}_{int} = \frac{\mp Ze^2}{4\pi\varepsilon_0 \varepsilon_s} \cdot \frac{e^{-r/L_D}}{r}$$

leading to the interaction Hamiltonian

$$\boxed{\hat{H}_{int}^{scr.} = \frac{\mp Ze^2}{4\pi\varepsilon_0 \varepsilon_s} \cdot \frac{e^{-r/L_D}}{r}}$$

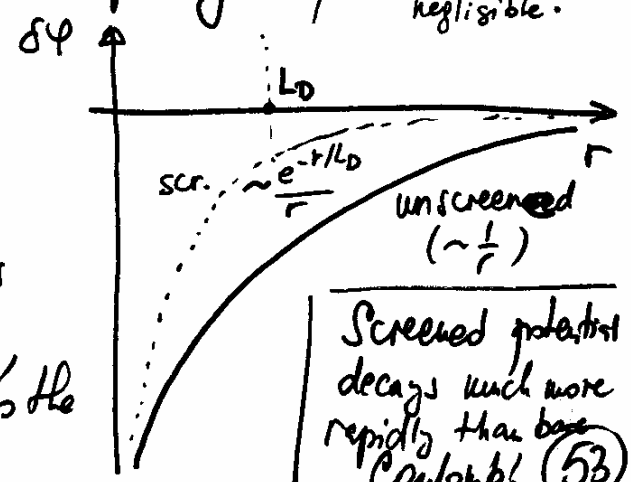
Before proceeding with calculation of scattering rates from this potential, there are a few things to note:

$|\vec{k}| = |\vec{k}'|$



1) The screened impurity can be thought of as having effective radius equal to L_D.

Beyond L_D, the impurity's potential is negligible.

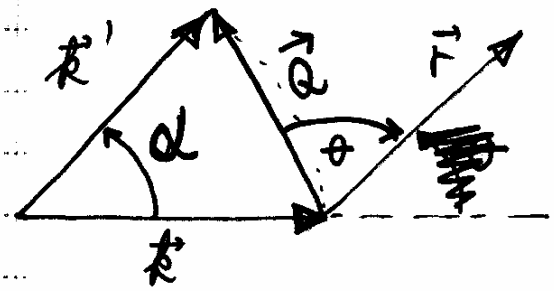


Screened potential decays much more rapidly than bare Coulomb!

2) Scattering is elastic: total energy is conserved, so far from the impurity, after scattering, kinetic energy is the same as before scattering!

$$\langle \vec{k}' | \hat{H}_{int} | \vec{k} \rangle = \frac{1}{Vol.} \cdot \int d^3\vec{r}\, e^{-i\vec{k}'\vec{r}}\, \hat{H}_{int}(\vec{r})\, e^{i\vec{k}\vec{r}}$$

$$= \frac{1}{V} \cdot \frac{\mp Z e^2}{4\pi\varepsilon_0 \varepsilon_s} \cdot \int d^3\vec{r}\, e^{-i(\vec{k}'-\vec{k})\vec{r}}\, \frac{e^{-r/L_D}}{r}$$



<u>For ionized impurity scattering:</u>
It is customary to view things in terms of the angle α, which is the angle between the final wavevector ($\vec{k}'$) and the initial wavevector ($\vec{k}$).

$|\vec{k}| = |\vec{k}'|$ Theta is the angle between $\vec{Q}$ and $\vec{r}$.
The magnitude of $\vec{Q}$ is given by the cosine theorem

$$Q^2 = k'^2 + k^2 - 2\vec{k}'\cdot\vec{k} = 2k^2 - 2k^2\cos\alpha$$
$$= 2k^2(1-\cos\alpha) = 4k^2 \sin^2\frac{\alpha}{2}$$

$$Q = 2k \sin\frac{\alpha}{2}$$

$$\int d^3\vec{r}\, e^{-iQr\cos\theta}\, \frac{e^{-r/L_D}}{r} = 2\pi \int_0^\infty r^{\cancel{2}}\, \frac{e^{-r/L_D}}{\cancel{r}}\, dr \int_{-1}^{1} d(\cos\theta) \times$$

$$\times\, e^{-iQr\cos\theta} = 2\pi \int_0^\infty \cancel{r}\, e^{-r/L_D} \cdot \frac{e^{-iQr} - e^{iQr}}{-iQ\cancel{r}}\, dr$$

$$= i\frac{2\pi}{Q} \cdot \int_0^\infty dr \left(e^{-iQr - r/L_D} - e^{iQr - r/L_D} \right)$$

$$= i\frac{2\pi}{Q} \cdot \left[\frac{1}{iQ + \frac{1}{L_D}} - \frac{1}{-iQ + \frac{1}{L_D}} \right] = i\frac{2\pi}{\cancel{Q}}\, \frac{-2i\cancel{Q}}{Q^2 + \frac{1}{L_D^2}}$$

$$= \boxed{4\pi / (Q^2 + 1/L_D^2)}$$

$$M(\vec{k},\vec{k}') = \langle \vec{k}' | \hat{H}_{int} | \vec{k} \rangle =$$

$$= \frac{1}{V} \cdot \frac{\mp Z e^2}{4\pi\varepsilon_0 \varepsilon_s} \cdot \frac{4\pi}{Q^2 + \frac{1}{L_D^2}} =$$

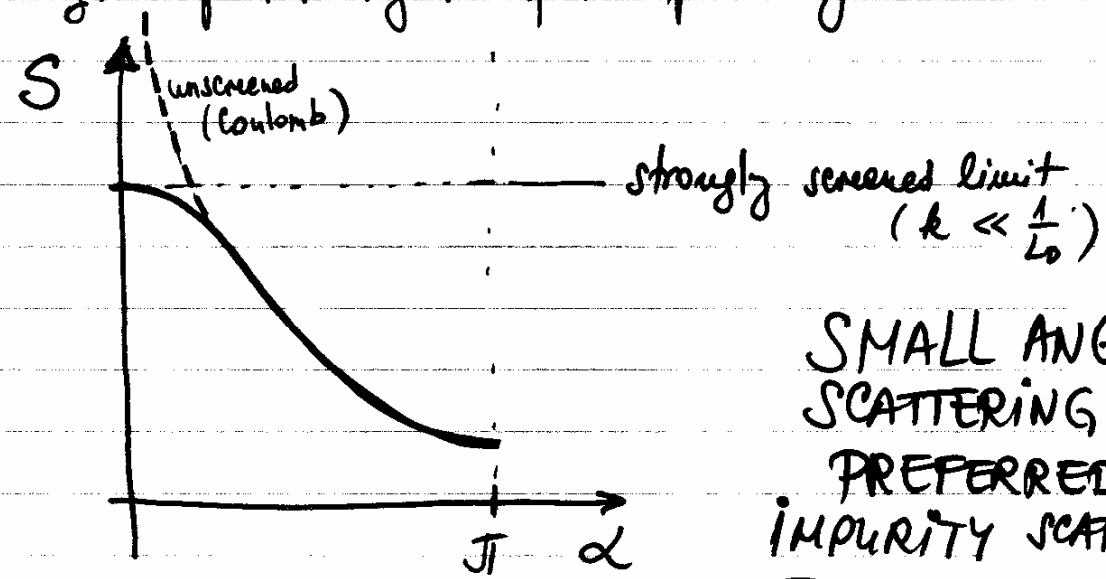
$$= \frac{1}{V} \cdot \frac{\mp Z e^2}{\cancel{4\pi}\varepsilon_0 \varepsilon_s} \cdot \frac{\cancel{4\pi}}{4k^2 \sin^2\left(\frac{\alpha}{2}\right) + \frac{1}{L_D^2}}$$

This is from a single impurity!

Transition rate, for $N_I V$ being the total number of impurities

$$\boxed{S(\vec{k},\vec{k}') = \frac{2\pi}{\hbar} \cdot N_I \cdot V \cdot \frac{Z^2 e^4}{V^2 \varepsilon_0^2 \varepsilon_s^2} \cdot \frac{\delta(\mathcal{E}(\vec{k}') - \mathcal{E}(\vec{k}))}{\left[4k^2 \sin^2\left(\frac{\alpha}{2}\right) + \frac{1}{L_D^2}\right]^2}}$$

Actually, the density that is present in the Debye length is the mobile carrier density (will be very different than the doping density in, e.g. depletion region of a p-n junction $n \to 0, L_D \to \infty$



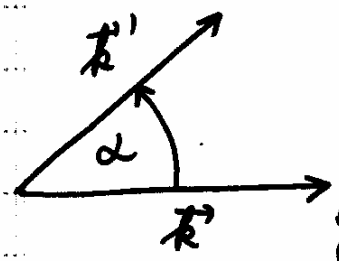
SMALL ANGLE SCATTERING PREFERRED!!!

IMPURITY SCATTERING NOT VERY GOOD AT RANDOMIZING MOMENTUM!!!

Total scattering rate:

$$\frac{1}{\tau(\vec{k})} = \Gamma(\vec{k}) = \sum_{\vec{k}'} S(\vec{k},\vec{k}') =$$

$$= \frac{2\pi}{\hbar}\cdot\frac{N_I Z^2 e^4}{\cancel{V}\,\varepsilon_0^2\varepsilon_s^2}\,\frac{\cancel{V}}{(2\pi)^3}\int d^3\vec{k}'\,\frac{\delta(\varepsilon(\vec{k}')-\varepsilon(\vec{k}))}{\left[4k^2\sin^2\left(\frac{\alpha}{2}\right)+\frac{1}{L_D^2}\right]^2}$$



$$= \frac{N_I Z^2 e^4}{\hbar(2\pi)^2\varepsilon_0^2\varepsilon_s^2}\cdot \text{integral}$$

$$\text{Integral} = 2\pi\int_0^\infty k'^2 dk' \int_{-1}^{1} d(\cos\alpha)\,\frac{\delta(\varepsilon(\vec{k}')-\varepsilon(\vec{k}))}{\left[4k^2\sin^2\left(\frac{\alpha}{2}\right)+\frac{1}{L_D^2}\right]^2}$$

$$\delta(f(x)) = \frac{\delta(x-x_0)}{\left|\frac{df}{dx}\right|_{x_0}}$$ (if $f(x)-f(x_0)=0$ has only one solution; otherwise, sum over all soln's.

$$\delta(\varepsilon(\vec{k}')-\varepsilon(\vec{k})) = \delta\left(\frac{\hbar^2}{2m^*}k'^2-\frac{\hbar^2}{2m^*}k^2\right)$$

$$= \frac{\delta(k'-k)}{\frac{\hbar^2 k}{m^*}}$$

$$\text{Integral} = 2\pi\cdot\frac{m^*}{\hbar^2 k}\underbrace{\int_0^\infty k'^2 dk'\cdot\delta(k'-k)}\int_{-1}^{1} d(\cos\alpha)\cdot\frac{1}{\left(4k^2\sin^2\left(\frac{\alpha}{2}\right)+\frac{1}{L_D^2}\right)^2}$$

$$= 2\pi\cdot\frac{m^*}{\hbar^2 k}\cdot k^2\cdot\int_{-1}^{1} d(\cos\alpha)\,\frac{1}{\left(2k^2(1-\cos\alpha)+\frac{1}{L_D^2}\right)^2}$$

In general $\int dx \frac{1}{(ax+b)^2} = -\frac{1}{a} \cdot \frac{1}{ax+b}$

Therefore,

$$\text{Integral} = 2\pi \frac{m^* \cancel{k}}{\hbar^2} \cdot \frac{1}{2k^{\cancel{2}}} \cdot \frac{1}{\left(4k^2 \sin^2\left(\frac{\alpha}{2}\right) + \frac{1}{L_D^2}\right)} \Bigg|_{\pi}^{0}$$

$$= \frac{\pi m^*}{\hbar^2 k} \cdot \left[\frac{-1}{4k^2 + \frac{1}{L_D^2}} + \frac{1}{\frac{1}{L_D^2}} \right]$$

$$= \frac{\pi m^*}{\hbar^2 k} \cdot \frac{4k^2 L_D^4}{4k^2 L_D^2 + 1} = \frac{4\pi m^* k L_D^4}{\hbar^2 (4k^2 L_D^2 + 1)}$$

$$\Gamma(k) = \frac{N_I Z^2 e^4 L_D^4}{\hbar (2\pi)^2 \varepsilon_0^2 \varepsilon_s^2} \cdot \frac{4\pi m^*}{\hbar^2} \cdot \frac{k}{(4k^2 L_D^2 + 1)}$$

$$= \frac{N_I Z^2 e^4 m^* L_D^4}{\hbar^3 \pi \varepsilon_0^2 \varepsilon_s^2} \left(\frac{k}{4k^2 L_D^2 + 1} \right)$$

Momentum relaxation rate (needed for Rode's method in problem 4 of your final)

$$\frac{1}{\tau_m(k)} = \frac{N_I Z^2 e^4}{\hbar (2\pi)^2 \varepsilon_0^2 \varepsilon_s^2} \cdot \underbrace{\int d^3 k' \frac{\delta(\varepsilon(k') - \varepsilon(k)) \cdot \left(1 - \frac{k' \cdot k}{k^2}\right)}{\left[4k^2 \sin^2\left(\frac{\alpha}{2}\right) + \frac{1}{L_D^2}\right]^2}}_{\text{Integral}}$$

$$\text{Integral} = 2\pi \int_0^\infty k'^2 dk' \; \frac{\delta(k'-k)}{\frac{\hbar^2 k}{m^*}} \int_{-1}^{1} d(\cos\alpha) \frac{(1-\cos\alpha)}{\left(2k^2(1-\cos\alpha)+\frac{1}{L_D^2}\right)^2}$$

$$x = 1-\cos\alpha$$

$$= 2\pi \cdot \frac{m^*}{\hbar^2 k} \cdot k^2 \cdot (-) \int_2^0 dx \frac{x}{\left(2k^2 x + \frac{1}{L_D^2}\right)^2}$$

$$= \frac{2\pi m^* k}{\hbar^2} \int_0^2 dx \frac{x}{\left(2k^2 x + \frac{1}{L_D^2}\right)^2} =$$

$$= \frac{2\pi m^* k}{\hbar^2} \left[\frac{1}{(2k^2)^2} \int_0^{4k^2} dy \frac{dy}{\left(y + \frac{1}{L_D^2}\right)^2} \right]$$

$$= \frac{\pi m^*}{2\hbar^2 k^3} \cdot \left[\int_0^{4k^2} dy \frac{\cancel{y + \frac{1}{L_D^2}}}{(y + 1/L_D^2)^{\cancel{2}}} - \frac{1}{L_D^2} \int_0^{4k^2} \frac{dy}{(y + 1/L_D^2)^2} \right]$$

$$= \frac{\pi m^*}{2\hbar^2 k^3} \left[\ln(y + 1/L_D^2) \Big|_0^{4k^2} + \frac{1}{L_D^2} \frac{1}{(y + 1/L_D^2)} \Big|_0^{4k^2} \right]$$

$$= \frac{\pi m^*}{2\hbar^2 k^3} \left[\ln(1 + 4k^2 L_D^2) + \frac{1}{L_D^2} \left(\frac{1}{4k^2 + 1/L_D^2} - \frac{1}{1/L_D^2} \right) \right]$$

$$= \frac{\pi m^*}{2\hbar^2 k^3} \left[\ln(1 + 4k^2 L_D^2) - \frac{4k^2 L_D^2}{4k^2 L_D^2 + 1} \right]$$

$$\Gamma_m(\vec{k}) = \frac{N_I Z^2 e^4}{\hbar (2\pi)^2 \varepsilon_0^2 \varepsilon_s^2} \cdot \frac{\pi m^*}{2\hbar^2 k^3} \cdot \left[\ln(1 + 4k^2 L_D^2) - \frac{4k^2 L_D^2}{1 + 4k^2 L_D^2} \right]$$

$$= \frac{N_I Z^2 e^4 m^*}{8\pi \hbar^3 \varepsilon_0^2 \varepsilon_s^2 k^3} \left[\ln(1 + 4k^2 L_D^2) - \frac{4k^2 L_D^2}{1 + 4k^2 L_D^2} \right]$$

Boltzmann Transport Equation

The central quantity of semiclassical (i.e., not quantum) transport, which is still the adequate approach to transport at room temperature in most semiconductor devices, even quite small ones, is the DISTRIBUTION FUNCTION

$$f(\vec{r}, \vec{p}, t)$$

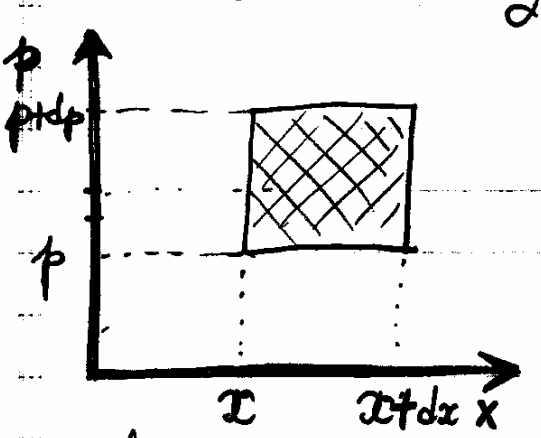
that describes how many particles at time t are found in a tiny volume $d^3\vec{r}$ around $\vec{r}$, and have momentum within $d^3\vec{p}$ of $\vec{p}$. (See p. 14 of the transport chapter in the notes, on why we say it is a "semiclassical" distribution function).

We have answered the first of the questions from page 15: why does f change in time? Due to external fields, scattering (we have covered most of the important scattering mechanisms in bulk semiconductors), and particles drifting out of the tiny $d^3\vec{r}$ volume.

These effects are all ~~described~~ incorporated in the BOLTZMANN TRANSPORT EQUATION, that describes temporal evolution of the distribution function:

$$\boxed{\frac{\partial f}{\partial t} + \left(\frac{\vec{p}}{m}\cdot\vec{\nabla}\right) f + \vec{F}\cdot\frac{\partial f}{\partial \vec{p}} = \left.\frac{\partial f}{\partial t}\right|_{\text{scattering}}}$$

What does this equation mean?



Say we are, for simplicity, considering just 1 spatial dimension. The distribution function was, at time t,

$$f(x,p,t)$$

What happens to the particles that were at time t in $dx\,dp$ (the space of all coordinates & momenta is called the PHASE SPACE: for d spatial dimensions, the phase space is $2d$-dimensional; $dx\,dp$ is a little volume in phase space corresponding to one real-space dimension)?

If the particle has velocity v, it will after dt be at $x+v\,dt$. However, the one that used to be at $x-v\,dt$ will now be at x. Due to the drift of particles, f has changed by

$$-f(x,p,t)+f(x-v\,dt,p,t)$$

Also, if there is external force applied $F=\frac{dp}{dt}$, those particles that had momentum p will leave the tiny phase-space volume and go to the one with $p+dt\cdot F$. However, those particles that were at $p-F\,dt$ will now be at p, which causes a net change

in the number of particles per $dx\,dp$ to be

$$-f(x,p,t) + f(x, p - F\,dt, t)$$

Last but not least, there are particles which are scattered into $dx\,dp$, and those scattered out

Scattered into during dt

$$dt \cdot \sum_{\vec{k}'} \underset{\substack{\uparrow \\ \text{initial}}}{S(\vec{k}', \vec{k})} \; \underset{\substack{\uparrow \\ \text{final} \\ \text{is } \vec{k}}}{f(\vec{k}')} \; \underset{\substack{\uparrow \\ \text{initial state} \\ \text{occupation}}}{(1 - f(\vec{k}))} \; \underbrace{\phantom{(1-f(\vec{k}))}}_{\substack{\uparrow \\ \text{final state} \\ \text{availability}}}$$

Scattered out of $dx\,dp$, during dt

$$dt \cdot \sum_{\vec{k}'} \underset{\substack{\uparrow \\ \text{initial}}}{S(\vec{k}, \vec{k}')} f(\vec{k})(1 - f(\vec{k}'))$$

So the total change in f is

$$df = f(x,p,t+dt) - f(x,p,t) =$$

$$= -f(x,p,t) + f(x - v\,dt, p, t) \quad \leftarrow \text{drift}$$

$$-f(x,p,t) + f(x, p - F\,dt, t) \quad \leftarrow \text{external forces}$$

$$+ dt \underbrace{\sum_{\vec{k}'} \left\{ S(\vec{k}', \vec{k}) f(\vec{k}')(1 - f(\vec{k})) - S(\vec{k}, \vec{k}') f(\vec{k})(1 - f(\vec{k}')) \right\}}_{\left.\frac{\partial f}{\partial t}\right|_{\text{scattering}}}$$

Since $f(x,p,t) - f(x-v\,dt,p,t) \approx v\,dt \frac{\partial f}{\partial x}(x-v\,dt,p,t)$
$\approx v\,dt \frac{\partial f}{\partial x}(x,p,t)$

and $f(x,p,t) - f(x,p-F\,dt,t) \approx F\,dt \frac{\partial f}{\partial p}(x,p,t)$,

we obtain

$$\underbrace{f(x,p,t+dt) - f(x,p,t)}_{\cancel{dt}\cdot \frac{\partial f}{\partial t}} = -v\,\cancel{dt}\frac{\partial f}{\partial x} - F\,\cancel{dt}\frac{\partial f}{\partial p} + \cancel{dt}\left(\frac{\partial f}{\partial t}\right)_{\text{scattering}}$$

$$\boxed{\frac{\partial f}{\partial t} + v\frac{\partial f}{\partial x} + F\frac{\partial f}{\partial p} = \left(\frac{\partial f}{\partial t}\right)_{\text{scattering}}}$$

1D version of Boltzmann equation

In 3D

$$\boxed{\frac{\partial f}{\partial t} + \frac{\vec{p}}{m}\cdot\underbrace{\frac{\partial f}{\partial \vec{r}}}_{\text{spatial gradient}} + \vec{F}\cdot\underbrace{\frac{\partial f}{\partial \vec{p}}}_{\text{momentum gradient}} = \left(\frac{\partial f}{\partial t}\right)_{\text{scattering}}}$$

BOLTZMANN TRANSPORT EQUATION (BTE)

Even when we know what scattering mechanisms are important, solving the BTE is not easy. Methods chosen depend strongly on how far we are from an equilibrium (Maxwell-Boltzman or Fermi-Dirac) distribution. Generally, low electric fields — fairly close to equilibrium. For high electric

fields, techniques utilized can become quite involved and will not be covered in this course.

For electronic transport in low electric fields, these two approaches will be covered:

1) RTA - relaxation time approximation
2) Rode's iterative method

Equilibrium and the Boltzmann Transport Equation

In equilibrium, in-scattering and out-scattering events are balanced

$$\left(\frac{\partial f}{\partial t}\right)\Big|_{scatt} = 0 \quad \left(\text{Collision integral on RHS of BTE is zero.}\right)$$

Also, the equilibrium distribution function does not depend explicitly on time

$$\frac{\partial f(\vec{r},\vec{p},t)}{\partial t} = 0$$

We know that in that case $f(\vec{r},\vec{p},t) = f_0(\vec{r},\vec{p})$ – the Fermi–Dirac distribution function

$$f_0(\vec{r},\vec{p}) = \frac{1}{\exp\underbrace{\left(\frac{\mathcal{E}_c(\vec{r}) + \frac{p^2}{2m} - \mathcal{E}_F(\vec{r})}{k_B T(\vec{r})}\right)}_{\theta} + 1}$$

According to the Boltzmann transport equation

$$\cancel{\frac{\partial f_0}{\partial t}} + \frac{\vec{p}}{m}\cdot\frac{\partial f_0}{\partial \vec{r}} + \vec{F}\cdot\frac{\partial f_0}{\partial \vec{r}} = \cancel{\left(\frac{\partial f}{\partial t}\right)_{scatt}} \to 0$$

$$\vec{F} = -e\vec{E} = e\frac{\partial \varphi}{\partial \vec{r}} = -\frac{\partial \mathcal{E}_c(\vec{r})}{\partial \vec{r}} \quad \leftarrow \text{this is built-in field}$$

$$\frac{\partial f_0}{\partial \vec{r}} = \frac{df_0}{d\theta}\cdot\frac{\partial \theta}{\partial \vec{r}} = \frac{df_0}{d\theta}\cdot\frac{\partial}{\partial \vec{r}}\left[\frac{\mathcal{E}_c(\vec{r}) + \frac{p^2}{2m} - \mathcal{E}_F(\vec{r})}{k_B T(\vec{r})}\right]$$

$$= \frac{df_0}{d\theta}\cdot\left(\frac{1}{k_B T}\right)^2\left[(k_B T)\left(\frac{\partial \mathcal{E}_c(\vec{r})}{\partial \vec{r}} - \frac{\partial \mathcal{E}_F(\vec{r})}{\partial \vec{r}}\right) - \left[\mathcal{E}_c + \frac{p^2}{2m} - \mathcal{E}_F\right]\cdot\frac{\partial k_B T}{\partial \vec{r}}\right]$$

$$\frac{\partial f_0}{\partial \vec{p}} = \frac{df_0}{d\theta}\cdot\frac{\partial\theta}{\partial\vec{p}} = \frac{df_0}{d\theta}\cdot\frac{1}{k_BT}\cdot\frac{\vec{p}}{m}$$

Into Boltzmann Transport eqn:

$$\frac{df_0}{d\theta}\left[\frac{\vec{p}}{m}\cdot\left(\frac{1}{k_BT}\right)\left(\overset{-\vec{F}}{\cancel{\frac{\partial\varepsilon_c}{\partial\vec{r}}}}-\frac{\partial\varepsilon_F}{\partial\vec{r}}\right)-\left(\varepsilon_c+\frac{p^2}{2m}-\varepsilon_F\right)\frac{1}{k_BT^2}\frac{\partial T}{\partial\vec{r}}\right.$$

$$\left.+\cancel{\vec{F}\cdot\frac{\vec{p}}{m}\cdot\frac{1}{k_BT}}\right]=0$$

Since $\frac{df_0}{d\theta}=0$

$$-\frac{\vec{p}}{m}\cdot\frac{\partial\varepsilon_F}{\partial\vec{r}}-\left(\varepsilon_c+\frac{p^2}{2m}-\varepsilon_F\right)\cdot\frac{1}{T}\frac{\partial T}{\partial\vec{r}}=0$$

Since this has to hold for any $\vec{p}$, we conclude:

$$\boxed{\frac{\partial\varepsilon_F}{\partial\vec{r}}=0}\quad\boxed{\frac{\partial T}{\partial\vec{r}}=0}$$

So the built in electric fields can be zero, but in equilibrium:
- the Fermi level is flat
- temperature is constant.

What makes the distribution reach its equilibrium form: electron-electron scattering!

This type of scattering is not crucial for estimating mobility, but it is what forces the distribution to the equilibrium one.

Maxwellian ($10^{17}-10^{18}\,cm^{-3}$ mobile carriers)
Fermi Dirac — above that — (degenerate case)

Relaxation Time Approximation (RTA)

In case of low external electric (and magnetic) fields, for some types of scattering, the solution to the Boltzmann transport equation can be found using the so-called relaxation time approximation.

The idea is to assume that the distribution function is close to its equilibrium form, i.e., that it can be written as a sum of a large symmetric and a small asymmetric part (symmetric & asymmetric refer to the behavior with respect to inversion of momentum).

$$f = f_S + f_A$$

So that if external fields are turned off, $f_S = f_0$, and $f_A = 0$.

The collision integral is then

$$\left.\frac{\partial f}{\partial t}\right|_{scatt} = \left.\frac{\partial f_S}{\partial t}\right|_{scatt} + \left.\frac{\partial f_A}{\partial t}\right|_{scatt}$$

$$\left.\frac{\partial f_S}{\partial t}\right|_{scatt} = \sum_{\vec{p}'} f_S(\vec{p})\, S(\vec{p},\vec{p}') - f_S(\vec{p}')\, S(\vec{p}',\vec{p})$$

If the applied field is low, then $f_S \approx f_0$, and we know that the collision integral vanishes in equil.

Therefore, the total collision integral is pretty much determined by the shape of the asymmetric function

$$\left.\frac{\partial f}{\partial t}\right|_{scat} = \left.\frac{\partial f_A}{\partial t}\right|_{scat} = \sum_{\vec{p}'} f_A(\vec{p})S(\vec{p},\vec{p}') - f_A(\vec{p}')S(\vec{p}',\vec{p})$$

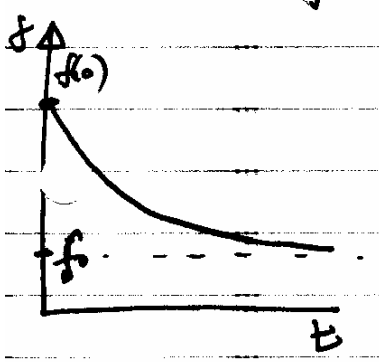
The relaxation time approximation introduces a characteristic time with which the distribution function relaxes (relaxation time) to approximate the collision integral, i.e.

$$\boxed{\left.\frac{\partial f}{\partial t}\right|_{scat} = \left.\frac{\partial f_A}{\partial t}\right|_{scat} = -\frac{f_A}{\tau_f}} \quad (RTA)$$

- Example 1: Spatially uniform semiconductor, no applied force (say we have perturbed it with bias and then left it alone

$$\frac{\partial f}{\partial t} + \frac{\vec{p}}{m}\cdot\underbrace{\cancel{\frac{\partial f}{\partial \vec{r}}}}_{\text{uniform}} + \underbrace{\cancel{\vec{F}}}_{\text{no force}}\cdot\frac{\partial f}{\partial \vec{p}} = \left.\frac{\partial f}{\partial t}\right|_{scat} = -\frac{f-f_0}{\tau_f} \quad RTA$$

$(f_s \approx f_0,\ f - f_0 = f_A)$



$$\frac{\partial f}{\partial t} = -\frac{f-f_0}{\tau_f}, \quad f = \text{const}\, e^{-t/\tau_f} + f_0$$

$(\text{const} = f(0) - f_0)$

$$f(t) = f_0 + (f(0) - f_0)e^{-t/\tau_f}$$

Example 2: uniform (spatially homogeneous) sample, low electric field $\vec{E}$, steady state, time-independent relaxation time.

$$\underbrace{\cancel{\frac{\partial f}{\partial t}}}_{\text{steady state}} + \frac{\vec{p}}{m}\cdot\underbrace{\cancel{\frac{\partial f}{\partial \vec{r}}}}_{\text{homogeneous}} + \vec{F}\cdot\frac{\partial f}{\partial \vec{p}} = \underbrace{\cancel{\frac{\partial f}{\partial t}\Big|_{scatt}}}_{-\frac{f_A}{\tau}\ \text{(relax. time approx)}}$$

$$\vec{F} = -e\vec{E} \qquad -e\vec{E}\cdot\frac{\partial f}{\partial \vec{p}} = -\frac{f_A}{\tau}$$

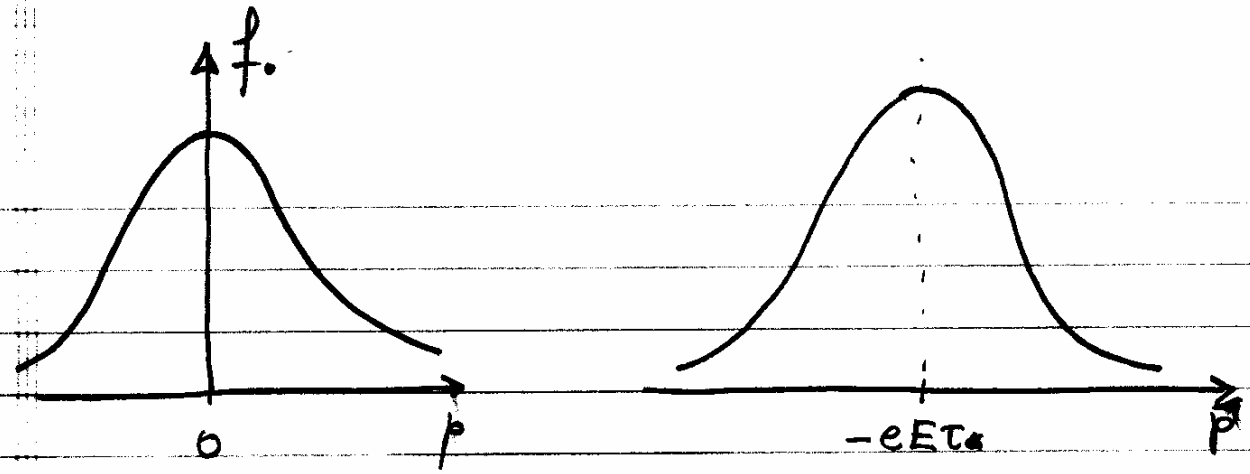
$$f = \underbrace{f_S + f_A}_{\text{low-field (near equil.)}} \approx \underbrace{f_0 + \tau e\vec{E}\cdot\frac{\partial f_0}{\partial \vec{p}}}_{\text{looks like 1st order expansion of } f_0(\vec{r},\vec{p}+\tau e\vec{E},t)}$$

f_0 - the equilibrium distribution
- will not depend explicitly on t
- will bear information on built-in fields in case of inhomogeneous doping; for a homogeneous case like here, there is not explicit $\vec{r}$-dependence, i.e.,

$$f_0 = f_0(\vec{p} + \tau e\vec{E})$$

How do we compute current?

$$\vec{J} = -ne\langle\vec{v}\rangle, \quad \langle\vec{v}\rangle = \frac{\int d^3\vec{p}\,\frac{\vec{p}}{m}\cdot f_0(\vec{p})}{\int d^3\vec{p}\, f_0(\vec{p})}$$



equilibrium low-field

$\langle \vec{v} \rangle = \frac{1}{m^*} \cdot$ where the peak is $= -\frac{e\tau}{m^*}\vec{E}$

We see that the low-field mobility is given by

$$\boxed{\mu = \frac{e\tau}{m^*}}$$

Current density then follows as

$$\vec{J} = -en\langle \vec{v} \rangle = \underbrace{\frac{e^2\tau n}{m^*}}_{\sigma} \vec{E}$$

σ conductivity
Drude result

High mobility — long relaxation time
small mass

Example 3

Spatially homogeneous sample, low-field, steady state $\rightarrow$ energy dependent relaxation time:

$$\underbrace{\cancel{\frac{\partial f}{\partial t}}}_{\text{steady state}} + \frac{\vec{p}}{m^*}\cdot\underbrace{\cancel{\frac{\partial f}{\partial \vec{r}}}}_{\text{homog}} + \vec{F}\cdot\frac{\partial f}{\partial \vec{p}} = \left.\frac{\partial f}{\partial t}\right|_{scatt}$$

$$\left.\frac{\partial f}{\partial t}\right|_{scatt} = -\frac{f_A}{\tau_f(\varepsilon)} \leftarrow \text{energy dependent relax. time}$$

$$-e\vec{E}\cdot\frac{\partial f}{\partial \vec{p}} = -\frac{f_A}{\tau_f(\varepsilon)} \qquad f_A(\vec{p}) = e\vec{E}\cdot\frac{\partial f}{\partial \vec{p}}\cdot\tau_f(\varepsilon(\vec{p}))$$

If we want just the first order in terms of the electric field (because it is low)

$$f_A(\vec{p}) \simeq e\vec{E}\cdot\frac{\partial f_0}{\partial \vec{p}}\,\tau_f(\varepsilon(\vec{p}))$$

Average velocity in the direction of the field

$$\underset{\substack{\uparrow\\ \text{drift}}}{v_d} = \langle v_\parallel \rangle = \frac{\int d^3\vec{p}\, v_\parallel f_A(\vec{p})}{\int d^3\vec{p}\, f_0(\vec{p})} =$$

$$= \frac{\int d^3\vec{p}\, v_\parallel\, eE\,\frac{df_0}{d\varepsilon}\cdot\frac{d\varepsilon}{dp_\parallel}\cdot\tau_f(\varepsilon(\vec{p}))}{\underbrace{\int d^3\vec{p}\, f_0(\vec{p})}_{n}}$$

If f_0 is Maxwell-Boltzmann, $\frac{df_0}{d\varepsilon} = -\frac{1}{k_B T} f_0(\varepsilon)$

$$v_d \equiv \langle v_\parallel \rangle = \frac{\int d^3\vec{p}\, \frac{p_\parallel}{m^*} \cdot eE \cdot \left(-\frac{1}{k_BT}\right) \cdot \frac{p_\parallel}{m^*}\, \tau_f(\varepsilon(\vec{p}))\, f_0(\varepsilon)}{n}$$

$$= \frac{-eE}{m^*} \cdot \frac{\int d^3\vec{p}\, (p_\parallel^2/2m^*)\, \tau_f(\varepsilon(\vec{p}))\, f_0(\varepsilon)}{\frac{k_BT \cdot n}{2}}$$

ε

$$\frac{k_BT \cdot n}{2} = \frac{1}{3}\langle \varepsilon \rangle$$

one third of average energy

$$= -\frac{eE}{m^*} \cdot \frac{1}{\cancel{\frac{1}{3}}\langle \varepsilon \rangle} \cdot \frac{1}{\cancel{3}} \int d^3\vec{p}\, \varepsilon\, \tau_f(\varepsilon)\, f_0(\varepsilon)$$

$\frac{p_\parallel^2}{2m^*}$ when averaged will give 1/3 of all the $\frac{p^2}{2m}$ averaged

$$\boxed{\mu \equiv \frac{|v_d|}{E} = \frac{e\langle\langle \tau \rangle\rangle}{m^*}}$$

$$\langle\langle \tau \rangle\rangle = \frac{\int d^3\vec{p}\, \varepsilon(\vec{p})\, \tau_f(\varepsilon(\vec{p}))\, f_0(\varepsilon(\vec{p}))}{\int d^3\vec{p}\, \varepsilon(\vec{p})\, f_0(\varepsilon(\vec{p}))} = \frac{\langle \varepsilon \tau_f(\varepsilon) \rangle}{\langle \varepsilon \rangle}$$

$$\langle \varepsilon \rangle = \int d^3\vec{p}\, \varepsilon(\vec{p})\, e^{-\varepsilon/k_BT} = \text{const}$$

$$= 4\pi \int_0^\infty p^2 dp\, \varepsilon(p)\, e^{-\varepsilon(p)/k_BT} \cdot \text{const}$$

$$x = \frac{\varepsilon(p)}{k_BT} = \frac{p^2}{2mk_BT} \qquad dx = \frac{p\,dp}{m^* k_BT}, \quad p = \sqrt{x}\,\sqrt{2m^* k_BT}$$

$$\langle \varepsilon \rangle = 4\pi \cdot \sqrt{2} \cdot m^{*3/2} (k_BT)^{5/2} \underbrace{\int_0^\infty x^{3/2} dx\, e^{-x}}_{\Gamma(5/2) = \frac{3\sqrt{\pi}}{4}} \cdot \text{const}$$

$$\langle \varepsilon \tau_f(\varepsilon) \rangle = \int d^3\vec{p}\, \varepsilon\, \tau_f(\varepsilon)\, e^{-\varepsilon/k_BT} \cdot \text{const}$$

For $\tau_f(\varepsilon) = \tau_0 (\varepsilon / k_BT)^s$, ($s = -1/2$ for acoustic phonons for instance)

$$\langle \varepsilon \tau_f(\varepsilon) \rangle = 4\pi\sqrt{2}\, m^{3/2} (k_BT)^{5/2} \tau_0 \cdot \text{const} \cdot \int_0^\infty x^{3/2+s} e^{-x} dx = \ldots \cdot \tau_0 (k_BT)^{5/2} \cdot \Gamma(5/2+s)$$

$$\langle\langle \tau \rangle\rangle = \tau_0 \frac{\Gamma(5/2+s)}{\Gamma(5/2)}$$

Acoustic phonons $s = -1/2$; $\Gamma(5/2 - 1/2) = \Gamma(2) = 1$

$$\boxed{\langle\langle \tau_{ac} \rangle\rangle = \tau_0 \frac{4}{3\sqrt{\pi}}} \qquad \boxed{\mu_{ac} = \frac{e\tau_0}{m^*} \cdot \frac{4}{3\sqrt{\pi}}}$$

τ_0 – contains Ξ, sound velocity

Relaxation-time approximation is valid only for either elastic or isotropic scattering events:

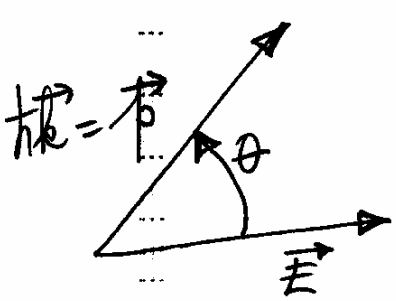
elastic	isotropic
acoustic	acoustic
ionized imp.	non-polar optical intervalley

Rode's Method for Low-Field Transport

In case of scattering processes that are neither elastic nor isotropic, the relaxation time approximation fails (an example is polar optical phonon scattering). Rode's method, which is iterative in nature, enables calculation of the STEADY STATE DISTRIBUTION FUNCTION IN A HOMOGENEOUS SEMICONDUCTOR UNDER LOW-FIELD CONDITIONS. (When only elastic & isotropic processes are present, it gives the same result as the relaxation time approximation, and "iteration" requires only one step.)

$$\underbrace{\cancel{\frac{\partial f}{\partial t}}}_{\substack{\to 0 \\ \text{steady state}}} + \frac{\vec{p}}{m}\cdot\underbrace{\cancel{\frac{\partial f}{\partial \vec{r}}}}_{\substack{\to 0 \\ \text{homogen.}}} + \vec{F}\cdot\frac{\partial f}{\partial \vec{p}} = \left.\frac{\partial f}{\partial t}\right|_{scatt}$$

$\vec{F} = -e\vec{E}$, $\vec{E}$ low ($|\vec{E}| < 10\,kV/cm$)



The direction of the external electric field is obviously preferred. Therefore, we assume the distribution function to be of the form

$$f(\vec{k}) = \underbrace{f_0(\vec{k})}_{\text{equilibrium}} + g(\vec{k})\cos\theta + O(\cos^2\theta)$$

We keep only the first term in $\cos\theta$. From a more general expansion order (so-called Legendre polynom. expansion), that is valid at even higher fields, one

can deduce that indeed the very-low field behavior is well-described by the $g(k)\cos\theta$ form. ‖

$$-e\vec{E}\cdot\frac{\partial f}{\partial \vec{p}} = -\frac{e}{\hbar}\vec{E}\frac{\partial f}{\partial \vec{k}} = -\frac{e}{\hbar}\vec{E}\cdot\left(\frac{\partial f}{\partial k}\cdot\vec{e}_k + \right.$$

$$\left. + \frac{1}{k}\frac{\partial f}{\partial \theta}\vec{e}_\theta + \cancel{\frac{1}{k\sin\theta}\frac{\partial f}{\partial \varphi}\vec{e}_\varphi}\right) =$$

$$= -\frac{e\vec{E}}{\hbar}\cdot\left(\left\{\frac{df_0}{dk} + \cos\theta\frac{\partial g}{\partial k}\right\}\vec{e}_k - \frac{1}{k}g(k)\sin\theta\,\vec{e}_\theta\right)$$

$$= -\frac{eE}{\hbar}\cos\theta\left\{\frac{df_0}{dk} + \cos\theta\frac{dg}{dk}\right\} + \frac{e}{\hbar}g(k)\sin\theta\,\underbrace{\vec{E}\cdot\vec{e}_\theta}_{-E\sin\theta}$$

Keeping only the lowest-order terms in $\cos\theta$

$$-e\vec{E}\cdot\frac{\partial f}{\partial \vec{p}} \simeq -\frac{eE}{\hbar}\frac{df_0}{dk}\cdot\cos\theta = -\frac{eE}{\hbar}\frac{df_0}{d\varepsilon}\cdot\frac{d\varepsilon}{dk}\cdot\cos\theta$$

$$\frac{d\varepsilon}{dk} = \underbrace{\frac{\hbar^2}{m^*}k}_{=\hbar\cdot v} \Rightarrow -e\vec{E}\cdot\frac{\partial f}{\partial \vec{p}} = \underline{\underline{-eEv\frac{df_0}{d\varepsilon}\cdot\cos\theta}}\,\|$$

The collision integral:

$$\left.\frac{\partial f}{\partial t}\right|_{coll} = \sum_{\vec{k}'} S(\vec{k}',\vec{k})\left[f_0(k') + g(k')\cos\theta'\right]\times$$
$$\times\left[1 - f_0(k) - g(k)\cos\theta\right]$$
$$-\sum_{\vec{k}'} S(\vec{k},\vec{k}')\left[f_0(k) + g(k)\cos\theta\right]$$
$$\left[1 - f_0(k') - g(k')\cos\theta'\right]$$

In equilibrium $\quad S(\vec{k}',\vec{k}) f_0(\vec{k}')(1-f_0(\vec{k})) =$
$$= S(\vec{k},\vec{k}') f_0(\vec{k})(1-f_0(\vec{k}'))$$

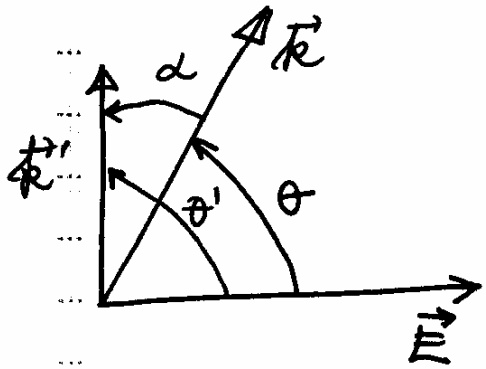
so when these cancel, we obtain

$$\left.\frac{\partial f}{\partial t}\right|_{scatt} = \sum_{\vec{k}'} -S(\vec{k}',\vec{k}) f_0(\vec{k}') g(\vec{k}) \cos\theta + S(\vec{k}',\vec{k})(1-f_0(\vec{k})) g(\vec{k}') \cos\theta' + \underset{\cos\theta'}{\mathcal{O}(\cos\theta)}$$
$$+ S(\vec{k},\vec{k}') f_0(\vec{k}) g(\vec{k}') \cos\theta'$$
$$- S(\vec{k},\vec{k}') g(\vec{k}) \cos\theta (1-f_0(\vec{k}')) + \mathcal{O}(\cos\theta\cos\theta')$$

$$\left.\frac{\partial f}{\partial t}\right|_{scatt} = \sum_{\vec{k}'} g(\vec{k}') \cos\theta' \left[S(\vec{k}',\vec{k})(1-f_0(\vec{k})) + S(\vec{k},\vec{k}') f_0(\vec{k}) \right]$$
$$- g(\vec{k}) \cos\theta \left[S(\vec{k}',\vec{k}) f_0(\vec{k}') + S(\vec{k},\vec{k}')(1-f_0(\vec{k}')) \right]$$

We now distinguish between elastic & inelastic scattering
$$S = S^{el} + S^{in}$$

For elastic processes $k' = k$ so $g(k) = g(k')$, $f_0(k) = f_0(k')$, and also $S(\vec{k},\vec{k}') = S(\vec{k}',\vec{k})$



$$\frac{\cos\theta'}{\cos\theta} = \operatorname{tg}\theta \sin\alpha \sin\varphi + \cos\alpha$$

averages to zero

$$\left.\frac{\partial f}{\partial t}\right|_{scatt}^{el} = \sum S^{el}(\vec{k},\vec{k}')\, g(k) \cos\theta \times$$
$$\times \left[-\cancel{f_0(k)} - (1-\cancel{f_0(k)}) + (1-\cancel{f_0(k)}) \cos\alpha + \cancel{f_0(k) \cos\alpha} \right]$$
$$= -g(k) \cos\theta \sum_{\vec{k}'} S^{el}(\vec{k},\vec{k}')\,(1-\cos\alpha)$$
$$= -g(k) \cos\theta \cdot \frac{1}{\tau_m^{el}(k)}$$

Inelastic part of the collision integral

$$\left.\frac{\partial f}{\partial t}\right|_{scatt}^{in} = \cos\theta \sum_{\vec{k}'} g(k') \left[S^{in}(\vec{k}',\vec{k})\,(1-f_0(k)) + S^{in}(\vec{k},\vec{k}')\, f_0(k) \right] \cos\alpha$$
$$- g(k) \left[f_0(k')\, S^{in}(\vec{k}',\vec{k}) \cancel{f_0(k)} + S^{in}(\vec{k},\vec{k}')\,(1-f_0(k')) \right]$$

$$\tilde{I} = \sum_{\vec{k}'} g(k') \cos\alpha \left[S^{in}(\vec{k}',\vec{k})\,(1-f_0(k)) + S^{in}(\vec{k},\vec{k}')\, f_0(k) \right]$$

$$I_0 = \sum_{\vec{k}'} S^{in}(\vec{k},\vec{k}') + \sum_{\vec{k}'} f_0(\vec{k}')\, S^{in}(\vec{k}',\vec{k}) - S^{in}(\vec{k},\vec{k}')$$

$$\left.\frac{\partial f}{\partial t}\right|_{coll}^{in} = \cos\theta \left\{ \tilde{I}(\vec{k}) - g(k)\, I_0(\vec{k}) \right\}$$

$$-eEv\frac{df_0}{d\varepsilon}\cancel{\cos\theta} = -g(k)\cancel{\cos\theta}\cdot\frac{1}{\tau_m^{el}(k)}$$
$$+\cancel{\cos\theta}\left\{\tilde{I}(k) - g(k)I_0(k)\right\}$$

$$-eEv\frac{df_0}{d\varepsilon} = -g(k)\left[\frac{1}{\tau_m^{el}(k)} + I_0(k)\right] + \tilde{I}(k)$$

$$\boxed{g(k) = \frac{\tilde{I}(k) + eEv\frac{df_0}{d\varepsilon}}{\frac{1}{\tau_m^{el}(k)} + I_0(k)}} \qquad \left(v = \frac{\hbar k}{m^*}\right)$$

- If the scattering process is isotropic, $\tilde{I} = 0$.

$$g(k) = \frac{evE\frac{df}{d\varepsilon}}{\underbrace{I_0(k) + \frac{1}{\tau_m^{el}(k)}}_{\frac{1}{\tau_{tot}(k)}}} = \underbrace{ev\,\tau_{tot}(k)\frac{df}{d\varepsilon}}_{\text{relax. time approx. result}}\cdot E$$

- <u>Set up iterative procedure</u>: First, evaluate τ_m^{el} and $I_0(k)$.

For multiple elastic scattering mechanisms

$$\frac{1}{\tau_m^{el}} = \frac{1}{\tau_{m,1}^{el}} + \frac{1}{\tau_{2,m}^{el}} + \cdots$$

(For nondegenerate case, you can easily show that $I_0(k) = \Gamma(k) \leftarrow$ total scattering rate, $\frac{1}{\tau(k)}$.)

Assume $g^{(0)} = 0 \Rightarrow \tilde{I}^{(0)} = 0$ ($\tilde{I}$ is the only thing that needs to be iterated.)

$$g^{(1)}(k) = \underbrace{\frac{ev\frac{df_0}{d\varepsilon}}{\frac{1}{\tau_m^{el}(k)} + I_0(k)}}_{\equiv\, \tilde{a}^{(1)}(k)} \cdot E$$

$$\tilde{I}^{(1)}(k) = E \underbrace{\sum_{\vec{k}'} \tilde{a}^{(1)}(k') \cos\alpha \left[S^{in}(\vec{k}', \vec{k}) + f_0(k)\left[S^{in}(\vec{k}, \vec{k}') - S^{in}(\vec{k}', \vec{k})\right]\right]}_{\tilde{b}^{(1)}}$$

$$g^{(2)} = E \boxed{\frac{\tilde{b}^{(1)}(k) + ev\frac{df_0}{d\varepsilon}}{\frac{1}{\tau_m^{el}(k)} + I_0(k)}} \tilde{a}^{(2)}(k)$$

And so forth; n-th step

$$g^{(n)} = E\,\tilde{a}^{(n)} \Rightarrow \tilde{I}^{(n)}(k) = E \underbrace{\sum_{\vec{k}'} \tilde{a}^{(n)}(k') \cos\alpha(\ldots)}_{\tilde{b}^{(n)}(k)}$$

$$g^{(n+1)}(k) = E \boxed{\frac{\tilde{b}^{(n)} + ev\frac{df_0}{d\varepsilon}}{\frac{1}{\tau_m^{el}(k)} + I_0(k)}} = \tilde{a}^{(n+1)}$$

(do the loop until converges)

Mobility is found from

$$\mu = \frac{|\langle v_\parallel \rangle|}{E} = \frac{\int d^3\vec{k}\, g(k) \cos\theta \cdot \overbrace{(v\cos\theta)}^{v_\parallel}}{\int d^3\vec{k}\, f_0(k)} \cdot \frac{1}{E}$$