

Solid State Physics

Alessio Cimma

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1 10-03-25: — Introduction (Forneris)

1.1 Correction of the test

Linearly polarized light:

$$\vec{\mathcal{E}} = \mathcal{E}_0 \hat{e}_x \cos(\omega t) \quad (1)$$

Remember that the \vec{B} and $\vec{\mathcal{E}}$ fields are \perp . We can obtain the value of the speed of light as:

$$c = \frac{1}{\sqrt{\mu_0 \varepsilon_0}} \quad (2)$$

Since we want to consider a linearly polarized plane, we consider the 1D case. We can then derive all informations about the period, frequency and pulse.

Band diagram of a crystal: We have regions where some energies are permitted and others where they are prohibited. The difference in the prohibited regions generate the difference between metals, semiconductors and insulators. The band diagram is a function of the crystal structure.

- Metals: valence band occupied at lowest energy.
- Semiconductors: valence band not occupied at lowest energy, and there is a small gap between the valence and conduction bands.
- Insulators: valence band not occupied at lowest energy, and there is a large gap between the valence and conduction bands.

The energy gap is the difference between the valence and conduction bands. From the following equation we can obtain the value of the energy gap:

$$E_T = k_B T \simeq 0.026 \text{ eV} \text{ (@ } 300 \text{ K)} \quad (3)$$

Between 1 and 3 eV we have the energy gap for semiconductors, while for insulators it is greater than 3 eV. Remember that the probability follows:

$$\text{prob.} \propto e^{k_B T / E_g} \quad (4)$$

This means that the definition of semiconductor or not depends on the temperature.

What is a photon: A photon is a wave-particle duality. And we can obtain its energy from the following equation:

$$E = h\nu = \frac{hc}{\lambda} = \frac{1240}{\lambda} \text{ eV} \quad (5)$$

Another important information is its momentum:

$$p = \hbar \hat{k} \quad (6)$$

What is a phonon: A phonon is a quantized vibration of the crystal lattice (elementary quantum of lattice vibration). It is a wave-particle duality. The energy of an individual phonon is:

$$E = \hbar\Omega = E_{\Omega,n} = \left(\frac{1}{2} + n\right) \hbar\Omega, \quad n \in \mathbb{N} \quad (7)$$

The phonon density is given by:

$$\rho_{\Omega} \propto \frac{1}{\exp\left[\frac{\hbar\Omega}{kT}\right] - 1} \quad (8)$$

Snell's law: The refraction index is the relative speed of light in a medium. The refraction index is given by:

$$n = \frac{c}{v} \quad (9)$$

If we want to know how much the light is refracted, we can use Snell's law:

$$n_1 \sin(\theta_1) = n_2 \sin(\theta_2) \quad (10)$$

Quantum states superposition: Let's consider a system that can be in many different states. The total wavefunction is given by:

$$|\Psi\rangle = \sum_{i=1}^N c_i |\psi_i\rangle \quad (11)$$

Photon absorption: This phenomenon depends mostly on the energy of the photon and the energy gap of the material ($h\nu \geq E_g$).

P-type semiconductor: We have acceptors creating new energy levels in the forbidden gap. The acceptors are positive ions. The energy levels are close to the valence band, effectively lowering the band gap. If I call N_a the number of acceptors, the hole density is $\rho \simeq N_a$ and most importantly $p \gg n$.

Ohm's law (Macro & Micro): The current is given by:

$$I = \frac{V}{R} \quad (12)$$

In microscopic terms, the current is given by the Drude's model.

2 12-03-25: — Tight binding model (Rigid Spheres) (Forneris)

Introduction: It's a formal way to describe the Band structure of crystals using a quantum mechanical approach. We can define a wavefunction for an electron bounded to the wavefunction (orbitals).

$$\hat{H}_{at} |\Psi\rangle = E_0 |\Psi\rangle \quad (13)$$

Next we move from a single atom to the periodic lattice.

Atomic radius: This can be considered the first thing that changes when using different elements. Consequentially the interatomic distance changes. We can use the rigid sphere model, where the sum of 2 radii gives us the interatomic distance. Since usually all the distances are expressed as chemical bonds, we will have the following type of radii, based on the bond nature:

- Ionic Radius (NaCl)
- Covalent Radius (Si, Ge)
- Metallic Radius (Metallic Na)
- Van der Waals Radius

Na example: Na values for different radii are 154pm for ionic and 186pm for metallic, which has a difference $\sim 20\%$. So the choice strongly depends on the usage.

If we consider the electronic configuration we have $[Na] = (1S)^2(2S)^2(2P)^6(3S)^1$, which are 4 different wavefunctions. We can also consider the Hamiltonian as:

$$\hat{H} = \hat{T} + \hat{V}(x) \quad (14)$$

$$\hat{T} = \frac{\hat{p}^2}{2m} \quad (15)$$

$$\hat{V}(x) = -\frac{1}{4\pi\epsilon} \frac{Ze^2}{x} \quad (16)$$

While the Ψ is considered as a product of a Radial component and Angular component:

$$\Psi(\vec{x}) = R_{n,l}(r) \cdot Y_{l,m}(\theta, \phi) \quad (17)$$

Additionally we replace the value of the radius with a new term ρ which is related to the Hydrogen radius (a_0 is the Bohr radius $\sim 53\text{pm}$). Just to have more relative values:

$$r \rightarrow \rho = \frac{r}{a_0} \quad (18)$$

From the notes we can note that we have essentially 2 different classes of electrons: localized and not localized (core and valence), this is because by plotting the Radial probability we see how the most external electrons are way out the ionic radius, so we can consider them as a 'lattice electron'. We can then divide the orbitals into 'core', 'valence' and 'lattice'. In addition we consider that Ψ are different superpositions of orbitals wavefunctions.

$$|\Psi\rangle \rightarrow |\varphi\rangle \quad (19)$$

Where the φ is a repetition of Ψ that create the crystal structure. We can see that the different Ψ are overlapping between each other. And each Ψ is just traslated in space:

$$|\Psi_i\rangle = |\Psi(x = x_i)\rangle \quad (20)$$

Overlapping, bonding and anti-bonding: In the overlapped Ψ we can have a bonding or anti-bonding configuration of electrons. If this is taken to infinity we generate bands. We recover the LCAO model, generalizing $|\varphi\rangle$ as a linear combination of $|\Psi\rangle$:

$$|\varphi(x)\rangle = \underbrace{\frac{1}{A}}_{\text{normalization}} \cdot \sum_{i=1}^N \underbrace{c_i}_{\text{weights}} |\Psi(x - x_i)\rangle \quad (21)$$

If in this simple example we have identical atoms, $|c_i|^2 = 1; \forall i$. Limit cases: maximally symmetric with $c_i = 1; \forall i$ and $c_i = (-1)^i; \forall i$ which is the maximally antisymmetric case.

$$|\varphi_+(x)\rangle = \frac{1}{A} \sum_{i=1}^N |\Psi(x - x_i)\rangle \quad (22)$$

$$|\varphi_-(x)\rangle = \frac{1}{A} (-1)^i \sum_{i=1}^N |\Psi(x - x_i)\rangle \quad (23)$$

To interpolate between them we will use c_j which is a phase defined as $e^{i\phi_j}$ where ϕ_j ranges between 0 and $j\pi$.

Potential: We can also describe how consequentially the potential changes:

$$V_{\text{at}} \propto -\frac{1}{x} \quad (24)$$

And with infinity of these equation we have overlaps, so we actually see the sum of all of them. (they go lower and smoother because values are negative). So how do we write the \hat{H}_{crystal} ?

$$\hat{H}_{\text{crystal}} = \hat{T} + \hat{V}_{\text{crystal}} \quad (25)$$

$$\hat{V}_{\text{crystal}} = \hat{V}_{\text{crystal}} + \underbrace{\left[\sum_{i=1}^N \hat{V}_{\text{at}}(x - x_i) - \sum_{i=1}^N \hat{V}_{\text{at}}(x - x_i) \right]}_{=0} \quad (26)$$

This means that we can actually rewrite it as:

$$\hat{H}_{\text{single}} = \underbrace{\frac{p^2}{2m} + \sum_{i=1}^N \hat{V}_{\text{at}}(x - x_i)}_{\text{Isolated}} + \underbrace{\left[\hat{V}_{\text{crystal}}(x - x_i) - \sum_{i=1}^N \hat{V}_{\text{at}}(x - x_i) \right]}_{\hat{V}_{\text{Perturbation}}} \quad (27)$$

So essentially we are considering the fact that the crystal exist and exchanges some energy as a perturbation of the isolated atom, which can be seen as a veery slow correction term that looks like a small sine negative wave. (look at Obsidian images) which has its maximum in the interatomic space (max distance between atoms). Of course the infinite limit goes like this:

$$\lim_{d \rightarrow \infty} \hat{V}_{\text{pert}}(x, d) = 0 \quad (28)$$

What happens when we switch again to the linear combination $|\varphi\rangle$? Well, $|\varphi\rangle$ is an eigenfunction of the Hamiltonian of the crystal, so it gives us the possibility to collapse it perfectly into the corresponding eigenvalue, which we couldn't do with the $|\Psi\rangle$, since being the isolated atom, it couldn't resolve the crystal perturbation:

$$\text{Eigenvalue} = (E_0 + \Delta E) \quad (29)$$

$$\Delta E = \int \langle \varphi(x) | \hat{V}_{\text{pert.}} | \varphi(x) \rangle \quad (30)$$

$$\frac{\Delta E}{E_0} \ll 1 \quad (31)$$

3 13-03-25: — Continuation of Tight model (Forneris)

When we consider functions that are very broad, they can sum such that the $|\varphi_+\rangle$ almost creates a continuous line, which means that's as if the $\lambda \rightarrow \infty$. But for the rest nothing changes, the periodicity stays the same nonetheless.

1° Brillouin zone: This is the smallest zone of the crystal where i can define the physical properties that describe the properties of all the crystal. It is defined in the reciprocal space because everything ranges from:

$$k \in \left[0, \frac{\pi}{d}\right] \quad (32)$$

Where the range indicates the frequency range assumed by k , so 0 is the φ_+ and the other the negative wavefunction. We can take a step further and calculate the ΔE_{\pm} which means the maximum difference in energy for both the $+$ version and the $-$ version.

$$\Delta E_{\pm} = \int dx \langle \varphi_{\pm} | \hat{V}_{\text{pert}} | \varphi_{\pm} \rangle \quad (33)$$

The question is which delta energy will be greater? We must consider that the $+$ one, has a smaller excursion, but the higher area covered. So in conclusion, yeah, the $\Delta E_+ < \Delta E_-$.

If we compare and plot the ΔE with the interatomic distance, we notice the difference between the 2 tends both to 0, this is because at extreme distances, there are no overlaps. While as long as they differ, we have an energy band, indicating the *Difference between the maximum excursion of energy generated from the different frequency of the wavefunction..* It generates the pictures we studied with Scarano, where we have the continues variation of energy when travelling inside the Brillouin zone.

3.1 Direct & Indirect lattice

Direct / Bravais: In the direct lattice we have the position of the nodes and they can be reached by using traslation vectors multiplied an integer number of times.

Indirect / Reciprocal: All representad using the wave vector \vec{k} , all the positions can again be reached by using a complex number times the base vectors.

Primitive cell: Smallest amount of space needed to describe the whole crystal by just applying a range of traslations. You can see some examples / exercises in the Obsidian file. Next follows a representation of energy bands, DOS and points of itnerest.

4 17-03-25: — Direct & Indirect band gap (Forneris)

In the indirect energy gap the jump is not straight, or more correctly, there's a change in the momentum of the electron, which will change its position. The momentum is calculated as:

$$p_\gamma = \hbar \vec{\chi} \quad \longrightarrow \quad \chi = \frac{2\pi}{\lambda} \quad (34)$$

This means that the photon is not carrying enough momentum to make the transition happen (3-4 orders of magnitude off). It's only enough to make the promotion, but not enough to move it.

Phonons: These are the answer to the momentum check. According to the conservation of energy we must have:

- $E_i + h\nu + \hbar\Omega = E_f$, meaning that the initial energy + photon's energy + phonon's energy gives us the final energy.
- $\hbar k_i + \hbar\chi + \hbar K = \hbar k_f$, meaning that the initial wave vector + the phonon's momentum (we can neglect the photon's momentum).

The energy of a phonon is:

$$\hbar\Omega = \hbar c \Delta \left(\frac{1}{\lambda} \right) \sim 10^{-2} eV \quad (35)$$

Which is negligible in the energy calculation. See it like this: photons are very high frequency (high energy) but very small (low momentum), the phonons on the other hand are very low frequency (low energy) but big particles (high momentum). Since they have a small frequency, it's easy to find a phonon which vibrates at the right (low) frequency to get the right energy and jump, making the prohibited transition happen.

4.1 Electro-Magnetic fields in materials

We will focus on electric changes through interactions. We will have *elastic* and *inelastic* interactions. Most of them will be considered as dipoles. For example we can start with:

Coulomb's law: It describes the interaction between two charges (in void).

$$\vec{F} = \frac{q_1 q_2}{4\pi\epsilon_0 r^2} \hat{r} \quad (36)$$

The ϵ_0 refers to vacuum, so in a material we will have a different magnitude of the force. Additionally the electric field associated to a charge is:

$$\vec{\mathcal{E}}_1 = \frac{q_1}{4\pi\epsilon_0 r^2} \hat{r} \rightarrow \vec{F} = q_2 \vec{\mathcal{E}}_1 \quad (37)$$

$$-\nabla V = \vec{\mathcal{E}} \quad (38)$$

General writing:

$$\vec{\nabla} \mathcal{E} = \frac{\rho}{\epsilon_0} \quad (39)$$

And remember, $\vec{\mathcal{E}}$ has its source from the + and sinks into the -.

Dipoles: We will not focus on understanding why and how some things happens, but remember that dipoles create EMW when oscillating and charges generate a EMW when moving (each of them have their associated equations).

Maxwell's equations: Quick recap of the equations, we will use them in the future to explain some behaviours in the materials. Also we saw how they are interlinked.

- $\nabla \cdot \mathcal{E} = \frac{\rho}{\varepsilon_0}$
- $\nabla \cdot B = 0$
- $\nabla \wedge \vec{B} = \mu_0 \vec{j} + \mu_0 \varepsilon_0 \frac{\partial \mathcal{E}}{\partial t}$
- $\nabla \wedge \mathcal{E} = -\frac{\partial \vec{B}}{\partial t}$

Combining them we can obtain this bad boy, that relates everything with everything:

$$\nabla^2 \mathcal{E} = \frac{1}{c^2} \frac{\partial^2 \mathcal{E}}{\partial t^2} \quad \mu_0 \varepsilon_0 = \frac{1}{c^2} \quad (40)$$

Displacement field: It's introduced as $\vec{D} = \varepsilon \vec{\mathcal{E}} = \varepsilon_0 \varepsilon_r \vec{\mathcal{E}} + \vec{P}$ where \vec{P} is the polarization field.

$$\vec{P} = \varepsilon_0 (\varepsilon_r - 1) \vec{\mathcal{E}} \quad (41)$$

So it's like the additional response we got from the material reacting to the wave.

$$\vec{P} = n_c \hat{p} \quad (42)$$

We have n_c density of dipoles and \hat{p} microscopic dipole moment. Essentially it measures how well the charges are aligned with the electric field.

Magnetic strength field:

$$\vec{H} = \frac{\vec{B}}{\mu} \quad (43)$$

Where \vec{B} is the magnetic induction field. This considers the material effect on the magnetic field. We can consider both electric and magnetic field as separate issues for their description. In the obsidian file there's the formula derivation, resulting in:

$$\vec{\nabla} \wedge \vec{H} = \vec{j} + \frac{\partial \vec{D}}{\partial t} \quad (44)$$

This has consequences on the Drude's model, since it describes how the electric and magnetic field interact when current goes through a wire.

5 19-03-25: — Electrical properties (Olivero)

Bands, electron states in crystals. This is mainly all we need to know. Bloch theorem which describes delocalized electrons in crystals. This plots the energy of the electron and the momentum (k which is also the k in $p = \hbar k$).

What is interesting is that at almost 0°K we got all the electrons in the valence band. So in ideal conditions an insulator or something with a band gap do not let pass any current. But at room temperature, something passes.

When talking about ‘free’ charges, we refer to charges that move under the action of an Electrical field. The value of n and p are expressed in [cm^{-3}], they are concentrations.

We will use the Fermi-Dirac statistical distribution for electrons. Quick recap: We have E on the x, and Probability function on the y. The form of this function depends on the E_F Fermi’s energy. It’s the ‘Scalino Function’. Combining this with the DOS function we obtain that the E_F is considered to be in the middle of the forbidden gap.

The Fermi-Dirac is applied to states. If they do not exist in the forbidden gap, regardless of the distribution, we will not have electrons there. This statistic is the following:

$$f(E) = \frac{1}{\exp\left[\frac{E-E_F}{kT}\right] + 1} \quad (45)$$

$$g(E) = \text{DOS} \quad (46)$$

$$g(E)f(E) = \text{Electrons per unit of Volume} \quad (47)$$

We do not derive the $g(E)f(E)$, but let’s just say we have a square root dependency on the energy. Just a side note, the $g(E)$ is already the product of the energy band and the $f(E)$.

The important formulas we need to know are:

5.1 Charge carriers & Doping

$$\begin{cases} n^- = N_c \exp\left(\frac{E_F - E_C}{kT}\right) \\ p^+ = N_v \exp\left(\frac{E_V - E_F}{kT}\right) \end{cases} \quad (48)$$

N_c are the actual states that can be occupied in the conduction band and there are about 10^{19} if them in a cubic cm, while we have $\sim 10^{22}$ atoms. This means that the actual free electrons are 10^{10} (from $f(E)g(E)$). This means that the free electrons generated from the doping ($\sim 10^{14}$) make this intrinsic free electrons negligible. For Silicon additionally we know that the E_g is 1.12eV. These are given from doping elements from the *III* and the *VI* element groups. This means that n and p are not equal, we will refer to n_i as $n_i = n = p$, which in an intrinsic semiconductor: $n_i^2 = np$, since the product needs to be the same, by the ‘law of mass action’ if one increases the other one decreases.

Donors and Acceptors energy levels: They are a little it higher and lower the conductive and valence band. They can help (thanks to heat) to make little jumps and complete the transition. (*VI* close to conduction band, and *III* close to valence band). The distances depend on the temperature!

So an assumption we can make is that at room temperature (300K) we can use the ‘full ionization hypothesis’ which says that all impurities are ionized, which means that $N_D = N_D^+$. **Remember:**

$$1C \ 1V = 1J \quad (49)$$

$$1.6 \cdot 10^{-19}C \ 1V = 1e1V = 1eV \quad (50)$$

Majority and Minority carriers: Usually $n_i^2 = 10^{20}cm^{-6}$, but by the law of mass etc, $pn = n_i^2$. And if from doping we have that n for example $\sim 10^{14}$, we have that the minority charge is $\sim 10^6$. They are negligible. As well as the intrinsic $\sim 10^{10}$ free electrons. In this case we can see as if the Energy levels gets closer to one of the bands. The degenerate doping is when we have so much doping that the semiconductor start behaving as a conductor (The Fermi’s level is inside one of the bands, conduction I suppose).

As a final note, we need ‘*shallow*’ levels and not ‘*deep*’ levels, so that get as close as possible to the conduction bands. And nothing (for now) beats Phosphorous and Borum for Silicon.

6 21-03-25: — Drift & Diffusion (Olivero)

These are the methods by which a charge can move through a material. We have the Drude model which we will not derive, but we know has as consequence (remember, same sign):

Drude's Model:

$$v_{\text{drift}} \propto \mathcal{E} \quad (51)$$

We introduce the mobility μ , which is measured as $[\mu] = [v]/[\mathcal{E}] = \text{cm s}^{-1}/\text{V cm}^{-1} = \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$:

$$v_{\text{drift, p}} = \mu_p \mathcal{E} \quad (52)$$

$$v_{\text{drift, n}} = \mu_n \mathcal{E} \quad (53)$$

We can introduce the current density j as:

$$J = i/S \rightarrow i = q/\Delta t \quad (54)$$

To write it with v :

$$\begin{aligned} j_{\text{drift, p}} &= (+e)pv_{\text{drift, p}} = ep\mu_p \mathcal{E} = \sigma_p \mathcal{E} \\ j_{\text{drift, n}} &= (-e)nv_{\text{drift, n}} = en\mu_n \mathcal{E} = \sigma_n \mathcal{E} \end{aligned} \quad (55)$$

Meaning that the total j is:

$$j_{\text{total}} = j_n + j_p \quad (56)$$

This is not equal to 0, because the face the same direction (electrons are negative, so they generate a positive current in the opposite direction). The energy on the other hand changes as:

$$E = (-e)V \quad (57)$$

Since this energy can be seen as the energy levels, if they are not horizontal, the Fermi level will change as well (intrinsic Fermi level).

Diffusion: Another case is when we have a disparity of charge for whatever reason they try to diffuse to homogenise.

$$j_{\text{diff}} \propto -eD_p \partial p / \partial x = A \text{cm}^{-2} = C[D] \text{cm}^{-3} \text{cm}^{-1} \rightarrow [D] = \text{cm}^4 C^{-1} C \text{s}^{-1} \text{cm}^{-2} = \text{cm}^2 \text{s}^{-1} \quad (58)$$

So the concentration is negative since we go from a place with lots of holes into a place with low holes. That's why we have the “-”, it's because the current goes into the opposite direction of the gradient. Also we have the Diffusion parameter that tells us (based on the material analyzed) how easy the electrons or holes move. If they are 0, we are in intrinsic semiconductor with no diffusion.

If the concentration of carriers is not constant, the distance between a band and Fermi level will not be constant. We also have a relation between μ and D :

$$D = \frac{kT\mu}{e} \quad (59)$$

6.1 PN Junction

We have lot of positive charge carriers and low negative charge carriers, but overall the piece of semiconductor is neutral, since the electrons are bounded to their atoms. The same things goes for bot donors and acceptors.

If we put them together a depletion zone generates, where free holes and free electrons recombine, leaving only fixed charges. Thi generates a built-in electrical field pointing from positive to negative zone.

Also, if we are in equilibrium, the ferm levels are horizontal. Now the difficult thing is to describe what happens in the juntion. The point is that indipendetely of the charge carrier, when they move the overall current goes into one direction, from high density to low density.

If intereseted, the built-in votlage is:

$$V_{bi} = \frac{kT}{e} \ln \left(\frac{N_D N_A}{n^2} \right) \quad (60)$$

The approximation called 'sharp junction approximation' describes in a sharp way the total gcharge across the junction. In this course is not done, but its possible to calculate where does the depletion zone ends for both parts.

$$x_n = \sqrt{\frac{2\epsilon_0\epsilon_r V_{bi}}{eN_D \left(1 + \frac{N_D}{N_A}\right)}} \quad (61)$$

7 24-03-25: — (Forneris)

EM waves in materials:

$$\underbrace{\vec{p}}_{\text{Polarization field}} = \underbrace{n_c}_{\text{density of micr. dipoles}} \cdot \underbrace{\hat{p}}_{\text{micr. dipole moment}} \quad (62)$$

Displacement field:

$$\vec{D} = \varepsilon_0 \mathcal{E} + \vec{P} \quad (63)$$

Now we can rewrite the Displacement field as:

$$\vec{D} = \varepsilon_0 \varepsilon_r \mathcal{E} \quad (64)$$

We also can introduce:

$$\vec{H} = \frac{\vec{B}}{\mu_0 \mu_r} \quad (65)$$

And lastly rewrite the Maxwell equations (previous section). We can then use the Ohm's law to express how the charges are moving in the material:

$$V = RI \quad (66)$$

$$\vec{j} = \underbrace{\sigma}_{\text{conductivity}} \vec{\mathcal{E}} \quad (67)$$

As an anticipation, this conductivity will depend on the frequency of the EM. So the dipoles of the material will oscillate when interacting with it, but also the opposite happens: the dipoles will change the EM.

So to proceed we can combine two equations and get:

$$\vec{\nabla} \left(\vec{\nabla} \cdot \vec{\mathcal{E}} \right) = -\frac{\partial}{\partial t} \left(\vec{\nabla} \times \vec{B} \right) \quad (68)$$

Continua una dimostrazione sulle wave equations for materials, fai riferimento ai file obsidian. It seems that the result will be similar to the description of the prism and rainbows. We obtain at the end the refractive index. Lambert-Beer law.

7.1 Free electrons - plasma oscillation

Using Drude's model we can have a point charge when we apply a static electric field.