University of Strasbourg

Tutorial I
Basic Properties of Homogeneous Semiconductors

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Introduction

This first exercise sheet focuses on the electronic properties of homogeneous semiconductors. We will first express the Fermi level in an *intrinsic* semiconductor before considering the case of homogeneously doped semiconductors. In a third part, we will perform a simplified description of impurity levels in homogeneously doped semiconductors. As a preliminary homework, it will be useful to retrieve the expression of the electronic density of states in a one-, two- and three-dimensional crystal within the effective mass ($m^\star$) approximation. We will consider a semiconductor (or insulator) with and energy gap $E_g = E_c - E_v$ between the conduction (c) and valence (v) band edges. The electrons follow a Fermi-Dirac distribution :

$$f_0(E) = \frac{1}{e^{(E-E_\mathrm{F})/k_B T} + 1} \tag{0.1}$$

with E_F the Fermi energy, k_B the Boltzmann constant and T the temperature. Similarly, holes follow the distribution $1 - f(E)$. The electronic density of states in the valence and conduction bands are denoted ρ_v and ρ_c, respectively.

- *homogeneous* means that there is no gradient of charge density,

$$\vec{\nabla}(n) = \vec{0}$$

- *intrisic* means that there is no states in the gap from valence to conduction band.
- *non-degenerate* means that the Fermi energy level E_F is in the gap (meaning that we have non-metallic behavior).

Density of states,

$$n(E) = \frac{1}{V}\frac{\mathrm{d}N(E)}{\mathrm{d}E}$$

each state occupies $(2\pi)^3/V$ in k space. Usually, we assume that the effective mass approximation holds, this means that

$$E = E_c + \frac{\hbar^2 k^2}{2m_c}$$

where m_c is the effective mass for the conduction band, and similarly for the valence band ($m_v < 0$),

$$E = E_v + \frac{\hbar^2 k^2}{2m_v}$$

Thus, for 3D space we get

$$n(E^\star) = \frac{m}{\pi^2\hbar^3}\sqrt{2m^\star E}$$

with $E^\star = |E - E_{c,v}|$ and where $m^\star = m_c, m_v$.

Note : For 2D,

$$n(E) = \frac{m^\star}{\pi\hbar^2}$$

For 1D,

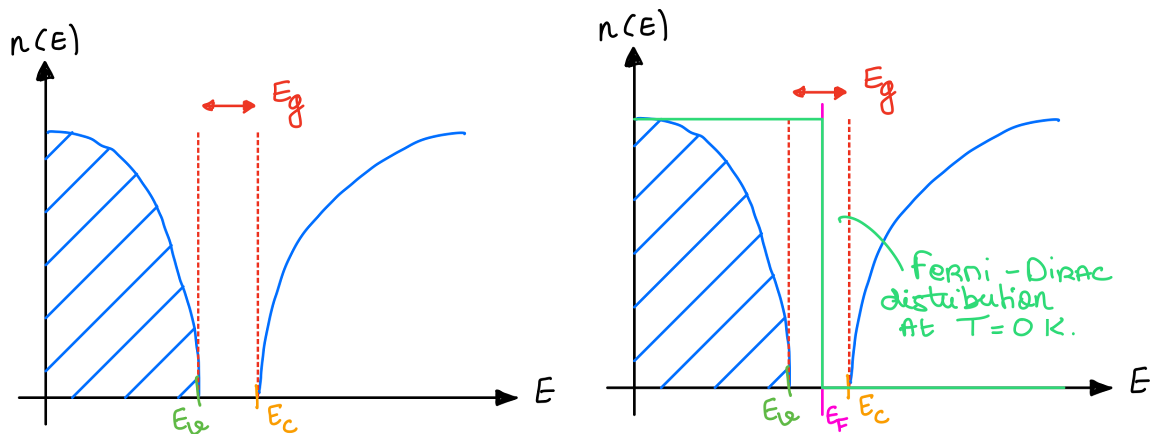
$$n(E) = \frac{\sqrt{2m}}{\pi\hbar\sqrt{E}}$$

1 Fermi Level and Charge Carrier Density in Intrinsic Semiconductors

We consider an intrinsic semiconductor with a filled valence band and an empty conduction band. The electron density in the conduction band and the hole density in the valence band are denoted n_0 and p_0, respectively.

i - Express $n_0(T)$ and $p_0(T)$. Express the neutrality condition. What does it imply for E_F ?

n_0 (p_0) is electron (hole) density in an intrinsic semiconductor,



$$\begin{cases} n_0(T) = \displaystyle\int_{E_c}^{+\infty} \mathrm{d}E n_c(E) f(E,T) \\ p_0(T) = \displaystyle\int_{-\infty}^{E_v} \mathrm{d}E n_v(E)(1 - f(E,T)) \end{cases}$$

We can express the neutrality condition as $n_0 = p_0$. Thus, at $T = 0$ K, we have that $n_0 = p_0 = 0$, thus the Fermi energy E_F has to be in the gap.

ii - We now assume that $k_BT \ll E_g$. Provide a sensible approximation for $f(E)$ and rewrite $n_0(T)$ and $p_0(T)$ in the form :

$$n_0(T) = N_{\mathrm{c}}(T)e^{-\frac{E_{\mathrm{c}}-E_{\mathrm{F}}}{k_BT}} \tag{1.1}$$

$$p_0(T) = N_{\mathrm{v}}(T)e^{-\frac{E_{\mathrm{F}}-E_{\mathrm{v}}}{k_BT}} \tag{1.2}$$

where $N_{\mathrm{c}}(T)$ and $N_{\mathrm{v}}(T)$ are the effective electron and hole densities of states in the conduction and valence bands, respectively.

In the following, we assume that $k_BT \ll E_g$ (the typical order of magnitude for k_BT is 25 meV at room temperature and semiconductor gap is 1 eV, thus motivate this approximation). This means that we can approximate Fermi-Dirac distribution by Boltzmannian,

$$f(E,T) \approx e^{-\frac{E-E_{\mathrm{F}}}{k_BT}}$$

Meaning we can simplify n_0 and p_0,

$$n_0(T) = \int_{E_c}^{+\infty} \mathrm{d}E n_c(E) e^{-\frac{E-E_{\mathrm{F}}}{k_BT}}$$

Writing $E - E_{\mathrm{F}} = E - E_{\mathrm{c}} + E_{\mathrm{c}} - E_{\mathrm{F}}$ allows us to write,

$$n_0(T) = N_c(T)e^{-\frac{E_{\mathrm{c}}-E_{\mathrm{F}}}{k_BT}}, \qquad N_c = \int_{E_c}^{+\infty} \mathrm{d}E n_c(E) e^{-\frac{E-E_{\mathrm{c}}}{k_BT}}$$

And similarly for p_0,

$$p_0(T) = N_v(T)e^{-\frac{E_{\mathrm{F}}-E_{\mathrm{v}}}{k_BT}}, \qquad N_v = \int_{-\infty}^{E_v} \mathrm{d}E n_v(E) e^{-\frac{E_{\mathrm{v}}-E}{k_BT}}$$

iii - Deduce the temperature dependent intrinsic Fermi level $E_{\mathrm{F},i}$ in the case of an undoped semiconductor as well the intrinsic electron and hole densities $n_i(T)$ and $p_i(T)$, respectively.

We know that $n_0(T) = p_0(T)$, thus,

$$N_c(T)e^{-\frac{E_{\mathrm{c}}-E_{\mathrm{F}}}{k_BT}} = N_v(T)e^{-\frac{E_{\mathrm{F}}-E_{\mathrm{v}}}{k_BT}}$$

Using the log allows us to get,

$$E_{\mathrm{F}} = \frac{1}{2}\left[(E_{\mathrm{c}} + E_{\mathrm{v}}) + k_BT \ln\left(\frac{N_v(T)}{N_c(T)}\right)\right]$$

Thus, we find that E_{F} is *close to* the middle of the gap in the intrinsic case.

iv - Calculate the product $n_0(T)p_0(T)$ and show that it does not depend on E_F.

This is leading us to what is called the **mass-action law**, since we already know that $n_0(T) = p_0(T) = n_i(T) = p_i(T)$, so we can write,

$$n_0(T)p_0(T) = n_i^2(T)$$

And this relation is *always* valid (even for extrinsic semiconductor). n_0 and p_0 may depend on E_F but their product won't,

$$n_i(T) = \sqrt{N_c(T)N_v(T)}e^{\frac{E_\mathrm{v}-E_\mathrm{c}}{k_BT}} = \sqrt{N_c(T)N_v(T)}e^{-\frac{E_\mathrm{g}}{2k_BT}}$$

v - We take the case of a simplified two-band (valence and conduction) three-dimensional system, with valence and conduction band effective mass m_v and m_c, respectively. Using $\int_0^\infty \sqrt{t}e^{-t}\mathrm{d}t = \sqrt{\pi}/2$, provide the expressions of $N_{\mathrm{v,c}}(T)$ and $E_{\mathrm{F},i}$ as a function of $m_{\mathrm{v,c}}$.

$$n_{\mathrm{c,v}} \propto \sqrt{|E - E_{\mathrm{c,v}}|}$$

Thus,

$$E_\mathrm{F} = \frac{1}{2}(E_\mathrm{c} + E_\mathrm{v}) + \frac{3}{4}k_BT\ln\left(\frac{m_\mathrm{v}}{m_\mathrm{c}}\right)$$

$$N_{\mathrm{c,v}} \approx 2.53 \times \left(\frac{m_{\mathrm{c,v}}}{m_0}\frac{T}{T_0}\right)^{3/2} \times 10^{25}\ \mathrm{m}^{-3}$$

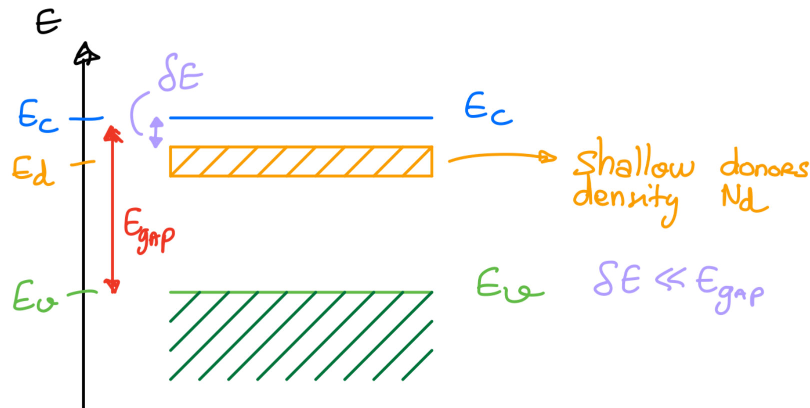
where $T_0 = 300$ K (room temperature) and m_0 is the free electron mass. It is still typically way less than the N for metals.

2 Fermi Level and Charge Carrier Density in Homogeneously Doped Semiconductors

We now consider an homogeneously n-doped semiconductor with an impurity band of shallow donors with density N_d and energy E_d located slightly below the conduction band edge such that $E_\mathrm{c} - E_\mathrm{d} = \delta E \ll E_g$. Due to the electrostatic energy cost to accommodate two electrons (with opposite spins) on one impurity level, the probability that the impurity level with energy E_d is occupied by an electron is given by :

$$\tilde{p}(E_\mathrm{d}) = \frac{1}{1/2e^{(E_\mathrm{d}-E_\mathrm{F})/k_BT} + 1} \tag{2.1}$$

i - Express the number of electrons $n_0(T)$ in the conduction band at a temperature T as a function of $N_{\mathrm{v,c,d}}$, $E_{\mathrm{v,c,d}}$ and E_F.



There is three regimes,

a) *frozen* regime, meaning $k_BT \ll \delta E$.

b) *intermediate* (room temperature) regime meaning $k_BT > \delta E$ but $k_BT \ll E_g$.

c) *high temperature* regime meaning $k_BT \lesssim E_g$.

We can write the neutrality condition,

$$n_0(T) = p_0(T) + N_d[1 - \tilde{p}(E_d)]$$

$N_d[1 - \tilde{p}(E_d)]$ can be seen as the probability that an extra-hole is present in the impurity band.

$$N_c(T)e^{-\frac{E_\mathrm{c}-E_\mathrm{F}}{k_BT}} = N_v(T)e^{-\frac{E_\mathrm{F}-E_\mathrm{v}}{k_BT}} + N_d\left[\frac{1/2e^{(E_\mathrm{d}-E_\mathrm{F})/k_BT}}{1/2e^{(E_\mathrm{d}-E_\mathrm{F})/k_BT} + 1}\right]$$

This is not trivial to solve, we need approximations.

ii - Let us define the temperature $T_\mathrm{d} = \delta E/k_B$. Express the Fermi energy E_F in the three following cases :

a) $T \ll T_\mathrm{d}$

b) $T_\mathrm{d} < T \ll E_g/k_B$

c) $T \sim E_g/k_B$ and $T \gg T_\mathrm{d}$

a) E_F lies between E_d and E_c, and very few donors are ionized, we can simply in first approximation, say that the valence band is filled (because $E_g \gg \delta E$). Thus $p_0(T) \to 0$. We can simply express (after simplification of the exponential in $\tilde{p}$,

$$N_c(T)\exp\left(-\frac{E_\mathrm{c}-E_\mathrm{F}}{k_BT}\right) \approx \frac{N_d}{2}\exp\left(\frac{E_\mathrm{d}-E_\mathrm{F}}{k_BT}\right)$$

Leading to,

$$E_\mathrm{F} = \frac{E_\mathrm{d}+E_\mathrm{c}}{2} + \frac{1}{2}k_BT\ln\left(\frac{N_\mathrm{d}}{2N_\mathrm{c}(T)}\right)$$

Thus,

$$n_0(T) = \sqrt{N_\mathrm{c}(T)\frac{N_\mathrm{d}}{2}}\exp\left(-\frac{\delta E}{2k_BT}\right)$$

b) We can still assume that $p_0 \simeq 0$ and now $n_0(T) \simeq N_\mathrm{d}$,

$$E_\mathrm{F} = E_\mathrm{c} + k_BT\ln\left(\frac{N_\mathrm{d}}{N_\mathrm{c}(T)}\right)$$

typically, $n_i \sim 10^{16}$ m^{-3} in Si at 300 K and $n_0 = N_\mathrm{d} \sim 10^{20}$ m^{-3}, thus $p_0 \sim 10^{12}$ m^{-3} $= n_i^2/N_\mathrm{d}$. And so we can estimate that

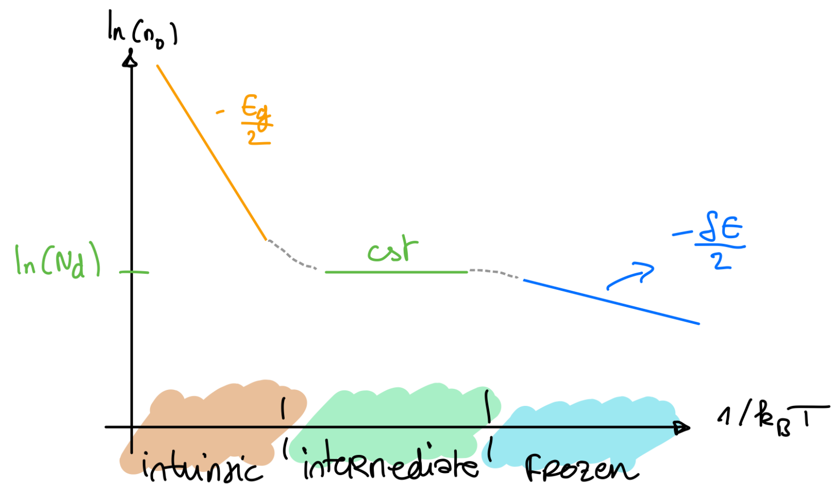
$$\frac{N_\mathrm{d}}{N_\mathrm{c}(T)} \sim 10^{-5} \text{ at room temperature}$$

So, $E_\mathrm{F} = E_\mathrm{c} - 10k_BT$.

c) In this limit, we are back in the intrinsic case, the contribution of the impurity band is negligible and so we get back to what we did in section 1,

$$n_0(T) \approx n_i(T) = \sqrt{N_\mathrm{c}(T)N_\mathrm{v}(T)}e^{-\frac{E_g}{2k_BT}}$$

iii - Draw schematically $n_0(T)$.



3 Impurity Levels

Having determined how the presence of dopants affects the Fermi level in semiconductors, we now provide a simple microscopic description of such impurities, with the aim to estimate the spatial extent of their wavefunctions and their eigenenergies. In bulk semiconductors (such as Si, Ge, from the column IV), impurities consist of substituent atoms from a neighboring column. Here, we shall consider donor atoms from the column V (e.g., As), which can provide one additional electron into the host semiconductor conduction band. Since the presence of defects breaks translational invariance, the wavefunctions of the doped crystal do no longer obey Bloch theorem but may be expanded on the basis composed by the intrinsic crystal wavefunctions $\psi(\boldsymbol{k},\boldsymbol{r}) = u(\boldsymbol{k},\boldsymbol{r})e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$. For simplicity, we shall also consider a single parabolic conduction band with effective mass m_c. The Schrödinger equation writes :

$$\left[-\frac{\hbar^2}{2m_c}\nabla^2 + \mathcal{V}(\boldsymbol{r}) + \mathcal{V}_I(\boldsymbol{r})\right]|\phi(\boldsymbol{r})\rangle = E\,|\phi(\boldsymbol{r})\rangle\,, \tag{3.1}$$

where the wavefunction of the doped crystal $|\phi(\boldsymbol{r})\rangle$ writes :

$$|\phi(\boldsymbol{r})\rangle = \sum_{\boldsymbol{k}'}\mathcal{A}(\boldsymbol{k}')\,|\psi(\boldsymbol{k}',\boldsymbol{r})\rangle \tag{3.2}$$

i - Show that (3.1) writes :

$$\left[\frac{\hbar^2k^2}{2m_c} + E_c - E\right]\mathcal{A}(\boldsymbol{k}) + \sum_{\boldsymbol{k}'}\mathcal{U}(\boldsymbol{k},\boldsymbol{k}')\mathcal{A}(\boldsymbol{k}') = 0 \tag{3.3}$$

where

$$\mathcal{U}(\boldsymbol{k},\boldsymbol{k}') = \langle\psi(\boldsymbol{k},\boldsymbol{r})|\,\mathcal{V}_I(\boldsymbol{r})\,|\psi(\boldsymbol{k}',\boldsymbol{r})\rangle \tag{3.4}$$

$$\left\langle \psi(\vec{k},\vec{r}) \middle| (3.1) \right\rangle$$

If you perform this calculation, one indeed get

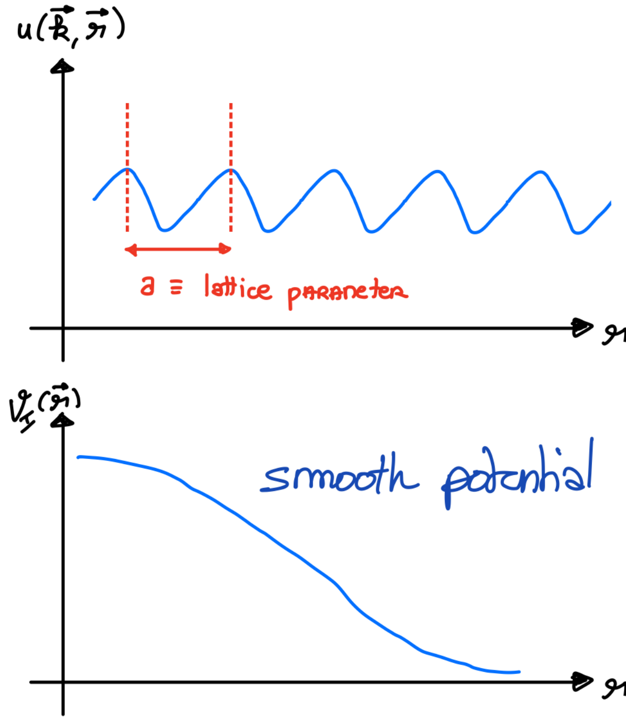
$$\left[\frac{\hbar^2k^2}{2m_c} + E_c - E\right]\mathcal{A}(\boldsymbol{k}) + \sum_{\boldsymbol{k}'}\langle\psi(\boldsymbol{k},\boldsymbol{r})|\,\mathcal{V}_I(\boldsymbol{r})\,|\psi(\boldsymbol{k}',\boldsymbol{r})\rangle\,\mathcal{A}(\boldsymbol{k}') = 0$$

ii - In the following we will consider, for simplicity, that the impurity potential is sufficiently smooth over the unperturbed crystal unit cell. Justify that one can make the following approximation in the limit where $\boldsymbol{k} \approx \boldsymbol{k}'$:

$$\mathcal{U}(\boldsymbol{k},\boldsymbol{k}') \approx \frac{1}{V}\int e^{-i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{r}}\mathcal{V}_I(\boldsymbol{r})\mathrm{d}\boldsymbol{r}. \tag{3.5}$$

Comment on this expression.

$$\mathcal{U}(\vec{k},\vec{k}') = \int \mathrm{d}\vec{r}\psi^*(\vec{k},\vec{r})\mathcal{V}_I(\vec{r})\psi(\vec{k},\vec{r})$$
$$= \int \mathrm{d}\vec{r}u^*(\vec{k}',\vec{r})u(\vec{k},\vec{r})\mathcal{V}_I e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}$$



Thus the product $u^*(\vec{k}',\vec{r})u(\vec{k},\vec{r})$ can be replaced by its mean value,

$$u^*(\vec{k}',\vec{r})u(\vec{k},\vec{r}) \approx \frac{1}{V}\int \mathrm{d}\vec{r}u^\star(\vec{k}',\vec{r})u(\vec{k},\vec{r}) \approx \frac{1}{V}\times 1 \qquad (\text{for } \vec{k}\approx\vec{k}')$$

A smooth $\mathcal{V}_I$ in real space, means that its Fourier transform $\tilde{\mathcal{V}}_I(|\vec{k}-\vec{k}'|$ is peaked near $|\vec{k}-\vec{k}'| = 0$, and thus we get,

$$\mathcal{U}(\boldsymbol{k},\boldsymbol{k}') \approx \frac{1}{V}\int e^{-i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{r}}\mathcal{V}_I(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = \tilde{\mathcal{V}}_I(|\vec{k}-\vec{k}'|)$$

where $\tilde{\mathcal{V}}_I$ is the Fourier transform of $\mathcal{V}_I$

iii - We introduce the envelope wavefunction

$$\mathcal{F}(\boldsymbol{r}) = \frac{1}{\sqrt{V}}\sum_{\boldsymbol{k}}\mathcal{A}(\boldsymbol{k})e^{i\boldsymbol{k}\cdot\boldsymbol{r}}. \qquad (3.6)$$

Show that (3.3) can be written as :

$$\left[-\frac{\hbar^2}{2m_c}\nabla^2 + \mathcal{V}_I(\boldsymbol{r})\right]\mathcal{F}(\boldsymbol{r}) = (E - E_c)\mathcal{F}(\boldsymbol{r}) \tag{3.7}$$

We do,

$$(3.3) \times e^{i\vec{k}\cdot\vec{r}}$$

and then we can take the sum over k, getting us 0, directly getting us (3.7).

$$\sum_{\vec{k},\vec{k}'} \tilde{V}_I(\vec{k} - \vec{k}')\mathcal{A}(\vec{k}')e^{i\vec{k}\cdot\vec{r}} = 0$$

We can rewrite $\vec{k} = \vec{k} - \vec{k}' + \vec{k}'$, and thus,

$$\sum_{k} \tilde{V}_I(\vec{k} - \vec{k}')e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}e^{i\vec{k}\cdot\vec{r}} \simeq V_I(\vec{r})e^{i\vec{k}'\cdot\vec{r}}$$

And so we write,

$$\left[\frac{\hbar^2}{2m_c}k^2 + E_c - E\right]\mathcal{F}(\vec{r}) + \underbrace{\sum_{k'} V_I(\vec{r})e^{i\vec{k}'\cdot\vec{r}}\mathcal{A}(\vec{k}')}_{=V_I(\vec{r})\mathcal{F}(\vec{r})} = 0$$

Leading to,

$$\left[-\frac{\hbar^2}{2m_c}\nabla^2 + V_I(\vec{r})\right]\mathcal{F}(\vec{r}) = (E - E_c)\mathcal{F}(\vec{r})$$

iv - We assume that the impurity potential takes the simplest form $\mathcal{V}_I(r) = \frac{e^2}{4\pi\epsilon_0\epsilon_s r}$ (the latter is realistic in the long-range approximation), where e is the electron charge, ϵ_0 is the vacuum dielectric permittivity, ϵ_s is the static dielectric constant of the host semiconductor. Comment on (3.7). What are the solutions of this equation ?

Eq. (3.7) is just the Schrödinger equation for the hydrogen atom (with the assumption that we take a simple Coulombic potential). ϵ_s is the screening of the Coulomb potential.

v - We recall the expression of the Bohr radius $a_\mathrm{B} = \hbar/(m_e \alpha c)$ and of the Rydberg energy $\mathrm{Ry} = \frac{1}{2}\alpha^2 m_e c^2$, with $\alpha = e^2/(4\pi\epsilon_0\hbar c)$ the fine structure constant, m_e the free electron mass, c the speed of light. For Silicium (Germanium) $\epsilon_s = 11.7$ (16) and $m_c \approx 0.3$ (0.2). Estimate the effective radius of the donor ground state wavefunction and the binding energy of the donor ground state. Comment these values.

$$
\begin{aligned}
a_\mathrm{B} = \frac{\hbar}{m_e \alpha c} &: \text{ Bohr radius.} \\
a_\mathrm{B}^* &: \text{ Bohr radius (effective).} \\
\mathrm{Ry} = \frac{1}{2}\alpha m_e c^2 &: \text{ Binding energy.} \\
\mathrm{Ry}^* &: \text{ Binding energy of the impurity level.} \\
\alpha = \frac{e^2}{(4\pi\epsilon_0)\hbar c} &: \text{ fine structure constant.} \\
\alpha^* = \frac{e^2}{(4\pi\epsilon_0\epsilon_s)\hbar c} &: \text{ effective fine structure constant.}
\end{aligned}
$$

Thus,

$$
\mathrm{Ry}^* = \mathrm{Ry}\frac{m_c}{m_e}\frac{1}{\epsilon_s^2}, \qquad a_\mathrm{B}^* = a_\mathrm{B}\epsilon_s\frac{m_e}{m_c}
$$

Typical values are $\epsilon \sim 10$ and thus, $m_e/m_c \sim 5$. Thus,

$$
\mathrm{Ry}^* = \mathrm{Ry} \times 10^{-3} \sim 25 \text{ meV}, \qquad a_\mathrm{B}^* = a_\mathrm{B} \times 50 \sim 25 \text{ nm} \gg \text{ lattice parameter}
$$

Thus the smooth potential approximation we made earlier is valid.