Physics of Semiconductors (4)

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4.1.1 Boltzmann equation and Drude conductivity (continued)

On the other hand, when the concentration is low and the temperature is high, thus approximation of the distribution function with the Maxwell distribution holds, $f_0 \approx A \exp(-E/k_\mathrm{B}T)$,

$$-\frac{\partial f_0}{\partial E} = -\frac{A}{k_\mathrm{B}T} \exp\left[-\frac{E}{k_\mathrm{B}T}\right] = -\frac{f_0}{k_\mathrm{B}T} = -\frac{f_0}{(2\langle E\rangle/3n)}.$$

In the last line, we have used the fact that the averaged kinetic energy for a single kinetic freedom is $k_\mathrm{B}T/2$. The electric conductivity is given as

$$\sigma = e^2 \int \tau(E)\mathscr{D}(E)\frac{2E}{3m}\frac{3nf_0}{2\langle E\rangle}dE = \frac{ne^2\langle\tau\rangle_E}{m}, \tag{4.1}$$

which is again of Drude type. Here the expression $\langle E\rangle_E$ means an average with the weight of energy as

$$\langle\tau\rangle_E = \frac{\langle\tau E\rangle}{\langle E\rangle} = \int_0^\infty \tau(E)E^{3/2}f_0 dE \Big/ \int_0^\infty E^{3/2}f_0 dE. \tag{4.2}$$

Next we consider the diffusion current caused by non-uniformity of f in real space. In Boltzmann equation (**??**), we put $\boldsymbol{F} = 0$ and apply the relaxation time approximation (**??**) to the spatial distribution represented by $f = f_0 + f_1$ to obtain

$$\boldsymbol{v}\cdot\boldsymbol{\nabla}f = -f_1/\tau, \quad \text{taking the first order of } f_1 \quad f_1 = -\tau\boldsymbol{v}\cdot\boldsymbol{\nabla}f_0. \tag{4.3}$$

We take a volume V and a constant diffusion current $\boldsymbol{J}$ in it, then

$$\boldsymbol{J} = (-e) \int_V \tau\boldsymbol{v}(\boldsymbol{v}\cdot\boldsymbol{\nabla}f_0)d\boldsymbol{r}.$$

We take the direction of $\boldsymbol{\nabla}f_0$ as x axis, then again just like (**??**), the integrations other than for v_x vanish due to the parity. $\langle v_x^2\rangle = \langle v^2\rangle/3$ and we assume that the temperature, $\langle v^2\rangle$ and others are uniform in space. Now for a unit volume

$$j_x \text{ (current density)} = -e \int_{\text{unit volume}} \tau v_x^2 \frac{\partial f_0}{\partial x}d\boldsymbol{r} = -e\left\langle\frac{\tau v^2}{3}\right\rangle\frac{\partial n}{\partial x}.$$

Therefore

$$\boldsymbol{j} = (-e)D\boldsymbol{\nabla}n, \quad D = \langle\tau v^2/3\rangle. \tag{4.4}$$

D is called **diffusion constant** and within the constant relaxation time approximation expressed as

$$D = \frac{\tau}{3}\langle v^2\rangle = \frac{\tau k_\mathrm{B}T}{m^*} = \frac{\mu}{e}k_\mathrm{B}T. \tag{4.5}$$

Equation (4.5) is called **Einstein relation**.

4.1.2 Hall effect

In the calculation of drift current when a magnetic flux density $\mathbf{B}$ along z axis exists, we substitue the Lorentz force $-e(\mathbf{E} + \mathbf{v} \times \mathbf{B})$ to $\mathbf{F}$ in (**??**). The calculation is straightforward but needs some space to be shown and here summarized in Appendix E. Here we just give a handwaving argument shown in Fig.4.1.

Let us consider a specimen with a finite width along y and infinite along x with an external electric field $\mathbf{E} = (\mathcal{E}_x, 0, 0)$. The Lorentz force raises current j_y along y-axis though the carriers brought by j_y accumulate at the ends of the specimen as illustrated in Fig.4.1, build up **Hall electric field** $\mathbf{E}_{\text{int}} = (0, \mathcal{E}_y, 0)$ inside the specimen and finally block j_y to be zero in a steady state.

The above electromagnetic effect that causes electric field perpendicular to the applied field (and flowing current) is called **Hall effect**. The coefficient

$$R_{\text{H}} = \frac{\mathcal{E}_y}{J_x B_z} \tag{4.6}$$

is called **Hall coefficient**. Hall electric field $\mathcal{E}_y$ is obtained from the condition $j_y = 0$ that

$$\mathcal{E}_y = -(A_t/A_l)\mathcal{E}_x. \tag{4.7}$$

Hence, by using (E.11b) for (4.6), the conductivity tensor defined as $\mathbf{j} = \hat{\sigma}\mathbf{E}$ is expressed as

$$\sigma_{xx} = \frac{ne^2}{m^*}A_l = \frac{ne^2}{m^*}\left\langle \frac{\tau}{1 + (\omega_c\tau)^2} \right\rangle_E, \quad \sigma_{xy} = \frac{ne^2}{m^*}\left\langle \frac{\omega_c\tau^2}{1 + (\omega_c\tau)^2} \right\rangle_E, \tag{4.8}$$

$$R_{\text{H}} = -\frac{1}{ne}\frac{A_t}{\omega_c(A_l^2 + A_t^2)}. \tag{4.9}$$

When the magnetic field is weak enough and $\omega_c\tau \ll 1$,

$$R_{\text{H}} = -\frac{1}{ne}\frac{\langle\tau^2\rangle_E}{\langle\tau\rangle_E^2} = \frac{1}{n(-e)}\frac{\Gamma(2s + 5/2)\Gamma(5/2)}{(\Gamma(s + 5/2))^2} = \frac{r_{\text{H}}}{n(-e)}. \tag{4.10}$$

This means if we could know s with knowing the scattering mechanism, we can know both the carrier concentration and the sign of carriers. (In the case of holes, $-e$ is replaced with $+e$). Here r_{H} is called **Hall factor**, which depends on the mechanism of scattering at high temperatures, though in many cases it is close to 1 (see Tab.1). r_{H} is 1 for constant relaxation time approximation ($s = 0$) or for the system under Fermi degeneracy. In such cases (4.10) holds even for non-Maxwellian distribution as we can know from (E.9).

4.2 Thermal transport and electric transport

In the presence of a temperature gradient, a thermal flux (or heat current) emerges in response. A big difference between thermal transport and electric transport is that the former has a powerful carrier phonon other than charge carriers. The thermal transport with phonon is called **phonon drag** and often is important in real systems through in this section we neglect it for simplicity. Also the Joule heating, caused by inelastic scattering of carriers is out of scope here.
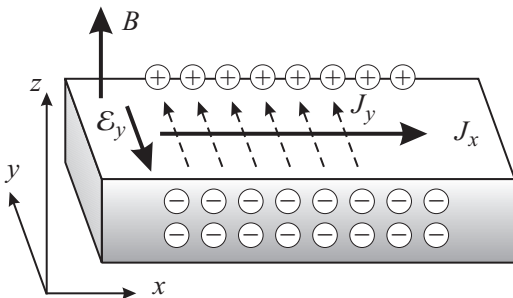

Figure 4.1: When a magnetic field is applied along z-axis, an electric current along x-axis causes a Lorentz force, which give rise to a current J_y to the y direction. J_y should be zero in a steady state canceled by the electric field (Hall field) due to the charge accumulation at the edges of the specimen.

Scattering mechanism	E exponent	T exponent	Hall factor
acoustic phonon	$-1/2$	$-3/2$	1.18
ionized impurity (weak screening)	$+3/2$	$+3/2$	1.93
ionized impurity (strong screening)	$+1/2$	$+1/2$	1.18
neutral impurity	0		1.00
piezoelectric phonon	$+1/2$		1.10

Table 1: Hall factors for various scattering mechanisms. See *e.g.* [1] for E and T.

4.2.1 Thermal conductivity

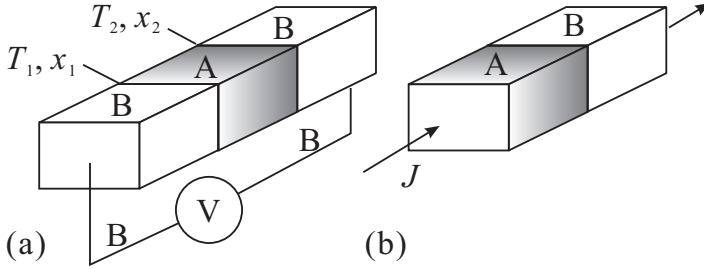We define the thermal flux density by charge carriers with the concentration n along x-axis as

$$j_{qx} = \langle nv_x(E - \mu) \rangle = \int_0^\infty v_x(E - \mu)f(E)\mathscr{D}(E)dE. \tag{4.11}$$

And **thermal conductivity** κ_n with charge carriers in the presence of **temperature gradient** ∇T is defined from

$$\kappa_n = -\frac{j_{qx}}{\partial T/\partial x}. \tag{4.12}$$

In vector representation $\boldsymbol{j}_q = -\hat{\kappa}\nabla T$

4.2.2 Thermoelectric effect

Because the thermal flux in (4.12) is carried by charge carriers, some electric effects should exist simultaneously. Such complex effects of temperature gradient and electric transport are called **thermoelectric effects**.

Consider an electric conductor A with a finite width illustrated in (a) of the left figure and let the temperatures of the two edges as T_1, T_2 respectively. The edges are connected to two electrodes of another conductor B. The electrodes are elongated to some other point with a temperature in-between T_1 and T_2, where we have a voltmeter with infinite input impedance.

In a steady state, the net charge current should be zero because the circuit is open and there should be a voltage V_{AB} at an A-B junction, which compensates the difference in the electric currents in conductors A and B driven by the temperature gradient. This effect is called **Seebeck effect** and the ration of the voltage to the temperautre difference $\Delta T = T_1 - T_2$

$$S_{AB} = \frac{V_{AB}}{\Delta T} \tag{4.13}$$

is called **Seebeck coefficient**.

On the other hand as illustrated in (b), initially a junction of A-B is placed under uniform temperature condition and an electric current J is externally applied. J gives rise to a thermal flux Q. If there is no charge accumulation at the junction plane, J should be continuous at the interface and common for the two conductors while the ratios to the thermal flux are different resulting in a discontinuity of thermal flux at the interface and cooling or heating should occur due to pile up or removal of the heat. This is called **Peltier effect** and the ratio of heating (cooling) velocity Q_{AB} and J,

$$\Pi_{AB} = \frac{Q_{AB}}{J}, \tag{4.14}$$

is called **Peltier coefficient**. If we repeat the same experiment on a BAB junction illustrated in (a), the same electric current flows with opposite directions for the two interfaces, thus if cooling occurs in one junction, heating occurs in another with the same heat quantity.

Even apart from junctions, in a uniform conductor, if there exist an electric current J and a temperature gradient $\partial T/\partial x$, also cooling and heating occur. The product of J and $\partial T/\partial x$ and the heat quantity per unit length and unit time $\partial Q/\partial x$ are in linear relationship, which is called **Thomson effect** and the coefficient

$$\tau = \frac{\partial Q/\partial x}{J(\partial T/\partial x)}, \tag{4.15}$$

is called **Thomson coefficient**.

There are simple relations between these coefficients as

$$\Pi_{\mathrm{AB}} = S_{\mathrm{AB}}T, \quad \tau_{\mathrm{A}} - \tau_{\mathrm{B}} = T\frac{dS_{\mathrm{AB}}}{dT}, \tag{4.16}$$

which are called **Kelvin relations** (or Thomson relations) (Appendix F). Therefore we can define, *e.g.* Seebeck coefficient S, which is specific to the material and does not depend on the combination at the junctions as

$$S_{\mathrm{A}}(T) \equiv \int_0^T \frac{\tau_{\mathrm{A}}(T')}{T'}dT'. \tag{4.17}$$

And for the junction A-B, the Seebeck coefficient is given as $S_{\mathrm{AB}} = S_{\mathrm{A}} - S_{\mathrm{B}}$.

4.2.3 Boltzmann equation and thermoelectric coefficients

We consider the thermoelectric effects within the relaxation time approximation of Boltzmann equation (**??**) (**??**). We restrict ourselves to steady states with $\partial f/\partial t = 0$ hence write down the equation as

$$\boldsymbol{v} \cdot \nabla f + \frac{\boldsymbol{F}}{m}\nabla_v f = -\frac{f - f_0}{\tau(E)}. \tag{4.18}$$

Again we assume the shift from the equilibrium is small and replace the distribution function f in RHS with the one for the thermal equilibrium f_0.

In the presence of temperature gradient ∇T, ∇f_0 is rewritten as follows.

$$\nabla f_0 = \nabla T\frac{\partial f_0}{\partial T}.$$

In f_0, E and T always appear as the combination $-(E - E_{\mathrm{F}})/k_{\mathrm{B}}T$. Let a be the combination expression, then

$$\frac{\partial f_0}{\partial T} = \frac{\partial f_0}{\partial E}\frac{\partial E}{\partial a}\frac{\partial a}{\partial T} = \frac{\partial f_0}{\partial E}(-k_{\mathrm{B}}T)\frac{E - E_{\mathrm{F}}}{k_{\mathrm{B}}T^2} = \frac{\partial f_0}{\partial E}\frac{E_{\mathrm{F}} - E}{T}$$

$$\nabla f_0 = \nabla T\frac{E_{\mathrm{F}} - E}{T}\frac{\partial f_0}{\partial E}. \tag{4.19a}$$

$$\text{and} \quad \nabla_v f_0 = \nabla_v E\frac{\partial f_0}{\partial E} = m\boldsymbol{v}\frac{\partial f_0}{\partial E}. \tag{4.19b}$$

Next we rewrite (4.18) in the case of the co-existence of an electric field **E** and a temperature gradient ∇T with use of (4.19) as

$$f = f_0 - \tau(E)\boldsymbol{v} \cdot \left[-e\mathbf{E} + \frac{E_{\mathrm{F}} - E}{T}\nabla T \right]\frac{\partial f_0}{\partial E}. \tag{4.20}$$

Here we apply this to Seebeck coefficient. We apply an electric field $\mathcal{E}_x$ to the x direction. Just like in (**??**), the current along x-axis j_x can be calculated as

$$j_x = -e\langle nv_x \rangle = -e\int_0^\infty v_x f(E)\mathscr{D}(E)dE = e\int_0^\infty v_x^2\tau\left[-e\mathcal{E}_x + \frac{E_{\mathrm{F}} - E}{T}\frac{\partial T}{\partial x} \right]\frac{\partial f_0}{\partial E}\mathscr{D}(E)dE.$$
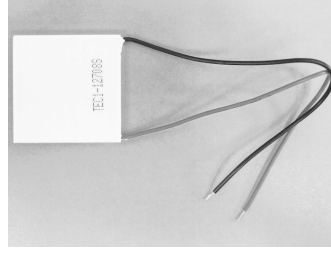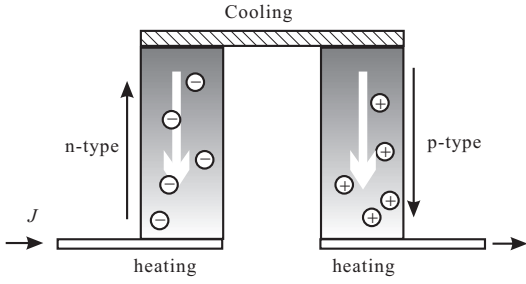
Figure 4.2: Left: Schematic cross section of a Peltier device. p-type semiconductors and n-type ones are alternatively connected. The current flow carriers heat from an edged to the other. Right: Photograph of a Peltier device. From the online shopping site of Akizuki Denshi Tsusho.

The Seebeck coefficient is measured as the ration of $\mathcal{E}_x$ and $\partial T/\partial x$ under the condition of $j_x = 0$,

$$S = \frac{\mathcal{E}_x}{\partial T/\partial x} = \int_0^\infty \frac{E_F - E}{eT} \frac{\partial f_0}{\partial E} \mathscr{D}(E) dE \Big/ \int_0^\infty v_x^2 \tau \frac{\partial f_0}{\partial E} \mathscr{D}(E) dE$$

$$= \frac{1}{eT} \left[E_F - \int_0^\infty \tau E^2 \frac{\partial f_0}{\partial E} \mathscr{D}(E) dE \Big/ \int_0^\infty \tau E \frac{\partial f_0}{\partial E} \mathscr{D}(E) dE \right]. \quad (4.21)$$

If we can adopt Maxwellian approximation $\partial f_0/\partial E = -f_0/k_B T$, and assume the energy dependence of τ as $\tau \propto E^s$,

$$S = -\frac{1}{eT} \left[\frac{\langle \tau E \rangle_E}{\langle \tau \rangle_E} - E_F \right] = -\frac{1}{eT} \left[\left(\frac{5}{2} + s \right) k_B T - E_F \right]. \quad (4.22)$$

The above tells that just like the Hall coefficient, if we know s (*i.e.*, the dominant mechanism of carrier scattering), we can measure the position of E_F from the temperature dependence of S. Similarly, in the case of holes, $-e$ should be replaces with $+e$ and we can also know the sign of charges for the carriers.

4.2.4 Peltier thermo-device

From Kelvin relation, we know that Peltier coefficients change their signs with those of carriers. This fact can be utilized for heat transfer, with connecting n-type and p-type semiconductors alternatively. The electric current through the circuit causes, as illustrated in Fig.4.2(a), heat transfer from one end of the device to the other. Hence they cause cooling on one end, heating on the other. They are called Peltier devices.

Peltier devices have been often used for cooling CPUs in PCs in combination with cooling fans. Longer history it has as cooling engines of noiseless refrigerators in bedrooms.

4.3 Metal-Insulator transition

So far we treat the impurity states in semiconductors as isolated. In such cases, as shown in Fig.3.2, charge carriers disappear at low temperatures, the conductivity is lost, and the system is insulating. Now we consider doping to higher impurity densities, where the average distance between the dopants is similar to or less than the spatial size of the wavefunctions. Then the overlapping of wavefunctions enables tunneling between the impurity sites. Such tunnleings may form a kind of conducting network in the crystal and with further increasing the impurity concentration finally spreads the network over the whole crystal, which now has a finite conductance at the lowest temperature, thus is a metal.

This problem – **metal-insulator transitions**, MIT – has been one of the most important problems in condensed matter physics, and huge amount of efforts have been devoted for years. The field of MIT extends over various phenomena in condensed matter physics, far beyond the doped semiconductors. We have not reached the final answer through great amount of knowledges have been accumulated. There are so many textbooks, very few of which are listed in references ([2]~[5]).

In the above we have defined the MIT as the spatial size of the wavefunctions at the Fermi level. The phenomenon is observed in the energy space as follows. With overlapping of neighboring wavefunctions, as
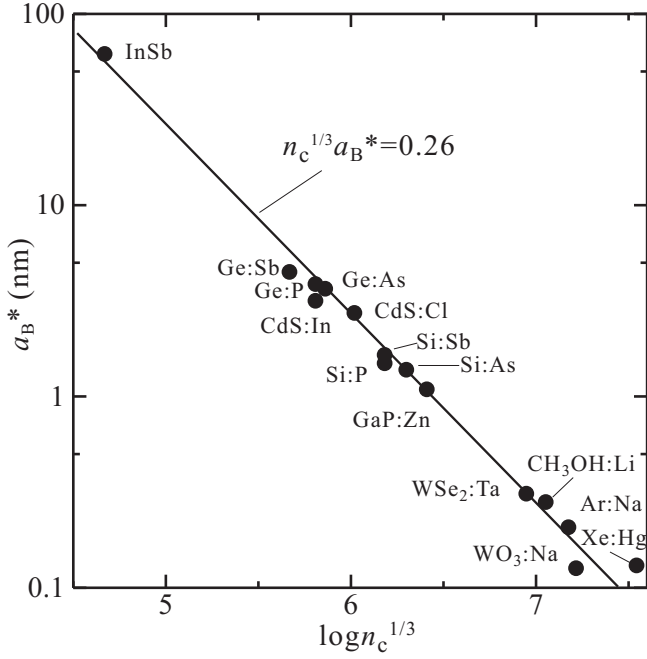
Figure 4.3: Experimental values for the critical concentrations of the MIT and the effective Bohr radiuses for various matrix semiconductors and dopants (the element symbols put after the colons). The data are plotted in log scale. The unit for n_c is cm^{-3}. The line indicates the empirical relation in eq.(4.23). The data are taken from P. Edwards and M. Sienko, Phys. Rev. B **17**, 2575 (1978).

we have seen in the tight binding model (regular, coherent case), the energy levels broadened and a band is formed, which we call an **impurity band**. Even under the formation of impurity band, in which the density of states is continuous, the wavefunction at the Fermi level is not necessarily spread over the entire crystal. It was first pointed out by Anderson that the electrons in a potential with a certain degree of disorder are spatially localized. This is called **Anderson localization**. Hence, some lower part of the impurity band is usually localized and the boundary is called a mobility edge.

It is well known that as shown in Fig.4.3, in many matrix crystals and species of dopants, an empirical relation,

$$n_c^{1/3} a_{\mathrm{B}}^* = 0.26 \tag{4.23}$$

holds between the critical impurity concentration n_c for the MIT and the effective Bohr radius a_{B}^*. This criterion is natural from the view of impurity band formation and there are many trials to derive it from more rigorous theoretical background.

The largest difficulty in solving this problem lies in the treatment of disorder, which makes it impossible to utilize the coherence of the scattering from the crystal lattice. In the band theory, the coherence brings about great simplicity. In the case of MIT in disordered systems, one should directly treat the disorder itself.

Though the final answer has not been found, or it is not even known whether there is such one or not, many new physical idea have been developed, which have greatly expanded our knowledges on random systems. The concepts have been applied various fields such as organic semiconductors. We do not go into this problem further due to the space-time limitations.

5 Optical response

The interaction of charge carriers with electromagnetic waves, *i.e.*, photons also affects the nature of carriers. Absorption of light depends on the more details of band structures in comparison with carrier concentration. Thus it gives important information in determining the detailed band structures. Needless to say, in the field of device application, it is the most important property for optical detectors and solar cells. Though it covers a large area of the optical science, we only have a look at very basics for understanding the experiments in quantum wells or characteristics of solar cells.

Both absorption and emission of photons are closely related with the quantum mechanical properties of structured materials which interact with the electromagnetic field. We would observe more specified examples in the later sections devoted to those individual structures. And here, we restrict ourselves to the very general

descriptions. Even more elementary description of absorption and emission of light by a two-level system is summarized in Appendix G.

References

[1] M. Lundstrom, "Fundamentals of Carrier Transport" (Cambridge, 2000).

[2] N. F. Mott, "Metal-Insulator transitions" (CRC Press, 1990).

[3] H. Kamimura and H. Aoki, "The Physics of Interacting Electrons in Disordered Systems" (Oxford, 1990).

[4] Y. Ono, "Metal-Insulator Transitions" (in Japanese, Asakura, 2002).

[5] D. Stauffer and A. Aharony, "Introduction to Percolation Theory" (CRC Press, 1994).

Appendix E: Electromagnetic effect

We go back to the drift current and consider the response to the magnetic flux density $\mathbf{B}$. Now the external force is the Lorentz force $\mathbf{F} = -e(\mathbf{E} + \boldsymbol{v} \times \mathbf{B})$. In the relaxation time approximation (3.21) of the Boltzmann equation eq. (3.20), we put $f_1 \equiv f - f_0$ and

$$-\frac{e}{\hbar}(\mathbf{E} + \boldsymbol{v} \times \mathbf{B}) \cdot \frac{\partial f}{\partial \boldsymbol{k}} = -\frac{f_1}{\tau} \quad (\boldsymbol{p} = \hbar \boldsymbol{k}). \tag{E.1}$$

We approximate f in $\partial f/\partial \boldsymbol{k}$ on the first term on the left hand side as f_0. From $dE = \boldsymbol{v} \cdot d\boldsymbol{p}$ the second term becomes $\partial f_0/\partial \boldsymbol{k} = \hbar(\partial f_0/\partial E)\boldsymbol{v}$, and the term of f_0 vanishes being orthogonal to $\boldsymbol{v} \times \mathbf{B}$. This is natural considering that the force from the magnetic field is orthogonal to $\boldsymbol{v}$ and does not give work. In the second term we take the term of f_1 to get

$$-e\boldsymbol{v} \cdot \mathbf{E}\frac{\partial f_0}{\partial E} - \frac{e}{\hbar}(\boldsymbol{v} \times \mathbf{B}) \cdot \frac{\partial f_1}{\partial \boldsymbol{k}} = -\frac{f_1}{\tau}. \tag{E.2}$$

Here we introduce a vector in the dimension of electric field $\mathbf{E}_a$ as

$$f_1 = e\tau(\boldsymbol{v} \cdot \mathbf{E}_a)\frac{\partial f_0}{\partial E}. \tag{E.3}$$

This equation represents the model of the shift of the Fermi sphere with the Lorentz force just as illustrated in Fig.3.3, in which the origin of the shift is "normalized" into an electric field. Hence

$$-\boldsymbol{v} \cdot \mathbf{E} = -\boldsymbol{v} \cdot \mathbf{E}_a + \frac{e\tau}{m}(\boldsymbol{v} \times \mathbf{B}) \cdot \mathbf{E}_a, \quad \therefore \mathbf{E} = \mathbf{E}_a - \frac{e\tau}{m^*}\mathbf{B} \times \mathbf{E}_a, \tag{E.4}$$

of which the solution is given as

$$\mathbf{E}_a = \frac{1}{1 + \omega_c^2 \tau^2}\left[\mathbf{E} + \frac{e\tau}{m^*}\mathbf{B} \times \mathbf{E} + \left(\frac{e\tau}{m^*}\right)^2 (\mathbf{B} \cdot \mathbf{E})\mathbf{B}\right], \tag{E.5}$$

$$\omega_c = \frac{e|\mathbf{B}|}{m^*}. \tag{E.6}$$

ω_c is called **cyclotron frequency**. After all f_1 is given as

$$f_1 = \frac{e\tau\mathbf{E}}{1 + \omega_c^2 \tau^2} \cdot \left[\boldsymbol{v} + \frac{e\tau}{m^*}\boldsymbol{v} \times \mathbf{B} + \left(\frac{e\tau}{m^*}\right)^2 (\mathbf{B} \cdot \boldsymbol{v})\mathbf{B}\right]\frac{\partial f_0}{\partial E}. \tag{E.7}$$

Let us consider the case in which the magnetic field and the electric field are given as $\mathbf{B} = (0, 0, \mathcal{B}_z)$, $\mathbf{E} = (\mathcal{E}_x, \mathcal{E}_y, 0)$. Because $v_z = 0$, (E.7) gives f_1 as

$$f_1 = e\frac{\partial f_0}{\partial E}\left[v_x\left(\frac{\tau}{1 + (\omega_c\tau)^2}\mathcal{E}_x - \frac{\omega_c\tau^2}{1 + (\omega_c\tau)^2}\mathcal{E}_y\right) + v_y\left(\frac{\omega_c\tau^2}{1 + (\omega_c\tau)^2}\mathcal{E}_x + \frac{\tau}{1 + (\omega_c\tau)^2}\mathcal{E}_y\right)\right]. \tag{E.8}$$

From this result to obtain $j_x = -en\langle v_x \rangle$, for example, we need to calculate the expectation value of v_x with $f = f_0 + f_1$. The expectation value in f_0 is zero and the odd part in v vanishes with integration on $\boldsymbol{k}$. Then we obtain

$$j_x = 2\int (-e)v_x f(\boldsymbol{k})\frac{d\boldsymbol{k}}{(2\pi)^3} = -\frac{e^2}{4\pi^3}\int \frac{\tau v_x^2}{1+(\omega_c\tau)^2}(\mathcal{E}_x - (\omega_c\tau)\mathcal{E}_y)\frac{\partial f_0}{\partial E}d\boldsymbol{k}. \tag{E.9}$$

The integrand in (E.9) is the same as that of thermal equilibrium, which is a function of energy E, other than the part of v_x^2. Generally for a function $\xi(E)$, the equipartition law results in

$$\int v_x^2\xi(E)d\boldsymbol{k} = \frac{2}{3m^*}\int E\xi(E)d\boldsymbol{k}. \tag{E.10}$$

If we adopt Maxwellian approximation $f_0 = A\exp(-E/k_{\mathrm{B}}T)$ for a semiconductor at high temperatures and as the density of states $\mathscr{D}(E) = A_D E^{1/2}$, use (E.10), then we get

$$\frac{\partial f_0}{\partial E} = \frac{f_0}{-k_{\mathrm{B}}T}, \quad n = A_D\int_0^\infty f_0 E^{1/2}dE = \frac{2A_D}{3k_{\mathrm{B}}T}\int_0^\infty E^{3/2}f_0 dE.$$

Applying these to (E.9) we obtain

$$j_x = \frac{ne^2}{m^*}\left[\left\langle \frac{\tau}{1+(\omega_c\tau)^2}\right\rangle_E \mathcal{E}_x - \left\langle \frac{\omega_c\tau^2}{1+(\omega_c\tau)^2}\right\rangle_E \mathcal{E}_y\right], \tag{E.11a}$$

$$\equiv (ne^2/m^*)(A_l\mathcal{E}_x - A_t\mathcal{E}_y). \tag{E.11b}$$

The last line is the definition of A_l and A_t. Here $\langle\cdots\rangle_E$ means the same as the energy weighted average in (**??**). j_y is obtained in a similar way and the conductivity tensor in xy plane is finally obtained as

$$\boldsymbol{j} = \frac{ne^2}{m^*}\begin{pmatrix} A_l & -A_t \\ A_t & A_l \end{pmatrix}\mathbf{E}. \tag{E.12}$$

Appendix F: Kelvin relations

Consider a junction of BAB, where A and B are two species of metals as shown in the right. Let us move a unit charge from one end of the junction sys-

tem to the other quasi-statically keeping the temperatures at the both ends of the metal B at T_{m}. Let the temperatures at two junctions as T and $T + \Delta T$ respectively.
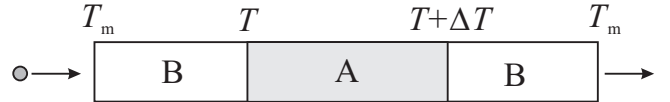
From the quasi-stationariness of the process we can apply the first and the second laws of thermodynamics as

$$V_{\mathrm{BA}} = \Pi_{\mathrm{BA}}(T) - \Pi_{\mathrm{BA}}(T+\Delta T) + (\tau_{\mathrm{B}} - \tau_{\mathrm{A}})\Delta T = 0$$

$$\frac{V_{\mathrm{BA}}(T)}{T} - \frac{\Pi_{\mathrm{BA}}(T+\Delta T)}{T+\Delta T} + \frac{\tau_{\mathrm{B}} - \tau_{\mathrm{A}}}{T}\Delta T = 0.$$

In the differential forms we get

$$\frac{dV_{\mathrm{BA}}}{dT} - \frac{d\Pi_{\mathrm{BA}}}{dT} + \tau_{\mathrm{B}} - \tau_{\mathrm{A}} = 0, \quad \frac{d}{dT}\left(\frac{\Pi_{\mathrm{BA}}}{T}\right) = \frac{\tau_{\mathrm{B}} - \tau_{\mathrm{A}}}{T}.$$

$$\therefore S_{\mathrm{AB}} = \frac{\Pi_{\mathrm{AB}}}{T}, \quad \frac{dS_{\mathrm{AB}}}{dT} = \frac{\tau_{\mathrm{A}} - \tau_{\mathrm{B}}}{T}. \tag{F.1}$$

Appendix G: Absorption and emission of radiation, Rabi oscillation

Here we teat absorption and emission of radiation in semiclassical approximation by giving a time-dependence to the perturbation Hamiltonian in a two-level system already treated in Appendix A (Lecture No.1). The treatment is semiclassical because the electromagnetic wave will be treated as a classical wave.

In App.A, we labeled the two levels as L R but here we use a, b, which rather label lower and upper energy levels. We write the unperturbed Hamiltonian as $\mathscr{H}^0 = \mathscr{H}^a + \mathscr{H}^b$, the perturbation Hamiltonian as $\mathscr{H}'$. We use simplified notation $\langle a|\mathscr{H}^0|b\rangle = \mathscr{H}^0_{ab}$ and assume $\mathscr{H}'_{aa} = \mathscr{H}'_{bb} = 0$.

Just as in App.A, we write the time dependent wavefunction as

$$\psi(t) = c_a(t)\phi_a e^{-E_a t/\hbar} + c_b(t)\phi_b e^{-E_b t/\hbar} \tag{G.1}$$

and substitute it into Schrödinger equation $\mathscr{H}\psi = i\hbar\partial\psi/\partial t$ to obtain

$$c_a \mathscr{H}'|a\rangle e^{-iE_a t/\hbar} + c_b \mathscr{H}'|b\rangle e^{-iE_b t/\hbar} = i\hbar[\dot{c}_a|a\rangle e^{-iE_a t/\hbar} + \dot{c}_b|b\rangle e^{-iE_b t/\hbar}].$$

By taking inner products with $\langle a|$ $\langle b|$, the following simultaneous differential equations for c_a and c_b.

$$\begin{cases} \dfrac{dc_a}{dt} = -\dfrac{i}{\hbar}c_b \mathscr{H}'_{ab} e^{-i\omega_0 t}, \\ \dfrac{dc_b}{dt} = -\dfrac{i}{\hbar}c_a \mathscr{H}'_{ba} e^{i\omega_0 t}, \end{cases} \tag{G.2}$$

where

$$\omega_0 \equiv \frac{E_b - E_a}{\hbar}. \tag{G.3}$$

The above is formally the same as Appendix A, where we saw that the tunneling causes the level anti-crossing (avoided level crossing) and the energy levels split though here we rather see the effect of external time-dependent perturbation on the transition between the two levels that have energy difference $\hbar\omega_0$. Let a be the label of the ground state with lower energy and we take the initial state as $c_a(0) = 1$, $c_b(0) = 0$.

As a simplest way to treat time-dependent perturbation, here we substitute the results in the lower order perturbation approximation into c_a and c_b in the right hand side of eq.(G.13) and solve the differential equation to obtain the next order results. In the 0-th order, from $dc_a/dt = dc_b/dt = 0$, $c_a^{(0)}(t) = 1$ and $c_b^{(0)}(t) = 0$. Starting from this the following two steps give

$$c_a^{(1)}(t) = 1, \quad c_b^{(1)}(t) = -\frac{i}{\hbar}\int_0^t \mathscr{H}'_{ba}(t') e^{i\omega_0 t'} dt', \tag{G.4a}$$

$$c_a^{(2)}(t) = 1 - \frac{1}{\hbar^2}\int_0^t dt' \mathscr{H}'_{ab}(t') e^{-i\omega_0 t'}\left[\int_0^{t'} dt'' \mathscr{H}'_{ba}(t'') e^{i\omega_0 t''}\right], \quad c_b^{(2)}(t) = -\frac{i}{\hbar}\int_0^t \mathscr{H}'_{ba}(t') e^{i\omega_0 t'} dt. \tag{G.4b}$$

We consider also simplest sinusoidal perturbation

$$\mathscr{H}'(t) = V\cos\omega t. \tag{G.5}$$

As ω, we take the value close to the energy difference between a and b, that is the values around ω_0. We simplify notation as $V_{ab} = \langle a|V|b\rangle$. From eq.(G.4b), we obtain

$$c_b(t) \simeq -\frac{i}{\hbar}V_{ba}\int_0^t dt' \cos\omega t' e^{i\omega_0 t'} = -\frac{V_{ba}}{2\hbar}\left[\frac{e^{i(\omega_0+\omega)t} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0-\omega)t} - 1}{\omega_0 - \omega}\right]$$

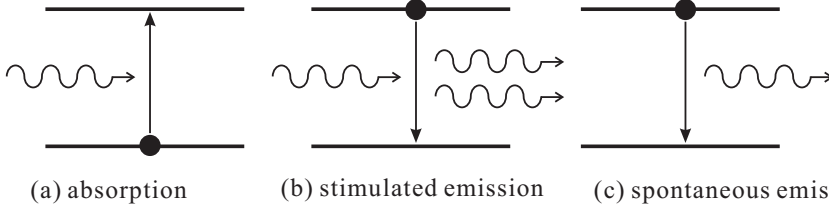$$\simeq -i\frac{V_{ba}}{\hbar}\frac{\sin[(\omega_0-\omega)t/2]}{\omega_0 - \omega}e^{i(\omega_0-\omega)t/2}. \tag{G.6}$$

Figure 4.4: Sketches for three interaction processes between a two-level system and electromagnetic waves (photons).

(a) absorption

(b) stimulated emission

(c) spontaneous emission

In the last line, from $\omega \sim \omega_0$ we estimate $\omega_0 + \omega \gg |\omega_0 - \omega|$ and drop the first term and transform the second term into the present form. Finally we obtain

$$P_b(t) = |c_b(t)|^2 \simeq \frac{|V_{ba}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2}. \qquad (G.7)$$

The result in (G.7) tells that the probability of occupying b state at time t oscillates with frequency $(\omega_0 - \omega)/(2\pi)$ and the oscillation amplitude is proportional to the square of the absolute value of Perturbation Hamiltonian matrix element V_{ba}. And if we fix the time delay t and sweep the angular frequency ω of the perturbation, the probability varies just like Fraunhofer diffraction as shown in the figure on the right.
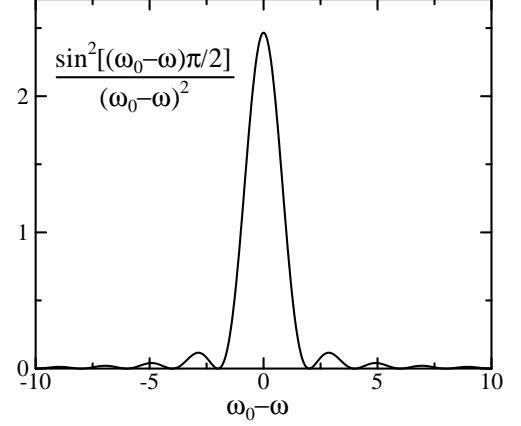
If we treat electromagnetic wave classical y, we can write the perturbation by the radiation field of electromagnetic wave as

$$\mathcal{H}' = -e\mathcal{E}_0 z \cos \omega t, \qquad (G.8)$$

which is just in the form of (G.5). Hence we can apply the result (G.7) to this case and get

$$P_b(t) \simeq \frac{|p\mathcal{E}_0|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2}, \qquad p \equiv e\langle a|z|b\rangle. \qquad (G.9)$$

From eq.(G.9), the excitation probability from a to b is proportional to the square of amplitude in electric field. If we quantise the electromagnetic field to photons, the above means that the probability is proportional to the number of photons in the vicinity of the two-level system. The transition $a \leftrightarrow b$ is, as illustrated in Fig.4.4, caused by the absorption and emission of photons. It is natural that the absorption probability illustrated in (a) is proportional to the photon density. On the other hand, the expression of transition probability in (G.9) holds not only for $c_a(0) = 1$ but for $c_b(0) = 1$. That is, eq.(G.9) also represents the stimulated emission process illustrated in (b).

Now if we start with the excited state in which the electron occupies the state b, and there is absolutely no electromagnetic field, there is no incident to cause the transition and hence no emission of photon occurs. That is, surprisingly in this classical treatment of electromagnetic field, we have no spontaneous emission illustrated in Fig.4.4(c).

Actually as, say, illumination with LED, the most of the emission processes we use are those of spontaneous emission. In order to have an insight on this problem, we rewrite the perturbation Hamiltonian in (G.8) with second quantization as

$$\mathcal{H}' = ie\sqrt{\frac{\hbar\omega_k}{2\epsilon_0 V_s}} z[a_{k\lambda}^\dagger e^{-ikr} - a_{k\lambda} e^{ikr}], \qquad (G.10)$$

where $a_k^\dagger$ is the creation operator of the photon with wavenumber $\boldsymbol{k}$, V_s is the system volume. The coefficient can be understood as the electric field amplitude $\mathcal{E}_0$ of a single photon, obtained by equating the energy of photon $\hbar\omega_k$ to the energy of electromagnetic field $V_s\epsilon_0\mathcal{E}_0^2$.

Here we use the Fermi's golden rule approximation for the transition probability then can ignore the time dependence of the perturbation and put $\cos \omega_k t$ as 1. Let n_k be the number of photons in the vicinity of the

two-level system and apply the Fermi's golden rule to the process $|b, n_k\rangle \to |a, n_k + 1\rangle$, then the transition probability is

$$W = \frac{2\pi}{\hbar} |\mathscr{H}'_{ba}|^2 \delta(E_b - E_a - \hbar\omega_k) = \frac{2\pi e^2}{\hbar} \left(\frac{\hbar\omega_k}{2\epsilon_0 V_s}\right) |\langle 1, n_{k+1}|a^\dagger_{k\lambda} z|2, n_{k\lambda}\rangle|^2 \delta(E_b - E_a - \hbar\omega_k)$$

$$= \frac{2\pi e^2}{\hbar} \left(\frac{\hbar\omega_k}{2\epsilon_0 V_s}\right) |\langle a|z|b\rangle|^2 (n_k + 1)\delta(E_b - E_a - \hbar\omega_k). \tag{G.11}$$

This result tells that there is the term 1 arising from the zero-point motion of vacuum other than the term proportional to the photon number n_k. This term 1 corresponds to the spontaneous emission. That is the spontaneous emission comes from the perturbation Hamiltonian matrix element coming from the vacuum zero point motion.

In eq.(G.6) we have dropped the first term as an approximation but this is equivalent to put

$$\mathscr{H}'_{ab} = \frac{V_{ab}}{2} e^{i\omega t}. \tag{G.12}$$

For hermicity, $\mathscr{H}'_{ba} = (V_{ba}/2)e^{-i\omega t}$.

Then the simultaneous differential equation (G.13) becomes

$$\begin{cases} \dfrac{dc_a}{dt} = -\dfrac{i}{2\hbar} c_b V_{ab} e^{-i(\omega_0 - \omega)t}, \\ \dfrac{dc_b}{dt} = -\dfrac{i}{2\hbar} c_a V_{ba} e^{i(\omega_0 - \omega)t}. \end{cases} \tag{G.13}$$

c_a can be erased and we get a homogeneous differential equation

$$\frac{d^2 c_b}{dt^2} + i(\omega - \omega_0)\frac{dc_a}{dt} + \frac{|V_{ab}|^2}{(2\hbar)^2} = 0, \tag{G.14}$$

which is readily solved to give the following answer. We define

$$\lambda_\pm \equiv \frac{1}{2}(\delta \pm \sqrt{\delta^2 + |V_{ab}|^2/\hbar^2}), \quad \delta \equiv \omega_0 - \omega. \tag{G.15}$$

And we can write

$$c_b(t) = c_+ e^{i\lambda_+ t} + c_- e^{\lambda_- t}. \tag{G.16}$$

If we apply the boundary condition $|c_a(0)| = 1$, $c_b(0) = 0$, we get

$$c_b(t) = \frac{i|V_{ab}|}{\omega_R \hbar} e^{i\delta t/2} \sin(\omega_R t/2),$$

$$c_a(t) = e^{i\delta t/2} \left[\cos\left(\frac{\omega_R t}{2}\right) - i\frac{\delta}{\omega_R}\sin\left(\frac{\omega_R t}{2}\right)\right], \tag{G.17}$$

where ω_R is the **Rabi frequency**

$$\omega_R \equiv \sqrt{(\omega_0 - \omega)^2 + |V_{ab}|^2/\hbar^2}. \tag{G.18}$$

From this result of Rabi model (G.17), in case of large electromagnetic amplitude and small detuning δ, the occupation probability oscillates between a and b with the frequency *proportional to the amplitude*. This is called **Rabi oscillation**.