

Light and Matter: Lecture 16

Introduction

The first 15 lectures of this course have been about the electronic structure of atoms and molecules and the interaction of light with atoms. For the next ten lectures we are going to look at the interaction of light with solids. The treatment differs on account of the properties of solids, namely, the density of atoms, the symmetry and structure in their organisation, the fact that the electronic coupling between atoms leads to continuous bands of electronic states rather than discrete energies, and the extended nature of the vibrational modes of the solid. We will address different classes of solids with different optical properties. We will study metals, dielectrics, semiconductors and molecular materials, including the special case of low dimensional structures. We will also look at how the properties of certain materials give rise to applications in the emission, detection and manipulation of light, and at how the optical properties are measured. We will see that optical properties of solids provide a window into their electronic structure.

1. Introduction and classical Lorentz oscillator model
2. Microscopic description of absorption
3. Absorption in a direct gap semiconductor
4. Luminescence
5. Low dimensional semiconductor structures
6. Optical properties of quantum wells, wires, dots
7. Absorption and emission by molecular materials
8. Interaction of light with vibrational states of solids
9. Metals and doped semiconductors
10. Applications

The main text book for this part of the course is *Optical Properties of Solids* by Mark Fox, (Oxford University Press, Second edition: 2010). For Lecture 16, Chapter 1 and Sections 2.1 and 2.2 of Fox are relevant.

16.1 Revision of some key concepts

We will need to use various physical relationships that you have studied in previous courses. Here we recall a few of the important definitions.

The complex dielectric function of a solid $\epsilon(\omega)$ relates the electric displacement field to the electric field \mathcal{E} .

$$\mathbf{D} = \epsilon_r \epsilon_0 \mathcal{E} \quad (16.1)$$

where we have expressed the complex dielectric function ϵ as $\epsilon = \epsilon_r \epsilon_0$.

The polarisation \mathbf{P} of the material can also be related to \mathcal{E} through the electric susceptibility χ

$$\mathbf{P} = \chi \epsilon_0 \mathcal{E} \quad (16.2)$$

And since $\mathbf{D} = \epsilon_0 \mathcal{E} + \mathbf{P}$ this means that

$$\mathbf{P} = \epsilon_0 (\epsilon_r - 1) \mathcal{E} \quad (16.3)$$

In general $\epsilon(\omega)$ is both complex and is frequency dependent. It can be expressed in terms of its real and imaginary parts:

$$\epsilon_r(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \quad (16.4)$$

The complex refractive index $\eta(\omega)$ is defined as

$$\eta = \sqrt{\epsilon_r} \quad (16.5)$$

where

$$\eta = n_r + i\kappa \quad (16.6)$$

This leads to expressions relating ϵ_1 and ϵ_2 to n_r and κ

$$\begin{aligned} \epsilon_1 &= n_r^2 - \kappa^2 \\ \epsilon_2 &= 2n_r\kappa \end{aligned} \quad (16.7)$$

In general ϵ_r and η are direction dependent, and this can be important in solids that have structural anisotropy. This gives rise to optical properties that depend on the direction and polarisation of the light field. In most cases however we will assume that ϵ_r and η are isotropic. When light passes through a material with imaginary part of refractive index κ , the intensity I of the light attenuates with distance x like

$$\frac{dI}{dx} = -\alpha I. \quad (16.8)$$

α is known as the absorption coefficient, it has dimensions of inverse length and is, like the other properties, frequency dependent. You have seen how to express the absorption coefficient in terms of the absorption cross section of an atom in the earlier part of the course. α relates directly to κ through

$$\alpha = \frac{4\pi\kappa}{\lambda} \quad (16.9)$$

where λ is the wavelength of light in vacuum.

We can relate the probability of reflection R of light from an interface to the difference in the real parts of the refractive index in the two materials. For normal incidence on a plane surface from medium of refractive index η_1 onto one of refractive index η_2 we have

$$R = \left| \frac{\eta_1 - \eta_2}{\eta_1 + \eta_2} \right|^2 \quad (16.10)$$

Absorption and reflection of light are important methods for the experimental determination of optical properties. Reflection is especially useful for solids where large optical density means that very little light is transmitted and spectral features are therefore hard to discern from changes in the transmitted light, but may be much more evident from the spectrum of reflected light.

16.2 Classical oscillator model for solids

Earlier in this course you have seen that when light of energy $\hbar\omega$ interacts with isolated atoms which have energy levels split by $E_2 - E_1 \approx \hbar\omega$, it can excite a transition between the levels. Note that for this effect to be strong, E_1 should be occupied and E_2 should be empty (or vice versa, which happens in a laser). The resulting oscillation in state occupancy looks like an oscillating dipole and can be treated with a classical oscillator model.

When we move from isolated atoms to solids, several other factors become important:

- There is a higher density of atoms, and therefore of possible transitions, so that the resulting relative permittivity ϵ_r is no longer close to 1.
- The electronic states form continuous bands, so that the transition energies are no longer discrete.

- The form of these bands, and the allowed transitions, is influenced by the symmetry of the structure of the solid and the dimensionality of the system.
- Extended vibrational modes form and transitions between them can occur.

A consequence of the band structure of solids is that the classical oscillator model is not always a good model for solids. It is good for some types of transitions, such as for atomic impurities in glasses where transitions between states of the impurity are still atomic-like, and it is good for metals and at low frequencies in doped semiconductors. It is not so good for inter-band transitions in semiconductors where there is a high density of transitions that changes rapidly with photon energy. In these cases we need to use a quantum mechanical description of the interaction of light with the solid. That will be the focus of the following six lectures. But first we will revise the classical oscillator model.

The equation of motion for an electron in an oscillating electric field is

$$m^* \frac{d^2x}{dt^2} + m^* \gamma \frac{dx}{dt} + Kx = -e\mathcal{E}_0 \exp(-i\omega t) \quad (16.11)$$

where γ is the coefficient of damping, m^* is the effective mass of the electron, e is the electronic charge and the field \mathcal{E} is polarised in the x direction. K represents the coefficient of the restoring force and can be written $K = m^* \omega_0^2$. The displacement x of the electron from its equilibrium position has the form

$$x = x_0 \exp(-i\omega t) \quad (16.12)$$

We will take the real parts of the complex quantities \mathcal{E} and x for the electric field and position, respectively. Substituting for x we find

$$(-\omega^2 - i\gamma\omega + \omega_0^2)x_0 = -\frac{e\mathcal{E}_0}{m^*} \quad (16.13)$$

From which we have

$$x(t) = -\frac{e}{m^*} \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega} \mathcal{E}(t) \quad (16.14)$$

Now, we can find the complex dielectric function $\epsilon_r(\omega)$ from the definition of the polarisation field

$$\mathbf{P} = \epsilon_0(\epsilon_r - 1)\mathcal{E} \quad (16.15)$$

The electron displacement leads to a contribution to the polarisation \mathbf{P} of the form

$$\mathbf{P}_{\text{resonant}} = -Nex \quad (16.16)$$

where N is the density of oscillators per unit volume. In the case when there are no other contributions to the polarisation field than these oscillations then $\mathbf{P} = \mathbf{P}_{\text{resonant}}$ and we can find ϵ_r from equations 16.14 to 16.16.

$$\epsilon_r(\omega) = 1 + \frac{Ne^2}{m^* \epsilon_0} \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}. \quad (16.17)$$

This can also be written as

$$\epsilon_r(\omega) = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega}. \quad (16.18)$$

where $\omega_p = \sqrt{Ne^2/m^* \epsilon_0}$ is known as the *plasma frequency*.

Separating this into the real and imaginary parts of ϵ_r we have

$$\epsilon_1(\omega) = 1 + \frac{Ne^2}{m^* \epsilon_0} \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}. \quad (16.19)$$

$$\epsilon_2(\omega) = \frac{Ne^2}{m^* \epsilon_0} \frac{\gamma\omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}. \quad (16.20)$$

If we look at the form of ϵ_1 and ϵ_2 for a single oscillator resonance we may notice several features.

- $\epsilon_2(\omega)$ has an approximately symmetric lineshape and is relatively narrow (the width and height depend on γ)

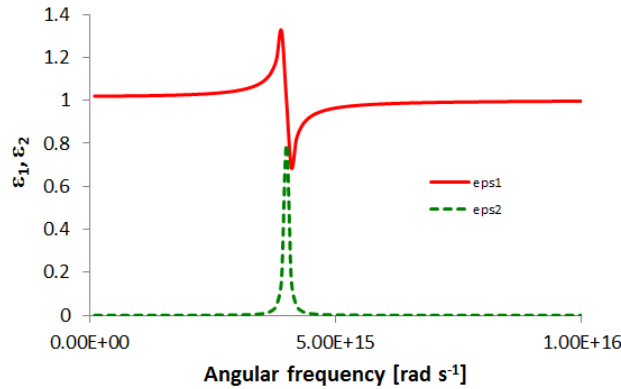


Figure 16.1: Real and imaginary parts of the complex dielectric function ϵ for a system containing a single oscillator of resonant frequency $\omega_0 = 4 \times 10^{15} \text{ s}^{-1}$.

- $\epsilon_1(\omega)$ is asymmetric with a rapid change in value around ω_0 ; ϵ_1 has a rather slower dependence on ω away from the resonance than ϵ_2
- $\epsilon_1(\omega)$ tends to different values at high and low ω . Specifically, $\epsilon_1(0) = 1 + \frac{Ne^2}{m^* \epsilon_0 \omega_0^2}$ and $\epsilon_1(\infty) = 1$. So $\epsilon_1(\omega)$ has dropped by an amount $\frac{Ne^2}{m^* \epsilon_0 \omega_0^2}$ as we cross from low frequency to high frequency across the resonance at ω_0 .

We can obtain expressions for n_r and κ from their definitions (see Problem 6.1) and we will see that n_r shows roughly similar behaviour to ϵ_1 and κ shows similar behaviour to ϵ_2 . You have been through a similar exercise earlier in this course when you worked out ϵ_r and the real and imaginary parts of η for a dilute gas. You have also used a treatment like this to find the frequency dependent conductivity of conductors in second year EM: in the case of a conductor, $\omega_0 = 0$. In the present case, the formulation is different from that for atoms in that (i) for a solid that can be treated in the nearly free electron model we use the effective mass m^* instead of the free electron mass, and (ii) because the density of atoms is high in a solid, N is large enough that we can no longer assume ϵ_r to be very close to 1. So we cannot make the simple approximations to n_r and κ that were made earlier in Lecture 11.

In addition, in a solid we are often concerned with multiple transitions at different energies. The contributions to ϵ_r from these transition can simply be added. For a system with several alternative oscillator-like transitions of different frequencies ω_{0i} from the same electronic ground state,

$$\epsilon_1(\omega) = 1 + \frac{Ne^2}{m^* \epsilon_0} \sum_i \frac{f_i (\omega_{0i}^2 - \omega^2)}{(\omega_{0i}^2 - \omega^2)^2 + \gamma_i^2 \omega^2}. \quad (16.21)$$

$$\epsilon_2(\omega) = \frac{Ne^2}{m^* \epsilon_0} \sum_i \frac{f_i \gamma_i \omega}{(\omega_{0i}^2 - \omega^2)^2 + \gamma_i^2 \omega^2}. \quad (16.22)$$

where f_i represents the *oscillator strength* of the i th transition. It can be shown that the transitions obey a sum rule whereby $\sum_i f_i = 1$. When we consider a frequency range that contains just one transition, then we can represent the effect of transitions at higher frequencies using the electric susceptibility χ . χ is the sum of contributions to ϵ_1 from higher frequency transitions. If these higher energy transitions are sufficiently narrow then χ can be taken as a constant over the range of interest, and thus

$$\epsilon_1(\omega) = 1 + \chi + \frac{Ne^2}{m^* \epsilon_0} \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}. \quad (16.23)$$

$$\epsilon_2(\omega) = \frac{Ne^2}{m^* \epsilon_0} \frac{\gamma \omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}. \quad (16.24)$$

The higher energy transitions contribute a background to the polarisation field

$$\mathbf{P}_{\text{background}} = \epsilon_0 \chi \mathbf{E} \quad (16.25)$$

and the total polarisation close to the resonance is due to the sum of background and resonant contributions:

$$\mathbf{P} = \mathbf{P}_{\text{background}} + \mathbf{P}_{\text{resonant}}. \quad (16.26)$$

This is the reason why in spectra for solids we often see ϵ_1 tend to an apparent constant value higher than 1 on the high frequency side of the resonance.

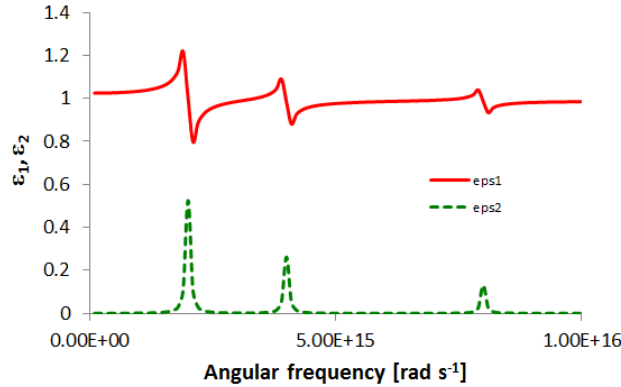


Figure 16.2: Real and imaginary parts of the complex dielectric function ϵ for a system containing three classical oscillators of equal strength and resonant frequencies $\omega_0 = 2 \times 10^{15} \text{ s}^{-1}$, $4 \times 10^{15} \text{ s}^{-1}$ and $8 \times 10^{15} \text{ s}^{-1}$.

It is worth noting that the real and imaginary parts of ϵ_r are not independent but are related to each other through a pair of integral equations called the Kramers-Kronig relations:

$$\begin{aligned} \epsilon_1(\omega) - 1 &= \frac{2}{\pi} P \int_0^\infty \omega' \frac{\epsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \\ \epsilon_2(\omega) &= -\frac{2}{\pi} P \int_0^\infty \omega' \frac{\epsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega' \end{aligned} \quad (16.27)$$

where P is the principal value of the integral. A similar set of relations exists for the real and imaginary parts of other complex functions, such as for the real and imaginary parts of η . This means that refractive index can be calculated from measurements of absorption over a wide range of frequencies, and vice versa. (See Problem 6.2).

The oscillator model is widely used but is not a good physical model for transitions between the occupied and unoccupied bands of states in solids. In these cases we need to use a quantum mechanical description in which the frequency dependence of an optical transition is related to the form of the electronic density of states near that energy. This will be treated next.

16.3 Main points of the lecture

- Light interacts with matter through photon absorption, emission and scattering (reflection).
- The physical description of optical processes in solids depends on the electronic structure of the material. Some solids, such as metals can be treated with the classical oscillator model while interband transitions in semiconductors require a QM treatment.
- In the classical oscillator model, the real and imaginary parts of the dielectric function are built up from a series of Lorentzian functions representing different transitions.
- Understanding optical properties is important for understanding the operation of optoelectronic and photonic devices, but also because optical methods are used as probes of electronic structure.

Light and Matter: Lecture 17

Microscopic description of absorption

For the next six lectures we will consider the interaction of light with electrons in solids, leading to transitions between energy levels, and the emission of light as a result of electronic transitions. We will use the nearly free electron model for the electronic states in solids that you learnt in second year Solid State Physics. First we will establish a general form for the absorption coefficient. For this lecture, Appendix B2 of Fox is relevant.

17.1 Transition rate

We will consider a two level system with electron states at energies E_1 and E_2 ($E_2 > E_1$). When light of energy $\hbar\omega = E_2 - E_1$ interacts with this system, it can promote an electron from E_1 to E_2 (absorption), or, if E_2 is partly occupied, it can stimulate a transition from E_2 to E_1 (stimulated emission). In general, to find the rate of transitions from one state of a system to another under the influence of an external perturbation, we can use an expression known as Fermi's Golden Rule (FGR). Fermi's Golden Rule is a result from time dependent perturbation theory. We are not going to derive it, but if you are interested you will find a derivation in many QM text books, for example, it is covered briefly in Chapter 9 of *Introduction to Quantum Mechanics* by Griffiths and Chapter 8 of *Quantum Mechanics* by Rae. In the case of a two level system where the lower state is occupied and the upper state is not, the rate of electronic transitions from state $|1\rangle$ of energy E_1 to state $|2\rangle$ of energy E_2 under the influence of a perturbing field H' is given by:

$$\Gamma_{1 \rightarrow 2} = \frac{2\pi}{\hbar} \left| \langle 2 | \hat{H}' | 1 \rangle \right|^2 \delta(E - E_2 + E_1) \quad (17.1)$$

If we allow for the two levels to have degeneracy g_1 and g_2 and allow for the two states to have occupation probabilities f_1 and f_2 then the rate becomes:

$$\Gamma_{1 \rightarrow 2} = \frac{2\pi}{\hbar} \left| \langle 2 | \hat{H}' | 1 \rangle \right|^2 \delta(E - E_2 + E_1) g_1 g_2 f_1 (1 - f_2) \quad (17.2)$$

Since the perturbing field can also stimulate a transition from E_2 to E_1 , we can define a rate for downward transitions $\Gamma_{2 \rightarrow 1}$ which is identical to $\Gamma_{1 \rightarrow 2}$ but with the subscripts 1, 2 swapped. Then the net transition rate is

$$\Gamma_{12} = \Gamma_{1 \rightarrow 2} - \Gamma_{2 \rightarrow 1} = \frac{2\pi}{\hbar} \left| \langle 2 | \hat{H}' | 1 \rangle \right|^2 \delta(E - E_2 + E_1) g_1 g_2 (f_1 - f_2) \quad (17.3)$$

where we use the fact that $\left| \langle 2 | \hat{H}' | 1 \rangle \right| = \left| \langle 1 | \hat{H}' | 2 \rangle \right|$.

When we apply this to solids where there is an ensemble of states or continuous bands of states, we will replace the delta function and degeneracy terms with a function that accounts for the density of initial states and the density of final states where the initial and final state energies differ by $\hbar\omega$. Such a function is called the joint density of states. For the moment, we will consider only the system containing two discrete levels.

17.2 Dipole approximation

In the presence of an electromagnetic field the total Hamiltonian H is given by

$$H = H_0 + H' = \frac{(\mathbf{p} + e\mathbf{A})^2}{2m_0}, \quad (17.4)$$

where H_0 is the Hamiltonian in the absence of the applied field. \mathbf{A} is the vector potential of the field and has the form

$$\mathbf{A} = \mathbf{A}_0 \exp(i(\mathbf{k} \cdot \mathbf{r} - \omega t)) \quad (17.5)$$

Expanding the terms we have

$$H_0 + H' = \frac{\mathbf{p}^2}{2m_0} + \frac{e\mathbf{p}\cdot\mathbf{A}}{m_0} + \frac{(e\mathbf{A})^2}{2m_0}, \quad (17.6)$$

where we have used the fact that $\mathbf{p}\cdot\mathbf{A} = \mathbf{A}\cdot\mathbf{p}$ because p and A commute. In the case of a weak electromagnetic field, which in practice is almost always the case, we can neglect the last term, in \mathbf{A}^2 , leaving

$$H' = \frac{e\mathbf{p}\cdot\mathbf{A}}{m_0}, \quad (17.7)$$

where we have used the definition of the unperturbed Hamiltonian

$$H_0 = \frac{\mathbf{p}^2}{2m_0}. \quad (17.8)$$

Since the wavelength of light λ , is large compared to atomic distances within a solid (for visible light, $2\pi/\lambda \approx 10^7$ while $|r| < 10^{-9}$, so $\mathbf{k}\cdot\mathbf{r} \ll 1$) we can expand the spatial part of the exponent in \mathbf{A}

$$\mathbf{A} = \mathbf{A}_0 \exp(-i\omega t)(1 + \mathbf{k}\cdot\mathbf{r} + \dots) \approx \mathbf{A}_0 \exp(-i\omega t) \quad (17.9)$$

For an electromagnetic wave in a system where the scalar potential is zero \mathbf{A} relates to the electric field through $\mathcal{E} = -\frac{d\mathbf{A}}{dt}$. From this we find $\mathcal{E}_0 \exp(-i\omega t) = i\omega \mathbf{A}_0 \exp(-i\omega t)$ and then can write H' in terms of \mathcal{E}

$$H' = \frac{e\mathbf{p}\cdot\mathbf{A}}{m_0} = \frac{e}{i\omega m_0} \mathbf{p}\cdot\mathcal{E}_0 \exp(-i\omega t) \quad (17.10)$$

The matrix element $\langle 2|\hat{H}'|1\rangle$ in the transition rate now has the form:

$$\langle 2|\hat{H}'|1\rangle = \frac{e}{im_0\omega_{12}} \langle 2|\mathbf{p}\cdot\mathcal{E}_0|1\rangle \quad (17.11)$$

where we have set $\omega = \omega_{12}$ since the delta function in Equation 17.3 selects the photon energy $\hbar\omega_{12} = E_2 - E_1$: i.e., the rate is zero for any other value of ω . The time dependence of the field does not appear in the matrix element because a time dependence of the form $e^{-i\omega t}$ was accounted for in the derivation of Fermi's Golden Rule. The matrix element can be simplified further by making use of a commutation relationship from quantum mechanics (this is developed in Problem 6.3):

$$[\hat{H}_0 \hat{r} - \hat{r} \hat{H}_0] = \frac{\hbar}{im_0} \hat{p} \quad (17.12)$$

This allows us to express the matrix element in terms of the position operator \hat{r} using:

$$\langle 2|\hat{p}|1\rangle = \frac{im_0}{\hbar} \langle 2|\hat{H}_0 \hat{r} - \hat{r} \hat{H}_0|1\rangle = \frac{im_0(E_2 - E_1)}{\hbar} \langle 2|\hat{r}|1\rangle = im_0\omega_{12} \langle 2|\hat{r}|1\rangle \quad (17.13)$$

Which leaves

$$\langle 2|\hat{H}'|1\rangle = e \langle 2|\mathbf{r}\cdot\mathbf{e}_0|1\rangle |\mathcal{E}_0| = d_{12} |\mathcal{E}_0| \quad (17.14)$$

where \mathbf{e}_0 is the unit vector along the direction of \mathcal{E} and $d_{12} = e \langle 2|\mathbf{r}\cdot\mathbf{e}_0|1\rangle$. d_{12} is known as the *transition dipole matrix element* because it is proportional to the dipole moment of the electron undergoing the transition. You will recognise this from the matrix element in Lecture 9 (and second year atomic physics) where you used $H = -\mathbf{d}\cdot\mathcal{E}_0$ where \mathbf{d} is the dipole moment of an electron.

Finally, the transition rate is

$$\Gamma_{12} = \frac{2\pi}{\hbar} d_{12}^2 |\mathcal{E}_0|^2 \delta(E - E_2 + E_1) g_1 g_2 (f_1 - f_2) \quad (17.15)$$

17.3 Absorption coefficient

Now we will find the coefficient of absorption, α_{12} , in an isotropic medium containing N such two-level systems per unit volume. We know that the absorption coefficient describes the attenuation of light of intensity I with distance

$$\frac{dI}{dx} = -\alpha_{12}I \quad (17.16)$$

The intensity I on the right hand side of Equation 17.16 is given by the energy density in the electromagnetic field $U = \frac{1}{2}n_r^2\epsilon_0|\mathcal{E}_0|^2$ times the speed of light in the medium c/n_r :

$$I = \frac{1}{2}n_r c \epsilon_0 |\mathcal{E}_0|^2 \quad (17.17)$$

while the left hand side of Eqn. 17.16 is equal to the rate of loss of energy density from the field $\frac{dI}{dx} = -\frac{dU}{dt}$, which is given by the product of transition rate and transition energy

$$\frac{dI}{dx} = -N\Gamma_{12}\hbar\omega_{12} \quad (17.18)$$

Substituting for $\frac{dI}{dx}$ (Equation 17.17) and I (Equation 17.18), we obtain the absorption coefficient in terms of transition rate :

$$\alpha_{12} = \frac{2N\hbar\omega_{12}\Gamma_{12}}{n_r c \epsilon_0 |\mathcal{E}_0|^2} \quad (17.19)$$

Using equation 17.15 for Γ_{12} and cancelling the terms in $|\mathcal{E}_0|^2$ we find

$$\alpha_{12}(\hbar\omega) = \frac{4\pi N\omega}{n_r c \epsilon_0} d_{12}^2 \delta(\hbar\omega - E_2 + E_1) g_1 g_2 (f_1 - f_2) \quad (17.20)$$

The delta function must be retained to make the expression dimensionally correct.

In the case of transitions from a singly degenerate, occupied lower state ($g_1 = 1$, $f_1 = 1$) to a singly degenerate, empty lower state ($g_2 = 1$, $f_2 = 0$), α_{12} becomes:

$$\alpha_{12}(\hbar\omega) = \frac{4\pi N\omega}{n_r c \epsilon_0} d_{12}^2 \delta(\hbar\omega - E_2 + E_1) \quad (17.21)$$

Now α_{12} depends only on

- The density N of such two-level electronic systems
- The magnitude of the transition dipole matrix element d_{12}
- The energy of the transition $E_2 - E_1$
- The refractive index of the medium n_r .

In a medium containing multiple levels and multiple possible transitions then to find the rate at which light of energy $\hbar\omega$ is absorbed we need to add together contributions from different transitions where the initial and final state energies differ by $\hbar\omega$.

$$\alpha(\hbar\omega) = \sum_{i,j} \alpha_{ij}(\hbar\omega) \quad (17.22)$$

where each contribution α_{ij} has the form of eqn. 17.20 with different d_{ij} and subject to $\delta(\hbar\omega - E_j + E_i)$. In the case of continuous bands of states, the sum becomes an integral. In the next section we will apply this formalism to find the absorption coefficient for interband transitions in a semiconductor. We will see that the symmetry imposed by the position operator in the matrix element will lead to strong selection rules controlling which transitions are optically allowed.

17.4 Main points of lecture

- An electromagnetic field induces optical transitions between electronic levels separated by the photon energy. The transition rate can be described using Fermi's Golden Rule.
- Because the wavelength of light is much larger than the distances involved in electronic transitions, the effect of the electromagnetic field is reduced to that of a dipole operator coupling initial and final states.
- The transition rate then depends on the transition dipole matrix element and the light intensity.
- We find that the absorption coefficient is proportional to the square of the transition dipole matrix element.
- For a system with multiple transitions, the contributions to the absorption coefficient can be added.

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Absorption in direct gap semiconductor

In the last lecture we derived the absorption coefficient in terms of dipole matrix element. Now we will evaluate this for interband transitions in a direct band gap semiconductor. From Fox's book, Appendix D and Chapter 3, Sections 3.1 to 3.3 are relevant for this lecture.

18.1 Bloch wavefunctions

In second year Solid State you studied the form of the electronic states in a crystalline solid. You learnt that, in the nearly free electron model, the wave functions of electrons in a crystalline solid have the Bloch form. The wavefunction is the product of a periodic function that reflects the electronic structure of the unit cell and a slowly varying plane wave term. The rapidly varying, periodic part is specific to the band (e.g., conduction or valence band) and it is related to the orbitals of the constituent atoms that are involved in that particular band. The plane wave part arises from the requirement that the electron density should be periodic in a crystal, as stated by the Bloch theorem. The Bloch Theorem is covered in Dr Lee's lecture notes (Chapter 5) from second year.

You have also learnt in second year Solid State that the electronic states in a crystal form a set of bands separated by energy gaps in which no electronic states are allowed. The band structure depends upon the electron wavevector \mathbf{k} and is in general different for \mathbf{k} directed along different axes within the crystal. You learnt that the bands are filled by the available electrons, following Pauli's exclusion principle, up to some level which is called the Fermi level. (In fact, the Fermi level denotes the highest occupied level at $T = 0$; at $T > 0$ some empty states will be found below the Fermi level and some occupied states above it.) If the Fermi level falls within a band then the solid has metallic properties: the electrons in the highest occupied levels can easily be scattered into empty levels at a similar energy, for example by an applied electrostatic field. If the Fermi level falls within a gap which is around 1 - 3 eV in size then the solid is a semiconductor: at low temperature the lower band (the valence band) is completely filled and the upper band (the conduction band) completely empty. If the Fermi level falls within a gap which is larger than about 3 eV the material is an insulator.

We are going to consider optical transitions across the valence - conduction band gap in a semiconductor.

The Bloch wavefunction, ψ_{n,\mathbf{k}_n} , or $|n, \mathbf{k}_n\rangle$ in Dirac notation, is defined by two quantities, the principal quantum number n of the band involved and the electron wavevector \mathbf{k}_n :

$$|n, \mathbf{k}_n\rangle = \frac{1}{\sqrt{V}} u_n(\mathbf{r}) e^{i\mathbf{k}_n \cdot \mathbf{r}} \quad (18.1)$$

where V is a normalisation volume. We will assume that the periodic functions u_n are independent of \mathbf{k} . The periodic parts of the wavefunction and the entire wavefunction satisfy orthogonality such that

$$\int_{\text{unit cell}} u_m^*(\mathbf{r}) u_n(\mathbf{r}) dV = \delta_{nm} \quad (18.2)$$

and

$$\frac{1}{V} \int u_m^*(\mathbf{r}) e^{-i\mathbf{k}_m \cdot \mathbf{r}} u_n(\mathbf{r}) e^{i\mathbf{k}_n \cdot \mathbf{r}} dV = \delta_{nm} \delta_{\mathbf{k}_m \mathbf{k}_n} \quad (18.3)$$

To calculate the absorption coefficient using the formalism from the last lecture we will need to know the dipole matrix element for transitions between valence and conduction bands and the degeneracies of the energy levels.

18.2 Transition dipole matrix element for interband transitions

The dipole matrix element for a transition between a valence band state $|v, \mathbf{k}_v\rangle = u_v(\mathbf{r})e^{i\mathbf{k}_v \cdot \mathbf{r}}$ and conduction band state $|c, \mathbf{k}_c\rangle = u_c(\mathbf{r})e^{i\mathbf{k}_c \cdot \mathbf{r}}$ is given by

$$d_{cv} = e \frac{1}{V} \int u_c^*(\mathbf{r}) e^{-i\mathbf{k}_c \cdot \mathbf{r}} \mathbf{r} \cdot \mathbf{e}_0 u_v(\mathbf{r}) e^{i\mathbf{k}_v \cdot \mathbf{r}} dV \quad (18.4)$$

The integral in Equation 18.4 is non-zero only if the exponential terms cancel out, i.e. if $e^{-i\mathbf{k}_c \cdot \mathbf{r}} * e^{i\mathbf{k}_v \cdot \mathbf{r}} = 1$ and hence if $\mathbf{k}_v = \mathbf{k}_c$. The same conclusion follows from considering that the crystal momentum before and after the transition must be conserved.

The condition $\mathbf{k}_v = \mathbf{k}_c$ means that only vertical transitions between the bands are permitted. The matrix element becomes

$$d_{cv} = e \int_{\text{unit cell}} u_c^*(\mathbf{r}) \mathbf{r} \cdot \mathbf{e}_0 u_v(\mathbf{r}) dV \delta_{\mathbf{k}_m \mathbf{k}_n} \quad (18.5)$$

where the integral is now taken over the unit cell. The delta function provides a selection rule on the \mathbf{k} values of the states: it says that only vertical transitions (with $\Delta\mathbf{k} = 0$) are optically allowed. In an isotropic material we may choose a direction for the electric field, say z , so

$$d_{cv} = e \int_{\text{unit cell}} u_c^*(\mathbf{r}) z u_v(\mathbf{r}) dV \quad (18.6)$$

(In a crystal with cubic symmetry, d_{cv} will be the same for polarisation in the x , y and z directions.) The value of the integral depends on the symmetry of the functions $u_c(\mathbf{r})$ and $u_v(\mathbf{r})$. Usually the atomic functions possess even or odd symmetry, like the atomic orbitals, and therefore the integral will be non-zero only if $u_c(\mathbf{r})$ and $u_v(\mathbf{r})$ have different parity. That is often the case in semiconductors.

For example in gallium arsenide (GaAs) the valence and conduction bands result from the mixing of the 4s and 4p atomic orbitals of Ga (valence configuration $4s^2 4p^1$) and As (valence configuration $4s^2 4p^3$) and inherit the atomic symmetry. In GaAs, the valence bands have p like symmetry near the valence band maximum and the conduction band has s like symmetry near the conduction band minimum. As a result of the opposite parity of $u_c(r)$ and $u_v(r)$, the matrix element for GaAs is non-zero. In rare cases where the conduction and valence bands have the same parity near the band extrema d_{cv} is zero and optical transitions between those bands are dipole forbidden.

For interband transitions in practical semiconductors the dipole matrix element has been calculated or derived from experimental measurements and is available as a parameter of the material. We do not have to work it out. Notice that the requirement for different parity of the $u(\mathbf{r})$ functions will automatically rule out optical transitions between occupied and unoccupied electronic states in the same band ('intraband' transitions).

18.3 Form of $\alpha(\hbar\omega)$ in direct gap semiconductor

Now we work out the form of $\alpha(\hbar\omega)$ in a direct gap semiconductor. We will take the case where the valence band maximum has energy E_v and occurs at $\mathbf{k} = \mathbf{0}$, and the conduction band minimum E_c occurs at the same point $\mathbf{k} = \mathbf{0}$. We will assume that the material's band structure is isotropic near this point. You should recall from second year Solid State that in the Nearly Free Electron model the electronic states in a crystal are defined by their wavevector \mathbf{k} and that the energy of an electron in a state defined by \mathbf{k} is given by

$$E_c(\mathbf{k}) = E_c(0) + \hbar^2 \frac{\mathbf{k}^2}{2m_e^*} \quad (18.7)$$

where m_e^* is the electron effective mass. The electrons behave as though they are free electrons with the energy and momentum of a plane wave, but with a different effective mass m_e^* , rather than m_0 . Similarly the energy of a hole in a state defined by \mathbf{k} is given by

$$E_v(\mathbf{k}) = E_v(0) - \hbar^2 \frac{\mathbf{k}^2}{2m_h^*} \quad (18.8)$$

where m_h^* is the hole effective mass. These two relationships mean that the energy difference between electron and hole states of the same \mathbf{k} is given by

$$E(\mathbf{k}) = E_g + \frac{\hbar^2 \mathbf{k}^2}{2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) = E_g + \frac{\hbar^2 \mathbf{k}^2}{2\mu^*} \quad (18.9)$$

where we define a reduced effective mass,

$$\mu^* = (1/m_e^* + 1/m_h^*)^{-1} \quad (18.10)$$

and we define the band gap energy

$$E_g = E_c(0) - E_v(0). \quad (18.11)$$

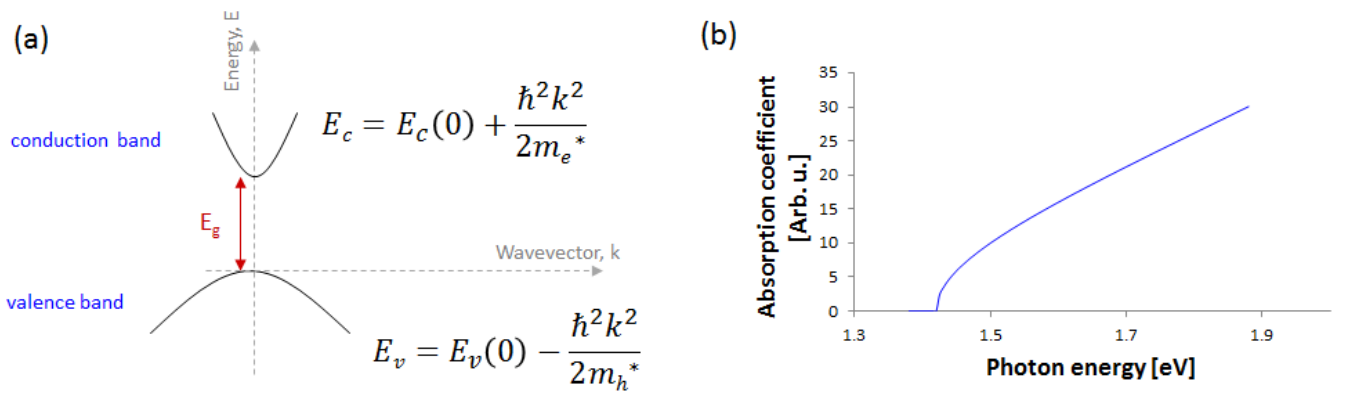


Figure 18.1: (a) Band structure (b) Absorption coefficient of an ideal direct band gap semiconductor.

The above dispersion relations result from the form of the density of states in three dimensions. We use similar physics to obtain the form of $\alpha(\hbar\omega)$. We will assume that the valence band is fully occupied and the conduction band is empty so the occupation factor $f_1 - f_2 = 1$. This is reasonable for a semiconductor at equilibrium at room temperature. Eqn. 17.20 (Lecture 17) gave us the absorption coefficient for a medium contain N pairs of levels per unit volume when the levels have degeneracies g_1, g_2 . In a continuous solid we need to express the degeneracies in terms of the density of transitions per unit volume, or the joint density of states (JDOS), $\rho(\hbar\omega)$

The JDOS is the density of initial states from which a transition of energy $\hbar\omega$ is allowed, multiplied by the density of those final states. It results from a sum over \mathbf{k} states of the form

$$\rho(\hbar\omega) = N \sum_{\mathbf{k}} g_c(\mathbf{k}) g_v(\mathbf{k}) \delta(\hbar\omega - E_c(\mathbf{k}) + E_v(\mathbf{k})) \quad (18.12)$$

where the delta function ensures the $\Delta\mathbf{k} = 0$ selection rule is obeyed. In the case of the direct interband transition the JDOS is easily calculated. Eqn. 18.9 tells us that the transition energy is directly related to \mathbf{k} through $\hbar\omega = E(\mathbf{k}) = E_g + \frac{\hbar^2 \mathbf{k}^2}{2\mu^*}$. The density of states in \mathbf{k} space in three dimensions is given by

$$g(\mathbf{k}) d^3\mathbf{k} = g_{3D}(k) dk = \left(\frac{1}{2\pi} \right)^3 4\pi k^2 dk \quad (18.13)$$

where we have used the symmetry of the system to express $g(\mathbf{k})$ in terms of k . We can convert the density of states into terms of transition energy $E = \hbar\omega$ using eq. 18.9 and letting

$$\rho(E) dE = 2g_{3D}(k) dk \quad (18.14)$$

where the additional factor of 2 is included to account for spin degeneracy. This yields

$$\rho(\hbar\omega) = \frac{1}{2\pi^2} \left(\frac{2\mu^*}{\hbar^2} \right)^{3/2} \sqrt{\hbar\omega - E_g} \quad (18.15)$$

(The full exercise is worked through in Problem 6.5.) An important point to notice here is that the JDOS, and hence the absorption strength, will be high whenever the gradient of the band dispersion, dE/dk , approaches zero. This means we can expect features in the absorption spectra of a solid at energies corresponding to band extrema at the Brillouin zone boundaries. In fact, optical measurements of these features are often used in order to learn about the electronic structure of the material.

Finally, we reconstruct the absorption coefficient. Using eq. 17.20, and substituting in our expression for the JDOS in place of the terms in N , degeneracies and delta function, we obtain:

$$\alpha_{cv}(\hbar\omega) = \frac{4\pi\omega}{n_r c \epsilon_0} |d_{cv}|^2 \rho(\hbar\omega) \quad (18.16)$$

Now we can write

$$\begin{aligned} \alpha_{cv}(\hbar\omega) &= \frac{2(2\mu^*)^{3/2}\omega}{\pi n_r c \epsilon_0 \hbar^3} |d_{cv}|^2 \sqrt{\hbar\omega - E_g} && \text{for } \hbar\omega > E_g \\ \alpha_{cv}(\hbar\omega) &= 0 && \text{otherwise} \end{aligned} \quad (18.17)$$

or, in a more friendly way,

$$\begin{aligned} \alpha_{cv}(\hbar\omega) &= A\omega \sqrt{\hbar\omega - E_g} && \text{for } \hbar\omega > E_g \\ \alpha_{cv}(\hbar\omega) &= 0 && \text{otherwise} \end{aligned} \quad (18.18)$$

where A is a material dependent constant.

The absorption coefficient thus has a distinct shape, where alpha rises sharply from zero at the band gap and follows a square root form, with a magnitude that depends on the transition dipole matrix element, i.e. on the overlap and symmetry of the atomic parts of the conduction and valence band Bloch functions, and on the effective masses of the electron and hole in the material. The additional factor of ω will influence the shape of $\alpha(\omega)$ only weakly near the band edge.

In practice, direct gap semiconductors tend to show a sharp turn on in absorption. However the exact square root dependence on $\hbar\omega - E_g$ predicted by Eqn. 18.18 is seldom seen. This can be because other critical points in the band structure occur close to E_g and distort the trend; the assumption of a parabolic band (energy independent effective masses) is not good; defects in the material lead to states within the gap and an absorption tail; excitonic absorption at energies close to the band gap. The absorption spectra of indirect gap semiconductors are also completely different; we will deal with this in a later lecture.

18.4 Main points of lecture

- In crystalline solids, the electronic wavefunction can be written in the Bloch form, as the product of a rapidly varying, periodic part and a plane wave.
- The transition dipole matrix element for an interband transition, d_{cv} is constructed from the periodic functions for the two bands and is non zero only when the electron wavevector \mathbf{k} is conserved.
- This means that only transitions that are *vertical* in the $E(\mathbf{k})$ diagram for a solid are optically allowed.
- The joint density of states $\rho(\hbar\omega)$ determines the density of allowed transitions per unit energy and volume for a system with continuous energy bands. It replaces the term $N g_1 g_2 \delta(\hbar\omega - E_2 + E_1)$ for a two level system.
- In the nearly free electron model, the energy difference between initial and final states of a vertical transition depends quadratically on k . This leads to a joint density of states (for a three dimensional material) which varies like $\sqrt{\hbar\omega - E_g}$
- The absorption coefficient for an interband transition in a direct gap semiconductor depends on $\sqrt{\hbar\omega - E_g}$ and the interband transition dipole matrix element for the material.

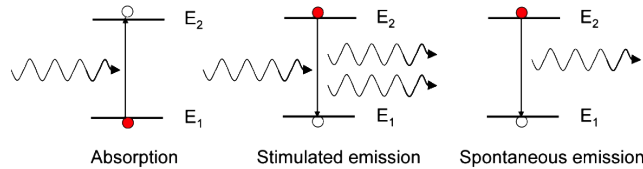
Light and Matter: Lecture 19

Luminescence

Until now we have been dealing with the absorption of light by solids. You already know that any material that can absorb light can also emit light: the selection rules that enable a photon to excite an electron from level 1 to level 2 (absorption) also enable a photon to de-excite an electron from level 2 to level 1 along with emission of a photon (stimulated emission) and allow an electron to decay spontaneously from level 2 to level 1 along with the emission of a photon (spontaneous emission). In a set of identical atoms containing two levels the rates of these three processes are related by the Einstein A and B coefficients that you studied in Lecture 12 and in previous courses. A similar reciprocity principle applies to solids. The main difference is that in a solid where the electron population shares the same set of energy levels we need to consider the state of occupation of the levels involved in a transition as defined by the Fermi-Dirac occupation factors. In a set of atoms the electrons in different atoms do not interact and it is not necessary to consider the effect of level occupation. Also in the case of solids, light emission (like absorption) is influenced by the continuous nature of the energy levels and the higher density of states compared to a gas of atoms.

Emission of light by solids, especially by semiconductors, is an area of huge practical importance, with efforts to control the colour, bandwidth, speed and efficiency of light emitting devices, displays, lighting devices and lasers. In this lecture we will obtain a relationship between the rate and spectrum of spontaneous emission and the absorption coefficient for a solid and will consider the special case of interband transitions in a direct band-gap semiconductor. For this lecture, Chapter 5 of Fox is relevant but does not cover mathematical details and the notes from Lecture 12 may be helpful. Some additional background on units is given in the paper by Robert C. Hilborn at this link: <http://arxiv.org/abs/physics/0202029>.

19.1 Relation between absorption and emission rates



Let's consider a two level system where the lower level at E_1 is occupied with probability f_1 and the upper level E_2 with probability f_2 . We will assume the two levels have the same degeneracy $g_1 = g_2 = 1$. The main result will be independent of g_1 and g_2 since absorption and emission are both proportional to $g_1 g_2$. We want to find the rate of spontaneous emission in terms of the parameters that control photon absorption, the occupation of the two levels and the energy of the gap.

First recall how f is defined. You will remember from second year Solid State that the electronic occupation probability f_1 of the level at energy E_1 is given by $f_1 = 1/(e^{(E_1 - E_F)/k_B T} + 1)$ where E_F is the Fermi level and k_B is Boltzmann's constant. When the system is not at thermal equilibrium, e.g when additional electrons have been excited into the upper level, we can still define the occupation probabilities in terms of two different *quasi*-Fermi levels E_{F1} and E_{F2} for the electrons at E_1 and E_2 , respectively.

$$f_1 = \frac{1}{e^{(E_1 - E_{F1})/k_B T} + 1}, \quad f_2 = \frac{1}{e^{(E_2 - E_{F2})/k_B T} + 1} \quad (19.1)$$

The difference in quasi Fermi levels $\Delta\mu = E_{F2} - E_{F1}$ is sometimes called the chemical potential.

Let's define a rate of spontaneous emission from the upper level to the lower level in analogy with the Einstein A and B coefficient analysis:

$$-\frac{dn_2}{dt} = aNf_2(1 - f_1) \quad (19.2)$$

where $n_2 = Nf_2$, N is the density of systems (e.g. atoms) that make up the solid and f_2 the occupation probability of level 2. Compared to equation 12.1, the occupation probability of the final state f_1 is included. We can also define a rate of net photon absorption (i.e. of absorption minus stimulated emission) of

$$-\frac{dn_1}{dt} = bNu(\hbar\omega)(f_1 - f_2) \quad (19.3)$$

where $n_1 = Nf_1$ and we have added the net rates of absorption and stimulated emission following Lecture 17. $u(\hbar\omega)$ is the energy density in the photon field per unit photon energy. In the steady state the rates of spontaneous emission and net absorption are equal and therefore

$$a = bu(\hbar\omega) \frac{(f_1 - f_2)}{f_2(1 - f_1)}. \quad (19.4)$$

We relate a to b by considering thermal equilibrium. At thermal equilibrium $u(\hbar\omega)$ is given by Planck's law for black body radiation in a medium of refractive index n_r at temperature T

$$u(\hbar\omega)d(\hbar\omega) = \frac{\omega^3 n_r^3}{\pi^2 c^3} \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} d(\hbar\omega). \quad (19.5)$$

Because $E_{F1} = E_{F2} = E_F$ at thermal equilibrium, the last factor in equation 19.4 simplifies to

$$\frac{(f_1 - f_2)}{f_2(1 - f_1)} = e^{\frac{E_2 - E_1}{k_B T}} - 1. \quad (19.6)$$

and since $\hbar\omega = E_2 - E_1$ for our system the two terms containing $e^{\frac{\hbar\omega}{k_B T}} - 1$ cancel to leave

$$a = b \frac{\omega^3 n_r^3}{\pi^2 c^3}. \quad (19.7)$$

Until now we have effectively been dealing with the case of a narrow resonance and broadband light. For a solid it is more appropriate to deal with the case of monochromatic light of energy $\hbar\omega$. In that case we replace $u(\hbar\omega)$ by $Ug(\hbar\omega)$ where $g(\hbar\omega)$ is a lineshape function, so the rate of absorption events in an energy range $\hbar\omega$ to $\hbar\omega + d(\hbar\omega)$ is given by $-dn_1/dt = bNUg(\hbar\omega)(f_1 - f_2)$ where U is the total energy density of the radiation.

We can now relate b to the absorption coefficient α that we obtained in Lecture 17. The net rate of absorption events is given by $-dn_1/dt = N\Gamma_{12}$ where Γ_{12} was related to α by eqs. 17.16 to 17.18.

$$N\Gamma_{12} = \frac{\alpha U c}{n_r \hbar\omega} \quad (19.8)$$

Equating the two expressions for the net absorption rate we find

$$\alpha(\hbar\omega) = \frac{n_r}{c} b \hbar\omega g(\hbar\omega) N (f_1 - f_2) \quad (19.9)$$

We can now find the spontaneous emission rate using $-\frac{dn_2}{dt} = aNf_2(1 - f_1)$ and substituting for a using eq. 19.7 and substituting for b in terms of α using eq. 19.9. Since we consider events within a narrow energy range of width $d(\hbar\omega)$ the most useful quantity is the spontaneous emission rate per unit volume per unit photon energy, $r_{sp}(\hbar\omega)$. r_{sp} is obtained by weighting the expression for $\frac{dn_2}{dt}$ by $g(\hbar\omega)$, i.e. $r_{sp} = ag(\hbar\omega)Nf_2(1 - f_1)$:

$$r_{sp} = \frac{n_r^2}{\pi^2 c^2} \frac{\alpha(\hbar\omega)\omega^2}{\hbar} \frac{f_2(1 - f_1)}{f_1 - f_2} \quad (19.10)$$

The final factor simplifies, using the definitions of the quasi-Fermi levels and $\Delta\mu = E_{F2} - E_{F1}$ to give

$$\frac{f_2(1 - f_1)}{f_1 - f_2} = \frac{1}{e^{\frac{E_2 - E_1 - \Delta\mu}{k_B T}} - 1}. \quad (19.11)$$

Thence, letting $E_2 - E_1 = \hbar\omega$, we obtain the spectral emission rate in all directions

$$r_{sp} = \frac{n_r^2}{\pi^2 c^2 \hbar^3} \frac{\alpha(\hbar\omega)(\hbar\omega)^2}{e^{\frac{\hbar\omega - \Delta\mu}{k_B T}} - 1} \quad (19.12)$$

To find the spectral spontaneous emission rate through a planar surface we have to resolve the isotropic expression along one (say, the z) direction (Problem 7.5). This yields the directional emission rate

$$r_{sp}(\hbar\omega) = \frac{n_r^2}{4\pi^2\hbar^3 c^2} \frac{\alpha(\hbar\omega)(\hbar\omega)^2}{e^{(\hbar\omega - \Delta\mu)/kT} - 1} \quad (19.13)$$

At thermal equilibrium $\Delta\mu = 0$ and the final factor becomes the spectral photon flux density emitted from a black body at temperature T . In most situations $\hbar\omega - \Delta\mu \gg kT$ and we can write

$$r_{sp}(\hbar\omega) = \frac{n_r^2}{4\pi^2\hbar^3 c^2} \alpha(\hbar\omega)(\hbar\omega)^2 e^{-\hbar\omega/kT} e^{\Delta\mu/kT} \quad (19.14)$$

19.2 Spontaneous emission from a direct gap semiconductor

The expression for r_{sp} can be applied to any material with continuous densities of electronic states and a corresponding absorption spectrum $\alpha(\hbar\omega)$, such as the direct band gap semiconductor that we considered in Lecture 18. The requirement for Equation 18.18 to be valid is that all of the electrons in the conduction band should behave as though they share the same quasi-Fermi level E_{Fc} and all the electrons (and holes) in the valence band behave as though they share the same quasi-Fermi level E_{Fv} where $\Delta\mu = E_{Fc} - E_{Fv}$. This will be valid for semiconductors that are in quasi-thermal equilibrium with their surroundings. That means that the electrons within each band have exchanged energy with each other and the lattice by scattering and have thermally relaxed. Such relaxation would normally occur on the time scale of tens of femtoseconds, which is much faster than the rate of electron relaxation between the bands by spontaneous emission. A semiconductor can be maintained in a constant state of quasi thermal equilibrium by means of steady-state optical excitation or a steady-state electrical bias in a semiconductor device.

We can make some remarks about our expression for r_{sp} (Eqn.19.14):

- $r_{sp} \propto \alpha$. Strong absorption leads to strong spontaneous emission; weak absorption leads to weak emission. Both processes are controlled by the same transition dipole matrix element.
- The photon energy dependence of the spectrum is strongly biased by the term $e^{-\hbar\omega/kT}$, so emission is strongest from the lowest allowed transitions.
- The emission rate, and therefore the overall intensity of the emission increases exponentially with $e^{\Delta\mu/kT}$. This reflects the enhanced emission when the population of electrons in E_2 or holes in E_1 is increased.
- $r_{sp} \propto n_r^2$. Forward emission is stronger into a medium of higher refractive index.

In the case of a direct gap semiconductor as studied in Lecture 18, r_{sp} is non zero for $\hbar\omega > E_g$ and

$$\begin{aligned} r_{sp}(\hbar\omega) &\propto n_r d_{cv}^2 \sqrt{\hbar\omega - E_g} (\hbar\omega)^3 e^{-\hbar\omega/kT} e^{\Delta\mu/kT} && \text{for } \hbar\omega > E_g \\ r_{sp}(\hbar\omega) &= 0 && \text{otherwise} \end{aligned} \quad (19.15)$$

The shape of the spectrum in eqn. 19.15 is dominated by the square root term, which switches on the emission at $\hbar\omega = E_g$ and the exponential which strongly reduces the emission at higher photon energies. Comparing the shape of absorption and emission spectra, we can see that the emission is strong only for photon energies within $\sim kT$ of the band gap. The colour of the emitted light is therefore determined by the band gap.

In the case of a material such as an imperfect crystal where there are isolated, defect states lying within the band gap, then if transitions between that defect level and the conduction or valence bands are optically allowed, the luminescence spectrum will contain emission corresponding to that transition. Because lower photon energies are less strongly suppressed by the exponential in eqn 19.15, the defect emission may dominate the spectrum, even if the density of defects is too low for it to be visible in the absorption spectrum. This means that luminescence can be a useful way to monitor the electronic quality of a material.

19.3 Photoluminescence and electroluminescence

Spontaneous emission will occur only weakly for the semiconductor at equilibrium. To make spontaneous emission visible, we need to increase $\Delta\mu$ by applying an optical or electrical bias.

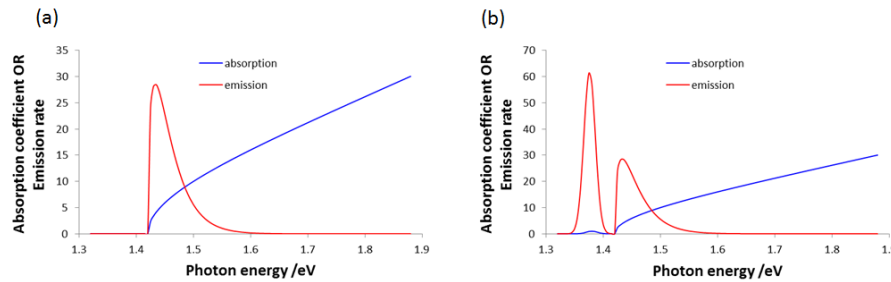


Figure 19.1: (a) Absorption coefficient and spontaneous emission spectrum from an ideal direct band-gap semiconductor (b) As for (a) with a defect centred at 0.04 eV below the band gap.

In photoluminescence, the material is illuminated with light of energy larger than the band gap and emitted photons with energy close to E_g are detected. The intensity of this emitted light is increased by increasing the intensity of the applied bias light. The bias light generates electron hole pairs, the photo-generated electrons and holes relax to the conduction and valence band edges, respectively, and form populations that are larger than the equilibrium populations of the material. The electron and hole populations under bias are related to the respective quasi-Fermi levels by $n = N_c \exp(-(E_c - E_{Fc})/kT)$ and $p = N_v \exp(-(E_{Fv} - E_v)/kT)$ where N_c and N_v are the conduction and valence band effective densities of states that you met in second year solid state physics. You can see that since $\Delta\mu = E_{Fc} - E_{Fv}$ the last factor in eqn. 19.15 is proportional to np . So the emission intensity increases like the product of electron and hole densities. Strictly, we should subtract the emission in equilibrium, so the net emission under bias is proportional to $(\exp(\Delta\mu/kT) - 1)$ or to $(np - n_0p_0)$ where n_0, p_0 are the electron and hole densities in the semiconductor at equilibrium.

Whilst the emission spectrum per unit volume can be determined in terms of material parameters and $\Delta\mu$, by integrating eqn. 19.15 over photon energies, we cannot define a unique *lifetime* for the spontaneous emission. The radiative lifetime and the form of the kinetics depend on whether and how strongly the material is doped (Problem 7.5). The lifetime also depends on competing, non-radiative processes that allow electrons to relax back to the valence band without emitting photons.

The second way to increase $\Delta\mu$ is by applying an electrical bias, to induce electroluminescence. The quasi-Fermi levels of the electrons and holes can be separated by building the semiconductor into a diode structure such as a $p-n$ or $p-i-n$ junction, and then applying an electrical bias V between the p and n terminals. For good electrical contacts and a semiconductor of good electronic quality the quasi-Fermi level separation is given by $\Delta E_F = eV$. When the p contact is made positive relative to the n contact, $\Delta\mu$ is raised, the populations of electrons and holes are both amplified and the spontaneous emission rate increases. This is the working principle of a light emitting diode. To a first approximation the emission spectrum does not change, only the intensity. This is explained by the fact that the amplification factor in eq.19.14 is separate from the energy dependent factors.

19.4 Main points of the lecture

- The rate of spontaneous emission can be obtained by considering a detailed balance between the rates of absorption and emission in a two level system.
- In a direct gap semiconductor, the emission spectrum is proportional to the product of the absorption spectrum a term of the form $(\hbar\omega)^2 \exp(-\hbar\omega/kT)$. The exponential strongly selects transitions of lowest energy, close to the band gap.
- The intensity of emission increases exponentially with the separation between the quasi-Fermi levels of the electron and hole, and linearly with the product of electron and hole densities.
- Spontaneous emission results from illuminating a semiconductor with light of energy $> E_g$ (in photoluminescence) and from injecting of charge pairs into a light emitting diode (in electroluminescence).

Light and Matter: Lecture 20

Low dimensional structures

Until now we have dealt with solids which are three dimensional crystalline materials. When we calculate the absorption coefficient for interband transitions we take into account the dispersion relation between the wavevector and energy of the states, to find the joint density of states. If we consider a periodic system that is confined to 2, 1 or 0 dimensions then the density of \mathbf{k} states is different and that leads to a different form for the absorption and emission spectra. In low dimensional semiconductor structures, the features of a 2D, 1D or 0D density of states can be observed using thin layers, or wires, or particles of one semiconductor embedded within another semiconductor of different band structure. In addition, the energies of optical transitions in the low dimensional structure can be controlled by controlling the size of the structure.

20.1 Density of states and joint density of states in 2D and 1D

Recall from Lecture 18 that in order to find the optical transition rate, and hence the absorption coefficient for interband transitions in semiconductors using Fermi's Golden Rule that we needed to find the density of pairs of states of the same \mathbf{k} whose energies differ by the photon energy $E = \hbar\omega$, i.e. we needed to find the density of states that satisfy $\hbar\omega = E_c(\mathbf{k}) - E_v(\mathbf{k})$. In the nearly free electron theory, $\hbar\omega$ is related to \mathbf{k} through:

$$\hbar\omega = E_c(0) + \frac{\hbar^2 \mathbf{k}^2}{2m_e^*} - E_v(0) + \frac{\hbar^2 \mathbf{k}^2}{2m_h^*} = E_g + \frac{\hbar^2 \mathbf{k}^2}{2\mu^*} \quad (20.1)$$

where μ^* is the reduced effective mass of the electron and hole in the semiconductor and we have assumed isotropic, parabolic bands. The dependence of photon energy on \mathbf{k} means that the JDOS for photon energy $\hbar\omega = E$ can be mapped directly on to the density of states in \mathbf{k} -space, $\rho(E)dE = 2g(k)dk$, whence

$$\rho(E) = \frac{2g(k)}{\frac{dE}{dk}} \quad (20.2)$$

where the factor 2 allows for spin degeneracy. Substituting for $\frac{dE}{dk}$ from Equation 20.1 with $E = \hbar\omega$ we have

$$\rho(E) = \frac{2\mu^*}{\hbar^2} \frac{g(k)}{k} \quad (20.3)$$

The above steps apply irrespective of the dimension of the periodic medium. In a uniform medium the density of \mathbf{k} states is isotropic. However the form of the density of states in \mathbf{k} space depends on the dimensionality of the space. In three dimensions, the density of states per unit volume, g_{3D} is given by

$$g_{3D}(k)dk = \frac{1}{(2\pi)^3} 4\pi k^2 dk \quad (20.4)$$

from which we found in Lecture 18 that

$$g_{3D}(\hbar\omega) = \frac{1}{2\pi^2} \left(\frac{2\mu^*}{\hbar^2} \right)^{3/2} (\hbar\omega - E_g)^{1/2} \quad (20.5)$$

We can use a similar procedure to find the JDOS in lower dimensions (Problem 7.2). You should find that in two dimensions $\rho(\hbar\omega)$ has the form of a step:

$$\rho_{2D}(\hbar\omega) = \frac{\mu^*}{\pi\hbar^2} \Theta(\hbar\omega - E_g) \quad (20.6)$$

where $\Theta(E)$ is the Heaviside function, defined so that $\Theta(E) = 1$ when $E > 0$ and $\Theta(E) = 0$ otherwise. In one dimension,

$$\rho_{1D}(\hbar\omega) = 2 \left(\frac{2\mu^*}{\hbar^2} \right)^{1/2} (\hbar\omega - E_g)^{-1/2} \quad (20.7)$$

The singularity at $\hbar\omega = E_g$ in $\rho_{1D}(\hbar\omega)$ is known as a Van Hove singularity. Since the absorption coefficient is proportional to $\omega\rho(\hbar\omega)$ the shape of the optical absorption spectrum will depend strongly on the dimensionality of the system. The forms of the JDOS in different dimensions reflect the form of the electron density of states in those systems.

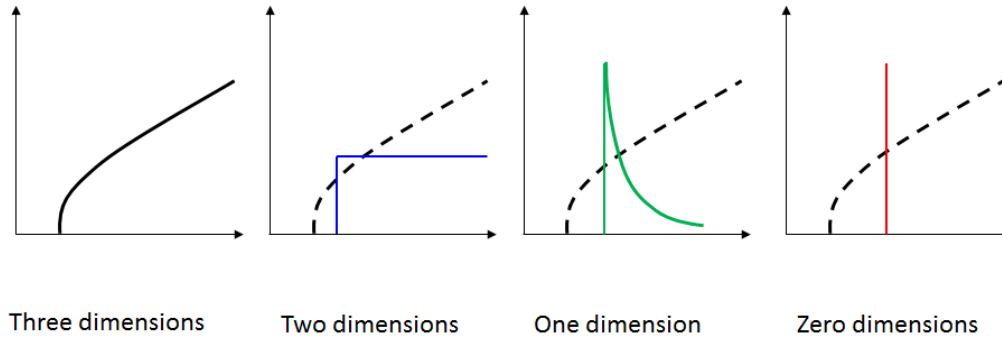


Figure 20.1: Form of the density of states as a function of energy for structures in three, two, one and zero dimensions. The dashed line indicates the density of states of the three dimensional structure of equivalent material parameters.

We haven't yet considered the special case of zero dimensions. In 0D, no propagating states can exist and so the wavefunction cannot have Bloch form. In these cases, the energy level spectrum consists of discrete states and optical transitions can occur between pairs of states which have different parity and are dipole allowed, just as in the case of an atom. The interband JDOS linking the 'valence' and 'conduction' states would be a single delta function.

How are low dimensional solids relevant to us? Some periodic materials do exist in reduced dimensions, because they form layers or wires of atomic width. An important example in 2D is graphene. In 1D, polymers and carbon nanotubes have been studied as examples of periodic systems. The different types of JDOS corresponding to different dimensions is also useful for classifying features seen in the optical spectra of real solids. The model we used for the 3D case was for an ideal isotropic system with parabolic bands. In practice band structure is much more complex and may feature regions where the valence and conduction bands are parallel, leading to peaks in the JDOS where $\frac{dE}{dk}$ is close to zero, as well as peaks near band extrema. These features in the optical spectra are sometimes called critical points.

The physics of low dimensional structures is also relevant for understanding and designing semiconductor heterostructures where very thin layers of different crystalline semiconductors can be grown on top of each other, and semiconductor nanostructures where crystals of very small dimensions, such as nanoparticles and nanorods, are grown.

20.2 Quantum confinement and semiconductor heterostructures

The optical and electronic properties of a crystalline solid are not normally dependent on the size of the crystal. Normally, electronic states are determined by the electronic structure of the component atoms and their arrangement within the crystal, which will determine the rapidly varying parts of the wavefunction. When the crystal becomes small enough the electronic states are also influenced by the crystal size, due to the confinement of the electronic states within a small volume. We can estimate the size at which this occurs.

According to the uncertainty principle, $|\Delta p| > \frac{\hbar}{2|\Delta x|}$. The electron's energy relates to momentum via $E = \frac{p^2}{2m_0}$ so the uncertainty in energy due to confinement in one dimension within a length Δx is of order $\Delta E = \frac{\hbar^2}{2m_0\Delta x^2}$. Such an effect will be relevant and visible when ΔE is comparable to or larger than the thermal energy $\frac{1}{2}k_B T$, so when $\Delta x < \frac{\hbar}{\sqrt{m_0 k_B T}}$ where k_B is Boltzmann's constant. At room temperature, for electrons in free space, that means $\Delta x < 5$ nm. Inside a semiconductor in the nearly free electron approximation we use the effective mass m^* , which leads to quantum confinement at larger Δx for some common materials where $m^* < m_0$. As we shall see below, the confinement of electronic energy levels by using small structures leads to enhancement of the optical gap above the value of the bulk material, and importantly, the ability to tune

the optical gap by varying the size of the structure. The optical properties will also depend on the number of dimensions in which the electrons are confined.

Semiconductor nanostructures can be grown by the direct growth of nanocrystals or nanorods using chemical processes, or by the epitaxial growth of layered structures (quantum wells), linear structures (quantum well wires) or islands (quantum dots). In epitaxial growth methods, a semiconductor of lower band gap is grown atomic layer by atomic layer on top of a crystalline layer of a wider band gap semiconductor such that the two semiconductors share the same crystal structure and growth axis. An important consequence of this is that if the two semiconductors are similar enough that the periodic parts of their Bloch wavefunctions are the same, then a nearly free electron model can be applied to electronic states *across* the interface between the materials. Only the parameters that determine the electron or hole energy and wavevector, i.e. the band edge energy and effective mass, change across the interface. Such ideal interfaces can be grown for some combinations of compound semiconductors such as GaAs with the ternary compound semiconductor $\text{Al}_x\text{Ga}_{1-x}\text{As}$. (Here x represents the fraction of Ga atoms that have been replaced by Al atoms in the material.)

20.3 Electronic states of a semiconductor quantum well

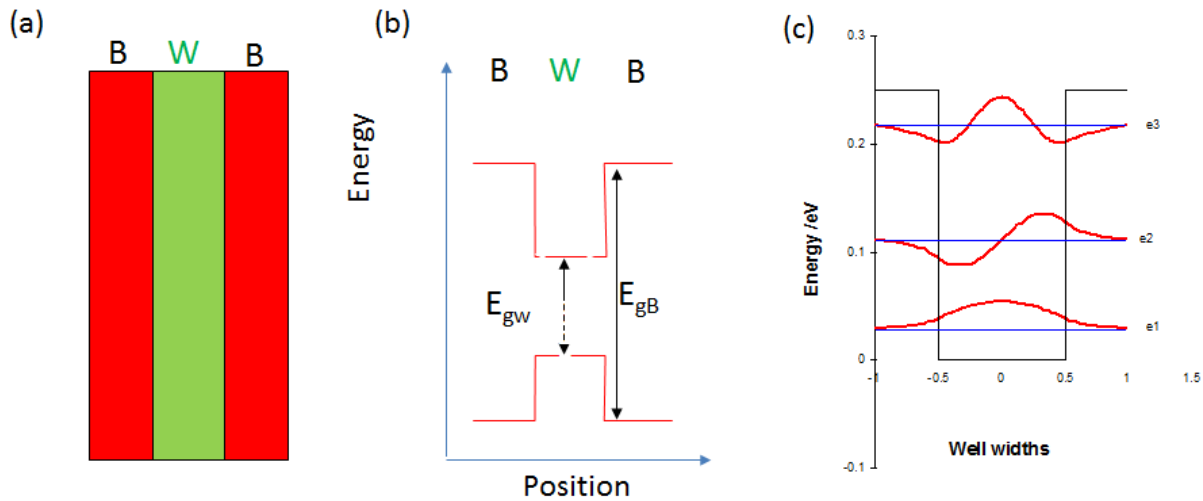


Figure 20.2: (a) Layer structure of a Quantum well (QW). (b) Energy profiles of the conduction and valence bands of a QW. (c) Calculated envelope functions in the conduction band of a QW.

In second year Solid State you used the nearly free electron model to develop the Bloch wavefunctions for electrons in a crystalline solid. The Bloch wavefunction is the product of a rapidly varying, periodic part and a plane wave. Close to band extrema, the energy of the electron is given by $E(0) + \frac{\hbar^2 \mathbf{k}^2}{2m^*}$ where m^* is the effective mass. Thus it behaves like a free electron with a plane wave wavefunction but with a different electron mass, m_0 is replaced by m^* . We can write the electron wavefunction in the conduction band as

$$\Psi_c(\mathbf{r}) = u_c(\mathbf{r})F_c(\mathbf{r}) \quad (20.8)$$

where $F(\mathbf{r})$ is called the envelope function and in the case of a Bloch electron in a 3D crystal it has the form $e^{i\mathbf{k}\cdot\mathbf{r}}$. It can be shown that the envelope function obeys a differential equation that is very similar to the time independent Schrodinger equation which we call the effective mass equation (EME). For electron states in the conduction band the EME has the form

$$\left[-\frac{\hbar^2}{2m_0} \left(\nabla \cdot \frac{m_0}{m_{ij}} \nabla \right) + V_c(\mathbf{r}) \right] F_c(\mathbf{r}) = (E_c - E_c(0))F_c(\mathbf{r}) \quad (20.9)$$

where m_{ij} is the effective mass tensor, $V_c(\mathbf{r})$ is the position of the conduction minimum as a function of position and $E_c(0)$ the electronic energy at the band minimum, assumed here to be at $\mathbf{k} = 0$. In the case of an isotropic

medium where the effective mass is independent of position and orientation

$$\left[-\frac{\hbar^2 \nabla^2}{2m_e^*} + V_c(\mathbf{r}) \right] F_c(\mathbf{r}) = (E_c - E_c(0)) F_c(\mathbf{r}) \quad (20.10)$$

If we have a uniform, infinite medium $V_c(\mathbf{r}) = 0$ everywhere and $F(\mathbf{r})$ has the form $e^{i\mathbf{k}\cdot\mathbf{r}}$. Now suppose we have a layered structure where there is a region made from a material with a lower V_c lying between two regions with higher V_c ,

$$\begin{aligned} V_c(z) &= 0 & -\frac{L}{2} < z < \frac{L}{2} \\ V_c(z) &= V_0 & |z| \geq \frac{L}{2} \end{aligned} \quad (20.11)$$

This would be the case, for example, for a layer of GaAs between two layers of $\text{Al}_x\text{Ga}_{1-x}\text{As}$. Now $F(\mathbf{r})$ will have different form for the (x, y) and z dependences. We can write $F(\mathbf{r})$ as a product

$$F(\mathbf{r}) = f(z)h(x, y) \quad (20.12)$$

and the EME becomes

$$\left[-\frac{\hbar^2}{2m_e^*} \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} \right) - \frac{\hbar^2}{2m_e^*} \frac{d^2}{dz^2} + V_c(z) \right] f(z)h(x, y) = (E_c - E_c(0))f(z)h(x, y) \quad (20.13)$$

This can be separated into two parts

$$-\frac{\hbar^2}{2m_e^*} \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} \right) h(x, y) = E_{||} h(x, y) \quad (20.14)$$

and

$$\left[-\frac{\hbar^2}{2m_e^*} \frac{d^2}{dz^2} + V_c(z) \right] f(z) = \epsilon_n f(z) \quad (20.15)$$

where the energies satisfy

$$E_c = E_c(0) + \epsilon_n + E_{||} \quad (20.16)$$

The differential equation in x and y has a plane wave solution of the form

$$h(x, y) = e^{i\mathbf{k}_{||}\cdot\mathbf{r}_{||}} \quad (20.17)$$

Where $r_{||} = \sqrt{x^2 + y^2}$ and $\mathbf{k}_{||}$ is the wavevector in the (x, y) plane. The differential equation in z is an eigenvalue equation with discrete solutions for $\epsilon_n < V_0$. Let's first consider the special case when V_0 is infinite. Then the problem of finding the ϵ_n is the familiar 'particle in a box' problem from quantum mechanics. The z part of the envelope function, $f(z)$, has the form

$$\begin{aligned} f(z) &= A_n \cos(k_n z) & \text{for } n = 1, 3, 5 \dots & & \text{for } -\frac{L}{2} \leq z \leq \frac{L}{2} \\ f(z) &= A_n \sin(k_n z) & \text{for } n = 2, 4, 6 \dots & & \text{for } -\frac{L}{2} \leq z \leq \frac{L}{2} \\ f(z) &= 0 & & & \text{for } |z| > \frac{L}{2} \end{aligned} \quad (20.18)$$

where k_n is quantized through the boundary condition that $f(z) = 0$ at $z = \pm \frac{L}{2}$ such that $k_n = n\frac{\pi}{L}$. Then

$$\epsilon_n = \frac{\hbar^2 \pi^2 n^2}{2m_e^* L^2} \quad (20.19)$$

When V_0 is finite we cannot determine the ϵ_n analytically. In this case, $f(z)$ has the same form as in Equations 20.18 above, but no longer vanishes at $z = \pm \frac{L}{2}$ and the condition on k_n no longer applies. Now the wavefunction is finite but exponentially decaying in the barrier regions where $|z| > \frac{L}{2}$ and $\epsilon_n < V_0$. We can find a transcendental equation for k_n by matching the wavefunction at the barriers; you have studied this problem in second year QM.

The $f(z)$ envelope functions for the finite well have the following properties:

- They are always even or odd
- The probability density $|f(z)|^2$ is non zero in the barrier region
- The lowest eigenstate always lies above the bottom of the well ($\epsilon_n > 0$). This is an example for zero point energy resulting from quantum confinement.
- A limited number of states, but at least one, is confined in the well
- The energies ϵ_n for the finite well are always lower than those of the infinite well.

Finally we can express the form of the electron wavefunction in terms of the bound and propagating parts of the envelope function and the periodic function $u(\mathbf{r})$ appropriate for the band (e.g., c or v),

$$\psi(\mathbf{r}) = u_c(\mathbf{r})e^{i\mathbf{k}_{||}\cdot\mathbf{r}_{||}}f(z) \quad (20.20)$$

For systems that are confined in two or three dimensions a similar analysis can be followed. For the quantum wire the envelope function is the product of a plane wave in one dimension and a function that is confined in two dimensions, while for the nanoparticle or quantum dot there is no plane wave part, and the solutions are eigenstates of a three dimensional ‘particle in a box’ type of problem but for a box with finite barriers.

20.4 Main points of the lecture

- The form of the density of electron and hole states in \mathbf{k} space depends on the dimension of the space. This also influences the form of the joint density of states at photon energies close to the band gap. In two dimensions, the JDOS is a step function and in 1D it has a singularity at the band edge.
- Electronic states in structures of small linear dimension are quantised in the confinement direction. For semiconductors, significant changes in electron energies are achieved for sizes ($< \sim 10$ nm).
- The electronic states of quasi-two dimensional system (a ‘quantum well’) can be described by a plane wave component in the x and y directions and a bound function in the z direction. The energies and wavefunctions for the z component are those of a finite square well.
- Conduction band energies are shifted up and valence band energies are shifted down through quantum confinement, by an amount that depends on the thickness of the well. This means that the ‘band gap’ of the semiconductor is raised relative to that of the same semiconductor in the bulk.

Light and Matter: Lecture 21

Optical properties of quantum wells

We have seen that the form of the density of electronic states depends upon the dimensionality of the system, and that low dimensional semiconductor structures with linear dimensions of 1-10 nm can be made. In this lecture we will see how the features of the low dimensional structures control the optical properties, and how they are used in practice. We will focus on the case of the quantum well, where a thin layer of semiconductor is embedded within another material of larger band gap. Chapter 6, sections 6.1 to 6.4 of Fox's book are relevant to this lecture.

21.1 Density of states of quantum wells, wires and dots

We can now construct the band structure for the quantum well. Considering a QW in the conduction band, the electron energies satisfy

$$E_c(\mathbf{k}_{||}, j) = E_c(0) + \epsilon_{c,j} + \frac{\hbar^2 \mathbf{k}_{||}^2}{2m_e^*} \quad (21.1)$$

where j is the index of the state confined in the z direction and $\mathbf{k}_{||,c}$ is the wavevector in the (x, y) plane. The electron's energy is raised above the conduction band minimum by two effects, (i) confinement in the z direction and (ii) by its kinetic energy in the (x, y) plane. The graph of energy against $\mathbf{k}_{||}$ is a set of parabolic bands, or mini-bands, each of which has a minimum at $E_c(0) + \epsilon_{c,j}$. To find the density of electronic states for each mini-band, remember that $\mathbf{k}_{||}$ is continuous only in the x and y directions, so the density of states in $\mathbf{k}_{||}$ space is two-dimensional. Each of the mini-bands corresponding to different $\epsilon_{c,j}$ contributes a two dimensional (step-function) term to the density of states, turning on at the energy $E_c(0) + \epsilon_{c,j}$. So the density of electronic states $g(E)$ has the form of a staircase,

$$g_c(E) = \frac{m_e^*}{\pi \hbar^2 L} \sum_j \Theta(E - E_c(0) - \epsilon_{c,j}) \quad (21.2)$$

where the Heaviside function has $\Theta(E) = 1$ for $E > 0$ and $\Theta(E) = 0$ elsewhere. The factor $\frac{1}{L}$, where L is the width of the quantum well, is required to obtain a density of states per unit volume, rather than per unit area as for a pure 2D system.

For hole states in the valence band,

$$E_v(\mathbf{k}_{||}, l) = E_v(0) - \epsilon_{v,l} - \frac{\hbar^2 \mathbf{k}_{||}^2}{2m_h^*} \quad (21.3)$$

and the corresponding density of hole states is

$$g_v(E) = \frac{m_h^*}{\pi \hbar^2 L} \sum_l \Theta(E - E_v(0) + \epsilon_{v,l}). \quad (21.4)$$

In the case of a quantum wire (quasi-1D system), the analysis is exactly the same as for the quantum well except that, because the potential $V_c(\mathbf{r})$ is confined in two dimensions, the resulting envelope function $F(\mathbf{r})$ is the product of an exponential term in one dimension $e^{ik_x x}$ and a set of discrete levels due to confinement in the y and z directions. The density of states is then a sequence of one-dimensional DoS functions at different energies. In the case of a quantum dot the envelope function has no propagating part and the density of states is a sequence of delta functions corresponding to the different confined states.

21.2 Selection rules for optical transitions in a quantum well

Recall from Lecture 17 that the optical absorption coefficient for transitions between states 1 and 2 has the form

$$\alpha_{12}(\hbar\omega) = A\omega d_{12}^2 \delta(\hbar\omega - E_2 + E_1) g_1 g_2 (f_1 - f_2) \quad (21.5)$$

where the transition dipole matrix element is $d_{12} = e \langle 2 | \mathbf{r} \cdot \mathbf{e}_0 | 1 \rangle$ and A is a constant for the material. In order to find $\alpha(\hbar\omega)$ for a transition between two mini-bands in a quantum well (QW) we will need to find the transition dipole matrix element linking initial and final states. In the last lecture we found that the electron wavefunction has the form $\psi(\mathbf{r}) = u_c(\mathbf{r}) e^{i\mathbf{k}_{||} \cdot \mathbf{r}_{||}} f(z)$. In order to distinguish electron and hole states we can write the wavefunction of the electron in the conduction band as

$$\psi_e(\mathbf{r}, \mathbf{k}_{||,c}, j) = u_c(\mathbf{r}) e^{i\mathbf{k}_{||,c} \cdot \mathbf{r}_{||}} f_{c,j}(z) \quad (21.6)$$

where the indices c, j refer to the j^{th} miniband of the conduction band, and the wavefunction of the hole in the valence band as

$$\psi_h(\mathbf{r}, \mathbf{k}_{||,v}, l) = u_v(\mathbf{r}) e^{i\mathbf{k}_{||,v} \cdot \mathbf{r}_{||}} f_{v,l}(z) \quad (21.7)$$

where the indices v, l refers to the l^{th} miniband of the valence band.

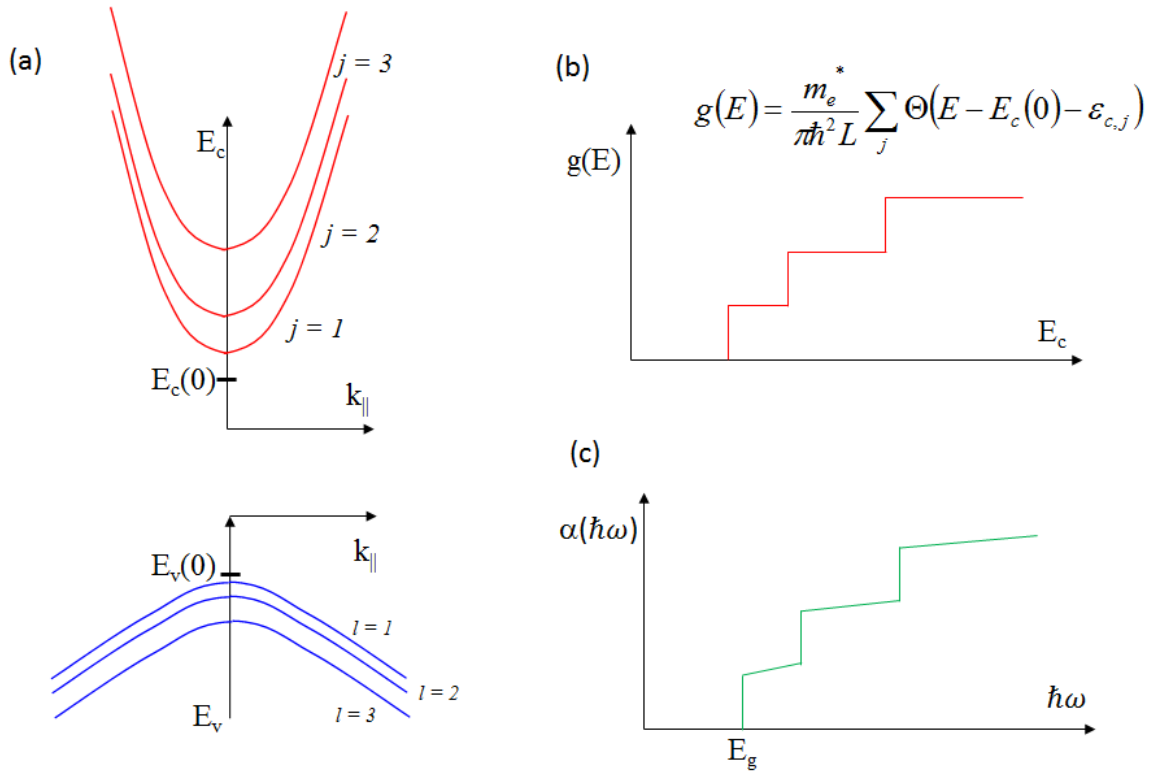


Figure 21.1: (a) Band structure of a Quantum well showing the energy of minibands in the conduction band and valence band as a function of in-plane wavevector $k_{||}$. (b) Density of states for electrons in the conduction band of the QW. (c) Schematic absorption spectrum, showing only the contributions from miniband to miniband transitions.

Let's consider a transition from state $\psi_h(\mathbf{r}, \mathbf{k}_{||,v}, l)$ to state $\psi_e(\mathbf{r}, \mathbf{k}_{||,c}, j)$. The dipole matrix element that controls this transition is given by

$$d_{cjl} = e \int u_c^*(\mathbf{r}) e^{-i\mathbf{k}_{||,c} \cdot \mathbf{r}_{||}} f_{c,j}(z) \mathbf{r} \cdot \mathbf{e}_0 u_v(\mathbf{r}) e^{i\mathbf{k}_{||,v} \cdot \mathbf{r}_{||}} f_{v,l}(z) dV \quad (21.8)$$

In contrast to the case for an isotropic bulk semiconductor, the value of the transition dipole matrix element now depends on the direction of polarisation of the electric field, \mathbf{e}_0 , relative to the growth (z) direction of

the QW. The integral can be simplified as described in the Appendix to this lecture. You are not going to be examined on this!

The analysis shows that different selection rules apply for transitions between mini-bands in the conduction and valence bands (*inter-band* transitions) and those between mini-bands that are both in the conduction or the valence band (*intra-band* transitions). Let's consider the two cases separately.

Interband transitions ($v \rightarrow c$) If the light is incident normally on the QW the field will be polarised in the plane of the QW (e.g. $\mathbf{r} \cdot \mathbf{e}_0 = x$) and the transition dipole matrix element can be expressed as

$$d_{cjl} = d_{cv} M_{jl} \quad (21.9)$$

where d_{cv} is the interband transition dipole matrix element of the bulk material, and we define the overlap integral of envelope functions M_{jl} as

$$M_{jl} = \int f_{c,j}(z) f_{v,l}(z) dz \quad (21.10)$$

The overall transition dipole matrix element is now clearly proportional to the overlap of the envelope functions for the initial and final states in the confinement (z) direction. Since the $f(z)$ are either even or odd, this overlap integral is non-zero only when the two functions are both even or both odd. Moreover, it will be large only when $l = j$. For transitions where $j \neq l$ but the functions have the same parity, then the function will be non-zero but small in the case of wells of different depth or where electron and hole have different effective mass. These weak transitions are often neglected.

Intraband transitions ($\nu \rightarrow \nu$ or $c \rightarrow c$) For optical transitions between different mini-bands in the same principal (conduction or valence) band of a QW structure, the dipole matrix element d_{cjl} vanishes unless $\mathbf{r} \cdot \mathbf{e}_0 = z$, i.e. \mathbf{e}_0 is perpendicular to the plane of the QW. That corresponds to light incident *in the plane of* the QW. This type of transition also requires that $f_l(z)$ and $f_j(z)$ have opposite parity. Since QW heterostructures are thin layered structures it is difficult to couple light in to the structure so that it has a significant component of \mathbf{e}_0 in the z direction. A second issue is that for strong optical transitions we need the two levels to have very different occupation, which may require the material to be doped. Nevertheless, these structures are used in order to absorb and emit light of wavelengths in the mid infrared region, something which is hard to do with other semiconductor materials.

To summarise the selection rules for optical transitions in a QW:

- Only vertical transitions ($\Delta \mathbf{k}_{||} = 0$) are allowed.
- For interband transitions, transitions are allowed for light polarised in the plane of the QW (normal incidence). Only transitions between mini-bands of the same quantum number are strong.
- For intraband transitions, transitions are allowed only for light polarised normal to the plane of the QW (lateral incidence).

21.3 Absorption coefficient for interband transitions in a QW

Once we apply the selection rule that transitions have $\Delta \mathbf{k}_{||} = 0$ we can write the transition energy in terms of $\mathbf{k}_{||}$. Let's consider transitions between the l^{th} valence miniband and the j^{th} conduction miniband. Substituting for $E_v(\mathbf{k}_{||}, l)$ and $E_c(\mathbf{k}_{||}, j)$ from eqns. 21.3 and 21.1 we have

$$\hbar\omega = E_c(\mathbf{k}_{||}, j) - E_v(\mathbf{k}_{||}, l) = E_g + \epsilon_{c,j} + \epsilon_{v,l} + \frac{\hbar^2 \mathbf{k}_{||}^2}{2\mu^*} \quad (21.11)$$

where we use $E_g = E_c(0) - E_v(0)$. Assuming that the valence subband is filled ($f_v = 1$) and the conduction subband is empty ($f_c = 0$) and using the fact that both levels have degeneracy equal to 1 per spin state the absorption coefficient becomes

$$\alpha_{cjl}(\hbar\omega) = A d_{cv}^2 M_{jl}^2 \omega \delta(\hbar\omega - E_g - \epsilon_{c,j} - \epsilon_{v,l} - \frac{\hbar^2 \mathbf{k}_{||}^2}{2\mu^*}) \quad (21.12)$$

As before we convert the density of initial and final states in $\mathbf{k}_{||}$ space into a joint density of states in energy where $E = \hbar\omega$:

$$\rho(E) dE = 2g(k_{||}) dk_{||} \quad (21.13)$$

But now the density of states has the quasi two dimensional form $\rho(\hbar\omega) = \frac{\mu^*}{\pi\hbar^2 L} \Theta(\hbar\omega - E_g - \epsilon_{c,j} - \epsilon_{v,l})$ which is similar to the form in Section 20.1 except that the factor $\frac{1}{L}$ is introduced to make it a density of states per unit volume rather than per area. This yields

$$\alpha_{cjl}(\hbar\omega) = A \frac{\mu^*}{\pi\hbar^2 L} d_{cv}^2 M_{jl}^2 \omega \Theta(\hbar\omega - E_g - \epsilon_{c,j} - \epsilon_{v,l}) \quad (21.14)$$

Which has the form of a step function turning on at $\hbar\omega = E_g + \epsilon_{c,j} + \epsilon_{v,l}$. Finally, to take into account the transitions between different subbands, and including only those with $j = l$ we have

$$\alpha_{cjl}(\hbar\omega) = A \frac{\mu^*}{\pi\hbar^2 L} d_{cv}^2 \sum_j M_{jj}^2 \Theta(\hbar\omega - E_g - \epsilon_{c,j} - \epsilon_{v,j}) \quad (21.15)$$

To explain observed spectra of QWs we need to address one more factor. In bulk semiconductors a type of state known as an *exciton* can exist, where the electron and hole are bound together through their mutual Coulomb attraction. Exciton states have a lower energy than E_g , they can be optically excited so long as the net wavevector is zero, appears as a sharp peak (or series of peaks) in the absorption spectrum at a certain energy, known as the binding energy, below the onset of bulk absorption. The exciton binding energy is determined by the average separation of the electron and hole. In a QW, excitons are more strongly bound because the electron and hole are now confined to the same restricted volume of space. As a consequence the exciton is more likely to be observed at room temperature in the QW than in a bulk semiconductor and so excitons are a more prominent feature of the optical spectra of good quality QWs. Since the lowest energy absorbing states are selected in luminescence, the excitonic states can also dominate the emission from QWs.

21.4 Applications of low dimensional semiconductor structures

The special optical properties of QWs have led to a number of practical applications of QW technology. First, the tuneability of the absorption edge and emission wavelength means that QW structures have been used to achieve LED and laser emission at wavelengths that could not be achieved with bulk semiconductors, usually because a good quality bulk semiconductor with the required band gap did not exist. This has been important for blue emitting LEDs which can be used to produce white light by pumping a phosphor, and have the advantage of relatively low power consumption. It has also been important for achieving optical communications, because InGaAsP based QW structures could be used to emit and modulate light in the infra-red at a wavelength (1.55 μm) where silica transmits with the least optical losses. This technology has been used for transatlantic data communications since the 1990s. QW structures made from GaAs/AlGaAs were also used in local e.g. ethernet data communications at IR wavelengths. QW lasers are used in data reading in DVD technology, and the advent of efficient blue LEDs allowed DVDs (operating at red/IR wavelengths) to be overtaken by blu-ray technology, which offers higher density data storage because of the shorter optical wavelength. Finally, QW laser structures can be grown in a vertical cavity surface emitting laser structure, which allows for very compact optical componentry. Quantum dot technology is less well developed, but QD structures are attractive for light emission because of the high absorption strength that comes from the confinement of the wavefunctions.

21.5 Main points of the lecture

- The optical spectra of QWs differ from those of the well material in the bulk in several respects:
 - The first optical transition occurs at a higher energy than the band gap, determined by the QW thickness. In the infinite well approximation the band gap increase is $\frac{\hbar^2 \pi^2}{2\mu^* L^2}$.
 - The absorption edge is a step function rather than a square root. This means that emission is sharper (narrower band width) and population inversion in lasers can be achieved more easily.
 - The absorption spectrum shows a characteristic staircase function.
- The tuneable emission wavelength means that particular colours (e.g. in LEDs and lasers) can be selected by tuning thickness, while the sharp absorption edge means that narrower emission bandwidth can be achieved. These properties have led to a wide range of practical applications of QW structures.

21.6 Appendix to Lecture 21: Evaluating the transition dipole matrix element for transitions in a quantum well

To simplify the integral 21.8,

- First we express the dipole matrix element in terms of the momentum operator: From Lecture 17, we had that $\langle 2|\hat{r}|1\rangle = \frac{1}{im_0\omega_{12}} \langle 2|\hat{p}|1\rangle$. Since $\hat{p} = i\hbar\nabla$ we can expand the integrand as a product, hence $\hat{p}(u(\mathbf{r})F(\mathbf{r})) = u(\mathbf{r})\hat{p}F(\mathbf{r}) + F(\mathbf{r})\hat{p}u(\mathbf{r})$ and an integral of the form $\int F_c(\mathbf{r})^* u_c^*(\mathbf{r}) \hat{p} F_v(\mathbf{r}) u_v(\mathbf{r}) dV$ breaks into two terms.
- Then we use the fact that $F(\mathbf{r})$ varies slowly over a unit cell compared to $u(\mathbf{r})$ to separate each term in into a product of two integrals, one concerning the $u(\mathbf{r})$ and taken over the unit cell and one concerning the envelope functions and taken over all space. Together these give

$$\begin{aligned} d_{cjl} &= \frac{e}{im_0\omega} \int F_{c,j}^*(\mathbf{r}) u_c^*(\mathbf{r}) \mathbf{p} \cdot \mathbf{e}_0 F_{v,l}(\mathbf{r}) u_v(\mathbf{r}) dV \\ &= \frac{e}{im_0\omega} \int_{\text{unit cell}} u_c^*(\mathbf{r}) u_v(\mathbf{r}) dV \int F_{c,j}^*(\mathbf{r}) \mathbf{p} \cdot \mathbf{e}_0 F_{v,l}(\mathbf{r}) dV + \frac{e}{im_0\omega} \int_{\text{unit cell}} u_c^*(\mathbf{r}) \mathbf{p} \cdot \mathbf{e}_0 u_v(\mathbf{r}) dV \int F_{c,j}(\mathbf{r}) F_{v,l}(\mathbf{r}) dV \end{aligned} \quad (21.16)$$

- Then we write the envelope function $F(\mathbf{r}) = e^{i\mathbf{k}_{||} \cdot \mathbf{r}_{||}} f(z)$. The integrals involving the $F(\mathbf{r})$ will be non-zero only when $\mathbf{k}'_{||} = \mathbf{k}_{||}$, so that the slowly varying exponential factors cancel. This is also required physically by the conservation of momentum in the plane of the QW. This leaves

$$\begin{aligned} d_{cjl} &= \left[e \int_{\text{unit cell}} u_c^*(\mathbf{r}) u_v(\mathbf{r}) dV \frac{1}{im_0\omega} \int f_{c,j}(z) \mathbf{p} \cdot \mathbf{e}_0 f_{v,l}(z) dz \right. \\ &\quad \left. + e \int_{\text{unit cell}} u_c^*(\mathbf{r}) \mathbf{r} \cdot \mathbf{e}_0 u_v(\mathbf{r}) dV \int f_{c,j}(z) f_{v,l}(z) dz \right] \delta_{\mathbf{k}_{||,c}, \mathbf{k}_{||,v}} \end{aligned} \quad (21.17)$$

This tells us that different selection rules apply for transitions between different bands (in particular, inter-band and intra-band) and for different polarisation of the light. Since the functions $u_i(\mathbf{r})$ are orthogonal to each other, the first term is zero for transitions between bands and the second term is normally zero for transitions within bands.

Now we can find the selection rules for optical transitions in a QW. We will consider separately the cases of interband transitions (from valence to conduction band) and intraband transitions (when an electron is excited, e.g., from one miniband to another within the conduction band).

Interband transitions ($v \rightarrow c$) If the light is incident normally on the QW the field will be polarised in the plane of the QW (e.g. $\mathbf{r} \cdot \mathbf{e}_0 = x$) and

$$d_{cjl} = e \int_{\text{unit cell}} u_c^*(\mathbf{r}) x u_v(\mathbf{r}) dV \int f_{c,j}(z) f_{v,l}(z) dz = d_{cv} M_{jl} \quad (21.18)$$

where we have substituted in the interband transition dipole matrix element of the bulk material, d_{cv} and have defined the overlap integral $M_{jl} = \int f_{c,j}(z) f_{v,l}(z) dz$.

The overall transition dipole matrix element is now clearly proportional to the overlap of the envelope functions for the initial and final states in the confinement (z) direction. Since the $f(z)$ are either even or odd, this overlap integral is non zero only when the two functions are both even or both odd. Moreover, it will be large only when $l = j$. For transitions where $j \neq l$ but the functions have the same parity, then the function will be zero in the case of wells of the same depth where electron and hole have the same effective mass, and non-zero but small, otherwise. These weak transitions are usually neglected.

Intraband transitions ($\nu \rightarrow \nu$ or $c \rightarrow c$) For optical transitions between different subbands in the same principal band (conduction or valence) of a QW structure, the second term in Equation 21.17 vanishes. The first term also vanishes unless $\mathbf{r} \cdot \mathbf{e}_0 = z$, i.e. \mathbf{e}_0 is perpendicular to plane of QW. That corresponds to light incident in the plane of the QW. Then, the integral containing the $f(z)$ will be non-zero only for $f(z)$ functions with opposite parity. Since QW heterostructures are thin layered structures it is difficult to couple light in to the structure so that it has a significant component of \mathbf{e}_0 in the z direction.

Light and Matter: Lecture 22

Optical properties of molecular electronic materials

22.1 Non-crystalline semiconductors

Until now we have considered crystalline semiconducting materials where the atomic structure is periodic in three (or, in the case of quantum heterostructures, in two or one) dimensions and the electronic states are delocalised in space and are characterised by a wavevector \mathbf{k} . Periodicity is not essential for a material to have semiconducting properties. Amorphous semiconductors, where there is a good degree of order in the local atomic arrangement but enough variation in bond angles and length for the material to lack long range crystalline order, can function well as semiconductors. A widely used example in thin film electronics is amorphous silicon. The properties of such materials are often limited by the presence of defects - isolated electronic states that are localised in space and may fall within the band gap. Such defects serve to reduce electronic conduction by trapping charges, and can dominate light emission. In an amorphous semiconductor the electronic states are not characterised by \mathbf{k} and the $\Delta\mathbf{k} = 0$ selection rule is relaxed. The JDOS is then built up from the product of the electron and hole densities of states in energy.

In this course, we are not going to deal with amorphous semiconductors in general, but we will focus in part of this lecture on one group of materials which is important because of their optical and material properties. These are organic semiconductors, sometimes called molecular electronic materials or pi-conjugated materials. In the solid state, they consist of carbon based molecules packed into a dense assembly - which may be amorphous or semicrystalline - in which the molecules interact weakly through van der Waals forces whilst the atoms within the molecules are bound by strong covalent bonds. The result is that the optical properties of the solid are dominated by the optical properties of the molecule, whilst the interactions between the molecules are strong enough for electric charge to 'hop' between them, making them semiconducting. Organic semiconductors are of great interest for applications for several reasons: the optical properties can be tuned by altering the chemical structure of the molecules; they can have strong luminescent efficiency; and, importantly, in many cases they can be made soluble in various solvents, so that the active layers can be processed cheaply from solution.

In this lecture, we will first introduce the concept of an exciton, which is relevant to the optical properties of both inorganic and organic semiconductors, and then look at the electronic structure, light absorption and emission by organic semiconductors. Sections 4.1 and 4.2 of Fox are relevant to the part on excitons and Sections 8.1 to 8.4 are relevant to the part on molecular materials.

22.2 Excitons

In Lectures 18-21 we considered the electron and hole independently. However, an electron and a hole that are located in the same region of a solid will interact through their mutual Coulombic potential. This allows them to form a coupled states called an *exciton*. In periodic systems the Coulomb interaction can be treated as a perturbation applied to the Bloch electron and hole eigenstates of the system. The resulting exciton states F are built up from products of electron and hole Bloch states $F = \psi_{c,\mathbf{k}_c} \psi_{v,\mathbf{k}_v}$ and have energies that are reduced relative to the unbound electron-hole pair energy by E_{ex} . For an exciton state to be stable, the group velocities of the electron and hole that make up the exciton must be the same. This means that the gradient of the electron and hole dispersion curves $\frac{\partial E}{\partial \mathbf{k}}$ must be equal, and for such a state to be excited optically we also require that electron and hole k values are equal. These two conditions are satisfied when $\mathbf{k} = 0$. So an exciton can be formed as a result of a direct transition at $\mathbf{k} = 0$. These type of excitons are known as Wannier excitons.

In an isotropic 3D system, the exciton binding energies E_{ex} and wavefunctions are the solutions to a Schrodinger-like equation of the form

$$-\frac{\hbar^2}{2\mu^*}\nabla_r^2 F - \frac{e^2}{4\pi\epsilon_r\epsilon_0 r}F = E_{ex}F \quad (22.1)$$

where μ^* is the reduced effective mass $(1/m_e^* + 1/m_h^*)^{-1}$ and ϵ_r is the real part of the relative dielectric constant of the medium. This problem is analogous to the hydrogen atom and has solutions for the energy of

$$E_{ex} = -\frac{\mu^*}{m_0\epsilon_r^2} \frac{Ry}{n^2} \quad (22.2)$$

where $n = 1, 2, 3, \dots$ and Ry is the Rydberg energy of 13.6 eV. The ground state ($n = 1$) exciton has a radius of $a_{ex} = \frac{m_0}{\mu^*}\epsilon_r a_B$ where a_B is the Bohr radius. Using typical values of μ^* and ϵ_r for semiconductors we find that the exciton binding energy is usually less than $k_B T$, with the result that the excitons are typically ionised at room temperature, while a_{ex} is of the order of 10 nm. Therefore excitons are not usually visible in absorption spectra of solids at room temperature, but they may be visible at low temperatures or in emission spectra.

In a non-periodic system, an exciton can form where the electron and hole wavefunction are confined within the same volume of space. For example, in the case of a quantum confined system such as a nanoparticle, or a molecular semiconductor (considered below), electron and hole wavefunctions are confined to individual nanoparticles or molecules. Absorption of a photon leads to a coupled state of electron and hole which is known as a Frenkel exciton. Because a nanoparticle or molecule is typically only a few nm in size, the electron and hole are much more tightly bound than in a Wannier exciton and the binding energy is larger, typically some tenths of an eV.

22.3 Electronic structure of π -conjugated molecular materials

You studied the electronic states of diatomic molecules in Lectures 14 and 15 of this course. There, you learnt that the wavefunction can be expressed as the product of an electronic function ψ , a vibrational function χ and a rotational function, and the energy as a sum of corresponding terms. In a solid we can neglect the rotational states of the molecule but, to study optical transitions, we need to introduce a component that describes the state of spin of the wavefunction, φ . Thus,

$$\Psi(\mathbf{r}, \mathbf{R}, s) = \psi(\mathbf{r})\chi(\mathbf{R})\varphi(s) \quad (22.3)$$

The energy is given by the sum of contributions,

$$E_{\text{total}} \approx E_{\text{electronic}} + E_{\text{vibrational}} \quad (22.4)$$

where we have neglected the small rotational contribution to the energy. The separation of variables in Equation 22.3 results from using the Born-Oppenheimer approximation, in which we assume that the nuclei move much more slowly than the electrons, due to their much greater mass, to separate out the dependence on the electronic (\mathbf{r}) and nuclear (\mathbf{R}) coordinates. The electronic wavefunction is then found for some particular configuration of the nuclei. The ground state will occur in the nuclear configuration where the overall energy is minimised. You also learnt in Lecture 14 that when two atoms come together their atomic orbitals combine into pairs of bonding and antibonding orbitals and that in a stable molecule most electrons occupy bonding orbitals. In simple diatomic molecules the bonding and antibonding electronic states are typically spaced by $O(10)$ eV while the vibrational states are spaced by $O(0.1)$ eV. Simple diatomic molecules therefore absorb in the IR and the UV. π conjugated molecules are more complex molecules whose bonding and antibonding orbitals are spaced closely enough to absorb and emit light in the visible. When these molecules are assembled into a solid film they can also conduct charge, while the electronic structure of the solid is fairly well approximated by the molecule.

π conjugated molecules are distinguished by being based on a network of carbon atoms in the sp^2 configuration. In this configuration the carbon atom can form three strong trigonally directed bonds with neighbouring atoms and has one additional, more loosely bound p_z electron that is available to form an additional bond with the p_z electron of a second C atom. The strong, directional bonds due the sp^2 orbitals are called σ bonds and the weaker bond, formed from the p_z orbitals is called a π bond. In a π conjugated system containing several linked sp^2 carbon atoms, the π electrons from the network of linked sp^2 carbon atoms can delocalise over the molecule, or a fragment of the molecule, in a set of extended π molecular orbitals. These π orbitals extend in space above and below the plane that contains the network of sp^2 hybridised C atoms and the σ bonds. Since the p_z electrons are weakly bound, the highest π bonding orbital is the highest occupied molecular orbital

(HOMO) of the system. The lowest π antibonding orbital is the lowest unoccupied molecular orbital (LUMO). The increasing delocalisation of π electrons with molecular size leads to reducing energy difference between the highest bonding and lowest antibonding orbitals such that for molecules of tens of sp^2 C atoms, the energy gap typically lies in the range 1 - 3 eV and can be bridged by visible photons. Each electronic state can exist in different vibrational states, leading to a set of ‘vibronic’ levels that are typically separated by 0.1-0.2 eV.

22.4 Optical transitions in π -conjugated molecular materials

When a molecule absorbs light, an electron is excited from a filled (e.g. HOMO) to an unfilled (e.g. LUMO) orbital, generating a Frenkel exciton. In general the excited state has a different potential energy surface to the ground state with the result that the minimum-energy geometry in the excited state is different from that in the ground state. However, because the nuclei move slowly compared to electrons, when the molecule is excited by a photon it initially keeps its ground state nuclear configuration, which is normally not the optimum for the excited state. The transition is vertical in the potential energy - nuclear coordinate space. We call this the Frank-Condon principle. The freshly excited molecule can thermally relax to its new optimum configuration. This happens quickly (in tens of fs) compared to electron relaxation to the ground state e.g. through spontaneous emission (\sim ns). When an electron decays from an occupied LUMO state to an unoccupied HOMO state a similar process occurs but now a vertical downward transition takes the molecule from the minimum-energy excited state to a non-optimum ground state geometry, after which the nuclei relax to the true ground state configuration. A consequence of this is that the transitions that are strongly observed in emission are generally lower in energy than those that are strongly involved in absorption.

A second important point is that the molecule possesses a well defined spin state. When the electrons are all paired as in the ground state the total spin quantum number is normally $S = 0$. When one electron is excited from π to π^* the unpaired electrons could then exist in different ($S = 0$) or the same ($S = 1$) spin state. The states are called singlet and triplet, respectively, on account of the number of different ways of combining the spins. Only singlet states can be optically excited because the transition dipole moment vanishes for different spin states.

22.5 Absorption and emission spectra for π -conjugated molecular materials

Here we will find the absorption coefficient and emission rate for optical transitions between the HOMO, which we will label as state **0** and the LUMO, which we will label as state **1**. Recall that the transition dipole matrix element is given by

$$d_{ij} = e \langle j | \mathbf{r} \cdot \mathbf{e}_0 | i \rangle \quad (22.5)$$

This can be factorised by a similar process to that used in Lecture 21: the action of the dipole operator on the two position dependent parts of the wavefunction can be expanded as a product to give a sum of terms:

$$d_{ij} = e \langle \psi_j | \mathbf{r} \cdot \mathbf{e}_0 | \psi_i \rangle \langle \chi_j | \chi_i \rangle \langle \varphi_j | \varphi_i \rangle + e \langle \psi_j | \psi_i \rangle \langle \chi_j | \mathbf{r} \cdot \mathbf{e}_0 | \chi_i \rangle \langle \varphi_j | \varphi_i \rangle \quad (22.6)$$

The second term vanishes for transitions between different electronic states because of the orthogonality of initial and final electronic states in the same molecule, leaving, for our HOMO to LUMO transition:

$$d_{0m1n} = e \langle \psi_1 | \mathbf{r} \cdot \mathbf{e}_0 | \psi_0 \rangle \langle \chi_{1n} | \chi_{0m} \rangle \langle \varphi_1 | \varphi_0 \rangle \quad (22.7)$$

The indices m, n are added to distinguish vibronic levels, as explained below. The first factor expresses the selection rule that the initial and final electronic parts of the wavefunction should have different parity. For most molecular materials this term is non-zero since the HOMO and LUMO usually have different parity. The central factor is the spatial overlap integral of the initial and final vibrational parts of the wavefunction, called the Franck Condon factor. Since these belong to different electronic states the two functions don’t obey any particular orthogonality relation and so this term is generally non-zero. This vibrational term modulates the strength of transitions between different pairs of vibronic states, as shown below (also Problem 8.1). The final factor requires that the initial and final states should have the same total spin quantum number. This means that only singlet excitons (with $S = 0$) may be generated from the ground state which for organic semiconductors normally has zero total spin.

There is normally a very small number, typically one or two, of bright electronic transitions in the visible absorption spectrum of a molecular material. The spectrum nevertheless has a significant bandwidth because of the different vibronic levels available in the excited state, each of which can absorb light in proportion to the vibrational overlap integral. This leads to a series of evenly spaced spectral lines of different intensities for each electronic transition. In practice the lines are broadened due to variations in environment and molecular conformation. The shape and breadth of the spectrum thus depends on the size of the different vibrational overlap integrals, while the overall absorption strength is determined by the electronic part of the matrix element. To illustrate this, let's consider transitions from the ground state to the first singlet excited state of a molecule. The initial and final states will be defined by the vibrational quantum number of the initial state, m , and of the final state, n . Because spin is conserved the matrix element can be written as

$$d_{0m1n} = d_{01}^e \langle \chi_{0m} | \chi_{1n} \rangle \quad (22.8)$$

where d_{01}^e refers to the electronic part of the matrix element coupling HOMO to LUMO. We model the ground state nuclear potential as a parabolic potential energy surface $V_0 = \frac{1}{2}\mu\Omega^2 Q^2$ and the excited state as a second potential energy surface $V_1 = E_g + \frac{1}{2}\mu\Omega^2(Q + \Delta Q)^2$, where E_g is the difference between the energies of the relaxed ground and relaxed excited states, $\hbar\Omega$ is the spacing of vibrational states, ΔQ represents the difference in nuclear coordinates between the two states and μ is the nuclear effective mass. Here, Q is a so-called normal coordinate that quantifies the displacement from equilibrium of all the atoms in the system due to a particular vibrational mode. It is a way of representing many nuclear positions with a single parameter. Similar curvatures may be used for the two potential energy surfaces since the same set of bonds and force constants is involved. The energies of the initial states are then given by

$$E_{0m} = \left(m + \frac{1}{2}\right) \hbar\Omega \quad (22.9)$$

and those of the final states by

$$E_{1n} = E_g + \left(n + \frac{1}{2}\right) \hbar\Omega \quad (22.10)$$

The wavefunctions χ_{0m} and χ_{1n} are solutions to the Schroedinger equation for the harmonic oscillator,

$$\chi_n(u) = \left(\frac{1}{\sqrt{\pi}2^n n!}\right)^{1/2} e^{-\frac{u^2}{2}} H_n(u) \quad (22.11)$$

where for the ground states, $u = \mu\Omega Q/\hbar$ and for the excited states, $u = \mu\Omega(Q + \Delta Q)/\hbar$ and $H_n(x)$ is a function known as a Hermite polynomial of order n . The relevant quantity in calculating the transition strengths will thus be the overlap integral between two of the Hermite polynomials, which will depend only on n , m and the shift in equilibrium coordinate, $\Delta u = \mu\Omega\Delta Q/\hbar$. Denoting this integral as F_{mn} where

$$F_{mn} = \int \chi_n(u + \Delta u) \chi_m(u) du \quad (22.12)$$

and using eqn. 17.20 for the absorption coefficient α we finally have

$$\alpha(\hbar\omega) = \frac{4\pi N\omega}{n_r c \epsilon_0} d_{01}^e{}^2 \sum_{n,m} F_{mn}^2 (f_m - f_n) \delta(\hbar\omega - E_{1n} + E_{0m}) \quad (22.13)$$

where we have assumed state degeneracies of one. The spectrum is a series of evenly spaced lines, each weighted by the overlap of the initial and final vibrational wavefunctions. The delta function may be replaced by a lineshape $D(E)$ such as a Gaussian or Lorentzian function, to account for the broadening of the spectral lines in practice. To approximate the absorption spectrum, it is common to assume that only the first ground state vibronic level is occupied ($f_0 = 1$, $f_m = 0$ for $m \geq 1$) and that all excited levels are empty ($f_n = 0$). This is reasonable when $\hbar\omega \gg k_B T$. Then

$$\alpha(\hbar\omega) = \frac{4\pi N\omega}{n_r c \epsilon_0} d_{01}^e{}^2 \sum_n F_{0n}^2 D(\hbar\omega - E_{1n} + E_{00}) \quad (22.14)$$

The emission spectrum can be determined using similar principles. In Lecture 19 when dealing with interband transitions in a direct gap semiconductor we showed that the spontaneous emission rate is proportional to

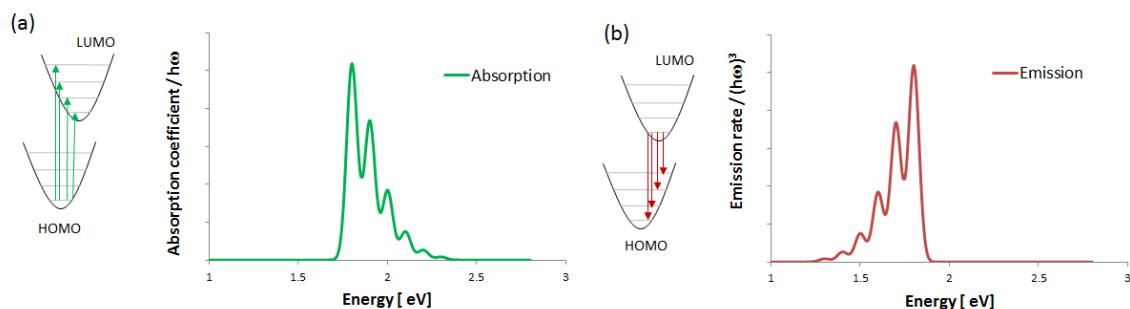


Figure 22.1: (a) Schematic of transitions involved in absorption process and typical absorption spectrum, and (b) transitions involved in emission process and typical emission spectrum for a molecule. In the ideal case the weighted emission and absorption spectra are mirror images.

$\alpha_{12}(\hbar\omega)(\hbar\omega)^2 e^{-\hbar\omega/k_B T}$. The same physics applies here, and when we account for all possible initial and final states at finite temperature (i.e. all m and n) we can show that r_{sp} is approximated by

$$r_{sp}(\hbar\omega) \propto (\hbar\omega)^3 d_{01}^2 \sum_m F_{m0}^2 D(\hbar\omega - E_{10} + E_{0m}) \quad (22.15)$$

The dominant transitions in emission are those from the lowest vibrational state of the LUMO ($n = 0$) to any vibrational state (any m) of the HOMO. Qualitatively, this is because when the excited state reaches quasi thermal equilibrium, most of the excited electrons will lie in the $n = 0$ excited vibrational state while all vibronic levels of the ground state of that molecule are available. The total intensity will also depend on the optical or electrical bias applied, which modulates the population of the ground and excited states.

Once corrected for the different dependence on $\hbar\omega$, the emission spectrum is a mirror image of the absorption spectrum, reflected around the photon energy $\hbar\omega = E_{10} - E_{00}$. The shape of both spectra is modulated by the relative strength of the different vibronic-vibronic transitions and this depends on the difference in geometry of ground and excited state. We now consider some features of molecular absorption and emission spectra.

- Absorption and emission spectra comprise a series of peaks spaced by the vibrational energy $\hbar\Omega \sim 0.1\text{eV}$
- The absorption spectrum occurs at higher energies than the emission spectrum; the two spectra are approximate mirror images of each other (although emission is sharper in practice).
- The shift between absorption and emission peaks (known as the Stokes shift) depends upon the change in molecule shape upon excitation.

22.6 Main points of lecture

- Electrons and holes interact to form Coulombically bound states called excitons. A Wannier exciton occurs in a periodic semiconductor and is loosely bound while a Frenkel exciton is tightly bound and occurs in nanoparticle or molecular materials.
- Organic semiconductors are composed of π conjugated molecules bound by van der Waals forces. The optical properties of the solid are determined by the properties of the molecule.
- Transitions energies between the highest π bonding state (HOMO) and the lowest π^* anti-bonding state (LUMO) occur at visible - UV photon energies.
- The wavefunction has electronic, vibrational and spin components. In optical transitions, both electronic and vibrational state can change but spin is conserved.
- The transition dipole matrix element contains the overlap of initial and final vibrational states. The absorption and emission spectra consists of a series of peaks of different height.
- Organic semiconductors are useful for applications in light emission because of the ability to tune the colour, the high resulting luminescent efficiency and ease of processing materials.

Light and Matter: Lecture 23

Interaction of light with vibrational states of solids

23.1 Optical transitions across the range of wavelengths

Up until now we have been studying the interaction between solids and light waves with frequencies in the visible and near visible region ($\sim 1 \times 10^{15}$ to 6×10^{15} rad s⁻¹ or ~ 1 to 4 eV). Light of these energies is typically able to excite electrons between different electronic states, e.g., the valence and conduction bands of a semiconductor or different electronic states of a π -conjugated molecule. We have also seen that the interaction of light with solids provides insight into the electronic structure and symmetry of the solid. Electromagnetic fields of higher and lower frequency are also useful as probes of the structure of solids and can give rise to useful effects. Below is a summary of some types of light - solid interaction at different frequencies.

- X-ray and γ ray photons can release core electrons from atoms and act as probes of the internal electronic structure. High energy photoelectron spectroscopy uses x-rays to identify the presence and the electronic state of particular atoms inside a solid.
- Visible, UV and near-infrared (IR) photons probe electronic interband processes.
- Infrared photons can probe transitions between phonon states in crystals and vibrational states in molecules. IR spectroscopy is particularly useful for identifying species because the IR spectra of a material can be sharp enough to act as a fingerprint. Vibrational transitions are also probed in inelastic scattering processes such as Raman scattering. Note that not all vibrational transitions are optically active.
- Lower energy (far IR) photons probe free carrier absorption in conductors and doped semiconductors.
- Microwaves can probe transitions between rotational states of a molecule
- Very low energy transitions between different spin states are probed with magnetic resonance techniques.

In this lecture we will focus on the interaction of IR light with the vibrational states of solids. Solid - light interactions in the IR range are useful for a variety of reasons. IR spectroscopy helps us to identify particular materials and distinguish their properties, such as purity. For molecular materials IR spectra are highly structured and can be used to identify the presence or absence of compounds. IR absorption and reflection can be used as a probe of electronic structure, involving low energy electronic transitions. It can also be used to help to characterise the dispersion properties and losses of optical materials that we want to use for IR transmission. And there are various applications that exploit the detection and emission of IR radiation. Chapter 10, Sections 10.1, 10.2 and 10.5 of Fox are relevant to this lecture.

23.2 Phonon modes

In second year Solid State you learnt that a periodic solid supports collective vibrational states of the atoms called phonons. Phonons are quantised - like electronic states - and characterised by wavevector \mathbf{q} and energy $\hbar\Omega_{\mathbf{q}}$. In the case of a diatomic periodic solid, there are two types of phonon: *acoustic* phonons where the different neighbouring atoms move together and *optical* modes where they move in opposite directions. The two types of mode have different dispersion relations between $\Omega_{\mathbf{q}}$ and \mathbf{q} . In one dimension the relations are given by:

$$\Omega_{\mathbf{q}}^2 = \frac{K}{\mu} \pm K \left[\frac{1}{\mu^2} - \frac{4\sin^2(qa)}{M_1 M_2} \right]^{1/2} \quad (23.1)$$

where K is the force constant, M_1 and M_2 the atomic masses and μ their reduced mass ($\mu = (1/m_e^* + 1/m_h^*)^{-1}$) and a the atomic spacing. The acoustic branch ($-$ sign) has lower energy and vanishes at low \mathbf{q} . The optical branch ($+$ sign) has higher energy and can support a mode of finite energy at zero \mathbf{q} . This $\mathbf{q} = 0$ optical phonon is effectively a standing wave where neighbouring atoms oscillate relative to each other. In three dimensional solids the phonons may involve transverse displacements of the atoms as well as longitudinal displacements, leading to four types of phonon: longitudinal acoustic (LA), transverse acoustic (TA), longitudinal optical (LO) and transverse optical (TO). The phonon energy is typically $\sim 10 - 100$ meV so $10^{-21} - 10^{-20}$ J.

Only optical phonons are capable of interacting with light because only when two atoms are different and carry different charge can the atomic vibrations lead to a time varying dipole. We reach the same conclusion from the dispersion curves: because the IR photon has very low wavevector \mathbf{k} (due to the high speed of light) and because both energy and momentum must be conserved when the photon is absorbed to generate a phonon, a photon can only generate phonons of low \mathbf{q} and finite energy, therefore only those on the optical branch.

Moreover, since the photon of wavevector \mathbf{k} generates a phonon of wavevector \mathbf{q} and since the polarisation of the light \mathbf{e}_0 is perpendicular to \mathbf{k} , the electric field along \mathbf{e}_0 can only affect motions that are perpendicular to \mathbf{k} . Therefore, only *transverse* optical (TO) phonons can interact directly with light. When the required conditions are met, for example for polar compound semiconductor or insulator materials, then the absorption by phonons at long wavelength can be strong. This is sometimes called lattice absorption. The strong absorption means that IR properties are better studied using reflectivity rather than transmission measurements.

23.3 Optical response of transverse optical (TO) phonon

The classical oscillator model that we studied in Lecture 16 is a good model for an electron oscillating near an isolated atom, where a resonant frequency ω_0 could be well defined, but less suitable for interband electronic transitions in solids where a continuum of transition energies is present. The response to light of atoms in an optical phonon close to $\mathbf{q} = 0$ is in fact very well modelled by the oscillator model. The analysis is similar to that in Lecture 16, except that now we need to consider two masses. The equations of motion for atoms of mass M_1 and M_2 in response to an applied electric field \mathcal{E} are

$$\begin{aligned} M_1 \frac{d^2 x_1}{dt^2} + \gamma M_1 \frac{dx_1}{dt} + K(x_1 - x_2) &= +\delta Q \mathcal{E} \\ M_2 \frac{d^2 x_2}{dt^2} + \gamma M_2 \frac{dx_2}{dt} + K(x_2 - x_1) &= -\delta Q \mathcal{E} \end{aligned} \quad (23.2)$$

where γ is a damping coefficient. Combining Equations 23.2, letting $x = x_1 - x_2$, using the reduced mass $\frac{1}{\mu} = \frac{1}{M_1} + \frac{1}{M_2}$ and writing $\Omega_{TO} = \sqrt{\frac{K}{\mu}}$ we have:

$$\frac{d^2 x}{dt^2} + \gamma \frac{dx}{dt} + \Omega_{TO}^2 x = \frac{\delta Q}{\mu} \mathcal{E} \quad (23.3)$$

This is exactly the same as the classical oscillator problem that we studied in Lecture 16 with m^* , ω_0 and $-e$ replaced by μ , Ω_{TO} and δQ , respectively. So we can use the solution for ϵ_r that we found there. The solution in an oscillating field $\mathcal{E} = \mathcal{E}_0 e^{-i\omega t}$ is:

$$\epsilon_r = 1 + \chi + \frac{N(\delta Q)^2}{\epsilon_0 \mu} \frac{1}{\Omega_{TO}^2 - \omega^2 - i\gamma\omega} \quad (23.4)$$

where we have included the susceptibility χ to allow for the effect of other transitions at higher ω . We write ϵ_r in terms of the low frequency (ϵ_{st}) and higher frequency ($\epsilon_\infty = 1 + \chi$) limits as

$$\epsilon_r = \epsilon_\infty + (\epsilon_{st} - \epsilon_\infty) \frac{\Omega_{TO}^2}{\Omega_{TO}^2 - \omega^2 - i\gamma\omega} \quad (23.5)$$

and separate out real and imaginary parts:

$$\begin{aligned} \epsilon_1 &= \epsilon_\infty + (\epsilon_{st} - \epsilon_\infty) \frac{\Omega_{TO}^2(\Omega_{TO}^2 - \omega^2)}{(\Omega_{TO}^2 - \omega^2)^2 + \gamma^2\omega^2} \\ \epsilon_2 &= \frac{\omega\gamma(\Omega_{TO}^2 - \omega^2)}{(\Omega_{TO}^2 - \omega^2)^2 + \gamma^2\omega^2} \end{aligned} \quad (23.6)$$

It is clear from eq. 23.6 that in the limit of weak damping ($\gamma \rightarrow 0$), there is some frequency ω_R at which $\epsilon_1 = 0$,

$$\omega_R = \left(\frac{\epsilon_{st}}{\epsilon_\infty}\right)^{1/2} \Omega_{TO} \quad (23.7)$$

and a range of frequencies $\Omega_{TO} < \omega < \omega_R$ over which $\epsilon_1 < 0$. Over this range the refractive index η is purely imaginary and the reflectivity R is equal to 1. In practice, finite damping reduces R to less than 1 but in general, strong reflective bands are seen close to Ω_{TO} for materials that are IR active. These are called *Rehstrahl bands*.

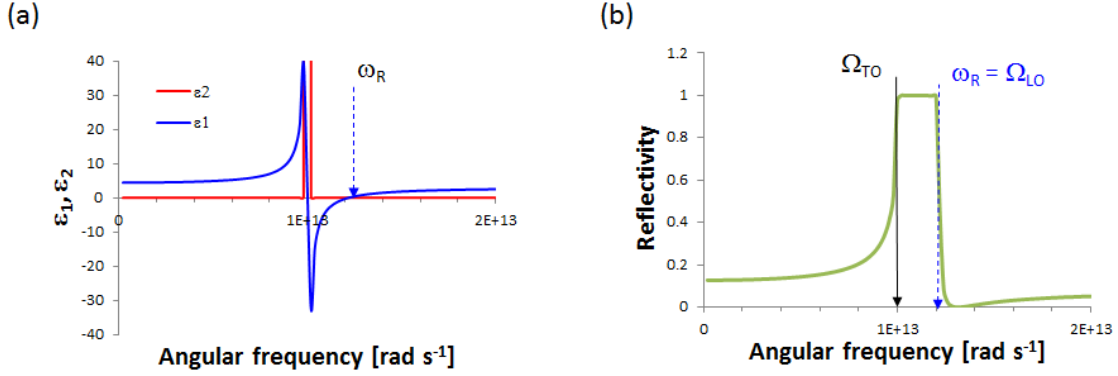


Figure 23.1: (a) Real and imaginary part of ϵ_r for a weakly damped TO phonon mode (b) Reflectivity spectrum for (a). The frequency at which $\epsilon_1 = 0$ is known as the Rehstrahl frequency ω_R .

Let's consider the special case when $\epsilon_1 = 0$ ($\omega = \omega_R$). At this point, the condition on \mathcal{E} to satisfy Gauss' law ($\nabla \cdot (\epsilon_r \epsilon_0 \mathcal{E}) = 0$) is relaxed. Normally, when $\epsilon_1 \neq 0$, $\nabla \cdot \mathcal{E} = 0$ is required. However, when $\epsilon_r = 0$ $\nabla \cdot \mathcal{E} = 0$ is no longer required and therefore longitudinal electric field waves can propagate in the dielectric and these waves can excite LO phonons. The difference between the LO and TO phonon frequencies can be found from the width of the Rehstrahl band.

23.4 Inelastic scattering

We have seen that infrared radiation can excite TO phonon modes leading to strong absorption. However, this is only possible in polar materials where the optical phonons have a dipole. Non polar materials such as diamond, silicon, have no direct IR absorption (if they are pure). Even in polar materials only TO modes can normally be excited directly, and moreover, there are selection rules that determine which TO modes can be excited with light. An alternative way to observe lattice vibrations that allows us to see some of the modes that can not be directly excited is to use *inelastic* scattering techniques. Here, we illuminate the solid with, say, visible frequency to excite electronic transitions and observe the frequency of scattered light. A small fraction of the incident photons will interact with phonon modes in the solid to give up or absorb a quantum of energy and will be scattered with a different frequency and wavevector. If the incident and scattered photons have wavevector \mathbf{k}_{inc} , \mathbf{k}_{sca} and energy ω_{inc} , ω_{sca} then

$$\mathbf{k}_{sca} = \mathbf{k}_{inc} \pm \mathbf{q} \quad (23.8)$$

$$\hbar\omega_{sca} = \hbar\omega_{inc} \pm \hbar\Omega_{\mathbf{q}} \quad (23.9)$$

where \mathbf{q} , $\hbar\Omega_{\mathbf{q}}$ are the wavevector and energy of the phonon, and the $-$ and $+$ signs refer to phonon emission (Stokes scattering) and phonon absorption (anti-Stokes). The maximum phonon energy absorbed or emitted corresponds to backscattered light and this limits the size of phonon energies. The signal detected in inelastic scattering processes is generally very weak, because the process requires both photon and phonon to be available.

Raman scattering is an inelastic scattering technique that can be used to probe the energies of optical (LO and TO) phonons near $\mathbf{q} = 0$. Because the phonon structure of solids in different crystal structures is different, Raman can also be used to distinguish different polymorphs of a crystalline material. It is also very powerful for probing the physical state of molecular materials, because the vibrational frequencies detected relate directly to the chemical and physical environment of the bonds being probed.

23.5 Absorption in indirect bandgap semiconductors

Inelastic scattering events are second order processes that depend upon the availability of a phonon and a photon with particular combination of energy and momentum to stimulate a transition that would otherwise be forbidden by optical selection rules. Here we introduce a very important example of such a phenomenon in semiconductors, optical transitions across an *indirect* band gap. We have seen in Lecture 18 that crystal momentum \mathbf{k} must be conserved in an optical transition in a crystal. This means that the lowest optically allowed transition in a semiconductor should occur where the difference between the conduction band energy $E_c(\mathbf{k})$ and valence band energy $E_v(\mathbf{k})$ is the lowest. In a number of semiconductors - importantly, in silicon - the conduction band minimum and valence band maximum occur at different \mathbf{k} , say at \mathbf{k}_{c0} and \mathbf{k}_{v0} , respectively. A photon cannot bridge that transition because the photon wavevector is too small to conserve \mathbf{k} . However if the photon absorption is accompanied by the absorption or emission of a phonon of wavevector $\mathbf{q} = \mathbf{k}_{c0} - \mathbf{k}_{v0}$ then an electron transition from $E_c(\mathbf{k}_{c0})$ to $E_v(\mathbf{k}_{v0})$ is allowed. The rate of this process (and therefore, the size of the absorption coefficient and emission rate) will depend not only on the density of electron and hole states, as previously, but also on the probability that there is a phonon of appropriate \mathbf{k} .

Consider the process where a phonon is emitted. Then

$$\hbar\omega = E_c(\mathbf{k}_{c0}) - E_v(\mathbf{k}_{v0}) + \hbar\Omega_{\mathbf{q}} \quad (23.10)$$

where $\hbar\Omega_{\mathbf{q}}$ is the energy of the phonon with $\mathbf{q} = \mathbf{k}_{c0} - \mathbf{k}_{v0}$.

For direct gap semiconductors we found that the probability of absorption was proportional to the joint density of states,

$$\rho(\hbar\omega) = N \sum_{\mathbf{k}} g_c(\mathbf{k}) g_v(\mathbf{k}) \delta(\hbar\omega - E_c(\mathbf{k}) + E_v(\mathbf{k})) \quad (23.11)$$

For indirect gap semiconductors, the probability of the electron transition (and therefore the absorption and emission rate) is also proportional to the probability of having a phonon of wavevector \mathbf{q} and energy $\hbar\Omega_{\mathbf{q}}$. This probability involves a sum also over phonon states, involving the phonon density of states $g_p(\mathbf{q})$:

$$N \sum_{\mathbf{k}, \mathbf{q}} g_c(\mathbf{k}_c) g_v(\mathbf{k}_v) \delta(\hbar\omega - E_c(\mathbf{k}_c) + E_v(\mathbf{k}_v) - \hbar\Omega_{\mathbf{q}}) g_p(\mathbf{q}) \delta(\mathbf{k}_c - \mathbf{k}_v - \mathbf{q}) \quad (23.12)$$

It can be shown (though you are not expected to do this!) that this leads to a weak energy dependence of the absorption coefficient close to the band edge of

$$\alpha_{cv}(\hbar\omega) = A\omega(\hbar\omega - E_g - \hbar\Omega)^2 \quad (23.13)$$

where A is some material dependent constant. The slow rise of α with photon energy is a distinguishing feature of indirect gap semiconductors such as silicon. In such materials, absorption rises sharply at higher photon energies when the optically allowed direct transitions turn on. The low probability of optical transitions near the band gap of indirect gap semiconductors also means that spontaneous emission is very unlikely and is effectively non-existent.

23.6 Main points of the lecture

- Different part of the electromagnetic spectrum interact with solids in different ways. Radiation at infrared (IR) frequencies is useful for probing the vibrational state of solids.
- Infrared radiation can directly excite the transverse optical (TO) phonon modes of a solid. This leads to strong infrared absorption bands in polar solids.
- The interaction of light with these optical phonons can be treated with a classical oscillator model.
- At the frequency where $\epsilon_1 = 0$ longitudinal phonon modes may also be excited.
- Inelastic scattering techniques such as Raman scattering can be used to probe vibrational modes that cannot be directly excited optically. These second order processes are relatively weak, but informative.
- Inter-band transitions near to the band gap of an *indirect* gap semiconductor are also weak second order processes involving phonon absorption and emission. This is the reason why indirect gap semiconductors have weaker absorption close to the band gap than direct gap semiconductors.

Light and Matter: Lecture 24

Optical properties of metals

The last lecture specific to a group of materials concerns probably the simplest case, the case of metals. Metals crystallise into one of a number of basic structures (simple, body centres or face centred cubic or hexagonal) and have a Fermi level that lies within one of the bands, rather than in the band gap as with a semiconductor. The electrons within the outer, unfilled atomic shell partially fill the conduction band. They can move easily in response to an applied electric field because of the availability of unfilled electronic states at close energies. The high density of mobile electrons gives rise to a high conductivity and, as we shall see, to distinct optical properties. Chapter 7, Sections 7.1 to 7.4 of Fox are relevant to this lecture.

24.1 Classical oscillator model applied to metals

Because the electronic states are delocalised across the structure, the valence electrons can be treated as nearly free electrons. In fact the effective mass m^* is close to m_0 in the case of common conductive metals such as Cu, Ag and Au so they may be considered as free electrons; in the following analysis for metals we will take $m^* = m_0$. Because the electrons are not bound to particular atoms the electrons do not experience a restoring force, so we can write the equation of motion as

$$m_0 \frac{d^2 \mathbf{x}}{dt^2} + m_0 \gamma \frac{d\mathbf{x}}{dt} = -e\mathcal{E} \quad (24.1)$$

Here, the second term represents damping due to frictional forces in the medium. When the applied field is oscillatory, $\mathcal{E} = \mathcal{E}_0 e^{-i\omega t}$ and we use a trial solution of the form $\mathbf{x} = \mathbf{x}_0 e^{-i\omega t}$ we find that the electron displacement \mathbf{x} has the form

$$\mathbf{x} = \frac{e\mathcal{E}}{m_0(\omega^2 + i\gamma\omega)} \quad (24.2)$$

Using the same argument as in Lecture 16, that the electron displacement gives rise to a contribution to the polarisation \mathbf{P} ($\mathbf{P} = -Ne\mathbf{x}$) where N is the density of free electrons, we can find the complex dielectric function $\epsilon_r(\omega)$. In the case where there is no significant contribution to ϵ_r from higher transitions (i.e. $\chi = 0$) we find

$$\epsilon_r(\omega) = 1 - \frac{Ne}{\epsilon_0} \frac{\mathbf{x}}{\mathcal{E}} = 1 - \frac{Ne^2}{\epsilon_0 m_0} \frac{1}{\omega^2 + i\gamma\omega} \quad (24.3)$$

This is identical to the result in Lecture 16 with the resonant frequency $\omega_0 = 0$ and $m^* = m_0$. In dealing with metals, it is typical that a lifetime τ is used rather than a rate γ , where $\tau = 1/\gamma$, to characterise the damping. In that case, and after defining the plasma frequency

$$\omega_p = \left(\frac{Ne^2}{\epsilon_0 m_0} \right)^{1/2} \quad (24.4)$$

we have

$$\epsilon_r(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + \frac{i}{\tau})} \quad (24.5)$$

Breaking ϵ_r into real and imaginary parts

$$\begin{aligned} \epsilon_1 &= 1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2} \\ \epsilon_2 &= \frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)} \end{aligned} \quad (24.6)$$

A similar treatment of electrons under an oscillating electric field delivers the conductivity of the medium. To find the frequency dependent conductivity $\sigma(\omega)$, we express the electric current density \mathbf{j} in terms of electron velocity \mathbf{v} , $\mathbf{j} = -Ne\mathbf{v}$ and use the definition of conductivity $\mathbf{j} = \sigma\mathbf{E}$. Thus

$$\sigma = -\frac{Ne\mathbf{v}}{\mathbf{E}} \quad (24.7)$$

And then use the solution for \mathbf{x} (Equation 24.2) and the definition $\mathbf{v} = -i\omega\mathbf{x}$ to find

$$\sigma = i\frac{Ne^2\omega}{m_0(\omega^2 + i\frac{\omega}{\tau})} \quad (24.8)$$

which we can write as

$$\sigma = \frac{Ne^2\tau}{m_0} \frac{1}{1 - i\omega\tau} = \frac{\sigma_0}{1 - i\omega\tau} \quad (24.9)$$

where

$$\sigma_0 = \frac{Ne^2\tau}{m_0} \quad (24.10)$$

is the DC conductivity. You have already met this behaviour in second year Electromagnetism.

Comparing expressions for σ and ϵ_r , we see that conductivity and complex dielectric function are related through

$$\epsilon_r(\omega) = 1 + \frac{i\sigma(\omega)}{\epsilon_0\omega} \quad (24.11)$$

Equation 24.11 tells us that a metal with high conductivity will have high absorption at low frequencies.

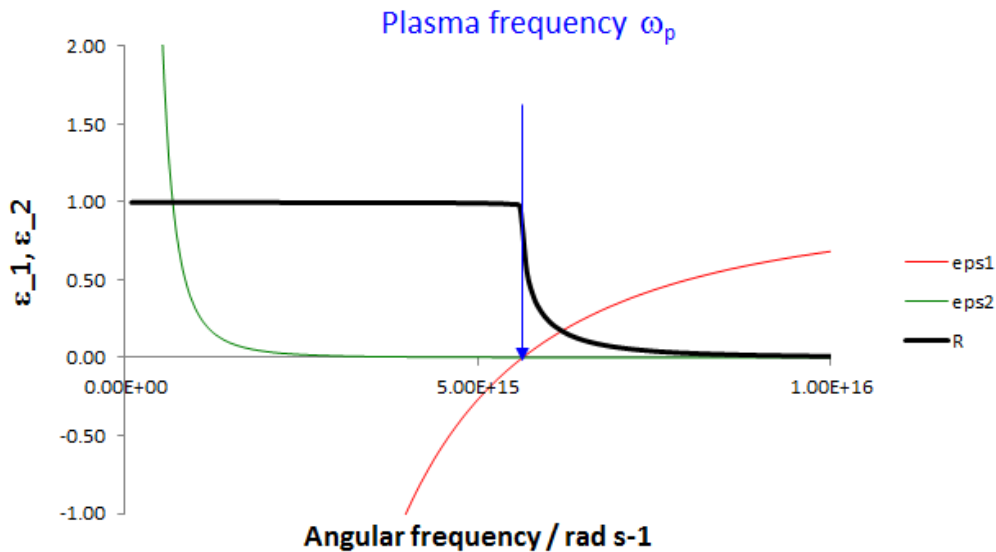


Figure 24.1: Real and imaginary part of ϵ_r and the corresponding reflectivity R for a metal.

24.2 Reflection and Absorption by metals

Now we can find the absorption and reflectivity of a metal as a function of frequency. We will see that there are two important frequency regimes: low frequency ($\omega < \omega_p$ for low damping) where the medium shows metallic behaviour and high frequency ($\omega > \omega_p$) where it starts to behave like a dielectric. We consider the case where $\chi \approx 0$ but χ can easily be included as an additive term in the expressions for ϵ_1 .

If we consider the low frequency regime of a lightly damped system ($\omega < \omega_p$, $\omega\tau \gg 1$), we find that ϵ_1 is negative ($\epsilon_1 \approx -\omega_p^2/\omega^2$) and greater in magnitude than ϵ_2 ($\epsilon_2 \approx \omega_p^2/\omega^3\tau$). As a consequence, in this regime we find that the imaginary part of the refractive index η , κ , is much larger than the real part, n_r , which is close to

zero. To see the physical consequences, consider the reflection coefficient for light incident normally from free space. Evaluating $R = \left| \frac{1-\eta}{1+\eta} \right|^2$ we find that

$$R \sim 1 - \frac{4n_r}{\kappa^2} \quad (24.12)$$

Therefore in the low frequency regime where $\epsilon_1 < 0$ and $\kappa \gg n_r$ the reflectivity is very close to 1. If damping is sufficiently low, the metal is completely reflective. If the damping is significant (so $\omega\tau$ is neither small nor large) this reduces reflectivity from 1 and narrows the regime where $\epsilon_1 < 0$ following eqn. 24.6. In practice the scattering time τ can be estimated from the DC conductivity using eqn. 24.10.

We can also find the absorption coefficient from $\alpha = \frac{4\pi\kappa}{\lambda}$ where λ is the wavelength of light in free space $\lambda = 2\pi c/\omega$. In the very low frequency limit ($\omega\tau \ll 1$), we can show that $\kappa \approx \sqrt{(\epsilon_2/2)}$ and hence that

$$\alpha = \sqrt{\frac{2\omega_p^2\omega\tau}{c^2}}. \quad (24.13)$$

Since α and σ_0 both depend on τ , α can be expressed in terms of the DC conductivity σ_0 using the definition of ω_p

$$\alpha = \sqrt{2\sigma_0\mu_0\omega} \quad (24.14)$$

where we also used $c^2 = 1/\mu_0\epsilon_0$. Remembering that light intensity attenuates like $e^{-\alpha x}$ we can see that in the low frequency regime, the electromagnetic field penetrates a distance of

$$\frac{2}{\alpha} \sim \frac{2}{\sqrt{\sigma_0\omega\mu_0}} \quad (24.15)$$

Comparing these results we see that a conductive metal has a high absorption coefficient at low frequencies, but because the light doesn't penetrate into the medium, incident light is mainly reflected rather than being absorbed.

Now let's consider the behaviour at high frequencies. When $\omega\tau \gg 1$ we have

$$\begin{aligned} \epsilon_1 &= 1 - \frac{\omega_p^2}{\omega^2} \\ \epsilon_2 &= \frac{\omega_p^2}{\omega^2} \frac{1}{\omega\tau} \end{aligned} \quad (24.16)$$

Now the behaviour is like that of a dielectric far from a resonance. ϵ_r is dominated by the real part, the refractive index n_r is real and the medium can support propagating electromagnetic waves. The reflectivity falls towards zero so that at sufficiently high frequencies the metal becomes transparent.

The threshold between these two regimes, the low ω metallic and high ω dielectric regime occurs when $\epsilon_1 = 0$. In the limit of low damping and when $\chi = 0$ (as we assumed) this happens at $\omega = \omega_p$. With finite damping or $\chi > 0$ the threshold is simply shifted away from ω_p but the same behaviour results.

We can estimate the value of ω_p from the density and valency of metals. For example, from the density of valence electrons in copper ($N = 8.5 \times 10^{28} m^{-3}$), gold ($N = 5.9 \times 10^{28} m^{-3}$) and aluminium ($N = 1.8 \times 10^{29} m^{-3}$) we find plasma frequencies ω_p of 2.6×10^{15} Hz, 2.2×10^{15} Hz and 3.8×10^{15} Hz, all of which lie in the UV part of the spectrum. From this we would expect UV light to be transmitted and all visible wavelengths of light to be reflected. In fact, metals can be coloured: copper (Cu) appears red and gold (Au) appears yellow. The actual reflectivity data for Cu and Au falls off at lower frequencies than the expected ω_p . This is because in Cu and Au interband absorption occurs from d to s bands at some $\omega < \omega_p$ and this means some visible light can be absorbed to promote electrons from the tenfold degenerate d valence band to empty s conduction states, changing the spectrum of reflected light. Interband transitions can also introduce other features into the frequency dependence of reflectivity.

24.3 Reflection and Absorption by doped semiconductors

When a semiconductor is doped (by adding controlled amounts of impurity atoms that have either an excess or a deficit of valence electrons compared to the host material) the density of holes (for p type) or electrons (for n type) is greatly increased above the intrinsic carrier density. At the same time the density of the other

carrier type is reduced and the position of the Fermi level in the band gap is modulated. The optical properties of the doped semiconductor are changed by the addition of the excess free electrons or holes. Specifically, the materials will absorb light strongly at low ω through free carrier absorption just like in a metal. The analysis is the same as above except that N should now be the doping density of the material, which is orders of magnitude smaller than the density of valence electrons in a metal, and m_0 should be replaced by the effective mass m^* . As a result, $\omega_p (= \sqrt{Ne^2/\epsilon_0 m^*})$ is smaller and typically falls in the mid to far-IR region, depending on doping level. Because the optical properties are less dominated by the free electron response than those of a metal, we will keep the electric susceptibility χ in our expression for ϵ_r , to account for higher frequency transitions.

Because ω_p falls at lower frequencies than in a metal, the doped semiconductor is normally in the dielectric (i.e. non reflective) regime at visible frequencies. If damping is low enough that $\tau\omega \gg 1$ in the visible then we expect

$$\epsilon_1 \approx 1 + \chi - \frac{\omega_p^2}{\omega^2} \quad (24.17)$$

$$\epsilon_2 \approx \frac{\omega_p^2}{\omega^3 \tau} \quad (24.18)$$

This leads to a free carrier absorption coefficient that falls like ω^{-2} as ω increases.

24.4 Plasmons

If we solve Maxwell's equations in a conductive medium we find that the medium supports transverse electromagnetic waves subject to the dispersion relation $c^2 k^2 = \omega^2 - \omega_p^2$ and can support longitudinal solutions only when $\omega = \omega_p$. The latter type of solution can exist when $\epsilon_1 = 0$ at $\omega = \omega_p$, as we saw in Lecture 23 for the case of LO phonons. The plasmons are quantised longitudinal oscillations of the electrons in the medium.

Plasmons in the bulk of a metal have only longitudinal components and cannot be excited optically, although they can be observed by inelastic scattering, like LO phonons. However, localised plasmons can exist close to the metal-air or metal-dielectric interface and these surface plasmons possess both transverse and longitudinal components. The transverse components means they can couple to electromagnetic radiation. These surface plasmons (or surface plasmon polaritons) are highly localised to the metal surface. This has led to interest in the idea of transmitting electromagnetic waves in reduced dimensions (smaller than the wavelength of light) by using the surface plasmons. The electric field can be strongly enhanced close to the metal-dielectric interface, and especially when close to curved interfaces. This can be used to enhance the intensity of signals, for example in Raman scattering. Surface plasmons confined in gold nanoparticles give rise to a change in colour compared to the bulk material, by strongly absorbing around a plasmon resonance that occurs at a lower frequency than that of the bulk metal. The colour change depends on the dielectric environment and the particle shape. You can learn all about plasmonics in the option course on '*Plasmonics and Metamaterials*'.

24.5 Main points of the lecture

- A metal can be modelled as a classical oscillator with zero resonant frequency. In the limit of low damping there are two regimes: a metallic regime for $\omega < \omega_p$ where the metal is reflective and a dielectric regime at $\omega > \omega_p$ where the metal transmits.
- The optical response of real metals is influenced by interband transitions.
- The absorption of a metal is correlated to the conductivity, and both are high at low frequency.
- Doped semiconductors behave like metals with a much lower density of oscillators, and so free carrier absorption is only significant for infrared light.
- Although bulk plasmon modes cannot be optically excited, surface plasmon modes that are localized close to the metal surface can interact with light. In metal nanoparticles, localised surface plasmons lead to colour changes compared to the bulk metal.

Light and Matter: Lecture 25

Applications of the optical properties of solids

In our last lecture on the optical properties of solids we will look at some examples of how the properties we have studied are used in applications, and at how different applications make use of different aspects of the optical properties. We will take examples from semiconductor optoelectronics, namely, solar cell and photodetector, light emitting diodes and semiconductor diode lasers. In all cases the devices operate by converting electrical current into photon flux, or vice versa. This basic operation is performed by a semiconductor photodiode: a p-n junction or similar structure built around a semiconductor layer that can absorb or emit light. You met the *p-n* junction in second year Solid State Physics. In this lecture we will first revise the basic principles of the p-n junction diode and then study the operation of photodetectors and solar cells, light emitting diodes and diode lasers. From Fox's book, Sections 3.7, 5.4, 6.6 and 8.4 are relevant.

25.1 *p-n* junction (photo)diode

In second year solid state you learnt that a p-n junction is made when p-doped and n-doped layers of the same semiconductor are brought together. The doping gradient at the junction leads to redistribution of free charge in the material so that an electrostatic field is established, opposing the motion of electrons from the **n** doped side to the **p** doped side. the effect of this asymmetry is that the diode passes current easily in one direction: when a negative potential is applied to the n side the quasi Fermi level of the electrons is raised relative to that of the holes. This reduces the barrier seen by the electrons and current flows more easily. When a positive potential is applied to the **n** side the barrier remains and little current flows. When light is absorbed in the p-n junction to generate electron-hole pairs the built in electrostatic field drives the electrons to the **n**-side and holes to the **p**-side. This can drive an electric current through an external circuit. This is the operating principle of a *photodetector*. In a *solar cell*, a photocurrent is also generated but now the generated current passes through an external load, with the result that a potential difference is maintained between the **n** and **p** contacts. If we inject electrons and holes from the contacts using an electric bias then some of the charge pairs will recombine radiatively to generate a photon via the process of spontaneous emission. This is the basic mechanism of a *light emitting diode*. Charge injection is also required for operation of a *diode laser*.

The operation of any one of these semiconductor devices can be modelled using a set of differential equations that relate the electron and hole carrier densities at a point, n and p , respectively, and the electron and hole current densities, J_n and J_p , to the applied light and electrical bias. In a one dimensional device at steady state, the current densities obey

$$\frac{1}{e} \frac{dJ_n}{dx} + G - U = 0 \quad (25.1)$$

$$-\frac{1}{e} \frac{dJ_p}{dx} + G - U = 0 \quad (25.2)$$

where G is the density of charge pairs generated (by light absorption) per unit time (the volume charge generation rate) and U the density of charge pairs that recombine per unit time either by photon emission or by other, non-radiative processes (the volume recombination rate). In practice the non-radiative processes dominate over the radiative ones. The current densities can be expressed in terms of charge densities through

$$J_n = eD_n \frac{dn}{dx} + e\mu_n n \mathcal{E} \quad (25.3)$$

$$J_p = -eD_p \frac{dp}{dx} + e\mu_p p \mathcal{E} \quad (25.4)$$

where μ , D are the charge mobilities and diffusion coefficients and \mathcal{E} is the local electrostatic field. The charge carrier profile can be worked out by solving these differential equations for some form of G and U for given boundary conditions on n , p , J_n and J_p . One of these will be the applied bias between the contacts, V . The applied bias at the **n** and **p** contacts determines the populations of electrons (at the **n** side) and holes (at the **p** side) through the relationships between n or p and the respective quasi Fermi level: $n = N_c \exp(-(E_c - E_{Fn})/k_B T)$, $p = N_v \exp(-(E_{Fp} - E_v)/k_B T)$, where eV is equal to the difference in the quasi Fermi levels $\Delta\mu$,

$$eV = \Delta = E_{Fn} - E_{Fp} \quad (25.5)$$

This section has been included mainly for background to the applications described below.

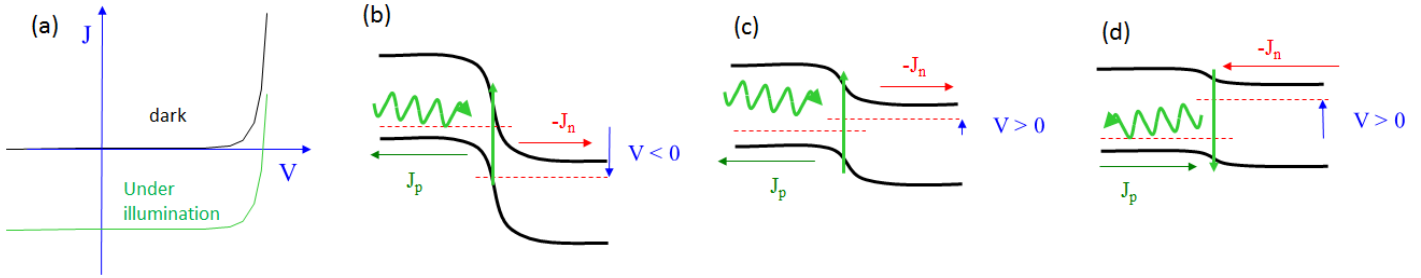


Figure 25.1: (a) Current density - voltage (J - V) characteristic of a diode in the dark and under illumination. Band profiles when operating as (b) a photodetector (under reverse bias with $V < 0$), (c) a solar cell (with a load present so $V > 0$) and (d) a light-emitting diode (V must be large enough to inject enough charges for the emitted light flux to be significant).

25.2 Solar cells and photodetectors

In both of these device types, a photon of energy $\hbar\omega > E_g$ is absorbed to generate an electron-hole pair and the pair is separated by the asymmetric diode structure to deliver one electron to the external circuit. In eqn. 25.2, the term G dominates over U so that $G - U$ is positive. The resulting 'photocurrent' acts in the opposite sense to the diode current and usually is given with negative sign. For both solar cells and photodetectors we want a high probability of photon absorption, a high probability of pair collection and normally, sensitivity to a broad range of photon energies. Since light intensity attenuates like $I = I_0 \exp(-\alpha x)$, and allowing a fraction R of the light to be reflected, the pair generation rate at a depth x in response to light of energy $\hbar\omega$ is given by

$$G(\hbar\omega, x) = (1 - R(\hbar\omega)) \frac{I_0(\hbar\omega) e^{-\alpha(\hbar\omega)x}}{\hbar\omega} \alpha(\hbar\omega) \quad (25.6)$$

where $I_0(\hbar\omega)$ is the spectral irradiance (for example, the solar spectrum) and the factor $\frac{I_0(\hbar\omega) e^{-\alpha(\hbar\omega)x}}{\hbar\omega}$ represents the density of photons of energy $\hbar\omega$ that reach depth x per unit time. The photocurrent density J_{ph} is found by integrating over both thickness and photon energy:

$$J_{ph} = -e \int_{E_g}^{\infty} \int_0^d G(\hbar\omega, x) dx d(\hbar\omega) = -e \int_{E_g}^{\infty} (1 - R(\hbar\omega)) \frac{I_0(\hbar\omega)}{\hbar\omega} (1 - e^{-\alpha(\hbar\omega)d}) d(\hbar\omega) \quad (25.7)$$

where d is the absorbing layer thickness and noting that the probability of photon absorption in a layer of thickness d is then proportional to $(1 - R)(1 - e^{-\alpha d})$. For a good solar cell at short circuit (i.e. no load applied) then $G \gg U$ and the device current is approximated by J_{ph} . Also for a photodetector, the device will be optimised to minimise U and it may be operated at reverse bias to reduce U further.

Thus the factors that influence solar cell and photodetector response are:

- Strength of the absorption coefficient and active layer thickness d , giving the optical depth αd .
- The onset of absorption E_g
- Front surface reflectivity R

We have seen that $\alpha(\hbar\omega)$ varies like $\hbar\omega\sqrt{(\hbar\omega - E_g)}$ for a direct gap semiconductor, rising sharply from zero at E_g . At photon energies a few tenths of an eV above E_g , experimental values for α for direct gap semiconductors are on the order of 10^6 to 10^7 m⁻¹. Therefore around 2 microns of semiconductor are enough to absorb more than 90% of the light.

An indirect semiconductor (see Lecture 23) absorbs light of $\hbar\omega > E_g$ where E_g is measured between the lowest point on the conduction band and the highest point on the valence band, but with a much lower probability because absorption depends on the availability of a phonon of correct wavevector. In this case $\alpha(\hbar\omega)$ rises more slowly with energy near E_g , $\alpha(\hbar\omega) \sim (\hbar\omega - E_g \pm \hbar\Omega)^2$ where $\hbar\Omega$ is the phonon energy. Experimental values of $\alpha(\hbar\omega)$ are much lower near E_g than for direct gap semiconductors. In silicon, $\alpha(\hbar\omega)$ increases from 10^3 m⁻¹ in the near infrared to 10^7 m⁻¹ in the blue. Therefore in order to absorb 90% of IR light, a layer hundreds of microns thick is needed. This is feasible so long as the electrical quality of the material (specifically, the charge mobilities and the charge lifetimes) are high enough for U to remain low even when integrated over a large thickness. In fact, most solar cells and photodetectors are made from silicon, because in spite of its weak absorption the non-radiative loss rate U can be made small. Other advantages of silicon outweigh the need for thick films.

The second parameter determining choice of material is the band gap E_g . It is clear that J_{ph} will increase as E_g reduces. However, if E_g is too low the solar cell will generate too little electrical work as the separation in Fermi levels, $\Delta\mu$, that can be generated by the light is too small. It can be shown that there is an optimum E_g of ~ 1.4 eV for conversion in the solar spectrum.

For photodetectors the choice of E_g depends on the range of photon energies that it is intended to detect. Photodetectors that can detect low energy photons, and so have low E_g , tend to suffer from high noise due to the large thermal generation in low band gap semiconductors.

In both solar cells and photodetectors, light absorption can be enhanced by applying an antireflection coating, with refractive index at the geometrical mean of the semiconductor and free space.

25.3 Light emitting diodes

In an LED electrical current is injected and charge pairs recombine near the junction of the diode, a fraction of these via spontaneous emission with the emission of a photon. The photons that escape through the semiconductor surface contribute to the emitted light. In this type of device $G = 0$ and U contains radiative and non-radiative terms $U = U_{rad} + U_{nonrad}$. The injected current is maintained by an applied bias $eV = E_{Fn} - E_{Fp}$ that fixes n and p at the contacts. The radiative part of the volume recombination rate is given by

$$U_{rad} = \int_{E_g}^{\infty} r_{sp}(\hbar\omega) d\hbar\omega \quad (25.8)$$

where r_{sp} is the spontaneous emission rate that we found in Lecture 19:

$$r_{sp}(\hbar\omega) = \frac{n_r^2}{4\pi^2 \hbar^3 c^2} \alpha(\hbar\omega) (\hbar\omega)^2 e^{-\hbar\omega/kT} e^{\Delta\mu/kT} \quad (25.9)$$

The output of an LED will thus depend on the following factors:

- Band gap E_g . Because of the exponential term in $\hbar\omega$ in eq. 19.14, emission peaks close to E_g . The range of emitted energies is of order 0.1 eV (usually < 100 nm).
- The shape of the absorption edge near E_g . Low dimensional structures like QWs and quantum dots have sharper $\alpha(\hbar\omega)$ resulting in narrower emission bandwidth.
- Applied bias V . The dependence of r_{sp} on $\exp(\Delta\mu/k_B T)$, given that $eV = \Delta\mu = E_{Fn} - E_{Fp}$ means that r_{sp} depends on the product of electron and hole densities np and so will increase with increasing injected current density J . (See problem 7.5.)
- Strength of competing recombination processes. The radiative efficiency $U_{rad}/(U_{rad} + U_{nonrad})$ tends to improve with applied bias.
- The refractive index n_r . The high n_r of a semiconductor means that some of the emitted light is internally reflected. To overcome this an optical medium of intermediate n_r is used to encase the semiconductor.

Note that spontaneous emission from an *indirect* gap semiconductor is extremely weak because, like absorption, it is a second order process requiring a phonon and in practice is overwhelmed by non-radiative processes.

Quantum wells are used in order to access particular emission colours. Use of QWs or other heterostructures where the n and p regions are made from a wider E_g material means that recombination can be located in the junction region and reabsorption of light in the n and p regions avoided. In comparison to solar cells, the presence of optically allowed transitions with $\hbar\omega < E_g$ is much more problematic since this will pollute the colour of emitted light in an LED; optically forbidden transitions will increase U_{nonrad} and reduce device efficiency but not affect colour. The difference in photon energy dependence of α and r_{sp} mean that whilst a solar cell is normally panchromatic (absorbing over a wide range of energies), an LED emits only over a small range of $\hbar\omega$.

To achieve white light emission using LEDs, some other process is needed. One (mentioned in Lecture 19) is to pump a phosphor that has a broad emission spectrum with blue LEDs. Another is to build structures containing several, separately addressed active layers in the same complex layer structure. Another would be to combine, say, two different emission colours in the same device. This can be done with organic semiconductors using molecules combining two different chemical groups.

An important requirement for efficient LED and solar cell operation is that the optical window to the device should be both conductive and transmissive. From Lecture 24 you know that a conductive medium becomes transmissive only at $\omega > \omega_p$ where the plasma frequency $\omega_p = \sqrt{Ne^2/m^*\epsilon_0}$. You also know that the dc conductivity of the material σ_0 also depends on the density of free electrons N (eq. 24.10). This leads to a compromise: higher conductivity leads to reduced optical transmission in the visible. But high transmissivity, which can be achieved with materials of low N , leads to a series resistance opposing the collection (in a solar cell) or injection (in an LED) of charge carriers. As a guide, the potential dropped across the electrode due to this series resistance, $\Delta V = JR_s$, where R_s is the sheet resistance and relates to σ_0 through $R_s = \frac{1}{\sigma_0 t}$ where t is the electrode thickness. JR_s , should be small compared to the potential difference V between the **n** and **p** contacts.

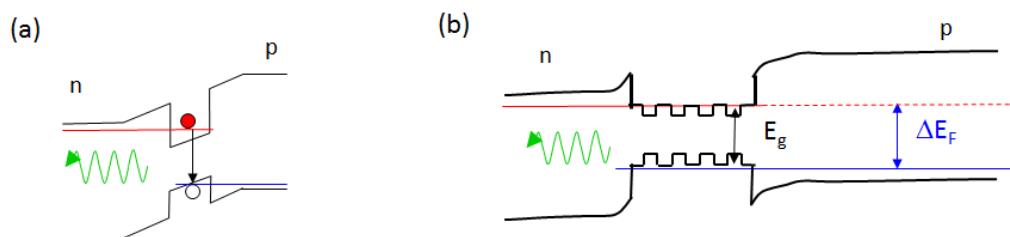


Figure 25.2: (a) Band profile of a quantum well LED. The QW width is chosen to control the colour of emitted light. (b) Band profile of a quantum-well diode laser. The QWs are contained between p and n layers of a wider band gap semiconductor that serves both to inject electrons and holes and to optically confine the emitted light.

25.4 Quantum well lasers

In Lecture 13 of this course you learnt that stimulated emission, which requires the upper level occupation probability exceed that of the lower level, $f_2 > f_1$, can't be achieved with a two level system alone. It can be achieved with a four level system where electrons are supplied to the upper level and removed from the lower level by another source. When $f_2 > f_1$ the net rate of absorption (absorption minus stimulated emission) becomes negative and we have what we call 'gain' in the device, the process whereby the density of photons can be amplified through absorption and stimulated emission.

Laser action can be achieved in a semiconductor diode by embedding the emissive semiconductor between n and p doped layers made from a wider band gap semiconductor. The conduction and valence band of the emissive semiconductor are populated by electrical injection of charges from the external circuit via the wider gap semiconductor. The wider gap material can also provide optical confinement via refractive index contrast if it has n_r lower than that of the emissive layer; this can help to provide the optical cavity that is necessary for lasing. When low current densities are injected, light is emitted from the low band gap layer through spontaneous emission. As injected current is increased, the Fermi level separation in the emissive layer is increased until $f_2 > f_1$. At this point, the photon density in the emitted layer starts to increase. Photon density can be amplified through repeated reflection from the ends of the laser, but only for those photon energies where the

length of the cavity is a whole number of wavelengths. The amplified modes lead to additional peaks in the emission spectrum, on top of the spontaneous emission, and are much narrower. For applications, usually only one mode is required.

In tuning the emission wavelength of a semiconductor diode laser, we have the same challenge as with LEDs: not all band gaps are available in naturally occurring direct gap semiconductors. Although laser emission energy can be tuned within the range of spontaneous emission energies by choice of cavity length, this range is limited to a energies close to the available direct gap semiconductors. As with LEDs, this problem can be addressed using quantum heterostructures. When a quantum well is placed in the lower gap region, photon emission will come from the quantum well, at energies close to the lowest allowed transition of the QW. This energy can be tuned by tuning the well width. When gain is achieved and when the structure is embedded in a cavity, then one or more photon energy that lies within the spontaneous emission spectrum of the QW will be selected and amplified. Two further advantages of QW structures for lasers are (i) that gain is achieved more easily with increased injection, due to the abrupt shape of the joint density of states in QWs, and (ii) the same epitaxial growth method that is used to make quantum wells can be used to grown multilayer stacks of materials of contrasting n_r above and below the emissive layer, resulting in a cavity structure integrated with the device. These so called vertical cavity surface emitting lasers (VCSELs) are relatively straightforward to process and are widely used in communications.

25.5 Main points of the lecture

- The optical properties of semiconductors are exploited in applications in light detection and emission, often based on a semiconductor diode structure.
- In a diode structure such as a p - n junction, applied electrical bias can lead to light emission whilst absorption of light leads to a photocurrent and / or an internal electrical bias.
- Direct or indirect gap semiconductors can be used for solar cells and photodetectors, so long as the electrical properties of optically thick layers are good enough. All photon energies above E_g contribute to the current.
- Only direct gap semiconductors can be used for LEDs. Photon emission comes from energies fairly close to E_g , so single junction LEDs are \sim single colour. White light emission requires pumping a phosphor or using two or more emissive materials at once.
- In semiconductor lasers a diode structure pumps charges into a lower gap, emissive layer and achieve population inversion. QW structures allow a wide range of laser wavelengths to be realised.
- When transparent electrodes are needed, there is a compromise between the conductivity (which affects device efficiency) and optical transmissivity.