CHAPTER 12

Quantum Mechanical Treatment of the Optical Properties

12.1. Introduction

We assumed in the preceding chapter that the electrons behave like particles. This working hypothesis provided us (at least for small frequencies) with equations which reproduce the optical spectra of solids reasonably well. Unfortunately, the treatment had one flaw: For calculation and interpretation of the infrared (IR) absorption we used the concept that electrons in metals are free; whereas the absorption bands in the visible and ultraviolet (UV) spectrum could only be explained by postulating harmonic oscillators. From the classical point of view, however, it is not immediately evident why the electrons should behave freely at low frequencies and respond as if they would be bound at higher frequencies. An unconstrained interpretation for this is only possible by applying wave mechanics. This will be done in the present chapter. We make use of the material presented in Chapters 5 and 6.

12.2. Absorption of Light by Interband and Intraband Transitions

When light (photons) having sufficiently large energy impinges on a solid, the electrons in this crystal are thought to be excited into a higher energy level, provided that unoccupied higher energy levels are available. For these transitions the total momentum of electrons and photons must remain constant (conservation of momentum). For optical frequencies, the momentum of a photon, and thus its wave vector $\mathbf{k}_{\text{phot}} = p/h$ (see (4.7)), is much smaller than that of an electron. Thus, $\mathbf{k}_{\text{phot}}$ is much smaller than the

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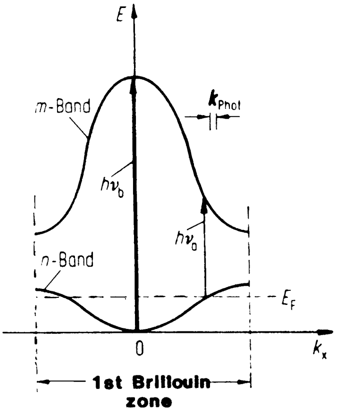

Figure 12.1. Electron bands and direct interband transitions in a reduced zone. (Compare with Fig. 5.4).

diameter of the Brillouin zone (Fig. 12.1). Electron transitions at which **k** remains constant (vertical transitions) are called "**direct interband transitions**". Optical spectra for metals are dominated by direct interband transitions.

Another type of interband transition is possible however. It involves the absorption of a light quantum under participation of a *phonon* (lattice vibration quantum, see Chapter 20). To better understand these "**indirect interband transitions**" (Fig. 12.2) we have to know that a phonon can only absorb very small energies, but is able to absorb a large momentum comparable to that of an electron. During an indirect interband transition, the excess momentum (i.e., the wave number vector) is transferred to the lattice (or is absorbed from the lattice). In other words, a phonon is exchanged with

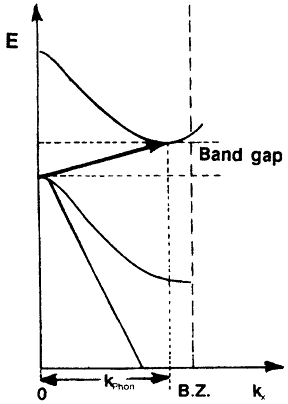

Figure 12.2. Indirect interband transition. (The properties of phonons are explained in Chapter 20).

the solid. Indirect interband transitions may be disregarded for the interpretation of metal spectra, because they are generally weaker than direct transitions by two or three orders of magnitude. They are only observed in the absence of direct transitions. In the case of semiconductors, however, and for the interpretation of photoemission, indirect interband transitions play an important role.

We now make use of the simplified model depicted in Fig. 12.1 and consider direct interband transitions from the n to the m band. The smallest photon energy in this model is absorbed by those electrons whose energy equals the Fermi energy, E_F, i.e., by electrons which already possess the highest possible energy at $T = 0$ K. This energy is marked in Fig. 12.1 by $h\nu_a$. Similarly, $h\nu_b$ is the *largest* energy, which leads to an interband transition from the n to the m band. In the present case, a variety of interband transitions may take place between the energy interval $h\nu_a$ and $h\nu_b$.

Interband transitions are also possible by skipping one or more bands, which occur by involving photons with even larger energies. Thus, a multitude of absorption bands are possible. These bands may partially overlap.

As an example for interband transitions in an actual case, we consider the band diagram for copper. In Fig. 12.3, a portion of Fig. 5.22 is shown, i.e., the pertinent bands around the L-symmetry point are depicted. The interband transition having the smallest possible energy difference is shown to occur between the upper d-band and the Fermi energy. This smallest energy is called the "**threshold energy for interband transitions**" (or the "**fundamental edge**") and is marked in Fig. 12.3 by a solid arrow. We mention in passing that this transition, which can be stimulated by a photon energy of

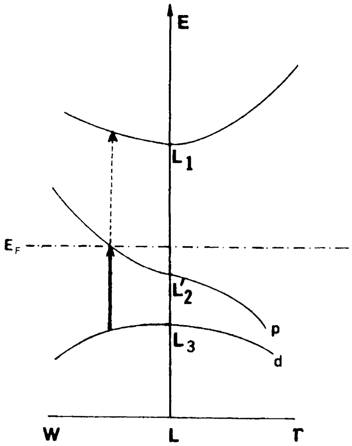

Figure 12.3. Section of the band diagram for copper (schematic). Two pertinent interband transitions are shown with arrows. The smallest possible interband transition occurs from a filled d-state to an unfilled state just above the Fermi energy.

2.2 eV, is responsible for the red color of copper. At slightly higher photon energies, a second transition takes place, which originates *from* the Fermi energy. It is marked in Fig. 12.3 by a dashed arrow. Needless to say, many more transitions are possible. They can take place over a wide range in the Brillouin zone. This will become clearer in Chapter 13 when we return to the optical spectra of materials and their interpretation.

We now turn to another photon-induced absorption mechanism. Under certain conditions photons may excite electrons into a higher energy level *within the same band*. This occurs with participation of a phonon, i.e., a lattice vibration quantum. We call such a transition, appropriately, an **intraband transition** (Fig. 12.4). It should be kept in mind, however, that because of the Pauli principle, electrons can only be excited into *empty* states. Thus, intraband transitions are mainly observed in metals because metals have unfilled electron bands. We recognize, however, that semiconductors with high doping levels or which are kept at high temperatures may likewise have partially filled conduction bands.

*Intra*band transitions are equivalent to the behavior of *free* electrons in classical physics, i.e., to the "classical infrared absorption." Insulators and semiconductors have no classical infrared absorption because their bands are either completely filled or completely empty (except at high temperatures and due to doping). This explains why some insulators (such as glass) are transparent in the visible spectrum. The largest photon energy, E_{max}, that can be absorbed by means of an intraband transition corresponds to an excitation from the lower to the upper band edge, see Fig. 12.4. All energies smaller than E_{max} are absorbed continuously.

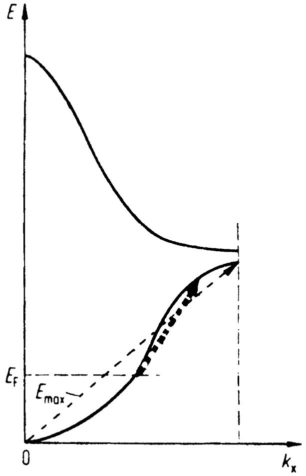

Figure 12.4. Intraband transitions. The largest energy that can be absorbed by intraband transitions is obtained by projecting the arrow marked "E_{max}" onto the energy axis.

In summary, at low photon energies, *intra*band transitions (if possible) are the prevailing absorption mechanism. Intraband transitions are not quantized and occur essentially in metals only. Above a critical light energy *inter*band transitions set in. Only certain energies or energy intervals are absorbed in this case. The onset of this absorption mechanism depends on the energy difference between the bands in question. *Interband* transitions occur in metals as well as in insulators or semiconductors. They are analogous to optical excitations in solids with *bound* electrons. In an intermediate frequency range, interband as well as intraband transitions may take place (see Fig. 11.1).

12.3. Optical Spectra of Materials

Optical spectra are the principal means to obtain experimentally the band gaps and energies for interband transitions. For isolated atoms and ions, the absorption and emission spectra are known to be extremely sharp. Thus, absorption and emission energies for atoms can be determined with great accuracy. The same is basically true for molecular spectra. In contrast to this, the optical spectra of solids are rather broad. This stems from the high particle density in solids and from the interatomic interactions, which split the atomic levels into quasi-continuous bands. The latter extend through the three-dimensional momentum space of a Brillouin zone.

A further factor has to be considered, too. Plain *reflection* spectra of solids are, in general, not too useful for the deduction of transition energies, mainly because R is a rather involved function of ε_1 and ε_2 (see (10.29)). Thus, ε_2 (i.e., absorption) spectra are often utilized instead. The characteristic features in the ε_2-spectra of solids stem from discontinuities in the energy profile of the density of states. However, relatively sharp features in ε_2-spectra are superimposed on noncharacteristic transitions from other parts of the Brillouin zone. In other words, the ε_2-spectra derive their shape from a summation over extended, rather than localized, regions in the Brillouin zone. Modulated optical spectra (see Section 13.1.3) separate the small contributions stemming from points of high symmetry (such as the centers and edges of a Brillouin zone) from the general, much larger background. This will become clearer in the next chapter.

*12.4. Dispersion

To calculate the behavior of electrons in a periodic lattice we used, in Section 4.4, the periodic potential shown in Fig. 4.9. We implied at that time that the potential does not vary with time. This proposition needs to be dropped when the interaction of light with a solid is considered. The alternating electric field of the light which impinges on the solid perturbs the potential field of the lattice periodically. Thus, we need to add to the potential energy a correction term, the so-called perturbation potential, V',

$$V = V_0 + V' \tag{12.1}$$

(V_0 = unperturbed potential energy). It goes without saying that this perturbational potential oscillates with the frequency, ν, of the light.

We consider, as always, plane-polarized light. The momentary value of the field strength, $\mathscr{E}$, is

$$\mathscr{E} = A\cos\omega t, \tag{12.2}$$

where A is the maximal value of the field strength. Then, the perturbation potential (potential energy of the perturbation, or force times displacement x) is

$$V' = e\mathscr{E}x = eA\cos(\omega t)\cdot x. \tag{12.3}$$

Since the potential now varies with time, we need to make use of the time-dependent Schrödinger equation (3.8),

$$\nabla^2\Psi - \frac{2m}{\hbar^2}V\Psi - \frac{2im}{\hbar}\frac{\partial\Psi}{\partial t} = 0, \tag{12.4}$$

which reads, with (12.1) and (12.3),

$$\nabla^2\Psi - \frac{2m}{\hbar^2}(V_0 + eAx\cos\omega t)\Psi - \frac{2im}{\hbar}\frac{\partial\Psi}{\partial t} = 0. \tag{12.5}$$

Our goal is to calculate the optical constants from the polarization, in a similar way as it was done in Sections 11.2, 11.3, and 11.6. We have to note, however, the following: In wave mechanics, the electron is not considered to be a point, but instead is thought to be "smeared" about the space $d\tau$. The locus of the electron in classical mechanics is thus replaced by the probability, $\Psi\Psi^*$, of finding an electron in space (see (2.12)). The classical polarization

$$P = Nex$$

(11.4) is replaced in wave mechanics by

$$P = Ne\int x\Psi\Psi^* d\tau. \tag{12.6}$$

We seek to find a solution Ψ of the *perturbed Schrödinger equation* (12.5) and calculate from that the *norm* $\Psi\Psi^*$; then, by using (12.6) we can calculate the polarization P. The equation for the optical constants thus obtained is given in (12.31).

The detailed calculation of this approach will be given below. The first step is to transform the space- *and* time-dependent Schrödinger equation into a Schrödinger equation that is only space-dependent. The perturbed Schrödinger equation (12.5) is rewritten, using the Euler equation[7] $\cos\rho = \frac{1}{2}(e^{i\rho} + e^{-i\rho})$, as

$$\nabla^2\Psi - \frac{2m}{\hbar^2}V_0\Psi - \frac{2im}{\hbar}\frac{\partial\Psi}{\partial t} = \frac{2m}{\hbar^2}eAx\frac{1}{2}\left[e^{i\omega t} + e^{-i\omega t}\right]\Psi. \tag{12.7}$$

Now, the left side of (12.7) has the form of the unperturbed Schrödinger equation (12.4). We assume that the perturbation is very small. Then, we can insert in the perturbation term (right side of (12.7)) the expression (3.4), and get

$$\Psi_i^0(x,y,z,t) = \psi_i^0(x,y,z)e^{i\omega_i t} \tag{12.8}$$

for the unperturbed *i*th eigenfunction. This yields

$$\nabla^2\Psi - \frac{2m}{\hbar^2}V_0\Psi - \frac{2im}{\hbar}\frac{\partial\Psi}{\partial t} = \frac{m}{\hbar^2}eAx\psi_i^0\left[e^{i(\omega_i+\omega)t} + e^{i(\omega_i-\omega)t}\right]. \tag{12.9}$$

The right-hand side will be contracted to simplify the calculation:

$$\nabla^2\Psi - \frac{2m}{\hbar^2}V_0\Psi - \frac{2im}{\hbar}\frac{\partial\Psi}{\partial t} = \frac{m}{\hbar^2}eAx\psi_i^0 e^{i(\omega_i\pm\omega)t}. \tag{12.10}$$

To solve (12.10), we seek a trial solution which consists of an unperturbed solution and two terms with the angular frequencies $(\omega_i + \omega)$ and $(\omega_i - \omega)$:

$$\Psi = \Psi_i^0 + \psi_+ e^{i(\omega_i+\omega)t} + \psi_- e^{i(\omega_i-\omega)t}. \tag{12.11}$$

This trial solution is condensed as before

$$\Psi = \Psi_i^0 + \psi_\pm e^{i(\omega_i\pm\omega)t}. \tag{12.12}$$

Equation (12.12) is differentiated twice with respect to space and once with respect to time, and the results are inserted into (12.10). This yields

$$\begin{aligned}\underline{\nabla^2\Psi_i^0} + \nabla^2\psi_\pm e^{i(\omega_i\pm\omega)t} \underline{- \frac{2m}{\hbar^2}V_0\Psi_i^0} - \frac{2m}{\hbar}V_0\psi_\pm e^{i(\omega_i\pm\omega)t}\\ \underline{-\frac{2im}{\hbar}\frac{\partial\Psi_i^0}{\partial t}} + \frac{2m}{\hbar}(\omega_i\pm\omega)\psi_\pm e^{i(\omega_i\pm\omega)t} = \frac{m}{\hbar^2}eAx\psi_i^0 e^{i(\omega_i\pm\omega)t}.\end{aligned} \tag{12.13}$$

The underlined terms in (12.13) vanish according to (12.4) if Ψ_i^0 is the solution to the unperturbed Schrödinger equation. In the remaining terms, the exponential factors can be cancelled, which yields, with $\hbar\omega = h\nu = E$,

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[7] See Appendix 2.

$$\nabla^2\psi_\pm + \frac{2m}{\hbar^2}\psi_\pm(E_i \pm h\nu - V_0) = \frac{m}{\hbar^2}eAx\psi_i^0. \tag{12.14}$$

In writing (12.14) we have reached our first goal, i.e., to obtain a time-independent, perturbed Schrödinger equation. We solve this equation with a procedure that is common in perturbation theory. We develop the function $x\psi_i^0$ (the right side of (12.14)) in a series of eigenfunctions

$$x\psi_i^0 = a_{1i}\psi_1^0 + a_{2i}\psi_2^0 + \cdots + a_{ni}\psi_n^0 + \cdots = \sum a_{ni}\psi_n^0. \tag{12.15}$$

multiply (12.15) by ψ_n^{0*}, and integrate over the entire space $d\tau$. Then, due to $\int\psi\psi^*\,d\tau = 1$ (3.15) and $\int\psi_m\psi_n^*\,d\tau = 0$ (for $m \neq n$), we obtain

$$\int x\psi_i^0\psi_n^{0*}d\tau = a_{1i}\underbrace{\int \psi_1^0\psi_n^{0*}d\tau}_{0} \underset{0}{+\cdots+} a_{ni}\, l \underbrace{\int \psi_n^0\psi_n^{0*}d\tau}_{1} + \cdots = a_{ni}. \tag{12.16}$$

Similarly, we develop the function $\psi_\pm$ in a series of eigenfunctions

$$\psi_\pm = \sum b_{\pm n}\psi_n^0. \tag{12.17}$$

Inserting (12.15) and (12.17) into (12.14) yields

$$\sum b_{\pm n}\left(\underline{\nabla^2\psi_n^0} + \frac{2m}{\hbar^2}E_i\psi_n^0 \pm \frac{2m}{\hbar^2}h\nu\psi_n^0 - \underline{\frac{2m}{\hbar^2}V_0\psi_n^0}\right) = \frac{m}{\hbar^2}eA\sum a_{ni}\psi_n^0. \tag{12.18}$$

Rewriting the unperturbed time-independent Schrödinger equation (3.1) yields

$$\nabla^2\psi_n^0 - \frac{2m}{\hbar^2}V_0\psi_n^0 = -\frac{2m}{\hbar^2}E_n\psi_n^0. \tag{12.19}$$

Equation (12.19) shows that the underlined terms in (12.18) may be equated to the right side of (12.19). Thus, (12.18) may be rewritten as

$$\frac{2m}{\hbar^2}\sum \psi_n^0 b_{\pm n}(E_i - E_n \pm h\nu) = \frac{2m}{\hbar^2}\frac{eA}{2}\sum \psi_n^0 a_{ni}. \tag{12.20}$$

Comparing the coefficients in (12.20) yields, with

$$E_i - E_n = E_{ni} = h\nu_{ni}, \tag{12.21}$$

the following expression:

$$b_{\pm n} = \frac{eAa_{ni}}{2(E_i - E_n \pm h\nu)} = \frac{eAa_{ni}}{2h(\nu_{ni} \pm \nu)}. \tag{12.22}$$

Now we are able to determine the functions ψ_+ and ψ_- by using (12.22) and (12.17). We insert these functions together with (3.4) into the trial solution

(12.11) and obtain a solution for the time-dependent, perturbed Schrödinger equation (12.5)

$$\Psi = \psi_i^0 e^{i\omega_i t} + \frac{1}{2h}\sum eAa_{ni}\psi_n^0\left[\frac{e^{i(\omega_i+\omega)t}}{\nu_{ni}+\nu} + \frac{e^{i(\omega_i-\omega)t}}{\nu_{ni}-\nu}\right], \tag{12.23}$$

and thus

$$\Psi^* = \psi_i^{0*} e^{-i\omega_i t} + \frac{1}{2h}\sum eAa_{ni}^*\psi_n^{0*}\left[\frac{e^{-i(\omega_i+\omega)t}}{\nu_{ni}+\nu} + \frac{e^{-i(\omega_i-\omega)t}}{\nu_{ni}-\nu}\right]. \tag{12.24}$$

In order to write the polarization (12.6) we have to form the product $\Psi\Psi^*$. As can be seen from (12.23) and (12.24), this calculation yields time-dependent as well as time-independent terms. The latter ones need not be considered here, since they provided only an additive constant to the polarization (light scattering). The time-dependent part of the norm $\Psi\Psi^*$ is

$$\begin{aligned}\Psi\Psi^* = \frac{eA}{2h}\Bigg[&\sum a_{ni}^*\psi_n^{0*}\psi_i^0\left(\underbrace{\frac{e^{-i\omega t}}{\nu_{ni}+\nu} + \frac{e^{i\omega t}}{\nu_{ni}-\nu}}_{Q}\right)\\ &+\sum a_{ni}\psi_n^0\psi_i^{0*}\left(\underbrace{\frac{e^{i\omega t}}{\nu_{ni}+\nu} + \frac{e^{-i\omega t}}{\nu_{ni}-\nu}}_{R}\right)\Bigg].\end{aligned} \tag{12.25}$$

To simplify, we abbreviate the terms in parentheses by Q and R, respectively. The polarization (12.6) is then

$$P = \frac{Ne^2A}{2h}\left[\sum a_{ni}^*Q\underbrace{\int x\psi_n^{0*}\psi_i^0 d\tau}_{a_{ni}} + \sum a_{ni}R\underbrace{\int x\psi_n^0\psi_i^{0*} d\tau}_{a_{ni}^*}\right], \tag{12.26}$$

which reduces, with (12.16),

$$\int x\psi_i^0\psi_n^{0*}\,d\tau = a_{ni}$$

and

$$a_{ni}\cdot a_{ni}^* = |a_{ni}|^2 \equiv a_{ni}^2 \tag{12.27}$$

to

$$P = \frac{Ne^2A}{2h}\sum a_{ni}^2(Q+R)\ . \tag{12.28}$$

A numerical calculation applying the above-quoted Euler equation yields

$$Q + R = \frac{2\nu_{ni} e^{-i\omega t}}{\nu_{ni}^2 - \nu^2} + \frac{2\nu_{ni} e^{i\omega t}}{\nu_{ni}^2 - \nu^2} = \frac{4\nu_{ni} \cos \omega t}{\nu_{ni}^2 - \nu^2}, \tag{12.29}$$

which gives, with (12.2),

$$P = \frac{Ne^2 \mathscr{E}}{\pi \hbar} \sum a_{ni}^2 \frac{\nu_{ni}}{\nu_{ni}^2 - \nu^2}. \tag{12.30}$$

Finally, we make use of (10.13) and (11.5) and obtain with, (12.30),

$$\boxed{\varepsilon_1 = n^2 - k^2 = 1 + \frac{Ne^2}{\varepsilon_0 \pi \hbar} \sum a_{ni}^2 \frac{\nu_{ni}}{\nu_{ni}^2 - \nu^2}.} \tag{12.31}$$

Equation (12.31) is the sought-after relation for the optical properties of solids, obtained by wave mechanics. It is similar in form to the classical dispersion equation (11.51). A comparison of classical and quantum mechanical results might be helpful to better understand the meaning of the empirically introduced oscillator strength, f_i. We obtain

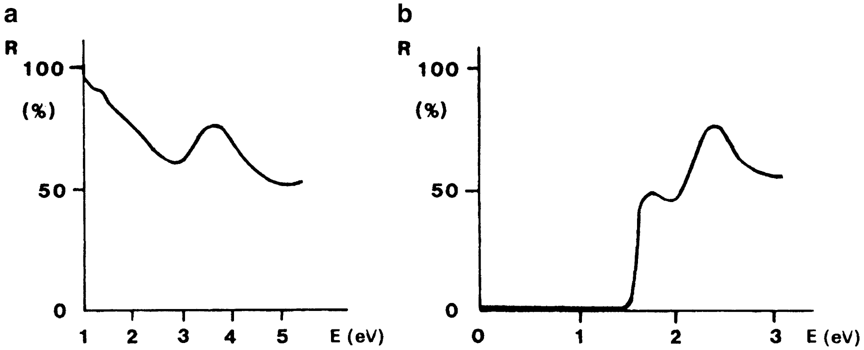
$$\boxed{f_i = \frac{4\pi m}{\hbar} a_{ni}^2 \nu_{ni}.} \tag{12.32}$$

We know that $h\nu_{ni}$ is that energy which an electron absorbs when it is excited from the n-band into the i-band (e.g., the m-band). Thus, the resonance frequency, ν_{oi}, of the ith oscillator introduced in Section 11.7.4 is replaced in wave mechanics by a frequency, ν_{ni}, that corresponds to an allowed electron transition from the nth into the ith band. Furthermore, we see from (12.16) that a_{ni} is proportional to the probability of an electron transition from the nth into the ith band. The oscillator strength, f_i, is, therefore, essentially the probability for a certain interband transition.

Problems

1. What information can be gained from the quantum mechanical treatment of the optical properties of metals which cannot be obtained by the classical treatment?
2. What can we conclude from the fact that the spectral reflectivity of a metal (e.g., copper) has "structure"?
3. Below the reflection spectra for two materials A and B are given.
   a. What type of material belongs to reflection spectrum A, what type to B? (Justify). Note the scale difference! Some reflection takes place below 1.5 eV in material B!
   b. For which colors are these (bulk) materials transparent?
   c. What is the approximate threshold energy for interband transitions for these materials?

d. For which of the materials would you expect intraband transitions in the infrared region? (Justify.)
e. Why do these intraband transitions occur in this region?



4. What is the smallest possible energy for interband transitions for aluminum? (*Hint*: Consult the band diagram in Fig. 5.21.)

5. Are intraband transitions possible in semiconductors at high temperatures?