Chapter 1

Introduction

A very long time ago, light and matter were one [1]. At present, we use light to study matter in order to understand more about its properties and behaviour.

Depending on the wavelength of the light, different solid-state excitations can be probed, and a variety of information can be obtained. This is schematically illustrated in Fig. 1.1, where the absorption coefficient of a typical doped semiconductor is plotted as a function of energy. In the lowest energy region [2], free carriers (electrons in the conduction band or holes in the valence band) can absorb radiation, resulting in intraband transitions. Plasmons (collective excitations of these conduction electrons) can be observed in the range of 0.02 to 0.1 eV [3]. Ionic or partially ionic solids can absorb infrared (IR) radiation at specific resonances corresponding to the lattice vibrations (the so-called phonons). In the visible region, the sharp rise in absorption is the fundamental absorption edge, also called the conductivity gap: electrons are excited from the highest occupied band to the lowest unoccupied band (interband transitions). Just below the conductivity gap there are excitons, which are bound electron-hole pairs. At much higher energies, at X-ray frequencies, electrons can be excited from the core levels.

Since the density of free carriers is very low in semiconductors, their contribution is small and limited to the microwave (low energy) part of the electromagnetic spectrum [2]. For metals, the free-carrier contribution is much larger and extends to higher frequency, while the conductivity gap is absent. Conversely, for insulators, free-carrier absorption is absent and the conductivity gap shifts toward higher frequency.

However, which excitations one can observe using certain experimental techniques is not just determined by the energy of the light used. Symmetry considerations and selection rules also play an important role, and so does the intensity of the light. At the relatively low intensities of natural light, the optical properties of materials are essentially independent of the intensity of illumination [4]. In this case we operate in the linear optical regime. However, when the illumination is sufficiently intense, the optical properties start to depend on the intensity of the
light and nonlinear optics (NLO) comes into play, with its own selection rules and criteria, opening up a completely new and fascinating field of optical phenomena and applications.

In order to create these nonlinear effects, very strong electromagnetic \((e.m.)\) fields are needed, fields typically produced by lasers. In fact, the first observation of second-harmonic generation by Franken \textit{et al.} \cite{Franken}, which is marked as the beginning of nonlinear optics, took place shortly after the demonstration of the first working laser by Maiman in 1960. Within a few years, Bloembergen and co-workers developed the full theory describing the propagation of \(e.m.\) waves through NLO active media \cite{Bloembergen1, Bloembergen2, Bloembergen3}.

In this thesis we focus on the visible part of the spectrum, and especially on the excitons and interband transitions, using light intensities in the nonlinear optical regime. Both subjects, excitons and nonlinear optics, will be introduced further below.

### 1.1 Excitons

As already mentioned above, an exciton is a bound electron-hole pair. A more sophisticated definition is given by Dexter and Knox \cite{Dexter}: "an exciton is a quantum of electronic excitation energy traveling in a periodic structure, whose motion is characterized by a wave vector." This is a clear and concise description of the idealized exciton, at least to those who already know all about it. In this section excitons
of several kinds will be discussed, in the hope that at the end, the concept of an exciton is clear to everyone.

We first introduce some experimental observations related to excitons. In Fig. 1.2 the absorption spectrum of a thin film of solid xenon is shown. The band gap of solid xenon is found to be 9.28 eV [10]. The absorption lines below 9.28 eV are due to excitons. A sample of gaseous xenon would display two sharp absorption lines. Their positions are marked by the vertical dashes in Fig. 1.2. For this material, the solid exhibits absorption characteristics reminiscent of those of the gas phase [9]. This is not always the case, as it is shown in Fig. 1.3, where the absorption spectrum of Cu$_2$O is presented [11]. The sharp absorption lines are due to excitons, but in this case there is no resemblance to the absorption characteristic of either copper or oxygen [9]. Hence, the presence and the kind of excitons both depend on the characteristics of the material.

![Fig. 1.2. Absorption spectrum of solid xenon, after Baldini [10]. The vertical dashes indicate the energy of the resonances in the free atom.](image)

Let us take a closer look at the example of xenon. In the case of a molecular solid, we may visualize the solid as a periodic array of atoms (molecules). The interaction between the atoms (molecules) is very weak. If we consider an exciton as an electron and a hole which are held together by their electrostatic attraction then, in the atomic picture of the solid, the electron and hole will be on one site [9]. This is depicted in the upper part of Fig. 1.4(a). Such a strongly bound exciton is known as a **Frenkel exciton**. The excitation spectrum of such excitons is the result of on-site excitations and can therefore resemble the excitation spectrum of the gas phase. When the binding energy of an exciton is defined as the energy difference
between the conductivity gap and the exciton energy, then a Frenkel exciton has a binding energy of the order of eV’s. Frenkel excitons are electron-hole correlated states, lying well within the conductivity gap as is schematically shown in the lower part of Fig. 1.4(a). Although in a tightly bound exciton the excitation is localized on or near a single atom, the pair may be anywhere in the crystal. A Frenkel exciton is essentially an excited state of a single atom, but the excitation can hop (not at random but in a regular and coherent motion) from one atom to another by virtue of the coupling between neighbours [12]. Like all excitations in a periodic system, also the states of Frenkels excitons have the form of propagating waves, characterized by a wave vector $k$. In the next chapter this will be considered in more detail. Frenkel excitons are found in many molecular crystals, for instance in the $\pi$ to $\pi^*$ transitions in aromatic molecules such as anthracene [13]. In this thesis we will study the Frenkel excitons in solid $C_{60}$ (Chapter 4). Other examples are the excitations of localized $d$ electrons, such as in nickel oxide.

When the interaction between the atoms (molecules) is stronger than for a molecular solid, the electron bands will broaden. As a result, an electron and a hole can be on nearest-neighbour sites, while still forming a bound pair, i.e., an exciton (Fig. 1.4(b)). Such excitons are called charge-transfer excitons [14]. Charge-transfer excitons have a reduced binding energy compared to Frenkel excitons. Their binding energy is of the order of 0.5 eV. Excitons in alkali halides and other strongly ionic insulators involve such a charge transfer to nearest neighbours [14]. We have observed and studied charge-transfer excitons in NiO (Chapter 5).

In semiconductors, the interaction between the atoms is stronger than for ionic insulators. The bands are, therefore, even more broadened. In this case, the electron
and hole can be separated by many interatomic spacings, as shown in Fig. 1.4(c) [9]. Such a weakly bound exciton is called a Wannier exciton [9]. The binding energies of Wannier excitons are in the order of tens of meV’s. Note that these excitons lie very close to the conductivity gap, however, they are still excitons: electron-hole pairs carrying no charge. They propagate through the lattice together, transporting energy but no charge [9]. The example shown in Fig. 1.3, the absorption spectrum of Cu$_2$O, displays Wannier excitons. We have studied the Wannier excitons in CuCl (Chapter 6).

In the case of an interband transition (Fig. 1.4(d)), an electron is excited across the conductivity gap. The electron and hole are moving freely, independently in the entire electron-hole continuum, resulting in two independent particles carrying charge.

Since an exciton is a two-particle system, it is much more complicated to calculate its energy levels and wave functions than for the corresponding electron case [14]. However, in the limit, where the electron and hole are separated by many interatomic spacings, the effective mass approximation can be used, and this simplifies the problem enormously [14]. Using the effective mass approximation, the
Chapter 1. Introduction

Fig. 1.5. (a) An electron-hole pair excitation in the scheme of valence and conduction band. (b) A corresponding pair excitation in the scheme of the exciton picture for a direct gap semiconductor, after Klingshirn [15].

Coulomb interaction between the electron and the hole (see Fig. 1.5(a)) leads to a hydrogen-like problem with a Coulomb potential term $-e^2/(4\pi\varepsilon_0|\mathbf{r}_e - \mathbf{r}_h|)$ [15]. This approach works especially well for the Wannier excitons in semiconductors. They form, to a good approximation, a hydrogen-like series of states below the gap, as shown schematically in Fig. 1.5(b). The dispersion relation of excitons can be expressed as [15]:

$$E_{\text{ex}}(n, K) = E_g - R_y^* \frac{1}{m^2} + \frac{\hbar^2 K^2}{2M}$$  \hspace{1cm} (1.1)

where $n = 1, 2, ..., \infty$. The energy $E_g$ is the band gap energy $\epsilon_e(0)-\epsilon_v(0)$. The kinetic term involves the effective mass of the exciton, $M = m_e^* + m_h^*$, and the total wave vector of the exciton, $K = k_e + k_h$. The exciton binding energy contains an effective Rydberg energy:

$$R_y^* = 13.6 \text{eV} \frac{\mu}{e^2}$$  \hspace{1cm} (1.2)

where $\mu$ is the reduced mass of the electron and hole, $\mu^{-1} = (m_e^*)^{-1} + (m_h^*)^{-1}$, and $\epsilon$ is the dielectric constant of the medium in which these particles move. The radius of the exciton equals the Bohr radius of the H-atom, $a_B^H$, again modified by $\epsilon$ and $\mu$ [15]:

$$a_{B}^{ex} = a_B^H \frac{\epsilon}{\mu}$$  \hspace{1cm} (1.3)

These simple expressions show the dependence of the radius and binding energy of a Wannier exciton on the type of material through the dielectric constant $\epsilon$. For example [14], InSb has $\mu = 0.015$ and $\epsilon = 18$. This results in an exciton binding energy of 0.6 meV and an exciton Bohr radius of 600 Å.
1.2 Nonlinear Optics

The induced polarization $\mathbf{P}$ describes the optical response of a medium. In the linear optical regime, i.e., for relatively weak applied $e.m.$ fields, the relation between $\mathbf{P}$ and the macroscopic electric field $\mathbf{E}$ is linear:

$$\mathbf{P} = \chi \cdot \mathbf{E}$$  \hspace{1cm} (1.4)

where the susceptibility $\chi$ is a material parameter, and a second rank tensor.

In the nonlinear optical regime, the response function $\chi$ now becomes $\mathbf{E}$-dependent, and the induced polarization can be written as an expansion of the electric field [16, 17]:

$$\mathbf{P} = \chi^{(1)} \cdot \mathbf{E} + \chi^{(2)} : \mathbf{E} \mathbf{E} + \chi^{(3)} : \mathbf{E} \mathbf{E} \mathbf{E} + ...$$  \hspace{1cm} (1.5)

$$\equiv \mathbf{P}^{(1)} + \mathbf{P}^{(2)} + \mathbf{P}^{(3)} + ...$$

where $\chi^{(n)}$ is the $n$-th order susceptibility tensor of rank $n+1$. Hence, in a nonlinear optical experiment, the light "retransmitted" from the material contains not only the fundamental (input) frequency, but also the double frequency (second-harmonic generation), the triple frequency (third-harmonic generation), and so on. Eq. 1.5 holds within the electric-dipole approximation. This means that all $\chi$'s are local properties [18]: $\chi(\mathbf{r}, t) = \chi(t)$, $\chi(\mathbf{k}, \omega) = \chi(\omega)$.

As an example of a nonlinear optical interaction, we consider the process of second-harmonic generation (SHG), closely following the derivations of Boyd [19]. The monochromatic input electric field (the laser beam) is represented as:

$$\mathbf{E}(t) = \mathbf{E} e^{-i\omega t} + c.c.$$  \hspace{1cm} (1.6)

where $c.c.$ stands for the complex conjugate, and $\mathbf{E}$ is the amplitude at the fundamental frequency. The nonlinear polarization created in a crystal with a nonzero $\chi^{(2)}$ is given as:

$$\mathbf{P}^{(2)}(t) = 2 \chi^{(2)} \mathbf{E} \mathbf{E}^* + (\chi^{(2)} \mathbf{E}^2 e^{-i2\omega t} + c.c.)$$  \hspace{1cm} (1.7)

where we have substituted Eq. 1.6 into the $\mathbf{P}^{(2)}$ part of Eq. 1.5. This second-order polarization consists of a contribution at zero frequency (the first term) and a contribution at frequency $2\omega$ (the second term). The first contribution leads to a process known as optical rectification in which a static electric field is created within the nonlinear crystal. The second contribution leads to the generation of radiation at the second-harmonic frequency.

It is convenient to express the result of Eq. 1.7 using the notation:

$$\mathbf{P}(t) = \sum_{n} \mathbf{P}(\omega_n) e^{-i\omega_n t}$$  \hspace{1cm} (1.8)
where the summation extends over positive (incoming) and negative (outgoing) frequencies $\omega_n$. The complex amplitudes of the nonlinear polarization are hence given by:

$$P(0) = 2\chi^{(2)} E E^*$$

$$P(2\omega) = \chi^{(2)} E^2$$

The $n$-th order polarization can be written as [4]:

$$P^{(n)}(\omega) = \sum_{\omega_1,\omega_2,\ldots,\omega_n} \chi^{(n)}(-\omega;\omega_1,\omega_2,\ldots,\omega_n) : E(\omega_1) E(\omega_2) \ldots E(\omega_n)$$  \hspace{1cm} (1.10)

where $\sum_{\omega_1,\omega_2,\ldots,\omega_n}$ denotes a summation over all distinct sets of frequencies $(\omega_1, \omega_2, \ldots, \omega_n)$ which satisfy $\omega = \omega_1 + \omega_2 + \ldots + \omega_n$. The most common optical processes of low order are given in Table 1.1.

<table>
<thead>
<tr>
<th>$\chi^{(n)}(-\omega; \omega_1, \ldots, \omega_n)$</th>
<th>Process</th>
<th>Order n</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-\omega; \omega$</td>
<td>Linear absorption/emission and refractive index</td>
<td>1</td>
</tr>
<tr>
<td>$0; \omega_1, -\omega$</td>
<td>Optical rectification (optically-induced d.c. field)</td>
<td>2</td>
</tr>
<tr>
<td>$-\omega; 0, \omega$</td>
<td>Pockels effect (linear electrooptic effect)</td>
<td>2</td>
</tr>
<tr>
<td>$-2\omega; \omega, \omega$</td>
<td>Second-harmonic generation (SHG)</td>
<td>2</td>
</tr>
<tr>
<td>$-(\omega_1 + \omega_2); \omega_1, \omega_2$</td>
<td>Sum-frequency generation (SFG)</td>
<td>2</td>
</tr>
<tr>
<td>$-(\omega_1 - \omega_2); \omega_1, \omega_2$</td>
<td>Difference-frequency generation (DFG) Parametric amplification and oscillation</td>
<td>2</td>
</tr>
<tr>
<td>$-\omega; 0, 0, \omega$</td>
<td>d.c. Kerr effect (quadratic electrooptic effect)</td>
<td>3</td>
</tr>
<tr>
<td>$-2\omega; 0, \omega, \omega$</td>
<td>Electric field induced SHG (EFISH)</td>
<td>3</td>
</tr>
<tr>
<td>$-3\omega; \omega, \omega, \omega$</td>
<td>Third-harmonic generation (THG)</td>
<td>3</td>
</tr>
<tr>
<td>$-\omega; \omega, -\omega, \omega$</td>
<td>Degenerate four-wave mixing (DFWM)</td>
<td>3</td>
</tr>
<tr>
<td>$-\omega; -\omega_2, \omega_2, \omega_1$ or $-\omega; -\omega, \omega_1$</td>
<td>Two-photon absorption (TPA)/ionization / emission</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 1.1: Optical processes described by $\chi^{(n)}(-\omega; \omega_1, \ldots, \omega_n)$.

Before discussing possible applications of nonlinear optics, we should point out that $\chi^{(n)}$ vanishes for even-$n$ in media with inversion symmetry\(^1\). Let us consider

---

\(^1\)As Koopmans pointed out [16], an "average" inversion symmetry is sufficient, i.e., averaged over a length scale smaller than the wavelength of the radiation applied.
for the moment a second-order process. If the medium has inversion symmetry, the incoming fields $E(\omega)$ and $-E(\omega)$ must induce dipoles of opposite direction, $P(2\omega)$ and $-P(2\omega)$, respectively [20]. However, Eq. 1.7 demonstrates that this is impossible unless $\chi^{(2)}=0$, indicating that SHG (or any even-order process) is forbidden. Only when the inversion symmetry is broken, such as at a surface or an interface, an even-order $\chi^{(n)}$ is no longer forbidden. Consequently, even-order optical processes are highly surface and interface specific. This is all considered within the electric-dipole approximation, i.e., the electric fields are assumed to be spatially homogeneous. In the next chapter we will see in more detail that, when the gradient of the electric field is taken into account, higher order contributions of electric-quadrupole and magnetic-dipole character originating from the bulk are possible.

During the past, decade experiments have demonstrated the versatility of SHG as an analytical tool to monitor processes at surfaces and interfaces in different environments. Shen has given several reviews on this subject [20, 21, 22]. A few examples to illustrate the versatility are the following. For instance, Rasing [23] used optical SHG to study the technologically important buried semiconductor-metal (GaAs-Au) and magnetic multilayer interfaces of M/Co/M, with M = Cu or Au. Buck [24] showed that in-situ monitoring of thin-film formation by SHG can differentiate between the reaction at the interface and the subsequent film growth. The chemical vapor deposition of polyamic acid is presented as an example [24]. SHG has also been used in investigations of electrode-electrolyte interfaces during electrochemical reactions. In Richmond’s paper [25] one finds a review of this field.

Apart from its interface sensitive properties, SHG has many more specific properties. To that end Fiebig et al. [26] found that antiferromagnetic 180° domains of bulk Cr$_2$O$_3$ can be observed directly in SHG transmission, leading to the first photographs ever taken of antiferromagnetic domains$^2$ [29]. Also Kirilyuk et al. showed that nonlinear magneto-optical imaging of ferromagnetic domains reveals new information that is absent in the linear equivalent [30].

In this thesis, second-harmonic generation is used as a spectroscopic tool. Since SHG has strict selection rules, which can be different from the linear optics selection rules, it is a powerful tool to investigate certain specific excitations, in particular excitons, as we will show.

### 1.3 Scope of this thesis

In this thesis several materials are studied in spectroscopic second-harmonic generation (SHG) and sum-frequency generation (SFG) experiments. The experiments show that SHG and SFG are selective tools to probe all different kinds of excitons,

$^2$As noted by Muthukumar et al. [27] domain walls can be observed optically in certain antiferromagnets when they are associated with crystal distortions. See Roth [28].
even when their energy is close to the conductivity gap. The latter appears to give
no resonant enhancement in a SHG or SFG experiment.

In Chapter 2 a phenomenological theory is presented on optical excitations and
SHG, and in Chapter 3 the experimental set-up for the SHG and SFG experiments
is described.

In Chapter 4 the Frenkel excitons in C$_{60}$ are studied in SHG and SFG experi-
ments. Temperature-dependent SHG shows that the propagation of the lowest
Frenkel exciton occurs via a charge-transfer mediated mechanism. Moreover, a
strong enhancement of the second-harmonic resonance intensity is found for de-
creasing temperature.

The second-harmonic response of NiO is studied in Chapter 5, since NiO has
several d-d Frenkel excitons within the conductivity gap as well as charge-transfer
excitons just below the conductivity gap. Temperature- and polarization-dependent
SHG and SFG experiments, performed on NiO films of different thicknesses, will be
presented. The influence of the magnetic structure on the SHG is also investigated
and discussed.

The spectroscopic SHG study of CuCl, investigating the Wannier excitons and
the interband transition, is presented in Chapter 6. Since the excitonic and interband
transitions in CuCl are already known from literature, a direct comparison of the
SHG arising from these different excitations is possible.

In Chapter 7 the results of the SHG from the various kinds of excitons will be
summarized. A few ideas of why excitons might exhibit more second-harmonic in-
tensity than interband transitions are discussed at a phenomenological level. With
this picture in mind, a new interpretation on the SHG data of Si measured by Daum
et al. [31] is presented.

References

(1961).
1918 (1962).