Chapter 2

Optical spectroscopy and SHG

2.1 Optical electron-hole spectrum

As we have seen in Chapter 1, the optical spectrum of solid-state materials contains many possible excitations. One kind of excitation, typically a few eV above the ground state, is the exciton, which involves a bound state of an electron and hole pair. Since the exciton is a charge neutral excitation, one of the best ways of studying it is by optical spectroscopy. In the optical spectra of solid-state materials one also observes interband transitions across the conductivity gap, which can also be described in terms of electron-hole pairs, but now free, moving as independent particles. In this section we consider the nature of excitons showing up in optical spectra and compare them to the interband transitions. The theoretical level adopted is elementary, because our aim is to explain some basic facts. More information can be found in a pioneering publication [1] and in a number of text books [2, 3, 4, 5].

2.1.1 Oscillator strength

Collective excitations in solids can be described as quantized oscillators and the corresponding transition probability as an oscillator strength. The simplest way to look at a crystal is as a periodic array of identical atoms, each of which still has its own atomic electronic states, leading however to crystal energy bands because of the lattice periodicity. To get a feeling, let us consider two atoms which have a filled s-orbital and empty p-orbitals. The ground state of this system can be depicted schematically as follows:

```
p  ——  ——

s  ⚫⚫⚫  ⚫⚫⚫
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In the next picture both atoms are far apart (in the periodic array of atoms) and an electron is excited from the s-orbital of one atom to the p-orbital of the "far-away"
The conductivity gap is defined by the energy needed for such an excitation ($E_{\text{gap}}$). $E_{\text{gap}}$ can be determined from Photonemission (PES) and Inverse-photonemission (IPES) spectra in which the ionization energy ($E_I$) and the electron affinity ($E_A$) is measured, respectively. The total Coulomb energy for the ground state of these two atoms is $2U$, where $U$ is the on-site electron-electron Coulomb repulsion energy. The excited state, depicted above, has a total Coulomb energy of $3U$. Hence, the conductivity gap is $E_{\text{gap}} = E_I - E_A = U + \Delta E$, where $\Delta E = \epsilon_p - \epsilon_s$, the difference in the energy between the p- and s-orbital on an atom.

In the next picture an optical excitation, localized on one atom is shown, i.e., an on-site excitation:

We have already seen that the ground state has a total Coulomb energy of $2U$. For this case the excited state has a total Coulomb energy of $2U$ as well, so that the excitation energy is $E_{\text{loc}}^{\text{exc}} = \Delta E$.

If we consider an excitation to a nearest-neighbour atom, the following situation can be depicted:

In this case the nearest neighbour Coulomb repulsion energy ($V$) has to be taken into account as well. The total Coulomb energy for the ground state is $2U + 4V$, and for the excited state $3U + 3V$. Hence, the energy for a nearest-neighbour (n-n) excitation is $E_{\text{exc}}^{n-n} = \Delta E + U - V$.

Sometimes it is convenient to speak of the energy of a localized excitation compared with a delocalized excitation (across the conductivity gap). We see from the above that the localized excitation is $U$ lower in energy, and we can redefine $U$ as the on-site Coulomb attraction between the electron and the hole. The various excitation energies relative to the ground state energy are then defined as follows: $E_{\text{exc}}^{\text{loc}} = \Delta E - U$, $E_{\text{exc}}^{n-n} = \Delta E - V$, and $E_{\text{exc}}^{\text{deloc}} = \Delta E$. In general, these definitions are used throughout this thesis.
Below, we consider the two extreme cases. The first case is a localized excitation, where the electron-hole pair will be strongly bound and close together spatially. This Frenkel exciton case is valid when $U \gg V$ (i.e., the on-site Coulomb attraction between the electron and the hole is much larger than the Coulomb repulsion between the electrons of neighbouring atoms), and $U-V \gg t$, where $t$ is the one-electron or one-hole hopping integral between neighbouring atoms (as we will see in the next section). The other extreme case is when $U = 0$, and the electron and hole will move freely and independently. In this delocalized case the excitation corresponds to an interband transition into the electron-hole continuum (across the conductivity gap).

Back to the first case ($U \gg V$ and $U-V \gg t$) where interatomic coupling can be neglected. By using Bloch's theorem for wave functions in a periodic lattice, the wave function of the excited state (exciton final state) can be expressed in the following form [3]:

$$\Psi_{FS, k}^\text{exc}(r) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} e^{i\mathbf{k} \cdot \mathbf{R}_i} \phi_{p_i}^\text{exc} (r - \mathbf{R}_i) \phi_{s_i}^\text{GS} (r - \mathbf{R}_i),$$

(2.1)

where $\mathbf{k}$ is the wave vector of an excitation wave, $\hbar\mathbf{k}$ is the momentum of the associated exciton, and $\mathbf{R}_i$ is the position vector of atom $i$. Since the excitation can be on any atom, we have to sum over all $N$ atoms in the system.

In a second quantization scheme, the following Hamiltonian describes the optical excitation of the electron from the s-level to the p-level on same site assuming an infinite wave length of the light:

$$H_1 = M \sum_{i=1}^{N} c_{p_i}^+ c_{s_i},$$

(2.2)

where $c_{p_i}^+$ and $c_{s_i}$ are the creation and annihilation operators of a p-electron state and s-electron state at the site $i$, respectively, $H_1$ describes the interaction with electromagnetic radiation, and $M = M_i = \langle c_{p_i}^+ c_{s_i} | H_1 | c_{p_i}^+ c_{s_i} \rangle$ is the atomic transition matrix element. Using Eq. (2.1) and Eq. (2.2) the transition probability aside from the energy conservation part for the exciton excitation can be calculated:

$$| \langle \Psi_{FS, k}^\text{exc} | H_1 | \Psi_{GS, k} \rangle |^2 = N M^2 \delta(\mathbf{k}).$$

(2.3)

Here, we use the optical selection rule, $\Delta \mathbf{k} = 0$, because of momentum conservation in conjunction with the momentum of the photon being negligible compared to the momentum of the crystal. From Eq. (2.3) we see that the transition probability for the localized exciton state is proportional to the total number of atoms.

If we now consider the second extreme case, where $U=0$, the electron and the hole are no longer bound to each other, but they propagate independently, each having its own wave vector. This is rather different from the exciton, which has a
single $k$-vector. The final state (FS) of the free electron and hole for a certain $k$ and $k'$ can be expressed as:

$$
\Psi_{FS,kk'}(\mathbf{r}) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} e^{ik\mathbf{R}_i} e^{ik'\mathbf{R}_j} \phi_p^{e}(\mathbf{r} - \mathbf{R}_i) \phi_p^{h}(\mathbf{r} - \mathbf{R}_j).
$$

(2.4)

The transition probability for this excitation is:

$$
| < \Psi_{FS,kk'}^{\text{e-h}} | H_1 | \Psi_{\text{GS}} > |^2 = M^2 \delta(k + k').
$$

(2.5)

Hence, because of the on-site Hamiltonian of Eq. (2.2), an excitation is only possible if it occurs on the same atom ($\mathbf{R}_i = \mathbf{R}_j$) and again because of momentum conservation $k + k' = 0$. Moreover, the free electron-hole excitation probability is a factor of $1/N$ smaller than the probability of the exciton excitation (compare Eq. (2.3) and Eq. (2.5)). This is because in Eq. (2.5) the transition probability is calculated for a specific $k$ and $k'$. The sum rule in optics implies summation of Eq. (2.5) over all $k$-values. This summation gives an additional factor $N$ in the free electron-hole case, so that the exciton and the free electron-hole pair have the same total transition probability.

### 2.1.2 Energy dispersion

One way of looking at the features in an optical spectrum due to excitonic transitions and free electron-hole excitations, is by considering their energy dispersion and their corresponding density of states.

The density of states represents the number of states in the energy interval from $E$ to $E + dE$ [6]. If we know the specific dispersion relation $E(k)$ and its inverse $k(E)$, it is possible to calculate the density of states $\rho(E)dE$ [6]:

$$
\rho(E)dE = \rho[k(E)] \frac{1}{|\nabla_k E(k)|} dE.
$$

(2.6)

Let us first consider the case for $U=0$. In Fig. 2.1(b) we show a simplified picture of the energy bands for a case where the conduction band and the valence band have the same dispersion, i.e., they are parallel over the entire $k$-range. The corresponding density of states is shown in Fig. 2.1(a). Since all optical excitations have to be excitations at $\Delta k = 0$, they all occur at the same energy, $E_o$. Therefore, for this particular case, the optical absorption spectrum will show a very sharp peak at $E_o$ (Fig. 2.1(c)).

A more realistic tight-binding-like energy dispersion is shown in Fig. 2.2(b) along with the corresponding density of states (Fig. 2.2(a)). In this case the energy bands exhibit a strong dispersion. Optical transitions are possible over a broad energy range. The optical absorption spectrum will therefore show a broad structure, spread
over all possible energies above a threshold energy, $E_0$ (Fig. 2.2(c)). If the total area underneath the curve would be the same as in Fig. 2.1(c), due to conservation of spectral weight, the intensity of the transitions will decrease considerably.

Up to now, we have considered a one-electron band (conduction band) and a one-hole band (valence band), and their corresponding density of states. In order to obtain the density of states of an electron-hole pair, the convolution of the electron density of states ($\rho_e$) and the hole density of states ($\rho_h$) has to be taken. If we assume that $\rho_e$ and $\rho_h$ both have a bandwidth $W$, the density of states of the electron-hole pair will have a bandwidth of $2W$. Keep in mind, that this $2W$ electron-hole band contains all possible excitations, also the $\Delta k \neq 0$ transitions.

Let us return to the strongly bound exciton states, thus the case that $U \gg V$ and $U-V \gg t$, and consider their corresponding electron-hole pair density of states. Due to the strong attraction (large $U$) between the electron and the hole localized on one
atom, the excitonic state is pulled below the electron-hole continuum (Fig. 2.3(a)). Since there are $N$ atoms, there are $N$ such states, which together form the exciton band. In an optical experiment the $\Delta k=0$ selection rule applies, and therefore, only the $\Delta k=0$ part of the exciton band will be observed (Fig. 2.3(b)).

A strongly bound exciton, i.e., a Frenkel exciton, can propagate via dipole-dipole interaction. This is usually the case when the exciton is due to an electric-dipole allowed transition from the ground state. A molecule (or atom) in an allowed excited state has an effective dipole moment. Dipole-dipole interaction can induce an upward transition in the second (nearest-neighbour) molecule, de-exciting the first [2]; hence the exciton can move. In Chapter 4 we study a Frenkel exciton due to an electric-dipole forbidden transition and we will see that an exciton can also propagate via a charge-transfer-mediated mechanism. This exciton propagation mechanism (shown schematically in Fig. 11 of Chapter 4) involves an electron hopping to its nearest-neighbour with a one-electron hopping integral ($t_e$), while the hole follows the electron with a one-hole hopping integral ($t_h$). As a result the entire exciton has moved one site. The intermediate state, in which the electron and hole are on nearest-neighbours, is at an energy $U - V$. The effective exciton hopping integral is given from perturbation theory by:

$$T_{\text{exciton}} = \frac{2t_et_h}{U - V}. \quad (2.7)$$

Hence, the propagation of the exciton by this mechanism is accompanied by mixing of the exciton $k=0$ states with states from the free electron-hole continuum. This mixing will give rise to some intensity in the electron-hole continuum. In an optical experiment the $k=0$ character is probed, hence not only an exciton peak will be observed but in addition some spectral weight will be present at the interband
transition region (as schematically indicated in Fig. 2.3(b)). One could say that the intensity detected in the energy range of the electron-hole continuum is a measure for the optical extent of the electron-hole pair in the excitonic state. Since the spectral weight is conserved in linear optics, this process reduces the intensity of the exciton peak.

A broadening of the exciton peak in the optical spectrum will occur due to processes such as impurity scattering and atomic rotations. These processes destroy $k$ as a good quantum number, leading to a breakdown of the $\Delta k=0$ selection rule. This means that in an optical spectrum not only the $\Delta k=0$ transition will be observed, but also transitions with other $k$-vectors. In Chapter 4 and Chapter 6, i.e., for the case of C$_{60}$ and CuCl, we discuss the broadening of the observed exciton resonance due to molecular rotations and acoustic phonon scattering, respectively.

It should be mentioned that the situation is more complicated when the valence and conduction bands have the same dispersion over a broad $k$-range, as depicted in Fig. 2.1(b). In this case it is more difficult to distinguish, on the basis of the optical spectrum, whether a resonance is due to a direct interband transition or to an exciton, lying close to the conductivity gap. Fig. 2.1(c) and Fig. 2.3(b) show that both cases give rise to a sharp resonance. This point will be raised in Chapter 7, where the optical spectrum of Si will be discussed in connection with the coherence of the processes involved.

### 2.1.3 Coherence and relaxation processes

As we have mentioned above, scattering processes can give rise to the breakdown of the $\Delta k=0$ selection rule. Another way to visualize their influence is the following: we consider an electronic excitation. The induced polarizations, $P_i$, at all different sites in the solid are initially all in phase with each other; they are coherent. The coherence is maintained until scattering processes change their phase and thereby destroy their coherence. The characteristic time in which the fraction of polarization still in phase with the "overall" induced polarization of the system is reduced by a factor of $e^{-1}$ is called the dephasing time $T_2$. Scattering processes which destroy the phase include:

1. impurity or lattice defect scattering
2. phonon scattering
3. scattering with other electronic excitations, e.g., elastic and inelastic exciton-exciton or exciton-electron scattering
4. recombination.

The last process occurs if there are no other phase-destroying processes; finally the phase will be lost in the recombination process, either radiatively or non-radiatively. This process has a characteristic lifetime $T_1$, called the population relaxation time.
The first and third of the above mentioned scattering processes are especially important for free electron-hole pairs (in ordered structures), while the significance of these processes can be considerably reduced for a strongly bound exciton. One reason for this argument is that a free electron and a free hole are charged particles. They will, therefore, be easier susceptible to scattering processes in general, than an exciton which is a charge neutral particle.

Impurity or lattice defect scattering, which limits $T_2$, might change the energy of the state or the direction or magnitude of its $k$ vector as well. However, for limiting $T_2$, it is already sufficient that the phase correlation is destroyed. Phonon scattering and electronic scattering increase significantly with increasing lattice temperature and excitation intensity, respectively. In addition to the processes mentioned above, the lifetime of an electron-hole pair is determined by intraband relaxation. This process is sometimes described by a time constant $T_3$ [6]. It is particular importance when the excess energy of the created pair is considerably larger than $k_BT$.

The essential point of the arguments presented above is that a free electron-hole excitation is considerably more susceptible to loss of its coherence than a bound exciton. It is therefore not surprising to see, that, for example, in the optical absorption spectrum of GaAs, the resonance at the onset of the absorption is due to an exciton and not to an interband transition [2, 7]. Before considering the implications on an optical second-harmonic generation (SHG) spectrum, we would like to make a few comments on the typical time scales for $T_1$ and $T_2$, and the broadening of the resonance due to relaxation processes.

$T_1$ is generally in the $ns$ regime for direct gap semiconductors and reaches values in the $\mu s$ or even $ms$ range for indirect gap materials [6], whereas $T_2$ typically lies in the $ps$ range.

To get a feeling for the broadening of the resonance, we consider a two-level atom. If we assume that all two-level systems in the ensemble share the same resonance frequency, $\omega_{ba}$, the ensemble is homogeneously affected by incoherent interactions. Examples of such processes are collisions, radiative decay determined by $T_1$, and coupling between rotational, vibrational and electronic excitations. These processes, which determine the dephasing lifetime $T_2$ as we saw above, cause a broadening of the resonance. This has to be distinguished from dephasing due to inhomogeneous effects. In the latter case the transition frequency, $\omega_{ba}$, varies from atom to atom, since the local environment of two atoms may be different, for instance because a given atom lies close to a defect or an impurity and this perturbs its energy [8]. In a pump-probe experiment, like a photon-echo experiment, the influence of homogeneous and inhomogeneous broadening can be studied separately.

Related to the population relaxation time $T_1$ (or longitudinal relaxation time) and the dephasing relaxation time $T_2$, is the pure dephasing relaxation time $T_2^*$ (or transverse relaxation time) which can be defined as follows:
2.2. SHG and SFG

2.1.4 Optical SHG spectrum

A second-harmonic generation (SHG) process is a coherent process. This means, that we will only measure a SHG signal if the first excited state \((n')\), and the second excited state \((n'')\), have the same phase as at the beginning of the excitation, i.e., the excited states should not dephase during the SHG process. A picture of this excitation scheme is shown in Fig. 2.4. We consider only the case where \(n'\) and \(n''\) are one-exciton states. The transition matrix element for a SHG process can be written as:

\[
T = \sum_{n', n'' \neq g} < \Psi_g \mid H_1 \mid \Psi_{n'} > < \Psi_{n'} \mid H_1 \mid \Psi_{n''} > < \Psi_{n''} \mid H_1 \mid \Psi_g >, \tag{2.9}
\]

where \(H_1\) described the interaction with electromagnetic radiation. If we calculate each transition matrix element in Eq. (2.9) in the same way as we did in the beginning of this chapter (Eq. (2.3) and Eq. (2.5)), we obtain:

\[
< \Psi_{n'} \mid H_1 \mid \Psi_g > = \sqrt{N} M_1, \\
< \Psi_{n'} \mid H_1 \mid \Psi_{n''} > = M_2, \\
< \Psi_g \mid H_1 \mid \Psi_{n''} > = \sqrt{N} M_3. \tag{2.10}
\]

Substituting Eq. (2.10) in Eq. (2.9) and squaring the latter gives the transition probability for a SHG process: \(N^2 (M_1^2 \cdot M_2^2 \cdot M_3^2)\). Hence, the second-harmonic intensity is proportional to the square of the number of coherent atoms or molecules \((N_{coh}^2)\) involved. Above we discussed that the \(T_2\)-like dephasing processes due to impurities, dislocations, rotations and vibrations of the atoms, reduce the periodicity and the coherence of the system. These dephasing processes directly affect the second-harmonic intensity in a SHG experiment, since the second-harmonic intensity depends quadratically on the number of coherent atoms, i.e., atoms still in phase with the ground state throughout the SHG process. Moreover, the interband transitions, which give rise to free electron-hole pairs, are much more susceptible to dephasing processes than a bound exciton. All of the above indicates that the excitonic states will be preferentially seen in a SHG experiment.

2.2 SHG and SFG

This section is based on works by Guyot-Sionnest [9, 10, 11], Koopmans [12, 13], Shen [14, 15], and van Hasselt [16].
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Fig. 2.4. Schematic representation of the states appearing in Eq. 2.9 for a second-order optical process. The dark circle denotes an electron and the open circle a hole.

2.2.1 Basic concepts

In the Introduction (Chapter 1) we have seen that, since optical SHG is an even-order process, it is forbidden in a medium with inversion symmetry, but it is allowed at an interface, where space inversion symmetry is broken. This holds within the electric-dipole approximation, in which the induced polarization $P$ at a certain position $r$ depends only on the local electric field at that position.

Beyond the electric-dipole approximation, we obtain an effective nonlinear polarization $P_{\text{eff}}^{(2)}(2\omega)$ which consists of a series of multipole terms [9]:

$$P_{\text{eff}}^{(2)}(2\omega) = P^{(2)}(2\omega) - \nabla \hat{\chi}^{(Q)}(2\omega) + \frac{c}{i2\omega} \nabla \times M^{(2)}(2\omega) + \ldots \quad (2.11)$$

where $P$, $\hat{Q}$ and $M$ stands for the electric-dipole polarization, electric-quadrupole polarization and magnetic-dipole magnetization, respectively.

By taking all second-harmonic sources in $P_{\text{eff}}^{(2)}$ up to the first order in the spatial derivative, these three terms can be written as [9]:

$$P^{(2)}(2\omega) = \hat{\chi}^{(D)}: E(\omega) E(\omega),$$
$$\hat{Q}^{(2)}(2\omega) = \hat{\chi}^{(Q)}: E(\omega) E(\omega),$$
$$M^{(2)}(2\omega) = \hat{\chi}^{(M)}: E(\omega) E(\omega),$$

with $\chi^{(Q)}_{ijkl} = \chi^{(Q)}_{P,ijkl} - 2\chi^{(Q)}_{Q,ijkl}$ [12]. For a second-order process $\hat{\chi}^{(D)}$ and $\hat{\chi}^{(M)}$ are third rank tensors describing the electric-dipole and magnetic contributions, whereas $\hat{\chi}^{(Q)}$ (and so also $\hat{\chi}^{(Q)}_P$ and $\hat{\chi}^{(Q)}_Q$) is a fourth rank tensor describing the quadrupole contributions.

The tensor $\hat{\chi}^{(Q)}_P$ describes processes for which the induced electric-dipole polarization $P^{(2)}$ is proportional to the gradient of the fundamental field, whereas $\hat{\chi}^{(Q)}_Q$ describes processes for which the generalized polarization $P_{\text{eff}}^{(2)}$ is proportional to the gradient of the induced quadrupole polarization [12]. The contribution from the tensor $\hat{\chi}^{(Q)}_P$ can be divided in electric-quadrupole (EQ) and magnetic-dipole (MD) contributions due to $\hat{\chi}^{(EQ)}_P$ and $\hat{\chi}^{(MD)}_P$, respectively [13].
For a medium with inversion symmetry both in space and in time, i.e., a non-magnetic material, the second-order magnetization \( M^{(2)}(2\omega) \) vanishes. The effective second-harmonic polarization is then given by:

\[
P_{\text{eff}}^{(2)} = \hat{\chi}^{(D)}: \mathbf{E} \mathbf{E} + \hat{\chi}^{(Q)}: \mathbf{E} \nabla \mathbf{E} - (\nabla \hat{\chi}^{(Q)}): \mathbf{E} \mathbf{E}. \tag{2.13}
\]

In the bulk of a centrosymmetric and homogeneous medium \( \hat{\chi}^{(D)} \) and \( \nabla \hat{\chi}^{(Q)} \) vanish, so that the effective bulk SHG polarization can be written as:

\[
P_{B}^{(2)} = \hat{\chi}^{(Q)}: \mathbf{E} \nabla_{B} \mathbf{E}, \tag{2.14}
\]

where \( \nabla_{B} \) denotes the field gradient in the bulk.

At an interface the term \( \nabla \hat{\chi}^{(Q)} \) has to be included \([16, 13, 12]\). Therefore, the effective surface (interface) polarization is given by:

\[
P_{S}^{(2)} = \hat{\chi}^{(D)}: \mathbf{E} \mathbf{E} + \hat{\chi}^{(Q)}: \mathbf{E} \nabla_{S} \mathbf{E} - \nabla \hat{\chi}^{(Q)}: \mathbf{E} \mathbf{E}, \tag{2.15}
\]

where \( \nabla_{S} \) refers to the field gradient across the interface. Since \( \hat{\chi}^{(Q)} \) is present in the bulk expression 2.14 as well as in the surface expression 2.15, it is difficult to separate surface contributions from bulk contributions. In the next section we consider this problem in more detail.

### 2.2.2 Surface and bulk contributions

An experimental way to obtain the surface information is by modifying the surface, and subsequently observe the induced second-harmonic changes \([9, 10]\). However, it is not always possible to modify the surface, and even when this is possible, one still needs to be careful with interpreting the observed changes. For instance, the second-harmonic intensity from a metallic surface drops by an order of magnitude when it is exposed to oxidizing adsorbates \([15, 17]\). But, as Koopmans et al. \([13]\) pointed out in an example of almost equal surface and bulk second-harmonic susceptibilities, quenching of the surface signal reduces the second-harmonic intensity by a factor of 10. This calls for another separation method, like the one developed by Koopmans \([12, 18, 19]\), outlined briefly below.

For isotropic media the bulk SHG is described by four nonzero tensor components: \( \chi_{2}^{B} \equiv \chi_{xx}^{(Q)}, \chi_{3}^{B} \equiv \chi_{xy}^{(Q)}, \chi_{4}^{B} \equiv \chi_{x}^{(Q)}, \) and \( \chi_{1}^{B} \equiv \chi_{xxxx}^{(Q)} \), where \( \chi_{1}^{B} \) is related to the other three by: \( \chi_{1}^{B} = \chi_{2}^{B} + \chi_{3}^{B} + \chi_{4}^{B} \).

The nonlocal bulk polarization written in the vector notation is then given by:\(^{1}\)

\[
P^{B} = \chi_{2}^{B} \mathbf{E} (\nabla \cdot \mathbf{E}) + \frac{1}{2} \chi_{3}^{B} \nabla (\mathbf{E} \cdot \mathbf{E}) + \chi_{4}^{B} (\mathbf{E} \cdot \nabla) \mathbf{E}. \tag{2.16}
\]

---

\(^{1}\)In the original work of Bloembergen \([20]\) the parameters \( \beta, \gamma, \) and \( \delta \) are used. Koopmans \([12]\) introduced \( \chi_{2}^{B} = \beta, \chi_{3}^{B} = 2\gamma, \) and \( \chi_{4}^{B} = (\delta - \beta - 2\gamma) \). Sipe et al. \([21]\) defined, for convenience, a parameter \( \delta^{0} = (\delta - \beta - 2\gamma) \).
Since the divergence of the macroscopic electric field in the bulk is zero, the $\chi_2^B$ term does not contribute. If only a single plane wave is present inside the medium, also the $\chi_4^B$ term will not contribute, since $\mathbf{E} \cdot \mathbf{k} = 0$ for a transverse $\text{e.m.}$ wave. In that case only the $\chi_3^B$ contribution will be nonzero. However, it is known that the $\chi_3^B$ component is indistinguishable from a certain combination of surface contributions [21, 9]. Koopmans pointed out that in the thin film geometry, reflection from the lower interface causes a second plane wave, hence allowing $\chi_4^B$ contributions.

When a thickness dependent SHG measurement is carried out in different polarization geometries, $\chi_4^B$ is separable. By exploiting relations between $\chi_4^B$ and $\chi_3^B$, a full separation of all surface and bulk tensor components is possible. For the case of $\text{C}_60$, group theoretical arguments were used to find that $\chi_4^B = -\chi_3^B$ for the quadrupole excitation of magnetic-dipole character, i.e., the magnetic-dipole allowed transition at $\hbar\omega = 1.8 \text{ eV}$ [18]. All tensor components have been resolved for this particular resonance. Wilk et al. [22] used the same separation method for another resonance in $\text{C}_60$ ($\hbar\omega \simeq 1.17 \text{ eV}$) and found the surface and bulk contributions for this case.

### 2.2.3 Symmetry

A tensor describing the physical properties of a crystalline medium is invariant with respect to the point group of the crystal. This is the so-called Neumann principle [23, 24, 25]. If we consider the expression for the second-order sum-frequency polarization:

$$ P_i^{(2)}(\omega_1 + \omega_2) = \sum_{j,k} \chi^{(2)}_{ijk} E_j(\omega_1) E_k(\omega_2), \tag{2.17} $$

each component of the tensor $\chi^{(2)}$ has to be invariant under any symmetry operation of the point group. This can reduce the number of independent and nonzero components significantly. The point group of a crystal reflects a geometrical property and this symmetry determines what is called the *external tensor symmetry*. In addition, there are symmetry relations of non-geometrical nature due to, for example, thermodynamical properties or the experimental set-up, which show up in relations involving permutation of the tensorial indices. This is the so-called *internal symmetry* [26] or *intrinsic permutation symmetry* [27].

For example, a general third rank tensor $\chi^{(2)}$ in Eq. (2.17) has 27 independent elements (e.g., for a sum-frequency generation (SFG) process). However, for a SHG process, the order of the last two indices is arbitrary, implying that the second-harmonic susceptibility tensor has a maximum of 18 independent elements. This number can be reduced further by the point group symmetry.

A typical internal symmetry is for instance the *overall permutation symmetry*, which is valid when all of the optical frequencies occurring in the expression for the susceptibility are far from the transition frequencies of the nonlinear medium. In
other words, the medium is transparent at all relevant frequencies [27]. The overall permutation symmetry states that all of the frequency arguments of the nonlinear susceptibility can be freely interchanged, as long as the corresponding Cartesian indices are interchanged simultaneously [28]. For instance,
\[
\chi^{(2)}_{ijk}(-\omega_3; \omega_1, \omega_2) = \chi^{(2)}_{jki}(\omega_1; \omega_2, -\omega_3) = \chi^{(2)}_{kji}(\omega_2; \omega_1, -\omega_3).
\]
(2.18)

When the optical frequencies \(\omega_i\) involved in the nonlinear optical interactions are much smaller than the lowest resonance frequency of the material under study, the nonlinear susceptibility is essentially independent of frequency [28]. This is called the Kleinman symmetry condition and means for the example used above that:
\[
\chi^{(2)}_{ijk}(-\omega_3; \omega_1, \omega_2) = \chi^{(2)}_{jki}(-\omega_3; \omega_1, \omega_2) = \chi^{(2)}_{kji}(-\omega_3; \omega_1, \omega_2).
\]
(2.19)

### 2.2.4 Microscopic description

The classical anharmonic oscillator can provide a good description of the nonlinear susceptibility, when all of the optical frequencies are considerably smaller than the lowest electronic resonance frequency of the material under study [28]. A better description of the nonlinear susceptibility, especially for cases where at least one resonance is involved, can be obtained using quantum-mechanical theory, in particular the density matrix formalism. The derivation of the microscopic expressions for the resulting nonlinear response can be found in various books [14, 28, 27]. The expressions consist of a sum of several terms of the form [25]:
\[
\chi^{(2)}_{ijk}(-\omega_3; \omega_1, \omega_2) = -N \frac{e^3}{\hbar} \sum_{n', n'' \neq g} \left[ \frac{<g|\gamma_n|n''> <n''|\gamma_j|n'|<n'|\gamma_k|g>}{(\omega_3 - \omega_{n'g} + i, n''_g)(\omega_{12} - \omega_{n'g} + i, n''_g)} + \ldots \right] \rho_g^{(0)}.
\]
(2.20)

where \(n'\) and \(n''\) range over the full set of eigenstates of the localized system and \(\omega_{12}\) stands for \(\omega_1\) or \(\omega_2\). The quantities \(\omega_{n'g}\) and \(\omega_{n''g}\) are the energy difference and line widths for transitions between different quantum states of the material system, respectively; \(\rho_g^{(0)}\) denotes the population of state \(|g\rangle\), the initial state which at \(T=0\) is the ground state. In this expression, the material is broken into small units (typically molecules) and each of these units is treated in the electric-dipole approximation. \(N\) represents the volumetric density of the units. The matrix elements represent a sequence of transitions from ground state \(|g\rangle\) to an available intermediate state \(|n'\rangle\) induced by the first pump photon \(\hbar \omega_1\), followed by a second transition to another intermediate state \(|n''\rangle\) induced by the second pump photon \(\hbar \omega_2\). Next, a photon at sum-frequency \(\hbar (\omega_1 + \omega_2)\) is emitted upon a transition returning to the ground state \(|g\rangle\) of the system [25]. The transitions may occur either on- or off-resonance. Note that in this entire process, momentum has to be conserved in every step, and energy must be conserved between the initial and final states [6].
A resonant enhancement is expected whenever the frequency of any of the transitions \((g \rightarrow n')\), \((n' \rightarrow n'')\) or \((n'' \rightarrow g)\) matches either the fundamental frequency \((\omega_1\) or \(\omega_2)\) or the sum-frequency \((\omega_3 = \omega_1 + \omega_2)\). The nonlinear susceptibility is obtained by performing a summation over all possible initial and intermediate states.

### 2.2.5 Spectroscopic SHG and SFG

With the use of a tunable laser, SHG can be employed for (surface) spectroscopy. From section 2.2.4 it is clear that when either one of the frequencies, \(\omega\) or \(2\omega\), is close to a material excitation, the nonlinear susceptibility \(\chi^{(2)}\) should exhibit a resonant enhancement. SHG, however, has two drawbacks. First, it is often not evident whether the observed resonance occurs at the fundamental frequency or at the second-harmonic frequency. Secondly, to achieve monolayer sensitivity, a high-gain photodetector, such as a photomultiplier, is needed. This limits spectroscopic study to electronic transitions in the visible. Sometimes infrared vibrational spectra are more useful, for instance to study adsorbed molecules selectively, but no appropriate photomultiplier is available in the infrared. Sum-frequency generation (SFG) offers a solution to both problems.

In particular, the photomultiplier problem can be overcome by performing infrared visible SFG [15]. If \(\omega_1\) is chosen in the infrared and \(\omega_2\) in the visible range, \(\omega_1 + \omega_2\) will be in the near-infrared or visible and can be detected by a photomultiplier. Moreover, \(\omega_1\) can excite vibrational transitions so that the SFG has the selective detection of molecules through their characteristic vibrational transitions. An example of a surface vibrational spectroscopic study by SFG is the work done by Guyot-Sionnest et al. [29]. They studied the molecular orientation of pentadecanoic acid on a water surface at different surface densities. An example of spectroscopic SHG and SFG is the study of a buried \(\text{CaF}_2/\text{Si}(111)\) interface through 50 nm of \(\text{CaF}_2\) done by Heinz et al. [30]. Since the dispersion of the sum-frequency signal matches the second-harmonic signal, when plotted as a function of the dye-laser frequency, their observed resonance must occur at the fundamental frequency of the dye laser, rather than at the second-harmonic frequency. In this way they determined that the band gap of the buried interface is 2.4 eV by assigning the main spectral feature (at 2.4 eV) to direct transitions at the two-dimensional band gap. In addition they observed a weaker feature at 2.25 eV, which they tentatively assigned to a two-dimensional exciton.

Other examples of spectroscopic SHG and SFG are the study of oxidized, clean and hydrogen terminated singular \(\text{Si}(001)\) samples by Daum and co-workers [31] (discussed in section 7.3), and the study of a buried \(\text{ZnSe}/\text{GaAs}(001)\) interface done by Yeganeh et al. [32].

In section 2.2.3 we have seen that, due to the intrinsic permutation symmetry, the nonlinear susceptibility for SHG has fewer independent isotropic tensor elements.
than the more general process of SFG. Hence, by a proper choice of pump polarization and crystal orientation, additional information concerning tensor elements can be obtained when SHG and SFG spectra are compared.

In the next chapter our SHG and SFG experimental set-up will be described. We have performed SFG experiments, in order to resolve whether a particular resonance occurs at the fundamental frequency or at the second-harmonic frequency. For the case of $C_{60}$ we found that the fundamental frequency was resonant (Chapter 4), whereas NiO turned out to be resonant at the second-harmonic frequency (Chapter 5).

References


