Pulse Propagation in Nonlinear Media and Photonic Crystals

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Abstract

The present thesis is devoted to theoretical studies of pulse propagation of light through linear and nonlinear media, and of light-induced nuclear dynamics.

The first part of the thesis addresses propagation of light pulses in linear periodical media - photonic crystals. The main accent was put on studies of the angular properties of two qualitatively different types of photonic crystals: holographic photonic crystals, and impurity band based photonic crystals. The anisotropy of band structure, group velocity and pulse delay with respect to the light polarization are analyzed.

In the second part of the thesis a strict theory of nonlinear propagation of a few strong interacting light beams is presented. The key idea of this approach is a self-consistent solution of the nonlinear wave equation and the density matrix equations of the material. This technique is applied to studies of dynamics of cavityless lasing generated by ultra-fast multi-photon excitation. It is shown that interaction of co- and counter-propagating pulses of amplified spontaneous emission (ASE) affects the dynamics and efficiency of nonlinear conversion. Our dynamical theory allows to explain the asymmetric spectral properties of the forward and backward ASE pulses, which were observed in recent experiment with different dye molecules. It is shown that the ASE spectral profile changes drastically when the pump intensity approaches the threshold level. The effect of the temporal self-pulsation of ASE is studied in detail.

The third part of the thesis is devoted to light-induced nuclear dynamics. Time- and frequency-resolved X-ray spectroscopy of molecules driven by strong and coherent infrared (IR) pulses shows that the phase of the IR field strongly influences the trajectory of the nuclear wave packet, and hence, the X-ray spectrum. Such a dependence arises due to the interference of one (X-ray) and two-photon (X-ray + IR) excitation channels. The phase of the light influences the dynamics also when the Rabi frequency is the vibrational frequency, breaking down the rotating-wave approximation. The probe X-ray spectra are also sensitive to the delay time, the duration, and the shape of the pulses. The evolution of the nuclear wave packets in the dissociative core-excited state affects the dynamics of resonant Auger scattering from fixed-in-space molecules. One of the important dynamical effects is the atomic-like resonance which experiences electronic Doppler shift. We predict that the scattering of the Auger electrons by nearby atoms leads to new Doppler shifted resonances. These extra resonances show sharp maxima in the bond directions, which makes them very promising as probes for local molecular structure using energy and angular resolved electron-ion coincidence techniques. Our theory provides prediction of several new effects, but also results that are in good agreement with the available experimental data.
Preface

Over the last decade, the development of nanotechnologies together with the availability of ultrashort strong laser pulses has stimulated a rapid development of new experimental techniques making it possible to analyze different physical, chemical, and biological processes in unprecedented detail. This fast progress in the precise experimental tools requires an adequate development of theoretical language and methods which are combined with simulation techniques.

During my work on the present thesis I was involved in development of theory, coding and applications in order to predict and explain different aspects of the dynamics of light-matter interaction. The research has mostly started from analytical models, which allow to get insight into the physics of the processes, and which gradually includes numerical methods to make our models applicable to the real experiments. Different physical problems related to different equations need various computational methods, like the transfer matrix technique for photonic crystals, and finite-difference technique for the time-dependent solution of the Schrödinger, density matrix and Maxwell’s equations. Ab initio quantum-chemical methods are used for calculations of microscopic molecular properties.

However, even a brilliant theory is just a theory until it is proved by experiment. Having this in mind, we were always looking for connection of our theory with available experimental data. Most of our theoretical studies were in fact initiated by experimental results in order to give a clear physical explanation of the observed phenomena. Part of my studies addresses, new experiments and some of these predictions have already been verified by recent measurements.

Applications of the present studies cover a rather wide range of modern science and technology: from ultra-fast optical connections and time-resolved pump-probe spectroscopy to cavityless lasing and femtochemistry.

The work in this thesis has been carried out at the Laboratory of Theoretical Chemistry, Department of Biotechnology, Royal Institute of Technology, Stockholm, Sweden during four years: 2002 - 2006.
List of papers included in the thesis


List of related papers not included in the thesis


**Comments on my contributions to the papers**

- I was responsible for theory, calculations, writing and editing of manuscript in Papers I, II, V, VII, VIII, IX and X.
- I participated in discussions and theoretical work, and I was responsible for calculations in Papers III, IV, VI and XI.
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Chapter 1

Introduction

“Reality is merely an illusion, albeit a very persistent one.”
Albert Einstein

From the Newton’s time until the middle of the 1800’s, the particle picture of light was the generally accepted theory. Light was considered to be a stream of tiny particles. However, in the late 1800’s Maxwell created the Theory of Electromagnetism, which replaced the particle picture. Many phenomena associated with light, such as refraction, diffraction and interference, were successfully explained by the new wave picture, which expressed that visible light is just one particular type of electromagnetic radiation. Other types of radiation outside the visible spectrum with wavelengths longer than red light were also encompassed in the theory, like, for example, infrared (heat), microwave and radio waves, also radiation with wavelengths shorter than blue light, like ultraviolet radiation, X- and γ -rays.

However, in the early 20th century experiments showed many phenomena which could only be explained by a particle picture of light. For example, experiments such as blackbody radiation, the photoelectric effect, and Compton scattering could be explained using the photon picture of light, but not with the wave picture. But, as was mentioned, experiments on diffraction and interference need the wave picture in order to be explained. Thus, light as it is now understood, has attributes of both particles and waves. Both pictures are needed in different circumstances. Light has a dual nature: in some cases it behaves as waves, and in other cases it behaves as photons. This wave-particle duality is the basis of the quantum theory of light, and has some profound physical and philosophical implications which are still being debated today.

The present thesis deals with light pulse propagation through linear and nonlinear media,
as well as with light-induced dynamics of matter. Many scientific and technological problems are related to propagation of rather weak light which does not change the properties of the medium. For example, this is the case of light propagation through waveguides and photonic crystals. In the case of a photonic crystal, or periodical dielectric medium with the periodicity of the order of the wave length of the light, low intense light does not affect the susceptibilities of the material. All phenomena appear due to diffraction and interference of the scattered waves and can be described in the framework of Maxwell’s equations with a periodic boundary condition (see Sec.2). However, in case when strong coherent radiation interacts with nonlinear media, we face the problem of solving Maxwell’s equations coupled to the wave equation of the medium (see Sec.3). In this case, the interaction of the electromagnetic wave with different matter waves, like electronic, spin or vibrational wave packets, becomes very important (see Sec.4).

1.1 Pulses in linear periodical media

In 1913, the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg explained why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence. They introduced the so-called Bragg’s law of diffration, which is an interesting property of periodical structures that has attracted much attention ever since. There were many detailed analyzes of the phenomena of propagation of optical waves in crystals and layered structures before Eli Yablonovitch introduced the term “Photonic Crystal” (PC) in 1987. The pioneer works of Yablonovitch and John gave birth to a whole new area of optical physics and technology which deals with molding the flow of light in PCs. PCs manipulate optical or microwave photons in very similar ways as when X-rays propagate through crystals or as semiconductors influence the motion of electrons. Many ideas and terms in PC physics, such as photonic band gap, defect mode, impurity band, were borrowed from solid state physics.

Nowadays, PCs are discussed widely as a basis for high-speed computers of the next generation. Progress has already been made towards replacing the slow copper connections in computers with ultra-fast optical interconnects. Then photons, rather than electrons, will pass signals from board to board, from chip to chip and even from one part of a chip to another. In the future, it will be possible to implement optical manipulation, signal processing and electronic circuitry all in one chip. In this field, to get shorter operation time one needs to use a shorter signal, or light pulse.

The band structure of PCs defines the main properties of light propagating through a device. Propagation of short pulses through PCs looks different in many aspects compared...
to propagation of monochromatic continuum wave light. The main reason for this is that a short light pulse is a superposition of many harmonics according to the uncertainty relation:

\[ \Delta \omega \geq \frac{1}{\tau}. \]  \hspace{1cm} (1.1)

These harmonics correspond to different parts of the band structure, and therefore propagate with different velocities. This results in an undesirable effect, namely, the distortion of the pulse, often called dispersion.

One important application of PCs is the fabrication of delay lines for optical pulses. The simplest idea of pulse delay is related to the fact that the group velocity approaches zero near the band edge. However, large physical distances are needed in this case. An alternative way is forcing the light to traverse a small distance many times making use of the defect mode (optical cavity). These problems are discussed in Sec.2.3.

### 1.2 Light propagation through nonlinear media

A light wave consists of two components: electric and magnetic fields. These fields oscillate sinusoidally with high frequencies. Interaction of light and matter results in some displacement of the charge distribution inside the atoms or molecules of the material. This effect can be easily understood with the help of the model of a forced harmonic oscillator. The atoms, constructing the material, are seen as charge distributions pushed away from their equilibrium state when exposed to the electro-magnetic field. When the field is weak, light interacts linearly with the material. In the case of high intensity of the light, the electromagnetic field strongly modifies the optical properties of the medium, which affects the propagation of the radiation. Broadly speaking, nonlinear matter is a medium whose optical response depends on the intensity of the optical field that propagates through it. One typical nonlinearity is the change of the dielectric constant due to the Kerr effect. The Kerr nonlinearity enriches optics in general, and, in particular, the light propagation through nonlinear PCs.\(^5\) Nonlinear PCs and nonlinear PC-based fibers were successfully applied in the fields of frequency mixing and harmonic generation,\(^6,7\) efficient phase matching of several wavelengths,\(^8\) in manufacturing optical diodes,\(^9\) optical switchers and limiters,\(^9,10\) to mention just a few examples.

Nowadays, a lot of nonlinear effects are being discovered and studied in different materials (gases, liquids and solids). One can mention a few of them, like, nonlinear photoabsorption, harmonic generation, self-focusing, nonlinear photoionization, photodissociation, phase conjugation, etc. The area of applications of these nonlinear phenomena is vast. They are applied in medicine, biology, telecommunications, military and industrial applications.
There are two qualitatively different nonlinear interactions. The first one occurs when the light frequency is close to the resonant frequency of the medium. In this case, nonlinear effects appear at rather small intensities (\(\approx W/cm^2\)). The nonlinear optical effects are accompanied in this case by undesirable strong photoabsorption. To avoid absorption, one can induce nonlinearity by a nonresonant field. However, much higher intensities are demanded in that case.

Ordinary light sources have rather low intensity and interact with matter linearly. The creation of lasers in the 1960’s gave birth to a new area in optics – nonlinear optics – by opening the possibilities to observe and manipulate the nonlinear effects mentioned above. The nonlinear effects can be classified by the order of nonlinearity they exhibit. The quadratic electric field term in the Taylor expansion of the polarization gives rise to many important effects such as frequency doubling or second-harmonic generation, sum- and difference-frequency generation (if instead of monochromatic two fields with different frequencies are applied) and many others. Generally, the quadratic term involves the mixing of three different fields (it multiplies two fields to generate a third). The cubic term is important for materials with inversion symmetry (isotropic materials, such as glasses, liquids and gasses). There are no even powers of the electric field in the expansion of the polarization for symmetry reasons, and the lowest-order nonlinearity is then the cubic term. Four-wave mixing and intensity dependent refractive index effects, stimulated Raman and stimulated Brillouin scattering, third-harmonic generation and the quadratic electro-optic effect are all results of third-order polarization. The effects due to higher-order nonlinearities are usually very small and not so widely studied as the quadratic and cubic terms.

In the case when the intensity of the laser field is so high, that the conventional expansion of the nonlinear polarization in the Taylor series ceases to be a good approximation, the corresponding language of susceptibilities breaks down. A typical example is the two-photon absorption which is accompanied by saturation effects. Such high intensities are widely used in current experiments. The strict solution of the density matrix equations of the material is in these cases needed for the explicit treatment of the nonlinear polarization without addressing a Taylor expansion. In Sec.3.1 we review a generalized formalism for the nonlinear propagation of a multi-mode field without any restriction on the field strength. The theory was applied to studying amplified stimulated emission induced by three-photon absorption in an organic chromophore molecule (Sec.3).
1.3 Light-induced ultrafast processes

Investigation of ultrafast processes in solids, biomolecules and chemical reactions is a hot topic of modern science. The characteristic times of nuclear and electronic dynamics are femto- and attoseconds, respectively. Ultrashort optical and X-ray pulses are needed to study such fast processes. Much attention is paid nowadays to investigation of interactions of ultrashort intense light pulses with matter. On the other hand, strong short pulses give unique opportunities to modify the optical properties of matter. For example, laser radiation can orient molecules, it can create a coherent superposition of electronic, spin, and nuclear quantum states - so-called wave packets. The wave packet technique used in the thesis is nicely suited for studies of the dynamical aspects of light-matter interaction.

The concept of wave packets was introduced by Erwin Schrödinger in 1926 in order to make a bridge between the classical and quantum description of nature. For a long time the wave packets, which follow a classical trajectory, had no practical use because their preparation seemed impossible. However, recent advances in the physics and chemistry of laser interaction with atoms and molecules have brought wave packets and their dynamics into the limelight. In the 1990’s it became possible to prepare electronic wave packets by exciting atoms to Rydberg states with short pulses and to create nuclear wave packets in X-ray Raman scattering. A whole new realm of phenomena opened when femtosecond pulse technology emerged. With ultrashort pulses one can prepare a molecular wave packet and probe its evolution, observe molecular reactions on a real time scale (femtoseconds and tens of femtoseconds). The possibility to manipulate the reaction in order to achieve precise control over the output products appeared. In the field of molecular reactions, it gave birth to the field of femtochemistry.

Recent development of ultrafast control of coherent molecular dynamics has stimulated many theoretical and experimental efforts to realize logical gates and quantum computing algorithms in atoms and molecules. The analogs of several quantum bits within the shape of a single wave packet were defined based on wave packet symmetries. Recently, it was recognized that the trajectory of a wave packet is very sensitive to the phase of the pump radiation. This constitutes the background of phase sensitive pump-probe spectroscopy (see Secs. 4.1, 4.2).

The evolution of nuclear wave packets in a dissociative core-excited state affects the dynamics of resonant Auger scattering from fixed-in-space molecules, which can be tested making use of newly developed photoelectron-photoion coincidence technique. One of the important dynamical effects is the atomic-like resonance which experiences an electronic Doppler shift. The scattering of the Auger electrons by nearby atoms leads to new Doppler shifted resonances (see Sec. 4.3). These Doppler shifts allow to select different scattering processes
in the energy domain giving a unique opportunity to study electron-molecular interaction in details. Sharp scattering anisotropy together with the Doppler shifted resonances makes this phenomenon useful in structure studies.
Chapter 2

Photonic crystals

Photonic crystals (PCs) are periodic dielectric structures that control the propagation of light. The periodicity of the dielectric constant removes the degeneracies of the free-photon states at Bragg planes and produces a range of forbidden energies for the photons. This leads to the concept of photonic band gaps (PBGs) which underscores the analogy between electrons in semiconductors and photons in a PC. Any material which exhibits spatial periodicity in the refractive index is a PC. There are some examples of PCs in the nature; the sharp colors of natural opals and butterfly wings are manifestations of the periodic structure of these objects (Fig. 2.1). The periodicity defines the dimensionality of a PC (Fig. 2.2). Usually, one dimensional (1D) PCs pose a PBG for only one particular direction of the incident light, two dimensional PCs are able to stop the light beams in one particular plane, while some dielectric structures with a three-dimensional periodicity, have no propagation modes in any direction at all for a range of frequencies, giving rise to a complete PBG.

In 1987 a theoretical description of PBGs\cite{2,3} was proposed for the first time. In 1991 the first three dimensional PC was fabricated\cite{26}, based on a face-centered cubic structure. Since that time, numerous structures which pose PBG have been invented\cite{4}. By proper design of the PC (for example, lattice type, dielectric constants of the material, size of the unit cell, introduction of defects or impurity bands, choosing the angle of incidence of the light), one can manipulate the PBG of the PC and, hence, control the light propagation through the...
PC device. PCs are successfully used in many applications now: optical fibers, nanoscopic lasers, perfect mirrors, radio-frequency antennas and reflectors, and many others. Photonic integrated circuits is the hot topic of modern developments for PC applications. In 1968 Victor Veselago invented the concept of materials with negative refractive index and predicted a wide variety of new optical phenomena based on these so-called ‘left-handed’ materials. The fabrication of PCs based on left-handed materials is one of the important directions in the physics of PCs.

In the present chapter we will discuss the properties and applications of 1D periodical structures, namely 1D holographic PCs (see Sec.2.2) and 1D impurity band based PCs (see Sec.2.3).

2.1 Basic theory of photonic band gaps

The usual way to understand the properties of a PC is to analyze the solution of the Maxwell’s equations in the periodic system. Using Maxwell’s equations we can set up a wave equation or, in the stationary case, a Helmholtz equation (CGS units):

\[
(\Delta + (\omega/c)^2 \varepsilon(x)) E_k(x) = 0, \quad \varepsilon(x) = \varepsilon_0 + \varepsilon_1(x)
\]  

(2.1)

where \(\varepsilon_1(x)\) is a periodic function: \(\varepsilon_1(x) = \varepsilon_1(x + R)\). Because of the periodicity of the medium, we can expand the function \(\varepsilon_1(x)\) in a Fourier series over the reciprocal lattice vector:

\[
\varepsilon_1(x) = \varepsilon_1 \sum_G U_G e^{iGx},
\]  

(2.2)

here, \(\varepsilon_1\) is the amplitude of oscillation of the dielectric constant, and \(G\) is the reciprocal lattice vector. The electric field can also be expanded in a Fourier series over the vectors \(G\):

\[
E_k(x) = \sum_\alpha \sum_G E^\alpha_{k-G} \exp[i(k - G)x].
\]  

(2.3)
2.1 Basic theory of photonic band gaps

where $\alpha$ is the index of photon polarization. Any polarization can be expanded in two components: $\alpha = (x, y)$ for linear polarization, or $(+, -)$ for circular photon polarization.

Due to space inhomogeneity, the harmonics $E^\alpha_k$ are coupled. Introducing (2.2), (2.3) into (2.1) we obtain approximate amplitude equations for the harmonics:

$$\sum_{\alpha} E^\alpha_k \left[ k^2 - (\omega/c)^2 \varepsilon_0 \right] = \sum_{\alpha} (\omega/c)^2 \varepsilon_1 (U_G E^\alpha_{k-G} + U_{-G} E^\alpha_{k+G}),$$

$$\sum_{\alpha} E^\alpha_{k-G} \left[ (k - G)^2 - (\omega/c)^2 \varepsilon_0 \right] = \sum_{\alpha} (\omega/c)^2 \varepsilon_1 (U_{-G} E^\alpha_k + U_G E^\alpha_{k-2G})$$  (2.4)

which are valid when $\varepsilon_1(x)$ is rather small.

Let us discuss the 1D PC (Fig.2.3(a)). For the case of normal incidence ($k \parallel G$), all polarizations are decoupled and eqs.(2.4) become scalar. Near the band edge ($k \approx G/2$), only the scattering from the 1st Bragg plane is important:

$$E^\alpha_k \left[ k^2 - (\omega/c)^2 \varepsilon_0 \right] = (\omega/c)^2 \varepsilon_1 U_G E^\alpha_{k-G},$$

$$E^\alpha_{k-G} \left[ (k - G)^2 - (\omega/c)^2 \varepsilon_0 \right] = (\omega/c)^2 \varepsilon_1 U_{-G} E^\alpha_k.$$  (2.5)

These equations result in the following dispersion relation:

$$\left[ k^2 - (\omega/c)^2 \varepsilon_0 \right] \left[ (k - G)^2 - (\omega/c)^2 \varepsilon_0 \right] - (\omega/c)^4 \varepsilon_1^2 U_G U_{-G} = 0.$$  (2.6)

When $k = G/2$ and $U_G = U_{-G}$, we get

$$\omega_{\pm}/c = k/\sqrt{\varepsilon_0} \pm \varepsilon_1 U_G.$$  (2.7)

Thus, the forbidden band gap appears at the edge of the Brillouin zone (Fig. 2.3(b)) $\Delta \omega = \omega_{-} - \omega_{+} \approx \omega |\varepsilon_1 U_G|/\varepsilon_0$. The picture changes drastically when the light propagates parallel to the layers. In this case a photonic band gap does not appear (Fig. 2.3(c)).
Holographic photonic crystals

There are many methods of creating a PC: mechanical techniques (drilling holes etc.), chemically assisted ion beam etching, self-assembled aggregation of small particles, thin films or multilayer methods. One promising way to fabricate PCs is holographic lithography. With the help of several intercrossed laser beams, one can create a periodical interference pattern which can be saved employing a photoresistant recording medium (Fig. 2.4(a),(b)). The main advantage of this method is that one can prepare the interference pattern by adjusting the writing laser beams, and create a PC with desired properties. The disadvantage is that the existing photopolymers exhibit rather small contrast in the refraction index after light exposure (the bigger dielectric contrast, the wider the PBG).

Holographic photonic crystals (HPC) are exemplified in the present section as a 1D analog of the structure shown in Fig. 2.4(b). This structure was fabricated as a 1D reflection hologram by focusing two intercrossed laser beams on a photoresistant sample (Paper I). The principle difference of the HPC from an ordinary PC is that the refractive index changes continuously,
2.2 Holographic photonic crystals

Figure 2.5: (a) Experimental transmission spectra for different incident angles of the probe beam ($\theta_a$). (b) Dependence of the position of the BG center on the incident angle in air ($\theta_a$) (experiment and theory).

Figure 2.6: (a) The Brewster angle, $\Theta_B = \arctan(n_2/n_1)$. (b) Angular dependence of the band structure of a 1D HPC. The refraction index varies from $n_{max} = 2.5$ to $n_{min} = 2.1$. The shaded regions show the band gaps.
and not step-like (Fig. 2.4(c)). Based on an experimental observation of angular properties of the 1D HPC (Fig. 2.5(a)) made by our co-authors, we analyzed such a system theoretically with the help of a conventional transfer matrix technique. For this purpose we divided each elementary unit cell of the 1D HPC into sublayers with approximately constant value of refractive index and then solved the Maxwell’s equations for each sublayer (Fig. 2.4(c)). A comparison of the theory with the experimental data (Fig. 2.5(b)) allowed us to define the parameters of the HPC – the dielectric contrast and the shrinkage of the hologram.

As it could be seen from the equations in Sec. 2.1, when the incident light enters the PC at an angle other then 0° or 90°, the degeneracy of light polarization is removed. Then, light with $p$– and $s$–polarization (or TM and TE modes) interacts differently with the PC. In this context, it is important to notice the presence of a Brewster angle for the TM mode (Fig. 2.6(a)). It is an angle at which the reflection of this light component equals zero and the PBG disappears (Fig. 2.6(b)). The theoretical analysis (Paper I) showed that the value of the Brewster angle for different bands is different (Fig. 2.6(b)). This differs qualitatively from the conventional two-layer Bragg reflector with a step-like distribution of the dielectric constant, where the Brewster angle is the same for all bands, $\Theta_B = \arctan(n_2/n_1)$. The band gap of the TE does not have such a particularity and increases monotonically with an increase of the incident angle (see Paper I).
2.3 Pulse propagation through impurity band based photonic crystals

As it is well known from solid state physics, an impurity creates a localized mode inside the electronic band gap. Similarly, one can obtain a very narrow defect mode inside the photonic band gap by introducing a defect in a perfect PC structure (see Fig. 2.7). By varying the parameters of the defect and the photonic crystal, one can change the position and the width of this defect mode. This technique was applied for creating tunable wavelength filters for continuous radiation and optical delay lines. Optical delay lines provide the delay time of an optical signal. These devices have many applications, for example they are essential elements for all-optical switching nodes in photonic network systems and quantum computers. An enhanced delay is also desirable in nonlinear optical systems as it increases the effective interaction time.

A short pulse has a wide frequency dispersion. When such radiation enters a PC with
a narrow defect mode, the pulse is damaged, and part of the radiation (which corresponds to the defect mode frequency region) goes through the PC, while the rest is reflected. It means that in order to manipulate the propagation of the pulses, it is necessary to satisfy, to some extent, two contradictory requirements: a small spectral width of the defect mode and a rather broad spectrum of the short pulse. A method to overcome that contradiction was presented in the papers of Lan et al\textsuperscript{41} devoted to theoretical and experimental studies of pulse propagation through coupled cavity waveguides. The key idea for reducing pulse distortion in such delay lines is based on the possibility of creating a quasi-flat transmission spectrum in the impurity band\textsuperscript{42}. Impurity bands, in analogy with semiconductors, can be implemented in 1D PCs by periodically introducing N defect layers (see Fig.2.8). Due to the overlap, different defect modes interact with each other and form an impurity band (IB). Figure 2.9(a) shows the forming of an impurity band inside the photonic band gap frequency region. The IB spectra depends strongly on the number of defects in the PC, N, and the number of layers which form the cavity resonators, m and n.

It is well established that transmission spectra of 1D PCs is very sensitive to the angle of incidence of the light\textsuperscript{1}. The possibility of altering the properties of 1D PCs with the help of the incidence angle has become apparent and has generated substantial interest in this

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**Figure 2.10:** (a) Transmission spectrum of the impurity band (solid) and spectral distribution of the incident Gaussian pulse (dashed). (b) Time dependence of the incident TE-polarized (dashed), transmitted (solid) and reflected (dash-dotted) pulses. The carrier frequency is $\omega_0 = 0.37752(2\pi c/a)$, angle of incidence is $\theta_0 = 60^\circ$. 

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\textsuperscript{1} It is well established that transmission spectra of 1D PCs is very sensitive to the angle of incidence of the light. 

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**Photonic crystals**
field. In Paper II we presented a theoretical study of the angular dependence of the delay time of IB based PCs. The main goal of our study was to establish the angular anisotropy of the delay time.

Angular anisotropy of the group velocity of the impurity band is the reason behind the angular anisotropy of the delay time. We have shown that the group velocity of the TE and TM modes of the impurity band has qualitatively different angular behavior: the group velocity of the TM mode increases with increasing the incidence angle up to the Brewster angle (Fig.2.6(a)), where the delay time for the TM mode equals zero (Fig.2.9(b)). The group velocity decreases when the incident angle exceeds the Brewster angle. On the other hand, the group velocity of the TE mode decreases monotonically with increasing the incident angle (Fig.2.9(b)). Thus, the TM and TE modes are separated in the time domain due to qualitatively different angular dependence of the group velocity, and hence, of the delay time for these modes. Moreover, the edges of the impurity band spectrum have narrow defect peaks, while at the central part of the spectrum they are broader (Fig.2.10(a)), and hence the group velocity dispersion is large for different spectral components of the incident pulse. This results in a distortion of the TE-polarized incident pulse (Fig.2.10(b)). It splits in few transmitted pulses with different delay times (see insets in Fig.2.10(b)).

The role of the incident angle, $\theta$, is important in applications, because the delay time can be changed easily by varying $\theta$ without changing the optical device itself (see Paper II for further details).
Chapter 3

Interaction of short light pulses with nonlinear media

Nonlinear optics constitutes one of the most important areas of modern science and technology. It has already revolutionized telecommunications and is expected to soon make a similar impact on computer technology. Nonlinear techniques cover a wide region of different applications now, such as sum frequency and harmonic generations, frequency upconverted lasing, optical power limiting, optical data storage and photodynamic therapy.

One of the most important directions in nonlinear optics and quantum electronics nowadays is constituted by many-photon pumped frequency-upconverted lasing. Studies of stimulated emission were earlier performed using two-photon pump of dye solutions and dye-doped polymer matrices. Quite recently, three- and four-photon pumped (3PP and 4PP) amplified spontaneous emission (ASE) in solutions was studied both experimentally and theoretically. In the case of 3PP and 4PP ASE, the pump mechanism is based on three- and four-photon absorption; therefore an ultra-short laser pulse source is required to provide high peak power.

It is a common view that for future use more sophisticated understanding of the basic mechanisms underlying non-linear phenomena of this kind will be required. This motivates us to explore non-linear propagation of light pulses through complex media, where details of the quantum structure of the molecular units become essential. The present chapter is devoted to a review of some essential theoretical aspects of the dynamics of cavityless lasing generated by ultra-fast multi-photon excitation.
3.1 Density matrix equations for multi-mode beam propagation

Real laser experiments deal with many factors which act simultaneously, something that can make special models inadequate for use in proper analysis of experimental measurements. For example, the standard theoretical way to explore the nonlinear propagation of strong interacting electromagnetic fields is based on the solution of the nonlinear equation for a specific nonlinearity (quadratic, cubic, etc.). But in many experiments the intensity of the laser fields is so high that the conventional expansion of the nonlinear polarization in a Taylor series over the electric field strength ceases to be a good approximation, and the corresponding language of susceptibilities is no longer valid. These cases require a strict solution of the density matrix equations of the material for the explicit description of the nonlinear polarization without addressing the Taylor expansion. The character of many-photon absorption in condensed phases is often complicated by the competition between one-step and sequential absorption channels. In Paper III we presented a generalized formalism for the nonlinear propagation of a multi-mode field without any restrictions on the field strength.

In the case of multi-mode interaction, we seek a solution of the density matrix equations\(^\text{65}\)

\[
\left( \frac{\partial}{\partial t} + \hat{\Gamma} \right) \rho = \frac{i}{\hbar}[\rho V]
\]

(3.1)

making use of the Fourier transform:

\[
\rho_{\alpha\beta} = e^{i\omega_{\alpha\beta}t} \sum_n n_{\alpha\beta} e^{i(n_o k \cdot r - n_o \omega t - n_o \phi)},
\]

(3.2)

where \(\hat{\Gamma}\) is the relaxation operator, \(V\) is the interaction between a molecule and the electromagnetic field, \(\omega_{\alpha\beta} = (E_\alpha - E_\beta)/\hbar\) is the frequency of the transition \(\alpha \rightarrow \beta\). Here, we introduced the \(N\)-dimensional vector \(n\) and the \(N\)-dimensional scalar product

\[
n \equiv (n_1, n_2, ..., n_N), \quad n \circ \omega \equiv \sum_{j=1}^{N} n_j \omega_j, \quad n \circ k \equiv \sum_{j=1}^{N} n_j k_j, \quad (3.3)
\]

with \(n_j = 0, \pm 1, \pm 2, ..., \pm \infty\) as the numbers of photons of the field \(\mathcal{E}_j\); \(\omega = (\omega_1, \omega_2, ..., \omega_N)\), and \(k = (k_1, k_2, ..., k_N)\).
3.2 Dynamics of amplified spontaneous emission generated by long pump pulses

A substitution of the expansion (3.2) into (3.1) gives the following equations:

$$\left\{ \frac{\partial}{\partial t} - i [n \circ (\omega - \mathbf{k} \cdot \mathbf{v} - \omega_{\alpha \beta}) + \Gamma_{\alpha \beta}^\gamma] \right\} r_n^{\alpha \beta} = \delta_{\alpha \beta} \sum_{\gamma > \alpha} \Gamma_{\gamma \gamma}^\alpha r_n^{\gamma}$$

$$+ i \sum_{j=1}^N \sum_{\gamma} \left[ (r_n^{\alpha \gamma -1 j} + r_n^{\alpha \gamma +1 j}) G^{(j)}_{\gamma \beta} - G^{(j)}_{\gamma \beta} \left( r_n^{\alpha \gamma -1 j} + r_n^{\alpha \gamma +1 j} \right) \right], \quad (3.4)$$

where \( G_{\alpha \beta}^{(j)} = \mathbf{E}_j \cdot \mathbf{d}_{\alpha \beta} / 2\hbar \) is the Rabi frequency of the \( j \)th field for the transition \( \alpha \rightarrow \beta \). The origin of the the upper indices of the density matrix in the field term \( n \pm 1_j \equiv (n_1, n_2, ..., n_j \pm 1, ..., n_N) \) is the absorption or emission of one photon of the \( j \)th mode due to the molecular field interaction. This representation is a key to solve the problem of propagation of strong pump and probe fields through a nonlinear many-level medium. The nonlinear polarization can be expressed in terms of the density matrix elements as:

$$\mathcal{P}_j = \sum_{\beta \alpha} \mathbf{d}_{\beta \alpha} r_n^{1_j}_{\alpha \beta}. \quad (3.5)$$

Here \( r_n^{1_j}_{\alpha \beta} \) means \( r_n^{\alpha \beta} \) with \( n = (0, 0, ..., 1_j, ..., 0) \). Equations (3.4) and (3.5) together with the paraxial wave equation

$$\left( -\frac{i}{c} \frac{\partial}{\partial t} + \frac{1}{2c^2} \nabla^2 - \frac{i}{2k_j} \Delta_\perp \right) \mathbf{E}_j = \frac{i k_j}{\varepsilon_0} \mathcal{P}_j, \quad (3.6)$$

solve the problem of propagation of the strong multi-mode field through a nonlinear many-level medium without restrictions on the mode intensities.

3.2 Dynamics of amplified spontaneous emission generated by long pump pulses

In this section we will exemplify the theory described above by discussing amplified spontaneous emission (ASE) induced by three-photon absorption in an organic stilbenochromophore (APSS) (Fig.3.1(A)) dissolved in solvent (see Paper IV). Our work was initiated by recent experimental studies of this system. The scheme of transitions is shown in Fig.3.1(B). The pump laser populates vibrational level 4 by three-photon absorption. Level 4 decays non-radiatively to the lowest vibrational level 3, giving rise to a population inversion between levels 3 and 2. Thus, two lasing transitions are possible, – from the pumped level 4, and from the bottom of the potential well \( S_1 \). The duration of the pulse used in the experiment was rather long, \( \tau_p \approx 2 \) ps. This duration is comparable with the time of vibrational quenching
Figure 3.1: Structure of APSS and the reduced molecule\textsuperscript{60} (A). Energy level scheme for ASE lasing (B).

Figure 3.2: Scheme of the co- and counter propagating ASE pulses (A). ASE intensity dynamics (B).
3.3 Dynamics of ultra-fast three-photon pumped amplified stimulated emission

of the pumped level (few ps). Under such conditions, the population of level 3 is largest due to the long lifetime of this level (about 1 ns). This motivates us to consider only the $3 \rightarrow 2$ ASE channel (Fig.3.1(B)). The ASE channel $4 \rightarrow 2$ becomes important for shorter pump pulses (See Section 3.3).

We explored the dynamics of co- and counter (relative to the pump) propagating ASE pulses (Fig. 3.2(A)). The pump pulse creates population inversion $\rho_3 - \rho_2$ and, hence, gain $g$. The front of the gain grows very fast, with characteristic time equal to the pulse duration (2 ps). In this example, the ASE pulse (Fig. 3.2(B)) displays a long tail with width of several tenths of ps, which depends on $\Gamma_3$ and it is sensitive to the saturation of the ASE transition. Due to the small inhomogeneous broadening the saturation effect is rather strong.

Interaction of the forward and backward pulses results in self-pulsations (Fig.3.2(B)) and, hence, smaller efficiency of non-linear conversion for the forward ASE compared to the case when the forward emission is considered alone. This is a result caused by the partial re-pump of the absorbed energy to the backward ASE component; the overall efficiency is nevertheless higher than for the forward emission considered alone (see Paper IV). The efficiency of the non-linear conversion of the pump energy to the counter-propagating ASE pulses is strongly dependent on the concentration of active molecules so that a particular combination of concentration and cell length maximizes the conversion coefficient.

3.3 Dynamics of ultra-fast three-photon pumped amplified stimulated emission

The shortening of the pump pulse changes considerably cavityless lasing due to two reasons. The first one is the increase of the peak intensity of the pump pulse. The second reason is the shortening of the pump pulse itself which influences strongly the population of the lasing levels (see eqs. (14) and (15) in Paper V) and, hence, the ASE dynamics.

Recent experiment studies, devoted to ASE generation by ultra-fast three-photon excitation in stilbazolium dye solution PRL-L3 (Fig.3.3), showed an unusually strong dependence of the ASE spectral profile on the pump intensity: The peak position of forward (relative to the pump pulse) ASE almost coincides with the maximum of fluorescence for the low pump level, while it experiences a blue shift ($\sim 20$ nm) relative to the fluorescence, as well as relative to the backward ASE when the pump exceeds some energy threshold. To explain this apparently new and surprising strong dependence of the ASE spectral profile on the pump intensity, we developed a dynamical theory of ASE based on two different models: a 'molecular' and a 'solvent' model (Paper V). Analysis of the experimental data prompts
that this effect is essentially a dynamical one and related to the relaxation dynamics of the excited states.

The first, molecular, model (see Fig. 3.4(A)), is based on the phenomenon of vibrational relaxation of the excited electronic state. The pump radiation promotes the molecule from the ground to the first excited electronic state and populates the group of vibrational levels in the Franck-Condon (FC) region near the vertical transition energy. The radiative decay from these “vertical” levels to the ground electronic state starts immediately and opens the first ASE channel $3 \rightarrow 1$ (Fig. 3.4(A)). At the same time, these pumped vibrational levels relax nonradiatively to the bottom of the excited state potential due to intramolecular interaction and due to interaction with the solvent. The radiative decay from the lowest vibrational level of the excited state also leads to ASE. Apparently, this second ASE channel $2 \rightarrow 1$
3.3 Dynamics of ultra-fast three-photon pumped amplified stimulated emission

Figure 3.5: Branching ratio versus pump intensity $I_p$, computed at the entry ($z = 0$) and at the end ($z = L$) of the cell for the backward and forward ASE, respectively (A). The forward (B) and backward (C) ASE rates $\gamma_{31}$ and $\gamma_{21}$ as functions of the pump intensity (molecular model). $d_{31} = 5.67$ D, $d_{21} = 8.12$ D; $I_0 = 276$ GW/cm$^2$.

(Fig. 3.4(A)) is delayed and red-shifted relative to the first channel. Both ASE channels compete with each other and the appearance of each channel depends on the FC factors of the decay transitions, as well as on the pump level.

The branching ratios of these two channels for the forward and backward ASE pulses as function of the pump intensity are shown in Fig.3.5(A). When the pump intensity $I_p$ is larger than a certain threshold level $I_0$, defined by the equation

$$\gamma_{31}(I_0) = \Gamma_{32},$$

the ASE rate of the first channel $\gamma_{31}(I_p)$ for forward pulse exceeds the rate of nonradiative quenching of the pumped vibrational levels $\Gamma_{32}$ (see Fig. 3.5(B)), and the first blue-shifted ASE channel starts to dominate (Fig. 3.6(A)). This is in agreement with the experiment (Fig. 3.6(B)) which shows a blue shift of the forward pulse when $I_p \geq I_0$.

In the case of backward ASE, the ASE rate $\gamma_{31}$ is smaller than $\Gamma_{32}$ for pump intensities up to $1.4I_0$ (Fig. 3.5(C)). Due to this circumstance, the second delayed ASE channel dominates for the backward ASE pulse (Fig. 3.6(A)) and the maximum of its spectrum coincides with the peak position of the fluorescence, in agreement with the experiment (compare panels A and B in Fig. 3.6). The temporal profiles of the forward and backward ASE pulses for the $2 \rightarrow 1$ transitions are shown in Figure 3.7(A).

The background of the second, so-called “solvent”, model is an instantaneous change of the permanent dipole moment of the dye molecule upon excitation, $d_0 \rightarrow d_1$ (Fig. 3.4(B)). The first ASE channel $3 \rightarrow 1$ (Fig. 3.4(C)) starts from the lower vibrational level of the
Figure 3.6: Theoretical (A) and experimental\textsuperscript{61} (B) spectra of the forward and backward ASE pulses generated from a solution of PRL-L3 dye (Fig.3.3) in DMSO solvent by ultra-fast three-photon excitation.
3.3 Dynamics of ultra-fast three-photon pumped amplified stimulated emission

Figure 3.7: (A) Solid and dashed lines display the forward and backward $2 \rightarrow 1$ ASE pulses which interact with each other; the dashed-dotted line shows the forward $2 \rightarrow 1$ pulse calculated without taking into account interaction with the backward pulses (molecular model). $I_p = I_0$. The remaining parameters are the same as in Fig. 3.5. (B) Shapes of ASE pulses for forward and backward ASE for $3 \rightarrow 1$ and $2 \rightarrow 1$ channels (solvent model). $I_p = 1.09I_0$, $I_0 = 271 \text{ GW/cm}^2$, $d_{31} = 6.18 \text{ D}$, $d_{21} = 7.73 \text{ D}$.

non-equilibrium state $S_1$ after nonradiative relaxation of the level 4 (Fig. 3.4(B)).

Due to solute-solvent relaxation around the newly formed dipole, the state $S_1$ relaxes to a new state $\tilde{S}_1$ with lower energy,\(^{66}\) $E(\tilde{S}_1) = E(S_1) + \hbar \Delta \omega$,

$$\hbar \Delta \omega = \frac{1}{4 \pi \varepsilon_0 \alpha^3} \left[ 2\mathbf{d}_0 \cdot (\mathbf{d}_0 - \mathbf{d}_1) F(\varepsilon, n) + (d_0^2 - d_1^2) \left( \frac{n^2 - 1}{n^2 + 2} \right) \right]$$  \hspace{1cm} (3.8)

Here, $\alpha$ is the radius of the spherical cavity of the solute, $F(\varepsilon, n) = (\varepsilon - 1)/(\varepsilon + 2) - (n^2 - 1)/(n^2 + 2)$ is the reaction field factor, $\varepsilon$ and $n$ are the static dielectric constant and the optical refractive index of the solvent, respectively. Ab-initio simulations based on the Dalton code\(^{67}\) give $\Delta \omega \approx -379.7 \text{ cm}^{-1}$ or $\Delta \lambda \approx 13.5 \text{ nm}$ for the PRL-L3 molecule in dimethyl sulfoxide (DMSO) (see Paper V). This value is in a reasonable agreement with the experimental value\(^{61}\) $\Delta \lambda_{\text{exp}} \approx 20 \text{ nm}$. The solute-solvent relaxation takes time within tens to a hundred picoseconds.\(^{66}\) Radiative decay from the relaxed state $\tilde{S}_1$ forms the second ASE channel $2 \rightarrow 1$ (Fig. 3.4(C)). Similar to the molecular model, the threshold occurs when the rate of stimulated emission of the first channel approaches the rate of solute-solvent relaxation in the excited state (3.7). It is worth noting that similar to the molecular model, ASE from the pumped level 4 also occurs, $4 \rightarrow 1$ (Fig. 3.4(C)). The threshold pump level of the $4 \rightarrow 1$ ASE channel is comparable with the threshold of the $3 \rightarrow 1$ channel (see Paper
V). Generally, one can expect three ASE channels in the solvent model: first the $4 \rightarrow 1$ blue shifted ASE pulse appears, the $3 \rightarrow 1$ pulse arrives later. The $2 \rightarrow 1$ red-shifted ASE pulse experiences largest delay caused by the solute-solvent relaxation of the excited state. The relative intensity of the $4 \rightarrow 1$ ASE channel is given by the corresponding Franck-Condon (FC) factor. The FC factor of the $4 \rightarrow 1$ ASE channel is assumed to be small in the numerical simulations and, due to this, the $4 \rightarrow 1$ channel is neglected. The simulated shape of the forward and backward ASE pulses, taking into account channels $3 \rightarrow 1$ and $2 \rightarrow 1$ are shown in Fig. 3.7(B).

Both forward and backward $2 \rightarrow 1$ ASE pulses experience modulation (see Fig. 3.7(A),(B)). The origin of this self-pulsation of the ASE is the interaction of these contrary propagating pulses (see Sec.3.4 and Paper VI for details). Indeed, our simulations of the ASE profiles, which neglect the interaction between the forward and the backward pulses, does not show any oscillations (Fig. 3.7(A), Fig. 3.2(B)).

We show (see Paper V) that both models can explain the current experiments. To select one of the models, further experimental and theoretical studies are needed. The applicability of the model is sensitive to the system and both mechanisms can simultaneously affect the ASE dynamics for some of the molecules.

### 3.4 Self-sustained pulsation of amplified spontaneous emission

Theoretical (Paper IV, V), as well as experimental,\textsuperscript{46,61–63} studies show that under certain specified conditions the ASE effect becomes oscillatory (see Figs. 3.2(B), 3.7). Two different mechanisms of the origin of such temporal self-pulsations of the forward and backward propagating ASE pulses were proposed (see Paper VI): i) interaction between co- and counter-propagating ASE (see Sec. 3.2, 3.3), and ii) dynamical competition between the stimulated emission and the off-resonant absorption.
To understand the dynamics of ASE qualitatively, let us discuss the scheme of ASE depicted in Fig. 3.8, which extracts the most essential part of the energy level diagrams shown in Figs. 3.1(B) and 3.4. In this model the ASE process can be described by two rate equations for populations of level 1 ($\rho_1$) and 0 ($\rho_0$):

\[
\begin{align*}
\left( \frac{\partial}{\partial t} + \Gamma_1 \right) \rho_1 &= \Gamma_N N - \gamma (\rho_1 - \rho_0), \\
\left( \frac{\partial}{\partial t} + \Gamma_0 \right) \rho_0 &= \Gamma_1 \rho_1 + \gamma (\rho_1 - \rho_0),
\end{align*}
\]

and the wave equations for the intensity of the forward $I^+$ and backward $I^-$ propagating ASE fields (Fig. 3.2(A))

\[
\left( \frac{1}{c} \frac{\partial}{\partial t} \pm \frac{\partial}{\partial z} \right) I^\pm = g I^\pm, \quad g = B(\rho_1 - \rho_0) - \alpha.
\]

Here, $g$ is the gain and $\alpha$ is the weak non-resonant absorption; $N = N(z,t)$ is a population of the pumped level created by the pump pulse (see eq. (13) in Paper VI); this state decays with rate $\Gamma_N$ to the lasing level 1 (Fig. 3.8) creating the population inversion between levels 1 and 0. This triggers the ASE process in both backward and forward directions.

The ASE rate $\gamma = p I$ and, hence, the population inversion $\rho_1 - \rho_0$ depends on the total ASE intensity $I = I^+ + I^-$ (3.9). Due to this the forward and backward ASE pulses affect each other.

### 3.4.1 Oscillations caused by interaction of co- and counter-propagating ASE pulses

The interaction of forward and backward ASE pulses causes self-pulsation of the ASE as mentioned in the previous Sections 3.2 and 3.3 (see Figs. 3.2(B) and 3.7). These self-pulsations occur when the ASE intensities are high enough to saturate the ASE transition $1 \rightarrow 0$. The oscillatory pattern is absent when the interaction of the opposite propagating ASE pulses is neglected, $I = I^+$ or $I = I^-$ (see Fig.3.2(B), Fig.3.7(A)).

To give insight into the mechanism of these oscillations it is useful to analyze the map of the gain $g$ (Fig.3.9) which is computed for $\alpha = 0$. The gain grows during the lifetime of the excited state, $0 \leq t \lesssim \Gamma_N^{-1}$. Due to this, the intensity $I^+$ of the forward ASE increases faster along the pathway corresponding to longer time. Because $I^+$ is larger near the end of the cavity ($z = L$), the forward pulse depopulates level 1 and quenches the gain in the region $F_1$ (Fig.3.9). This makes the enhancement length of the backward pulse shorter. Due to
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\[ \Gamma N^{-1} - \Gamma 0^{-1} \]

\[ z \]

\[ z_0 \]

\[ \tau_B \]

\[ \tau_F \]

\[ A \]

\[ B \]

\[ C \]

\[ r_N^{-1} \]

\[ r_0^{-1} \]

\[ Time \]

\[ Forward ASE \]

\[ Rearward ASE \]

\[ \text{Figure 3.9: Map of the gain } (g = B(\rho_1 - \rho_0)) \). Physical picture of the self-sustained pulsation caused by the interaction of co- and counter-propagating ASE pulses.

this circumstance, the counter-propagating pulse is suppressed in the region \( B_2 \) (Fig. 3.9). Contrary to the forward pulse the counter-propagating ASE component assumes maximum near the entry of the cavity \((z = 0)\), where it saturates the \( 1 \rightarrow 0 \) transition decreasing the gain (see region \( B_1 \) in Fig.3.9). Thus, the enhancement length of the forward ASE is shortened in the region \( B_1 \). This explains the minimum of the forward ASE in the region \( F_2 \) (Fig. 3.9). The inversion is restored after time \( \Gamma_0^{-1} \) due to the fast decay of the level 0 and the scenario is repeated.

### 3.4.2 Self-pulsation of ASE caused by competition between stimulated emission and off-resonant absorption

The other possible mechanism causing self-pulsations is the dynamical competition between the stimulated emission and the absorption \( \alpha \). It is necessary to note that the absorption by active molecules on ASE transition \( 1 \rightarrow 0 \) is taken into account in the term \( \gamma(\rho_1 - \rho_0) \) (see eq.(3.9)). Thus, \( \alpha \) includes the non-resonant absorption by active molecules as well as a possible resonant excited state absorption. We assume that the solvent contains some admixture of the buffer molecules which absorb resonantly the ASE radiation. Thus the absorption coefficient

\[ \alpha \equiv \alpha(I) = \alpha_0/(1 + I/I_s), \]

\( (3.11) \)
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Figure 3.10: (A) Self-sustained pulsation of ASE. The ASE intensity, gain and populations of levels 1 and 0 are depicted in plots (a), (b) and (c), respectively. (B) Physical picture of the origin of self-pulsations. The ASE intensity (a), the gain (b), $\alpha$ and $B(\rho_1 - \rho_0)$ (c) in the region of steady state self-sustained pulsations (panel A).

depends on the ASE intensity when $I$ approaches the saturation value $I_s$. Here, $\alpha_0$ is the absorption coefficient at zero intensity. The saturation intensity $I_s$ can be changed by variation of the concentration of the buffer molecules.

Fig.3.10 A shows the self-pulsations of the ASE caused by saturable absorption. To avoid the modulation of the ASE profile due to interaction of the co- and counter-propagating ASE pulses we neglect the propagation effects in eq. (3.10) assuming $\partial I/\partial z = 0$. Due to the pump, the stimulated emission $B(\rho_1 - \rho_0)$ exceeds the losses ($\alpha$) and the gain ($g$) becomes positive (Fig. 3.10(B)). The ASE intensity grows reducing the inversion $(\rho_1 - \rho_0)$ until the gain vanishes, $g = 0$ (Fig. 3.10(B), plot (b)). At this instant the ASE intensity and the absorption coefficient take maximum and minimum values, respectively, because $\dot{I} \propto \dot{\alpha} \propto g = 0$. However, the derivative of the inversion (3.9) is not equal to zero here. This results in a shift of the minima of $\alpha$ and $B(\rho_1 - \rho_0)$ relative to each other (Fig. 3.10(B), plot (c)). Due to this circumstance, the gain becomes later on negative, and the ASE intensity, $I = I_0 \exp(\int^t g(\tau) d\tau)$, starts to decrease. A smaller ASE intensity lowers the saturation of the ASE transition and the inversion increases. Through a while the gain begins to grow and becomes positive again (Fig. 3.10(B), plot (b)). The scenario is then repeated. A more detailed explanation of the steady self-pulsations of ASE (Fig. 3.10) based on stability analysis is given in Paper VI.
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Chapter 4

X-ray time-resolved spectroscopy of light-induced nuclear dynamics

In the previous sections we studied the dynamics of light pulses in linear and nonlinear media. However, the short and brilliant laser pulses can disturb the medium, creating coherent superpositions of quantum states. The powerful concept of coherence lies at the core of femtochemistry and is a key in the observation of dynamical effects. The creation of new sources of intense and short pulses of coherent radiation has opened new opportunities and experimental tools for active operation and probing of electronic and nuclear wave packets. Recent progress in the field of femto- and sub-femtosecond laser pulses has made it possible to measure the continuous time evolution of nuclear and electronic motion.

Our main objective was to perform time-resolved pump-probe studies of nuclear motion. The nuclear wave packet is here the key concept and theoretical tool. With the help of wave packets it is possible to monitor molecules at various stages of vibrational distortion, recording "stop-action" spectroscopic events corresponding to well defined molecular geometries far from equilibrium, including stretched and/or bent unstable transient structures.

The name “wave packet” embraces a broad range of approaches including also various semiclassical methods. We treat here only strictly quantum methods using a finite difference representation of the wave packets. The finite difference method represents a function by sampling its values at a grid of, usually, equidistant points.
X-ray time-resolved spectroscopy of light-induced nuclear dynamics

4.1 Phase-sensitive spectroscopy of molecules driven by a strong infrared field

This section is devoted to time- and frequency-resolved X-ray spectroscopy of molecules driven by strong and coherent infrared (IR) pulses. Studies of IR-induced nuclear dynamics require quite short X-ray pulses (< 100 fs). As reviewed in Ref.\textsuperscript{70}, several kinds of such sources are available already today. In fact, ultrashort X-ray pulses (≈ 250 attosecond) have recently been reported.\textsuperscript{71} X-ray pump-probe spectroscopy together with recent development of femtosecond lasers brings new possibilities into time-resolved X-ray spectroscopy.\textsuperscript{13} It becomes possible to investigate the nuclear dynamics within the time scale of molecular vibrations.

The principle of IR – X-ray pump-probe spectroscopy is illustrated in Fig.4.1(a) using the NO molecule as an example (see Paper VIII). The coherent IR pump pulse resonantly excites the vibrational levels of the ground electronic state, thereby creating a coherent superposition of vibrational states or a wave packet. The short probe X-ray pulse exposes the molecule at different moments of time, and excites the wave packet to a certain point at the core-excited potential. A change of the delay time between the probe and the pump pulses allows to investigate the dynamics of nuclear wave packets in the ground state, as
4.1 Phase-sensitive spectroscopy of molecules driven by a strong infrared field

well as to map the core-excited potential surface.

The nuclear wave packet created in the ground state (Fig. 4.1(a)) by the coherent IR field with strength $E_L(t)$, frequency $\omega_L$ and phase $\varphi_L$, obeys the time-dependent Schrödinger equation:

$$i\frac{\partial}{\partial t}\phi(t) = [H_0 - (d \cdot E_L(t)) \cos(\omega_L t + \varphi_L)] \phi(t), \quad (4.1)$$

where $H_0$ is the nuclear Hamiltonian of the ground electronic state. The interaction with the coherent IR field makes the dynamics of the nuclear wave packet sensitive to the phase of the IR field, $\varphi_L$. This is seen from the perturbation solution of the Schrödinger equation (4.1) for $\omega_L = \omega_{10}$

$$|\phi(t)\rangle = \sum_{\nu=0}^{\infty} |\nu\rangle c_{\nu}(t) e^{-i(\nu\varphi_L + c_{\nu}t)} \propto \left[ 1 + c_1(t) \sqrt{2}(r - r_e)/a_0 e^{-i(\omega_{10} t + \varphi_L)} + \ldots \right] e^{-(r-r_e)^2/2a_0^2}, \quad (4.2)$$

where the coefficients $c_{\nu}(t)$ do not depend on $\varphi_L$ in the rotating wave approximation. Here, $r$ and $r_e$ denote the internuclear distance and equilibrium distance, respectively; $a_0$ is the amplitude of vibrations and the coefficients $c_{\nu}(t)$ are proportional to the strength of the electromagnetic interaction. The sensitivity of the nuclear dynamics to the phase of the IR field is seen directly from the trajectory of the center of gravity of the wave packet,

$$\langle r(t) \rangle = \langle \phi(t)|r|\phi(t) \rangle, \quad (4.3)$$

which is displayed in Fig. 4.1(b). This effect has nothing to do with the role of the phase in few-cycle experiments. Indeed, in our case the duration of the IR pulse is longer than the inverse frequencies of the IR field.

Fig. 4.1(b) displays two-scale dynamics. One can see both fast and slow oscillations of the wave packet in the potential well. The wave packet performs fast back and forth oscillations with vibrational frequency $\omega_{10}$ (Fig. 4.1(b)). These oscillations are slowly modulated, due to anharmonicity of the ground state potential, with a period, $T_a = \pi/\omega_e x_e$ (see left panel in Fig. 4.1(b)). A measurement of the revival time $T_a$ using X-ray absorption gives a new opportunity to determine the anharmonicity constant $\omega_e x_e$. Here, we face a paradoxical situation, namely that the ultrafast X-ray measurements allow to determine the fine structure of the spectrum (anharmonicity).

The absorption of X-ray probe radiation by laser-excited molecules is defined as the expectation value of the interaction of the X-ray field with the system. As it is shown in Paper VIII, the absorption probability

$$P(\Omega) = -\Im m \int_{-\infty}^{\infty} \text{Tr} [\rho(t_1)(E_X(t_1) \cdot D)] \, dt_1 = \langle \phi_e(\Omega)|\phi_e(\Omega) \rangle \quad (4.4)$$
Figure 4.2: Population of the vibrational levels of the ground electronic state versus time for different switching off times of the pump field. The inset shows population for the case of $\varphi = 0$ (solid line) and $\varphi = \pi/2$ (dashed line). $\tau_L = 100$ fs (a), $\Delta T \approx 715$ fs (b).

is equal to the norm of the Fourier transform of the wave packet

$$|\phi_c(\Omega)| = \int_{-\infty}^{\infty} dt \ e^{-i\Omega t} E_X(t) |\phi_c(t)|,$$

(4.5)

where $\rho(t, \Omega)$ is the density matrix of the molecule, $|\phi_c(t)| = e^{iH_c t} \zeta(t) |\phi(t)|$ is the nuclear wave packet in the potential surface of the core-excited state, $\zeta = (E_X \cdot D)/2E_X$, $E_X(t)$ is the strength of the X-ray field, $D$ is the dipole moment of the X-ray transition, $\Omega = \omega_X - \omega_{\text{ad}}$ is the detuning of the frequency of the X-ray photons from the adiabatic excitation energy $\omega_{\text{ad}}$. The phase sensitivity of the trajectory of the wave packet results in, according to Fig.4.1(a), strong phase sensitivity of the probe X-ray spectra (dashed bands in Fig.4.1(b)).

We would like to pay attention to another interesting effect: The probe X-ray spectra depend on the phase of the pump field $\varphi_L$ even after the pump pulse leaves the system (Fig. 4.1(b)). The origin for such a long phase memory is found in the long lifetime of the vibrational levels of the ground state of diatomic molecules, $\sim 1$ msec (see Fig. 4.2(A)). During such a long lifetime the wave packet remains coherent and keeps memory about the pump pulse and, in particular, about its phase.

A first impression is that the long lifetime of the ground state vibrational levels guarantees the effect of phase memory. However, this is not true. The phase memory effect depends on the ratio of the Rabi period $T_R$ and the time of switching off the IR pulse $\Delta T$ (see Fig. 4.2(B)). Figures 4.1(b) and 4.2(A) illustrate the case when the duration of the IR pulse, $\tau_L = 100$ fs, is much shorter than the Rabi period, $T_R$.

$$T_R = \frac{2\pi}{G_R}, \quad G_R = |E_L \cdot d_0|,$$

(4.6)
4.2 Phase-sensitive dynamics caused by break down of the rotating wave approximation

where $G_R$ is the Rabi frequency of the system. This corresponds to the limiting case of a sudden switching off the pump field: The IR field is shut off faster than the Rabi period and the molecule remains in the vibrationally excited state after the pulse leaves the system (Fig. 4.2 (A)). The scenario changes drastically when the time for the switching-off of the IR pulse, $\Delta T \approx 715$ fs, is long and becomes comparable with the Rabi period, $T_R \approx 750$ fs (see Fig. 4.2 (B)). In this case, the system follows adiabatically the slow decrease of the light intensity up to zero, where only the lowest vibrational level is populated (Fig. 4.2 (B)). Because a single vibrational level does not depend on the phase, the effect of the phase memory is absent, and the X-ray spectrum coincides with the spectrum of the molecules that are not exposed to an IR field.

4.2 Phase-sensitive dynamics caused by break down of the rotating wave approximation

In the previous Section we discussed the phase sensitivity of the wave packet, created by direct mixing of vibrational states by the pump field (see Fig. 4.1). However, another mechanism of phase dependence of the nuclear dynamics exists. The origin of this phase dependence is the off-resonant interaction of the pump field with the molecule, which becomes to be important when the Rabi frequency (4.6) approaches the frequency of the vibrational transition, $\omega_{10} = \omega_L$. In this case, the intensity of the pump pulse is strong enough to violate the rotating wave approximation (RWA). The off-resonant or non-RWA (NRWA) contribution oscillates with double frequency and has a double phase shift, $2\varphi$ (see Paper IX).

We consider now the resonant interaction of the IR field with the OH vibrational mode, $\omega_L \approx \omega_{10} \equiv \omega_{OH}$ of the water dimer (Paper IX). Both the zero-point energy and the energy of the next OH vibrational state depend on the OO distance (Fig. 4.3 (A)). We separate the fast OH and slow OO vibrational modes in the Born-Oppenheimer approximation. Coherent IR radiation induces transitions between the two OH wells and creates wave packets in both. These wave packets perform oscillations along the OO bond. It is worthwhile to note that contrary to the situation discussed earlier in Sec. 4.1, the pump field does not mix the OO vibrational states directly. Now, the vibrational levels of the slow OO mode are mixed because of transitions through the upper OH well. Due to such up and down transitions, the phase of the IR field is canceled in the RWA approximation. Thus, the phase dependence

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1The rotating wave approximation ignores the fast oscillating terms in the dynamical equations. This is true when the resonant electromagnetic field is rather weak. In this case, only slow oscillations with frequency $\omega_{10} - \omega_L$ are kept, while the fast oscillations with frequency $\omega_{10} + \omega_L$ are neglected.
Figure 4.3: (A) The water dimer. (B) Phase dependence of the square of the wave packets of the ground and excited states at different times. The left panel shows the electric field of the pump pulse $E(t) = E(t) \cos(\omega_L t + \varphi)$. Solid and dashed lines correspond to $\varphi = 0$ and $\varphi = \pi/2$, respectively. Duration of the pump pulse $\tau = 50$ fs; the peak position corresponds to $T = 250$ fs; the peak intensity is $I = 10^{15}$ W/cm$^2$.

of the wave packet, which is presented in Fig. 4.3 (B), occurs only due to the break down of the RWA.

Our simulations show that the populations of the ground ($\rho_g$) and the excited ($\rho_e$) states (Fig. 4.3 (A)) experience weak modulations with the double frequency of the laser field, which appear due to the NRWA contribution (see Fig. 4.4 (A)). The character of these weak oscillations is similar to the NRWA modulations in the NO molecule (see inset in Fig.4.2(a)). Contrary to populations $\rho_g$ and $\rho_e$, the dynamics of the wave packet is strongly influenced by the NRWA terms (Fig. 4.3(B)). The reason for this is that the break down of the RWA affects the spatial distribution of the nuclear wave packet much stronger than such an integral characteristic as the population.

Snapshots of wave packets of the ground and excited states (Fig. 4.3(B)) show that the difference between wave packets induced by the pump field with a phase $\varphi = 0$ and $\pi/2$ is maximal when the intensity of the pump field and, hence, the Rabi frequency (4.6), reaches maximum (see left panel of Fig. 4.3(B)). We see that the wave packets depend on the doubled phase, $2\varphi$, due to the NRWA terms. Indeed, the simulations show that the wave packet does not change its shape when $2\varphi = 0 \rightarrow 2\pi$, contrary to the change of the phase $\varphi$ in $\pi/2$. The phase effect takes maximum value when $2\varphi = 0 \rightarrow \pi$. 
4.2 Phase-sensitive dynamics caused by break down of the rotating wave approximation

To observe the NRWA effects, one can measure the absorption or enhancement of the weak probe radiation with the same frequency as the pump field. The results of calculations of the probe signal are depicted in Fig. 4.4. One can see that the relative phase of the pump \( \varphi \) and the probe \( \varphi_p \) fields, \( \Delta \varphi = |\varphi - \varphi_p| \), affects strongly the work of the probe field \( P_p(t) \): compare panels (c), (d) where \( \Delta \varphi = 0 \) with the panel (e) where \( \Delta \varphi = \pi/2 \) (Fig. 4.4). The effect of the relative phase appears in the rotating wave approximation and the origin of this effect is the coherent interaction of the pump and probe fields.\(^{74}\)

To see the effect of the absolute phase, we need to compare panels (c) and (d) of Fig. 4.4 with different absolute phases, \( \varphi = \varphi_p = 0 \) and \( \varphi = \varphi_p = \pi/2 \). At a first glance, the work of the probe field is almost the same in both panels. However, the fine time structure of the populations and of \( P_p(t) \) (see right panel of Fig. 4.4) depends strongly on the absolute phase. Due to the break down of the RWA, the populations of the ground and excited states, as well as the work of the probe field \( P_p(t) \), oscillate with double frequency, \( 2\omega_L \). One can see that the change of the absolute phases \( \varphi = \varphi_p = 0 \rightarrow \pi/2 \) results in a shift of the fine structure of the populations and \( P_p(t) \) on \( \Delta t = 2\varphi/2\omega = 2\pi/4\omega \), which demonstrate that the probe signal depends on \( 2\varphi \) and \( \varphi + \varphi_p \) (Paper IX). It is interesting to note that in the region of strong pump field the probe signal \( P_p(t) \) experiences Rabi oscillations with a period \( T_R = 2\pi/G_{00} \approx 17 \) fs, which are strongly suppressed for the populations \( \rho_g(t) \) (Fig. 4.4).
4.3 Role of electron scattering in X-ray Doppler spectroscopy

Core excitations of molecules strongly change the interatomic interactions. As an X-ray photon transfers a molecule to a highly excited state it will, as a rule, dissociate. The dynamics of nuclear wave packets in a dissociative state is one of the hot topics of modern resonant Auger spectroscopy (RAS). We discuss here the electronic Doppler effect which is surprisingly large in RAS.

When a molecule $A_1A_2$ is core-excited in a dissociative state the fragments speed apart. The kinetic energy release, $\Delta E = \mu v^2/2 \approx 5 \div 10 \text{ eV}$, is much larger than the thermal energy, $k_B T \approx 0.03 \text{ eV}$. This results in a large velocity $v_1 = \alpha v$ [$\alpha = m_2/(m_1 + m_2)$] of the core-excited atom $A_1$. Large $v_1$, together with large momentum of the Auger electron ($k \approx 5 \div 10 \text{ a.u.}$), leads to a Doppler shift

$$\Delta \alpha = kv_1 \cos \theta, \quad kv_1 \sim 0.5 \div 1 \text{ eV}$$

(4.7)

which is one order of magnitude larger than the well-known electronic Doppler broadening caused by thermal motion. Because the Doppler shift exceeds considerably the lifetime broadening, $\Gamma \sim 0.1 \text{ eV}$, it has been readily observed in resonant Auger spectra of many molecules using the effect of Doppler splitting. The lifetime of the core excited state $\Gamma^{-1}$ is very important for the discussed Doppler effect. Indeed, the Doppler shift takes maximum value in the region of dissociation, $\Delta R = R - R_0 \sim 1 \div 2 \text{ a.u.}$ This means that the time of flight of the atom must be comparable with $\Gamma^{-1}$

$$\frac{\Delta R}{v_1} \sim \Gamma^{-1}.$$  (4.8)

The fundamental aim of spectroscopy is to determine molecular structure. However, the fact that molecules generally are randomly oriented significantly reduces the informational content. Because of the large kinetic energy release of the ionized fragment, the dissociation process is fast compared to the typical rotational times of the molecule. This means that measurements of the directions of the fragments in coincidence give a possibility to measure X-ray spectra of fixed-in-space molecules. The scheme of photoelectron-photoion coincidence (PEPICO) technique, which allows to obtain angular- and energy-resolved electronic spectra, is shown in Fig.4.5 (A). The PEPICO technique gives an opportunity to study the Doppler effect. Here, we focus our attention on the role of electron scattering by the surrounding atoms on the Doppler effect. This scattering gives information about bond angles of polyatomic molecules (see Paper X).
4.3 Role of electron scattering in X-ray Doppler spectroscopy

![Diagram](image)

Figure 4.5: (A) Scheme of electron-ion coincidence measurements of electronic spectra from fixed-in-space molecules. (B) Multiple-scattering contributions to the wave function of the Auger electron.

To give more insight in to the physics of the studied process we consider here only diatomic molecules. The Doppler effect is related to the momentum conservation law which is hidden in the generalized FC amplitude $\langle p_e | Q | p_f \rangle \propto \langle p_e | \psi | p_f \rangle$:

$$
\langle p_e | \psi | p_f \rangle, \quad \psi = e^{i K \mathbf{R}} \left[ f_2^{\ast}(\theta)\frac{e^{i(kR-k\mathbf{R})}}{R^2} + f_2(\pi) f_1(\pi-\theta)\frac{e^{2i k R}}{R^2} \right] \quad (4.9)
$$

where the amplitude of the K-Auger decay is proportional to the photoelectron wave function near the atom $A_1$, $Q \sim \psi$;19 $f_n(\theta)$ is the scattering amplitude on atoms $n$; $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$ is the internuclear radius vector; $|p_e\rangle$ and $|p_f\rangle$ are the nuclear wave functions of dissociative core-excited and final states, respectively; $\theta = \angle k, \mathbf{R}$. The last two terms in equation (4.9) describe single and double scattering events.

Integration over the displacements $q$ ($R \to R + q$) in the matrix element $\langle p_e | \psi | p_f \rangle$ (4.9) gives the following expression for the scattering amplitude of RAS from oriented diatomic molecules (Paper X)

$$
F \propto (\mathbf{e} \cdot \mathbf{d}) \left[ \frac{1}{\varepsilon + \Delta_0} + \frac{e^{-ikR(1-cos\theta)}}{\varepsilon + \Delta_0 + \Delta_\alpha - i\Gamma} + \frac{e^{-2ikR}}{\varepsilon + \Delta_0 + \Delta_\alpha - i\Gamma} \right] \quad (4.10)
$$

where $\varepsilon = E - \omega^\infty_{ej}$ is the energy of the Auger electron relative to the resonant frequency $\omega^\infty_{ej}$ of decay in an isolated core-excited atom; the complex dimensionless parameter $\rho = \rho(\theta)$ has a magnitude of the order of 1. The first, and the largest, term at the right-hand side of eq. (4.10) displays the ordinary Doppler shift (4.7). What perhaps is surprising, is that the
single and double scattering contributions have extra Doppler shifts, \( \Delta_b \) and \( \Delta_c \), respectively (see Fig.4.5 (B)). One can see that the origins of the Doppler shifts \( \Delta_a = \alpha k v \cos \theta \), \( \Delta_b = k v (1 - \cos \theta) \) and \( \Delta_c = 2 k v \) lay in the phase factors \( \exp (i k R_1) \), \( \exp (i (k R - k R)) \), and \( \exp (2 i k R) \) in the the wave function of the Auger electron (4.9). It is important to note that, contrary to \( \Delta_a \), the scattering induced Doppler shifts, \( \Delta_b \) and \( \Delta_c \), do not depend on the mass factor \( \alpha \). These Doppler shifts allow to select different scattering channels from the whole signal. The intensities of the new Doppler resonances are proportional to the scattering amplitude \( f(\theta) \) which takes maximum value in the forward direction. The strong anisotropy of the electron scattering combined with the Doppler effect makes the studied phenomenon a promising tool for molecular structure determination (see Paper X, XI).

Fig.4.6 shows results of simulations of eq.(4.10) for the IO molecule with core excitation of the oxygen atom. Scattering induced peaks B and C are displaced relative to the main peak A (the first term in (4.10)) by the Doppler shifts \( \Delta_b \) and \( \Delta_c \), respectively. The strong peak C appears only near the backward direction, \( \theta = 180^\circ \) (Fig.4.6). It is worthwhile here to note that the intensity of the diffractional peak C is comparable with the main peak A. It is because the smallness of \( |f_2(\pi)| \) is compensated by the large forward scattering amplitude, \( |f_1(0)| \). See Paper X and XI for more details.

Recently, the predicted effects were observed in PEPICO experiments with molecular oxygen.\(^{85}\) The scheme of experiment is shown in Fig.4.7 (a). The peaks A and B (Fig.4.7 (b)) are related to the first term in eq.(4.10) with Doppler shift \( \Delta_a = \alpha k v \cos \theta \). These peaks have opposite Doppler shifts because they correspond to reverse orientations of the ionized oxygen molecules (Fig.4.7 (a)). As shown in Fig.4.7 the intensities of the peaks A and B depend strongly on the time-of-flight. The peak A is more intense for longer time-of-flight; indeed, the ion needs longer time to reach the detector because it needs to change its propagation direction. In case B the ion moves directly to the detector; due to this the intensity of this peak is higher for short ion time-of-flight, Fig.4.7 (a). Peak \( C_B \) corresponds to backward...
single scattering with Doppler shift $\alpha k v - 2kv$, peak C$_F$ describes forward single-scattering with the Doppler shift $-\alpha k v$. This peak coincides with peak B (see Fig. 4.7 (b)). A similar experiment with tetrafluoromethane was performed in Ref. $^8$.
X-ray time-resolved spectroscopy of light-induced nuclear dynamics
Summary of results

The following main results have been obtained during my PhD studies:

Photonic crystals

- It was shown that the Brewster angles for different bands are different in 1D holographic photonic crystals, in contrast to the conventional two-layer Bragg reflector. The parameters of the hologram were found from comparison of the experimental data and theoretical results.
- A strong angular anisotropy of the delay time of short pulses in 1D impurity band based photonic crystals was shown.
- The strong anisotropy of the delay time was traced to the anisotropy of the group velocity, which is related to the angular dependence of the impurity band structure.

Dynamics of amplified spontaneous emission

- A strict theory of nonlinear propagation of few interacting strong light beams was developed: The self-consistent solutions of the nonlinear wave equation and the density matrix equation of the material were derived.
- A theory for bi-directional description of ASE induced by three-photon absorption was derived. It was shown that the interaction of co- and counter-propagating ASE pulses affects the dynamics and efficiency of nonlinear conversion. The efficiency of ASE is strongly dependent on the concentration of active molecules so that a particular combination of concentration and cell length maximizes the conversion coefficient.
- The dynamical theory explains the threshold behavior as well as the asymmetric properties between the forward and backward ASE pulses generated by ultra-fast multi-photon excitation. It is shown that these phenomena appear due to competition of different ASE channels.
- It is shown that the ASE spectral profile changes drastically when the pump intensity ap-
proaches the threshold level. Such a phase transition occurs when the ASE rate approaches the rate of vibrational relaxation or the rate of solute-solvent relaxation in the first excited state.

- Under certain conditions the ASE effect is found to be oscillatory. Two different mechanisms of temporal self-pulsations of forward and backward propagating ASE pulses were found: i) the interaction of co- and counter-propagating ASE, and ii) the dynamical competition between the stimulated emission and off-resonant absorption.

**Light-induced nuclear dynamics**

- It was shown that in time- and frequency-resolved X-ray spectroscopy of molecules driven by strong and coherent IR pulses, the phase of the pump field strongly influences the trajectory of the nuclear wave packet, and hence, the X-ray spectrum.
- The trajectory of the nuclear wave packet experiences fast oscillations with the vibrational frequency, which are modulated due to the anharmonicity of the potential.
- It is shown that the X-ray spectrum keeps memory about the infrared phase even after the pump field left the system. This memory effect is sensitive to the relation of the time of switching-off the pump field and the Rabi frequency.
- The phase effect takes maximum value when the duration of the X-ray pulse is of the order of the infrared field period, and can be enhanced by a proper control of the duration and intensity of the pump pulse.
- It was shown that the phase of the light influences the dynamics of the nuclear wave packets when the Rabi frequency approaches the vibrational frequency, thus breaking down the rotating-wave approximation.
- In this regime, the absorption profile of the probe field also experiences dependence on the absolute phase of the pump field. The fast temporal oscillation of the probe field profile has a slower envelope which corresponds to the Rabi oscillation of the system.
- It was predicted that when fixed-in-space molecules are considered, there will appear extra Doppler resonances resulting from the diffractional scattering of the Auger electrons by the surrounding atoms.
- These resonances show sharp maxima in the bond directions. That makes them very promising as probes for local molecular structure using current energy and angular resolved electron-ion coincidence experiments.
Bibliography


