

Theoretical study of light-molecule nonlinear interactions

Ke Zhao



Department of Theoretical Chemistry
School of Biotechnology
Royal Institute of Technology
Stockholm, Sweden 2007

© Ke Zhao, 2007

ISBN 978-91-7178-642-5

Printed by Universitetservice US AB,

Stockholm, Sweden, 2007

Abstract

The work presented in the thesis concerned theoretical study of light-matter nonlinear interactions. Two important aspects of such interactions have been examined, namely the nonlinear optical properties of a series of organic charge transfer molecules in solutions induced by the laser light and the propagation of the ultrafast high power laser through the nonlinear molecular medium.

Special attention has been paid to understand the solvent effects on the two-photon absorption of a symmetrical diamino substituted distyrylbenzene chromophore, for which time-dependent density functional theory in combination with polarizable continuum model (PCM) have been employed. The dielectric medium alone has a rather small effect both on the bond length alternation and on the one-photon absorption spectrum, but noticeable effects on the two-photon absorption cross section. Both one- and two-photon absorptions are found to be extremely sensitive to the planarity of the molecule. Our calculations indicate that the experimentally observed anomalous solvent effect on the two-photon absorption of dialkylamino substituted distyrylbenzene chromophores can not be attributed to the intrinsic properties of a single molecule and its interaction with solvents. With the same theoretical approaches, two-photon absorption properties of interacting polar chromophores have been investigated to examine the validity of the widely used exciton model. Our first principles calculations have shown that the exciton model offers a conceptually simple interpretation for experimental observations, but is lack of predictability.

The second part of the thesis is to investigate the propagation of ultrashort laser pulse through a one-dimensional asymmetric organic molecular medium by solving full Maxwell-Bloch equations using predictor-corrector finite-difference time-domain method. It focuses on the supercontinuum generation of spectra and the formation of attosecond pulses. It is shown that the supercontinuum generation is strongly modulated by both area and width of the pulse, which results from the interference between the splitting pulses in time-domain and is the implication of the time-energy uncertainty relation. The presence of permanent dipole moment in molecular medium has noticeable effects on the supercontinuum generation. Our calculations show that a well-shaped 132 attosecond pulse can be generated from a two femtosecond incoming pulse under certain conditions. Influences of carrier-envelope phase and time-dependent ionization on the spectral and temporal evolutions of the ultrashort pulses have also been discussed.

Preface

The work presented in this thesis has been carried out at the Department of Theoretical Chemistry, School of Biotechnology, Royal Institute of Technology, Stockholm, Sweden.

List of papers included in the thesis

Paper I. **Ke Zhao**, Lara Ferrighi, Luca Frediani, Chuan-Kui Wang, and Yi Luo, *Solvent effects on two-photon absorption of dialkylamino substituted distyrylbenzene chromophore*, J. Chem. Phys. 00, 000, 2007.

Paper II. **Ke Zhao**, Chuan-Kui Wang, and Yi Luo, *Two-photon absorption activities of interacting dipolar chromophores: a DFT Study*, in manuscript.

Paper III. **Ke Zhao**, Ji-Cai Liu, Chuan-Kui Wang, and Yi Luo, *Modulation of supercontinuum generation and formation of attosecond pulse from a generalized two-level medium*, J. Phys. B: At. Mol. Opt. Phys. **40**, 1523, 2007.

List of papers not included in the thesis

Paper I. Chuan-Kui Wang, Ji-Cai Liu, **Ke Zhao**, Yu-Ping Sun, and Yi Luo, *The breakdown of optical power limiting and dynamical two-photon absorption under femtosecond laser pulses in molecular medium*, J. Chem. Phys., submitted.

Comments on my contribution to the papers included

- I was responsible for most of calculations and the writing of the first draft for Paper I.
- I was responsible for calculations and writing of Paper II.
- I was responsible for most of calculations and the writing of the first draft for Paper III.

Acknowledgments

First of all, I would like to express my deep gratitude to my supervisor Prof. Yi Luo. It is you who give me the chance to have access to the first-class research environment. Your patient guidance and fruitful ideas give me great helps and make this thesis possible. I would also like to thank Prof. Hans Ågren, the head of our department. Your kindness makes me feel our group like a whole family.

I wish to thank my supervisor in China Dr. Chuankui Wang. You introduce me to my research field and give me great guidance.

I would also like to express my thanks to Prof. Faris Gel'mukhanov, Dr. Ying Fu, Dr. Fahmi Himo, Dr. Åsa Larson, Dr. Zilvinas Rinkevicius, Dr. Pawel Salek, Dr. Yaoquan Tu, Prof. Boris Minaev, Dr. Prakash Chandra Jha. Thank you for teaching me so much useful knowledge.

I would like to acknowledge the following people for the discussions and assistances: Yanhua Wang, Jun Jiang, Kai Liu, Shilu Chen, Yong Zeng, Tiantian Han, Bin Gao, Feng Zhang (phoenix), Guangde Tu, Qiong Zhang, Na Lin, Wenhua Zhang, Kathrin Hopmann, Elias Rudberg, Cornel Oprea, Emil Jansson, Peter Hammar, Robin Sevastik, Katia Julia de Almeida, Rongzhen Liao, Ying Hou, Kai Fu, Jikai Liu. Thank all colleagues at the group of theoretical chemistry.

Finally, I want to thank my mother for taking care of my son and giving me great support.

Contents

1	Introduction	9
2	Quantum chemistry methods	13
2.1	Hartree-Fock method	14
2.2	Density functional theory	16
2.2.1	Hohenberg-Kohn theorem	16
2.2.2	Kohn-Sham equation	17
2.2.3	Functional	17
3	Two-photon absorption	19
3.1	Cross sections	19
3.2	Response Theory	21
3.2.1	Response functions	21
3.2.2	Residues of response functions	23
3.3	Few-states model	23
3.4	Solvent effects	25
3.4.1	Solvent models	26
3.4.2	Solvent effects on two-photon absorption	28
4	Frenkel Exciton Model	31
4.1	Heitler-London approximation	31
4.2	The interaction-energy operator	33
4.3	In Second-Quantization representation	34
5	Propagation of few-cycle pulse in generalized two-level medium	37
5.1	Maxwell-Bloch equations	38
5.2	The McCall-Hahn “Area Theorem”	41
5.3	Predictor-corrector FDTD method	43

Chapter 1

Introduction

In 1931, Maria Göppert-Mayer[1] calculated the probability of the simultaneous absorption of two photons in a medium and found that the typical nonresonant cross section for two-photon absorption (TPA) is exceedingly small. Therefore, the experimental confirmation of such a process had to wait the advent of laser sources with sufficient intensity. The first experimental verification of TPA processes was reported in 1961 by W. Kaiser and C. G. B. Garrett[2].

In the last two decades, many organic molecules have been found to have large TPA cross sections. Materials possessing large TPA response have many potential applications, for instance two-photon excited fluorescence microscopy[3,4], optical limiting[5], upconverted lasing[6,7], three-dimensional (3D) optical data storage[8,9], and microfabrication, just to mention a few. The ability to achieve 3D spatial resolution arises from the fact that the rate of the simultaneous absorption of two photons depends quadratically on the intensity of the incident laser light. It means that if a tightly focus beam is used, the intensity of the beam decreases quadratically with the distance from the focal plane, so that the excitation is confined in a small volume around the focus (on the order of λ^3). The linear absorption of a material may be very weak in the wavelength range where the TPA occurs, providing the possibility to excite materials at greater depth than might be possible via one-photon excitation. Moreover, because the wavelength used for TP excitation is roughly twice that for one-photon excitation, the influence of scattering on beam intensity is greatly reduced. These are clear advantages for applications such as imaging in absorbing or scattering media, like biological

tissues.

Theoretical simulations have provided many useful guidelines for the design and synthesis of TPA materials. Development of detailed structure-property relationships is important for systematically increasing the TPA cross section at desirable wavelengths. It has been shown that the TPA cross sections can be enhanced by several structural factors, such as the electron richness of the π -conjugation center, the strength of donor and/or acceptor substituents, the molecular symmetry, the dimensionality of charge transfer networks, and the planarity of the π -conjugation center.[10-14]

In recent years, the structure of active TPA organic molecules moved from symmetrically or asymmetrically substituted linear π -conjugated unit to multi-branched architectures with increased dimensionality[15-22]. As for multi-branched molecules, the interplay and the coupling among the branches has a significant effect on nonlinear optical response. Both Frenkel exciton model and “supermolecular” quantum chemical methods are employed to interpret experimental results. Frenkel excitons are used to describe the elementary collective electronic excitations of molecular crystals that consist of weakly interacting molecules. With this model, the one- and two-photon excitation spectra of multi-branched molecule can be constructed from those of single-branched sub-unit. Frenkel exciton model is conceptually simple, but relies on experimental data as inputs. Its predictability is thus questionable. A better choice for such systems is the first principles, or *ab initio*, quantum chemical methods. The fast growth of the computer power and the constant improvement of computational techniques have allowed us to treat very large systems without introducing empirical approximations. Quantum chemical approaches have not only been used to confirm the experimental observations, but also provided many useful design strategies to guide the chemical synthesis. Most of the experiments, as well as technical applications, are performed in solutions, matrices, thin films or in the solid phase. It has been shown that optical properties of molecules can be modified dramatically in condensed phase[23-28]. It is thus necessary to include the effects of surroundings in the quantum chemical methods.

In this thesis, the validity of Frenkel exciton model has been examined by comparing with density functional response theory calculations for the linear and two-photon absorption spectra of these interacting polar chromophores. It is found that

the molecular parameters used in the Frenkel exciton model are often unrealistic. Furthermore, solvent effects on the one- and two-photon absorption spectra of charge transfer molecules have been studied by means of polarizable continuum model (PCM), which treats the solvent environment as a homogenous dielectric continuum medium characterized by its dielectric constant. All of the calculations were performed with the GAUSSIAN 03[29] and DALTON[30] quantum chemical program packages.

The light-molecule nonlinear interaction can induce nonlinear polarization of the molecule as we just discussed. It can also result in the change of the character of the laser light. An impressive progress has been achieved recently in the generation of ultrashort light pulses with a duration corresponding to a few cycles of the optical field[31,32], which offers an unique opportunity to perform spectral measurements with an unprecedented high resolution and has stimulated many applications in diverse fields. Coherent control of chemical reactions, the acceleration of particles and the generation of coherent soft-X-ray radiation are only a few examples to mention here. Several methods of generating subfemtosecond and attosecond pulses using high-order harmonic generation and coherent Raman sidebands have been extensively discussed.

One of the most important processes is the supercontinuum generation (SCG), which is the formation of broad continuous spectra by propagation of high power pulses through nonlinear media. This phenomenon was first observed in 1970 [33] and have been utilized in solids, liquids, and gases under a wide variety of experimental conditions since then[34-36]. SCG is a universal feature of the laser-matter interaction because the shapes of the observed spectra for various media are very similar. As a broadly tunable ultrafast light source, SCG is promised to have applications in a number of areas, including time-resolved broadband absorption and excitation spectroscopy, optical pulse compression, and optical parametric amplification. SCG is a result of many complicated nonlinear optical processes, such as stimulated Raman scattering (SRS)[37] and four-wave mixing (FWM)[33,38].

A full description of interaction between ultra-fast high power pulses and matter presents a great challenge for theory. Most of theoretical models are based on a two-level system following the seminal work of MaCall and Hahn [39]. Under the rotating-wave approximation (RWA) and slowly varying envelope approximation (SVEA), interesting effects such as self-induced transparency and Rabi flopping were

observed[40,41]. Without employing SVEA and RWA, Ziolkowski et al. [42] applied the finite-difference time-domain (FDTD) technique to numerically solve the semi-classical Maxwell-Bloch (MB) equations and provided a more detailed analysis of the self-induced transparency (SIT) effects. Hughes [43,44] has recently employed the FDTD approach to stimulate the propagation of an 18fs pulse propagating through a two-level medium. It was found that for large area laser pulse, the area under individual carriers might cause Rabi flopping, which can lead to carrier-wave reshaping, higher spectral components and even soft-x-ray generation.

It is known that nonlinear optical processes of charge-transfer molecules can often be described by a few-state model due to the presence of charge-transfer states that dominate the optical absorptions. However, a two-level atomic model can not be directly used for a two-state molecular system, since the latter often possesses permanent dipole moments. The interaction between ultrashort laser pulses and dipolar molecular medium has become an interesting subject.[45-47]

The work presented in this thesis is concerned with the propagation of ultrashort pulses in a generalized two-level system, consisting of permanent dipole moments. It is simulated by solving the full Maxwell-Bloch equations using predictor-corrector FDTD method. Special attention has been paid to the supercontinuum generation of spectra and the formation of attosecond pulses. The effect of the permanent dipole moment on the supercontinuum generation is discussed in detail. Influences of carrier-envelope phase and time-dependent ionization on the spectral and temporal evolutions of the ultrashort pulses are also considered.

Chapter 2

Quantum Chemistry Methods

Nowadays quantum chemistry methods have become the basic and effective tools to explore the structure, properties and behavior of atoms and molecules. The main object of all nonrelativistic *ab initio* computational methods is to solve the Schrödinger equation of system usually containing many electrons. Although the Schrödinger equation has a relatively simple form, it is impossible to solve it exactly except for the simplest cases like H_2^+ . Many reasonable approximations have to be adopted.

Given a molecular system with M nuclei and N electrons, the Hamiltonian associated with the total energy is the sum of the kinetic operators of nuclei and electrons, the potential operator which accounts for the electrostatic repulsion between nuclei and between electrons, and the electrostatic attraction between nuclei and electrons. In atomic units,

$$H = -\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} \quad (2.1)$$

where i, j refer to electrons, A, B to nuclei.

The time-independent Schrödinger equation is written as

$$H(\{\bar{R}_A\}, \{\bar{r}_i\})\Phi(\{\bar{R}_A\}, \{\bar{r}_i\}) = \varepsilon\Phi(\{\bar{R}_A\}, \{\bar{r}_i\}) \quad (2.2)$$

where Φ is the stationary wave function.

The large difference between the masses of the nuclei and the electron allows us to neglect the motion of the nuclei and to consider the electrons to be moving in a field of

M fixed positive point charges, that is, Born-Oppenheimer approximation. With the Born-Oppenheimer approximation, the coupling of electronic and nuclear motions can thus be neglected and their position variables can be separated, so that,

$$\Phi(\{\bar{\mathbf{R}}_A\}, \{\bar{\mathbf{r}}_i\}) = \Phi_{elec}(\{\bar{\mathbf{r}}_i\}; \{\bar{\mathbf{R}}_A\}) \Phi_{nucl}(\{\bar{\mathbf{R}}_A\}) \quad (2.3)$$

The electron wave function is solved from the Schrödinger equation of electrons,

$$H_{elec} \Phi_{elec} = \varepsilon_{elec} \Phi_{elec} \quad (2.4)$$

in which

$$\varepsilon_{elec} = \varepsilon_{elec}(\{\bar{\mathbf{R}}_A\}) \quad (2.5)$$

depends parametrically on the nuclei coordinates. The electronic Hamiltonian H_{elec} includes the second, fourth and fifth terms in (2.1). When the electronic problem is solved, $\varepsilon_{elec}(\{\bar{\mathbf{R}}_A\})$ can provide an average potential for the motion of nuclei. The nuclei Hamiltonian is thus

$$H_{nucl} = -\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} + \varepsilon_{elec}(\{\bar{\mathbf{R}}_A\}) \quad (2.6)$$

The nuclei wave function solved from the nuclear Schrödinger equation

$$H_{nucl} \Phi_{nucl} = \varepsilon \Phi_{nucl} \quad (2.7)$$

$\Phi_{nucl}(\{\bar{\mathbf{R}}_A\})$ describes the translation, rotation and vibration of the molecule. The total energy ε now includes not only electronic but also translational, rotational and vibrational energies.

2.1 Hartree-Fock method

The Hartree-Fock approximation is a one-electron molecular orbital approximation that introduces one-electron wavefunctions (molecular orbital) to describe the electrons in the molecule. Each molecular orbital is composed of the spatial orbital $\psi_i(\bar{\mathbf{r}})$ and the spin function, either $\alpha(\omega)$ (spin up) or $\beta(\omega)$ (spin down). The total N-electron wave function can be constructed from the occupied N molecular orbitals ($\chi_i, \chi_j, \dots, \chi_k$) in a determinantal form, namely, the Slater determinant

$$\psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = (N!)^{-1/2} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) & \cdots & \chi_k(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) & \cdots & \chi_k(\mathbf{x}_2) \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \chi_i(\mathbf{x}_N) & \chi_j(\mathbf{x}_N) & \cdots & \chi_k(\mathbf{x}_N) \end{vmatrix} \quad (2.8)$$

where \mathbf{x}_i is the collective notation for the spatial and spin coordinates of the i -th electron. Such a determinant satisfies antisymmetry requirement of multi-electron wave functions, i.e, Pauli exclusion principle.

The variation principle of quantum mechanics states that the best approximation to the exact solution of the Schrödinger equation for a certain type trial function is the one that gives the minimal energy with respect to the variation of all the parameters it contains. If we use Slater determinant as the ansatz for the wavefunction and write the molecular orbitals (spatial part) as a linear combination of atomic orbitals (basis sets), then employ the variational principle, we can derive a set of N coupled equations (Hartree-Fock equations) for the N orbitals. Solution of these equations yields the Hartree-Fock wavefunction and energy of the system, which are approximations of the exact one. The Hartree-Fock method is also called the self-consistent field method (SCF) because the solving of the HF equations is an iterative self-consistent procedure.

The one-electron molecular orbital approximation is also equivalent to assuming that the electron is independent of each other so that the electron interacts only with the average potential from the rest of the electrons, hence the electronic Hamiltonian can be expressed as a sum of one-electron Hamiltonians. The Hartree-Fock approximation inevitably neglects the interactions among electrons. The difference between the total ground state exact energy and the HF energy is defined as the correlation energy:

$$E_{corr} = E_{tot} - E_{HF} \quad (2.9)$$

It should be noted that the exchange energy which derives from the electron-electron repulsion interaction due to Pauli exclusion principle is fully accounted for in the Hartree-Fock method. The neglect of the electron correlation can lead to large deviations from experimental results. A number of approaches that improve this weakness are collectively called post-Hartree-Fock methods which include electron correlation of

different degree in the many-electron wave function. Among many, Configuration Interaction (CI), Multi-configurational self-consistent fields (MCSCF), complete active space SCF (CASSCF), and Møller-Plesset perturbation theory (MPn) are the frequently used ones. Another quite different way of including the electron correlation is the density-functional theory (DFT), which is based on the electron density instead of the wavefunction.

2.2 Density functional theory

DFT developed by Hohenberg, Kohn and Sham gives a relatively simple prescription for the total energy of a system. In DFT the energy is not obtained as eigenvalues of a wavefunction, but rather as a functional of the electron density. In recent years, DFT has become a very popular method for large molecular systems.

If the number of electrons is N , then the electron density is defined as

$$n(\mathbf{r}) = N \int \cdots \int |\psi|^2 d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \quad (2.10)$$

2.2.1 Hohenberg-Kohn theorem

In 1964, Hohenberg-Kohn gave the proofs of two important theorems:[48]

Theorem I: For any system of electrons, the external potential $V_{ext}(\mathbf{r})$ is determined uniquely, except a constant, by the ground state density $n(\mathbf{r})$.

Theorem II: There exists a universal functional for the energy $E[n]$ of the density $n(\mathbf{r})$. For a given $V_{ext}(\mathbf{r})$, the global minimum of $E[n]$ is the exact ground state energy which occurs for the exact ground state density $n(\mathbf{r})$.

Hohenberg-Kohn theorem guarantees the existence of an energy functional $E[n]$ that reaches its minimum for the correct density $n(\mathbf{r})$. For molecules with non-degenerate ground state, the ground state energy and all other molecular electronic properties are uniquely determined by the ground state electronic density.

2.2.2 Kohn-Sham equation

One can always find the non-interacting electron system with the same $n(\mathbf{r})$ as the exact, interacting system. For this fictitious system with non-interacting electrons Kohn-Sham introduced the orbitals ϕ_i (Kohn-Sham orbital), [49] which give the exact ground state electron density as

$$n(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2 \quad (2.11)$$

The exact total electronic energy can be written as sum of terms, each dependent on the density

$$E_{exact} = E_T + E_V + E_J + E_{xc} \quad (2.12)$$

where E_T is the kinetic energy of a system of non-interacting electrons with the same density as the real system, E_V is the external potential energy, E_J is the classical interaction between two charge densities, and E_{xc} is the exchange-correlation energy which contains not only exchange and correlation contributions, but also a contribution due to the difference between the true kinetic energy of the system and the E_T .

Applying the variational theorem we can derive the Kohn-Sham equations for the orbital

$$\left[-\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \quad (2.13)$$

where the V_{xc} is the exchange-correlation potential defined as the functional derivative of the exchange-correlation energy with respect to the density $V_{xc}(r) = \delta E_{xc} / \delta n(\mathbf{r})$. Similar to Hartree-Fock orbitals, the Kohn-Sham orbitals are obtained by using a SCF approach to solve the Kohn-Sham equations.

2.2.3 Functional

Although Eq. (2.12) can give the exact energy of system, the main problem is that the exact functional for exchange and correlation are not known except for the free electron gas. Thus, approximated functional must be introduced. The local density approximation (LDA), the local spin density approximation (LSDA) and generalized gradient approximation (GGA) are some examples. One of the most popular functional

is Becke's [50] three-parameter gradient-correlated exchange functional with the Lee-Yang-Parr [51] gradient-correlated correlation (B3LYP)

$$E_{xc}^{B3LYP} = (1 - a_0)E_x^{LSDA} + a_0E_x^{HF} + a_x\Delta E_x^{B88} + a_cE_c^{LYP} + (1 - a_c)E_c^{VWN} \quad (2.14)$$

where a_0 , a_x and a_c are empirical coefficients obtained by least-square fitting to experimental data. Their values are $a_0 = 0.20$, $a_x = 0.72$ and $a_c = 0.81$. Because it uses the Hartree-Fock exchange, it is also called as hybrid exchange-correlation functional. B3LYP functional has been used in all the work presented in this thesis.

Chapter 3

Two-photon absorption

Two-photon absorption (TPA) process involves the concerted interaction of two photons with individual atom or molecule, see Figure 3.1. The probability of a molecule simultaneously absorbing two identical photons is proportional to the square of the laser intensity. Compared to one-photon absorption, TPA has different selection rules and it is dependent on the polarization of the light. These features make the TPA a complementary spectroscopic tool to study the excited states of molecule.

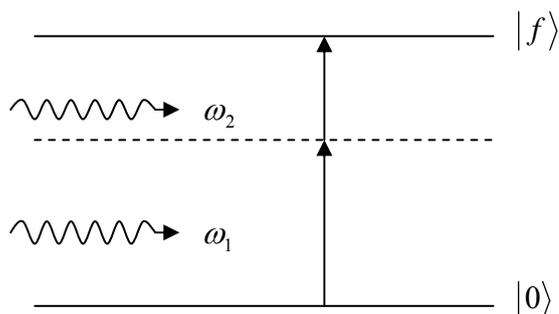


Figure 3.1 Two-photon absorption.

3.1 Cross sections

A relationship between molecular structure and two-photon absorption cross section can be derived from standard time-dependent perturbation theory[52]. The two-photon absorption cross section of randomly oriented systems is directly related to the imaginary part of the third susceptibility $\chi^{(3)}$.

$$\sigma = \frac{8\pi^2\hbar\omega^2}{n^2c^2N} \text{Im}(\chi^{(3)}) = \frac{8\pi^2\hbar\omega^2}{n^2c^2} \text{Im}(\gamma) \quad (3.1)$$

where γ is the second hyperpolarizability and n is the refractive index.

Alternatively, the two-photon absorption cross section can be obtained by computing the individual two-photon transition matrix elements S_{ab} between the initial state $|i\rangle$ and final state $|f\rangle$. For simplicity we shall consider the case of one beam with frequency ω being close to half of the excitation energy of the final state ω_f .

$$\gamma_{\alpha\beta\gamma\delta}(-\omega; \omega, -\omega, \omega) = i \frac{2\hbar^{-1}}{\Gamma_f} S_{\alpha\gamma} S_{\beta\delta}^* \quad (3.2)$$

$S_{\alpha\beta}$ is defined as

$$S_{\alpha\beta} = \sum_s \left(\frac{\langle i | \mu_\alpha | s \rangle \langle s | \mu_\beta | f \rangle}{(\omega_{si} - \omega)} + \frac{\langle i | \mu_\beta | s \rangle \langle s | \mu_\alpha | f \rangle}{(\omega_{si} - \omega)} \right) \quad (3.3)$$

where $\alpha, \beta \in (x, y, z)$, μ is the dipole moment operator, ω_{si} represents the excitation energy to each intermediate state $|s\rangle$, and the summation here includes all intermediate, initial and final states.

The TPA transition probability is dependent on the polarization of the laser beams[53]. The orientationally averaged two-photon probability is given by

$$\delta_{ip} = \sum_{\alpha\beta} [F \times S_{\alpha\beta} S_{\beta\alpha}^* + G \times S_{\alpha\beta} S_{\alpha\beta}^* + H \times S_{\alpha\beta} S_{\beta\alpha}^*] \quad (3.4)$$

Here F, G and H are coefficients dependent on the polarization of the light. The values of F, G and H are 2, 2 and 2 for linearly polarized light and -2, 3 and 3 for the circular case. The microscopic TPA cross section of molecules excited by a linearly polarized monochromatic beam can thus be described by

$$\delta_{ip} = 6(S_{xx} + S_{yy} + S_{zz})^2 + 8(S_{xy}^2 + S_{xz}^2 + S_{yz}^2 - S_{xx}S_{yy} - S_{xx}S_{zz} - S_{yy}S_{zz}) \quad (3.5)$$

The TPA cross section that can be directly compared with the experiment is defined as

$$\sigma_p = \frac{4\pi^2 a_0^5 \alpha \omega^2 L^4}{15c \Gamma_f n^2} \delta_p \quad (3.6)$$

where a_0 is the Bohr radius, α is the fine structure constant, L is the Lorentz field factor, n is the refractive index and the level broadening Γ_f of final state is assumed to have the commonly used value $\Gamma_f = 0.1$ eV, corresponding to a lifetime of a few fs.

Using Eq. (3.3) to calculate the TP transition matrix elements is called the sum-over-states (SOS) method. Its application is limited because it requires the knowledge of all excited states which makes the *ab initio* calculations very expensive. In practice, it is used by truncation of the SOS expression to only include the dominating states. The convergence rates with respect to the inclusion of states in summation are known to be slow except for special systems, like the charge-transfer molecules. Now the most accurate and rigorous method to evaluate the TPA transition matrix is by the response theory.

3.2 Response Theory

Response theory[54] is a way of formulating time-dependent perturbation theory. As the name implies, response functions describe how a property of a system responds to an external perturbation. The main advantage is that the explicit summation over excited states is substituted by the solution of a set of coupled response equations. The TP transition matrix elements can be identified from the residue of the quadratic response function.

3.2.1 Response functions

The Hamiltonian operator of a molecular system experienced external field can be expressed as

$$H = H_0 + V(t) \quad (3.7)$$

where H_0 is the time-independent Hamiltonian of the unperturbed system, and $V(t)$ is the time-dependent perturbation.

In the frequency domain, the perturbation operator can be written as

$$V(t) = \int_{-\infty}^{+\infty} V^\omega e^{(-i\omega + \varepsilon)t} d\omega \quad (3.8)$$

where ε is a small positive infinitesimal that ensures the field vanishes at $t = -\infty$.

The average value of time-dependent operator A can be expanded in the series

$$\begin{aligned} \langle A \rangle(t) &= \langle A \rangle_0 + \int_{-\infty}^{+\infty} \langle \langle A; V^{\omega_1} \rangle \rangle_{\omega_1} e^{(-i\omega_1 + \varepsilon)t} d\omega_1 \\ &+ \frac{1}{2!} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \langle \langle A; V^{\omega_1}, V^{\omega_2} \rangle \rangle_{\omega_1, \omega_2} e^{[-i(\omega_1 + \omega_2) + 2\varepsilon]t} d\omega_1 d\omega_2 \\ &+ \frac{1}{3!} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \langle \langle \langle A; V^{\omega_1}, V^{\omega_2}, V^{\omega_3} \rangle \rangle \rangle_{\omega_1, \omega_2, \omega_3} e^{[-i(\omega_1 + \omega_2 + \omega_3) + 3\varepsilon]t} d\omega_1 d\omega_2 d\omega_3 + \dots \end{aligned} \quad (3.9)$$

where $\langle \langle A; V^{\omega_1} \rangle \rangle_{\omega_1}$, $\langle \langle A; V^{\omega_1}, V^{\omega_2} \rangle \rangle_{\omega_1, \omega_2}$ and $\langle \langle \langle A; V^{\omega_1}, V^{\omega_2}, V^{\omega_3} \rangle \rangle \rangle_{\omega_1, \omega_2, \omega_3}$ denote the linear, quadratic, and cubic response functions, respectively. According to these response functions, all time-dependent properties of the molecule can be determined. For example, when A denotes the electric dipole operator, the total dipole moment induced by the external field may be expressed by response functions which correspond to, for instance, the polarizability and hyperpolarizability of the molecule.

$$\alpha_{ij}(-\omega_1; \omega_1) = -\langle \langle \mu_i, \mu_j \rangle \rangle_{\omega_1} \quad (3.10)$$

$$\beta_{ijk}(-\omega_1 - \omega_2; \omega_1, \omega_2) = -\langle \langle \mu_i; \mu_j, \mu_k \rangle \rangle_{\omega_1, \omega_2} \quad (3.11)$$

$$\gamma_{ijkl}(-\omega_1 - \omega_2 - \omega_3; \omega_1, \omega_2, \omega_3) = -\langle \langle \mu_i; \mu_j, \mu_k, \mu_l \rangle \rangle_{\omega_1, \omega_2, \omega_3} \quad (3.12)$$

For exact states these response functions can be given in their special representation with

$$-\langle \langle A; B \rangle \rangle_{\omega_1} = \sum_{\mathbf{P}} \sum_n \frac{\langle 0|A|n\rangle \langle n|B|0\rangle}{\omega_n - \omega_1} \quad (3.13)$$

as the linear response function and

$$-\langle \langle A; B, C \rangle \rangle_{\omega_1, \omega_2} = \sum_{\mathbf{P}} \sum_{n, m \neq 0} \frac{\langle 0|A|n\rangle \langle n|\bar{B}|m\rangle \langle m|C|0\rangle}{(\omega_n - \omega_\sigma)(\omega_m - \omega_2)} \quad (3.14)$$

as the quadratic response function, where $\langle n|\bar{B}|m\rangle = \langle n|B - \langle 0|B|0\rangle|m\rangle$ and $\omega_\sigma = \omega_1 + \omega_2 + \dots$. \mathbf{P} is the permutation operator.

3.2.2 Residues of response functions

The linear response function has poles at frequencies equal to plus or minus the excitation energies of the unperturbed system. The corresponding residues are

$$\lim_{\omega_1 \rightarrow \omega_f} (\omega_1 - \omega_f) \langle\langle \mu_i; \mu_j \rangle\rangle_{\omega_1} = \langle 0 | \mu_i | f \rangle \langle f | \mu_j | 0 \rangle \quad (3.15)$$

$$\lim_{\omega_1 \rightarrow -\omega_f} (\omega_1 + \omega_f) \langle\langle \mu_i; \mu_j \rangle\rangle_{\omega_1} = -\langle 0 | \mu_j | f \rangle \langle f | \mu_i | 0 \rangle \quad (3.16)$$

The linear response functions thus provide the information about the excitation energies from the initial state $|0\rangle$ to final state $|f\rangle$ and the corresponding transition dipole moments. It can be used to describe the one-photon processes. The single residue of the quadratic response function gives the information on the two-photon transition matrix elements

$$\begin{aligned} & \lim_{\omega_2 \rightarrow \omega_f} (\omega_2 - \omega_f) \langle\langle \mu_i; \mu_j, \mu_k \rangle\rangle_{-\omega_1, \omega_2} \\ &= -\sum_{n>0} \left[\frac{\langle 0 | \mu_i | n \rangle \langle n | (\mu_j - \langle 0 | \mu_j | 0 \rangle) | f \rangle}{\omega_n - \omega_2} + \frac{\langle 0 | \mu_j | n \rangle \langle n | (\mu_i - \langle 0 | \mu_i | 0 \rangle) | f \rangle}{\omega_n - \omega_1} \right] \langle f | \mu_k | 0 \rangle \end{aligned} \quad (3.17)$$

where $\omega_1 + \omega_2 = \omega_f$.

It is noted that the two-photon absorption cross section is an observable which is described by the cubic response function. The quadratic response function may only be used to identify formal expressions for the TPA matrix element. It makes the calculations more convenient.

From the double residue of the same response function one can deduce the transition dipole moments between excited states

$$\begin{aligned} & \lim_{\omega_1 \rightarrow -\omega_f} (\omega_1 + \omega_f) \left[\lim_{\omega_2 \rightarrow \omega_i} (\omega_2 - \omega_i) \langle\langle \mu_i; \mu_j, \mu_k \rangle\rangle_{\omega_1, \omega_2} \right] \\ &= -\langle 0 | \mu_j | f \rangle \langle f | (\mu_i - \langle 0 | \mu_i | 0 \rangle) | i \rangle \langle i | \mu_k | 0 \rangle \end{aligned} \quad (3.18)$$

3.3 Few-states model

As mentioned above, for some special molecular systems, the optical properties are found to be dominated by a few electronic states. In this case, the SOS expression only needs to include a few dominating states. The so-called few-states model[55,56,10,24,] not only makes the SOS approach to a manageable extent, but also provides a better

understanding for the revealed structure-to-property relations.

For one-dimensional molecules, the TPA cross section is completely dominated by the component along the molecular axis S_{zz} , and only this component will be considered in a few-states model. For the symmetrically substituted one-dimensional molecules, the first excited state is two-photon forbidden. Thus we have to use at least a three-states model for calculation of the TPA cross section, which has a simple form as

$$S_{zz} = \frac{2\mu_z^{01}\mu_z^{1f}}{\omega_1 - \omega} \quad (3.19)$$

For asymmetrically substituted molecules it is sufficient to include only two states

$$S_{zz} = \frac{2\mu_z^{0f}(\mu_z^{ff} - \mu_z^{00})}{\omega_f - \omega} \quad (3.20)$$

The validity of the few-states model has been verified by comparing its results with those obtained from the analytical response theory, see Table 3.1 for an example.

Molecule	ΔE (eV)	μ_z^{0f} (D)	$\Delta\mu_z$ (D)	S_{zz}		σ_{tpa}	
				Two states	Response	Two states	Response
DTT-DA(102)	1.66	13.6	4.5	309	293	498	446
DTT-DA(104)	1.63	14.6	4.7	355	334	645	568
Molecule	ΔE (eV)	μ_z^{01} (D)	μ_z^{1f} (D)	Three states	Response	Three states	Response
DTT-AA	1.19	13.5	2.5	243	273	541	687
Stilbene-DD (6)	1.44	13.7	3.1	246	258	613	636
DTT-DD (101)	1.15	13.4	2.9	286	302	755	842
DTT-DD (103)	1.17	15.3	4.0	441	461	1594	1727

Table 3.1 Comparison of the few-states models with the response theory calculations for strong charge-transfer one-dimensional donor/acceptor substituted molecules. Copied from Ref[10].

By comparing the transition energy, transition dipole moments and the difference of the permanent dipole moment between the ground and the TPA final states, the dependence of the TPA properties on the molecular electronic structure is clearly demonstrated. For example, the DTT-DD molecule given in Table 3.1 should have the largest TPA cross section because it possesses the smallest energy ΔE and the largest transition dipole moments μ_z^{01} , μ_z^{12} among all these molecules.

For two-dimensional charge-transfer molecules, when the excitation scheme is dominated by two major transitions, from ground state $|0\rangle$ to the final excited state $|f\rangle$ via the intermediate state $|1\rangle$, the TPA transition matrix for symmetric molecules can be expressed by a three-states model

$$S_{\alpha\beta} = \frac{\mu_{\alpha}^{01} \mu_{\beta}^{1f}}{\Delta E} + \frac{\mu_{\beta}^{01} \mu_{\alpha}^{1f}}{\Delta E} \quad (3.21)$$

where $\Delta E = \omega_1 - \omega = \omega_1 - \omega_f / 2$, μ_{α}^{ij} is the dipole moment between the state $|i\rangle$ and $|j\rangle$ and $\alpha, \beta \in \{x, y\}$.

For asymmetric planar molecules, when the excitation is dominated by the transition from ground state $|0\rangle$ to the final excited state $|f\rangle$, the two-state model can be used.

$$S_{\alpha\beta} = \frac{\mu_{\alpha}^{0f} \Delta\mu_{\beta}}{\Delta E} + \frac{\mu_{\beta}^{0f} \Delta\mu_{\alpha}}{\Delta E} \quad (3.22)$$

where $\Delta E = \omega_f - \omega = \omega_f / 2$, $\Delta\mu$ denotes the difference of dipole moments between the ground state and the final state. More general, if an asymmetric molecule has more than one charge transfer state, more than one dominant excitation channel can occur (see Fig 3.2). For instance, the asymmetric PVPHC and DPVPA molecules both have two charge transfer states S_1 and S_2 . If the final TPA state is the S_1 , there are two dominant scattering processes involved, i.e. $S_0 \rightarrow S_2 \rightarrow S_1$ and $S_0 \rightarrow S_1$. Therefore, a three-states model should be employed, which can be written as

$$S_{\alpha\beta} = \frac{\mu_{\alpha}^{01} \Delta\mu_{\beta} + \mu_{\beta}^{01} \Delta\mu_{\alpha}}{\Delta E_1} + \frac{\mu_{\alpha}^{02} \mu_{\beta}^{21} + \mu_{\beta}^{02} \mu_{\alpha}^{21}}{\Delta E_2} \quad (3.23)$$

3.4 Solvent effects

Results from calculations of a single isolated molecule are directly related to the experimental measurements in gas phase. However, most of the experiments, as well as technical applications, do take place in solutions. The presence of solvents can screen the external applied field and induce changes in the electronic and geometrical structures of the solute molecule. It has been well demonstrated that the optical properties of molecules can be modified dramatically in condensed phase. It is therefore

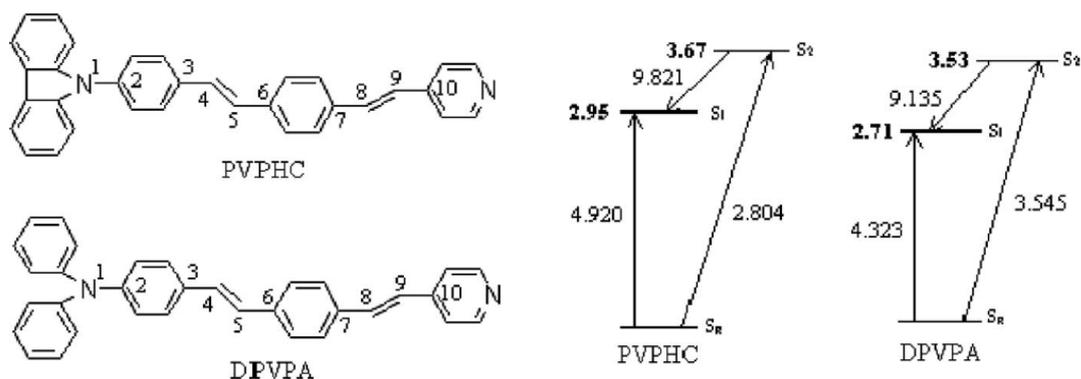


Figure 3.2 Molecular structures and the corresponding excitation channels: $S_0 \rightarrow S_2 \rightarrow S_1$ and $S_0 \rightarrow S_1$, the numbers beside the lines are the transition moments. Copied from Ref. [57]

highly relevant to develop theoretical methods that can effectively describe the effects of the surroundings.

3.4.1 Solvent models

Basically there are two fundamentally different ways to account for the solvent effects: the discrete and the continuum approaches. The discrete approach or explicit solvent models include individual solvent molecules and to do so we have to either restrict to small clusters of molecules (supermolecular approach) or treat a large part of the molecules in a more classical way such as molecular dynamics (MD) simulations. Supermolecular approach considers the solute molecule and some of its neighboring solvent molecules together and describes all of them in a quantum mechanical manner, by which the specific short-range intermolecular interaction can be explicitly treated. The molecular dynamics simulation aims to model molecular motions by Newtons classical equations. The potential of inter-atomic interactions can be derived either from quantum mechanical calculations or a predetermined molecular mechanical force field.

The commonly used continuum approach or implicit solvent models are represented by Onsager reaction field model[58] or more sophisticated polarizable continuum model (PCM)[59,60]. The continuum models view the solvent environment as a homogenous dielectric continuum medium characterized by its dielectric constant ϵ , while the solute molecule inside a cavity embedded in the continuum medium is described by

quantum mechanics. The physics of the electrostatic solute-solvent interaction is quite simple. The charge distribution of the solute polarizes the dielectric continuum, which in turn polarizes the solute charge distribution and at the end a stabilization could be reached for such an interaction. Such a self-consistent process can be numerically solved by an iterative procedure. In this model, no overlap of electronic clouds of solute and solvent molecules is considered, thus the short-range interactions such as hydrogen bonding are not included.

In the originally Onsager reaction field model, the solute molecule is considered as a dipole at the center of spherical or ellipsoids cavity. The solvent effects can be regards as a perturbation, H_1 , to the Hamiltonian of an isolated solute molecule, H_0 .

$$H = H_0 + H_1 \quad (3.24)$$

And the perturbation term represents the coupling between the reaction field \mathbf{F}^R and the dipole moment operator $\boldsymbol{\mu}$.

$$H_1 = -\boldsymbol{\mu} \cdot \mathbf{F}^R \quad (3.25)$$

The connection between the dipole moment and the reaction field is linear.

$$\mathbf{F}^R = f^R \cdot \boldsymbol{\mu} \quad f^R = \frac{2(\varepsilon - 1)}{(2\varepsilon + 1)a^3} \quad (3.26)$$

where a is the radius of the cavity and f^R is the so-called reaction field factor. Obviously the shape and the size of the cavity are quite important parameters for the total Hamiltonian. The computational procedure will be far simpler and faster when simple shapes are used, such as spheres and ellipsoids, but molecules do not often possess a spherical or ellipsoidal shape. Naturally a realistic cavity shape should reproduce the molecular shape as close as possible, which is exact what the PCM model is based on. In this model, the cavity follows the molecular shape and its size is defined through interlocking *van der Waals*-spheres centered at atomic positions. In this thesis, we employed the PCM model to study the solvent effects on the TPA properties of molecules.

In dielectric continuum model, the charge distribution of the solute molecule induces polarization vector \mathbf{P}^{tot} in the solvent molecules. To describe the solvent response function a common approximation [61] is to divide the polarization into two components: one, called the optical polarization vector, \mathbf{P}^{op} , connected to polarization

of the electronic clouds, and another, \mathbf{P}^{in} , to nuclear degrees of freedom of the solvent molecules, as well as the solvent molecular motions: vibrations, rotations, and translations. The latter is often called the orientational polarization or inertial polarization.

$$\mathbf{P}^{tot} = \mathbf{P}^{op} + \mathbf{P}^{in} \quad (3.27)$$

The relaxation times of the two components of \mathbf{P}^{tot} are very different. When the solute charge distribution changes, the optical polarization is considered to instantaneously adjust to the changes in the solute electronic state. On the contrary, at the same time, the inertial polarization remains fixed to the value corresponding to the solute charge distribution of the initial state. It needs a longer time to come to equilibrium and the relaxation time constant, a characteristic of the solvent, is by far larger than that of optical polarization. This assumption is completely analogous to the so-called Frank-Condon approximation frequently used in the analysis of electronic spectra.

The total and optical polarization of the medium can be related to the static dielectric constants (ϵ_{st}) and optical dielectric constants (ϵ_{op}), respectively. For example, as known, the static dielectric constant of water is 78.39, but the optical dielectric constant is 1.776. The difference is quite substantial.

3.4.2 Solvent effects on two-photon absorption

In contrast to extensive work on establishing useful structure-property relationship for isolated molecules, theoretical efforts to address solvent effects on the TPA have been quite limited. Luo et al.[23] studied the solvent effects on the TPA of the push-pull molecule $\text{NO}_2(\text{C}_2\text{H}_5)_2\text{NH}_2$ by using both self-consistent reaction field and internal finite field approaches. Their calculations have shown that the TPA cross section (δ) of the push-pull molecule strongly depends on the geometrical changes associated with the polarities of the solvents: polar solvents lead to larger bond length alternation (BLA) and in turn to bigger TPA cross sections. A prototype donor-acceptor system (D- π -A) was used to study solvent effects on TPA by Wang et al.[24] employing polarizable continuum model (PCM) combined with a two-state approach. It was also revealed that the enhancement of the TPA cross section in solution can also be attributed to the

electronic structure changes induced by the solvent. The solvent dependence of the TPA cross section displayed a non-monotonic behavior with respect to the solvent polarity, see Fig.3.3(a). The most sophisticated theoretical approach so far is the one developed by Frediani et al.[27] who have evaluated the solvent induced TPA cross sections by means of the quadratic response theory and the PCM. They have found that the TPA cross section of a charge-transfer molecule is more dependent on the optical dielectric constant rather than the static dielectric constant of the solvent: a very polar solvent, such as water, does not necessary yield a higher TPA cross section.

On the experimental side, the recent work of Woo et al.[28] measured the TPA cross sections of a series of distyrylbenzene chromophores and systematically studied the solvent effects on TPA properties. It is found that the effect of solvent on TPA cross section is nonmonotonic: maximum cross section was measured in an intermediate polarity solvent (THF) and was lowest in water, see Fig. 3.3(b). We have performed quantum chemical calculations to explore the possible mechanism for the observed behavior. The details can be found in Paper I.

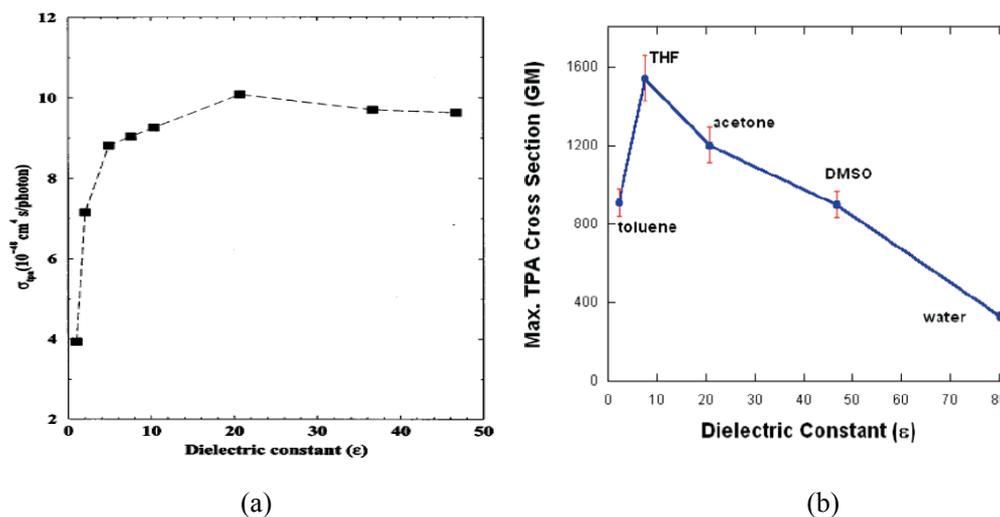


Figure 3.3 Solvent dependence of TPA cross section, (a) from ref.[24] and (b) from ref.[28].

Chapter 4

Frenkel Exciton Model

The nonlinear optical properties of aggregates or interacting chromophores can be described qualitatively by means of the classical Frenkel exciton model which takes into account the dipolar interactions among molecules. The concept of exciton was first introduced into physics by Frenkel in 1931[62]. Frenkel excitons are usually used to describe the elementary collective electronic excitations of molecular crystals that consist of weakly interacting molecules. It is assumed, hence, that the wave functions of the adjacent molecules are slightly overlapped. The basis molecular functions form the many-electron wave functions of the total system. For example, in Heitler-London approximation, the ground wavefunction is assumed to be the product of the ground-state wavefunctions of each single molecule, and the excited states are described as superpositions of the products in which a constant number of molecules are excited at a time. This approximation has proved to be valid in describing electronic excitations in many molecular crystals. A brief description of the Frenkel exciton model for the example of molecular crystal is given below[63].

4.1 Heitler-London approximation

Let H_n be the energy operator of the molecule that occupies point n , and let V_{nm} be the interaction-energy operator of the two molecules at points n and m . The total energy operator of the crystal can be written as

$$H = \sum_n H_n + \frac{1}{2} \sum_{n,m} V_{nm} \quad (4.1)$$

Summation in (4.1) is over all molecules. The prime on the second summation indicates that terms with $n=m$ are absent.

The energy operator H_n has a set of eigenfunctions $\varphi_n^f(\xi_n)$ that correspond to the eigenvalues ε_f , i.e.

$$H_n \varphi_n^f(\xi_n) = \varepsilon_f \varphi_n^f(\xi_n) \quad (4.2)$$

The energy ε_f characterizes the internal electronic excitation of a molecule. The symbol ξ_n indicates the set of coordinates corresponds to the internal degrees of freedom of the molecule occupying point \mathbf{n} .

It is assumed that the overlap of wave functions of adjacent molecules can be neglected. This approximation works out particularly well in crystals consisting of molecules of aromatic compounds (benzene, naphthalene, anthracene, etc.). In such molecules, transitions to the first electronic excited state involve changes in the motion of the π electrons of the molecule and excitation occurs between states in which the spatial distribution of the π -electron densities differs slightly.

The ground state of a crystal with the energy operator $H_0 = \sum_n H_n$ has the energy $N\varepsilon_0$ and is described by the wave function

$$\psi^0 = \prod_n \varphi_n^0 \quad (4.3)$$

The excited states corresponding to the f -th excitation of one molecule of the crystal have the energy $(N-1)\varepsilon_0 + \varepsilon_f$. These states are N -fold degenerate. If the molecule at \mathbf{n} is excited, the corresponding wave function will have the form

$$\psi_n^f = \varphi_n^f \prod_m \varphi_m^0 \quad m \neq n \quad (4.4)$$

Since all of the molecules are the same, we can introduce N new orthonormal functions

$$\psi^f = N^{-1/2} \sum_n \psi_n^f \quad (4.5)$$

In a system with operator H_0 , all the states in Eq. (4.5) have the same energy. This degeneracy is removed if we take into account the interactions between molecules. In molecular crystals, the intermolecular interaction is small, so in the first approximation

of perturbation theory the energy of the crystal is equal to the mean value of the operator (4.2) in states corresponding to wave functions (4.3) and (4.5) of the zeroth approximation. If we take their difference, we find the excitation energy for transition from the ground state (4.3) to excited state (4.5):

$$E_f = \Delta\varepsilon_f + D_f + L_f \quad (4.6)$$

where $\Delta\varepsilon_f$ is the excitation energy of a free molecule;

$$D_f = \sum_m \left\{ \int |\varphi_n^f|^2 V_{nm} |\varphi_m^0|^2 d\tau - \int |\varphi_n^0|^2 V_{nm} |\varphi_m^0|^2 d\tau \right\} \quad (4.7)$$

is the change in the interaction energy of one molecule with all of the surrounding molecules in its transition to the f -th excited state; and

$$L_f = \sum_m M_{nm}^f \quad (4.8)$$

The matrix element

$$M_{nm}^f = \int \varphi_n^{*0} \varphi_m^{*f} V_{nm} \varphi_m^0 \varphi_n^f d\tau \quad (4.9)$$

determines the transition of excitation f from molecule \mathbf{n} to molecule \mathbf{m} .

Thus, N different excited states correspond to a nondegenerate excited state of a free molecule. Each of these excited states is a collective excited state of the entire crystal and is called exciton.

4.2 The interaction-energy operator

The interaction-energy operator V_{nm} of two molecules, which characterizes the Coulomb interaction of the electrons and nuclei of both molecules, is usually expanded into a series in inverse powers of the distance between the centers of the molecules. The individual terms of the series characterize multipole-multipole interactions of the various orders. If the molecules are neutral, the first term of the series in the interaction operator corresponds to dipole-dipole interaction. If the electric dipole moment transition of molecule differs from zero, usually only the dipole-dipole interaction is retained. In this approximation,

$$E_{dipole} = \frac{\mu_A \mu_B}{\varepsilon (R_{AB})^3} (\cos \chi - 3 \cos \alpha_A \cos \alpha_B) \quad (4.10)$$

ε is the dielectric constant of the solvent, χ is the angle between two dipoles μ_A

and μ_B , α_A, α_B are the angles between the dipoles and the vector connecting the two dipoles, R_{AB} is the distance between the dipoles, see Fig. 4.1.

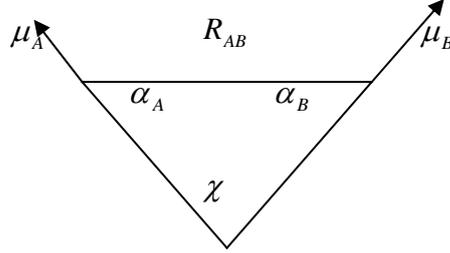


Figure 4.1 Dipole-Dipole interaction.

4.3 In Second-Quantization representation

As is well known, systems consisting of a large number of identical interacting subsystems are more conveniently described by the second-quantization representation. In the occupation number representation, the state of the crystal is characterized by functions of the occupation numbers N_{nf} . The occupation numbers N_{nf} are equal to either zero or unity and must satisfy the condition

$$\begin{aligned} \sum_f N_{nf} &= 1 \\ \sum_{n,f} N_{nf} &= N \end{aligned} \quad (4.11)$$

The wave function is, in the occupation number representation, a function of all of the numbers N_{nf} denoted by the symbol $\psi(\dots N_{nf} \dots)$. The number-of-states operator \hat{N}_{nf} is diagonal and its eigenvalues are the numbers N_{nf}

$$\hat{N}_{nf} \psi(\dots N_{nf} \dots) = N_{nf} \psi(\dots N_{nf} \dots) \quad (4.12)$$

The \hat{N}_{nf} can be expressed as

$$\hat{N}_{nf} = b_{nf}^+ b_{nf} \quad (4.13)$$

and

$$\begin{aligned} b_{nf}^+ \psi(\dots N_{nf} \dots) &= (1 - N_{nf}) \psi(\dots, N_{nf} + 1, \dots), \\ b_{nf} \psi(\dots N_{nf} \dots) &= N_{nf} \psi(\dots, N_{nf} - 1, \dots) \end{aligned} \quad (4.14)$$

b_{nf}^+ and b_{nf} are creation and annihilate operator of the state nf .

Introduce the operators

$$\left. \begin{aligned} \hat{\Psi}(\xi) &= \sum_{n,f} b_{nf} \varphi_{nf}(\xi), \\ \hat{\Psi}^+(\xi) &= \sum_{n,f} b_{nf}^+ \varphi_{nf}^*(\xi), \end{aligned} \right\} \quad (4.15)$$

Where $\varphi_{nf}(\xi)$ are the eigenfunctions of the operators $H_n(\xi)$. The energy operator of the non-interacting molecules in the coordinate representation is transformed in the occupation-number representation to

$$H_0 = \int \hat{\Psi}^+ H_n \hat{\Psi} d\xi = \sum_{n,f} b_{nf}^+ b_{nf} \varepsilon_f \quad (4.16)$$

In the occupation number representation,

$$\begin{aligned} \sum_{n,m} ' V_{nm} &= \int \hat{\Psi}^+(\xi) \hat{\Psi}^+(\eta) V(\xi, \eta) \hat{\Psi}(\xi) \hat{\Psi}(\eta) d\xi d\eta \\ &= \sum_{n,m} ' \sum_{f,f'} \sum_{g,g'} b_{nf}^+ b_{mg}^+ b_{mg} b_{nf} \langle f' g' | V_{nm} | gf \rangle \end{aligned} \quad (4.17)$$

Where $\langle f' g' | V_{nm} | gf \rangle = \int \varphi_{nf}^* \varphi_{mg}^* V_{nm} \varphi_{mg} \varphi_{nf} d\xi d\eta$

Then the energy operator is

$$H = \sum_f \varepsilon_f b_{nf}^+ b_{nf} + \frac{1}{2} \sum_{n,m} ' b_{nf}^+ b_{mg}^+ b_{mg} b_{nf} \langle f' g' | V_{nm} | gf \rangle \quad (4.18)$$

where f, f', g, g' , are the quantum numbers that characterize all of the steady states of the molecules. In the first sum of (4.18), summation is over all n and f . The second summation is over all n, m, f, f', g, g' at $n \neq m$.

When we consider only the ground state and the one of the excited states, the f, f', g, g' equal to 0 or f . Then the energy operator takes the form

$$H = H_0 + H_1 + H_2 + H_3 \quad (4.19)$$

where $H_0 = N\varepsilon_0 + \frac{1}{2} \sum_{n,m} ' \langle 00 | V_{nm} | 00 \rangle$ is a constant term. Further,

$$H_1 = \sum_n (\Delta\varepsilon_f + \sum_{m(\neq n)} D_{nm}^f) \hat{N}_{nf} \quad (4.20)$$

in which

$$\Delta\varepsilon_f = \varepsilon_f - \varepsilon_0$$

$$D_{nm}^f = \langle 0f | V_{nm} | f0 \rangle - \langle 00 | V_{nm} | 00 \rangle$$

$$H_2 = \sum_{n,m} ' M_{nm}^f b_{n0}^+ b_{mf}^+ b_{m0} b_{nf} \quad (4.21)$$

$$H_3 = \frac{1}{2} \sum_{n,m} ' M_{nm}^f (b_{n0}^+ b_{m0}^+ b_{mf} b_{nf} + b_{nf}^+ b_{mf}^+ b_{m0} b_{n0}) \quad (4.22)$$

Energy operator is further simplified by introducing the new operators

$$B_{nf} = b_{n0}^+ b_{nf}, \quad B_{nf}^+ = b_{nf}^+ b_{n0} \quad (4.23)$$

The operator B_{nf} corresponds to transition of the molecule \mathbf{n} from the f -th excited state to the ground state. The operator B_{nf}^+ corresponds to the reverse process-transition of the molecule \mathbf{n} from the ground state to an excited state.

Using the commutation relations, we have

$$H_1 = \sum_n (\Delta \varepsilon_f + D_f) B_{nf}^+ B_{nf} \quad (4.24)$$

$$H_2 = \sum_{n,m} ' M_{nm}^f B_{mf}^+ B_{nf} \quad (4.25)$$

$$H_3 = \frac{1}{2} \sum_{n,m} ' M_{nm}^f (B_{mf}^+ B_{nf}^+ + B_{mf} B_{nf}) \quad (4.26)$$

Consider the operator (4.19) without the operator H_3 , the excitation-energy operator takes the form

$$\Delta H = H - H_0 = \sum_n (\Delta \varepsilon_f + D_f) B_{nf}^+ B_{nf} + \sum_{n,m} ' M_{nm}^f B_{mf}^+ B_{nf} \quad (4.27)$$

This approximation corresponds to the Heitler-London approximation, which was considered in section 4.1.

Chapter 5

Ultrashort pulse in generalized two-level medium

Recent progress in ultrafast laser technology has allowed the generation of extremely short and intense light pulse consisting of a few oscillation cycles. The interaction of femtosecond laser pulses with two-level medium has attracted much attention. The semiclassical method is often used, in which the electromagnetic field is described by classical Maxwell equations, while the medium is treated quantum mechanically by means of Bloch equation. For a few-cycle pulse, it has been found the conventional slowly varying envelope approximation (SVEA) and the rotation-wave approximation (RWA) are not valid any more. The propagation of few-cycle pulse laser in a resonance two-level atom medium possesses many novel features which are different from the case of long pulses can be found, such as the carrier-wave Rabi flopping (CWRf), carrier-envelope phase (CEP) effects, and breakdown of area theorem, just to mention a few.

In this thesis, the propagation of one-dimensional electromagnetic field in a two-level molecular system has been investigated. The full Maxwell-Bloch equation beyond SVEA and RWA is solved by using iterative predictor-corrector finite-difference time-domain method (FDTD). By solving Maxwell-Bloch equation numerically, the propagation of laser pulse and the corresponding spectral evolution can be explored. The realistic one-dimensional asymmetric organic molecules have been chosen as the two-level medium model. These molecules possess large nonlinear properties and have only one charge-transfer (CT) state in the visible or ultraviolet region. Furthermore, for asymmetric molecule, it has nonzero permanent dipole moment, which is different from

commonly used two-level atom system and can result in many interesting new phenomena.

5.1 Maxwell-Bloch equations

The behavior of electromagnetic field in medium is described by the well known Maxwell equation

$$\begin{cases} \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \\ \nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \\ \nabla \cdot \mathbf{D} = \rho \\ \nabla \cdot \mathbf{B} = 0 \end{cases} \quad (5.1)$$

Here, ρ , \mathbf{J} are charge and current density, respectively. For electromagnetic field with visible light frequency, the charge and current density in medium will be zero. The relationship between electromagnetic field and the electric polarization \mathbf{P} and magnetization \mathbf{M} of the medium can take the form

$$\mathbf{B} = \mu \mathbf{H} = \mu_0 (\mathbf{H} + \mathbf{M}) \quad \mathbf{D} = \varepsilon \mathbf{E} = \varepsilon_0 \mathbf{E} + \mathbf{P} \quad (5.2)$$

Here ε and μ are constants known as the medium permittivity and permeability. In nonferromagnetic material, $\mathbf{B} \approx \mu_0 \mathbf{H}$.

The incident electric field is assumed to be polarized along the x axis and propagates along the z axis to an input interface of the medium at $z=0$, i.e., $\mathbf{E}(\mathbf{r}, t) = E_x(z, t) \hat{\mathbf{x}}$ and $\mathbf{H}(\mathbf{r}, t) = H_y(z, t) \hat{\mathbf{y}}$. The polarization is $\mathbf{P} = P_x \hat{\mathbf{x}}$. Then Maxwell equation has the following form

$$\frac{\partial H_y}{\partial t} = -\frac{1}{\mu_0} \frac{\partial E_x}{\partial z} \quad \frac{\partial E_x}{\partial t} = -\frac{1}{\varepsilon_0} \frac{\partial H_y}{\partial z} - \frac{1}{\varepsilon_0} \frac{\partial P_x}{\partial t} \quad (5.3)$$

where μ_0 and ε_0 are the permeability and permittivity of free space. The macroscopic nonlinear polarization P_x is related to the ensemble average of the expectation value of dipole moment operator for a molecule.

Atom and molecule are multilevel systems, and their interaction with a radiation field can involve many levels. Nevertheless, for a radiation field with a single

frequency, ω , it is often necessary to consider only the ground state and those levels that are different in energy from the ground state energy by $\hbar\omega$. When only one such excited level exists, a two-level approximation can be made[64]. The Hamiltonian for the two-level system interacting with the radiation field is given by

$$H(t) = H_0 + V(t) \quad (5.4)$$

where H_0 is the free molecule Hamiltonian and the time-dependent interaction potential $V(t)$ is given in the electric dipole approximation by

$$V(t) = -\boldsymbol{\mu} \cdot \mathbf{E}(t) \quad (5.5)$$

where $\boldsymbol{\mu} = -e\mathbf{r}$ is the dipole moment operator and $\mathbf{E}(t)$ is the time-dependent electric field.

Using the density matrix to treat medium, the Schrödinger equation is replaced by the Liouville equation

$$\frac{\partial}{\partial t} \rho_{nm} = -\frac{i}{\hbar} [H, \rho]_{nm} \quad (5.6)$$

With it we can obtain the Bloch equation

$$\frac{\partial}{\partial t} \rho_{lk} = -i\omega_{lk} \rho_{lk} + \frac{i\mathbf{E}}{\hbar} \cdot \sum_{j=1}^N (\boldsymbol{\mu}_{lj} \rho_{jk} - \boldsymbol{\mu}_{jk} \rho_{lj}) \quad (5.7)$$

The elements of the density matrix have the following physical interpretation: The diagonal elements ρ_{nn} give the probability that the system is in energy eigenstate n . The off-diagonal elements ρ_{mn} provide the ‘‘coherence’’ between level n and m , in the sense that ρ_{mn} will be nonzero only if the system is in a coherent superposition of energy eigenstates n and m . In some circumstances, it is proportional to the induced electric dipole moment of the medium.

Equation (5.7) is the density matrix equations of motion absent of relaxation processes. If we consider a closed two-level system, 1 and 2, and add phenomenological damping terms: γ_{22} , γ_{12} and γ_{21} , which are called population and polarization relaxation constants, the density matrix equations become

$$\frac{\partial \rho_{11}}{\partial t} = -\frac{iE_x}{\hbar} (\mu_{21} \rho_{12} - \mu_{12} \rho_{21}) + \gamma_{22} \rho_{22} \quad (5.8)$$

$$\frac{\partial \rho_{22}}{\partial t} = \frac{iE_x}{\hbar} (\mu_{21} \rho_{12} - \mu_{12} \rho_{21}) - \gamma_{22} \rho_{22} \quad (5.9)$$

$$\frac{\partial \rho_{12}}{\partial t} = i\omega_{12}\rho_{12} + \frac{iE_x}{\hbar} [\mu_{12}(\rho_{22} - \rho_{11}) + (\mu_{11} - \mu_{22})\rho_{12}] - \gamma_{12}\rho_{12} \quad (5.10)$$

$$\frac{\partial \rho_{21}}{\partial t} = i\omega_{12}\rho_{21} + \frac{iE_x}{\hbar} [\mu_{21}(\rho_{11} - \rho_{22}) + (\mu_{22} - \mu_{11})\rho_{21}] - \gamma_{21}\rho_{21} \quad (5.11)$$

Let $\Delta\mu = \mu_{22} - \mu_{11}$, $u = \rho_{12} + \rho_{21}$, $v = i(\rho_{21} - \rho_{12})$ and $d = \rho_{22} - \rho_{11}$ which denotes the population difference of two levels, we have

$$\frac{\partial u}{\partial t} = -\gamma_{12}u - \omega_0v + \frac{\Delta\mu}{\hbar} E_x v \quad (5.12)$$

$$\frac{\partial v}{\partial t} = -\gamma_{21}v + \omega_0u + 2\frac{\mu E_x}{\hbar} d - \frac{\Delta\mu}{\hbar} E_x u \quad (5.13)$$

$$\frac{\partial d}{\partial t} = -\gamma_{22}(d+1) - 2\frac{\mu E_x}{\hbar} v \quad (5.14)$$

where $\omega_0 = \omega_{12}$ is the frequency difference of two levels and $\mu = \mu_{12} = \mu_{21}$ is the transition dipole moment between two states. The (5.3) and (5.12-14) are our Maxwell-Bloch equation used for simulating propagation of pulse in closed two-level molecules. The polarization P_x fulfills the following relation

$$\frac{\partial P_x}{\partial t} = -\gamma_{22} \frac{N\Delta\mu}{2} (d+1) - \gamma_{12} N\mu u - N\mu\omega_0 v \quad (5.15)$$

Here N is molecular number density.

During the course of interaction between the intense laser pulse and the quantum system such as atom and molecule, the quantum system can experience ultraintense radiation without ionization. However, when the laser intensity is much higher, it becomes questionable whether ionization of the quantum system affects the evolution of the pulse in the medium. So we also consider the time-dependent ionization effects on the evolution of the pulse in two-level-plus-continuum medium, i.e. an open two-level system. In this case, the Bloch equations have the form

$$\frac{\partial u}{\partial t} = -\gamma_{12}u - \omega_0v + \frac{\Delta\mu}{\hbar} E_x v - \frac{\gamma_i(t)}{2} u \quad (5.16)$$

$$\frac{\partial v}{\partial t} = -\gamma_{21}v + \omega_0u + 2\frac{\mu E_x}{\hbar} (\rho_{22} - \rho_{11}) - \frac{\Delta\mu}{\hbar} E_x u - \frac{\gamma_i(t)}{2} v \quad (5.17)$$

$$\frac{\partial \rho_{11}}{\partial t} = \gamma_{22} \rho_{22} + \frac{\mu E_x}{\hbar} v \quad (5.18)$$

$$\frac{\partial \rho_{22}}{\partial t} = -\gamma_{22} \rho_{22} - \frac{\mu E_x}{\hbar} v - \gamma_i(t) \rho_{22} \quad (5.19)$$

where $\gamma_i(t)$ is the time-dependent ionization rate of the excited state. For two-photon ionization, $\gamma_i(t) = \sigma_i^{(2)} I(t)^2 / (\hbar \omega)^2$ and $\sigma_i^{(2)}$ is the two-photon ionization cross section of the excited state. And the polarization P_x takes the following form

$$\frac{\partial P_x}{\partial t} = -\gamma_{22} N \Delta \mu \rho_{22} - \gamma_{12} N \mu u - N \mu \omega_0 v + \frac{\gamma_i}{2} N \mu u + \gamma_i N \mu_{22} \rho_{22} \quad (5.20)$$

5.2 The McCall-Hahn “Area Theorem”

The “area theorem” was first derived by McCall and Hahn in 1967[65]. It governs the coherent nonlinear transmission of short light pulses (pulse temporal duration is much smaller compared with the decay times of two levels) through resonance two-level media. It is derived from Maxwell-Bloch equation using SVEA and RWA, so, for the case of few-cycle pulse it is not exactly true. But for the sake of comparison, we also use it to define our pulse.

It is convenient to define the pulse area at position z , $\theta(z)$, as

$$\theta(z) = \frac{\mu}{\hbar} \int_{-\infty}^{\infty} E_0(z, t) dt \quad (5.21)$$

where $E_0(z, t)$ is the electric field envelope.

McCall and Hahn[63] found that the pulse area satisfies the equation

$$\frac{d\theta(z)}{dz} = \frac{\alpha}{2} \sin \theta(z) \quad (5.22)$$

where α is the absorption coefficient in terms of the transition dipole moment, the index of refraction, etc. This equation is known as “pulse area theorem”. It is an extended version of Beer’s law.

Figure 5.1 plots $\theta(z)$ vs z for several values of $\theta(0)$. Here we only consider the absorbing media. According to the area theorem, it is clear that $\lim_{z \rightarrow \infty} \theta(z) = 2n\pi$, where n is determined by $\theta(0)$. For example, for $\theta(0) < \pi$, $n = 0$; for $\pi < \theta(0) < 3\pi$,

$n=1$. If $\theta(0) = n\pi$, for any n , the pulse area suffers no attenuation in propagation, since $\partial\theta/\partial z = 0$. The areas that are even multiples of π are more stable than those that are odd multiples. With deeper penetration of the pulse into the absorber, the area tends toward even multiples of π . Especially, for $\theta(0) = 2\pi$, the pulse can propagate without shape change (solitary wave), which is called self-induced transparency (SIT).

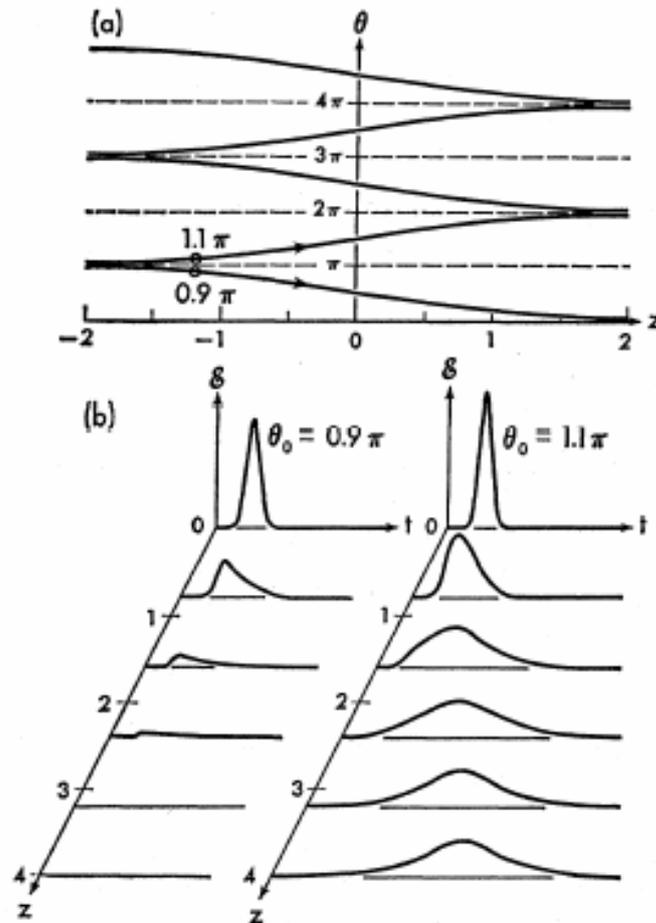


Figure 5.1 Pulse area evolution. Ref[65]

The area theorem only tells the evolution of total area, but it can not give information at all about possible breakup of a pulse into two or more pulses with the same total area. It has been observed, both experimentally and theoretically [40,41,66], that the 4π pulse does not propagate as a single pulse but rather separates into two individual 2π pulses and the 6π is also decomposed into three 2π pulses accompanied by pulse delay and pulse compressing or broadening. These result in many

interesting phenomena on this subject. Moreover, currently, it has been shown that there are many different properties of area evolution between few-cycle ultrashort pulse and long pulse.

5.3 Predictor-corrector FDTD method

The predictor-corrector finite-difference time-domain (FDTD) technique of Ziolkowski [42] is applied to solve numerically the semiclassical Maxwell-Bloch equations. The FDTD method belongs to grid-based differential time-domain numerical modeling method. The equations are solved in leapfrog manner: the electric field is solved at a given instant in time, then the magnetic field is solved at the next instant in time, and the progress is repeated over and over again. In our case, the z-propagating magnetic field (H_y) and the electric field (E_x) are spatially separated by $\Delta z/2$ and temporally by $\Delta t/2$, as shown in Fig.5.2, in which the i and j denote the temporal and spatial discretization steps, respectively. The magnetic-field component is at the “edge” of the cell in the grid (intersection point of solid line) and the electric field component lies at the “center” of the cell (intersection point of dash line). We associate all of the material properties (P_x) with the location of the electric field.

Introducing the quantities $u_i(z, t)$ through the definitions

$$u = e^{-t\gamma_{21}} u_1(z, t) \quad (5.23)$$

$$v = e^{-t\gamma_{21}} u_2(z, t) \quad (5.24)$$

$$d = e^{-t\gamma_{22}} u_3(z, t) - 1 \quad (5.25)$$

One obtains the electric-field and two-level system equations in the form

$$\frac{\partial H}{\partial t} = -\frac{1}{\mu_0} \frac{\partial E}{\partial z} \quad (5.26)$$

$$\frac{\partial E}{\partial t} = -\frac{1}{\epsilon_0} \frac{\partial H}{\partial z} + Au_1 + Bu_2 + Ku_3 \quad (5.27)$$

$$\frac{\partial u_1}{\partial t} = -\omega_0 u_2 + GEu_2 \quad (5.28)$$

$$\frac{\partial u_2}{\partial t} = \omega_0 u_1 + C_1 Eu_3 + DE - GEu_1 \quad (5.29)$$

$$\frac{\partial u_3}{\partial t} = -C_2 E u_2 \quad (5.30)$$

where the time-varying coefficients

$$\begin{aligned} A(t) &= \frac{N\mu_{12}\omega_0}{\varepsilon_0} e^{-t\gamma_{21}} & B(t) &= \frac{N\mu_{12}\omega_0}{\varepsilon_0} e^{-t\gamma_{21}} \\ C_1(t) &= 2\frac{\mu_{12}}{\hbar} e^{-t(\gamma_{22}-\gamma_{21})} & C_2(t) &= 2\frac{\mu_{12}}{\hbar} e^{-t(\gamma_{21}-\gamma_{22})} \\ D(t) &= -\frac{2}{\hbar}\mu_{12}e^{t\gamma_{22}} & K(t) &= \frac{N\Delta\mu\gamma_{22}}{2\varepsilon_0} e^{-t\gamma_{22}} & G &= \frac{\Delta\mu}{\hbar} \end{aligned} \quad (5.31)$$

The magnetic-field equation is solved at the space steps $(j + \frac{1}{2})\Delta z$ for the time step $(i + \frac{1}{2})\Delta t$, while the electric field and the medium term u_1, u_2 , and u_3 are solved at the space steps $j\Delta z$ for the time steps $i\Delta t$. The discretized version of the Maxwell-Bloch system is of the following form

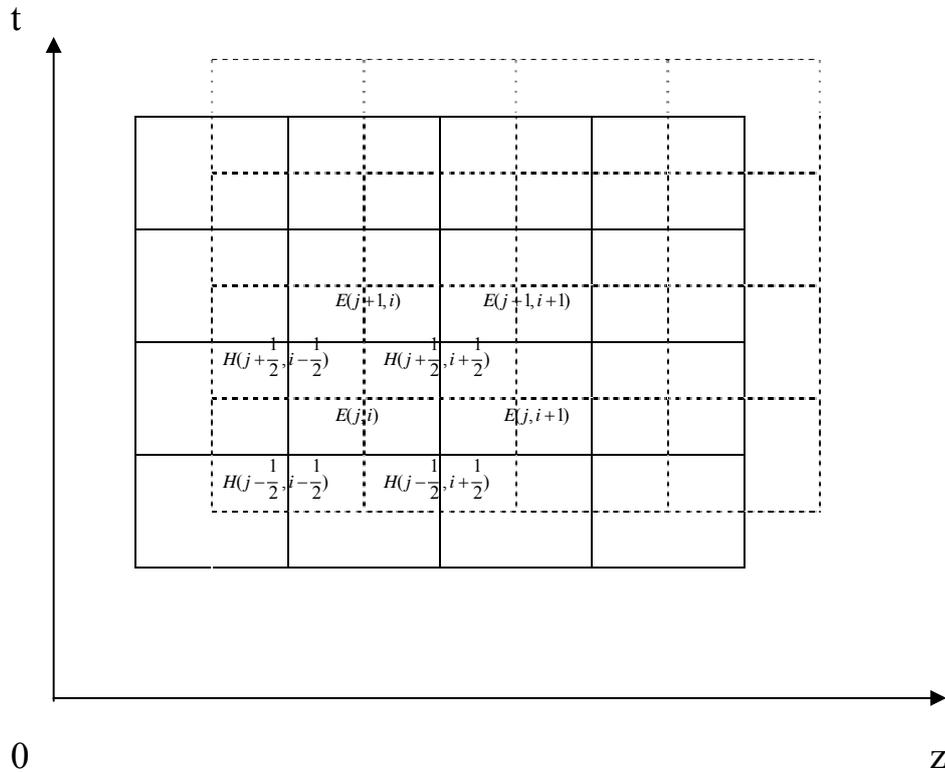


Figure 5.2 Illustration of the cell used in FDTD.

$$H(j + \frac{1}{2}, i + \frac{1}{2}) = H(j + \frac{1}{2}, i - \frac{1}{2}) - \frac{\Delta t}{\mu_0 \Delta z} [E(j+1, i) - E(j, i)] \quad (5.32)$$

$$\begin{aligned} E(j, i+1) = E(j, i) - \frac{\Delta t}{\varepsilon_0 \Delta z} & \left[H(j + \frac{1}{2}, i + \frac{1}{2}) - H(j - \frac{1}{2}, i + \frac{1}{2}) \right] \\ & + \Delta t A (i + \frac{1}{2}) \frac{[u_1(j, i+1) + u_1(j, i)]}{2} + \Delta t B (i + \frac{1}{2}) \frac{[u_2(j, i+1) + u_2(j, i)]}{2} \\ & + \Delta t K (i + \frac{1}{2}) \frac{[u_3(j, i+1) + u_3(j, i)]}{2} \end{aligned} \quad (5.33)$$

Bloch equation becomes

$$\begin{aligned} u_1(j, i+1) = u_1(j, i) - \Delta t \omega_0 & \frac{[u_2(j, i+1) + u_2(j, i)]}{2} \\ & + \Delta t G \frac{[E(j, i+1) + E(j, i)] [u_2(j, i+1) + u_2(j, i)]}{2} \end{aligned} \quad (5.34)$$

$$\begin{aligned} u_2(j, i+1) = u_2(j, i) + \Delta t \omega_0 & \frac{[u_1(j, i+1) + u_1(j, i)]}{2} \\ & + \Delta t \frac{[E(j, i+1) + E(j, i)]}{2} \left\{ C_1 (i + \frac{1}{2}) \frac{[u_3(j, i+1) + u_3(j, i)]}{2} + D (i + \frac{1}{2}) \right\} \\ & - \Delta t G \frac{[E(j, i+1) + E(j, i)] [u_1(j, i+1) + u_1(j, i)]}{2} \end{aligned} \quad (5.35)$$

$$u_3(j, i+1) = u_3(j, i) - \Delta t C_2 (i + \frac{1}{2}) \frac{[E(j, i+1) + E(j, i)] [u_2(j, i+1) + u_2(j, i)]}{2} \quad (5.36)$$

Since the electric field equations and the Bloch equation are coupled, they can not be integrated in the typical FDTD method. It has to be solved via a predictor-corrector scheme. The equations (5.33-36) can be expressed in the form

$$U_i^{new} = U_i^{old} + \Delta t F_i(U^{old}, U^{new}) \quad (5.37)$$

where U_i denotes E , u_1 , u_2 , u_3 and the functional F_i represent the right-hand sides of equations (5.33-36). Eq. (5.37) can thus be solved iteratively. The critical converge value we used is 0.001%.

References

- [1] M. Göppert-Mayer. *Ann. Phys. Lpz*, 9:273, 1931.
- [2] W. Kaiser and C. G. Garret. *Phys. Rev. Lett.*, 7:129, 1961.
- [3] W. Denk, J. H. Strickler, and W. W. Webb. *Science*, 248:73, 1990.
- [4] R. H. Köhler, J. Cao, W. R. Zipfel, W. W. Webb, and M. R. Hansen. *Science*, 276:2039, 1997.
- [5] J. E. Ehrlich, X. L. Wu, I.-Y. Lee, Z. -Y. Hu, H. Roeckel, S. R. Marder, and J. Perry. *Opt. Lett.*, 22:1843, 1997.
- [6] G. S. He, C. F. Zhao, J. D. Bhawalkar, and P. N. Prasad. *Appl. Phys. Lett.*, 67:3703, 1995.
- [7] J. D. Bhawalkar, G. S. He, and P. N. Prasad. *Rep. Prog. Phys.*, 59:1041, 1996.
- [8] D. A. Parthenopoulos, P. M. Rentzepis. *Science*, 245:843, 1989.
- [9] A. S. Dvornikov, P. M. Rentzepis. *Opt. Commun.*, 119:341, 1995.
- [10] C. K. Wang, P. Macak, Y. Luo, and H. Ågren. *J. Chem. Phys.*, 114:9813, 2001.
- [11] P. Macak, Y. Luo, P. Norman, and H. Ågren. *J. Chem. Phys.*, 113:7055, 2000.
- [12] J. Yoo, S. K. Yang, M. Y. Jeong, H. C. Ahn, S. J. Jeon, and B. R. Cho. *Org. Lett.*, 5:645, 2003.
- [13] M. Albota, et al. *Science*, 281:1653, 1998.
- [14] S. K. Pati, T. J. Marks, and M. A. Ratner. *J. Am. Chem. Soc.*, 123:7287, 2001.
- [15] S.-J. Chung, K.-S Kim, T.-C. Lin, G. S. He, J. Swiatkiewicz, and P. N. Prasad. *J. Phys. Chem. B.*, 103:10741, 1999.
- [16] A. Adronov, J. M. J. Fréchet, G. S. He, K.-S Kim, S.-J. Chung, J. Swiatkiewicz, and P. N. Prasad. *Chem. Mater.*, 12:2838, 2000.
- [17] S.-J. Chung, T.-C. Lin, K.-S Kim, G. S. He, J. Swiatkiewicz, P. N. Prasad, G. A. Baker, and F. V. Bright. *Chem. Mater.*, 13:4071, 2001.

- [18] M. Drobizhev, A. Karotki, A. Rebane, and C. W. Spangler. *Opt. Lett.*, 26:1081, 2001.
- [19] M. Drobizhev, A. Karotki, Y. Dzenis, A. Rebane, Z. Suo, and C. W. Spangler. *J. Phys. Chem. B.*, 107:7540, 2003.
- [20] W. J. Yang, D. Y. Kim, C. H. Kim, M.-Y. Jeong, S. K. Lee, S.-J. Jeon and B. R. Cho. *Org. Lett.*, 6:1389, 2004.
- [21] L. Porrès, O. Mongin, C. Katan, M. Charlot, T. Pons, J. Mertz, and M. Blanchard-Desce. *Org. Lett.*, 6:47, 2004.
- [22] F. Meng, B. Li, S. Qian, K. Chen, and H. Tian. *Chem. Lett.*, 33:470, 2004.
- [23] Y. Luo, P. Norman, P. Macak, and H. Ågren. *J. Phys. Chem. A*, 104:4718, 2000.
- [24] C. K. Wang, K. Zhao, Y. Su, R. Yan, X. Zhao, and Y. Luo. *J. Chem. Phys.* 119:1208, 2003.
- [25] Y. L. Huang, H. Lei, N. Li, Z. R. Qiu, H. Z. Wang, J.-D. Guo, Y. Luo, Z. P. Zhong, and Z. H. Zhou. *J. Mater. Chem.*, 13:708, 2003.
- [26] R. Zaleśny, W. Bartkowiak, S. Styrzcz, and J. Leszczynski. *J. Phys. Chem. A*, 106:4032, 2002.
- [27] L. Frediani, Z. Rinkevicius, and H. Ågren. *J. Chem. Phys.*, 122:244104, 2005.
- [28] H. Y. Woo, B. Liu, B. Kohler, D. Korystov, A. Mikhailovsky, and G. C. Bazan. *J. Am. Chem. Soc.*, 127:14721, 2005.
- [29] **Gaussian 03**, Revision A.1, M. J. Frisch, et al. Gaussian, Inc., Pittsburgh PA, 2003.
- [30] **DALTON**, a molecular electronic structure program, Release 2.0 (2005), see <http://www.kjemi.uio.no/software/dalton/dalton.html>.
- [31] M. Nisoli, S. De Silvestri, O. Svelto, R. Szipocs, K. Ferencz, Ch. Spielmann, S. Sartania, and F. Krausz. *Opt. Lett.*, 22:522, 1997.
- [32] A. Baltuska, Z. Wei, M. S. Pshenichnikov, and D.A.Wiersma. *Opt. Lett.*, 22:102, 1997.
- [33] R. R. Alfano and S. L. Shapiro. *Phys. Rev. Lett.*, 24:592, 1970.
- [34] P. B. Corkum et al. *Opt. Lett.*, 10:624, 1985.
- [35] W. L. Smith and N. Bloembergen. *Phys. Rev. A*, 15:2396, 1977.
- [36] P. B. Corkum et al. *Phys. Rev. Lett.*, 57:2268, 1986.
- [37] A. Brodeur and S. L. Chin. *J. Opt. Soc. Am. B*, 16:637, 1999.
- [38] A. Penzkofer et al. *Phys. Rev. Lett.*, 31:863, 1973.

- [39] S. L. McCall and E. L. Hahn. *Phys. Rev.*, 183:457, 1969.
- [40] G. L. Lamb, Jr. *Rev. Mod. Phys.*, 43:99, 1971.
- [41] L. Allen and J.H. Eberly. *Optical resonance and two-level atoms*. Wiley:New York, 1987.
- [42] R.W. Ziolkowski, J.M.Arnold, and D.M.Gogny. *Phys. Rev. A*, 52:3082, 1995.
- [43] S. Hughes. *Phys. Rev. A*, 62:055401, 2000.
- [44] S. Hughes. *Phys. Rev. Lett.*, 81:3363, 1998.
- [45] W. J. Meath, R. A. Thuraisingham, and M. A. Kemtic. *Adv. Chem. Phys.*, 73:307, 1989.
- [46] A. F. Kondo and W. J. Meath. *Mol. Phys.*, 92:805, 1997.
- [47] A. Brown, W. J. Meath, and P. Tran. *Phys. Rev. A*, 63:013403, 2000.
- [48] P. Hohenberg and W. Kohn. *Phys. Rev.*, 136:B864, 1964.
- [49] W. Kohn and L. J. Sham. *Phys. Rev.*, 140:A1133, 1965.
- [50] A. D. Becke. *J. Chem. Phys.*, 98:5648, 1993.
- [51] C. Lee, W. Yang, and R. G. Parr. *Phys. Rev. B*, 37:785, 1988.
- [52] R. W. Boyd. *Nonlinear Optics*. 2nd Edn. Academic Press: San Diego, CA, 2003.
- [53] P. R. Monson and W. M. McClain. *J. Chem. Phys.*, 53:29, 1970.
- [54] J. Olsen, P. Jørgensen. *J. Chem. Phys.*, 82:3235, 1985.
- [55] P. Cronstrand, Y. Luo, and H. Ågren. *J. Chem. Phys.*, 117:11102, 2002.
- [56] J. D. Guo, C. K. Wang, Y. Luo, and H. Ågren. *Phys. Chem. Chem. Phys.*, 5: 3869, 2003.
- [57] Y. H. Sun, K. Zhao, C. K. Wang, Y. Luo, Y. X. Yan, X. T. Tao, and M. H. Jiang. *Chem. Phys. Lett.*, 394:176, 2004.
- [58] L. Onsager. *J. Am. Chem. Soc.*, 58:1486, 1936.
- [59] J. Tomasi, B. Menncci, and R. Cammi. *Chem. Rev.*, 105:2999, 2005.
- [60] J. Tomasi and M. Persico. *Chem. Rev.*, 94:2027, 1994.
- [61] S. Lee and J. T. Hynes. *J. Chem. Phys.*, 88:6853, 1988.
- [62] J. Frenkel. *Phys.Rev.*, 37:1276, 1931.
- [63] A. S. Davidov. *Theory of molecular excitons*. Plenum Press: New York, 1971.
- [64] Y. B. Band. *Light and matter*. Wiley & Sons:Chichester, 2006.
- [65] S. L. McCall and E. L. Hahn. *Phys. Rev. Lett.*, 18:908, 1967.
- [66] R. E. Slusher and H. M. Gibbs. *Phys. Rev. A.*, 5:1634, 1972.

