Quantum Chemical Calculations of Nonlinear Optical Absorption

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Abstract

This thesis represents a quantum chemical treatise of various types of interactions between radiation and molecular systems, with special emphasis on the nonlinear optical processes of Multi-Photon Absorption and Excited State Absorption. Excitation energies, transition dipole moments, two-photon and three-photon tensor elements have been calculated from different approaches; density functional theory and ab-initio theory, employing different orders of correlation treatment with the purpose to provide accurate values as well as evaluate the quality of the lower order methods. A combined study of the Multi-Photon Absorption and Excited State Absorption processes is motivated partly because they both contribute to the total optical response of a system subjected to intense radiation, but also because of their connection through so-called sum-over-states expressions. The latter feature is exploited in a generalized few-states model, which incorporates the polarization of the light and the directions of the transition dipole moments constructing an excitation channel, which thereby enables a more comprehensive comparison of the attained transition dipole moments with experimental data. Moreover, by decomposing a complex nonlinear response process such as Two-Photon Absorption into more intuitive quantities, generalized few-states models may also enable a more elaborate interpretation of computed or experimental results from which guidelines can be extracted in order to control or optimize the property of interest. A general conclusion originating from these models is that the transition dipole moments in an excitation channel should be aligned in order to maximize the Two-Photon Absorption probability. The computational framework employed is response theory which through the response functions (linear, quadratic, cubic) offers alternative routes for evaluating the properties in focus; either directly and untruncated through the single residue of the quadratic or cubic response functions or through various schemes of truncated sum-over-states expressions where the key ingredients, transition dipole moments, can be identified from the single residue of the linear response function and double residue of the quadratic response function. The range of systems treated in the thesis stretches from diatomics, such as carbon monoxide and lithium hydride, via small to large fundamental organic molecules, such as formaldehyde, tetrazine and the trans-polyenes, to large chromophores, such as trans-stilbene, cumulenes, dithienothiophene, paracyclophane and organo-metallic systems, such as the platinum(II)ethynyl compounds.
Publications

Publications included in the thesis


Publications not included in the thesis


Own contributions

In papers 1-2 I performed the structure optimizations and some of the calculations, I was also responsible for planning and interpreting the results and contributed with the first preliminary version of the manuscript. In papers 3-5, 7-9, 11 I performed all calculations and was responsible for planning, interpretation and the preparation of the manuscript. In paper 6 I performed some calculations and participated in the discussions. In paper 10 I was responsible for the calculations of the three-photon probabilities and the discussions related to them.
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Chapter 1

Introduction

The interaction between light and matter is perhaps one of the most fundamental processes in nature. Throughout the history of science it has been a primary object of investigation. Theoretical and experimental methods have in a dynamic interplay generated descriptions and theories of the separate nature of light and matter and of the nature of the interaction between them. To some extent, quantum mechanics can be seen as the theoretical response in order to explain experimental results arising in the interface between light and matter in the early 1900’s. The photoelectric effect, the UV catastrophe associated with black-body radiation, the spectroscopy of the hydrogen atom, all showed anomalous behavior that contributed to the emerging quantum picture. When firmly established, the theory proposed a manifold of bold predictions, of which several could not be experimentally verified until the advent of the laser half a century later. One of these predictions was the capability of multi-photon absorption, that is the probability of a system to absorb two or more photons simultaneously, which originally was described already 1930 by Göppert-Mayer[1]. A pioneering observation in this field is attributed to J. Kerr who already 1875 noted birefringencies when applying a static electric field over a glass crystal[2]. In this experiment the observed nonlinearity was related to the external static field. Experimental evidence of nonlinearities exclusively induced by light itself were not detected until the early 1960’s[3], with the first types of laser. Since then a manifold of nonlinear optical properties have been verified by increasingly intense light sources; second harmonic generation (SHG)[3], third harmonic generation (THG)[4], two-photon absorption (TPA)[5] and three-photon absorption (3PA)[6] are all examples of the potentially eccentric behavior hiding in the higher order corrections in the descriptions of light-matter interaction. For a long time, multi-photon absorption processes were merely considered as exotic phenomena with only minor technological relevance, except as a method of spectroscopy i.e. an experimental method using light to probe matter.

This thesis is in a simplistic picture devoted to the complete opposite; using theory to describe matter capable of controlling light. This have become of rapidly growing interest in times when optics is being considered as a complement to, or replacement for, conventional electronics. New materials with highly improved nonlinear behavior are in novel applications believed to manipulate the new carrier of information; light. Other applications of nonlinear absorption enter such
diverse fields as 3D optical storage, bio-imaging and photo-dynamic therapy [7]. In the latter applications, the essential feature is the ability of accessing excited states by radiation with half or third of the actual energy threshold. Thereby less noxious radiation with increased penetration depth in human tissue can be employed in order to populate excited states and potentially initiate reactions strongly destructive to cancer cells. The quadratic or cubic dependence on the intensity ensures a spatial confinement of the reaction.

Initially, inorganic crystals were employed to achieve optical nonlinearities, but basically all atoms, molecules or even free electrons exhibit these properties when subjected to sufficiently intense radiation. However, the synthesis of organic molecules with enhanced two-photon absorption cross sections have restored the activity in this field. Unlike their inorganic counterparts, organic systems offer nonlinear response in a broad frequency range accompanied with a natural versatility which should make them readily integrable in various electronic devices.

Owing to the number of organic molecules and sometimes specific technological demands, theoretical guidelines and design strategies are becoming increasingly important. These can be evaluated from simulations of matter at the molecular level. Simulations can confirm or reject, explain or interpret and predict new results and thereby avoid often tedious and expensive synthesis. By estimating not only the desired property but also related quantities, occasionally out of reach of experiments, valuable structure-to-property relations can be obtained. The tools for accomplishing such analysis have traditionally been developed within the discipline of quantum chemistry. The starting point is the attempt to solve the Schrödinger equation for systems beyond the realms of analytical solutions. Therefore it is necessary to introduce carefully chosen approximations and accompanying techniques for estimating the effects of these approximations. The last feature is of special significance in situations where experimental data are scarce, dubious or even absent. The key notion is to introduce approximations in a systematic and hierarchical fashion in order to determine any convergence to a more exact solution. In such a benchmarking procedure lower order methods can be evaluated against higher order methods for smaller systems before applied to large scale systems. Hence, when confidence has been established for the method determining the electronic structure, additional and modifying effects such as vibration, solvent effects subsequently can be included in order to bring the estimations closer to experiment. Ultimately all the effects can be included in a dynamical model derived from first principles. In such a model it will also be necessary to consider the duration of the pulse and saturation effects.

Response theory is the main theoretical foundation utilized in the thesis. It provides a general and powerful computational framework from which a rich variety of molecular properties can be retrieved in a highly consistent manner. Due to the computational complexity, all calculations benefit greatly from improved computational facilities. In particular, parallel computers have proved to be useful in this context enabling the addressing of large scale structures at an accuracy nearly in parity with experiments.

The three major topics in this thesis are Two-Photon Absorption (TPA), Three-Photon Absorption (3PA) and Excited State Absorption (ESA), all with potential applications for instance within optical limiting devices. The entreated
quantity is a material which is transparent at lower intensities, but ideally opaque at higher intensities, *e.g.* laser pulses. This feature can be utilized in, for instance, protection of optical sensors. A second - twofold - reason for studying TPA and ESA in accordance to each other is that the quantities are deeply connected through so-called sum-over-states (SOS) expressions. In fact, these expressions constitute one of the few sources for evaluating experimental values of the microscopic property that determines the ESA; the transition dipole moments between excited states. Another attractive feature is the ability to construct generalized few-states model from which design strategies for optimum nonlinear response can be extracted.
Chapter 2

Quantum chemistry methods

2.1 The Schrödinger equation

The properties in focus in this thesis need to be addressed by means of quantum chemical methods [8, 9, 10, 11]. From a microscopic point of view, all information resides in the wave function, \( \Psi \), of the system. A particular physical quantity, \( Q \), can be determined by calculating the expectation value of the corresponding operator as \( \langle \Psi | Q | \Psi \rangle \). The fundamental and initial issue in quantum chemistry is therefore to solve the Schrödinger equation, either in the time-dependent

\[
\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = H \Psi
\]

(2.1)

or the corresponding time-independent version

\[
H \Psi = E \Psi
\]

(2.2)

In both forms, \( H \) represents the Hamiltonian operator which extracts the kinetic and potential energies from the wave function of the system. Because no analytical solutions are possible even for the smallest organic system, it is essential to introduce several approximations. In addition, it is also useful to have some means of estimating the effects of these approximations. The first step in a series of approximations is the Born-Oppenheimer approximation which states the separation of the electronic and the nuclear motion. This is motivated by the considerable difference in mass between the nuclei and the electrons which leads to a considerable difference in momentum. Accordingly,

\[
\Psi = \Psi_e(R,r) \psi_n(R)
\]

(2.3)

where the nuclear wave function \( \psi_n \) depends on the coordinates of the nuclei, \( R \), while the electronic wave function, \( \Psi_e \), depends on the electronic coordinates, \( r \), and only parametrically on the nuclear coordinates. This implies a consideration of the coordinates, but not of the momentum of the nuclei for the electronic wave function and implicit results of this approximation are such basic concepts as the potential energy surface and the notion of molecular geometry. The Hamiltonian for \( N \) electrons and \( M \) nuclei has in this case and in atomic units (a.u.) the
following structure

\[ H = - \sum_i^N \frac{1}{2} \nabla_i^2 - \sum_i^N M \sum_A Z_A \nabla_i r_{iA} + \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}} \]  

(2.4)

where clearly the last term, the electron-electron repulsion, constitutes the most computationally challenging term. Semi-empirical methods attack this by modifying the Hamiltonian, while \textit{ab-initio} methods keep the Hamiltonian unchanged—at a higher computational cost—and tries instead to approximate the wave function. Introducing approximations to the Hamiltonian leads to computationally less demanding schemes, but also in general to a strong dependence on a wide set of empirical parameters that need to be fitted to experiment.

2.1.1 Hartree-Fock

If the Hamiltonian above did not include the electron-electron interaction, it would only be a sum of one-electron operators. The product of spin orbitals, \( \chi \), defined as

\[ \chi(x) = \begin{cases} \psi(r)_\alpha = \psi \\ \text{or} \\ \psi(r)_\beta = \bar{\psi} \end{cases} \]  

(2.5)

where \( \psi(r) \) is a pure spatial orbital and \( \alpha \) and \( \beta \) denote the spin functions up (\( \uparrow \)) and down (\( \downarrow \)), respectively, may thus appear as a fairly reasonable start for solving the Schrödinger equation. Because of the Pauli principle that requires that the wave function should be antisymmetric with respect to the interchange of the coordinates of any two electrons, this idea has to be recast in the context of Slater determinants. A single determinant represents a constrained approach, but also a starting point for more advanced methods:

\[ \Psi_0 = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \ldots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \ldots & \chi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \ldots & \chi_N(x_N) \end{vmatrix} \]  

(2.6)

The inevitable confinement to a finite number of determinants is usually referred to as a truncation in \( n \)-electron space. Each spatial molecular orbital is expanded from a linear combination of basis functions, \( \phi_\mu \), as

\[ \psi_i(r) = \sum_\mu c_{i\mu} \phi_\mu(r) \]  

(2.7)

A complete expansion will in theory give the exact solution within the single determinant approximation. For computational reasons this series is not only truncated, but also modified by choosing functions for their mathematical properties rather than their physical content. These functions, denoted basis functions, are commonly - but not necessarily - attached to the individual atoms. For instance, molecule centered diffuse functions may be efficient in order to describe diffuse excited states or the weak interactions in van der Waals complexes. The
2.1 The Schrödinger equation

accuracy lost when employing a finite basis set will, analogously to the use of a
finite number of Slater determinants, be referred to as a truncation in 1-electron
space. The equations obtained from one single determinant and a finite basis set,

\[ \sum_a \int d\mathbf{x}_2 \chi_a^\ast (\mathbf{x}_2) r_{12}^{-1}(1 - P_{12}) \chi_a (\mathbf{x}_2) \]

(2.8)

where \( P \) is an operator interchanging electron 1 and electron 2. The Hartree–Fock
operator acts on the spin orbitals as

\[ f(\mathbf{x}_1) \chi_i (\mathbf{x}_1) = \epsilon_i \chi (\mathbf{x}_1) \]

(2.9)

The solutions are denoted Hartree–Fock (HF) or sometimes self-consistent field solu-
tions (SCF) and the limit of a complete basis set defines the Hartree–Fock limit.
The difference between the lowest eigenvalue of the non-relativistic Hamiltonian
and the Hartree–Fock limit energy is called the correlation energy. This is often
separated in two parts; the static and the dynamic correlation. The dynamical
correlation arises from the singular term \( r_{ij}^{-1} - v_{HF}(i) \), where \( v_{HF}(i) \) denotes the
average potential from the surrounding electrons experienced by the \( i^{th} \) electron.
The non-dynamic correlation originates because of the mixing between other low
lying configurations with the Hartree-Fock configuration. The latter is small for
closed shell molecules at equilibrium geometry, but increases when the molecule
is distorted.

Hitherto, we have not made any assumptions of the occupancy of the obtained
orbitals. For closed shell systems one normally imposes the restriction that each
spatial orbital should contain two electrons of opposite spin. This is referred to
as closed shell Hartree-Fock and the corresponding ground state is

\[ |\Psi\rangle = |\chi_1\chi_2\chi_3\cdots\chi_N\rangle = |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2\cdots\psi_{N/2}\bar{\psi}_{N/2}\rangle \]

(2.10)
CHAPTER 2. QUANTUM CHEMISTRY METHODS

Through the expansion in Eq. 2.7 the Hartree-Fock equation can be transformed into the matrix equation

\[ \sum_{\nu} c_{\nu i} \int \phi_{\mu}^*(1) f(1) \phi_{\nu}(1) d\mathbf{r}_1 = \epsilon_i \sum_{\nu} \int \phi_{\mu}^*(1) \phi_{\nu}(1) d\mathbf{r}_1 \]  

(2.11)

which by defining the matrices \( S \) and \( F \) as

\[ S_{\mu\nu} = \int \phi_{\mu}^*(1) \phi_{\nu}(1) d\mathbf{r}_1 \]  

(2.12)

and

\[ F_{\mu\nu} = \int \phi_{\mu}^*(1) f(1) \phi_{\nu}(1) d\mathbf{r}_1 \]  

(2.13)

can be further compressed to

\[ \sum_{\nu} F_{\mu\nu} c_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} c_{\nu i} \]  

(2.14)

or equivalently

\[ FC = SC\epsilon \]  

(2.15)

A formulation capable to describe open shell systems can be constructed by decoupling the spin orbitals in two mutually excluding sets of opposite spin and thereby allowing each electron an individual orbital. This approach denoted unrestricted Hartree-Fock (UHF) enables description of high spin states such as doublets, triplets..., but have the drawback of producing wavefunctions which are not true eigenfunction of the \( S^2 \) operator. The optimization of a singlet UHF wavefunction can therefore steal contributions from higher lying triplet, quintet etc. states. This mixing of pure spin states is referred to as spin-contamination and several approaches for removing the spin contamination by for instance various projection methods have been developed. By explicitly releasing only those electrons responsible for the open shell character, letting the remaining stay in doubly occupied orbitals and using combinations of determinants that are eigenfunctions of \( S^2 \) leads to the scheme of restricted open shell Hartree-Fock (ROHF). This re-establishes proper eigenfunctions of the spin operator and inhibits the proneness to spin-contamination, but adds some additional computational complexity.

2.2 Beyond the single determinant approximation

The straightforward way to leave the single determinant picture and recover some correlation energy is to simply expand the wave function in multiple excited determinant configurations as

\[ |\psi_{CI}\rangle = a_0|\theta_{HF}\rangle + \sum_S a_S|\theta_{S}\rangle + \sum_D a_D|\theta_{D}\rangle + \sum_T a_T|\theta_{T}\rangle + \cdot \]  

(2.16)

where \( S, D, T \) denotes singly (S), doubly (D) and triply (T) excited configurations respectively. This is referred to as a Configuration Interaction (CI) expansion. Including all possible excitations within the given basis set forms the Full Configuration Interaction (FCI) approach. This is very computationally expensive,
2.2 Beyond the single determinant approximation

since the numbers of excited determinants grows factorially with the basis set size, but FCI is possible for small basis sets/molecules and is occasionally used as a benchmark. The diagonalization of the CI matrix leads, however, only to a solution exact within the 1-electron subspace spanned by the chosen basis set. The ultimate solution would be FCI in a complete basis set.

Except for small basis sets and molecules the CI expansion has to be truncated according to some scheme for selecting the proper configurations. In the multi-configurational SCF (MCSCF) method both the coefficients, $a_i$, as well as the MOs employed for constructing the determinants are optimized. The question of which configurations to choose, however, still remains open. In complete active space (CAS) the highest occupied and the lowest unoccupied orbitals are selected to construct the active space in which all possible determinants are considered. However, the MCSCF method is not foremost employed for retrieving a large fraction of the correlation energy, perhaps more frequently the reasons are related to the necessity to address the multi-configurational character of a system. In practice MCSCF also forms a fairly robust method for optimizing states different from the singlet ground state.

2.2.1 Coupled cluster

The observation that the solution of the Hartree-Fock equation only should differ slightly from the true eigenvalue seems to motivate the use of perturbation theory. In many-body perturbation theory a part of the correlation is added as a perturbation on top of an approximate wave function. In Møller-Plesset (MP) perturbation theory the Hamiltonian is chosen as a sum over Fock operators. By restricting to the second order corrections, the widely applied method, MP2, is obtained which qualitatively describes the interaction of pairs of electrons. A major advantage of this approach is that it predicts correct scaling of the correlation energy with the number of particles, which is not generally true for truncated CI. A drawback of the MP(n) technique is that each type of correction (S, D, T etc) is only summed up to a limited order (2, 3, 4 etc). However, this can be improved by expanding the configurations differently. Let the excited configurations be denoted as

$$\Psi_{IJ}^{AB} = a_{B}^\dagger a_{J} a_{A}^\dagger a_{I} \Psi_0$$

and label the excitation operators by $T$ as

$$T = T_1 + T_2 + T_3 \cdots$$

$$T_1 = \sum_A \sum_I t_{A}^I a_{I} \Psi_0$$

$$T_2 = \sum_{A>B} \sum_{I>J} t_{IJ}^{AB} a_{B}^\dagger a_{J} a_{A}^\dagger a_{I}$$

The letter $t$ is usually denoted the cluster amplitude. If now the cluster operators are expanded exponentially as
\[ \exp(T) = 1 + T_1 + \left( T_2 + \frac{1}{2} T_1^2 \right) + \left( T_3 + T_2 T_1 + \frac{1}{6} T_1^3 \right) + \ldots \quad (2.21) \]

then all corrections of a certain type are included to infinite order. Each term, 1, \( T_1 \) and the following parentheses represents all excited states at a given order. For instance, the terms in the second parenthesis generate all doubly excited states, both connected \( T_2 \) as well as disconnected \( \frac{1}{2} T_1^2 \). The equations for \( t \) can be obtained by projecting \( (H - E) \exp(T) \Psi_0 \) on the \( N \)-fold excitation manifold as

\[
\langle \Psi_0 | H | \exp(T) \Psi_0 \rangle = \epsilon 
\]

\[
\langle \Psi_I^A | H | \exp(T) \Psi_0 \rangle = \epsilon t_I^A 
\]

\[
\langle \Psi_{IJ}^{AB} | H | \exp(T) \Psi_0 \rangle = \epsilon (t_{IJ}^{AB} + t_I^A t_J^B - t_I^B t_J^A) 
\]

where

\[
\mathcal{H} = H - E_0 
\]

This is rigorously size-extensive irrespective of truncation. Different levels of coupled cluster (CC) methods are obtained by truncating \( T \) at different orders. By including only single excited configurations, i.e. truncating \( T \) as \( T \approx T_1 \) one obtains CCS, double excited configurations, \( T \approx T_1 + T_2 \), give CCSD and triple excited configurations, \( T \approx T_1 + T_2 + T_3 \), give CCSDT. Since already CCSDT scales as \( N^8 \), several intermediate methods, such as CC2 and CC3, have been obtained by a perturbative approach. From this it is possible to construct hierarchies in \( n \)-electron space, CCS < CC2 < CCSD < CC3, which together with the basis set hierarchies in 1-electron space form an exquisite tool for monitoring the effects of the applied approximations. Unfortunately, this is not completely trivial since basis set effects are not systematic in general. According to the Brillouin theorem the pure singles, \( T_1 \), should not add any direct correction to the energy, but through the interaction with doubles has the similar effect as MO relaxation. This feature may improve the description of the response of the energy to a perturbation when evaluating molecular properties.

### 2.3 Density functional theory

A completely different strategy for determining molecular properties is Density Functional Theory (DFT), where the focus is on the electron density rather than the wave function and the orbitals. The foundation is the observation\[^{12}\] that the ground state energy is completely determined as a functional of the electron density, \( \rho \), as

\[
E[\rho] = T[\rho] + V_{\text{NE}}[\rho] + J[\rho] + E_{\text{xc}}[\rho] 
\]

where \( T \) is the kinetic energy, \( V_{\text{NE}} \) the nuclear-electron attraction and \( J \) the coulomb part of the electron-electron interaction. The remaining contributions to the exact energy, the exchange and the correlation energy, are absorbed in the exchange-correlation functional, \( E_{\text{xc}} \). In general orbitals, the so called Kohn-Sham (KS) orbitals, \( \phi \), are re-introduced as

\[
\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2 
\]
in order to construct the Kohn-Sham equations

\[
\left[-\frac{1}{2} \nabla^2 + v_{\text{NE}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' + v_{\text{XC}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})
\] (2.28)

The KS orbitals can similarly to Hartree–Fock be expanded in basis functions and well established techniques for retrieving molecular properties can therefore be applied once the KS orbitals have been determined.

If \( E \) is taken as the exact energy in Eq. 2.26 this could serve as a definition of the unknown exchange-correlation functional \( E_{\text{xc}} \). The true functional \( E_{\text{xc}} \) may be as, or even more, computationally expensive as any high order correlation method. In general though, the implemented approximations of \( E_{\text{xc}} \) make the computational cost of the order of the Hartree–Fock method. Among the species in the extensive fauna of functionals in use, the local density approximation (LDA) has a special place because it is based on the assumption that the electrons locally can be treated as a uniform electron gas. Because of the poor performance and somewhat crude underlying approximation it was soon realized that additional corrections were required. A first step was to permit the functional to depend on the derivatives of the density in order more accurately handle a non-uniform electron gas. This approach, denoted Generalized Gradients Approximation (GGA), led to substantial improvements and an explosion of functionals reflecting the high expectations associated with the method. One successful route devised by Becke was the inclusion of fractions of exact Hartree–Fock exchange. In particular, the hybrid functional B3LYP[13], has been widely used because of good performance with respect to experimental data. A drawback of DFT is that, unlike regular \textit{ab-initio} quantum chemistry, there is no clear way of establishing systematic improvements by forming hierarchies in n-electron space. Nevertheless, DFT has been, and is, extensively used in a broad range of applications because of its computationally inexpensive way of treating the electronic correlation. Analogously to Hartree–Fock, open shell system can be addressed by unrestricted or restricted approaches. An advantage of DFT in this context is its inherent tolerance to spin-contamination.
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Chapter 3

Molecular optical transitions

3.1 The excitation scheme

The overall optical response of a molecular system can be incorporated in the Jablonski scheme, as seen in Fig. 3.1. On top of a singlet ground state, $S_0$, and a gap energy of a few electron volts, resides a manifold of singlet excited states, $S_n$. These are accessible, depending on symmetry selection rules, by one-photon absorption or by absorbing two or more photons simultaneously in a multi-photon absorption process. The transition probabilities from an excited state to additional excited states determine the excited state absorption characteristics; they may either be smaller, which corresponds to bleaching, or larger, which corresponds to reversed bleaching (reversed saturable absorption, RSA). Spin conversion induced by heavy atom spin-orbit effects may cause an intersystem crossing to $T_1$, followed by triplet-triplet transitions to $T_n$. A total description requires thus both the location of the excited states and the coupling between them within the manifold of singlet and triplet states. All transitions within the scheme can in principle be addressed at an arbitrary level of approximation, both with respect to the choice of quantum chemical method and basis set, but also by different treatments of

Fig. 3.1: Example of some transitions within a molecular system
additional effects like geometrical relaxation and vibration. Especially the latter have proved to add considerable contributions to the total TPA cross section for multi-branched structures. For a realistic simulation and a proper interpretation of an experiment such effects as the duration of the pulse, dephasing, saturation and the interaction with the solvent should also should be taken into account. Less influence on the final accuracy are provided by effects related to the fact that molecular systems will be treated quantum mechanically while light will be described as purely classical. Moreover, since the wavelength of the light (> 1000 Å) will be substantially larger than the dimension of the molecular system (<10 Å) one can assume a uniform field across the molecule and apply the dipole approximation:

\[ e^{ikr} = 1 + (ik \cdot r) + \frac{1}{2}(ik \cdot r)^2 + \ldots \]  

(3.1)

Apparently several, more or less, independent effects contribute to the total optical response. Hence, the field of nonlinear optics appears divided in one part concerned with the propagation and evolution of the fields and one with the intrinsic response associated with the nonlinear susceptibility. This thesis is constrained to the quantum chemical part and various means of estimating transition probabilities and does mainly assume pure vertical transitions. Both the one-photon and the multi-photon absorption probabilities can be accomplished by traditional time-dependent perturbation theory under the assumption that the unperturbed solution is known exactly. Since this is not the case in general, the derived expressions should be regarded as tools for interpretation rather than foundations for implementing efficient computational schemes.

3.2 Electromagnetic fields

A natural starting point for discussing linear as well as nonlinear optics is the set of Maxwells equations

\[ \nabla \cdot \mathbf{D} = \rho \]  

(3.2)

\[ \nabla \cdot \mathbf{B} = 0 \]  

(3.3)

\[ \nabla \times \mathbf{E} = \frac{\partial \mathbf{B}}{\partial t} \]  

(3.4)

\[ \nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \]  

(3.5)

which unites the charge density, \( \rho \), current density, \( \mathbf{J} \), the electric field strength, \( \mathbf{E} \), the electric flux density, \( \mathbf{D} \), the magnetic field strength, \( \mathbf{H} \), and the magnetic flux density, \( \mathbf{B} \) and together with the constitutive matter-specific relations

\[ \mathbf{D} = \varepsilon \mathbf{E} \]  

(3.6)

\[ \mathbf{B} = \mu \mathbf{H} \]  

(3.7)

provides the foundation for describing the classical propagation of electro-magnetic waves. The mere writing of the permitivity, \( \varepsilon \), and the permeability, \( \mu \), as scalar constants, indicates the assumption of a linear, homogeneous and isotropic medium.
Although all these assumptions will be violated in the field of nonlinear optics, it is instructive to incipiently derive some cardinal relations within this simplified regime. For a given material the presence of an electric field will induce a polarization, \( P \)

\[
P = \epsilon_0 \chi E
\]

which within the prescribed space of assumptions will be linear and ascertained by the first order susceptibility, \( \chi \). The electric flux density will consequently be written as

\[
D = \epsilon_0 E + P = \epsilon_0 (1 + \chi) E = \epsilon_0 \epsilon_r E = \epsilon E
\]

and the wave equation for a homogeneous media free of charges and currents

\[
\frac{\partial^2 D}{\partial t^2} - \frac{1}{\mu_0} \nabla^2 E = 0
\]

A first unavoidable step in order to incorporate nonlinear effects is to allow higher order terms of the polarization

\[
D = \epsilon_0 E + P = \epsilon_0 E + P^L + P^{NL} = \epsilon_0 (1 + \chi^L) E + P^{NL}
\]

which when introduced in the wave equation 3.10 leads to\([14, 15, 16]\)

\[
\frac{\partial^2 E}{\partial t^2} - \frac{1}{\mu_0 \epsilon} \nabla^2 E = \frac{1}{\epsilon} \frac{\partial^2 P^{NL}}{\partial t^2}
\]

Unlike for vacuum, we are confronted with a term, \( P^{NL} \), which may strongly affect the wave along its propagation through the medium. Thus, through the design of materials with certain nonlinear polarization we are provided means of controlling the propagation of light. Another important relation concerns the conservation of energy and can be written as

\[
\frac{\partial}{\partial t} \left( \frac{1}{2} \epsilon |E|^2 + \frac{1}{2 \mu_0 \epsilon} |B|^2 \right) + \nabla \cdot \frac{(E \times B)}{\mu_0} = - J \cdot E
\]

The left side represents the rate of the energy density of the electric and the magnetic field as balanced by the flow of electromagnetic energy, \((E \times B)/\mu_0\), whereas the right hand side describes the rate work exerted on the field by the medium. Conversely, the rate work, \( \partial W/\partial t \), done on the medium by the electromagnetic field, i.e. the absorption, can be written as

\[
\frac{\partial W}{\partial t} = J \cdot E
\]

### 3.3 Nonlinear susceptibilities

In order to describe an anisotropic medium, the relation describing the polarization, \( P \), of a material when exposed to an electric field, \( E \), will benefit from being casted in the Einstein’s summation convention as

\[
P_i = \epsilon_0 \chi_{ij} E_j
\]
As mentioned in previous section, this is perfectly valid for weak fields and covers the microscopic phenomena of charge deformation and dipole re-orientation. Analogously, for a magnetic field

$$M_i = \frac{\chi^M_{ij} B_j}{\mu_0}$$  (3.16)

where $\chi^M$ denotes the magnetic susceptibility. The decoupling of electric and magnetic fields is obviously legitimate for static fields, but in general also for dynamical fields in materials with a low density of free charge carriers, even though intrinsically entangled through Maxwell’s relations for propagating waves. A general prerequisite for the presence of nonlinear optical phenomena is high intensity fields, $E$, in the order of the field strength in molecules and atoms, $E_{at} \approx 10^{10} - 10^{12}$ V/m. On a macroscopic scale this field induces a polarization of the medium, which unlike in the case of lower intensities, also is dependent on the second, the third or even higher powers of the perturbing field. One can show the following approximate relation[17]

$$\left| \frac{P^{(n+1)}}{P^{(n)}} \right| \approx \left| \frac{E}{E_{at}} \right|$$  (3.17)

which justifies the right hand side as an expansion parameter in perturbation calculations. The effect of higher order terms of $P$ can readily be illustrated by expanding the polarization to include nonlinear terms as

$$P_i = \epsilon_0 \left[ \chi^{(1)}_{ij} E_j + \chi^{(2)}_{ijkl} E_j E_k + \chi^{(3)}_{ijklm} E_j E_k E_l \ldots \right]$$  (3.18)

Inserted in the familiar derivatives of Maxwell’s equations, as Eq. 3.10 the presence of $\chi^{(n)}$ give rise to a manifold of nonlinear phenomena[17, 18, 19, 20]. This can be exemplified by assuming the presence of two harmonic waves with the frequencies $\omega_1$ and $\omega_2$.

$$E_i = E^{(1)}_i e^{-i\omega_1 t} + E^{(2)}_i e^{-i\omega_2 t} + c.c.$$  (3.19)

and by confining the attention to their exclusive effect on the quadratic response

$$P^{(2)}_i = \epsilon_0 \chi^{(2)}_{ijk} \left[ E^{(1)}_j E^{(1)}_k e^{-2i\omega_1 t} + E^{(2)}_j E^{(2)}_k e^{-2i\omega_2 t} + E^{(1)}_j E^{(2)}_k e^{-i(\omega_1+\omega_2) t} + E^{(2)}_j E^{(1)}_k e^{-i(\omega_1-\omega_2) t} + c.c. \right]$$

$$+ 2\epsilon_0 \chi^{(2)}_{ijk} \left[ E^{(1)}_j E^{(1)}_k \right]^* + E^{(2)}_j E^{(2)}_k \right]^*$$  (3.20)

Clearly, all linear combinations of the two original frequencies is present in this expansion, leading to a variety of nonlinear effects; second harmonic generation (SHG), sum of frequency generation (SFG) difference frequency generation (DFG). Even a static field can be induced as seen from the last term and which is referred to as optical rectification (OR).

If one of the perturbing fields instead would have been static, $E^{(0)}$, then we would, among a pure static effect and terms of types already included in the expansion above, witness a correction, $\chi^{(2)}_{ijk}(-\omega; \omega, 0)$ linear with the static field
3.3 Nonlinear susceptibilities

which would modify the effective refractive index. This effect is denoted Pockels
or short Pockel effect and could in principle be employed
to control the propagation of light through a sample by an electrical field. The
nonlinear effects related to the second order susceptibility are summarized in Ta-
ble 3.3

<table>
<thead>
<tr>
<th>Quadratic term</th>
<th>interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi^{(2)}_{ijk}(-2\omega_1;\omega_1,\omega_1)E^{(1)}_jE^{(1)}_k e^{-2i\omega_2 t}$</td>
<td>SHG$^a$</td>
</tr>
<tr>
<td>$\chi^{(2)}_{ijk}(-2\omega_2;\omega_1,\omega_2)E^{(2)}_jE^{(2)}_k e^{-2i\omega_2 t}$</td>
<td>SHG$^a$</td>
</tr>
<tr>
<td>$\chi^{(2)}_{ijk}(-\omega_1 + \omega_2;\omega_1,\omega_2)E^{(1)}_jE^{(2)}_k e^{-i(\omega_1+\omega_2)t}$</td>
<td>SFG$^b$</td>
</tr>
<tr>
<td>$\chi^{(2)}_{ijk}(-\omega_1 - \omega_2;\omega_1,\omega_2)E^{(1)}_jE^{(2)}_k [E^{(2)}_k]^* e^{-i(\omega_1-\omega_2)t}$</td>
<td>DFG$^c$</td>
</tr>
<tr>
<td>$\chi^{(2)}_{ijk}(0;\omega_1,\omega_1)E^{(1)}_jE^{(1)}_k [E^{(1)}_k]^*$</td>
<td>OR$^d$</td>
</tr>
<tr>
<td>$\chi^{(2)}_{ijk}(0;\omega_2,\omega_2)E^{(2)}_jE^{(2)}_k [E^{(2)}_k]^*$</td>
<td>OR$^d$</td>
</tr>
<tr>
<td>$\chi^{(2)}_{ijk}(\omega_1;0,\omega_1)E^{(0)}_jE^{(1)}_k [E^{(1)}_k]^* e^{i\omega_1}$</td>
<td>EOPE$^e$</td>
</tr>
</tbody>
</table>

$^a$Second-harmonic generation, $^b$Sum-frequency generation, $^c$Difference-frequency generation,
$^d$Optical rectification, $^e$Electro-optical Pockels effect

Table 3.1: Nonlinear optical effects derived from the second order susceptibility.

The identical approach, but applied to the third order polarization can similarly cause various types of wave mixing, and an analog to the Pockel effect; the Kerr electro-optical effect which is quadratic with respect to the static field. Again, by assuming a perturbation of the type

$$E_i = E^{(0)}_i + E^{(1)}_i e^{-i\omega_1 t} + E^{(2)}_i e^{-i\omega_2 t} + E^{(3)}_i e^{-i\omega_3 t} + \text{c.c.}$$ (3.22)

and inserting it in Eq. 3.18, one can highlight a few terms in the manifold of emerging combinations

$$P^{(3)}_i = \epsilon_0 \chi^{(3)}_{ijk}[E^{(1)}_jE^{(1)}_kE^{(1)}_l e^{-3i\omega_1 t} + \cdots + E^{(1)}_jE^{(2)}_kE^{(3)}_l e^{-i(\omega_1+\omega_2+\omega_3)t} + \cdots$$

$$+ E^{(0)}_jE^{(0)}_kE^{(1)}_l e^{-i\omega_1 t} + \cdots + E^{(0)}_jE^{(1)}_kE^{(4)}_l e^{-2i\omega_2 t} + \cdots \text{c.c.}]$$ (3.23)

One finds terms associated to tripled frequencies and additions and/or subtractions of the ingoing fields of which some may be static. Some of the most prominent terms are summarized in Table 3.3.

Susceptibilities are strongly affected by spatial symmetries. The relation between the second order polarization and the electric field in one dimension reads

$$P^{(2)} = \chi^{(2)} E^2$$ (3.24)

For a centrosymmetric medium, the act of reversing the electric field should correspond to reversing the polarization i.e.

$$-P^{(2)} = \chi^{(2)} (-E)^2 = \chi^{(2)} E^2$$ (3.25)

which implies that $\chi^{(2)} = 0$. The consequences of symmetry can be generalized further. In conjunction with the assumption of frequency independence of the susceptibilities for a lossless medium (Kleinman’s symmetry rules), the reality of the
### Table 3.2: Nonlinear optical effects derived from the third-order susceptibility.

<table>
<thead>
<tr>
<th>Cubic term</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi^{(3)}_{ijkl}(-3\omega_1;\omega_1,\omega_1,\omega_1)E_j^{(1)}E_k^{(1)}E_l^{(1)}e^{-3i\omega_1 t}$</td>
<td>THG\textsuperscript{a}</td>
</tr>
<tr>
<td>$\chi^{(3)}_{ijkl}(-2\omega_1;\omega_1,\omega_1,0)E_j^{(1)}E_k^{(1)}E_l^{(0)}e^{-2i\omega_1 t}$</td>
<td>ESHG\textsuperscript{b}</td>
</tr>
<tr>
<td>$\chi^{(3)}_{ijkl}(-\omega_1;\omega_1,0,0)E_j^{(1)}E_k^{(0)}E_l^{(0)}e^{-i\omega_1 t}$</td>
<td>EOEK\textsuperscript{c}</td>
</tr>
<tr>
<td>$\chi^{(3)}_{ijkl}(-\omega_1;\omega_1,-\omega_1,\omega_1)E_j^{(1)}E_k^{(1)}E_l^{(1)}e^{-i(\omega_1-\omega_2)t}$</td>
<td>IDRI\textsuperscript{d}</td>
</tr>
<tr>
<td>$\chi^{(3)}_{ijkl}(-\omega_1+\omega_2+\omega_3;\omega_1,\omega_2,\omega_3)E_j^{(1)}E_k^{(2)}E_l^{(3)}e^{-i(\omega_1+\omega_2+\omega_3)t}$</td>
<td>SFG\textsuperscript{e}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Third-harmonic generation, \textsuperscript{b}Electric-field-induced harmonic generation \textsuperscript{c}Electro-optical Kerr effect, \textsuperscript{d}Intensity-dependent refractive index, \textsuperscript{e}Sum frequency generation

**3.4 Multi-photon absorption**

All the nonlinear phenomena discussed in the previous section seemingly concern the propagation of light. Another notation for these phenomena is parametric processes, meaning processes where the populations of the quantum mechanical states are invariant in time, except for the brief and sublime time intervals supplied by the uncertainty principle. Non-parametric processes relate on the other hand to processes with an explicit transfer of populations to real states, such as in absorption.

From considering a plane electromagnetic wave propagating through a medium

\[ \mathbf{E} = E_0 e^{i(n\mathbf{k} \cdot \mathbf{x} - \omega t)} = E_0 e^{-n_f \mathbf{k} \cdot \mathbf{x} e^{i(n_R \mathbf{k} \cdot \mathbf{x} - \omega t)}} \]  

(3.26)

it is clear that technically it is the real part of the refractive index, $n_R$, that relates to propagation. Dissipative losses due to absorption relates on the other hand to the imaginary part, $n_f$. A computational scheme where each order of the susceptibility is associated with its corresponding order of photonic transition can be derived from energy considerations. For a non-magnetic medium with no free charge carriers the average change of absorbed energy per volume unit when subjected to an external electric field, $\mathbf{E}$, can be written as

\[ \left\langle \frac{d}{dt} \left( \frac{\text{absorbed energy}}{\text{volume}} \right) \right\rangle_{\text{time}} = \langle \mathbf{j} \cdot \mathbf{E} \rangle \]  

(3.27)

The current density, $\mathbf{j}$, induced in the medium can be expanded as

\[ \mathbf{j} = \frac{\partial \mathbf{P}}{\partial t} + c \nabla \times \mathbf{M} - \frac{\partial}{\partial t} \nabla \times \mathbf{Q} + \cdots \]  

(3.28)

where the terms represent the electric dipole, magnetic dipole and electric quadrupole polarization. In the field of nonlinear optics the latter terms are neglected in general and the electric dipole term is expanded as

\[ \mathbf{P} = \mathbf{P}^{(1)} + \mathbf{P}^{(2)} + \mathbf{P}^{(3)} + \mathbf{P}^{(4)} + \mathbf{P}^{(5)} \cdots \]  

(3.29)
3.4 Multi-photon absorption

where it is sufficient to consider terms of odd order, because contributions from terms of even order will cancel out in the time averaging procedure[23]

\[
P_1^{(1)} = \epsilon_0 \chi_{ij}^{(1)}(E_j e^{-i\omega t} + E_j^* e^{i\omega t}),
\]

(3.30)

\[
P_1^{(3)} = \epsilon_0 \chi_{ijkl}^{(3)}(E_j e^{-i\omega t} + E_j^* e^{i\omega t})(E_k e^{-i\omega t} + E_k^* e^{i\omega t}),
\]

(3.31)

\[
P_1^{(5)} = \epsilon_0 \chi_{ijklmn}^{(5)}(E_j e^{-i\omega t} + E_j^* e^{i\omega t})(E_k e^{-i\omega t} + E_k^* e^{i\omega t})(E_l e^{-i\omega t} + E_l^* e^{i\omega t})(E_m e^{-i\omega t} + E_m^* e^{i\omega t})(E_n e^{-i\omega t} + E_n^* e^{i\omega t}).
\]

(3.32)

Moreover, we can anticipate the effect of the time averaging by confining the attention to the following highlighted terms

\[
P_1^{(1)} = \epsilon_0 \chi_{ij}^{(1)}(-\omega;\omega)E_j e^{-i\omega t} + c.c. + \ldots,
\]

(3.33)

\[
P_1^{(3)} = 3\epsilon_0 \chi_{ijkl}^{(3)}(-\omega;\omega,-\omega,\omega)E_j e^{-i\omega t}E_k^* e^{i\omega t}E_l e^{-i\omega t} + c.c. + \ldots
\]

(3.34)

\[
P_1^{(5)} = 10\epsilon_0 \chi_{ijklmn}^{(5)}(-\omega;\omega,-\omega,\omega,-\omega,\omega)E_j e^{-i\omega t}E_k^* e^{i\omega t}E_l e^{-i\omega t}E_m e^{i\omega t}E_n e^{-i\omega t} + c.c. + \ldots
\]

(3.35)

which in the expansion of the the rate of absorbed energy

\[
\left\langle \frac{d}{dt} \left( \frac{\text{absorbed energy}}{\text{volume}} \right) \right\rangle_{\text{time}} = \langle \mathbf{j} \cdot \mathbf{E} \rangle = \left\langle \frac{\partial \mathbf{P}^{(1)}}{\partial t} \cdot \mathbf{E} \right\rangle + \left\langle \frac{\partial \mathbf{P}^{(3)}}{\partial t} \cdot \mathbf{E} \right\rangle + \left\langle \frac{\partial \mathbf{P}^{(5)}}{\partial t} \cdot \mathbf{E} \right\rangle \ldots
\]

(3.36)

will determine the first order contribution of the rate of absorbed energy as

\[
\left\langle \frac{\partial \mathbf{P}^{(1)}}{\partial t} \cdot \mathbf{E} \right\rangle = 2\epsilon_0 \omega \text{Im}[\chi_{ij}^{(1)}(-\omega;\omega)]E_j E_j^*.
\]

(3.37)

This correspond to one-photon transitions and the remaining terms can be ascertained as

\[
\left\langle \frac{\partial \mathbf{P}^{(3)}}{\partial t} \cdot \mathbf{E} \right\rangle = 6\epsilon_0 \omega \text{Im} \left[ \chi_{ijkl}^{(3)}(-\omega;\omega,-\omega,\omega) \right] E_j E_k^* E_l E_l^*.
\]

(3.38)

\[
\left\langle \frac{\partial \mathbf{P}^{(5)}}{\partial t} \cdot \mathbf{E} \right\rangle = 20\epsilon_0 \omega \text{Im} \left[ \chi_{ijklmn}^{(5)}(-\omega;\omega,-\omega,\omega,-\omega,\omega) \right] E_i E_j E_k E_l E_m E_m^*.
\]

(3.39)

which correspond to two- and three-photon absorption. The expressions can be abbreviated further by introducing the intensity, I, as \( I = \frac{mc}{\pi \hbar} E^2 \) (in cgs units)[24] which ensures that the more frequently employed unit for multi-photon cross sections, photons cm\(^{-2}\) s\(^{-1}\), later is evaluated (in this system of units we also have to drop \( \epsilon_0 \) in front of \( \chi^{(n)} \)).

\[
\left\langle \frac{\partial \mathbf{P}^{(1)}}{\partial t} \cdot \mathbf{E} \right\rangle = \frac{4\pi \hbar \omega}{nc} \text{Im} \left[ \chi^{(1)}(-\omega;\omega) \right] I.
\]

(3.40)
\[ \left\langle \frac{\partial \mathbf{P}^{(3)}}{\partial t} \cdot \mathbf{E} \right\rangle = \frac{24\pi^2 \omega}{n^2 c^2} \text{Im} \left[ \chi^{(3)}(-\omega; \omega, -\omega, \omega) \right] I^2 \] (3.41)

\[ \left\langle \frac{\partial \mathbf{P}^{(5)}}{\partial t} \cdot \mathbf{E} \right\rangle = \frac{160\pi^3 \omega}{n^3 c^3} \text{Im} \left[ \chi^{(5)}(-\omega; \omega, -\omega, -\omega, \omega) \right] I^3 \] (3.42)

Finally, the one-, two- and three-photon absorption coefficients, \( \alpha \), \( \beta \) and \( \gamma \), can be identified as

\[ \alpha = \frac{2\pi \hbar \omega}{nc} \text{Im} \left[ \chi^{(1)}_{ij}(-\omega; \omega) \right] \] (3.43)

\[ \beta = \frac{24\pi^2 \hbar^2 \omega}{n^2 c^2} \text{Im} \left[ \chi^{(3)}_{ijkl}(-\omega; \omega, -\omega, \omega) \right] \] (3.44)

\[ \gamma = \frac{160\pi^3 \hbar^3 \omega}{n^3 c^3} \text{Im} \left[ \chi^{(5)}_{ijklmn}(-\omega; \omega, -\omega, \omega, -\omega, \omega) \right] \] (3.45)

which can be related to the phenomenological equations describing the attenuation of a light beam experiencing OPA, TPA and 3PA as

\[ \frac{dI}{dz} = -\alpha I - \beta I^2 - \gamma I^3 \] (3.46)

Trough the relations

\[ \sigma^{\text{TPA}} = \frac{\hbar \omega \beta}{N} \] (3.47)

and

\[ \sigma^{\text{3PA}} = \frac{\hbar^2 \omega^2 \gamma}{N} \] (3.48)

one can define the OPA, TPA and 3PA cross sections, \( \sigma^{\text{OPA}} \), \( \sigma^{\text{TPA}} \) and \( \sigma^{\text{3PA}} \).

Multi-photon absorption in general is characterized by several attractive features. From a spectroscopically point of view it enables the exploration of states that are inaccessible for ordinary one-photon excitations due to symmetry or parity rules. Since this is accomplished at a frequency half of the actual energy gap, it furthermore stretches the accessible range for conventional lasers. Two-photon absorption also appears promising in optical limiting applications. The principal idea is that a bandgap of \( 2\omega \) is unsurmountable for ordinary one-photon absorption of frequency \( \omega \), whereas the competing two-photon process will hit resonance, but only be significant at higher intensities, because of the squared dependence on the intensity. Ideally this would lead to a material that is transparent for lower intensities, but opaque for the higher intensities of a laser pulse. The process is believed to be enhanced further if the TPA is followed by additional transitions to even higher excited states in an excited state absorption (ESA) process. Three-photon absorption (3PA) share the characteristics of TPA, but with a somewhat more distinct flavor since the dependence on intensity is cubic and the spatial confinement therefore even higher. Excitation gaps of a typical chromophore can by 3PA in general be surmounted by light in the IR region which is preferable in various bio-physical application where increased penetration depth is desirable.
3.5 Polarizabilities

Despite the focus on molecular materials, the previous sections implicitly have addressed nonlinear properties as bulk properties. Molecular materials differ though in many aspects from inorganic crystals. Since the constituting molecules in general only are weakly bond through van der Waals interactions, the nonlinear response can be traced to a distinct unit, with a separate delimited electronic environment. The essential building block in organic systems, carbon, offers four orbitals for bonding, 2s- and 2p-orbitals, with the ability to form two types of bonds \( \sigma \)− and \( \pi \)-types. Whereas the former are confined to the actual bonding site, the latter are characterized by a high degree of delocalization. In compounds with alternating single and multiple bonds, also denoted \( \pi \)-conjugated systems, the \( \pi \)-orbitals are delocalized over the effective conjugation length which makes the electronic distribution highly deformable, freely responding to the optical perturbation. For this class of molecules, the nonlinear optical properties are therefore in general significantly enhanced, but is also sensitive to various modifications of the electronic structure through for instance the attachment of electron accepting and electron donating groups. Thus, the combined effect of strong nonlinearities and the inherited versatility renders \( \pi \)-conjugated systems a great potential. In addition, when congregated as polymers, they present a structural flexibility, which enable an extraordinarily variety of shapes and structures e.g. crystals, fibers, films and liquid crystals [25].

In order to pursue the theoretical survey, it is essential to relate the macroscopic observable to a corresponding property at the molecular level. The common ground for the manifold of nonlinear optical properties is the higher order susceptibilities. On a microscopical level the susceptibilities are determined by the corresponding molecular property: the polarizabilities. The energy, \( V \), for a dipole, \( \mu \), when interacting with an electric field, \( E \), is given by

\[
V = -\mu \cdot E
\]

A classical interpretation of the interaction between an uncharged molecule and an electric field is that the electrons experience a force which alters the electron density of the molecule and/or the external field re-orient a permanent dipole moment, thereby inducing a correction, \( \mu^{\text{ind}} \), to the permanent dipole moment, \( \mu^0 \).

\[
\mu(t) = \mu^0 + \mu^{\text{ind}}
\]

The permanent molecular dipole moment can be separated in a nuclear and an electronic part

\[
\mu^0 = \mu_{\text{nuclei}} + \mu_{\text{electronic}}
\]

where the nuclear term is treated classically as a sum over the nuclei, represented as point charges, and their positions. The electronic term requires a quantum mechanical description and is calculated from an unperturbed wave function, \( |0\rangle \) as

\[
\mu_{\text{electronic}}^0 = -e\langle 0|\mathbf{r}|0\rangle = -e\langle 0| \sum_i \mathbf{r}_i |0\rangle
\]
The dynamical term of the dipole moment, the induced dipole moment, \( \mu_{\text{ind}} \), will require both linear and nonlinear corrections in order to describe the response to a strong external field. Clearly, this is more indispensable the closer the external field is to the internal atomic field. The linear and the nonlinear corrections to the polarizabilities can therefore be expanded in a power series as

\[
\mu_{\text{ind}}^{i} = \alpha_{ij}^{0} E_{j} + \frac{1}{2!} \beta_{ijk}^{0} E_{j} E_{k} + \frac{1}{3!} \gamma_{ijkl}^{0} E_{j} E_{k} E_{l} + \cdots
\]

(3.53)

where the terms denote the polarizability, \( \alpha \), first hyperpolarizability, \( \beta \), and second hyperpolarizability, \( \gamma \) tensors. These can be expected to increase for species with a more diffuse electron density, where the electrons are more free to respond to the electric field.

Properties can be extracted from the functional dependence of the molecular polarization, \( p(E) \), as

\[
\mu_{i}^{0} = p_{i}\big|_{E=0}
\]

(3.54)

\[
\alpha_{ij}^{0} = \frac{\partial p_{i}}{\partial E_{j}}\big|_{E=0}
\]

(3.55)

\[
\beta_{ijk}^{0} = \frac{\partial^2 p_{i}}{\partial E_{j} \partial E_{k}}|_{E=0}
\]

(3.56)

\[
\gamma_{ijkl}^{0} = \frac{\partial^3 p_{i}}{\partial E_{j} \partial E_{k} \partial E_{l}}|_{E=0}
\]

(3.57)

The corresponding macroscopic properties, the susceptibilities, can be obtained by applying thermal averaging by considering an averaged ensemble of molecules as

\[
P_{i} = N\langle p_{i} \rangle
\]

(3.58)

Within a Boltzmann distribution the averaging can be performed as

\[
\langle p_{i} \rangle = \frac{\int_{0}^{2\pi} \int_{0}^{\pi} \mu_{i} e^{-\frac{\Delta E}{kT}} \sin \theta d\theta d\phi}{\int_{0}^{2\pi} \int_{0}^{\pi} \sin \theta d\theta d\phi}
\]

(3.59)

where the interaction energy only relates to a static field since the rotational and translational degrees of freedom of the molecules cannot follow the high frequencies corresponding to the optical field.

In conclusion for molecules in gas phase

\[
\chi_{ij}^{(1)} = \frac{\partial P_{i}}{\partial E_{j}}|_{E=0}
\]

(3.60)

\[
\chi_{ijk}^{(2)} = \frac{\partial^2 P_{i}}{\partial E_{j} \partial E_{k}}|_{E=0}
\]

(3.61)

\[
\chi_{ijkl}^{(3)} = \frac{\partial^3 P_{i}}{\partial E_{j} \partial E_{k} \partial E_{l}}|_{E=0}
\]

(3.62)

Hereby a set of relations are established between the macroscopic observables, \( \chi^{(1)} \), \( \chi^{(2)} \) and \( \chi^{(3)} \), in dilute gas phase and the corresponding microscopic interpretation.
that can be addressed by means of quantum chemistry, \( \alpha \), \( \beta \) and \( \gamma \). In solution additional techniques are needed to relate the applied external field with the local field experienced by the molecule and mediated by the polarizable medium. A general relation can be written as follows

\[
\chi^{(1)}(-\omega_1; \omega_1) = l^\omega_1 \langle \alpha \rangle 
\]

\[
\chi^{(2)}(-\omega_3; \omega_1, \omega_2) = l^\omega_1 l^\omega_2 l^\omega_3 \langle \beta \rangle 
\]

\[
\chi^{(3)}(-\omega_4; \omega_1, \omega_2, \omega_3) = l^\omega_1 l^\omega_2 l^\omega_3 l^\omega_4 \langle \gamma \rangle 
\]

where \( l^\omega \) denotes local field factors and \( \langle \alpha \rangle \), \( \langle \beta \rangle \) and \( \langle \gamma \rangle \) the orientationally averaged values of the (hyper)polarizabilities. The principle branches of approaches for relating microscopic properties with the macroscopic observables can be classified as supermolecular or continuum models. The first approach accounts explicitly the interaction by a finite number of neighboring molecules. The second approach assumes a homogeneous medium and considers instead a cavity of various degrees of sophistication, ranging from single spheres to iso-density surfaces, embedded in a dielectric continuum. The exact representations of both these approaches are beyond the scope of this thesis.
Chapter 4

Time-dependent perturbation theory

4.1 General background

A molecular property can, in a general picture, be viewed as the response to a perturbation. Ground, excited state and transition properties for a system can be obtained within the framework of time-dependent perturbation theory\[10, 26, 27\]. We consider a Hamiltonian consisting of an unperturbed Hamiltonian, $H_0$ and a perturbation $V$.

\[ H = H_0 + V \]  

(4.1)

The wave function, $\Psi$, is expanded in the unperturbed functions, $\psi_n^{(0)}$, where

\[ \omega_n = \frac{E_n^{(0)}}{\hbar} \]

in an attempt to solve the time-dependent Schrödinger equation

\[ H\Psi = i\hbar \frac{\partial}{\partial t} \Psi \]  

(4.3)

We multiply from left by $\psi_k e^{i\omega_k t} = \langle k|e^{i\omega_k t} and get

\[ \dot{c}_k(t) = \frac{1}{i\hbar} \sum_n c_n(t) V_{kn}(t) e^{i\omega_{kn} t} \]  

(4.4)

where $V_{kn}$ denotes $\langle k|V|n\rangle$ and $\omega_{kn} = \omega_k - \omega_n$. This is exact, but requires all other coefficients, in order to determine one single coefficient. Provided that $\Psi$ is normalized to unity and all $\psi_n$ are orthonormal we can interpret $|c_n(t)|^2$ as the probability to observe the system in the unperturbed state $|n\rangle$ at time $t$. A solution to Eq. 4.4 can be achieved by expanding $c_n(t)$ in a power series as

\[ c_n(t) = c_n^{(0)}(t) + c_n^{(1)}(t) + c_n^{(2)}(t) + \ldots \]  

(4.5)

By integrating - or by employing the Dyson equation - recursive relations for the coefficients can be obtained

\[ c_k^{(p+1)}(t) = \frac{1}{i\hbar} \sum_n \int_{t_0}^t c_n^{(p)}(t') V_{kn}(t') e^{i\omega_{kn} t'} dt' \]  

(4.6)
Hence, when the correction coefficients, $c_n^{(p)}$, are determined we can construct a similar expansion of corrections to the wavefunction as

$$
\Psi(t) = \Psi^{(0)}(t) + \Psi^{(1)}(t) + \Psi^{(2)}(t) + \Psi^{(3)}(t) + \ldots
$$

(4.7)

where

$$
\Psi^{(p)}(t) = \sum_n c_n^{(p)}(t)e^{-i\omega_nt}|n\rangle
$$

(4.8)

A further simplification can be established by assuming that initially at $t=0$ the system is in the unperturbed reference state $|a\rangle$, i.e.

$$
c_n^{(0)} = \delta_{na}
$$

(4.9)

and exclusively focusing on transitions to the final state $|b\rangle$. A first order correction can in such case be written as

$$
c_b^{(1)}(t) = \frac{1}{i\hbar} \sum_n \int_{t_0}^{t} c_n^{(0)}(t')V_{bn}(t')e^{i\omega_{bn}t'}dt' = \frac{1}{i\hbar} \sum_n \int_{t_0}^{t} \delta_{na}V_{bn}(t')e^{i\omega_{bn}t'}dt' = \frac{1}{i\hbar} \int_{t_0}^{t} V_{ba}(t')e^{i\omega_{ba}t'}dt'
$$

(4.10)

This is the first order correction for a general perturbation and also the starting point for generating higher order corrections.

### 4.2 One-photon absorption

Within the dipole approximation the interaction with radiation can be described by the following perturbation

$$
V(t) = -\hat{\mu} \cdot E = -\hat{\mu}_iE_i(e^{-i\omega t} + c.c)e^{i\epsilon t}
$$

(4.11)

Only the dipole moment is associated with an operator, which reflects the convention of treating light classically, but matter quantum mechanically. The last term containing an infinitesimal $\epsilon$ in the exponent is included to (i) physically assure an adiabatic onset of the perturbation and (ii) mathematically terminate unwanted contributions when integrating from $\infty$. To the first order in the perturbation, the correction, $c_b^{(1)}(t)$, reads

$$
c_b^{(1)}(t) = -\frac{1}{i\hbar} \int_{t_0}^{t} V_{ab}(t')e^{i\omega_{ba}t'}e^{i\epsilon t'}dt' = -\frac{1}{i\hbar} V_{ab} \int_{-\infty}^{t} (e^{-i\omega t} + c.c)e^{i\omega_{ba}t'}e^{i\epsilon t'}dt' = -\frac{1}{i\hbar} V_{ab} \int_{-\infty}^{t} \left[ e^{i(\omega_{ba}+\epsilon)t'} - e^{i(\omega_{ba}-\epsilon)t'} \right] e^{i\epsilon t'}dt' = \frac{1}{\hbar} V_{ab} \left[ \frac{e^{i(\omega_{ba}+\epsilon)t}e^{i\epsilon t'} \omega_{ba} + \omega - i\epsilon}{\omega_{ba} - \omega - i\epsilon} - \frac{e^{i(\omega_{ba}-\epsilon)t}e^{i\epsilon t'} \omega_{ba} - \omega - i\epsilon}{\omega_{ba} - \omega - i\epsilon} \right]
$$

(4.12)
Only the latter term relates to the process of interest, namely absorption, and the exclusion of the former term is often referred to as the rotating wave approximation. Even though $\epsilon$ can be interpreted as an inverse lifetime, we can assume laser detuning and safely remove it for the sake of simplicity.

$$c_b^{(1)}(t) = \frac{1}{\hbar} V_{ab} e^{i(\omega_{na} - \omega)t}$$ (4.13)

The remaining time independent part $V_{ba}$ can be written as

$$V_{ba} = \langle b|\hat{\mu}_iE_i|a \rangle = \cos(\theta)E\langle b|\hat{\mu}|a \rangle = \cos(\theta)\mu_{ba}$$ (4.14)

where $\theta$ is the angle between the polarization of the field $E$ and the transition dipole moment, $\mu$. The probability for absorption can now be written as

$$P_{ba}^{(1)}(t) = |c_b^{(1)}(0)|^2 = \frac{E^2}{\hbar^2} \cos^2(\theta)|\mu_{ba}|^2F(t, \omega_{ba} - \omega)$$

$$= \frac{I(\omega)}{\hbar^2 c\epsilon_0} \cos^2(\theta)|\mu_{ba}|^2F(t, \omega_{ba} - \omega)$$ (4.15)

where $E^2$ has been identified with an intensity, $I(\omega)/c\epsilon_0$ and $F(t, \omega_{ba} - \omega)$ is identified from $|\exp(i(\omega_{ba} - \omega)t)/(\omega_{ba} - \omega)|^2$ for sufficiently large $t$. If either the polarization vector is at random or the ensemble of molecules is isotropic, as in gas phase or in solution, the term $\cos^2(\theta)$ is replaced by its average $1/3$ and conclusively we write the final expression for the probability for the transition to occur as

$$P_{ba}^{(1)}(t) = \frac{I(\omega)}{3\hbar^2 c\epsilon_0} |\mu_{ba}|^2F(t, \omega_{ba} - \omega)$$ (4.16)

The dimensionless quantity, the oscillator strength, is frequently employed in discussions of relative intensities in spectra. This is defined as

$$f_{ba} = \frac{2\omega_{ba}}{3} \sum_i |\mu_{ai}|^2$$ (4.17)

where $i \in \{x, y, z\}$ in cartesian coordinates. This measure will - sometimes exclusively - be employed to estimate the strength of various transitions, both for ground-to-excited state and excited-to-excited state transitions. A close comparison with experiment will though, especially for the latter type of transitions, inevitably compel a treatise of several dynamical aspects, which may be both system and experiment specific. In particular, issues connected to the relation between the potential energy surfaces of the two participating states can be significant. In principle, this is possible to accomplish, but presumably for smaller systems where adequate potential energy surfaces can be constructed. An approach based on the assumption of vertical excitations will thus ineluctably suffer some limitations, which makes it perhaps less appropriate for providing highly accurate values, rather than supplying qualitative correct predictions and general trends.
4.3 Two- and three-photon absorption

The first order transition probability for the transition \( |a \rangle \rightarrow |b \rangle \) was, as shown in Eq. 4.12, given by \( |c_b^{(1)}|^2 \). This result can be generalized further by considering higher order transitions moments. These can readily be evaluated recursively from Eq. 4.6 to arbitrary order. We proceed as for the first order transition in previous section, but switch notation reflecting the primary interest in transitions from the ground state to final state, \( |0 \rangle \rightarrow |f \rangle \). The first order correction in this notation is

\[
c_f^{(1)}(t) = \frac{1}{\hbar} \langle f | \hat{\mu}_f | 0 \rangle E_f e^{i(\omega_f - \omega)t} \tag{4.18}
\]

By re-cycling this result in the recursive relation in Eq. 4.6 the second order corrections can be evaluated as

\[
c_f^{(2)}(t) = \frac{1}{\hbar} \int_{-\infty}^{t} \sum_n \frac{1}{\hbar^2} c_n^{(1)} \langle f | \hat{\mu}_f | 0 \rangle E_f e^{-i\omega t'} e^{i\omega_f t'} e^{i\epsilon t'} dt'
\]

\[
= \frac{1}{\hbar^2} \sum_n \frac{1}{\hbar} \frac{\langle n | \hat{\mu}_n | 0 \rangle \langle f | \hat{\mu}_f | n \rangle E_f E_j}{(\omega_n - \omega)} \int_{-\infty}^{t} e^{i(\omega_{fn} + \omega_n - 2\omega)t'} e^{i\epsilon t'} dt'
\]

\[
= \frac{1}{\hbar^2} \sum_n \frac{\langle n | \hat{\mu}_n | 0 \rangle \langle f | \hat{\mu}_f | n \rangle E_f E_j}{(\omega_n - \omega)} e^{i(\omega_{fn} - 2\omega)t} e^{i\epsilon t} \tag{4.19}
\]

Furthermore, by symmetrizing over dummy indices, removing \( \epsilon \)-related terms and inter-changing the states to a more intuitive order we finally reach the expression for the two-photon elements;

\[
S_{ij} = \frac{1}{2\hbar} \sum_n \left[ \frac{\langle 0 | \hat{\mu}_i | n \rangle \langle n | \hat{\mu}_j | f \rangle}{\omega_n - \omega} + \frac{\langle 0 | \hat{\mu}_j | n \rangle \langle n | \hat{\mu}_i | f \rangle}{\omega_n - \omega} \right] \tag{4.20}
\]

Third order amplitudes can be derived by repeating the procedure above

\[
c_f^{(3)}(t) = \frac{1}{\hbar^3} \sum_{n,p} \frac{1}{\hbar^2} \langle f | \hat{\mu}_f | 0 \rangle \langle p | \hat{\mu}_p | n \rangle \langle n | \hat{\mu}_n | f \rangle E_f E_j E_k \sum_n \frac{\langle n | \hat{\mu}_n | 0 \rangle \langle f | \hat{\mu}_f | n \rangle \langle n | \hat{\mu}_n | f \rangle}{(\omega_n - \omega)} \int_{-\infty}^{t} e^{i(\omega_{fn} + \omega_n - 3\omega)t'} e^{i\epsilon t'} dt'
\]

\[
= \frac{1}{\hbar^3} \sum_n \frac{\langle n | \hat{\mu}_n | p \rangle \langle p | \hat{\mu}_p | 0 \rangle \langle f | \hat{\mu}_f | 0 \rangle \langle 0 | \hat{\mu}_0 | n \rangle \langle n | \hat{\mu}_n | f \rangle E_f E_j E_k}{(\omega_n - \omega)} \int_{-\infty}^{t} e^{i(\omega_{fn} - 3\omega)t} e^{i\epsilon t} dt
\]

\[
= \frac{1}{\hbar^3} \sum_n \frac{\langle n | \hat{\mu}_n | p \rangle \langle p | \hat{\mu}_p | 0 \rangle \langle f | \hat{\mu}_f | 0 \rangle \langle 0 | \hat{\mu}_0 | n \rangle \langle n | \hat{\mu}_n | f \rangle}{(\omega_n - \omega)} \int_{-\infty}^{t} e^{i(\omega_{fn} - 3\omega)t} e^{i\epsilon t} dt
\]

Again symmetrizing over dummy indices and re-ordering the states leads to the three-photon matrix elements

\[
T_{ijk} = \frac{1}{\hbar^2} \sum_{np} P_{ijk} \sum_n \frac{\langle 0 | \hat{\mu}_i | m \rangle \langle m | \hat{\mu}_m | n \rangle \langle n | \hat{\mu}_n | f \rangle}{(\omega_n - 2\omega)(\omega_{m0} - \omega)} \tag{4.22}
\]
where $\mathcal{P}_{i,j,k}$ denotes permutation with respect to the indices $i, j, k$. These derivations confine to absorption of two or three photons of identical frequency. The procedure can easily be generalized for radiation containing multiple frequencies by expanding the field in Fourier amplitudes as

$$E_i = \sum_\omega E_i^\omega e^{-i\omega t}$$

and proceed as above.

### 4.4 Hyperpolarizabilities

Properties can also be extracted from the perturbed wave function by calculating expectation values. The expectation value of the dipole moment can be written as

$$\langle \Psi(t) | \hat{\mu}_i | \Psi(t) \rangle = \langle \hat{\mu}_i \rangle^{(0)} + \langle \hat{\mu}_i \rangle^{(1)} + \langle \hat{\mu}_i \rangle^{(2)} + \langle \hat{\mu}_i \rangle^{(3)} + \ldots$$

where contributions of each order have been collected as

$$\langle \hat{\mu}_i \rangle^{(0)} = \langle \Psi(0) | \hat{\mu}_i | \Psi(0) \rangle$$

$$\langle \hat{\mu}_i \rangle^{(1)} = \langle \Psi(0) | \hat{\mu}_i | \Psi(1) \rangle + \langle \Psi(1) | \hat{\mu}_i | \Psi(0) \rangle$$

$$\langle \hat{\mu}_i \rangle^{(2)} = \langle \Psi(0) | \hat{\mu}_i | \Psi(2) \rangle + \langle \Psi(2) | \hat{\mu}_i | \Psi(1) \rangle + \langle \Psi(1) | \hat{\mu}_i | \Psi(2) \rangle + \langle \Psi(2) | \hat{\mu}_i | \Psi(1) \rangle + \langle \Psi(3) | \hat{\mu}_i | \Psi(0) \rangle$$

$$\vdots$$

In order to evaluate these expressions we need the wavefunction corrections of the desired order, $\Psi^{(n)}$, which in turn rely on the coefficients, $c^{(n)}$. Thus, the iterative scheme will be based on Eq. 4.6 and summarized as: (i) determining the coefficients of order $c^{(n)}$ from $c^{(n-1)}$ (ii) constructing the wavefunctions of the same order (iii) evaluating $\langle \hat{\mu} \rangle^{(n)}$ (iv) repeatedly determining the coefficients $c^{(n+1)}$ from $c^{(n)}$. In order to allow multiple frequencies of the field as well as simplify bookkeeping of terms, the field is expanded as

$$E_i = \sum_\omega E_i^\omega e^{-i\omega t} e^{i\epsilon t}$$

The first order correction as determined in previous section but with the perturbation in Eq. 4.29 is

$$c_m^{(1)}(t) = \frac{1}{\hbar} \sum_\omega \left\{ \langle n | \hat{\mu}_j | 0 \rangle E_i^{\omega t} e^{-i(\omega_{m0} - \omega_1) t} e^{i\epsilon t} \right\}$$

so the linear polarizability can be written

$$\langle \hat{\mu}_j \rangle^{(1)} = \langle \psi^{(0)} | \hat{\mu}_j | \psi^{(1)} \rangle + \langle \psi^{(1)} | \hat{\mu}_j | \psi^{(0)} \rangle$$

$$= \langle 0 | e^{i\omega_0 t} \hat{\mu}_j \sum_n \frac{1}{\hbar} \sum_\omega \langle n | \hat{\mu}_i | 0 \rangle E_i^{\omega t} e^{-i(\omega_{n0} - \omega_1) t} e^{i\epsilon t} \langle n | \hat{\mu}_j e^{-i\omega_0 t} | 0 \rangle$$

$$+ \sum_n \frac{1}{\hbar} \sum_\omega \langle 0 | \hat{\mu}_i | n \rangle E_i^{\omega t} e^{-i(\omega_{n0} - \omega_1) t} e^{i\epsilon t} \langle n | \hat{\mu}_j e^{-i\omega_0 t} | 0 \rangle$$
\[ = \sum_n \frac{1}{\hbar} \sum_{\omega_1} \frac{\langle 0|\hat{\mu}_j|n\rangle \langle n|\hat{\mu}_i|0 \rangle}{\omega_n - \omega_1 - i\epsilon} E_1^{\omega_1} e^{-i\omega_1 t} e^{\text{i}t} + \frac{1}{\hbar} \sum_{\omega_1} \frac{\langle 0|\hat{\mu}_i|n\rangle \langle n|\hat{\mu}_j|0 \rangle}{\omega_n + \omega_1 + i\epsilon} E_1^{\omega_1} e^{i\omega_1 t} e^{\text{i}t} \]

\[ = \sum_n \frac{1}{\hbar} \sum_{\omega_1} \left[ \frac{\langle 0|\hat{\mu}_j|n\rangle \langle n|\hat{\mu}_i|0 \rangle}{\omega_n - \omega_1 - i\epsilon} + \frac{\langle 0|\hat{\mu}_i|n\rangle \langle n|\hat{\mu}_j|0 \rangle}{\omega_n + \omega_1 + i\epsilon} \right] E_1^{\omega_1} e^{-i\omega_1 t} e^{\text{i}t} \]

Since \(\omega_1\) runs over both positive and negative frequencies, the complex conjugation conveniently can be included in the summation \([E_1^{\omega_1}]^* = E_{-\omega_1}\) since we require the field to be real. Finally, the linear polarizability, \(\alpha_{ij}(\omega;\omega)\), can be identified from Eq. 3.53 as

\[ \alpha_{ij}(\omega;\omega) = \sum_{n \neq 0} \left[ \frac{\langle 0|\hat{\mu}_i|n\rangle \langle n|\hat{\mu}_j|0 \rangle}{\omega_n - \omega_1} + \frac{\langle 0|\hat{\mu}_j|n\rangle \langle n|\hat{\mu}_i|0 \rangle}{\omega_n + \omega_1} \right] \]

The first and second order hyperpolarizabilities, \(\beta_{ijk}(\omega_1;\omega,\omega)\) and \(\gamma_{ijk}(\omega_1;\omega,\omega,\omega)\), can be retrieved in exactly the same manner. For \(\beta_{ijk}(\omega_1;\omega,\omega)\) we initially need to evaluate the terms \(\langle \Psi^{(0)}|\hat{\mu}_k|\Psi^{(2)}\rangle\), \(\langle \Psi^{(1)}|\hat{\mu}_k|\Psi^{(1)}\rangle\) and \(\langle \Psi^{(2)}|\hat{\mu}_k|\Psi^{(0)}\rangle\).

\[ \langle \Psi^{(0)}|\hat{\mu}_k|\Psi^{(2)}\rangle = \langle 0|e^{\text{i}x_0 t}\hat{\mu}_k \]

\[ \times \sum_n \frac{1}{\hbar^2} \sum_{\omega_1,\omega_2,\omega} \frac{\langle n|\hat{\mu}_j|p\rangle \langle p|\hat{\mu}_i|0 \rangle E_j^{2\omega_1} E_i^{\omega_1}}{\omega_n - \omega_1 - \omega_2 - i\epsilon} \]

\[ = \frac{1}{\hbar^2} \sum_{\omega_1,\omega_2,\omega} \sum_{np} \frac{\langle 0|\hat{\mu}_j|n\rangle \langle n|\hat{\mu}_i|p\rangle \langle p|\hat{\mu}_i|0 \rangle E_j^{2\omega_1} E_i^{\omega_1}}{\omega_n - \omega_1 - i\epsilon} e^{-i\omega_1 t} e^{\text{i}t} \]

\[ \langle \Psi^{(1)}|\hat{\mu}_k|\Psi^{(1)}\rangle = \sum_n \frac{1}{\hbar} \sum_{\omega_2} \frac{\langle 0|\hat{\mu}_j|n\rangle [E_j^{2\omega_1}]^*}{\omega_n - \omega_2 + i\epsilon} e^{-i\omega_0 t} e^{\text{i}t} \]

\[ \times \langle n|\hat{\mu}_k \]

\[ \sum_{\omega_1} \frac{\langle p|\hat{\mu}_i|0 \rangle E_i^{\omega_1}}{\omega_n - \omega_1 - i\epsilon} e^{-i\omega_1 t} e^{\text{i}t} \]

\[ = \frac{1}{\hbar^2} \sum_{\omega_1,\omega_2,\omega} \sum_{np} \frac{\langle 0|\hat{\mu}_j|n\rangle \langle n|\hat{\mu}_i|p\rangle \langle p|\hat{\mu}_i|0 \rangle E_j^{2\omega_1} E_i^{\omega_1}}{\omega_n + \omega_1 + i\epsilon} e^{-i\omega_1 t} e^{\text{i}t} \]

and

\[ \langle \Psi^{(2)}|\hat{\mu}_k|\Psi^{(0)}\rangle = \sum_n \frac{1}{\hbar^2} \sum_{\omega_1,\omega_2,\omega} \frac{\langle p|\hat{\mu}_j|n\rangle \langle 0|\hat{\mu}_i|p\rangle [E_j^{\omega_1}]^* [E_i^{\omega_1}]^*}{\omega_n - \omega_1 - \omega_2 + i\epsilon} \]

\[ \times e^{-i\omega_0 t} e^{\text{i}t} e^{\text{i}t} \]

\[ = \frac{1}{\hbar^2} \sum_{\omega_1,\omega_2,\omega} \sum_{np} \frac{\langle 0|\hat{\mu}_j|n\rangle \langle n|\hat{\mu}_k|0 \rangle E_j^{\omega_1} E_k^{\omega_1}}{\omega_n + \omega_1 + \omega_2 + i\epsilon} e^{-i\omega_1 t} e^{\text{i}t} \]

By forming the sum of these terms, introducing the term \(\omega_\sigma = \omega_1 + \omega_2\) and a permutation operator \(P_{1,2}\) which permutes the pairs \((i, \omega)\) and \((j, \omega)\) and again remove the \(\epsilon\) related terms, \(\beta_{ijk}(\omega_\sigma;\omega_1,\omega_2)\) can be identified from Eq. 3.53 as

\[ \beta_{ijk}(\omega_\sigma;\omega_1,\omega_2) = \sum_{P_{1,2}} \sum_{p,q} \frac{\langle 0|\hat{\mu}_j|p\rangle \langle p|\hat{\mu}_i|q\rangle \langle q|\hat{\mu}_k|0 \rangle}{(\omega_n - \omega_\sigma)(\omega_n - \omega_2)} \]
which can be compressed even further by generalizing the permutation operator and introducing the fluctuation dipole moment as $\mu_j - \langle 0|\mu_j|0 \rangle$ to

$$\beta_{ijk}(-\omega; \omega_1, \omega_2) = \sum_{\sigma=1,2} \mathcal{P}_{-\sigma, \sigma} \sum_{p,q,r \neq 0} \frac{\langle 0|\mu_i|p \rangle \langle p|\mu_j|q \rangle \langle q|\mu_k|0 \rangle}{(\omega_p - \omega_\sigma)(\omega_q - \omega_2)}$$

(4.37)

The identical approach, but with increasing complexity, can be employed in order to retrieve formulas for the second order hyperpolarizability, $\gamma_{ijkl}(-\omega; \omega_1, \omega_2, \omega_3)$. We refer to[17, 23] for an explicit derivation and merely present the result:

$$\gamma_{ijkl}(-\omega; \omega_1, \omega_2, \omega_3) = \sum \mathcal{P} \sum_{p,q,r \neq 0} \frac{\langle 0|\mu_i|p \rangle \langle p|m_\mu_j|q \rangle \langle q|m_\mu_k|r \rangle \langle r|\mu_l|0 \rangle}{(\omega_p - \omega_1)(\omega_q - \omega_2)} + \sum_{p,q,r \neq 0} \frac{\langle 0|\mu_i|p \rangle \langle p|\mu_j|0 \rangle \langle 0|\mu_k|q \rangle \langle q|\mu_l|0 \rangle}{(\omega_p - \omega_\sigma)(\omega_p - \omega_1)(\omega_q + \omega_2)}$$

(4.38)

Here $\omega_\sigma$ again is defined as $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$ and $\sum \mathcal{P}$ denotes a summation over the simultaneous permutations of the operators and their corresponding frequencies, $(i, \omega_1)$, $(j, \omega_2)$, $(k, \omega_3)$ and $(l, \omega_\sigma)$.

The expressions derived above, for one-, two- and three-photon absorption and the (hyper)polarizabilities are somewhat misleading in their deceitful simplicity. First of all, the summation is given to infinite order which naturally is unfeasible unless some convergence assumptions can be legitimized. Secondly, the condition that all states $|n\rangle$ are orthogonal will certainly be violated for a real molecular system with MCSCF optimized states of the same symmetry. Moreover, the two sets of orbitals for the two molecular states will, independent of symmetry, be different[28]. Optimizing an excited state under the condition that it should be orthogonal to lower states may appear appealing, but poses in fact a computational problem of substantial complexity. Another approach is to regain orthogonality by transforming the two sets of MOs to a bi-orthonormal basis. This technique is inherent in the so called CAS State Interaction (CASSI) method and is described elsewhere[29]. Yet another approach is to circumvent the actual optimization of the excited states themselves and extract excitation energies, excited state properties and transition properties indirectly from a perturbative technique. Excited state properties will in this scheme be accessible even for a low cost method, such as SCF or DFT, which is essential if large scale systems are at focus. A concerted advantage, is that the summations displayed in the formulas above implicitly can be performed to infinite order.

### 4.5 Residues of (hyper)polarizabilities

All derived properties within the time-dependent perturbation scheme share the structure of infinite summations. This may appear deterring at first glance, but
it can also provide alternative routes for evaluations of various properties through the use of residues. From inspection of the given expression for $\alpha$ in Eq. 4.32 it is evident that the transition dipole moments between the ground state and a final state should be derivable by extracting the proper residue

$$\lim_{\omega \to \omega_f} (\omega - \omega_f) \alpha_{ij}(-\omega; \omega) = \langle 0|\hat{\mu}_i|f\rangle \langle f|\hat{\mu}_j|0\rangle$$  \hspace{1cm} (4.39)

Note that the property actually evaluated is the product of $\mu_i^{0f} \mu_j^{0f}$ or if $i = j$ the square of $|\mu_i^{0f}|^2$, which in both cases destroys any information about the sign of the transition dipole moment. This is in general not critical, since the property of interest normally is given as a square, as for instance the oscillator strengths.

Similar technique can be applied to $\beta$, though the sum-over-states expression contains two potential poles and consequently both single and double residues can be evaluated. For the single residue given as

$$\lim_{\omega_2 \to -\omega_f} (\omega_2 - \omega_f) \beta_{ijk}(-\omega; \omega_1, \omega_2) = \frac{1}{\hbar} \sum_n \left[ \frac{\langle 0|\mu_i|n\rangle \langle n|\mu_j|f\rangle \langle f|\mu_k|0\rangle}{(\omega_n - \omega_1 - \omega_f)} + \frac{\langle 0|\mu_j|n\rangle \langle n|\mu_i|f\rangle \langle f|\mu_k|0\rangle}{(\omega_n + \omega_f)} \right]$$

$$= \frac{1}{\hbar} \sum_n \left[ \frac{\langle 0|\mu_i|n\rangle \langle n|\mu_j|f\rangle}{(\omega_{nf} - \omega_1)} + \frac{\langle 0|\mu_j|n\rangle \langle n|\mu_i|f\rangle}{(\omega_{n0} + \omega_1)} \right] \langle f|\mu_k|0\rangle$$  \hspace{1cm} (4.40)

it is clear that the term inside the brackets is connected to the two-photon absorption matrix element given by Eq. 4.20, when evaluated for $\omega_1 = -\omega_f/2$. For the double residue we restrict the attention to the choice $\omega_1 = -\omega_f$ and $\omega_2 = \omega_{e0}$, where $e$ relates to the excited state $|e\rangle$.

$$\lim_{\omega_1 \to -\omega_f} (\omega_{e0} + \omega_1) \right) \lim_{\omega_2 \to \omega_{e0}} (\omega_{e0} + \omega_2) \beta_{ijk}(-\omega; \omega_1, \omega_2)$$

$$= \langle 0|\hat{\mu}_j|f\rangle \langle f|\hat{\mu}_i|e\rangle \langle e|\hat{\mu}_k|0\rangle$$  \hspace{1cm} (4.41)

The middle term represents the transition dipole moment between two excited states or if $e = f$, the dipole moment of the excited state $|f\rangle$. In any case it is noteworthy that is sufficient to apply the perturbation theory technique and the succeeding residue analysis from a ground state in order to achieve information intrinsically related to the excited states. Two other important features have been revealed here; first, a considerable downshift of the order of the property can be achieved. A property originally given at third order, as the two-photon absorption, can be accomplished through elements identified at second order, the single residue of the first order hyperpolarizability, $\beta$. Secondly, a property can be determined through another – occasionally much more readily obtained – property. This facilitating technique opens a computational back-door to a variety of properties. In this context we have primarily restricted the attention to optical properties. However, the technique can be generalized much further since the results are not confined to the electric dipole operator. The perturbing operators could equally well be a component of the electric quadrupole moment, a magnetic moment, orbital angular momentum operator, spin-orbit operator, the Hamiltonian at infinitesimal displaced nuclear geometry etc.. In combination with the
optional frequencies, where the static case is represented by the choice $\omega = 0$, a manifold of properties can be accomplished within a unified and systematic scheme.

We conclude by showing the similar results for 3PA probabilities, essentially a fifth order property, but also available through third order transition elements which in turn can be identified from the single residue of the second order hyperpolarizability, $\gamma$, as

$$\lim_{\omega_3 \to -\omega_f} (\omega_f - \omega_3) \gamma_{ijkl}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = 1$$

$$\frac{1}{\hbar^3} \sum P \sum_{nm \neq 0} \frac{\langle 0|\mu_i|n\rangle \langle n|\mu_j|m\rangle \langle m|\mu_k|f\rangle \langle f|\mu_l|0\rangle}{(\omega_n - \omega_k)(\omega_m - \omega_2 - \omega_f)}$$

$$= 1 \frac{1}{\hbar^3} \sum \sum_{nm} \frac{\langle 0|\mu_i|n\rangle \langle n|\mu_j|m\rangle \langle m|\mu_k|f\rangle \langle f|\mu_l|0\rangle}{(\omega_nf - \omega_1 - \omega_2)(\omega_mf - \omega_2)}$$

The downshift from fifth to third order represents a decisive simplification which makes 3PA absorption computable for extensive systems.
Chapter 5

The response method

5.1 Response theory for exact states

A more elaborate scheme of time-dependent perturbation theory is response theory\cite{30, 31} which exhibits two major attractive features. By means of this theory we can avoid the explicit summation of the expressions attained in the previous section by solving algebraic equations. Secondly, the formalism is analytically transferable, \textit{i.e.} the same technique may subsequently be applied to retrieve properties from a wave function irrespective of the actual parametrization of the wave function. This supplies the means to use hierarchies in the 1- and $n$-electron space not only for ground state energies but for excited state properties as well.

At a most general level, the issue is to add a time-dependence to a set of time-independent solutions. This can be done, either in ordinary time-dependent perturbation-theory through the coefficients, $c(t)$, in an expansion of the time-dependent wave function in the unperturbed wave functions, or in a slightly more advanced way through unitary transformations within the set of eigenstates of the system. This leads to a formulation applicable even to approximate wave functions, but will require some additional conditions to hold in order to determine the introduced parameters. A natural choice is the presumption that the system on the average should evolve according to a quantum mechanical version of Newtons dynamical equation, which technically means solving the Ehrenfest equation for each order of the perturbation. This enables an expansion of the average of an operator to obtain the so-called response functions which describe the evolution in each order of the applied perturbation.

Similar to ordinary time-dependent perturbation-theory, the starting point in response theory is the separation of the Hamiltonian as

$$H = H_0 + V(t)$$  \hspace{1cm} (5.1)

where the unperturbed Hamiltonian solves

$$H_0|0\rangle = E_0|0\rangle$$  \hspace{1cm} (5.2)

and

$$H_0|n\rangle = E_n|n\rangle$$  \hspace{1cm} (5.3)
The perturbation can be expressed as decomposed in frequencies as
\[ V(t) = \int_{-\infty}^{\infty} d\omega V^w \exp(-i\omega t) \] (5.4)

Now we introduce time-dependency by parameterizing the unperturbed wave function in terms of unitary transformations within the set of eigenstates of the system as
\[ |\tilde{0}\rangle = \exp(\Lambda(t)) |0\rangle \] (5.5)

where \( \Lambda \) is an anti-hermitean operator defined as
\[ \Lambda(t) = \sum_{m>0} (\lambda_m(t)q^\dagger_m - \lambda^*_m(t)q_m) \] (5.6)

where \((q^\dagger_m, q_m)\) denote the transfer operators
\[ q^\dagger_m = |m\rangle \langle 0| \] (5.7)
\[ q_m = |0\rangle \langle m| \] (5.8)

The operator \( \Lambda \) can also be written as
\[ \Lambda(t) = \sum_{m>0} (\lambda_m(t)q^\dagger_m - \lambda^*_m(t)q_m) = \sum_m (\lambda_m(t)O_m) \] (5.9)

where the summation over excitations and deexcitations have been absorbed in one summation over positive and negative \( m \). We expand \( |\tilde{0}\rangle \) as
\[ |\tilde{0}\rangle = |0^{(0)}\rangle + |0^{(1)}\rangle + |0^{(2)}\rangle + |0^{(3)}\rangle + \ldots \] (5.10)

and, in order to determine the \( \lambda \)s, we require that Ehrenfests equation should hold for each order of the perturbation
\[ \langle \tilde{0} | O | \dot{\tilde{0}} \rangle + \langle \dot{\tilde{0}} | O | \tilde{0} \rangle = -i \langle \tilde{0} | [O, H_0 + V^t] | \tilde{0} \rangle \] (5.11)

where \( |\dot{\tilde{0}}\rangle \) denotes the time derivative of \( |\tilde{0}\rangle \). When the time dependence is determined, the average of the expectation value of an operator, \( A \), can be expanded as
\[ A_{av}(t) = \langle \tilde{0} | A | \tilde{0} \rangle = \langle 0 | A | 0 \rangle + \int_{-\infty}^{\infty} d\omega_1 \langle \langle A; V^{\omega_1} \rangle \rangle_\omega \exp(i\omega_1 t) \]
\[ + \frac{1}{2} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \langle \langle A; V^{\omega_1}, V^{\omega_2} \rangle \rangle_{\omega_1,\omega_2} \exp(i\omega_1 t - i\omega_2 t) \ldots \] (5.12)

For exact states these can be given in their spectral representation with
\[ -\langle \langle A; B \rangle \rangle_{\omega_1} = \sum_{P} \sum_{m} \langle 0 | A | p \rangle \langle p | B | 0 \rangle \frac{\omega_p - \omega_1}{\omega_p - \omega_1} \] (5.13)
as the linear response function and

\[-\langle \langle A; B, C \rangle \rangle_{\omega_1, \omega_2} = \sum P \sum_{p,q \neq 0} \frac{\langle 0 | A | p \rangle \langle p | B | q \rangle \langle q | C | 0 \rangle}{(\omega_p + \omega_0)(\omega_q - \omega_2)} \] (5.14)

as the quadratic response function, where \( \langle p | B | q \rangle = \langle p | B - \langle 0 | B | 0 \rangle | q \rangle \) and \(-\omega_0 = \omega_1 + \omega_2 + \ldots \). If the chosen operator is the dipole operator, \( \mu \), the response functions, \( \langle \langle \mu_i; \mu_j, \mu_k \cdots \rangle \rangle_{\omega_1, \omega_2, \ldots} \) will correspond to the (hyper)polarizabilities \( \alpha \), \( \beta \) and \( \gamma \).

The response functions contain inherently information about the excited states. The poles determine the location of the excitation energies and further information can be retrieved by examining resonance conditions through a residue analysis. From the expression for the linear response function for an exact wave function, where the unperturbed Hamiltonian is diagonal, we can easily evaluate transition dipole moments between the ground state, \( | 0 \rangle \), and an excited state, \( | f \rangle \) as

\[ \lim_{\omega_1 \to \omega_f} (\omega_1 - \omega_f) \langle \langle \mu_i; \mu_j \rangle \rangle_{\omega_1} = \langle 0 | \mu_i | f \rangle \langle f | \mu_j | 0 \rangle \] (5.15)

The single residue of the quadratic response function provides information on the two-photon transition matrix elements

\[ \lim_{\omega_2 \to \omega_f} (\omega_2 - \omega_f) \langle \langle \mu_i; \mu_j, \mu_k \rangle \rangle_{-\omega_1, \omega_2} = \]

\[-\sum_n \left( \frac{\langle 0 | \mu_i | n \rangle \langle n | (\mu_j - \langle 0 | \mu_j | 0 \rangle) | f \rangle}{\omega_n - \omega_2} + \frac{\langle 0 | \mu_j | n \rangle \langle n | (\mu_i - \langle 0 | \mu_i | 0 \rangle) | f \rangle}{\omega_n - \omega_1} \right) \langle f | \mu_k | 0 \rangle \] (5.16)

where \( \omega_1 + \omega_2 = \omega_m \). From the double residue of the same response function one can deduce the transition dipole moments between excited states

\[ \lim_{\omega_1 \to \omega_f} (\omega_1 - \omega_f) \left[ \lim_{\omega_2 \to \omega_m} (\omega_2 - \omega_m) \langle \langle \mu_i; \mu_j, \mu_k \rangle \rangle_{-\omega_1, \omega_2} \right] = \]

\[-\langle 0 | \mu_i | f \rangle \langle f | (\mu_i - \langle 0 | \mu_i | 0 \rangle) | i \rangle \langle i | \mu_k | 0 \rangle \] (5.17)

For an approximate wave function the parameterization will be slightly different and add some new computational difficulties. For a SCF wavefunction, the transfer operators will be

\[ \Lambda(t) = \sum (\lambda_m(t) q^\dagger_m - \lambda^*_m(t) q_m) \] (5.18)

where \( (q^\dagger_m, q_m) \) now are the orbital rotation generators

\[ q^\dagger_m = E_{pq} = a^\dagger_{p\alpha} a_{q\alpha} + a^\dagger_{p\beta} a_{q\beta} \] (5.19)

The terms, \( \lambda \), can be expressed in terms of following matrices when solving Ehrenfest equation

\[ S^2_{jk} = \langle 0 | [O_j, O_k] | 0 \rangle \] (5.20)

\[ S^3_{jkl} = -\frac{1}{2} \langle 0 | [O_j, [O_k, [O_l, O_k]]] | 0 \rangle \] (5.21)

\[ E^1_j = \langle 0 | [O_j, H_0] | 0 \rangle \] (5.22)

\[ E^2_j = \langle 0 | [O_j, [O_k, H_0]] | 0 \rangle \] (5.23)

\[ E^3_{jk} = \frac{1}{2} \langle 0 | [O_j, [O_k, [O_l, H_0]]] | 0 \rangle \] (5.24)
which all will be diagonal for exact and orthogonal states, but already for a moderate system computationally intractable. In fact, they constitute the major task in calculations of any specific response property and are hardly ever constructed explicitly. The remaining evaluation of the response function follows two steps; first a determination of the excitation energies, \( \omega_f \), and response vector, \( N_j^B \), from

\[
N_j^B(\omega) = \left( E_{\omega}^{[2]} - \omega S^{[2]} \right)^{-1}_{jk} B_k^{[1]}, \tag{5.25}
\]

and then a subsequent matrix multiplication to obtain the response function of interest.

\[
\langle \langle A; B \rangle \rangle_\omega = -AN_j^B(\omega) \tag{5.26}
\]

### 5.2 The two-photon transition matrix elements

As shown in previous chapters, the two-photon cross section, \( \sigma_{\text{TPA}} \), was related to the third order susceptibility, \( \chi^3(-\omega;F,-\omega,F) \) which on a microscopic level corresponds to the second hyperpolarizability, \( \gamma \). By only considering the resonant terms for \( \gamma(-\omega;F,-\omega,F) \) with \( \omega = \frac{i}{2} \omega_f \) where \( \omega_f \) is the excitation energy to the final two-photon state \( |f \rangle \) it is possible to rewrite \( \gamma \) as

\[
\gamma_{\alpha\beta\gamma\delta}(-\omega;F,-\omega,F) = \hbar^{-3} \sum_{k} \mathcal{P}_{1,3}
\]

\[
\times \sum_{km} \left[ \frac{\langle 0|\mu_\alpha|k \rangle \langle k|\mu_\gamma|f \rangle \langle f|\mu_\beta|m \rangle \langle m|\mu_\delta|0 \rangle}{(\omega_k - \omega)(-i\Gamma_f/2)(\omega_m - \omega)} + \frac{\langle 0|\mu_\gamma|k \rangle \langle k|\mu_\alpha|f \rangle \langle f|\mu_\beta|m \rangle \langle m|\mu_\delta|0 \rangle}{(\omega_k - \omega)(-i\Gamma_f/2)(\omega_m - \omega)} \right]
\]

\[
= i \frac{2\hbar^{-3}}{\Gamma_f} \sum_{\alpha\beta\gamma\delta} \mathcal{P}_{\sigma,2} \sum_k \frac{\langle 0|\mu_\alpha|k \rangle \langle k|\mu_\gamma|f \rangle}{(\omega_k - \omega)} \sum_{m} \frac{\langle f|\mu_\beta|m \rangle \langle m|\mu_\delta|0 \rangle}{(\omega_m - \omega)}
\]

\[
= i \frac{2\hbar^{-1}}{\Gamma_f} S_{\alpha\beta} S_{\gamma\delta}^*,
\]

from which the two-photon transition matrix elements \( S_{\alpha\beta} \) have been identified as

\[
S_{\alpha\beta} = \hbar^{-1} \sum_k \left[ \frac{\langle 0|\mu_\alpha|k \rangle \langle k|\mu_\beta|f \rangle}{\omega_k - \omega} + \frac{\langle 0|\mu_\beta|k \rangle \langle k|\mu_\alpha|f \rangle}{\omega_k - \omega} \right]. \tag{5.28}
\]

Apparently, the TPA cross section can either be determined from \( \gamma \) or by evaluating each individual transition matrix element, \( S_{\alpha\beta} \), from a lower order method, namely as the single residue of the quadratic response function. In the latter approach the two-photon transition matrix element, \( S_{\alpha\beta} \), can be identified as [30]

\[
\lim_{\omega_2 \rightarrow -\omega_f} \langle \omega_2 - \omega_f \rangle \langle \mu_\alpha;\mu_\beta,\mu_\gamma \rangle_{-\omega_f/2,\omega_2} = S_{\alpha\beta}(f|\mu_\gamma|0), \tag{5.29}
\]

which now in the response terminology can be evaluated directly as

\[
S_{AB} = -N_j^A(\omega_f/2)B_{jk}^{[2]}N_k^F(\omega_f) - N_j^B(-\omega_f/2)A_{jk}^{[2]}N_k^F(\omega_f)
\]

\[
- N_j^A(\omega_f/2) \left( E_{j(kl)}^{[3]} + \frac{i}{2} \omega_f S_{jkl}^{[3]} - \omega_f S_{jkl}^{[3]} \right) N_j^B(-\omega_f/2)N_k^F(\omega_f) \tag{5.30}
\]
5.3 The three-photon transition matrix elements

We emphasize that this is done from the reference state, \(|0\rangle\), preferably the ground state, with no further reference to any excited state. From a comparison with the expression derived in the previous chapter, it is also striking that the property originally given as a summation here is evaluated in a non-truncated condition.

\[ T_{abc} = \sum \mathcal{P}_{a,b,c} \sum_{n,m} \frac{\langle 0|\mu_a|m\rangle\langle m|\mu_b|n\rangle\langle n|\mu_c|f\rangle}{(\omega_m - 2\omega_f/3)(\omega_n - \omega_f/3)} \]  

(5.31)

where \(\sum \mathcal{P}_{a,b,c}\) performs the summation over the six permutations with respect to the indices \(a, b,\) and \(c\). In response formalism this can be evaluated from

\[
T_{abc} = N_j^A(\omega_f/3)T_{klm}^{[4]}(\omega_f/3, \omega_f/3, \omega_f/3)N_k^B(-\omega_f/3)N_l^C(-\omega_f/3)N_m^F(\omega_f) \\
- N_j^A(\omega_f/3)[T_{klm}^{[3]}(-\omega_f/3, \omega_f/3 - \omega_f/3)N_k^B(\omega_f/3)N_l^C(-\omega_f/3, \omega_f/3)] \\
+ T_{klm}^{[3]}(-\omega_f/3, 2\omega_f/3)N_k^F(-\omega_f/3)N_l^B(\omega_f/3) \\
+ T_{klm}^{[3]}(-\omega_f/3, -2\omega_f/3)N_k^F(\omega_f)N_l^BC(\omega_f/3, -\omega_f/3) \\
- N_j^A(\omega_f/3)[B_{klm}^{[3]}N_k^C(-\omega_f/3)N_l^F(\omega_f) + C_{klm}^{[3]}N_k^B(-\omega_f/3, \omega_f)] \\
+ N_j^A(\omega_f/3)[B_{klm}^{[2]}N_k^C(-\omega_f/3, \omega_f) + C_{klm}^{[2]}N_k^B(-\omega_f/3, \omega_f)] \\
+ A_{klm}^{[2]}N_j^F(-\omega_f/3)N_k^BC(-\omega_f/3, \omega_f) + N_j^F(-\omega_f/3)N_k^B(-\omega_f/3, \omega_f) \\
+ N_j^F(\omega_f)N_k^BC(-\omega_f/3, -\omega_f/3) - A_{klm}^{[3]}N_j^B(\omega_f/3)N_k^C(-\omega_f/3)N_l^F(\omega_f) \\
(5.32)
\]

where

\[
N_j^X(\omega_a) = (E_j^{[2]} - \omega_a S_j^{[2]})^{-1} X_k^{[1]}, \quad X \in \{A, B, C\} \\
(5.33)
\]

\[
(E_j^{[2]} - \omega_a S_j^{[2]})_{jk} N_k^F(\omega_f) = 0 \\
(5.34)
\]

and

\[
(E_j^{[2]} - (\omega_1 + \omega_2) S_j^{[2]}) N_j^{BC}(\omega_1, \omega_2) = T_{klm}^{[3]}(\omega_1, \omega_2) N_l^B(\omega_1) N_m^C(\omega_2) \\
- C_{klm}^{[2]} N_l^B(\omega_1) - B_{klm}^{[2]} N_l^C(\omega_2) \\
(5.35)
\]

\[
(E_j^{[2]} - (\omega_f - \omega_a) S_j^{[2]}) N_j^{XF}(\omega_a, \omega_f) = T_{klm}^{[3]}(-\omega_a, \omega_f) N_l^X(-\omega_a) N_m^F(\omega_f) \\
- X_{klm}^{[3]} N_l^F(\omega_f) \\
X \in \{B, C\} \\
(5.36)
\]
The terms $T_{jkl}^{[3]}$ and $T_{jklm}^{[4]}$, which are separate from the three-photon transition matrix elements, are short-hand notation for

\[
T_{jkl}^{[3]}(\omega_1, \omega_2) = (E_{jk}^{[3]} - \omega_1 S_{jkl}^{[3]} - \omega_2 S_{jkl}^{[3]}),
\]

(5.36)

\[
T_{jklm}^{[4]}(\omega_1, \omega_2, \omega_3) = (E_{jklm}^{[4]} - \omega_1 S_{jklm}^{[4]} - \omega_2 S_{jklm}^{[4]} - \omega_3 S_{jklm}^{[4]}),
\]

(5.37)

### 5.4 Transition dipole moments

The response functions potentially contain a manifold of properties extractible through residue analysis. Even though the TPA and 3PA probabilities can be determined directly as the single residue of the quadratic or the cubic response function, there may be reasons for explicitly evaluating truncated versions of the sum-over-states (SOS) expressions. As seen from Eq. 5.28, the relevant quantities for accomplishing such tasks are the excitation energies and the transition dipole moments, which all are attainable within the same formalism.

The transition dipole moment between the ground state $|0\rangle$ and an excited state $|f\rangle$ is given by the residue of the linear response function as

\[
\langle 0|A|f\rangle \langle f|B|0\rangle = A_f^{[1]} B_f^{[1]},
\]

(5.38)

whereas the transition dipole moments between excited states ($e \neq f$) as well as the excited state dipole moments ($e = f$) are evaluated as double residues of the quadratic response function as

\[
\langle e|A|f\rangle - \delta_{ef} \langle 0|A|0\rangle = (A_{kl}^{[2]} + A_{lk}^{[2]}) N_k^E (\omega_e) N_l^E (\omega_f) + N_f^E (\omega_f - \omega_e) (E_{jkl}^{[3]} + E_{jlk}^{[3]} - S_{jkl}^{[3]} \omega_e + S_{jkl}^{[3]} \omega_f) N_j^E (\omega_e) N_l^E (\omega_e).
\]

(5.39)

Again it is noteworthy that the calculation of excited state properties such as transition dipole moment between excited state or the dipole of an excited state can be retrieved from the ground state $|0\rangle$. 
Chapter 6

Few-states models

6.1 Orientational averaging

Even though the two-photon matrix elements can be addressed directly by response theory without performing the explicit summation, there may still be reasons for studying the sum-over-states (SOS) expressions given in the previous chapter. Due to their slow convergence an explicit summation does not form a viable option for \textit{ab-initio} methods, except when they can be truncated to a few leading terms. These truncations have traditionally been considered legitimate for so-called charge transfer (CT) systems, where the excitation scheme is completely dominated by a few major excitation channels. In addition, they may also serve as a valuable tool for interpretation purposes because of their ability to display the relation of the TPA probability, $\delta_{\text{TPA}}$, to other somewhat more intuitive quantities. Moreover, truncated SOS expressions for the two-photon probability, $\delta_{\text{TPA}}$, can under certain assumptions be employed to evaluate transition dipole moments between excited states from experimental data. In fact they represent one of the few available sources to perform such comparisons.

The resonant two-photon matrix element, $S_{\alpha\beta}$, for a one color beam can be identified from the sum-over-states formula

$$S_{\alpha\beta} = \sum_i \left[ \frac{\langle 0|\mu_\alpha|i\rangle\langle i|\mu_\beta|f\rangle}{\omega_i - \omega_f/2} + \frac{\langle 0|\mu_\beta|i\rangle\langle i|\mu_\alpha|f\rangle}{\omega_i - \omega_f/2} \right]$$

(6.1)

where $\mu$ is the dipole operator in the directions $\alpha, \beta \in \{x, y, z\}$, $\omega_i$ and $\omega_f$ the excitation energies for the intermediate state, $|i\rangle$, and the final two-photon state, $|f\rangle$, respectively.

The route between microscopic origin to macroscopic detection requires among many other things relations between the two coordinate systems; that of the laboratory and that of the molecules. Specifically we need to be able to relate the quantity that defines the macroscopic coordinates in the microscopic realm, that is the polarization of light, with the transition dipole moments evaluated at the quantum level. Since experiments rarely are made on single molecules, but an ensemble of molecules which for gases or liquids has no preferred direction, the relation must include a full orientational averaging. The principle was incidentally demonstrated in the previous chapter for one-photon absorption, where the
CHAPTER 6. FEW-STATES MODELS

isotropic average of $|\mu^0 f \cos \theta|^2$ was replaced by $|\mu^0 f|^2/3$. For a second order transition moment, $S^0 f$, yet a coordinate is involved and for two photons of identical frequency but different polarization vectors, $\lambda$ and $\nu$ in lab coordinates we have [32, 33, 34]

$$S_{\alpha\beta} = \sum_i \left[ \frac{(\lambda \cdot \mu^0 i)(\mu^i f \cdot \nu)}{\omega_i - \omega f/2} + \frac{(\nu \cdot \mu^0 i)(\mu^i f \cdot \lambda)}{\omega_i - \omega f/2} \right]$$  \hspace{1cm} (6.2)

On a macroscopic scale we thus want to establish a relation such as

$$S^0 f_{AB} = l_A a l_B b S^0 f_{ab}$$  \hspace{1cm} (6.3)

where $l_{x,x}$ denotes the cosine angle between the $X$-axis of the laboratory and the $x$-axis in the coordinate system of the molecule. However, the quantity of interest is not transition moments as such, but two-photon probabilities, $\delta_{\text{TPA}}$

$$\delta_{\text{TPA}} = |S^0 f(\lambda, \nu)|^2 = (\lambda A \nu B S^0 f_{AB})(\lambda C \nu D S^0 f_{DE})^*$$  \hspace{1cm} (6.4)

which when averaged corresponds to

$$\langle |S^0 f(\lambda, \nu)|^2 \rangle = \langle (\lambda A \nu B \lambda^* C \nu^* D)(l_A a l_B b l_C a l_D b)(S^0 f_{AB} S^0 f_{DE})^* \rangle$$  \hspace{1cm} (6.5)

The complete contraction of this expression will contain $3^8 = 6561$ terms, but by identifying three unique types of groups and the postulate that it is irrelevant whether the averaging occurs in the molecule or the lab coordinates, Monson and McClain[35, 36] derived the following relations

$$\delta_{\text{TPA}} = F \delta_F + G \delta_G + H \delta_H$$  \hspace{1cm} (6.6)

where $F$, $G$ and $H$ are defined as

$$F = -|\lambda \cdot \nu^*|^2 + 4|\lambda \cdot \nu|^2 - 1$$  \hspace{1cm} (6.7)

$$G = -|\lambda \cdot \nu|^2 - |\lambda \cdot \nu|^2 + 4$$  \hspace{1cm} (6.8)

$$H = 4|\lambda \cdot \nu^*|^2 - |\lambda \cdot \nu|^2 - 1$$  \hspace{1cm} (6.9)

and

$$\delta_F = \sum_{a,b} S_{aa} S_{bb}^*, \quad \delta_G = \sum_{a,b} S_{ab} S_{ab}^*, \quad \delta_H = \sum_{a,b} S_{ab} S_{ba}^*$$  \hspace{1cm} (6.10)

For linearly polarized light this implies that $F=G=H=2$. The terms $\delta_F$, $\delta_G$ and $\delta_H$ can be regarded as three-dimensional vectors and any measurement of $\langle \delta_{\text{TPA}} \rangle$ should be interpreted as the dot product between $\delta_{\text{TPA}}$ and $(\delta_F \delta_G \delta_H)$. By applying different combinations of polarized light one can uniquely specify various linearly independent values of the vector $(\delta_F \delta_G \delta_H)$ which along with the given symmetry of the molecule provides a comprehensive basis for assigning excited states. This is a distinct key feature of multi-photon phenomena in general; unlike one-photon processes even randomly orientated molecules may supply valuable information due to the transition rates dependence on the polarization of the ingoing photons. The approach can straightforwardly be extrapolated to embrace related nonlinear optical effects as for instance electric field induced TPA [37, 38, 40, 41].
The polarization ratio, $\Omega$, defined as

$$\Omega = \frac{\delta_{TPA}^F}{\delta_{TPA}^L} = -\frac{\delta_F + 3\delta_G}{\delta_F + 2\delta_G} \tag{6.11}$$

is a constrained version of the same approach and may reveal some information of the symmetry of the excited state[36, 43].

The remaining issue is to relate the two-photon probabilities with the two-photon cross section, $\sigma_{TPA}$, which previously was identified from the imaginary part of $\chi^{(3)}$. Since $\chi^{(3)}$ is expressed through $\delta_{TPA}$ which normally is given in atomic units, we initially need to convert the latter to a macroscopically more adequate property. In practice, however, it has shown useful to employ a mixed relation, which can be evaluated through the conversion factors in Table 6.1 as

$$\sigma_{TPA} = 24\pi^2\hbar\omega^2 \text{Im}[\chi^{(3)}] = 4\pi^2\hbar\omega^2 e^4 a_0^4 E_h^{-3}\delta_{TPA} = \frac{4\pi^2\alpha a_0^5\omega^2}{c}\delta_{TPA} \tag{6.12}$$

Provided the Bohr radius, $a_0$ and the speed of light are given in cgs units and the frequency, $\omega$ and the TPA probability, $\delta_{TPA}$ in atomic units the resulting unit will be cm$^4$ s photon$^{-1}$. The result can be generalized further by introducing the finite lifetime broadening as

$$\sigma_{TPA} = 4\pi^3\alpha a_0^5\omega^2 \delta_{TPA} \Delta(\omega_f - 2\omega, \Gamma_f) \tag{6.13}$$

through the normalized Lorentzian

$$\Delta(\omega_f - 2\omega, \Gamma_f) = \frac{1}{\pi} \frac{\Gamma_f}{(\omega_f - 2\omega)^2 + \Gamma_f^2} \tag{6.14}$$

<table>
<thead>
<tr>
<th>Property</th>
<th>a.u.</th>
<th>S.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$</td>
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<td>$8.4784 \times 10^{-30}$ C m</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$e^2 a_0^3 E_h^{-1}$</td>
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<td>$\beta$</td>
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<tr>
<td>$\gamma$</td>
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<tr>
<td>$\delta$</td>
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<td>$1.2126 \times 10^{-65}$ C$^5$m$^5$J$^{-4}$</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>$e^6 a_0^7 E_h^{-5}$</td>
<td>$2.3581 \times 10^{-88}$ C$^6$m$^6$J$^{-5}$</td>
</tr>
</tbody>
</table>

Table 6.1: Conversion factors for hyperpolarizabilities.[42]. $E_h$ denotes the energy given in Hartrees.

### 6.2 Few-states models for two-photon absorption

Few-states models are obtained by truncating the summation in Eq. (6.2) to include a finite number of excited states. By confining to two states and a linear polarized light, the long-in-plane component $S_{zz}$ of the TPA transition matrix can be written as

$$S_{zz} = \frac{4\mu_{zz}^{0f}(\mu_{zz}^{ff} - \mu_{zz}^{00})}{\omega_f} = \frac{4\mu_{zz}^{0f} \Delta \mu_{zz}}{\omega_f} \tag{6.15}$$
where \( \mu^0_f \) denotes the \( z \)-component of the transition dipole moment between the ground state \( |0\rangle \) and the final excited state \(|f\rangle\), and \( \mu^0_z \) and \( \mu^f_z \) are the permanent dipole moments of the ground and final states, respectively. It is clear that the two-states model is not applicable to molecules with an inversion center. For such molecules, an intermediate state \(|1\rangle\) is required and the corresponding three-states model is written as

\[
S_{zz} = \frac{2\mu^0_1 \mu^f_z}{\omega_1 - \omega_f/2} \tag{6.16}
\]

The corresponding two-photon absorption probability with a linearly polarized light source is

\[
\delta_{\text{TPA}}^L = 6(S_{zz})^2. \tag{6.17}
\]

The latter equation is motivated either when evaluating single long-in-plane moments or for systems that can be considered as one-dimensional. The means for enhancing the nonlinear response suggested by these few-states models are obviously minimizing the denominator and increasing the transition dipole moments. For systems with more dimensions and/or more excitation channels the formulas has to be improved in order to describe both multi-dimensional contributions, but also the effect of interference between different excitation paths to the final TP-state. A general formula to incorporate these effects is

\[
\delta_{\text{TPA}}^L = 8 \sum_{ij} \frac{3(\mu^0_i \cdot \mu^f_j)(\mu^0_j \cdot \mu^f_i) + (\mu^0_i \times \mu^f_j) \cdot (\mu^0_j \times \mu^f_i) - 2(\mu^0_i \times \mu^0_j) \cdot (\mu^f_j \times \mu^f_i)}{\Delta E_i \Delta E_j} \tag{6.18}
\]

This reformulation emphasizes the vector nature of the transition dipole moments. A natural decomposition would be in the terms \( \delta_1 \), \( \delta_2 \) and \( \delta_3 \) as

\[
\delta_1 = \sum_{ij} \frac{(\mu^0_i \cdot \mu^f_j)(\mu^0_j \cdot \mu^f_i)}{\Delta E_i \Delta E_j} \tag{6.19}
\]

\[
\delta_2 = \sum_{ij} \frac{(\mu^0_i \times \mu^f_j) \cdot (\mu^0_j \times \mu^f_i)}{\Delta E_i \Delta E_j} \tag{6.20}
\]

\[
\delta_3 = \sum_{ij} \frac{(\mu^0_i \times \mu^0_j) \cdot (\mu^f_j \times \mu^f_i)}{\Delta E_i \Delta E_j} \tag{6.21}
\]

and express the two-photon probability for linear polarized light, \( \delta_{\text{TPA}}^L \), and circular polarized light, \( \delta_{\text{TPA}}^C \), as

\[
\delta_{\text{TPA}}^L = 24\delta_1 + 8\delta_2 - 16\delta_3 \tag{6.22}
\]

\[
\delta_{\text{TPA}}^C = 16\delta_1 + 12\delta_2 - 24\delta_3 \tag{6.23}
\]

The terms \( \delta_1 \) and \( \delta_2 \) thus describes the alignments - or absence of alignments - of the channels leading to the actual two-photon state, i.e. indirectly the symmetry of the excited state.

Obviously, a perfect alignment is preferable, however not possible in each molecular point group. Far more intriguing is the task of controlling the interference term, \( \delta_3 \). In order to avoid negative contribution the summation would
ultimately consist of terms entangled in arrangements such as $\mu_{00}^0$, $\mu_{11}^1 \perp \mu_{01}^0$ and where $\mu_{00}^0$ is directed in the opposite direction to $\mu_{11}^1$. These conditions can easily be fulfilled by arbitrary vectors, but not likely to occur for transition dipole moments for a real system. From inspection it is also clear that the $D_{2h}$ molecular point group is less appropriate, since all excitation paths unavoidably will be orthogonal. The distribution between the different terms $\delta_1$, $\delta_2$ and $\delta_3$ defines a clarifying signature of the processes underlying a particular TPA cross section. As depicted for the dipolar structure PCP0 ($C_s$ molecular point group) and for the highly symmetric PCP2 ($D_{2h}$ molecular point group) in Fig. 6.1, the alignments of the excitation sub-paths can be of substantial importance for the final TPA cross section. Another consequence of this reformulation is that the ratio, $\Omega$, between circular and linear polarized light can be rewritten as

$$\Omega = \frac{\delta_{TPA}^C}{\delta_{TPA}^L} = \frac{4\delta_1 + 3\delta_2 - 6\delta_3}{6\delta_1 + 4\delta_2 - 4\delta_3}$$

(6.24)

A strictly dipolar system with completely aligned transition dipole moments will therefore have a ratio $\Omega = 2/3$, whereas systems with orthogonal excitation sub-paths are more inclined to have $\Omega \approx 3/2$.

### 6.3 Effective transition dipole moments

Three-state models may be applied to evaluate transition dipole moments between excited states[44] from TPA cross sections. Even in cases where a three-state models appears perfectly valid, e.g. only one dominating channel leading to the final excited states, the angle, $\theta$, between the relevant transition dipole moments, $\mu_{01}^0$ and $\mu_{1f}^1$, constitutes a problem. This can perhaps most easily be seen by truncating Eq. 6.18 to three states and restrict to two dimensions.

$$\delta_{TPA}^i = \delta_{TPA}^i \left( \frac{(\mu_{0i}^0 \mu_{1f}^1)^2(2\cos^2(\theta_{0f}^i) + 1)}{(\Delta E_i)^2} \right)$$

(6.25)
The angle, \( \theta_{f01}^{1f} \) is unknown from an experimentally point a view and have to be assumed to be zero, which may be motivated for purely one-dimensional systems. Another way would be to employ an effective transition dipole moments as defined by

\[
\left( \mu_{\text{eff}}^{1f} \right)^2 = \frac{\left( \mu_{\text{f01}}^{1f} \right)^2}{3} \left( 2 \cos^2(\theta_{f01}^{1f}) + 1 \right)
\]

in order to enable a proper comparison. The difference between parallel and orthogonal transition dipole moments apparently is a factor 3 within a three-state model. When the excitation scheme is not completely dominated by one single excitation channel it is necessary to comprise additional excitation channels and the interference between them. In addition it is still possible to define an effective transition dipole moment as

\[
\left( \mu_{\text{eff}}^{2f} \right)^2 = \frac{\left( \mu_{\text{f01}}^{2f} \right)^2}{3} \left( 2 \cos^2(\theta_{f02}^{2f}) + 1 \right) \left( \Delta E_1 \right)^2 + \frac{\left( \mu_{\text{f02}}^{2f} \right)^2}{(\Delta E_2)^2} \left( \mu_{\text{f01}}^{2f} \mu_{\text{f02}}^{2f} \right)^2 \left( \Delta E_2 \right)^2 - \frac{4 \sin(\theta_{f01}^{1f}) \sin(\theta_{f02}^{2f}) \sin(\theta_{f01}^{1f})}{\Delta E_2} \left( \Delta E_2 \right)^2 \left( \mu_{\text{f01}}^{2f} \mu_{\text{f02}}^{2f} \right)^2
\]

where \( \theta_{ij}^{kl} \) is the angle between \( \mu_{ij} \) versus \( \mu_{kl} \) and \( \mu_{ij} \) denotes \( |\mu_{ij}| \).

### 6.4 Three-photon absorption

The three-photon transition tensor element \( T_{abc} \) for three photons of identical frequency is defined as

\[
T_{abc} = \sum_{a,b,c} P_{a,b,c} \sum_{n,m} \langle 0 | \mu_a | m \rangle \langle m | \mu_b | n \rangle \langle n | \mu_c | f \rangle \left( \omega_n - 2 \omega_f / 3 \right) \left( \omega_m - \omega_f / 3 \right)
\]

where \( \sum P_{a,b,c} \) performs the summation over the six permutations with respect to the indices \( a, b, \) and \( c. \) As for TPA, orientational averaging is performed in order to relate the intrinsic coordinates of a single molecule to the ensemble of freely moving particles as measured in the laboratory coordinate system. In complete analog with TPA one therefore seeks to evaluate:

\[
\delta_{3\text{PA}} = |T^{0f}(\lambda, \nu, \xi)|^2 = (\lambda_{\nu E_F} T_{ABC}^{0f})(\lambda_{\nu E_F} T_{DEF}^{0f})^* \quad (6.29)
\]

According to McClain [45] the orientational averaged values for the 3PA probability \( \delta_{3\text{PA}} \) for linearly (\( L \)) and circularly (\( C \)) polarized light can be written as:

\[
\delta_{3\text{PA}}^L = \frac{1}{35} \left( 2 \delta_G + 3 \delta_F \right), \quad (6.30)
\]

\[
\delta_{3\text{PA}}^C = \frac{1}{35} \left( 5 \delta_G - 3 \delta_F \right), \quad (6.31)
\]

where

\[
\delta_F = \sum_{i,j,k} T_{iij} T_{kkj}, \quad (6.32)
\]

\[
\delta_G = \sum_{i,j,k} T_{ijk} T_{ijk}. \quad (6.33)
\]
The theory can rather easily be generalized to address various combinations of multi-photon phenomena\cite{46, 47, 48} in order to guide spectroscopy when exploring excited states.

By proceeding exactly the same way as for TPA, $\delta^{3\text{PA}}$ can be related to a three-photon cross section, $\sigma^{3\text{PA}}$ as

$$\sigma^{3\text{PA}} = \frac{120\pi^3 h^2 \omega^3}{c^3} \text{Im}[\chi^{(5)}] = \frac{4\pi^3 h^2 \omega^3}{3c^3} e^6 d^6 E_i^5 \delta^{3\text{PA}}$$

$$= \frac{4\pi^3 \alpha a_0^3 \omega^3}{3c^2} \delta^{3\text{PA}} = \frac{4\pi^4 \alpha a_0^3 \omega^3}{3c^2} \delta^{3\text{PA}} \Delta(\omega_f - 3\omega, \Gamma_f) \quad (6.34)$$

### 6.4.1 Few-states models for three-photon absorption

For a confinement to two states and one single long-in-plane component the third order transition moments $T_{zzz}$ can be written as

$$T_{zzz} = 27 \times \frac{2 \mu_{0f}^3 (\mu_{00} - \mu_{ff})^2 - (\mu_{0f}^3)^3}{2\omega_f^2} = 27 \times \frac{\mu_{0f}^3 [2(\Delta \mu_{0})^2 - (\mu_{0f}^3)^2]}{2\omega_f^2} \quad (6.35)$$

and for one-dimensional systems, the total three-photon absorption probability $\delta^{3\text{PA}}$ for linearly polarized light will become

$$\delta^{3\text{PA}}_L = \frac{(T_{zzz})^2}{7}. \quad (6.36)$$

Unlike TPA, a two-state model is sufficient to capture the essential parameters behind a 3PA probability for both molecules without (non-symmetric) and with (symmetric) a center of inversion. A second conclusion revealed from this is that for non-symmetric, polar, molecules, the transition dipole moment between the ground and final states $\mu_{0f}$ and the corresponding dipole moment fluctuation $\Delta \mu$ always will counteract. A strategy for maximizing $T_{zzz}$ which is suggested by Eq. (6.35) is to enhance the transition dipole moment between the ground and the final states while minimizing the dipole moment fluctuation. This seems to argue for symmetric molecules, however, charge-transfer units at terminal locations will not only remove symmetries and introduce the competing term of $\Delta \mu$, but also in general lead to a stronger $\mu_{0f}^3$. Therefore, compared to TPA, it is less trivial to suggest general guidelines in order to maximize the 3PA cross sections. For the second excited state and above it is essential to comprise yet another state in the expansion which in total leads to 5 additional terms

$$T_{zzz}^{3\text{sn}} = T_{zzz}^{2\text{sm}} + \frac{\mu_{01}^1 \mu_{1f}^f \mu_{1f}^f}{\omega_f/3(\omega_1 - \omega_f/3)} + \frac{\mu_{01}^1 \mu_{1f}^f \mu_{1f}^f}{2\omega_f/3(\omega_1 - 2\omega_f/3)}$$

$$+ \frac{\mu_{01}^1 \mu_{1f}^f \mu_{1f}^f}{(\omega_1 - 2\omega_f/3)(\omega_1 - \omega_f/3)} - \frac{\mu_{00}^0 \mu_{1f}^f \mu_{1f}^f}{\omega_f/3(\omega_1 - 2\omega_f/3)}$$

$$- \frac{\mu_{01}^1 \mu_{10}^{10} \mu_{0f}^f}{2\omega_f/3(\omega_1 - \omega_f/3)} \quad (6.37)$$

Each term could potentially contain a singularity $\omega_1 \approx 2\omega_f/3$ (or $\omega_1 \approx \omega_f/3$). and as seen in Eq. 6.37 the final outcome when close to resonance is highly unpredictable. Therefore, calculations of $\delta^{3\text{PA}}$ above the threshold of resonance are not reliable.
Chapter 7

Summary

The present thesis consists of a collection of attempts to describe various types of nonlinear optical absorption for molecules through a variety of quantum chemical methods. The order of the articles enclosed in the thesis—with a few exceptions—reflects the chronological order e.g. excited state absorption (ESA), two-photon absorption (TPA), three-photon absorption (3PA) and triplet-triplet (TT) absorption. The first two papers are concerned with transition dipole moments between excited states in order to estimate the suitability of certain methods for predicting ESA. The low scaling method Hartree–Fock (HF) is shown to qualitatively follow the highly correlated coupled-cluster (CC) results, but also to blue-shift the spectra. The succeeding article repeats the methodology, but for the first members in the polyene family serving as prototypes of the general class of π-conjugated systems. In addition to displaying theoretical ESA spectra as evolving with conjugation length, the long debated and anticipated crossing between the $2A_g$ and the $1B_u$ state is reported to occur for octatetraene at the CC3-level. Transition dipole moments between excited states are experimentally hard to attain and probably only derivable from TPA cross sections. By the proposal of a generalized few-states model it is shown that such comparisons have to rely on the assumptions of perfectly aligned excitation sub-paths in one completely dominating excitation channel. Another possibility is to include the directions of the ingoing transition dipole moments and possibly additional excitation channels in a redefined effective transition dipole moment. An alternative use of the model is to characterize the TPA of multi-dimensional chromophores and guide the attachment of electron donating (D) and electron accepting (A) substituents for maximum TPA response. Initially this approach was applied to a series of explicit two-dimensional systems based on cumulens, but subsequently also to the three-dimensional template of [2.2]paracyclophane (PCP). The major conclusion realized forms a general emphasize on alignments of excitation sub-paths, which clearly promotes dipolar structures. Certain molecular point groups, as $D_{2h}$ are definitely unfavorable while inevitably introducing orthogonal excitation sub-paths.

Through effective core potentials (ECP) the response approach can be broadened to address TPA of organo-metallic systems including heavy elements. From the outset of optical limiting, TPA could contribute with a substantial nonlinear absorption from the ground state and thereby complementing the documented features of linear absorption in the near UV-region, inter-system crossing followed
by triplet-triplet absorption, spin-forbidden transition to triplet-states, and ultimately yields limiting capacity covering the entire visible spectra.

In a first survey, three-photon absorption (3PA), have been explored by \textit{ab initio} response calculations applied to a set of chromophores based on dithieniophehene (DTT). Compared to TPA, the substitution effects by attaching acceptors and donors are shown to be less dramatic, though still pointing out the AD charge transfer systems as the most intense 3PA molecules. One viable option for improving the accuracy of the estimations of multi-photon probabilities, is employing few-states models with ingredients obtained at a higher correlated level. Despite the well documented agreement between few-states models and full response results reported for TPA, this conclusion can not be transferred to 3PA. Deviations can occasionally be substantial and not even entirely systematic which clearly reduces the potential utility of the approach. Thus, full response at the DFT level protrudes as the only candidate for extensive systems. This conclusion is fortified further in a minor benchmark where DFT-3PA elicits the results obtained within the coupled-cluster hierarchy. For a set of chromophores the qualitative conclusions already attained at the HF level are confirmed by DFT/BLYP, but with a more salient characteristics in predicting the AD-compounds as the most 3PA active.

In order to pursue the predictions closer to performed measurements it is essential to estimate the impact of experiment specific parameters such as pulse duration and saturation effects. In an all dynamical model it is demonstrated that pulse propagation in a nonlinear medium strongly is influenced by saturation effects for longer pulses.
Bibliography


