Nonlinear Optical Properties Of Organic Chromophores
Calculated Within Time Dependent Density Functional Theory

Sergio Tafur
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NONLINEAR OPTICAL PROPERTIES OF ORGANIC
CHROMOPHORES CALCULATED WITHIN
TIME DEPENDENT
DENSITY FUNCTIONAL THEORY

by
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B.Sc. University of Central Florida, 2005

A thesis submitted in partial fulfillment of the requirements
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Committee Chair: Dr. Viatcheslav Kokouline
ABSTRACT

Time Dependent Density Functional Theory offers a good accuracy/computational cost ratio among different methods used to predict the electronic structure for molecules of practical interest. The Coupled Electronic Oscillator (CEO) formalism was recently shown to accurately predict Nonlinear Optical (NLO) properties of organic chromophores when combined with Time Dependent Density Functional Theory. Unfortunately, CEO does not lend itself easily to interpretation of the structure activity relationships of chromophores. On the other hand, the Sum Over States formalism in combination with semiempirical wavefunction methods has been used in the past for the design of simplified essential states models. These models can be applied to optimization of NLO properties of interest for applications. Unfortunately, TD-DFT can not be combined directly with SOS because state-to-state transition dipoles are not defined in the linear response TD approach. In this work, a second order CEO approach to TD-DFT is simplified so that properties of double excited states and state-to-state transition dipoles may be expressed through the combination of linear response properties. This approach is termed the *a posteriori* Tamm-Dancoff approximation (ATDA), and validated against high-level wavefunction theory methods. Sum over States (SOS) and related Two-Photon Transition Matrix formalism are then used to predict Two-Photon Absorption (2PA) profiles and anisotropy, as well as Second Harmonic Generation (SHG) properties. Numerical results for several conjugated molecules are in excellent agreement with CEO and finite field calculations, and reproduce experimental measurements well.
This work is dedicated to
Myriam, Diana, Bonnie, and Chuck
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KeyWords: Two Photon Absorption, Nonlinear Optics, polarizability
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CHAPTER I
INTRODUCTION

1.1 Motivation

Second harmonic generation (SHG) and two-photon absorption (2PA) are respectively second and third-order nonlinear optical effects which have found a wide range of applications in the fields of engineering, medicine, and information technology. Presently 2PA applications include lithographic micro-fabrication, three dimensional data storage, photonic devices [1], quantum information technology [2], optical power limiting, two-photon pumped lasing in organic chromophores and quantum dots [2, 3], in-vivo imaging, and cell-selective photodynamic therapy [3]. SHG has found applications in mimicking operations of electronic devices by providing the possibility of phase and/or amplitude modulation [4] as well as frequency conversion and optical switching [5]. Prediction of 2PA and SHG can be employed in material design and Time Dependent Density Functional Theory (TD-DFT) offers arguably the best accuracy/computational cost ratio among different methods used to predict the nonlinear response of materials in both cases [6, 7].

It is the scope of this thesis to present calculations of 2PA (Ch.3,4) and SHG (Ch.5) carried out within TD-DFT. Coupled electronic oscillators (CEO), sum over states (SOS), and 2PA transition matrix formalisms were used to carry out the prediction of the nonlinear response of materials. These results were compared to experimental results for the studied molecular structures. The application of the SOS formalism required writing a new computer program to calculate NLO properties and modifications to Gaussian 2003 D.01, implementing TD-DFT, to calculate state to state transition dipole moments. This is detailed in Ch.2.
1.2 Material response to external fields

Nonlinear optical properties (NLOs) of materials are strongly dependent on the intensity of an external field in the local neighborhood of elements of the material [8]. In this section a very limited discussion on the linear and nonlinear response of materials is presented to lead the presentation of the discussion of NLO studies carried out here in.

The response of materials to an incident/external electric field, as learned by a student in an electromagnetism/electrodynamics course, is given by an internal polarization field that arises within the material and is linearly proportional to the incident/external field. The manner or calculating these internal polarization fields are introduced in standard texts such as Pollack & Stump’s Electromagnetism [9] or Introduction to Electrodynamics by David Griffiths [10]. In centimeter-gram-second (cgs) units the polarization is represented as:

\[ \mathbf{P} = \chi_E \mathbf{E} \]

According to this notation \( \mathbf{E} \) is the electric vector field and \( \chi_E \) is the electric susceptibility. For the remainder of the text \( \chi \equiv \chi_E \) will be referred to as the susceptibility and will be understood to mean the electric susceptibility. As a first assumption there is no treatment or regard for the magnetic susceptibility in this text, and any material response to an external electric field is considered to be treated as through it were due entirely to the electronic susceptibility.

Following the treatment, as presented in Boyd [8], for vector fields, the nonlinear response to \( \mathbf{E} \) by the polarization field is given by a power series expansion of \( \mathbf{P} \) in orders of \( \mathbf{E} \):

\[ \mathbf{P} = \sum_r \mathbf{\chi}^{(r)}(\mathbf{E})^r \]
Another approach using the Taylor expansion convention in terms a coupled formalism gives the increasing order corrections to the susceptibilities estimated as higher order derivatives of the dipole moment with respect to the applied field. This can be done numerically which is usually called finite field (FF) method or analytically as increasing order derivatives of energy \((W)\) with respect to an applied field. In the power series expansion, by \((E)^k\) it is meant that, a vector field \(\mathbf{E} \rightarrow \mathbf{E}(r, t) = \sum_{i=1}^{3} \vec{E}_i(r, t)\), with the spatial components of the electric vector field contribute to components of the responding polarization vector by:

\[
P_i = \chi^{(1)}_{ij} \vec{E}_j + \chi^{(2)}_{ijk} \vec{E}_j \vec{E}_k + \chi^{(3)}_{ijk\ell} \vec{E}_j \vec{E}_k \vec{E}_\ell + \chi^{(4)}_{ijklmn} \vec{E}_j \vec{E}_k \vec{E}_l \vec{E}_m + \chi^{(5)}_{ijklmn\ell} \vec{E}_j \vec{E}_k \vec{E}_l \vec{E}_m \vec{E}_\ell + \cdots \tag{1.3}
\]

The electric field vector of an optical wave is assumed to be a discrete sum of a series of frequency components, \(N\) numerated by \(n\), so that each complex spatial component of the vector can be represented by:

\[
\vec{E}_i(r, t) = \sum_{n}^{N} E_i(\mathbf{r}, \omega_n t) \tag{1.4}
\]

That is to say that the polarization field is now treated as dependent on the frequencies (meaning that each frequency of the field may vary independently of other frequencies) of the external incident fields as well as their spatial components, spatial location, and time. To account for the response of \(\mathbf{P}\) to the frequency dependence of electric fields incident on a given material, it may be possible to allow the susceptibility \(\chi\) to determine this response for each order of \(\mathbf{P}\). In this fashion \(\vec{E}^{(k)} \rightarrow \chi^{(k)}_{\ell \ldots k+1} \left( \sum_{i}^{n} \omega_i ; \omega_1, \ldots, \omega_n \right)\) making the susceptibility a tensor of rank \(k+1\), dependent on the \(n\)th field frequency [8].

The focus of this thesis lies in calculating NLO properties from microscopic polarizabilities (ie. the response of a single molecule to electric fields incident upon it).
Therefore, it is required to establish a relationship between the macroscopic susceptibilities and
the microscopic polarizabilities. Referring back\(^1\) to introductory texts like [9] and [10], the
polarization field arises due to the creation of a dipole moment in matter in response to an
electric field. That is to say that after the charge density of a molecule has reached equilibrium
(ie. the molecule has been polarized) in the presence of an electric field \(\mathbf{E}\), the molecule is left
with a small (or large) dipole moment \(\mathbf{p}\) dependent on the intensity of the field incident field.
This linear relationship is given by:
\[
\mathbf{p} = \tilde{\alpha} \mathbf{E} .
\] (1.5)

An elegant case of a classical example is given in Chapter 4 of Griffiths [10]. The linear
relationship between \(\mathbf{P}\) and \(\mathbf{p}\) is given by the definition of the polarization as:
\[
\mathbf{P} \equiv \text{dipole moment per volume}
\] (1.6)

This definition is not sufficient for developing a relationship between the susceptibilities
and the polarizabilities to account for NLO properties. In the treatment given by Boyd [8] the
relationship becomes one of a net effect of dipoles \(\mathbf{p}\) generating a polarization field in matter.
Given that an induced dipole moment per atom, to a \(k\)th order \(\langle \mathbf{p}^{(k)} \rangle\), may be derived from
perturbation theory in quantum mechanics, by multiplying this expectation value of the \(k\)th order
contribution by the total number \(N\) of molecules, with \(n\) as the molecular density, yields the \(k\)th
order correction to \(\mathbf{P}\).
\[
\mathbf{P}^{(k)} \equiv n\langle \mathbf{p}^{(k)} \rangle
\] (1.7)

This is sufficient to lead to the conclusion that, when local–field corrections can be ignored\(^1\)
microscopically:

\(^1\) a discussion on local field corrections is, regrettably, beyond the scope of this thesis. The reader is directed to
Section 3.8 in Boyd [8] for a brief treatment of the topic.
\[ \langle \mathbf{p} \rangle = \sum_k \langle \mathbf{p}^{(k)} \rangle \]
\[ \langle \mathbf{p}^{(k)} \rangle = \tilde{\alpha}^{(k)} (\mathbf{E})^k \]  
\hspace{1cm} (1.8)

Where macroscopically:

\[ \mathbf{P}^{(k)} = \tilde{\chi}^{(k)} (\mathbf{E})^k \]  
\hspace{1cm} (1.9)

Such that the polarizability will relate to the susceptibility by:

\[ \tilde{\chi}^{(k)} = N \tilde{\alpha}^{(k)} \]  
\hspace{1cm} (1.10)

[8].

This thesis focuses on effects dependent on the second and third order susceptibilities on a single molecule and only polarizabilities will be treated. Predicted effects will be compared to experiment. The net effect will be assumed to be a result of the independent contributions of the independent elements of a collection of molecules.

Following the treatment in Boyd [8] and Cronstrand’s work [11], the polarizabilities will be labeled as:

\[ \langle p \rangle_j = \alpha^{(1)}_{ij} \mathbf{E}_j + \beta^{(2)}_{ijk} \mathbf{E}_j \mathbf{E}_k + \gamma^{(3)}_{ijkl} \mathbf{E}_j \mathbf{E}_k \mathbf{E}_l + \cdots \]  
\hspace{1cm} (1.11)

A permanent dipole term is omitted in (1.11) by the assumption that the dipole to be modeled will arise purely due to the response of the charge density to the incident electric field \( \mathbf{E} \) and that the sum between \( \langle p \rangle_i \) and \( p_0 \) (the permanent dipole) will give the total dipole moment of a given molecule. As shown above \( \alpha_{ij} \) is the linear polarizability, \( \beta_{ijk} \) is the second order polarizability (also referred to as the first hyper-polarizability) and \( \gamma_{ijkl} \) is the third order polarizability (also referred to as the second hyper-polarizability). No susceptibilities will be predicted in this thesis. Only comparisons to experimental measurements of cross-sections, anisotropies, or polarizabilities for independent molecules will be made.
1.3 Sum over States (SOS) Formalism

The sum over state (SOS) expressions for the (hyper)-polarizabilities arise from applying time dependent perturbation theory, in the Schrödinger picture, to calculate $\langle \mathbf{p} \rangle$. In this formalism grouping terms of $\langle \mathbf{p} \rangle$ that are of the same order yields the $k^{th}$ order correction in (1.12), and therefore the $k^{th}$ order polarizability. Following the formalism presented in [8] and [11]:

$$
\langle \mathbf{p}^{(k)} \rangle = \langle \Psi^{(0)} | \mu | \Psi^{(k)} \rangle + \cdots + \langle \Psi^{(r)} | \mu | \Psi^{(s)} \rangle + \cdots + \langle \Psi^{(k)} | \mu | \Psi^{(0)} \rangle
$$

(1.12)

Expression (1.12) is true where the sum of $r$ and $s$ equates to $k$. In (1.12) $\mu$ represents the dipole-moment operator and $\langle \Psi^{(k)} | \mu | \Psi^{(0)} \rangle$ represent the $k^{th}$ order corrections to bras and kets that solve the time dependent Schrödinger equation:

$$
\mathbf{H} | \Psi \rangle = i\hbar \partial_t | \Psi \rangle
$$

(1.13)

When looking for polarizabilities, $\mathbf{H}$ represents the Hamiltonian for a collection of atoms arranged to represent a molecular system in the presence of a perturbative classical optical electric field. Rewriting the Hamiltonian to as $\mathbf{H}_0 + \mathbf{V}$ where $\mathbf{V}$, given as a perturbation to $\mathbf{H}$, is the classical interaction of a dipole in the presence of an electric field given by:

$$
\mathbf{V} = -\mathbf{p} \cdot \mathbf{E}
$$

(1.14)

In (1.14) $\mathbf{p}$ is treated as the quantum mechanical dipole-moment operator $\mu$. The SOS (hyper)-polarizabilities will be listed and their derivation will be omitted for the sake of brevity. The derivation of these expressions is straight-forward and may be carried out by an analysis implementing perturbation theory up to the $k^{th}$ order correction of corresponding to the $k^{th}$ order polarizability and comparing to the expressions corresponding to the $k^{th}$ order correction of the
microscopic dipole moment \( \langle \mathbf{p} \rangle \). The resulting (hyper)-polarizabilities are listed as results following the discussion from Boyd [8] and Cronstrand [11] by:

\[
\alpha_{ij}^{(1)}(\omega_p) = \frac{1}{\hbar} \sum_{m} \left( \frac{\mu^i_{gm} \mu^j_{mg}}{\omega_{mg} - \omega_p} + \frac{\mu^j_{gm} \mu^i_{mg}}{\omega_{mg} + \omega_p} \right) \tag{1.15}
\]

\[
\beta_{ijkl}^{(2)}(\omega_p + \omega_q; \omega_p, \omega_q) = \frac{\varphi_{pq}^{ij}}{\hbar^2} \sum_{n,m} \left( \frac{\mu^i_{gn} \mu^j_{nm} \mu^k_{mg}}{(\omega_{ng} - \omega_p - \omega_q) (\omega_{mg} - \omega_p)} + \frac{\mu^j_{gn} \mu^i_{nm} \mu^k_{mg}}{(\omega^*_{ng} + \omega_q) (\omega_{mg} - \omega_p)} \right) \tag{1.16}
\]

\[
\gamma_{ijkl}^{(3)}(\omega_p + \omega_q + \omega_r; \omega_p, \omega_q, \omega_r) = \frac{\varphi_{pq}^{iqr}}{\hbar^3} \sum_{n,m} \left( \frac{\mu^i_{vn} \mu^j_{mn} \mu^k_{mg}}{(\omega_{vg} - \omega_p - \omega_q - \omega_r) (\omega_{mg} - \omega_p)} + \frac{\mu^j_{vn} \mu^i_{mn} \mu^k_{mg}}{(\omega^*_{vg} + \omega_r) (\omega_{mg} - \omega_p)} \right) \tag{1.17}
\]

In these expressions \( \omega_{nm} \) represents the resonant transition frequency of states \( n \) and \( m \) of the modeled molecule \( \omega_{nm} = \omega_{nm}^0 - i \Gamma_m \), \( i,j,k,l \) represent the spatial coordinates (ie. \( x,y,z \)), \( v,n,m,g \) represent states of the modeled molecule, \( p,q,r \) represent frequencies of the applied fields, and \( \varphi_{pq}^{iqr} \) and \( \varphi_{pq}^{ij} \) represent an averaging permutation operation over the dummy indices \( j,k,l \) and
$p,q,r$ to force the characteristic symmetry of the (hyper)-polarizability tensors.

1.4 Density Functional Theory (DFT)

Density Functional Theory (DFT) in the Kohn-Sham (KS) approximation [12] has been the method of choice in solid state theory studies for a long time. It has received recognition as a reasonably accurate first principles method for the calculation of ground states of large molecular systems after Generalized Gradient approximation was combined with fraction of Hartree Fock (HF) exchange (hybrid GGA) [13]. Instead of starting with a multi-configuration wave function, the KS method accounts for the electron correlation through an exchange-correlation potential. In particular, the contribution of double and higher excited configurations to the ground state are included as a single Slater determinant KS description implicitly. It was shown that the exact electron density obtained in multi-reference \textit{ab initio} methods (such as Full CI) can be mapped onto effective single-particle KS description even for molecules far from equilibrium [14].

A ground state wave function is not available in DFT for use in analysis, and the single determinant describes a hypothetical system of noninteracting electrons (quasi particles) used in KS theory, rather than the molecular system of interest. Despite this single determinant appearance, DFT is not a single reference method. This statement becomes apparent when Fermi broadening is applied to occupation numbers and these fractionally occupied KS orbitals are compared with Natural Orbitals obtained from methods based on a single wave function [15]. Approximate hybrid exchange-correlation functionals (such as B3LYP[16]) result in energies close to couple cluster models in quality [13].

There are several extensions of DFT developed to describe the excited states. One approach is to use the multi-reference strategies described above [17-20]. However, it is more
common to combine DFT with a time dependent perturbation theory approach. This approach will be briefly described next.

1.5 Time Dependent Density Functional Theory (TD-DFT)

Instead of obtaining lowest energy solutions to the Schrödinger equation, based on variational principle, the excited states can be described by a time-dependent perturbation theory treatment as the interaction between the molecular system and the electric field [21]. Several formalisms have been developed to obtain excitation energies and transition dipoles directly,[22] including the equation of motion (EOM) and polarization propagator approaches. When the ground state is described in the HF method and terms of order higher than linear in the external filed are neglected (linear response, LR); this approach results in the Time-Dependent Hartree-Fock (TDHF) method. This is also known as the random phase approximation (RPA). When applied to a DFT ground state,[23, 24] the LR approximation is often referred to as LR-DFT, or TD-DFT. LR-DFT method results in a non-Hermitian eigenvalue problem:

\[
\begin{pmatrix}
A & B \\
-B & -A
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix}
= \Omega
\begin{pmatrix}
X \\
Y
\end{pmatrix}
\]

(1.18)

A solution to which are the excitation energies \( \Omega_\alpha \) and transition density matrices \( \xi_\alpha \equiv \begin{pmatrix} X \\ Y \end{pmatrix} \) for the ground to excited state transitions. In the basis of occupied \((i,j)\) and vacant \((a,b)\) KS orbitals of \(\sigma,\tau\) subsets \((\sigma,\tau=a,\beta)\), the transition density matrix is of block-diagonal form with occupied-vacant \(X = (\xi)_{ia}\) and vacant-occupied \(Y = (\xi)_{ai}\) blocks being nonzero. Matrices \(A\) and \(B\) are defined as

\[
A_{ai\sigma, bj\tau} = \delta_{ai} \delta_{\sigma} \delta_{\tau} (\varepsilon_a - \varepsilon_i) + K_{ai\sigma, bj\tau} \quad \text{and} \quad B_{ai\sigma, bj\tau} = K_{ai\sigma, jb\tau}
\]

(1.19)
For the case of hybrid DFT with a $c_{HF}$ fraction of HF exchange, the coupling matrix $K$ is expressed through the second derivatives of the exchange-correlation functional $w$ in the Coulomb and exchange integrals by:

$$K_{a_{i\sigma}, b_{j\tau}} = (1 - c_{HF})(ia \mid w \mid jb) + (ia \mid jb) - c_{HF}\delta_{\sigma\tau}(ab \mid ij) \quad (1.20)$$

The RPA or TDHF equation is then a limiting case with $c_{HF}=1$, where the matrix $A$ consists of interactions between two singly-excited configurations $(a \leftarrow i \mid H \mid b \leftarrow j)$. $H$ is referred to as the CIS Hamiltonian. The matrix $B$ includes, by virtue of swapping indexes, the excitations from virtual to occupied MOs (de-excitations) of the form $(a \leftarrow i \mid H \mid j \leftarrow b)$. Mathematically, they are equivalent to the matrix elements between the ground and doubly excited states [25]. Thus, LR-DFT accounts for double excitations in two ways: implicitly, though exchange-correlation functional, and explicitly, through de-excitation matrix $B$.

An additional approximation that may be introduced to the LR formalism is the Tamm-Dancoff approximation (TDA) [26, 27]. This approximation consists of neglecting de-excitation matrix $B$ in equation (1.18). When applied to the HF ground state this approximation is equivalent to configuration interaction method limited to singles (CIS).

1.6 Coupled Electronic Oscillators (CEO)

The SOS formalism requires state-to-state transition dipoles that are not available in linear response TD-DFT. For that reason another approach to calculate NLO properties, called the Coupled Electronic Oscillators (CEO) formalism, was used in [28]. Unlike the SOS approach, the CEO formalism does not lend itself to a clear interpretation of the nature of NLO properties. As presented by [28], the CEO formalism treats transition densities from TD-DFT as solutions to the equation of motion for coupled harmonic oscillators. In this formalism all of the
information of the Hamiltonian is contained in the excitation energies $\Omega_\alpha$ and what are called the “anharmonicities” of the coupled system $V_{\alpha\beta\gamma}, V_{\alpha\beta\delta}, \mu^{(s)}_{\alpha}, \mu^{(s)}_{\alpha\beta}$, and $\mu^{(s)}_{\alpha\beta\gamma}$ [29] are given by:

$$
\mu^{(s)}_{\alpha} = \text{Tr}\left(\mu^{(s)}_{\alpha}\xi_\alpha\right) \quad (1.21)
$$

$$
\mu^{(s)}_{\alpha\beta} = \sum_{\text{perm}}^\alpha \text{Tr}\left[\mu^{(s)}_{\alpha}(I - 2\overline{\rho})\xi_\alpha\xi_\beta\right] \quad (1.22)
$$

$$
\mu^{(s)}_{\alpha\beta\gamma} = -\frac{1}{3} \sum_{\text{perm}}^\alpha \text{Tr}\left[\mu^{(s)}_{\alpha}(I - 2\overline{\rho})\xi_\alpha\xi_\beta\xi_\gamma\right] \quad (1.23)
$$

$$
V_{\alpha\beta\gamma} = \frac{1}{2} \sum_{\text{perm}}^\alpha \text{Tr}\left[(I - 2\overline{\rho})\xi_\alpha\xi_\beta\tilde{V}(\xi_\gamma)\right] + \frac{1}{6} \sum_{\text{perm}}^\alpha \text{Tr}\left[\xi_\alpha U^{(2)}(\xi_\beta, \xi_\gamma)\right] \quad (1.24)
$$

$$
V_{\alpha\beta\gamma\delta} = \frac{1}{12} \sum_{\text{perm}}^\alpha \text{Tr}\left[(I - 2\overline{\rho})\xi_\alpha\xi_\beta\tilde{V}(\xi_\gamma, \xi_\delta)\right] + \frac{1}{12} \sum_{\text{perm}}^\alpha \text{Tr}\left[\xi_\alpha \tilde{V}(\xi_\beta, \xi_\gamma)\right] + \frac{1}{12} \sum_{\text{perm}}^\alpha \text{Tr}\left[\xi_\alpha U^{(2)}(\xi_\beta, \xi_\gamma, \xi_\delta)\right] + \frac{1}{12} \sum_{\text{perm}}^\alpha \text{Tr}\left[\xi_\alpha U^{(3)}(\xi_\beta, \xi_\gamma, \xi_\delta)\right] \quad (1.25)
$$

These expressions are also referred to as coupling terms $\mu^{(s)}_{\alpha}, V_{\alpha\beta\gamma}$, and $V_{\alpha\beta\gamma\delta}$. In the expressions below, $\mu^{(s)}_{\alpha}$ represent the dipole components along the spatial direction $(s) = x,y,z$, $\text{Tr}$ represents the trace of the matrix, $\xi_\alpha$ are the transition densities to state $\alpha$ calculated from LR-DFT (described in Ch.2), and $\tilde{V}$ are two-electron integrals (Coulomb matrix elements) evaluated on transition densities and their combinations [28, 29]. The second and third order
polarizability tensors derived from (1.21-25) in the Coupled Electronic Oscillator (CEO) formalism and implemented here in are given by the expressions (1.26,27) below [28].

\[
\beta_{ijkl}(\omega_1, \omega_2) = \frac{1}{2} \sum_{a\beta\gamma} \left( \sum_{a\beta\gamma} \frac{V_{-\alpha\beta\gamma} \mu_{-\alpha\beta\gamma} \mu_{-\alpha\beta\gamma} \gamma S_a S_{\beta} S_{\gamma}}{(\Omega_\alpha - \omega_1 - \omega_2)(\Omega_\beta - \omega_1)(\Omega_\gamma - \omega_2)} + \frac{1}{2} \sum_{a\beta\gamma} \frac{\mu_{a\beta\gamma} \mu_{-\alpha\beta\gamma} \gamma S_a S_{\beta} S_{\gamma}}{(\Omega_\alpha - \omega_1)(\Omega_\beta - \omega_2)} \right) + \frac{1}{2} \sum_{a\beta\gamma} \left( \sum_{a\beta\gamma} \frac{\mu_{-\alpha\beta\gamma} \mu_{-\alpha\beta\gamma} \gamma S_a S_{\beta} S_{\gamma}}{(\Omega_\alpha - \omega_1 - \omega_2)(\Omega_\beta - \omega_1)} + \frac{1}{2} \sum_{a\beta\gamma} \frac{\mu_{-\alpha\beta\gamma} \mu_{-\alpha\beta\gamma} \gamma S_a S_{\beta} S_{\gamma}}{(\Omega_\alpha - \omega_1 - \omega_2)(\Omega_\beta - \omega_2)} \right).
\]

(1.26)

\[
\gamma(\omega_1, \omega_2, \omega_3) = \sum_{\omega_1 \omega_2 \omega_3} \left( \gamma^{(I)} + \gamma^{(II)} + \gamma^{(III)} + \ldots \gamma^{(VIII)} \right),
\]

\[
\gamma^{(I)}_{ijkl} = \sum_{\alpha\beta\gamma\delta} \left( \sum_{\alpha\beta\gamma\delta} \frac{\mu_{-\alpha\beta\gamma} \mu_{-\alpha\beta\gamma} \gamma S_a S_{\beta} S_{\gamma}}{(\Omega_\alpha - \omega_1 - \omega_2 - \omega_3)(\Omega_\beta - \omega_2 - \omega_3)(\Omega_\gamma - \omega_3)} \right).
\]

\[
\gamma^{(II)}_{ijkl} = \sum_{\alpha\beta\gamma\delta} \left( \sum_{\alpha\beta\gamma\delta} \frac{\mu_{-\alpha\beta\gamma} \mu_{-\alpha\beta\gamma} \gamma S_a S_{\beta} S_{\gamma}}{(\Omega_\alpha - \omega_1 - \omega_2 - \omega_3)(\Omega_\beta - \omega_2 - \omega_3)(\Omega_\gamma - \omega_3)} \right).n
\]

(1.27)

In (1.26,27) $S_\alpha$ is the sign of $\alpha$, $\Omega_\alpha$ is the excitation energy calculated from the linear response at the same time as $\mu_{\alpha\beta\gamma}$, $\mu_{\alpha\beta\gamma}$, $\mu_{\alpha\beta\gamma}$, $\mu_{\alpha\beta\gamma}$, $\mu_{\alpha\beta\gamma}$, $\mu_{\alpha\beta\gamma}$, and $V_{\alpha\beta\gamma}$ [29].
2.0 Summary

The focus of the discussion in this chapter is the definition and validation of the *a posteriori* Tamm-Dancoff approximation (ATDA). ATDA is validated through a direct comparison to experiment and other levels of theory including first principles calculations. The extraction of state to state transition dipoles from TD-DFT calculations implementing ATDA are also discussed here in.

2.1 Motivation

Accurate numerical values of transition dipoles between excited states of molecules are important for prediction of nonlinear photonic processes [30, 31] such as excited state absorption and two-photon absorption. States, involved in these processes, are often not observable in linear absorption spectra and appear to possess a strong double excited character [32-34]. The relation between two-photon absorption and other nonlinear optical (NLO) properties of ground states is provided by high order corrections to the induced dipole moment $\mathbf{p}$ in the SOS expressions derived within a perturbation theory approach [35]. *(See section 1.3)* Several authors [36-38] had noticed that first and second hyperpolarizability values, obtained for the linear polyenes at a semiempirical theory level within the SOS approach, are dominated by contributions from a few, so called “essential” states, so that all other states might be excluded from consideration. This approximation appeared attractive for structure-property relationship schemes [39, 40], but later *ab initio* studies [41, 42] reported it to be an oversimplification. This chapter investigates the
matter of implementing a more advanced correlation treatment, analyzes the structure of the higher excited states in details, and identifies approximations responsible for disagreements between different \textit{ab initio} approaches.

\subsection*{2.2 Theory}

Conjugated hydrocarbons (also known as polyenes) and their derivatives present an important class of compounds with rich photo-physical and photo-chemical properties. These properties originate from a highly polarizable $\pi$-electron system present in these compounds and find a wide use in organic electronics\cite{43} and photonics\cite{44} applications. Another reason for interest in electronically excited states of polyenes is their role in biological processes of vision and photosynthesis. Theoretical description of electronic structure and electronic excited states in conjugated molecules plays a critical role in understanding natural and engineered processes and may assist in the rational design of the new materials with improved properties.

Polyenes often serve as a testing ground for new theoretical methods and a comprehensive review of the published results seems to be an impossible venture. The consensus over the ordering of state symmetries seems to be that the lowest excited state $2A_g$ is above $1B_u$ (but close in energy) for all-trans butadiene and hexatriene and below the $1B_u$ state for larger hydrocarbons. Transition dipole moments between excited states of polyenes are much less studied and the double-excited nature of $2A_g$ states is still a matter of discussion \cite{45}. At the same time the double-excited nature of select excited states remain an important challenge to TD-DFT \cite{46}. These aspects of electronic structure, as well as the ability of TD-DFT methods to describe nonlinear properties of this type of molecular system, are the focus of the following study.
An alternative formulation of time-dependent perturbation theory for excited states is known as CEO the approach [28, 47]. (See section 1.6) CEO uses a density matrix (Liouville space) representation and is based on the Heisenberg equation of motion when looking for the ground state density. CEO was recently extended from HF to DFT methods [29].

When only terms of first order, in an external field perturbation, are retained an equation equivalent to LR formalism (1.18) is obtained. When considering second order terms the solutions are sought in the basis of LR transition densities. As a result, linear excitations remain unchanged in the quadratic formalism and combined states $\xi_\alpha^\beta \xi_\gamma^\delta$, of a double excited nature, are added to the picture. The excitation energy for each of these new states is the sum of single excitations:

$$\Omega_{a\beta} = \Omega_\alpha + \Omega_\beta$$

(2.1)

Second order CEO gives transition dipole terms between the ground and double excited states by

$$\mu_{a^\beta} = \sum_{a^\beta} perm Tr(\mu I - 2\rho)_{\xi_\alpha^\beta \xi_\gamma^\delta} + \sum_{\gamma > 0} \left( \frac{V_{a^\beta - \gamma} \mu_{\gamma}}{\Omega_\alpha + \Omega_\beta - \Omega_\gamma} \right)$$

(2.2)

In (2.2) the first summation runs over symmetrized permutations of the indexes and the second summation includes negative indexes. $I$ above is the identity matrix, $\rho$ is ground state density matrix, and $V_{a^\beta - \gamma}$ is an exchange-correlation coupling term, expressed via Kohn-Sham operators $V(\xi)$ on transition densities. The exchange-correlation coupling term is given by:

$$V_{a^\beta - \gamma} = \frac{1}{2} \sum_{a^\beta \gamma} Tr((I - 2\rho)_{\xi_\alpha^\beta \xi_\gamma^\delta} V(\xi_\gamma))$$

(2.3)

Further, transition dipoles between double excited states and any other excited state are zero, unless the other state presents one of the components of the double state:

$$\mu_{a^\beta} = \mu_\beta; \; \mu_{a^\beta} = 0$$

(2.4)
In the CEO formalism, state to state transition dipole moments between two single excited states, $\alpha \& \beta$, are given by:

$$\mu_{\alpha,\beta} = \sum_{-\alpha,\beta} \text{perm} \left[ \frac{1}{2} \sum_{\gamma > 0} \left( \frac{V_{-\alpha\beta\gamma} \mu_{\gamma}}{-\Omega_{\alpha} + \Omega_{\beta} - \Omega_{\gamma}} + \frac{V_{\alpha-\beta\gamma} \mu_{\gamma}}{\Omega_{\alpha} - \Omega_{\beta} - \Omega_{\gamma}} \right) \right] (2.5)$$

In second order CEO the first double excited state of $(\text{HOMO})^2 \rightarrow (\text{LUMO})^2$ type is always twice higher in energy than HOMO$\rightarrow$LUMO excited state and (unlike wavefunction based methods), it never mixes with higher lying single excitations.

Double excited states do not appear when TDA is invoked, and exchange-correlation coupling terms $V_{\alpha\beta\gamma}$ vanish. As a result, state-to-state transition dipole moments coincide with the ones obtained in the CIS method for TDA. State to state transition dipole moments are given by the first term on the RHS of (2.5) and are:

$$\mu_{\alpha,\beta} = \sum_{-\alpha,\beta} \text{perm} \left[ \frac{1}{2} \sum_{\gamma > 0} \left( \frac{V_{-\alpha\beta\gamma} \mu_{\gamma}}{-\Omega_{\alpha} + \Omega_{\beta} - \Omega_{\gamma}} + \frac{V_{\alpha-\beta\gamma} \mu_{\gamma}}{\Omega_{\alpha} - \Omega_{\beta} - \Omega_{\gamma}} \right) \right] (2.6)$$

A Tamm-Dancoff approximation (TDA) that annihilates the $Y$ component of transition density $a posteriori$ after the LR equation has been solved yields excitation energies and ground to excited transition dipole moments that remain unaffected while the CIS formula is applied to calculate state-to-state transition dipole moments. We will call this scheme the $a posteriori$ Tamm-Dancoff (ADTA) approximation. ATDA is a scheme that acts as an intermediate between TDA and full second order TD-DFT. It allows the calculation of second order properties without solving the equations of full QR-DFT by making a simple modification to existing LR codes. Next the effect of ATDA and TDA on transition dipoles between excited states is examined and compared in numerical values with the ones obtained from higher theory levels and experimental studies.
The simplest scheme of higher theory levels restricts expansion of the wavefunction to single substitutions (CI Singles, or CIS), another one limits the substitutions to singles and doubles (CISD). To reduce the computational effort, amplitudes for double substitutions can be evaluated perturbatively (instead of in a variational approach), resulting in the CIS(D) method [48]. When applied to the ground state, the method is known as MP2 (Moeller-Plesset second order perturbation theory). Second-order Algebraic Diagrammatic Construction, or ADC(2), presents yet another perturbation correction method, where the correction is applied to the matrix elements before solving CIS equations [49]. Some higher excitations may also be added to the wavefunction in the form of products of single and double excited configurations. This approach results in coupled cluster expansions (CCSD, CC2, etc.) [50]. At the moment the couple cluster methodology provides probably the best accuracy/cost ratio among wavefunction based methods. Configuration interaction methods, based on the couple cluster reference (SAC-CI)[51, 52] extend this treatment to the excited states. Both single and double (SD-R)[53] and up to six-order (General-R)[52] excitation truncation schemes have been developed. Both SD-R and General-R were shown to yield similar results for $2A_g$ state of trans-butadiene. This motivated adoption of the SAC-CI(SD-R) method as a benchmark \textit{ab initio} method to validate ATDA [54].

2.3 Computational details

This section will focus on the acquisition of state to state transition dipole moments. In linear response DFT (LR-DFT) they are readily obtained as a convolution of the dipole moment operator with the transition densities $\xi_\alpha$:

$$\mu_\alpha = \text{Tr}(\mu_\alpha \xi_\alpha)$$ \hspace{1cm} (2.7)

State-to-state transition dipoles $\mu_{\alpha\beta}$ do not appear in the LR approximation, unless the excited
state $\alpha$ is taken as the reference state. In order to obtain the expressions for $\mu_{a\beta}$ one has to extend
time dependent perturbation theory to Quadratic Response (QR).

For all SAC-CI and TD-B3LYP calculations the revision D.1 of Gaussian 2003 suite of
programs was used [55]. General-R, MaxR=2, and FullRGeneration options were used in the
SAC-CI method to include double excited states in the initial guess. State-to-state transition
dipole moments at the ATDA-B3LYP level were obtained with a locally modified version of
Gaussian 2003 (G’03) code. ATDA was implemented in modifications to G’03 by using
equation (2.6) with $\xi = \begin{bmatrix} X \\ 0 \end{bmatrix}$ instead of $\xi = \begin{bmatrix} X \\ Y \end{bmatrix}$ after the RPA LR equations (1.18) are solved.

These modifications were made to the SSDiag subroutine of of link 914 (I914.F) in Gaussian
2003 revision D. 01. The first modification included forcing this subroutine to output state to
state transition dipoles once the calculation was completed, in the case that the AllTransitions
keyword was used, by commenting out a variable that when rewritten did not allow the DoRPA
subroutine to be called. The second modification was made to the CISRho subroutine of I914.F.
This required that original counts in this section of code, normally running in iterations from the
$J^{th}$ state to the $I^{th}$ state, run from the $J^{th}$ state to the $I^{th}$. That is to say, to include transition
dipoles named $\mu_{ii}$ to be calculated and output in the standard log file. The third modification was
to set matrices $(X+Y)$ and $(X-Y)$, the standard format in which G’03 stores transition matrices, to
$(X)$ and $(Y)$, after allowing the program to solve the LR-DFT eigen-value problem. This was
accomplished by means of the programming the operations $(X+Y)-(X-Y) & (X-Y)+(X+Y)$ into
G’03 and replacing these vectors into the original addresses for $(X+Y)$ & $(X-Y)$). These were then
re-normalized and again sent to the same addresses that were previously occupied by $(X+Y)$ and
$(X-Y)$. Once these operations were carried out, a fourth and final modification was made, to
implement ATDA following the prescription presented above to approximate the eigen-vectors (transition densities) letting \((Y) \rightarrow 0\). NLOs of double excited states and single excited states in ATDA were then calculated by use of a new program coded by the author, external to G’03, that used transition dipole moments interpreted according to the formulas (2.2, 2.5) as discussed above [54].

2.4 Results and Discussion

The numerical results of ATDA are validated on 3 examples of all-trans hydrocarbons. The valence \(\pi \pi^*\)-excited states are considered to be primarily responsible for the second and higher order polarizabilities of conjugated hydrocarbons. Linear all-\(\text{trans}\) polyenes are planar molecules of \(C_{2h}\) symmetry, their \(\pi\)-orbitals belong to \(a_u\) and \(b_g\) irreducible representations. Configurations (Slater determinants) describing the electron transitions between the orbitals of the same symmetry contribute to \(A_g\) states, while transitions between the orbitals of different symmetry contribute to \(B_u\) states. Since the ground state is \(1A_g\), one-photon transitions to \(mB_u\) states are dipole-allowed and transitions to \(nA_g\) states are dipole-forbidden in the one-photon regime. In the two-photon regime transitions are forbidden to \(mB_u\) states, but are allowed to \(nA_g\) states.

The accuracy of ATDA vs SAC-CI(SD-R) were verified by [54] to describe the excited states in butadiene. The five lowest excited \(\pi \pi^*\)-states are presented on table 1 in agreement with previously published SAC-CI results [51, 52, 54]. Including the higher excited configurations (up to MaxR=4) does not have any appreciable effect on the excitation energies, compared to SD-R (MaxR=2) results. Increasing size of the basis set from DZp to QZ3p uniformly lowers the excitation energies by about 0.5 eV, in agreement with MRMP results [56]. The remaining stabilization energy of the excited states is close to 0.6 eV (as compared to the best high-level \(ab\)
Apparently the addition of diffuse and Rydberg functions to the basis set is necessary to recover more accurate values. The conclusion that the SAC-CI(SD-R)/DZp theory level overestimates the excitation energies by about 1eV for the lowest \( \pi\pi^* \)-states [54].

The results for the singlet \( \pi\pi^* \)-states of butadiene, hexatriene, and octatetraene are presented in tables 1-3 [54]. The Slater determinants, combined to form excited states, were analyzed and major contributions were tabulated. In short notation, (1-1’) correspond to HOMO \( \rightarrow \) LUMO transitions, (1-2’) corresponds to HOMO \( \rightarrow \) LUMO+1, etc. and a comparison of the major configurations in the SAC-CI and ATDA-DFT states show that there is a 1 to 1 correspondence between the two. Observations for \( A_g \) states show a large transition dipole from the \( 1B_u \) state. For \( mB_u \) states, transition dipoles from the ground state are much lower.

The double-excited nature of \( 2A_g \) in the linear polyenes is well described at the TD-B3LYP level of theory. Excitation energies obtained in time-dependent density functional theory, even with the modest DZp basis sets, are in good agreement with published high-level \textit{ab initio} values [54]. This confirms that the same electron correlation effects, which are described by double excited configurations in the wavefunction, are accounted for by the approximate exchange-correlation functional B3LYP.

Much higher (40-80%) contributions of the doubly excited configurations are observed in some of the higher-lying states. Excitation energies of these states are very close to the sum of the excitation energies of the respective predominantly single excited states. These states, again, are well reproduced by TD-DFT, but entirely missing in the list of CIS and CIS(D) states [54]. Double excited states are not present in the output of standard computer codes implementing TD-
DFT in linear response. They were added to the code according to (2.4-6) simplified with \textit{a posteriori} Tamm-Dancoff approximation.

Transition dipole moments calculated with ATDA-DFT are in better agreement with SAC-CI valued than CIS ones. They also compare favorably with QR-DFT results. While ground to \textit{mB}_u transition dipole moments are the same at ATDA and QR-DFT methods (being LR values), \textit{1B}_u to \textit{nA}_g transition dipoles are shown to be different [54]. \textit{nA}_g states of mostly single excited character are bright in SAC-CI, darker with ATDA, and even darker with QR. Covalent states of mostly double excited character are completely absent in QR, but their transition dipoles are borrowed by other states close in energy. In Octatetraene as many as four states borrow their intensity from this missing double excitation and need to be added together for fair comparison with SAC-CI. Even with this in mind, ATDA values are still closer to SAC-CI ones [54]. The absorption spectrum of a \textit{1B}_u state in octatetraene is determined to be dominated by the \textit{2A}_g state and higher \textit{nA}_g states with twice as large transition dipole and an energy nearly twice that of the energy of the \textit{1B}_u state. This is well reproduced by the second order TD-DFT/CEO formalism, and closely approximated by the ATDA method [54].
Table 1: Excitation energies $\Delta E$ (eV), major contributing configurations of all-trans butadiene, and % contributions of the leading double excited configurations for the lowest $\pi$-states. Transition dipoles $\mu$ (a.u.), form the ground state to Bu states, and from 1Bu to Ag states are also reported. All basis sets are DZp, unless noted otherwise.

<table>
<thead>
<tr>
<th>State</th>
<th>$\Delta E$, eV</th>
<th>Configurations</th>
<th>$\Delta E$, eV</th>
<th>CIS</th>
<th>Configurations</th>
<th>%D</th>
<th>$\Delta E$, eV</th>
<th>Configurations</th>
<th>ATDA-B3LYP</th>
<th>QR-B3LYP</th>
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</thead>
<tbody>
<tr>
<td>1Bu</td>
<td>6.66</td>
<td>(1-1')</td>
<td>2.661</td>
<td>6.77</td>
<td>(1-1')</td>
<td>0</td>
<td>2.291</td>
<td>(1-1')</td>
<td>5.94</td>
<td>2.131</td>
</tr>
<tr>
<td></td>
<td>12.15</td>
<td>(2-2')</td>
<td>0.784</td>
<td>11.33</td>
<td>(2-2')+(11-1'2')</td>
<td>2</td>
<td>0.874</td>
<td>(2-2')+(1-2')(1-1')(2-1')</td>
<td>10.33</td>
<td>0.706</td>
</tr>
<tr>
<td></td>
<td>15.31</td>
<td>(11-1'2')-(12-1'1')</td>
<td>78</td>
<td>0.170</td>
<td></td>
<td></td>
<td>(11-1'2')-(12-1'1')</td>
<td>14.51</td>
<td>1'')</td>
<td>-</td>
</tr>
<tr>
<td>2Ag</td>
<td>9.66</td>
<td>(1-2')+2-1')</td>
<td>2.682</td>
<td>9.95</td>
<td>(2-1')+1-2'-(11-1'1')</td>
<td>13</td>
<td>1.695</td>
<td>(2-1')+1-2'-(11-1'1')</td>
<td>7.11</td>
<td>1.845</td>
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<tr>
<td></td>
<td>9.03</td>
<td>(1-2')-(2-1')</td>
<td>0.112</td>
<td>9.28</td>
<td>(1-2')-(2-1')</td>
<td>0</td>
<td>0.306</td>
<td>(1-2')-(2-1')</td>
<td>8.57</td>
<td>0.086</td>
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<tr>
<td>3Ag</td>
<td>-</td>
<td>(2-1')+1-2'-(11-1'1')</td>
<td>53</td>
<td>2.698</td>
<td></td>
<td></td>
<td>(2-1')+1-2'-(11-1'1')</td>
<td>11.89</td>
<td>(1-1')(1-1')</td>
<td>2.131</td>
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<tr>
<td></td>
<td>-</td>
<td>(12-1'2')+(22-1'1')+(11-1'2')</td>
<td></td>
<td>16.71</td>
<td>2-2'</td>
<td>83</td>
<td>0.557</td>
<td>(1-1')(2-2')</td>
<td>16.28</td>
<td>0.706</td>
</tr>
<tr>
<td>3Ag</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>(1-1')(2-2')</td>
<td>0.706</td>
<td>-</td>
<td>(1-1')(2-2')</td>
<td>0.706</td>
<td>-</td>
</tr>
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Table 2: Excitation energies $\Delta E$ (eV), major contributing configurations of all-trans hexatriene, and % contributions of the leading double excited configurations for the lowest $\pi$-states of all-trans hexatriene. Transition dipoles $\mu$ (a.u.), form the ground state to Bu states, and from 1Bu to Ag states are also reported. All basis sets are DZp.

<table>
<thead>
<tr>
<th>State</th>
<th>CIS</th>
<th>CIS(D)</th>
<th>SAC-CI(SD-R)</th>
<th>ATDA-B3LYP</th>
<th>QR-B3LYP</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta E, eV$</td>
<td>configurations</td>
<td>$\mu, \text{a.u.}$</td>
<td>$\Delta E, eV$</td>
<td>configurations</td>
</tr>
<tr>
<td>1Bu</td>
<td>5.59 (1-1')</td>
<td>2.353</td>
<td>5.62 (1-1')</td>
<td>0</td>
<td>3.108</td>
</tr>
<tr>
<td>2Bu</td>
<td>9.05 (1-3')(3-1')(2-2')</td>
<td>0.31</td>
<td>9.2</td>
<td>7.28 (3-1')(1-3')</td>
<td>7</td>
</tr>
<tr>
<td>3Bu</td>
<td>9.57 (3-1')(2-3')</td>
<td>0.13</td>
<td>7.76</td>
<td>9.19 (3-1')(1-3')</td>
<td>0</td>
</tr>
<tr>
<td>4Bu</td>
<td>11.32 (2-2')(3-3')</td>
<td>0.581</td>
<td>10.13</td>
<td>10.46 (2-2')</td>
<td>2</td>
</tr>
<tr>
<td>5Bu</td>
<td>14.30 (2-2')(3-3')</td>
<td>0.578</td>
<td>11.85</td>
<td>12.7 (3-3')</td>
<td>4</td>
</tr>
<tr>
<td>2Ag</td>
<td>8.58 (1-2')(2-1')</td>
<td>3.705</td>
<td>6.91</td>
<td>6.38 (1-2')(2-1')(11-11')</td>
<td>12</td>
</tr>
<tr>
<td>3Ag</td>
<td>7.99 (1-2')(2-1')</td>
<td>0.779</td>
<td>7.9</td>
<td>8.08 (1-2')(2-1')</td>
<td>0</td>
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<tr>
<td>4Ag</td>
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<td>0.387</td>
<td>10.84</td>
<td>10.45 (2-3')(3-2')</td>
<td>8</td>
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<tr>
<td>5Ag</td>
<td>11.12 (2-1')(1-2')(11-11')</td>
<td>45</td>
<td>4.033</td>
<td>9.60 (1-1')(1-1')</td>
<td>3.108</td>
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<td>6Ag</td>
<td>11.67 (2-3')(3-2')</td>
<td>0.105</td>
<td>10.73</td>
<td>11.16 (3-2')(2-3')</td>
<td>1</td>
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Table 3: Excitation energies $\Delta E$ (eV), major contributing configurations of all-trans octatetraen,
and % contributions of the leading double excited configurations for the lowest $\pi$-states. Transition dipoles $\mu$ (a.u.) form the ground state to Bu states, and from 1Bu to Ag states are also reported.

<table>
<thead>
<tr>
<th>State</th>
<th>$\Delta E$, eV</th>
<th>CIS configurations</th>
<th>$\Delta E$, eV</th>
<th>CIS(D) configurations</th>
<th>$\Delta E$, eV</th>
<th>SAC-CI(SD-R) configurations</th>
<th>$%D$</th>
<th>$\mu$, a.u.</th>
<th>ATDA-B3LYP $\Delta E$, eV</th>
<th>configurations</th>
<th>$\mu$, a.u.</th>
<th>QR-B3LYP $\Delta E$, eV</th>
<th>configurations</th>
<th>$\mu$, a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Bu</td>
<td>4.89</td>
<td>(1-1')-(2-2')</td>
<td>4.333</td>
<td></td>
<td>4.89</td>
<td>(1-1')</td>
<td>0</td>
<td>3.108</td>
<td>4.09</td>
<td>(1-1')</td>
<td>3.816</td>
<td>-</td>
<td>-</td>
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<td></td>
<td>4.78</td>
<td>(1-1')</td>
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<td></td>
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2.5 Review

A simplified approach to calculate state to state transition dipole moments within TD-DFT was developed and implemented as a modification in existing computer code. The ATDA was defined and shown to yield excitation energies and ground to excited transition dipole moments that remain unaffected while the CIS formula is applied to calculate state-to-state transition dipole moments. Numerical values for linear polyenes were shown to be in good agreement with higher levels of theory and experimental results for the ATDA approximation.
CHAPTER III
QUANTITATIVE SIMULATIONS OF TWO PHOTON ABSORPTION PROFILES

3.0 Summary

The focus of the discussion in this chapter revolves around the calculation of two photon absorption profiles. A brief background to two photon absorption and its applications are presented. Experimental results from studies found in the literature for two photon absorption cross-sections are compared to those calculated in the 2PA transition matrix formalism and the CEO formalism. Structure activity relationships for states exhibiting 2PA are also discussed.

3.1 Background and Applications

Two-photon absorption (2PA) is an electronic excitation process involving simultaneous absorption of two photons. 2PA probability is quadratically dependent on the intensity of incident light, so it may be localized in space with a tightly focused laser beam. There are a wide range of 2PA applications, such as lithographic micro-fabrication, three dimensional data storage, photonic devices [1], quantum information technology [2], optical limiting, two-photon pumped lasing in organic chromophores and quantum dots [2, 3], in-vivo imaging, and cell-selective photo-dynamic therapy [3]. Most applications require chromophores with large 2PA cross-sections to minimize laser intensity requirements and prevent overheating of targets [1]. To design more efficient TPA chromophores, it is important to understand their structure/activity relationships (SAR). Computer modeling of 2PA spectra facilitates understanding of these
relationships [40] and represents a rational approach that may accelerate progress in chromophore design.

Recently, Time Dependent Density Functional Theory (TD-DFT) was successfully used to simulate 2PA electronic spectra in large conjugated molecules [6, 58, 59]. This approach was shown to achieve superior accuracy for 2PA excitation energies, when compared to semiempirical wave function theory methods. We describe the couple electronic oscillator (CEO) formalism in Section 2. Approximations to the high order TD-DFT formalism are also mentioned. The tools used for implementation of the third order CEO at TD-DFT level are detailed in the computational details section.

Approximate state to state transition dipole moments were used to identify the essential states governing the 2PA process and evaluate the accuracy of few-state SOS models against CEO results, neglecting contributions from all the other states. The results of this interpretation are described below, along with simulated profiles and relationship between the electronic-structure given over states exhibiting large 2PA absorption cross-sections. The results of the present study and directions for future work are outlined in the results section.

The probability of one-photon absorption (1PA) depends linearly on the intensity of the incident light:

\[ P_{1PA} = t \cdot \sigma_{OPA} \cdot \frac{I}{h\omega} \]  

(3.1)

In this equation \( I \) is intensity, \( h \) is Planck's constant, \( \omega \) as the frequency of the beam, \( t \) is the time of exposure, and \( \sigma_{OPA} \) is the cross-section. In 1PA, the absorption cross-section describes the ability a molecule has to absorb light linearly with respect to the incident flux of photons. This linear cross-section is verbally defined as:
In contrast to 1PA, two-photon absorption (2PA) is an electronic excitation process involving the simultaneous absorption of two photons. 2PA is a non-linear process, which is quadratically dependent on the intensity of light incident on a molecule:

\[
P_{2PA} = I \cdot \sigma_{2PA} \cdot \frac{I^2}{\hbar \omega}
\]

In this case, the non-linear cross-section describes the ability of a molecule to absorb light as dependent on the square of the incident flux of photons. This non-linear cross-section may be described as:

\[
\frac{\partial \sigma}{\partial \omega} = \frac{\text{Absorbed Irradiance/Solid Angle}}{\text{Incident Irradiance/Area}}
\]

The quadratic dependence of 2PA probability allows for spatial localization of the absorption and subsequent processes (such as emission or photo-reactivity) with a tightly focused laser beam.

### 3.2 Motivation

To design more efficient 2PA chromophores, it is important to understand their structure/activity relationships (SAR). Computer simulations of 2PA spectra facilitate understanding of these relationships [40] and represent a rational approach that may accelerate progress in chromophore design. Accurate predictions of 2PA spectral profiles would greatly assist in the design of more effective 2PA chromophores while eliminating poor candidates from the synthetic pipeline. The goal of this study is improvement in quantitative predictions of 2PA.
Molecular absorption cross-sections are proportional to the imaginary part of their respective frequency-dependent polarizability [6]. In the case of 1PA, the cross-section is defined by the first order (linear) polarizability:

$$\sigma_{1PA} = \frac{4\pi\hbar\omega}{\eta c} \Im(\alpha(-\omega;\omega_1))$$

(3.3)

The linear polarizability $\alpha$, given by Expression 1, is obtained from perturbation theory. In turn, the third-order polarizability (second hyperpolarizability) that defines two-photon absorption cross-section is given by:

$$\sigma_{TPA} = \frac{4\pi^2\hbar\omega^2}{\eta^2 c^2} L^4 \Im(\gamma(-\omega;\omega,\omega,-\omega))$$

(3.4)

In this expressions $\omega$ is the optical frequency of the beam, $\eta$ is a dielectric constant, $c$ is the speed of light in vacuo, $\hbar$ is Planck's constant, and $\gamma$ is the third order polarizability tensor.

**3.3 Theory**

Within the CEO formalism, the third order polarizability tensor is given by the expression presented in figure 3 of section 1.6 from [29] and the SOS expression is presented in (1.17) of section 1.3 [8]. In the SOS formalism the 2PA cross-section may be approximated by implementing the 2PA cross-section amplitude derived from the 2PA transition matrix. The 2PA transition matrix approximation of the 2PA cross-section is given by:

$$\sigma_{TPA} = \frac{8\pi^3\omega^2}{c^2} \langle |M_{JJ}^{(2)}|^2 \rangle g(2\omega)$$

(3.5)

Where $g(2\omega)$ is a Lorentzian line shape [60, 61]. In (3.5) $\langle |M_{JJ}^{(2)}|^2 \rangle$ is the orientationally averaged 2PA probability given by [61, 62]:

29
\[
\left\langle |M_{jk}^{(2)}|^2 \right\rangle = \frac{1}{15} \sum_{a,b}^{3} \left( M_{aa} M_{bb}^* + 2M_{ab} M_{ab}^* \right) \quad (3.6)
\]

In (3.6) \(M_{ab}\) is an element of the 2PA transition matrix given by:

\[
M_{ij} = \frac{1}{2\hbar} \sum_{k}^{N} \left( \frac{\mu_{jk}^i \mu_{kg}^j + \mu_{jk}^j \mu_{kg}^i}{\omega_{kg} - \omega - i\frac{\Gamma}{\hbar}} \right) \quad (3.7)
\]

Here \(g, k, f\) represent few states which contribute strongly to the 2PA effect in an approximation referred to as “few state models” in the literature [61, 63].

### 3.4 Computational Details

The conjugated chromophores selected as the subjects of study are presented in **table 4**. These chromophores were derived from experimentally studied ones by truncation of the aliphatic chains to methyl groups. The abbreviations of the model molecules and the systematic names of the corresponding experimentally studied ones are: **BzFBz**: 2,7-Bisbenzothiazolyl-9,9-didecylfluorene; **BzFDp**: (7-benzothiazol-2-yl-9,9-didecylfluoren-2-yl)diphenylamine; **DpFDp**: 9,9-didecyl-2,7-bis(N,N-phenylamino)-fluorene; **BzPFPBz**: 2,7-Bis[4-(9,9-didecylfluoren-2-yl)vinyl]-phenylbenzothiazole; **(DpFPBz)**: (7-[2-(4-Benzothiazol-2ylphenyl)vinyl]-9,9-didecylfluorene-2yl)diphenylamine.
Table 4: Studied Conjugated Chromophores

*Molecules studied; from top to bottom BzFDp; BzFBz; DpFDp; BzPFPBz; DpFPBz*

Studies of these conjugated chromophores implemented SOS in the 2PA transition matrix formalism with and without double excited states in ATDA as well as CEO. All molecular structures that were optimized at HF/STO-3G theory level are shown in figure 4. HF/STO3G favors planar geometry of conjugated molecules and was shown to give the best agreement for the bond lengths as compared to the results of X-Ray diffraction experiments for stilbene [64] and its three derivatives [6]. The optimized geometries were confirmed by the absence of imaginary frequencies in the following normal mode calculations. Two essential excited states were optimized at CIS/STO-3G level, which was shown [64] to describe the important focal...
points on the potential energy surface of stylobene in good agreement with high level \textit{ab initio} predictions due to fortuitous cancellation of errors.

Figure 1: Molecule Optimized Geometries
Molecules optimized at the HF/STO-3G level. From top to bottom BzFDp; BzFBz; DpFDp; BzPFPBz; DpFPBz

The first excited state S1 was always among the essential states of interest. The second essential state Sn was identified by large value of transition dipole moment with either S1 (for symmetric molecules BzFBz, BzPFPBz and DpFDp) or S0 (for asymmetric molecules DpFBz and DpFPBz). The active space was limited to 40 electrons on 40 orbitals. Both ground and excited states of molecules were optimized on the assumption of highest possible symmetry ($C_{2v}$ for BzFBz and BzPFPBz and $C_2$ for DpFDp). Symmetry was confirmed by comparing the total
energies with the results of optimization with no symmetry constraints. The single point energy and transition dipole calculations were performed at TD-DFT/MIDIx levels.

A TD-DFT approach was used to simulate the 1PA and 2PA absorption profiles. The B3LYP exchange-correlation functional was used in combination with MIDI! basis set, which uses polarization basis functions on hetero-atoms [65, 66]. Transition density matrices for the 24 lowest excited states, as well as Kohn-Sham operators on these transition densities were printed out. Contributions of the second and third derivatives of the exchange-correlation potentials into Kohn-Sham operators, and operators on the pair combinations of transition densities were neglected. A modified version of Gaussian 98 A11 [67] was implemented, as described in previous studies [6], in order to enable this printout. The frequency-dependent orientationally averaged first- and third-order polarizability tensors were generated from the transition matrices using expression 3, as implemented in CEO program [28]. SOS 2PA cross-sections for single and double excitations were implemented via a 2PA transition matrix with the use of a Lorentzian line shape. These calculations were carried out via the development of a new piece of software. This new code utilizes as input the print out of a version of Gaussian 2003 D1 [55] modified to carry out ATDA calculations and output single and double excited state to state transition dipole moments. A habitual empirical line width of 0.1 eV was used for both 1PA and 2PA. Natural Transition Orbitals (NTOs), which diagonalize the transition density matrix and give the best representation of the electronic excitation in single-particle terms [68], were used to analyze the electronic structure of the excited states we used. In the molecules studied, the highest occupied NTO (HOTO) and lowest unoccupied NTO (LUTO) were found to make 90-96% of the contributions to the transition density matrices. For this reason, only HOTO and
LUTO are reported for each excited state of interest. The graphical software XCrysDen [69] was used to plot NTOs.

3.5 Results and Discussion

The predicted, CEO and 2PA transition matrix with single and double excitations, linear and two-photon absorption profiles are presented in Figs. 5-10. The experimental measurements of these conjugated chromophores, reported previously [70-72] are also shown for comparison along with NTOs for select states. The resonant maxima are listed in Table 5. NTO’s were calculated and plotted for the states in resonance with 2PA maxima for all 5 molecules (Figures 5-10) to discuss the nature of 2PA excitations in the chromophores studied. The NTOs can be interpreted as describing charge transfer upon the electronic excitation of the molecule from the highest occupied transition orbitals (HOTO) to the lowest unoccupied transition orbitals (LUTO). From the NTO plots the charge redistribution upon 2PA excitation is visible from the terminal groups to the Fluorine core. Although this redistribution is in agreement with electron donating nature of Dimethylamino groups, it is rather counterintuitive considering electron withdrawing nature of Benzothiazolyl groups. The seeming contradiction is resolved when considering that the higher excitation (to states S3 and S4) is responsible for 2PA transition. While electron transfer during 1PA transition follows an intuitive direction, 2PA transition may be thought of as associated with the re-donation of an electron. The simulated linear and two-photon absorption profiles (Figs. 5-10) agreed well with experimental data. For the most molecules the agreement between the resonant wavelength maxima is better than 10 nm, better than 0.1 eV. For the case of DpFPBz the predicted maxima are red-shifted by relative to experimental maxima by approximately 0.44 eV (55 nm) for both 1PA and 2PA spectra. Typically, longer chains of conjugated bonds result in lower excitation energies and red shifts of
resonance maxima on electronic spectra, relative to shorter-chain analogs. This is qualitatively explained by simple model of particle in the box of increasing length. Spectra of \textit{BzPFPBz} and \textit{BzFBz} chromophores exemplify this trend. In the contrast, \textit{BzFDp} and \textit{DpFPBz} chromophores have resonance maxima on both 1PA and 2PA spectra at approximately the same wavelength. A sum over states formalism was used to describe states that strongly contribute to 2PA according to the relative strength of their corresponding transition dipole moments and are reported in tables 1 & 2.

In order to investigate and explain the apparent contradiction to the general trend by the case of \textit{DpFPBz}, the conformational flexibility of this chromophore was evoked and a calculation of the adiabatic transition energies carried out; the adiabatic transition energies are defined by the difference between the ground and excited state energies both taken in their respective equilibrium geometries. In order to verify the hypothesis that the conformational flexibility of the chromophore was responsible for the discrepancy, three rotational degrees of freedom were identified to study the effect of non-planarity of the chromophore. The three rotational degrees for freedom expected to be flexible for \textit{DpFPBz} are shown in figure 10. A representative conformational ensemble of \textit{DpFPBz} rotamers was generated by twisting each dihedral from 0 to 90 degrees in a 5 degree incremental step. The second dihedral was found to have the most profound effect on the predicted spectral bands. \textit{Figures 11 and 12} show predicted 1PA spectra for each rotamer along the second dihedral. According to these figures, experimentally observed spectra can be explained by an increased intensity of new bands and decrease in intensity of the existing bands. This behavior is observed for conformations between 60 and 80 degrees.
The estimated contributions of each rotamer according to an equilibrium Boltzmann distribution is presented in figure 13. At HF/6-31G* theory level, the most probable value of the dihedral angle around bond 3 is 0 (planar conformation), while the dihedral angles around bonds 1 and 2 have the most probable values of approximately 23 degrees. The contributions of 60 to 80 degree twisted rotamers are insignificantly low. The theoretical spectra averaged over the conformal ensemble with these rotamer concentrations is not significantly different from the spectrum of the planar conformer (not shown). As a result, rotamer energies at HF/6-31G* theory level are insufficient to explain discrepancies between theoretical and experimental spectra. It is possible that these differences can be explained by taking into account the effect of simultaneous rotation around two or three bonds, and/or solvent effects. This work is presently in progress.
Results for BzFBz. Top panel: calculated 1PA (left) and 2PA (right) profiles represented by solid lines and experimental measurements are represented by diamonds. Bottom panels: NTO plots for the excited states S1 and S4, corresponding to 1PA and 2PA resonances respectively. Experimental profiles were obtained from [71].
Figure 3: BzFDp 1PA, 2PA, NTO properties

Results for BzFDp. Top panel: calculated 1PA (left) and 2PA (right) profiles represented by solid lines and experimental measurements are represented by diamonds. Bottom panels: NTO plots for the excited states S1 and S3, corresponding to 1PA and 2PA resonances respectively. Experimental profiles were obtained from [72].
Figure 4: DpFDp 1PA, 2PA, NTO properties

Results for DpFDp. Top panel: calculated 1PA (left) and 2PA (right) profiles represented by solid lines and experimental measurements are represented by diamonds. Bottom panels: NTO plots for the excited states S1 and S3, corresponding to 1PA and 2PA resonances respectively. Experimental Profiles were obtained from [72].
Results for BzPFPBz. Top panel: calculated 1PA (left) and 2PA (right) profiles represented by solid lines and experimental measurements are represented by diamonds. Bottom panels: NTO plots for the excited states S1 and S2, corresponding to 1PA and 2PA resonances respectively. Experimental profiles were obtained from [70] and [73].
Figure 6: DpFPBz 1PA, 2PA, NTO properties

Results for DpFPBz. Top panel: calculated 1PA (left) and 2PA (right) profiles represented by solid lines, and experimental measurements are represented by diamonds. Bottom panels: NTO plots for the excited states S1 and S2, corresponding to 1PA and 2PA resonances respectively. Experimental Profiles were obtained from [70] and [73].
Table 5: Numerical 2PA Cross-Sections for 5 conjugated Chromophores

Energies, absorbance, and cross-sections for the linear and 2PA absorbing states in the molecules studied. Energy measured in eV, 2PA Cross Sections in GM, and wavelengths in nm.

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Table 6: Essential States & Transition Dipoles for 5 conjugated chromophores
states (α,β), symmetries, wavelengths, energy differences (ΔE), and transition dipoles (μ, a.u. ≈ 2.3D) studied at ATDA-B3LYP/MIDIx//HF/STO-3G theory level.

| α | β | Symmetry | ΔE_{αβ}, eV | λ_{β}, nm | (μ_{αβ})_x, a.u. | (μ_{αβ})_y, a.u. | (μ_{αβ})_z, a.u. | |μ_{αβ}|, a.u. |
|---|---|----------|-------------|-----------|----------------|----------------|----------------|--------------|
| S0 | S1 | B2 | 3.5904 | 345.27 | 0.0000 | -4.3856 | 0.0000 | 4.3856 |
| S1 | S2 | A1 | 4.2289 | 293.14 | 0.0000 | 1.4393 | 0.0000 | 1.4393 |
| S1 | S4 | A1 | 4.2767 | 289.87 | 0.0000 | -4.8998 | 0.0000 | 4.8998 |

BzFBz

| Symmetry | ΔE_{αβ}, eV | λ_{β}, nm | (μ_{αβ})_x, a.u. | (μ_{αβ})_y, a.u. | (μ_{αβ})_z, a.u. | |μ_{αβ}|, a.u. |
|----------|-------------|-----------|----------------|----------------|----------------|--------------|
| S0 | S1 | A | 3.0766 | 402.94 | 3.1011 | 0.0610 | -0.0114 | 3.1017 |
| S0 | S3 | A | 4.0974 | 302.55 | -2.2573 | -0.4189 | 0.0062 | 2.2958 |
| S0 | S4 | A | 4.1207 | 300.84 | -1.0477 | 1.3394 | -0.2805 | 1.7235 |
| S0 | S5 | A | 4.1989 | 295.24 | -1.4262 | 0.1916 | 0.2337 | 1.4579 |
| S1 | S3 | A | 4.0974 | 302.55 | 3.5143 | 0.1342 | -0.0411 | 3.5171 |
| S1 | S4 | A | 4.1207 | 300.84 | 1.1000 | -0.3755 | 0.0856 | 1.1655 |
| S3 | S4 | A | 4.1207 | 300.84 | 1.0865 | 0.7010 | -0.0798 | 1.2955 |

BzFDp

| Symmetry | ΔE_{αβ}, eV | λ_{β}, nm | (μ_{αβ})_x, a.u. | (μ_{αβ})_y, a.u. | (μ_{αβ})_z, a.u. | |μ_{αβ}|, a.u. |
|----------|-------------|-----------|----------------|----------------|----------------|--------------|
| S0 | S1 | B | 3.3841 | 366.32 | -0.0467 | 3.5284 | 0.0000 | 3.5287 |
| S0 | S5 | B | 4.0102 | 309.13 | 1.1756 | 0.3474 | 0.0000 | 1.2259 |
| S0 | S6 | A | 4.0107 | 309.09 | 0.0000 | 0.0000 | 1.3743 | 1.3743 |
| S1 | S3 | A | 3.8556 | 321.53 | 0.0422 | 3.5412 | 0.0000 | 3.5415 |
| S1 | S15 | A | 4.6025 | 269.35 | 0.0546 | 2.0276 | 0.0000 | 2.0283 |
| S5 | S11 | A | 4.5036 | 275.26 | -0.4029 | 0.9241 | 0.0000 | 1.0081 |
| S5 | S14 | A | 4.5630 | 271.68 | 0.2486 | 3.4655 | 0.0000 | 3.4744 |
| S5 | S6 | A | 4.0107 | 309.09 | -0.0004 | 3.4380 | 0.0000 | 3.4380 |
| S6 | S13 | B | 4.5599 | 271.86 | -0.0381 | 3.4660 | 0.0000 | 3.4662 |
| S6 | S15 | A | 4.6025 | 269.35 | 0.0000 | 0.0000 | 1.0307 | 1.0307 |

BzPFPBz

| Symmetry | ΔE_{αβ}, eV | λ_{β}, nm | (μ_{αβ})_x, a.u. | (μ_{αβ})_y, a.u. | (μ_{αβ})_z, a.u. | |μ_{αβ}|, a.u. |
|----------|-------------|-----------|----------------|----------------|----------------|--------------|
| S0 | S1 | B2 | 3.0613 | 404.95 | 6.3633 | 0.0001 | 0.0000 | 6.3633 |
| S0 | S4 | B2 | 3.9882 | 310.84 | -3.0797 | -0.0001 | 0.0000 | 3.0797 |
| S1 | S2 | A1 | 3.4601 | 358.28 | 7.0643 | 0.0001 | 0.0000 | 7.0643 |
| S1 | S3 | A1 | 3.7247 | 332.82 | 2.9295 | 0.0000 | 0.0000 | 2.9295 |
| S4 | S10 | A1 | 4.3938 | 282.14 | 1.1448 | 0.0001 | 0.0000 | 1.1448 |
| S4 | S11 | A1 | 4.4548 | 278.28 | -5.9306 | -0.0001 | 0.0000 | 5.9306 |
| S4 | S13 | A1 | 4.5562 | 272.08 | 3.5097 | 0.0000 | 0.0000 | 3.5097 |
| S4 | S14 | A1 | 4.5622 | 271.73 | -2.4774 | 0.0000 | 0.0000 | 2.4774 |

DpFPBz

| Symmetry | ΔE_{αβ}, eV | λ_{β}, nm | (μ_{αβ})_x, a.u. | (μ_{αβ})_y, a.u. | (μ_{αβ})_z, a.u. | |μ_{αβ}|, a.u. |
|----------|-------------|-----------|----------------|----------------|----------------|--------------|
| S0 | S1 | A | 2.8316 | 437.80 | 3.5821 | 0.0408 | 0.0006 | 3.5823 |
| S0 | S2 | A | 3.5616 | 348.07 | -4.2364 | 0.0480 | 0.0497 | 4.2370 |
| S0 | S5 | A | 4.0942 | 302.79 | -0.2784 | 1.3615 | -0.3534 | 1.4339 |
| S1 | S2 | A | 3.5616 | 348.07 | 5.0199 | 0.0802 | 0.0146 | 5.0206 |
| S1 | S3 | A | 3.6703 | 337.76 | -1.4908 | 0.3444 | 0.1709 | 1.5396 |
| S2 | S3 | A | 3.6703 | 337.76 | -1.7347 | -0.0408 | -0.0241 | 1.7353 |
| S2 | S6 | A | 4.2465 | 291.93 | 1.4593 | 0.0301 | -0.0365 | 1.4601 |
| S2 | S8 | A | 4.2734 | 290.09 | 5.4800 | -0.1812 | -0.0822 | 5.4836 |
| S2 | S9 | A | 4.3776 | 283.19 | 2.6735 | 0.0083 | -0.0617 | 2.6742 |
| S2 | S12 | A | 4.5091 | 274.93 | -1.6377 | 0.0754 | 0.0040 | 1.6394 |
**Figure 7: Rotamers of DpFPBz**

Flexible dihedral angles used to generate rotamer ensemble for chromophore DpFPBz in order to account for thermal broadening effects.

**Figure 8: 0 to 55 degree twist for DpFPBz**

Calculated linear absorption profiles for conformers of molecule DpFPBz corresponding from 0-55.

**Figure 9: 60 to 80 degree twist for DpFPBz**

Calculated linear absorption profiles for conformers of molecule DpFPBz corresponding from 60-80 degrees twist about Bond 2. Figures 8 and 9 are separated for clarity.
Figure 10: DpFPBz rotamer Boltzmann weighting factors

Boltzmann weights for the DpFPBz rotamer ensemble at HF/6-31G* theory level. Varying dihedral angles for three bonds are defined above.
3.4 Review

2PA absorption profiles calculated in the 2PA transition matrix formalism within ATDA were shown to be close to CEO results and both were qualitatively comparable to experiment. It was also shown that ATDA double excitations affect 2PA profiles more significantly close to 1PA resonance. It was observed that there was a somewhat systemic decrease across resonant 2PA cross-sections when comparing CEO results those predicted by the 2PA transition matrix formalism. The systematic decrease may be due in part or in whole to the nature of the 2PA matrix formalism or an underestimation of state to state transition dipole moments in ATDA. Further investigations into this effect are in progress. From the rotamer study carried out for DpFPBz it can be concluded that the distortion of the molecular geometry along the selected rotamers from planar geometry does not account for the ~50nm deviation observed with respect to experimental excitation energies of resonant maxima for its 1PA and 2PA profiles. Further efforts that implement Franck-Condon factors and adiabatic excitations instead of vertical excitation are underway in this area to account for the deviation.
4.0 Summary

In this chapter the SOS formalism is applied in the form of the 2PA transition matrix to predict the two-photon anisotropy ($r_{2\text{PA}}$) spectra of BzFBz. Predicted $r_{2\text{PA}}$ values are then compared to a previous experimental study the anisotropy for this chromophore. A short discussion on $r_{2\text{PA}}$ and the experimental study focused on the $r_{2\text{PA}}$ of BzFBz is also presented. The discussion is then followed by the results from the predicted $r_{2\text{PA}}$ utilizing the information generated by an ATDA modified version of Gaussian 2003. The results are shown to be in good agreement with experimental $r_{2\text{PA}}$ spectra; predicted to be approximately constant with respect to wavelength across the 2PA range, if no essential state approximation is made. A previous explanation involving vibronic coupling and ground state symmetry breaking is shown to no longer be necessary to explain experimental observations.

4.1 Motivation & Background

Studies of chromophores that exhibit strong 2PA are currently an area of research under active development. Though there has been progress in the study of structure–activity relationships of organic molecules more studies are necessary to understand the NLO’s of conjugated chromophores. Recently a theoretical approach to investigate 2PA steady state anisotropy originally presented by Callis [74] and McClain [75] was used to experimentally study BzFBz and extended for three- and four-level molecular models of this conjugated chromophore [76]. In that recent study a few-state-model was implemented for the case of two-
photon excitations of BzFBz to the S1 state. Two simultaneous channels of excitation were considered: first, involving $\mu_{01}$ and $\Delta \mu$; and second, involving transition dipole moments $\mu_{01}$ and $\mu_{12}$. Theoretical analysis in the study showed that the high $r_{2PA}$ values can only be explained by taking into account the effect of vibronic coupling within the forbidden by symmetry rules $S_0 \rightarrow S_1$. It was presented that the vibronic coupling could change the angle between $\mu_{01}$ and $\Delta \mu$ leading to a proposed ground-state symmetry breaking [76]. The symmetry breaking phenomenon was suggested to affect 2PA into the S2 state so that experimental values of $r_{2PA}$ for BzFBz, with a dominant $S_0 \rightarrow S_1$ transition, might be explained by deviations of participating transition dipole moments from the ‘‘classical’’ parallel and perpendicular orientation [76]. The measurements and analysis performed found that $r_{2PA}$ was nearly constant. The apparently flat behavior of $r_{2PA}$ was also attributed to symmetry breaking via the strong influence of the mechanism on $\Delta \mu$. Predicted values of $r_{2PA}$ in the study conducted for BzFBz were found to be in the close vicinity of 0.53 for $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_2$ transitions [76].

Through the implementation of the 2PA transition matrix it is possible to establish the orientations and spectral positions of transition dipole moments from the ground to the first excited state, $\mu_{01}$, as well as higher excited-states, $\mu_{0n}$, with respect to the orientation of the emission transition dipole moment, $\mu_{10}$ (required to be the emission transition dipole moment through Kasha’s rule). It is suggested that this may be accomplished by studying one-photon anisotropy measurements for a desired conjugated chromophore and linking analysis of results with quantum-chemical calculations [76].

In this chapter, $r_{2PA}$ spectra of BzFBz is predicted theoretically and compared to experimental results presented in the framework of a three-state model with one-intermediate-level and a four-state model with two intermediate-levels presented from [76]. The reasons for
the unusual behavior of 2PA anisotropy are investigated via an interpretative SOS formalism that may provide deeper insight into the nature of 2PA processes and the failure 3 state models. In the following section a brief background touching on the derivation of \( r_{2PA} \) formulas for a molecule assumed to be planar on an experimental xy-plane will be presented according to [74-76] to model \( r_{2PA} \) via an SOS formalism since a CEO formalism does not implement this type of calculations.

4.2 Theory

The anisotropy of linearly polarized light is given by ratio of the difference between horizontally and vertically polarized fluorescence intensities with respect to the total fluorescence intensity. By this definition the anisotropy \( r \) is given by:

\[
  r = \frac{I_{VV} - I_{VH}}{I_{VV} + 2I_{VH}}
\]

[77]. For the case of 2PA anisotropy (\( r_{2PA} \)) the intensity is described by:

\[
  I = \sum_{i,j=1}^{4} P_i M_{ij} Q_j.
\]

[74]. Here \( P \) represents geometric factors that depend on the polarization vectors of the excitation and emission of photons in a given experimental setup, \( M \) represents an averaging matrix connecting geometric and molecular factors, and \( Q \) depends on the *symmetrized* molecular 2PA transition matrix. Components of \( Q \) are given by:
\[Q_1 = 1\]
\[Q_2 = \frac{|F \cdot S|^2}{|F|^2 |S|^2}\]
\[Q_3 = \frac{\left| \text{Tr} S \right|^2}{|S|^2}\]
\[Q_4 = \frac{(F \cdot S \cdot F) \text{Tr} S}{|F|^2 |S|^2}\]  \hfill (4.3)

In this fashion, for the case of identical photons for a non-planar molecule, the anisotropy is given by:
\[r_{2\text{pa}} = \frac{-4 + 12Q_2 + Q_3 + 4Q_4}{14 + 7Q_3}\]  \hfill (4.4)

[74, 75]. The molecules described in the motivation section above are of a planar conformation and may be assumed to be placed on the x-y plane [76]. For this geometry \(Q_4 = Q_2 + \frac{1}{2}(Q_3 - 1)\) and the anisotropy is then given by:
\[r_{2\text{pa}} = \frac{18Q_2 + Q_3 - 7}{14 + 7Q_3}. \]  \hfill (4.4.b)

Explicitly, in terms of fluorescence transition dipole moments and elements of the 2PA transition matrix, \(r_{2\text{pa}}\)'s are given by:
\[r_{2\text{pa}} = \frac{2}{7} \frac{9\left(f_x^2 s_{xx}^2 + 2f_x f_y s_{xy} + f_y^2 s_{yy}^2\right)\left(s_{xx} + s_{yy}\right) - 4\left(s_{xx} + s_{yy}\right)^2 + 1}{\left(s_{xx} + s_{yy}\right)^2 + 2} \]  \hfill (4.4.c)

[74, 76]. In expression (4.4.c) \(f_i\) is interpreted to be the same as the normalized transition dipole moment from the first excited state to the ground state of the molecule under study, according to Kasha’s Rule, and \(s_{ij}\) is a normalized 2PA transition matrix element. These two expressions are given by:
\[ f_i = \frac{\mu_{i0}}{|\mu_{i0}|} \]  \hspace{1cm} (4.5)

\[ s_{ij} = \frac{M_{ij}}{|M|} \]  \hspace{1cm} (4.6)

The contribution of independent states may be studied on a state by state basis since \( M \) requires a sum over all contributing states. It is possible to determine which states may be considered essential to \( r_{2PA} \) by isolating states in the evaluation of the 2PA transition matrix elements. This may be implemented explicitly by recording the \( N^{th} \) contribution in:

\[
M_{ij} = \sum_{k}^{N} \left( \frac{\mu_{jk} \mu_{ik} + \mu_{jk} \mu_{ik}}{\omega_{kg} - \omega - i \frac{\Gamma}{\hbar}} \right)
\]  \hspace{1cm} (4.7)

### 4.3 Computational Details

The optimization scheme conducted for BzFBz was the same that was implemented for 2PA cross-section calculations. A B3LYP/Midi! level was used in an ATDA approximation via a modified version of G’03 to extract state to state transition dipole moments. The 2PA transition matrix elements from (3.7) were calculated and implemented in the calculation for \( r_{2PA} \) following 4.4.c. according to the discussion from [74] and [76]. The prediction of \( r_{2PA} \) was carried out with a new NLO program developed by the author to carryout high-order optical effect predictions from output of a modified version of Gaussian 2003 that implements ATDA.

### 4.4 Results and Discussion

The modeled \( r_{2PA} \) calculations matched well with experimental results when including
more that one intermediate state into the model. It was observed that the same results of $r_{2PA}=0.14$ were observed when describing the S0 to S1 transition as were predicted in [76]. Upon inclusion of more states, up to the 24 total states, it was observed that the values of $r_{2PA}$ compared well to experimental values of $r_{2PA} = 0.53$, where $S0 \rightarrow S1-24$ were in the acceptable range of $r_{2PA} \approx 0.54 – 0.57$. The results imply that more essential states were needed in few state models to accurately describe $r_{2PA}$ for fluorescence intensities from the S1 state when only treating $f_i$ for $S1 \rightarrow S0$, according to Kasha’s rule, in the $r_{2PA}$ calculations.

Figure 11: BzFBz $r_{2PA}$ for S1 & S1 - S24

Results from 2PA transition matrix for $r_{2PA}$ for S1 (green) and all contributions from S1 – S24. Experimental $r_{2PA}$ for BzFBz presented from [76].
Incremental contribution from states S1 to S24 for $r_{\text{2PA}}$ at the level of B3LYP/Midi!. Experimental $r_{\text{2PA}}$ for BzFBz presented from [76].

4.5 Review

A two state model depending on $S_0 \rightarrow S_1$ with S1 as an intermediate state was found to be insufficient to predict experimental behavior of $r_{\text{2PA}}$ for BzFBz. By incrementally taking into account the number of contributing states, a value $r_{\text{2PA}}$ close to the experimental result was observed by means of a 2PA transition matrix formalism and transition dipoles found from ATDA. A detailed analysis exploring this behavior of $r_{\text{2PA}}$ and extending this approach to study $r_{\text{2PA}}$ of non-planar molecules is on the way as of the writing of this thesis.
5.0 Summary

In this chapter the newly presented ATDA was used to predict transition dipole moments for the calculation of SHG properties of $p$NA in the SOS formalism. Several TD-DFT functionals and HF approaches were used and compared to available experimental values. The SOS, CEO, and FF formalisms were then implemented to calculate SHG properties of $p$NA using results arising from the HF and TD-DFT description of $p$NA. SOS used state to state transition dipoles and excited state energies available from ATDA. It was concluded that the FF, CEO, and SOS treatment were in close agreement. A plot of the SHG $\beta$ shows that CEO and SOS are in good agreement of a range of several eV. It is also established in this chapter that a new exchange and correlation functional with correct asymptotics needs to be found to appropriately account for the exchange and correlation effects of $p$NA.

5.1 Motivation

Organic materials are rapidly gaining practical interest for nonlinear optical applications [78-83]. Donor and/or acceptor substituted $\pi$-conjugated organic molecules exhibit an extremely fast nonlinear optical (NLO) response time that is purely electronic in origin. This makes organics promising candidates for optoelectronic applications. Design of the molecules with high molecular hyperpolarizabilities ($\beta$) and appropriate optical transparency is an important step in the search for effective NLO materials. The use of quantum chemical approaches for prediction
of the molecular NLO properties is expected to provide guidance and accelerate experimental studies active in this search.

The reliable estimation of NLO properties requires quantum chemical methods that include electron correlation and large basis sets with polarization as well as diffused functions [84, 85]. It was shown that MP2 and coupled cluster methods can reproduce molecular hyperpolarizabilities with high accuracy [86, 87]. However, the application to molecules of practical interest composed of more than dozens of atoms can hardly be considered a routine task. Density Functional Theory (DFT) emerges as an attractive alternative to approach this task. It is feasible for calculation of electronic structure properties of large molecules [88, 89] and presents a promising tool for prediction NLO properties. However, the numerical performance of DFT for estimation of molecular NLO properties was criticized [90-92]. The inadequacy of conventional DFT functionals for both LDA and GGA were reported. At the same time, according to a comparison given in [87], conventional DFT methods B3LYP and B971 give reliable results for small molecules. From [91] it can also be concluded that B3LYP performs better than pure DFT functionals. For easily polarizable molecules, conventional DFT methods lead to somewhat of an overestimation of NLO properties. However such easily polarized structures usually have low stability and are not optically transparent while molecules of practical interest contain a combination of aromatic and ethylene fragments. The representative series of such molecules was recently considered by Robinson at al [93, 94]. The authors in those contributions came to conclusion that molecules containing up to 8 –C=C– fragments in a \( \pi \)-system are in the “safe domain” to be systematically studied by conventional DFT methods, at least at a qualitative level. In the systematic search for promising materials with NLO applications the main purpose is to find trends and structure-activity relations in
hyperpolarizabilities, in a series of proposed compounds, which may provide guidance for experimentalists. However, the comparison of calculated hyperpolarizabilities to experimental values might be problematic due to use of different conventions in the definition of SHG $\beta$s and standards by experimentalists. This problem was specially addressed recently by [95-98]. In review [98] it was not recommended to compare results obtained by different authors. For the $p$NA molecule most of the available experimental NLO data was critically analyzed and tabulated in a unified scale by Reis [96]. After a rigorous search in the literature, it was determined that at the present time, para-nitroaniline is the only molecule with D/A substituents connected by a $\pi$-conjugated bridge which may be considered as a prototype of push-pull molecules of practical meaning and which has reliably determined gas-phase values of the molecular hyperpolarizability. This allows direct comparison to calculated values obtained for an isolated molecule. Unfortunately all other accurate gas-phase measurements were carried out for small molecules like water, acetonitrile etc. which are of interest only for the development and testing of rigorous quantum chemical approaches.

The NLO properties on $p$NA have been the subject of theoretical study in numerous publications. Salek at al.[99, 100] has found that B3LYP value of $\beta$ of pNA is in good agreement with a more sophisticated CCSD method. The first hyperpolarizability of $p$NA was recently calculated using the TDDFT/SOS formalism [101]. Several DFT methods including pure DFT as well as HGGA methods were considered. It was shown, in agreement with other literature data [91], that hybrid functionals perform better. Also, it was concluded that the SHG $\beta$ of $p$NA is nearly insensitive to the choice of basis set, while earlier it was shown that an augmentation of the basis set, with both polarization and diffused functions, is necessary to obtain reliable values of NLO properties [84, 85]. At the same time, the series of basis sets with both polarization and
diffused functions give results for the hyperpolarizability of $p$NA which do not vary significantly[102].

In this chapter a systematic study of the DFT functional dependence of the static first hyperpolarizability described. Frequency-dependent hyperpolarizabilities are estimated with finite field FF[103-106] as well as SOS [35, 107] methods and comparisons between these methods are presented. The reference molecule considered is $p$NA. $p$NA is a medium-size $\pi$-system and was chosen due to availability of both experimental[96, 108] (reliably measured) and theoretical hyperpolarizabilities, calculated at different levels of theory, and the availability of the X-ray structure.[109]

5.2 Theory

In the Sum over States (SOS) formalism the second harmonic generation (SHG) $\beta_{ijk}$ may be explicitly calculated from [8]:

$$\beta_{ijk}(2\omega, \omega, \omega) = \frac{1}{2\hbar^2} \sum_{n,m} \left(\frac{\mu_n^i \mu_{nm}^j \mu_{mg}^k}{\Omega_{ng} - 2\omega (\Omega_{mg} - \omega)} + \frac{\mu_n^j \mu_{nm}^i \mu_{mg}^k}{\Omega_{ng}^* + \omega (\Omega_{mg}^* - \omega)} + \frac{\mu_n^k \mu_{nm}^j \mu_{mg}^i}{\Omega_{ng} + \omega (\Omega_{mg}^* + 2\omega)} \right) \right)$$

(5.1)
Here, $\mu_{nm}^i$ are the state to state transition dipole moments between states $n$ & $m$ along the $i$th spatial direction, $\Omega_{nm} = \omega_{nm} - i\Gamma$, & $\Omega_{nm}^* = \omega_{nm} + i\Gamma$, where gamma is a habitually used empirical broadening factor $\Gamma = 0.1/\hbar$ [40], $\omega_{nm}$ is the energy difference between excited states $n$ & $m$ $\omega_{nm} = \Delta E_{nm}/\hbar$, and $\omega$ is the frequency of the modeled field [8]. Above, $\mu_{nm}^i$ state to state transition dipole moments were calculated in ATDA setting $\xi = \begin{bmatrix} X \\ 0 \end{bmatrix}$ [54]. The state to state transition dipoles have the form given in expression (2.6) of the CEO formalism. The vectorial part of $\beta$ is then calculated by:

$$\beta_{\text{vec}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2},$$

where $\beta_j = \frac{1}{3} \sum_{i=1}^{3} \left( \beta_{ji} + \beta_{ij} + \beta_{ij} \right)$, $i, j = x, y, z$

### 5.3 Computational details

Several DFT functionals B972, B3LYP, PBE0, and BMK were chosen for the study of SHG in $p$NA. The geometry optimization of $p$NA was carried out with a 6-31G(d) basis set at the HF level while the hyperpolarizability properties were carried out with a 6-31+G(d) basis set. As it was discussed in the theory section, hybrid functionals are more suitable for calculations of NLO properties and pure density functionals were not considered. A modified version of G98 was used to print out information required by the CEO formalism to calculate SHG properties of $p$NA, while a modified version of G’03 was used to implement ATDA and output state to state transition dipoles to be used in the NLO program written by the author to produce SHG spectra.
5.4. Results and Discussion

Results obtained for pNA using the SOS and FF methods are given in Table 7 and figure 13. Necessary data for SOS expressions were obtained using the TDHF and TDDFT methods by use of a modified version of the gaussian03 suite of programs. It can be seen that the static SOS hyperpolarizabilities ($\lambda=\infty$) agree well with FF calculations; SOS values are 2-10% higher. Frequency corrections obtained at the HF level are slightly lower; however the ones calculated with DFT appear to be significantly higher. A comparison of SHG $\beta$'s are calculated for both the CEO and SOS formalism and are plotted in figure 16. It appears that in the treatment of the SHG properties of pNA within the SOS formalism some characteristics are lost in the region between ~3.75 and ~4.25 eV. While over the reminder of the energy domain CEO is in good agreement with SOS [110].

Table 7: Hyperpolarizabilities obtained by FF and SOS methods

<table>
<thead>
<tr>
<th>$\beta_{xxx}(0)/FF$</th>
<th>B972</th>
<th>PBE0</th>
<th>B3LYP</th>
<th>BMK</th>
<th>HF</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1675</td>
<td>1571</td>
<td>1745</td>
<td>1557</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\beta_{xxx}(0)/SOS$</td>
<td>1735</td>
<td>1661</td>
<td>1938</td>
<td>1537</td>
<td>687</td>
<td>-</td>
</tr>
<tr>
<td>$\beta_{xxx}(2\omega,\omega,\omega)/SOS$</td>
<td>2940</td>
<td>2754</td>
<td>3433</td>
<td>2409</td>
<td>863</td>
<td>1787</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>1.69</td>
<td>1.66</td>
<td>1.77</td>
<td>1.57</td>
<td>1.26</td>
<td>-</td>
</tr>
</tbody>
</table>

Static and dynamic ($\lambda=1064$ nm). $\Delta = \frac{\beta_{xxx}(2\omega,\omega,\omega)}{\beta_{xxx}(0)}$ is the multiplicative correction factor.
Figure 13: Second Harmonic Generation (SHG) of pNA

Comparison between SHG $\beta_{xxx}$ as calculated from the SOS formalism with state to state transition dipole moments calculated from ATDA modified version of G’03 and CEO formalism. Results for $\beta_{xxx}$ are presented in Debye$^3$/eV$^2$. *(To convert to table values multiply by 27.21142/2.54173)*

5.5 Review

SOS predictions of SHG compare well to CEO predictions of SHG as concluded from figure 16. An improved exchange and correlation functional is needed with the correct asymptotics to properly predict SHG in pNA when compared to experiment and FF. It was observed that dynamic $\beta$s in TD-DFT are overestimated and underestimated at the HF level.
CHAPTER VI
CONCLUSION

A variation of the second order TD-DFT method, termed the \textit{posteriori} Tamm-Dancoff approximation (ATDA) was proposed. It consists of solving full linear response equations, the evaluation of permanent and state-to-state transition dipoles in the Tamm-Dancoff approximation, and the calculation of excitation energies and transition dipoles as a combination of corresponding linear response values. For benchmarking purposes excited states in the short linear polyenes were studied with a wave function-based method SAC-CI, including the description of both static and dynamic electron correlation. The numerical results were found to be in better agreement with SAC-CI values than those calculated within QR-DFT. ATDA-DFT is recommended for the calculation of nonlinear optical properties.

Both CEO- and SOS-based TD-DFT descriptions of excited states for 1PA and 2PA profiles of 5 conjugated chromophores were found to be in good agreement with each other and close to experimental data. An empirical broadening constant is sufficient for qualitative agreement in most cases, although calculated peaks show a systematic red-shift with respect to experimental resonance peaks. Minor differences between experimental and calculated peaks of the planar orientations for the studied chromophores may be attributed to unaccounted factors such as thermal broadening and solvent effects on charge transfer for figures 5 and 6. Large (55nm) discrepancies between theory and experiment were observed for one chromophore (DpFPBz). An explicit thermal broadening methodology was developed based on Boltzmann distribution of rotamers around single chemical bond for 3 bonds of this molecule. This methodology was found insufficient to explain the observed discrepancies so that additional accuracy in the calculation of broadening factors needs to be taken into account. This work is
under way in the form of a formal study of the effects of Franck-Condon factors on inhomogeneous broadening of spectra.

A two state model depending on $S_0 \rightarrow S_1$ was found to be insufficient to predict experimental behavior of $r_{2PA}$. $r_{2PA}$ was predicted by incrementally taking into account the number of contributing states. A value for $r_{2PA}$ close to the experimental result was observed when taking into account more than 2 intermediate states by means of the 2PA transition matrix formalism and transition dipoles found from ATDA. A detailed analysis exploring the behavior of $r_{2PA}$ is on the way.

The SOS method was applied to calculate SHG of the first hyper-polarizability of pNA. TD-DFT functionals, which are most popular and easily available in most of quantum chemical programs, were considered to generate output which may then be utilized to calculate the dynamics of SHG in the FF, CEO, and SOS formalisms. The geometry of pNA, optimized with a 6-31G basis, was used in conjunction with the basis set 6-31+G(d) to obtain the results for estimation of relative changes in the hyperpolarizability for pNA that provide a realistic estimation of NLO properties. Both CEO and SOS are in good agreement when describing the SHG properties pNA, though a better exchange and correlation functional with correct asymptotics is needed.

SOS calculations of high order corrections to the Polarization field $P$, whether incorporating or not incorporating double excitations, proved to be in good agreement with the CEO calculations. A major advantage presented with the SOS formalism is the speed up time in the calculation of NLOs when compared to CEO. It was observed that when using the CEO formalism explicitly it takes several days to calculate the 2$\text{nd}$ and 3$\text{rd}$ order response of a molecule, while the SOS formalism takes seconds to carry out results in good agreement with
those from CEO. ATDA-DFT was shown to provide a close agreement with experimental results when used to predict the nonlinear response of materials and is recommended for the calculation of nonlinear optical properties.
LIST OF REFERENCES


