

CHAPTER 2

Theoretical background of computational methods

Abstract

The second chapter represents a brief report on the basic theoretical background related to various optical properties along with theoretical techniques to quantify hyperpolarizability (β) and two-photon absorption cross section (σ). For theoretical determination of first hyperpolarizability (β), early models, equivalent field model (EIF), additivity model and two-state model along with quantum chemical approaches *viz.*, sum over states (SOS) methods and coupled perturbed HF (CPHF) methods are also discussed here. A short description of “few-states model” for quantifying two-photon absorption cross section (σ) is also presented. In case of luminescent materials, principles of computational phosphorescence are clearly stated.

2.1. Theoretical determination of first hyperpolarizability (β)

2.1.1. Early models for the calculation of β

2.1.1.1. Equivalent field model (EIF)

Equivalent field model was developed by Oduar and Chemla^{67, 68} for interpreting the second-order nonlinear optical responses. This method represents β by quantifying the ground state asymmetry of a π -network in a systematic fashion. It is reported that the major portion of the second order response can be predicted by the deformation of the electron distribution due to appended substituents to the chromophore molecules. The perturbation of the π -cloud caused by particular substituents is known as substituent mesomeric moment (μ_R) and is related with β as

$$\beta_{\pi} = \frac{3\gamma\Delta\mu_R}{\alpha} \quad (2.1)$$

Where α is polarizability, γ is second order hyperpolarizability and β_{π} is the static hyperpolarizability at $h\omega = 0.0$.

In this model determining the μ_R is complicated in predicating the β_{π} . For mono substituted benzenes and stilbenes, the π -deformation caused by substituent R is defined as the difference between the ground-state μ to the mono substituted aromatic derivative and that for the analogous mono substituted aliphatic molecule. The σ -contributions to the μ of the π -chromophores are eliminated. Using the μ_R ,⁶⁹ the β_{π} for a considerable number of mono substituted π -conjugation systems are predicted, which are well correlated with experimental trends in the second order response.^{68, 70} This model also accounts for the negative sign in the second order response when the added group is an electron acceptor and a positive β when the attached moiety is an electron donor.

2.1.1.2. Additivity model

This model is an extension of the EIF model and is generally used for predicting the second-order response for disubstituted derivatives *i.e.*, push/pull systems (push/pull substituted benzene). It has been proposed that the total molecular nonlinearity for a complex system should be the sum of the contributions of each important structural component of the system.^{71, 72} However this additivity model works well for weakly coupled systems, such as *D* and *A* σ -

networks⁷³ but fails for strongly coupled disubstituted systems^{73, 74} as proposed by Zyss et al. This model also fails predicting high β -values for highly asymmetric systems.

Thus difficulties with both the EIF and additivity model is based on the assumption that β is governed by ground-state electronic distributions and that the substituents act independently of each other.

2.1.1.3. Two-state model

In order to explain the high β -value for asymmetric systems, Oudar and Chemla^{68, 75} proposed the two-state model. This model proposed that the large NLO response for these type of systems arises due to intramolecular charge transfer (CT) between D and A . Hence not only the ground state, the excited state is also responsible for the NLO response. The β can be represented as a sum of two contributions, β_{add} and β_{CT} .

$$\beta = \beta_{CT} + \beta_{add} \quad (2.2)$$

β_{add} accounts for the interaction between the individual substituents and spacer (*i.e.*, chromophore) and β_{CT} represents the charge transfer interactions between the D and A moieties and is described in terms of a two-level interaction between the ground state (g) and the first excited state (n) as follows .

$$\beta_{CT} = \frac{3e^2}{2m} \frac{h\omega_{gn} f_{gn} \Delta_{\mu_{gn}}}{[(h\omega_{gn})^2 - (2h\omega)^2][(h\omega_{gn})^2 - (h\omega)^2]} \quad (2.3)$$

Here,

$h\omega$ is the energy of the laser photon,

$h\omega_{gn}$ is the energy difference between ground state (g) and the first excited state (n),

f_{gn} is the oscillator strength of a g - n transition,

Δ_{gn} is the difference in dipole moments between the ground and first excited state.

Thus high β -value for a system is related to the charge transfer excited states and any method that seeks to predict hyperpolarizability must adequately represent the excitation to these states.⁷⁶

2.2. Quantum chemical approach for the calculation of β

Reliable theoretical predictions of nonlinear optical responses are useful for providing guidelines to the synthetic chemists for exploring species of potential interest. Moreover this will

give us a concrete idea about the structure-optical-property relationship which is a key step to search the possible suitable candidate for NLO materials. There are two basic methodologies which can be used with an electronic structure method to compute NLO response *viz.*, Sum over states (SOS) methods and Coupled perturbed HF (CPHF) methods. Both the SOS (field-independent) and CPHF (field-dependent) methods are useful for any model Hamiltonian (*i.e.*, *ab initio*, semiempirical) for the computation of β .

2.2.1. Sum over states (SOS) methods

Sum over states (SOS) approaches constitute one of the most commonly used class of methodologies for theoretical estimation of hyperpolarizabilities. These methods are field independent and calculations are carried out on free molecule where NLO response involves the coupling of the excited state. According to SOS methods, NLO responses calculated by applying perturbation theory to an unperturbed molecule^{77, 78} and are suited for studying the interaction between individual orbitals. In the uncoupled formulation, electronic excited states created by the perturbing laser field are treated as an infinite sum over unperturbed particle-hole states. The SOS perturbation equation for calculating β is given here (2.4).

$$\beta_{ijk}^{SHG} = -\frac{e^3}{8h^2} \left[\begin{aligned} & \sum_{n \neq g} \sum_{\substack{n' \neq g \\ n' \neq n}} \left\{ (r_{gn'}^j r_{n'n}^i r_{gn}^k + r_{gn'}^k r_{n'n}^i r_{gn}^j) \left(\frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - \omega)} \right) + \right. \\ & (r_{gn'}^i r_{n'n}^j r_{gn}^k + r_{gn'}^k r_{n'n}^j r_{gn}^i) \left(\frac{1}{(\omega_{n'g} + 2\omega)(\omega_{ng} + \omega)} \right) \left(\frac{1}{(\omega_{n'g} - 2\omega)(\omega_{ng} - \omega)} \right) + \\ & \left. (r_{gn'}^j r_{n'n}^k r_{gn}^i + r_{gn'}^k r_{n'n}^j r_{gn}^i) \left(\frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} - 2\omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} + 2\omega)} \right) \right\} + \\ & \{ [r_{gn'}^j r_{gn}^k \Delta r_n^i (\omega_{ng}^2 - 4\omega^2) + r_{gn'}^i (r_{gn}^k \Delta r_n^j + r_{gn}^j \Delta r_n^k) (\omega_{ng}^2 + 2\omega^2)] \times \\ & 4 \sum_{n \neq g} \frac{1}{(\omega_{ng}^2 - \omega^2)(\omega_{ng}^2 - 4\omega^2)} \} \end{aligned} \right] \quad (2.4)$$

where, ω is the frequency of the applied electric field, $r_{n,n'}^i$ is the matrix element of displacement operator r^i along the i th molecular axis between electronic states n and n' and $h\omega_{ng}$ is the energy separation between the ground state (g) and an excited state (n). The term $\Delta r_n^i (= r_{nn}^i - r_{gg}^i)$ is the dipole moment difference between excited and ground state.

From this equation it is clear that in order to compute β , one needs to know the dipole matrix elements between the ground and excited states, excitation energy and excited state dipole moments. Since the ground state is of single determinant type, the polarizability involves only

monoexcited configurations. However, the applied fields mix the molecular ground state with many excited states, the SOS expansion is infinite and generally the sum is truncated after apparent convergence has been reached.

2.2.2. Coupled perturbed Hartree Fock (CPHF) methods

These formalism involves molecular Hamiltonian as field term $(-r.F)$, which describes the interaction between the external uniform static field and the electronic structure. At a given field strength the molecular wave function is found, from which the appropriated expectation values of the field-dependent molecular energy $(E(F))$ and the field-dependent dipole moment $(\mu(F))$ can be evaluated by following equation

$$E(F) = \langle \psi(F) | H(F) | \psi(F) \rangle \quad (2.5)$$

$$\mu(F) = \langle \psi(F) | \sum q_i(F) r_i(F) | \psi(F) \rangle \quad (2.6)$$

The relationship between the μ of a molecule interacting with an external electric field and the NLO response can be given as

$$\mu_i(F) = \mu_i^0 + \sum_j \alpha_{ij} F_j + \sum_{j<k} \beta_{ijk} F_j F_k + \sum_{j<k<l} \gamma_{ijkl} F_j F_k F_l + \dots \quad (2.7)$$

where μ_i^0 is the dipole moment in the absence of the field and $(\mu_i - \mu_i^0)$ is the polarization in the i^{th} direction (P_i) as defined in equation (1.3). The (hyper) polarizabilities of increased order may be obtained by differentiating $\mu(F)$ with respect to the field.

The partial derivative of the polarization (P_i) with respect to the field can give the polarizability, while the second partial derivative of the polarization gives β and third partial derivative gives γ evaluated at zero field,⁷⁹⁻⁸¹

$$\alpha_{ij} = (\partial \mu_i / \partial F_j)_{F=0} \quad (2.8)$$

$$\beta_{ijk} = (\partial^2 \mu_i / \partial F_j \partial F_k)_{F=0} \quad (2.9)$$

$$\gamma_{ijkl} = (\partial^3 \mu_i / \partial F_j \partial F_k \partial F_l)_{F=0} \quad (2.10)$$

Similarly the α , β and γ coefficients can be obtained from the molecular energy expansion^{80, 81} as follows. The molecular dipole moment is the negative field derivative of the energy. Thus

$$\mu_i = -(\partial E / \partial F_i) \quad (2.11)$$

$$\alpha_{ij} = -(\partial^2 E / \partial F_i \partial F_j)_{F=0} \quad (2.12)$$

$$\beta_{ijk} = (\partial^3 E / \partial F_i \partial F_j \partial F_k)_{F=0} \quad (2.13)$$

$$\gamma_{ijkl} = (\partial^4 E / \partial F_i \partial F_j \partial F_k \partial F_l)_{F=0} \quad (2.14)$$

The relationships given for α , β and γ are valid for the static field limit. Thus, the majority of derivative based NLO response computations have been reported at zero frequency. Numerical differentiation strategies^{82, 83} are used to compute the above derivatives. Pulay and others^{84, 85} have developed analytic gradient techniques to compute the above derivatives. Generally in CPHF methods analytical gradients techniques are used to compute NLO and other properties. While in FF, numerical methods are used to calculate the derivatives.

2.3. One- and two-photon absorptions

The one-photon absorption rate is proportional to the imaginary part of the linear susceptibility that can be derived by time-dependent perturbation theory.⁸⁶ It is useful to introduce the oscillator strength to specify the “strength” of the transition. The dimensionless oscillator strength of the $g \rightarrow e$ transition is defined as⁸⁶

$$f_{eg} = \frac{2m\omega_{eg} \sum_{\alpha}^{x,y,z} \left| \langle e | \mu_{\alpha} | g \rangle \right|^2}{3\hbar e^2} \quad (2.15)$$

where the μ_{α} is the dipole moment operator. The name of “oscillator” derives from the classical theory of radiation, imaging the atom as an oscillating electric dipole. The one-photon absorption spectra can be obtained by the calculation of oscillator strength through Lorentzian lineshape broadening

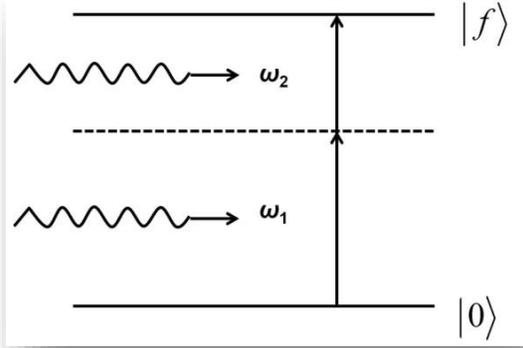
$$g(\omega_f - \omega) = \frac{1}{\pi} \frac{\Gamma_f}{(\omega_f - \omega)^2 + \Gamma_f^2} \quad (2.16)$$

where Γ_f corresponds to level broadening of the final state.

A typical nonlinear absorption process is two-photon absorption which means the molecule can absorb two photons at the same time under the interaction of light field, see Figure 2.1. The probability of a molecule simultaneously absorbing two identical photons is proportional to the square of the light intensity. In comparison with one-photon absorption, TPA has different selection rules and also it is related to the polarization of the light. These properties

make the TPA as a complementary spectroscopic tool for determining the position of energy levels that are not connected to the one photon absorption.

Usually the TPA activity of molecules is described by TPA cross section. The



relationship between molecular structure and two-photon absorption cross section can be also derived from standard time-dependent perturbation theory.⁸⁶ The TPA cross sections of random orientated systems are related to imaginary part of the second hyperpolarizability $Im\gamma(-\omega;\omega,-\omega,\omega)$ by⁸⁷

Figure 2.1. Two-photon absorption

$$\sigma = \frac{8\pi^2 \hbar \omega^2}{n^2 c^2} L^4 \text{Im}(\gamma) \quad (2.17)$$

where n is the refractive index and L is the local field factor.

Alternatively, the two-photon absorption cross section can be obtained by calculating the two-photon transition matrix elements $S_{\alpha\beta}$ between the initial state I and final state f . Consider $Im\gamma(-\omega;\omega,-\omega,\omega)$ for frequency ω being close to half of the excitation energy of the final state f and neglect all nonresonant contributions, the expression for γ becomes

$$\gamma_{\alpha\beta\gamma\delta}(-\omega;\omega,-\omega,\omega) = i \frac{2\hbar^{-1}}{\Gamma_f} S_{\alpha\gamma} S_{\beta\delta}^* \quad (2.18)$$

where $S_{\alpha\beta}$ is the two-photon transition matrix elements defined as⁸⁸

$$S_{\alpha\beta} = \sum_s \left(\frac{\langle i|\mu_\alpha|s\rangle\langle s|\mu_\beta|f\rangle}{\omega_{si} - \omega} + \frac{\langle i|\mu_\beta|s\rangle\langle s|\mu_\alpha|f\rangle}{\omega_{si} - \omega} \right) \quad (2.19)$$

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

The TPA transition probability for a molecule is dependent on the polarization of the laser beams. The orientationally averaged two-photon probability is given by⁸⁹

$$\delta_{tp} = \sum_{\alpha\beta} [F \times S_{\alpha\beta} S_{\beta\alpha}^* + G \times S_{\alpha\beta} S_{\alpha\beta}^* + H \times S_{\alpha\beta} S_{\beta\alpha}^*] \quad (2.20)$$

Here F , G and H are coefficients dependent on the polarization of the light and are defined as

$$F = -|\lambda \cdot \nu^*| + 4|\lambda \cdot \nu|^2 - 1 \quad (2.20a)$$

$$G = -|\lambda \cdot \nu^*|^2 - |\lambda \cdot \nu|^2 + 4 \quad (2.20b)$$

$$H = 4|\lambda \cdot \nu^*| - |\lambda \cdot \nu|^2 - 1 \quad (2.20c)$$

where λ and ν are the polarization vectors of the laser beam. The values of F , G and H are 2, 2 and 2 for linearly polarized light and -2, 3 and 3 for the circular case.

The macroscopic TPA cross section that can be directly compared with the experiment can be obtained by^{88, 90}

$$\sigma_{tp} = \frac{4\pi^2 a_0^5 \alpha \omega^2 L^4}{15c \Gamma_f n^2} g(\omega) \delta_{tp} \quad (2.21)$$

where a_0 is the Bohr radius, α is the fine structure constant, L is the Lorentz field factor, $g(\omega)$ provides the spectral line profile, n is the refractive index and the level broadening Γ_f of final state is assumed to have the commonly used value $\Gamma = 0.1 f eV$. If the Bohr radius and the speed of light are given in cgs units and the frequency ω and the TPA probability δ_{tp} are in atomic units, the resulting unit will be cm^4s which is often expressed as the Göppert-Mayer unit ($1GM = 10^{50} cm^4s$).

2.3.1. Few-states model

Equation (2.7), which includes the summation of all the intermediate, initial and final states for computing TP transition matrix elements, represents the so-called sum-over-states (SOS) method. Since it requires the information of all excited states, it means that the *ab initio* calculations could be too expensive to use. In practice, especially for charge-transfer molecules, it is used by truncation of the SOS expression to only include the dominating states and

excitation channels. That is the few-states model.^{90, 91} This model not only makes the SOS approach to a manageable extent, but also provides a better understanding for the structure-to-property relations. The validity of the few-states model has been confirmed by comparing its results with those obtained from the analytical response theory.

In the few-states model, for the symmetrically substituted one-dimensional molecules, usually its first excited state is a charge-transfer state, but the two-photon transition is forbidden in this situation. Thus we have to use at least a three-state model for calculation of the TPA cross section, which has a simple form as

$$S_{zz} = \frac{2\mu_z^{01}\mu_z^{1f}}{\omega_1 - \omega} \quad (2.22)$$

As to asymmetrically substituted one-dimensional molecules it is sufficient to include only the ground state and final TPA state because the final TPA state is usually the charge-transfer state

$$S_{zz} = \frac{2\mu_z^{0f}(\mu_z^{ff} - \mu_z^{00})}{\omega_f - \omega} \quad (2.23)$$

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

$$S_{\alpha\beta} = \frac{\mu_\alpha^{01}\mu_\beta^{1f}}{\Delta E} + \frac{\mu_\beta^{01}\mu_\alpha^{1f}}{\Delta E} \quad (2.24)$$

Where $\Delta E = \omega_1 - \omega = \omega_1 - \omega_f / 2$, μ_α^{ij} is the dipole moment between the state $|i\rangle$ and $|j\rangle$ and $\alpha, \beta \in \{x, y\}$. In asymmetric planer molecules, when the excitation is dominated by the transition from ground state $|0\rangle$ to the final excited state $|f\rangle$, the two-state model can be used.

$$S_{\alpha\beta} = \frac{\mu_\alpha^{0f}\Delta\mu_\beta}{\Delta E} + \frac{\mu_\beta^{0f}\Delta\mu_\alpha}{\Delta E} \quad (2.25)$$

Where $\Delta E = \omega_f - \omega = \omega_f / 2$, $\Delta\mu$ denotes the dipole moments between the ground state and the final state. More general, if an asymmetric molecule has more than one charge transfer state, there will be several dominant excitation channels (see Figure 2.2). For instance, an

asymmetric molecule has two charge transfer states S_1 and S_2 . If the TPA state is the S_1 , there are two dominant scattering processes involved, *i.e.*, $S_0 \rightarrow S_2 \rightarrow S_1$ and $S_0 \rightarrow S_1 \rightarrow S_1$. Therefore, three-state model should be employed, which can be written as

$$S_{\alpha\beta} = \frac{\mu_{\alpha}^{01}\Delta\mu_{\beta} + \mu_{\beta}^{01}\Delta\mu_{\alpha}}{\Delta E_1} + \frac{\mu_{\alpha}^{02}\mu_{\beta}^{21} + \mu_{\beta}^{02}\mu_{\alpha}^{21}}{\Delta E_2} \quad (2.26)$$

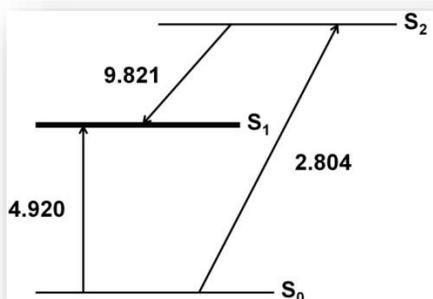


Figure 2.2. The excitation channels: $S_0 \rightarrow S_2 \rightarrow S_1$ and $S_0 \rightarrow S_1 \rightarrow S_1$, the numbers beside the lines are transition moments.

Using the few-states model, the transition energy, transition dipole moments and the difference of the permanent dipole moment between the ground and excited states are specified. Then the dependence of the TPA properties on the molecular electronic structure is clearly illustrated. In this thesis, the few-states model is employed to explain the TPA properties of several interacting polar chromophores.

2.4. Principles of computational phosphorescence

According to the molecular analogue of Hund's rule in atomic physics, the triplet excited states are always placed lower in energy than the corresponding singlet excited states, which are formulated by this equation,

$$E(S_1) - E(T_1) = 2 \iint \psi_i^*(1)\psi_u^*(2) \left(\frac{e^2}{r_{1,2}} \right) \psi_i(2)\psi_u(1) dv_1 dv_2 \quad (2.27)$$

In the framework of the electric-dipole approximation, the electronic transitions between the ground singlet (S_0) and excited singlet (S_n) states are spin allowed and are also usually allowed by the orbital symmetry selection rules. In contrast, the absorption and emission involving singlet and triplet states (T_n) are strongly spin-forbidden since they proceed as second-order, or nonlinear processes involving both spin-orbit and dipole couplings.

2.4.1. Spin-orbit coupling and S-T mixing

Neglecting spin-orbit coupling and other relativistic effects, any singlet state ($^1\psi$) can be represented as a product of a symmetrical spatial wave function (Φ_+) and an unsymmetrical spin wave function (Ω_-):

$$^1\psi = \Phi_+ \Omega_- \quad (2.28)$$

For two electrons, the spatial and spin parts for the singlet state can be written as follows:

$$\Phi_+ = \frac{1}{\sqrt{2}} [\varphi_a(1)\varphi_b(2) + \varphi_a(2)\varphi_b(1)] \quad (2.29)$$

$$\Omega_- = \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha) \quad (2.30)$$

where $\varphi_a(1)$ and $\varphi_b(2)$ are the molecular orbitals which depend on the spatial coordinates x_1, y_1 and z_1 and x_2, y_2 and z_2 for the first and second electrons, respectively; α and β are the eigenfunctions of the one-electron S_z operator, with quantum numbers $M_s = \pm 1/2$.

The triplet state wave function ($^3\psi$) is also asymmetrical and can be represented as a product between an asymmetrical spatial wave function (Φ_-) and three different symmetrical spin wave functions ($\Omega_+^1, \Omega_+^{-1}$ and Ω_+^0):

$$^3\psi = \Phi_- \Omega_+ \quad (2.31)$$

$$\Phi_- = \frac{1}{\sqrt{2}} [\varphi_a(1)\varphi_b(2) - \varphi_a(2)\varphi_b(1)] \quad (2.32)$$

$$\Omega_+^1 = \alpha\alpha, \Omega_+^{-1} = \beta\beta, \Omega_+^0 = \frac{1}{\sqrt{2}} (\alpha\beta + \beta\alpha) \quad (2.33)$$

If ($^1\psi$) and ($^3\psi$) corresponds to the same electronic configuration, the “-” sign in the spatial part of $^3\psi$ (equation 2.32) leads to the fact that the T state energy is lower than the S state energy (the first Hund’s rule) since the exchange integral between the orthogonal MOs φ_a and φ_b is always positive.

Actually, the $^1\psi$ and $^3\psi$ functions are never “pure” singlets or triplets (even for helium and noble gases) because the spin-orbit coupling always mixes the $^1\psi$ and $^3\psi$ eigenfunctions.^{92, 93} The S-T mixing is responsible for phosphorescence intensity, lifetime and quantum yield.

2.4.2. Perturbation theory for S-T transitions

Due to the SOC effect, the singlet states of polyatomic molecules contain some admixture of triplet character. At the same time, the T_1 state is contaminated by singlet state wave functions that can be described by first-order perturbation theory.^{92, 94}

$$\tilde{T}_1 = T_1 + \sum_n \delta_n S_n \quad (2.34)$$

where δ_n is an admixture coefficient:

$$\delta_n = \frac{\langle S_n | H_{SO} | T_1 \rangle}{E(T_1) - E(S_n)} \quad (2.35)$$

Typically the admixture coefficient values vary in the range of 0.001-0.1 depending on the system. As follows from equation (2.35), larger the value of δ_n , the larger the $\langle S_n | H_{SO} | T_1 \rangle$ integral in the numerator and the smaller the ΔE_{ST} gap in the denominator. For radiative T_1 decay (phosphorescence), the intensity of the S_0 - T_1 interaction is proportional to the square of the $\langle S_0 | M | T_1 \rangle$ transition moment (M is the electric dipole moment operator). Accounting for equations (2.34) and (2.35) and a similar mixing of the T_n and S_0 states one can get:

$$\begin{aligned} \langle \tilde{S}_0 | M | \tilde{T}_1 \rangle = & \left[\langle T_1 | M | T_1 \rangle - \langle S_0 | M | S_0 \rangle \right] \frac{\langle T_1 | H_{SO} | S_0 \rangle}{E(T_1) - E(S_0)} \\ & + \sum_n \langle S_n | M | S_0 \rangle \frac{\langle S_n | H_{SO} | T_1 \rangle}{E(T_1) - E(S_n)} \\ & + \sum_n \langle T_1 | M | T_n \rangle \frac{\langle T_n | H_{SO} | S_0 \rangle}{E(S_0) - E(T_n)} \end{aligned} \quad (2.36)$$

In general, the multipole expansion for the interaction between a molecular electronic shell and a light electromagnetic wave can be truncated with account of the electric dipole, magnetic dipole, and electric quadrupole terms. Thus, the transition moment for the S - T radiation process has the following general definition:

$$\begin{aligned} |M_{S-T}|^2 = & \left\langle S_0 \left| \sum_i e r_i \right| T_1 \right\rangle^2 + \left\langle S_0 \left| \left(\frac{1}{2mc} \sum_i e r_i \right) \times \left(\frac{\hbar}{i} \sum_i \frac{\partial}{\partial r_i} \right) \right| T_1 \right\rangle \\ & + \frac{3\pi^3 (\Delta E_{S-T})^3}{10c^2 h^3} \left\langle S_0 \left| \left(m \sum_i e r_i \right) \times \left(\sum_i r_i \right) \right| T_1 \right\rangle^2 \end{aligned} \quad (2.37)$$

The first component in equation (2.37) is the electric dipole moment contribution, while the second and third terms corresponds to the magnetic dipole moment and electric quadrupole moment contributions respectively. Both magnetic dipole and quadrupole terms are negligibly small compared with the first component, but in the case when the electronic transition is forbidden in the electric dipole approximation due to some selection rules, these small magnetic dipole and quadrupole contributions become very important for molecular phosphorescence.

2.4.3. Phosphorescence intensity and lifetime

The oscillator strength of the $S_0 \rightarrow T_1$ absorption is proportional to the square of the transition moment value M_{S-T} :

$$M_{S-T}^2 = \sum_{\gamma} \left| \langle \tilde{S}_0 | M_{\gamma} | \tilde{T}_1 \rangle \right|^2 \quad (2.38)$$

and is equal to

$$f_{S-T} = \frac{2}{3} \Delta E_{S-T} M_{S-T}^2 \quad (2.39)$$

where M and ΔE_{S-T} values are in atomic units (a.u.), γ sets the polarization of the transition momentum M along x, y, or z axes.

The radiative lifetime (τ_{α}) and corresponding rate constant (k_{α}) for the selected spin sublevel T_1^{α} can be estimated as⁹⁴

$$k_{\alpha} = \frac{1}{\tau_{\alpha}} = \frac{64\pi^4 (\Delta E_{TS})^3}{3h^4 c^3} \sum_{\gamma} |M_{\gamma}(T_1^{\alpha})|^2 \quad (2.40)$$

2.4.4. Quadratic response theory and phosphorescence

Response theory^{95, 96} can be considered as a special representation of time-dependant (TD) perturbation theory⁹⁷ where the selected molecular property (at an external perturbation) is characterized by response functions. In the presence of a TD-perturbing field V^t , a molecular property “A” can be Fourier-transformed yielding coefficient that define the response functions of different orders (indices 1, 2, 3,.....):

$$\begin{aligned} \langle \tilde{O}(t) | A | \tilde{O}(t) \rangle &= \langle 0 | A | 0 \rangle + \int_{-\infty}^{\infty} \langle \langle A; V^{\omega_1} \rangle \rangle e^{-i\omega_1 t} d\omega_1 \\ &+ \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \langle \langle A; V^{\omega_1}, V^{\omega_2} \rangle \rangle e^{-i(\omega_1 + \omega_2)t} d\omega_1 d\omega_2 \\ &+ \frac{1}{6} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \langle \langle A; V^{\omega_1}, V^{\omega_2}, V^{\omega_3} \rangle \rangle e^{-i(\omega_1 + \omega_2 + \omega_3)t} d\omega_1 d\omega_2 d\omega_3 \dots \end{aligned} \quad (2.41)$$

A main feature of the response theory is that the usual algorithms for the excited state summation is replaced by the solving of linear equation sets that can be accomplished without prior calculations of the excited states.⁹⁶