

## CHAPTER 2

### *Theoretical background of computational methods*

#### **Abstract**

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The present chapter constitutes a brief report on the basic theoretical information associated with fluorescence property, nonlinear optical property and photovoltaic property of dye sensitized solar cell (DSSC). For theoretical determination of first hyperpolarizability ( $\beta$ ) different models on the basis of quantum chemical approaches have been discussed here.

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## 2.1. Theoretical Determination of Fluorescence

### 2.1.1. Spectroscopic transition strengths

When a molecule absorbs or emits a photon, the probability of the molecule changing its state depends upon several factors, like the nature of the wavefunctions of the initial and final states, the strength of the interaction of light with the molecule and intensity of the incident light. Generally the probability of a transition of a molecule is depicted by the transition strength. Where, transition strengths are dominated by selection rule and this is determined by whether the transition is allowed or not. According to classical theory of light absorption, charges are aligned in a matter. By oscillating electromagnetic field of the light, the charges can be set into motion. The electric dipole oscillators contain specific characteristics, which is frequencies ( $\nu_i$ ), this is depends on the material. Absorption of a photon occurs when frequency of the radiation is close to the oscillator frequency and the radiation intensity reduces on passing through the substance. Oscillator strength ( $f_i$ ) is the intensity of the interaction; it can be also defined by the number of electrons per molecule that oscillate with the characteristic frequency ( $\nu_i$ ),  $f_i$  of a transition is a dimensionless number which is used for the comparison of different transitions. In quantum mechanics for a fully allowed transition, oscillator strength has 1.0 value. In experiment, oscillator strength,  $f$ , is connected to the intensity of absorption is described by:

$$f = \frac{2303mc}{nN_A e^2} \int \epsilon(\nu) d\nu \quad (2.1)$$

here,  $m$  is the mass of an electron,  $\epsilon$  represents molar absorptivity,  $c$  denotes velocity of the light,  $N_A$  is the Avogadro's number,  $e$  represents electron charge and  $n$  stands for refractive index of the medium. The integration is done over the frequency range connected with the absorption band. In quantum mechanical approximation complete explanation of the absorption of radiation by a substance is depended on the time-dependent wave mechanics. In wave mechanics, the connection between the two

states in a transition is explained by the transition dipole moment ( $\mu_{GE}$ ) by the following equation.

$$\mu_{GE} = \int \psi_G \mu \psi_E dv \quad (2.2)$$

Where ground and excited state wavefunctions are represented by  $\psi_G$  and  $\psi_E$  respectively  $dv$  is the volume element. When symmetry of the ground and excited states are different, the transition dipole moment will be a nonzero quantity.

### 2.1.2. Einstein coefficients

In 1917 Albert Einstein first described absorption and emission quantitatively.<sup>1</sup> In a time interval the rate of change of the probability of finding a molecule in the excited state is related with the transition rate of stimulated absorption. The frequency of transition from the ground to the excited state is given by the following equation.

$$W_{g \rightarrow e} = B \rho(\nu_{ge}) \quad (2.3)$$

where B represents Einstein coefficient, which is related to the square of the transition dipole moment,  $\rho$  is the energy density of radiation. By the same equation (equation no 2.3) Einstein described stimulated emission, where excitation occurs excited state to ground state (e $\rightarrow$ g). Einstein also proposed that for the radiative de-excitation there must be another way which is independent of the incident light. He suggested that the excited state of a molecule could experience spontaneous emission characterized by the coefficient A. The coefficient is directly related to the coefficient B by the following equation.

$$A_{eg} = \frac{8\pi h n^3 \nu_{eg}^3}{c^3} B_{eg} \quad (2.4)$$

here  $h$ ,  $c$  and  $n$  represent Planck constant, velocity of light in vacuum and refractive index of the environment. As spontaneous emission is directly associated with the intensity of the absorption, therefore strong absorption inherently signifies strong emission. As the coefficient A is directly proportional to the cube of the transition

frequency, as a result spontaneous emission starts to dominate with increasing the frequency of the incident light. Depending upon the nature of the ground and excited states wavefunctions, spontaneous emission can be separated into fluorescence and phosphorescence. The fluorescence can be characterized as the transition among ground and excited singlet states (S). Here singlet state wavefunction has symmetric spatial part and antisymmetric spin part; with the zero-total angular momentum i.e. electron spin is zero.

### 2.1.3. Radiative rate constant

Absorption and fluorescence related Einstein relationship is strictly valid only for systems that absorb and emit at a single frequency. This relationship is not valid for the case for dissolved molecules which shows broad absorption and fluorescence spectra. For spontaneous emission from the excited to the ground state, the radiative rate constant ( $k_r$ ) and Einstein coefficient  $A$ , can be linked to the electronic transition dipole moment.<sup>2,3</sup> If the emission transition dipole moment is same with the absorption one, it can be said that  $\mu_{ge} = \mu_{eg} = M$ , then the radiative transition can be expressed as

$$k_r = \alpha \langle \nu_f^{-3} \rangle^{-1} |M|^2 \quad (2.5)$$

here  $\langle \nu_f^{-3} \rangle^{-1}$  can be defines as

$$\langle \nu_f^{-3} \rangle^{-1} = \frac{\int F(\nu) d\nu}{\nu^{-3} F(\nu) d\nu} \quad (2.6)$$

In the above equations  $F(\nu)$  signifies the fluorescence spectrum and  $\alpha$  is the constant term which depends on the refractive index of the solvent.

#### 2.1.4. Fluorescence quantum yield

Fluorescence quantum yield is defined by the number of photons emitted relative to the number of photons absorbed. The quantum yield is associated to the radiative constant and lifetime by the following equation.

$$\phi = \frac{k_r}{k_{\text{total}}} = \frac{\tau}{\tau_r} \quad (2.7)$$

Here  $k_{\text{total}}$  is the total rate constant and  $\tau$  is the actual lifetime. This can be defined by

$$\tau = \frac{1}{k_{\text{tot}}} = \frac{1}{k_r + k_{ic} + k_{isc} + k_{ret} + k_{et} + \dots} = \frac{1}{k_r + k_{nr}} \quad (2.8)$$

The non-radiative mechanisms include internal conversion ( $k_{ic}$ ), intersystem crossing ( $k_{isc}$ ), electron transfer ( $k_{et}$ ) and resonant energy transfer ( $k_{ret}$ ).  $k_{nr}$  represents sum of all non-radiative competing processes which is involved in the deactivation of the excited state.

#### 2.1.5. Fluorescence lifetime

Upon excitation fluorophore molecule is excited to the higher energy states and then returns to the ground state, either radiatively or non-radiatively. The rate of change of the number of excited molecules with respect to time is directly associated with the number of excited molecules and rate constants by the following equation.

$$\frac{dN(t)}{dt} = -(k_r + k_{nr})N(t) \quad (2.9)$$

The solution of the equation no. 2.9 is

$$I(t) = I_0 \exp\left(-\frac{t}{\tau}\right) \quad (2.10)$$

where  $I(t)$  is the fluorescence intensity,  $I_0$  represents intensity at time zero. This equation represents mono-exponential decays. In general, in depopulation of the excited state or fluorophores, more than one process is involved. For this case, it is assumed that the intensity decay is the sum of individual single exponential decays and the intensity decay is multi-exponential.

$$I(t) = \sum_{i=1}^n \alpha_i \exp\left(-\frac{t}{\tau_i}\right) \quad (2.11)$$

where  $\tau_i$  represents decay times and  $\alpha_i$  is the amplitudes of components at time zero.  $\tau_i$  and  $\alpha_i$  parameters are rely on the studied system. For the difficulty to interpret the parameters, the mean fluorescence lifetime can be used as

$$\langle \tau \rangle = \frac{\int_0^{\infty} t I(t) dt}{\int_0^{\infty} I(t) dt} = \frac{\sum_i A_i \tau_i^2}{\sum_i A_i \tau_i} \quad (2.12)$$

### 2.1.6. Solvatochromism

Due to the different property of the ground and excited states of the fluorophore, upon excitation dipole moment changes ( $\Delta\mu = \mu_e - \mu_g$ ), which cause shift in the absorption and emission band. This relies on the solvent polarity i.e. solvatochromism. For the entire discussion of the solvatochromism effect, dielectric constant of the solvent ( $\epsilon_s$ ), refractive index ( $n$ ), and change in dipole moment ( $\Delta\mu$ ) should be considered. According to Lippert equation,<sup>4,5</sup> the stokes shift can be designated as

$$\nu_{\text{abs}} - \nu_{\text{em}} = \frac{2(\mu_e - \mu_g)^2}{c h a^3} \left[ \frac{2(\epsilon_s - 1)}{(2\epsilon_s + 1)} - \frac{2(n^2 - 1)}{(2n^2 + 1)} \right] \quad (2.13)$$

where  $h$  signifies Planck's const,  $c$  is the velocity of the light in the vacuum.  $a$  represents onsager radius of the fluorophore in the respective solvent.  $\mu_e$  and  $\mu_g$  represent excited state and ground state dipole moment.

## 2.2. Theoretical Determination of First Hyperpolarizability ( $\beta$ )

### 2.2.1. Early models for the calculation of $\beta$

#### 2.2.1.1. Equivalent field model (EIF)

Oduar and Chemla<sup>6,7</sup> developed the equivalent field model to interpret the second-order nonlinear optical responses. In this method  $\beta$  is quantified by the ground state asymmetry of a systematic  $\pi$ -chain. It is demonstrated that the second order response can be calculated by the electron distribution deformation because of appended substituents to the chromophore molecules. Due to particular substituents perturbation of the  $\pi$ -cloud occurs which is recognized as substituent mesomeric moment ( $\mu_R$ ) and this is related to  $\beta$  by the following equation.

$$\beta_{\pi} = \frac{3\gamma\Delta\mu_R}{\alpha} \quad (2.14)$$

Where  $\alpha$ ,  $\gamma$  represent polarizability and second order hyperpolarizability.  $\beta_{\pi}$  is the static hyperpolarizability at  $h\omega = 0.0$ .

In this model calculation of the  $\beta_{\pi}$  by determining the  $\mu_R$  is difficult. For mono substituted benzenes and stilbenes, the  $\pi$ -deformation caused by substituent R is defined as the difference between the ground-state  $\mu$  to the mono substituted aromatic derivative and that for the analogous mono substituted aliphatic molecule. The  $\sigma$ -contributions to the  $\mu$  of the  $\pi$ -chromophores are eliminated. Using the  $\mu_R$ ,<sup>8</sup> the  $\beta_{\pi}$  for a considerable number of mono substituted  $\pi$ -conjugation systems are predicted, which are well correlated with experimental trends in the second order response.<sup>7,9</sup> This model also accounts for the negative sign in the second order response when the added group is an electron acceptor and a positive  $\beta$  when the attached moiety is an electron donor.

### 2.2.1.2. Additivity model

This model is used to calculate the second order response for push-pull type di-substituted systems (e.g. donor-acceptor substituted benzene). It is postulated that the total nonlinear polarizability is the sum of contribution of significant structural component of the systems.<sup>10,11</sup> According to Zyss et al. this model can well explain the nonlinear behaviour of the weakly coupled *D* and *A*  $\sigma$ -networks system but failed to explain the nonlinearity of strongly coupled disubstituted systems<sup>12,13</sup> and highly asymmetric system.

The complications of EIF and additivity model are due to postulation of nonlinearity which is comprised of ground-state electronic distributions.

### 2.2.1.3. Two-state model

The nonlinearity of the highly asymmetric system is well explained in the two-state model by Oudar and Chemla<sup>7,14</sup>. This model suggested that the high nonlinearity i.e. high  $\beta$  arises due to the intramolecular charge transfer (CT) from donor to acceptor moiety. Nonlinear optical property is dependent on ground state as well as excited state electronic distribution. The  $\beta$  value is sum of two contributions. One is interaction between the spacer group and individual substituent ( $\beta_{add}$ ) and another is intramolecular charge transfer interactions ( $\beta_{CT}$ ) between the *D* and *A* groups. This can be represented as

$$\beta = \beta_{CT} + \beta_{add} \quad (2.15)$$

The two-level interaction between the ground state (*g*) and the first excited state (*n*) can be described as

$$\beta_{CT} = \frac{3e^2}{2m} \frac{\hbar\omega_{gn} f_{gn} \Delta\mu_{gn}}{[(\hbar\omega_{gn})^2 - (2\hbar\omega)^2][(\hbar\omega_{gn})^2 - (\hbar\omega)^2]} \quad (2.16)$$

In the above equation  $h\omega$  represents 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 ground state to the first excited state transition and  $\Delta_{gn}$  represent the difference in dipole moments between the  $g$  and  $n$  state.

### 2.3. Quantum Chemical Calculation for the Calculation of NLO Response

It is very important for the theoretical chemist to predict the NLO response accurately as this gives the guideline to the synthetic chemist to explore molecules which have potential interest. For suitable NLO material, structure-optical property relationship is very important parameter. For the computation of NLO response two basic methodologies i.e., Sum over states (SOS) methods and Coupled perturbed HF (CPHF) methods can be used. The SOS method is field-independent and the CPHF method is field-dependent. For the computation of  $\beta$  both model can be used for any model Hamiltonian (*i.e.*, ab initio, semiempirical).

#### 2.3.1. Sum over states (SOS) methods

For the determination of theoretical hyperpolarizabilities, sum over states (SOS) methods are one of the popular methodologies. In this method calculations are done on free molecule where NLO response is associated with the coupling of the excited state. In the SOS methods, perturbation theory is applied to an unperturbed molecule<sup>15,16</sup> for the estimation of  $\beta$  value. This is an uncoupled formulation where perturbing laser field creates electronic excited states, which are behaved as infinite sum over unperturbed particle-hole states.

The perturbation equation of SOS methods for the determination of  $\beta$  is given in the following (2.17).

$$\beta_{ijk}^{SHG} = -\frac{e^3}{8h^2} \left[ \begin{aligned} & \sum_{n \neq g} \sum_{\substack{n' \neq g \\ n' \neq n}} \left\{ (r_{gn}^j r_{n'n}^i r_{gn}^k + r_{gn}^k r_{n'n}^i r_{gn}^j) \left( \frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - \omega)} \right) + \right. \\ & (r_{gn}^i r_{n'n}^j r_{gn}^k + r_{gn}^i r_{n'n}^k r_{gn}^j) \left( \frac{1}{(\omega_{n'g} + 2\omega)(\omega_{ng} + \omega)} \right) \left( \frac{1}{(\omega_{n'g} - 2\omega)(\omega_{ng} - \omega)} \right) + \\ & \left. (r_{gn}^j r_{n'n}^k r_{gn}^i + r_{gn}^k r_{n'n}^j r_{gn}^i) \left( \frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} - 2\omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} + 2\omega)} \right) \right\} + \\ & \left\{ [r_{gn}^j r_{gn}^k \Delta r_n^i (\omega_{ng}^2 - 4\omega^2) + r_{gn}^i (r_{gn}^k \Delta r_n^j + r_{gn}^j \Delta r_n^k) (\omega_{ng}^2 + 2\omega^2)] \times \right. \\ & \left. 4 \sum_{n \neq g} \frac{1}{(\omega_{ng}^2 - \omega^2)(\omega_{ng}^2 - 4\omega^2)} \right\} \end{aligned} \right] \quad (2.17)$$

here,  $\omega$  = frequency of the applied electric field

$r_{n,n'}^i$  = matrix element of displacement operator  $r^i$  along the  $i^{\text{th}}$  molecular axis

between electronic states  $n$  and  $n'$

$h\omega_{ng}$  = difference of energy between the ground state ( $g$ ) and an excited state ( $n$ ).

And  $\Delta r_n^i (= r_{nn}^i - r_{gg}^i)$  = difference of excited and ground state dipole moment.

For the calculation of  $\beta$ , ground and excited states dipole matrix elements, excited state dipole moment and excitation energy are important parameters.

As the molecular ground state is of single determinant type, the polarizability of a molecule is associated with the monoexcited configurations only. Although the SOS expansion is infinite because in these methods the applied fields mix the molecular ground state with many excited states.

### 2.3.2. Coupled perturbed Hartree Fock (CPHF) methods

In this methodology molecular Hamiltonian acts as field term ( $-r \cdot F$ ) which explains the interaction between the electronic structure and the uniform external static field. At particular field strength the molecular wavefunction is obtained and the expectation values of the field-dependent molecular energy ( $E(F)$ ) and the dipole moment ( $\mu(F)$ ) can be assessed by following equations

$$E(F) = \langle \psi(F) | H(F) | \psi(F) \rangle \quad (2.18)$$

$$\mu(F) = \langle \psi(F) | \sum q_i(F) r_i(F) | \psi(F) \rangle \quad (2.19)$$

The interaction of the dipole moment with the external electric field and the NLO response can be described as follows

$$\mu_i(F) = \mu_i^0 + \sum_j \alpha_{ij} F_j + \sum_{j < k} \beta_{ijk} F_j F_k + \sum_{j < k < l} \gamma_{ijkl} F_j F_k F_l + \dots \quad (2.20)$$

here  $\mu_i^0$  signifies the dipole moment (in absence of the field) and  $(\mu_i - \mu_i^0)$  represents polarization in the  $i^{\text{th}}$  direction ( $P_i$ ). By differentiation of  $\mu(F)$  with respect to the electric field the higher order (hyper) can be obtained.

The first, second and third partial derivative of the polarization ( $P_i$ ) with respect to the field can provide the polarizability,  $\beta$  and  $\gamma$  at zero field.<sup>17-19</sup>

$$\alpha_{ij} = (\partial \mu_i / \partial F_j)_{F=0} \quad (2.21)$$

$$\beta_{ijk} = (\partial^2 \mu_i / \partial F_j \partial F_k)_{F=0} \quad (2.22)$$

$$\gamma_{ijkl} = (\partial^3 \mu_i / \partial F_j \partial F_k \partial F_l)_{F=0} \quad (2.23)$$

The  $\alpha$ ,  $\beta$  and  $\gamma$  coefficients can also be determined from the molecular energy expansion<sup>18,19</sup>. As the dipole moment of a molecule is the negative field derivative of the energy. Thereby this can be represented as follows

$$\mu_i = -(\partial E / \partial F_i) \quad (2.24)$$

$$\alpha_{ij} = -(\partial^2 E / \partial F_i \partial F_j)_{F=0} \quad (2.25)$$

$$\beta_{ijk} = (\partial^3 E / \partial F_i \partial F_j \partial F_k)_{F=0} \quad (2.26)$$

$$\gamma_{ijkl} = (\partial^4 E / \partial F_i \partial F_j \partial F_k \partial F_l)_{F=0} \quad (2.27)$$

These relationships provided for  $\alpha$ ,  $\beta$  and  $\gamma$  are applicable for the static field limit. Therefore for the computations of NLO response zero frequency has been reported usually. For the computation of the above derivatives numerical differentiation strategies<sup>20,21</sup> are used. Analytic gradient techniques developed by Pulay and others<sup>22,23</sup> are also used to compute the above derivatives. In this methodology to compute NLO response and other properties usually gradients techniques are employed.

## 2.4. Theoretical Determination of Dye-Sensitized Solar Cells (DSSSC)

### 2.4.1. Working Principle of Dye-Sensitized Solar Cells

The working principle of DSSC stands upon four basic steps:

1. Light absorption
2. Electron injection
3. Transportation of carrier
4. Collection of current.

**Step 1:** At the 1<sup>st</sup> step photosensitizer absorbed incident light (photon), therefore electrons of the dye in the ground state ( $S^+/S$ ) gets promoted to the excited state ( $S^+/S^*$ ). Generally the absorption wavelength for maximum cases is in the range of 700 nm which is corresponding to 1.72 eV of the photon energy.

**Step 2:** In the next step the excited electrons with a nanosecond lifetime are injected into the electrode of  $TiO_2$  conduction band. The conduction band of  $TiO_2$  electrons lies below the excited state of the dye. Here small portion of solar photons can be absorbed by the  $TiO_2$  electrode in the UV region.<sup>24</sup> Hence the oxidization of the dye occurs.



**Step 3:** The electrons which are injected in  $TiO_2$  nanoparticles are now transported and the electrons are diffused towards the back contact (transparent conducting oxide [TCO]). The electrons reach at the counter electrode through the external circuit.

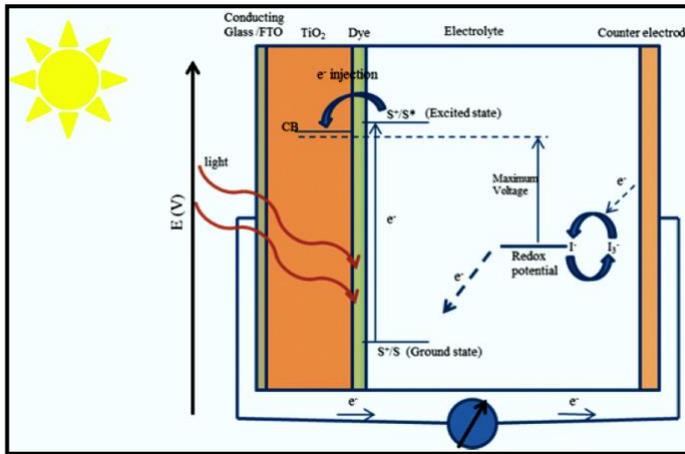
**Step 4:** At the counter electrode electrons reduce  $I_3^-$  to  $I^-$ . In this step dye regeneration occurs or it can be said that regeneration of the ground state of the dye happens. As  $I^-$  gets oxidized to  $I_3^-$  (oxidized state) and the electrons of the  $I^-$  ion are accepted by dye.



**Step 5:** In the last step  $I_3^-$  reduces to  $I^-$  as the oxidized mediator ( $I_3^-$ ) diffuses towards the counter electrode.



In the conversion of light into electricity the following steps are involved which is shown in figure 2.4.1.



**Figure 2.4.1.** Working principle of dye-sensitized solar cells

## 2.4.2. Photovoltaic properties of dye sensitized Solar cell (DSSC)

The efficiency of electron injection process to the surface of conduction band of semiconductor and electron accumulation efficiency at the transparent conductive oxide electrode regulate the short-circuit current density ( $J_{sc}$ ) of DSSC. The efficiency ( $\eta$ ) of DSSC can be expressed using the following equation:<sup>25</sup>

$$\eta = \frac{J_{sc} FF V_{oc}}{P_{IN}} \quad (2.32)$$

where  $V_{OC}$  is the open-circuit photovoltage, which is the potential difference between the Fermi level of the electrons in the semiconductor and redox potential of the electrolyte. FF is the fill factor and  $P_{IN}$  is the input power of incident solar light. The short-circuit density ( $J_{SC}$ ) in DSSC is determined as:<sup>26</sup>

$$J_{SC} = \int_{\lambda} \mathbf{LHE}(\lambda) \phi_{\text{inject}} \eta_{\text{collect}} \mathbf{d}\lambda \quad (2.33)$$

LHE ( $\lambda$ ) is light harvesting efficiency,  $\phi_{\text{inject}}$  is the electron injection efficiency and  $\eta_{\text{collect}}$  is the charge collection efficiency. Equation 2.33 describe that, large LHE and  $\phi_{\text{inject}}$  of the sensitizer, assist to achieve high  $J_{SC}$  value. The LHE is described by:<sup>27</sup>

$$\mathbf{LHE} = \mathbf{1} - \mathbf{10}^{-A} = \mathbf{1} - \mathbf{10}^{-f} \quad (2.34)$$

where  $A$  ( $f$ ) is the absorption (oscillator strength) of the dye. So, larger  $f$  value imparts higher light harvesting efficiency.

$\phi_{\text{inject}}$  is correlated with the free energy change ( $\Delta G$ ), which is linked to the electron injection process from the photoinduced excited state of the dye into the  $\text{TiO}_2$  surface.<sup>27,28</sup>

$$\phi_{\text{inject}} \propto f(-\Delta G^{\text{inject}}) \quad (2.35)$$

$$\Delta G^{\text{inject}} = E^{\text{dye}^*} - E_{CB} = E^{\text{dye}} - E_{0-0} - E_{CB} \quad (2.36)$$

$E^{\text{dye}^*}$  and  $E^{\text{dye}}$  are the excited state and ground state oxidation potential energy of the dye.  $E_{CB}$  is reduction potential of  $\text{TiO}_2$  conduction band. Herein  $E_{CB}$  is  $-4.0$  eV for  $\text{TiO}_2$ .  $E_{0-0}$  represents electronic vertical transition energy.<sup>29</sup> To achieve high energy-conversion efficiency, dye molecules should overcome the binding energy barrier, i.e., dye should hold low exciton binding energy ( $E_b$ ).  $E_b$  is determined as:<sup>30,31</sup>

$$E_b = E_g - E_x = E_{H-L} - \lambda_{\text{max}} \quad (2.37)$$

$E_g$  is band gap of dye molecule and estimated as the difference of HOMO–LUMO energy and  $E_x$  is the optical band gap and defined as electronic vertical transition energy.

### 2.4.3. Electron injection

For the efficient electron injection process the calculation of electron injection lifetime ( $\tau$ ) for adsorbates on the surface is an important parameter which can be calculated by employing the Newns–Anderson model. The electron injection lifetime is inversely proportional to the electron injection efficiency ( $\Phi_{inj}$ ). The simulation is depended on the energy shift of the LUMO after the adsorption of dye on the semiconductor surface. The lifetime broadening ( $\hbar\Gamma$ ) can be illustrated by a Lorentzian distribution:<sup>32,33</sup>

$$L_{LUMO}(E) = \frac{1}{(E - E_{LUMO})^2 + \left(\frac{\hbar\Gamma}{2}\right)^2} \quad (2.38)$$

here distribution of the LUMO level of dye is represented by  $L_{LUMO}(E)$  and  $E_{LUMO}$  signifies adsorbate LUMO level, which is calculated from a weighted average of the computed energies. In convenient numerical units the approximate electron injection lifetime can be illustrated as

$$\tau = 658 / \hbar\Gamma \quad (2.39)$$

by using this method in DSSC the electron transfer process of the dye/TiO<sub>2</sub> interface could accurately simulated.

### 2.4.4. Open circuit photovoltage ( $V_{oc}$ )

The difference of voltage between the electrolyte redox potential ( $E_{redox}/q$ ) and the quasi-Fermi potential of electrons ( $E_{F,n}/q$ ) in the TiO<sub>2</sub> semiconductor are defined by open circuit photovoltage ( $V_{oc}$ ). In the DSSC,  $V_{oc}$  can be represented by the following equation<sup>34</sup>

$$V_{OC} = \frac{E_{CB} + \Delta CB}{q} + \frac{K_B T}{q} \ln \left( \frac{n_c}{N_{CB}} \right) - \frac{E_{redox}}{q} \quad (2.40)$$

in the above equation  $K_B$  is the Boltzmann constant,  $E_{CB}$  signifies conduction band edge of the semiconductor,  $q$  represents unit charge,  $E_{redox}$  stands for the electrolyte Fermi level,  $T$  is the absolute temperature, the number of electron in the conduction band is represented by  $n_c$ , and  $N_{CB}$  signifies accessible density of conduction band states.  $\Delta CB$  represents shift of  $E_{CB}$  after adsorption of the dyes on the semiconductor and can be expressed as<sup>26</sup>

$$\Delta CB = - \frac{q \mu_{normal} \gamma}{\epsilon_0 \epsilon} \quad (2.41)$$

here electron charge is represented by  $q$ ,  $\mu_{normal}$  signifies the dipole moment component of the sensitizer perpendicular to the semiconductor surface, surface concentration of dye is represented by  $\gamma$ ,  $\epsilon_0$  signifies permittivity of vacuum and  $\epsilon$  represents permittivity of the dipole layer.

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