

# On few-state (VB- $n$ CT) theory

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## 1 Introduction

In nonlinear optics (NLO), promising molecular architectures often belong to the push-pull family. These structures typically consist of electron donor and acceptor groups connected by a  $\pi$ -conjugated segment that facilitates electronic “communication” between the two moieties.

To elucidate the relationships between NLO properties and structure, simplified models have been developed to capture complex phenomena with minimal parameters. The valence-bond charge-transfer (VB-CT) model, pioneered by Mulliken [1], has been particularly successful in describing the first hyperpolarizabilities of push-pull polyenes. It also applies to other properties, such as UV/VIS absorption spectra and various physico-chemical characteristics [2]. This model represents a system as a superposition of two limiting states, a valence-bond state,  $\phi_{VB}$ , and a charge-transfer state,  $\phi_{CT}$ , connected by electron displacement from the donor to the acceptor (see Fig. 1). Using fundamental parameters, such as the ionization energy of the donor, electron affinity of the acceptor, and the coupling between these states, the VB-CT model provides valuable insight into structure-activity relationships. Indeed, when combined with the sum-over-states (SOS) theory developed by Orr and Ward [3], these models provide estimate of NLO properties and identification of valuable structure-activity relationships.

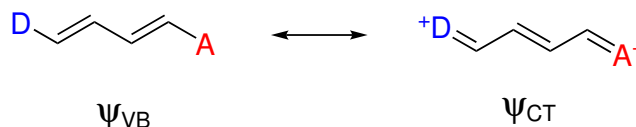


Figure 1: Limiting forms of the VB-CT model.

Despite its simplicity, this model has proven versatile, allowing extensions to systems with multiple donor/acceptor groups through 3-state [4, 5, 6], 4-state [7], and 5-state [8] descriptions. The goal of this document is to quickly review these models few-state models and to introduce a few useful relationships.

## 2 Theory

### 2.1 A model Hamiltonian

Given a set of basis functions  $\{\phi_i\}$ , the energy of a trial function  $\Psi = \sum_i c_i \phi_i$  is always greater than or equal to the true ground state energy,  $\varepsilon_0$ :

$$\varepsilon_0 \leq \varepsilon, \text{ where } \varepsilon = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle},$$

One minimizes the energy of the trial function by setting  $\frac{d\varepsilon}{dc_i} = 0$ . This yields a set of so-called secular equations of the form:

$$\forall k : \sum_i c_i (H_{ki} - \varepsilon_k S_{ki}) = 0, \quad (1)$$

where  $S_{ki} = \langle \phi_k | \phi_i \rangle$  (overlap matrix) and  $H_{ki} = \langle \phi_k | \hat{H} | \phi_i \rangle$  (Hamiltonian matrix). This is a generalized eigenvalue problem. If the basis functions are orthogonal, i.e.,  $S_{ki} = \delta_{k,i}$ , this reduces to a standard eigenvalue problem,  $HC = C\varepsilon$ , where diagonalizing  $H$  gives the energy levels,  $\varepsilon$ .  $C$  is the matrix of coefficients, also referred to as the eigenfunctions of the system.

In the VB- $n$ CT framework, corresponding to a  $(n+1)$ -state model, a set of orthogonal functions is employed consisting of one valence-bond (VB) state,  $\phi_{VB}$ , and  $n$  charge-transfer (CT) states,  $\{\phi_{CT,i} | 0 < i \leq n\}$ . This leads to a model Hamiltonian, given by a  $(n+1) \times (n+1)$  matrix and parameterized as follows:

$$\langle \phi_{VB} | \hat{H} | \phi_{VB} \rangle = E_{VB}, \langle \phi_{VB} | \hat{H} | \phi_{CT,i} \rangle = -t, \text{ and } \langle \phi_{CT,i} | \hat{H} | \phi_{CT,j} \rangle = \begin{cases} E_{CT} & \text{if } i = j, \\ -T & \text{otherwise,} \end{cases} \quad (2)$$

where  $E_{VB}$  and  $E_{CT}$  denote the energies of the VB and CT states, respectively, while  $t$  and  $T$  are the transfer integrals.

Solving the eigenvalue problem yields a ground state,  $|0\rangle$ , with minimal energy, a set of  $(n-1)$ -fold degenerate excited states,  $\{|e_i\rangle | 0 < i < n\}$  (which does not exist when  $n = 1$ ), and a single non-degenerate excited state,  $|f\rangle$ . Corresponding eigenvalues were provided by Cho *et al.* [8] and are, in all generality, given by:

$$\begin{aligned} E_0 &= \frac{1}{2} \left[ E_{VB} + E_{CT} - (n-1)T - \sqrt{(V - (n-1)T)^2 + 4nt^2} \right], \\ E_{e_i} &= E_{CT} + T, \\ E_f &= \frac{1}{2} \left[ E_{VB} + E_{CT} - (n-1)T + \sqrt{(V - (n-1)T)^2 + 4nt^2} \right], \end{aligned} \quad (3)$$

where  $V = E_{CT} - E_{VB}$ . The associated eigenfunctions are:

$$|0\rangle = \cos \delta |\phi_{VB}\rangle + \frac{\sin \delta}{\sqrt{n}} \sum_{0 < j \leq n} |\phi_{CT,j}\rangle,$$

$$\begin{aligned}
|e_i\rangle &= \frac{1}{\sqrt{i(i+1)}} \left[ - \sum_{0 < j \leq i} |\phi_{CT,j}\rangle + i |\phi_{CT,i+1}\rangle \right], \\
|f\rangle &= \sin \delta |\phi_{VB}\rangle - \frac{\cos \delta}{\sqrt{n}} \sum_{0 < j \leq n} |\phi_{CT,j}\rangle,
\end{aligned} \tag{4}$$

where the mixing angle  $\delta \in [0, \pi/2]$  is introduced. For  $0 \leq \delta < \pi/4$ , the ground state is VB-dominated, whereas for  $\pi/4 < \delta \leq \pi/2$ , the CT state dominates. The point  $\delta = \pi/4$  is referred to as the *cyanine limit*.

Minimizing the ground-state energy  $E_g$  with respect to  $\delta$  provides a condition linking the parameters:

$$\frac{\partial E_g(\delta)}{\partial \delta} = 0 \Rightarrow V - (n-1)T = 2t\sqrt{n} \cot(2\delta). \tag{5}$$

Setting the energy origin to:

$$E_{VB} + E_{CT} - (n-1)T = 0, \tag{6}$$

simplifies the eigenvalues to:

$$E_0 = -\sqrt{n} \frac{t}{\sin(2\delta)}, E_{e_i} = nT + t\sqrt{n} \cot(2\delta), \text{ and } E_f = \frac{t}{\sin(2\delta)} \sqrt{n}. \tag{7}$$

To monitor variations in molecular properties, the charge-transfer (CT) character of the ground state,  $\ell_{CT}$ , can be introduced as follows [8, 7, 6]:

$$\ell_{CT} = \frac{1}{n} \sin^2 \delta. \tag{8}$$

With  $\delta \in [0, \pi/2]$ ,  $\ell_{CT}$  varies in the range  $\ell_{CT} \in [0, 1/n]$ . A value of  $\ell_{CT} = 0$  indicates a ground state fully described by the VB form, while  $\ell_{CT} = 1/n$  corresponds to a state entirely characterized by CT. An additional parameter, introduced by Barzoukas and collaborators [9, 10, 11], measures the VB-CT mixing:

$$m_{CT} = -\cos(2\delta) = 2n\ell_{CT} - 1. \tag{9}$$

This parameter,  $m_{CT}$ , ranges from  $-1$  (VB-dominated) to  $+1$  (CT-dominated), effectively capturing the balance between VB and CT character in the ground state.

## 2.2 A set of dipole moments

To utilize the SOS expression, both excitation energies (calculated, in the VB- $n$ CT model, as differences between eigenvalues, given in Eq. (7)) and transition dipoles are required. In general, transition dipoles are computed as follows:

$$\vec{\mu}_{ij} = \langle i | \hat{\mu} | j \rangle = \sum_{\nu\kappa} C_{i\nu} C_{j\kappa} \langle \phi_\nu | \hat{\mu} | \phi_\kappa \rangle = C M C^\dagger, \tag{10}$$

where  $|i\rangle = \sum_{\nu} C_{i\nu} |\phi_{\nu}\rangle$  represents the electronic states of the system,  $C_{i\nu}$  are the coefficients in the state expansion, and  $|\phi_{\nu}\rangle$  are the basis functions.

In the VB- $n$ CT model, the dipole matrix elements  $M_{\mu\nu} = \langle\phi_{\nu}|\hat{\mu}|\phi_{\kappa}\rangle$  are given as follows [12]:

$$\langle\phi_{VB}|\hat{\mu}|\phi_{VB}\rangle = \langle\phi_{VB}|\hat{\mu}|\phi_{CT,i}\rangle = 0, \langle\phi_{CT,i}|\hat{\mu}|\phi_{CT,j}\rangle = \begin{cases} \vec{\mu}_{CT,i} & \text{if } i = j, \\ 0 & \text{otherwise.} \end{cases} \quad (11)$$

This results in a sparse, diagonal dipole matrix parameterized by a select set of CT dipole moments associated to each CT state,  $\{\vec{\mu}_{CT,i} \mid 0 < i \leq n\}$ . Generally,  $\vec{\mu}_{CT,i} = \mu_{CT} \vec{e}_i$ , where  $\vec{e}_i$  is a unit vector, so that all dipole have the same length, given by the quantity  $\mu_{CT}$ .

### 2.3 Parameterization of a VB- $n$ CT model

As outlined in Sections 2.1 and 2.2, a VB- $n$ CT model is uniquely defined by a set of  $n$  CT dipole moments,  $\{\vec{\mu}_{CT,i} \mid 0 < i \leq n\}$ , and either of the following parameterizations:

1. Using Eq. (2): specified by  $E_{VB}$ ,  $E_{CT}$  (or equivalently  $V$ ),  $t$ , and  $T$ ;
2. Alternatively, by applying the conditions in Eqs. (5) and (6): specified by  $t$ ,  $T$ , and one of the mixing parameters defined in Section 2.1 (such as  $\delta$ ,  $\ell_{CT}$ , or  $m_{CT}$ ).

This allows a straightforward implementation of this model in Python, which outputs excitation energies and transition dipole moments.

## 3 Results

Using Eqs. A2-A6 allows to check the implementation. It works ;)

## A Practical expressions for static $\beta$

Let's assume the parameterization from Section 2.3 (with  $m_{CT}$  as the mixing parameter), and a (non-divergent) SOS expression for the static  $\beta$  tensor elements [13]:

$$\beta_{(\zeta\eta\kappa)} = \hbar^{-2} \sum_{\mathcal{P}} \sum_{a'_1, a'_2} \frac{(\zeta\bar{\eta}\kappa)_{a_1 a_2}}{\omega_{a_1} \omega_{a_2}}, \quad (\text{A1})$$

where  $\zeta, \eta, \kappa$  are the Cartesian coordinates  $x, y, z$  (in the molecular frame, the parenthesis indicates that one can freely permute the indices),  $(\zeta\bar{\eta}\kappa)_{a_1 a_2}$  is the notation of Bishop for the product of transition dipole moments,  $\sum_{a'_1, a'_2}$  is a sum over the  $n$  excited states, and  $\sum_{\mathcal{P}}$  is the sum over the different permutations. On that ground, one can derive practical expressions for the components of  $\beta$  in different cases, presented below. For an in-depth derivation, see Chapter 11 of Ref. [14] and the references therein.

**2-state ( $C_{\infty v}$ ) model.** These systems consist of a donor-acceptor (D/A) pair typically located at the ends of a  $\pi$ -conjugated linker, oriented along the  $z$ -axis for convenience. Assuming that the CT dipole moment,  $\mu_{CT}$ , lies entirely along the  $z$ -axis, one obtains the following expression for the only non-null component,  $\beta_{zzz}$  [9, 10, 11]:

$$\beta_{zzz} = -\frac{3}{8} m_{CT} (1 - m_{CT}^2)^2 \frac{\mu_{CT}^3}{t^2}. \quad (\text{A2})$$

**3-state ( $C_{2v}$ ) model.** Assuming that the two CT axes form an angle  $\theta \in [0, \pi/2]$  from the  $z$  axis [6], as represented in Fig. 2, one has:

$$\vec{\mu}_{CT,1} = \mu_{CT} (\sin \theta, 0, \cos \theta) \text{ and } \vec{\mu}_{CT,2} = \mu_{CT} (-\sin \theta, 0, \cos \theta). \quad (\text{A3})$$

There are only two non-null independent components:  $\beta_{zzz}$  and  $\beta_{(zxx)}$ :

$$\begin{aligned} \beta_{zzz} &= -\frac{3}{16} m_{CT} (1 - m_{CT}^2)^2 \frac{\mu_{CT}^3}{t^2} \cos^3 \theta, \\ \beta_{(zxx)} &= \frac{1 - m_{CT}^2}{2} \mu_{CT}^3 \sin^2 \theta \cos \theta \\ &\quad \times \left\{ \frac{1}{\left(2T + t \left[2 \frac{1 - m_{CT}}{1 + m_{CT}}\right]^{1/2}\right)^2} + \frac{2}{2t \left[\frac{2}{1 - m_{CT}^2}\right]^{1/2} \left(2T + t \left[2 \frac{1 - m_{CT}}{1 + m_{CT}}\right]^{1/2}\right)} \right\}. \end{aligned} \quad (\text{A4})$$

Note that when  $\theta = 90^\circ$ , both  $\beta_{zzz}$  and  $\beta_{(zxx)}$  goes to zero, since it corresponds to a situation with a center of inversion ( $D_{\infty h}$ ).

**4-state ( $C_{3v}$ ) system.** Let's, this time, assume that the three dipole moments are at  $120^\circ$  from each other in the  $xy$  plane (and the first one point to the  $y$  direction), but that there is a

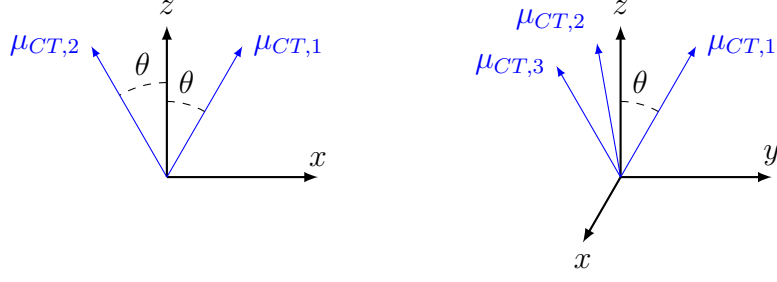


Figure 2: Representation of the charge-transfer dipoles ( $\mu_{CT}$ ) in the 3-state (left) and 4-state (right) models.

$\theta \in [0, \pi/2]$  angle between the dipoles and the  $z$  axis, as in Fig. 2. Thus,

$$\vec{\mu}_{CT,1} = \mu_{CT} (0, \sin \theta, \cos \theta), \vec{\mu}_{CT,2} = \vec{\mu}_{CT,3} = \frac{\mu_{CT}}{2} (\pm \sqrt{3} \sin \theta, -\sin \theta, 2 \cos \theta) \quad (\text{A5})$$

There are three non-null independent components:  $\beta_{zzz}$ ,  $\beta_{(zyy)}$ , and  $\beta_{yyy}$ . Their expressions are:

$$\begin{aligned} \beta_{zzz} &= -\frac{1}{8} m_{CT} (1 - m_{CT}^2)^2 \frac{\mu_{CT}^3}{t^2} \cos^3 \theta, \\ \beta_{(zyy)} &= \frac{1 - m_{CT}^2}{4} \mu_{CT}^3 \sin^2 \theta \cos \theta \\ &\quad \times \left\{ \frac{1}{\left( 3T + t \left[ 3 \frac{1 - m_{CT}}{1 + m_{CT}} \right]^{1/2} \right)^2} + \frac{2}{2t \left[ \frac{3}{1 - m_{CT}^2} \right]^{1/2} \left( 3T + t \left[ 3 \frac{1 - m_{CT}}{1 + m_{CT}} \right]^{1/2} \right)} \right\}, \\ \beta_{yyy} &= \frac{3}{4} (1 + m_{CT}) \frac{\mu_{CT}^3}{\left( 3T + t \left[ 3 \frac{1 - m_{CT}}{1 + m_{CT}} \right]^{1/2} \right)^2} \sin^3 \theta. \end{aligned} \quad (\text{A6})$$

The relationship  $\beta_{yyy} = -\beta_{(yxx)}$  holds in this model,<sup>1</sup> as expected from  $C_{3v}$  symmetry. Note that when  $\theta = 90$ , the system correspond to a  $D_{3h}$  symmetry, with  $\beta_{zzz} = \beta_{(zyy)} = \beta_{(zxx)} = 0$ , and  $\beta_{yyy}$  is the only remaining component.

**5-states ( $T_d$ ) system.** For the sake of completeness, lets finally consider the  $T_d$  geometry, which was first reviewed by Cho *et al.* [8]. The dipole moments are (arbitrarily) given by

$$\begin{aligned} \vec{\mu}_{CT,1} &= \mu_{CT} \frac{\sqrt{3}}{3} (1, 1, 1), \vec{\mu}_{CT,2} = \mu_{CT} \frac{\sqrt{3}}{3} (1, -1, -1), \\ \vec{\mu}_{CT,3} &= \mu_{CT} \frac{\sqrt{3}}{3} (-1, -1, 1), \text{ and } \vec{\mu}_{CT,4} = \mu_{CT} \frac{\sqrt{3}}{3} (-1, 1, -1). \end{aligned} \quad (\text{A7})$$

<sup>1</sup>Symmetry tables generally reports  $\beta_{yyy} = -\beta_{(yxx)}$ , but it is just a matter of defining the  $\sigma_v$ . Also, this definition is consistent with  $D_{3h}$ .

In this case, there is only one non-null independent component:

$$\beta_{(xyz)} = (1 + m_{CT}) \frac{\sqrt{3}}{3} \frac{\mu_{CT}^3}{\left(4T + 2t \left[\frac{1-m_{CT}}{1+m_{CT}}\right]^{1/2}\right)^2}. \quad (\text{A8})$$

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