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Article

Chiroptical Symmetry Analysis (CSA): Exciton Chirality-Based Formulae to Understand the Chiroptical Responses of C_n and D_n Symmetric Systems

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Abstract: The high sensitivity of chiroptical responses to conformational changes and supramolecular interactions has prompted an increasing interest in the development of chiroptical applications. However, prediction and understanding the chiroptical responses of the necessary large systems may not be affordable for calculations at high levels of theory. In order to facilitate the development of chiroptical applications, methodologies capable of evaluating the chiroptical responses of large systems are necessary. Exciton chirality method has been extensively used for the interaction between two independent chromophores through the Davydov model. For systems presenting C_2 or D_2 symmetry one can get to the same results by applying the selection rules. In the present article, analysis of the selection rules for systems with symmetries C_n and D_n with n = 3 and 4 is used to uncover the origin of their chiroptical responses. We hope that the use of the chiroptical symmetry analysis (CSA) for systems presenting the symmetries explored herein as well as for systems presenting higher symmetries will serve as a useful tool for the development of chiroptical applications.

Keywords: Chirality; Chiroptical Responses; Exciton Chirality; Selection Rules; Symmetry.

1. Introduction

Chirality, or the existence of a pair of non-superimposable mirror-image shapes, is a natural property present in a wide variety of biological systems. While enantiomeric molecules present the same interaction with other achiral molecules, they may interact differently with other chiral molecules or entities. Besides its impact in the biological world is ubiquitous[1-2], chirality can also be exploited in other areas such as materials science. For example, the interaction of chiral compounds with light has been used for the construction of light powered molecular motors[3] or in the development of more sensitive and specific sensors[4-5]. The increasing interest in the potentiality of chiral systems for miscellaneous applications makes essential the understanding of their chiroptical responses and the development of methodologies to study them.

When a linearly polarized light passes through a chiral medium, the resulting light can become elliptically polarized due to the different absorption of the right and left circularly polarized light by the chiral medium[6]. This phenomenon is known as circular dichroism which can exists in two forms, electronic (U.V.-visible range) or vibrational (I.R. range). Derived from the particular interaction of chiral molecules with light, optical methodologies were developed to characterize enantiomers according to their absolute configurations[7].

The electronic circular dichroism (ECD) is one of the most used chiroptical spectroscopies [8,9]. Comparison of the experimental and theoretically predicted ECD spectra is routinely used not only

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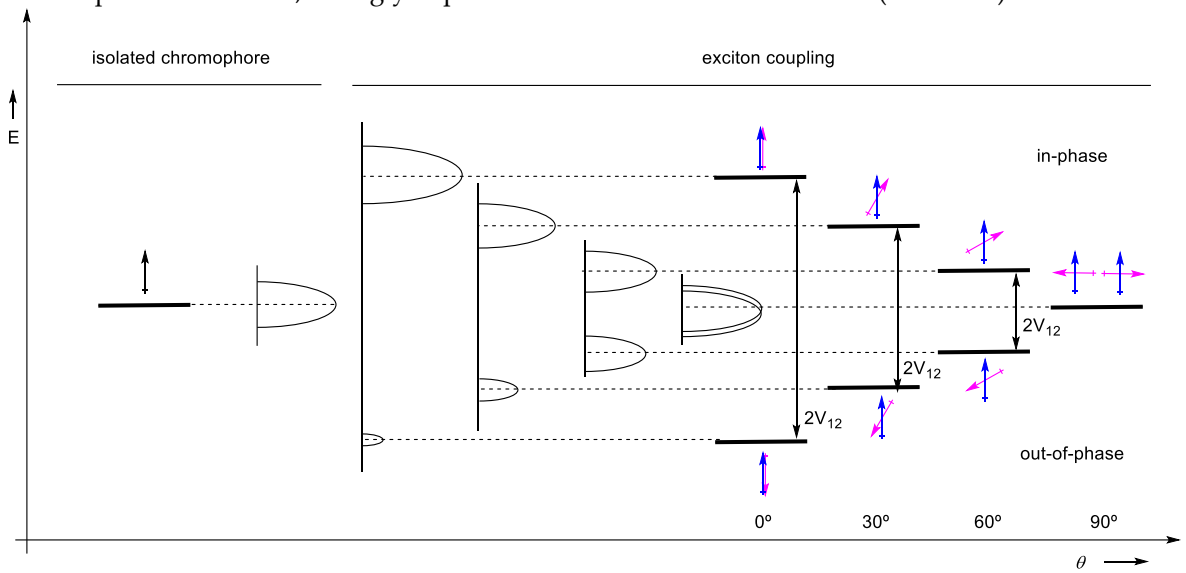
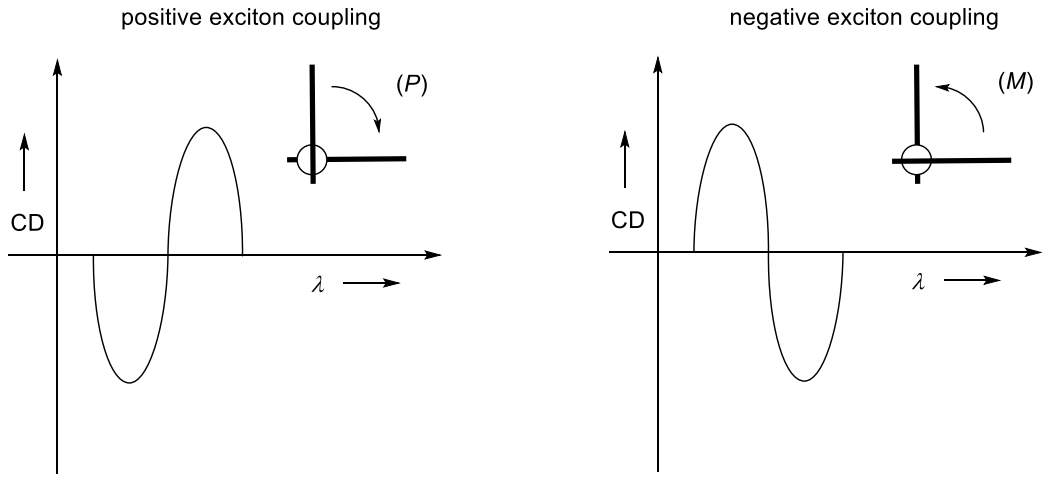
for absolute and relative configuration assignment of small and medium sized molecules[10], but also for elucidating the conformational preferences of the systems under study[11,12]. The level of theory employed for the simulation of the ECD spectra must be carefully chosen according to the nature of the systems under study[13]. As an alternative to the use of *ab initio* calculations, the exciton chirality method can be applied when two independent chromophores are present in the molecule[14]. The more general phenomenon known as the Davydov splitting[15], $2V_{12}$, emerges from the excitation energy splitting between the in-phase and out-of-phase simultaneous two chromophore transitions, strongly dependent on their relative orientation (Scheme 1).



Scheme 1. Representation of the splitting of the energy excitation of two interacting chromophores due to the in-phase and out-of-phase interactions. Arrows represent the electronic transition for two chromophores, blue and magenta. Curves represent the absorption band in the UV/Vis spectra. Different torsion angles between the two chromophores lead to different relative intensity and ΔE between the two possible transitions.

When the arrangement between the interacting chromophores is chiral, the Cotton effects emerging from the in-phase and out-of-phase excitations in the CD spectrum present opposite sign. Notable, the sing of the less energetic band in the resulting bisignated CD signal is diagnostic of the handedness of the chiral arrangement between the chromophores allowing the absolute configuration determination of many compounds[14,16] (Scheme 2).



Scheme 2. Representation of bisignated CD signal arising for the interaction between two independent chromophores with a relative positive (left) or negative (right) twist.

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The Davydov model considers an ideal system formed by two non-conjugated chromophores with two-fold degenerate excited states. Perturbation theory allows breaking degeneracy considering the interaction between two chromophores. If two chromophores are represented by the corresponding electric transition dipole moment (ETDM), $\vec{\mu}_i^t$, the interaction between them, V_{12}, is given (in au) by equation (1), where $\vec{R}_{12}$ is the vector connecting the origin of $\vec{\mu}_1^t$ and $\vec{\mu}_2^t$. When these chromophores display also permanent dipoles in excited or ground state, represented respectively by, $\vec{\mu}_i^0$ and $\vec{\mu}_i^a$ additional terms have to be considered within V_{12}, as it will be shown below.

$$V_{12} = R_{12}^{-3}\left[\vec{\mu}_1^t \cdot \vec{\mu}_2^t - 3R_{12}^{-2}\left(\vec{\mu}_1^t \cdot \vec{R}_{12}\right)\left(\vec{\mu}_2^t \cdot \vec{R}_{12}\right)\right], \quad (1)$$

The application of the perturbation theory to the (originally degenerate) first electronically excited level yields an energy splitting, ΔE, between these two states (usually named α and β) given by equation (2).

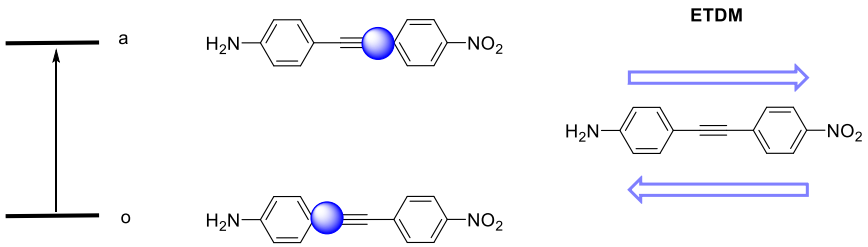
$$\Delta E = 2V_{12}, \quad (2)$$

This outcome is comparable with the analysis of a C_2 and D_2 symmetric systems in terms of the selection rules. In recent years we have contributed with a number of highly symmetric systems such as linear[5] and cyclic oligomers[17], molecular containers[18,19] or even all-carbon double helices[20] presenting remarkable chiroptical responses have been developed on the search for valuable materials for everyday chiroptical applications[21]. However, analysis of the chiroptical responses is often tedious[22,23]. In order to have a more accessible understanding of the behavior of highly symmetric systems, herein we perform the chiroptical symmetry analysis (CSA) and apply it to systems with D_n symmetry for n = 2, 3 or 4. Additionally, since the CSA is general, it could be applied to any other symmetry, and therefore, we hope that it will serve as a design tool for the development of everyday chiroptical applications in the near future.

2. Results and discussion

2.1. Theoretical background

The interaction of UV-visible light with a molecule can result in an electric excitation, usually depicted, within the Hartree-Fock framework, as the transition from one of the occupied molecular orbitals, ϕ_i^0, to an empty (virtual) one, ϕ_j^a. This produces a rearrangement of the electron density of the molecule, basically described by the ETDM as a linear displacement of electron density during the transition (Scheme 3). Moreover, the intensity of the transition between the two states is proportional to the square of the modulus of the ETDM, and forbidden electronic transitions yield null values of ETDM. The selection rules stablish that for a transition to be allowed at least one of the components of the ETDM must contain the totally symmetric representation of the system point group, and, consequently, the direct product for the representations of the involved wave functions must contain at least one of the representations of the electric dipole moment components.



Scheme 3. Representation of the *o* → *a* electronic excitation of a model compound. The electron density redistribution from the ground state *o* to the excited state *a* results in the electric transition dipole moment (ETDM). ETDM has a defined direction and two equally probably orientations. The blue spheres represent the center of electron density for the electronic states.

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Davydov's molecular exciton model provides an elegant explanation for the CD Cotton effects in a molecule with two identical chromophores[15]. The model predicts that dipole interaction between chromophores splits the ideally degenerate excited state. Neglecting all kind of interactions between the chromophores (zero-order approximation), the relative energy of the excited state with regard to the ground state would be the same as in an isolated chromophore, E^a. In fact, when considering that the electronic transition only affects the chromophores, it is assumed that the rest of the molecule remains unchanged by the transition. Therefore, in the zero-order approach, the ground state, $\Psi^{0(0)}$, can be represented by the product of two ground state wave functions for the isolated chromophore (4), ψ^0, whereas the zero-order degenerate excited electronic state, $\Psi^{a(0)}$, can be expressed by the product of ground and excited states, ψ^a, of single chromophores, with two equivalent possibilities: $\Psi_1^{a(0)}=\psi^0\psi^a$ and $\Psi_2^{a(0)}=\psi^a\psi^0$, where the former refers to the chromophore 1 in the ground state and the chromophore 2 in the excited state.

$$\Psi^{0(0)} = \psi^0\psi^0, \quad (4)$$

The application of the perturbation theory to the ground state (non degenerate) provides for the first order correction to the energy, $E^{0(1)}$, the usual expression given by equation (5). Considering only the dipole-dipole interaction between the chromophores, the first-order correction for the energy of the ground state is that shown by equation (6), where $\vec{\mu}_i^0$ are the dipole moments of the chromophores in the ground state, named V_{12}^{00}.

$$E^{0(1)} = \left\langle \psi^0\psi^0 \middle| \hat{V}_{12} \middle| \psi^0\psi^0 \right\rangle, \quad (5)$$

$$E^{0(1)} = V_{12}^{00} = R_{12}^{-3}\left[\vec{\mu}_1^0 \cdot \vec{\mu}_2^0 - 3R_{12}^{-2}\left(\vec{\mu}_1^0 \cdot \vec{R}_{12}\right)\left(\vec{\mu}_2^0 \cdot \vec{R}_{12}\right)\right], \quad (6)$$

Obtaining the first order correction for the energy of the degenerate states leads to a set of linear homogenous equations, with non-trivial solution only when the condition (7) is verified. $E^{a(1)}$ being the first-order correction to the energy of the excited state for the two-chromophores system. Condition (7) is only fulfilled by the two $E^{a(1)}$ values contained in expression (8). We observe these values involve the dipole-dipole interaction between one chromophore in ground state and another in the excited state, V_{12}^{0a}, and a term where the interaction applies over the electronic transition, V_{12}^{tt}, shown in (9).

$$\begin{vmatrix} \left\langle \psi^0\psi^a \middle| \hat{V}_{12} \middle| \psi^0\psi^a \right\rangle - E^{a(1)} & \left\langle \psi^0\psi^a \middle| \hat{V}_{12} \middle| \psi^a\psi^0 \right\rangle \\ \left\langle \psi^a\psi^0 \middle| \hat{V}_{12} \middle| \psi^0\psi^a \right\rangle & \left\langle \psi^a\psi^0 \middle| \hat{V}_{12} \middle| \psi^a\psi^0 \right\rangle - E^{a(1)} \end{vmatrix} = 0, \quad (7)$$

$$E^{a(1)} = V_{12}^{0a} \pm V_{12}^{tt}, \quad (8)$$

$$V_{12}^{tt} = \left\langle \psi^0\psi^a \middle| \hat{V}_{12} \middle| \psi^a\psi^0 \right\rangle = R_{12}^{-3}\left[\vec{\mu}_1^t \cdot \vec{\mu}_2^t - 3R_{12}^{-2}\left(\vec{\mu}_1^t \cdot \vec{R}_{12}\right)\left(\vec{\mu}_2^t \cdot \vec{R}_{12}\right)\right], \quad (9)$$

Thus, after introducing the first-order corrections obtained with perturbation theory for ground and excited electronic states, the relative energy of the excited state, ΔE^a, can be expressed by equation (10). Obviously, the reliability of the formula can be improved including further corrections, but the most significant fact is the splitting of the excited level in two different states (usually named α and β) whose energy differs in $2V_{12}^{tt}$. Moreover, replacing the two solutions for energy correction (8) in the system of homogeneous equation and normalizing, it is found that the zero-order wave functions for α and β states follow, respectively, expressions (11) and (12).

$$\Delta E^a \cong \Delta E^{a(0)} + \Delta E^{a(1)} = E^a + V_{12}^{0a} - V_{12}^{00} \pm V_{12}^{tt}, \quad (10)$$

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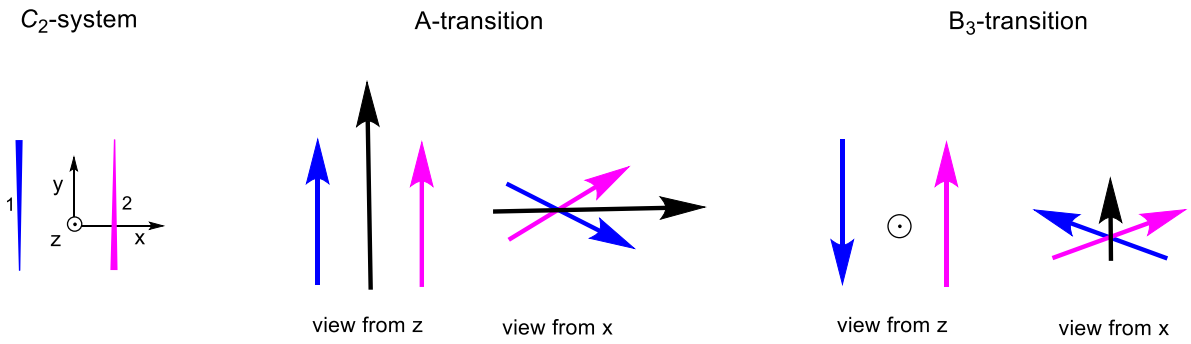
$$\psi_{\alpha}^{(0)} = \frac{1}{\sqrt{2}}\left(\psi^{a}\psi^{0} - \psi^{0}\psi^{a}\right), (11)$$

$$\psi_{\beta}^{(0)} = \frac{1}{\sqrt{2}}\left(\psi^{a}\psi^{0} + \psi^{0}\psi^{a}\right), (12)$$

One can directly obtain wave functions (11) and (12) by means of group theory if chromophores are in C_2 arrangement. Also, their relative energies appear as their averaged V_{12} values (Scheme 4) (13).

$$\left\langle \psi_{\beta}^{(0)} \middle| \hat{V}_{12} \middle| \psi_{\beta}^{(0)} \right\rangle = \left\langle \psi_{\alpha}^{(0)} \middle| \hat{V}_{12} \middle| \psi_{\alpha}^{(0)} \right\rangle + 2V_{12}^{tt}, (13)$$



Scheme 4. Representation of a system presenting D_2 symmetry. According to the selection rules, the two equivalent chromophores 1 (blue) and 2 (magenta) can undergo a simultaneous excitation following A or B_3 symmetry leading to total ETDMs (black) parallel to y or z respectively as a result of the summation of the ETDM of each chromophore. A circle with a dot in the middle represents an arrow perpendicular to the plane pointing to the reader.

2.2. Excited state splitting with 3 and 4 chromophores

Following, we apply the independent exciton model to systems formed by three or four identical chromophores which are in different chiral symmetric arrangements (C_3, D_3, C_4, D_4). Our aim is obtaining expressions for the splitting between those first electronic excited states attainable from the ground state by absorption of electromagnetic radiation allowed by electric dipole transition.

2.2.1. C_3 and D_3 geometries.

Assuming that the electronic structure of the three chromophores is basically unchanged with regard to the isolated one, the ground state wave functions could be zero-order approached by equation (14), and belongs to the totally symmetry irreducible representation of this point group, A. We can expect three equivalent monoexcitations from the ground state, described by the wave functions shown in (15) (Scheme 5). They can be used as a basis set for constructing C_3 symmetry-adapted linear combinations (SALC) for first electronically excited states. In this case, the reducible representation decomposes into the symmetry irreducible species A and the pseudodegenerate reducible species E, as shown in (16). Thus, one A excited state and two E excited electronic states can be predicted. They are represented in the zero-order approach, respectively, by equations (17-19). We stress that transitions from A to E states (E1 and E2) are both orbitally allowed.

$$\Psi^{0(0)} = \psi^{0}\psi^{0}\psi^{0}, (14)$$

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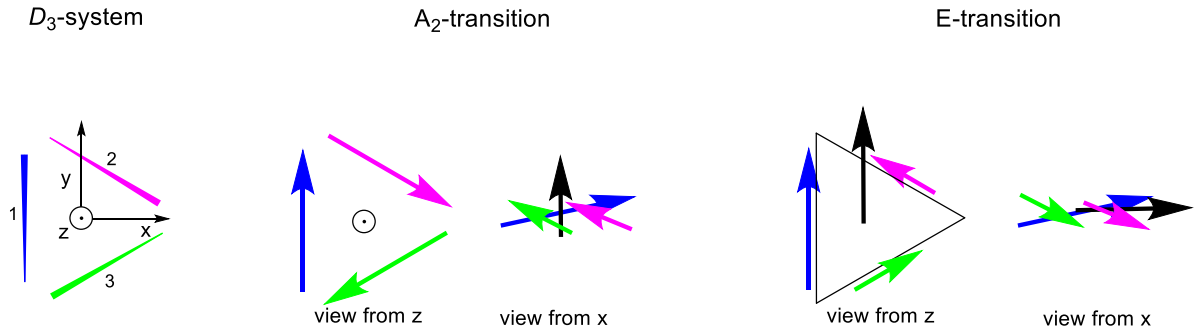
$$\Psi_1^{a(0)} = \psi^a\psi^0\psi^0\,,\quad \Psi_2^{a(0)} = \psi^0\psi^a\psi^0\,,\quad \Psi_3^{a(0)} = \psi^0\psi^0\psi^a\,, \quad (15)$$

$$\Gamma\left(\Psi_1^{a(0)}, \Psi_2^{a(0)}, \Psi_3^{a(0)}\right) = A \oplus E\,, \quad (16)$$

$$\Psi_A^{a(0)} = \frac{1}{\sqrt{3}}\left[\psi^a\psi^0\psi^0 + \psi^0\psi^a\psi^0 + \psi^0\psi^0\psi^a\right], \quad (17)$$

$$\Psi_{E1}^{a(0)} = \frac{1}{\sqrt{3}}\left[\psi^a\psi^0\psi^0 + \psi^0\psi^a\psi^0 e^{2\pi i/3} + \psi^0\psi^0\psi^a e^{-2\pi i/3}\right], \quad (18)$$

$$\Psi_{E2}^{a(0)} = \frac{1}{\sqrt{3}}\left[\psi^a\psi^0\psi^0 + \psi^0\psi^a\psi^0 e^{-2\pi i/3} + \psi^0\psi^0\psi^a e^{2\pi i/3}\right], \quad (19)$$



Scheme 5. Representation of a system presenting D_3 symmetry. According to the selection rules, the three equivalent chromophores 1 (blue), 2 (magenta), and 3 (green) can undergo a simultaneous excitation following A_2 or E symmetry leading to total ETDMs (black) parallel to z or y respectively as a result of the summation of the ETDM of each chromophore. A circle with a dot in the middle represents an arrow perpendicular to the plane pointing to the reader.

Considering the interaction between the three chromophores is pair additive (20), and the interactions between all pairs are equal, the first order correction for the energies of the ground, A, and E states are respectively shown by (21)-(23). We highlight that, within the first order approach, both pseudodegenerate states display the same energy (23). Thus, in this case, the excited level splitting is $3V_{12}^{tt}$, and therefore can be also calculated by means of Davydov´s equation.

$$\hat{V} = \hat{V}_{12} + \hat{V}_{13} + \hat{V}_{23}\,, \quad (20)$$

$$E^{0(1)} = 3V_{12}^{00}\,, \quad (21)$$

$$E_A^{a(1)} = 2V_{12}^{a0} + V_{12}^{00} + 2V_{12}^{tt}\,, \quad (22)$$

$$E_E^{a(1)} = 2V_{12}^{a0} + V_{12}^{00} - V_{12}^{tt}\,, \quad (23)$$

In a D_3 arrangement the totally symmetry species is represented as A_1 (ground electronic state). There are again three equivalent monoexcitations given by (15). They form a suitable basis set for constructing D_3 SALCs for the first electronically excited states. The reducible representation of this basis, Γ^a, decomposes into different symmetry irreducible species depending on how the rotation around any of the three perpendicular C_2 axis affects the first electronically excited state of the isolated chromophore, ψ^a. When $\hat{C}_2\psi^a = \psi^a$, the typical situation when all the MOs describing

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the excited state are σ, Γ^a decomposes into A_1 and the truly degenerate reducible species E. In contrast, when the excited state of the chromophore contains one π MO: $\hat{C}_2\psi^a = -\psi^a$, and Γ^a contains A_2 and E species. Thus, the two degenerate E excited electronic states, represented in the zero-order approach by any linear combination of equations (24) and (25), can be accompanied by one A_1 or A_2 state, represented by a common expression (26).

The transition from the ground state is orbitally allowed for the three states only when the excited state of the isolated chromophore is antisymmetric for C_2 rotations. In this case, the application of the first order perturbation theory leads to the same splitting of the excited level obtained for C_3 geometries: $3V_{12}^{tt}$. On the other hand, when C_2 rotations are symmetric, the transition to the A_1 excited state is orbitally forbidden and there is no splitting.

$$\Psi_{E1}^{a(0)} = \frac{1}{2}\left[2\psi^a\psi^0\psi^0 - \psi^0\psi^a\psi^0 - \psi^0\psi^0\psi^a\right], \quad (24)$$

$$\Psi_{E2}^{a(0)} = \frac{1}{\sqrt{2}}\left[\psi^0\psi^a\psi^0 - \psi^0\psi^0\psi^a\right], \quad (25)$$

$$\Psi_{A_1,A_2}^{a(0)} = \frac{1}{\sqrt{3}}\left[\psi^a\psi^0\psi^0 + \psi^0\psi^a\psi^0 + \psi^0\psi^0\psi^a\right], \quad (26)$$

2.2.2. C_4 and D_4 geometries.

Considering a C_4 structure including 4 chromophores (Scheme 6), a pairwise approach for the interaction among them, where V_{12} and V_{13} are not equivalent, (27) the same approximations, and a similar treatment to that shown above (see Supporting Information), leads to the following conclusions: i) There are four monoexcited states, two of them pseudodegenerate, belonging to the E symmetry species, the other with A and B symmetry; ii) The electronic transition from the ground state to the B one is orbitally forbidden, whereas those to A and E are allowed; and iii) The energy of state A differs from those of E (equivalent within the first order approach) in $2\left(V_{12}^{tt} + V_{13}^{tt}\right)$; which is the splitting in this case.

$$\hat{V} = 4\hat{V}_{12} + 2\hat{V}_{13}, \quad (27)$$

As in the 3-chromophores case, replacing C_n symmetry by D_n splits some symmetry species (A into A_1 and A_2 and B into B_1 and B_2), while pseudodegenerate E states become degenerate. A_1 and B_1 species are symmetric for C_2 rotations over any perpendicular axis and correspond to excited states with forbidden transitions from the ground state. In contrast, A_2 and B_2 states are antisymmetric for these perpendicular rotations and the transitions between ground state and A_2 are orbitally-allowed. As a consequence, the excited state splitting is only observed for excited states involving the excitation of one chromophore to an antisymmetric state with regard to a perpendicular rotation. In this case, the energy of state A_2 differs from the E ones again by $2\left(V_{12}^{tt} + V_{13}^{tt}\right)$ (Supporting Information).

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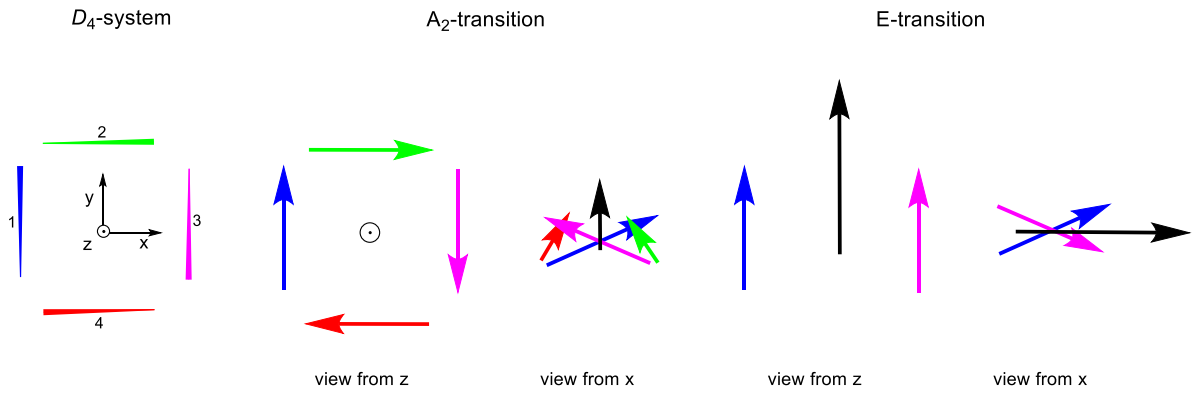

Scheme 6. Representation of a system presenting D_4 symmetry. According to the selection rules, the four equivalent chromophores 1 (blue), 2 (magenta), 3 (green), and 4 (red) can undergo a simultaneous excitation following A_2 or E symmetry leading to total ETDMs (black) parallel to z or y respectively as a result of the summation of the ETDM of each chromophore. A circle with a dot in the middle represents an arrow perpendicular to the plane pointing to the reader.

2.3. Rotatory strength

According to Rosenfeld´s quantum theory,[24] the rotatory strength, *R*, defined as the difference between the absorption rate of left circular polarized light (LCP) and right circular polarized light (RCP) in a certain transition, is given by (28), where $\hat{\mu}_e$ and $\hat{\mu}_m$ are, respectively the operators for electric (29) and magnetic dipole moment (30). Both are summation of one-electron operators. Within the context of the independent exciton model the summation only involves the *N* electrons provided by the chromophores and these electrons can be assigned to a certain chromophore *j*. Moreover, the ratio between *R* and the integrated absorption coefficient, *A*, (experimentally measurable) is a constant, *C*, (31).

$$R = \mathrm{Im}\left[\left\langle \Psi^0 \middle| \hat{\mu}_e \middle| \Psi^a \right\rangle \cdot \left\langle \Psi^a \middle| \hat{\mu}_m \middle| \Psi^0 \right\rangle\right], \quad (28)$$

$$\hat{\mu}_e = e\sum_j \sum_k \hat{r}_{jk}\,, \quad (29)$$

$$\hat{\mu}_e = \frac{e\eta}{2mci}\sum_j \sum_k \hat{r}_{jk} \times \nabla_{jk} = \frac{e}{2mc}\sum_j \sum_k \hat{r}_{jk} \times \hat{p}_{jk}\,, \quad (30)$$

$$A = \int \frac{\varepsilon(\nu)}{\nu} d\nu = CR\,, \quad (31)$$

Rosenfeld's equation states that *R* depends on the scalar product of the ETDM and the corresponding magnetic transition dipole moment (MTDM) as it will be described below. Consequently, optical activity in a certain transition implies: i) transition is both electric dipole and magnetic dipole allowed; and ii) ETDM and MTDM for the process are not mutually orthogonal.

2.3.1. Electric transition dipole moment

The fact that ETDM are origin independent and the form of equation (29) allows defining an ETDM vector for each chromophore, $\hat{\mu}_j^t$ (32). The molecular ETDM results in a specific combination of individual vectors for each state (*e.g.* α or β, represented, respectively, by wave functions (11) and (12)). For example, in the binary system, ETDM follows expression (33) in the α state and expression

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(34) in the β one. The square modulus of the molecular ETDM (directly related to Einstein coefficients in ETDM transitions) depends, in both cases, on the angle between these vectors, γ. Thus, in the case of two identical chromophores, expressions (35) and (36) are respectively followed for transitions to α and β states. Let us now think about the γ angle. For two isolated identical chromophores, the three components of their vectors will be equal. The only difference in the independent exciton model is the chromophores are placed in specific positions in the molecule, introducing different orientation for the groups. The γ angle is the one measuring this relative orientation. As a consequence, when the two chromophores are not orthogonally arranged in the molecule the absorptions for 0→α and 0→β transitions are of different intensity.

$$\vec{\mu}_j^t = e\sum_k \left\langle \psi^0\left(\vec{r}_{jk}\right)\middle|\vec{r}_{jk}\middle|\psi^a\left(\vec{r}_{jk}\right)\right\rangle, \quad (32)$$

$$\vec{\mu}^{t\alpha} = \frac{\vec{\mu}_1^t - \vec{\mu}_2^t}{\sqrt{2}}, \quad (33)$$

$$\vec{\mu}^{t\beta} = \frac{\vec{\mu}_1^t + \vec{\mu}_2^t}{\sqrt{2}}, \quad (34)$$

$$\left|\vec{\mu}^{t\alpha}\right|^2 = \left|\vec{\mu}_1^t\right|^2\left(1-\cos\gamma\right), \quad (35)$$

$$\left|\vec{\mu}^{t\beta}\right|^2 = \left|\vec{\mu}_1^t\right|^2\left(1+\cos\gamma\right), \quad (36)$$

Extending this procedure to C_3 systems, the expressions (37) and (38) are obtained for molecular ETDM from ground to E and A electronically excited states, and (39) and (40) for the corresponding squared modulus in a system formed by identical chromophores.

$$\vec{\mu}^{tE} = \frac{\vec{\mu}_1^t - \vec{\mu}_2^t}{\sqrt{2}}, \quad (37)$$

$$\vec{\mu}^{tA} = \frac{\vec{\mu}_1^t + \vec{\mu}_2^t + \vec{\mu}_3^t}{\sqrt{3}}, \quad (38)$$

$$\left|\vec{\mu}^{tE}\right|^2 = \left|\vec{\mu}_1^t\right|^2\left(1-\cos\gamma\right), \quad (39)$$

$$\left|\vec{\mu}^{tA}\right|^2 = \left|\vec{\mu}_1^t\right|^2\left(1+2\cos\gamma\right), \quad (40)$$

Similarly, the expressions for molecular ETDM in C_4 systems ((41) and (42)) show that the absorption for 0 → A and 0→E transitions depends on the molecular geometry. In this case the angles between $\vec{\mu}_c^t$ vectors interchanged by $\hat{C}^4$ and $\hat{C}^2$ operations are respectively represented by γ_{12} and γ_{13} in equations (43) and (44), derived for a system with identical chromophores.

$$\vec{\mu}^{tE} = \frac{\vec{\mu}_1^t - \vec{\mu}_3^t}{\sqrt{2}}, \quad (41)$$

$$\vec{\mu}^{tA} = \frac{\vec{\mu}_1^t + \vec{\mu}_2^t + \vec{\mu}_3^t + \vec{\mu}_4^t}{2}, \quad (42)$$

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$$\left|\vec{\mu}^{tE}\right|^2 = \left|\vec{\mu}_1^t\right|^2 \left(1-\cos\gamma_{13}\right), \quad (43)$$

$$\left|\vec{\mu}^{tA}\right|^2 = \left|\vec{\mu}_1^t\right|^2 \left(1+2\cos\gamma_{12}+\cos\gamma_{13}\right), \quad (44)$$

2.3.2. Magnetic transition dipole moment

Within the hypothesis of the independent exciton model, the molecular MTDM for a certain transition (t: 0→a) contained in Rosenfeld's expression can be obtained as the vector summation of group MTDM defined for each chromophore, j. Every one of these group MTDM is represented by a vector, $\vec{M}_j^t$, defined by expression (45), where subscript k refers to the electrons in chromophore j.

$$\vec{M}_j^t = \frac{e}{2mc}\sum_k \left\langle \psi^0\left(\vec{r}_{jk}\right)\left|\vec{r}_{jk}\times\vec{p}_{jk}\right|\psi^a\left(\vec{r}_{jk}\right)\right\rangle, \quad (45)$$

$\vec{M}_j^t$ vectors are origin-dependent. Thus, their summation should be done considering a common origin for all the electron position vectors, $\vec{r}_{jk}$. Introducing a reference point for each chromophore (*e.g.* its center of mass), with position vector $\vec{R}_j$, and the relative positions for the electrons in their chromophore, $\vec{r}'_{jk}$, (45) turns into (46), where $\vec{M}_j^t$ splits into two parts.

$$\vec{M}_j^t = \frac{e}{2mc}\left[\vec{R}_j\times\sum_k \left\langle \psi^0\left(\vec{r}_{jk}\right)\left|\vec{p}_{jk}\right|\psi^a\left(\vec{r}_{jk}\right)\right\rangle\right] + \frac{e}{2mc}\sum_k \left\langle \psi^0\left(\vec{r}_{jk}\right)\left|\vec{r}'_{jk}\times\vec{p}_{jk}\right|\psi^a\left(\vec{r}_{jk}\right)\right\rangle, \quad (46)$$

The first addend contains the linear transition moment of the chromophore, $\vec{p}_j^t$, defined by (47), whereas the second one defines the MTDM of the isolated chromophore, $\vec{m}_j^t$, (48). This allows to relate (equation (49)) the MTDM of the chromophore in the molecule, $\vec{M}_j^t$, with its value in an isolated species, $\vec{m}_j^t$.

$$\vec{p}_j^t = \sum_k \left\langle \psi^0\left(\vec{r}_{jk}\right)\left|\vec{p}_{jk}\right|\psi^a\left(\vec{r}_{jk}\right)\right\rangle, \quad (47)$$

$$\vec{m}_j^t = \frac{e}{2mc}\sum_k \left\langle \psi^0\left(\vec{r}_{jk}\right)\left|\vec{r}'_{jk}\times\vec{p}_{jk}\right|\psi^a\left(\vec{r}_{jk}\right)\right\rangle, \quad (48)$$

$$\vec{M}_j^t = \frac{e\left(\vec{R}_j\times\vec{p}_j^t\right)}{2mc} + \vec{m}_j^t, \quad (49)$$

The replacement of $\vec{p}_j^t$ in terms of the ETDM of the isolated chromophore, $\vec{\mu}_j^t$, (Supporting Information) leads to equation (50), where ν^t is the wave number for the transition.

$$\vec{M}_j^t = i\pi\nu^t\left(\vec{R}_j\times\vec{\mu}_j^t\right) + \vec{m}_j^t, \quad (50)$$

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At this point, summation of $\vec{M}_j^{\omega_t}$ vectors leads to molecular MTDM. This is shown for a binary system in states α and β in equations (51) and (52), for a C_3 one in states E and A in equations (53) and (54), and for C_4 in E and A states in (55) and (56).

$$\vec{M}^{t\alpha} = \frac{1}{\sqrt{2}}\left[i\pi\nu^t\left(\vec{R}_1 \times \vec{\mu}_1^{\omega} - \vec{R}_2 \times \vec{\mu}_2^{\omega}\right) + \left(\vec{m}_1^t - \vec{m}_2^t\right)\right], \quad (51)$$

$$\vec{M}^{t\beta} = \frac{1}{\sqrt{2}}\left[i\pi\nu^t\left(\vec{R}_1 \times \vec{\mu}_1^{\omega} + \vec{R}_2 \times \vec{\mu}_2^{\omega}\right) + \left(\vec{m}_1^t + \vec{m}_2^t\right)\right], \quad (52)$$

$$\vec{M}^{tE} = \frac{1}{\sqrt{2}}\left[i\pi\nu^t\left(\vec{R}_1 \times \vec{\mu}_1^{\omega} - \vec{R}_2 \times \vec{\mu}_2^{\omega}\right) + \left(\vec{m}_1^t - \vec{m}_2^t\right)\right], \quad (53)$$

$$\vec{M}^{tA} = \frac{1}{\sqrt{3}}\left[i\pi\nu^t\left(\vec{R}_1 \times \vec{\mu}_1^{\omega} + \vec{R}_2 \times \vec{\mu}_2^{\omega} + \vec{R}_3 \times \vec{\mu}_3^{\omega}\right) + \left(\vec{m}_1^t + \vec{m}_2^t + \vec{m}_3^t\right)\right], \quad (54)$$

$$\vec{M}^{tE} = \frac{1}{\sqrt{2}}\left[i\pi\nu^t\left(\vec{R}_1 \times \vec{\mu}_1^{\omega} - \vec{R}_3 \times \vec{\mu}_3^{\omega}\right) + \left(\vec{m}_1^t - \vec{m}_3^t\right)\right], \quad (55)$$

$$\vec{M}^{tA} = \frac{1}{2}\left[i\pi\nu^t\left(\vec{R}_1 \times \vec{\mu}_1^{\omega} + \vec{R}_2 \times \vec{\mu}_2^{\omega} + \vec{R}_3 \times \vec{\mu}_3^{\omega} + \vec{R}_4 \times \vec{\mu}_4^{\omega}\right) + \left(\vec{m}_1^t + \vec{m}_2^t + \vec{m}_3^t + \vec{m}_4^t\right)\right], \quad (56)$$

2.3.3. Rotatory strength in C_n systems ($2 \le n \le 4$)

The application of Rosenfeld's equation in a binary system to excitations with negligible MTDM for isolated chromophores leads to conclude that rotatory strengths for transitions to α and β states are equivalent but with opposite signs (57). In a general case the component due to MTDM are not null. Therefore, the absolute value of the rotatory strength is different for α (58) and β states (59).

$$R^{\alpha} = -R^{\beta} = \frac{\pi\nu^t}{2}\left(\vec{R}_2 - \vec{R}_1\right)\cdot\left(\vec{\mu}_1^t \times \vec{\mu}_2^t\right), \quad (57)$$

$$R^{\alpha} = \frac{1}{2}\mathrm{Im}\left\{\left(\vec{\mu}_1^t - \vec{\mu}_2^t\right)\cdot\left(\vec{m}_1^t - \vec{m}_2^t\right)\right\} + \frac{\pi\nu^t}{2}\left(\vec{R}_2 - \vec{R}_1\right)\cdot\left(\vec{\mu}_1^t \times \vec{\mu}_2^t\right) = R^E(C_3), \quad (58)$$

$$R^{\beta} = \frac{1}{2}\mathrm{Im}\left\{\left(\vec{\mu}_1^t + \vec{\mu}_2^t\right)\cdot\left(\vec{m}_1^t + \vec{m}_2^t\right)\right\} - \frac{\pi\nu^t}{2}\left(\vec{R}_2 - \vec{R}_1\right)\cdot\left(\vec{\mu}_1^t \times \vec{\mu}_2^t\right), \quad (59)$$

Expression (58) is also valid for the transitions to E states in a C_3 system. In fact, the expression for ETDM and MTDM in one of the E SALC are equivalent to those of the α state in a binary system. In contrast, the rotatory strength for the transition to the A state follows expression (60), which generalizes all transitions to A states in C_n systems.

$$R^A = \frac{1}{3}\mathrm{Im}\left\{\left(\vec{\mu}_1^t + \vec{\mu}_2^t + \vec{\mu}_3^t\right)\cdot\left(\vec{m}_1^t + \vec{m}_2^t + \vec{m}_3^t\right)\right\} + \\ -\frac{\pi\nu^t}{3}\left[\left(\vec{R}_2 - \vec{R}_1\right)\cdot\left(\vec{\mu}_1^t \times \vec{\mu}_2^t\right) + \left(\vec{R}_3 - \vec{R}_2\right)\cdot\left(\vec{\mu}_2^t \times \vec{\mu}_3^t\right) + \left(\vec{R}_3 - \vec{R}_1\right)\cdot\left(\vec{\mu}_1^t \times \vec{\mu}_3^t\right)\right], \quad (60)$$

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Finally, the rotatory strength for C_4 systems for both allowed transitions follow specific expressions: (61) for E states, where ETDM and MTDM involved correspond to chromophores in 1,3-arrangements, and (62) for the A state.

$$R^E(C_4) = \frac{1}{2}\mathrm{Im}\left\{\left(\vec{\mu}_1^t - \vec{\mu}_3^t\right)\cdot\left(\vec{m}_1^t - \vec{m}_3^t\right)\right\} + \frac{\pi\nu^t}{2}\left(\vec{R}_3 - \vec{R}_1\right)\cdot\left(\vec{\mu}_1^t \times \vec{\mu}_3^t\right), \quad (61)$$

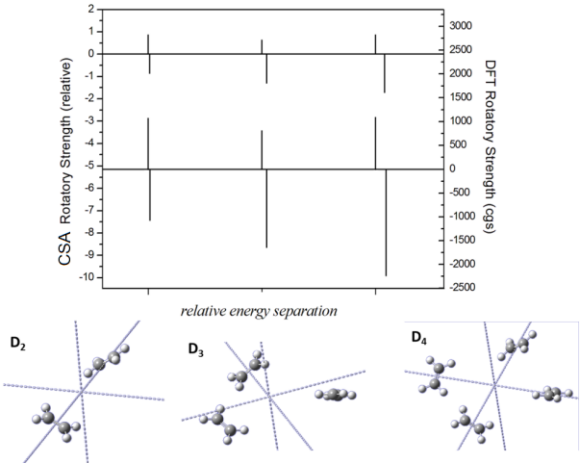
$$R^A = \frac{1}{n}\mathrm{Im}\left\{\left(\sum_{i=1}^{n}\vec{\mu}_i^t\right)\cdot\left(\sum_{i=1}^{n}\vec{m}_1^t\right)\right\} - \frac{\pi\bar{\nu}^t}{n}\left[\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\left(\vec{R}_j - \vec{R}_i\right)\cdot\left(\vec{\mu}_i^t \times \vec{\mu}_j^t\right)\right], \quad (62)$$

Alternatively, since the total ETDM and MTDM can be calculated as discussed above, the rotatory strength for each allowed transition, R^I, can be directly calculated from the dot product between both total transition dipole moments associated to such transition (63):

$$R^I = \mathrm{Im}\left\{\vec{\mu}^{tI}\cdot\vec{M}^{tI}\right\}, \quad (63)$$

2.4. Comparison with DFT calculations

The RS for the two lower energetic transitions where calculated with DFT and CSA for three systems bearing two, three, and four ethene moieties with, 5Å distance to the center of mass and 30º torsion angle respect to the *y* axis with D_2, D_3, and D_4 symmetry respectively (Scheme 7).



Scheme 7. Top: DFT predicted (graph bottom) and CSA predicted (graph top) rotatory strengths for D_2, D_3 and D_4 (from left to right) symmetries. The bottom axis represents the relative energy for each symmetry (from left to right: higher to lower). Bottom: D_n acetylenic systems.

The sign of the energy difference between the two allowed transitions, which is reflected on the order of the two RS at the spectrum, was correctly predicted by the CSA model giving the same chirality than the DFT calculations. Also the relative $\overrightarrow{\mu^n}$ and $\overrightarrow{m^n}$ intensities are correctly predicted which leads to correctly predict the relative RS compared with the DFT results.

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3. Conclusions

It has been shown how the chiroptical symmetry analysis (CSA) may significantly contribute in uncovering the chiroptical responses of highly symmetric systems bearing independent chromophores given that: i) V_{ij} can be calculated according to Davydov equation; ii) the allow transitions can be predicted by applying the selection rules; iii) ΔE between those transitions can be calculated according to theory; iv) the symmetry of the allowed transitions enables simple calculation of the total ETDM, MTDM, and rotatory strength associated.

This approach is not intended to accurately predict the experimental CD response of a particular system, but rather to be employed as a useful tool for the design of valuable systems for chiroptical applications. Next, we intend to develop a software for a straight forward analysis of diverse systems to explore the scope of the chiroptical symmetry analysis (CSA).

Author Contributions: Analysis of the selection rules for the different symmetries, S.C.F.; Contextualization of the chiroptical symmetry analysis within the state-of-the-art, A.P.G.; Theoretical demonstration, R.A.M.C; Conceptualization, J.L.A.G.

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S1. Excited state splitting for C_4 geometries.

The wave function for the electronic ground state is given, within the zero-order approximation by equation (S1.1) and belongs to the totally symmetric irreducible representation A. The functions shown in (S1.2) allow expanding the four independent C_4 SALCs for the first excited level in this approach: two of them are pseudodegenerate and belong to the E irreducible symmetry species, whereas the other are of A and B symmetry (equations S1.3 to S1.6, respectively). The transitions from the totally symmetric ground state are only orbitally-allowed to excited states which have the same symmetry of, at least, one of the components of the dipole moment operator. Therefore, the transition to the B state is forbidden, whereas those to A, E1, and E2 are allowed.

$$\Psi^{0(0)} = \psi^0\psi^0\psi^0\psi^0, \quad \text{(S1.1)}$$

$$\Psi_1^{a(0)} = \psi^a\psi^0\psi^0\psi^0, \quad \Psi_2^{a(0)} = \psi^0\psi^a\psi^0\psi^0, \quad \Psi_3^{a(0)} = \psi^0\psi^0\psi^a\psi^0, \Psi_4^{a(0)} = \psi^0\psi^0\psi^0\psi^a, \quad \text{(S1.2)}$$

$$\Psi_{E1}^{a(0)} = \frac{1}{2}\left[\left(\psi^a\psi^0\psi^0\psi^0 - \psi^0\psi^0\psi^a\psi^0\right) + i\left(\psi^0\psi^a\psi^0\psi^0 - \psi^0\psi^0\psi^0\psi^a\right)\right], \quad \text{(S1.3)}$$

$$\Psi_{E2}^{a(0)} = \frac{1}{2}\left[\left(\psi^a\psi^0\psi^0\psi^0 - \psi^0\psi^0\psi^a\psi^0\right) - i\left(\psi^0\psi^a\psi^0\psi^0 - \psi^0\psi^0\psi^0\psi^a\right)\right], \quad \text{(S1.4)}$$

$$\Psi_A^{a(0)} = \frac{1}{2}\left[\psi^a\psi^0\psi^0\psi^0 + \psi^0\psi^a\psi^0\psi^0 + \psi^0\psi^0\psi^a\psi^0 + \psi^0\psi^0\psi^0\psi^a\right], \quad \text{(S1.5)}$$

$$\Psi_B^{a(0)} = \frac{1}{2}\left[\psi^a\psi^0\psi^0\psi^0 - \psi^0\psi^a\psi^0\psi^0 + \psi^0\psi^0\psi^a\psi^0 - \psi^0\psi^0\psi^0\psi^a\right], \quad \text{(S1.6)}$$

Application of the first order perturbation theory, when the potential energy is given by (27), gives rise to identical corrections for the energy of E1 and E2 states, given by (S1.7), whereas that of the A excited state is represented by (S1.8).

$$E_{E1}^{a(1)} = E_{E2}^{a(1)} = 2\left(V_{12}^{a0} + V_{12}^{00}\right) + \left(V_{13}^{a0} + V_{13}^{00} - V_{13}^{tt}\right), \quad \text{(S1.7)}$$

$$E_A^{a(1)} = 2\left(V_{12}^{a0} + V_{12}^{00} + V_{12}^{tt}\right) + \left(V_{13}^{a0} + V_{13}^{00} + V_{13}^{tt}\right), \quad \text{(S1.8)}$$

S2. Excited state splitting for D_4 geometries.

The wave function for the electronic ground state displays, within the zero-order approximation, the same expression shown above for C_4 symmetry (S1.1), and belongs to the totally symmetric irreducible representation A_1. The functions shown in (S1.2) allow expanding the four independent D_4 SALCs for the first excited level in this approach. In this case, as it happens with D_3-symmetry, it is necessary two distinguish two possibilities: i) chromophores symmetric for C_2' rotations; and ii) chromophores antisymmetric for C_2' rotations, which can be, respectively exemplified by σ and π chromophores. The reducible representation for case i) contains A_1, B_1 and E representations, whereas for case ii) contains A_2, B_2 and E. As a consequence, D_4 symmetry structures with σ

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chromophores display a single orbitally-allowed electronic transition to the first set of excited states. In contrast, when the chromophores are π the single transition is replaced by two bands, representing the transitions from the A_1 ground level to A_2 and E states, whose wave functions are, represented by equation (S2.1) (A_1) and any linear combination of (S2.2) and (S2.3) (E).

$$\Psi_{A_2}^{a(0)} = \frac{1}{2}\left[\psi^a\psi^0\psi^0\psi^0 + \psi^0\psi^a\psi^0\psi^0 + \psi^0\psi^0\psi^a\psi^0 + \psi^0\psi^0\psi^0\psi^a\right], \text{(S2.1)}$$

$$\Psi_{E1}^{a(0)} = \frac{1}{\sqrt{2}}\left(\psi^a\psi^0\psi^0\psi^0 - \psi^0\psi^0\psi^a\psi^0\right), \text{(S2.2)}$$

$$\Psi_{E2}^{a(0)} = \frac{1}{\sqrt{2}}\left(\psi^0\psi^a\psi^0\psi^0 - \psi^0\psi^0\psi^0\psi^a\right), \text{(S2.3)}$$

Application of the first order perturbation theory, when the potential energy is given by (27), gives rise to a correction for the energy of E states, given by (S2.4), whereas that of the A_1 is represented by (S2.5).

$$E_E^{a(1)} = 2\left(V_{12}^{a0} + V_{12}^{00}\right) + \left(V_{13}^{a0} + V_{13}^{00} - V_{13}^{tt}\right), \text{(S2.4)}$$

$$E_{A_2}^{a(1)} = 2\left(V_{12}^{a0} + V_{12}^{00} + V_{12}^{tt}\right) + \left(V_{13}^{a0} + V_{13}^{00} + V_{13}^{tt}\right), \text{(S2.5)}$$

S3. Deriving the relationship between $\vec{p}$ and $\vec{\mu}^t$ vectors.

Simple relations of operators algebra outlined below (equations (S3.1) to (S3.3)) allow to replace $\vec{p}_j^t$ by the ETDM of the isolated chromophore, $\vec{\mu}_j^t$, through expressions involving the wave number for the transition, ν^t.

$$\left\langle\psi^0\left|\left[\hat{H},\hat{r}_k\right]\right|\psi^a\right\rangle = \left\langle\psi^0\left|\hat{H}\hat{r}_k\right|\psi^a\right\rangle - \left\langle\psi^0\left|\hat{r}_k\right|\hat{H}\psi^a\right\rangle =$$
$$= \left\langle\hat{r}_k\psi^a\left|\hat{H}\right|\psi^0\right\rangle - \left\langle\psi^0\left|\hat{r}_k\right|\hat{H}\psi^a\right\rangle = \left(E^0 - E^a\right)\left\langle\psi^0\left|\hat{r}_k\right|\psi^a\right\rangle = \frac{\left(E^0 - E^a\right)\vec{\mu}^t}{e}, \text{(S3.1)}$$

$$\left\langle\psi^0\left|\left[\hat{H},\hat{r}_k\right]\right|\psi^a\right\rangle = \left\langle\psi^0\left|\left[\left(\frac{\hat{p}_k^2}{2m} + \hat{V}\right),\hat{r}_k\right]\right|\psi^a\right\rangle = \frac{1}{2m}\left\langle\psi^0\left|\left[\hat{p}_k\hat{p}_k,\hat{r}_k\right]\right|\psi^a\right\rangle =$$
$$= \frac{1}{2m}\left\langle\psi^0\left|\hat{p}_k\hat{p}_k\hat{r}_k - \hat{r}_k\hat{p}_k\hat{p}_k + \hat{p}_k\hat{r}_k\hat{p}_k - \hat{p}_k\hat{r}_k\hat{p}_k\right|\psi^a\right\rangle = \frac{1}{2m}\left\langle\psi^0\left|\hat{p}_k\left[\hat{p}_k,\hat{r}_k\right] - \left[\hat{r}_k,\hat{p}_k\right]\hat{p}_k\right|\psi^a\right\rangle = \frac{\eta}{mi}\vec{p}, \text{(S3.2)}$$

$$\vec{p} = \frac{mi\left(E^0 - E^a\right)}{e\eta}\vec{\mu}^t = \frac{2\pi mci\nu^t}{e}\vec{\mu}^t, \text{(S3.3)}$$