Coupling between two identical monomers.

Objectives:
1. Develop a simple and intuitive mathematical framework for describing dimer sum and difference states.
2. Extend to biopolymers: the nonlinear optical properties of proteins.
3. Generalization to coupling between dissimilar dimers and multimers.

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In general, the wavefunctions in a coupled dimer of two identical chromophores will mix to form sum and difference combinations.

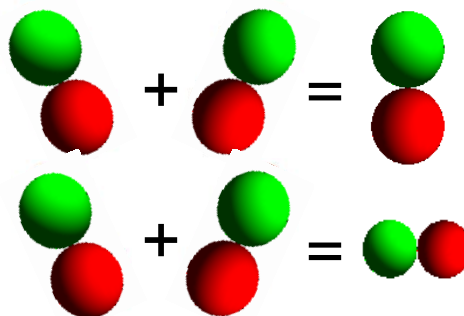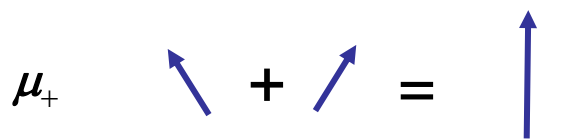$$\psi_{\pm} = \tfrac{1}{\sqrt{2}}\left(\psi_1 \pm \psi_2\right)$$

The NLO properties of each mixed state are given by the sum and difference tensors.

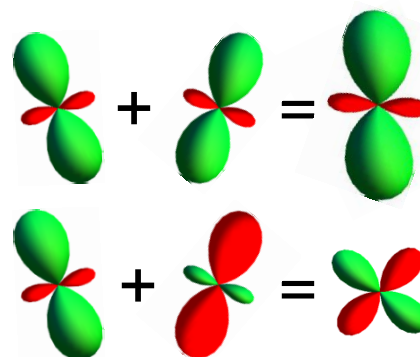$$\vec{\mu}_{\pm} = \tfrac{1}{\sqrt{2}}\left(\vec{\mu}_1 \pm \vec{\mu}_2\right)$$
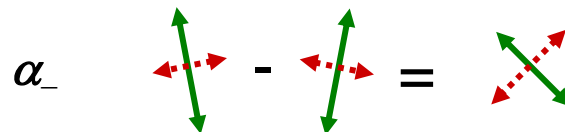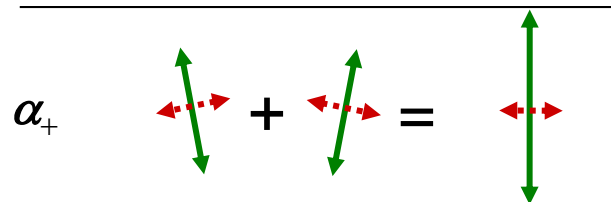
$$\alpha^{(1)}{}_{\pm} = \tfrac{1}{\sqrt{2}}\left(\alpha^{(1)}{}_1 \pm \alpha^{(1)}{}_2\right)$$

$$\beta^{(2)}{}_{\pm} = \tfrac{1}{\sqrt{2}}\left(\beta^{(2)}{}_1 \pm \beta^{(2)}{}_2\right)$$
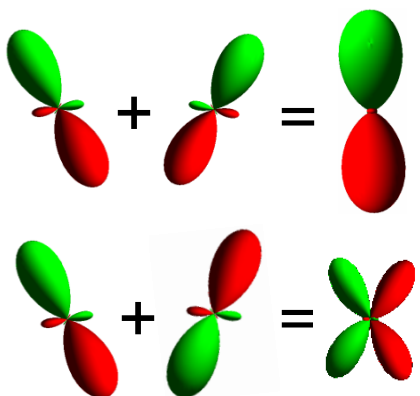
etc.

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μ_+ ↘ + ↗ = ↑

μ_- ↘ - ↗ = ←
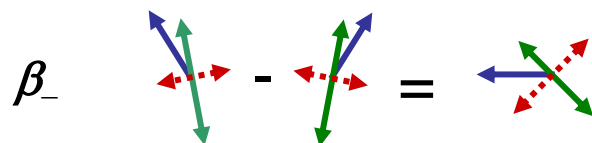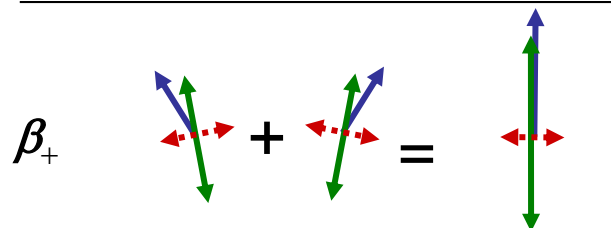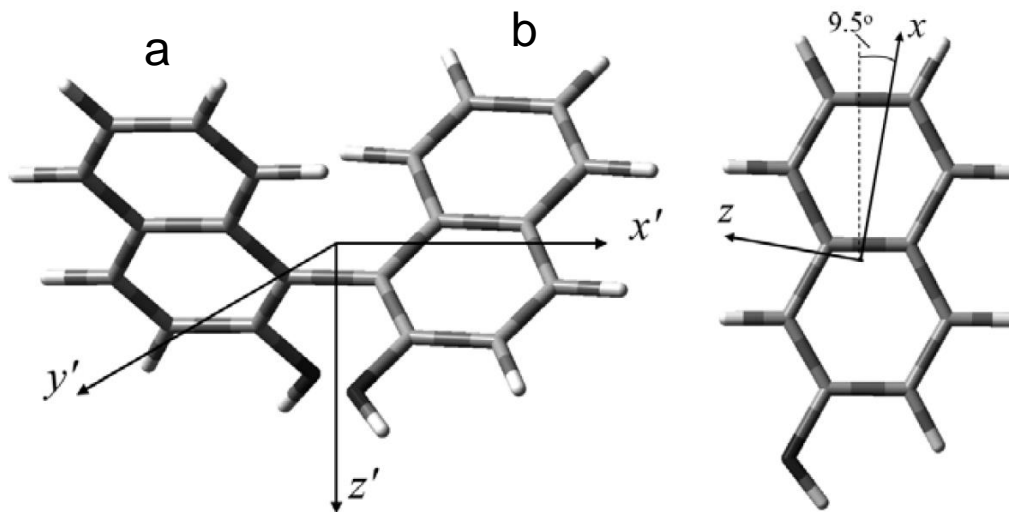
Vector addition is straightforward for the sum and difference states.

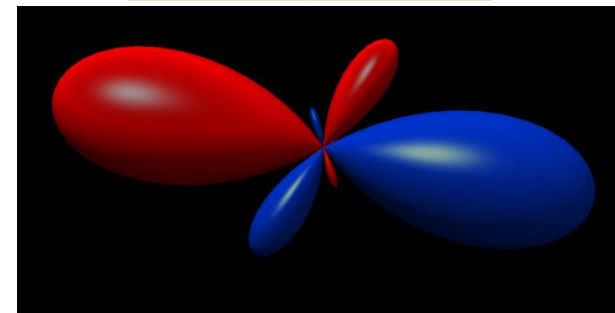α_+

α_-

Matrix addition is not as trivial, but simple numerically. Easy to rationalize in hindsight, though

β_+

β_-

Tensor addition can be done either by the combination of μ and α from above, or by combinations of the full $\beta^{(2)}$ tensors.

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a

b

9.5°

Monomer

$$\vec{\beta}\,' = \left(\boldsymbol{R}^a_{\theta\psi\phi} + \boldsymbol{R}^b_{\theta\psi\phi} \right) \cdot S \cdot \vec{\beta}$$

-R is the full 27×27 rotation matrix generated from the Kronecker product of three 3×3 rotation matrices (see Coordinate Transformations)
-S is the symmetry matrix, populating the set of 27 elements within $\beta^{(2)}$ from the subset of four unique, nonzero values.
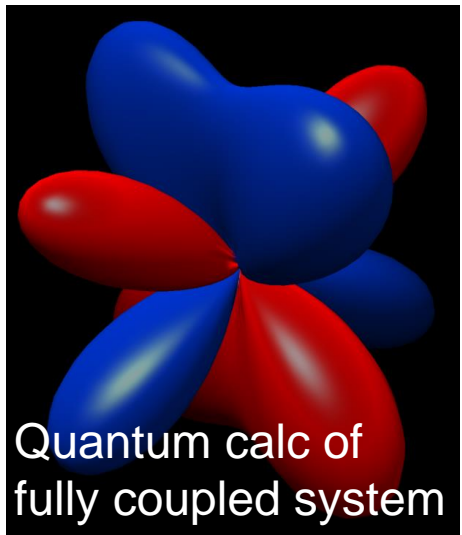
Quantum calc of fully coupled system
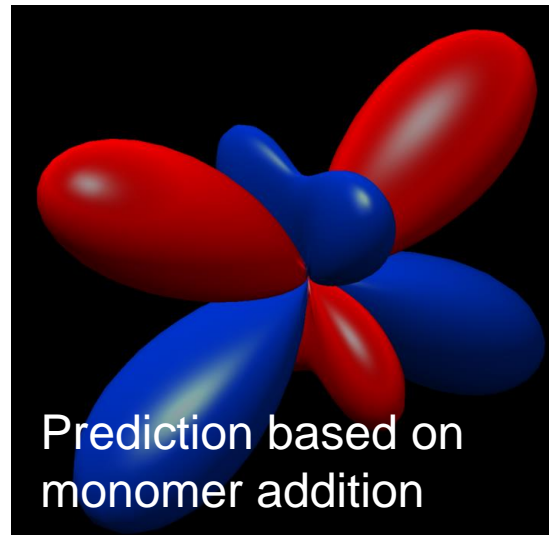
Prediction based on monomer addition

Summation of *A* and *B* states

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(a)

(b) 9.5° x

A-symmetry state

B-symmetry state

Quantum calc of fully coupled system

Symmetry-additive prediction
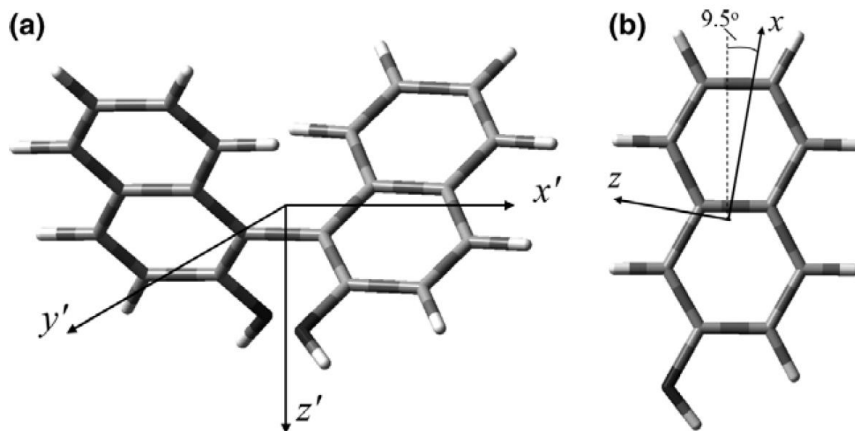
From inspection of the **character table** for a molecule with C_2 symmetry, the transitions are either of *A* or *B* symmetry. For SHG, the resonant hyperpolarizability is given by;

$$\vec{\beta}_n = S_n\left(2\omega\right)\vec{\mu}\otimes\vec{\alpha}$$

Based on the symmetry requirements of the transition moment and TPA matrix, the contributions to β from each exciton state can be separated.

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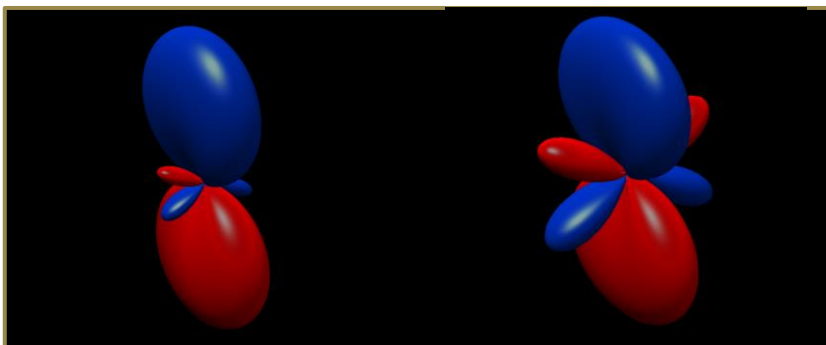
Calculated for the NV_1 electronic transition (CIS calculations with a 3-21G* basis set).
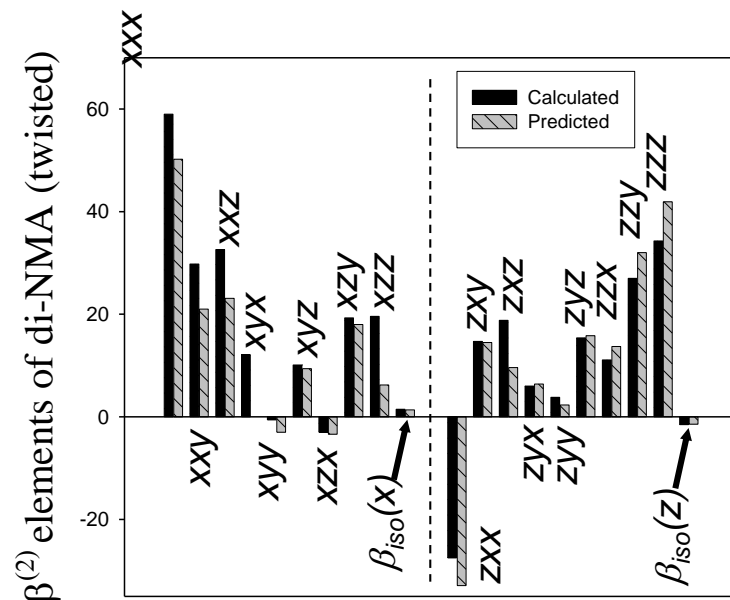
Extension to multimers: Symmetry-additive model for an α-helix.

Chautauqua

a)

b)
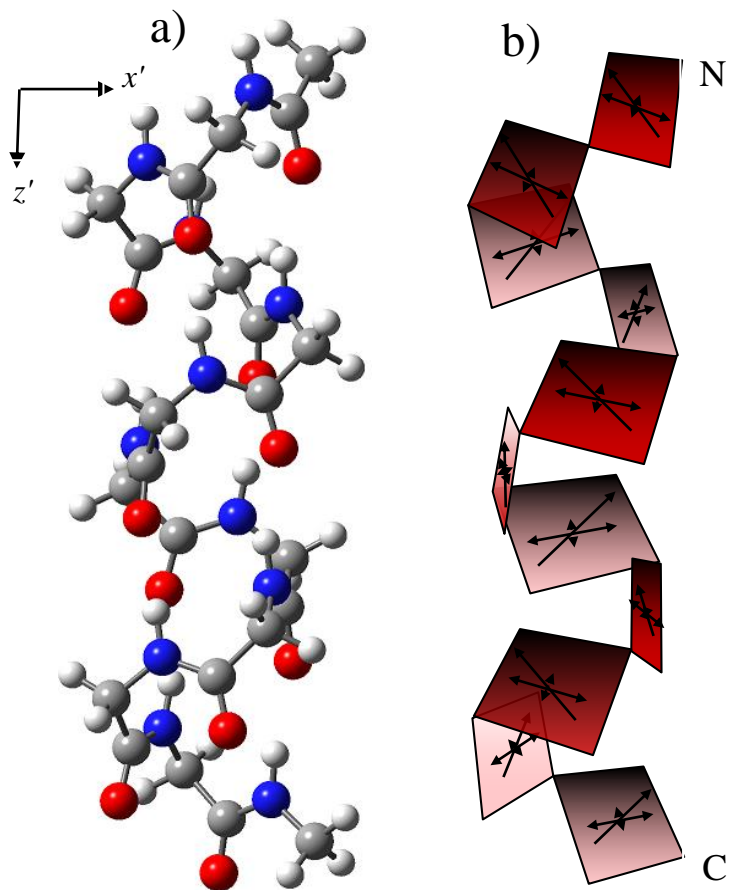
The monomer contributions are projected in the coordinate system of the dimer/polymer prior to summation. An α-helix has 3.6 residues per turn, effectively corresponding to 18-fold rotational symmetry. In practice, the hardest part about generating the dimer/polymer tensor is keeping track of the changes in reference frame (see lecture on Coordinate Transformations).

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a)

b)

N

C
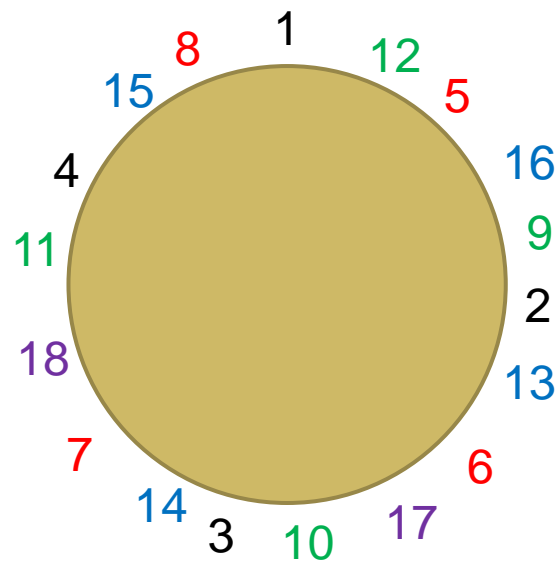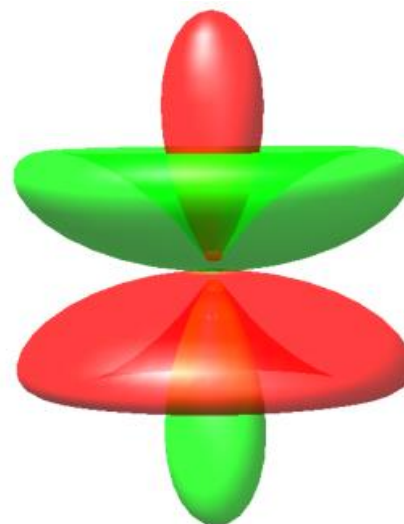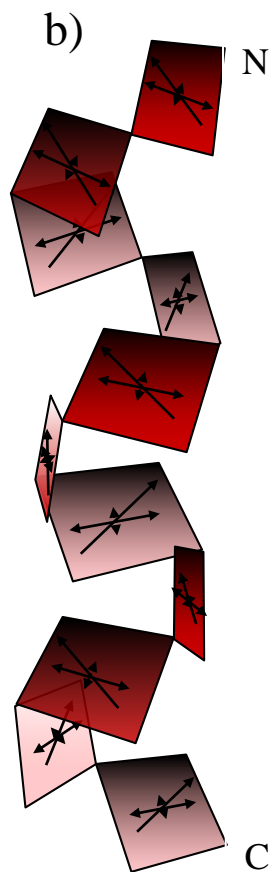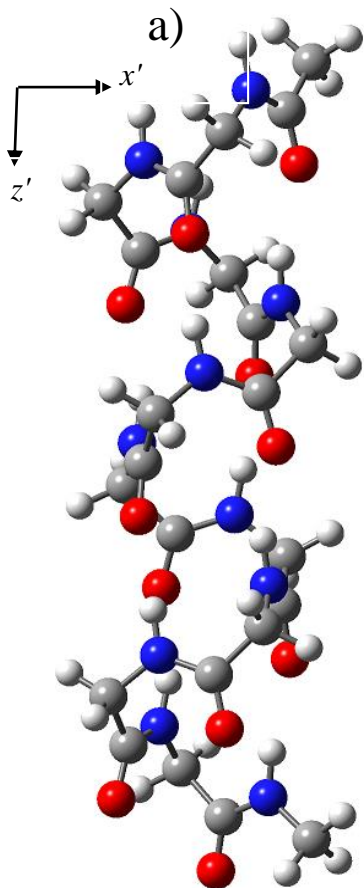
Coherent summation
(nonresonant and/or
weakly coupled limit)

In the absence of energy splitting between the excited states of the helix, the hyperpolarizability is estimated by the coherent summation of each amide contribution.

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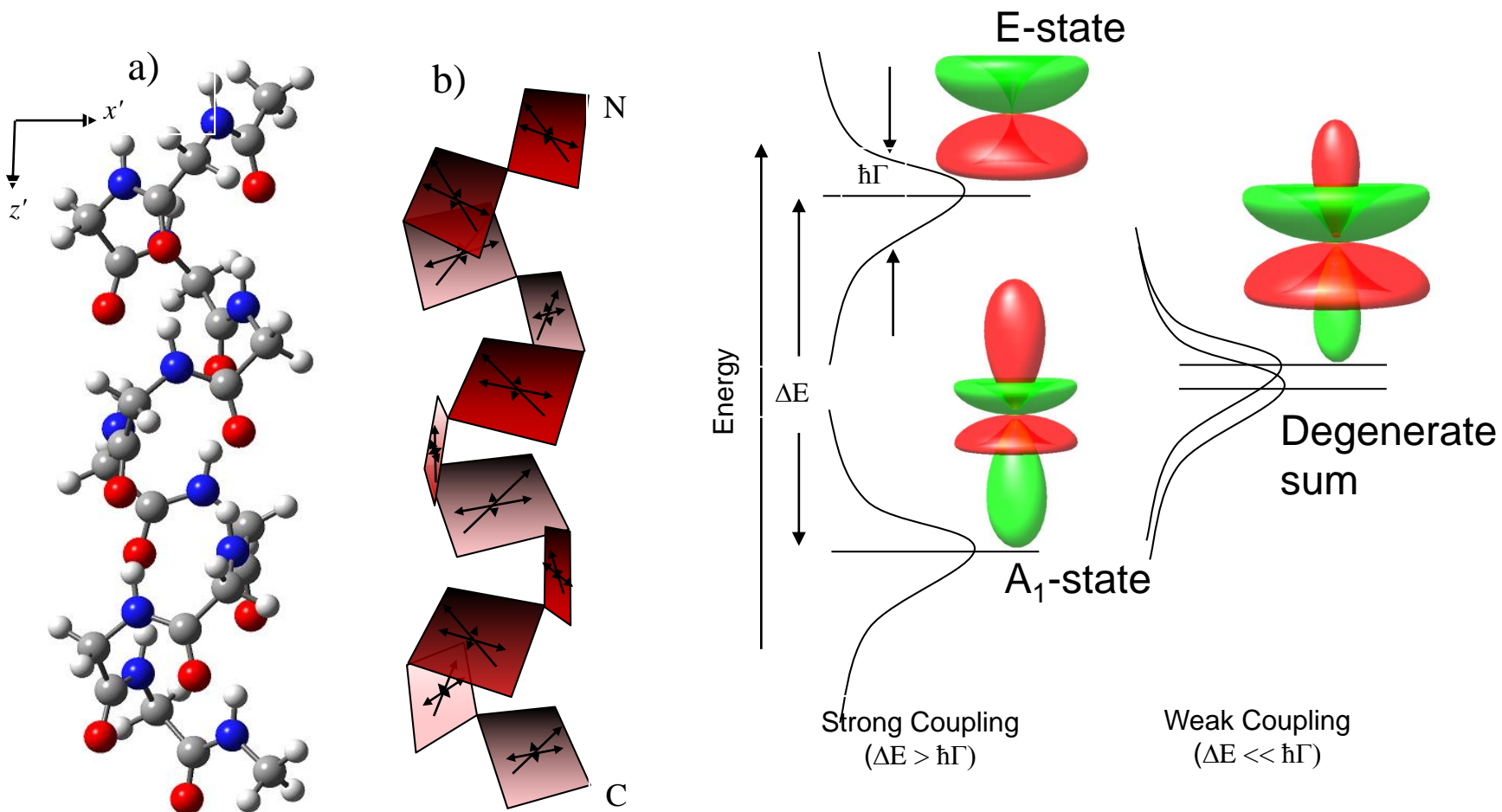
The 1-photon allowed transitions will be either of A_1 or E symmetry.

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- Provides an initial estimate for the NLO properties of extended structures at minimal computational cost.

- Equally applicable for both vibrational SFG and electronic SHG.

- In the simplest implementation for proteins, each amide is assumed to be identical. Differences (e.g., for aromatic amino acids) can result in splittings of the exciton states in manners not easily recoverable by the simple symmetry-additive approach (see later discussion of coupling bertween dissimilar chromophores).

- Quantitative reliability of the symmetry additive approach depends on the ability to describe exciton states using the monomer states as a basis.

- For extended conjugation or interactions involving multiple excited electronic states, the symmetry additive approach may prove problematic.

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(Vibrational resonances)

(collagen and other motifs)
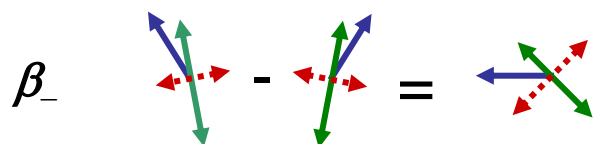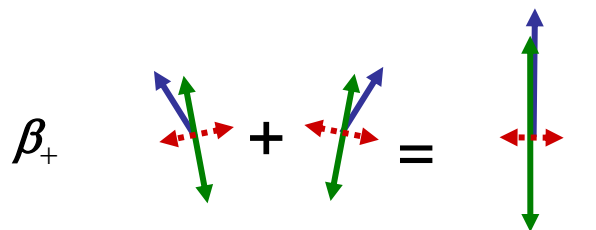
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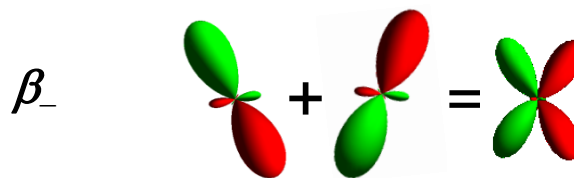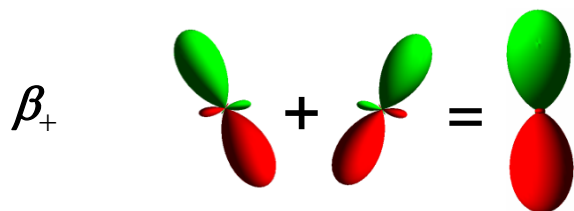
Note: Citations to the contents of these slides should reference the following textbook:
Simpson, Garth J. (2017) *Nonlinear Optical Polarization Analysis in Chemistry and Biology* (Cambridge University Press, ISBN 978-0-521-51908-3).

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In dimer coupling between dissimilar monomers A and B, the sum / difference states will have unequal contributions from each monomer, one looking more like A with some B character and vice versa. The fraction of each wavefunction contributing to the coupled states is generated from diagonalizing the Hamiltonian to construct the new stationary states of the coupled system.

$$H = \begin{bmatrix} \hbar\omega_A & \kappa_{AB} \\ \kappa_{AB} & \hbar\omega_B \end{bmatrix}$$

Coupling can arise from any number of intermolecular interactions. For free-space dipole-dipole coupling, the off-diagonal coupling energies can be calculated explicitly.

$$\kappa_{AB} = \frac{1}{4\pi\varepsilon_0}\left(\frac{\vec{\mu}_A \cdot \vec{\mu}_B}{\left|\vec{r}_{AB}\right|^3} - 3\frac{\left(\vec{r}_{AB} \cdot \vec{\mu}_A\right)\left(\vec{r}_{AB} \cdot \vec{\mu}_B\right)}{\left|\vec{r}_{AB}\right|^5} \right)$$

In the equation above, μ refers to the transition moments in the dimer reference frame and r_{AB} the vector connecting the origins of the two dipoles. For large separations between dipoles, the coupling approaches zero.

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In the case of a 2×2 matrix, expressions for the eigenvalues and corresponding eigenvectors can be written analytically.

$$H = \begin{bmatrix} \hbar\omega_A & \kappa_{AB} \\ \kappa_{AB} & \hbar\omega_B \end{bmatrix} = \begin{bmatrix} E_A & \kappa \\ \kappa & E_B \end{bmatrix}$$

$$\begin{bmatrix} \lambda_+ \\ \lambda_- \end{bmatrix} = \frac{1}{2}\begin{bmatrix} (E_A + E_B) + \sqrt{(E_A - E_B)^2 + (2\kappa)^2} \\ (E_A + E_B) - \sqrt{(E_A - E_B)^2 + (2\kappa)^2} \end{bmatrix}$$

The eigenvalues yield the energies of the sum and difference states.

$$\psi_+ = \begin{bmatrix} E_A - \lambda_+ \\ -\kappa \end{bmatrix} \frac{1}{\sqrt{(E_A - \lambda_+)^2 + \kappa^2}}$$

The normalized eigenvectors yield the fractions each monomer contributes to the sum and difference states.

$$\psi_- = \begin{bmatrix} -\kappa \\ E_B - \lambda_- \end{bmatrix} \frac{1}{\sqrt{(E_B - \lambda_-)^2 + \kappa^2}}$$

$$\psi_+ = \frac{1}{\sqrt{(E_A - \lambda_+)^2 + \kappa^2}}\left[(E_A - \lambda_+)\psi_A - \kappa\psi_B\right]$$

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In the limit of identical monomers with $E_A = E_B$, we should recover the simple sum and difference for the eigenvectors describing the linear combinations.

$$H = \begin{bmatrix} \hbar\omega_A & \kappa \\ \kappa & \hbar\omega_A \end{bmatrix} = \begin{bmatrix} E & \kappa \\ \kappa & E \end{bmatrix}$$

$$\begin{bmatrix} \lambda_+ \\ \lambda_- \end{bmatrix} = \begin{bmatrix} E + \kappa \\ E - \kappa \end{bmatrix}$$

$$\psi_+ = \begin{bmatrix} E - (E + \kappa) \\ -\kappa \end{bmatrix} \frac{1}{\sqrt{(E - (E + \kappa))^2 + \kappa^2}} = \begin{bmatrix} -\kappa \\ -\kappa \end{bmatrix} \frac{1}{\sqrt{2\kappa^2}} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

Absolute sign of the eigenvector is irrelevant.

$$\psi_- = \begin{bmatrix} -\kappa \\ E - (E - \kappa) \end{bmatrix} \frac{1}{\sqrt{(E - (E - \kappa))^2 + \kappa^2}} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

Sure enough, the sum and difference states emerge.

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This coupling model can be easily extended to include multiple coupling interactions in extended structures.

$$\hbar\omega_n^0 = \text{Transition energy for the uncoupled chromophore } n.$$

$$H = \begin{pmatrix} \hbar\omega_1^0 & \kappa_{12} & \kappa_{13} & \cdots \\ \kappa_{12} & \hbar\omega_2^0 & \kappa_{23} & \\ \kappa_{13} & \kappa_{23} & \hbar\omega_3^0 & \\ \vdots & & & \ddots \end{pmatrix}$$

$$\vec{\lambda} = \text{Full set of eigenvalues for the matrix } H.$$

$$S_\lambda = \text{Matrix of column eigenvectors.}$$

$$D = S_\lambda^{-1} H S_\lambda = \text{Diagonal matrix of eigenvalues.}$$

The elements of S_λ contain the relative contributions of each monomer to the stationary states emerging upon incorporating couplings. Only couplings between physically adjacent monomers are typically included.

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Summary

1. For identical monomers, coupling can be treated handily by summation followed by separation based on symmetry within the dimer.

2. A similar separation approach can be performed for biopolymers and secondary structural motifs. Summation followed by division into different symmetry-allowed elements reliably recovers the NLO properties of extended polymeric structures.

3. Creating a Hamiltonian that includes inter-chromophore coupling allows generalization for describing the NLO tensors of states produced from coupling between dissimilar monomers. This general approach converges properly to the simple sum and difference for identical monomers and offers greater overall flexibility. Furthermore, the energies of the different resulting eigenstates are directly recovered provided a good model for the coupling strengths is available.

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