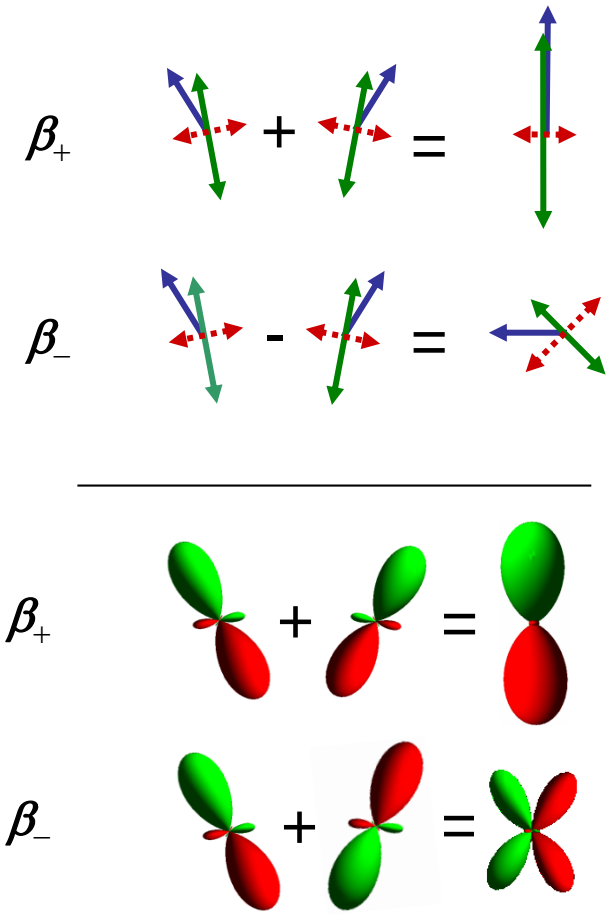
Coupling between two identical monomers.



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.

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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Dimer of two Identical Monomers

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

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

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

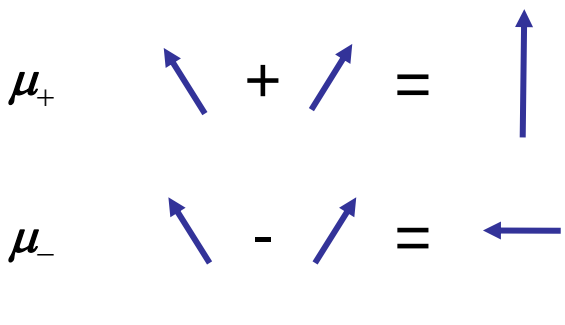
$$\vec{\mu}_{\pm} = \frac{1}{\sqrt{2}}\left(\vec{\mu}_1 \pm \vec{\mu}_2\right)$$

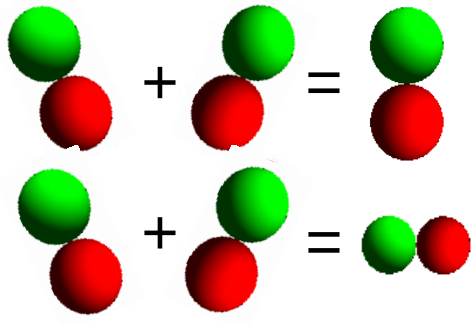
$$\alpha^{(1)}{}_{\pm} = \frac{1}{\sqrt{2}}\left(\alpha^{(1)}{}_1 \pm \alpha^{(1)}{}_2\right)$$

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

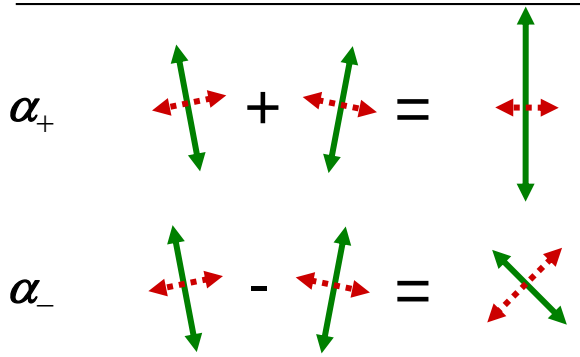
etc.

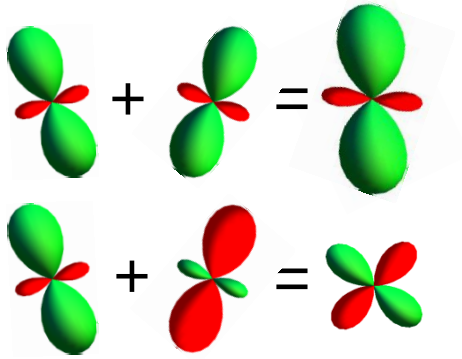
Dimer of two identical monomers



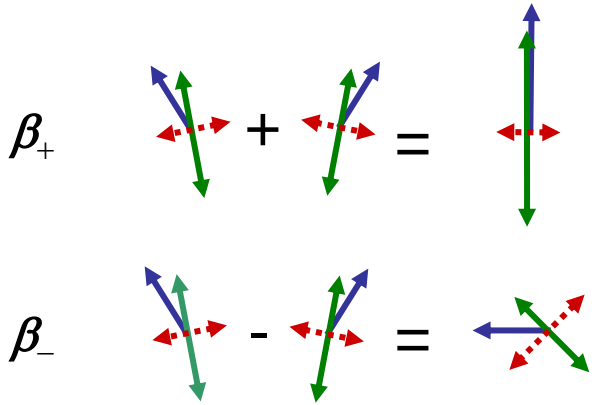


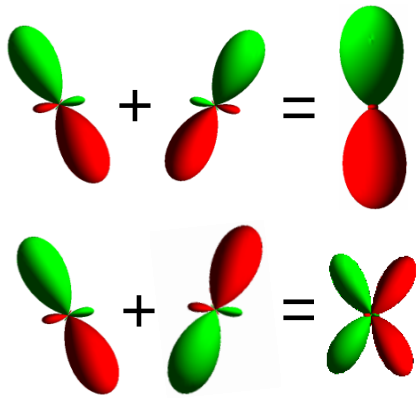
Vector addition is straightforward for the sum and difference states.





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





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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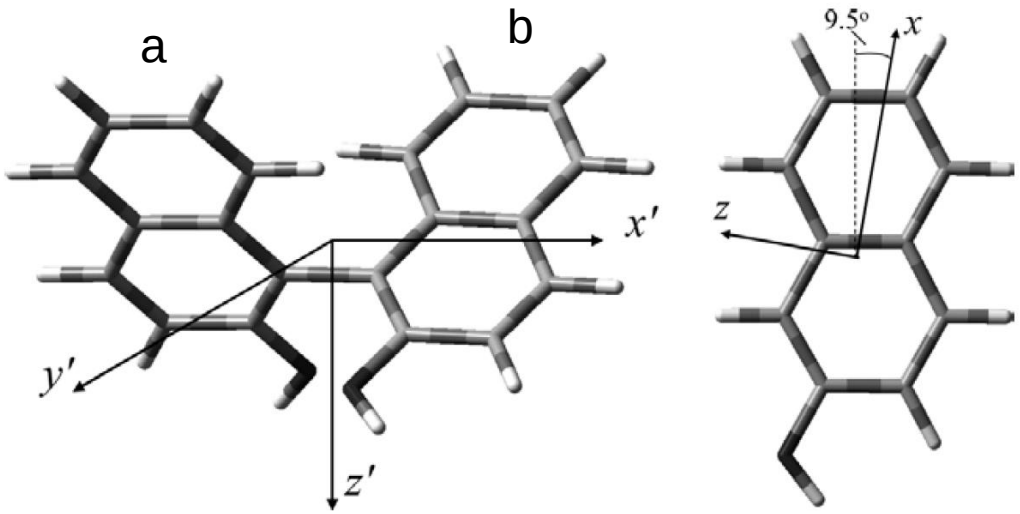
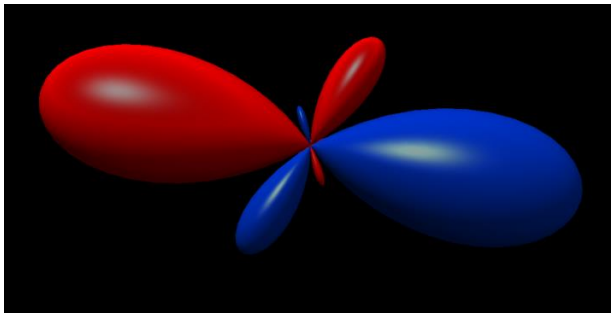
Example: Binaphthol



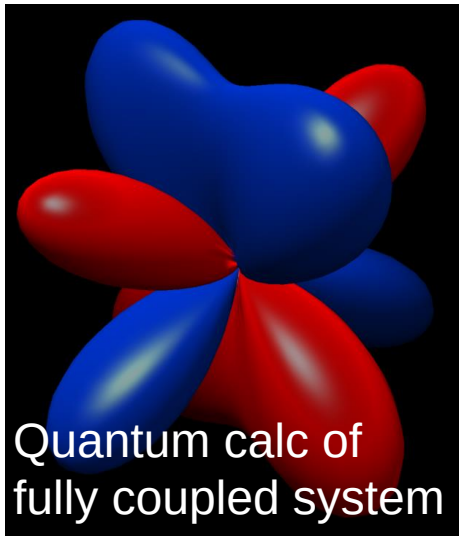
Monomer

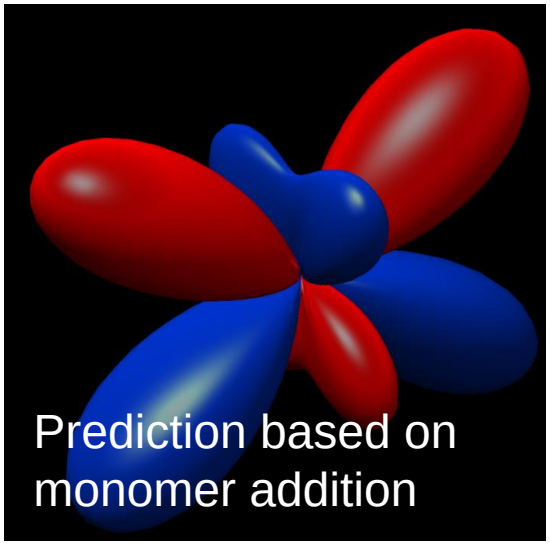


$$\vec{\beta}' = \left(\boldsymbol{R}^{a}_{\theta\psi\phi} + \boldsymbol{R}^{b}_{\theta\psi\phi} \right) \cdot S \cdot \vec{\beta}$$

-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.





Summation of *A* and *B* states

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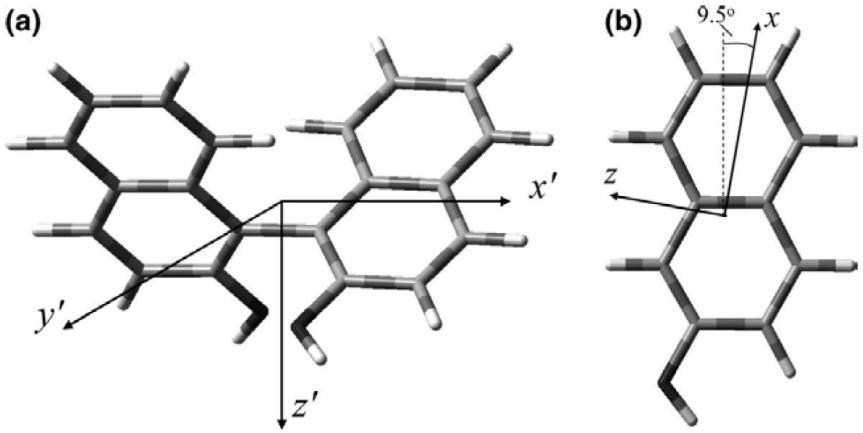
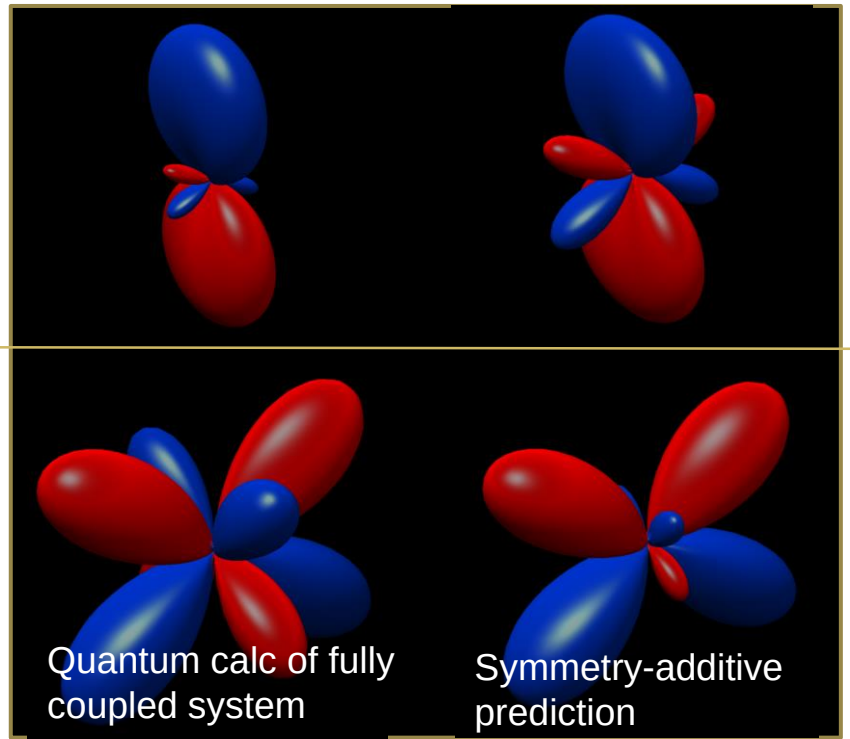
Example: Binaphthol



A-symmetry state

B-symmetry state



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;

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

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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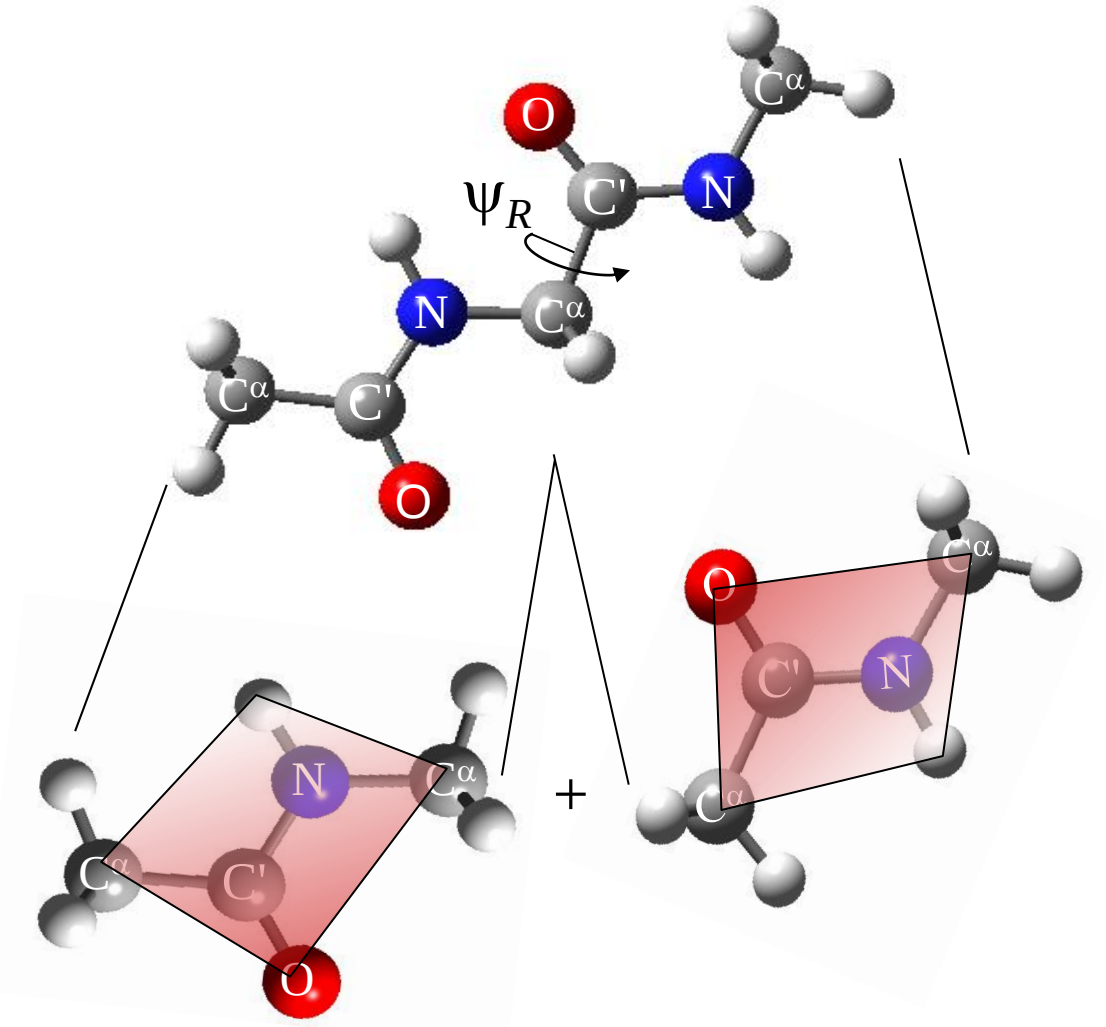
Amide dimer



Calculated for the NV_1 electronic transition (CIS calculations with a 3-21G* basis set).