Molecular Symmetry

General objective: Apply real or pseudo-symmetry to simplify the NLO properties of individual chromophores.

$$\vec{\beta}' = S \cdot \vec{\beta}$$

Specific Objectives:

1. Introduce a general architecture for incorporating symmetry operations.

2. The molecular symmetry matrix ***S***; how to populate it.

3. Relationships between the character tables for transitions of different symmetry and the molecular tensor.

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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).

Vector Properties

How are vector properties transformed by the application of particular symmetry operations?

Let's consider the specific example of a mirror-plane reflection operation σ_{xz}.

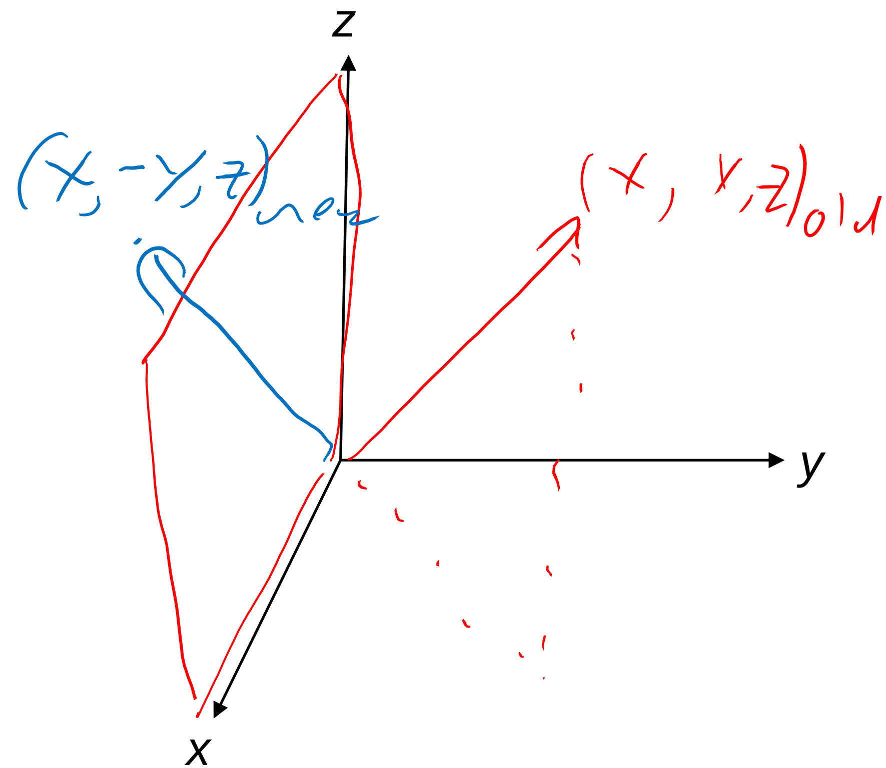
$$\vec{\mu}^{new} = \sigma_{xz} \cdot \vec{\mu}^{old}$$

$x \rightarrow x$

$y \rightarrow -y$

$z \rightarrow z$

$$\boxed{\sigma_{xz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}$$



Vector Properties

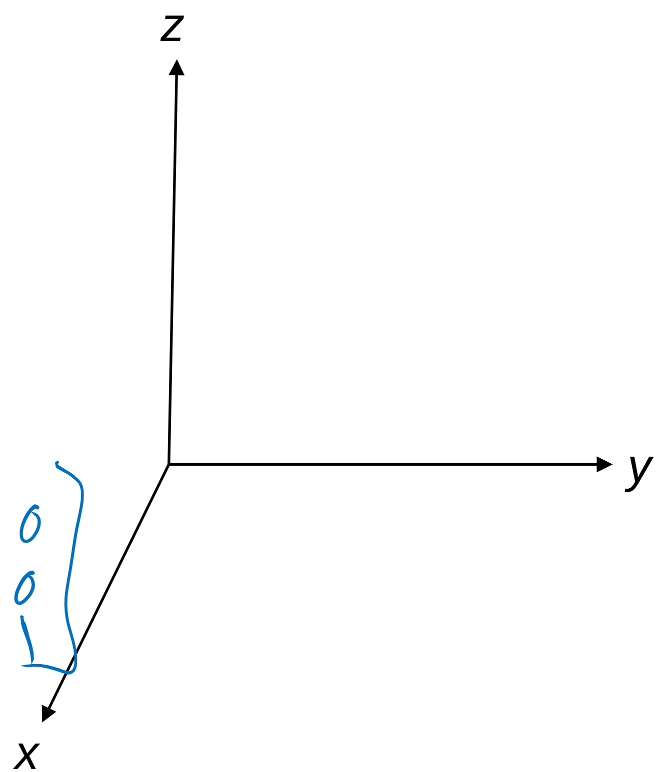
How are vector properties transformed by the application of particular symmetry operations?

Let's consider the specific example of a mirror-plane reflection operation σ_{xz}.

$$\vec{\mu}^{new} = \sigma_{xz} \cdot \vec{\mu}^{old}$$

$$\left(I + \sigma_{xz}\right)\frac{1}{2}$$

$$= \frac{1}{2}\left(\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} + \begin{pmatrix}1&0&0\\0&-1&0\\0&0&1\end{pmatrix}\right) = \begin{pmatrix}1&0&0\\0&0&0\\0&0&1\end{pmatrix}$$



If the symmetry operation leaves the system unchanged by definition, the sum of the two vectors isolates the symmetry-allowed elements.

$$\tfrac{1}{2}\left(I + \sigma_{xz}\right)$$

Matrix Properties

How are matrices transformed by the application of particular symmetry operations?

Let's consider the specific example of a mirror-plane reflection operation σ_{xz}.

$$\boxed{\alpha^{new} \neq \sigma_{xz} \cdot \alpha^{old}}$$

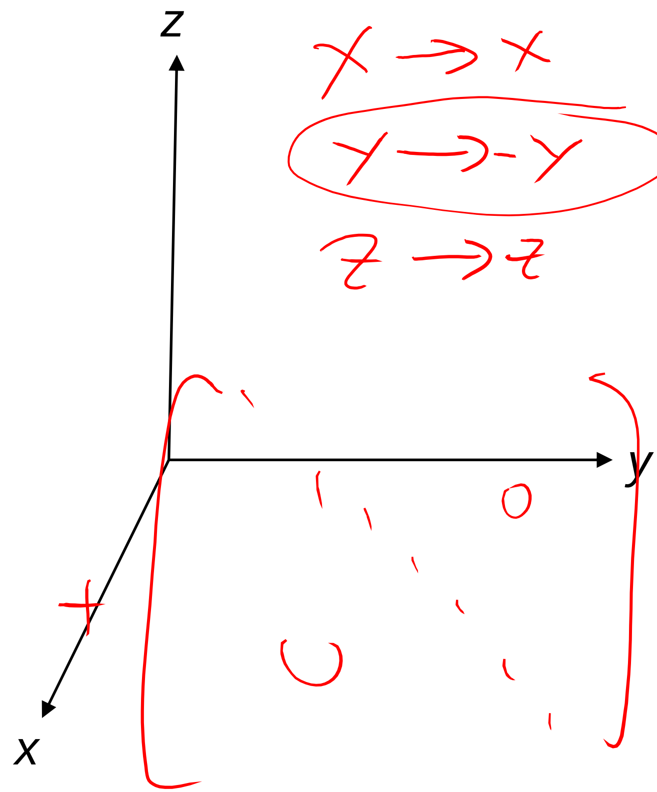
$$\boxed{\vec{\alpha}^{new} = \left(\sigma_{xz} \otimes \sigma_{xz}\right) \cdot \vec{\alpha}^{old}}$$

$$\begin{bmatrix} \alpha_{xx} \\ \cancel{\alpha_{xy}} \\ \alpha_{xz} \\ \cancel{\alpha_{yx}} \\ \alpha_{yy} \\ \cancel{\alpha_{yz}} \\ \alpha_{zx} \\ \cancel{\alpha_{zy}} \\ \alpha_{zz} \end{bmatrix}^{new} = \begin{bmatrix} 1 & & & & & & & & \\ & -1 & & & & & & \mathbf{0} & \\ & & 1 & & & & & & \\ & & & -1 & & & & & \\ & & & & 1 & & & & \\ & & & & & -1 & & & \\ & & & & & & 1 & & \\ & \mathbf{0} & & & & & & -1 & \\ & & & & & & & & 1 \end{bmatrix} \cdot \begin{bmatrix} \alpha_{xx} \\ \alpha_{xy} \\ \alpha_{xz} \\ \alpha_{yx} \\ \alpha_{yy} \\ \alpha_{yz} \\ \alpha_{zx} \\ \alpha_{zy} \\ \alpha_{zz} \end{bmatrix}^{old}$$

x → x

y → -y

z → z



Tensor Properties

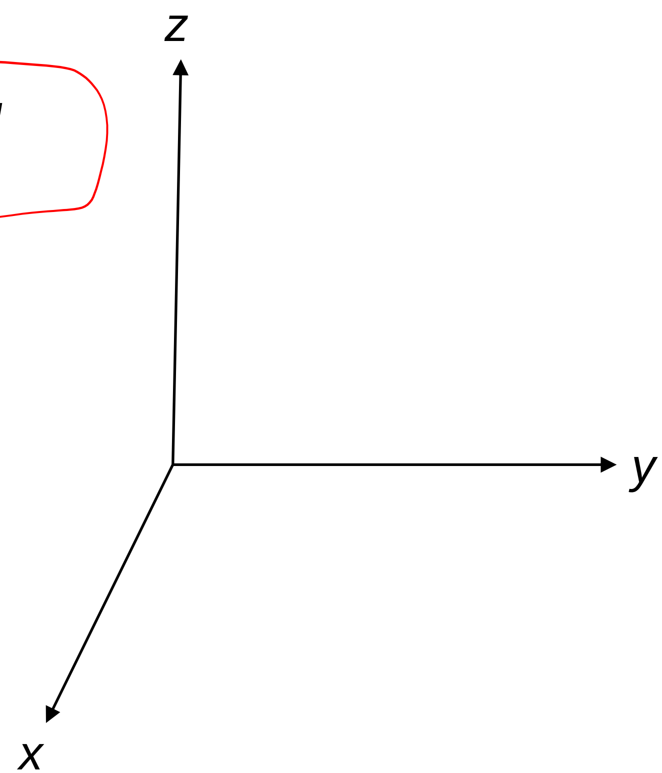
How are tensors transformed by the application of particular symmetry operations?

…by extension of the framework described for vectors and matrices!

$$\vec{\beta}^{new} = \left(\sigma_{xz} \otimes \sigma_{xz} \otimes \sigma_{xz}\right) \cdot \vec{\beta}^{old}$$

$$\frac{1}{2}\left[\left(\sigma_{xz} \otimes \sigma_{xz} \otimes \sigma_{xz}\right) + I\right]$$

Nonzero rows correspond to the set of symmetry-allowed elements.



Vector Properties

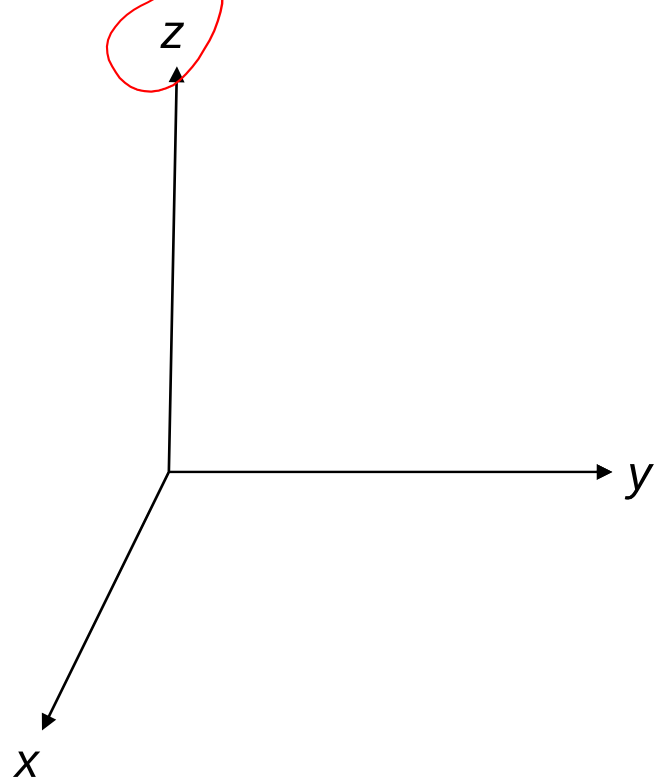
How are vector properties transformed by the application of a particular symmetry operation?

Let's next consider the $C_3(z)$ operation…

$$\vec{\mu}^{new1} = R\left(\frac{2\pi}{3}\right) \cdot \vec{\mu}^{old}$$

$$\vec{\mu}^{new2} = R\left(2\frac{2\pi}{3}\right) \cdot \vec{\mu}^{old}$$

$$\tfrac{1}{3}\left(I + R\left(\frac{2\pi}{3}\right) + R\left(2\frac{2\pi}{3}\right)\right)$$



If the symmetry operation leaves the system unchanged by definition, the sum of the three symmetry operators isolates the invariant elements.

Molecular symmetry: C_3

$\vec{\beta}' = \boxed{C_3^1(z)\otimes C_3^1(z)\otimes C_3^1(z)}\cdot\vec{\beta}$

Matrix for $I + \left[C_3^1(z)\otimes C_3^1(z)\otimes C_3^1(z)\right] + \left[C_3^2(z)\otimes C_3^2(z)\otimes C_3^2(z)\right]$

Sum the expanded transformation matrices for $C_3^0 + C_3^1 + C_3^2$ operations to reveal the symmetry relationships from the C_3 operation.

$$\boxed{-\beta_{xxx} = \beta_{xyy} = \beta_{yxy} = \beta_{yyx}}$$

	xxx	Xxy	xxz	xyx	xyy	xyz	xzx	xzy	xzz	yxx	yxy	yxz	yyx	yyy	yyz	yzx	yzy	yzz	zxx	zxy	zxz	zyx	zyy	zyz	zzx	zzy	zzz
xxx	0.75	0	0	0	-0.75	0	0	0	0	0	-0.75	0	-0.75	0	0	0	0	0	0	0	0	0	0	0	0	0	0
xxy	0	0.75	0	0.75	0	0	0	0	0	0.75	0	0	0	-0.75	0	0	0	0	0	0	0	0	0	0	0	0	0
xxz	0	0	1.5	0	0	0	0	0	0	0	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0	0	0	0
xyx	0	0.75	0	0.75	0	0	0	0	0	0.75	0	0	0	-0.75	0	0	0	0	0	0	0	0	0	0	0	0	0
xyy	-0.75	0	0	0	0.75	0	0	0	0	0	0.75	0	0.75	0	0	0	0	0	0	0	0	0	0	0	0	0	0
xyz	0	0	0	0	0	1.5	0	0	0	0	0	-1.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
xzx	0	0	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0	0
xzy	0	0	0	0	0	0	0	1.5	0	0	0	0	0	0	0	-1.5	0	0	0	0	0	0	0	0	0	0	0
xzz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
yxx	0	0.75	0	0.75	0	0	0	0	0	0.75	0	0	0	-0.75	0	0	0	0	0	0	0	0	0	0	0	0	0
yxy	-0.75	0	0	0	0.75	0	0	0	0	0	0.75	0	0.75	0	0	0	0	0	0	0	0	0	0	0	0	0	0
yxz	0	0	0	0	0	-1.5	0	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
yyx	-0.75	0	0	0	0.75	0	0	0	0	0	0.75	0	0.75	0	0	0	0	0	0	0	0	0	0	0	0	0	0
yyy	0	-0.75	0	-0.75	0	0	0	0	0	-0.75	0	0	0	0.75	0	0	0	0	0	0	0	0	0	0	0	0	0
yyz	0	0	1.5	0	0	0	0	0	0	0	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0	0	0	0
yzx	0	0	0	0	0	0	0	-1.5	0	0	0	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0	0	0
yzy	0	0	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0	0
yzz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
zxx	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.5	0	0	0	1.5	0	0	0	0
zxy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.5	0	-1.5	0	0	0	0	0
zxz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
zyx	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-1.5	0	1.5	0	0	0	0	0
zyy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.5	0	0	0	1.5	0	0	0	0
zyz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
zzx	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
zzy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
zzz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3

Molecular symmetry: C_3

$$\vec{\beta}\,' = \boxed{C_3^1(z)\otimes C_3^1(z)\otimes C_3^1(z)}\cdot\vec{\beta}$$

Matrix for $I+\left[C_3^1(z)\otimes C_3^1(z)\otimes C_3^1(z)\right]+\left[C_3^2(z)\otimes C_3^2(z)\otimes C_3^2(z)\right]$

	xxx	Xxy	xxz	xyx	xyy	xyz	xzx	xzy	xzz	yxx	yxy	yxz	yyx	yyy	yyz	yzx	yzy	yzz	zxx	zxy	zxz	zyx	zyy	zyz	zzx	zzy	zzz
xxx	0.75	0	0	0	-0.75	0	0	0	0	0	-0.75	0	-0.75	0	0	0	0	0	0	0	0	0	0	0	0	0	0
xxy	0	0.75	0	0.75	0	0	0	0	0	0.75	0	0	0	-0.75	0	0	0	0	0	0	0	0	0	0	0	0	0
xxz	0	0	1.5	0	0	0	0	0	0	0	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0	0	0	0
xyx	0	0.75	0	0.75	0	0	0	0	0	0.75	0	0	0	-0.75	0	0	0	0	0	0	0	0	0	0	0	0	0
xyy	-0.75	0	0	0	0.75	0	0	0	0	0	0.75	0	0.75	0	0	0	0	0	0	0	0	0	0	0	0	0	0
xyz	0	0	0	0	0	1.5	0	0	0	0	0	-1.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
xzx	0	0	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0	0
xzy	0	0	0	0	0	0	0	1.5	0	0	0	0	0	0	0	-1.5	0	0	0	0	0	0	0	0	0	0	0
xzz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
yxx	0	0.75	0	0.75	0	0	0	0	0	0.75	0	0	0	-0.75	0	0	0	0	0	0	0	0	0	0	0	0	0
yxy	-0.75	0	0	0	0.75	0	0	0	0	0	0.75	0	0.75	0	0	0	0	0	0	0	0	0	0	0	0	0	0
yxz	0	0	0	0	0	-1.5	0	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
yyx	-0.75	0	0	0	0.75	0	0	0	0	0	0.75	0	0.75	0	0	0	0	0	0	0	0	0	0	0	0	0	0
yyy	0	-0.75	0	-0.75	0	0	0	0	0	-0.75	0	0	0	0.75	0	0	0	0	0	0	0	0	0	0	0	0	0
yyz	0	0	1.5	0	0	0	0	0	0	0	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0	0	0	0
yzx	0	0	0	0	0	0	0	-1.5	0	0	0	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0	0	0
yzy	0	0	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0	0
yzz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
zxx	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.5	0	0	0	1.5	0	0	0	0
zxy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.5	0	-1.5	0	0	0	0	0
zxz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
zyx	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-1.5	0	1.5	0	0	0	0	0
zyy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.5	0	0	0	1.5	0	0	0	0
zyz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
zzx	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
zzy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
zzz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3

Sum the expanded transformation matrices for $C_3^0 + C_3^1 + C_3^2$ operations to reveal the symmetry relationships from the C_3 operation.

$$-\beta_{xxx} = \beta_{xyy} = \beta_{yxy} = \beta_{yyx}$$

$$-\beta_{yyy} = \beta_{xxy} = \beta_{xyx} = \beta_{yxx}$$

$$\beta_{xxz} = \beta_{yyz} \qquad \beta_{xyz} = -\beta_{yxz}$$

$$\beta_{xzx} = \beta_{yzy} \qquad \beta_{xzy} = -\beta_{yzx}$$

$$\beta_{zxx} = \beta_{zyy} \qquad \beta_{zxy} = -\beta_{zyx}$$

$$\beta_{zzz}$$