Lecture 12: Strong coupling

Strong coupling

$$\gamma_1 = \gamma_2, \quad \omega_{0,1} \approx \omega_{0,2}, \quad \Omega_1 \approx \Omega_2$$

Secular approximation not applicable:

$$\mathscr{H} = +\omega_{0,1}\mathscr{I}_{1z} + \omega_{0,2}\mathscr{I}_{2z} + \pi J\left(2\mathscr{I}_{1z}\mathscr{I}_{2z} + 2\mathscr{I}_{1x}\mathscr{I}_{2x} + 2\mathscr{I}_{1y}\mathscr{I}_{2y}\right)$$

$\mathscr{I}_{1z}$ and $\mathscr{I}_{2z}$ do not commute with $2\mathscr{I}_{1x}\mathscr{I}_{2x}$ and $2\mathscr{I}_{1y}\mathscr{I}_{2y}$:

$$[\mathscr{I}_{1z}, 2\mathscr{I}_{1x}\mathscr{I}_{2x}] = 2[\mathscr{I}_{1z}, \mathscr{I}_{1x}]\mathscr{I}_{2x} = \mathrm{i}2\mathscr{I}_{1y}\mathscr{I}_{2x}$$
$$[\mathscr{I}_{1z}, 2\mathscr{I}_{1y}\mathscr{I}_{2y}] = 2[\mathscr{I}_{1z}, \mathscr{I}_{1y}]\mathscr{I}_{2y} = -\mathrm{i}2\mathscr{I}_{1x}\mathscr{I}_{2y}$$
$$[\mathscr{I}_{2z}, 2\mathscr{I}_{1x}\mathscr{I}_{2x}] = 2\mathscr{I}_{1x}[\mathscr{I}_{2z}, \mathscr{I}_{2x}] = \mathrm{i}2\mathscr{I}_{1x}\mathscr{I}_{2y}$$
$$[\mathscr{I}_{2z}, 2\mathscr{I}_{1y}\mathscr{I}_{2y}] = 2\mathscr{I}_{1y}[\mathscr{I}_{2z}, \mathscr{I}_{2y}] = -\mathrm{i}2\mathscr{I}_{1y}\mathscr{I}_{2x}$$

Effects of $2\mathscr{I}_{1x}\mathscr{I}_{2x}$, $2\mathscr{I}_{1y}\mathscr{I}_{2y}$ and $\mathscr{I}_{1z}$, $\mathscr{I}_{2z}$
cannot be analyzed separately in any order

Strong coupling

$$\mathscr{H} = +\omega_{0,1}\mathscr{I}_{1z} + \omega_{0,2}\mathscr{I}_{2z} + \pi J\left(2\mathscr{I}_{1z}\mathscr{I}_{2z} + 2\mathscr{I}_{1x}\mathscr{I}_{2x} + 2\mathscr{I}_{1y}\mathscr{I}_{2y}\right)$$

Hamiltonian not diagonal:

$$\mathscr{H} = \frac{\pi}{2}\begin{pmatrix} \Sigma + J & 0 & 0 & 0 \\ 0 & \Delta - J & 2J & 0 \\ 0 & 2J & -\Delta - J & 0 \\ 0 & 0 & 0 & -\Sigma + J \end{pmatrix}$$

$$\Sigma = (\omega_{0,1} + \omega_{0,2})/\pi$$

$$\Delta = (\omega_{0,1} - \omega_{0,2})/\pi$$

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

NOT stationary states (eigenfunctions of $\mathscr{H}$)

New basis $\Rightarrow$ diagonalized Hamiltonian

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ \sqrt{\frac{1}{2} + \frac{\Delta}{2\sqrt{4J^2+\Delta^2}}} \\ \sqrt{\frac{1}{2} - \frac{\Delta}{2\sqrt{4J^2+\Delta^2}}} \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ -\sqrt{\frac{1}{2} - \frac{\Delta}{2\sqrt{4J^2+\Delta^2}}} \\ \sqrt{\frac{1}{2} + \frac{\Delta}{2\sqrt{4J^2+\Delta^2}}} \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

$$\Delta = (\omega_{0,1} - \omega_{0,2})/\pi$$

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ c_\xi \\ s_\xi \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ -s_\xi \\ c_\xi \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

stationary states (eigenfunctions of $\mathscr{H}'$)

Diagonalized Hamiltonian

$$\mathscr{H}' = \frac{\pi}{2}\begin{pmatrix} \Sigma + J & 0 & 0 & 0 \\ 0 & \sqrt{\Delta^2 + 4J^2} - J & 0 & 0 \\ 0 & 0 & -\sqrt{\Delta + 4J^2} - J & 0 \\ 0 & 0 & 0 & -\Sigma + J \end{pmatrix}$$

$$= \frac{\omega'_{0,1}}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} + \frac{\omega'_{0,1}}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} + \pi J \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\begin{aligned} \mathscr{H}' &= \omega'_{0,1}\mathscr{I}_{1z} + \omega'_{0,2}\mathscr{I}_{2z} + \pi J \cdot 2\mathscr{I}_{1z}\mathscr{I}_{2z} \\ \omega'_{0,1} &= \frac{1}{2}\left(\omega_{0,1} + \omega_{0,2} + \sqrt{(\omega_{0,1} - \omega_{0,2})^2 + 4\pi^2 J^2}\right) \\ \omega'_{0,2} &= \frac{1}{2}\left(\omega_{0,1} + \omega_{0,2} - \sqrt{(\omega_{0,1} - \omega_{0,2})^2 + 4\pi^2 J^2}\right) \end{aligned}$$

$\hat{\rho}$ and $\widehat{M}_+$ in the new basis

$$
\begin{aligned}
\mathscr{I}'_{1y} + \mathscr{I}'_{2y} &= c_\xi(\mathscr{I}_{1y} + \mathscr{I}_{2y}) + s_\xi(2\mathscr{I}_{1z}\mathscr{I}_{2y} - 2\mathscr{I}_{1y}\mathscr{I}_{2z}) \\
\mathscr{I}'_{1x} + \mathscr{I}'_{2x} &= c_\xi(\mathscr{I}_{1x} + \mathscr{I}_{2x}) + s_\xi(2\mathscr{I}_{1z}\mathscr{I}_{2x} - 2\mathscr{I}_{1x}\mathscr{I}_{2z}) \\
\mathscr{I}'_{1+} + \mathscr{I}'_{2+} &= c_\xi(\mathscr{I}_{1x} + \mathscr{I}_{2x} + \mathrm{i}\mathscr{I}_{1y} + \mathrm{i}\mathscr{I}_{2y}) \\
&+ s_\xi(2\mathscr{I}_{1z}\mathscr{I}_{2x} - 2\mathscr{I}_{1x}\mathscr{I}_{2z} + \mathrm{i}2\mathscr{I}_{1z}\mathscr{I}_{2y} - \mathrm{i}2\mathscr{I}_{1y}\mathscr{I}_{2z})
\end{aligned}
$$

Contribution	$\frac{2}{\kappa}\hat{\rho}'_1(\mathrm{b})$	$\xrightarrow{\omega'_{0,1}\mathscr{I}_{1z}}$	$\xrightarrow{\pi J\cdot 2\mathscr{I}_{1z}\mathscr{I}_{2z}}$
$\mathscr{I}_{1y}$	$+c_\xi$	$+c_\xi c'_1$	$+c_\xi c'_1 c_J - s_\xi s'_1 s_J$
$2\mathscr{I}_{1y}\mathscr{I}_{2z}$	$+s_\xi$	$+s_\xi c'_1$	$+s_\xi c'_1 c_J - c_\xi s'_1 s_J$
$\mathscr{I}_{1x}$	0	$-c_\xi s'_1$	$-c_\xi s'_1 c_J - s_\xi c'_1 s_J$
$2\mathscr{I}_{1y}\mathscr{I}_{2z}$	0	$-s_\xi s'_1$	$-s_\xi s'_1 c_J - c_\xi c'_1 s_J$

Signal of a strongly coupled pair

Contribution	$\frac{2}{\kappa}\hat{\rho}'_1(\mathrm{b})$	$\xrightarrow{\omega'_{0,1}\mathscr{I}_{1z}}$	$\xrightarrow{\pi J\cdot 2\mathscr{I}_{1z}\mathscr{I}_{2z}}$
$\mathscr{I}_{1y}$	$+c_\xi$	$+c_\xi c'_1$	$+c_\xi c'_1 c_J - s_\xi s'_1 s_J$
$2\mathscr{I}_{1y}\mathscr{I}_{2z}$	$+s_\xi$	$+s_\xi c'_1$	$+s_\xi c'_1 c_J - c_\xi s'_1 s_J$
$\mathscr{I}_{1x}$	0	$-c_\xi s'_1$	$-c_\xi s'_1 c_J - s_\xi c'_1 s_J$
$2\mathscr{I}_{1y}\mathscr{I}_{2z}$	0	$-s_\xi s'_1$	$-s_\xi s'_1 c_J - c_\xi c'_1 s_J$

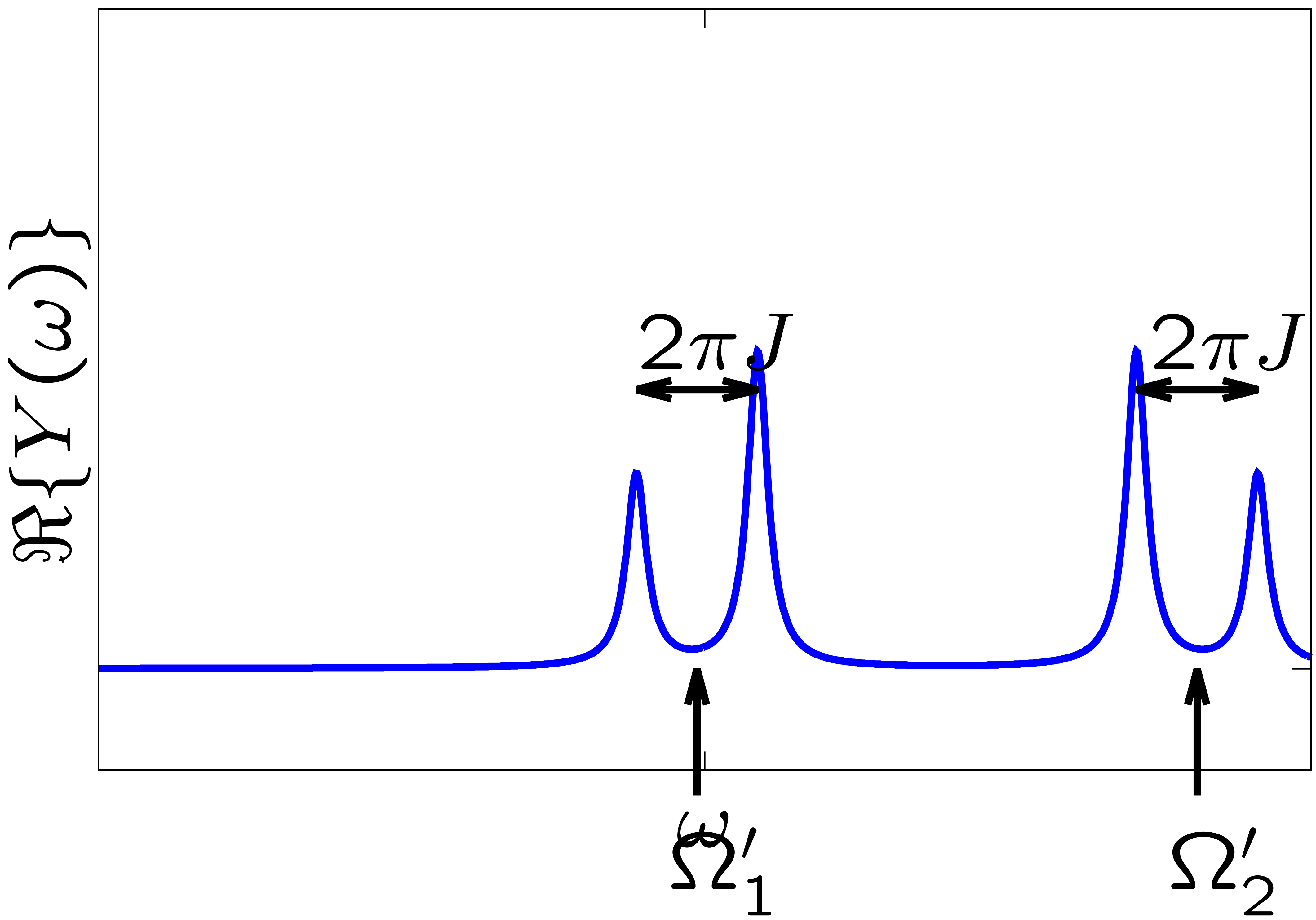
Contrib.	$\mathrm{Tr}\{\frac{2}{\kappa}\hat{\rho}'_1(t)\mathscr{I}'_{1+}\}$
$\mathscr{I}_{1y}$ $2\mathscr{I}_{1y}\mathscr{I}_{2z}$	$\left.\begin{matrix} +\mathrm{i}c_\xi^2 c'_1 c_J - \mathrm{i}c_\xi s_\xi s'_1 s_J \\ +\mathrm{i}s_\xi^2 c'_1 c_J - \mathrm{i}c_\xi s_\xi s'_1 s_J \end{matrix}\right\} = \mathrm{i}\left(c'_1 c_J - \frac{2J}{\sqrt{4J^2+\Delta^2}} s'_1 s_J\right)$
$\mathscr{I}_{1x}$ $2\mathscr{I}_{1y}\mathscr{I}_{2z}$	$\left.\begin{matrix} -c_\xi^2 s'_1 c_J - c_\xi s_\xi c'_1 s_J \\ -s_\xi^2 s'_1 c_J - c_\xi s_\xi c'_1 s_J \end{matrix}\right\} = -\left(s'_1 c_J + \frac{2J}{\sqrt{4J^2+\Delta^2}} c'_1 s_J\right)$

Signal of a strongly coupled pair

$$
\begin{aligned}
\Re\{Y(\omega)\} = &\left(1 - \frac{J}{\sqrt{\Delta^2 + 4J^2}}\right) \frac{\mathcal{N}\gamma^2\hbar^2 B_0}{16 k_\mathrm{B} T} \frac{\overline{R}_2}{\overline{R}_2^2 + (\omega - \Omega_1' - \pi J)^2} \\
&+ \left(1 + \frac{J}{\sqrt{\Delta^2 + 4J^2}}\right) \frac{\mathcal{N}\gamma^2\hbar^2 B_0}{16 k_\mathrm{B} T} \frac{\overline{R}_2}{\overline{R}_2^2 + (\omega - \Omega_1' - \pi J)^2} \\
&+ \left(1 + \frac{J}{\sqrt{\Delta^2 + 4J^2}}\right) \frac{\mathcal{N}\gamma^2\hbar^2 B_0}{16 k_\mathrm{B} T} \frac{\overline{R}_2}{\overline{R}_2^2 + (\omega - \Omega_2' + \pi J)^2} \\
&+ \left(1 - \frac{J}{\sqrt{\Delta^2 + 4J^2}}\right) \frac{\mathcal{N}\gamma^2\hbar^2 B_0}{16 k_\mathrm{B} T} \frac{\overline{R}_2}{\overline{R}_2^2 + (\omega - \Omega_2' + \pi J)^2}
\end{aligned}
$$

$$
\begin{aligned}
\Omega_1' &= \frac{1}{2}\left(\Omega_1 + \Omega_2 + \sqrt{(\Omega_1 - \Omega_2)^2 + 4\pi^2 J^2}\right) \\
\Omega_2' &= \frac{1}{2}\left(\Omega_1 + \Omega_2 - \sqrt{(\Omega_1 - \Omega_2)^2 + 4\pi^2 J^2}\right)
\end{aligned}
$$

Spectrum of a strongly coupled pair

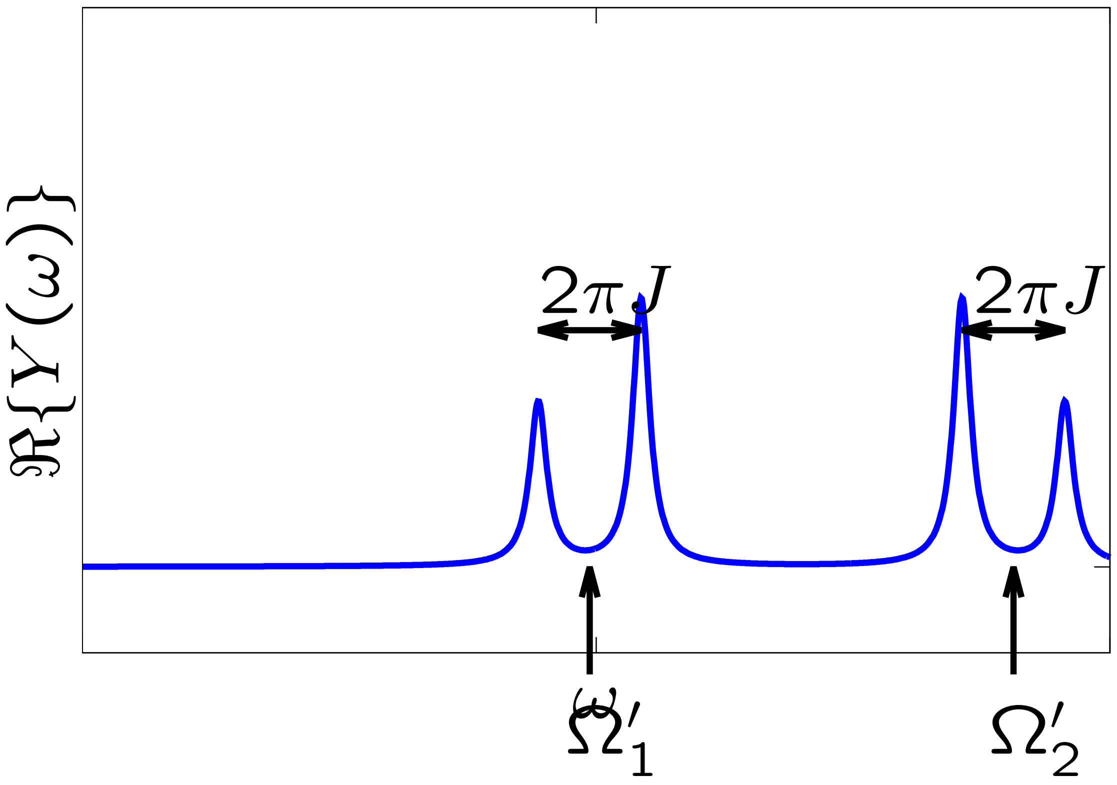


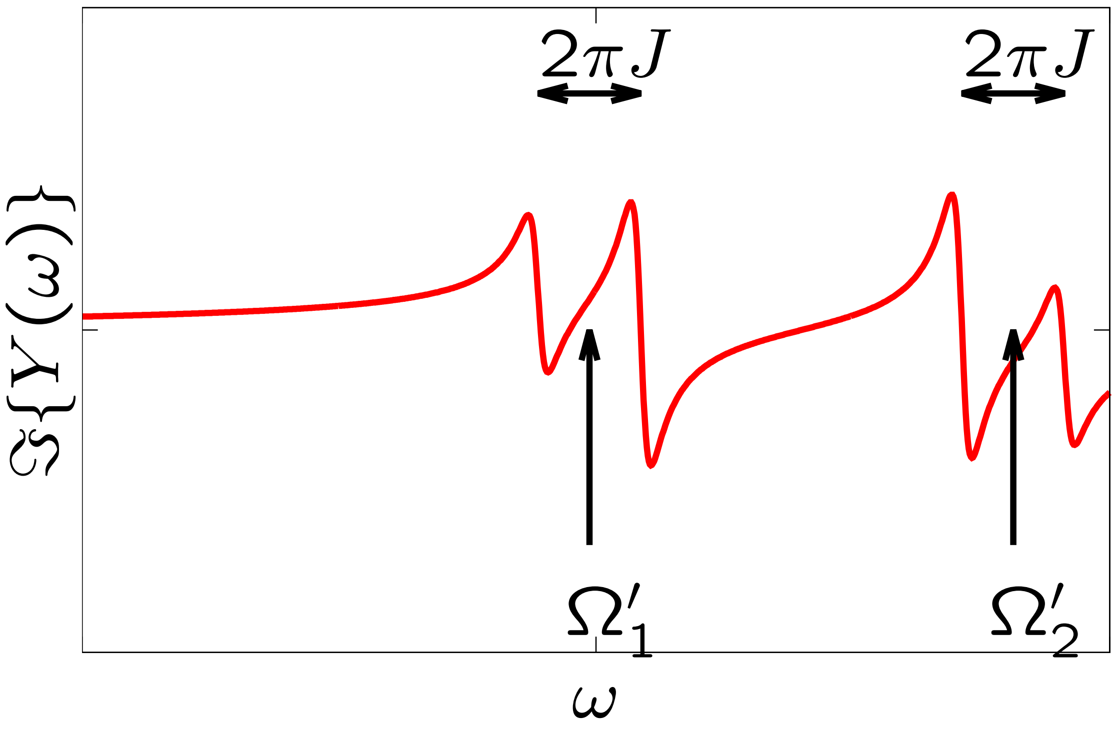
Strong vs. weak J-coupling

- Centers of doublets shifted from Ω_1 and Ω_1 by
  $\pm\left(\Omega_1 - \Omega_2 - \sqrt{(\Omega_1 - \Omega_2)^2 + 4\pi^2 J^2}\right)/2$
- Intensities of inner/outer peaks increased/decreased by
  $2\pi J/\sqrt{(\Omega_1 - \Omega_2)^2 + 4\pi^2 J^2}$
- $\sqrt{(\Omega_1 - \Omega_2)^2 + 4\pi^2 J^2}$ makes the difference
  $|\Omega_1 - \Omega_2| \gg 2\pi|J|$ weak

Spectrum of a strongly coupled pair

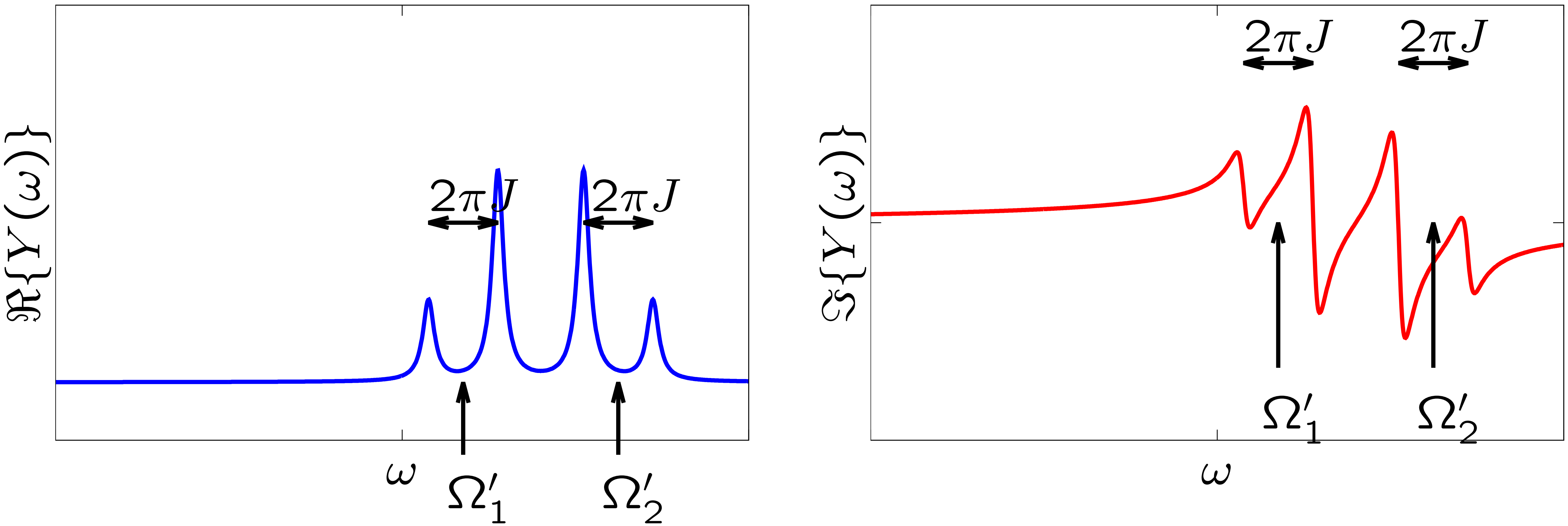
$$\Omega_1 - \Omega_2 = 8.0\pi J$$





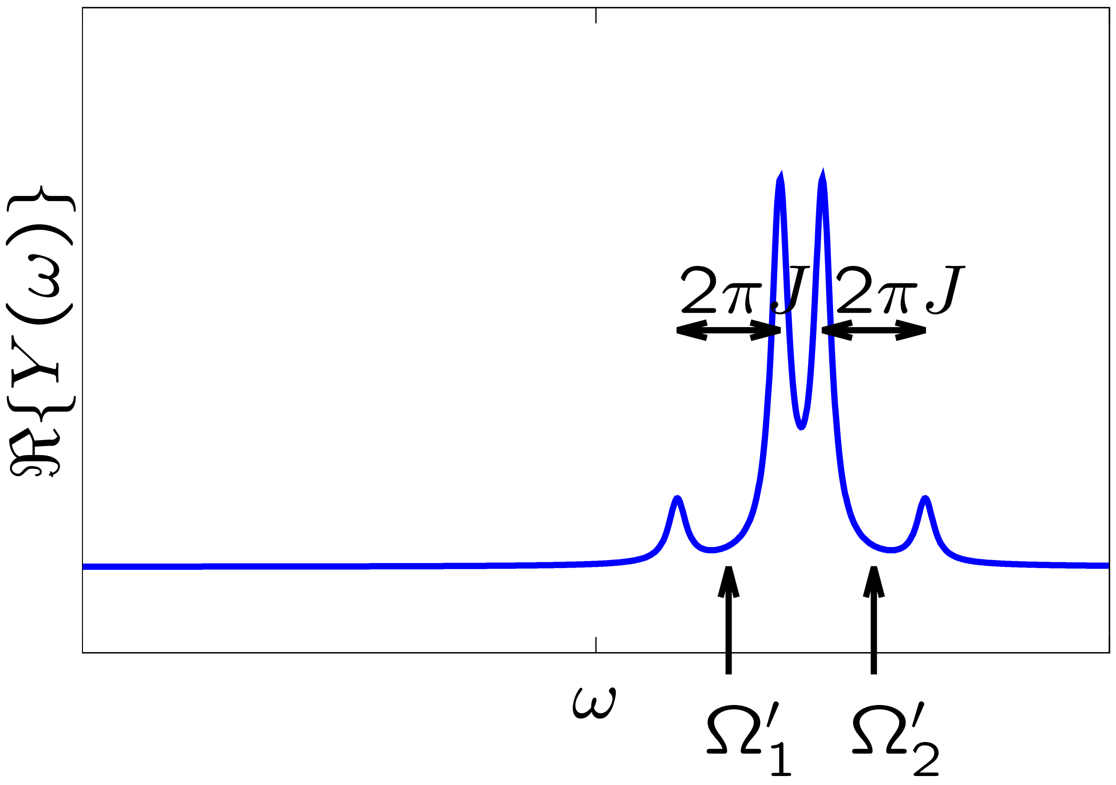
Spectrum of a strongly coupled pair

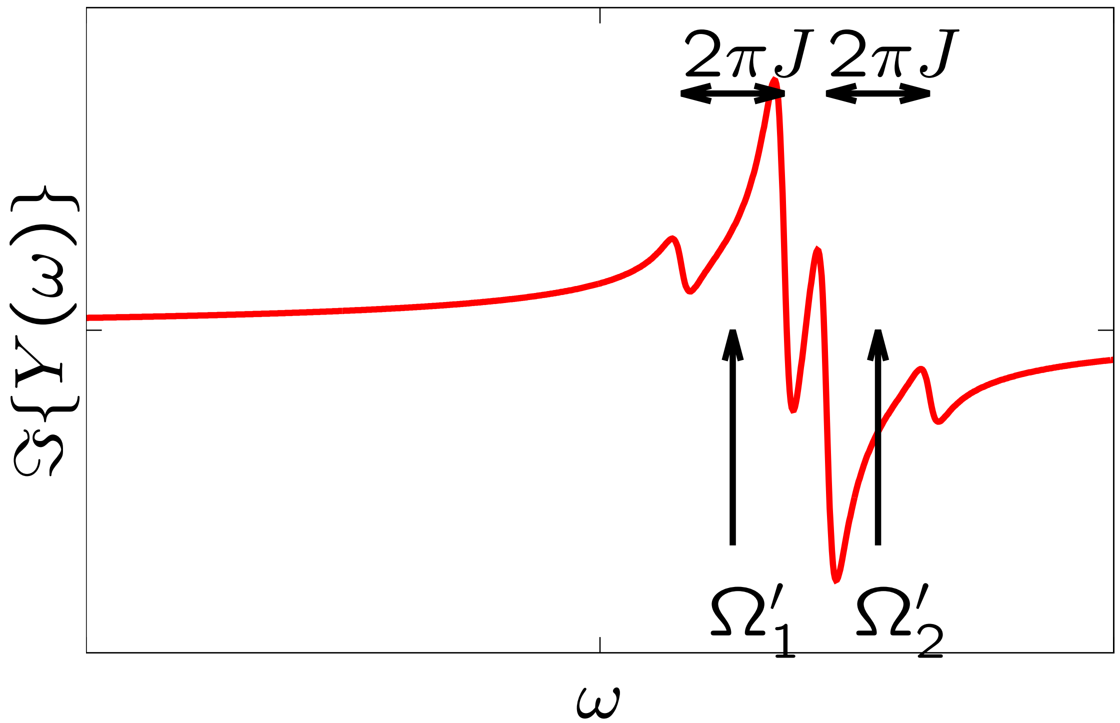
$$\Omega_1 - \Omega_2 = 4.0\pi J$$



Spectrum of a strongly coupled pair

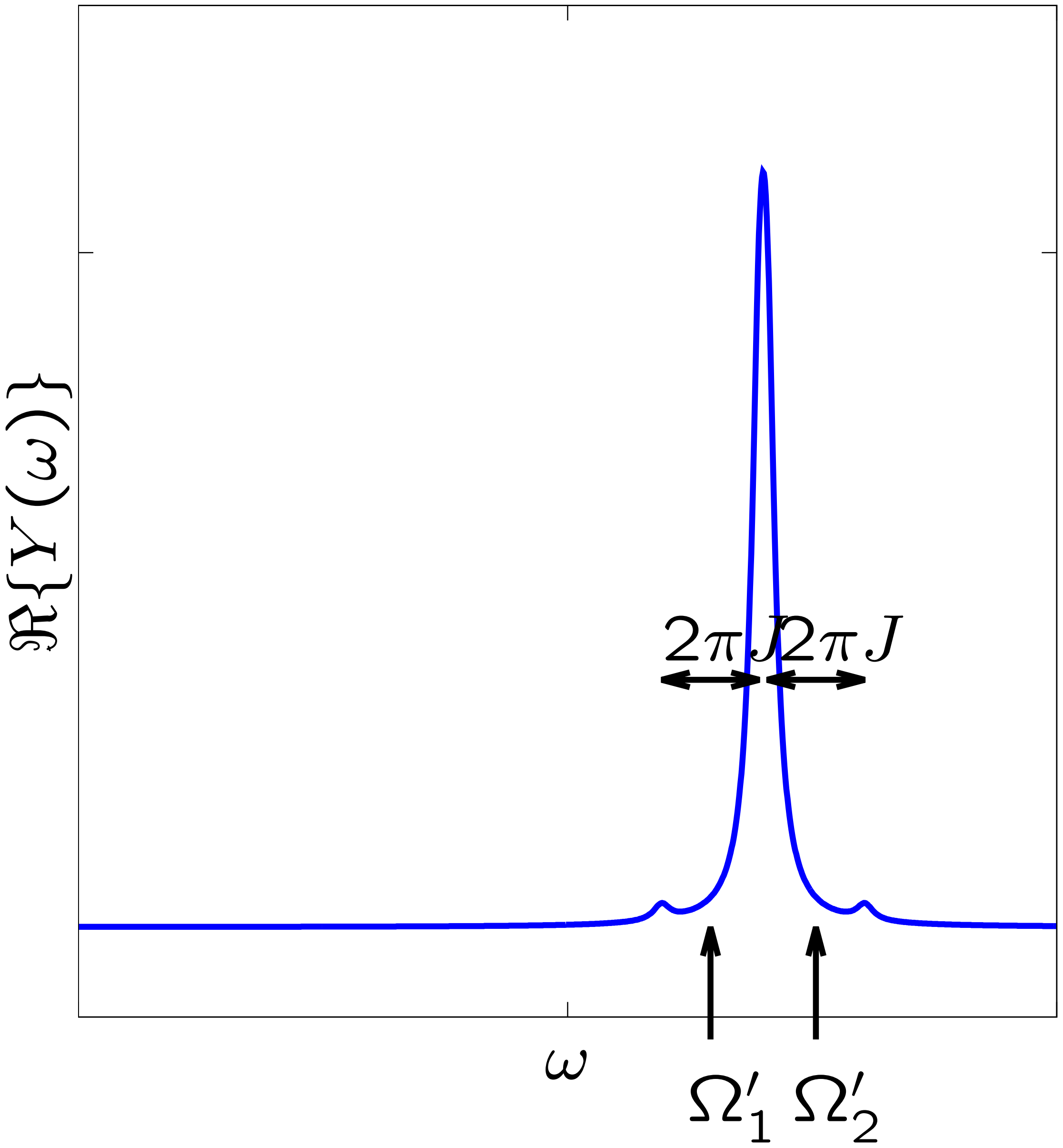
$$\Omega_1 - \Omega_2 = 2.0\pi J$$

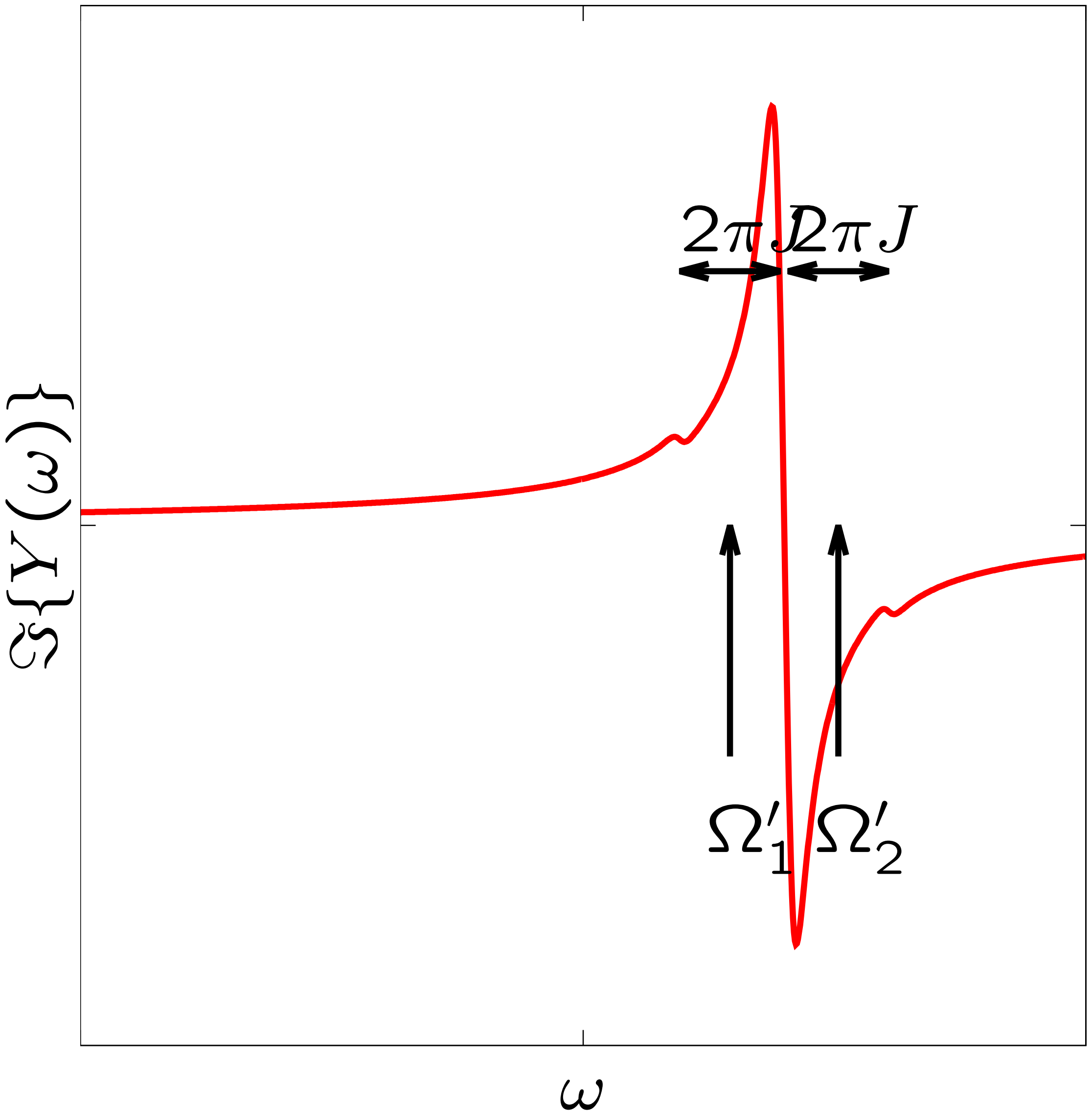




Spectrum of a strongly coupled pair

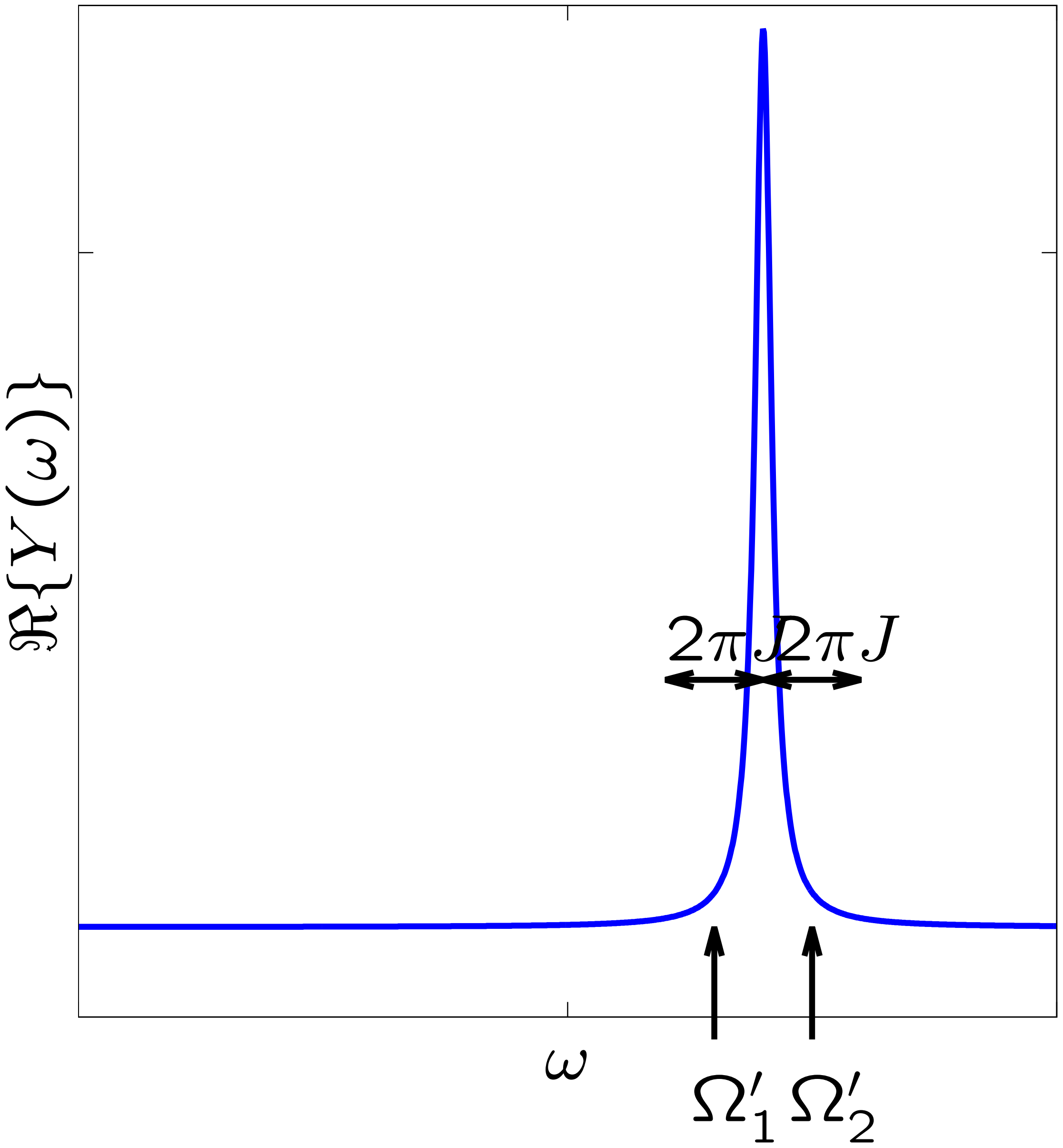
$$\Omega_1 - \Omega_2 = 0.8\pi J$$

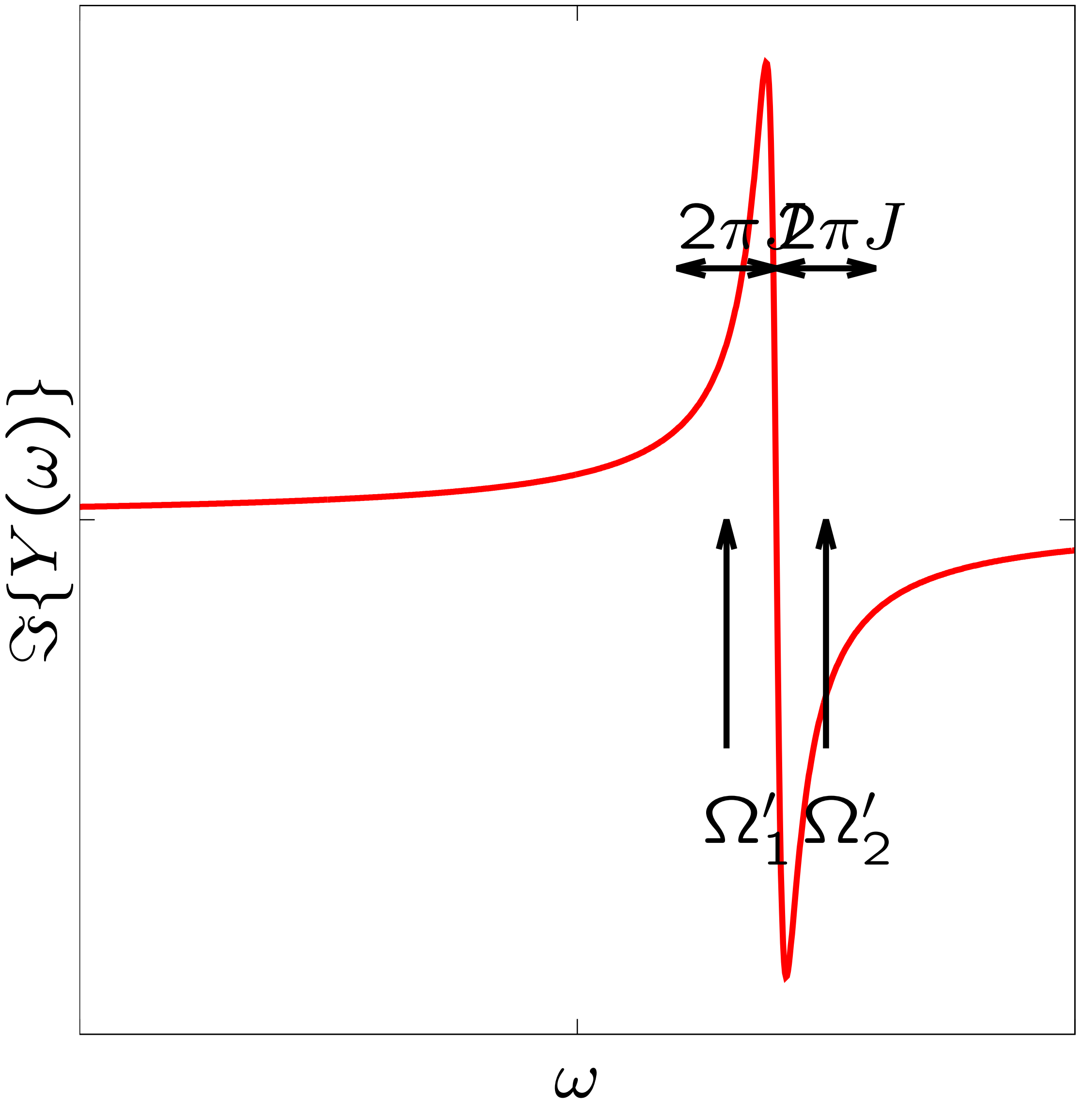




Spectrum of a strongly coupled pair

$$\Omega_1 - \Omega_2 = 0.0\pi J$$





Magnetic equivalence

- $\omega_{0,1} = \omega_{0,2}$ molecular symmetry or accident

- $J_{13} = J_{23}, \quad J_{14} = J_{24}, \ldots$

Existence of a plane of symmetry is not sufficient, the plane must bisect the particular pair of nuclei.

Magnetic equivalence: eigenfunctions

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 1/\sqrt{2} \\ 1/\sqrt{2} \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ -1/\sqrt{2} \\ 1/\sqrt{2} \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

stationary states (eigenfunctions of $\mathscr{H}'$)

Magnetic equivalence: eigenvalues

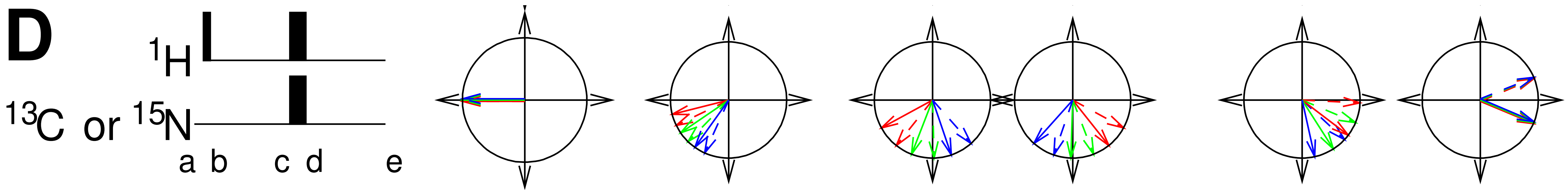
$$\hat{I}^2 = \left(\hat{\vec{I}}_1 + \hat{\vec{I}}_2\right)^2 = \hat{I}_1^2 + \hat{I}_2^2 + 2\hat{I}_{1x}\hat{I}_{2x} + 2\hat{I}_{1y}\hat{I}_{2y} + 2\hat{I}_{1z}\hat{I}_{2z}$$

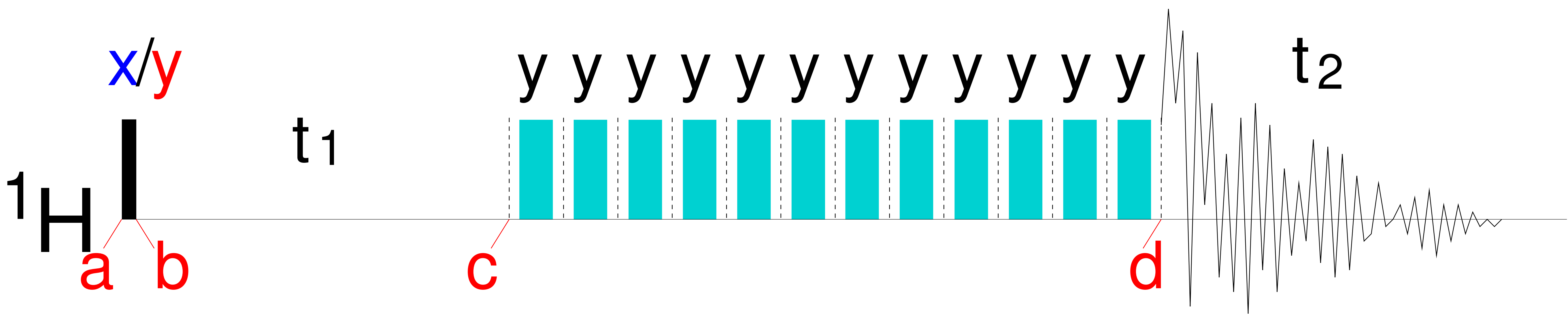
$$\mathscr{H}' = (\omega_0 + \pi J)\mathscr{I}_{1z} + (\omega_0 - \pi J)\mathscr{I}_{2z} + \pi J \cdot 2\mathscr{I}_{1z}\mathscr{I}_{2z}$$

Eigenfunction	$\hat{I}_1^2$	$\hat{I}_2^2$	$\hat{I}^{2\prime}$	$\hat{I}_z'$	$\mathscr{H}'$
$\lvert\alpha\rangle \otimes \lvert\alpha\rangle$	$3\hbar^2/4$	$3\hbar^2/4$	$2\hbar^2$	$+\hbar$	$+\omega_0 + \frac{\pi}{2}J$
$\frac{1}{\sqrt{2}}\lvert\alpha\rangle \otimes \lvert\beta\rangle + \frac{1}{\sqrt{2}}\lvert\beta\rangle \otimes \lvert\alpha\rangle$	$3\hbar^2/4$	$3\hbar^2/4$	$2\hbar^2$	0	$+\frac{\pi}{2}J$
$\frac{1}{\sqrt{2}}\lvert\alpha\rangle \otimes \lvert\beta\rangle - \frac{1}{\sqrt{2}}\lvert\beta\rangle \otimes \lvert\alpha\rangle$	$3\hbar^2/4$	$3\hbar^2/4$	0	0	$-\frac{3\pi}{2}J$
$\lvert\beta\rangle \otimes \lvert\beta\rangle$	$3\hbar^2/4$	$3\hbar^2/4$	$2\hbar^2$	$-\hbar$	$-\omega_0 + \frac{\pi}{2}J$

TOCSY (TOtally Correlated SpectroscopY)

$$\gamma_1 = \gamma_2, \quad \omega_{0,1} = \omega_{0,2}, \quad \Omega_1 = \Omega_2$$



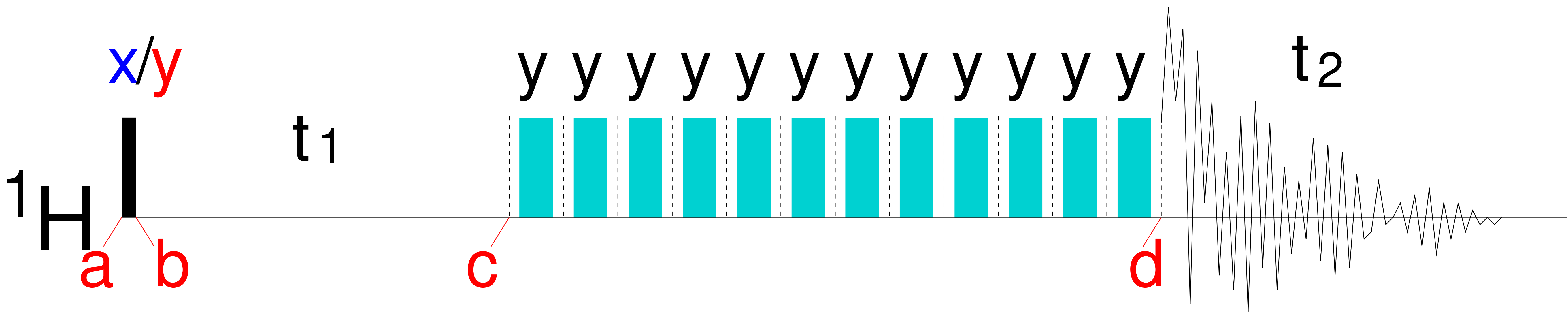


TOCSY

Simple example:

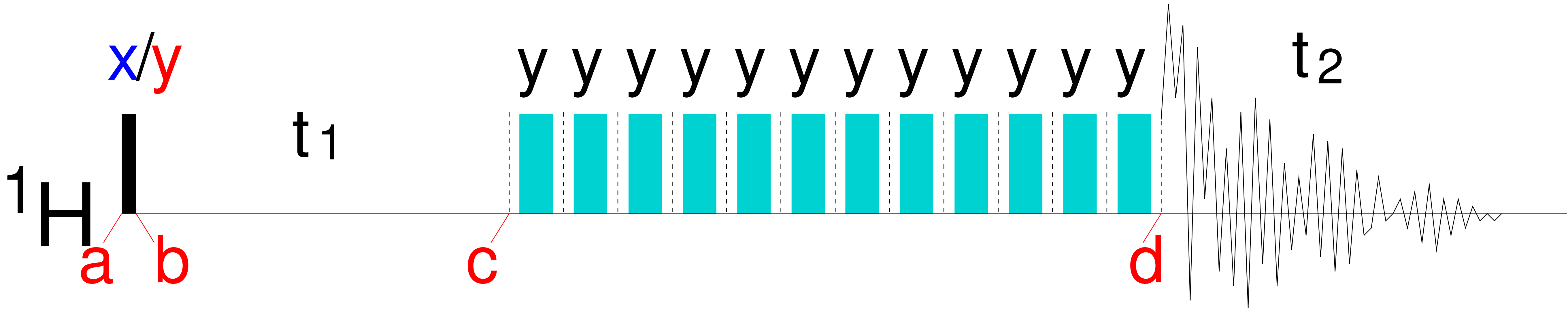
$$\mathrm{CH}\overbrace{-\mathrm{C}}^{J_{12}}\mathrm{H}\underbrace{-\mathrm{C}}_{J_{23}}\mathrm{H}$$

TOCSY



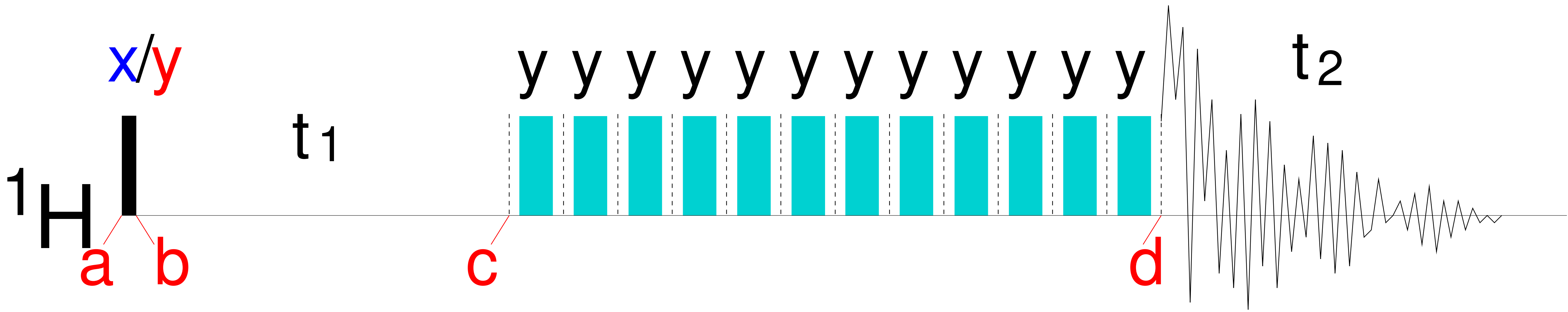
$$\hat{\rho}(\mathrm{a}) = \frac{1}{4}(\mathscr{I}_t + \kappa\mathscr{I}_{1z} + \kappa\mathscr{I}_{2z} + \kappa\mathscr{I}_{3z})$$

TOCSY



$$\widehat{\rho}(\mathrm{b}) = \frac{1}{4}(\mathscr{I}_t - \kappa\mathscr{I}_{1y} - \kappa\mathscr{I}_{2y} - \kappa\mathscr{I}_{3y})$$

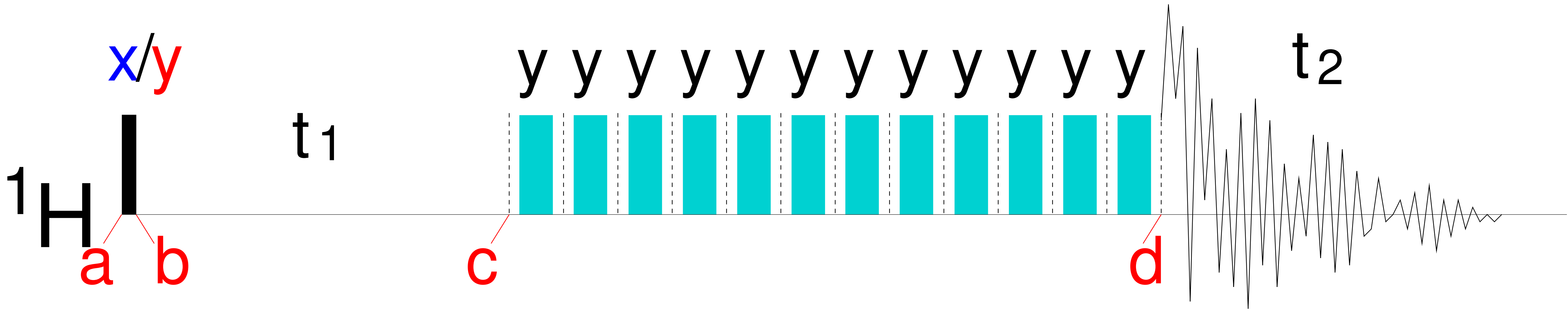
TOCSY



TOCSY pulse train applied with 90° (y) phases $\Rightarrow$

- $\mathscr{I}_{1y}$, $\mathscr{I}_{2y}$, $\mathscr{I}_{3y}$ components of the density matrix intact
- operators with $\mathscr{I}_{nx}$ and $\mathscr{I}_{nz}$ rotate "about" the $\mathscr{I}_{ny}$ "axis"
- long rotation randomizes polarization in x and z
- only the $\mathscr{I}_{1y}$, $\mathscr{I}_{2y}$, $\mathscr{I}_{3y}$, "locked" in y, survive
- only evolution of $\mathscr{I}_{1y}$, $\mathscr{I}_{2y}$, $\mathscr{I}_{3y}$ can give a signal

TOCSY



$$\hat{\rho}(\mathrm{c}) = \ldots - \frac{\kappa}{4}\cos(\Omega_1 t_1)\cos(\pi J_{12} t_1)\mathscr{I}_{1y}$$
$$- \frac{\kappa}{4}\cos(\Omega_2 t_1)\cos(\pi J_{12} t_1)\cos(\pi J_{23} t_1)\mathscr{I}_{2y}$$
$$- \frac{\kappa}{4}\cos(\Omega_3 t_1)\cos(\pi J_{23} t_1)\mathscr{I}_{3y}$$

TOCSY MIXING

$$\mathrm{CH}\overbrace{-\mathrm{C}}^{J_{12}}\mathrm{H}\underbrace{-\mathrm{C}}_{J_{23}}\mathrm{H}$$

$$\begin{aligned}\mathscr{H}_{\mathrm{TOCSY}} &= \pi J_{12}(2\mathscr{I}_{1x}\mathscr{I}_{2x} + 2\mathscr{I}_{1y}\mathscr{I}_{2y} + 2\mathscr{I}_{1z}\mathscr{I}_{2z}) \\ &+ \pi J_{23}(2\mathscr{I}_{2x}\mathscr{I}_{3x} + 2\mathscr{I}_{2y}\mathscr{I}_{3y} + 2\mathscr{I}_{2z}\mathscr{I}_{3z})\end{aligned}$$

All components of $\mathscr{H}_{\mathrm{TOCSY}}$ commute

their effects can be analyzed separately in any order

TOCSY MIXING

. . . but the analysis is not simple for > 2 nuclei

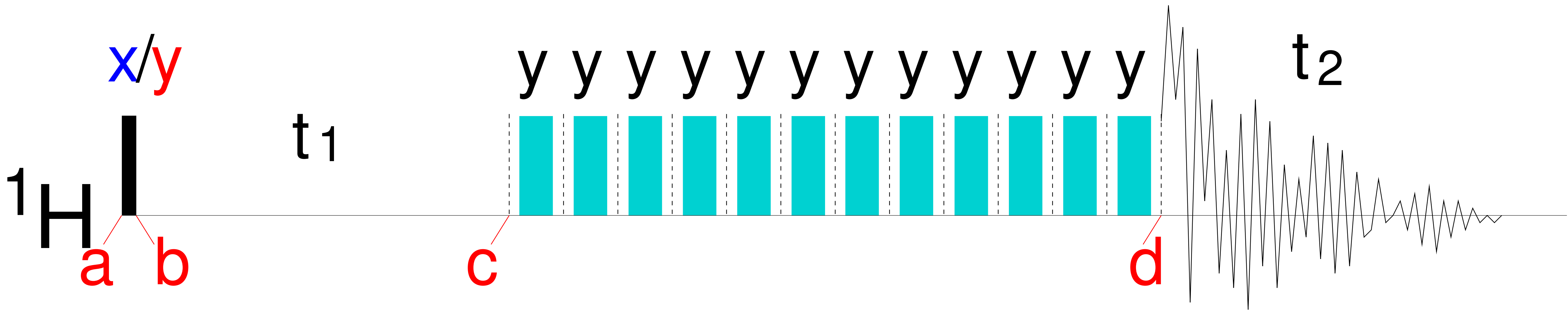
Commutator relations provide insight:

- $[\mathscr{I}_{1y}, \mathscr{H}_{\text{TOCSY}}] = -2\mathrm{i}\pi J_{12}(\mathscr{I}_{1z}\mathscr{I}_{2x} - \mathscr{I}_{1x}\mathscr{I}_{2z}) \neq 0$
  $\Rightarrow$ part of $\mathscr{I}_{1y}$ is lost

- $[\mathscr{I}_{1y} + \mathscr{I}_{2y}, \mathscr{H}_{\text{TOCSY}}] = 2\mathrm{i}\pi J_{23}(\mathscr{I}_{2x}\mathscr{I}_{3z} - \mathscr{I}_{2z}\mathscr{I}_{3x}) \neq 0$
  $\Rightarrow$ the loss of $\mathscr{I}_{1y}$ is not fully regained by $\mathscr{I}_{2y}$

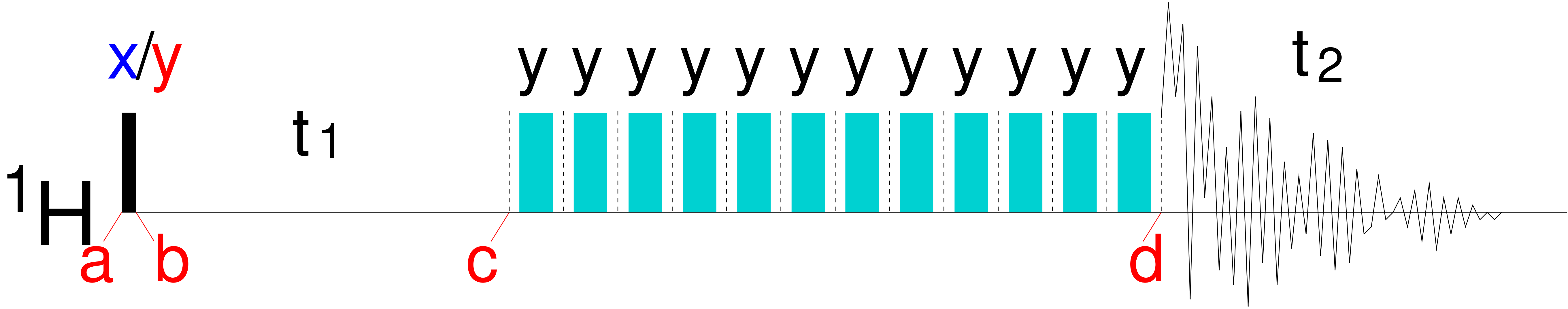
- $[\mathscr{I}_{1y} + \mathscr{I}_{2y} + \mathscr{I}_{3y}, \mathscr{H}_{\text{TOCSY}}] = 0$
  $\Rightarrow$ some $\mathscr{I}_{3y}$ must be created to keep $\mathscr{I}_{1y} + \mathscr{I}_{2y} + \mathscr{I}_{3y}$ constant despite $J_{13} = 0$!

TOCSY



$$
\begin{aligned}
\hat{\rho}(\mathrm{d}) = \\
& -\frac{\kappa}{4}\cos(\Omega_1 t_1)\cos(\pi J_{12}t_1)(a_{11}\mathscr{I}_{1y} + a_{12}\mathscr{I}_{2y} + a_{13}\mathscr{I}_{3y}) \\
& -\frac{\kappa}{4}\cos(\Omega_2 t_1)\cos(\pi J_{12}t_1)\cos(\pi J_{23}t_1) \\
& \qquad \times(a_{21}\mathscr{I}_{1y} + a_{22}\mathscr{I}_{2y} + a_{23}\mathscr{I}_{3y}) \\
& -\frac{\kappa}{4}\cos(\Omega_3 t_1)\cos(\pi J_{23}t_1)(a_{31}\mathscr{I}_{1y} + a_{32}\mathscr{I}_{2y} + a_{33}\mathscr{I}_{3y})
\end{aligned}
$$

TOCSY



Evolution of $\widehat{\rho}(t_2)$ analyzed as usually:

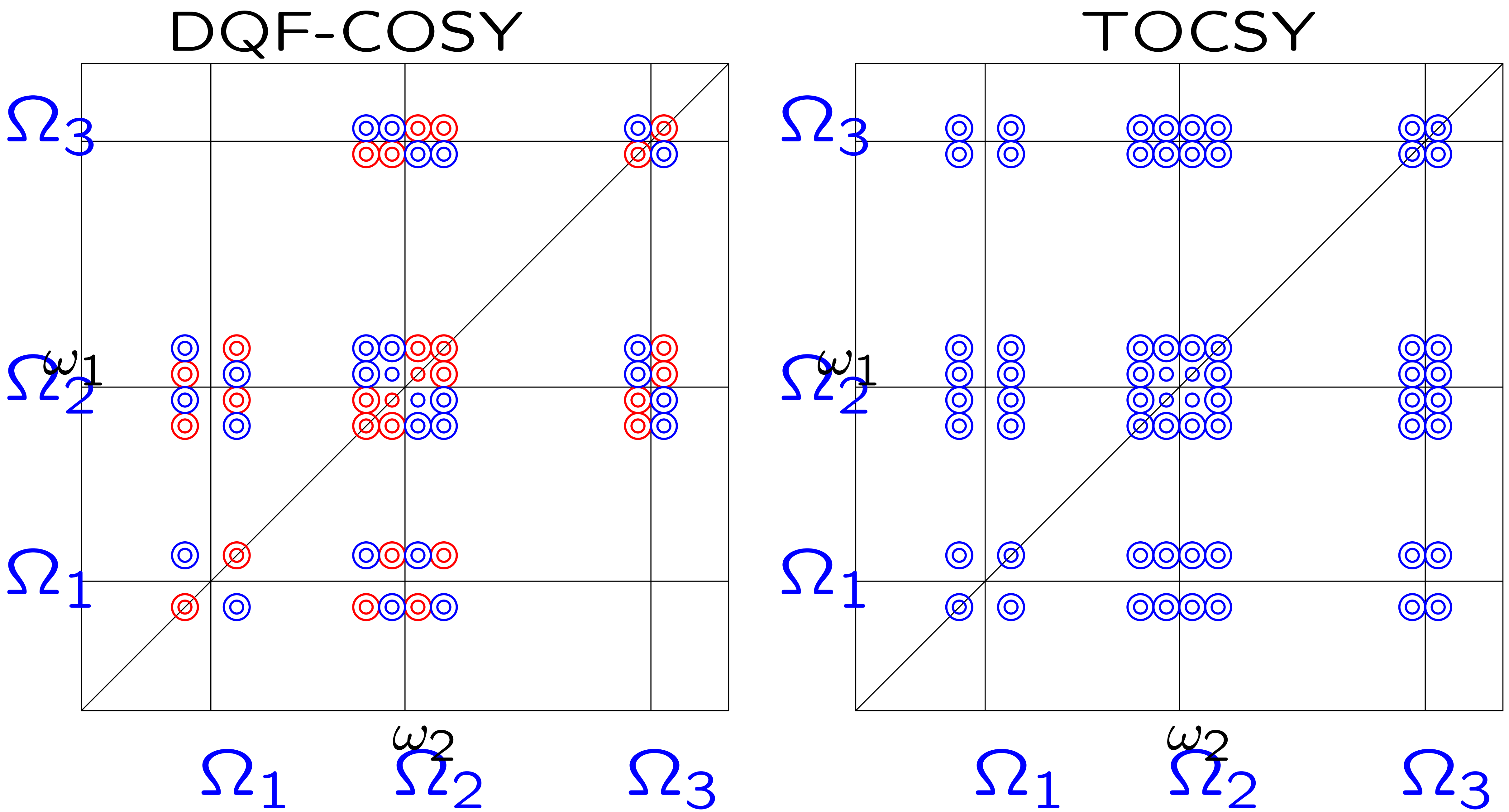
$$\frac{\kappa a_{11}}{16}\mathrm{e}^{-\overline{R}_2t_1}\left(\mathrm{e}^{-\mathrm{i}(\Omega_1-\pi J_{12})t_1}+\mathrm{e}^{-\mathrm{i}(\Omega_1+\pi J_{12})t_1}\right)\mathrm{e}^{-\overline{R}_2t_2}\left(\mathrm{e}^{-\mathrm{i}(\Omega_1-\pi J_{12})t_2}+\mathrm{e}^{-\mathrm{i}(\Omega_1+\pi J_{12})t_2}\right)+$$

$$\frac{\kappa a_{12}}{16}\mathrm{e}^{-\overline{R}_2t_1}\left(\mathrm{e}^{-\mathrm{i}(\Omega_1-\pi J_{12})t_1}+\mathrm{e}^{-\mathrm{i}(\Omega_1+\pi J_{12})t_1}\right)\mathrm{e}^{-\overline{R}_2t_2}\left(\mathrm{e}^{-\mathrm{i}(\Omega_2-\pi J_{12})t_2}+\mathrm{e}^{-\mathrm{i}(\Omega_2+\pi J_{12})t_2}\right)+$$

$$\frac{\kappa a_{13}}{16}\mathrm{e}^{-\overline{R}_2t_1}\left(\mathrm{e}^{-\mathrm{i}(\Omega_1-\pi J_{12})t_1}+\mathrm{e}^{-\mathrm{i}(\Omega_1+\pi J_{12})t_1}\right)\mathrm{e}^{-\overline{R}_2t_2}\left(\mathrm{e}^{-\mathrm{i}(\Omega_3-\pi J_{12})t_2}+\mathrm{e}^{-\mathrm{i}(\Omega_3+\pi J_{12})t_2}\right)+$$

$$+\ldots$$

TOCSY spectrum



TOCSY vs. COSY

- different structural information

- TOCSY:
  cross-peaks correlate all nuclei of a spin system
  (spin system = network of J-coupled nuclei)
  whole spin system in one spectrum

- COSY:
  cross-peaks correlate only directly coupled nuclei
  who is whose neighbor

HOMEWORK:

Section 12.4.2

Strong coupling