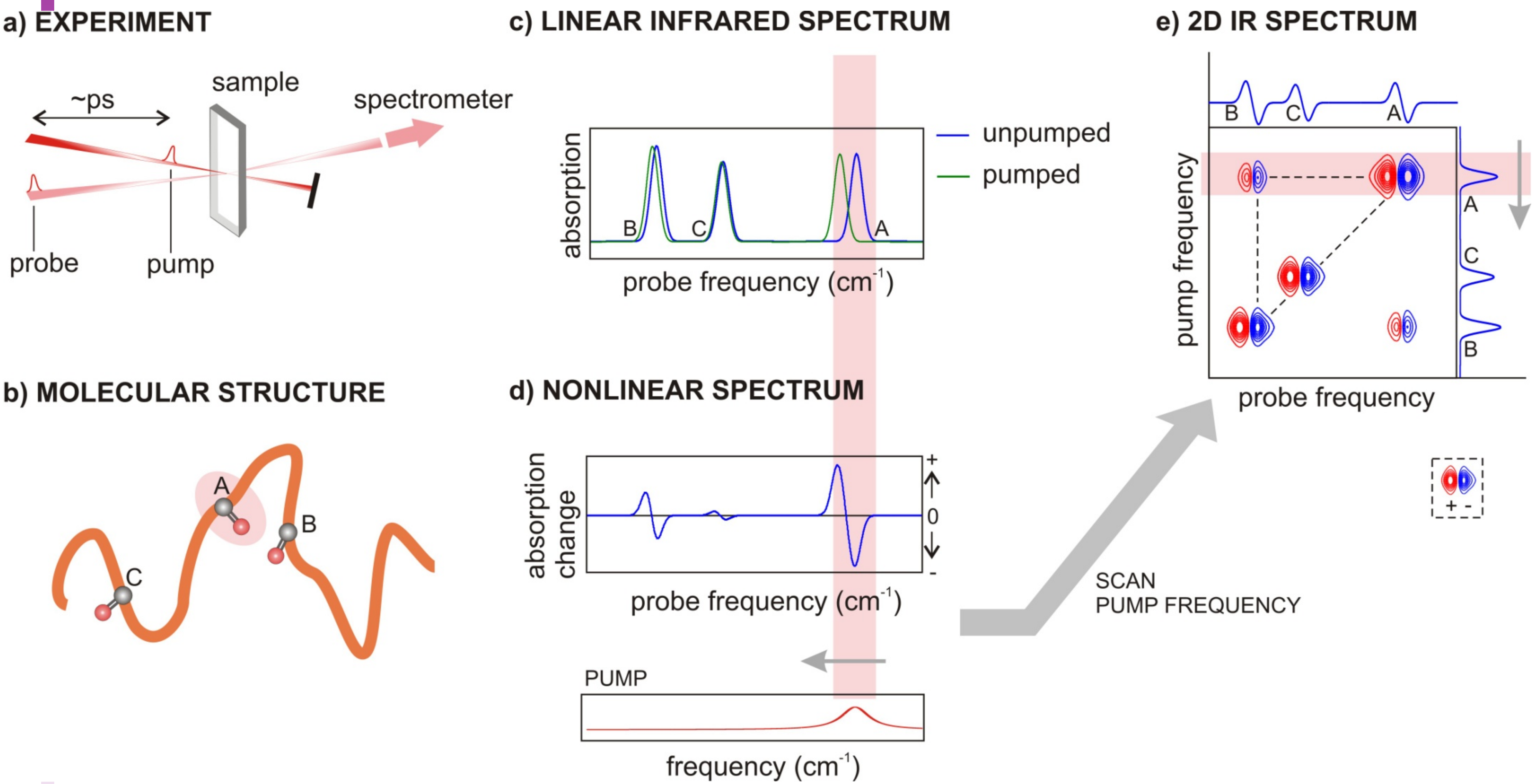
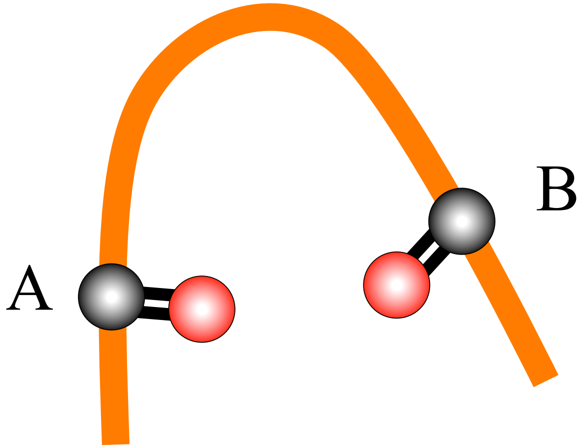
Vibrational couplings and 2DIR spectroscopy

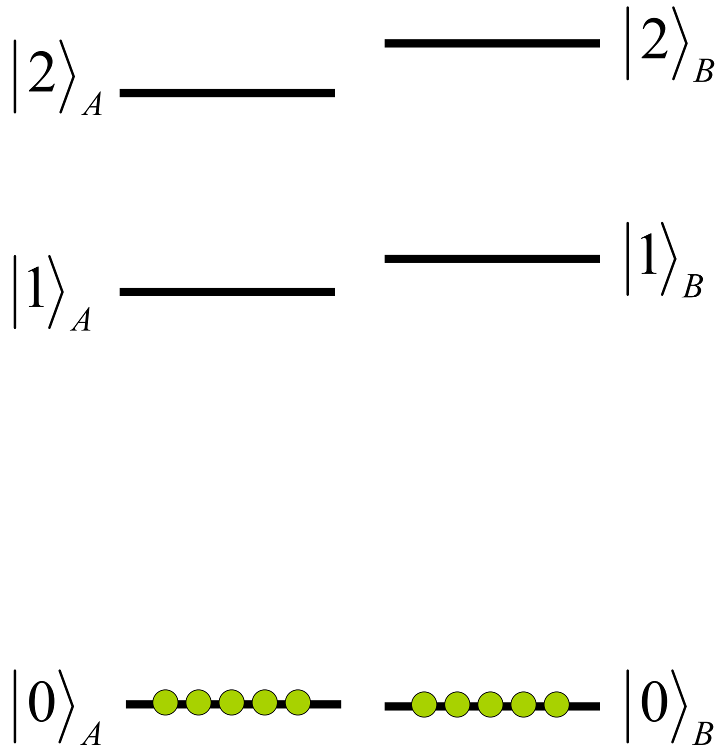
2DIR spectroscopy

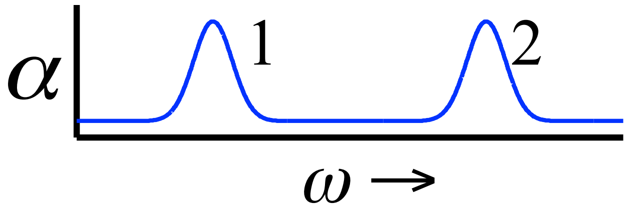


How do we describe a cross peak?

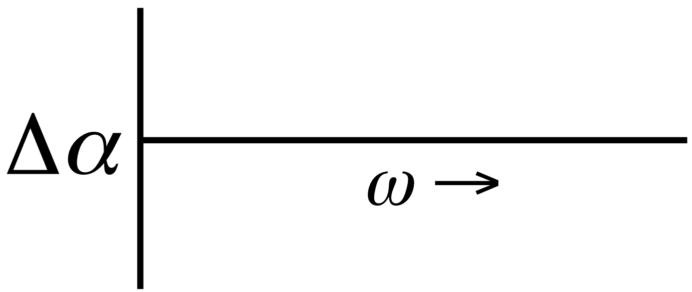


Two amide vibrations



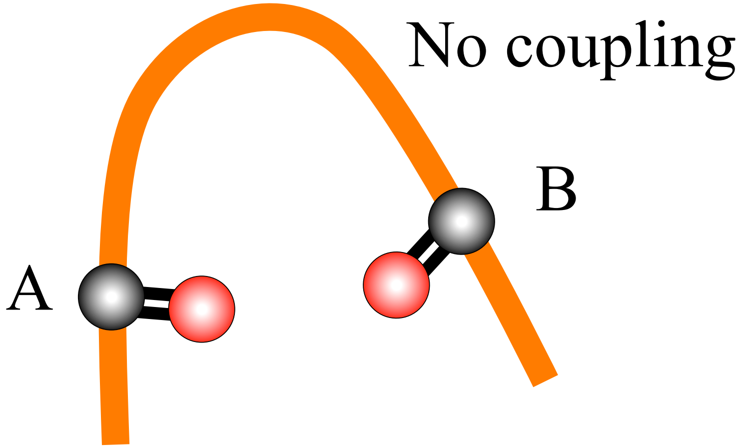


Absorption spectrum

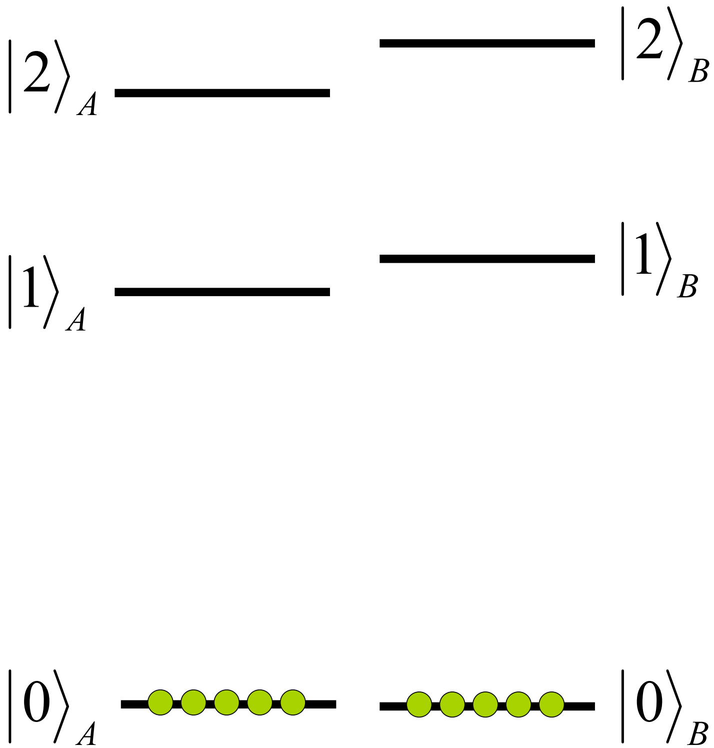


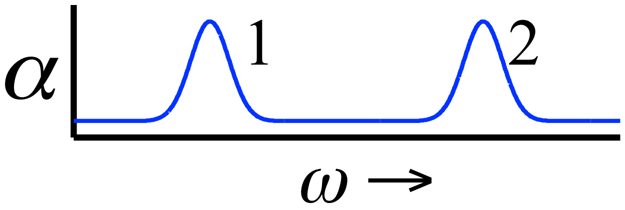
Pump-probe spectrum

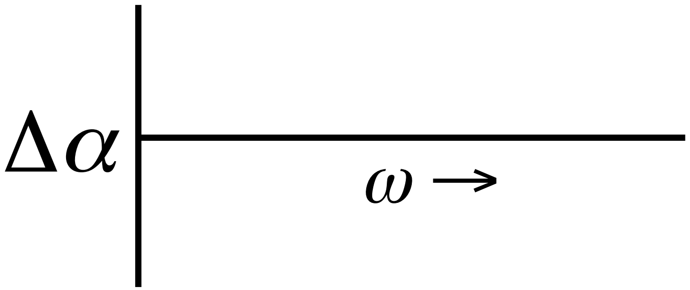
How do we describe a cross peak?



Energy levels







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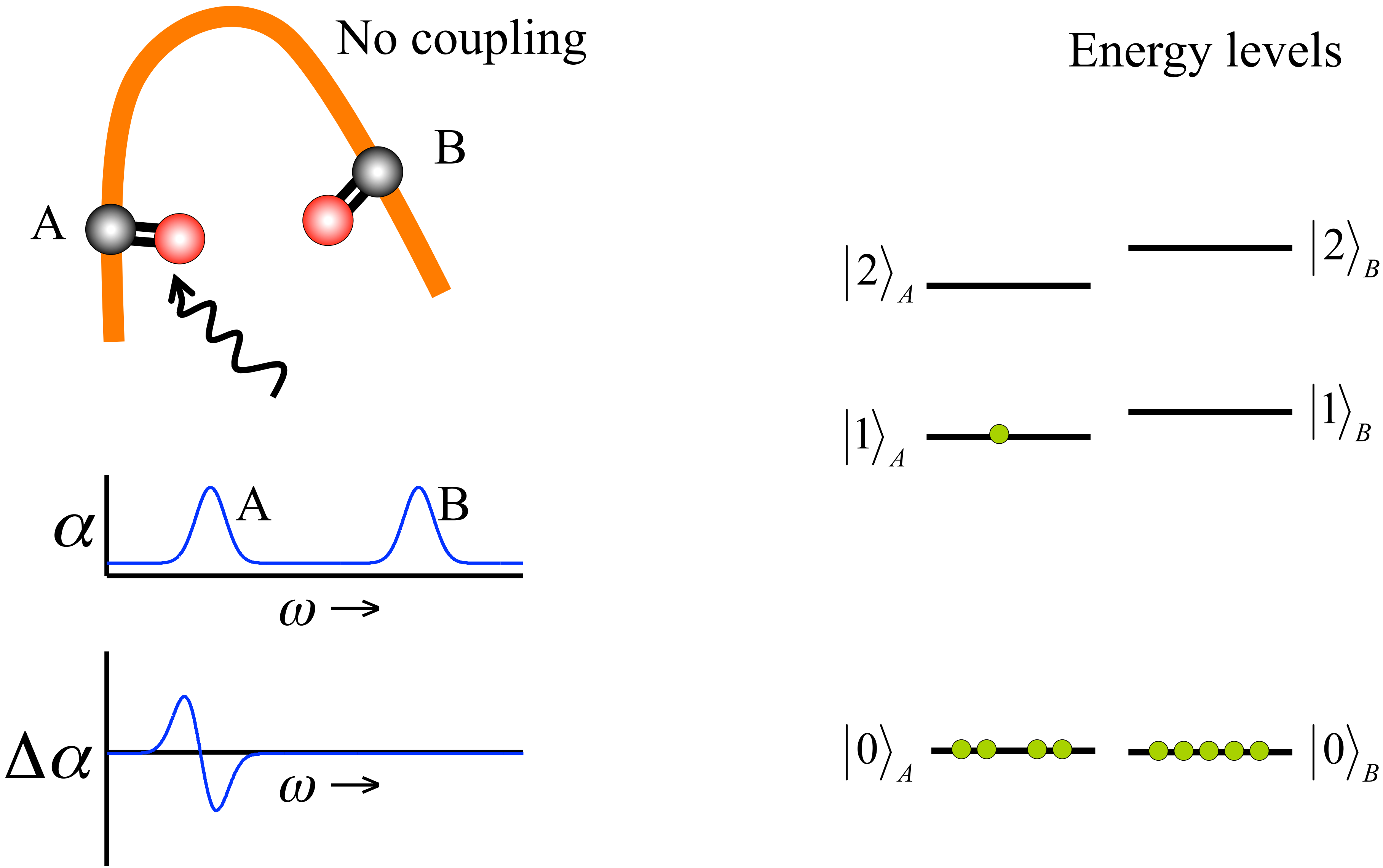

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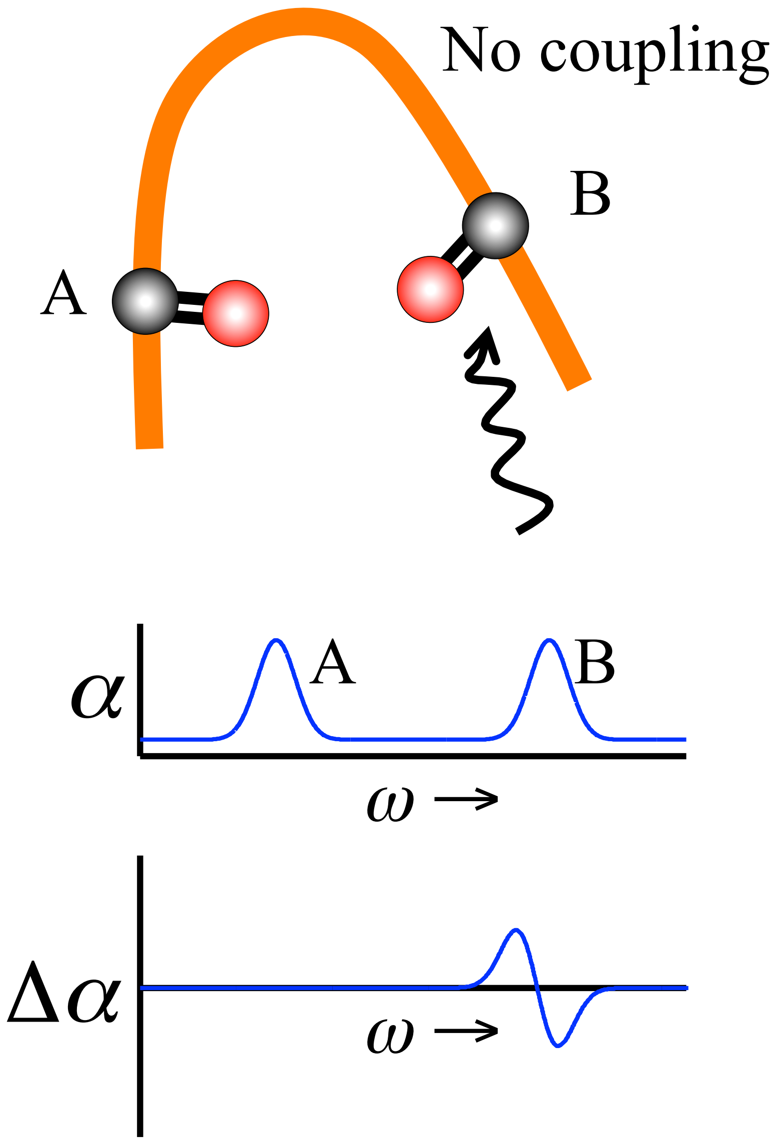
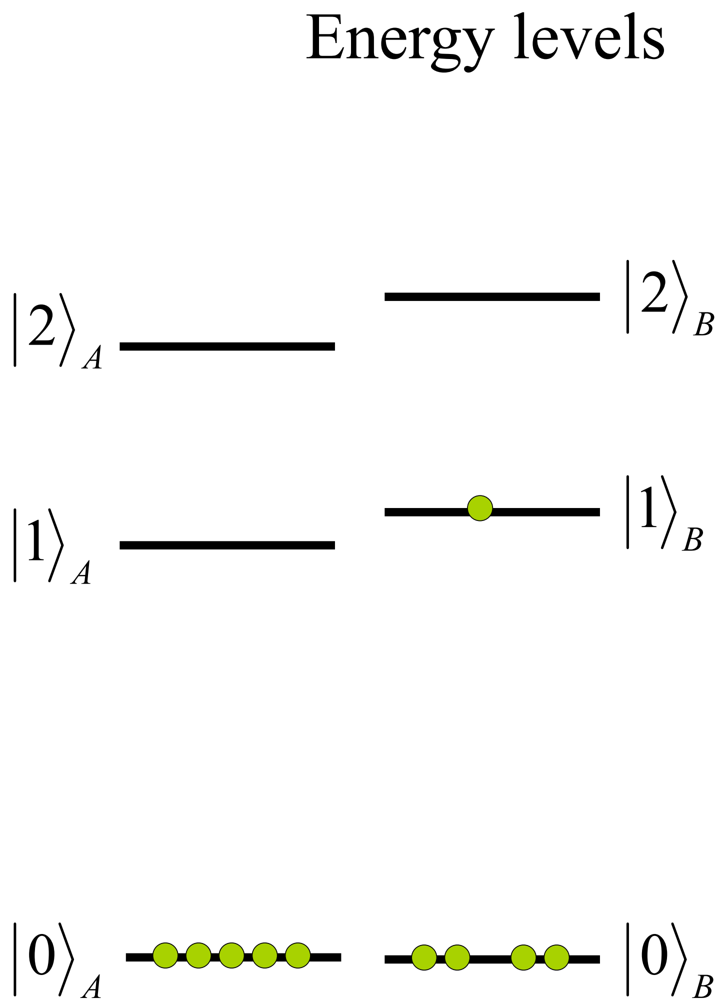
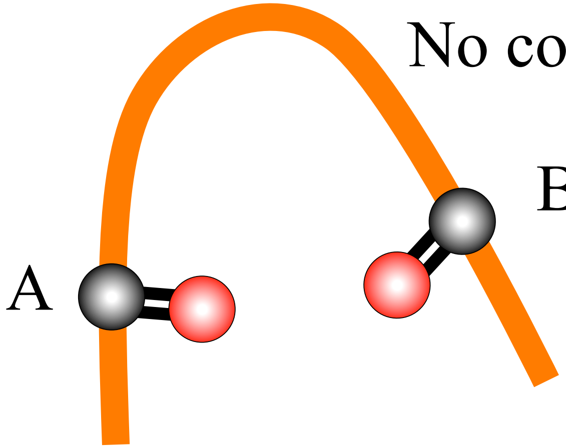
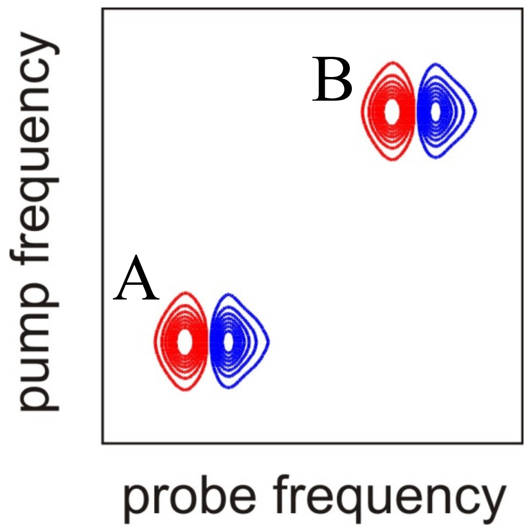


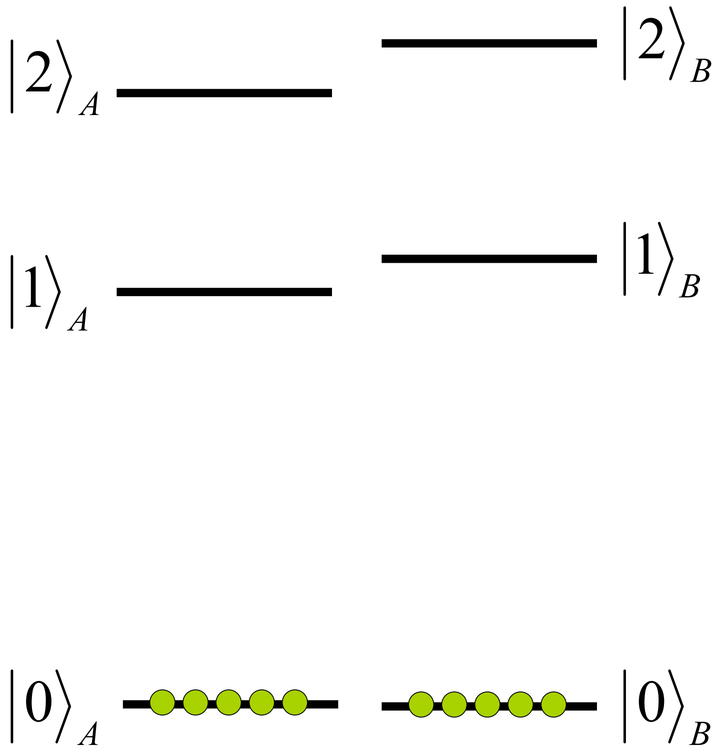


How do we describe a cross peak?

No coupling







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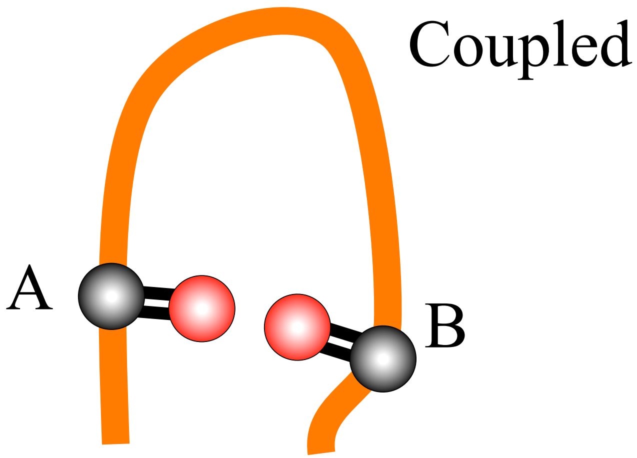

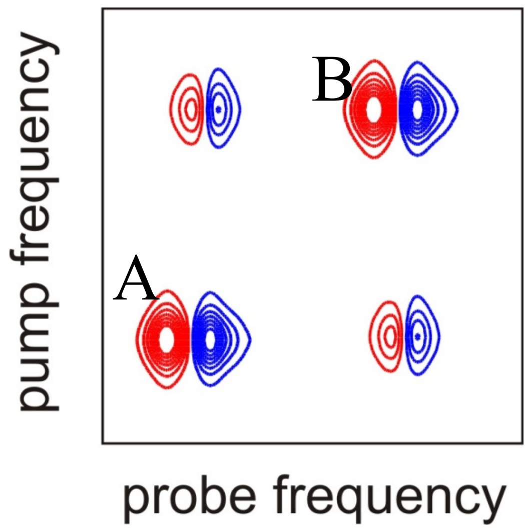

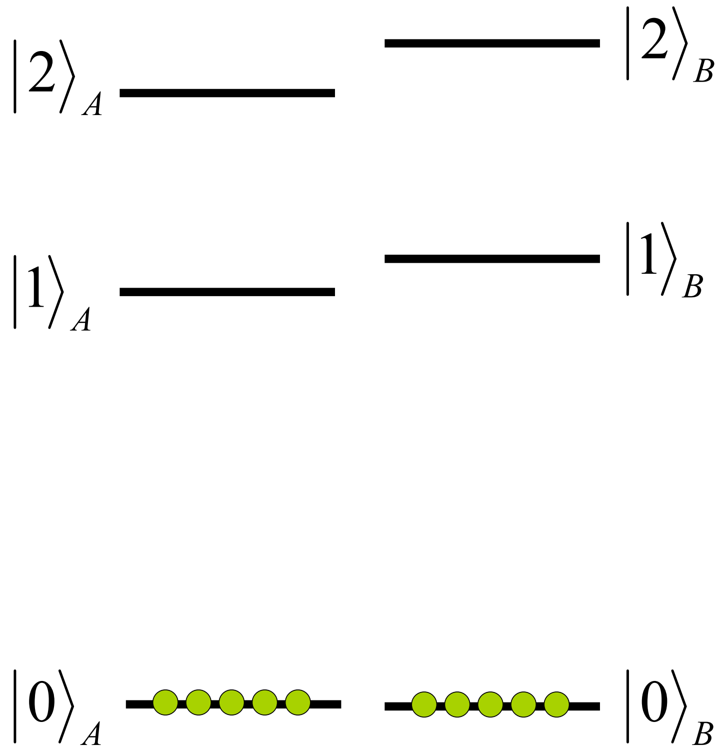

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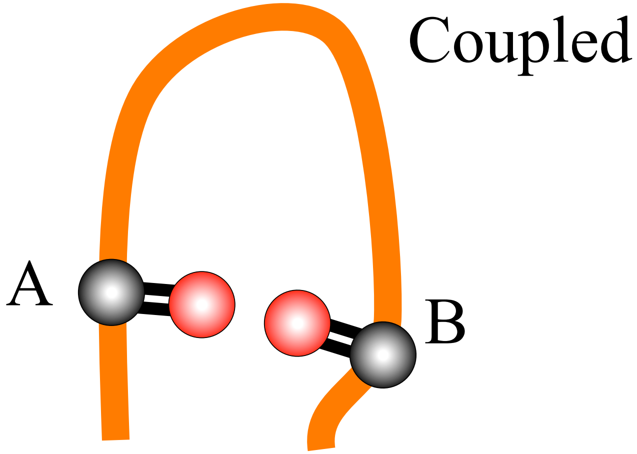

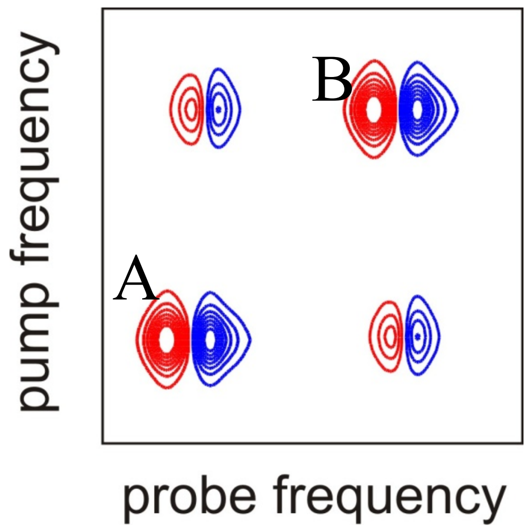

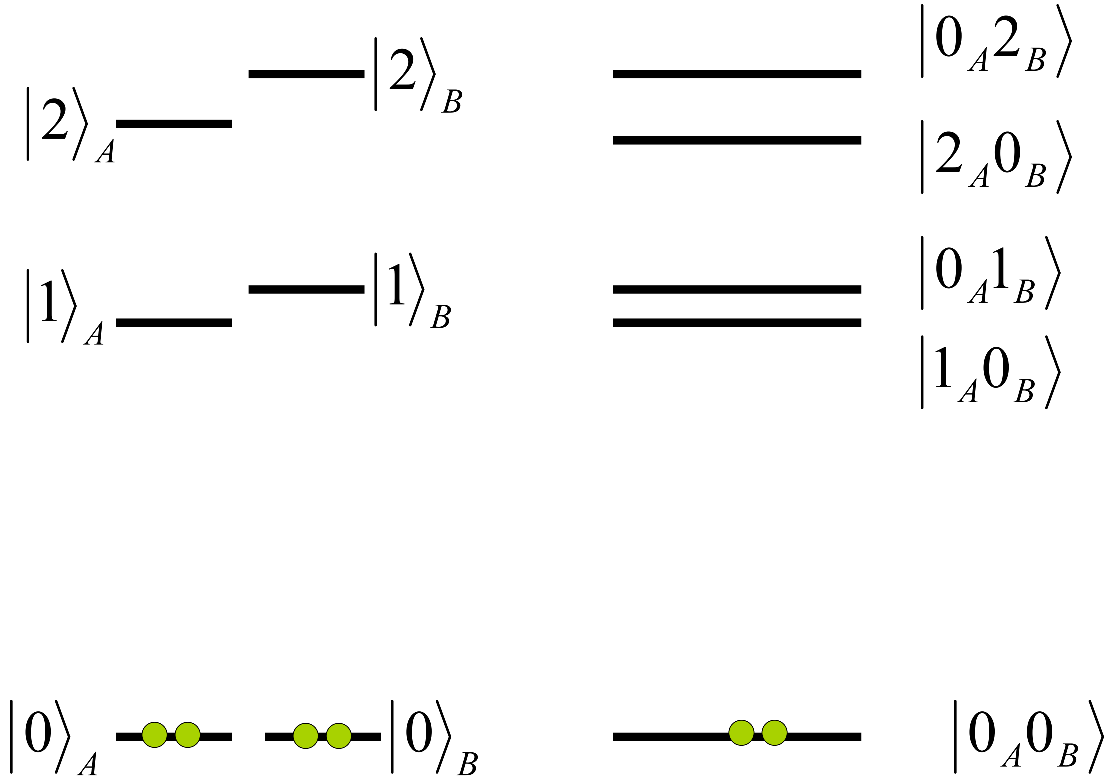

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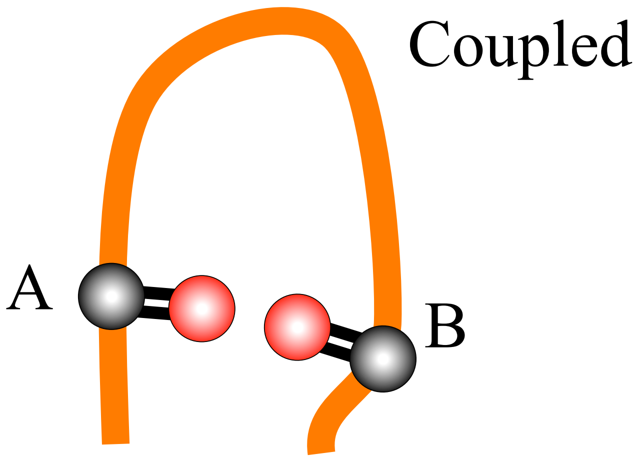

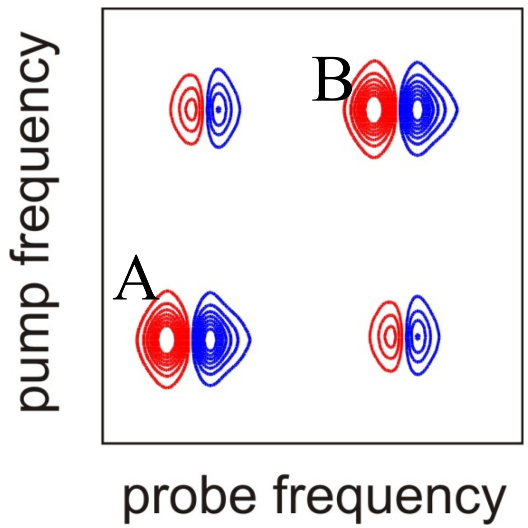

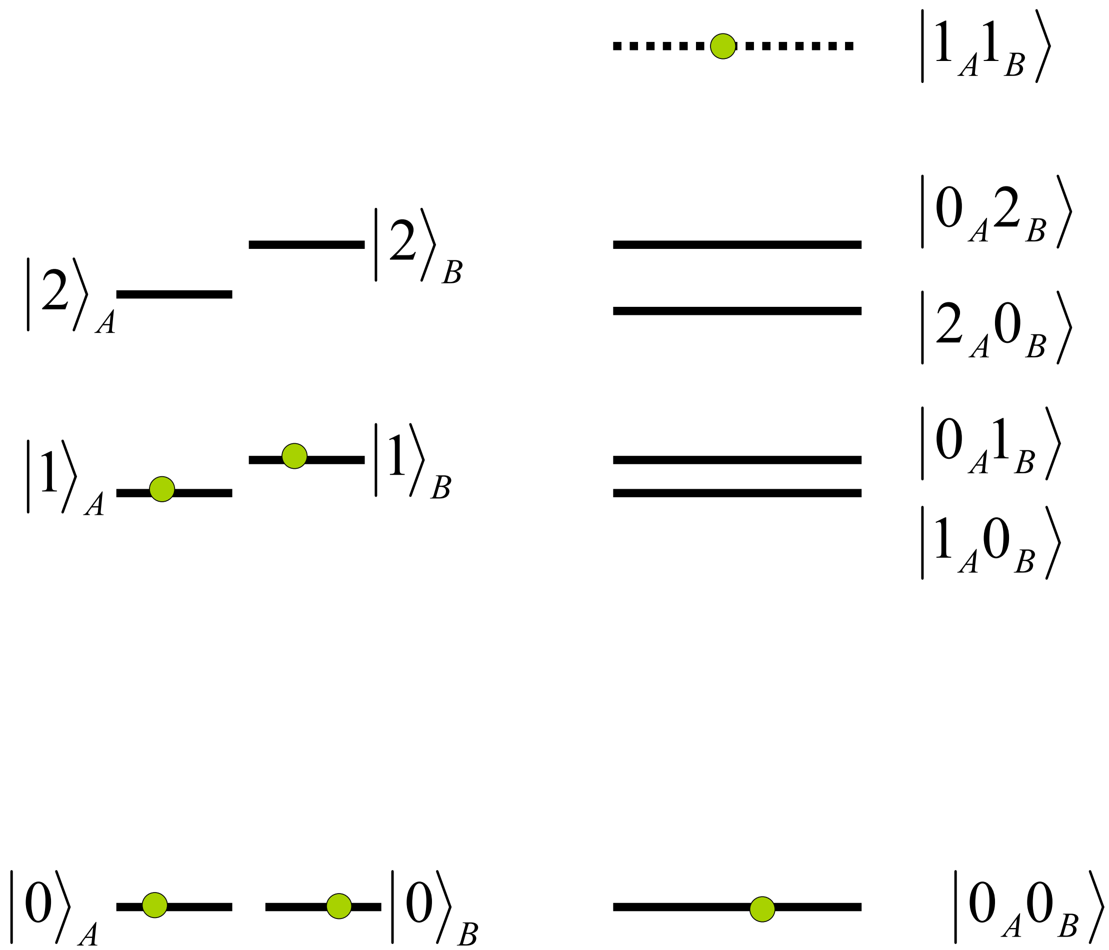

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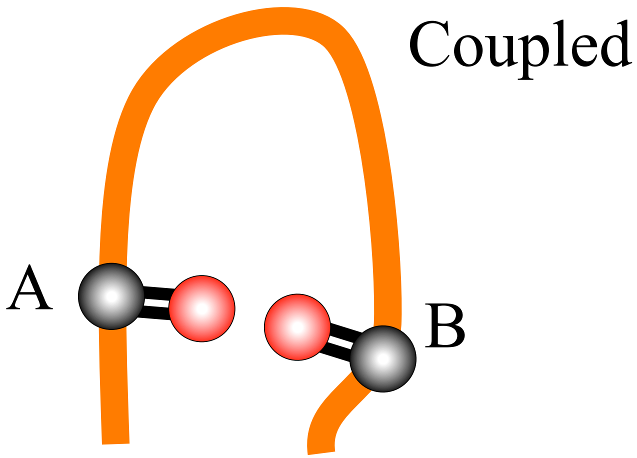

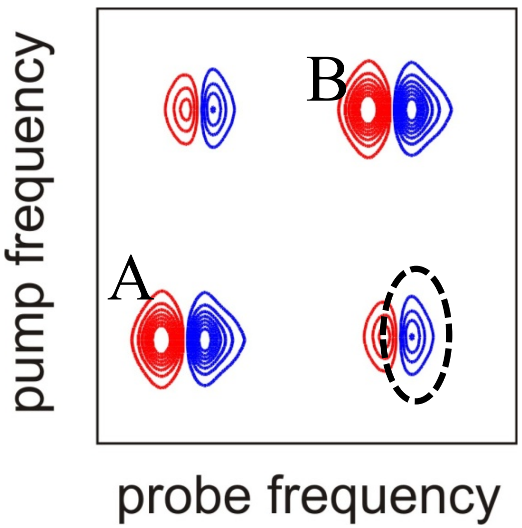

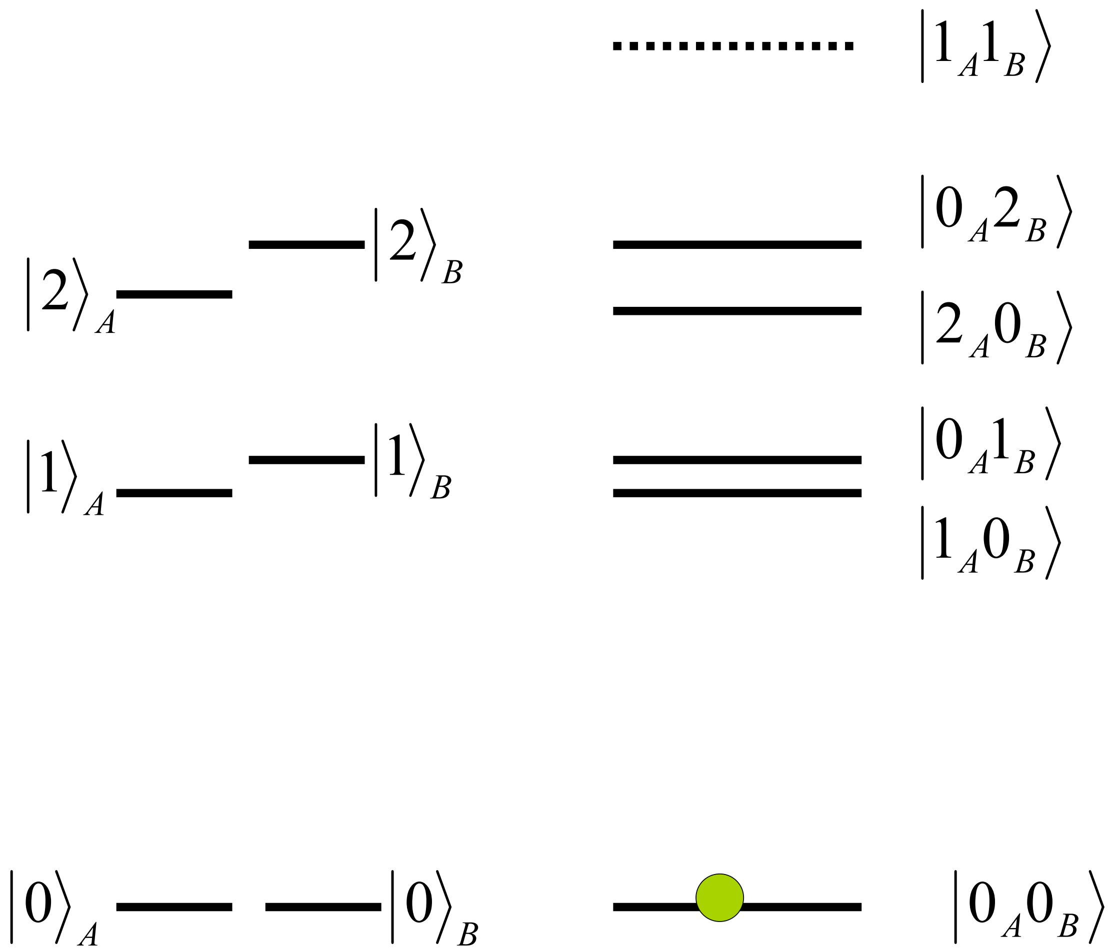

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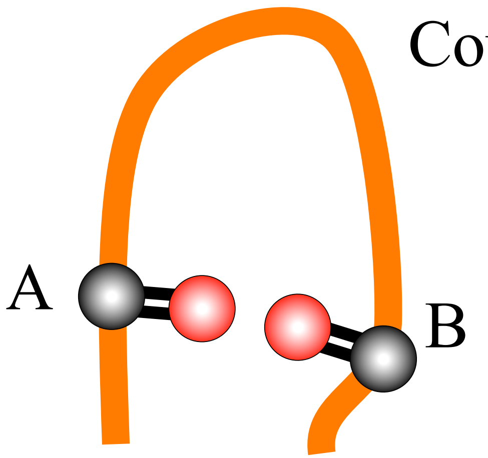
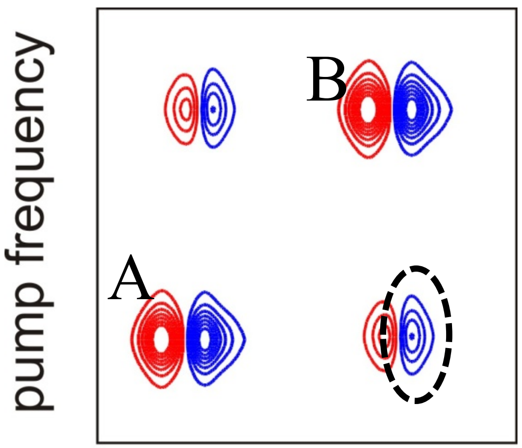
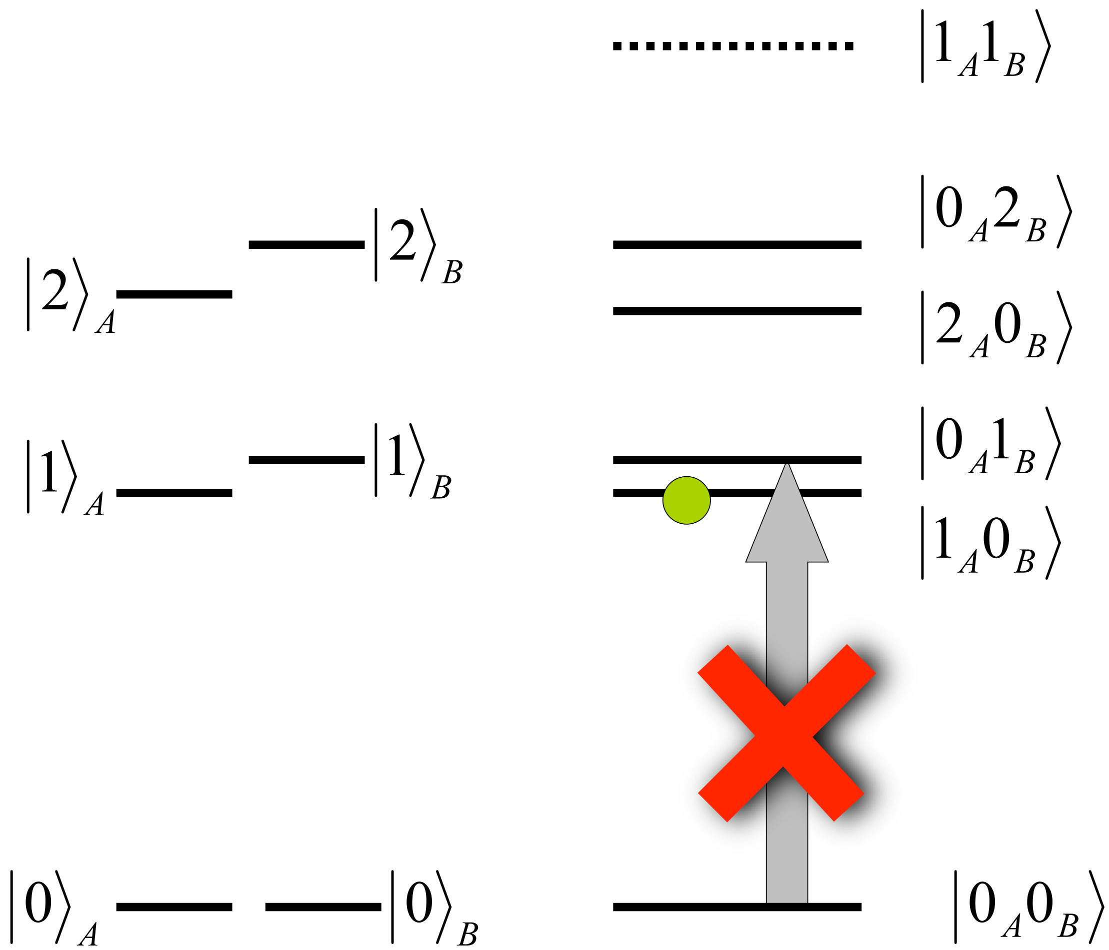
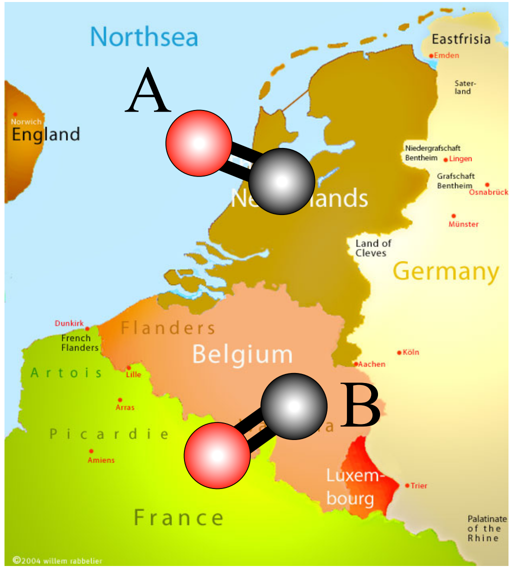


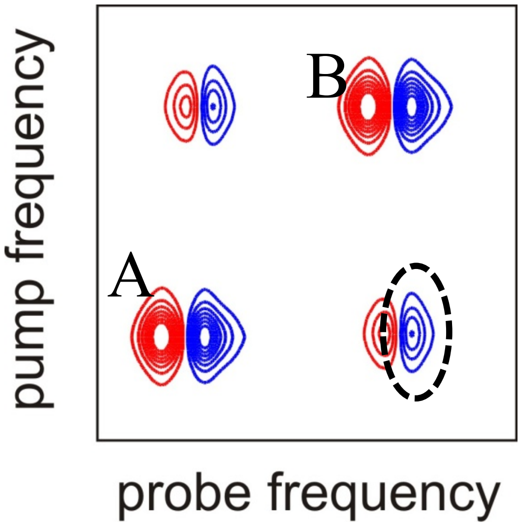




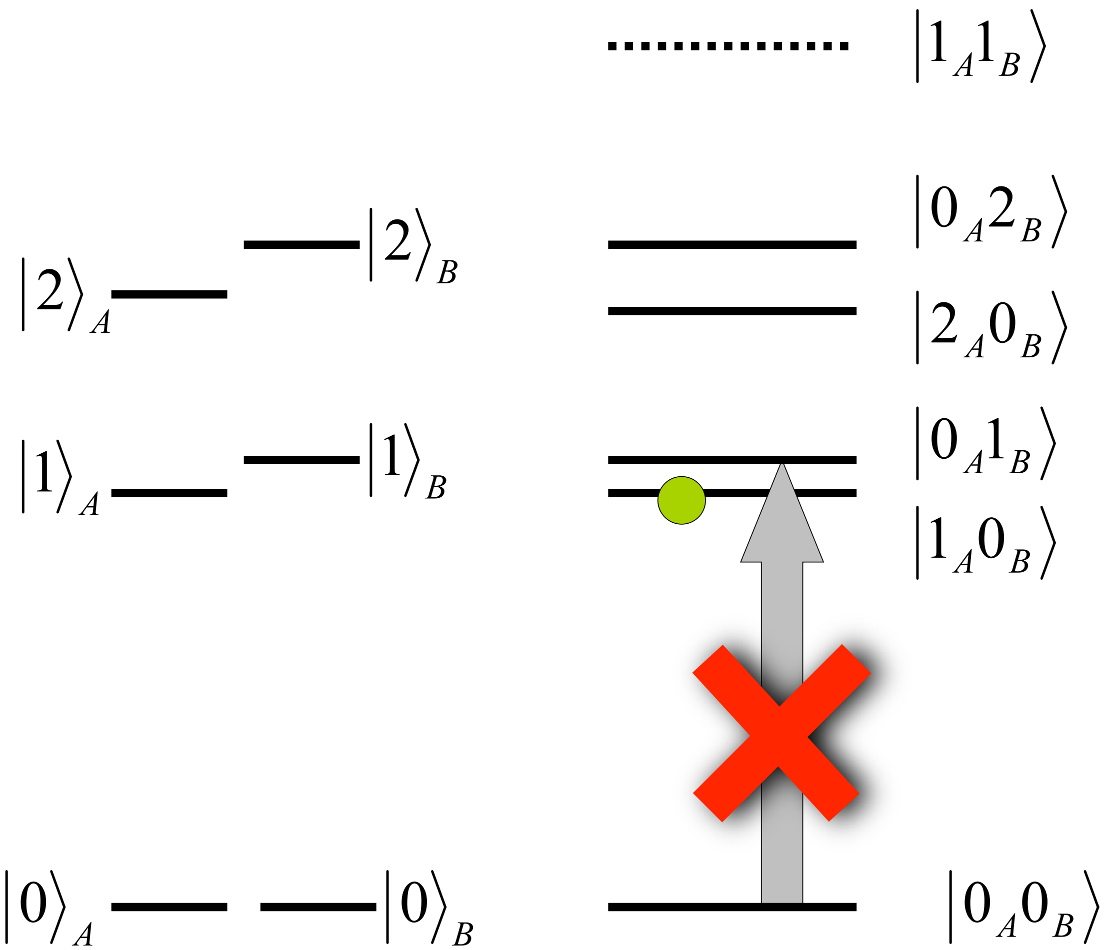
Hmmmm?!



Northsea
Eastfrisia
England
A
Germany
Flanders
Belgium
Artois
Picardie
B
Luxem-
bourg
France



B
A
pump frequency
probe frequency



$|2\rangle_A$
$|2\rangle_B$
$|1\rangle_A$
$|1\rangle_B$
$|0\rangle_A$
$|0\rangle_B$
$|1_A 1_B\rangle$
$|0_A 2_B\rangle$
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$|0_A 1_B\rangle$
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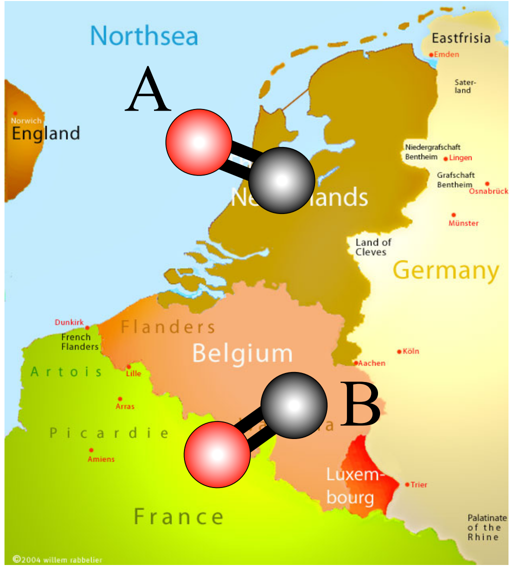
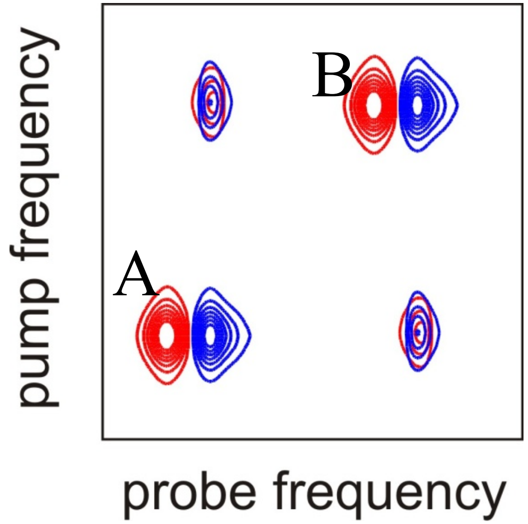
$|0_A 0_B\rangle$

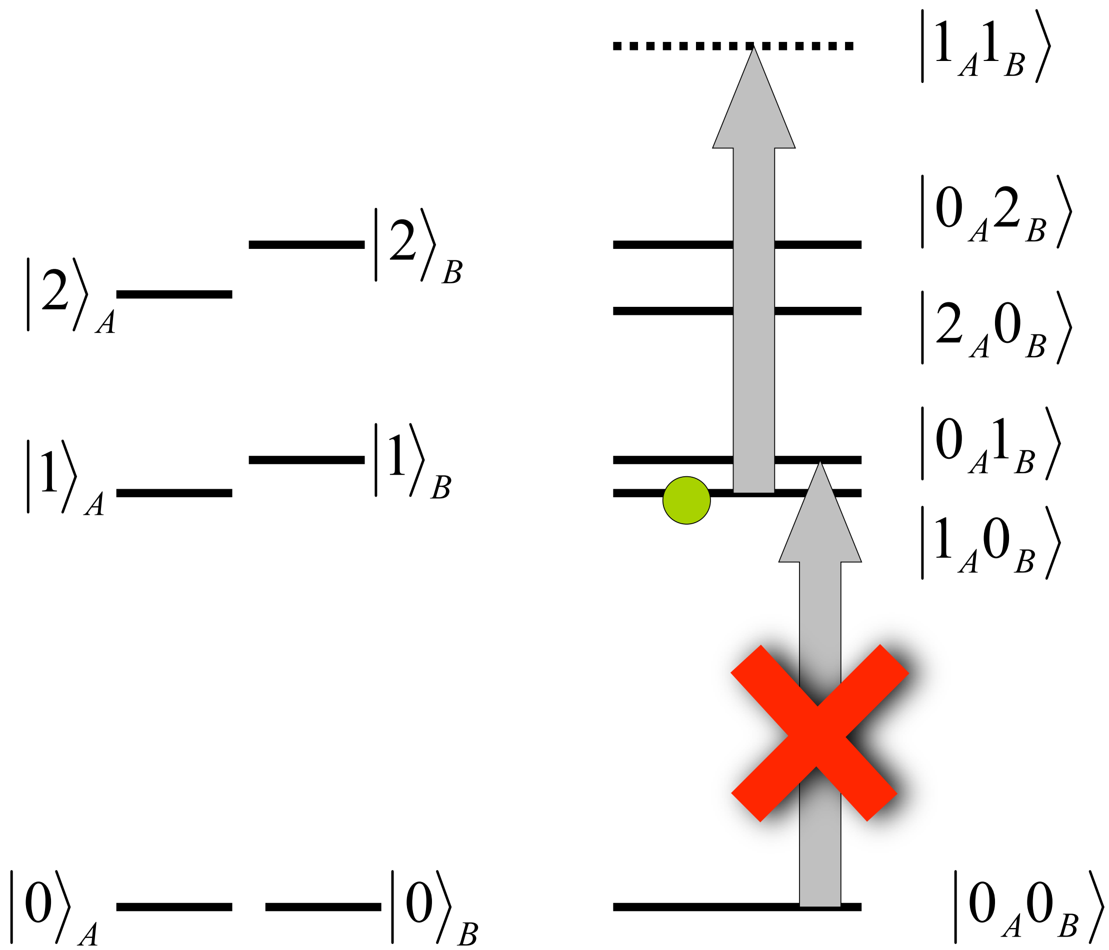
Hmmmm?!



Northsea
Eastfrisia
Emden
Sater-land
A
Norwich
England
Niedergrafschaft Bentheim
Lingen
Grafschaft Bentheim
Osnabrück
Münster
Land of Cleves
Germany
Dunkirk
French Flanders
Flanders
Belgium
Köln
Aachen
Artois
Lille
Arras
Picardie
Amiens
B
Luxem-bourg
Trier
France
Palatinate of the Rhine
©2004 willem rabbelier



pump frequency
B
A
probe frequency



$|2\rangle_A$
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$|1\rangle_B$
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$|1_A 1_B\rangle$
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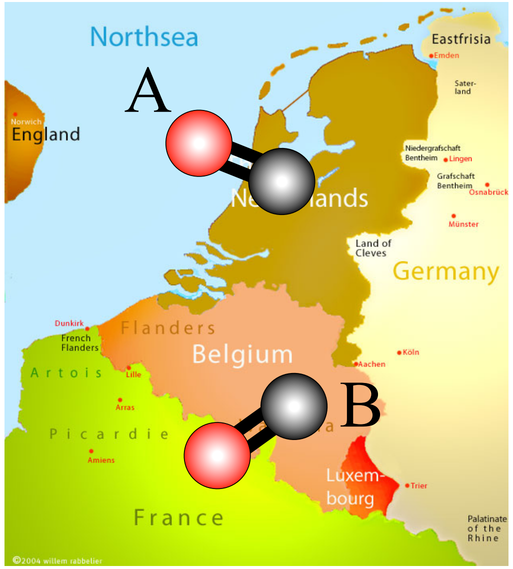
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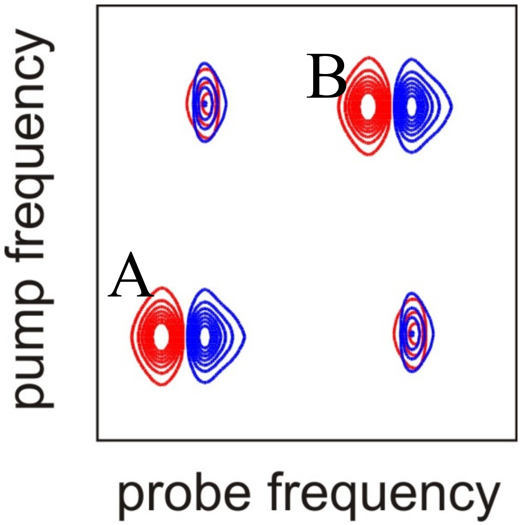
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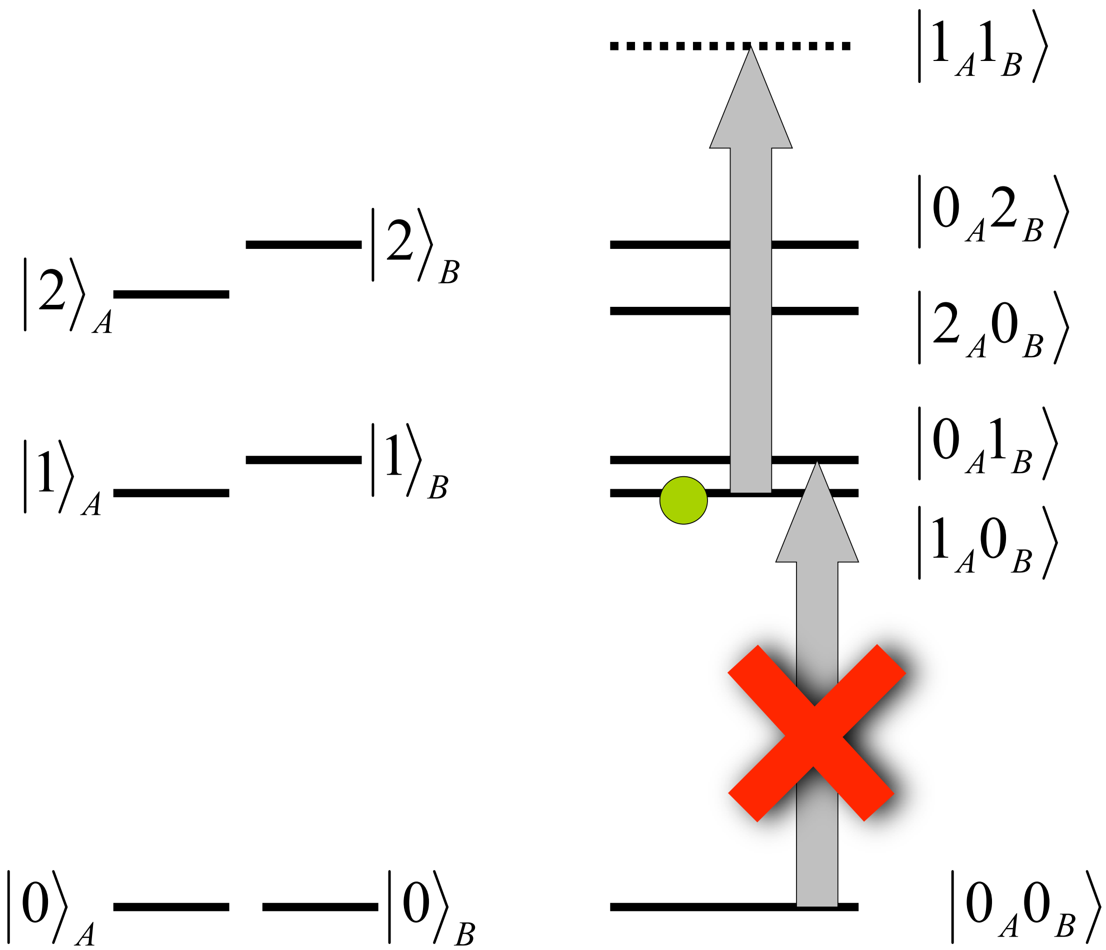
A
pump frequency
probe frequency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$|1\rangle_A$
$|1\rangle_B$
$|0\rangle_A$
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$|1_A 1_B\rangle$
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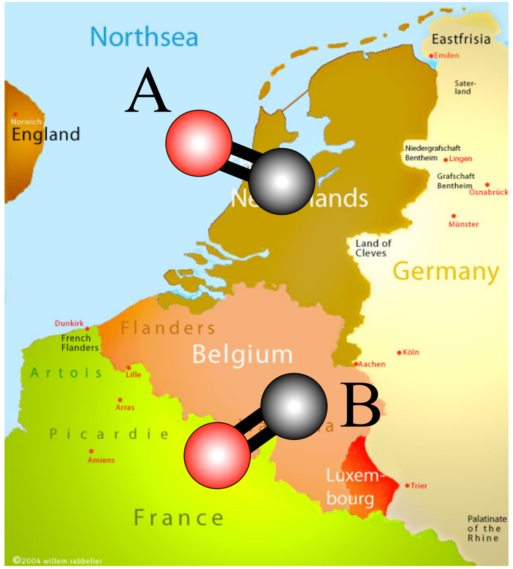

Northsea
Eastfrisia
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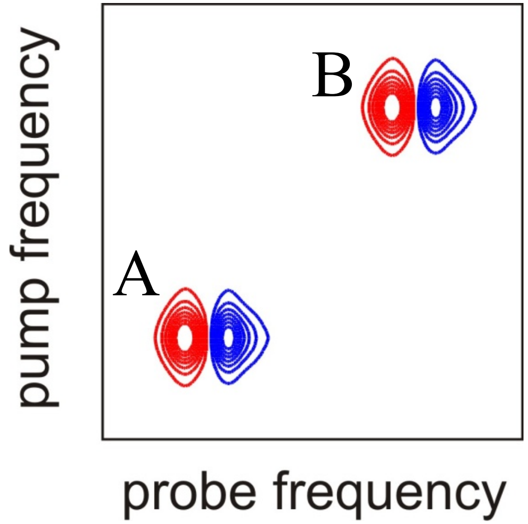
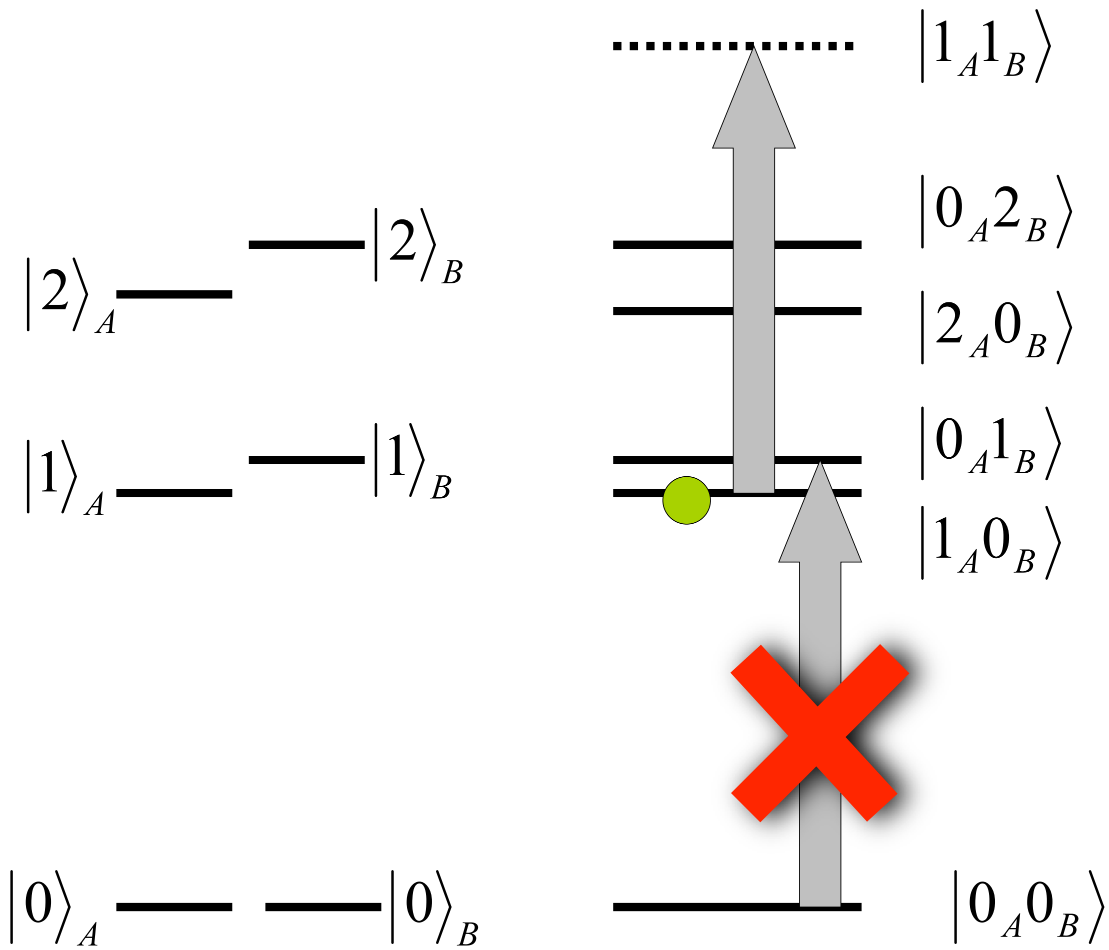


pump frequency
probe frequency
A
B



$|2\rangle_A$
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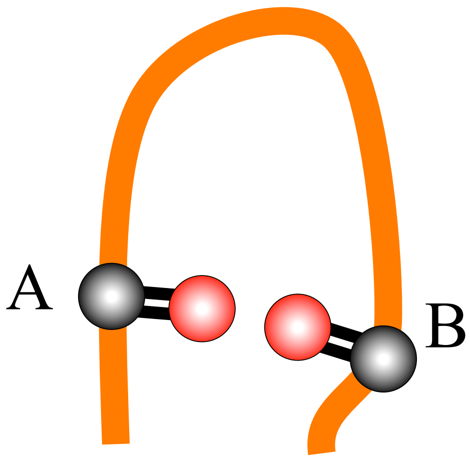
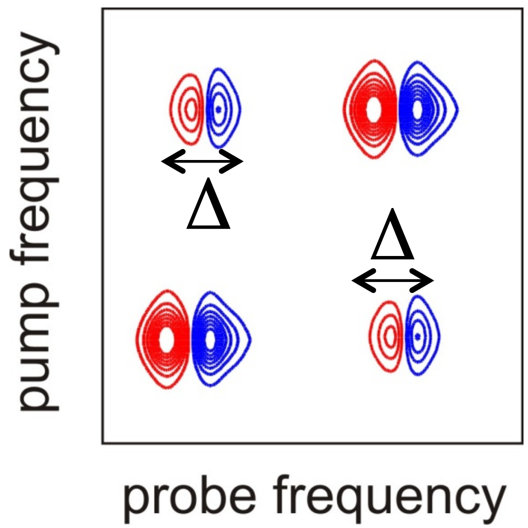
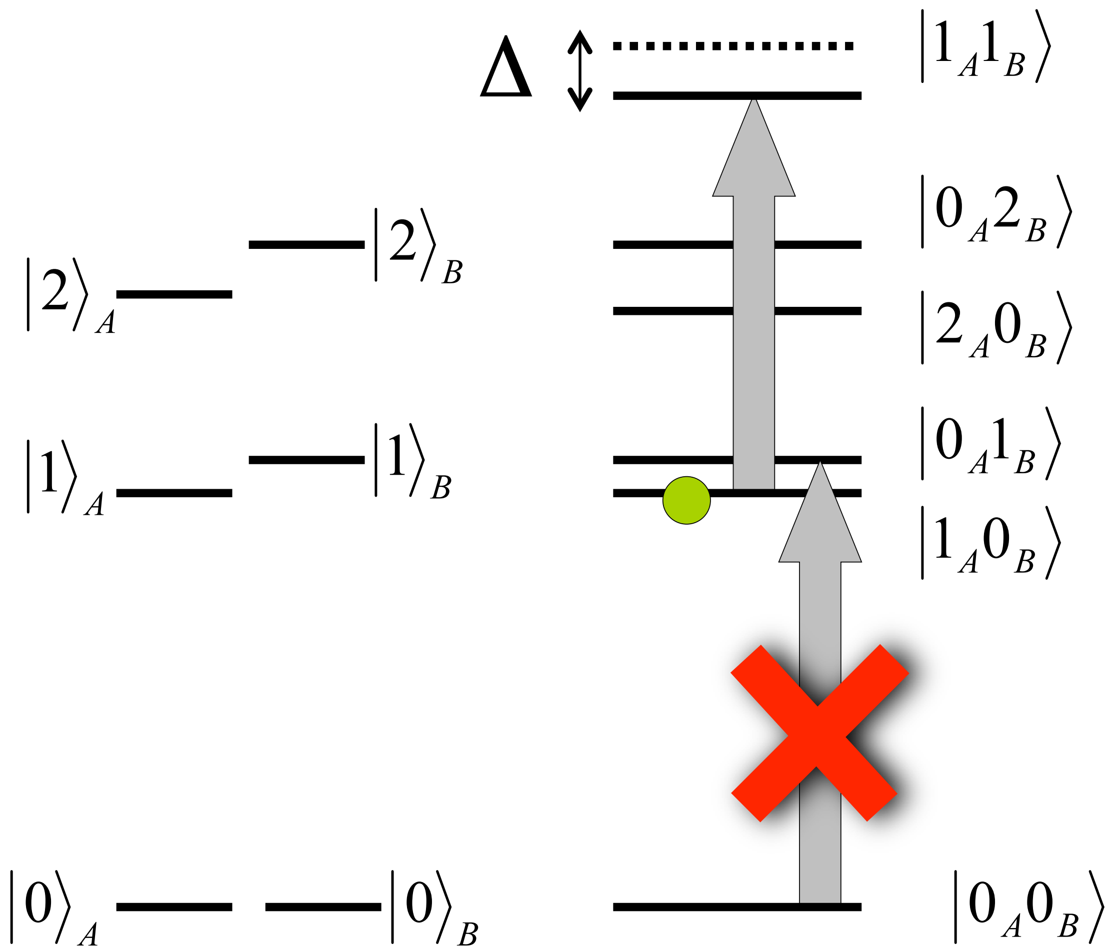
$|1_A 1_B\rangle$
$|0_A 2_B\rangle$
$|2_A 0_B\rangle$
$|0_A 1_B\rangle$
$|1_A 0_B\rangle$
$|0_A 0_B\rangle$

Needed: cross anharmonicity







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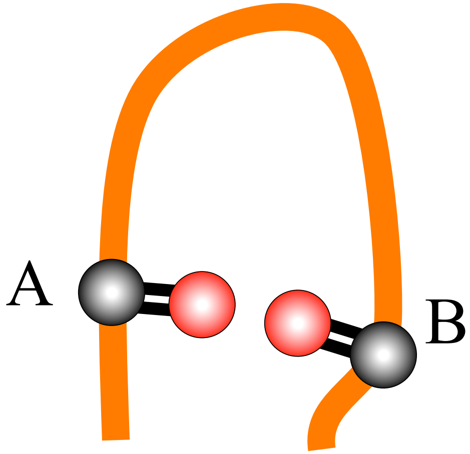
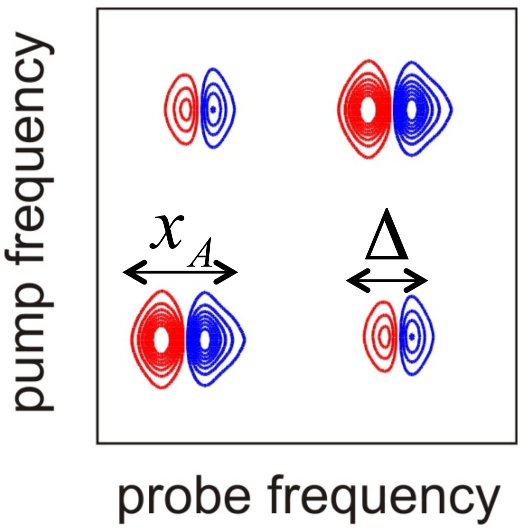
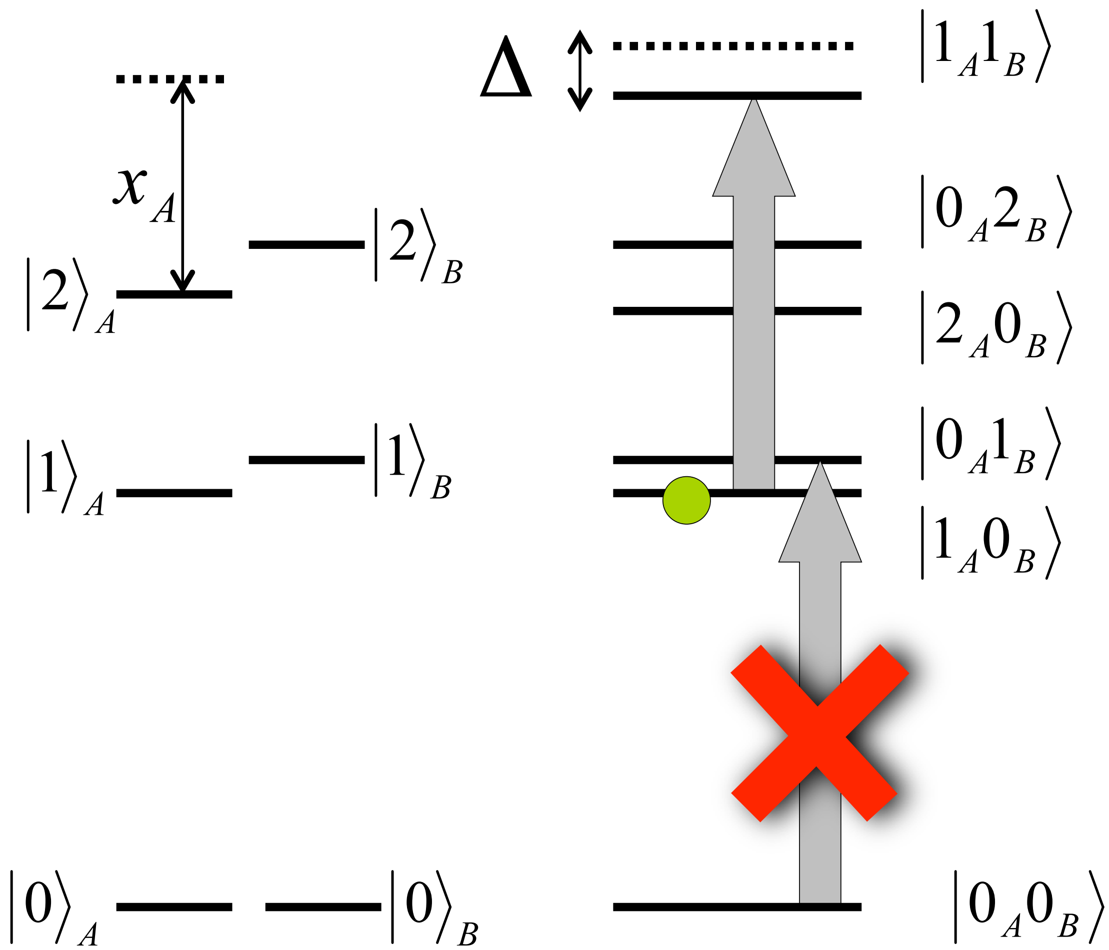
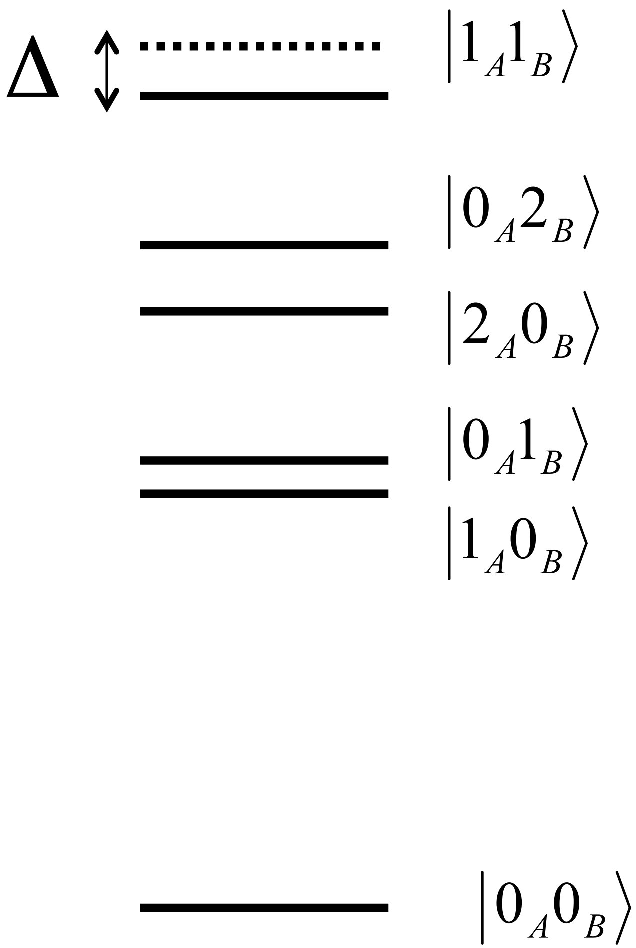






Cross anharmonicity: origin



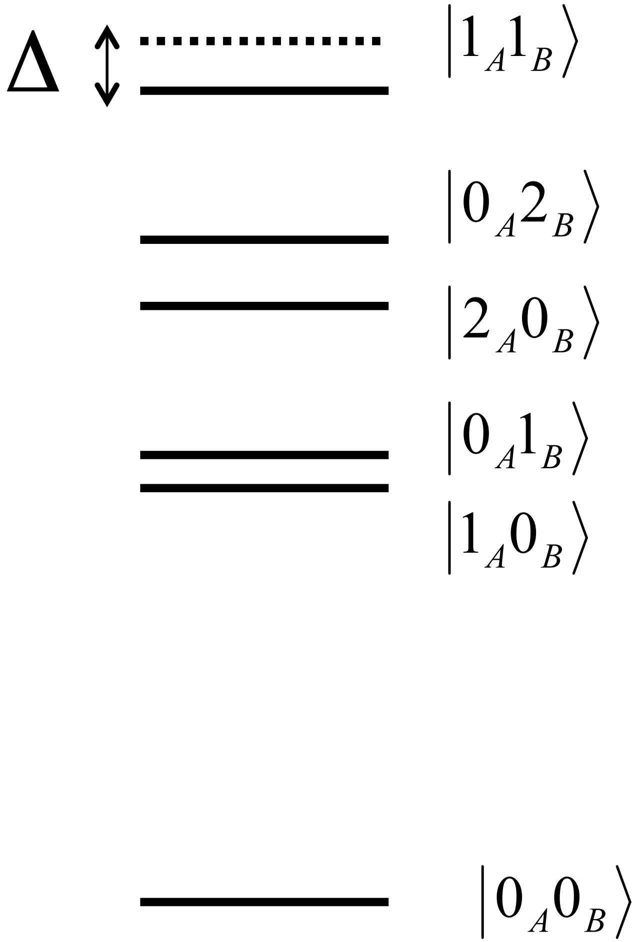
Classical

vibration A affects the frequency of vibration B

Quantum

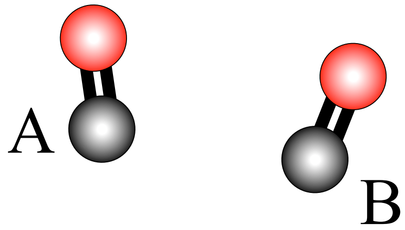
$$E_{11} \neq E_{10} + E_{01}$$

Cross anharmonicity: origin



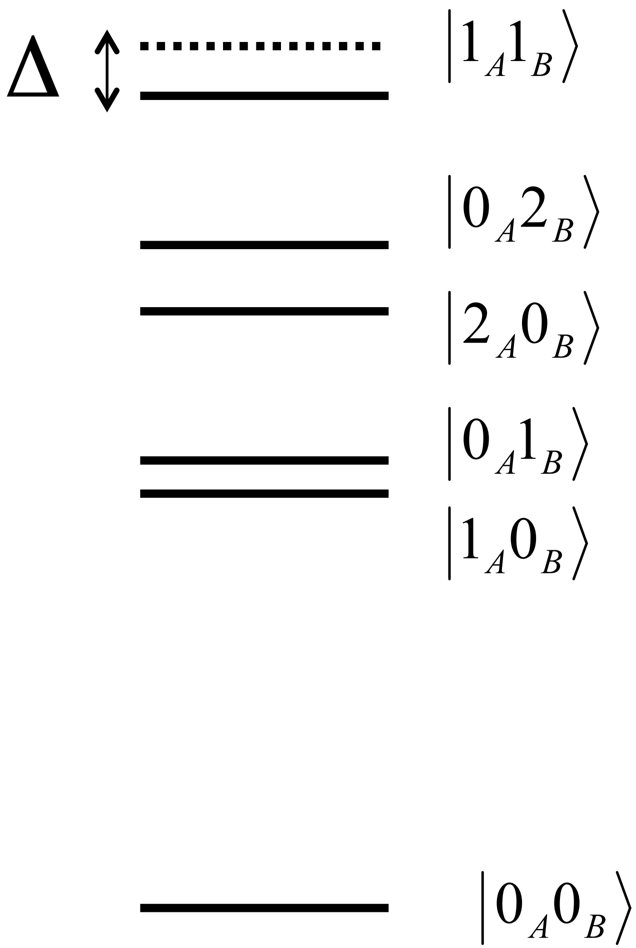
Energy levels we can calculate!

Dipole-dipole interaction



$$V = \frac{1}{4\pi\varepsilon_0}\left[\frac{\vec{\mu}_A \cdot \vec{\mu}_B}{r^3} - 3\frac{(\vec{\mu}_A \cdot \vec{r})(\vec{\mu}_B \cdot \vec{r})}{r^5}\right]$$

Cross anharmonicity: origin



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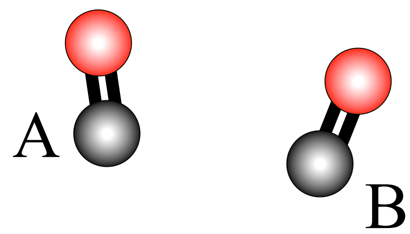


Interaction operator

$$\hat{V}_{AB} = \beta'_{AB}\hat{x}_A\hat{x}_B$$

Perturbative calculation

$$\hat{H} = \hat{H}_0 + \hat{V}$$

$$\hat{H}_0 = \hbar\omega_A\left(\hat{a}_A{}^{\pm}\hat{a}_A + \frac{1}{2}\right) + \hbar\omega_B\left(\hat{a}_B{}^{\pm}\hat{a}_B + \frac{1}{2}\right)$$

$$\hat{V}_{AB} = \beta'_{AB}\hat{x}_A\hat{x}_B$$ perturbation

Leave out constant term in $\hat{H}_0$

Perturbative calculation

$$\hat{H}_0 = \hbar\omega_A \hat{a}_A^{\pm}\hat{a}_A + \hbar\omega_B \hat{a}_B^{\pm}\hat{a}_B$$

$$\hat{V}_{AB} = \beta'_{AB}\hat{x}_A\hat{x}_B$$

$$\hat{V}_{AB} = \beta_{AB}\left(\hat{a}_A^{\pm}\hat{a}_B + \hat{a}_A\hat{a}_B^{\pm} + \underbrace{\hat{a}_A^{\pm}\hat{a}_B^{\pm} + \hat{a}_A\hat{a}_B}_{\substack{\text{Not energy conserving} \\ \to\ \text{ignore}}}\right)$$

Perturbative calculation

$$\hat{H}_0 = \hbar\omega_A \hat{a}_A^{\pm}\hat{a}_A + \hbar\omega_B \hat{a}_B^{\pm}\hat{a}_B \qquad \hat{V}_{AB} = \beta_{AB}\left(\hat{a}_A^{\pm}\hat{a}_B + \hat{a}_A\hat{a}_B^{\pm}\right)$$

$$\begin{array}{cc} \begin{matrix} |00\rangle & |10\rangle & |01\rangle & |02\rangle & |20\rangle & |11\rangle \end{matrix} & \\ \begin{bmatrix} 0 & & & & & \\ & \hbar\omega_A & \beta_{AB} & & & \\ & \beta_{AB} & \hbar\omega_B & & & \\ & & & 2\hbar\omega_A & 0 & \sqrt{2}\beta_{AB} \\ & & & 0 & 2\hbar\omega_B & \sqrt{2}\beta_{AB} \\ & & & \sqrt{2}\beta_{AB} & \sqrt{2}\beta_{AB} & \hbar(\omega_A + \omega_B) \end{bmatrix} & \begin{matrix} |00\rangle \\ |10\rangle \\ |01\rangle \\ |20\rangle \\ |02\rangle \\ |11\rangle \end{matrix} \end{array}$$

Formulas from perturbation theory

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \ldots$$

$$\hat{H} = \hat{H}_0 + \hat{V}$$

$$E_n^{(1)} = \langle n | \hat{V} | n \rangle$$

$$E_n^{(2)} = \sum_{k \neq n} \frac{\left| \langle k | \hat{V} | n \rangle \right|^2}{E_n^{(0)} - E_k^{(0)}}$$

E.g. Bransden And Joachain, ***Introduction to Quantum Mechanics***

Perturbative calculation

$$E_n^{(1)} = \langle n|\hat{V}|n\rangle$$

$$E_n^{(2)} = \sum_{k\neq n} \frac{\left|\langle k|\hat{V}|n\rangle\right|^2}{E_n^{(0)} - E_k^{(0)}}$$

$$\begin{array}{c}
\left[\begin{array}{c|cc|ccc}
0 & & & & & \\
\hline
 & \hbar\omega_A & \beta_{AB} & & & \\
 & \beta_{AB} & \hbar\omega_B & & & \\
\hline
 & & & 2\hbar\omega_A & 0 & \sqrt{2}\beta_{AB} \\
 & & & 0 & 2\hbar\omega_B & \sqrt{2}\beta_{AB} \\
 & & & \sqrt{2}\beta_{AB} & \sqrt{2}\beta_{AB} & \hbar(\omega_A + \omega_B)
\end{array}\right]
\end{array}
\begin{array}{l}
|00\rangle \\ |10\rangle \\ |01\rangle \\ |20\rangle \\ |02\rangle \\ |11\rangle
\end{array}$$

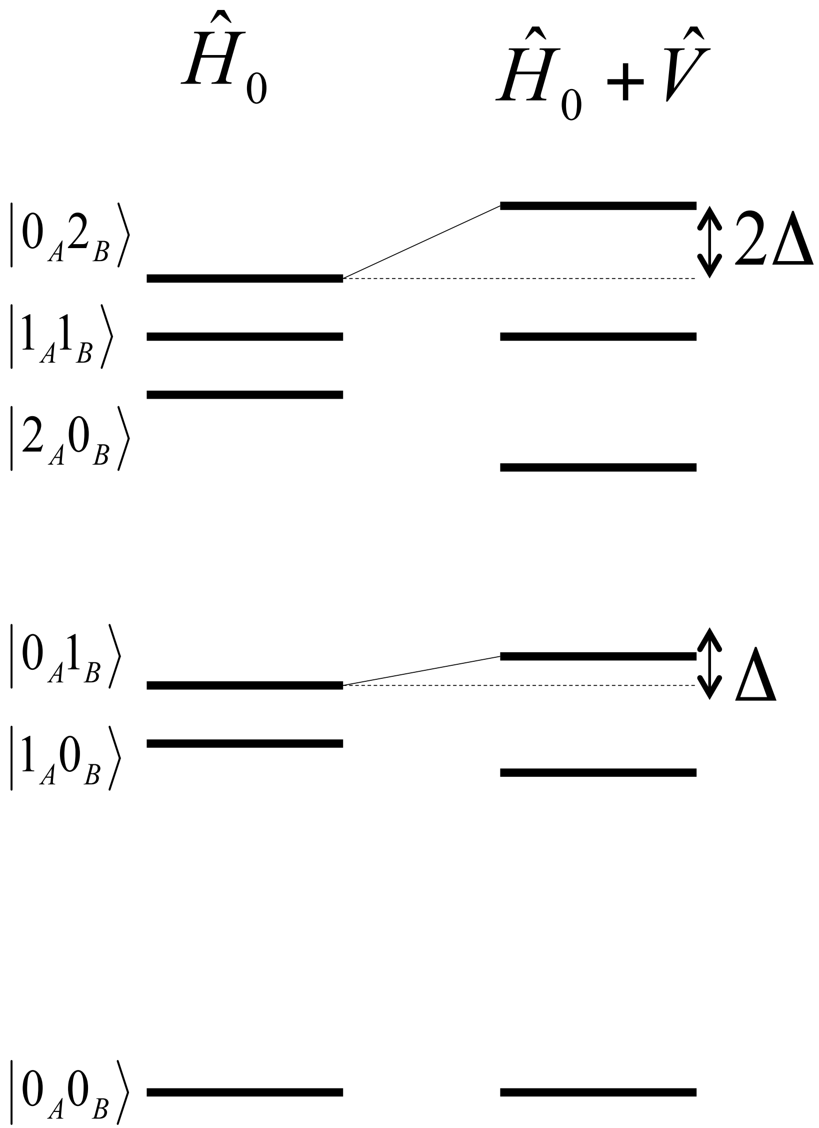
Perturbative calculation

$$E_n^{(2)} = \sum_{k \neq n} \frac{\left| \left\langle k \middle| \hat{V} \middle| n \right\rangle \right|^2}{E_n^{(0)} - E_k^{(0)}}$$

$$\hbar\omega_A - \frac{\beta_{AB}^2}{\hbar\omega_B - \hbar\omega_A} \qquad \hbar\omega_B + \frac{\beta_{AB}^2}{\hbar\omega_B - \hbar\omega_A}$$

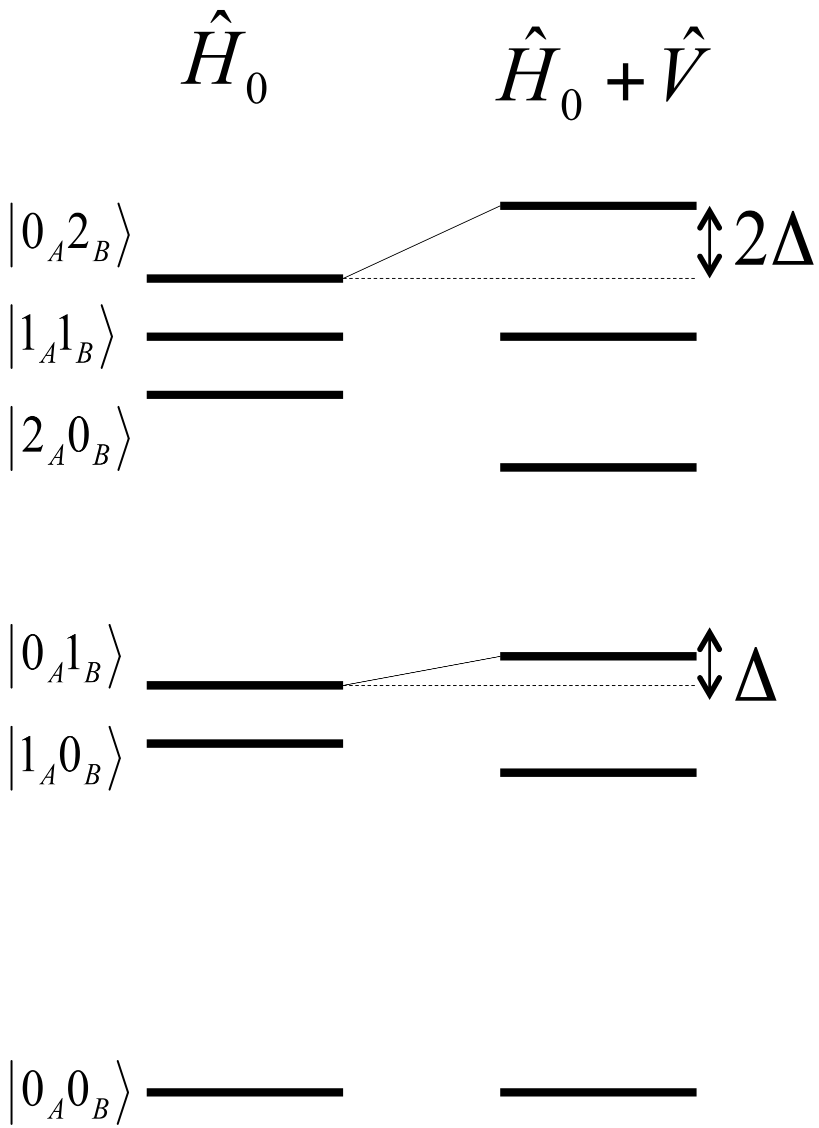
$$\left[\begin{array}{c|cc|ccc}
0 & & & & & \\
\hline
 & \hbar\omega_A & \beta_{AB} & & & \\
 & \beta_{AB} & \hbar\omega_B & & & \\
\hline
 & & & 2\hbar\omega_A & 0 & \sqrt{2}\beta_{AB} \\
 & & & 0 & 2\hbar\omega_B & \sqrt{2}\beta_{AB} \\
 & & & \sqrt{2}\beta_{AB} & \sqrt{2}\beta_{AB} & \hbar(\omega_A + \omega_B)
\end{array}\right]
\begin{array}{c}
|00\rangle \\
|10\rangle \\
|01\rangle \\
|20\rangle \\
|02\rangle \\
|11\rangle
\end{array}$$

Effect of coupling



$$\Delta = \frac{\beta_{AB}^2}{\hbar\omega_B - \hbar\omega_A}$$

Effect of coupling



$$\Delta = \frac{\beta_{AB}^2}{\hbar\omega_B - \hbar\omega_A}$$

•The new modes remain harmonic

$$E_{20} = 2E_{10}$$

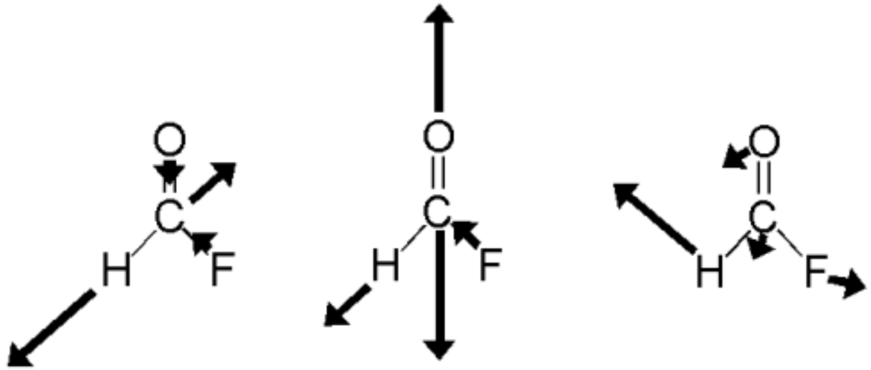
•There is no cross-anharmonicity

$$E_{11} \neq E_{10} + E_{01}$$

•No 2DIR spectrum

Summary normal modes

•A molecule has 3N-6 normal modes



•The normal modes can be obtained by solving the classical equations of motion → independent solutions

Adding anharmonicity

$$\hat{H}_0 = \hbar\omega_A \hat{a}_A^{\pm}\hat{a}_A + \hbar\omega_B \hat{a}_B^{\pm}\hat{a}_B \qquad \hat{V}_{AB} = \beta_{AB}\left(\hat{a}_A^{\pm}\hat{a}_B + \hat{a}_A\hat{a}_B^{\pm}\right)$$

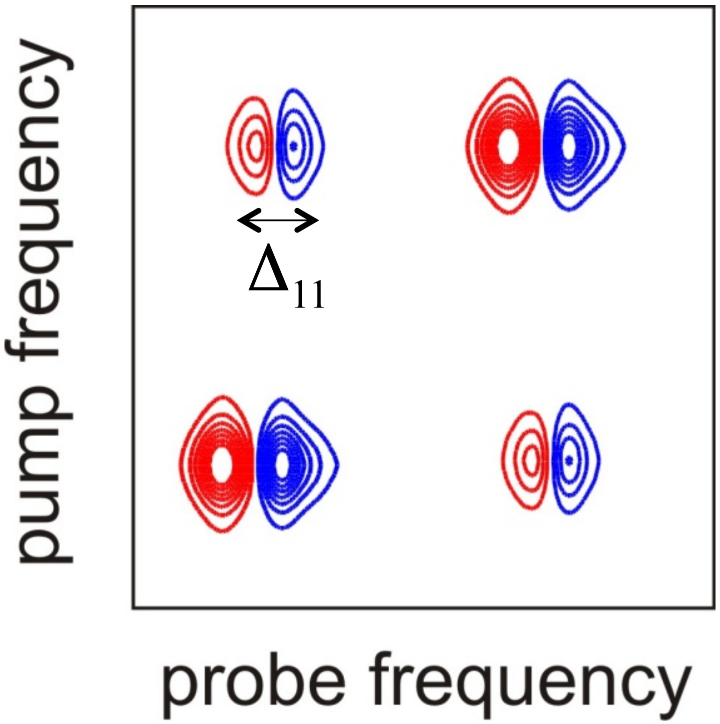
$$\hat{V}_{anh} = -\frac{\Delta}{2}\left(\hat{a}_A^{\pm}\hat{a}_A^{\pm}\hat{a}_A\hat{a}_A + \hat{a}_B^{\pm}\hat{a}_B^{\pm}\hat{a}_B\hat{a}_B\right)$$

$$\begin{array}{cc}
\left[\begin{array}{c|cc|ccc}
0 & & & & & \\
\hline
 & \hbar\omega_A & \beta_{AB} & & & \\
 & \beta_{AB} & \hbar\omega_B & & & \\
\hline
 & & & 2\hbar\omega_A - \Delta & 0 & \sqrt{2}\beta_{AB} \\
 & & & 0 & 2\hbar\omega_B - \Delta & \sqrt{2}\beta_{AB} \\
 & & & \sqrt{2}\beta_{AB} & \sqrt{2}\beta_{AB} & \hbar\left(\omega_A + \omega_B\right)
\end{array}\right]
&
\begin{array}{c}
|00\rangle \\
|10\rangle \\
|01\rangle \\
|20\rangle \\
|02\rangle \\
|11\rangle
\end{array}
\end{array}$$

Adding anharmonicity

$$E_{11} = \hbar(\omega_A + \omega_B) - \Delta_{11}$$

$$\Delta_{11} = -4\Delta \frac{\beta_{AB}^2}{(\hbar\omega_B - \hbar\omega_A)^2 - \Delta^2}$$



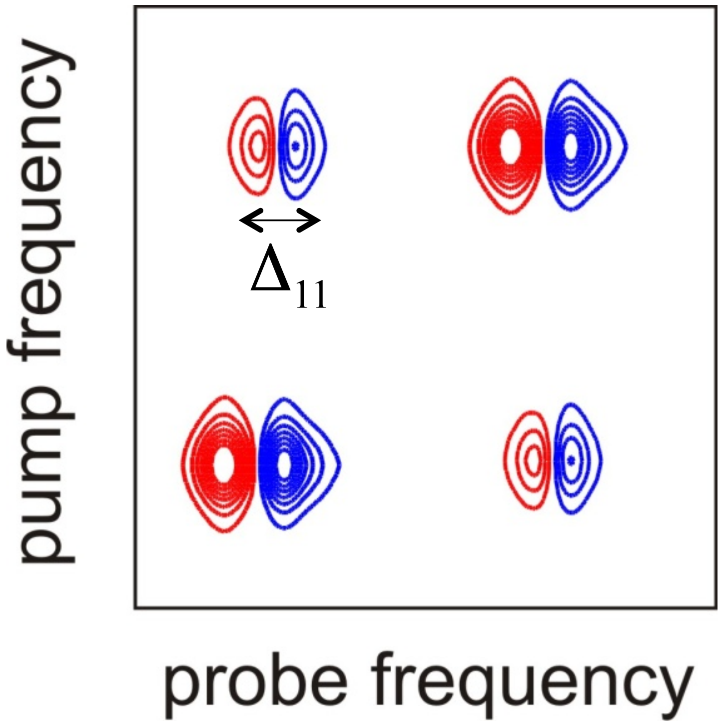
Remember:

$$V = \frac{1}{4\pi\varepsilon_0}\left[\frac{\vec{\mu}_A \cdot \vec{\mu}_B}{r^3} - 3\frac{(\vec{\mu}_A \cdot \vec{r})(\vec{\mu}_B \cdot \vec{r})}{r^5}\right]$$

Adding anharmonicity

$$E_{11} = \hbar(\omega_A + \omega_B) - \Delta_{11}$$

$$\Delta_{11} = 4\Delta \frac{\beta_{AB}^2}{(\hbar\omega_B - \hbar\omega_A)^2 - \Delta^2}$$



Remember:

$$\hat{V}_{AB} = \beta_{AB}\hat{x}_A\hat{x}_B$$