Density Operator Revised

Quantum Statistical Mechanics

$\begin{pmatrix}1\\0\end{pmatrix} \uparrow \qquad \begin{pmatrix}0\\1\end{pmatrix} \uparrow$

1 spin system – we can easily specify pure states eg. $|\uparrow\rangle$ and $|\downarrow\rangle$ or their combinations, eg. $|\rightarrow\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle)$, $\begin{pmatrix}1/\sqrt{2}\\1/\sqrt{2}\end{pmatrix}$

How do we represent statistical uncertainty (vs quantum uncertainty)?

eg. $|$50% chance of $\uparrow$, 50% change of $\downarrow\rangle = ?$

$\frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle)$? but that is just $|\rightarrow\rangle$.

Mixed state – cannot be written as any combination of basis states.
– can be represented as a density operator/matrix

Mixtures of states:

If we have a mixture $\{p_i, |\psi_i\rangle\}$ we can write the density operator:
not restricted to eigenstates

$$\rho = \sum p_i |\psi_i\rangle\langle\psi_i|$$

For above example: $\rho = \frac{1}{2}|\uparrow\rangle\langle\uparrow| + \frac{1}{2}|\downarrow\rangle\langle\downarrow|$

$$= \frac{1}{2}\begin{pmatrix}1\\0\end{pmatrix}\begin{pmatrix}1 & 0\end{pmatrix} + \frac{1}{2}\begin{pmatrix}0\\1\end{pmatrix}\begin{pmatrix}0 & 1\end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix}1 & 0\\0 & 0\end{pmatrix} + \frac{1}{2}\begin{pmatrix}0 & 0\\0 & 1\end{pmatrix} = \begin{pmatrix}1/2 & 0\\0 & 1/2\end{pmatrix}$$

diagonals don't need to be zero, eg.
$\{|\rightarrow\rangle\}$: $\rho = \frac{1}{2}\begin{pmatrix}1\\1\end{pmatrix}\cdot\begin{pmatrix}1 & 1\end{pmatrix}$
$= \begin{pmatrix}1/2 & 1/2\\1/2 & 1/2\end{pmatrix}$

$(\mathrm{Tr}\,\rho = 1)$

diagonals sum to 1

Measurement: Probability of measuring system to be in state $|\beta\rangle$:

$$P(|\beta\rangle) = \sum_j p_j |\langle\psi_j|\beta\rangle|^2 = \sum_j p_j \langle\beta|\psi_j\rangle\langle\psi_j|\beta\rangle$$

$$= \langle\beta|\Big(\sum_j p_j |\psi_j\rangle\langle\psi_j|\Big)|\beta\rangle = \langle\beta|\rho|\beta\rangle$$

If $|\beta\rangle$ is in the standard basis, ie. $|\beta\rangle = |\psi_k\rangle$

$$P(|\beta\rangle) = \langle\beta|\rho|\beta\rangle = \langle k|\left(\sum_j p_j |j\rangle\langle j|\right)|k\rangle = \rho_{jj}$$

using orthonormality.

i.e. diagonal terms are populations

Expectation values of operators:

$$\langle A\rangle = \sum_j p_j \langle j|A|j\rangle \cancel{= \sum_j p_j \langle j|}$$

$$= \sum_j p_j \sum_{x,y} \langle j|x\rangle\langle x|A|y\rangle\langle y|j\rangle$$

$$= \sum_{x,y}\sum_j p_j \langle y|j\rangle\langle j|x\rangle\langle x|A|y\rangle$$

$$= \sum_{x,y} \langle y|\rho|x\rangle\langle x|A|y\rangle$$

$$= \sum_y \langle y|\rho A|y\rangle = \mathrm{Tr}(\rho A).$$

Off-diagonal elements

Diagonal elements give the populations IN A GIVEN BASIS.
Off-diagonal elements are superpositions of states termed coherences.

In the Zeeman basis (eigenstates of the Hamiltonian)

$$\rho_{eq} = \frac{1}{Z} e^{-H/kT} \approx I - \frac{1}{kT} H + \dots$$

is diagonal.
Coherences therefore decay to zero.

But! Nothing special in general about off-diagonal terms: ρ is Hermitian operator therefore can always be diagonalised by an appropriate change of basis.

So – in a given basis the components of ρ change with time. In Zeeman basis, useful to think of relaxation of coherences → ρ_{eq}.

eg. ^1H-^{15}N TROSY: in basis $|\psi_H \psi_N\rangle$:

$$\rho = \begin{array}{c|cccc|} & \alpha\alpha & \alpha\beta & \beta\alpha & \beta\beta \\ & \cdot & \cdot & \cdot & \cdot \\ & |\alpha\alpha\rangle\langle\alpha\beta| & \cdot & \cdot & |\beta\beta\rangle\langle\alpha\beta| \\ & |\alpha\alpha\rangle\langle\beta\alpha| & \cdot & \cdot & |\beta\beta\rangle\langle\beta\alpha| \\ & \cdot & |\alpha\beta\rangle\langle\beta\beta| & |\beta\alpha\rangle\langle\beta\beta| & \cdot \end{array}$$

fast relaxing ^1H transition (^{15}N in α state)

fast relaxing ^{15}N transition (^1H in α state)

slow relaxation ^1H transition (^{15}N in β state)

slow relaxing ^{15}N transition (^1H in β state)

N.B. knowing which states relax fast/slow requires analysing the relaxation ~~measurement~~ mechanisms, ie. identifying DD/CSA interference.

Basis spaces

Choosing a sensible basis for calculations is crucial to simplifying the algebra and revealing the underlying spin physics.

Our choice hitherto has had the form of a tensor product of individual Zeeman eigenfunctions:

$$|\psi_I \psi_S\rangle = |\psi_I\rangle \otimes |\psi_S\rangle = |\psi_I\rangle|\psi_S\rangle$$

$$\longrightarrow \{|\alpha\alpha\rangle, |\alpha\beta\rangle, |\beta\alpha\rangle, |\beta\beta\rangle\}$$

In this basis the chemical shift + (weak) scalar coupling Hamiltonian is:

$$\mathcal{H} = \omega_I I_z + \omega_S S_z + 2\pi J I_z S_z$$

~~$= \omega_I$~~

Representations of 2-spin operators in tensor product spaces:

1-spin product operator representations (in basis $\{|\alpha\rangle, |\beta\rangle\}$):

$$\mathbf{E} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad I_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad I_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad I_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

Form 2-spin operators from the direct product:

$$I_z = I_z \otimes E_s = \begin{pmatrix} 1\times\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & 0\times\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ 0\times\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & -1\times\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \end{pmatrix} = \begin{pmatrix} 1 & & & \\ & 1 & & \\ & & -1 & \\ & & & -1 \end{pmatrix}$$

$$S_z = E_I \otimes S_z = \begin{pmatrix} 1 & & & \\ & -1 & & \\ & & 1 & \\ & & & -1 \end{pmatrix}$$

$$2I_zS_z = I_z \otimes S_z = \begin{pmatrix} 1 & & & \\ & -1 & & \\ & & -1 & \\ & & & 1 \end{pmatrix}$$

Therefore, the Hamiltonian is:

$$\mathcal{H} = \omega_I I_z + \omega_s S_z + 2\pi J\, I_z S_z$$

$$= \begin{pmatrix} \omega_I + \omega_s + \pi J & & & \\ & \omega_I - \omega_s - \pi J & & \\ & & -\omega_I + \omega_s - \pi J & \\ & & & -\omega_I - \omega_s + \pi J \end{pmatrix}$$

i.e. it is diagonalised in the Zeeman product basis – a very convenient property for calculations!

Strong coupling

If $\Delta\omega \lesssim J$, the system is strongly coupled. The strong coupling Hamiltonian is:

$$\mathcal{H} = \omega_1 I_{1z} + \omega_2 I_{2z} + 2\pi J \, \mathbf{I}_1 \cdot \mathbf{I}_2$$

$$2\mathbf{I}_1 \cdot \mathbf{I}_2 = 2I_{1x}I_{2x} + 2I_{1y}I_{2y} + 2I_{1z}I_{2z}$$

$$= \begin{pmatrix} & & & 1 \\ & & 1 & \\ & 1 & & \\ 1 & & & \end{pmatrix} + \begin{pmatrix} & & & -1 \\ & & 1 & \\ & 1 & & \\ -1 & & & \end{pmatrix} + \begin{pmatrix} 1 & & & \\ & -1 & & \\ & & -1 & \\ & & & 1 \end{pmatrix}$$

$$= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

off-diagonal terms!

$$\therefore \mathcal{H} = \begin{pmatrix} \omega_1 + \omega_2 + \pi J & 0 & 0 & 0 \\ 0 & \omega_1 - \omega_2 - \pi J & 2\pi J & 0 \\ 0 & 2\pi J & -\omega_1 + \omega_2 - \pi J & 0 \\ 0 & 0 & 0 & -\omega_1 - \omega_2 + \pi J \end{pmatrix}$$

Now the Hamiltonian is no longer diagonalised in the Zeeman product eigenbasis!

The eigenfunctions of $\mathcal{H}$ are:

$|1\rangle = |\Psi_1\rangle = |\alpha\alpha\rangle$

$|2\rangle = |\Psi_2\rangle = \cos\theta\,|\alpha\beta\rangle + \sin\theta\,|\beta\alpha\rangle$

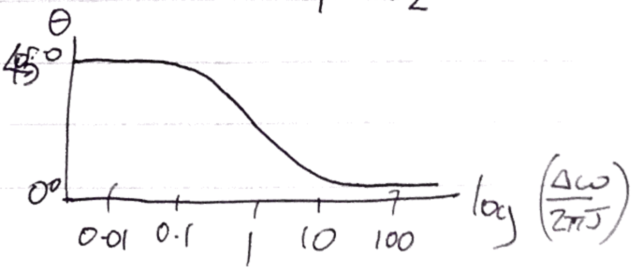
$|3\rangle = |\Psi_3\rangle = \cos\theta\,|\beta\alpha\rangle - \sin\theta\,|\alpha\beta\rangle$

$|4\rangle = |\Psi_4\rangle = |\beta\beta\rangle$

θ is the 'strong coupling angle' given by:

$$\tan(2\theta) = \frac{2\pi J}{\omega_1 - \omega_2}$$

$\theta = 45°$ in strong coupling limit.



Thus, in strong coupling limit, Hamiltonian ~~eigenstates~~ eigenfunctions and eigenvalues are:

$|1\rangle = |\alpha\alpha\rangle$ $\qquad E_1 = \frac{1}{2}\omega_1 + \frac{1}{2}\omega_2 + \frac{1}{2}\pi J$

$|2\rangle = 1/\sqrt{2}\,(|\alpha\beta\rangle + |\beta\alpha\rangle)$ $\qquad E_2 = D - \frac{1}{2}\pi J$

$|3\rangle = 1/\sqrt{2}\,(|\beta\alpha\rangle - |\alpha\beta\rangle)$ $\qquad E_3 = -D - \frac{1}{2}\pi J$

$|4\rangle = |\beta\beta\rangle$ $\qquad E_4 = -\frac{1}{2}\omega_1 - \frac{1}{2}\omega_2 + \frac{1}{2}\pi J$

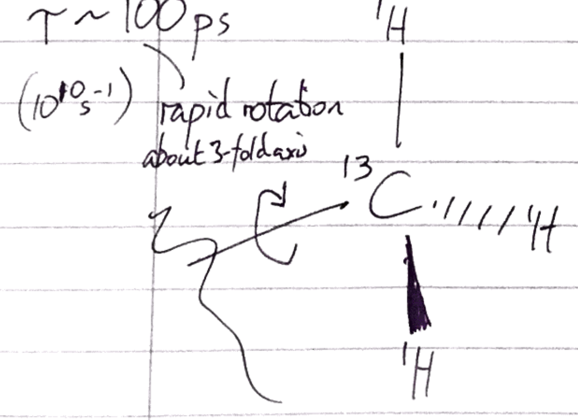
where $D = \frac{1}{2}\sqrt{(\omega_1 - \omega_2)^2 + 4\pi^2 J^2}$

N.B. eigenfunctions have become symmetrised! Wavefunctions are Symmetric / Anti-symmetric under exchange of identical particles
- fundamental requirement of QM
- c.f. weak coupling, particles are distinguishable.

In the strong coupling limit therefore it may be preferable to work in Hamiltonian eigenbasis rathan ~~than~~ Zeeman product basis:

$$\mathcal{H} = \begin{pmatrix} E_1 & & & \\ & E_2 & & \\ & & E_3 & \\ & & & E_4 \end{pmatrix}$$

Methyl groups



The methyl group is an AX_3 spin system. Rapid rotation renders all protons equivalent.

$^1J_{CH} \approx 140$ Hz

$\Delta\omega_H = 0$ (equivalent)

⇒ Protons are strongly coupled.

Coupling Angular Momenta

Angular momentum commutation relations:

$$[J_x, J_y] = i J_z$$

$\vec{J} = \vec{i} J_x + \vec{j} J_y + \vec{k} J_z$ does not commute with J_i

$J^2 = J \cdot J = J_x^2 + J_y^2 + J_z^2$ commutes with J_i :

$$\begin{aligned}
[J_z, J^2] &= [J_z, J_x^2] + [J_z, J_y^2] + [J_z, J_z^2] \\
&= J_x[J_z, J_x] + [J_z, J_x]J_x + J_y[J_z, J_y] + [J_z, J_y]J_y \\
&= -J_x J_y - J_y J_x + J_y J_x + J_x J_y \\
&= 0
\end{aligned}$$

angular momentum revision

Since J_z and J^2 commute, they have the same eigenstates – but different eigenvalues! Label them α and β:

$$\underset{\substack{\uparrow \\ \text{total magnitude of ang. mom.}}}{J^2|\alpha,\beta\rangle = \alpha|\alpha,\beta\rangle} \quad \text{and} \quad \underset{\substack{\uparrow \\ \text{ang. mom. along z-axis}}}{J_z|\alpha,\beta\rangle = \beta|\alpha,\beta\rangle}$$

or $J^2|j,m\rangle = j(j+1)|j,m\rangle$ and $J_z|j,m\rangle = m|j,m\rangle$

Two uncoupled angular momenta:

For two uncoupled spins can work in product basis:

$$|j_1, m_1\rangle \otimes |j_2, m_2\rangle$$

If $[J_1, J_2] = 0$, spins are uncoupled and have the same eigenstates, which can be specified by $|j_1, m_1; j_2, m_2\rangle$.

Coupled spins

If Hamiltonian contains an interaction between the spins like $\vec{J}_1 \cdot \vec{J}_2$, eigenstates will be a mixture of product basis vectors. Easier to work in coupled basis.

Total angular momentum $\vec{J} = \vec{J}_1 + \vec{J}_2$ obeys canonical commutation relations, ie. is also an angular momentum.

We can therefore define j and m quantum numbers for the total angular momentum. – but still need two more!

z-projections of individual spins do not commute with total angular momentum:

$$[J^2, J_{1z}] \neq 0 \quad \text{and} \quad [J^2, J_{2z}] \neq 0$$

ie. do not share eigenstates $\Rightarrow$ m_1 and m_2 are not good quantum numbers.

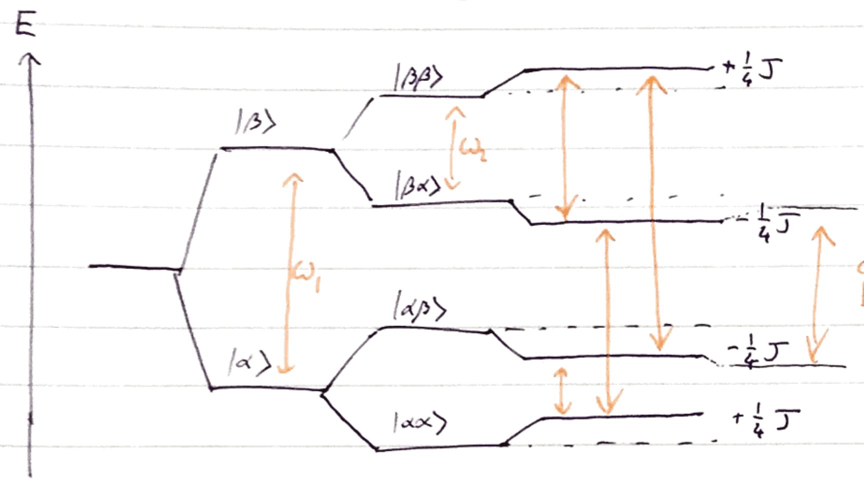
What about total angular momentum of individual spins?

$$[J^2, J_1^2] = [J^2, J_2^2] = [J_z, J_1^2) = [J_z, J_2^2] = 0.$$

So state is specified by:

$$J^2 |j, m, j_1, j_2\rangle = j(j+1) |---\rangle$$
$$J_z |j, m, j_1, j_2\rangle = m \ |---\rangle$$
$$J_1^2 |j, m, j_1, j_2\rangle = j_1(j_1+1) |\cdots\rangle$$
$$J_2^2 |j, m, j_1, j_2\rangle = j_2(j_2+1) |\cdots\rangle$$

Strong coupling: energy level picture

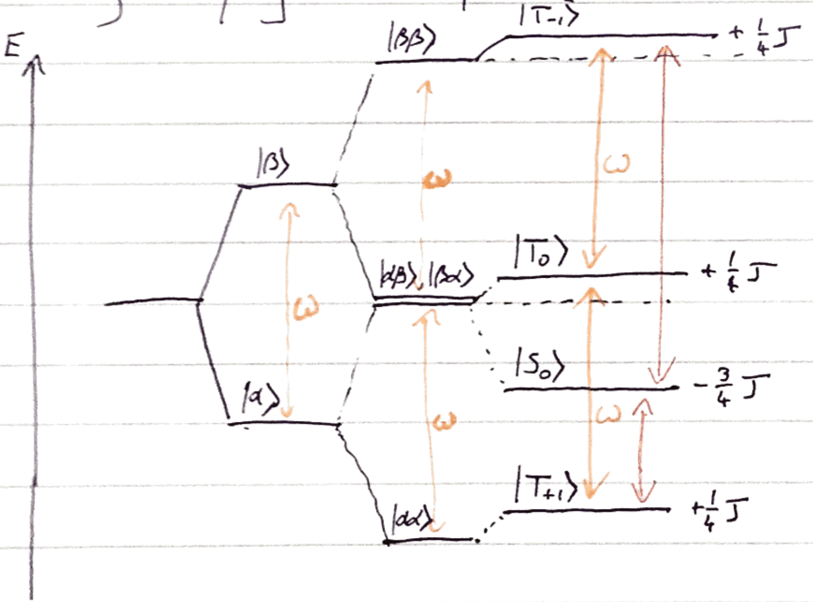


weak coupling
– 4 transitions

coupling introduces repulsion between $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$ states
-gets stronger as $\Delta\omega \to 0$
-arises from off-diagonal terms in Hamiltonian:

$$\begin{pmatrix} \Sigma+J & 0 & 0 & 0 \\ 0 & \Delta-J & 2J & 0 \\ 0 & 2J & -\Delta-J & 0 \\ 0 & 0 & 0 & -\Sigma+J \end{pmatrix}$$

Strong coupling limit: $\omega_1 = \omega_2$



$$|T_0\rangle = \frac{1}{\sqrt{2}}\left(|\alpha\beta\rangle + |\beta\alpha\rangle\right)$$

$$|S_0\rangle = \frac{1}{\sqrt{2}}\left(|\alpha\beta\rangle - |\beta\alpha\rangle\right)$$

Singlet-triplet transitions are forbidden!

Singlets + triplets:

Angular momentum eigenstates $|I, m_I\rangle$

$$\text{Spin } \tfrac{1}{2} + \text{Spin } \tfrac{1}{2} \longrightarrow \text{Spin } 0 \longrightarrow |0,0\rangle$$

$$\text{Spin } \tfrac{1}{2} + \text{Spin } \tfrac{1}{2} \longrightarrow \text{Spin } 1 \longrightarrow \left\{ \begin{matrix} |1,1\rangle \\ |1,0\rangle \\ |1,-1\rangle \end{matrix} \right\}$$

NMR selection rule is $\Delta m = \pm 1$,
– forbidden by symmetry.