

6.2: Product operator formalism with pseudo-secular interactions

Transformation of \hat{S}_x to the eigenbasis

Excitation and detection in EPR experiments are described by the \hat{S}_x and \hat{S}_y operators in the rotating frame. These operators act only on electron spin transitions and thus formalize the spectroscopic selection rules. If the spin Hamiltonian contains off-diagonal terms, such as the pseudo-secular $B\hat{S}_z\hat{I}_x$ term in Eq. (6.1), the eigenbasis deviates from the basis of the electron spin rotating frame/nuclear spin laboratory frame in which the Hamiltonian is written and in which the excitation and detection operators are linear combinations of \hat{S}_x and \hat{S}_y . In order to understand which transitions are driven and detected with what transition moment, we need to transform \hat{S}_x to the eigenbasis (the transformation of \hat{S}_y is analogous). This can be done by product operator formalism and can be understood in the local field picture.

The Hamiltonian in the eigenbasis has no off-diagonal elements, meaning that all quantization axes are along z . Thus, we can directly infer from Fig. 6.1 that, in the α_S state, we need a counterclockwise (mathematically positive) rotation by tilt angle η_α about the y axis, which is pointing into the paper plane. In the β_S state, we need a clockwise (mathematically negative) rotation by tilt angle η_β about the y axis. The electron spin states can be selected by the projection operators \hat{S}^α and \hat{S}^β , respectively. Hence, we have to apply rotations $\eta_\alpha\hat{S}^\alpha\hat{I}_y$ and $-\eta_\beta\hat{S}^\beta\hat{I}_y$. These two rotations commute, as the α_S and β_S subspaces are distinct when m_S is a good quantum number. For the rotation into the eigenbasis, we can write a unitary matrix

$$\begin{aligned}\hat{U}_{\text{EB}} &= \exp\left\{-i\left(\eta_\alpha\hat{S}^\alpha\hat{I}_y - \eta_\beta\hat{S}^\beta\hat{I}_y\right)\right\} \\ &= \exp\left\{-i\left(\xi\hat{I}_y + \eta 2\hat{S}_z\hat{I}_y\right)\right\}\end{aligned}$$

where $\xi = (\eta_\alpha - \eta_\beta)/2$ and $\eta = (\eta_\alpha + \eta_\beta)/2$. Note that the definition of angle η corresponds to the one given graphically in Fig. 6.1.² The two new rotations about \hat{I}_y and $\hat{S}_z\hat{I}_y$ also commute. Furthermore, \hat{I}_y commutes with \hat{S}_x (and \hat{S}_y), so that the transformation of \hat{S}_x to the eigenbasis reduces to

$$\hat{S}_x \xrightarrow{\eta 2\hat{S}_z\hat{I}_y} \cos\eta\hat{S}_x + \sin\eta 2\hat{S}_y\hat{I}_y \quad (6.2.1)$$

The transition moment for the allowed transitions that are driven by \hat{S}_x is multiplied by a factor $\cos\eta \leq 1$, i.e. it becomes smaller when $\eta \neq 0$. In order to interpret the second term, it is best rewritten in terms of ladder operators $\hat{S}^+ = \hat{S}_x + i\hat{S}_y$ and $\hat{S}^- = \hat{S}_x - i\hat{S}_y$. We find

$$2\hat{S}_y\hat{I}_y = \frac{1}{2}\left(\hat{S}^+\hat{I}^- + \hat{S}^-\hat{I}^+ - \hat{S}^+\hat{I}^+ - \hat{S}^-\hat{I}^-\right) \quad (6.2.2)$$

In other words, this term drives the forbidden electron-nuclear zero- and double-quantum transitions (Fig. 6.2(a)) with a transition proportional to $\sin\eta$.

In a CW EPR experiment, each transition must be both excited and detected. In other words, the amplitude is proportional to the square of the transition moment, which is the transition probability. Allowed transitions thus have an intensity proportional to $\cos^2\eta$ and forbidden transitions a transition probability proportional to $\sin^2\eta$ (Fig. 6.2(b)).

General product operator computations for a non-diagonal Hamiltonian

In a product operator computation, terms of the Hamiltonian can be applied one after the other if and only if they pairwise commute. This is not the case for the Hamiltonian in Eq. (6.1). However, application of \hat{U}_{EB} diagonalizes the Hamiltonian:

$$\hat{H}_0 \xrightarrow{\eta\hat{S}_z\hat{I}_y} \Omega_S\hat{S}_z + \omega_{\text{sum}}/2\hat{I}_z + \omega_{\text{hfi}}\hat{S}_z\hat{I}_z \quad (6.2.3)$$

This provides a simple recipe for product operator computations in the presence of the pseudosecular hyperfine coupling. Free evolution and transition-selective pulses are computed in the eigenbasis, using the Hamiltonian on the right-hand side of relation (6.9). For application of non-selective pulses, the density operator needs to be transformed to the electron spin rotating frame/nuclear spin laboratory frame basis by applying $\hat{U}_{\text{EB}}^\dagger$. In product operator formalism this corresponds to a product operator

transformation $\xrightarrow{-i\hat{S}_z\hat{I}_y}$. After application of non-selective pulses, the density operator needs to be backtransformed to the eigenbasis. Detection also needs to be performed in the electron spin rotating frame/nuclear spin laboratory frame basis.

This concept can be extended to any non-diagonal Hamiltonian as long as one can find a unitary transformation that transforms the Hamiltonian to its eigenbasis and can be expressed by a single product operator term or a sum of pairwise commuting product operator terms.

² We have used $\hat{S}^\alpha = \hat{I}/2 + \hat{S}_z$ and $\hat{S}^\beta = \hat{I}/2 - \hat{S}_z$.

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