

Tutorial

Fundamental theory of EPR; quantum mechanics.

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1. Angular momentum.

The spin angular momentum $\hbar\mathbf{S}$ is characterized by states $|s m_s\rangle$ that are eigenstates of \mathbf{S}^2 and one of the components of \mathbf{S} , say S_z :

$$\begin{aligned}\mathbf{S}^2 |s m_s\rangle &= s(s+1)|s m_s\rangle \\ S_z |s m_s\rangle &= m_s |s m_s\rangle.\end{aligned}$$

In cases where we need to know how S_x or S_y operate on a spin state, we make use of the so-called ladder operators S_+ or S_- : $S_{\mp} \equiv S_x \mp iS_y$.

In this exercise we show that

$$S_{\mp} |s m_s\rangle = \lambda_{\mp} |s m_s \mp 1\rangle,$$

with

$$\lambda_{\mp} = \sqrt{s(s+1) - m_s(m_s \mp 1)}.$$

Do so for S_+ step by step.

- Show that S_+ is the Hermitian conjugate of S_- (and vice versa).
- Show that the commutator of S_z and S_+ equals S_+ .
- Show that $S_+ |s m_s\rangle$ is an eigenstate of S_z with eigenvalue $(m_s + 1)$.
- Express $S_- S_+$ in terms of S^2 and S_z .
- Calculate the expectation value of $S_- S_+$ in the state $|s m_s\rangle$ in two ways using the result of (c) and (d), respectively, and find λ_+ .

2. Coupling of two spin $\frac{1}{2}$ systems: a biradical.

The total spin angular momentum $\hbar\mathbf{S} = \hbar\mathbf{s}_1 + \hbar\mathbf{s}_2$.

- Express the eigenstates as ket vectors in terms of the quantum numbers of the total spin.
- Express these states in terms of the eigenstates $|1/2\ 1/2\rangle$ and $|1/2\ -1/2\rangle$ of the individual spins.

Suppose the electron spins are in a magnetic field $(0, 0, B)$ and have an exchange interaction J . The spin Hamiltonian is given by

$$H = \beta_e B (g_1 s_{1z} + g_2 s_{2z}) + J \mathbf{s}_1 \cdot \mathbf{s}_2.$$

- Calculate the energies of the spin states and draw the energy-level diagram for two limiting cases:
 - Weak coupling $|J| \ll (|g_1 - g_2|)\beta_e B$
 - Strong coupling $|J| \gg (|g_1 - g_2|)\beta_e B$
- Indicate for both situations the allowed EPR transitions in the energy-level diagram.

3. Spin Hamiltonian.

In the spin Hamiltonian only spin operators occur, while the spatial distribution of the electron (and nuclear) spin density is absorbed in tensorial magnetic parameters. Here we will illustrate this concept through derivation of the explicit expression of the zero-field splitting tensor \mathbf{D} for the magnetic dipole-dipole interaction of two electron spins in a triplet state ($S=1$). We take $g_1 = g_2 = g$, a proper assumption for most organic triplets. The corresponding Hamilton operator is

$$H_{zfs} = \frac{\mu_0}{4\pi} g^2 \beta_e^2 \left\{ \frac{\mathbf{s}_1 \cdot \mathbf{s}_2}{r^3} - \frac{3(\mathbf{s}_1 \cdot \mathbf{r})(\mathbf{s}_2 \cdot \mathbf{r})}{r^5} \right\},$$

where \mathbf{r} represents the vector joining the two electrons.

- a. Prove the following operator relations for $s = \frac{1}{2}$:

$$s_x s_y = -s_y s_x = i/2 s_z,$$

$$s_x^2 = s_y^2 = s_z^2 = 1/4 \mathbf{1}.$$

- b. In terms of the total spin angular momentum $\hbar \mathbf{S} = \hbar \mathbf{s}_1 + \hbar \mathbf{s}_2$, prove the following operator relations:

$$S_j^2 = 2s_{1j}s_{2j} + 1/2 \mathbf{1},$$

$$(S_j S_k + S_k S_j) = 2(s_{1j}s_{2k} + s_{1k}s_{2j}),$$

for $j, k = x, y, z$.

- c. Rewrite the Hamilton operator in terms of the total spin angular momentum. The result can be identified with the spin Hamiltonian $H_{zfs} = \tilde{\mathbf{D}} \mathbf{S} \mathbf{S}$. To do so, we have to take the expectation value of the spatial observables, which yields the following expression for the elements of the \mathbf{D} tensor:

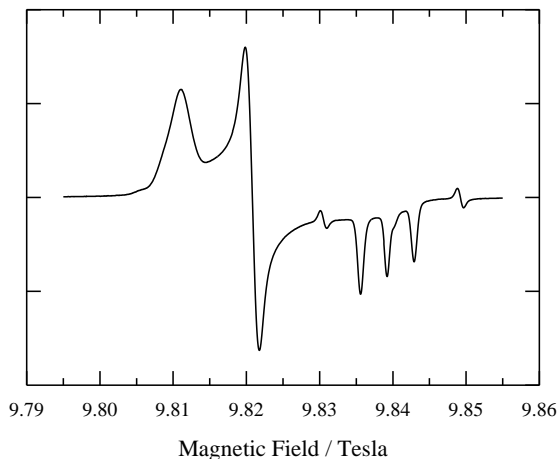
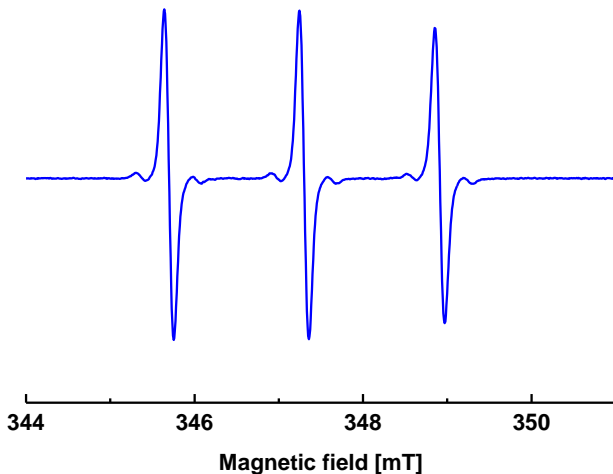
$$D_{jk} = \frac{1}{2} \frac{\mu_0}{4\pi} g^2 \beta_e^2 \left\langle \frac{\delta_{jk} r^2 - 3jk}{r^5} \right\rangle.$$

4. The EPR spectrum of a nitroxide radical at 9.5 and 275 GHz.

Below two EPR spectra are represented for the nitroxide spin label MTSL: one at 9 GHz (X-band) for a solution at room temperature, and the other at 275 GHz for a frozen sample at low temperature. In the spectra the effect of the nuclear spin of nitrogen ($I=1$) is visible.

The spectrum at 9 GHz extends over about 3.5 mT and consists of three peaks and small extra features on both sides of each peak. The spectrum at 275 GHz extends over 40 mT, and small extra features are visible at about 9.83 and 9.85 T.

- Which spin Hamiltonians describe the spectra? Provide a qualitative interpretation of the spectra.
- Speculate on the origin of the extra features in both spectra.
- Simulate the spectra with Easyspin.
- Use Easyspin to investigate the dependence of the EPR spectrum of MTSL on the rotational freedom of the spin label in solution, both at 9 and 275 GHz.



5. High-spin Co(III).

Consider high-spin Co(II), a $3d^7$ electron configuration with $S = \frac{3}{2}$. In zero-field, the magnetic sublevels form two degenerate doublets (so-called Kramers doublets) separated by the zero-field splitting.

- Determine the matrix representation of the spin Hamiltonian in zero-field in the basis of the eigenstates of S_z : $|3/2 \ 3/2\rangle, |3/2 \ 1/2\rangle, |3/2 \ -1/2\rangle, |3/2 \ -3/2\rangle$. Work in the principal axes system x, y, z of the zfs-tensor \mathbf{D} .
- Assume $\text{Tr}\mathbf{D} = 0$ and define $D \equiv \frac{3}{2}D_{zz}$ and $E \equiv \frac{1}{2}(D_{xx} - D_{yy})$. Determine the energies of the Kramers doublets in terms of D and E , and the corresponding eigenstates.

The eigenstates can be written as

$$\begin{aligned} & \cos \theta |3/2 \ \pm 3/2\rangle + \sin \theta |3/2 \ \mp 1/2\rangle \\ & \cos \theta |3/2 \ \pm 1/2\rangle - \sin \theta |3/2 \ \mp 3/2\rangle, \end{aligned}$$

where the angle θ is given by $\tan 2\theta = \sqrt{3} E/D$.

- Suppose \mathbf{g} is anisotropic with principal axes parallel to those of \mathbf{D} . Calculate for negative D the effect of a magnetic field on the energy of the lower doublet. When is it justified to neglect the upper doublet?
- Show that the result obtained under (c) is equivalent to that for an $s=1/2$ system with effective g -values. Express the effective g -values in terms of the true g -values and θ .

6. Density matrix.

Consider an isolated spin $\frac{1}{2}$ system in the state $|\chi\rangle = c_1|1\rangle + c_2|2\rangle$, where $|1\rangle$ and $|2\rangle$ refer to the orthonormal eigenstates $|1/2 \ 1/2\rangle$ and $|1/2 \ -1/2\rangle$, and $|c_1|^2 + |c_2|^2 = 1$.

- a. The density operator $\rho = |\chi\rangle\langle\chi|$. Set up the density matrix $\mathbf{\rho}$ in the basis $|1\rangle, |2\rangle$ and express the expectation values of $S_x, S_y,$ and S_z in terms of the elements of the density matrix. Remember $\langle A \rangle = \text{Tr}(\mathbf{\rho}\mathbf{A})$ and make use of the Pauli matrices.

For an ensemble of spin $\frac{1}{2}$ systems in a pure state, i.e., the coefficients c_1 and c_2 are the same for all spins, the description is equivalent to that for an isolated spin. Also in this case the system can be described just as well by the density operator as by the state vector. The density operator has advantages. First, the two state vectors $|\chi\rangle$ and $e^{i\theta}|\chi\rangle$ describe the same physical state, and the density operator eliminates the arbitrary phase factor. Secondly, expressions like the expectation value of an observable, while quadratic in the state vector, are linear in the density operator.

- b. If not obvious, check both assertions.

Subsequently we consider a non-pure case, a so-called mixed state, which corresponds to an incoherent superposition of states with different coefficients c_1 and c_2 . An important example concerns a macroscopic system at thermal equilibrium, in other words a statistical mixture of states $|1\rangle$ and $|2\rangle$. The density operator becomes

$$\rho = p_1|1\rangle\langle 1| + p_2|2\rangle\langle 2|,$$

where p_1 and p_2 are the probabilities of spins being in the two states as given by the Boltzmann distribution.

- c. Set up the density matrix and show that it can be written as

$$\rho = \frac{1}{2}\mathbf{1} + \frac{1}{2}(p_1 - p_2)\mathbf{S}_z.$$

7. A two-spin system and the evolution of the density matrix: electron-spin-echo spectroscopy of radical pairs.

(Adapted from the tutorial by Peter Hore, University of Oxford, at the 2010 Summer School on Advanced EPR Spectroscopy in Konstanz)

Consider a two-pulse electron-spin-echo experiment on a weakly coupled pair of electron spins A and B ($S = S_A + S_B$) with the spin Hamiltonian

$$H = \omega_A S_{Az} + \omega_B S_{Bz} + \omega_{dd} S_{Az} S_{Bz} + J S_{Az} S_{Bz}.$$

The eigenstates and the corresponding energies are:

$$|1\rangle = |\alpha_A \alpha_B\rangle \quad \varepsilon_1 = +\frac{1}{2}(\omega_A + \omega_B) + \frac{1}{4}(J + \omega_{dd})$$

$$|2\rangle = |\alpha_A \beta_B\rangle \quad \varepsilon_2 = +\frac{1}{2}(\omega_A - \omega_B) - \frac{1}{4}(J + \omega_{dd})$$

$$|3\rangle = |\beta_A \alpha_B\rangle \quad \varepsilon_3 = -\frac{1}{2}(\omega_A - \omega_B) - \frac{1}{4}(J + \omega_{dd})$$

$$|4\rangle = |\beta_A \beta_B\rangle \quad \varepsilon_4 = -\frac{1}{2}(\omega_A + \omega_B) + \frac{1}{4}(J + \omega_{dd}).$$

The resonance frequencies ω_A and ω_B correspond to isotropic Zeeman and hyperfine interactions, J is the exchange and ω_{dd} the dipolar coupling of the electron spins. The non-secular parts of the electron-electron interactions have been omitted.

Suppose the initial density matrix, at $t=0$, is diagonal in the basis of eigenstates of H :

$$\rho(0) = \begin{pmatrix} p_1 & 0 & 0 & 0 \\ 0 & p_2 & 0 & 0 \\ 0 & 0 & p_3 & 0 \\ 0 & 0 & 0 & p_4 \end{pmatrix},$$

where the p_j 's ($j=1, 4$) are the fractional populations of the four eigenstates.

We consider the pulse sequence

$$\beta_x - \tau - \pi_x - \tau - \text{echo},$$

where the microwave pulses with phase x and flip-angles β and π are separated by a time interval τ . The pulses are assumed to be hard so that off-resonance effects can be ignored. We calculate the echo amplitudes $\langle S_x \rangle$ and $\langle S_y \rangle$ detected along the x - and y -axes at time $t=2\tau$.

- Let $\rho(0_+)$, $\rho(\tau_-)$ and $\rho(\tau_+)$ represent the density operator at times immediately after the β -pulse, just before the π -pulse and immediately after the π -pulse. Show that solving the Liouville-von Neumann equation for the time interval 0 to 0_+ yields

$$\rho(0_+) = \exp(-i\beta S_x) \rho(0) \exp(+i\beta S_x).$$

- b. Express in a similar way the evolution of the density operator from 0_+ to τ_- , from τ_- to τ_+ , and from τ_+ to 2τ . Combination of these results yields the evolution of the density operator from time 0 to time 2τ .
- c. Determine the matrix representations in the basis of eigenstates of H of the following operators:

$$H, \exp(\pm iH\tau), S_x, S_y, \exp(\pm i\beta S_x).$$

- d. Combine all results to calculate the echo amplitudes $\langle S_x \rangle$ and $\langle S_y \rangle$ detected along the x- and y-axes at time $t=2\tau$. Hopefully you obtain:

$$\langle S_x \rangle(2\tau) = \frac{1}{2}(p_1 - p_2 - p_3 + p_4) \sin 2\beta \sin(J + \omega_{dd})\tau$$

$$\langle S_y \rangle(2\tau) = (p_1 - p_4) \sin\beta \cos(J + \omega_{dd})\tau$$

The matrix algebra is pretty tedious if done by hand. Alternatively, make use of, for example, *Mathematica*.

With the two microwave pulses having phase x , the echo is normally formed along the y-axis. The y-echo is therefore referred to as the “in-phase” echo and the x-echo as the “out-of-phase” echo. Both echoes are found to be modulated at the frequency of the electron-electron coupling.

- e. Comment on the dependence of the echo amplitudes on the flip-angle β and the mutual phase shift of the echoes along x and y.
- f. Comment on the echo amplitudes for
- a spin system in thermal equilibrium at $t=0$ (assuming the high-temperature approximation, $k_B T \gg \hbar\omega_A \approx \hbar\omega_B$)
 - a spin-correlated radical pair formed at $t=0$ in a pure singlet state.