Einführung in die EPR Spektroskopie

Übungsblatt 7

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The iPython notebook of this problem set is at
`https://colab.research.google.com/drive/1AwtekJeINmZlbeFjPZMmV2350uJeNNCp?usp=sharing`.

1 Molecular frame of the dipolar coupling

As you know from the lecture, the dipolar coupling between two spins, S and I, is described by the spin Hamiltonian

$$\hat{\mathcal{H}}_{\text{dip}} = \frac{\mu_0}{4\pi}(\hbar\gamma_S)(\hbar\gamma_I)\frac{1}{r^3}\left[\hat{\vec{S}}\cdot\hat{\vec{I}} - \frac{3(\hat{\vec{S}}\cdot\vec{r})(\hat{\vec{I}}\cdot\vec{r})}{r^2}\right]. \tag{1}$$

You already encountered this Hamiltonian in Problem Set 4 where you examined the prefactor in front of the square brackets. Here you will analyze the part inside the square brackets.

a) Matrix form of the dipole-dipole interaction

As abstract objects in the space of three physical dimensions, the vectors $\hat{\vec{S}}$, $\hat{\vec{I}}$, and $\vec{r}$ in eq. (1) do not depend on the choice of a coordinate system. However, when a system of coordinate axes for the 3D space is selected, these abstract vectors can be represented in terms of their components in this coordinate frame.

Let us say that the components of the vectors in some given system of coordinate axes, which we will call the "laboratory frame" (LAB), are as follows:

$$\hat{\vec{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z), \quad \hat{\vec{I}} = (\hat{I}_x, \hat{I}_y, \hat{I}_z), \quad \vec{r} = (x, y, z). \tag{2}$$

i) Expand the expression

$$\hat{\vec{S}}\cdot\hat{\vec{I}} - \frac{3(\hat{\vec{S}}\cdot\vec{r})(\hat{\vec{I}}\cdot\vec{r})}{r^2} \tag{3}$$

and write it down in terms of the coordinates of the three vectors, keeping in mind that the dot between two vectors indicates their inner (dot) product.

ii) The expression in eq. (3) can also be written as

$$\hat{\vec{S}}^{\top} \cdot \tilde{T} \cdot \hat{\vec{I}}, \tag{4}$$

where $\tilde{T}$ is a 3×3 *symmetric* matrix (i.e., $T_{ij} = T_{ji}$), and the superscript $\top$ denotes the transpose operation (in this case, turning the column vector $\hat{\vec{S}}$ into a row vector).

Just like the vectors, as an abstract object $\tilde{T}$ is independent of the choice of coordinate axes. Nevertheless, since we already have written the vectors in terms of their components in the LAB frame, we can also write the components of $\tilde{T}$ in the LAB frame.

Considering that

$$\hat{\vec{S}}^{\top} \cdot \tilde{T} \cdot \hat{\vec{I}} = \begin{pmatrix} \hat{S}_x & \hat{S}_y & \hat{S}_z \end{pmatrix} \begin{pmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{yx} & T_{yy} & T_{yz} \\ T_{zx} & T_{zy} & T_{zz} \end{pmatrix} \begin{pmatrix} \hat{I}_x \\ \hat{I}_y \\ \hat{I}_z \end{pmatrix}, \tag{5}$$

and using the expansion you obtained in part **i)**, identify all nine components of $\tilde{T}$ in the LAB frame in terms of the components of the vector $\vec{r}$.

iii) For concreteness, let the vector $\vec{r}$ lie in the y-z plane of the LAB frame. If we denote the angle this vector makes with the z axis of the LAB frame by θ, its components in this frame will be

$$\vec{r} = (0, r\sin\theta, r\cos\theta). \tag{6}$$

Express the components of the matrix $\tilde{T}$ that you obtained in part **ii)** in terms of the angle θ. Note how r cancels out and all components depend only on θ.

b) Transformation to the molecular frame

Let us transform the components of the matrix $\tilde{T}$ in the LAB frame, which you obtained above, to another coordinate frame. Denoting the components in the LAB frame by $\tilde{T}_{\text{LAB}}$ and those in the other frame by $\tilde{T}_{\text{other}}$, the relationship between the two is

$$\tilde{T}_{\text{LAB}} = \tilde{R} \cdot \tilde{T}_{\text{other}} \cdot \tilde{R}^{-1}, \tag{7}$$

where $\tilde{R}$ is a transformation matrix (in this case, rotation matrix) that specifies how the LAB axes need to be rotated to become the axes of the other coordinate frame. For such rotation matrices, the inverse matrix is simply equal to the transpose (i.e., $\tilde{R}^{-1} = \tilde{R}^{\top}$).

i) Use the matrix

$$\tilde{R} = \tilde{R}_x(\alpha) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & -\sin\alpha \\ 0 & \sin\alpha & \cos\alpha \end{pmatrix}, \tag{8}$$

which corresponds to rotation about the x axis by an angle α, to transform the components $\tilde{T}_{\mathrm{LAB}}$ to another system of axes with rotated y and z directions. That is, calculate the components of $\tilde{T}$ in this new coordinate frame. (Hint: The resulting components should be functions of both α and θ.)

ii) A rotation about the x axis by an angle of $-\theta$ (i.e., a clockwise rotation by θ) would make the z-axis of the LAB frame point along the direction of the vector $\vec{r}$. Let us call this new system of coordinate axes MOL. Use $\alpha = -\theta$ in your result from part **i)** to calculate the components of $\tilde{T}$ in the MOL frame. (Hint: You should find that $\tilde{T}_{\mathrm{MOL}}$ is diagonal.)

2 Anisotropic g tensor

In Problem Set 6 you encountered an anisotropic g tensor, whose components in some molecular system of coordinate axes were

$$\tilde{g}_{\mathrm{MOL}} = \begin{pmatrix} g_{xx} & & \\ & g_{yy} & \\ & & g_{zz} \end{pmatrix} \tag{9}$$

with

$$g_{xx} = 2.008, \quad g_{yy} = 2.006, \quad g_{zz} = 2.003. \tag{10}$$

Let us assume that the coordinate system MOL for this g tensor is exactly the same as the coordinate system MOL from question **1 b ii)**.

i) Use the transformation matrix

$$\tilde{R}_x(-\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{pmatrix} \tag{11}$$

to obtain the components of the g tensor in the LAB frame. (That is, find $\tilde{g}_{\mathrm{LAB}}$.)

ii) Calculate the numerical values of the components of $\tilde{g}_{\mathrm{LAB}}$ for $\theta = \pi/2$ and for $\theta = \pi/4$.