Einführung in die EPR Spektroskopie

Übungsblatt 8

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The iPython notebook of this problem set is at
`https://colab.research.google.com/drive/1kraf-gJwx7r2OOlC1N7H-WULxA78OC4j?usp=sharing`.

1 Diagonalizing the dipolar coupling matrix

In Problem Set 7 we wrote the dipole-dipole interaction between a spin S and a spin I as

$$\hat{\vec{S}} \cdot \tilde{T} \cdot \hat{\vec{I}} = \begin{pmatrix} \hat{S}_x & \hat{S}_y & \hat{S}_z \end{pmatrix} \begin{pmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{yx} & T_{yy} & T_{yz} \\ T_{zx} & T_{zy} & T_{zz} \end{pmatrix} \begin{pmatrix} \hat{I}_x \\ \hat{I}_y \\ \hat{I}_z \end{pmatrix}. \tag{1}$$

We also showed that the components of the matrix $\tilde{T}$ in some general coordinate frame, which we called the LAB frame, were

$$\tilde{T}_{\mathrm{LAB}}(x,y,z) = \begin{pmatrix} 1-3\frac{xx}{r^2} & -3\frac{xy}{r^2} & -3\frac{xz}{r^2} \\ -3\frac{yx}{r^2} & 1-3\frac{yy}{r^2} & -3\frac{yz}{r^2} \\ -3\frac{zx}{r^2} & -3\frac{zy}{r^2} & 1-3\frac{zz}{r^2} \end{pmatrix}, \tag{2}$$

where x, y, and z were the Cartesian components of the vector $\vec{r}$ in the same coordinate frame, i.e.

$$\vec{r}_{\mathrm{LAB}} = (x,y,z). \tag{3}$$

Note that

$$r^2 = x^2 + y^2 + z^2. \tag{4}$$

a) Dipolar coupling matrix in terms of two angles

Using spherical polar coordinates in the LAB frame, the Cartesian components of the vector $\vec{r}$ can be expressed in terms of the magnitude of the vector, r, and two angles, θ and ϕ, as follows:

$$\vec{r}_{\mathrm{LAB}} = (r\sin\theta\cos\phi, r\sin\theta\sin\phi, r\cos\theta). \tag{5}$$

Substitute this form of the components of $\vec{r}$ in eq. (2) to express the components of the matrix $\tilde{T}$ in the LAB frame in terms of the two angles θ and ϕ.

$$\tilde{T}_{\mathrm{LAB}}(\theta, \phi) = \ ? \ .$$

b) Diagonalization of the matrix

Use SymPy to diagonalize the matrix $\tilde{T}_{\mathrm{LAB}}(\theta, \phi)$ from part **a)**.

In your work, keep θ and ϕ as symbols. Once you have constructed the desired **sympy** matrix `T`, you can perform the diagonalization by calling the **sympy** function `diagonalize` as follows:

```
(P, D) = T.diagonalize(normalize=True)
```

When **sympy** is done with the diagonalization, the matrix `D` will be the diagonal form of `T`, and `P` will contain the transformation matrix relating the two matrices as follows

$$T = PDP^{-1}. \tag{6}$$

For our purposes, the diagonal matrix D contains the components of the dipolar coupling matrix $\tilde{T}$ but with respect to the axes of another coordinate frame, which I will call the molecular frame (MOL). In other words, $\tilde{T}_{\mathrm{MOL}} = D$.

c) Transformation to a new coordinate frame

Let $\tilde{R}_{\mathrm{L}\to\mathrm{M}}$ denote the matrix that transforms the unit vectors in the x, y and z directions of the LAB frame to the corresponding unit vectors in the MOL frame. Then, the components of the matrix $\tilde{T}$ in the two coordinate frames are related as follows:

$$\tilde{T}_{\mathrm{LAB}} = \tilde{R}_{\mathrm{L}\to\mathrm{M}} \cdot \tilde{T}_{\mathrm{MOL}} \cdot \tilde{R}^{-1}_{\mathrm{L}\to\mathrm{M}}. \tag{7}$$

Comparison with eq. (6) shows that the matrix P that **sympy** reported in part **b)** is in fact the transformation matrix $\tilde{R}_{\mathrm{L}\to\mathrm{M}}$.

Act with this matrix on the unit vector

$$\hat{x} = (1, 0, 0)$$

of the LAB frame, to determine the x direction of the MOL frame.

When displaying the result of the calculation, it may be useful to simplify the expression as much as possible. You can do this using the **sympy** function `simplify` as follows

```
sp.simplify(x_MOL)
```

Compare the vector that $\hat{x}$ was transformed to with the unit vector in the direction of $\vec{r}$, i.e.,

$$\hat{r}_{\mathrm{LAB}} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta).$$