

# The Hyperfine Splitting in the Hydrogen Atom

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The purpose of this tutorial is to provide a much abbreviated version of the first three sections in Chapter 12 of Volume III of *The Feynman Lectures on Physics*. These sections deal with the hyperfine interaction in the hydrogen atom.

At the introductory quantum chemistry-physics level we treat the hydrogen atom using an energy operator consisting of a kinetic energy term and an electron-proton potential energy term and calculate the ground-state energy. These are clearly the most important terms in the total energy operator, but they are not the only terms. The proton and electron are spin-1/2 fermions and as such have magnetic moments which interact with one another. This means that the ground state that we have calculated consists of four terms which have slightly different energies due to the magnetic interaction between the electron and proton (hyperfine splitting).

For example, listing the electron spin first we have the following four electron-proton states in the z-basis:  $|++\rangle$ ,  $|+-\rangle$ ,  $| -+\rangle$  and  $|--\rangle$ . The spin-spin operator is.

$$\widehat{H}_{SpinSpin} = A\sigma^e \cdot \sigma^p = A(\sigma_x^e \sigma_x^p + \sigma_y^e \sigma_y^p + \sigma_z^e \sigma_z^p)$$

where the Pauli spin operators appear on the right side and represent the magnetic interaction between the electron and proton. The identity operator, on the right, will be needed later.

$$\sigma_x := \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y := \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z := \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad I := \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Tensor multiplication is now used to represent the spin-spin operator in matrix format. In the interest of mathematical clarity the constant  $A$  is set equal to unity.

$$H_{SpinSpin} := (\text{kroncker}(\sigma_x, \sigma_x) + \text{kroncker}(\sigma_y, \sigma_y) + \text{kroncker}(\sigma_z, \sigma_z))$$

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

We now ask Mathcad to calculate the eigenvalues and eigenvectors of the spin-spin operator. These results are displayed by constructing a matrix which contains the eigenvalues in the top row, and their eigenvectors in the columns below the eigenvalues.

$$E := \text{eigenvals}(H_{SpinSpin}) \quad \text{EigenvalEigenvec} := \text{rsort}\left(\text{stack}\left(E^T, \text{eigenvecs}(H_{SpinSpin})\right), 1\right)$$

$$\text{EigenvalEigenvec} = \begin{pmatrix} -3 & 1 & 1 & 1 \\ 0 & 0 & 0 & 1 \\ 0.707 & 0.707 & 0 & 0 \\ -0.707 & 0.707 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

These results are expressed in more familiar form below.

$$\begin{aligned}
 |T\rangle_1 &= |\uparrow\rangle_p |\uparrow\rangle_e \\
 \text{Triplet state } E_T = 1 & \quad |T\rangle_0 = \frac{1}{\sqrt{2}} \left[ |\uparrow\rangle_p |\downarrow\rangle_e + |\downarrow\rangle_p |\uparrow\rangle_e \right] \\
 & \quad |T\rangle_{-1} = |\downarrow\rangle_p |\downarrow\rangle_e \\
 \text{Singlet state } E_S = -3 & \quad |S\rangle_0 = \frac{1}{\sqrt{2}} \left[ |\uparrow\rangle_p |\downarrow\rangle_e - |\downarrow\rangle_p |\uparrow\rangle_e \right]
 \end{aligned}$$

We can achieve the same result using these electron-proton states:  $|++\rangle$ ,  $|+-\rangle$ ,  $|-+\rangle$  and  $|--\rangle$ .

First we write the spin states in vector format:  $|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$       $|-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

Next we write the four electron-proton spin states in tensor format.

$$\begin{aligned}
 |++\rangle &= \begin{pmatrix} 1 \\ 0 \end{pmatrix} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} & \quad |+-\rangle &= \begin{pmatrix} 1 \\ 0 \end{pmatrix} \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} \\
 |-+\rangle &= \begin{pmatrix} 0 \\ 1 \end{pmatrix} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} & \quad |--\rangle &= \begin{pmatrix} 0 \\ 1 \end{pmatrix} \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}
 \end{aligned}$$

These spin states are given the following labels to facilitate the calculation of energy matrix.

$$\begin{aligned}
 \mathbf{a} &:= \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} & \mathbf{b} &:= \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} & \mathbf{c} &:= \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} & \mathbf{d} &:= \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}
 \end{aligned}$$

$$\text{eigenvals} \left( \begin{pmatrix} \mathbf{a}^T \cdot \mathbf{H}_{\text{SpinSpin}} \cdot \mathbf{a} & \mathbf{a}^T \cdot \mathbf{H}_{\text{SpinSpin}} \cdot \mathbf{b} & \mathbf{a}^T \cdot \mathbf{H}_{\text{SpinSpin}} \cdot \mathbf{c} & \mathbf{a}^T \cdot \mathbf{H}_{\text{SpinSpin}} \cdot \mathbf{d} \\ \mathbf{b}^T \cdot \mathbf{H}_{\text{SpinSpin}} \cdot \mathbf{a} & \mathbf{b}^T \cdot \mathbf{H}_{\text{SpinSpin}} \cdot \mathbf{b} & \mathbf{b}^T \cdot \mathbf{H}_{\text{SpinSpin}} \cdot \mathbf{c} & \mathbf{b}^T \cdot \mathbf{H}_{\text{SpinSpin}} \cdot \mathbf{d} \\ \mathbf{c}^T \cdot \mathbf{H}_{\text{SpinSpin}} \cdot \mathbf{a} & \mathbf{c}^T \cdot \mathbf{H}_{\text{SpinSpin}} \cdot \mathbf{b} & \mathbf{c}^T \cdot \mathbf{H}_{\text{SpinSpin}} \cdot \mathbf{c} & \mathbf{c}^T \cdot \mathbf{H}_{\text{SpinSpin}} \cdot \mathbf{d} \\ \mathbf{d}^T \cdot \mathbf{H}_{\text{SpinSpin}} \cdot \mathbf{a} & \mathbf{d}^T \cdot \mathbf{H}_{\text{SpinSpin}} \cdot \mathbf{b} & \mathbf{d}^T \cdot \mathbf{H}_{\text{SpinSpin}} \cdot \mathbf{c} & \mathbf{d}^T \cdot \mathbf{H}_{\text{SpinSpin}} \cdot \mathbf{d} \end{pmatrix} \right) = \begin{pmatrix} 1 \\ -3 \\ 1 \\ 1 \end{pmatrix}$$

$$\text{eigenvecs} \begin{pmatrix} a^T \cdot H_{\text{SpinSpin}} \cdot a & a^T \cdot H_{\text{SpinSpin}} \cdot b & a^T \cdot H_{\text{SpinSpin}} \cdot c & a^T \cdot H_{\text{SpinSpin}} \cdot d \\ b^T \cdot H_{\text{SpinSpin}} \cdot a & b^T \cdot H_{\text{SpinSpin}} \cdot b & b^T \cdot H_{\text{SpinSpin}} \cdot c & b^T \cdot H_{\text{SpinSpin}} \cdot d \\ c^T \cdot H_{\text{SpinSpin}} \cdot a & c^T \cdot H_{\text{SpinSpin}} \cdot b & c^T \cdot H_{\text{SpinSpin}} \cdot c & c^T \cdot H_{\text{SpinSpin}} \cdot d \\ d^T \cdot H_{\text{SpinSpin}} \cdot a & d^T \cdot H_{\text{SpinSpin}} \cdot b & d^T \cdot H_{\text{SpinSpin}} \cdot c & d^T \cdot H_{\text{SpinSpin}} \cdot d \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0.707 & 0.707 & 0 & 0 \\ 0.707 & -0.707 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Identical to the previous calculation, this method also yields an upper triplet state at  $E = 1$  and a lower singlet at  $E = -3$ . Two of the four final states are superpositions of  $|+-\rangle$  and  $|+-\rangle$ . In other words, we have found the eigenstates of the spin-spin energy operator as is shown below. Using these states the spin-spin energy matrix is diagonal.

$$a := \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad b := \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ 0 \end{pmatrix} \quad c := \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} \quad d := \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} a^T \cdot H_{\text{SpinSpin}} \cdot a & a^T \cdot H_{\text{SpinSpin}} \cdot b & a^T \cdot H_{\text{SpinSpin}} \cdot c & a^T \cdot H_{\text{SpinSpin}} \cdot d \\ b^T \cdot H_{\text{SpinSpin}} \cdot a & b^T \cdot H_{\text{SpinSpin}} \cdot b & b^T \cdot H_{\text{SpinSpin}} \cdot c & b^T \cdot H_{\text{SpinSpin}} \cdot d \\ c^T \cdot H_{\text{SpinSpin}} \cdot a & c^T \cdot H_{\text{SpinSpin}} \cdot b & c^T \cdot H_{\text{SpinSpin}} \cdot c & c^T \cdot H_{\text{SpinSpin}} \cdot d \\ d^T \cdot H_{\text{SpinSpin}} \cdot a & d^T \cdot H_{\text{SpinSpin}} \cdot b & d^T \cdot H_{\text{SpinSpin}} \cdot c & d^T \cdot H_{\text{SpinSpin}} \cdot d \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix}$$

The spin-spin hyperfine interaction is the basis of the hydrogen maser. The triplet state is selected using a Stern-Gerlach magnet and then 21 cm photons induce a triplet-singlet transition creating a coherent beam of photons.

The following table calculates expectation values for the z-direction spin for triplet and singlet states. In the first column, the expectation values for z-direction measurements jointly on the electron and proton are calculated. The next two columns calculate the z-direction expectation values for the electron and proton independently.

$$\begin{pmatrix} a^T \cdot \text{kroncker}(\sigma_z, \sigma_z) \cdot a & a^T \cdot \text{kroncker}(\sigma_z, I) \cdot a & a^T \cdot \text{kroncker}(I, \sigma_z) \cdot a \\ b^T \cdot \text{kroncker}(\sigma_z, \sigma_z) \cdot b & b^T \cdot \text{kroncker}(\sigma_z, I) \cdot b & b^T \cdot \text{kroncker}(I, \sigma_z) \cdot b \\ c^T \cdot \text{kroncker}(\sigma_z, \sigma_z) \cdot c & c^T \cdot \text{kroncker}(\sigma_z, I) \cdot c & c^T \cdot \text{kroncker}(I, \sigma_z) \cdot c \\ d^T \cdot \text{kroncker}(\sigma_z, \sigma_z) \cdot d & d^T \cdot \text{kroncker}(\sigma_z, I) \cdot d & d^T \cdot \text{kroncker}(I, \sigma_z) \cdot d \end{pmatrix} = \begin{pmatrix} 1 & 1 & 1 \\ -1 & 0 & 0 \\ 1 & -1 & -1 \\ -1 & 0 & 0 \end{pmatrix}$$

The **b** and **d** states are entangled Bell states. Note that in these states the expectation values for the individual spins are 0, indicating complete randomness. Collectively, however, the electron and proton always show opposite spin states leading to a joint expectation value of -1. In other words, the measurement result for the z-spin for either the electron or proton is completely random, but once the result for one of the particles is obtained, the other particle's spin state can be predicted with certainty.