

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.

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

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.

$$E := \text{eigenvals}(H_{SpinSpin}) \quad V := \text{eigenvecs}(H_{SpinSpin})$$

$$\text{augment}(E, V^T)^T = \begin{pmatrix} 1 & -3 & 1 & 1 \\ 0 & 0 & 1 & 0 \\ 0.707 & 0.707 & 0 & 0 \\ 0.707 & -0.707 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Using this approach we get, in short order, the same results as provided in the first three sections of Feynman's text. We have a singlet ground state and a triply degenerate excited state, and we haven't made explicit use of the obvious electron-proton states: $|++\rangle$, $|+-\rangle$, $|-\rangle$ and $|--\rangle$. If we write these states out in tensor format we can use them to achieve the same final result.

First we write the spin states in vector format:

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

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

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

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

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

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

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

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

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.

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

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

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.