The Hyperfine Splitting in the Hydrogen Atom

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The purpose of this tutorial is to provide a much abreviated 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: |++>, |+->, |-+> and |-->. The magnetic spin-spin operator is.

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

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.

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

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

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

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

We know 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.

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

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

These results are expressed in more familiar form below.

Triplet state $E_T = 1$

$$|T\rangle_1 = |\uparrow\rangle_p |\uparrow\rangle_e$$

$$|T\rangle_0 = \frac{1}{\sqrt{2}}\left[|\uparrow\rangle_p |\downarrow\rangle_e + |\downarrow\rangle_p |\uparrow\rangle_e\right]$$

$$|T\rangle_{-1} = |\downarrow\rangle_p |\downarrow\rangle_e$$

Singlet state $E_S = -3$

$$|S\rangle_0 = \frac{1}{\sqrt{2}}\left[|\uparrow\rangle_p |\downarrow\rangle_e - |\downarrow\rangle_p |\uparrow\rangle_e\right]$$

The hyperfine interaction can be analyzed in terms of the Bell states:

$$\Phi_p := \frac{1}{\sqrt{2}}\cdot\begin{pmatrix}1\\0\\0\\1\end{pmatrix} \qquad \Phi_m := \frac{1}{\sqrt{2}}\cdot\begin{pmatrix}1\\0\\0\\-1\end{pmatrix} \qquad \Psi_p := \frac{1}{\sqrt{2}}\cdot\begin{pmatrix}0\\1\\1\\0\end{pmatrix} \qquad \Psi_m := \frac{1}{\sqrt{2}}\cdot\begin{pmatrix}0\\1\\-1\\0\end{pmatrix}$$

T_0 and S_0 are Ψ_p and Ψ_m. $\quad \Psi_p{}^T\cdot H_{SpinSpin}\cdot\Psi_p = 1 \qquad \Psi_m{}^T\cdot H_{SpinSpin}\cdot\Psi_m = -3$

The first two Bell states, Φ_p and Φ_m, have eigenvalues of 1 and therefore belong to the triplet state.

$$\Phi_p{}^T\cdot H_{SpinSpin}\cdot\Phi_p = 1 \qquad \Phi_m{}^T\cdot H_{SpinSpin}\cdot\Phi_m = 1$$

T_1 and T_{-1} are superpositions of Φ_p and Φ_m.

$$\frac{\Phi_p + \Phi_m}{\sqrt{2}} = \begin{pmatrix}1\\0\\0\\0\end{pmatrix} \quad \begin{pmatrix}1\\0\\0\\0\end{pmatrix}^T\cdot H_{SpinSpin}\cdot\begin{pmatrix}1\\0\\0\\0\end{pmatrix} = 1 \qquad \frac{\Phi_p - \Phi_m}{\sqrt{2}} = \begin{pmatrix}0\\0\\0\\1\end{pmatrix} \quad \begin{pmatrix}0\\0\\0\\1\end{pmatrix}^T\cdot H_{SpinSpin}\cdot\begin{pmatrix}0\\0\\0\\1\end{pmatrix} = 1$$

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.