

# Quantum Mechanics I

## Week 14 (Solutions)

Spring Semester 2025

### 1 Finding Clebsch–Gordan coefficients

Consider two angular momenta  $\hat{\mathbf{J}}_1$  and  $\hat{\mathbf{J}}_2$  with  $j_1 = 1$  and  $j_2 = \frac{3}{2}$ . We define

- the (tensorial) product basis

$$B_1 = \left\{ |j_1 = 1, m_1\rangle \otimes |j_2 = \frac{3}{2}, m_2\rangle \right\} \equiv \{|m_1\rangle |m_2\rangle\}, \quad (1.1)$$

- the total angular momentum basis  $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$ ,

$$B_2 = \left\{ |j_1 = 1, j_2 = \frac{3}{2}, j, m\rangle \right\} \equiv \{|j, m\rangle\}. \quad (1.2)$$

(a) What is the dimension of the Hilbert space for this system?

The first angular momentum can be in  $3 = 2j_1 + 1$  basis states, and the second angular momentum can be in  $4 = 2j_2 + 1$  basis states. Thus the dimension of the Hilbert space is  $3 \times 4 = 12$ .

(b) What are the possible values of the total angular momentum  $j$ , obtained by adding  $\hat{\mathbf{J}}_1$  and  $\hat{\mathbf{J}}_2$ ?

Using the formulas of addition of angular momenta, the possible values of the total angular momentum are  $|j_1 - j_2|, \dots, |j_1 - j_2| + 1, \dots, j_1 + j_2$ . In this case, the possible values of the total angular momentum are  $j = 5/2, j = 3/2$ , and  $j = 1/2$ .

(c) On the plane  $(m_1, m_2)$ , plot the possible values of  $m_1$  and  $m_2$ , and draw the lines  $m = \text{constant}$ , where  $m = m_1 + m_2$ .

The possible values of  $m_1, m_2$ , and the lines of constant  $m = m_1 + m_2$  are shown in Fig. 1.

(d) What is the dimension of the subspace with a fixed  $m$  for each possible  $m$ ?

The dimension is equal to the number of points lying on the lines in Fig. 1. The space with  $m = 5/2$  has only one state ( $|+1, +3/2\rangle$ ). This corresponds to the top-right corner in Fig. 1.

The space with  $m = 3/2$  has two states ( $|0, +3/2\rangle, |+1, +1/2\rangle$ ). The space with  $m = 1/2$  has three states ( $| -1, +3/2\rangle, |0, +1/2\rangle, |+1, -1/2\rangle$ ).

The result for any  $m = -5/2, -3/2, -1/2, 1/2, 3/2, 5/2$  can be written compactly as:  $g(m) = |7/2 - |m||$ .

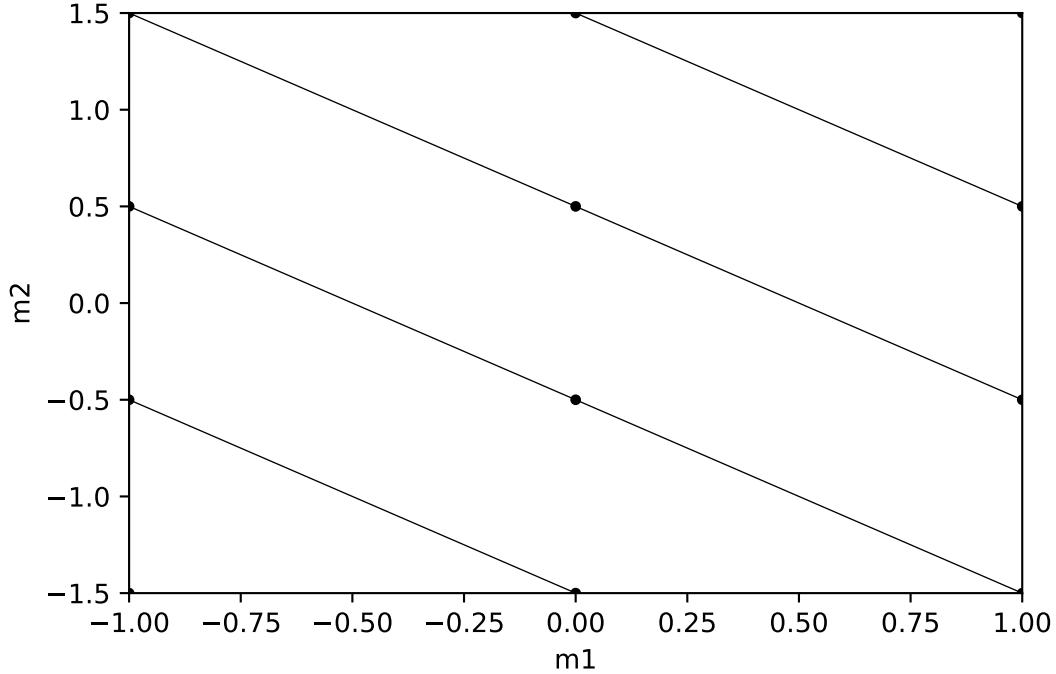


Figure 1: Possible values of  $m_1$  and  $m_2$ , and of the lines at which  $m_1 + m_2$  is constant.

(e) Calculate the Clebsch–Gordan coefficients  $\langle m_1, m_2 | j, m \rangle$  for  $j = 5/2$  and  $-\frac{5}{2} \leq m \leq \frac{5}{2}$ . Hint: Apply  $J^-$  to  $|j = \frac{5}{2}, m = \frac{5}{2}\rangle$  and go "up the ladder".

From the theory of addition of angular momenta, we know that we can break the Hilbert space of the 2 angular momenta, which as seen before is 12-dimensional, into a sector with  $j = 5/2$ , a sector with  $j = 3/2$ , and a sector with  $j = 1/2$ . The state<sup>1</sup>  $|m_1 = +1, m_2 = +3/2\rangle$  has  $m = +5/2$ , which is the maximum possible value of the angular momentum. This state must belong to the sector with  $j = 5/2$ . So the first Clebsch-Gordan coefficient which we find is  $\langle 1, +1, 3/2, +3/2 | 5/2, +5/2 \rangle = 1$ .

The states  $m = +3/2$  are as seen before,  $|1, 0; 3/2, +3/2\rangle$  and  $|1, 1; 3/2, 1/2\rangle$ , we have to find the linear combinations of these which belong respectively to the sector with  $j = 5/2$  and with  $j = 3/2$ .

To do this we can use that  $\hat{J}^- |5/2, +5/2\rangle$  must have  $j = 5/2$  (as  $J^-$  commutes with the operator  $\hat{J}^2$ ). Using  $\hat{J} = \hat{j}_1 + \hat{j}_2$  and using  $\hat{j}_1^- |j_1, m_1; j_2, m_2\rangle = \sqrt{j_1(j_1 + 1) - m_1(m_1 - 1)} |j_1, m_1 - 1; j_2, m_2\rangle$ ,

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<sup>1</sup>In the following, to clarify the notation, we include in the definition of the states their total angular momentum, so that the states are written as  $|j_1 m_1, j_2 m_2\rangle$ . For the states of the composite system in the  $j, m$  basis we write  $|j, m\rangle$ .

$\hat{j}_2^- |j_1, m_1; j_2, m_2\rangle = \sqrt{j_2(j_2+1) - m_2(m_2-1)} |j_1, m_1; j_2, m_2-1\rangle$  we find:

$$\begin{aligned}
\hat{j}^- |5/2, +5/2\rangle &= \left( \hat{j}_1 + \hat{j}_2 \right) |1, +1; 3/2, +3/2\rangle \\
&= \sqrt{\frac{5}{2} \times \left( \frac{5}{2} + 1 \right) - \frac{5}{2} \times \left( \frac{5}{2} - 1 \right)} |5/2, +3/2\rangle = \sqrt{5} |5/2, +3/2\rangle \\
&= \sqrt{1 \times 2 - 1 \times 0} |1, 0; 3/2, +3/2\rangle \\
&\quad + \sqrt{\frac{3}{2} \times \frac{5}{2} - \frac{3}{2} \times \frac{1}{2}} |1, +1; 3/2, +1/2\rangle \\
&= \sqrt{2} \left| 1, 0; \frac{3}{2}, +\frac{3}{2} \right\rangle + \sqrt{3} \left| 1, +1; \frac{3}{2}, +\frac{1}{2} \right\rangle , \\
\end{aligned} \tag{1.3}$$

which implies

$$\left| \frac{5}{2}, +\frac{3}{2} \right\rangle = \sqrt{\frac{2}{5}} \left| 1, 0; \frac{3}{2}, +\frac{3}{2} \right\rangle + \sqrt{\frac{3}{5}} \left| 1, +1; \frac{3}{2}, +\frac{1}{2} \right\rangle . \tag{1.4}$$

Applying  $\hat{J}^-$  other times, we get iteratively all states belonging to the  $j = 5/2$  sector. The result is:

$$\begin{aligned}
\left| \frac{5}{2}, +\frac{1}{2} \right\rangle &= \frac{1}{\sqrt{\frac{5}{2} \times (\frac{5}{2} + 1) - \frac{3}{2} \times (\frac{3}{2} - 1)}} \times \left( \sqrt{\frac{2}{5}} \left( \sqrt{2} \left| 1, -1; \frac{3}{2}, +\frac{3}{2} \right\rangle \right. \right. \\
&\quad \left. \left. + \sqrt{3} \left| 1, 0; \frac{3}{2}, +\frac{1}{2} \right\rangle \right) + \sqrt{\frac{3}{5}} \left( \sqrt{2} \left| 1, 0; \frac{3}{2}, +\frac{1}{2} \right\rangle + 2 \left| 1, +1; \frac{3}{2}, -\frac{1}{2} \right\rangle \right) \right) \\
&= \frac{1}{\sqrt{10}} \left( \left| 1, -1; \frac{3}{2}, +\frac{3}{2} \right\rangle + \sqrt{6} \left| 1, 0; \frac{3}{2}, +\frac{1}{2} \right\rangle + \sqrt{3} \left| 1, +1; \frac{3}{2}, -\frac{1}{2} \right\rangle \right) . \\
\end{aligned} \tag{1.5}$$

Similarly,

$$\left| \frac{5}{2}, -\frac{1}{2} \right\rangle = \frac{1}{\sqrt{10}} \left( \left| 1, 1; \frac{3}{2}, -\frac{3}{2} \right\rangle + \sqrt{6} \left| 1, 0; \frac{3}{2}, -\frac{1}{2} \right\rangle + \sqrt{3} \left| 1, -1; \frac{3}{2}, \frac{1}{2} \right\rangle \right) , \tag{1.6}$$

$$\left| \frac{5}{2}, -\frac{3}{2} \right\rangle = \sqrt{\frac{2}{5}} \left| 1, 0; \frac{3}{2}, -\frac{3}{2} \right\rangle + \sqrt{\frac{3}{5}} \left| 1, -1; \frac{3}{2}, -\frac{1}{2} \right\rangle , \tag{1.7}$$

$$\left| \frac{5}{2}, -\frac{5}{2} \right\rangle = \left| 1, -1; \frac{3}{2}, -\frac{3}{2} \right\rangle . \tag{1.8}$$

(f) Using the orthogonality relation  $\langle j', m' | j, m \rangle = \delta_{j'j}$ , express  $|j = \frac{3}{2}, m = \frac{3}{2}\rangle$  in the basis  $B_1$ .

We have expressed all the states  $|\frac{5}{2}, m\rangle$  in  $B_1$ , and now we move to  $|\frac{3}{2}, \frac{3}{2}\rangle$ . It will be a linear combination of  $|1\rangle |\frac{1}{2}\rangle$  and  $|0\rangle |\frac{3}{2}\rangle$ , just like  $|\frac{5}{2}, \frac{3}{2}\rangle$ . The idea here is that, using a linear combination of these two vectors we can build only two vectors (up to an overall phase) that are orthonormal. Thus,  $|\frac{3}{2}, \frac{3}{2}\rangle$  is the only vector in the

sub-space  $m = \frac{3}{2}$  orthonormal to  $|\frac{5}{2}, \frac{3}{2}\rangle$ . We express  $|\frac{3}{2}, \frac{3}{2}\rangle$  using the two states in  $B_1$  with  $m = \frac{3}{2}$ :

$$|\frac{3}{2}, \frac{3}{2}\rangle = \alpha |0\rangle |\frac{3}{2}\rangle + \beta |1\rangle |\frac{1}{2}\rangle. \quad (1.9)$$

Then, its product with  $|\frac{5}{2}, \frac{3}{2}\rangle$  is

$$\langle \frac{5}{2}, \frac{3}{2} | \frac{3}{2}, \frac{3}{2} \rangle = \sqrt{\frac{2}{5}} \alpha + \sqrt{\frac{3}{5}} \beta. \quad (1.10)$$

By the orthogonality relation this product must be zero, so we have  $\frac{\alpha}{\beta} = -\sqrt{\frac{3}{2}}$ . Using the normalization condition  $|\alpha|^2 + |\beta|^2 = 1$  and assuming the phase of  $\alpha$  to be zero, we obtain

$$|\frac{3}{2}, \frac{3}{2}\rangle = \sqrt{\frac{3}{5}} |0\rangle |\frac{3}{2}\rangle - \sqrt{\frac{2}{5}} |1\rangle |\frac{1}{2}\rangle. \quad (1.11)$$

(g) Calculate the Clebsch–Gordan coefficients  $\langle m_1, m_2 | j, m \rangle$  for  $j = 3/2$  and  $j = 1/2$ .

The coefficients for  $|\frac{3}{2}, \frac{3}{2}\rangle$  were determined in the previous question. Now, for the state  $|\frac{3}{2}, \frac{1}{2}\rangle$ , we use the same method as in part (e). We find

$$|\frac{3}{2}, \frac{1}{2}\rangle = \sqrt{\frac{2}{5}} | -1 \rangle |\frac{3}{2}\rangle + \sqrt{\frac{1}{15}} | 0 \rangle |\frac{1}{2}\rangle - \sqrt{\frac{8}{15}} | 1 \rangle | -\frac{1}{2}\rangle. \quad (1.12)$$

As for the states  $|\frac{3}{2}, m\rangle$  with  $m < 0$ , we resort to symmetries. In particular, for each pair of  $(j, m)$ , there exists a phase factor  $\alpha_j$  such that  $\forall m_1, m_2$ , we have:

$$\langle m_1, m_2 | j, m \rangle = e^{i\alpha_j} \langle -m_1, -m_2 | j, -m \rangle. \quad (1.13)$$

This phase depends only on  $j$  and not on  $m$ . Since all Clebsch–Gordan coefficients are real, the phase takes only two values,  $\pm 1$ . Thus,

$$\langle m_1, m_2 | j, m \rangle = (-1)^{j_1 + j_2 - j} \langle -m_1, -m_2 | j, -m \rangle \quad (1.14)$$

We only need to determine the sign for one term: for example, when applying  $\hat{J}^-$  to Eq. (1.12), the state  $|1\rangle | -\frac{1}{2}\rangle$  becomes  $|1\rangle | -\frac{3}{2}\rangle$  and its coefficient acquires a positive factor  $\hbar\sqrt{\dots}$ , which is therefore negative. We deduce that for  $j = \frac{3}{2}$  the Clebsch–Gordan coefficients are antisymmetric for  $m \rightarrow -m$ . Therefore we have

$$|\frac{3}{2}, -\frac{1}{2}\rangle = \sqrt{\frac{8}{15}} | -1 \rangle |\frac{1}{2}\rangle - \sqrt{\frac{1}{15}} | 0 \rangle | -\frac{1}{2}\rangle - \sqrt{\frac{2}{5}} | 1 \rangle | -\frac{3}{2}\rangle, \quad (1.15)$$

$$|\frac{3}{2}, -\frac{3}{2}\rangle = \sqrt{\frac{2}{5}} | -1 \rangle | -\frac{1}{2}\rangle - \sqrt{\frac{3}{5}} | 0 \rangle | -\frac{3}{2}\rangle. \quad (1.16)$$

For the case of  $j = 1/2$ , we follow the same procedure as with the  $j = 3/2$  case. The state  $|\frac{1}{2}, \frac{1}{2}\rangle$  belongs to the sub-space generated by the states  $| -1 \rangle |\frac{3}{2}\rangle$ ,  $| 0 \rangle |\frac{1}{2}\rangle$ , and  $| 1 \rangle | -\frac{1}{2}\rangle$ , and is orthogonal to the states  $|\frac{5}{2}, \frac{1}{2}\rangle$  and  $|\frac{3}{2}, \frac{1}{2}\rangle$  whose decompositions we already know in the basis  $|m_1\rangle |m_2\rangle$ . To simplify the calculations, we notice that, as  $|\frac{5}{2}, \frac{1}{2}\rangle$  and  $|\frac{3}{2}, \frac{1}{2}\rangle$  are normalized,  $|\frac{1}{2}, \frac{1}{2}\rangle$  is obtained (up to a phase) by the vector product of these two vectors (since all of them have to be orthogonal to each

other). In the basis  $\{|-1\rangle |\frac{3}{2}\rangle, |0\rangle |\frac{1}{2}\rangle, |1\rangle |-\frac{1}{2}\rangle\}$  we obtain the coefficients of this vector product:

$$\begin{pmatrix} \sqrt{\frac{1}{10}} \\ \sqrt{\frac{3}{5}} \\ \sqrt{\frac{3}{10}} \end{pmatrix} \times \begin{pmatrix} \sqrt{\frac{2}{5}} \\ \sqrt{\frac{1}{15}} \\ -\sqrt{\frac{8}{15}} \end{pmatrix} = \begin{pmatrix} -\sqrt{\frac{1}{2}} \\ \sqrt{\frac{1}{3}} \\ -\sqrt{\frac{1}{6}} \end{pmatrix}. \quad (1.17)$$

By convention, we choose  $\langle 1, \frac{1}{2} | \frac{1}{2}, \frac{1}{2} \rangle > 0$ ; therefore

$$|\frac{1}{2}, \frac{1}{2}\rangle = \frac{1}{\sqrt{2}} |-1\rangle |\frac{3}{2}\rangle - \frac{1}{\sqrt{3}} |0\rangle |\frac{1}{2}\rangle + \frac{1}{\sqrt{6}} |1\rangle |-\frac{1}{2}\rangle. \quad (1.18)$$

Applying the ladder operator  $\hat{J}^-$  to the left-hand side and  $\hat{J}_1^- + \hat{J}_2^-$  to the right-hand side, we obtain

$$|\frac{1}{2}, -\frac{1}{2}\rangle = \frac{1}{\sqrt{6}} |-1\rangle |\frac{1}{2}\rangle - \frac{1}{\sqrt{3}} |0\rangle |-\frac{1}{2}\rangle + \sqrt{\frac{1}{2}} |1\rangle |-\frac{3}{2}\rangle. \quad (1.19)$$

The coefficients are symmetric under the transformation  $m \rightarrow -m$ .

## 2 Pair of particles

We consider a system of two particles with spins  $s_1 = \frac{3}{2}$  and  $s_2 = \frac{1}{2}$ , and their interaction is described by the following approximate Hamiltonian

$$\hat{H} = \frac{4E_0}{\hbar^2} \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2, \quad (2.1)$$

where  $E_0$  is a constant with units of energy. The system is initialized in the following simultaneous eigenstate of  $S_1^2, S_2^2, S_{1z}, S_{2z}$ :

$$|\psi(0)\rangle = |\frac{3}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle. \quad (2.2)$$

Determine the state of the system at time  $t > 0$ . What is the probability of measuring the state  $|\frac{3}{2}, \frac{1}{2}; \frac{3}{2}, -\frac{1}{2}\rangle$ ? We use the notation  $|s_1, s_2; m_1, m_2\rangle$ .

Due to the coupling term between the two spins, the Hamiltonian is not diagonal in the uncoupled basis. We can circumvent this by expressing it in the coupled basis. Firstly, using  $\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2 = \hat{\mathbf{S}}$ , we can readily show that:

$$\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = \frac{1}{2} [\hat{\mathbf{S}}^2 - \hat{\mathbf{S}}_1^2 - \hat{\mathbf{S}}_2^2]. \quad (2.3)$$

Using this result, the Hamiltonian takes the following form:

$$\hat{H} = \frac{2E_0}{\hbar^2} [\hat{\mathbf{S}}^2 - \hat{\mathbf{S}}_1^2 - \hat{\mathbf{S}}_2^2]. \quad (2.4)$$

It is easily verified that the Hamiltonian is diagonal in the coupled basis  $|s_1, s_2; s, m\rangle$  since

$$S^2 |s_1, s_2; s, m\rangle = \hbar^2 s(s+1) |s_1, s_2; s, m\rangle, \quad (2.5)$$

$$S_{1/2}^2 |s_1, s_2; s, m\rangle = \hbar^2 s_{1,2}(s_{1,2}+1) |s_1, s_2; s, m\rangle. \quad (2.6)$$

To determine the time evolution of the system, we need to express the initial state, which is simultaneous eigenstate of  $S_1^2$ ,  $S_2^2$ ,  $S_{1z}$ ,  $S_{2z}$ , in the coupled basis  $|s_1, s_2; s, m\rangle$ . The initial state has a total quantum number  $m = 1$  and from this fact, we can write down a general superposition

$$|\frac{3}{2}, \frac{1}{2}; 1, 1\rangle = a |\frac{3}{2}, \frac{1}{2}; \frac{3}{2}, -\frac{1}{2}\rangle + b |\frac{3}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle, \quad (2.7)$$

$$|\frac{3}{2}, \frac{1}{2}; 2, 1\rangle = c |\frac{3}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle + d |\frac{3}{2}, \frac{1}{2}; \frac{3}{2}, -\frac{1}{2}\rangle \quad (2.8)$$

where we have used the convention  $|s_1, s_2; s, m\rangle$  and  $|s_1, s_2; m_1, m_2\rangle$  for the kets in the coupled and uncoupled bases, respectively. Our task now is to determine the coefficients. We start first by applying the raising operator on the first state,

$$\hat{S}^+ |\frac{3}{2}, \frac{1}{2}; 1, 1\rangle = a\hbar |\frac{3}{2}, \frac{1}{2}; \frac{3}{2}, \frac{1}{2}\rangle + b\hbar\sqrt{3} |\frac{3}{2}, \frac{1}{2}; \frac{3}{2}, \frac{1}{2}\rangle. \quad (2.9)$$

Since  $\hat{S}^+ |\frac{3}{2}, \frac{1}{2}; 1, 1\rangle$ , and due to the normalization condition, we find  $a = -\sqrt{3}/2$  and  $b = 1/2$ . Similarly, for the second state, we have:

$$\hat{S}^+ |\frac{3}{2}, \frac{1}{2}; 2, 1\rangle = c\hbar\sqrt{3} |\frac{3}{2}, \frac{1}{2}; \frac{3}{2}, \frac{1}{2}\rangle + d\hbar |\frac{3}{2}, \frac{1}{2}; \frac{3}{2}, \frac{1}{2}\rangle, \quad (2.10)$$

and since  $\hat{S}^+ |\frac{3}{2}, \frac{1}{2}; 2, 1\rangle$ , we obtain  $c = \sqrt{3}/2$  and  $d = 1/2$  (and the normalization condition was used). In summary, we have:

$$|\frac{3}{2}, \frac{1}{2}; 1, 1\rangle = -\frac{\sqrt{3}}{2} |\frac{3}{2}, \frac{1}{2}; \frac{3}{2}, -\frac{1}{2}\rangle + \frac{1}{2} |\frac{3}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle, \quad (2.11)$$

$$|\frac{3}{2}, \frac{1}{2}; 2, 1\rangle = \frac{\sqrt{3}}{2} |\frac{3}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle + \frac{1}{2} |\frac{3}{2}, \frac{1}{2}; \frac{3}{2}, -\frac{1}{2}\rangle. \quad (2.12)$$

Using this result, we can write our initial state in terms of the coupled states by simple algebraic manipulation,

$$|\frac{3}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle = \frac{\sqrt{3}}{2} |\frac{3}{2}, \frac{1}{2}; 2, 1\rangle + \frac{1}{2} |\frac{3}{2}, \frac{1}{2}; 1, 1\rangle. \quad (2.13)$$

We continue by considering the time-evolved state by applying the time evolution operator  $|\psi(t)\rangle = \exp\{-i\hat{H}t/\hbar\} |\psi(0)\rangle$ . We write this explicitly as follows:

$$\begin{aligned} |\psi(t)\rangle &= \exp\left\{-i\frac{(2E_0/\hbar^2)t}{\hbar} [\hat{\mathbf{S}}^2 - \hat{\mathbf{S}}_1^2 - \hat{\mathbf{S}}_2^2]\right\} \left[ \frac{\sqrt{3}}{2} |\frac{3}{2}, \frac{1}{2}; 2, 1\rangle + \frac{1}{2} |\frac{3}{2}, \frac{1}{2}; 1, 1\rangle \right] = \\ &= \frac{\sqrt{3}}{2} e^{-iE_2 t/\hbar} |\frac{3}{2}, \frac{1}{2}; 2, 1\rangle + \frac{1}{2} e^{-iE_1 t/\hbar} |\frac{3}{2}, \frac{1}{2}; 1, 1\rangle \end{aligned}$$

where  $E_1 = -5E_0$  and  $E_2 = 3E_0$ . In the first to second line, we have used Eqs. (2.5), (2.6).

Finally, the probability to find the system in the state  $|\frac{3}{2}, \frac{1}{2}; \frac{3}{2}, -\frac{1}{2}\rangle$  is given by:

$$P = |\langle \frac{3}{2}, \frac{1}{2}; \frac{3}{2}, -\frac{1}{2} | \psi(t) \rangle|^2 = \frac{3}{4} \sin^2 \frac{(E_2 - E_1)t}{\hbar} = \frac{3}{4} \sin^2 \frac{8E_0 t}{\hbar}. \quad (2.14)$$

### 3 Hyperfine Splitting of a Hydrogen Ground State in a Magnetic Field

A. The hyperfine splitting refers to the splitting of energy levels in an atom due to the interaction between the nucleus and the electron cloud. For the Hydrogen atom, this is the interaction between the proton and the electron. This splitting is caused by electromagnetic multipole interaction and results in very small energy shifts and splitting. The corresponding Hamiltonian of the interaction is:

$$H_{HFS} = \frac{4\epsilon}{\hbar^2} \mathbf{S}_e \cdot \mathbf{S}_p. \quad (3.1)$$

Note that this is the simplified form of the interaction, which is relevant for the ground state of the Hydrogen atom. The parameter  $\epsilon$  is a positive constant with units of energy, and it is defined as:

$$\epsilon = \frac{\mu_0 g_p e^2}{3\pi m_p m_e a^3}, \quad (3.2)$$

where  $\mu_0$  is the magnetic permeability of free space,  $g_p$  is the gyromagnetic ratio of the proton,  $e$  is the electron charge and  $m_p, m_e$  are the masses of the proton and electron, respectively.

There are two natural bases in this problem. The uncoupled basis  $|m_e, m_p\rangle$  (first entry: electron, second entry: proton) is

$$|1\rangle = |\uparrow\uparrow\rangle, \quad |2\rangle = |\uparrow\downarrow\rangle, \quad |3\rangle = |\downarrow\uparrow\rangle, \quad |4\rangle = |\downarrow\downarrow\rangle. \quad (3.3)$$

The coupled basis  $|j m\rangle$  of eigenstates of  $J^2$  and  $J_z$ , is

$$|1\rangle = |1, 1\rangle, \quad |2\rangle = |1, 0\rangle, \quad |3\rangle = |1, -1\rangle, \quad |4\rangle = |0, 0\rangle, \quad (3.4)$$

where  $\mathbf{J} = \mathbf{S}_e + \mathbf{S}_p$ .

(a) Find the matrix elements of  $H_{HFS}$  in the uncoupled basis. Calculate the energy eigenvalues and the eigenvectors.

We write the Hamiltonian in terms of the components of the spin operators of each particle, as follows:

$$\hat{H} = \epsilon[\sigma_e^x \sigma_p^x + \sigma_e^y \sigma_p^y + \sigma_e^z \sigma_p^z]. \quad (3.5)$$

where  $\sigma_{p,e}^{x,y,z}$  are the Pauli matrices. Acting on each ket of the uncoupled basis with the above Hamiltonian, and then taking the bra for all possible combinations, we find the matrix elements of the Hamiltonian  $\langle i | H | j \rangle$  where  $i, j \in \{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$ . The corresponding matrix form is

$$H = \begin{pmatrix} |\uparrow\uparrow\rangle & |\uparrow\downarrow\rangle & |\downarrow\uparrow\rangle & |\downarrow\downarrow\rangle \\ |\uparrow\downarrow\rangle & \epsilon & 0 & 0 \\ |\downarrow\uparrow\rangle & 0 & -\epsilon & 2\epsilon \\ |\downarrow\downarrow\rangle & 0 & 2\epsilon & -\epsilon \end{pmatrix}. \quad (3.6)$$

Due to the block-diagonal form of the above matrix, we can easily extract the energies and the corresponding eigenvectors. For the  $1 \times 1$  blocks, we have:

$$|\psi_1\rangle = |\uparrow, \uparrow\rangle \quad (E_1 = \epsilon), \quad |\psi_4\rangle = |\downarrow, \downarrow\rangle \quad (E_4 = \epsilon). \quad (3.7)$$

Then, we have one  $2 \times 2$  block, which we can diagonalize and find:

$$|\psi_2\rangle = \frac{1}{\sqrt{2}} \left[ |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right] \quad (E_3 = \epsilon), \quad |\psi_3\rangle = \frac{1}{\sqrt{2}} \left[ |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right], \quad (E_3 = -3\epsilon). \quad (3.8)$$

There is a three-fold degeneracy in the energy  $E = \epsilon$ , which we recognize as the triplet state.

(b) Find the matrix elements of  $H_{HFS}$  in the coupled basis. Calculate the energy eigenvalues and the eigenvectors.

The Hamiltonian is now expressed in terms of the total spin operator. By using the fact that  $\hat{\mathbf{S}}_e + \hat{\mathbf{S}}_p = \hat{\mathbf{S}}$ , we find:

$$\hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p = \frac{1}{2} \left[ \hat{\mathbf{S}}^2 - \hat{\mathbf{S}}_e^2 - \hat{\mathbf{S}}_p^2 \right]. \quad (3.9)$$

The Hamiltonian then takes the following form:

$$\hat{H} = \frac{2\epsilon}{\hbar^2} \left[ \hat{\mathbf{S}}^2 - \hat{\mathbf{S}}_e^2 - \hat{\mathbf{S}}_p^2 \right]. \quad (3.10)$$

Following a very similar procedure as in part (a), we can compute the matrix elements  $\langle i | H | j \rangle$  where  $i, j \in \{|1, 1\rangle, |1, 0\rangle, |1, -1\rangle, |0, 0\rangle\}$ . The corresponding matrix form is

$$H = \begin{matrix} & |1, 1\rangle & |1, 0\rangle & |1, -1\rangle & |0, 0\rangle \\ \begin{matrix} |1, 1\rangle \\ |1, 0\rangle \\ |1, -1\rangle \\ |0, 0\rangle \end{matrix} & \left( \begin{matrix} \epsilon & 0 & 0 & 0 \\ 0 & \epsilon & 0 & 0 \\ 0 & 0 & \epsilon & 0 \\ 0 & 0 & 0 & -3\epsilon \end{matrix} \right) \end{matrix}. \quad (3.11)$$

This matrix is already in diagonal form. The states  $|1, 1\rangle, |1, 0\rangle, |1, -1\rangle$  are degenerate with energy  $E = \epsilon$ , while the state  $|0, 0\rangle$  has energy  $E = -3\epsilon$ . Thus, we have shown that the Hamiltonian of the hyperfine structure is diagonal in the coupled basis.

(c) We now add an external magnetic field of magnitude  $B$  along the  $z$ -direction, and the magnetic moment of the electron interacts with that (Zeeman interaction). The corresponding Hamiltonian is:

$$\hat{H}_e^Z = -\frac{g_e \mu_B}{\hbar} \mathbf{S}_e \cdot \mathbf{B} = \frac{g_e \mu_B}{\hbar} (S_e)_z B \quad (3.12)$$

where  $g_e \approx -2$  is the gyromagnetic ratio of the electron and  $\mu_B = e\hbar/2m_e$  is the Bohr magneton. Find the matrix elements of  $\hat{H}_e^Z$  in the uncoupled and coupled bases. Calculate the energies and eigenvectors of the total Hamiltonian  $\hat{H} = \hat{H}_{HFS} + \hat{H}_e^Z$  in each case.

For the uncoupled basis, we use the Hamiltonian of Eq. (3.5) and that of the Zeeman coupling, and we find:

$$H_e^Z = \begin{vmatrix} | \uparrow\uparrow \rangle & | \uparrow\downarrow \rangle & | \downarrow\uparrow \rangle & | \downarrow\downarrow \rangle \\ | \uparrow\uparrow \rangle & \epsilon + A & 0 & 0 \\ | \uparrow\downarrow \rangle & 0 & -\epsilon + A & 2\epsilon \\ | \downarrow\uparrow \rangle & 0 & 2\epsilon & -\epsilon - A \\ | \downarrow\downarrow \rangle & 0 & 0 & \epsilon - A \end{vmatrix} \quad (3.13)$$

where  $A = g_e \mu_B B / 2$ . In a very similar fashion as in part (a), the matrix is yet again in block diagonal form. For the  $1 \times 1$  blocks, we find:

$$|\psi'_1\rangle = |\uparrow\uparrow\rangle \quad (E'_1 = \epsilon + A), \quad |\psi'_4\rangle = |\downarrow\downarrow\rangle \quad (E'_4 = \epsilon - A). \quad (3.14)$$

For the  $2 \times 2$  block, we find:

$$|\psi'_2\rangle = \cos \Theta |\uparrow\downarrow\rangle + \sin \Theta |\downarrow\uparrow\rangle \quad (E'_2 = -\epsilon + \sqrt{4\epsilon^2 + A^2}), \quad (3.15)$$

$$|\psi'_3\rangle = -\sin \Theta |\uparrow\downarrow\rangle + \cos \Theta |\downarrow\uparrow\rangle \quad (E'_3 = -\epsilon - \sqrt{4\epsilon^2 + A^2}) \quad (3.16)$$

where

$$\cos \Theta = \frac{1}{\sqrt{1 + \alpha^2}}, \quad \sin \Theta = \frac{\alpha}{\sqrt{1 + \alpha^2}}, \quad \alpha = \frac{\sqrt{4\epsilon^2 + A^2} - A}{2\epsilon}. \quad (3.17)$$

We move on to the coupled basis where we use the Hamiltonian of Eq. (3.10) and that of the Zeeman coupling. In matrix form, we have:

$$H_e^Z = \begin{vmatrix} |1,1\rangle & |1,0\rangle & |1,-1\rangle & |0,0\rangle \\ |1,1\rangle & \epsilon + A & 0 & 0 \\ |1,0\rangle & 0 & \epsilon & 0 \\ |1,-1\rangle & 0 & 0 & \epsilon - A \\ |0,0\rangle & 0 & A & 0 \end{vmatrix} \quad (3.18)$$

where we used the expansion of  $|1,0\rangle, |0,0\rangle$  in terms of the basis kets of the uncoupled state so that we can determine the action of  $(S_e)_z$ . The above matrix looks to be in a block-diagonal form with one  $1 \times 1$  and one  $3 \times 3$  matrices. However, we can further simplify it by swapping row 2 with row 3, and also swapping column 2 with column 3 (a permutation operation). This operation does not alter the resulting spectrum. You can think of it simply as relabeling of the basis states. The Hamiltonian then becomes:

$$H_e^Z = \begin{vmatrix} |1,1\rangle & |1,-1\rangle & |1,0\rangle & |0,0\rangle \\ |1,1\rangle & \epsilon + A & 0 & 0 \\ |1,-1\rangle & 0 & \epsilon - A & 0 \\ |1,0\rangle & 0 & 0 & \epsilon \\ |0,0\rangle & 0 & 0 & A \end{vmatrix}. \quad (3.19)$$

Diagonalizing the  $1 \times 1$  blocks yields:

$$|\psi_1^{Z,c}\rangle = |1,1\rangle \quad (E_1^{Z,c} = \epsilon + A), \quad |\psi_4^{Z,c}\rangle = |1,-1\rangle \quad (E_4^{Z,c} = \epsilon - A), \quad (3.20)$$

while from diagonalizing the  $2 \times 2$  block matrix, we get:

$$|\psi_2^{Z,c}\rangle = \cos \Phi |1,0\rangle + \sin \Phi |0,0\rangle \quad (E_2^{Z,c} = -\epsilon + \sqrt{4\epsilon^2 + A^2}), \quad (3.21)$$

$$|\psi_3^{Z,c}\rangle = -\sin \Phi |1,0\rangle + \cos \Phi |0,0\rangle \quad (E_3^{Z,c} = -\epsilon - \sqrt{4\epsilon^2 + A^2}) \quad (3.22)$$

where

$$\cos \Phi = \frac{1}{\sqrt{1 + \beta^2}}, \quad \sin \Phi = \frac{\beta}{\sqrt{1 + \beta^2}}, \quad \beta = \frac{\sqrt{4\epsilon^2 + A^2} - 2\epsilon}{A}. \quad (3.23)$$

You should verify that in both representations we obtain the correct expressions (according to the previous questions) in the limit of  $A \rightarrow 0$ .

(d) What form do the the energy eigenvalues take for small and large magnetic fields? Sketch the energy eigenvalues as a function of the magnetic field.

For small magnetic fields, we use the expansion  $\sqrt{1+x^2} \approx 1 + x^2/2$  for small  $x$ . Thus:

$$E'_{2,3} = -\epsilon \pm 2\epsilon \sqrt{1 + \frac{A^2}{4\epsilon^2}} \rightarrow -\epsilon \pm 2\epsilon \left(1 + \frac{A^2}{8\epsilon^2}\right). \quad (3.24)$$

This is true for the energies in both bases, although they correspond to different eigenstates. For low magnetic fields, the energies scale with the square of the magnetic field.

For large magnetic fields, we use the same expansion, thus

$$E'_{2,3} = -\epsilon \pm A \sqrt{1 + \frac{4\epsilon^2}{A^2}} \approx -\epsilon \pm A \left(1 + \frac{2\epsilon^2}{A^2}\right) \approx -\epsilon \pm A. \quad (3.25)$$

In this limit, all energies (including  $E_{1,4}$ ) scale linearly with the magnetic field. In Figure 2, we plot the energies as a function of the parameter  $A$ . We identify the correct behavior in the limiting cases of  $A \rightarrow 0$  and  $A \rightarrow \infty$ , that we have just studied.

(e) Which basis is more suitable for small magnetic fields and which basis is more suitable for large magnetic fields?

For small magnetic fields, the hyperfine Hamiltonian dominates the Zeeman term, thus the coupled basis is more suitable in this case, since it remains (roughly) diagonal for  $\epsilon \gg A$  (see parts (a,b) for this). However, for large magnetic fields  $\epsilon \ll A$ , the Zeeman term dominates. The total Hamiltonian the two bases are:

$$H_e^Z \rightarrow \begin{array}{c} |\uparrow\uparrow\rangle \quad |\uparrow\downarrow\rangle \quad |\downarrow\uparrow\rangle \quad |\downarrow\downarrow\rangle \\ \hline |\uparrow\uparrow\rangle \left( \begin{array}{cccc} A & 0 & 0 & 0 \\ 0 & A & 0 & 0 \\ 0 & 0 & -A & 0 \\ 0 & 0 & 0 & -A \end{array} \right) \end{array} \quad (3.26)$$

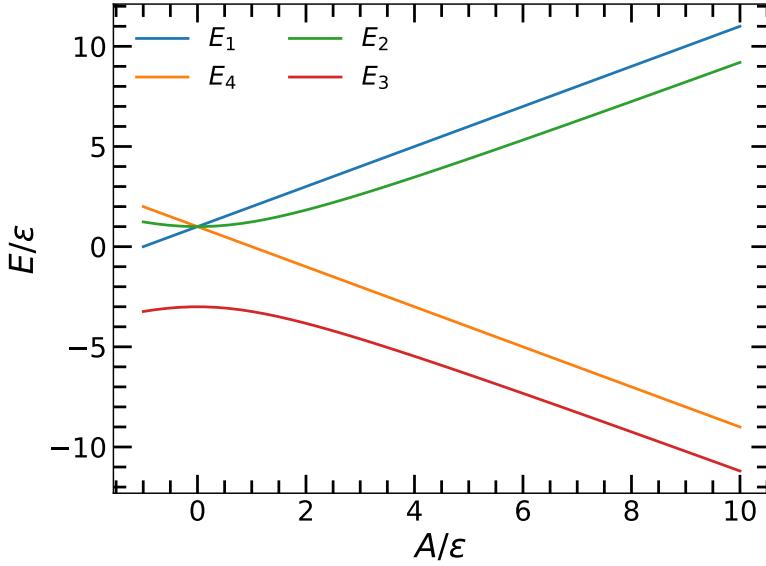


Figure 2: The energies as a function of the magnetic field  $A$ .

and

$$H_e^Z \rightarrow \begin{pmatrix} |1,1\rangle & |1,0\rangle & |1,-1\rangle & |0,0\rangle \\ |1,1\rangle & A & 0 & 0 \\ |1,0\rangle & 0 & 0 & A \\ |1,-1\rangle & 0 & 0 & -A \\ |0,0\rangle & 0 & A & 0 \end{pmatrix} \quad (3.27)$$

Thus, the uncoupled basis is more suitable in this case, since it is diagonal.

(f) Finally, we consider the interaction of the magnetic dipole moment of the proton to the magnetic field. The associated Hamiltonian is:

$$\hat{H}_p^Z = -\frac{g_p\mu_N}{\hbar}(S_p)_z B_z, \quad (3.28)$$

where  $g_p \approx 5.585$  is the gyromagnetic ratio of the proton and  $\mu_N = e\hbar/2m_p$  is the nuclear magneton. How does the energy scale associated with the magnetic dipole moment of the proton compare to that of the electron? What do you conclude? Is the Zeeman term for the proton important?

We take the ratio of the corresponding energy scales,

$$\frac{g_e\mu_B}{g_p\mu_N} = \frac{g_e(e\hbar/2m_e)}{g_p(e\hbar/2m_p)} = \frac{g_e m_p}{g_p m_e} \gg 1. \quad (3.29)$$

The mass of the proton is four orders of magnitude larger than that of the electron, and using the gyromagnetic ratios of the proton and electron, the ratio is found to be of the order of  $\sim 10^2$ . We conclude that the Zeeman term for the proton is not very important compared to that of the electron, and thus we neglect this contribution from the total Hamiltonian.