PHYS 3803: Quantum Mechanics I, Spring 2021

Lecture 27, May 06, 2021 (Thursday)

- Reading: Spin—Griffiths 4.4
- Final Exam on May 11 (Tuesday) 1:30 pm–3:30 pm.

Topics for Today: Spin [Griffiths 4.4]

6.6 Comparison with Experiments

6.6 Degeneracy in Hydrogen Atom

6.7 Spin and Addition of Angular Momentum

6.5 Comparison with Experiments

If an atom is in the state denoted by n, ℓ, m with energy E_n, it would remain there forever since that is a stationary state.

- However, if we disturb the system, it may make a transition to another state n', ℓ', m' with energy $E'_n \neq E_n$.
- Furthermore, if $E_{n'} < E_n$, the atom would emit a photon with energy $E_n - E_{n'}$. The frequency of the emitted photon would be

  $$\omega_{n,n'} = \frac{1}{\hbar}(E_n - E_{n'})$$

  and it can be measured in a laboratory.

Quantum mechanics predicts that

$$\omega_{n,n'} = \frac{R_y}{\hbar}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right) .$$

- For a fixed value of n', we get a family of lines (spectrum) as we vary n. Thus

$$\omega_{n,1} = \frac{R_y}{\hbar}\left(1 - \frac{1}{n^2}\right)$$

  is called the Lyman series.

- Similarly,

$$\omega_{n,2} = \frac{R_y}{\hbar}\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

  is known as the Balmer series and so on.

These lines are observed and verify quantum mechanical predictions.

To make the theoretical prediction more precise, we need ’ higher order ’ corrections.

- For example, we have to correct for the fact that the proton is not immobile, i.e., it does not have infinite mass.
- Furthermore, we have treated the electron like a non-relativistic particle whereas the relativistic effects are not negligible.
- These are known as fine structure corrections and are calculable.
- However, we must remember that all such corrections are extremely small and that the non-relativistic Schrödinger equation describes the Hydrogen atom extremely well.

6.6 Degeneracy in Hydrogen Atom

The Hydrogen atom possesses rotational symmetry. That implies that

$$\begin{aligned} [L_i, H] &= 0 \quad \text{or} \\ [L_\pm, H] &= 0\,. \end{aligned}$$

- $L_\pm$ change the $m-$quantum numbers for a given ℓ.
- Since $L_\pm$ commute with the Hamiltonian, this implies that all the $2\ell + 1$ states with different $m-$values have the same energy.
- Thus rotational invariance implies this degeneracy of the $m-$quantum numbers.
- In Hydrogen atom, for a given value of n, ℓ takes integer values from $0, 1, \cdots, n-1$. And furthermore, since the energy levels are characterized by the $n-$quantum numbers only, all these states with different $\ell-$quantum numbers also have the same energy.

Thus for example,

n	E_n	ℓ	m
1	-13.6 eV	0	0
2	$-13.6/4$ eV	0, 1	0; ± 1,0
3	$-13.6/9$ eV	0, 1, 2	0; ± 1, 0; ± 2, ± 1, 0

and so on.

Thus the total number of degeneracy in the case of Hydrogen atom for a given n is

$$\begin{aligned} \sum_{\ell=0}^{n-1}(2\ell+1) &= 2\cdot\frac{1}{2}(n-1)n+n \\ &= n(n-1+1) \;=\; n^2\,. \end{aligned}$$

We have seen similar degeneracy in the case of 3-dimensional harmonic oscillator and have characterized this as accidental degeneracy.

6.7 Spin and Addition of Angular Momentum

A. Spin

We have chosen $L_3 = L_z$ to share the same eigenvectors with L^2.

- The orbital angular momentum, defined as the operator

$$\vec{L} = \vec{r} \times \vec{P} = \vec{X} \times \vec{P} \quad \text{or} \quad L_i = \epsilon_{ijk} X_j P_k$$

and studied within the context of the Schrödinger equation, has only integer eigenvalues in units of $\hbar$

$$\begin{aligned} L^2|\ell, m\rangle &= \ell(\ell+1)\hbar^2|\ell, m\rangle \quad \text{and} \quad L_3|\ell, m\rangle = m\hbar|\ell, m\rangle \quad \text{or} \\ L^2 Y_{\ell,m}(\theta,\phi) &= \ell(\ell+1)\hbar^2 Y_{\ell,m}(\theta,\phi) \quad \text{and} \\ L_3 Y_{\ell,m}(\theta,\phi) &= m\hbar Y_{\ell,m}(\theta,\phi) \end{aligned}$$

with

$$\ell = 0, 1, 2, \cdots, \quad -\ell \leq m \leq \ell, \quad \text{and} \quad Y_{\ell,m}(\theta,\phi) \equiv \langle\theta,\phi|\ell, m\rangle.$$

- However, if we treat angular momentum as an abstract operator satisfying the same commutation relations as the orbital angular momentum, namely,

$$[J_i, J_j] = i\hbar\epsilon_{ijk}J_k \ ,$$

and study its representations, we find that J^2 has eigenvalues $j(j+1)\hbar^2$ where the quantum number j takes multiples of half integer values. The eigenvalue equations of J^2 and J_3 are

$$\begin{aligned} J^2|\ell, m\rangle &= j(j+1)\hbar^2|j, m\rangle\rangle \\ J_3|\ell, m\rangle &= m\hbar|j, m\rangle \ . \end{aligned}$$

There has been increasing evidence that half integer angular momentum must be associated with the electron.

The experiments to suggest this are as follows

- Anomalous Zeeman effect
- Fine structure
- Stern-Gerlach experiment

The definitive proof for half integer angular momentum comes from the Stern-Gerlach experiment.

In 1925, Uhlenbeck and Goudsmit introduced the idea that, in addition to the orbital angular momentum, the electron possesses an intrinsic spin angular momentum of magnitude $s = \hbar/2$

The total angular momentum of a particle consists of two parts, one due to its orbital motion and the other due to its spin. Thus we have

$$\vec{J} = \vec{L} + \vec{S}$$

where spin $\vec{S}$ is an intrinsic operator, i.e. it does not depend on coordinates and momenta.

Therefore $\vec{L}$ and $\vec{S}$ commute and

$$[J_i, J_j] = [L_i, L_j] + [S_i, S_j]$$

or

$$i\hbar\epsilon_{ijk}J_k = i\hbar\epsilon_{ijk}L_k + [S_i, S_j]\,.$$

That leads to

$$[S_i, S_j] = i\hbar\epsilon_{ijk}S_k\,.$$

The eigenvalue equations for spin operators are

$$\begin{aligned} S^2|s, s_z\rangle &= S^2|s, m_s\rangle = s(s+1)\hbar^2|s, m_s\rangle \quad \text{and} \\ S_z|s, s_z\rangle &= S_z|s, m_s\rangle = m_s\hbar|s, m_s\rangle\,. \end{aligned}$$

For a spin-1/2 state, there are two basis states $(2s+1=2)$

$$|s, m_s\rangle : |\frac{1}{2}, \frac{1}{2}\rangle \quad \text{and} \quad |\frac{1}{2}, -\frac{1}{2}\rangle \quad \text{with} \quad -s \leq m_s \leq s\,.$$

The eigenvalue equations for the electron with spin $s = \hbar/2$ become

$$\begin{aligned} S^2|\frac{1}{2}, m_s\rangle &= \frac{1}{2}(\frac{1}{2}+1)\hbar^2|\frac{1}{2}, m_s\rangle = \frac{3}{4}\hbar^2|\frac{1}{2}, m_s\rangle \\ S_z|\frac{1}{2}, \frac{1}{2}\rangle &= \frac{1}{2}\hbar|\frac{1}{2}, \frac{1}{2}\rangle\,, \quad \text{and} \\ S_z|\frac{1}{2}, -\frac{1}{2}\rangle &= -\frac{1}{2}\hbar|\frac{1}{2}, \frac{1}{2}\rangle\,. \end{aligned}$$

Sometimes, the basis states are also denoted by $|+\rangle$ and $|-\rangle$ respectively, corresponding to the signature of the z-component of the spin value:

$$|+\rangle = |\frac{1}{2}, \frac{1}{2}\rangle \quad \text{and} \quad |-\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle\,.$$

These states are orthonormal so that

$$\begin{aligned} \langle +|+\rangle &= \langle -|-\rangle = 1\,, \\ \langle +|-\rangle &= \langle -|+\rangle = 0\,. \end{aligned}$$

In a two dimensional matrix representation, we can choose,

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

Any vector, in this space, can be defined as a linear combination of these two basis vector. Thus, we can write

$$|\psi\rangle = \sum_i c_i |i\rangle = c_+ |+\rangle + c_- |-\rangle .$$

In this basis, the spin operators have the following matrix representations in this space

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} , \quad \text{and} \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} .$$

In addition, S_z and S^2 are diagonal matrices

$$S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \text{and} \quad S^2 = \frac{3\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

We can define the spin operators as

$$\vec{S} = \frac{\hbar}{2} \vec{\sigma}$$

where $\vec{\sigma}$'s are known as the Pauli matrices.

B. Addition of Angular Momentum

Let us consider a system with two particles. Each particle is associated with an angular momentum operator $\vec{J}_1$ and $\vec{J}_2$ respectively.

The commutation relations of these operators can be written as

$$\begin{aligned} [J_{1i}, J_{1j}] &= i\hbar\epsilon_{ijk}J_{1k} \\ [J_{2i}, J_{2j}] &= i\hbar\epsilon_{ijk}J_{2k} \\ [J_{1i}, J_{2j}] &= 0\,. \end{aligned}$$

Applying tensor notations $(\vec{A} \times \vec{B})_i = \epsilon_{ijk}A_jB_k$, we obtain commutation relations in the compact form

$$\begin{aligned} \vec{J}_1 \times \vec{J}_1 &= i\hbar\vec{J}_1 \\ \vec{J}_2 \times \vec{J}_2 &= i\hbar\vec{J}_2 \\ \left[\vec{J}_1, \vec{J}_2\right] &= 0\,. \end{aligned}$$

Let us assume that the values of te angular momenta for these two particles are j_1 and j_2 respectively. Thus

$$J_i^2|j_i, m_i\rangle = j_i(j_i+1)\hbar^2|j_i, m_i\rangle \quad \text{and}$$
$$J_{iz}|j_i, m_i\rangle = m_i\hbar|j_i, m_i\rangle \quad \text{and} i = 1, 2\,.$$

Since $\vec{J}_1$ and $\vec{J}_2$ commute, the total space is a direct product of the two spaces:

$$\begin{aligned} \mathcal{E} &= \mathcal{E}_1 \otimes \mathcal{E}_2 \quad \text{or} \\ |j_1, m_1; j_2, m_2\rangle &= |j_1, m_1\rangle \otimes |j_2, m_2\rangle\,. \end{aligned}$$

The total space must have dimension $(2j_1+1)(2j_2+1)$ with

$$\begin{aligned} J_z|j_1, m_1; j_2, m_2\rangle &= (J_{1z} + J_{2z})|j_1, m_1; j_2, m_2\rangle \\ &= J_{1z}|j_1, m_1\rangle \otimes |j_2, m_2\rangle + |j_1, m_1\rangle \otimes J_{2z}|j_2, m_2\rangle \\ &= (m_1 + m_2)\hbar|j_1, m_1; j_2, m_2\rangle\,. \end{aligned}$$

The total angular momentum operator takes values from $j_1 + j_2$ down to $|j_1 - j_2|$, decreasing in steps of unity and we have

$$\mathcal{E} = \mathcal{E}^{(j_1)} \otimes \mathcal{E}^{(j_2)} = \sum_{j=|j_1-j_2|}^{j_1+j_2} \oplus \mathcal{E}^{(j)} \, .$$

This simply means that the $j, m; j_1, j_2\rangle$ basis defines a reducible space and operators take block diagonal form in this basis

A system consisting of two angular momentum operators can be equivalently described in terms of two alternate basis, namely,

$$|j_1, m_1; j_2, m_2\rangle \quad \text{or} \quad |j, m; j_1, j_2\rangle$$

with $-j \leq m \leq j$.

Applying completeness relation of $|j_1, m_1; j_2, m_2\rangle$, we can write

$$|j, m; j_1, j_2\rangle = \sum_{m_1, m_2} |j_1, m_1; j_2, m_2\rangle\langle j_1, m_1; j_2, m_2|j, m; j_1, j_2\rangle\,.$$

That leads to

$$\begin{aligned} |j, m; j_1, j_2\rangle &= \sum_{m_1, m_2} \langle j_1, m_1; j_2, m_2|j, m; j_1, j_2\rangle |j_1, m_1; j_2, m_2\rangle \\ &= \sum_{m_1, m_2} C(j, j_1, j_2; m, m_1, m_2)\, |j_1, m_1; j_2, m_2\rangle\,. \end{aligned}$$

where

$$C(j, j_1, j_2; m, m_1, m_2) \equiv \langle j_1, m_1; j_2, m_2|j, m; j_1, j_2\rangle$$

and they are called the Clebsch-Gordon coefficients.

The orthonormal relations of basis vectors lead to

$$C(j, j_1, j_2; m, m_1, m_2) \equiv \langle j_1, m_1; j_2, m_2|j, m; j_1, j_2\rangle = 0$$

if $m \neq m_1 + m_2$ and $j_1 + j_2 \geq j \geq |j_1 - j_2|$ does not hold.

Similarly we can apply completeness relation of $|j, m; j_1, j_2\rangle$ and show that

$$|j_1, m_1; j_2, m_2\rangle = \sum_{j,m} |j, m; j_1, j_2\rangle\langle j, m; j_1, j_2||j_1, m_1; j_2, m_2\rangle \, .$$

That leads to

$$\begin{aligned} |j_1, m_1; j_2, m_2\rangle &= \sum_{j,m}\langle j, m; j_1, j_2||j_1, m_1; j_2, m_2\rangle \, |j, m; j_1, j_2\rangle \\ &= \sum_{j,m} C^*(j, j_1, j_2; m, m_1, m_2) \, |j, m; j_1, j_2\rangle \, , \end{aligned}$$

where

$$C^*(j, j_1, j_2; m, m_1, m_2) = \langle j, m; j_1, j_2|j_1, m_1; j_2, m_2\rangle \, .$$

Example:

Let us consider the sum of two angular momenta with eigenvalues 1/2 each and analyze the resulting eigenvalues and eigenstates. In this case we have

$$j_1 = \frac{1}{2}\,, \quad \text{and} \quad j_2 = \frac{1}{2}\,,$$

and, therefore,

$$m_1 = \frac{1}{2}, -\frac{1}{2}\,, \quad \text{and} \quad m_2 = \frac{1}{2}, -\frac{1}{2}\,.$$

The basis vectors are

$$|j_1, m_1\rangle : \quad |+\rangle = |\frac{1}{2}, \frac{1}{2}\rangle\,, \quad |-\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle\,,$$
$$|j_2, m_2\rangle : \quad |+\rangle = |\frac{1}{2}, \frac{1}{2}\rangle\,, \quad |-\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle\,.$$

Note that the total space is the tensor product of $|j_i, m_i\rangle$:

$$|j_1, m_1; j_2, m_2\rangle = |j_1, m_1\rangle \otimes |j_2, m_2\rangle$$

There are four independent basis states in the total space

$$|u_1\rangle = |+,+\rangle\,, \quad |u_2\rangle = |+,-\rangle\,, \quad |u_3\rangle = |-,+\rangle\,, \quad |u_4\rangle = |-,-\rangle\,.$$

We see that

$$\begin{aligned} J_z|+,+\rangle &= (J_{1z}+J_{2z})|+,+\rangle \\ &= (J_{1z}|+\rangle)\otimes|+\rangle\ +|+\rangle\,(J_{2z}|+\rangle) \\ &= \left(\frac{1}{2}+\frac{1}{2}\right)\hbar|+,+\rangle\ =\ \hbar|+,+\rangle\,. \end{aligned}$$

Similarly, we can show that

$$\begin{aligned} J_z|+,-\rangle &= 0\,, \\ J_z|-,+\rangle &= 0\,, \\ J_z|-,-\rangle &= -\hbar|-,-\rangle\,. \end{aligned}$$

In the product basis, the eigenvalues of J_z or the m quantum numbers are $m = 1, 0, -1$, and

$$J_z \rightarrow \begin{array}{c} (+,+) \\ (+,-) \\ (-,+) \\ (-,-) \end{array} \begin{pmatrix} \hbar & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\hbar \end{pmatrix} .$$

Furthermore, using the result

$$\begin{aligned} J^2 &= J_1^2 + J_2^2 + 2J_1 \cdot J_2 \\ &= J_1^2 + J_2^2 + 2J_{1z}J_{2z} + J_{1+}J_{2-} + J_{1-}J_{2+} \end{aligned}$$

we can show that in the product basis,

$$J^2 \to \hbar^2 \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix} .$$

We can diagonalize this matrix and show that

$$\begin{aligned} &|+,+\rangle \\ &\frac{1}{\sqrt{2}}\left(|+,-\rangle + |-,+\rangle\right) \\ &|-,-\rangle \end{aligned}$$

represent the eigenbasis corresponding to $j = 1$ (triplet), while

$$|-, -\rangle$$

corresponds to the eigenstate $j = 0$ (singlet).

We can identify

$$\begin{aligned} |j = 1, m = 1\rangle &= |+, +\rangle \\ |j = 1, m = 0\rangle &= \frac{1}{\sqrt{2}} \left(|+, -\rangle + |-, +\rangle \right) \\ |j = 1, m = -1\rangle &= |-, -\rangle \end{aligned}$$

and

$$|j = 0, m = 0\rangle = \frac{1}{\sqrt{2}} \left(|+, -\rangle - |-, +\rangle \right) .$$

We can identify

$$
\begin{aligned}
|j=1,m=1\rangle &= |+,+\rangle \\
|j=1,m=0\rangle &= \frac{1}{\sqrt{2}}\left(|+,-\rangle + |-,+\rangle\right) \\
|j=1,m=-1\rangle &= |-,-\rangle
\end{aligned}
$$

and

$$
|j=0,m=0\rangle = \frac{1}{\sqrt{2}}\left(|+,-\rangle - |-,+\rangle\right) .
$$

- The states with $j=1$ are known as the triplet states $(2j+1=3)$, where as the $j=0$ state is called the singlet state $(2j+1=1)$.
- The triplet states are symmetric under exchange whereas the singlet is anti-symmetric.

The relations between the total momentum basis $|j, m; j_1, j_2\rangle$ and the product basis $|j_1, m_1; j_2, m_2\rangle$ can be expressed in the matrix form as

$$\begin{pmatrix} |1,1\rangle \\ |1,0\rangle \\ |1,-1\rangle \\ |0,0\rangle \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \end{pmatrix} \cdot \begin{pmatrix} |+,+\rangle \\ |+,-\rangle \\ |-,+\rangle \\ |-,-\rangle \end{pmatrix} .$$

The elements of the matrix connecting the two sets of basis states are the Clebsch-Gordon coefficients for this problem.

We can write the composition of the angular momenta as

$$\frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0$$

where the numbers represent the quantum number j.