ANGULAR MOMENTUM AND CENTRAL FIELD

- To understand the motion of a particle in a central field, in particular to find the spectrum of a hydrogen atom, we need to use the conservation of the angular momentum which satisfies the $\mathfrak{su}(2)$ Lie algebra relations.

- This requires constructing irreducible representations of $\mathfrak{su}(2)$, and decomposing the tensor product of two representations into irreducible ones.

- We will develop the necessary technique to work with the angular momentum.

1 Irreducible representations of $\mathfrak{su}(2)$

The angular momentum satisfies the commutation relations

$$[J_\alpha\,,\; J_\beta] = \sum_{\gamma=1}^{3} \mathrm{i}\,\hbar\,\epsilon_{\alpha\beta\gamma} J_\gamma \tag{1}$$

- Up to a rescaling of J_α are the same as the $\mathfrak{su}(2)$ or $\mathfrak{sl}(2)$ Lie algebra relations.
- We are interested in unitary irreps of the universal enveloping algebra of $\mathfrak{su}(2)$ that is we want to realise the relations (1) by
  - (i) $n \times n$ hermitian matrices if a representation is finite-dimensional
  - (ii) hermitian operators acting in a Hilbert space if a representation is infinite-dimensional.

Let us show that all unitary irreps of $\mathfrak{su}(2)$ are finite-dimensional.

- Assume we have any representation of $\mathfrak{su}(2)$.
- Since $J_z \equiv J_3$ is hermitian there is a basis where it is diagonal
- The Casimir operator $J^2 \equiv \sum_{\alpha=1}^3 J_\alpha^2$ is hermitian and commutes with J_α.
- There is a basis where both J_z and J^2 are diagonal.
- Choose any mutual eigenvector of J^2 and J_z with eigenvalues $\hbar^2 f$ and $\hbar m$, and denote it by $|f, m\rangle$

$$J^2|f,m\rangle = \hbar^2 f\,|f,m\rangle\,, \quad J_z|f,m\rangle = \hbar\,m|f,m\rangle \tag{2}$$

- The irrep is obtained by acting on $|f, m\rangle$ with the remaining operators J_x and J_y.
- Since $[J_\alpha, J^2] = 0$ all vectors obtained this way are eigenkets of J^2 with the same eigenvalue $\hbar^2 f$.
- Introduce

$$J_\pm \equiv J_x \pm \mathrm{i}\, J_y \tag{3}$$

- They satisfy

$$\begin{aligned} [J_z\,,\ J_\pm] &= [J_z\,,\ J_x] \pm \mathrm{i}\,[J_z\,,\ J_y] = \mathrm{i}\,\hbar\, J_y \pm \hbar\, J_x = \pm\,\hbar\, J_\pm \\ [J_+\,,\ J_-] &= [J_x + \mathrm{i}\, J_y\,,\ J_x - \mathrm{i}\, J_y] = 2\,\hbar\, J_z \end{aligned} \tag{4}$$

- The Casimir operator

$$J^2 = \frac{1}{2} J_+ J_- + \frac{1}{2} J_- J_+ + J_z^2 = J_+ J_- + J_z^2 - \hbar\, J_z = J_- J_+ + J_z^2 + \hbar\, J_z \tag{5}$$

- Acting on $|f, m\rangle$ by $J_\pm$, we get two new vectors. Let us act on those vectors by J_z

$$J_z\, J_\pm |f, m\rangle = (\pm\hbar J_\pm + J_\pm\, J_z)|f, m\rangle = \hbar(m \pm 1)\, J_\pm |f, m\rangle \tag{6}$$

- $J_\pm|f, m\rangle$ is an eigenvector of J_z with the eigenvalue $\hbar(m \pm 1)$.
- J_+ and J_- are called the **raising or lowering operators**.
- Acting on $|f, m\rangle$ by $J_\pm^n$, we get eigenvectors of J_z with the eigenvalues $\hbar(m \pm n)$.
- Due to (5) the operators $J_\pm J_\mp$ do not produce any new vectors

- The irreps is spanned by the vectors

$$J_+^n|f,m\rangle\,,\quad J_-^n|f,m\rangle\,,\quad n=0,1,2,\dots \tag{7}$$

- Since the spectrum of J_z is discrete and nondegenerate, the vectors are orthogonal and normalisable

$$J_\pm^n|f,m\rangle = c_\pm(m,n)|f,m\pm n\rangle\,,\;\; J_z|f,m\pm n\rangle = \hbar(m\pm n)|f,m\pm n\rangle\,,\;\; \langle f,m+k|f,m+l\rangle = \delta_{kl} \tag{8}$$

where $c_\pm(m,n)$ are to be determined.

- Is it an infinite-dimensional irreducible representation?
- We have not used yet the unitarity condition.
- All vectors must have nonnegative norm.
- The norm of $J_+|f,m+n\rangle$ is found by using $J_+^\dagger = J_-$

$$\begin{aligned}\langle f,m+n|J_-J_+|f,m+n\rangle &= \langle f,m+n|J^2-J_z^2-\hbar\,J_z|f,m+n\rangle \\ &= \hbar^2(f-(m+n)(m+n+1))\ge 0\end{aligned} \tag{9}$$

- The nonnegativity condition will be broken unless there is $n_{\rm max}$ such that

$$J_+|f,m+n_{\rm max}\rangle = 0 \tag{10}$$

- Denoting $j_{\rm max}\equiv m+n_{\rm max}$, we get

$$J_+|f,j_{\rm max}\rangle = 0\,,\quad f=j_{\rm max}(j_{\rm max}+1) \tag{11}$$

- A vector satisfying the condition (11) is called the **highest weight vector**.
- Similarly, computing the norm of the vector $J_-|f, m-n\rangle$, we get

$$\begin{aligned}\langle f, m-n|J_+J_-|f, m-n\rangle &= \langle f, m-n|J^2 - J_z^2 + \hbar\, J_z|f, m-n\rangle \\ &= \hbar^2(f-(m-n)(m-n-1)) \geq 0\end{aligned} \tag{12}$$

- The nonnegativity condition will be broken unless there is another $\bar{n}_{\rm max}$ such that

$$J_-|f, m-\bar{n}_{\rm max}\rangle = 0 \tag{13}$$

- Denoting $j_{\rm min} \equiv m - \bar{n}_{\rm max}$, we get

$$J_-|f, j_{\rm min}\rangle = 0\,, \quad f = j_{\rm min}(j_{\rm min}-1) \tag{14}$$

- A vector satisfying the condition (14) is called the **lowest weight vector**.
- Comparing (11) and (14) and taking into account that $j_{\rm min} \leq j_{\rm max}$, we get

$$j \equiv j_{\rm max} = -j_{\rm min}\,, \quad f = j(j+1) \tag{15}$$

- Since $2j = j_{\rm max} - j_{\rm min} = n_{\rm max} + \bar{n}_{\rm max}$ is an integer, j can be either an integer and a half-integer.

- Denote the orthonormal basis vectors by $|j, m\rangle$

$$\begin{aligned} J^2|j,m\rangle &= \hbar^2 j(j+1)\,|j,m\rangle\,, \quad J_z|j,m\rangle = \hbar\, m|j,m\rangle\,, \quad m=-j,-j+1,\ldots,j-1,j \\ J_+|j,j\rangle &= 0\,, \quad J_-|j,-j\rangle = 0 \end{aligned} \tag{16}$$

- Constructed $2j+1$-dimensional irreducible unitary representation of $\mathfrak{su}(2)$ which in physics is called the spin-j (or angular momentum j) representation.
- Proven that any irreducible unitary representation of $\mathfrak{su}(2)$ is finite-dimensional.
- Having found a subrepresentation in the given representation, we can choose another mutual eigenvector of J^2 and J_z and repeat the process.
- Eventually, we decompose any given unitary representation of $\mathfrak{su}(2)$ into a direct sum of irreps.
- The raising and lowering operators act on $|j, m\rangle$ as

$$J_\pm|j,m\rangle = \hbar\, C_\pm(j,m)|j,m\pm 1\rangle \tag{17}$$

(i) To find the normalisation constants $C_\pm(j, m)$ we compute the norms of $J_\pm|j, m\rangle$

$$\langle j,m|J_\mp J_\pm|j,m\rangle = \langle j,m|J^2 - J_z^2 \mp \hbar\, J_z|j,m\rangle = \hbar^2(j(j+1) - m(m\pm 1)) = \hbar^2|c_\pm(m)|^2 \tag{18}$$

(ii) Choose

$$C_\pm(j,m) = \sqrt{j(j+1) - m(m\pm 1)} = \sqrt{(j\mp m)(j\pm m+1)} \tag{19}$$

(iii) $C_\pm(j,m)$ are fixed up to arbitrary phase factors, and this choice specifies the spin-j irrep

$$\begin{gathered} J^2|j,m\rangle = \hbar^2 j(j+1)\,|j,m\rangle\,, \quad J_z|j,m\rangle = \hbar\, m|j,m\rangle\,, \quad m=-j,-j+1,\ldots,j-1,j \\ J_+|j,m\rangle = \hbar\sqrt{(j-m)(j+m+1)}\,|j,m+1\rangle\,, \quad J_-|j,m\rangle = \hbar\sqrt{(j+m)(j-m+1)}\,|j,m-1\rangle \end{gathered} \tag{20}$$

(iv) The number m is often called the magnetic quantum number

(v) In the case of a spinning particle it encodes its spin orientation.

- If we exponentiate the operators J_α we get a representation of the rotation group

(i) The rotation operator through ϑ around $\vec{n}$ is represented by the $(2j+1)\times(2j+1)$ matrix

$$R(\vec{\vartheta}) = \exp\Big(-\mathrm{i}\,\vec{\vartheta}\cdot\vec{J}/\hbar\Big) = \exp\Big(-\mathrm{i}\,\vartheta\, J_{\vec{n}}/\hbar\Big)\,, \quad \vec{\vartheta} = \vartheta\,\vec{n}\,, \quad \vec{n}^{\,2}=1 \tag{21}$$

(ii) Rotations about the z-axis are represented by

$$R_z(\phi) = \exp\Big(-\mathrm{i}\,\phi J_z/\hbar\Big) \tag{22}$$

(iii) It acts on the basis vectors as

$$R_z(\phi)|j,m\rangle = \exp\Big(-\mathrm{i}\,\phi J_z/\hbar\Big)|j,m\rangle = e^{-\mathrm{i}\,\phi\, m}|j,m\rangle \tag{23}$$

(iv) A rotation through 2π around the z-axis gives

$$R_z(2\pi)|j,m\rangle = (-1)^{2m}|j,m\rangle \tag{24}$$

(v) A system with half integer angular momentum does not always return to its original state – the initial and final states may be minus one another.

2 The tensor product of irreducible repreentations

We have systems for which the total angular momentum is a sum of independent angular momenta.

(i) A system of two (or more) spinning particles in zero dimensions, say a spin chain, then the total spin of the system is the sum of spins of individual particles.

  (a) The spin operator $\vec{S}_a$ of the a-th particle acts in its Hilbert space $\mathscr{H}^{s_a}$ which is the $(2s_a + 1)$-dimensional irrep of $\mathfrak{su}(2)$.

  (b) The Hilbert space of the system is $\mathscr{H} = \mathscr{H}^{s_1} \otimes \mathscr{H}^{s_2}$ where the total spin $\vec{S} = \vec{S}_1 + \vec{S}_2$ acts

  (c) How is $\mathscr{H}$ decomposed into irreps of $\mathfrak{su}(2)$?

(ii) A single particle of spin s moving in the three-dimensional space.

  (a) Its total angular momentum $\vec{J} = \vec{L} + \vec{S}$ is the sum of its orbital angular momentum $\vec{L} = \vec{X} \times \vec{P}$ and its spin operator $\vec{S}$.

  (b) The Hilbert space is $\mathscr{H} = \mathscr{H}^{s} \otimes \mathscr{H}^{xp}$ of the Hilbert spaces $\mathscr{H}^{s}$ and $\mathscr{H}^{xp}$ of $\vec{S}$ and $\vec{L}$

  (c) We again need to decompose it into irreps of $\mathfrak{su}(2)$.

- Consider a system composed of two subsystems, e.g. two spinning particles
  (i) They have unvarying total angular momentum quantum numbers j_1 and j_2 not equal to 0.
  (ii) Any state
$$|\psi\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} c_{m_1 m_2} |j_1, m_1\rangle |j_2, m_2\rangle \,, \qquad |\psi\rangle \in \mathscr{H} = \mathscr{H}^{j_1} \otimes \mathscr{H}^{j_2} \tag{25}$$
  (iii) The kets $|j_1, m_1\rangle |j_2, m_2\rangle$ form a basis of $\mathscr{H}$
  (iv) $\vec{J} = \vec{J}_1 + \vec{J}_2$ acts on $|\psi\rangle$ as
$$\vec{J}\,|\psi\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} c_{m_1 m_2} \Big((\vec{J}_1 |j_1, m_1\rangle) |j_2, m_2\rangle + |j_1, m_1\rangle (\vec{J}_2 |j_2, m_2\rangle) \Big) \tag{26}$$
  (v) We want to know how $\mathscr{H}$ is decomposied
$$\mathscr{H} = \mathscr{H}^{j_1} \otimes \mathscr{H}^{j_2} = \sum_j \mathscr{H}^j \tag{27}$$
  into a sum $\mathscr{H}^j$ of irreducible representations.
- Any vector $|j_1, m_1\rangle |j_2, m_2\rangle$ is an eigenvector of J_z with the eigenvalue $m_1 + m_2$
$$J_z\,|j_1, m_1\rangle |j_2, m_2\rangle = J_{1z} |j_1, m_1\rangle) |j_2, m_2\rangle + |j_1, m_1\rangle (J_{2z} |j_2, m_2\rangle) = \hbar (m_1 + m_2) |j_1, m_1\rangle |j_2, m_2\rangle \tag{28}$$
- The Casimir operator J^2 is expressed as
$$\begin{aligned} J^2 &= (J_{1+} + J_{2+})(J_{1-} + J_{2-}) + (J_{1z} + J_{2z})^2 - \hbar (J_{1z} + J_{2z}) \\ &= J_1^2 + J_2^2 + J_{1+} J_{2-} + J_{1-} J_{2+} + 2\, J_{1z} J_{2z} \end{aligned} \tag{29}$$

- Analyse $|j_1, m_1\rangle|j_2, m_2\rangle$ with fixed $m = m_1 + m_2$ starting with the maximum possible value $j_1 + j_2$.
  1. $|j_1, j_1\rangle|j_2, j_2\rangle$ is the product of the hwv of $\mathscr{H}^{j_1}$ and $\mathscr{H}^{j_2}$
     (a) It is a hwv of $\mathscr{H}^{j_1} \otimes \mathscr{H}^{j_2}$.
     (b) By using (29) we find
     $$J^2|j_1, j_1\rangle|j_2, j_2\rangle = \hbar^2(j_1(j_1+1) + j_2(j_2+1) + 2\, j_1 j_2) = \hbar^2(j_1+j_2)(j_1+j_2+1) \tag{30}$$
     (c) Thus, it is the hwv of spin-$j_1 + j_2$ irrep $\mathscr{H}^{j_1+j_2}$, and we may write
     $$|j_1+j_2, j_1+j_2\rangle = |j_1, j_1\rangle|j_2, j_2\rangle \tag{31}$$
     (d) Acting on it with the lowering operator J_- we obtain all $2(j_1+j_2)+1$ vectors of $\mathscr{H}^{j_1+j_2}$.
  2. Two vectors $|j_1, j_1-1\rangle|j_2, j_2\rangle$ and $|j_1, j_1\rangle|j_2, j_2-1\rangle$ with the magnetic number $m = j_1+j_2-1$.
     (a) One combination is the vector $|j_1+j_2, j_1+j_2-1\rangle \in \mathscr{H}^{j_1+j_2}$
     $$\begin{aligned} |j_1+j_2, j_1+j_2-1\rangle &= \frac{1}{\hbar\sqrt{2(j_1+j_2)}} J_-|j_1+j_2, j_1+j_2\rangle \\ &= \sqrt{\frac{j_1}{j_1+j_2}}\,|j_1, j_1-1\rangle|j_2, j_2\rangle + \sqrt{\frac{j_2}{j_1+j_2}}\,|j_1, j_1\rangle|j_2, j_2-1\rangle \end{aligned} \tag{32}$$
     (b) The other one is the vector orthogonal to it which must be a hwv of $\mathscr{H}^{j_1} \otimes \mathscr{H}^{j_2}$.
     (c) Otherwise acting on it with J_+ we would get a vector with $m = j_1 + j_2$ that is impossible because there is only one such a vector which has been already used to get $|j_1+j_2, j_1+j_2-1\rangle$.

(d) This vector is the hwv of spin-j_1+j_2-1 irrep $\mathscr{H}^{j_1+j_2-1}$

$$|j_1+j_2-1, j_1+j_2-1\rangle = \sqrt{\frac{j_2}{j_1+j_2}}\,|j_1, j_1-1\rangle|j_2, j_2\rangle - \sqrt{\frac{j_1}{j_1+j_2}}\,|j_1, j_1\rangle|j_2, j_2-1\rangle \tag{33}$$

(e) Acting on it with J_- we obtain all $2(j_1+j_2-1)+1$ vectors of $\mathscr{H}^{j_1+j_2-1}$.

3. Three vectors $|j_1, j_1-2\rangle|j_2, j_2\rangle$, $|j_1, j_1-1\rangle|j_2, j_2-1\rangle$, $|j_1, j_1\rangle|j_2, j_2-2\rangle$ with $m = j_1+j_2-2$.
   (a) Two combinations are $|j_1+j_2, j_1+j_2-2\rangle \in \mathscr{H}^{j_1+j_2}$ and $|j_1+j_2-1, j_1+j_2-2\rangle \in \mathscr{H}^{j_1+j_2-1}$
   (b) A unit vector orthogonal to $|j_1+j_2, j_1+j_2-2\rangle$ and $|j_1+j_2-1, j_1+j_2-2\rangle$ must be a hwv of spin-j_1+j_2-2 irrep
4. This pattern continues until $m = |j_1-j_2|$ where we find the last hwv of spin-$|j_1-j_2|$ irrep
   (a) The Hilbert space, $\mathscr{H}$, therefore, has the decomposition

$$\mathscr{H} = \mathscr{H}^{j_1} \otimes \mathscr{H}^{j_2} = \sum_{j=|j_1-j_2|}^{j_1+j_2} \oplus \mathscr{H}^{j} \tag{34}$$

   (b) There are no more hwvs because the dimensions of the l.h.s. and r.h.s. are the same.

$$\dim \mathscr{H}^{j_1} \otimes \mathscr{H}^{j_2} = (2j_1+1)(2j_2+1) \tag{35}$$

$$\begin{aligned}
\dim \sum_{j=|j_1-j_2|}^{j_1+j_2} \mathscr{H}^{j} &= \sum_{j=|j_1-j_2|}^{j_1+j_2} (2j+1) \\
&= (j_1+j_2+|j_1-j_2|)(j_1+j_2-|j_1-j_2|+1) + j_1+j_2-|j_1-j_2|+1 \\
&= (j_1+j_2+|j_1-j_2|+1)(j_1+j_2-|j_1-j_2|+1) \\
&= (j_1+j_2+1)^2 - (j_1-j_2)^2 = \dim \mathscr{H}^{j_1} \otimes \mathscr{H}^{j_2}
\end{aligned} \tag{36}$$

- Due to the tensor product decomposition (34) we have two orthonormal bases of $\mathscr{H}^{j_1} \otimes \mathscr{H}^{j_2}$.

  (i) The original one is

$$|j_1, m_1\rangle |j_2, m_2\rangle\,, \quad m_1 = -j_1, -j_1 + 1, \ldots, j_1\,, \quad m_2 = -j_2, -j_2 + 1, \ldots, j_2 \tag{37}$$

  (ii) The decomposed one is

$$|j, m\rangle\,, \quad j = |j_1 - j_2|, |j_1 - j_2| + 1, \ldots, j_1 + j_2\,, \quad m = -j, -j + 1, \ldots, j \tag{38}$$

- We can decompose the basis vectors as

$$|j_1, m_1\rangle |j_2, m_2\rangle = \sum_{j=|j_1-j_2|}^{j_1+j_2} \sum_{m=-j}^{j} C^{jm}_{j_1,m_1;j_2,m_2} |j, m\rangle\,, \tag{39}$$

  and

$$|j, m\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} C^{j_1,m_1;j_2,m_2}_{jm} |j_1, m_1\rangle |j_2, m_2\rangle\,. \tag{40}$$

- The coefficients of the expansion

$$C^{jm}_{j_1,m_1;j_2,m_2} = \langle j, m | j_1, m_1\rangle |j_2, m_2\rangle\,, \quad C^{j_1,m_1;j_2,m_2}_{jm} = \langle j_1, m_1 | \langle j_2, m_2 | j, m\rangle = \bar{C}^{jm}_{j_1,m_1;j_2,m_2} \tag{41}$$

  are called the **Clebsch-Gordan coefficients**.

  (i) With our choice of the bases they are real numbers.

  (ii) There is an explicit expression for the Clebsch-Gordan coefficients

- Consider an important but simple case where $j_1 = 1/2$ and $j \equiv j_2 \geq 1/2$.
  1. The tensor product decomposition
$$\mathscr{H}^{1/2} \otimes \mathscr{H}^{j} = \mathscr{H}^{j+1/2} \oplus \mathscr{H}^{j-1/2} \tag{42}$$
  2. The hwvs
$$\begin{aligned} |j+\frac{1}{2}, j+\frac{1}{2}\rangle &= |\frac{1}{2}, \frac{1}{2}\rangle |j, j\rangle \\ |j-\frac{1}{2}, j-\frac{1}{2}\rangle &= \sqrt{\frac{2j}{2j+1}}\,|\frac{1}{2}, -\frac{1}{2}\rangle |j, j\rangle - \sqrt{\frac{1}{2j+1}}\,|\frac{1}{2}, \frac{1}{2}\rangle |j, j-1\rangle \end{aligned} \tag{43}$$
  3. Act on $|j+\frac{1}{2}, j+\frac{1}{2}\rangle$ by J_-
$$\begin{aligned} J_-|j+\frac{1}{2}, j+\frac{1}{2}\rangle &= C_-(j+\frac{1}{2}, j+\frac{1}{2})|j+\frac{1}{2}, j-\frac{1}{2}\rangle \\ &= C_-(\frac{1}{2}, \frac{1}{2})|\frac{1}{2}, -\frac{1}{2}\rangle |j, j\rangle + C_-(j, j)|\frac{1}{2}, \frac{1}{2}\rangle |j, j-1\rangle \end{aligned} \tag{44}$$
$$\begin{aligned} J_-^2|j+\frac{1}{2}, j+\frac{1}{2}\rangle &= C_-(j+\frac{1}{2}, j+\frac{1}{2})C_-(j+\frac{1}{2}, j-\frac{1}{2})|j+\frac{1}{2}, j-\frac{3}{2}\rangle \\ &= 2C_-(\frac{1}{2}, \frac{1}{2})C_-(j, j)|\frac{1}{2}, -\frac{1}{2}\rangle |j, j-1\rangle + C_-(j, j)C_-(j, j-1)|\frac{1}{2}, \frac{1}{2}\rangle |j, j-2\rangle \end{aligned} \tag{45}$$

$$
\begin{aligned}
J_-^3|j+\frac{1}{2},j+\frac{1}{2}\rangle &= C_-(j+\frac{1}{2},j+\frac{1}{2})C_-(j+\frac{1}{2},j-\frac{1}{2})C_-(j+\frac{1}{2},j-\frac{3}{2})|j+\frac{1}{2},j-\frac{5}{2}\rangle \\
&= 3C_-(\frac{1}{2},\frac{1}{2})C_-(j,j)C_-(j,j-1)|\frac{1}{2},-\frac{1}{2}\rangle|j,j-2\rangle \\
&+ C_-(j,j)C_-(j,j-1)C_-(j,j-2)|\frac{1}{2},\frac{1}{2}\rangle|j,j-3\rangle
\end{aligned} \tag{46}
$$

4. The pattern is clear, and taking into account that $C_-(\frac{1}{2},\frac{1}{2})=1$, we find

$$
\begin{aligned}
J_-^k|j+\frac{1}{2},j+\frac{1}{2}\rangle &= C_-(j+\frac{1}{2},j+\frac{1}{2})\prod_{p=0}^{k-2}C_-(j+\frac{1}{2},j-\frac{1}{2}-p)|j+\frac{1}{2},j+\frac{1}{2}-k\rangle \\
&= k\prod_{p=0}^{k-2}C_-(j,j-p)|\frac{1}{2},-\frac{1}{2}\rangle|j,j-k+1\rangle+\prod_{p=0}^{k-1}C_-(j,j-p)|\frac{1}{2},\frac{1}{2}\rangle|j,j-k\rangle
\end{aligned} \tag{47}
$$

5. Dividing both sides by $C_-(j+\frac{1}{2},j+\frac{1}{2})\prod_{p=0}^{k-2}C_-(j+\frac{1}{2},j-\frac{1}{2}-p)$, and using

$$
\frac{C_-(j,j-p)}{C_-(j+\frac{1}{2},j-\frac{1}{2}-p)}=\sqrt{\frac{p+1}{p+2}} \tag{48}
$$

we get

$$
|j+\frac{1}{2},j+\frac{1}{2}-k\rangle=\sqrt{\frac{k}{2j+1}}\,|\frac{1}{2},-\frac{1}{2}\rangle|j,j-k+1\rangle+\sqrt{\frac{2j+1-k}{2j+1}}\,|\frac{1}{2},\frac{1}{2}\rangle|j,j-k\rangle \tag{49}
$$

6. Finally, introducing the magnetic number $m \equiv j + \frac{1}{2} - k$, we get

$$|j + \frac{1}{2}, m\rangle = \sqrt{\frac{j + \frac{1}{2} - m}{2j + 1}}\, |\frac{1}{2}, -\frac{1}{2}\rangle |j, m + \frac{1}{2}\rangle + \sqrt{\frac{j + \frac{1}{2} + m}{2j + 1}}\, |\frac{1}{2}, \frac{1}{2}\rangle |j, m - \frac{1}{2}\rangle \tag{50}$$

and the Clebsch-Gordan coefficients are

$$\begin{aligned} C^{\frac{1}{2}, -\frac{1}{2}; j, m+\frac{1}{2}}_{j+\frac{1}{2}, m} &= \langle \frac{1}{2}, -\frac{1}{2} | \langle j, m + \frac{1}{2} | j + \frac{1}{2}, m\rangle = \sqrt{\frac{j + \frac{1}{2} - m}{2j + 1}} = C^{j+\frac{1}{2}, m}_{\frac{1}{2}, -\frac{1}{2}; j, m+\frac{1}{2}} \\ C^{\frac{1}{2}, \frac{1}{2}; j, m-\frac{1}{2}}_{j+\frac{1}{2}, m} &= \langle \frac{1}{2}, \frac{1}{2} | \langle j, m - \frac{1}{2} | j + \frac{1}{2}, m\rangle = \sqrt{\frac{j + \frac{1}{2} + m}{2j + 1}} = C^{j+\frac{1}{2}, m}_{\frac{1}{2}, \frac{1}{2}; j, m-\frac{1}{2}} \end{aligned} \tag{51}$$

7. The vectors $|j - \frac{1}{2}, m\rangle$ can be found from the condition that they are orthogonal to $|j + \frac{1}{2}, m\rangle$

$$|j - \frac{1}{2}, m\rangle = \sqrt{\frac{j + \frac{1}{2} + m}{2j + 1}}\, |\frac{1}{2}, -\frac{1}{2}\rangle |j, m + \frac{1}{2}\rangle - \sqrt{\frac{j + \frac{1}{2} - m}{2j + 1}}\, |\frac{1}{2}, \frac{1}{2}\rangle |j, m - \frac{1}{2}\rangle \tag{52}$$

$$\begin{aligned} C^{\frac{1}{2}, -\frac{1}{2}; j, m+\frac{1}{2}}_{j-\frac{1}{2}, m} &= \langle \frac{1}{2}, -\frac{1}{2} | \langle j, m + \frac{1}{2} | j - \frac{1}{2}, m\rangle = \sqrt{\frac{j + \frac{1}{2} + m}{2j + 1}} = C^{j-\frac{1}{2}, m}_{\frac{1}{2}, -\frac{1}{2}; j, m+\frac{1}{2}} \\ C^{\frac{1}{2}, \frac{1}{2}; j, m-\frac{1}{2}}_{j-\frac{1}{2}, m} &= \langle \frac{1}{2}, \frac{1}{2} | \langle j, m - \frac{1}{2} | j - \frac{1}{2}, m\rangle = -\sqrt{\frac{j + \frac{1}{2} - m}{2j + 1}} = C^{j+\frac{1}{2}, m}_{\frac{1}{2}, \frac{1}{2}; j, m-\frac{1}{2}} \end{aligned} \tag{53}$$

- This case includes a hydrogen atom in its ground state, when all angular momentum is contributed by the spins of the proton and the electron.
- Since both are spin-1/2 particles, there are four states in all and j takes two values, 1 and 0.

3 Orbital angular momentum eigenfunctions

The orbital angular momentum operator $\vec{L} = \vec{X} \times \vec{P}$ satisfies the $\mathfrak{so}(3) \cong \mathfrak{su}(2)$ algebra relations

- Any unitary repr of the Heisenberg algebra of $\vec{X}$ and $\vec{P}$ provides a unitary repr of $\mathfrak{su}(2)$.
- It is an infinite-dimensional representation
- It can be decomposed into a sum of finite-dimensional irreps.
- To find the decomposition we need to identify all hwvs in the infinite-dimensional representation.
- Since all representations of the Heisenberg algebra are unitarily equivalent, we can choose any.
- Find the spectrum of H invariant under rotations, e.g.for a particle moving in a central field.
- It is convenient to use the position representation, where L_α become linear differential operators

$$\vec{L} = -\mathrm{i}\hbar\,\vec{x} \times \vec{\nabla} \quad \Leftrightarrow \quad L_\alpha = -\mathrm{i}\hbar \sum_{\beta,\gamma=1}^{3} \epsilon_{\alpha\beta\gamma} x_\beta \frac{\partial}{\partial x_\gamma} \tag{54}$$

  acting in the Hilbert space $L^2(\mathbb{R}^3)$ of square-integrable functions $\psi(x, y, z)$ in $\mathbb{R}^3$.
- Because of the rotational symmetry it is convenient to use spherical coordinates.
- $\vec{X}^2$ and $\vec{P}^2$ commute with L_α therefore L_α cannot depend neither on $\partial/\partial r$ nor on r.
- Thus, L_α in spherical coordinates are differential operators depending only on the angles θ and ϕ, and their derivative operators $\partial/\partial\theta$ and $\partial/\partial\phi$.

- Then, vectors of a finite-dimensional irrep of the orbital angular momentum operator algebra become functions of the angles ϕ and θ called the spherical harmonics.
- Begin with the coordinate representation for $\vec{X}$ and $\vec{P}$

$$\vec{X}\,\psi(\vec{x}) = \vec{x}\,\psi(\vec{x})\,, \quad \vec{P}\,\psi(\vec{x}) = -\mathrm{i}\,\hbar\,\vec{\nabla}\,\psi(\vec{x}) \tag{55}$$

- Introduce the spherical coordinates

$$x = r\cos\phi\sin\theta\,, \quad y = r\sin\phi\sin\theta\,, \quad z = r\cos\theta\,, \quad r \geq 0\,,\ 0 \leq \theta \leq \pi\,,\ 0 \leq \phi \leq 2\pi \tag{56}$$

- $\psi(x, y, z)$ becomes

$$\varphi(r, \theta, \phi) = \psi(r\cos\phi\sin\theta, r\sin\phi\sin\theta, r\cos\theta)$$

  and it is a periodic function of ϕ
- The Hilbert space $L^2(\mathbb{R}^3)$ of square-integrable functions $\psi(x, y, z)$ on $\mathbb{R}^3$ can be thought of as the tensor product $L^2(\mathbb{R}) \otimes L^2(\mathbb{R}^2)$ or $L^2(\mathbb{R}) \otimes L^2(\mathbb{R}) \otimes L^2(\mathbb{R})$.

- In spherical coordinates we think about $L^2(\mathbb{R}^3)$ as

$$L^2(\mathbb{R}^3) \cong L^2(\mathbb{R}^+) \otimes L^2(S^2) \cong L^2(\mathbb{R}^+) \otimes L^2([0,\pi]) \otimes L^2(S^1) \tag{57}$$

  (i) $\mathbb{R}^+$ is the set of nonnegative real numbers,

  (ii) S^2 is a two-dimensional sphere of radius 1

  (iii) S^1 is a circle of radius 1.

- The inner products on the Hilbert spaces are not the usual ones.

  (i) They are induced from the inner product on $L^2(\mathbb{R}^3)$.

  (ii) Consider two square-integrable functions $\psi_1(x,y,z)$ and $\psi_2(x,y,z)$ on $\mathbb{R}^3$.

    (a) Their inner product in terms of spherical coordinates is

$$\langle\psi_1|\psi_2\rangle = \int dxdydz\,\psi_1^*(x,y,z)\psi_2(x,y,z) = \int_0^\infty dr\,r^2 \int_0^\pi d\theta\,\sin\theta \int_0^{2\pi} d\phi\,\varphi_1^*(r,\theta,\phi)\varphi_2(r,\theta,\phi) \tag{58}$$

    (b) Let φ_a have the factorised product form

$$\varphi_a(r,\theta,\phi) = \mathcal{R}_a(r)\,\mathcal{P}_a(\theta)\,\Phi_a(\phi)\,, \quad a = 1,2 \tag{59}$$

    (c) The inner product becomes

$$\langle\psi_1|\psi_2\rangle = \int_0^\infty dr\,r^2\,\mathcal{R}_1^*(r)\mathcal{R}_2(r) \int_0^\pi d\theta\,\sin\theta\,\mathcal{P}_1^*(\theta)\mathcal{P}_2(\theta) \int_0^{2\pi} d\phi\,\Phi_1^*(\phi)\Phi_2(\phi) \tag{60}$$

(iii) $L^2(\mathbb{R}^+)$ is the Hilbert space of square-integrable functions $\mathcal{R}(r)$ on $\mathbb{R}^+$ with **weight** r^2

(iv) $L^2([0,\pi])$ is the Hilbert space of square-integrable functions $\mathcal{P}(\theta)$ on $[0.\pi]$ with **weight** $\sin\theta$,

(v) $L^2(S^1)$ is the Hilbert space of square-integrable periodic functions $\Phi(\phi)$ on $[0,2\pi]$.

(vi) Since θ and ϕ parametrise a sphere of radius 1, the tensor product $L^2([0.\pi]) \otimes L^2(S^1)$ can be identified with the Hilbert space of square-integrable functions $Y(\vec{n})$, $\vec{n}^2 = 1$ on S^2 with the natural inner product

$$\langle Y_1|Y_2\rangle = \int_{S^2} d\Omega\, Y_1^*(\vec{n})Y_2(\vec{n}) = \int_0^\pi d\theta\, \sin\theta \int_0^{2\pi} d\phi\, Y_1^*(\theta,\phi)Y_2(\theta,\phi) \tag{61}$$

where $d\Omega$ is the surface (area) element of the unit sphere given in spherical coordinates by $\sin\theta\, d\theta\, d\phi$, and $\vec{n}$ is the unit vector to a point on the sphere.

- P_α become differential operators acting on $\varphi(r,\theta,\phi)$.
- To find theIr explicit form let us find momenta canonically conjugated to the spherical coordinates.

(i) Consider a free particle of mass $m = 1$ with Lagrangian

$$L = \frac{1}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) = \frac{1}{2}(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\dot{\phi}^2) \tag{62}$$

(ii) Their momenta are

$$p_x = \dot{x}\,, \quad p_y = \dot{y}\,, \quad p_z = \dot{z}\,, \quad p_r = \dot{r}\,, \quad p_\theta = r^2\dot{\theta}\,, \quad p_\phi = r^2\sin^2\theta\dot{\phi} \tag{63}$$

(iii) Differentiating (56) with respect to time, and using the formulae, we get

$$\begin{aligned} p_x &= \cos\phi\sin\theta\, p_r - \frac{\sin\phi}{r\sin\theta}\, p_\phi + \frac{1}{r}\cos\phi\cos\theta\, p_\theta \\ p_y &= \sin\phi\sin\theta\, p_r + \frac{\cos\phi}{r\sin\theta}\, p_\phi + \frac{1}{r}\sin\phi\cos\theta\, p_\theta \\ p_z &= \cos\theta\, p_r - \frac{1}{r}\sin\theta\, p_\theta \end{aligned} \tag{64}$$

(iv) It is easy to check that the point transformation (56), (64) is indeed canonical.

- Thus, the derivative operators which represent P_x, P_y, P_z and P_r, P_θ, P_ϕ are related as

$$\begin{aligned} \frac{\partial}{\partial x} &= \cos\phi\sin\theta\frac{\partial}{\partial r} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi} + \frac{1}{r}\cos\phi\cos\theta\frac{\partial}{\partial\theta}\,, \\ \frac{\partial}{\partial y} &= \sin\phi\sin\theta\frac{\partial}{\partial r} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi} + \frac{1}{r}\sin\phi\cos\theta\frac{\partial}{\partial\theta} \\ \frac{\partial}{\partial z} &= \cos\theta\frac{\partial}{\partial r} - \frac{1}{r}\sin\theta\frac{\partial}{\partial\theta} \end{aligned} \tag{65}$$

- By using these formulae we can find L_α in terms of the spherical coordinates

$$
\begin{aligned}
L_z &= -\mathrm{i}\,\hbar\,\frac{\partial}{\partial\phi}\\
L_x &= -\mathrm{i}\,\hbar\Big(-\sin\phi\frac{\partial}{\partial\theta}-\cot\theta\cos\phi\frac{\partial}{\partial\phi}\Big)\\
L_y &= -\mathrm{i}\,\hbar\Big(\cos\phi\frac{\partial}{\partial\theta}-\cot\theta\sin\phi\frac{\partial}{\partial\phi}\Big)
\end{aligned}
\tag{66}
$$

(i) As expected, L_α depend only on the angles θ and ϕ and their differential operators.

(ii) It is a new representation of $\mathfrak{su}(2)$ by differential operators acting in the Hilbert space $L^2(S^2)$.

(iii) It is an infinite-dimensional subrepresentation of the repr in $L^2(\mathbb{R}^3)$ we have begun with.

- To decompose it into a sum of finite-dimensional irreps

(i) Find $L_\pm$ and L^2

$$
\begin{aligned}
L_+ &= \hbar\,e^{\mathrm{i}\,\phi}\Big(\frac{\partial}{\partial\theta}+\mathrm{i}\,\cot\theta\frac{\partial}{\partial\phi}\Big)\\
L_- &= \hbar\,e^{-\mathrm{i}\,\phi}\Big(-\frac{\partial}{\partial\theta}+\mathrm{i}\,\cot\theta\frac{\partial}{\partial\phi}\Big)
\end{aligned}
\tag{67}
$$

$$
L^2 = -\hbar^2\Big(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Big) \tag{68}
$$

(ii) Find all hwvs in $L^2(S^2)$

$$
L_z\,Y_\ell^\ell(\theta,\phi) = \hbar\,\ell\,Y_\ell^\ell(\theta,\phi)\,, \quad L_+\,Y_\ell^\ell(\theta,\phi) = 0 \tag{69}
$$

(iii) By using (66), we get

$$-\mathrm{i}\frac{\partial Y_\ell^\ell(\theta,\phi)}{\partial\phi} = \ell\, Y_\ell^\ell(\theta,\phi) \tag{70}$$

(iv) The general solution is

$$Y_\ell^\ell(\theta,\phi) = \mathcal{P}_\ell^\ell(\theta)\Phi_\ell(\phi)\,, \qquad \Phi_\ell(\phi) = \frac{1}{\sqrt{2\pi}}e^{\mathrm{i}\,\ell\,\phi}\,, \quad \int_0^{2\pi} d\phi\,\Phi_\ell^*(\phi)\Phi_m(\phi) = \delta_{\ell m} \tag{71}$$

ℓ must be an integer because of the periodicity condition.

(v) Now, using (67), we find $\mathcal{P}_\ell^\ell(\theta)$

$$\Big(\frac{\partial}{\partial\theta} + \mathrm{i}\,\cot\theta\frac{\partial}{\partial\phi}\Big)\mathcal{P}_\ell^\ell(\theta)\Phi_\ell^\ell(\phi) = \Big(\frac{d\mathcal{P}_\ell^\ell(\theta)}{d\theta} - \ell\,\cot\theta\,\mathcal{P}_\ell^\ell(\theta)\Big)\Phi_\ell(\phi) = 0 \tag{72}$$

Thus

$$\frac{d\mathcal{P}_\ell^\ell(\theta)}{d\theta} - \ell\,\cot\theta\,\mathcal{P}_\ell^\ell(\theta) = 0 \quad \Rightarrow \quad \mathcal{P}_\ell^\ell(\theta) = c_l\sin^\ell\theta \tag{73}$$

(vi) The constant c_l can be chosen to be real, and it is found from the normalisation condition

$$\int_0^\pi d\theta\,\sin\theta\,\mathcal{P}_\ell^\ell(\theta)^2 = c_l^2\int_0^\pi d\theta\,\sin^{2\ell+1}\theta = c_l^2\,\frac{2^{2\ell+1}(\ell!)^2}{(2\ell+1)!} = 1 \quad \Rightarrow \quad c_l^2 = \frac{(2\ell+1)!}{2^{2\ell+1}(\ell!)^2} \tag{74}$$

- Found all hwvs of $\mathfrak{su}(2)$ in $L^2(S^2)$, and for each $\ell = 0, 1, 2, \ldots$ there is one vector

$$Y_\ell^\ell(\theta,\phi) = \mathcal{P}_\ell^\ell(\theta)\Phi_\ell(\phi) = \frac{(-1)^\ell}{\sqrt{4\pi}} \frac{\sqrt{(2\ell+1)!}}{2^\ell\,\ell!}\, e^{\mathrm{i}\,\ell\,\phi}\, \sin^\ell\theta \tag{75}$$

- This function is called the **highest weight-ℓ spherical harmonic**.
- $L^2(S^2)$ is decomposed into the sum of finite-dimensional irreps of $\mathfrak{su}(2)$

$$L^2(S^2) = \sum_{\ell=0}^{\infty} \mathscr{H}^\ell \tag{76}$$

- Vectors in each $\mathscr{H}^\ell$ are called **spherical harmonics**
  (i) denoted by Y_ℓ^m, $m = -\ell, -\ell+1, \ldots, \ell$
  (ii) obtained by acting on the highest weight-ℓ spherical harmonic by the lowering operator L_-

$$Y_\ell^m(\theta,\phi) = \frac{1}{\Pi_{k=0}^{\ell-m-1}\,\hbar\, C_-(\ell,\ell-k)}\, L_-^{\ell-m}\, Y_\ell^\ell(\theta,\phi) = \mathcal{P}_\ell^m(\theta)\Phi_m(\phi) \tag{77}$$

  (iii) For example

$$\begin{aligned} Y_\ell^{\ell-1}(\theta,\phi) &= \frac{1}{C_-(\ell,\ell)}\, e^{-\mathrm{i}\,\phi}\Big(-\frac{\partial}{\partial\theta} + \mathrm{i}\,\cot\theta\frac{\partial}{\partial\phi}\Big)\mathcal{P}_\ell^\ell(\theta)\Phi_\ell(\phi) = \frac{\Phi_{\ell-1}(\phi)}{\sqrt{2\ell}}\Big(-\frac{d}{d\theta} - \ell\,\cot\theta\Big)\mathcal{P}_\ell^\ell(\theta) \\ &= \Phi_{\ell-1}(\phi)\frac{\sqrt{(2\ell+1)!}}{2^\ell\,\ell!\sqrt{4\ell}}(-(-1)^\ell\,2\ell\,\cos\theta\,\sin^{\ell-1}\theta) \end{aligned} \tag{78}$$

Thus,

$$\mathcal{P}_\ell^{\ell-1}(\theta) = \frac{\sqrt{(2\ell+1)!}}{2^\ell\,\ell!\sqrt{4\ell}}(-(-1)^\ell\,2\ell\,\cos\theta\,\sin^{\ell-1}\theta) = \frac{\sqrt{(2\ell+1)!}}{2^\ell\,\ell!\sqrt{4\ell}}\frac{(-1)^\ell}{\sin^{\ell-1}\theta}\frac{d}{d(\cos\theta)}\sin^{2\ell}\theta \tag{79}$$

- It is not difficult to derive the general formula

$$\mathcal{P}_\ell^m(\theta) = \frac{\sqrt{(2\ell+1)!}}{2^\ell\,\ell!}\sqrt{\frac{(l+m)!}{2\,(2l)!(l-m)!}}\frac{(-1)^\ell}{\sin^m\theta}\frac{d^{\ell-m}}{d(\cos\theta)^{\ell-m}}\sin^{2\ell}\theta = P_\ell^m(\cos\theta) \tag{80}$$

  (i) $P_\ell^m(\mu)$, $-1 \le \mu \le 1$ are called the **normalised associated Legendre polynomials**.

  (ii) If $m=0$ then $P_\ell(\mu) \equiv P_\ell^0(\mu)$ are called the **normalised Legendre polynomials**.

  (iii) They differ from the Legendre polynomials whose normalisation is fixed by $P_\ell(1) = 1$.

- The normalised associated Legendre polynomials obey the relations

$$P_\ell^{-m}(\mu) = (-1)^m P_\ell^m(\mu)\,, \quad m = -\ell, -\ell+1, \dots, \ell \tag{81}$$

- Therefore the spherical harmonics obey

$$Y_\ell^{-m}(\theta,\phi) = (-1)^m \bar{Y}_\ell^m(\theta,\phi) \tag{82}$$

  (i) $\bar{Y}_\ell^\ell$ is up to a sign a lowest weight vector

  (ii) All spherical harmonics can be obtained by acting on it with the raising operators L_+.

  (iii) The sign is fixed from the requirement that Y_ℓ^0 and $\bar{Y}_\ell^0$ obtained from the highest and lowest weight vectors would be equal to each other.

- The spherical harmonics form an orthonormal basis of $L^2(S^2)$

$$\int_{S^2} d\Omega\, \bar{Y}_\ell^m(\theta,\phi) Y_{\ell'}^{m'}(\theta,\phi) = \delta_{\ell\ell'}\delta^{mm'} \tag{83}$$

- Any function in $L^2(S^2)$ can be expanded over the spherical harmonics.
- Coming back to our problem of decomposing the orbital momentum operators representation in $L^2(\mathbb{R}^3) \cong L^2(\mathbb{R}^+) \otimes L^2(S^2)$

  (i) Given any basis functions $\mathcal{R}_n(r)$ in $L^2(\mathbb{R}^+)$, the functions $\mathcal{R}_n(r)Y_\ell^m(\theta,\phi)$ form a basis of $L^2(\mathbb{R}^3)$

  (ii) Any function $\psi(\vec{x}) \in L^2(\mathbb{R}^3)$ can be expanded in a series

$$\psi(\vec{x}) = \sum_n \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} C_{n\ell m}\mathcal{R}_n(r)Y_\ell^m(\theta,\phi) \tag{84}$$

  (iii) Any irrep of $\mathfrak{su}(2)$ appears in a decomposition infinitely many times

  (iv) There are infinitely many ways to decompose $L^2(\mathbb{R}^3)$.
  Indeed given any function $\mathcal{R}(r) \in L^2(\mathbb{R}^3)$
  a set of function of the form $\mathcal{R}(r)\sum_{m=-\ell}^{\ell} C_m Y_\ell^m(\theta,\phi)$ forms an irrep of $\mathfrak{su}(2)$.

4 Central field

4.1 The radial Schrödinger equation

- In cartesian coordinates the Hamiltonian is

$$H = -\frac{\hbar^2}{2\mu}\vec{\nabla}^2 + V(r) \tag{85}$$

- $\vec{\nabla}^2$ in terms of spherical coordinates is

$$\vec{\nabla}^2 = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2}\Big(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Big) \tag{86}$$

- Comparing this expression with the Casimir operator L^2

$$L^2 = -\hbar^2\Big(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Big) \tag{87}$$

  we see that

$$\vec{\nabla}^2 = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2 r^2} \tag{88}$$

- In spherical coordinates the Hamiltonian of a particle moving in a central field takes the form

$$H = -\frac{\hbar^2}{2\mu\, r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{L^2}{2\mu\, r^2} + V(r) \tag{89}$$

- TISE becomes

$$\Big(-\frac{\hbar^2}{2\mu\, r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{L^2}{2\mu\, r^2} + V(r)\Big)\varphi_E(r,\theta,\phi) = E\,\varphi_E(r,\theta,\phi) \tag{90}$$

- Simultaneous eigenfunctions of H, L_z and L^2 are

$$\varphi_E(r,\theta,\phi) = \mathcal{R}_{E\ell m}(r)\, Y_\ell^m(\theta,\phi) \tag{91}$$

- $\mathcal{R}_{E\ell m}(r)$ satisfies the radial Schrödinger equation

$$\Big(-\frac{\hbar^2}{2\mu\, r^2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{\ell(\ell+1)\hbar^2}{2\mu\, r^2} + V(r)\Big)\mathcal{R}_{E\ell}(r) = E\,\mathcal{R}_{E\ell}(r) \tag{92}$$

  (i) The subscript m has been dropped because neither E nor the radial function depends on it.

  (ii) The energy spectrum has at least the $2\ell+1$-fold degeneracy.

- The reason for the degeneracy is in the rotational symmetry.

  (i) The Hamiltonian commutes with L_α

  (ii) Therefore, if $|\psi_{E\ell\ell}\rangle$ is a hwv and an eigenstate of H, then all the states $L_-^k|\psi_{E\ell\ell}\rangle$ are also eigenstates of H with the same energy.

- (92) takes the standard form of the one-dim TISE in terms of the function $\mathcal{U}_{E\ell}(r) = r\,\mathcal{R}_{E\ell}(r)$

$$\Big(-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V_{\text{eff}}(r)\Big)\mathcal{U}_{E\ell}(r) = E\,\mathcal{U}_{E\ell}(r)\,, \quad V_{\text{eff}}(r) \equiv V(r) + \frac{\ell(\ell+1)\hbar^2}{2\mu\,r^2} \tag{93}$$

  (i) Since $\mathcal{R}_{E\ell}(r)$ is regular at $r=0$, the function $\mathcal{U}_{E\ell}(r)$ must vanish at $r=0$.

  (ii) If $\mathcal{R}_{E\ell}(r)$ is normalisable then it belongs to the Hilbert space of square-integrable functions on $\mathbb{R}^+$ with weight r^2, and therefore $\mathcal{U}_{E\ell}(r)$ is normalised as

$$\int_0^\infty dr\,\mathcal{U}^*_{E\ell}(r)\mathcal{U}_{E\ell}(r) = 1 \tag{94}$$

  (iii) The spectrum is then discrete and can be parametrised by integer numbers n, ℓ, and m.

  (iv) The parameters n, ℓ, and m that determine the eigenfunctions of the discrete spectrum are called the radial, orbital, and magnetic quantum numbers, respectively.

- The radial equation (93) is equivalent to TISE with $V_{\text{eff}}(x)$ such that $V_{\text{eff}}(x) = \infty$ for $x < 0$.

- The effective potential includes for $\ell \neq 0$ the repulsive centrifugal barrier $\ell(\ell+1)\hbar^2/2\mu\,r^2$ that enforces $\mathcal{U}_{E\ell}(r)$ to vanish at $r=0$.

- Usually, $V(r)$ is less singular than $1/r^2$. It is the case for the two most important potentials

  (i) the Coulomb potential $V(r) = \alpha/r$ describing the interaction of charged particles

  (ii) the Yukawa potential $V(r) = ge^{-r/a}/r$ often used in nuclear physics.

- The small r behaviour of $\mathcal{U}_{E\ell}(r)$ for $\ell > 0$ is found by droppng the potential and the energy

$$\frac{d^2\mathcal{U}_{E\ell}(r)}{dr^2} = \frac{\ell(\ell+1)}{r^2}\mathcal{U}_{E\ell}(r) \tag{95}$$

  (i) Two linearly independent solutions $r^{\ell+1}$ and $1/r^{\ell}$ but only $r^{\ell+1}$ vanishes at $r = 0$.
  (ii) For this solution $\mathcal{R}_{E\ell}(r) \sim r^{\ell}$ and therefore the probability of finding a particle in the vicinity of the origin is decreasing with the angular momentum increasing in accord with intuition.
  (iii) If $\ell = 0$ the behaviour of $\mathcal{U}_{E\ell}(r)$ at the origin depends on the details of the potential.
  (iv) For some potentials $\mathcal{U}_{E\ell}(r) \sim r$, and the $\ell = 0$ state has a nonzero amplitude to be at the origin.

- Consider now the behaviour of $\mathcal{U}_{E\ell}(r)$ as $r \to \infty$.

  (a) If $V(r)$ diverges as $r \to \infty$ then the spectrum is discrete, and $\mathcal{U}_{E\ell}(r) \to 0$ as $r \to \infty$.
  (b) If $V(r) \to 0$ (or any constant) as $r \to \infty$ then there are two cases to consider

  1. $E > 0$: The particle escapes to infinity. We expect $\mathcal{U}_{E\ell}$ to oscillate as $r \to \infty$
  2. $E < 0$: The particle is bound. The region $r \to \infty$ is classically forbidden, and $\mathcal{U}_{E\ell}$ falls exponentially there

I. $E > 0$

At large r the solutions to (93) are of the form

$$\mathcal{U}_{E\ell}(r) = A_\pm(r)\, e^{\pm \mathrm{i}\, k\, r}\,, \quad k = \sqrt{\frac{2\mu E}{\hbar^2}} \tag{96}$$

i. The functions $A_\pm$ are slowly varying as $r \to \infty$.

ii. Substitute (96) into (93)

$$\frac{d^2 A_\pm}{dr^2} \pm 2\mathrm{i}\, k\, \frac{dA_\pm}{dr} - \frac{2\mu\, V_{\text{eff}}(r)}{\hbar^2} A_\pm = 0 \tag{97}$$

iii. Since $A_\pm$ vary slowly at large r we neglect $A_\pm''$ and find

$$\frac{d \ln\, A_\pm}{dr} = \mp \mathrm{i}\, \frac{\mu}{k\, \hbar^2} V_{\text{eff}}(r) \quad \Rightarrow \quad A_\pm(r) = \exp\Big(\mp \mathrm{i}\, \frac{\mu}{k\, \hbar^2} \int_{r_0}^{r} dr'\, V_{\text{eff}}(r') \Big) \tag{98}$$

where r_0 is some constant.

iv. Check that at large r $A_\pm''$ is much smaller than $A_\pm'$, and therefore we could drop $A_\pm''$.

The formula

$$A_\pm(r) = \exp\Big(\mp \,\mathrm{i}\frac{\mu}{k\,\hbar^2}\int_{r_0}^{r} dr'\, V_{\text{eff}}(r')\Big) \tag{99}$$

shows that potentials can be divided into two groups

1. Short-range potentials for which $r\,V(r) \to 0$ as $r \to \infty$, and $A_\pm \to$ constants as $r \to \infty$.
   - An example of such a potential is the Yukawa potential.
   - At large r the solutions to (93) are of the form

     $$\mathcal{U}_{E\ell}(r) = A\,e^{\mathrm{i}\,k\,r} + B\,e^{-\mathrm{i}\,k\,r} \tag{100}$$

   - The particle behaves as a free particle far from the origin.
   - Info about the potential is in A/B which is determined by the requirement that if $\mathcal{U}_{E\ell}$ is continued inward to $r = 0$, it must vanish.
   - There is therefore just one free parameter in the solution (the overall scale), and not two.
2. Long-range potentials for which $V(r) \to 0$ but $r\,V(r) \neq 0$ as $r \to \infty$, and $A_\pm$ remain nontrivial functions of r at large r.
   - An important example is the Coulomb potential $V = -\alpha/r$ for which, dropping the centrifugal potential subleading at large r, we get

     $$A_\pm(r) = \exp\Big(\pm \,\mathrm{i}\frac{\mu}{k\,\hbar^2}\alpha \ln\frac{r}{r_0}\Big) \tag{101}$$

   - This means that no matter how far away the particle is from the origin it is never completely free of the Coulomb potential.

II. $E < 0$.

– All the results from the $E > 0$ case carry over with the change

$$k \to \mathrm{i}\,\kappa\,, \quad \kappa = \sqrt{\frac{2\mu|E|}{\hbar^2}} \tag{102}$$

– For short-range potentials

$$\mathcal{U}_{E\ell}(r) = A\,e^{-\kappa\,r} + B\,e^{+\kappa\,r} \tag{103}$$

– The exponentially divergent term $B\,e^{+\kappa\,r}$ will be absent only for certain discrete values of E.

– For long-range potentials the exponential behaviour will be modified.

– In particular for the attractive Coulomb potential $V = -\alpha/r$ we get

$$\mathcal{U}_{E\ell}(r) \to \exp\Big(\frac{\mu}{\kappa\,\hbar^2}\alpha\ln\frac{r}{r_0} - \kappa\,r\Big) = \left(\frac{r}{r_0}\right)^{\frac{\mu\,\alpha}{\kappa\hbar^2}}\,e^{-\kappa\,r} \tag{104}$$

– When we solve the problem of the hydrogen atom, we will find that this is indeed the case.

4.2 The free particle in spherical coordinates

For a free particle the radial Schrödinger equation (92) takes the form

$$\frac{d^2\mathcal{R}_{E\ell}}{dr^2} + \frac{2}{r}\frac{d\mathcal{R}_{E\ell}}{dr} + \Big(k^2 - \frac{\ell(\ell+1)}{r^2}\Big)\mathcal{R}_{E\ell} = 0\,, \quad k \equiv \sqrt{\frac{2\mu}{\hbar^2}E} \tag{105}$$

- This differential equation is in fact equivalent to Bessel's equation

$$\frac{d^2\mathcal{B}}{dr^2} + \frac{1}{r}\frac{d\mathcal{B}}{dr} + \Big(k^2 - \frac{(\ell+\frac{1}{2})^2}{r^2}\Big)\mathcal{B} = 0\,, \qquad \mathcal{B}(r) = \sqrt{r}\,\mathcal{R}_{E\ell}(r) \tag{106}$$

  whose two linearly independent solutions are the **Bessel functions** $J_{\ell+1/2}(kr)$ and $Y_{\ell-1/2}(kr)$.

- The general solution to (105) is

$$\mathcal{R}_{E\ell}(r) = A\, j_\ell(k\,r) + B\, y_\ell(k\,r) \tag{107}$$

  where j_ℓ and y_ℓ are the **spherical Bessel functions**

$$j_\ell(x) \equiv \sqrt{\frac{\pi}{2x}}\, J_{\ell+1/2}(x)\,, \quad y_\ell(x) \equiv \sqrt{\frac{\pi}{2x}}\, Y_{\ell+1/2}(x) \tag{108}$$

- Since $Y_{\ell+1/2}(kr)$ diverges at $r = 0$, we have to set B to 0.

- To find A we use the orthogonality condition for spherical Bessel functions

$$\int_0^\infty dr\, r^2\, j_\nu(kr) j_\nu(k'r) = \frac{\pi}{2k^2}\delta(k-k')\,, \quad \nu > -\frac{1}{2}\,, \quad k > 0 \tag{109}$$

  and get

$$\mathcal{R}_{E\ell}(r) = \frac{\sqrt{\mu}}{\hbar}\sqrt{\frac{2k}{\pi}}\, j_\ell(kr)\,, \quad k = \sqrt{\frac{2\mu}{\hbar^2}E} \tag{110}$$

- The solution of TISE for a free particle with energy E and angular momentum $\hbar\,\ell$ is

$$\varphi_{E\ell m}(r,\theta,\phi) = \mathcal{R}_{E\ell m}(r)\,Y_\ell^m(\theta,\phi) = \frac{\sqrt{\mu}}{\hbar}\sqrt{\frac{2k}{\pi}}\,j_\ell(kr)\,Y_\ell^m(\theta,\phi)\,, \qquad E = \frac{\hbar^2}{2\mu}k^2 \tag{111}$$

- A wave packet in the spherical coordinates has the form

$$\varphi(r,\theta,\phi) = \sum_{\ell=-\infty}^{\infty}\sum_{m=-\ell}^{\ell}\int_0^\infty dE\,\varphi_{E\ell m}(r,\theta,\phi)\,C_{\ell m}(E)\,, \qquad \sum_{\ell=-\infty}^{\infty}\sum_{m=-\ell}^{\ell}\int_0^\infty dE\,|C_{\ell m}(E)|^2 = 1 \tag{112}$$

- It evolves as

$$\varphi(r,\theta,\phi,t) = \sum_{\ell=-\infty}^{\infty}\sum_{m=-\ell}^{\ell}\int_0^\infty dE\,e^{-\mathrm{i}\,E\,t/\hbar}\,\varphi_{E\ell m}(r,\theta,\phi)\,C_{\ell m}(E) \tag{113}$$

- The spectrum of L_z and L^2 is discrete $\Rightarrow$ normalise wave functions with definite ℓ and m.
- The corresponding wave packet is

$$\varphi(r,\theta,\phi,t) = \int_0^\infty dE\,e^{-\mathrm{i}\,E\,t/\hbar}\,\varphi_{E\ell m}(r,\theta,\phi)\,C(E) = \frac{e^{\mathrm{i}\,m\,\phi}}{\sqrt{2\pi}}\int_0^\infty dE\,e^{-\mathrm{i}\,E\,t/\hbar}\,\mathcal{R}_{E\ell}(r)\,\mathcal{P}_\ell^m(\theta)\,C(E) \tag{114}$$

- The probability of finding a particle with orbital number ℓ and magnetic number m at a point (r,θ,ϕ) is independent of ϕ.
- It is not surprising because ϕ and L_z are conjugate variables.

5 Gross structure of hydrogen

- We develop a model of the simplest atom, hydrogen, which is a system of an electron of charge $-e$ and mass m, and a proton of charge $+e$ and mass M.
- For future applications it is convenient to generalise from hydrogen to a hydrogen-like ion, in which a single electron is bound to a nucleus of charge Ze.
- We only consider a simplified model of a hydrogen-like ion.
- In this model neither the electron nor the nucleus has a spin, and the electron moves non-relativistically under purely electrostatic forces.
- The structure of an atom or ion that is obtained using these approximations is called its **gross structure**.

5.1 Energy spectrum of hydrogen

- The model is a two-body system
- We can reduce the problem to the dynamics of a single particle whose mass $\mu = mM/(m+M)$ is the reduced mass and whose coordinate r is the relative coordinate of the two particles.
- The Coulomb potential of a fixed charge Ze and a moving particle of charge $-e$ in CGS units is

$$V(r) = -\frac{Ze^2}{r} \tag{115}$$

- The energy spectrum is discrete for $E < 0$ and continuous for $E > 0$.
- We only consider the bound state spectrum determined by the radial Schrödinger equation (93)

$$\Big(\frac{d^2}{dr^2} + \frac{2\mu Ze^2}{\hbar^2}\frac{1}{r} - \frac{\ell(\ell+1)}{r^2}\Big)\mathcal{U}_{E\ell}(r) = \kappa^2\,\mathcal{U}_{E\ell}(r)\,, \quad \kappa \equiv \sqrt{-\frac{2\mu}{\hbar^2}E} \tag{116}$$

- The radial function $\mathcal{U}_{E\ell}$ behaves as $r^{\ell+1}$ as $r \to 0$, and as $r^\gamma\, e^{-\kappa r}$ as $r \to \infty$ where $\gamma = \mu Ze^2/\kappa\hbar^2$.
- Introduce the dimensionless variable

$$\rho \equiv 2\kappa\, r \tag{117}$$

and constant

$$\rho_0 \equiv \frac{\mu\, Ze^2}{\hbar^2\kappa} = \gamma \tag{118}$$

- (116) takes the form

$$\Big(\frac{d^2}{d\rho^2}+\frac{\rho_0}{\rho}-\frac{\ell(\ell+1)}{\rho^2}-\frac{1}{4}\Big)\mathcal{U}(\rho)=0\,,\quad \mathcal{U}(\rho)=\mathcal{U}_{E\ell}(\rho/2\kappa) \tag{119}$$

- It is convenient to remove from t $\mathcal{U}(\rho)$ the portions that describe its behaviour at $r=0$ and $r=\infty$.
- Introduce

$$\mathcal{W}(\rho)=\rho^{-\ell-1}\,e^{\rho/2}\,\mathcal{U}(\rho)\,,\quad \mathcal{W}(0)=w_0=\text{const}\ ,\quad \mathcal{W}(\rho)\to\rho^{-\ell-1+\gamma}\ \text{ as }\ \rho\to\infty \tag{120}$$

- It satisfies

$$\rho\,\frac{d^2\mathcal{W}}{d\rho^2}+(2\ell+2-\rho)\frac{d\mathcal{W}}{d\rho}+(\rho_0-\ell-1)\mathcal{W}=0 \tag{121}$$

- Look for a solution in terms of a power series in ρ

$$\mathcal{W}=\sum_{k=0}^{\infty}w_k\rho^k \tag{122}$$

- Substituting the series in (119), we get that the coefficients w_k satisfy the recursion relation

$$w_{k+1}=\frac{k+\ell+1-\rho_0}{(k+1)(k+2\ell+2)}\,w_k \tag{123}$$

- All the coefficients can be expressed through w_0, and for generic values of ρ_0 we get an infinite series in ρ.

- How does the series behave at large ρ ?

  (i) If $k \geq k_0 \gg \ell$ then the recursion relation can be approximated by

$$w_{k+1} \approx \frac{1}{k+1} w_k \quad w_k \approx \frac{1}{k!} c_0 \,, \quad k \geq k_0 \tag{124}$$

  (ii) The series behaves as

$$\sum_{k=0}^{\infty} w_k \rho^k \approx \sum_{k=0}^{k_0-1} w_k \rho^k + \sum_{k=k_0}^{\infty} \frac{1}{k!} \rho^k \, c_0 \quad \to \quad c_0 \, e^{\rho} \;\; \text{as} \;\; \rho \to \infty \tag{125}$$

  (iii) For generic values of ρ_0 the function $\mathcal{U}$ blows up as $e^{\rho/2}$ at large ρ.

- Thus, ρ_0 must be chosen so that the series terminates at some maximal integer, k_{max} such that

$$w_{k_{\text{max}}+1} = 0 \tag{126}$$

- From the recursion relation (123) we find

$$\rho_0 = k_{\text{max}} + \ell + 1 \tag{127}$$

- Define the **principal quantum number**

$$n \equiv k_{\text{max}} + \ell + 1 \geq 1 \tag{128}$$

- We have $\rho_0 = n$, and therefore the allowed energies are

$$E_n = -\frac{\mu \, Z^2 e^4}{2\hbar^2 \rho_0^2} = -\frac{\mu \, Z^2 e^4}{2\hbar^2} \frac{1}{n^2} = \frac{E_1}{n^2} \,, \quad n = 1, 2, 3, \ldots \tag{129}$$

- This is the famous **Bohr formula** obtained in 1913 well before quantum mechanics was created.
- Since at large r the wave function behaves as $e^{-\kappa r}$ the natural length scale is given by $1/\kappa$ which is expressed through the principal quantum number as follows

$$\frac{1}{\kappa} = \frac{\hbar^2 \rho_0}{\mu\, Z e^2} = \frac{\hbar^2}{\mu\, Z e^2} n = a_Z\, n\,, \quad a_Z \equiv \frac{\hbar^2}{\mu\, e^2\, Z} \tag{130}$$

(i) Here $a \equiv a_1$ is called the (first) **Bohr radius** of hydrogen

if $\mu = m_e m_p/(m_e + m_p)$, $m = m_e$, $M = m_p$ is the reduced mass and $-e$ the charge of the electron.

(ii) Its numerical value is

$$a = 5.29177 \times 10^{-9} cm \tag{131}$$

(iii) In the case of hydrogen one also defines the **Rydberg constant** $\mathcal{R}$

$$\mathcal{R} \equiv \frac{\mu\, e^4}{2\hbar^2} = 13.6056923\,\mathrm{eV} \tag{132}$$

and writes the expression for the permitted values of E and ℓ in hydrogen in the form

$$E_n = -\frac{\mathcal{R}}{n^2}\,, \quad n = 1, 2, \dots\,, \quad l = 0, 1, \dots, n-1 \tag{133}$$

(iv) The Rydberg constant is equal to the **binding energy** of hydrogen,

that is the amount of energy you would need to free the electron in the ground state which obviously corresponds to $n = 1$ and $\ell = 0$.

- The spectrum of a hydrogen-like ion is degenerate.

  (i) The usual $(2\ell+1)$-fold degeneracy for each ℓ

  (ii) An accidental degeneracy in ℓ. The number of states with the same energy is

$$\sum_{\ell=0}^{n-1}(2\ell+1) = n^2 \tag{134}$$

- Use n to label kets and wave functions: $|n,\ell,m\rangle$ is the stationary state of a hydrogen-like ion for the energy given by (129), and the stated angular-momentum quantum numbers.

  (i) The ground state is $|1,0,0\rangle$ and it is the only nondegenerate state.

  (ii) The energy level immediately above the ground state is four-fold degenerate.
  It is spanned by $|2,0,0\rangle$, $|2,1,0\rangle$ and $|2,1,\pm1\rangle$.

  (iii) The second excited energy level is 9-fold degenerate, and so on.

- In spectroscopy it is common to refer to the states with $\ell = 0,1,2,3,\ldots$ as $s,p,d,j,g,h,\ldots$ states.

  (i) $1s$ denotes the ground state $n=1, \ell=0$;

  (ii) $2s, 2p$ the $\ell=0$ and $\ell=1$ states at $n=2$;

  (iii) $3s, 3p, 3d$ the $\ell=0,1,2$ states at $n=3$, and so on.

  (iv) No attempt is made to keep track of m.

- The degeneracy of energy eigenstates with different values of ℓ is a special property of the Coulomb potential because the Hamiltonian of this system commutes with the Runge-Lenz vector

$$\vec{D} = \frac{\vec{P}\times\vec{L} - \vec{L}\times\vec{P}}{2m} \; - \; Ze^2\,\frac{\vec{X}}{|\vec{X}|} \tag{135}$$

  (i) It does not commute with $\vec{L}$, and maps a state with definite ℓ and m to a superposition of states with different values of ℓ and m.

  (ii) $\vec{L}$ and $\vec{D}$ generate $\mathfrak{so}(4) \cong \mathfrak{su}(2) \oplus \mathfrak{su}(2)$ on the subspace of the Hilbert space with $E < 0$.

  (iii) The generators $\vec{J}_1$ and $\vec{J}_2$ of the two $\mathfrak{su}(2)$'s satisfy $\vec{J}_1^2 = \vec{J}_2^2$, and are related to H as

$$H = -\frac{\mu\, Z^2 e^4}{2(2(\vec{J}_1^2 + \vec{J}_2^2) + \hbar^2)} \tag{136}$$

  (iv) An irrep of $\mathfrak{so}(4) \cong \mathfrak{su}(2) \oplus \mathfrak{su}(2)$ is the tensor product of two $(2j+1)$-dim irreps of $\mathfrak{su}(2)$

  (v) It is an eigenspace of the Hamiltonian with the eigenvalue

$$E = -\frac{\mu\, Z^2 e^4}{2(4j(j+1)\hbar^2 + \hbar^2)} = -\frac{\mu\, Z^2 e^4}{2\hbar^2(2j+1)^2} = -\frac{\mu\, Z^2 e^4}{2\hbar^2 n^2}\,, \qquad n = 2j+1 \tag{137}$$

  (vi) The principal quantum number n is equal to the dimension of the two $(2j+1)$-dim irreps.

  (vii) The bound states subspace admits the decomposition

$$\mathscr{H}_{E<0} = \sum_{2j=0}^{\infty} \mathscr{H}^j \otimes \mathscr{H}^j = \sum_{2j=0}^{\infty} \sum_{\ell=0}^{2j} \mathscr{H}^\ell = \sum_{n=1}^{\infty} \sum_{\ell=0}^{n-1} \mathscr{H}^\ell \tag{138}$$

  where $\mathscr{H}^\ell$ is the $(2\ell+1)$-dim irrep of the orbital momentum operator.

5.2 Emission-line spectra

- An isolated hydrogen atom in some stationary state would stay there forever.
- If you perturb the state by, say, collision with another atom or by shining light on it, the electron may undergo a **transition** or a **quantum jump** to some other stationary state by

  (i) absorbing energy, and moving up to a higher-energy state

  (ii) releasing energy, and moving down

- In practice such perturbations are always present, and a container of hydrogen emits photons.
- A single hydrogen atom usually emits a single photon with energy

$$E_\gamma = E_i - E_f = Z^2 \mathcal{R} \Big(\frac{1}{n_f^2} - \frac{1}{n_i^2} \Big) \tag{139}$$

- According to the **Planck formula**, the energy of a photon is proportional to its frequency

$$E = h\,\nu \tag{140}$$

  and its wavelength is given by $\lambda = c/\nu$, so

$$\frac{1}{\lambda} = \frac{Z^2 \mathcal{R}}{h\,c} \Big(\frac{1}{n_f^2} - \frac{1}{n_i^2} \Big)\,, \qquad \frac{\mathcal{R}}{h\,c} = 1.097 \times 10^7 \mathrm{m}^{-1}. \tag{141}$$

- For $Z = 1$ this is the **Rydberg formula** for the emission spectrum of hydrogen, and it was discovered empirically in the nineteenth century.

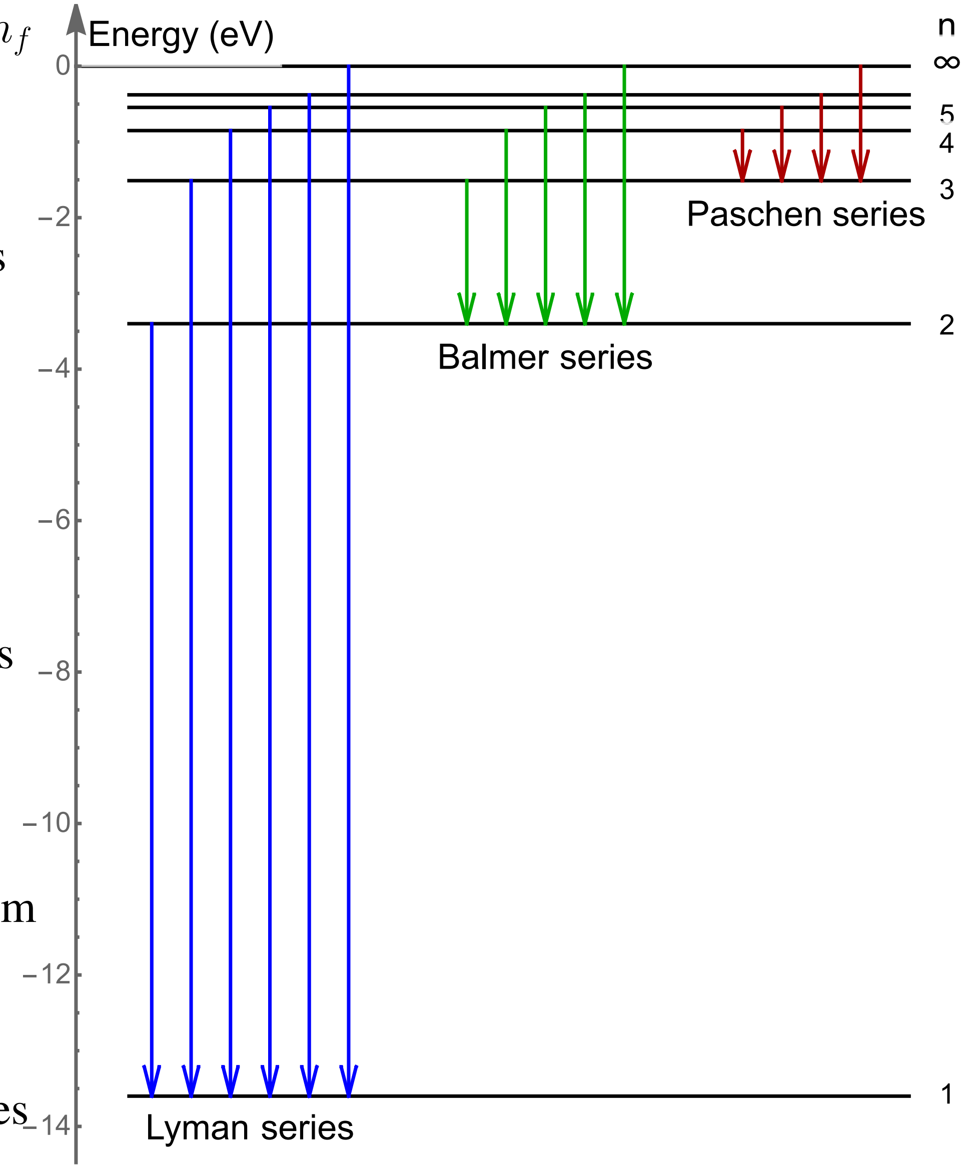
- The lines associated with a given lower level n_f form a series of lines of increasing frequency and decreasing wavelength.

  (i) The series with $n_f = 1$ is the Lyman series
  - the longest-wavelength member is the Lyman α line at 121.5nm
  - followed by the Lyβ line at 102.5nm,
  - the series limit line at 91.2nm.
  - They all lie in the ultraviolet.

  (ii) The series with $n_f = 2$ is the Balmer series
  - It was the first one to be discovered in 1885 because four of the Balmer lines fall in the visible region.
  - It starts with a line called Hα at 656.2nm
  - continues with Hβ at 486.1nm
  - towards the series limit at 364.6nm.

  (iii) The series with $n_f = 3$ is the Paschen series

  (iv) The serieswith $n_f = 4$ is the Brackett series



5.3 The wave functions

The wave functions for hydrogen are labeled by three quantum numbers n, ℓ and m

$$\varphi_{n\ell m}(r,\theta,\phi) = \mathcal{R}_{n\ell}(r)\, Y_\ell^m(\theta,\phi) \tag{142}$$

- The radial wave function

$$\begin{aligned} \mathcal{R}_{n\ell}(r) &= C_{n\ell}\,\frac{\sqrt{2\kappa_n}}{r}\rho^{\ell+1}e^{-\rho/2}\,\mathcal{W}_{n\ell}(\rho) = C_{n\ell}\,(2\kappa_n)^{3/2}\rho^\ell e^{-\rho/2}\,\mathcal{W}_{n\ell}(\rho)\,, \\ \rho &= 2\kappa_n\, r\,, \quad \kappa_n = \frac{1}{n\,a_Z}\,, \quad a_Z = \frac{\hbar^2}{\mu\, e^2\, Z} \end{aligned} \tag{143}$$

(i) $\mathcal{W}_{n\ell}(\rho)$ is a polynomial of degree $k_{\max} = n-\ell-1$ in ρ whose coefficients are determined by the recursion relation

$$w_{n\ell,k+1} = \frac{k+\ell+1-n}{(k+1)(k+2\ell+2)}\,w_{n\ell,k}\,, \quad w_{n\ell,0} = 1\,, \quad k = 0,1,\ldots,n-\ell-2 \tag{144}$$

(ii) The overall normalisation factor $C_{n\ell}$ can be chosen to be real positive

$$\int_0^\infty dr\, r^2\, |\mathcal{R}_{n\ell}(r)|^2 = C_{n\ell}^2\, 2\kappa_n \int_0^\infty dr\, \rho^{2\ell+2}e^{-\rho}\,\mathcal{W}_{n\ell}^2(\rho) = C_{n\ell}^2 \int_0^\infty d\rho\, e^{-\rho}\,\rho^{2\ell+2}\,\mathcal{W}_{n\ell}^2(\rho) = 1 \tag{145}$$

- To calculate $C_{n\ell}$ one needs the integral

$$\Gamma(z+1) \equiv \int_0^\infty d\rho\, e^{-\rho}\, \rho^z \tag{146}$$

for positive integer z.

(i) Integrating by parts, one shows

$$\Gamma(z+1) = z\,\Gamma(z) \tag{147}$$

(ii) Since $\Gamma(0) = 1$, one gets $\Gamma(k+1) = k!$ for any positive integer k.

(iii) Formula (146) is used to define $\Gamma(z+1)$ for any positive real number

(iv) The analytic continuation to any complex number gives a meromorphic function $\Gamma(z)$ with simple poles at $z = 0, -1, -2, \ldots$

(v) The function is called either the Gamma function or the factorial function.

- It is easy to find the radial function for any n and $\ell = n-1$ because $\mathcal{W}_{n,n-1}(\rho) = 1$, and

$$C_{n,n-1}^2 \int_0^\infty d\rho\, e^{-\rho}\, \rho^{2n} = C_{n,n-1}^2\, (2n)! = 1 \tag{148}$$

$$\mathcal{R}_{n,n-1}(r) = \frac{1}{\sqrt{(2n)!}}(2\kappa_n)^{3/2}\rho^{n-1}e^{-\rho/2} = \frac{1}{\sqrt{(2n)!}}\left(\frac{2}{n\,a_Z}\right)^{\frac{3}{2}}\left(\frac{2\,r}{n\,a_Z}\right)^{n-1} e^{-r/na_Z} \tag{149}$$

- The ground state wave function has $n = 1$, $\ell = 0$, and $Y_0^0(\theta,\phi) = 1/\sqrt{4\pi}$

$$\varphi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{2}}\left(\frac{2}{a_Z}\right)^{\frac{3}{2}} e^{-r/a_Z}\, Y_0^0(\theta,\phi) = \frac{1}{\sqrt{\pi\, a_Z^3}}\, e^{-r/a_Z} \tag{150}$$

- The probability of finding the electron in a spherical shell of radius r and thickness dr

$$dP(r) = \int_{S^2} d\Omega \, |Y^m_{n-1}(\theta,\phi)|^2 \, \mathcal{R}_{n,n-1}(r)^2 \, r^2 \, dr = \frac{1}{(2n)!} \left(\frac{2}{n\, a_Z}\right)^{2n+1} r^{2n} \, e^{-2r/na_Z} \, dr \tag{151}$$

  (i) The probability density in r reaches a maximum when

$$\frac{d}{dr} r^{2n} \, e^{-2r/na_Z} = 2n \, r^{2n-1} \, e^{-2r/na_Z} - \frac{2}{na_Z} r^{2n} \, e^{-2r/na_Z} = 0 \quad \Rightarrow \quad r = a_Z \, n^2 \tag{152}$$

  (ii) When $n = 1$ and $Z = 1$, this equals a.

  (iii) Thus the Bohr radius gives the most probable value of r in the ground state and this defines the "size" of the atom.

  (iv) If $n > 1$ we see that the size grows as n^2, at least in the state of $\ell = n-1$.

- The radial function for any n and $\ell = n-2$

  (i) $\mathcal{W}_{n,n-2}(\rho)$ is a linear function of ρ, and the recursion relation gives

$$w_1 = \frac{n-2+1-n}{(2n-4+2)} = -\frac{1}{2(n-1)} \tag{153}$$

$$\mathcal{W}_{n,n-2}(\rho) = 1 - \frac{\rho}{2(n-1)} \tag{154}$$

  (ii) Normalisation constant

$$\begin{aligned} C^2_{n\ell} \int_0^\infty d\rho \, e^{-\rho} \, \rho^{2n-2} \left(1 - \frac{\rho}{2(n-1)}\right)^2 &= C^2_{n\ell} \left((2n-2)! - \frac{(2n-1)!}{n-1} + \frac{(2n)!}{4(n-1)^2}\right) \\ &= C^2_{n\ell} \frac{(2n)!}{4(2n-1)(n-1)^2} = 1 \end{aligned} \tag{155}$$

(iii) The radial function is therefore given by

$$\begin{aligned}\mathcal{R}_{n,n-2}(r) &= \frac{2(n-1)\sqrt{2n-1}}{\sqrt{(2n)!}}\Big(1-\frac{\rho}{2(n-1)}\Big)(2\kappa_n)^{3/2}\rho^{n-2}e^{-\rho/2} \\ &= \frac{2(n-1)\sqrt{2n-1}}{\sqrt{(2n)!}}\Big(1-\frac{r}{n(n-1)a_Z}\Big)\left(\frac{2}{n\,a_Z}\right)^{\frac{3}{2}}\left(\frac{2\,r}{n\,a_Z}\right)^{n-2} e^{-r/na_Z}\end{aligned} \tag{156}$$

(iv) This wave function has a node at $r = n(n-1)a_Z$

- The polynomial $\mathcal{W}_{n\ell}(\rho)$ is proportional to the associated Laguerre polynomial, $L^{2\ell+1}_{n-\ell-1}(\rho)$

$$\mathcal{W}_{n\ell}(\rho) = \frac{(2\ell+1)!(n-\ell-1)!}{(n+\ell)!}\,L^{2\ell+1}_{n-\ell-1}(\rho) \tag{157}$$

(i) $L^k_n(x)$ is defined as in Mathematica

$$L^k_n(x) = \frac{e^x\,x^{-k}}{n!}\frac{d^n}{dx^n}\Big(e^{-x}\,x^{n+k}\Big) = \sum_{m=0}^{n}\frac{(-1)^m(k+n)!}{m!(k+m)!(n-m)!}\,x^m \tag{158}$$

(ii) The normalised radial wave function (143) is given by

$$\mathcal{R}_{n\ell}(r) = \sqrt{\frac{(n-\ell-1)!}{(n+\ell)!\,2n}}\,(2\kappa_n)^{3/2}\rho^\ell e^{-\rho/2}\,L^{2\ell+1}_{n-\ell-1}(\rho)\,, \tag{159}$$

and it has $n-\ell-1$ real zeroes.