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MENTOURI BROTHERS UNIVERSITY OF CONSTANTINE 1

كلية العلوم الدقيقة
FACULTY OF EXACT SCIENCES
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DEPARTMENT OF PHYSICS

Option : Physics

Specialization : PHYSICS OF MATERIALS

QUANTUM MECHANICS 2

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Preface

The Quantum Mechanics II course that I am teaching at the University of Constantine 1 is designed for students of 3rd-year bachelor's (License) in the field of Material Sciences. The course structure has been prepared in accordance with the national curriculum.

This module covers specific topics within quantum mechanics, expanding on the ideas presented in the Quantum Mechanics 1 course. In addition to exploring essential cases such as the hydrogen atom and emerging phenomena like spin, the module imparts essential concepts and mathematical techniques applicable to more advanced domains.

Students will be able to:

- Perform calculations using angular-momentum techniques, including the Wigner-Eckart theorem.
- Solve simple quantum mechanical problems.
- Use the approximate methods for solving the Schrödinger equation (the variational method, perturbation theory, WKB approximations)
- Calculate transition rates using time-dependent perturbation theory.

Prerequisite:

- Students must have completed Quantum Mechanics I.

Bilel Hamil, September 2023

Contents

Chapter 1

Angular Momentum and Spin

1.1 Definition

In classical physics, the angular momentum vector is defined with

$$\overrightarrow{L} = \overrightarrow{r} \wedge \overrightarrow{p}, \tag{1.1}$$

where $\overrightarrow{r}$ represents the position of the particle and $\overrightarrow{p}$ denotes the momentum of the particle. In Cartesian coordinates, the components of the angular momentum vector read

$$\begin{cases} L_x = yp_z - zp_y \\ L_y = zp_x - xp_z \\ L_z = xp_y - yp_x \end{cases} \tag{1.2}$$

The transition to quantum mechanics can be achieved by replacing the classical vectors "$\overrightarrow{r}$" and "$\overrightarrow{p}$" with their associated operators in the position representation,

$$\overrightarrow{r} \quad \hat{\to} \quad \hat{\mathbf{r}}, \tag{1.3}$$

$$\overrightarrow{p} \quad \to \quad \hat{\mathbf{p}} = -i\hbar\overrightarrow{\nabla}. \tag{1.4}$$

Hence, the angular momentum operator reads

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \wedge \hat{\mathbf{p}} = -i\hbar\hat{\mathbf{r}} \wedge \overrightarrow{\nabla}. \tag{1.5}$$

In Cartesian coordinates, the components of $\hat{\mathbf{L}}$ are

$$\begin{aligned}\hat{L}_x &= \frac{\hbar}{i}\left(\hat{y}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial y}\right)\\ \hat{L}_y &= \frac{\hbar}{i}\left(\hat{z}\frac{\partial}{\partial x} - \hat{x}\frac{\partial}{\partial z}\right)\\ \hat{L}_z &= \frac{\hbar}{i}\left(\hat{x}\frac{\partial}{\partial y} - \hat{y}\frac{\partial}{\partial x}\right)\end{aligned} \tag{1.6}$$

It is worth noting that the angular momentum cannot be applicable in a one-dimensional space. Another important point is that the square of the angular momentum operator, $\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$, and the components $\hat{L}_x, \hat{L}_y, \hat{L}_z$ are all Hermitian.

By introducing the Heisenberg uncertainty principle

$$[\hat{x}, \hat{p}_x] = i\hbar, \quad [\hat{y}, \hat{p}_y] = i\hbar, \quad [\hat{z}, \hat{p}_z] = i\hbar, \tag{1.7}$$

the angular momentum commutation relations of the form is derived

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z; \quad \left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x; \quad \left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y. \tag{1.8}$$

Please note that these commutation relations constitute the quantum mechanical concept of angular momentum, and its definition is broad enough to allow the inclusion of half-integer quantum numbers.

1.2 General Theory

Hereafter, we will consider a general Hermitian angular momentum operator, $\hat{\mathbf{J}}$, which is characterized by its components $\hat{J}_x, \hat{J}_y$, and $\hat{J}_z$. The three components $\hat{J}_x, \hat{J}_y$, and $\hat{J}_z$ obeys the following commutation relations

$$\left[\hat{J}_x, \hat{J}_y\right] = i\hbar\hat{J}_z; \quad \left[\hat{J}_y, \hat{J}_z\right] = i\hbar\hat{J}_x; \quad \left[\hat{J}_z, \hat{J}_x\right] = i\hbar\hat{J}_y, \tag{1.9}$$

with

$$\left[\hat{\mathbf{J}}^2, \hat{J}_y\right] = \left[\hat{\mathbf{J}}^2, \hat{J}_z\right] = \left[\hat{\mathbf{J}}^2, \hat{J}_x\right] = 0, \tag{1.10}$$

where the square of the general Hermitian angular momentum operator is defined as

$$\hat{\mathbf{J}}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2. \tag{1.11}$$

1.2.1 The eigenstates and eigenvalues of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$

Equations (1.9) and (1.10) can be readily understood from a straightforward physical interpretation. It's possible to determine the simultaneous eigenvalues of $\hat{\mathbf{J}}^2$ and one specific component, such as $\hat{J}_z$. However, it is not possible to precisely determine the eigenvalues of both $\hat{J}_x$ and $\hat{J}_z$ simultaneously.

Let us assume $|j,m\rangle$ as the common eigenstates of the operators $\hat{\mathbf{J}}^2$ and $\hat{J}_z$

$$\hat{\mathbf{J}}^2 |j,m\rangle = \hbar^2 \beta_j |j,m\rangle , \tag{1.12}$$

$$\hat{J}_z |j,m\rangle = \hbar m |j,m\rangle , \tag{1.13}$$

where j and m are quantum numbers to be determined. For simplification, we suppose that these eigenstates are orthogonal with each others

$$\langle j',m' |j,m\rangle = \delta_{j,j'} \delta_{m,m'}. \tag{1.14}$$

Now, we define the ladder (or raising and lowering) operators

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y, \tag{1.15}$$

to express the other operators in terms of them as

$$\hat{J}_x = \frac{\hat{J}_+ + \hat{J}_-}{2}; \quad \hat{J}_y = \frac{\hat{J}_+ - \hat{J}_-}{2i}, \tag{1.16}$$

and hence

$$\begin{cases} \hat{J}_x^2 = \frac{\hat{J}_+^2 + \hat{J}_-^2 + \hat{J}_+\hat{J}_- + \hat{J}_+\hat{J}_-}{4} \\ \hat{J}_y^2 = -\frac{\hat{J}_+^2 + \hat{J}_-^2 - \hat{J}_-\hat{J}_+ - \hat{J}_+\hat{J}_-}{4} \end{cases} . \tag{1.17}$$

Here, we also have

$$\begin{aligned} \left[\hat{J}_+, \hat{J}_-\right] &= \left[\hat{J}_x + i\hat{J}_y, \hat{J}_x - i\hat{J}_y\right] = -i\left[\hat{J}_x, \hat{J}_y\right] + i\left[\hat{J}_y, \hat{J}_x\right] \\ &= -2i\left[\hat{J}_x, \hat{J}_y\right] = 2\hbar\hat{J}_z, \end{aligned} \tag{1.18}$$

$$\begin{aligned} \left[\hat{J}_z, \hat{J}_\pm\right] &= \left[\hat{J}_z, \hat{J}_x\right] \pm i\left[\hat{J}_z, \hat{J}_y\right] = i\hbar\hat{J}_y \pm \hbar\hat{J}_x \\ &= \pm\hbar\hat{J}_\pm, \end{aligned} \tag{1.19}$$

in addition to

$$\left[\hat{J}_z, \hat{J}_\pm^2\right] = \hat{J}_\pm \left[\hat{J}_z, \hat{J}_\pm\right] + \left[\hat{J}_z, \hat{J}_\pm\right] \hat{J}_\pm = \pm 2\hbar \hat{J}_\pm^2. \tag{1.20}$$

By using equations (1.17) and (1.19), we get

$$\begin{aligned} \hat{J}_+ \hat{J}_- &= \hat{J}_x^2 + \hat{J}_y^2 + \hbar \hat{J}_z = \hat{\mathbf{J}}^2 - \hat{J}_z^2 + \hbar \hat{J}_z, \\ \hat{J}_- \hat{J}_+ &= \hat{J}_x^2 + \hat{J}_y^2 - \hbar \hat{J}_z = \hat{\mathbf{J}}^2 - \hat{J}_z^2 - \hbar \hat{J}_z, \end{aligned} \tag{1.21}$$

and via the equation (1.10) we obviously have

$$\left[\hat{\mathbf{J}}^2, \hat{J}_\pm\right] = 0. \tag{1.22}$$

Proposal 1

- The eigenvalues of $\hat{\mathbf{J}}^2$ are positive or zero.
- The quantum numbers β_j and m satisfy the inequality: $\beta_j \geq m^2 \geq 0$.

Demonstration

Since the operator $\hat{J}_i$ $(i = x, y, z)$ is Hermitian, we have

$$\left\langle \hat{J}_i^2 \right\rangle = \langle \psi | \hat{J}_i^2 | \psi \rangle = \left\| \hat{J}_i | \psi \rangle \right\|^2 \geq 0. \tag{1.23}$$

Thus

$$\begin{aligned} \left\langle \hat{\mathbf{J}}^2 \right\rangle &= \langle \psi | \hat{J}_x^2 | \psi \rangle + \langle \psi | \hat{J}_y^2 | \psi \rangle + \langle \psi | \hat{J}_z^2 | \psi \rangle, \\ &= \left\| \hat{J}_x | \psi \rangle \right\|^2 + \left\| \hat{J}_y | \psi \rangle \right\|^2 + \left\| \hat{J}_z | \psi \rangle \right\|^2 \geq 0. \end{aligned} \tag{1.24}$$

In particular, for an arbitrary state, $|j, m\rangle$, we have

$$\left\langle \hat{\mathbf{J}}^2 \right\rangle_{|j,m\rangle} = \langle j, m | \hat{\mathbf{J}}^2 | j, m \rangle = \hbar^2 \beta_j \geq 0. \tag{1.25}$$

Additionally, keeping in mind that $\langle \hat{\mathbf{J}}^2 \rangle \geq \langle \hat{J}_z^2 \rangle$, and employing the relations (1.12) and (1.13), we find

$$\left.\begin{array}{l} \langle \hat{\mathbf{J}}^2 \rangle_{|j,m\rangle} = \langle j,m|\hat{\mathbf{J}}^2|j,m\rangle = \hbar^2\beta_j \geq 0 \\ \langle \hat{J}_z^2 \rangle_{|j,m\rangle} = \langle j,m|\hat{J}_z^2|j,m\rangle = \hbar^2 m^2 \geq 0 \end{array}\right\} \Longrightarrow \beta_j \geq m^2 \geq 0. \tag{1.26}$$

Proposal 2

$$\hat{J}_\pm |j,m\rangle = C^\pm_{j,m}|j,m\pm 1\rangle$$

Demonstration

Initially, it's important to note that $\hat{J}_\pm$ does not commute with $\hat{J}_z$, which implies that the kets $|j,m\rangle$ are not the eigenstates of $\hat{J}_\pm$.

In order to demonstrate the proposal we utilize the relationship given in equation (1.19). We start with the following equality

$$\hat{J}_z\left(\hat{J}_\pm|j,m\rangle\right) = \left(\hbar\hat{J}_\pm \pm \hat{J}_\pm\hat{J}_z\right)|j,m\rangle = \hbar(1\pm m)\left(\hat{J}_\pm|j,m\rangle\right), \tag{1.27}$$

which states that $\hat{J}_\pm$ raises or lowers the eigenvalue m by one unit of $\hbar$. It's important to mention that $\left(\hat{J}_\pm|j,m\rangle\right)$ is an eigenstate of $\hat{J}_z$. On the other hand, $\hat{J}_z$ and $\hat{\mathbf{J}}^2$ commute, therefore, $\left(\hat{J}_\pm|j,m\rangle\right)$ should also be an eigenstate of $\hat{\mathbf{J}}^2$,

$$\hat{\mathbf{J}}^2\left(\hat{J}_\pm|j,m\rangle\right) = \hat{J}_\pm\hat{\mathbf{J}}^2|\psi_{j,m}\rangle = \beta_j\left(\hat{J}_\pm|j,m\rangle\right). \tag{1.28}$$

Based on equations (1.27) and (1.28), we can deduce that the action of the operator $\hat{J}_\pm$ on $|j,m\rangle$ does not alter the first quantum number j, but it does increase or decrease the quantum number m by one unit. This means that $\hat{J}_\pm|j,m\rangle$ is proportional to $|j,m\pm 1\rangle$

$$\hat{J}_\pm|j,m\rangle = C^\pm_{j,m}|j,m\pm 1\rangle. \tag{1.29}$$

Proposal 3

- If $m_{\max} = +j$, then $\beta_j = j(j+1)$
- If $m_{\min} = j'$, then $\beta_j = j'(j'-1)$

Demonstration

We remember

$$\hat{J}_+ |j,m\rangle = C^+_{j,m} |j,m+1\rangle , \tag{1.30}$$

from the previous proposal. For a maximal value to the quantum number, $m_{\max} = j$, it yields to

$$\hat{J}_+ |j,m_{\max}\rangle = 0. \tag{1.31}$$

Therefore, we can write

$$\left\| \hat{J}_+ |j,m_{\max}\rangle \right\|^2 = \langle j,m_{\max}| \hat{J}_- \hat{J}_+ |j,m_{\max}\rangle = 0. \tag{1.32}$$

Then, by using the relation $\hat{J}_- \hat{J}_+ = \hat{\mathbf{J}}^2 - \hat{J}_z^2 - \hbar \hat{J}_z$, we get

$$\begin{aligned} \left\| \hat{J}_+ |j,m_{\max}\rangle \right\|^2 &= \langle j,m_{\max}| \left(\hat{\mathbf{J}}^2 - \hat{J}_z^2 - \hbar \hat{J}_z \right) |j,m_{\max}\rangle , \\ &= \hbar^2 \left(\beta_j - j^2 - j \right) = 0 \Rightarrow \beta_j = j(j+1) . \end{aligned} \tag{1.33}$$

Let us now examine the state $|j,m_{\min} = j'\rangle$ which cannot be lowered further.

$$\hat{J}_- |j,m_{\min}\rangle = 0. \tag{1.34}$$

By employing the relation $\hat{J}_+ \hat{J}_- = \hat{\mathbf{J}}^2 - \hat{J}_z^2 + \hbar \hat{J}_z$, and repeating the similar algebra of equations (1.32) and (1.33), we obtain

$$\beta_j = j' \left(j' - 1 \right) . \tag{1.35}$$

The comparison of equations (1.33) and (1.35) leads to the following relation:

$$\beta_j = j(j+1) \quad \text{where} \qquad -j \leq m \leq j. \tag{1.36}$$

In summary, we conclude that $\hbar j(j+1)$ and $\hbar m$ are the eigenvalues of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ operators that act onto the joint eigenvectors $|j,m\rangle$, respectively:

$$\hat{\mathbf{J}}^2 |j,m\rangle = \hbar j(j+1) |j,m\rangle , \tag{1.37}$$

and

$$\hat{J}_z |j,m\rangle = \hbar m |j,m\rangle . \tag{1.38}$$

Proposal 4

The only possible values of j can be non-negative integers, non-negative half-integers or zero.

Demonstration

Let us consider the state $|j,-j\rangle$. If $\hat{J}_+$ acts on this state, then we will have to obtain a new state proportional to $|j,-j+1\rangle$. By repeating this procedure again and again (n times), we get

$$|j,-j\rangle \underbrace{\xrightarrow{\hat{J}_+} |j,-j+1\rangle \xrightarrow{\hat{J}_+} |j,-j+2\rangle \overset{\hat{J}_+}{\cdots} |j,-j+n\rangle} \equiv |j,j\rangle\,. \tag{1.39}$$

Therefore we can write,

$$-j = -j+n \Rightarrow j = \frac{n}{2}, \quad \text{where } n \in \mathbf{N}. \tag{1.40}$$

Recalling the range of the natural numbers, we easily conclude that

$$j \in \{0, 1/2, 1, 3/2, 2, ...\}\,, \tag{1.41}$$

with

$$m \in \{-j, -j+1, -j+2, , ..., j-1, j\}\,. \tag{1.42}$$

These results represent the fundamental quantization properties of angular momentum. In fact, they are applicable to all momenta including the orbital angular and spin angular momenta, in an arbitrary space in which equation (1.9) is satisfied.

Proposal 5

The action of the operator $\hat{J}_\pm$ on $|j,m\rangle$ is

$$\hat{J}_\pm |j,m\rangle = \hbar\sqrt{j(j+1) - m(m\pm 1)}\,|j,m\pm 1\rangle$$

Demonstration

Let us recall the second proposal

$$\hat{J}_\pm |j,m\rangle = C^\pm_{j,m} |j,m\pm 1\rangle\,. \tag{1.43}$$

Now, taking the inner product of Eq. (1.43) with its Hermitian conjugate, we get

$$\begin{aligned}\left\|\hat{J}_{\pm}|j,m\rangle\right\|^2 &= \langle j,m|\left(C^{\pm}_{j,m}\right)^* C^{\pm}_{j,m}|j,m\rangle = \left|C^{\pm}_{j,m}\right|^2,\\ &= \langle j,m|\hat{J}_{\mp}\hat{J}_{\pm}|j,m\rangle,\\ &= \langle j,m|\left(\hat{\mathbf{J}}^2-\hat{J}_z^2\mp\hbar\hat{J}_z\right)|j,m\rangle,\\ &= \hbar^2\left(j(j+1)-m(m\pm1)\right). \end{aligned} \tag{1.44}$$

If we consider the arbitrary phase of $C^{\pm}_{j,m}$ to be zero, then we obtain

$$C^{\pm}_{j,m} = \hbar\sqrt{j(j+1)-m(m\pm1)}. \tag{1.45}$$

1.2.2 The matrix element of the angular momentum

The states represented as $|j,m\rangle$ are a complete and orthonormal basis for angular momentum. They satisfy the following completeness and orthonormality relations, respectively:

$$\sum_{m=-j}^{j}|j,m\rangle\langle j,m| = \mathbf{1}, \tag{1.46}$$

$$\langle j,m|\ j',m'\rangle = \delta_{j,j'}\delta_{m,m'}. \tag{1.47}$$

Here, $\mathbf{1}$ corresponds to the unit matrix.

In equations (1.37) and (1.38), we have already shown that $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ operators have joint eigenstates. Now, by using the orthonormality condition, we construct their matrix representations

$$\left\langle j',m'\right|\hat{\mathbf{J}}^2|j,m\rangle = \hbar j(j+1)\,\delta_{j,j'}\delta_{m,m'}, \tag{1.48}$$

$$\left\langle j',m'\right|\hat{J}_z|j,m\rangle = \hbar m\delta_{j,j'}\delta_{m,m'}. \tag{1.49}$$

Hence, the matrices that depict $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ in the $|j,m\rangle$ eigenbasis are diagonal, with their diagonal components being equal to $\hbar j(j+1)$ and $\hbar m$, respectively.

On the other hand, as observed in equation (1.45), the impact of the ladder operators $\hat{J}_{\pm}$ on an angular momentum state is to create a state with the identical magnitude of the angular momentum. However, this new state's z component is

augmented or decreased by one unit of $\hbar$

$$\left\langle j',m'\right|\hat{J}_+\left|j,m\right\rangle = \hbar\sqrt{j(j+1)-m(m+1)}\,\delta_{j,j'}\delta_{m+1,m'}, \tag{1.50}$$

$$\left\langle j',m'\right|\hat{J}_-\left|j,m\right\rangle = \hbar\sqrt{j(j+1)-m(m-1)}\,\delta_{j,j'}\delta_{m-1,m'}. \tag{1.51}$$

Consequently, the matrix representations of the ladder operator, $\hat{J}_\pm$ in the $\{|j,m\rangle\}$ basis are characterized by the non-diagonal matrices.

Example

Let us consider a particle with angular momentum $j=3/2$ to answer the following questions

a. What are the possible values of m?

b. What are the matrix representations of $\hat{\mathbf{J}}^2$, $\hat{J}_z$, $\hat{J}_+$, $\hat{J}_-$ and $\hat{J}_x$, $\hat{J}_y$?

c. Find the energy levels of this particle when its Hamiltonian is given by

$$H = \frac{\varepsilon_0}{\hbar^2}\left(\hat{J}_x^2-\hat{J}_y^2\right) - \frac{\varepsilon_0}{\hbar}\hat{J}_z.$$

Solution

a. For $j=3/2$, four possible values of m exist: $3/2$, $1/2$, $-1/2$, and $-3/2$.

b. For $j=3/2$, we simply can list the states

$$\left|3/2,-3/2\right\rangle, \left|3/2,-1/2\right\rangle, \left|3/2,1/2\right\rangle, \left|3/2,3/2\right\rangle. \tag{1.52}$$

Following equations (1.48), (1.49), (1.50), and (1.51), we obtain the matrix representations of the operators, respectively as follows:

$$\hat{\mathbf{J}}^2 = \frac{15\hbar^2}{4}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \tag{1.53}$$

$$\hat{J}_z = \frac{\hbar}{2}\begin{pmatrix} -3 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 3 \end{pmatrix}, \tag{1.54}$$

$$\hat{J}_+ = \hbar\begin{pmatrix} 0 & 0 & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}, \tag{1.55}$$

$$\hat{J}_- = \hbar\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

which, when combined with $\hat{J}_x = \frac{\hat{J}_+ + \hat{J}_-}{2}$ and $\hat{J}_y = \frac{\hat{J}_+ - \hat{J}_-}{2i}$, lead to

$$\hat{J}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}; \hat{J}_- = \frac{\hbar}{2}\begin{pmatrix} 0 & -\sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & -2 & 0 \\ 0 & 2 & 0 & -\sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}.$$

c. The Hamiltonian is expressed as:

$$H = \frac{\varepsilon_0}{2}\begin{pmatrix} -3 & 0 & 2\sqrt{3} & 0 \\ 0 & -1 & 0 & 2\sqrt{3} \\ 2\sqrt{3} & 0 & 1 & 0 \\ 0 & 0 & 0 & 3 \end{pmatrix}.$$

The energy eigenvalues:

$$E_1 = -\frac{5}{2}\varepsilon_0, E_2 = -\frac{3}{2}\varepsilon_0, E_3 = \frac{3}{2}\varepsilon_0, E_4 = \frac{5}{2}\varepsilon_0.$$

1.3 Orbital Angular Momentum

1.3.1 Orbital angular momentum operators in spherical coordinates

We will now focus on expressing angular momentum in terms of coordinates. In this part, we will be operating within the spherical coordinate system. Let us use the notation "$|\ell,m\rangle$" to represent the joint eigenstates of the operators $\hat{\mathbf{L}}^2$ and $\hat{L}_z$,

$$\hat{\mathbf{L}}^2 |\ell,m\rangle = \hbar^2 \ell(\ell+1) |\ell,m\rangle , \tag{1.56}$$

$$\hat{L}_z |\ell,m\rangle = \hbar m |\ell,m\rangle . \tag{1.57}$$

We consider the transformation between the Cartesian and spherical coordinates

$$\begin{aligned} x &= r\sin\theta\cos\varphi; \quad y = r\sin\theta\sin\varphi; \quad z = r\cos\theta, \\ r &= \sqrt{x^2+y^2+z^2}; \quad \theta = \cos^{-1}\left(\frac{z}{r}\right); \quad \varphi = \tan^{-1}\left(\frac{y}{x}\right). \end{aligned} \tag{1.58}$$

The orthonormal Cartesian basis $(\overrightarrow{i}, \overrightarrow{j}, \overrightarrow{k})$, is related to its spherical basis $(\overrightarrow{e}_r, \overrightarrow{e}_\theta, \overrightarrow{e}_\varphi)$ through the following relations:

$$\overrightarrow{i} = \overrightarrow{e}_r \sin\theta\cos\varphi + \overrightarrow{e}_\theta \cos\theta\cos\varphi - \sin\varphi \overrightarrow{e}_\varphi . \tag{1.59}$$

$$\overrightarrow{j} = \overrightarrow{e}_r \sin\theta\sin\varphi + \overrightarrow{e}_\theta \cos\theta\sin\varphi + \cos\varphi \overrightarrow{e}_\varphi . \tag{1.60}$$

$$\overrightarrow{k} = \overrightarrow{e}_r \cos\theta - \overrightarrow{e}_\theta \sin\theta . \tag{1.61}$$

On the other hand, in spherical coordinates, the gradient operator $\overrightarrow{\nabla}$ is defined as follows:

$$\overrightarrow{\nabla} f = \overrightarrow{e}_r \frac{\partial f}{\partial r} + \frac{\overrightarrow{e}_\theta}{r}\frac{\partial f}{\partial \theta} + \frac{\overrightarrow{e}_\varphi}{r\sin\theta}\frac{\partial f}{\partial \varphi}. \tag{1.62}$$

Now, substitute the expression for the gradient operator $\overrightarrow{\nabla}$ (1.62) into the definition of the angular momentum (1.5), and after performing the cross product, we arrive at the expression for the angular momentum operator in spherical coordinates:

$$\hat{\mathbf{L}} = \frac{\hbar r}{i}\overrightarrow{e}_r \wedge \left(\overrightarrow{e}_r \frac{\partial}{\partial r} + \frac{\overrightarrow{e}_\theta}{r}\frac{\partial}{\partial \theta} + \frac{\overrightarrow{e}_\varphi}{r\sin\theta}\frac{\partial}{\partial \varphi} \right), \tag{1.63}$$

$$\hat{\mathbf{L}} = \frac{\hbar}{i}\left(\overrightarrow{e}_{\varphi}\frac{\partial}{\partial\theta} - \frac{\overrightarrow{e}_{\theta}}{\sin\theta}\frac{\partial}{\partial\varphi}\right). \tag{1.64}$$

By employing equation (1.64) along with equations (1.59) to (1.61), we express the components $\hat{L}_x, \hat{L}_y$ and $\hat{L}_z$ in spherical coordinates as:

$$\hat{L}_x = \overrightarrow{i}\cdot\hat{\mathbf{L}} = \frac{\hbar}{i}\left(\overrightarrow{e}_r\sin\theta\cos\varphi + \overrightarrow{e}_{\theta}\cos\theta\cos\varphi - \sin\varphi\overrightarrow{e}_{\varphi}\right)\cdot\left(\overrightarrow{e}_{\varphi}\frac{\partial}{\partial\theta} - \frac{\overrightarrow{e}_{\theta}}{\sin\theta}\frac{\partial}{\partial\varphi}\right),$$

$$= \frac{\hbar}{i}\left(-\sin\varphi\frac{\partial}{\partial\theta} - \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right). \tag{1.65}$$

$$\hat{L}_y = \overrightarrow{j}\cdot\hat{\mathbf{L}} = \frac{\hbar}{i}\left(\overrightarrow{e}_r\sin\theta\sin\varphi + \overrightarrow{e}_{\theta}\cos\theta\sin\varphi + \cos\varphi\overrightarrow{e}_{\varphi}\right)\cdot\left(\overrightarrow{e}_{\varphi}\frac{\partial}{\partial\theta} - \frac{\overrightarrow{e}_{\theta}}{\sin\theta}\frac{\partial}{\partial\varphi}\right),$$

$$= \frac{\hbar}{i}\left(\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right). \tag{1.66}$$

$$\hat{L}_z = \overrightarrow{k}\cdot\hat{\mathbf{L}} = \frac{\hbar}{i}\left(\overrightarrow{e}_r\cos\theta - \overrightarrow{e}_{\theta}\sin\theta\right)\left(\overrightarrow{e}_{\varphi}\frac{\partial}{\partial\theta} - \frac{\overrightarrow{e}_{\theta}}{\sin\theta}\frac{\partial}{\partial\varphi}\right),$$

$$= \frac{\hbar}{i}\frac{\partial}{\partial\varphi}. \tag{1.67}$$

Using equations (1.65) and (1.66), we rewrite the raising and lowering operators, namely $\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y$, in the spherical polar coordinates

$$\hat{L}_{+} = \hbar e^{i\varphi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right), \tag{1.68}$$

$$\hat{L}_{+} = -\hbar e^{-i\varphi}\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\varphi}\right). \tag{1.69}$$

Now, using the definition of the components $\hat{L}_x, \hat{L}_y$ and $\hat{L}_z$ in spherical coordinates, we can rewrite $\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ as

$$\hat{\mathbf{L}}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]. \tag{1.70}$$

The angular momentum operators $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ are functions of angular coordinates, θ and φ, their eigenstates depend only on θ and φ. Now, we introduce the spherical harmonics $\mathcal{Y}_{\ell,m}(\theta,\varphi) = \langle\theta,\varphi\,|\ell,m\rangle$, and re-express the eigenvalue equations (1.56)

and (1.57) as follows,

$$\hat{\mathbf{L}}^2 \mathcal{Y}_{\ell,m}(\theta,\varphi) = \hbar^2 \ell(\ell+1)\, \mathcal{Y}_{\ell,m}(\theta,\varphi), \tag{1.71}$$

$$\hat{L}_z \mathcal{Y}_{\ell,m}(\theta,\varphi) = \hbar m \mathcal{Y}_{\ell,m}(\theta,\varphi). \tag{1.72}$$

1.3.2 The eigenfunctions of $\hat{L}_z$ and $\hat{\mathbf{L}}^2$

To find the eigenfunctions $\mathcal{Y}_{\ell,m}(\theta,\varphi)$, we can employ the definition given in equation (1.70). In such case, we can start with

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \ell(\ell+1)\right]\mathcal{Y}_{\ell,m}(\theta,\varphi) = 0. \tag{1.73}$$

Then, we use the separation of variables method. We consider the solution

$$\mathcal{Y}_{\ell,m}(\theta,\varphi) = \Theta_{\ell,m}(\theta)\,\Phi_m(\varphi), \tag{1.74}$$

and substitute it in equation (1.73). Following several algebra, we obtain

$$\sin^2\theta\left[\frac{1}{\Theta_{\ell,m}(\theta)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta_{\ell,m}(\theta) + \ell(\ell+1)\right] = -\frac{1}{\Phi_m(\varphi)}\frac{\partial^2}{\partial\varphi^2}\Phi_m(\varphi). \tag{1.75}$$

The left-hand side of this equation is only dependent on the angle θ, while the right-hand side depends only on the angle φ. Since varying θ does not influence the right side, and changing φ does not affect the left side, we can consider both sides as a constant, m^2. Then, the equation for φ becomes

$$\left[\frac{\partial^2}{\partial\varphi^2} + m^2\right]\Phi_m(\varphi) = 0, \tag{1.76}$$

and its solution simply reads

$$\Phi_m(\varphi) = a e^{im\varphi}, \tag{1.77}$$

with an arbitrary constant a. Since $\Phi_m(\varphi)$ has to be a single-valued function, we must impose the periodicity condition

$$\begin{aligned} \Phi_m(\varphi+2\pi) &= \Phi_m(\varphi), \\ e^{im(\varphi+2\pi)} &= e^{im\varphi}, \\ e^{i2\pi m} &= 1 \Rightarrow m = 0, \pm 1, \pm 2, \ldots \end{aligned} \tag{1.78}$$

Then, by setting $a = \frac{1}{\sqrt{2\pi}}$, we derive the normalized solution of equation (1.76) in the form of

$$\Phi_m(\varphi) = \frac{e^{im\varphi}}{\sqrt{2\pi}} \quad \text{with } m = 0, \pm 1, \pm 2, \ldots \tag{1.79}$$

It's evident to note that the function $\Phi_m(\varphi)$ is an eigenfunction of the operator $\hat{L}_z$, possessing the eigenvalue m. Indeed, we observe that

$$\hat{L}_z \Phi_m(\varphi) = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}\Phi_m(\varphi) = \hbar m \Phi_m(\varphi). \tag{1.80}$$

Now, let us redirect our attention to equation (1.75). By introducing a change of variable $\varkappa = \cos\theta$, we get

$$\left[\frac{d}{d\varkappa}\left(1-\varkappa^2\right)\frac{d}{d\varkappa} + \ell(\ell+1) - \frac{m^2}{1-\varkappa^2}\right]\Theta_{\ell,m}(\varkappa) = 0, \tag{1.81}$$

which is known as the Legendre differential equation. The solution of the Legendre differential equation can be represented with the form

$$\Theta_{\ell,m}(\theta) = c_{\ell,m} P_\ell^m(\cos\theta), \tag{1.82}$$

where $c_{\ell,m}$ is the normalization constant, $P_\ell^m(\varkappa)$ are the associated Legendre functions defined by

$$P_\ell^m(\varkappa) = \left(1-\varkappa^2\right)^{\frac{|m|}{2}} \frac{d^{|m|}}{d\varkappa^{|m|}} P_\ell(\varkappa), \tag{1.83}$$

and

$$P_\ell(\varkappa) = \frac{(-1)^\ell}{2^\ell \ell!}\frac{d^\ell}{d\varkappa^\ell}\left(1-\varkappa^2\right)^\ell. \tag{1.84}$$

are the Legendre polynomials. The normalization constant, $c_{\ell,m}$, can be established through the orthonormalization condition

$$\begin{aligned}\left\langle \ell',m'\right| \left. \ell,m\right\rangle &= \int_0^{2\pi}\int_0^{\pi} d\varphi \sin\theta d\theta \left\langle \ell',m'\right| \left. \theta,\varphi\right\rangle \left\langle \theta,\varphi\right| \left. \ell,m\right\rangle = \delta_{\ell,\ell'}\delta_{m,m'},\\ &= \int_0^{2\pi}\int_0^{\pi} d\varphi \sin\theta d\theta \mathcal{Y}^*_{\ell',m'}(\theta,\varphi)\,\mathcal{Y}_{\ell,m}(\theta,\varphi),\\ &= \frac{\left|c_{\ell,m}\right|^2}{2\pi}\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \left|P_\ell^m(\cos\theta)\right|^2, \end{aligned} \tag{1.85}$$

and by the following integral property,

$$\int_0^{\pi} d\theta \sin\theta P_\ell^m(\cos\theta) P_{\ell'}^m(\cos\theta) = \frac{2(\ell+m)!}{(2\ell+1)(\ell-m)!}\delta_{\ell,\ell'}. \tag{1.86}$$

After some algebra, we can express the normalization constant in the form of

$$c_{\ell,m} = (-1)^m \sqrt{\frac{(2\ell+1)(\ell-m)!}{2(\ell+m)!}}. \tag{1.87}$$

By substituting this constant into equation (1.82), we obtain

$$\Theta_{\ell,m}(\theta) = (-1)^m \sqrt{\frac{(2\ell+1)(\ell-m)!}{2(\ell+m)!}} P_\ell^m(\cos\theta). \tag{1.88}$$

Finally, we can express the joint eigenfunctions of the operators $\hat{L}_z$ and $\hat{\mathbf{L}}^2$ by substituting equations (1.88) and (1.79) into equation (1.74):

$$\mathcal{Y}_{\ell,m}(\theta,\varphi) = (-1)^m \sqrt{\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}} P_\ell^m(\cos\theta), \qquad (m\geq 0). \tag{1.89}$$

$$\mathcal{Y}_{\ell,m}(\theta,\varphi) = (-1)^{|m|} \sqrt{\frac{(2\ell+1)(\ell-|m|)!}{4\pi(\ell+m)!}} P_\ell^{|m|}(\cos\theta), \qquad (m<0). \tag{1.90}$$

1.3.3 Some important properties of spherical harmonics

Here, we have to underline some important properties of the spherical harmonics.

Orthogonality and Normalization

$$\left\langle \ell', m' \right| \ell, m \rangle = \int_0^{2\pi} \int_0^{\pi} d\varphi \sin\theta d\theta \mathcal{Y}^*_{\ell',m'}(\theta,\varphi)\, \mathcal{Y}_{\ell,m}(\theta,\varphi) = \delta_{\ell,\ell'}\delta_{m,m'}. \tag{1.91}$$

The completeness relation

$$\begin{aligned} \sum_{m=-\ell}^{\ell} \langle \theta,\varphi\,|\ell,m\rangle \langle \ell,m\,|\theta',\varphi'\rangle &= \sum_{m=-\ell}^{\ell} \mathcal{Y}^*_{\ell,m}(\theta,\varphi)\, \mathcal{Y}_{\ell,m}(\theta',\varphi'), \\ &= \delta(\cos\theta - \cos\theta')\,\delta(\varphi-\varphi') \\ &= \frac{1}{\sin\theta}\delta(\theta-\theta')\,\delta(\varphi-\varphi'). \end{aligned} \tag{1.92}$$

The complex conjugate

$$\left[\mathcal{Y}_{\ell,m}(\theta,\varphi)\right]^* = (-1)^m \mathcal{Y}_{\ell,-m}(\theta,\varphi). \tag{1.93}$$

The parity operator

$\mathcal{Y}_{\ell,m}(\theta,\varphi)$ is an eigenstate of the parity operator $\mathcal{P}$ with an eigenvalue $(-1)^\ell$

$$\mathcal{P}\mathcal{Y}_{\ell,m}(\theta,\varphi) = \mathcal{Y}_{\ell,m}(\pi-\theta,\pi+\varphi) = (-1)^\ell \mathcal{Y}_{\ell,m}(\theta,\varphi). \tag{1.94}$$

Relation between the spherical harmonics and the Legendre polynomials

$$\mathcal{Y}_{\ell,0}(\theta,\varphi) = \sqrt{\frac{2\ell+1}{4\pi}} P_\ell(\cos\theta). \tag{1.95}$$

First few Spherical Harmonics

ℓ	m	Spherical Harmonics
0	0	$Y_{0,0}(\theta,\varphi) = \sqrt{\frac{1}{4\pi}}$,
1	0	$Y_{1,0}(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\theta$,
	± 1	$Y_{1,\pm 1}(\theta,\varphi) = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\varphi}$,
2	0	$Y_{2,0}(\theta,\varphi) = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right)$,
	± 1	$Y_{2,\pm 1}(\theta,\varphi) = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\varphi}$,
	± 2	$Y_{2,\pm 2}(\theta,\varphi) = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\varphi}$.

Table 1.1: First few Spherical Harmonics.

1.4 Spin

1.4.1 Stern - Gerlach Experiment

In 1921, O. Stern and W. Gerlach conducted a seminal experiment, revealing the existence of a magnetic moment associated with the electron's spin, even though the concept of electron spin was not yet recognized at that time. In their experiment, Stern and Gerlach prepared a beam of silver (Ag) atoms in their ground states and let them traverse a non-uniform magnetic field and reach a photographic plate, as depicted in figure 1.1. Essentially, they were planning to observe the deviations of the beam on the photographic plate when they turned on the magnetic field. According to them, they should observe one spot only because the atoms in the beam were in their ground state ($\ell = 0$). Moreover, they were expecting to observe three spots when the electrons are excited to the 5p state ($\ell = 1$). During the experiment, they observed that the beam produced a different number of peaks on the photographic plate, even when the magnetic field was turned off.

In 1925, Goudsmit and Uhlenbeck proposed a solution to this puzzle by suggesting that electrons should possess an intrinsic angular momentum, called **spin**. The concept of spin, which represents an intrinsic degree of freedom, is unique to quantum mechanics and lacks any classical analogs. Therefore, spin cannot be explained through the use of differential operators.

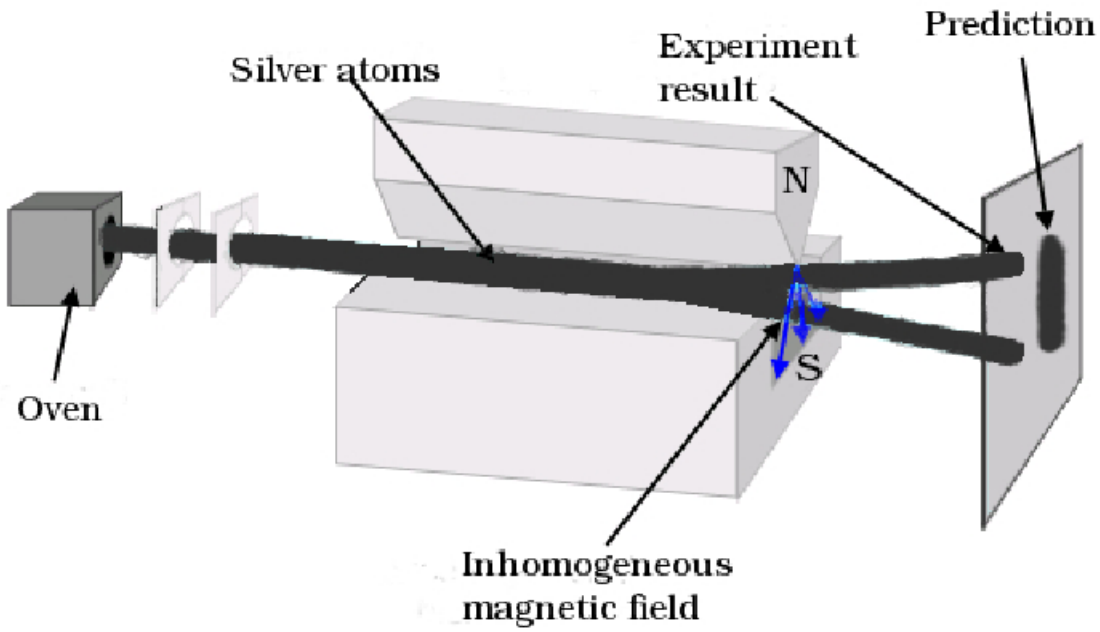

Figure 1.1: Stern-Gerlach experiment

1.4.2 Spin theory

Although the spin operator represents an intrinsic angular momentum, it follows the commutation relations similar to the ones derived for the orbital angular momentum. In order to distinguish the spin angular momentum from the orbital angular momentum, we utilize the symbol $\hat{\mathbf{S}}$ instead of $\hat{\mathbf{L}}$.

We consider spin operator components $\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$, which obey the following commutation relationships

$$\left[\hat{S}_x, \hat{S}_y\right] = i\hbar\hat{S}_z; \qquad \left[\hat{S}_y, \hat{S}_z\right] = i\hbar\hat{S}_x; \qquad \left[\hat{S}_z, \hat{S}_x\right] = i\hbar\hat{S}_y. \tag{1.96}$$

Then, with these components, we define a squared magnitude operator $\hat{\mathbf{S}}^2$ as

$$\hat{\mathbf{S}}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2, \tag{1.97}$$

where $\left[\hat{\mathbf{S}}^2, \hat{S}_j\right] = 0$ for $j = x, y, z$. Moreover, we consider raising and lowering operators, $\hat{S}_\pm$:

$$\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y. \tag{1.98}$$

Next, we write the eigenvalues of $\hat{\mathbf{S}}^2$ as $\hbar^2 s(s+1)$, by replacing the symbol ℓ with

s. Alike, we consider the eigenvalue of $\hat{S}_z$ as $\hbar m_s$. Altogether, they read

$$\hat{\mathbf{S}}^2 |s, m_s\rangle = \hbar^2 s(s+1) |s, m_s\rangle , \tag{1.99}$$

$$\hat{S}_z |s, m_s\rangle = \hbar m_s |s, m_s\rangle , \tag{1.100}$$

with

$$\hat{S}_\pm |s, m_s\rangle = \hbar \sqrt{s(s+1) - m_s(m_s \pm 1)} |s, m_s \pm 1\rangle .$$

Alike the orbital angular momentum, the allowed values for the quantum number s are 0, 1/2, 1, 3/2, $\cdots$. Furthermore, the admissible values of the quantum number m_s run between $-s$ to s, as we have proven in Section 1.2

1.4.3 Spin 1/2

Particles like electrons, protons, and neutrons are called fermions. This classification arises from their intrinsic properties, particularly from the fact that their spin angular momentum is quantized in half-integer values ($s = 1/2$). For $s = 1/2$, there are two values of m_s, namely $1/2$ and $-1/2$. Therefore, two eigenstates arise as

- $|1/2, 1/2\rangle$, which is called 'spin-up',
- $|1/2, -1/2\rangle$, which is called 'spin-down'.

For both cases, we can write

$$\begin{cases} \hat{\mathbf{S}}^2 |1/2,1/2\rangle = \frac{3\hbar^2}{4} |1/2,1/2\rangle ; \quad \hat{S}_z |1/2,1/2\rangle = \frac{\hbar}{2} |1/2,1/2\rangle \\ \hat{\mathbf{S}}^2 |1/2,-1/2\rangle = \frac{3\hbar^2}{4} |1/2,-1/2\rangle ; \quad \hat{S}_z |1/2,-1/2\rangle = -\frac{\hbar}{2} |1/2,-1/2\rangle \end{cases} . \tag{1.101}$$

Moreover, when we act $\hat{S}_\pm$ on these basis, we find

$$\begin{cases} \hat{S}_+ |1/2,1/2\rangle = 0; \quad \hat{S}_- |1/2,1/2\rangle = \hbar |1/2,-1/2\rangle \\ \hat{S}_+ |1/2,-1/2\rangle = \hbar |1/2,1/2\rangle ; \quad \hat{S}_- |1/2,-1/2\rangle = 0 \end{cases} . \tag{1.102}$$

If we associate the following matrices with the spin basis, we can write

$$|1/2,1/2\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} ; |1/2,-1/2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} . \tag{1.103}$$

Also, we can represent the operators $\hat{S}_x, \hat{S}_y$ and $\hat{S}_z$ as a 2×2 matrix form as follows:

$$\hat{S}_x = \frac{\hbar}{2}\sigma_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \tag{1.104}$$

$$\hat{S}_y = \frac{\hbar}{2}\sigma_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \tag{1.105}$$

$$\hat{S}_z = \frac{\hbar}{2}\sigma_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{1.106}$$

Here, σ_i are called Pauli matrices.

1.4.4 Properties of the Pauli matrices:

It is worth noting that the Pauli matrices satisfy a Lie algebra

$$\left[\sigma_i, \sigma_j\right] = i\varepsilon_{ijk}\sigma_k, \tag{1.107}$$

and their square is the identity matrix

$$\sigma_i^2 = \mathbf{1}. \tag{1.108}$$

Besides, they are traceless

$$tr\,\sigma_i = 0; tr\left(\sigma_i\sigma_j\right) = 2\delta_{ij}. \tag{1.109}$$

Furthermore, an interesting characteristic emerges when examining not only the square of the Pauli matrices but also the following object

$$\left(\overrightarrow{\sigma}\cdot\overrightarrow{a}\right)\left(\overrightarrow{\sigma}\cdot\overrightarrow{b}\right) = \left(\overrightarrow{a}\cdot\overrightarrow{b}\right) + i\overrightarrow{\sigma}\cdot\left(\overrightarrow{a}\times\overrightarrow{b}\right). \tag{1.110}$$

1.5 Exercises

Exercise 1

A certain state $|\phi\rangle$ is eigenstate of $\hat{\mathbf{L}}^2$ and $\hat{L}_z$

$$\hat{\mathbf{L}}^2|\phi\rangle = \hbar^2\ell(\ell+1)|\phi\rangle \text{ and } \hat{L}_z|\phi\rangle = \hbar m|\phi\rangle,$$

for this state calculate $\langle\hat{L}_x\rangle$ and $\langle\hat{L}_x^2\rangle$.

Solution

First, note that $\langle\hat{L}_x\rangle = 0$. Since

$$\hat{L}_x = \frac{1}{i\hbar}\left[\hat{L}_z, \hat{L}_y\right],$$

thus

$$\begin{aligned}\langle\hat{L}_x\rangle &= \frac{1}{i\hbar}\langle\phi|\left[\hat{L}_z,\hat{L}_y\right]|\phi\rangle = \frac{1}{i\hbar}\left(\langle\phi|\hat{L}_z\hat{L}_y|\phi\rangle - \langle\phi|\hat{L}_y\hat{L}_z|\phi\rangle\right),\\ &= \frac{m}{i}\left(\langle\phi|\hat{L}_y|\phi\rangle - \langle\phi|\hat{L}_y|\phi\rangle\right) = 0.\end{aligned}$$

Considering the symmetry with respect to x, y we have

$$\langle\hat{L}_x^2\rangle = \langle\hat{L}_y^2\rangle = \frac{1}{2}\left(\hat{\mathbf{L}}^2 - \hat{L}_z^2\right),$$

and so

$$\begin{aligned}\langle\hat{L}_x^2\rangle &= \frac{1}{2}\langle\phi|\left(\hat{\mathbf{L}}^2 - \hat{L}_z^2\right)|\phi\rangle = \frac{1}{2}\langle\phi|\hat{\mathbf{L}}^2|\phi\rangle - \frac{1}{2}\langle\phi|\hat{L}_z^2|\phi\rangle,\\ &= \frac{\hbar^2\ell(\ell+1) - \hbar^2m^2}{2}.\end{aligned}$$

Exercise 2

The spin function for a free electron in basis $\hat{S}_z$ is diagonal can be written as $\begin{pmatrix}1\\0\end{pmatrix}$ and $\begin{pmatrix}0\\1\end{pmatrix}$ with eigenvalues of $\hat{S}_z$ being $\hbar/2$ and $-\hbar/2$. Using this basis find a

normalized eigenfunction of $\hat{S}_y$ with eigenvalue $\hbar/2$.

Solution

In the diagonal representation of $\hat{S}_z$ and $\hat{\mathbf{S}}^2$we can represent $\hat{S}_y$ by

$$\hat{S}_y = \frac{\hbar}{2}.\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}.$$

Let the required eigenfunction of $\hat{S}_y$ be $\upsilon = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$. Then

$$\hat{S}_y \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \hbar/2 \begin{pmatrix} \alpha \\ \beta \end{pmatrix},$$

$$\frac{\hbar}{2}.\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \hbar/2 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}.$$

So, we have $\alpha = -i\beta$ and $\upsilon = \begin{pmatrix} \alpha \\ i\alpha \end{pmatrix}$.

Normalization

$$\upsilon^+\upsilon = \begin{pmatrix} \alpha & -i\alpha \end{pmatrix}\begin{pmatrix} \alpha \\ i\alpha \end{pmatrix} = 2\alpha^2 = 1,$$

gives $\alpha = \frac{1}{\sqrt{2}}$. Hence

$$\upsilon = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}.$$

Exercise 3

Use the following definitions of the angular momentum

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}},$$

$$\begin{aligned}\hat{L}_x &= \frac{\hbar}{i}\left(\hat{y}\frac{\partial}{\partial z}-\hat{z}\frac{\partial}{\partial y}\right),\\ \hat{L}_y &= \frac{\hbar}{i}\left(\hat{z}\frac{\partial}{\partial x}-\hat{x}\frac{\partial}{\partial z}\right),\\ \hat{L}_z &= \frac{\hbar}{i}\left(\hat{x}\frac{\partial}{\partial y}-\hat{y}\frac{\partial}{\partial x}\right),\end{aligned}$$

and the relationships:

$$[\hat{x},\hat{p}_x]=i\hbar;[\hat{y},\hat{p}_y]=i\hbar;[\hat{z},\hat{p}_z]=i\hbar,$$

to demonstrate the following operator identities

$$\left[\hat{L}_x,\hat{L}_y\right]=i\hbar\hat{L}_z;\left[\hat{L}_y,\hat{L}_z\right]=i\hbar\hat{L}_x;\left[\hat{L}_z,\hat{L}_x\right]=i\hbar\hat{L}_y.$$

$$\left[\hat{L}_x,\hat{\mathbf{L}}^2\right]=0;\left[\hat{L}_y,\hat{\mathbf{L}}^2\right]=0;\left[\hat{L}_z,\hat{\mathbf{L}}^2\right]=0.$$

Solution

Let us recall that the components of the vector cross-product can be expressed as

$$\hat{L}_i=(\hat{\mathbf{r}}\times\hat{\mathbf{p}})_i=\varepsilon_{ikl}\hat{x}_k\hat{p}_l$$

So, we can calculate the commutator $\left[\hat{L}_i,\hat{L}_j\right]$ in the following manner:

$$\begin{aligned}\left[\hat{L}_i,\hat{L}_j\right] &= \left[(\hat{\mathbf{r}}\times\hat{\mathbf{p}})_i,(\hat{\mathbf{r}}\times\hat{\mathbf{p}})_j\right]=\left[\varepsilon_{ikl}\hat{x}_k\hat{p}_l,\varepsilon_{jrs}\hat{x}_r\hat{p}_s\right]=\varepsilon_{ikl}\varepsilon_{jrs}\left[\hat{x}_k\hat{p}_l,\hat{x}_r\hat{p}_s\right],\\ &= \varepsilon_{ikl}\varepsilon_{jrs}\hat{x}_k\left[\hat{p}_l,\hat{x}_r\hat{p}_s\right]+\varepsilon_{ikl}\varepsilon_{jrs}\left[\hat{x}_k,\hat{x}_r\hat{p}_s\right]\hat{p}_l,\\ &= \varepsilon_{ikl}\varepsilon_{jrs}\hat{x}_k\left[\hat{p}_l,\hat{x}_r\right]\hat{p}_s+\varepsilon_{ikl}\varepsilon_{jrs}\hat{x}_r\left[\hat{x}_k,\hat{p}_s\right]\hat{p}_l,\\ &= -i\hbar\varepsilon_{ikl}\varepsilon_{jrs}\hat{x}_k\hat{p}_s\delta_{l,r}+i\hbar\varepsilon_{ikl}\varepsilon_{jrs}\hat{x}_r\hat{p}_l\delta_{k,s},\\ &= i\hbar\varepsilon_{ikl}\varepsilon_{ljs}\hat{x}_k\hat{p}_s-i\hbar\varepsilon_{jrk}\varepsilon_{kil}\hat{x}_r\hat{p}_l,\end{aligned}$$

Using the identity

$$\varepsilon_{ijk}\varepsilon_{krs}=\delta_{ir}\delta_{js}-\delta_{is}\delta_{jr},$$

one obtains

$$\begin{aligned}\left[\hat{L}_i,\hat{L}_j\right] &= i\hbar\left(\delta_{ij}\delta_{ks}-\delta_{is}\delta_{jk}\right)\hat{x}_k\hat{p}_s - i\hbar\left(\delta_{ji}\delta_{rl}-\delta_{jl}\delta_{ri}\right)\hat{x}_r\hat{p}_l,\\ &= i\hbar\left(\hat{x}_i\hat{p}_j-\hat{x}_j\hat{p}_i\right).\end{aligned}$$

But it is easy to see that

$$\begin{aligned}\varepsilon_{ijk}\hat{L}_k &= \varepsilon_{ijk}\left(\hat{\mathbf{r}}\times\hat{\mathbf{p}}\right)_k = \varepsilon_{ijk}\varepsilon_{krs}\hat{x}_r\hat{p}_s = \left(\delta_{ir}\delta_{js}-\delta_{is}\delta_{jr}\right)\hat{x}_r\hat{p}_s,\\ &= \hat{x}_i\hat{p}_j-\hat{x}_j\hat{p}_i,\end{aligned}$$

and hence we have the fundamental angular momentum commutation relation

$$\left[\hat{L}_i,\hat{L}_j\right] = i\hbar\varepsilon_{ijk}\hat{L}_k,$$

written out this says that

$$\left[\hat{L}_x,\hat{L}_y\right] = i\hbar\hat{L}_z;\left[\hat{L}_y,\hat{L}_z\right] = i\hbar\hat{L}_x;\left[\hat{L}_z,\hat{L}_x\right] = i\hbar\hat{L}_y.$$

Now the square of the orbital angular momentum operator is $\hat{\mathbf{L}}^2 = \hat{\mathbf{L}}\cdot\hat{\mathbf{L}} = \hat{L}_i\cdot\hat{L}_i$, and therefore

$$\begin{aligned}\left[\hat{\mathbf{L}}^2,\hat{L}_j\right] &= \left[\hat{L}_i\hat{L}_i,\hat{L}_j\right] = \hat{L}_i\left[\hat{L}_i,\hat{L}_j\right] + \left[\hat{L}_i,\hat{L}_j\right]\hat{L}_i,\\ &= i\hbar\varepsilon_{ijk}\hat{L}_i\hat{L}_k + i\hbar\varepsilon_{ijk}\hat{L}_k\hat{L}_i.\end{aligned}$$

But

$$\varepsilon_{ijk}\hat{L}_k\hat{L}_i = \varepsilon_{kij}\hat{L}_k\hat{L}_i = -\varepsilon_{kji}\hat{L}_k\hat{L}_i.$$

This leaves us with the important relation

$$\left[\hat{\mathbf{L}}^2,\hat{L}_j\right] = 0.$$

Exercise 4

Determine the eigenvalues and eigenvectors of the spin operato $\hat{\mathbf{S}}$ for an electron oriented along a unit vector $\mathbf{n}$; assume that $\mathbf{n}$; lies in the xz plane. Calculate the probability of measuring $\hat{S}_z = -\hbar/2$

Solution

In the xz plane, the vector $\mathbf{n}$ is defined as

$$\mathbf{n} = \sin\theta\,\overrightarrow{i} + \cos\theta\,\overrightarrow{k},$$

where $0 \leq \theta \leq \pi$. Thus we can write

$$\hat{\mathbf{S}}\cdot\mathbf{n} = \hat{S}_x \sin\theta + \hat{S}_z \cos\theta$$

Using the spin matrices, we can write $\hat{\mathbf{S}}\cdot\mathbf{n}$ in the following matrix form:

$$\hat{\mathbf{S}}\cdot\mathbf{n} = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\sin\theta + \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\cos\theta = \frac{\hbar}{2}\begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix}$$

The eigenvalues:

$$\det\left[\hat{\mathbf{S}}\cdot\mathbf{n} - \lambda\right] = \begin{vmatrix} \frac{\hbar}{2}\cos\theta - \lambda & \frac{\hbar}{2}\sin\theta \\ \frac{\hbar}{2}\sin\theta & -\frac{\hbar}{2}\cos\theta - \lambda \end{vmatrix} = \lambda^2 - \frac{\hbar^2}{4} = 0,$$

which in turn leads as expected to the eigenvalues $\lambda = \pm\hbar/2$.
The eigenvector:

- Case $\lambda_+ = +\hbar/2$:

$$\frac{\hbar}{2}\begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

This matrix equation can be reduced to a single equation

$$\begin{cases} \alpha(1-\cos\theta) = \beta\sin\theta \\ \beta(1+\cos\theta) = \alpha\sin\theta \end{cases} \Rightarrow \beta\cos\frac{\theta}{2} = \alpha\sin\frac{\theta}{2} \Rightarrow \beta = \alpha\tan\frac{\theta}{2}$$

normalization condition:

$$\alpha^*\alpha\begin{pmatrix} 1 & \tan\frac{\theta}{2} \end{pmatrix}\begin{pmatrix} 1 \\ \tan\frac{\theta}{2} \end{pmatrix} = 1 \Rightarrow |\alpha|^2\left(1+\tan^2\frac{\theta}{2}\right) = 1,$$

$$\alpha = \cos\frac{\theta}{2} \text{ and } \beta = \sin\frac{\theta}{2}.$$

Hence the eigenvector corresponding to $\lambda_+ = \frac{\hbar}{2}$ is

$$\begin{aligned} |\lambda_+\rangle &= \begin{pmatrix} \cos\frac{\theta}{2} \\ \sin\frac{\theta}{2} \end{pmatrix} = \cos\frac{\theta}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} + \sin\frac{\theta}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix}, \\ &= \cos\frac{\theta}{2}|+\rangle + \sin\frac{\theta}{2}|-\rangle. \end{aligned}$$

- Case $\lambda_- = -\hbar/2$:

  The eigenvector corresponding to $\lambda_- = \frac{\hbar}{2}$ can be obtained from

$$\frac{\hbar}{2}\begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix}\begin{pmatrix} \alpha' \\ \beta' \end{pmatrix} = -\frac{\hbar}{2}\begin{pmatrix} \alpha' \\ \beta' \end{pmatrix},$$

which leads to

$$\alpha' \cos\frac{\theta}{2} = \beta' \sin\frac{\theta}{2},$$

normalization condition:

$$\alpha'^{*}\alpha' \begin{pmatrix} 1 & \cot\frac{\theta}{2} \end{pmatrix}\begin{pmatrix} 1 \\ \cot\frac{\theta}{2} \end{pmatrix} = 1 \Rightarrow |\alpha'|^2\left(1+\cot^2\frac{\theta}{2}\right) = 1,$$

$$\alpha' = \sin\frac{\theta}{2} \quad \text{and } \beta' = \cos\frac{\theta}{2}.$$

Hence the eigenvector corresponding to $\lambda_- = -\frac{\hbar}{2}$ is

$$\begin{aligned} |\lambda_-\rangle &= \begin{pmatrix} \sin\frac{\theta}{2} \\ \cos\frac{\theta}{2} \end{pmatrix} = \sin\frac{\theta}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} + \cos\frac{\theta}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix}, \\ &= \sin\frac{\theta}{2}|+\rangle + \cos\frac{\theta}{2}|-\rangle. \end{aligned}$$

the probability of measuring $\hat{S}_z = -\hbar/2$ is given by

$$\mathcal{P}_{-\hbar/2} = |\langle - |\lambda_-\rangle|^2 = \cos^2\frac{\theta}{2}.$$

Exercise 5

Consider the following matrix representation of the x-and y-components of the angular momentum operator

$$\hat{L}_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}; \hat{L}_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

1. Compute $\hat{L}_z$ using the angular momentum operators' algebraic properties.
2. What is the corresponding value of ℓ, the angular momentum quantum number?
3. Calculate $\langle \hat{L}_x \rangle, \langle \hat{L}_x^2 \rangle$ and $\Delta \hat{L}_x$ belonging to the eigenvalue $+\hbar$

Solution

Using the relation $\hat{L}_z = \frac{1}{i\hbar} \left[\hat{L}_x, \hat{L}_y \right] = \frac{1}{i\hbar} \left(\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x \right)$, we have

$$\begin{aligned} \hat{L}_x \hat{L}_y &= \frac{\hbar^2}{2} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} = \frac{\hbar^2}{2} \begin{pmatrix} i & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & -i \end{pmatrix}, \\ \hat{L}_y \hat{L}_x &= \frac{\hbar^2}{2} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = \frac{\hbar^2}{2} \begin{pmatrix} -i & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & i \end{pmatrix}, \end{aligned}$$

$$\hat{L}_z = \frac{1}{i\hbar} \left(\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x \right) = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

The diagonalization of this matrix yields the following eigenvalues: $-\hbar, 0, +\hbar \Rightarrow \ell = 1$

The eigenvectors of $\hat{L}_z$:

$$\hat{L}_z |1, m\rangle = \hbar m |1, m\rangle$$

- Case $m = +1$:

$$\hat{L}_z|1,1\rangle = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = \hbar \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} \Rightarrow \beta = \gamma = 0.$$

normalization condition:

$$\langle 1,1\,|1,1\rangle = |\alpha|^2 = 1.$$

So, the eigenvector of $\hat{L}_z$ belonging to the eigenvalue $+\hbar$ is

$$|1,1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}.$$

Proceeding in the same way, we can easily obtain the eigenvector for $m = 0$ and $m = -1$:

$$|1,0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}; |1,-1\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

The mean value of $\hat{L}_x$ in the state $|1,1\rangle$

$$\langle 1,1\,|\hat{L}_x|\,1,1\rangle = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = 0.$$

The mean value of $\hat{L}_x^2$ in the state $|1,1\rangle$

$$\langle 1,1\,|\hat{L}_x^2|\,1,1\rangle = \frac{\hbar^2}{2} \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 1 \\ 0 & 2 & 0 \\ 1 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \frac{\hbar^2}{2}.$$

Finally,

$$\Delta\hat{L}_x = \sqrt{\left\langle \left[\hat{L}_x - \langle \hat{L}_x \rangle\right]^2 \right\rangle} = \frac{\hbar}{\sqrt{2}}.$$

Chapter 2

Addition of angular momenta

2.1 Addition of two angular momenta

2.1.1 Total angular momentum operator

Let us consider two angular momenta, represented by operators $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$, acting in two spaces $\mathcal{E}(1)$ and $\mathcal{E}(2)$, respectively. Here, $\mathcal{E}(i)$ is a vector space of dimension $d = (2j_i + 1)$ spanned by the vectors $|j_i; m_i\rangle$ $(i = 1, 2)$. In the space associated with a given particle, each angular momentum operator follows the usual commutation relationships

$$\left[\hat{J}_{1_i}; \hat{J}_{1_j}\right] = i\hbar\varepsilon_{ijk}\hat{J}_{1_k}, \qquad \text{and} \qquad \left[\hat{J}_{2_i}; \hat{J}_{2_j}\right] = i\hbar\varepsilon_{ijk}\hat{J}_{2_k}. \tag{2.1}$$

Since the operators belong to different spaces, their components commute:

$$\left[\hat{J}_{1_i}; \hat{J}_{2_j}\right] = 0 \qquad (\forall \;\; i, j)\,. \tag{2.2}$$

Now, let us examine the system considered by the combination of the two particles. We can describe this combined system's state space with the tensor product of $\mathcal{E}(1)$ and $\mathcal{E}(2)$,

$$\mathcal{E} = \mathcal{E}(1) \otimes \mathcal{E}(2)\,, \tag{2.3}$$

which means that the basis of the global system can be constructed by the combination of the tensor product of the selected bases from the $\mathcal{E}(1)$ and $\mathcal{E}(2)$ spaces:

$$|j_1; m_1\rangle \otimes |j_2; m_2\rangle = |j_1; j_2; m_1; m_2\rangle\,. \tag{2.4}$$

For the two-particle system, which has two subspaces, we have

$$\begin{aligned}
\hat{\mathbf{J}}_1^2 |j_1;j_2;m_1;m_2\rangle &= \hbar^2 j_1 (j_1+1) |j_1;j_2;m_1;m_2\rangle , && (2.5)\\
\hat{J}_{1_z} |j_1;j_2;m_1;m_2\rangle &= \hbar m_1 |j_1;j_2;m_1;m_2\rangle , && (2.6)\\
\hat{\mathbf{J}}_2^2 |j_1;j_2;m_1;m_2\rangle &= \hbar^2 j_2 (j_2+1) |j_1;j_2;m_1;m_2\rangle , && (2.7)\\
\hat{J}_{2_z} |j_1;j_2;m_1;m_2\rangle &= \hbar m_2 |j_1;j_2;m_1;m_2\rangle . && (2.8)
\end{aligned}$$

The action of the ladder operators $\hat{J}_{i_\pm} = \hat{J}_{i_x} \pm i\hat{J}_{i_y}$ on the eigenstate $|j_1;j_2;m_1;m_2\rangle$ reads

$$\begin{aligned}
\hat{J}_{1_\pm} |j_1;j_2;m_1;m_2\rangle &= \hbar\sqrt{j_1 (j_1+1) - m_1 (m_1 \pm 1)} |j_1;j_2;m_1 \pm 1;m_2\rangle , && (2.9)\\
\hat{J}_{2_\pm} |j_1;j_2;m_1;m_2\rangle &= \hbar\sqrt{j_2 (j_2+1) - m_2 (m_2 \pm 1)} |j_1;j_2;m_1;m_2 \pm 1\rangle . && (2.10)
\end{aligned}$$

It is worth to note that the product vectors $|j_1, j_2, m_1, m_2\rangle$ form a complete and orthonormal basis

$$\begin{cases} \sum_{m_1=-j_1}^{+j_1} \sum_{m_2=-j_2}^{+j_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2| = 1 \\ \langle j_1, j_2, m_1', m_2' |j_1, j_2, m_1, m_2\rangle = \delta_{m_1', m_1} \delta_{m_2', m_2} \end{cases} . \qquad (2.11)$$

Now, let us examine on the total angular momentum of the system, $\hat{\mathbf{J}}$, which is defined by

$$\begin{aligned}
\hat{\mathbf{J}} &= \hat{\mathbf{J}}_\mathbf{1} + \hat{\mathbf{J}}_\mathbf{2}, && (2.12)\\
\hat{J}_z &= \hat{J}_{1_z} + \hat{J}_{2_z}, && (2.13)
\end{aligned}$$

The square of the total angular momentum operator, $\hat{\mathbf{J}}^2$, commutes with $\hat{\mathbf{J}}_i^2$:

$$\left[\hat{\mathbf{J}}^2, \hat{\mathbf{J}}_1^2\right] = \left[\hat{\mathbf{J}}^2, \hat{\mathbf{J}}_2^2\right] = 0. \qquad (2.14)$$

In addition $\hat{J}_z = \hat{J}_{1_z} + \hat{J}_{2_z}$ commutes with $\hat{\mathbf{J}}^2$

$$\left[\hat{\mathbf{J}}^2, \hat{J}_z\right] = 0. \qquad (2.15)$$

Therefore, the four operators $\hat{\mathbf{J}}^2$, $\hat{\mathbf{J}}_1^2$, $\hat{\mathbf{J}}_2^2$ and $\hat{J}_z$ can be diagonalized simultaneously by the same states. Let us show the global (joint) eigenstate by $|J, M, j_1, j_2\rangle \equiv |J, M\rangle$.

Then, we can express

$$\hat{\mathbf{J}}^2 |J,M\rangle = \hbar^2 J(J+1)|J,M\rangle, \tag{2.16}$$
$$\hat{J}_z |J,M\rangle = \hbar M |J,M\rangle, \tag{2.17}$$
$$\hat{\mathbf{J}}_1^2 |J,M\rangle = \hbar^2 j_1(j_1+1)|J,M\rangle, \tag{2.18}$$
$$\hat{\mathbf{J}}_2^2 |J,M\rangle = \hbar^2 j_2(j_2+1)|J,M\rangle. \tag{2.19}$$

Here, the set of global eigenvectors $|J,M\rangle$ also form a complete and orthonormal basis:

$$\begin{cases} \sum_J \sum_{M=-J}^{J} |J,M\rangle\langle J,M| = 1, \\ \langle J',M'|J,M\rangle = \delta_{M',M}\delta_{J',J}. \end{cases} \tag{2.20}$$

Decoupled representation

A vector $|j_1;j_2;m_1;m_2\rangle = |j_1;m_1\rangle \otimes |j_2;m_2\rangle$ is a simultaneous eigenstate of the observables $\hat{\mathbf{J}}_1^2$; $\hat{\mathbf{J}}_2^2$; $\hat{J}_{1_z}$ and $\hat{J}_{2_z}$ with the respective eigenvalues $\hbar^2 j_1(j_1+1)$; $\hbar^2 j_2(j_2+1)$; $\hbar m_1$ and $\hbar m_2$. The basis $\{|j_1;j_2;m_1;m_2\rangle\}$ is particularly suited for analyzing the individual angular momenta, $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$, of the two subsystems. This basis is called the decoupled basis.

Coupled representation

A vector $|J,M\rangle$ is a simultaneous eigenstate of the observables $\hat{\mathbf{J}}^2$;$\hat{\mathbf{J}}_1^2$; $\hat{\mathbf{J}}_2^2$ and $\hat{J}_z$ with the respective eigenvalues $\hbar J(J+1)$;$\hbar^2 j_1(j_1+1)$; $\hbar^2 j_2(j_2+1)$ and $\hbar M$. The basis $\{|J,M\rangle\}$ is particularly suited for analyzing the total angular momenta. This basis is called the coupled basis.

2.1.2 Eigenvalues of $\hat{J}_z$

Theorem 1 *The eigenvalues of the $\hat{J}_z$ operator $\hbar M$, where $M = m_1 + m_2$, satisfy the following condition:*

$$-(j_1+j_2) \leq M \leq (j_1+j_2). \tag{2.21}$$

Proof:

First, we act $\hat{J}_z = \hat{J}_{1_z} + \hat{J}_{2_z}$, operators on the vectors $|j_1, j_2, m_1, m_2\rangle$ to obtain the eigenvalues of $\hat{J}_z$. We get

$$\begin{aligned}
\hat{J}_z |j_1, j_2, m_1, m_2\rangle &= \left(\hat{J}_{1z} + \hat{J}_{2z}\right) |j_1; m_1\rangle \otimes |j_2; m_2\rangle , \\
&= \hat{J}_{1z} |j_1; m_1\rangle \otimes |j_2; m_2\rangle + |j_1; m_1\rangle \otimes \hat{J}_{2z} |j_2; m_2\rangle , \\
&= \hbar m_1 |j_1; m_1\rangle \otimes |j_2; m_2\rangle + |j_1; m_1\rangle \otimes (\hbar m_2 |j_2; m_2\rangle) , \\
&= \hbar (m_1 + m_2) |j_1, j_2, m_1, m_2\rangle . \qquad (2.22)
\end{aligned}$$

Thus, $M = m_1 + m_2$. Then, we consider the maximum and minimum values of m_1 and m_2, respectively:

$$m_{1_{\max}} = j_1 \text{ and } m_{2_{\max}} = j_2 \Rightarrow M_{\max} = j_1 + j_2. \qquad (2.23)$$

$$m_{1_{\min}} = -j_1 \text{ and } m_{2_{\min}} = -j_2 \Rightarrow M_{\min} = -(j_1 + j_2) . \qquad (2.24)$$

Therefore, M can take values only in between the following range

$$-(j_1 + j_2) \leq M = m_1 + m_2 \leq (j_1 + j_2) . \qquad (2.25)$$

Now, let us study the degree of degeneracy.

- The eigenvalue $\hbar M = \hbar (j_1 + j_2)$ is non-degenerate since there is only one possibility to achieve the value $M = j_1 + j_2$, that is: $m_1 = j_1$ and $m_2 = j_2$. Thus, $g(M = j_1 + j_2) = 1$.

- The eigenvalue $\hbar M = -\hbar (j_1 + j_2)$, is also non-degenerate, since there exists only a single way to attain the given value $M = -(j_1 + j_2)$, that is: $m_1 = -j_1$ and $m_2 = -j_2$. Thus, $g(M = -(j_1 + j_2)) = g(M = j_1 + j_2) = 1$.

- The eigenvalue $\hbar M = \hbar (j_1 + j_2 - 1)$ is doubly degenerate, as there are two possibilities to achieve the value of $M = j_1 + j_2 - 1$, that is: $m_1 = j_1 - 1$ and $m_2 = j_2$, or $m_1 = j_1$ and $m_2 = j_2 - 1$. Therefore, $g(M = j_1 + j_2 - 1) = 2$.

- The eigenvalue $\hbar M = \hbar (-j_1 - j_2 + 1)$ is also doubly degenerate since it can be constructed either by $m_1 = -j_1 + 1$ and $m_2 = -j_2$ or $m_1 = -j_1$ and $m_2 = -j_2 + 1$. Thus, $g(M = (-j_1 - j_2 + 1)) = g(M = (j_1 + j_2 - 1)) = 2$.

In general, one can use the "rectangle method" to determine the quantum numbers and the degeneracy. The rectangle method consists of the following rules:

- On a coordinate system m_1 is plotted on the x-axis while m_2 is plotted on the y-axis. Each vector is represented by a point with coordinates (m_1, m_2).
- All points will be inside or on the sides of a rectangle whose four corners have coordinates:
$$(j_1, j_2);\ (-j_1, j_2);\ (j_1, -j_2);\ (, -j_1, -j_2)\,. \tag{2.26}$$
- All points located on the same parallel to the second bisector represent the same value of M, and thus, the same eigenvalue. Therefore, their quantity is equal to the degeneracy of that eigenvalue.

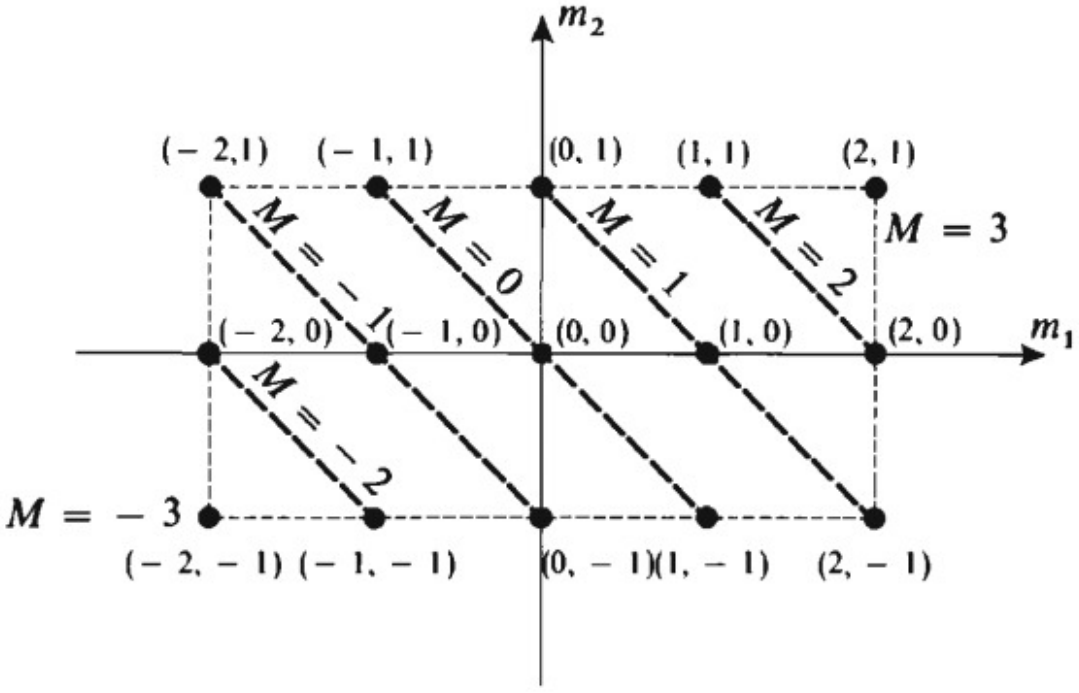

Figure 2.1: The rectangular method for the combined system of $j_1 = 2, j_2 = 1$. The points corresponding to a specific $M = m_1 + m_2$ are situated on a straight line of slope. (for more details see: [5] Cohen-Tannoudji: Quantum mechanics.)

2.1.3 Eigenvalues of $\hat{\mathbf{J}}^2$

Theorem 2 *Let us assume a system constituted of two particles with angular momenta $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$. The only possible values of the total angular momentum, J, can be in the range of*

$$|j_1 - j_2| \leq J \leq (j_1 + j_2)\,. \tag{2.27}$$

Proof:

Let us set m_1 and m_2 to their maximum values j_1 and j_2. Then, we can write the maximum value of J, which is

$$J_{\max} = j_1 + j_2. \tag{2.28}$$

To determine the minimum value for $J_{\max}$, we must utilize the information that there are a total of $(2j_1+1)(2j_2+1)$ eigenkets $|J,M\rangle$. For each value of J, there are a total of $2J+1$ eigenstates $|J,M\rangle$, so we have

$$(2j_1+1)(2j_2+1) = \sum_{J=J_{\min}}^{J_{\max}} (2J+1)\,. \tag{2.29}$$

This sum can be written as

$$\begin{aligned} \sum_{J=J_{\min}}^{J_{\max}} (2J+1) &= (2J_{\min}+1) + (2J_{\min}+3) + (2J_{\min}+5) + \ldots + (2J_{\max}+1)\,, \\ &= (2J_{\min}+1) + (2J_{\min}+3) + (2J_{\min}+5) + \ldots + (2(j_1+j_2)+1)\,, \end{aligned} \tag{2.30}$$

or

$$\sum_{J=J_{\min}}^{J_{\max}} (2J+1) = (2(j_1+j_2)+1) + (2(j_1+j_2)-1) + (2(j_1+j_2)-3) + \ldots + (2J_{\min}+1)\,. \tag{2.31}$$

By summing up equations (2.30) and (2.31) term by term, we get

$$\sum_{J=J_{\min}}^{J_{\max}} (2J+1) = [(j_1+j_2+1)+J_{\min}]\,[(j_1+j_2+1)-J_{\min}]\,. \tag{2.32}$$

By setting this expression equal to the left-hand side of the equation (2.29). We obtain

$$\begin{aligned}(j_1+j_2+1)^2-J_{\min}^2 &= (2j_1+1)(2j_2+1)\\ J_{\min}^2 &= (j_1-j_2)^2. \end{aligned} \tag{2.33}$$

Therefore, the allowed values of J lie within the range:

$$|j_1-j_2| \leq J \leq j_1+j_2. \tag{2.34}$$

2.1.4 Addition of the spin angular momentum of two electrons with $S=1/2$

Let $\mathcal{E}(1)$ and $\mathcal{E}(2)$ represent the two-dimensional state spaces of particles 1 and 2, respectively. In this case, the state space of the two-particles system becomes $\mathcal{E}$ is four-dimensional complex vector space, as defined with $\mathcal{E}=\mathcal{E}(1)\otimes\mathcal{E}(2)$.

Decoupled representation $|m_1,m_2\rangle$

The vectors $\{|1/2,1/2\rangle\equiv|+\rangle,|1/2,-1/2\rangle\equiv|-\rangle\}$ constitute a basis for the two-dimensional state space of each individual particle. The two-particle system's state space is spanned by the products of these states:

$$\begin{aligned}|+\rangle_1\otimes|+\rangle_2 &\equiv |+,+\rangle, \quad |+\rangle_1\otimes|-\rangle_2\equiv|+,-\rangle,\\ |-\rangle_1\otimes|+\rangle_2 &\equiv |-,+\rangle, \quad |-\rangle_1\otimes|-\rangle_2\equiv|-,-\rangle. \end{aligned} \tag{2.35}$$

By using the relations given in equations (2.5), (2.6), (2.7) and (2.8), we calculate the matrix of $\hat{S}_{1_z}$, $\hat{S}_{2_z}$, $\hat{\mathbf{S}}_1^2$ and $\hat{\mathbf{S}}_2^2$ in the $\{|+,+\rangle,|+,-\rangle,|-,+\rangle,|-,-\rangle\}$ basis. We find

$$\begin{cases} \langle m_1',m_2'|\hat{S}_{1_z}|m_1,m_2\rangle = \hbar m_1\delta_{m_1,m_1'}\delta_{m_2,m_2'} \\ \langle m_1',m_2'|\hat{S}_{2_z}|m_1,m_2\rangle = \hbar m_2\delta_{m_1,m_1'}\delta_{m_2,m_2'} \\ \langle m_1',m_2'|\hat{\mathbf{S}}_1^2|m_1,m_2\rangle = \langle m_1',m_2'|\hat{\mathbf{S}}_2^2|m_1,m_2\rangle = \frac{3\hbar^2}{4}\delta_{m_1,m_1'}\delta_{m_2,m_2'} \end{cases}, \tag{2.36}$$

In the matrix form, we can express $\hat{S}_{1_z}$ and $\hat{S}_{2_z}$

$$\hat{S}_{1_z} = \begin{pmatrix} \frac{\hbar}{2} & 0 & 0 & 0 \\ 0 & \frac{\hbar}{2} & 0 & 0 \\ 0 & 0 & -\frac{\hbar}{2} & 0 \\ 0 & 0 & 0 & -\frac{\hbar}{2} \end{pmatrix}; \qquad \hat{S}_{2_z} = \begin{pmatrix} \frac{\hbar}{2} & 0 & 0 & 0 \\ 0 & -\frac{\hbar}{2} & 0 & 0 \\ 0 & 0 & \frac{\hbar}{2} & 0 \\ 0 & 0 & 0 & -\frac{\hbar}{2} \end{pmatrix}, \tag{2.37}$$

with $\hat{\mathbf{S}}_1^2$ and $\hat{\mathbf{S}}_2^2$ in the form of

$$\hat{\mathbf{S}}_1^2 = \hat{\mathbf{S}}_2^2 = \begin{pmatrix} \frac{3\hbar}{4} & 0 & 0 & 0 \\ 0 & \frac{3\hbar}{4} & 0 & 0 \\ 0 & 0 & \frac{3\hbar}{4} & 0 \\ 0 & 0 & 0 & \frac{3\hbar}{4} \end{pmatrix}. \tag{2.38}$$

Coupled representation $|S,M\rangle$

Now, we intend to form the system's total spin with the help of

$$\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2, \tag{2.39}$$

$$\hat{S}_z = \hat{S}_{1_z} + \hat{S}_{2_z}. \tag{2.40}$$

We recall the allowed values of the total spin angular momentum of two electrons

$$\begin{aligned} |s_1 - s_2| \leq S \leq s_1 + s_2, \\ \Rightarrow 0 \leq S \leq 1. \end{aligned} \tag{2.41}$$

For a given S, the possible values ok M are as follows:

$$\begin{cases} S = 1;\ M = 0, \pm 1, \\ S = 0;\ M = 0. \end{cases} \tag{2.42}$$

The possible eigenstates in the $|S,M\rangle$ basis are

$$\overbrace{|1,1\rangle;\quad |1,0\rangle;\quad |1,-1\rangle}^{\text{triplet state}};\quad \overbrace{|0,0\rangle}^{\text{singlet state}}\quad . \tag{2.43}$$

The matrix of $\hat{\mathbf{S}}^2$ and $\hat{S}_z$ can be given via

$$\left\langle S', M' \right| \hat{\mathbf{S}}^2 \left| S, M \right\rangle = \hbar^2 S(S+1)\, \delta_{S,S'} \delta_{M,M'}, \tag{2.44}$$

$$\hat{\mathbf{S}}^2 = \hbar^2 \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \tag{2.45}$$

and

$$\left\langle S', M' \right| \hat{S}_z \left| S, M \right\rangle = \hbar M \delta_{S,S'} \delta_{M,M'}, \tag{2.46}$$

$$\hat{S}_z = \hbar \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{2.47}$$

For the two spin-up particles, each with eigenstate $|+\rangle$

$$S = \frac{1}{2} + \frac{1}{2} = 1, \tag{2.48}$$

hass the maximum value of total angular momentum. The maximum value of the total magnetic moment for the system is

$$M_{\max} = S = 1. \tag{2.49}$$

For two spin up particles, there is only one possibility, so, one eigenstate in the $|S, M\rangle$ basis is $|1,1\rangle$. This corresponds to $|+,+\rangle$ in the $|m_1, m_2\rangle$ basis

$$|1,1\rangle = |+,+\rangle\,. \tag{2.50}$$

Then, we employ the operator $\hat{S}_-$ on the state $|1,1\rangle$,

$$\hat{S}_- |1,1\rangle = \hbar\sqrt{2}\,|1,0\rangle \Rightarrow |1,0\rangle = \frac{\hat{S}_-}{\hbar\sqrt{2}} |1,1\rangle = \frac{\hat{S}_-}{\hbar\sqrt{2}} |+,+\rangle\,. \tag{2.51}$$

to find $|1,0\rangle$ in $\{|m_1,m_2\rangle\}$ basis. We simply apply $\hat{S}_- = \hat{S}_{1_-} + \hat{S}_{2_-}$ on $|m_1,m_2\rangle$:

$$\begin{aligned} |1,0\rangle &= \frac{\hat{S}_{1_-} + \hat{S}_{2_-}}{\hbar\sqrt{2}} |+,+\rangle, \\ &= \frac{1}{\sqrt{2}} \Big[|+,-\rangle + |-,+\rangle \Big]. \end{aligned} \tag{2.52}$$

Then, we proceed with the application of $\hat{S}_-$ on $|1,0\rangle$

$$\hat{S}_- |1,0\rangle = \hbar\sqrt{2}\,|1,-1\rangle \Rightarrow |1,-1\rangle = \frac{\hat{S}_-}{\hbar\sqrt{2}} |1,0\rangle,$$

$$\begin{aligned} |1,-1\rangle &= \frac{\hat{S}_{1_-} + \hat{S}_{2_-}}{2\hbar} [|+,-\rangle + |-,+\rangle], \\ &= |-,-\rangle. \end{aligned} \tag{2.53}$$

The vector $|0,0\rangle$ must be a linear combination of $|+,-\rangle$ and $|-,+\rangle$

$$|0,0\rangle = a\,|+,-\rangle + b\,|-,+\rangle, \tag{2.54}$$

where the combination of (2.52) with (2.54) leads to

$$\langle 0,0\,|1,0\rangle = \frac{a+b}{\sqrt{2}} = 0 \Rightarrow a = -b. \tag{2.55}$$

Since $|0,0\rangle$ has to be normalized, we get

$$\langle 0,0\,|0,0\rangle = |a|^2 + |b|^2 = 1 \Rightarrow a = \frac{1}{\sqrt{2}}. \tag{2.56}$$

After substituting this value into equation (2.54), we obtain

$$|0,0\rangle = \frac{1}{\sqrt{2}} \Big[|+,-\rangle - |-,+\rangle \Big]. \tag{2.57}$$

2.2 Clebsch–Gordan Coefficients (CG-C)

The angular momentum state vectors $\{|J,M\rangle\}$ form a complete basis set in space $\mathcal{E} = \mathcal{E}(1) \otimes \mathcal{E}(2)$, which is the same Hilbert space of the angular momentum state

vectors represented by $\{|j_1, j_2, m_1, m_2\rangle\}$. So, in this space $\mathcal{E} = \mathcal{E}(1) \otimes \mathcal{E}(2)$, we have 2-basis sets and our objective is to establish the connection between these two sets of bases.

First, we express the vectors $|J, M\rangle$ in term of $|j_1, j_2, m_1, m_2\rangle$ as follows:

$$|J, M\rangle = \mathbf{1}\,|J, M\rangle\,. \tag{2.58}$$

Then, we introduce the completeness relation

$$\mathbf{1} = \sum_{m_1=-j_1}^{+j_1} \sum_{m_2=-j_2}^{+j_2} |j_1, j_2, m_1, m_2\rangle\,\langle j_1, j_2, m_1, m_2|\,. \tag{2.59}$$

We find

$$\begin{aligned} |J, M\rangle &= \sum_{m_1=-j_1}^{+j_1} \sum_{m_2=-j_2}^{+j_2} \langle j_1, j_2, m_1, m_2\,|J, M\rangle\,|j_1, j_2, m_1, m_2\rangle\,, \\ &= \sum_{m_1=-j_1}^{+j_1} \sum_{m_2=-j_2}^{+j_2} \mathbf{C}^{J,M}_{j_1,m_1,j_2,m_2}\,|j_1, j_2, m_1, m_2\rangle\,, \end{aligned} \tag{2.60}$$

where

$$\mathbf{C}^{J,M}_{j_1,m_1,j_2,m_2} = \langle j_1, j_2, m_1, m_2\,|J, M\rangle\,, \tag{2.61}$$

are called Clebsch-Gordan Coefficients (CG-C). This term represents matrix elements of a unitary matrix that facilitate the the transformation between different bases, The dimension of the space $\mathcal{E}$ denoted by d_J is given by $(2j_1+1)(2j_2+1)$. Consequently, our unitary matrix has dimensions of d_J by d_J. Please note that, the (CG-C) goes to zero if $M \neq m_1 + m_2$

$$\langle j_1, j_2, m_1, m_2\,|J, M\rangle = 0 \quad \text{if} \quad M \neq m_1 + m_2. \tag{2.62}$$

Besides, the CG-C are real, in other words, the elements of the unitary matrix are real valued:

$$\langle j_1, j_2, m_1, m_2\,|J, M\rangle = \langle J, M\,|j_1, j_2, m_1, m_2\rangle\,. \tag{2.63}$$

We also know the orthonormality condition

$$\langle J', M'\,|J, M\rangle = \delta_{J,J'}\delta_{M,M'}. \tag{2.64}$$

Now, by employing the completeness relation, given in (2.59),

$$\sum_{m_1=-j_1}^{+j_1}\sum_{m_2=-j_2}^{+j_2}\langle J',M'\,|j_1,j_2,m_1,m_2\rangle\,\langle j_1,j_2,m_1,m_2\,|J,M\rangle=\delta_{J,J'}\delta_{M,M'}. \tag{2.65}$$

with equation (2.63), we get

$$\begin{aligned}\sum_{m_1=-j_1}^{+j_1}\sum_{m_2=-j_2}^{+j_2}\langle j_1,j_2,m_1,m_2\,\big|J',M'\rangle\,\langle j_1,j_2,m_1,m_2\,|J,M\rangle &= \delta_{J,J'}\delta_{M,M'},\\ \sum_{m_1=-j_1}^{+j_1}\sum_{m_2=-j_2}^{+j_2}\langle j_1,j_2,m_1,m_2\,|J,M\rangle\,\langle j_1,j_2,m_1,m_2\,|J,M\rangle &= \mathbf{1}.\end{aligned} \tag{2.66}$$

Since $\{|j_1,j_2,m_1,m_2\rangle\}$ satisfies the orthonormality condition,

$$\langle j_1,j_2,m_1,m_2\,\big|j_1,j_2,m_1',m_2'\rangle=\delta_{m_1,m_1'}\delta_{m_2,m_2'}, \tag{2.67}$$

we obtain

$$\sum_J\sum_{M=-J}^{J}\langle j_1,j_2,m_1,m_2\,|J,M\rangle\,\langle J,M\,\big|j_1,j_2,m_1',m_2'\rangle=\delta_{m_1,m_1'}\delta_{m_2,m_2'},$$

$$\sum_J\sum_{M=-J}^{J}\langle j_1,j_2,m_1,m_2\,|J,M\rangle\,\langle j_1,j_2,m_1,m_2\,|J,M\rangle=\mathbf{1}. \tag{2.68}$$

It is worth noting that, equations (2.66) and (2.68) represent the normality conditions of the global state $|J,M\rangle$.

$$||J,M\rangle|^2 = \sum_J\sum_{M=-J}^{J}\left(\langle j_1,j_2,m_1,m_2\,|J,M\rangle\right)^2. \tag{2.69}$$

$$= \sum_{m_1=-j_1}^{+j_1}\sum_{m_2=-j_2}^{+j_2}\left(\langle j_1,j_2,m_1,m_2\,|J,M\rangle\right)^2. \tag{2.70}$$

2.3 3J Symbols

The CG-C can be expressed in terms of the Wigner coefficients (3J symbols) as follows:

$$\begin{pmatrix} j_1 & j_2 & J\\ m_1 & m_2 & M\end{pmatrix}=\frac{(-1)^{2j_1+J+M}}{\sqrt{2J+1}}\,\langle j_1,j_2,-m_1,-m_2\,|J,M\rangle. \tag{2.71}$$

The inverse relation reads

$$\langle j_1, j_2, m_1, m_2 \,|J, M\rangle = (-1)^{j_1 - J + M} \sqrt{2J+1} \begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix}. \tag{2.72}$$

Here, the symbol $\begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix}$ is referred to as a Wigner coefficient. The $3J$ symbol has the following property

$$\begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & M \end{pmatrix} = 0, \quad \text{if} \quad m_1 + m_2 + M \neq 0. \tag{2.73}$$

The $3J$ symbol remains unchanged when the columns undergo on an even permutation

$$\begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & M \end{pmatrix} = \begin{pmatrix} J & j_1 & j_2 \\ M & m_1 & m_2 \end{pmatrix} = \begin{pmatrix} j_2 & J & j_1 \\ m_2 & M & m_1 \end{pmatrix}. \tag{2.74}$$

On the contrary, an odd permutation of the columns is analogous to multiplying by the coefficient $(-1)^{j_1+j_2+J}$

$$(-1)^{j_1+j_2+J} \begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & M \end{pmatrix} = \begin{pmatrix} j_2 & j_1 & J \\ m_2 & m_1 & M \end{pmatrix}. \tag{2.75}$$

Orthogonality properties of the Wigner 3j symbols read

$$\sum_{J,M} \begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & M \end{pmatrix} \begin{pmatrix} j_1 & j_2 & J \\ m_1' & m_2' & M \end{pmatrix} = \delta_{m_1, m_1'} \delta_{m_2, m_2'}. \tag{2.76}$$

$$\sum_{m_1, m_2} \begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & M \end{pmatrix} \begin{pmatrix} j_1 & j_2 & J' \\ m_1 & m_2 & M' \end{pmatrix} = \frac{\delta_{J',J} \delta_{M',M} \delta(j_1 j_2 J)}{2J+1}, \tag{2.77}$$

where

$$\delta(j_1 j_2 J) = \begin{cases} 1, & \text{if} \quad |j_1 - j_2| \leq J \leq j_1 + j_2 \\ 0, & \text{otherwise} \end{cases}. \tag{2.78}$$

2.4 Addition of three angular momenta

2.4.1 Total angular momentum operator

Consider 3-angular momentum operators $\hat{\mathbf{J}}_1$, $\hat{\mathbf{J}}_2$ and $\hat{\mathbf{J}}_3$ of magnitudes j_1, j_2 and j_3. Let us assume that these operators act in 3-spaces $\mathcal{E}(1), \mathcal{E}(2)$ and $\mathcal{E}(3)$ respectively. In this case, the total angular momentum reads $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2 + \hat{\mathbf{J}}_3$, where $\hat{\mathbf{J}}_1$, $\hat{\mathbf{J}}_2$ and $\hat{\mathbf{J}}_3$ stand for the commuting operators.

When combining three angular momenta, we have the following basis for Hilbert space

$$|j_1;m_1\rangle \otimes |j_2;m_2\rangle \otimes |j_3;m_3\rangle = |j_1;j_2;j_3;m_1;m_2;m_3\rangle . \tag{2.79}$$

The global system's state space can be described with the tensor product of $\mathcal{E}(1)$, $\mathcal{E}(2)$, and $\mathcal{E}(3)$

$$\mathcal{E} = \mathcal{E}(1) \otimes \mathcal{E}(2) \otimes \mathcal{E}(3) . \tag{2.80}$$

Therefore, the dimensionality of the global state space reads

$$d = (2j_1+1)(2j_2+1)(2j_3+1) . \tag{2.81}$$

There are different ways of forming the vector of total angular momentum $\hat{\mathbf{J}}$:

$$\underbrace{\underbrace{\hat{\mathbf{J}}_1 \quad , \quad \hat{\mathbf{J}}_2}_{\hat{\mathbf{J}}_{1,2}} \quad , \quad \hat{\mathbf{J}}_3}_{\hat{\mathbf{J}}} ; \qquad \underbrace{\underbrace{\hat{\mathbf{J}}_2 \quad , \quad \hat{\mathbf{J}}_3}_{\hat{\mathbf{J}}_{2,3}} \quad , \quad \hat{\mathbf{J}}_1}_{\hat{\mathbf{J}}} ; \qquad \underbrace{\underbrace{\hat{\mathbf{J}}_1 \quad , \quad \hat{\mathbf{J}}_3}_{\hat{\mathbf{J}}_{1,3}} \quad , \quad \hat{\mathbf{J}}_2}_{\hat{\mathbf{J}}}$$

1. We can first couple $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$ to construct the angular momentum $\hat{\mathbf{J}}_{1,2}$

$$\hat{\mathbf{J}}_{1,2} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2, \tag{2.82}$$

Then, we couple $\hat{\mathbf{J}}_{1,2}$ and $\hat{\mathbf{J}}_3$ to construct the total angular momentum $\hat{\mathbf{J}}$

$$\hat{\mathbf{J}} = \hat{\mathbf{J}}_{1,2} + \hat{\mathbf{J}}_3. \tag{2.83}$$

In this scheme, the eigenvector is as follows:

$$\begin{aligned}\left|(j_1,j_2)J_{1,2},j_3,J,M\right\rangle &= \sum_{m_i}\langle j_1,j_2,m_1,m_2\left|J_{1,2},M_{1,2}\right\rangle \\ &\left\langle J_{1,2},j_3,M_{1,2},m_3\left|J,M\right\rangle\right|j_1,j_2,j_3,m_1,m_2,m_3\rangle .\end{aligned} \tag{2.84}$$

and it is common for $\hat{\mathbf{J}}_1^2$, $\hat{\mathbf{J}}_2^2$, $\hat{\mathbf{J}}_3^2$, $\hat{\mathbf{J}}_{1,2}^2$, $\hat{\mathbf{J}}^2$ and $\hat{J}_z$. The corresponding quantum numbers j_1, j_2, j_3, $J_{1,2}$ and J satisfy the triangular conditions

$$|j_1-j_2|\leq J_{1,2}\leq j_1+j_2; \qquad \left|J_{1,2}-j_3\right|\leq J\leq J_{1,2}+j_3. \tag{2.85}$$

2. Instead of the first way, we can couple first $\hat{\mathbf{J}}_2+\hat{\mathbf{J}}_3=\hat{\mathbf{J}}_{2,3}$, and then $\hat{\mathbf{J}}_1+\hat{\mathbf{J}}_{2,3}=\hat{\mathbf{J}}$. In this way, the eigenvector reads

$$\begin{aligned}\left|j_1,(j_2,j_3)J_{2,3},J,M\right\rangle &= \sum_{m_i}\langle j_2,j_3,m_2,m_3\left|J_{2,3},M_{2,3}\right\rangle \\ &\left\langle j_1,J_{2,3},M_{2,3},m_1\left|J,M\right\rangle\right|j_1,j_2,j_3,m_1,m_2,m_3\rangle .\end{aligned} \tag{2.86}$$

and it is common for $\hat{\mathbf{J}}_1^2$, $\hat{\mathbf{J}}_2^2$, $\hat{\mathbf{J}}_3^2$, $\hat{\mathbf{J}}_{2,3}^2$, $\hat{\mathbf{J}}^2$ and $\hat{J}_z$. Here, the quantum numbers j_1, j_2, j_3, $J_{2,3}$ and J follow the following triangular conditions

$$|j_2-j_3|\leq J_{2,3}\leq j_2+j_3; \qquad \left|J_{2,3}-j_1\right|\leq J\leq J_{2,3}+j_1. \tag{2.87}$$

3. Instead of the previous two ways, one can couple first $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_3$, to obtain $\hat{\mathbf{J}}_{1,3}$. This vector gets values between $|j_1-j_3|$ and j_1+j_3. Then, the resulting vector can be derived via $\hat{\mathbf{J}}_{1,3}+\hat{\mathbf{J}}_2=\hat{\mathbf{J}}$. In this way, the eigenvector reads

$$\begin{aligned}\left|(j_1,j_3)J_{1,3},j_2,J,M\right\rangle &= \sum_{m_i}\langle j_1,j_3,m_1,m_3\left|J_{1,3},M_{1,3}\right\rangle \\ &\left\langle J_{1,3},j_2,M_{1,3},m_2\,|\,J,M\right\rangle|j_1,j_2,j_3,m_1,m_2,m_3\rangle\end{aligned} \tag{2.88}$$

and it is common for $\hat{\mathbf{J}}_1^2$, $\hat{\mathbf{J}}_2^2$, $\hat{\mathbf{J}}_3^2$, $\hat{\mathbf{J}}_{1,3}^2$, $\hat{\mathbf{J}}^2$ and $\hat{J}_z$. The quantum numbers J obeys the triangular conditions

$$\left|J_{1,3}-j_2\right|\leq J\leq J_{1,3}+j_2. \tag{2.89}$$

2.5 6J symbol

Among the three sets of eigenvectors, given in equations (2.84-2.88), it's possible to find transformations that establish connections between these different bases. We can express this type of transformation formally as follows:

$$\left|j_1,(j_2,j_3)J_{2,3},J,M\right\rangle = \sum_{J_{2,3}} \left\langle (j_1,j_2)J_{1,2},j_3,J \left| j_1,(j_2,j_3)J_{2,3},J\right\rangle \right| (j_1,j_2)J_{1,2},j_3,J,M\rangle\,. \tag{2.90}$$

The coefficients in (2.90) do not depend on the projection quantum number M. We can express this transformation in the following form:

$$\left\langle (j_1,j_2)J_{1,2},j_3,J \left| j_1,(j_2,j_3)J_{2,3},J\right\rangle = \sqrt{(2J_{1,2}+1)\,(2J_{2,3}+1)}\mathbf{W}\,(j_1,j_2,J,j_3;J_{1,2},J_{2,3})\,. \tag{2.91}$$

The term that stands on the right-hand side, $\mathbf{W}\,(j_1,j_2,J,j_3;J_{1,2},J_{2,3})$ is called the Racah $\mathbf{W}$-coefficient.

In this formalism, Wigner's 6J symbol is defined by

$$\left\{ \begin{array}{ccc} a & b & e \\ d & c & f \end{array} \right\} = (-1)^{a+b+c+d}\,\mathbf{W}\,(a,b,c,d;e,f)\,, \tag{2.92}$$

and sometimes it is utilized in place of the Racah coefficient. The definition of the 6J-symbol in terms of the 3J-symbols reads

$$\begin{aligned} \left\{ \begin{array}{ccc} j_1 & j_2 & J_{1,2} \\ j_3 & J & J_{2,3} \end{array} \right\} \;=\; & \sum_{m_1,m_2,m_3} \sum_{m_1',m_2',m_3'} (-1)^{\sum j_i+\sum \ell_i+\sum m_i+\sum m_i'} \times \\ & \left(\begin{array}{ccc} j_1 & j_2 & J_3 \\ m_1 & m_2 & m_3 \end{array} \right) \left(\begin{array}{ccc} j_1 & \ell_2 & \ell_3 \\ -m_1 & m_2' & -m_3' \end{array} \right) \\ & \times \left(\begin{array}{ccc} \ell_1 & j_2 & \ell_3 \\ -m_1' & -m_2 & m_3' \end{array} \right) \left(\begin{array}{ccc} \ell_1 & \ell_2 & j_3 \\ m_1' & -m_2' & m_3 \end{array} \right). \end{aligned} \tag{2.93}$$

It is worth noting that the 6J symbol remains unchanged under the following symmetry transformation:

- Any permutation of columns.

- Under exchange of the j's in rows 1 and 2 for any 2-columns

$$\left\{ \begin{array}{ccc} j_1 & j_2 & J_{1,2} \\ j_3 & J & J_{2,3} \end{array} \right\} = \left\{ \begin{array}{ccc} j_3 & J & J_{1,2} \\ j_1 & j_2 & J_{2,3} \end{array} \right\} = \left\{ \begin{array}{ccc} j_1 & J & J_{2,3} \\ j_3 & j_2 & J_{1,2} \end{array} \right\} = \left\{ \begin{array}{ccc} j_1 & j_2 & J_{2,3} \\ j_3 & J & J_{1,2} \end{array} \right\}. \tag{2.94}$$

2.6 Wigner-Eckart Theorem

Scalar operators

One can define a scalar operator, $\hat{\mathbf{A}}$, as an operator that commutes with the three components of the total angular momentum.

$$\left[\hat{J}_i, \hat{\mathbf{A}}\right] = 0. \tag{2.95}$$

Examples of scalar operators: $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$, $\hat{\mathbf{r}} \cdot \hat{\mathbf{p}}, \ldots$

Vector operators

An operator $\hat{\mathbf{V}}$ is considered a vector operator if its components $\hat{V}_x$, $\hat{V}_y$, and $\hat{V}_z$ satisfy the following commutation relations:

$$\left[\hat{J}_i, \hat{V}_j\right] = i\hbar\varepsilon_{ijk}\hat{V}_k. \tag{2.96}$$

Examples of vector operators: $\hat{\mathbf{p}}$, $\hat{\mathbf{r}}$, $\hat{\mathbf{J}}, \ldots$

Irreducible tensor operator

An irreducible tensor operator of rank k is defined as a set of $2k+1$ functions, denoted as $\hat{T}_q^{(k)}$ $(-k \leq q \leq k)$, which transform under the $2k+1$ dimensional representation of the rotation group.

$$\hat{T}_q'^{(k)} = \sum_{q'q}^{(k)} \hat{T}_q^{(k)} R_{q',q}^{(k)}. \tag{2.97}$$

The components of $\hat{T}_q^{(k)}$ of can be defined by their commutation relations with the components of the total angular momentum vector of the system on wich the tensor

component act. Specifically,

$$\left[\hat{J}_{\pm}, \hat{T}_q^{(k)}\right] = \hbar\sqrt{k(k+1) - q(q\pm 1)}\hat{T}_{q\pm 1}^{(k)}. \tag{2.98}$$

$$\left[\hat{J}_z, \hat{T}_q^{(k)}\right] = \hbar q \hat{T}_q^{(k)}. \tag{2.99}$$

Any scalar operator is an irreducible tensor operator of rank 0 and having only one component. The quantities $\hat{T}_q^{(1)}$ related to the components of vector operators $\hat{\mathbf{V}}$

$$\hat{T}_0^{(1)} = \hat{V}_0; \qquad \hat{T}_{\pm 1}^{(1)} = \frac{1}{\sqrt{2}}\left(\hat{V}_x \pm \hat{V}_y\right), \tag{2.100}$$

form an irreducible tensor operator of rank 1.

Wigner-Eckart theorem

The matrix element of spherical tensor operator $\hat{T}_q^{(k)}$ with respect to the angular momentum ($\hat{J}_z$ and $\hat{\mathbf{J}}$) takes the form

$$\left\langle \alpha', j', m' \mid \hat{T}_q^{(k)} \mid \alpha, j, m \right\rangle = \left\langle j, k, m, q \mid j', m' \right\rangle \left\langle \alpha', j' \mid\mid \hat{T}_q^{(k)} \mid\mid \alpha, j \right\rangle$$

where α, α' are quantum numbers. The factor $\left\langle \alpha', j' \mid\mid \hat{T}_q^{(k)} \mid\mid \alpha, j \right\rangle$ is called the reduced matrix element, and $\langle j, k, m, q, \mid j', m' \rangle$ is just the CG-C for two angular momenta. The proof of this theorem is given in several different textbooks.

The implication of the Wigner-Eckart theorem is that the matrix element $\left\langle \alpha', j', m' \mid \hat{T}_q^{(k)} \mid \alpha, j, m \right\rangle$ can be expressed as a product of terms that it's independent of q, m and m' , combined with the Clebsch-Gordan coefficient

Wigner-Eckart theorem for a scalar operator The scalar operator is an irreducible tensor operator of rank 0, we have

$$\left\langle \alpha', j', m' \mid \hat{\mathbf{A}} \mid \alpha, j, m \right\rangle = \left\langle j, 0, m, 0 \mid j', m' \right\rangle \left\langle \alpha', j' \mid\mid \hat{\mathbf{A}} \mid\mid \alpha, j \right\rangle, \tag{2.101}$$

the coefficient $\langle j, 0, m, 0 \mid j', m' \rangle$ is zero unless $j' = j$ and $m = m'$,

$$\left\langle \alpha', j', m' \mid \hat{\mathbf{A}} \mid \alpha, j, m \right\rangle = \left\langle \alpha', j \mid\mid \hat{\mathbf{A}} \mid\mid \alpha, j \right\rangle. \tag{2.102}$$

Wigner-Eckart theorem for a vector operator :

As we know, a vector operator is an irreducible tensor operator of rank 1

$$\left\langle \alpha', j', m' \mid \hat{\mathbf{V}}_q \mid \alpha, j, m \right\rangle = \left\langle j, 1, m, q \mid j', m' \right\rangle \left\langle \alpha', j' \mid\mid \hat{\mathbf{V}}_q \mid\mid \alpha, j \right\rangle, \tag{2.103}$$

here, the coefficients $\langle j,0,m,0 \mid j',m' \rangle$ equal to zero except for $|j-1| \leq j' \leq j+1$ and $m+q=m'$.

Projection Theorem

The Projection theorem asserts that for any vector operator $\hat{\mathbf{V}}_i$ and $j \neq 0$:

$$\left\langle \alpha', j', m' \mid \hat{\mathbf{V}}_i \mid \alpha, j, m \right\rangle = \frac{\left\langle \alpha', j, m \mid \left(\hat{\mathbf{J}} \cdot \hat{\mathbf{V}}\right) \mid \alpha, j, m \right\rangle}{\hbar^2 j(j+1)} \left\langle \alpha', j', m' \mid \hat{J} \mid \alpha, j, m \right\rangle. \tag{2.104}$$

An important application of the projection theorem is the calculation of the Landé g-factor for a particle possessing both orbital angular momentum ℓ and spin angular momentum s. By using the magnetic moment of an electron

$$\overrightarrow{\mu} = \frac{e}{2m}\left(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}\right). \tag{2.105}$$

and the Landé factor

$$\left\langle \alpha', j', m' \mid \overrightarrow{\mu} \mid \alpha, j, m \right\rangle = g_{\ell,s} \frac{e}{2m} \left\langle \alpha', j', m' \mid J \mid \alpha, j, m \right\rangle, \tag{2.106}$$

one can obtain

$$\begin{aligned} g_{\ell,s} &= \frac{\left\langle \alpha', j, m \mid \left(\hat{\mathbf{J}} \cdot \left(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}\right)\right) \mid \alpha, j, m \right\rangle}{\hbar^2 j(j+1)} \\ &= \frac{\left\langle \alpha', j, m \mid \left(\hat{\mathbf{J}} \cdot \left(\hat{\mathbf{J}} + \hat{\mathbf{S}}\right)\right) \mid \alpha, j, m \right\rangle}{\hbar^2 j(j+1)} \end{aligned}$$

In order to calculate factor "$\hat{\mathbf{J}} \cdot \left(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}\right)$", we employ

$$\hat{\mathbf{J}} \cdot \left(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}\right) = \hat{\mathbf{J}} \cdot \left(\hat{\mathbf{J}} + \hat{\mathbf{S}}\right) = \hat{\mathbf{J}}^2 + \hat{\mathbf{J}} \cdot \hat{\mathbf{S}}, \tag{2.107}$$

$$2\hat{\mathbf{J}} \cdot \hat{\mathbf{S}} = \hat{\mathbf{J}}^2 + \hat{\mathbf{S}}^2 - \hat{\mathbf{L}}^2. \tag{2.108}$$

thus,

$$\hat{\mathbf{J}}\cdot\left(\hat{\mathbf{L}}+2\hat{\mathbf{S}}\right)=\hat{\mathbf{J}}^2-\frac{\hat{\mathbf{L}}^2}{2}+\frac{\hat{\mathbf{J}}^2}{2}+\frac{\hat{\mathbf{S}}^2}{2}=\frac{3\hat{\mathbf{J}}^2}{2}-\frac{\hat{\mathbf{L}}^2}{2}+\frac{\hat{\mathbf{S}}^2}{2}.$$

Hence, in a state with definite values of j, s, and ℓ, we find

$$\begin{aligned} g_{\ell,s} &= \frac{\left\langle \alpha', j, m \mid \left(\frac{3\hat{\mathbf{J}}^2}{2}-\frac{\hat{\mathbf{L}}^2}{2}+\frac{\hat{\mathbf{S}}^2}{2}\right) \mid \alpha, j, m\right\rangle}{\hbar^2 j(j+1)}, \\ &= 1+\frac{1-\ell(\ell+1)+s(s+1)}{2j(j+1)}. \end{aligned} \tag{2.109}$$

2.7 Exercises

Exercise 1

Find the energy levels and their degeneracies for a system of two nonidentical spin 1/2 particles with Hamiltonian

$$H = \frac{\varepsilon_0}{\hbar^2}\left(\hat{\mathbf{S}}_1^2 + \hat{\mathbf{S}}_2^2\right) - \frac{\varepsilon_0}{\hbar}\left(\hat{S}_{1_z} + \hat{S}_{2_z}\right),$$

where ε_0 is a constant.

Solution

The four operators $\hat{\mathbf{S}}_1^2, \hat{\mathbf{S}}_2^2, \hat{S}_{1_z}, \hat{S}_{2_z}$ form a complete set of commuting operators; they can thus be jointly diagonalized by the same states. Denoting their joint eigenstates by $|s_1, s_2, m_1, m_2\rangle$,

$$\hat{\mathbf{S}}_i^2 |s_1, s_2, m_1, m_2\rangle = \hbar^2 s_i (s_i + 1) |s_1, s_2, m_1, m_2\rangle,$$

$$\hat{S}_{i_z} |s_1, s_2, m_1, m_2\rangle = \hbar m_i |s_1, s_2, m_1, m_2\rangle.$$

The eigenvalues of H are thus given by

$$H |s_1, s_2, m_1, m_2\rangle = \varepsilon_0 \left(s_1 (s_1 + 1) + s_2 (s_2 + 1) - m_1 - m_2\right) |s_1, s_2, m_1, m_2\rangle.$$

The matrix of H can be given via

$$H = \varepsilon_0 \begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 \\ 0 & \frac{3}{2} & 0 & 0 \\ 0 & 0 & \frac{3}{2} & 0 \\ 0 & 0 & 0 & \frac{5}{2} \end{pmatrix}.$$

The eigenvalues of H are

$$E_{1/2,1/2} = \frac{\varepsilon_0}{2}; E_{1/2,-1/2} = \frac{3\varepsilon_0}{2}; E_{-1/2,1/2} = \frac{3\varepsilon_0}{2}; E_{-1/2,-1/2} = \frac{5\varepsilon_0}{2}.$$

the energy $E_{1/2,-1/2} = E_{-1/2,1/2} = \frac{3\varepsilon_0}{2}$is twofold degenerate, since it corresponds to two different states.

Exercise 2

Consider two nonidentical spin s=1/2 particles with Hamiltonian

$$H = \frac{\varepsilon_0}{\hbar^2}\left(\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2\right)^2 - \frac{\varepsilon_0}{\hbar^2}\left(\hat{S}_{1_z} + \hat{S}_{2_z}\right)^2,$$

where ε_0 is a constant. Find the energy levels and their degeneracies

Solution

We introduce the total angular momentum of the system, $\hat{\mathbf{S}}$, which is defined by

$$\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2,$$

and

$$\hat{S}_z = \hat{S}_{1_z} + \hat{S}_{2_z}.$$

The square of the total angular momentum operator, $\hat{\mathbf{S}}^2$, commutes with $\hat{\mathbf{S}}_i$,

$$\left[\hat{\mathbf{S}}^2, \hat{\mathbf{S}}_1^2\right] = \left[\hat{\mathbf{S}}^2, \hat{\mathbf{S}}_2^2\right] = 0,$$

In addition $\hat{S}_z$ commutes with $\hat{\mathbf{S}}^2$

$$\left[\hat{\mathbf{S}}^2, \hat{S}_z\right] = 0$$

Therefore, the four operators $\hat{\mathbf{S}}^2, \hat{\mathbf{S}}_1^2, \hat{\mathbf{S}}_2^2$ and $\hat{S}_z$ can be diagonalized simultaneously by the same states,

$$\hat{\mathbf{S}}^2 |S,M\rangle = \hbar^2 S(S+1) |S,M\rangle ,$$

$$\hat{S}_z |S,M\rangle = \hbar M |S,M\rangle .$$

The allowed values of the total spin angular momentum of two particles are

$$0 \leq S \leq 1$$

and for a given S, the possible values of M are as follows:

$$-S \leq M \leq S$$

So, we may write H as

$$H = \frac{\varepsilon_0}{\hbar^2}\left(\hat{\mathbf{S}}^2 - \hat{S}_z^2\right).$$

The eigenvalues of H are thus given by

$$H\,|S,M\rangle = \varepsilon_0\left(S(S+1) - M^2\right)|S,M\rangle\,.$$

The matrix of H can be given via

$$H = \varepsilon_0 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

The eigenvalues of H are

$$E_{1,-1} = \varepsilon_0; E_{1,0} = 2\varepsilon_0; E_{1,1} = \varepsilon_0; E_{0,0} = 0.$$

the energy $E_{1,-1} = E_{1,1} = \varepsilon_0$ is twofold degenerate, since it corresponds to two different states.

Exercise 3

This problem demonstrates the Zeeman effect for a one-electron atom with the valency electron in a state with $\ell = 1$. The Hamiltonian for the system consists of the coupling of orbital and spin angular momenta and magnetic terms,

$$H = \frac{2W}{\hbar^2}\hat{\mathbf{L}}\cdot\hat{\mathbf{S}} + \frac{\mu_B B}{\hbar}\left(\hat{L}_z + 2\hat{S}_z\right).$$

Denote the 3-eigenfunction of $\hat{L}_z$ by m_1, m_0, m_{-1}, the eigenfunction of $\hat{S}_z$ by α and β and the product eigenfunction by

$$\begin{aligned} \chi_1 &= \alpha m_1, \chi_3 = \alpha m_0, \chi_5 = \alpha m_{-1}, \\ \chi_2 &= \beta m_1, \chi_4 = \beta m_0, \chi_6 = \beta m_{-1}, \end{aligned}$$

Show the following

$$\hat{\mathbf{L}}\cdot\hat{\mathbf{S}} = \frac{\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+}{2} + \hat{L}_z\hat{S}_z.$$

2

$$\begin{aligned}
H\chi_1 &= c_{11}\chi_1; \qquad H\chi_6 = c_{66}\chi_6,\\
H\chi_2 &= c_{22}\chi_2; \qquad H\chi_3 = c_{32}\chi_2 + c_{33}\chi_3,\\
H\chi_4 &= c_{44}\chi_4 + c_{45}\chi_5; \qquad H\chi_5 = c_{54}\chi_4 + c_{55}\chi_5,
\end{aligned}$$

where

$$\begin{aligned}
c_{11} &= 2\varepsilon + W; \quad c_{22} = c_{55} = -W,\\
c_{66} &= -2\varepsilon + W; \quad c_{33} = -c_{44} = \varepsilon,\\
23c &= c_{32} = c_{45} = c_{54} = \sqrt{2}W; \quad \varepsilon = \mu_B B
\end{aligned}$$

3 The eigenvalues E of the Hamiltonian have the values

$$W \pm \varepsilon; \quad \frac{1}{2}\left[(\varepsilon - W) \pm \sqrt{(\varepsilon + W)^2 + 2W^2}\right]; \quad \frac{1}{2}\left[-(\varepsilon + W) \pm \sqrt{(\varepsilon - W)^2 + 2W^2}\right].$$

Solution

1

$$\begin{aligned}
\hat{\mathbf{L}}\cdot\hat{\mathbf{S}} &= \hat{L}_x\hat{S}_x + \hat{L}_y\hat{S}_y + \hat{L}_z\hat{S}_z,\\
\hat{\mathbf{L}}\cdot\hat{\mathbf{S}} &= \frac{\left(\hat{L}_+ + \hat{L}_-\right)\left(\hat{S}_+ + \hat{S}_-\right)}{4} - \frac{\left(\hat{L}_+ - \hat{L}_-\right)\left(\hat{S}_+ - \hat{S}_-\right)}{4} + \hat{L}_z\hat{S}_z,\\
&= \frac{\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+}{2} + \hat{L}_z\hat{S}_z.
\end{aligned}$$

So, the Hamiltonian is

$$H = \frac{\mu_B B}{\hbar}\left(\hat{L}_z + 2\hat{S}_z\right) + \frac{W}{\hbar^2}\left(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+\right) + \frac{2W}{\hbar^2}\hat{L}_z\hat{S}_z.$$

For $\hat{L}_z$, and $\hat{S}_z$ we have

$$\hat{L}_z m_1 = \hbar m_1; \hat{L}_z m_0 = 0 m_1; \hat{L}_z m_{-1} = -\hbar m_{-1},$$

$$\hat{S}_z \alpha = \frac{\hbar}{2}\alpha; \hat{S}_z \beta = -\frac{\hbar}{2}\beta.$$

To obtain $H\chi_1$, we calculate the result of each term in H

$$\frac{1}{\hbar}\left(\hat{L}_z + 2\hat{S}_z\right)\chi_1 = \frac{1}{\hbar}\left(\hat{L}_z + 2\hat{S}_z\right) m_1 \alpha = 2 m_1 \alpha = \chi_1,$$

$$\frac{1}{\hbar^2}\hat{L}_z\hat{S}_z\chi_1 = \frac{1}{2}\chi_1,$$

$$\hat{L}_+\hat{S}_-\chi_1 = \hat{L}_-\hat{S}_+\chi_1 = 0,$$

$$H\chi_1 = \left(2\mu_B B + W\right)\chi_1.$$

For χ_2, we have

$$\begin{aligned} H\chi_2 &= \left[\frac{\mu_B B}{\hbar}\left(\hat{L}_z + 2\hat{S}_z\right) + \frac{2W}{\hbar^2}\hat{L}_z\hat{S}_z + \frac{W}{\hbar^2}\left(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+\right)\right]\beta m_1 \\ &= \left[\frac{\mu_B B}{\hbar}\left(\hat{L}_z + 2\hat{S}_z\right)\beta m_1 + \frac{2W}{\hbar^2}\hat{L}_z\hat{S}_z\beta m_1 + \frac{W}{\hbar^2}\left(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+\right)\beta m_1\right] \\ &= c_{22}\chi_2 + c_{23}\chi_3. \end{aligned}$$

The matrix of the operator H on the basis of the χ_i is

$$H = \begin{pmatrix} 2\varepsilon + W & 0 & 0 & 0 & 0 & 0 \\ 0 & -W & \sqrt{2}W & 0 & 0 & 0 \\ 0 & \sqrt{2}W & \varepsilon & 0 & 0 & 0 \\ 0 & 0 & 0 & -\varepsilon & \sqrt{2}W & 0 \\ 0 & 0 & 0 & \sqrt{2}W & -W & 0 \\ 0 & 0 & 0 & 0 & 0 & -2\varepsilon + W \end{pmatrix}.$$

The eigenvalues E of the Hamiltonian are

$$\frac{1}{2}(\varepsilon - W) \pm \frac{1}{2}\sqrt{\varepsilon^2 + 2\varepsilon W + 9W^2},$$

$$W \pm 2\varepsilon,$$

$$-(\varepsilon+W)\pm\frac{1}{2}\sqrt{\varepsilon^2-2\varepsilon W+9W^2}.$$

Exercise 4

Consider a hydrogen atom in the $1s$ state. Denote the z component of the Pauli spin operator for the electron by σ_{e_z} and its eigenstates by α_e and β_e, with corresponding notation for the proton nucleus. The Hamiltonian for the system is given by

$$H = B\left(\mu_e\sigma_{e_z}+\mu_p\sigma_{p_z}\right)+W\sigma_e\cdot\sigma_p,$$

For $B=0$, Show that the eigenstates of H are $\alpha\alpha$, $\beta\beta$, $(\alpha\beta+\beta\alpha)/\sqrt{2}$, with energy W, and$(\alpha\beta-\beta\alpha)/\sqrt{2}, -3W$. (The first α and β in each product refers to the electron and the second to the proton.)

Solution

When $B=0$, $H=W\sigma_e\cdot\sigma_p$. Then

$$\begin{aligned}\sigma_e\cdot\sigma_p\alpha\alpha &= \left(\sigma_{e_x}\sigma_{p_x}+\sigma_{e_y}\sigma_{p_y}+\sigma_{e_z}\sigma_{p_z}\right)\alpha\alpha,\\ &= \beta\beta-\beta\beta+\alpha\alpha=\alpha\alpha.\end{aligned}$$

$$\begin{aligned}\sigma_e\cdot\sigma_p\alpha\beta &= \left(\sigma_{e_x}\sigma_{p_x}+\sigma_{e_y}\sigma_{p_y}+\sigma_{e_z}\sigma_{p_z}\right)\alpha\beta,\\ &= (2\beta\alpha-\alpha\beta).\end{aligned}$$

$$\begin{aligned}\sigma_e\cdot\sigma_p\beta\alpha &= \left(\sigma_{e_x}\sigma_{p_x}+\sigma_{e_y}\sigma_{p_y}+\sigma_{e_z}\sigma_{p_z}\right)\beta\alpha,\\ &= 2\beta\alpha-\beta\alpha.\end{aligned}$$

Hence

$$\begin{aligned}\sigma_e\cdot\sigma_p(\alpha\beta+\beta\alpha) &= \alpha\beta+\beta\alpha,\\ \sigma_e\cdot\sigma_p(\alpha\beta-\beta\alpha) &= -3(\alpha\beta-\beta\alpha).\end{aligned}$$

The states $\alpha\alpha,(\alpha\beta+\beta\alpha)/\sqrt{2},\beta\beta$ are normalised eigenfunction of H with eigenvalue W, and the state $(\alpha\beta-\beta\alpha)/\sqrt{2}$ is a normalised eigenfunction with eigenvalue

$-3W$.

Exercise 5

Consider a set of 3-operators T_m, $m = 0, 1, -1$ such that

$$T_m^+ = (-1)^m T_m,$$

$$\left[\hat{J}_\pm, T_m\right] = \hbar\sqrt{2 - m(m \pm 1)}\, T_{m\pm 1},$$

$$\left[\hat{J}_z, T_m\right] = \hbar m T_m,$$

where $\hat{\mathbf{J}}$ are the total angular momentum operators. Evaluate the m', m" dependence of the matrix elements $\langle j, m' | T_m | j, m" \rangle$.

Express in terms of 3×3 matrices.

Solution

We begin by taking

$$T_0 = \begin{pmatrix} \alpha & \beta & \gamma \\ \delta & \varepsilon & \varepsilon \\ \mu & \nu & \kappa \end{pmatrix}.$$

Then using

$$\left[\hat{J}_z, T_0\right] = 0,$$

$$\begin{aligned} \hat{J}_z T_0 &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \alpha & \beta & \gamma \\ \delta & \varepsilon & \varepsilon \\ \mu & \nu & \kappa \end{pmatrix} = \begin{pmatrix} -\alpha & -\beta & -\gamma \\ 0 & 0 & 0 \\ \mu & \nu & \kappa \end{pmatrix}, \\ T_0 \hat{J}_z &= \begin{pmatrix} \alpha & \beta & \gamma \\ \delta & \varepsilon & \varepsilon \\ \mu & \nu & \kappa \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -\alpha & 0 & \gamma \\ -\delta & 0 & \varepsilon \\ -\mu & 0 & \kappa \end{pmatrix}, \end{aligned}$$

$$\left[\hat{J}_z, T_0\right] = \begin{pmatrix} 0 & -\beta & -2\gamma \\ \delta & 0 & -\varepsilon \\ 2\mu & \nu & 0 \end{pmatrix} = 0$$

we find

$$\beta = \gamma = \varepsilon = \delta = \mu = \nu = 0,$$

$$T_0 = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \varepsilon & 0 \\ 0 & 0 & \kappa \end{pmatrix}.$$

Next, we use

$$\left[\hat{J}_+, T_0\right] = \hbar\sqrt{2}T_1,$$

we find

$$T_1 = \begin{pmatrix} 0 & \varepsilon - \alpha & 0 \\ 0 & \varepsilon & \kappa - \varepsilon \\ 0 & 0 & 0 \end{pmatrix}.$$

Similarly, we use

$$\left[\hat{J}_-, T_0\right] = \hbar\sqrt{2}T_{-1},$$

we find

$$T_{-1} = \begin{pmatrix} 0 & 0 & 0 \\ \alpha - \varepsilon & \varepsilon & 0 \\ 0 & \varepsilon - \kappa & 0 \end{pmatrix}.$$

The condition $T_m^+ = (-1)^m T_m$ show that the 3-numbers $\alpha, \varepsilon, \kappa$ are real. Furthermore, if we use

$$\left[\hat{J}_+, T_{+1}\right] = \left[\hat{J}_-, T_{-1}\right] = 0,$$

we find

$$\alpha - 2\varepsilon + \kappa = 0 \Longrightarrow \varepsilon = \frac{\alpha + \kappa}{2}.$$

Therefore

$$T_+ = \frac{\kappa - \alpha}{2\sqrt{2}\hbar}\hat{J}_+,$$

$$T_- = -\frac{\kappa - \alpha}{2\sqrt{2}\hbar}\hat{J}_-,$$

$$T_0 = -\frac{\kappa - \alpha}{2\hbar}\hat{J}_+ - \frac{\kappa + \alpha}{2}.$$

Chapter 3

Central Potentials

3.1 General Treatment

In this chapter, we examine the structure of the three-dimensional Schrödinger equation for a particle of mass μ which moves under the effect of a spherically symmetric potential, $V(\hat{\mathbf{r}}) = V(\hat{r})$. The dynamics of the system is encoded in the solutions of the time-independent Schrodinger equation:

$$\left[\frac{\hat{\mathbf{p}}^2}{2\mu} + V(\hat{r})\right] \psi(\hat{\mathbf{r}}) = E\psi(\hat{\mathbf{r}}), \tag{3.1}$$

or

$$\left[\frac{-\hbar^2}{2\mu}\Delta + V(\hat{r})\right] \psi(\hat{\mathbf{r}}) = E\psi(\hat{\mathbf{r}}). \tag{3.2}$$

Since central potentials are spherically symmetric, using spherical coordinates is more appropriate. For the transformation between the cartesian and spherical coordinates, the usual definition

$$x = r\sin\theta\cos\varphi; \quad y = r\sin\theta\sin\varphi; \quad y = r\cos\theta. \tag{3.3}$$

can be used. In spherical coordinate systems, a three-dimensional volume element reads:

$$dV = r^2 dr \sin\theta d\theta d\varphi, \tag{3.4}$$

and therefore, the normalization integral for the wave function takes the form of

$$\int_0^{+\infty} dr \int_0^{\pi} d\theta \int_0^{2\pi} d\varphi r^2 \sin\theta \left|\psi(r,\theta,\varphi)\right|^2 = 1. \tag{3.5}$$

The Laplacian operator, Δ, can be separated into radial and angular components in the following manner

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right], \tag{3.6}$$

or alternatively as follows

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\hat{\mathbf{L}}^2}{r^2\hbar^2}, \tag{3.7}$$

where $\hat{\mathbf{L}}^2$ is the square of the orbital angular momentum. If we employ equation (3.7) in (3.2), we obtain the folowing equation

$$H\psi(\hat{\mathbf{r}}) = E\psi(\hat{\mathbf{r}}), \tag{3.8}$$

where

$$H = -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{\mathbf{L}}^2}{2\mu r^2} + V(\hat{r}). \tag{3.9}$$

It is worth noting that the Hamiltonian operator commutes with the square of the orbital angular operator $\hat{\mathbf{L}}^2$.

$$\left[H, \hat{\mathbf{L}}^2\right] = 0. \tag{3.10}$$

Moreover, it commutes with each angular momentum operator $\hat{L}_i$,

$$\left[H, \hat{L}_i\right] = 0. \tag{3.11}$$

Therefore, a common basis set of eigenfunctions for the operators H, $\hat{\mathbf{L}}^2$, $\hat{L}_z$ should exist. To obtain that solution, we focus on equation (3.9) which admits the decomposition of the wave function into radial and angular components

$$\psi(\hat{\mathbf{r}}) = R_{n,\ell}(r)\,\mathcal{Y}_{\ell,m}(\theta,\varphi). \tag{3.12}$$

Recalling

$$\hat{\mathbf{L}}^2 \mathcal{Y}_{\ell,m}(\theta,\varphi) = \hbar^2 \ell(\ell+1)\, \mathcal{Y}_{\ell,m}(\theta,\varphi), \tag{3.13}$$

we substitute equations (3.12) and (3.13) into equation (3.9). We get

$$\left[-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + V(r) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}\right] R_{n,\ell}(r) = E_{n,\ell} R_{n,\ell}(r). \tag{3.14}$$

The latter equation depends on radial coordinates and it does not stand with the same form of one-dimensional Schrödinger equation. However, with the following transformation

$$R_{n,\ell}(r) = \frac{U_{n,\ell}(r)}{r}. \tag{3.15}$$

equation (3.14) takes the same form with the Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \mathcal{V}_{eff}(r)\right] U_{n,\ell}(r) = E_{n,\ell} U_{n,\ell}(r), \tag{3.16}$$

with an effective potential definition

$$\mathcal{V}_{eff}(r) = V(r) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}. \tag{3.17}$$

Here, the term $\frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}$ is called the centrifugal force potential. It is worth noting that the energy eigenvalues of the system, $E_{n,\ell}$, do not rely upon the azimuthal quantum number, m. Consequently, the energy eigenvalues $E_{n,\ell}$ is just $(2\ell+1)$-fold degenerate.

3.2 Normalization conditions

As mentioned in the previous section (3.1), the solutions of the Schrödinger equation can be constructed in the following way:

$$\psi(\mathbf{r}) = \frac{U_{n,\ell}(r)}{r} \mathcal{Y}_{\ell,m}(\theta,\varphi). \tag{3.18}$$

Then, the radial wave function $U_{n,\ell}(r)$ has to satisfy the following equation

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V(r) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}\right] U_{n,\ell}(r) = E_{n,\ell} U_{n,\ell}(r). \tag{3.19}$$

On the other hand, the eigenfunctions must be normalizable. Given that the spherical harmonics are normalized to unity, the eigenfunctions corresponding to discrete eigenvalues need to satisfy the following condition:

$$\int d\mathbf{r}\,|\psi(\mathbf{r})|^2 = \int_0^{+\infty} dr\,\left|U_{n,\ell}(r)\right|^2 = 1. \tag{3.20}$$

If E lies in the continuous part of the spectrum, then the eigenfunctions should satisfy the following condition:

$$\int d\mathbf{r}\,|\psi(\mathbf{r})|^2 = \int_0^{+\infty} dr U^*_{E'}(r)\,U_E(r) = \delta\left(E-E'\right). \tag{3.21}$$

3.3 Free Particle

3.3.1 Radial equation

In this case, $V(r)=0$, and the spectrum energy varies continuously ($E \geq 0$). The free particle can be considered as a particular case of central potentials since the effective potential is not equal to zero. As demonstrated in section (3.1), the wave function can be separated into the radial and angular components as $\psi(\hat{\mathbf{r}}) = R_{n,\ell}(r)\,\mathcal{Y}_{\ell,m}(\theta,\varphi)$. The radial equation of a free particle reads

$$\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) - \frac{\ell(\ell+1)}{r^2} + k^2\right] R_{k,\ell}(r) = 0, \tag{3.22}$$

in spherical coordinates, or

$$\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} + k^2\right] \psi(\mathbf{r}) = 0, \tag{3.23}$$

in Cartesian coordinates. Here, $k^2 = \frac{2\mu E}{\hbar^2}$. One can easily verify that the de Broglie wave function. $\psi = e^{i\vec{k}\cdot\vec{r}}$, is a specific solution of the latter equation.

Now, let us introduce the dimensionless variable $\rho = kr$. Then, equation (3.22) takes the form

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} + 1 - \frac{\ell(\ell+1)}{\rho^2}\right] R_{k,\ell}(\rho) = 0. \tag{3.24}$$

This differential equation is Bessel's differential equation and its solutions are the

Bessel functions,

$$R_{k,\ell}(\rho) = A_\ell \overbrace{\underbrace{j_\ell(\rho)}}^{\text{regular at the origin}} + B_\ell \overbrace{\underbrace{n_\ell(\rho)}}^{\text{diverge at the origin}}, \tag{3.25}$$

where

$$j_\ell(\rho) = (-\rho)^\ell \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^\ell \frac{\sin\rho}{\rho}, \tag{3.26}$$

is the spherical Bessel function, and

$$n_\ell(\rho) = (-\rho)^\ell \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^\ell \frac{\cos\rho}{\rho}, \tag{3.27}$$

is the spherical Neumann function. The Neumann functions, $n_\ell(\rho)$, exhibit divergence at the origin. So they are not suitable solutions for this problem. Consequently, only the spherical Bessel functions, $j_\ell(\rho)$, constitute the eigenfunctions of the free particle

$$\psi(\hat{\mathbf{r}}) = \ j_\ell(\rho)\, \mathcal{Y}_{\ell,m}(\theta,\varphi). \tag{3.28}$$

Now, let us examine some specific cases, starting with the spherical states for which $\ell = 0$. In this case, we have

$$j_0(\rho) = \frac{\sin\rho}{\rho}, \quad \text{and} \ \lim_{\rho\longrightarrow 0} j_0(\rho) = 1, \tag{3.29}$$

Therefore,

$$R_{k,0}(\rho) = A_0 \frac{\sin\rho}{\rho} \overset{\rho\to 0}{\longrightarrow} A_0 \neq 0. \tag{3.30}$$

For $\ell = 0$, the probability density at the origin is non-zero $\left|R_{k,\ell}(\rho)\right|^2$. This is due to the absence of the centrifugal barrier for $\ell = 0$.

Finally, let us consider the case where $\ell >> 1$. In this situation, we have

$$j_\ell(\rho) \simeq \rho^\ell \overset{r\to 0}{\longrightarrow} 0,$$

$$R_{k,0}(\rho) = \rho^\ell \overset{r\to 0}{\longrightarrow} 0. \tag{3.31}$$

which shows that the wave function tends to zero.

3.3.2 Plane waves and spherical waves

The eigenfunction of a free particle in spherical coordinates stands

$$\psi_{k,\ell,m}(\overrightarrow{r}) = \; j_\ell(kr)\,\mathcal{Y}_{\ell,m}(\theta,\varphi)\,. \tag{3.32}$$

This function is the spherical plane wave

$$e^{i\overrightarrow{k}\cdot\overrightarrow{r}} = \sum_{\ell,m} a_{\ell,m} j_\ell(kr)\,\mathcal{Y}_{\ell,m}(\theta,\varphi)\,. \tag{3.33}$$

So, the problem is to find the expansion of the coefficients $a_{\ell,m}$.

We can always select the z-axis of our problem to lie along $\overrightarrow{k}$,

$$\overrightarrow{k}\cdot\overrightarrow{r} = kr\cos\theta, \quad \text{and } m = 0, \tag{3.34}$$

$$e^{ikr\cos\theta} = \sum_\ell \sqrt{\frac{2\ell+1}{4\pi}}\; a_\ell j_\ell(kr)\,P_\ell(\cos\theta)\,. \tag{3.35}$$

Here, we've utilized the relationship between $\mathcal{Y}_{\ell,0}(\theta,\varphi)$ and the Legendre polynomial, $P_\ell(\cos\theta)$. To determine the coefficient a_ℓ, we use the orthogonality relation of the Legendre polynomials, which is given by

$$\int P_\ell(\cos\theta)\,P_{\ell'}(\cos\theta)\,d\cos\theta = \frac{2}{2\ell+1}\delta_{\ell,\ell'}. \tag{3.36}$$

By multiplying both sides of equation (3.35) by $P_{\ell'}(\cos\theta)$, and subsequently integrating over θ using equation (3.36), we arrive at

$$\int_{-1}^{+1} e^{ikr\cos\theta} P_{\ell'}(\cos\theta)\,d\cos\theta = \frac{1}{\sqrt{\pi(2\ell+1)}}\; a_\ell j_\ell(kr)\,. \tag{3.37}$$

There exist various methods to derive a_ℓ. One approach involves a direct calculation of the integral on the right-hand side as outlined in (I. S. Gradshteyn: Table of Integrals, Series, and Products). The outcome is reiterated here:

$$\int_{-1}^{+1} e^{ikr\cos\theta} P_{\ell'}(\cos\theta)\,d\cos\theta = 2i^\ell j_\ell(kr)\,. \tag{3.38}$$

Comparing equations (3.37) and (3.38), we find

$$a_\ell = i^\ell \sqrt{4\pi\,(2\ell+1)}. \tag{3.39}$$

When we substitute equation (3.39) back into equation (3.35), we obtain

$$e^{ikr\cos\theta} = \sum_\ell i^\ell\,(2\ell+1)\,j_\ell\,(kr)\,P_\ell\,(\cos\theta)\,. \tag{3.40}$$

3.4 3-dimensional Square Well Potential

Now, let us examine another problem: a particle with a mass μ in a square well potential. Here, we consider the potential energy in the form of

$$V\,(r) = \begin{cases} -V_0, & r < a \\ 0, & r > a \end{cases}\,. \tag{3.41}$$

By substituting equation (3.41) into equation (3.14), we get

$$\left[-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\hbar^2\ell\,(\ell+1)}{2\mu r^2}\right] R_{n,\ell}\,(r) = (E+V_0)\,R_{n,\ell}\,(r)\,, \quad \text{for } 0 \le r < a, \tag{3.42}$$

and

$$\left[-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\hbar^2\ell\,(\ell+1)}{2\mu r^2}\right] R_{n,\ell}\,(r) = E R_{n,\ell}\,(r)\,, \quad \text{for } r > a. \tag{3.43}$$

For the bound state solutions, $-V_0 \le E \le 0$, first we perform a change of variable $\rho = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}\,r = \kappa r$. Then, equation (3.42) becomes

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} + 1 - \frac{\ell\,(\ell+1)}{\rho^2}\right] R_\ell\,(\rho) = 0, \quad \text{for } 0 \le r < a. \tag{3.44}$$

This differential equation is commonly known as the Bessel differential equation, it has a solution in terms of the Bessel functions,

$$R_{\kappa,\ell}\,(\kappa r) = C_\ell\;\, j_\ell\,(\rho) = C_\ell\;\, j_\ell\left(\sqrt{\frac{2m\,(E+V_0)}{\hbar^2}}\,r\right), \quad \text{for } 0 \le r < a. \tag{3.45}$$

where C_ℓ stands for the normalization constant. For the solution outside the well, $r > a$, we define

$$k_1 = i\sqrt{-\frac{2\mu E}{\hbar^2}}. \tag{3.46}$$

Then, the solutions outside the well potential will be expressed by the linear combinations of $j_\ell(ik_1 r)$ and $n_\ell(ik_1 r)$:

$$R_{\kappa,\ell}(r) = B_\ell \; h_\ell^{(1)}(ik_1 r) = B_\ell \; [j_\ell(k_1 r) + i n_\ell(k_1 r)], \qquad \text{for } r > a. \tag{3.47}$$

By using the fact that the radial wave function and its derivative must exhibit continuity at the point of potential discontinuity "$r = a$", we write

$$C_\ell \; j_\ell\left(\sqrt{\frac{2m(E+V_0)}{\hbar^2}}a\right) = B_\ell \; h_\ell(ik_1 a), \tag{3.48}$$

and,

$$\sqrt{\frac{2mV_0}{\hbar^2 k_1^2} - 1} C_\ell \; j'_\ell\left(\sqrt{\frac{2mV_0}{\hbar^2} - k_1^2}a\right) = B_\ell \; h_\ell^{(1)\prime}(ik_1 a). \tag{3.49}$$

These conditions yield an equation for the allowed discrete energy eigenvalues of the form

$$\frac{h_\ell^{(1)\prime}(ik_1 a)}{h_\ell^{(1)}(ik_1 a)} = \sqrt{\frac{2mV_0}{\hbar^2 k_1^2} - 1}\frac{j'_\ell\left(\sqrt{\frac{2mV_0}{k_1^2\hbar^2} - 1}k_1 a\right)}{j_\ell\left(\sqrt{\frac{2mV_0}{k_1^2\hbar^2} - 1}k_1 a\right)}. \tag{3.50}$$

3.5 Harmonic Oscillator

3.5.1 Anisotropic three-dimensional harmonic oscillator

Let us consider a scenario where a particle is moving in a three-dimensional anisotropic oscillator potential defined by

$$V(x,y,z) = \frac{\mu}{2}\omega_1^2 x^2 + \frac{\mu}{2}\omega_2^2 y^2 + \frac{\mu}{2}\omega_3^2 z^2, \tag{3.51}$$

In fact, this potential form allows us to consider it as the sum of three separate equations where the first, second, and third equations only depend on x, y, and z, respectively. Therefore, we can write the Schrödinger equation by utilizing variable

separation for x, y and z

$$H\psi = [H_x + H_y + H_z]\,\psi(x,y,z) = E\psi(x,y,z)\,, \tag{3.52}$$

where the Hamilton operator components stand for

$$\begin{cases} H_x = \frac{p_x^2}{2\mu} + \frac{\mu}{2}\omega_1^2 x^2 \\ H_y = \frac{p_y^2}{2\mu} + \frac{\mu}{2}\omega_2^2 y^2 \\ H_z = \frac{p_z^2}{2\mu} + \frac{\mu}{2}\omega_3^2 z^2 \end{cases} . \tag{3.53}$$

Because of the symmetry, we can consider the wave function, $\psi(x,y,z)$, as the product of three functions that depend on a single variable each

$$\psi(x,y,z) = \Phi(x)\,F(y)\,\Psi(z)\,. \tag{3.54}$$

By inserting equation (3.54) into equation (3.52), and then, dividing by the product $\Phi(x)F(y)\Psi(z)$, we arrive at the following expression:

$$\left[\frac{1}{\Phi}\frac{p_x^2}{2\mu}\Phi + \frac{\mu}{2}\omega_1^2 x^2\right] + \left[\frac{1}{F}\frac{p_x^2}{2\mu}F + \frac{\mu}{2}\omega_2^2 y^2\right] + \left[\frac{1}{\Psi}\frac{p_x^2}{2\mu}\Psi + \frac{\mu}{2}\omega_3^2 z^2\right] = E. \tag{3.55}$$

Here, we observe that each individual equation in the square brackets depends on one of the variables, and their sum is equal to a constant denoted with E. This shows us that each of these distinct equations can be taken as a constant, where their sum matches the value of E. In this case, the equations that depends on the x, y, and z-variables read:

$$\left[\frac{p_x^2}{2\mu} + \frac{\mu}{2}\omega_1^2 x^2\right]\Phi = \varepsilon_x\Phi. \tag{3.56}$$

$$\left[\frac{p_y^2}{2\mu} + \frac{\mu}{2}\omega_1^2 y^2\right]F = \varepsilon_y F, \tag{3.57}$$

$$\left[\frac{p_z^2}{2\mu} + \frac{\mu}{2}\omega_1^2 z^2\right]\Psi = \varepsilon_z\Psi, \tag{3.58}$$

where

$$\varepsilon_x + \varepsilon_y + \varepsilon_z = E. \tag{3.59}$$

We know that the energy eigenvalues corresponding to the potential $V(x) = \frac{m}{2}\omega_1^2 x^2$ can be expressed as

$$\varepsilon_x = \hbar\omega_1\left(n_x + \frac{1}{2}\right), \quad \text{with } n_x = 0,1,2,..., \tag{3.60}$$

with the corresponding wave function

$$\Phi_{n_x} = \frac{1}{\sqrt{\sqrt{\pi}2^{n_x}n_x!\sqrt{\hbar/\mu\omega_1}}} e^{-\frac{m\omega_1}{2\hbar}x^2} H_{n_x}\left(\sqrt{\hbar/\mu\omega_1}x\right). \tag{3.61}$$

where $H_{n_x}\left(\sqrt{\hbar/m\omega_1}x\right)$ denotes the Hermite polynomials. Taking into account the other two components, the total eigenvalue

$$E = \hbar\omega_1\left(n_x + \frac{1}{2}\right) + \hbar\omega_2\left(n_y + \frac{1}{2}\right) + \hbar\omega_3\left(n_z + \frac{1}{2}\right), \tag{3.62}$$

and wave functions read:

$$\begin{aligned}\psi_{n_x n_y n_z}(x,y,z) &= \frac{1}{\sqrt{\sqrt{\pi}2^{n_x}n_x!\sqrt{\hbar/\mu\omega_1}}} e^{-\frac{m\omega_1}{2\hbar}x^2} H_{n_x}\left(\sqrt{\hbar/\mu\omega_1}x\right) \\ &\times \frac{1}{\sqrt{\sqrt{\pi}2^{n_y}n_y!\sqrt{\hbar/\mu\omega_2}}} e^{-\frac{m\omega_2}{2\hbar}y^2} H_{n_y}\left(\sqrt{\hbar/\mu\omega_2}y\right) \\ &\times \frac{1}{\sqrt{\sqrt{\pi}2^{n_z}n_z!\sqrt{\hbar/\mu\omega_3}}} e^{-\frac{m\omega_3}{2\hbar}z^2} H_{n_z}\left(\sqrt{\hbar/\mu\omega_3}z\right),\end{aligned} \tag{3.63}$$

for $n_x, n_y, n_z = 0,1,2,...$

3.5.2 Isotropic three-dimensional harmonic oscillator

Now, let us handle a similar scenario where the particle moves under the influence of a three-dimensional isotropic oscillator potential,

$$V(r) = \frac{m\omega^2}{2}r^2. \tag{3.64}$$

Substituting equation (3.64) into equation (3.19), we get

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}+\frac{\mu\omega^2}{2}r^2+\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\right]U_{n',\ell}(r)=E_{n',\ell}U_{n',\ell}(r), \tag{3.65}$$

which can be rewritten as

$$\left[\frac{d^2}{dr^2}-\frac{\mu^2\omega^2}{\hbar^2}r^2-\frac{\ell(\ell+1)}{r^2}+\frac{2\mu E_{n',\ell}}{\hbar^2}\right]U_{n',\ell}(r)=0. \tag{3.66}$$

First, let us examine the behavior of the solutions at the asymptotic limits. At $r\to 0$, the dominant terms read:

$$\left[\frac{d^2}{dr^2}-\frac{\ell(\ell+1)}{r^2}\right]U_{n',\ell}(r)=0, \tag{3.67}$$

and they admit the following solution

$$U_{n',\ell}(r)\simeq A_\ell r^{\ell+1}+B_\ell r^{-\ell}. \tag{3.68}$$

For the normalization, we have to set $B=0$. Now, let us consider the other asymptotic limit, $r\to\infty$, where equation (3.66) takes the form

$$\left[\frac{d^2}{dr^2}-\frac{\mu^2\omega^2}{\hbar^2}r^2\right]U_{n',\ell}(r)=0. \tag{3.69}$$

In this case, the solution stands for:

$$U_{n',\ell}(r)\simeq e^{-\frac{\mu\omega}{2\hbar}r^2}. \tag{3.70}$$

By combining the asymptotic solutions obtained in equations (3.68) and (3.70), we formulate a general form of solution for equation (3.66) as follows:

$$U(r)=r^{\ell+1}e^{-\frac{\mu\omega}{2\hbar}r^2}\Xi_{n',\ell}(r), \tag{3.71}$$

Substituting the latter equation into (3.66), we obtain an equation that must be satisfied by $\Xi_{n,\ell}(r)$

$$\left[\frac{d^2}{dr^2}+2\left(\frac{\ell+1}{r}-\frac{\mu\omega}{\hbar}r\right)\frac{d}{dr}+\frac{2\mu E_{n',\ell}}{\hbar^2}-(2\ell+3)\frac{\mu\omega}{\hbar}\right]\Xi_{n',\ell}(r)=0. \tag{3.72}$$

Now, we define a dimensionless variable

$$\varkappa = \frac{\mu\omega}{\hbar} r^2, \tag{3.73}$$

which leads the equation to take the following form

$$\left[\varkappa \frac{d^2}{d\varkappa^2} + \left(\ell + \frac{3}{2} - \varkappa\right)\frac{d}{d\varkappa} + \frac{E_{n',\ell}}{2\hbar\omega} - \frac{(2\ell+3)}{4}\right] \Xi_{n',\ell}(\varkappa) = 0. \tag{3.74}$$

We find that this equation is the same equation as that for the associated Laguerre polynomials

$$\left[\varkappa \frac{d^2}{d\varkappa^2} + (\alpha + 1 - \varkappa)\frac{d}{d\varkappa} + n'\right] \Xi_{n',\ell}(\varkappa) = 0, \tag{3.75}$$

which has the following solutions

$$\Xi_{n',\ell}(\varkappa) = L_{n'}^{(\ell+1/2)}(\varkappa), \tag{3.76}$$

where n' is non-negative integer number. The simple match of these equations produces the energy quantization

$$\frac{E_{n',\ell}}{2\hbar\omega} - \frac{(2\ell+3)}{4} = n', \tag{3.77}$$

which can be rewritten as

$$E_{n,\ell} = \hbar\omega\left(n + \frac{3}{2}\right), \quad n = 0, 1, 2, ..., \tag{3.78}$$

where $n = 2n' + \ell$. Here, we observe that the quantum number ℓ is associated with n as follows:

$$\begin{array}{llll} n=0; & n'=0, \ell=0, & & \\ n=1; & n'=0, \ell=1, & & \\ n=2; & n'=0, \ell=2, & \text{or} & n'=1, \ell=0, \\ n=3; & n'=0, \ell=3, & \text{or} & n'=1, \ell=1. \end{array} . \tag{3.79}$$

This shows that the ground state of the isotropic three-dimensional harmonic oscillator, $(n=0; \ell=0)$, has an energy eigenvalue $E_{0,0} = \frac{3\hbar\omega}{2}$, is not degenerate. We note that all energy levels for $n > 1$ are degenerate, and the relationship describing

the degeneracy for the n^{th} energy level can be given as follows:

$$g_n = \frac{(n+1)(n+2)}{2}. \tag{3.80}$$

Before ending this problem. let us to sum up our findings about the radial eigenfunctions of the isotropic three-dimensional harmonic oscillator.

$$U_{n',\ell}(r) = \mathcal{C}_{n',\ell} r^{\ell+1} e^{-\frac{\mu\omega}{2\hbar}r^2} L_{n'}^{\left(\ell+\frac{1}{2}\right)}\left(\frac{\mu\omega}{\hbar}r^2\right), \tag{3.81}$$

where $\mathcal{C}_{n',\ell}$ is the normalization constant, which can be established through the following relation

$$\int_0^{+\infty} e^{-\varkappa}\varkappa^{\alpha} L_n^{\alpha}(\varkappa) L_m^{\alpha}(\varkappa)\, d\varkappa = \frac{(n+\alpha)!}{n!}\delta_{n,m}. \tag{3.82}$$

In this case, the normalization constant reads:

$$\mathcal{C}_{n',\ell} = \left(\frac{\mu\omega}{\hbar}\right)^{\frac{\ell}{2}+1/4} \sqrt{\frac{2n'!}{\left(n'+\ell+\frac{1}{2}\right)!}}. \tag{3.83}$$

Finally, we can write the most general expression of the wave functions of the isotropic three-dimensional harmonic oscillator as follows:

$$\psi_{n',\ell,m}(r,\theta,\varphi) = \left(\frac{\mu\omega}{\hbar}\right)^{\frac{\ell}{2}+1/4} \sqrt{\frac{2n'!}{\left(n'+\ell+\frac{1}{2}\right)!}} r^{\ell} e^{-\frac{\mu\omega}{2\hbar}r^2} L_{n'}^{\left(\ell+\frac{1}{2}\right)}\left(\frac{\mu\omega}{\hbar}r^2\right) \mathcal{Y}_{\ell,m}(\theta,\varphi), \tag{3.84}$$

where

$L_0^0(x) = 1$	$L_0^2(x) = 2$
$L_1^0(x) = -x+1$	$L_1^2(x) = -6x+18$
$L_2^0(x) = x^2-4x+2$	$L_2^2(x) = 12x^2-96x+144$
$L_0^1(x) = 1$	$L_0^3(x) = 6$
$L_1^1(x) = -2x+4$	$L_1^3(x) = -24x+96$
$L_2^1(x) = 2x^2-18x+18$	$L_2^3(x) = 60x^2-600x+1200$

Table 3.1: Some associated Laguerre polynomials.

3.6 Coulomb Potential

In this section, we will examine the radial Schrödinger equation of a single electron moving in a Coulomb potential

$$V(r) = -\frac{Ze^2}{r}, \tag{3.85}$$

Here, $-e$ is the electron charge. We start by substituting the Coulomb potential to equation (3.19).

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} - \frac{Ze^2}{r} + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\right] U_{n',\ell}(r) = E_{n',\ell}U_{n',\ell}(r). \tag{3.86}$$

To achieve our goal, which is to find the solution $U_{n',\ell}(r)$ and to determine the allowed energy levels $E_{n',\ell}$, we first analyze the behavior of the solution at $r \to \infty$,

$$\left[\frac{d^2}{dr^2} + \frac{2\mu E_{n',\ell}}{\hbar^2}\right] U_{n',\ell}(r) = 0, \tag{3.87}$$

that has the general solution as

$$U_{n',\ell}(r) \sim e^{-\frac{\sqrt{-2\mu E_{n',\ell}}}{\hbar}r}. \tag{3.88}$$

On the other hand, for $r \to 0$, equation (3.86) reduces to

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2}\right] U_{n',\ell}(r) = 0, \tag{3.89}$$

and it admits the solution

$$U_{n',\ell}(r) \sim r^{\ell+1}. \tag{3.90}$$

By combining equations (3.88) and (3.90), we represent the solution of equation (3.86) in the following form

$$U_{n',\ell}(r) = r^{\ell+1}e^{-\frac{\sqrt{-2\mu E_{n',\ell}}}{\hbar}r}F_{n',\ell}(r). \tag{3.91}$$

Then, we substitute equation (3.91) into equation (3.86). The radial equation becomes

$$\left[\frac{d^2}{dr^2}+2\left(\frac{\ell+1}{r}-\frac{\sqrt{-2\mu E_{n',\ell}}}{\hbar}\right)\frac{d}{dr}+2\left(\frac{-\frac{\sqrt{-2\mu E_{n',\ell}}}{\hbar}(\ell+1)+\frac{\mu Z e^2}{\hbar^2}}{r}\right)\right]F_{n',\ell}(r)=0. \tag{3.92}$$

Using the change of variables

$$\kappa=2\frac{\sqrt{-2\mu E_{n',\ell}}}{\hbar} \quad \text{and} \quad \rho=\kappa r, \tag{3.93}$$

equation (3.92) reduces to

$$\left[\rho\frac{d^2}{d\,\rho^2}+(2(\ell+1)-\rho)\frac{d}{d\,\rho}+\left(\frac{2\mu Z e^2}{\kappa\hbar^2}-(\ell+1)\right)\right]F_{n',\ell}(r)=0, \tag{3.94}$$

which admits solution in terms of the associated Laguerre polynomials

$$F_{n',\ell}(r)=L_{n+\ell}^{2\ell+1}\left(2\frac{\sqrt{-2\mu E_{n',\ell}}}{\hbar}r\right), \tag{3.95}$$

with

$$n'+(\ell+1)=n=\frac{2\mu Z e^2}{\kappa\hbar^2}. \tag{3.96}$$

With the help of the latter notation, $n=n'+\ell+1$ where n is called the principal quantum number and n' is the radial quantum number, we obtain the energy eigenvalue function in the form of

$$E_{n,\ell}=-\frac{\mu Z^2 e^4}{2\hbar^2 n^2}, \qquad \text{for } n=1,2,3,\cdots. \tag{3.97}$$

For a specific n value, the quantum number ℓ is restricted to a range of values from 0 to $n-1$, and for each ℓ, the quantum number m takes the following values $(2\ell+1)$, where $-\ell\leq m\leq\ell$. We observe that the degeneracy of state n , is given by the total number of different states associated with n, which is then

$$g_n=\sum_{\ell=0}^{n-1}(2\ell+1)=n^2. \tag{3.98}$$

3.7 The Hydrogen Atom

Essentially, the hydrogen atom is the simplest and most fundamental atom in the universe. It consists of two main components: proton and electron. In this case, the potential is not spherically symmetric, however, it depends upon the distance between the proton and the electron.

In non-relativistic quantum mechanics, we represent the Schrödinger equation for hydrogen atom as follows:

$$\left[-\frac{\hbar^2}{2\mu_p}\Delta_p - \frac{\hbar^2}{2\mu_e}\Delta_e + V\left(\left|\mathbf{r}_e - \mathbf{r}_p\right|\right)\right]\psi(\mathbf{r}_e,\mathbf{r}_p) = E\,\psi(\mathbf{r}_e,\mathbf{r}_p)\,. \tag{3.99}$$

Here, the subscripts "p" and "e" denote the proton and electron, respectively, and $V\left(\left|\mathbf{r}_e - \mathbf{r}_p\right|\right)$ corresponds to the Coulomb potential that depends only on the distance between the electron and the proton.
As done in standard textbooks, we introduce the relative coordinate "$\mathbf{r}$" and the center of mass coordinate "$\mathbf{R}$",

$$\mathbf{R} = \frac{\mu_e\mathbf{r}_e + \mu_p\mathbf{r}_p}{\mu_e + \mu_p}; \qquad \mathbf{r} = \mathbf{r}_e - \mathbf{r}_p, \tag{3.100}$$

Using the new variables in equation (3.99), we obtain

$$\left[-\frac{\hbar^2}{2M}\Delta_R - \frac{\hbar^2}{2\mu}\Delta_r + V(r)\right]\psi(\mathbf{R},\mathbf{r}) = E\,\psi(\mathbf{R},\mathbf{r})\,. \tag{3.101}$$

where

$$\mu = \mu_e + \mu_p \quad \text{and} \quad M = \frac{\mu_e\mu_p}{\mu_e + \mu_p}. \tag{3.102}$$

Now, let us seek the solution in the following form

$$\psi(\mathbf{R},\mathbf{r}) = \Phi(\mathbf{R})\Psi(\mathbf{r}) \qquad \text{and} \qquad E = E_R + E_r. \tag{3.103}$$

After we employ equation (3.103) in equation (3.101) and divide both sides with $\Phi(\mathbf{R})\Psi(\mathbf{r})$, we obtain the following set of equations:

$$-\frac{\hbar^2}{2M}\Delta_R\Phi(\mathbf{R}) = E_R\Phi(\mathbf{R})\,, \tag{3.104}$$

$$\left[-\frac{\hbar^2}{2\mu}\Delta_r + V(r)\right]\Psi(\mathbf{r}) = E_r\Psi(\mathbf{r}). \tag{3.105}$$

Here, $\Psi(\mathbf{r})$ describes the motion of a particle influenced by the Coulomb potential "$V(r)$", while $\Phi(\mathbf{R})$ dictates the motion of a free particle with the center of mass system. The solution of equation (3.104) has the form

$$\Phi(\mathbf{R}) = \frac{e^{i\overrightarrow{k}\cdot\overrightarrow{R}}}{(2\pi)}, \tag{3.106}$$

where $\overrightarrow{k}$ is the wave vector associated with the center of mass. The center of mass energy, $E_R = \frac{\hbar^2 k^2}{2M}$ is a constant and does not introduce a physical meaning.

On the other hand, equation (3.105) is the Schrödinger equation of the massive particle of μ that moves in a Coulomb potential which has the following solution already derived in the previous subsection

$$\Psi_{n,\ell,m}(\mathbf{r}) = -\left(\frac{2\mu e^2}{n\hbar^2}\right)^{3/2}\sqrt{\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}}\left(\frac{2\mu e^2 r}{n\hbar^2}\right)^{\ell} e^{-\frac{\mu e^2 r}{n\hbar^2}} L_{n+\ell}^{2\ell+1}\left(\frac{2\mu e^2 r}{n\hbar^2}\right)\mathcal{Y}_{\ell,m}(\theta,\varphi). \tag{3.107}$$

with

$$E_{r,n,\ell} = -\frac{\mu e^4}{2\hbar^2 n^2}, \qquad \text{for } n = 1,2,3,... \tag{3.108}$$

In table 3.2, we provide the first few wave functions $\Psi_{n,\ell,m}(\mathbf{r})$ associated with the particular set of quantum numbers (n,ℓ,m). In conclusion, the hydrogen atom's

n	ℓ	m	wave function
1	0	0	$\frac{1}{\sqrt{\pi}}a^{-3/2}e^{-r/a}$
2	0	0	$\frac{1}{4\sqrt{2\pi}}a^{-3/2}\left(2-\frac{r}{a}\right)e^{-r/2a}$
	1	0	$\frac{1}{4\sqrt{2\pi}}a^{-3/2}\frac{r}{a}\cos\theta e^{-r/2a}$
		1	$\frac{1}{4\sqrt{2\pi}}a^{-3/2}\frac{r}{a}\sin\theta e^{i\varphi}e^{-r/2a}$
		-1	$\frac{1}{4\sqrt{2\pi}}a^{-3/2}\frac{r}{a}\sin\theta e^{-i\varphi}e^{-r/2a}$

Table 3.2: The first few wave functions $\Psi_{n,\ell,m}(\mathbf{r})$ of the hydrogen atom (where $a = \frac{n\hbar^2}{\mu e^2}$).

bound states can be represented by using three subscripts, which correspond to the values of n, ℓ and m. Alternatively, in chemistry, the value of ℓ is denoted with the following letter formalism.

In fact, the letters s, p, d, and f have their origins in spectroscopy, and they

Letter	s	p	d	f	g	...
ℓ	0	1	2	3	4	...

represent the terms sharp, principal, diffuse, and fundamental. Consequently, the ground-state wave function $\Psi_{1,0,0}(\mathbf{r})$ is referred to as $\Psi_{1s}(\mathbf{r})$ or, more straightforwardly, as $1s$.

3.8 Exercises

Exercise 1

An electron is confined to the interior of a hollow spherical cavity of radius R with impenetrable walls. Determine the expression for the pressure exerted on the walls of the cavity by the electron in its ground state.

Solution

For the ground state, $\ell = 0$, and if we set the radial wave function as $U(r) = \frac{1}{r}\chi(r)$, then $\chi(r)$ is given by

$$\left[\frac{d^2}{dr^2} + \frac{2\mu E}{\hbar^2}\right]\chi(r) = 0 \quad \text{for } r < R,$$

$$\chi(r) = 0 \quad \text{for } r \geq R.$$

The solutions of the Schrödinger equation is

$$\chi(r) = Ae^{ikr} + Be^{-ikr}; \quad \text{with } k = \sqrt{\frac{2\mu E}{\hbar^2}}.$$

The continuity conditions of the wave function at $r = 0$ yield

$$\chi(0) = \chi(R) = 0,$$

$$\Longrightarrow A = -B \Longrightarrow \chi(r) = C\sin(kr).$$

the condition $\chi(0) = 0$, gives

$$A = -B \Longrightarrow \chi(r) = C\sin(kr),$$

while $\chi(R) = 0$, gives

$$k_n = \frac{n\pi}{R}; \quad n = 1, 2, 3, ..,$$

for which

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2\mu R^2}.$$

The average force F acting radially on the walls by the electron is given by

$$F = -\frac{\partial}{\partial R} E_n.$$

As the electron is in the ground state, $n = 1$ and

$$F = \frac{\pi^2}{R^3 \mu} \hbar^2.$$

The pressure exerted on the walls is

$$p = \frac{F}{4\pi R^2} = \frac{\pi \hbar^2}{4\mu R^5}.$$

Exercise 2

A particle of mass m is constrained to move between two concentric impermeable spheres of radius $r = a$ and $r = b$. Find the ground state energy and normalized wave function.

Solution

For the ground state, the radial wave function of the particle $U(r) = \frac{1}{r}\chi(r)$ satisfies the equation

$$\left[\frac{d^2}{dr^2} + \frac{2\mu E}{\hbar^2}\right] \chi(r) = 0 \quad \text{for } a \leq r \leq b,$$

the wave function of the particle must be zero outside the boundary. The solutions are

$$\chi(a) = Ae^{ikr} + Be^{-ikr}.$$

The wave function vanishes at $r = a$ and $r = b$,

1: at $r = a$

$$\chi(a) = Ae^{ika} + Be^{-ika} = 0 \rightarrow B = -Ae^{2ika},$$

$$\chi(r) = C \sin[k(r-a)].$$

2: at $r = b$

$$\chi(b) = C \sin[k(b-a)] = 0 \Longrightarrow k_n(b-a) = n\pi.$$

For the particle in the ground state, i.e., $n = 1$, we obtain the energy

$$E = \frac{\hbar^2 \pi^2}{2\mu (b-a)^2}.$$

From the normalization condition

$$\int_a^b |\chi(r)|^2 dr = |C|^2 \int_a^b \sin^2 [k_n (r-a)] = 1.$$

After some algebra we find

$$C = \sqrt{\frac{2}{b-a}}.$$

Exercise 3

a: The actions of the operators $\hat{p}_r$ and $\hat{r}$ on a radial wave function $\phi(r)$ are given by

$$\begin{aligned} \hat{p}_r \phi(r) &= \frac{\hbar}{i} \frac{1}{r} \frac{\partial}{\partial r} r\phi(r), \\ \hat{r}\phi(r) &= r\phi(r). \end{aligned}$$

a: Find the commutator $[\hat{p}_r, \hat{r}]$, and $\Delta p_r \Delta r$.

b: Show that $\hat{p}_r^2 = -\frac{\hbar^2}{r} \frac{\partial^2}{\partial r^2} r$

Solution

a: We have $\hat{r}\phi(r) = r\phi(r)$ and

$$\begin{aligned} [\hat{p}_r, \hat{r}]\phi(r) &= \left[\frac{\hbar}{i} \frac{1}{r} \frac{\partial}{\partial r} r, \hat{r}\right] \phi(r), \\ &= \frac{\hbar}{i} \frac{1}{r} \frac{\partial}{\partial r} r^2 \phi(r) - \frac{\hbar}{i} \frac{\partial}{\partial r} r\phi(r) \\ &= \frac{\hbar}{i} \phi(r). \end{aligned}$$

Using the uncertainty relation for a pair of operators A and B and $\Delta A \Delta B \geq \frac{1}{2} \langle [A, B] \rangle$, we write

$$\Delta p_r \Delta r \geq \frac{1}{2} \langle [\hat{p}_r, \hat{r}] \rangle \geq \frac{\hbar}{2}.$$

b: $\hat{p}_r^2$:

$$\hat{p}_r^2\phi(r) = \hat{p}_r\hat{p}_r\phi(r) = -\hbar^2\frac{1}{r}\frac{\partial^2}{\partial r^2}r\phi(r).$$

Exercise 4

For $n=1,\ell=0,m=0$ and $n=2,\ell=1,m=0$, determine the radius r at which the radial probability density of the hydrogen atom achieves its maximum value.

Solution

1: For $n=1,\ell=0$ the radial wave function is $R_{10}(r) = \frac{2}{a_0^{3/2}}e^{-\frac{r}{a_0}}$. The probability density is given by

$$P_{10} = r^2|R_{10}(r)|^2 = \frac{4r^2}{a_0^3}e^{-\frac{2r}{a_0}},$$

The maximum point $r_{\max}$:

$$\frac{\partial}{\partial r}P_{10} = \frac{8r}{a_0^3}\left(1-\frac{r}{a_0}\right)e^{-\frac{2r}{a_0}} = 0 \Longrightarrow r_{\max} = a_0.$$

2: For $n=2,\ell=1,m=0$ the the radial wave function is $R_{21}(r) = \frac{r}{2\sqrt{6}a_0^{5/2}}e^{-\frac{r}{2a_0}}$. The probability density is given by

$$P_{21} = r^2|R_{21}(r)|^2 = \frac{1}{24a_0^5}r^4e^{-\frac{r}{a_0}},$$

The maximum point $r_{\max}$:

$$\frac{\partial}{\partial r}P_{21} = \frac{r^3}{24a_0^5}\left(4-\frac{r}{a_0}\right)e^{-\frac{r}{a_0}} = 0 \Longrightarrow r_{\max} = 4a_0.$$

Chapter 4

Approximation Methods

4.1 Time-independent Perturbation Theory

4.1.1 Statement of the problem

A quantum system with the time-independent Hamiltonian H_0 is classified as an exactly solvable system if its energy eigenvalues and corresponding eigenstates can be determined analytically. However, there are many problems for which it becomes impossible to solve the Schrödinger equation directly. In such cases, it is necessary to use approximate methods to estimate the solutions.

4.1.2 The Method

Let us express the Hamiltonian of a given system in the following manner:

$$H = H_0 + W, \tag{4.1}$$

where H_0 represents the unperturbed Hamiltonian, which we know the exact energy levels and corresponding eigenstates, and W denotes the perturbing Hamiltonian. Let us show the known exact solution with

$$H_0 \left|\phi_n^{(0)}\right\rangle = E_n^{(0)} \left|\phi_n^{(0)}\right\rangle, \tag{4.2}$$

where $E_n^{(0)}$ corresponds to the unperturbed energies and is assumed to form a discrete spectrum. Here, $\left|\phi_n^{(0)}\right\rangle$ are the unperturbed states associated with these

energy eigenvalues. It is worth emphasizing that the set of vectors $\left|\phi_k^{(0)}\right\rangle$ form a complete and orthonormal basis:

$$\left\langle \phi_{k'}^{(0)} \middle| \phi_k^{(0)} \right\rangle = \delta_{k,k'}, \tag{4.3}$$

$$\sum_k \left|\phi_k^{(0)}\right\rangle \left\langle \phi_k^{(0)}\right| = \mathbf{1}. \tag{4.4}$$

Now, we intend to find the energy levels and eigenstates of the full Hamilton operator.

$$H|\Psi_n\rangle = (H_0 + W)|\Psi_n\rangle = E_n|\Psi_n\rangle. \tag{4.5}$$

For the perturbation, we assume

$$W = \lambda V, \quad \text{where} \quad \lambda << 1 \text{ and } \lambda \in \mathbf{R}. \tag{4.6}$$

Since eigenvectors may or may not be degenerate, we have to examine the formalism in two different scenarios each of which requires a unique approach.

4.1.3 Non-degenerate case

In the perturbation theory the energy, E_n, and the eigenvectors, $|\Psi_n\rangle$, rely on the perturbation parameter, λ, which can be expanded in powers of the perturbation parameter in the following manner:

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots + \lambda^k E_n^{(k)} + \cdots, \tag{4.7}$$

$$|\Psi_n\rangle = \left|\phi_n^{(0)}\right\rangle + \lambda \left|\phi_n^{(1)}\right\rangle + \lambda^2 \left|\phi_n^{(2)}\right\rangle + \cdots + \lambda^k \left|\phi_n^{(k)}\right\rangle + \cdots. \tag{4.8}$$

By substituting these expansions into the eigenvalue equation of H, we get

$$\begin{aligned}(H_0 + \lambda V)|\Psi_n\rangle &= (H_0 + \lambda V)\left(\left|\phi_n^{(0)}\right\rangle + \lambda \left|\phi_n^{(1)}\right\rangle + \ldots + \lambda^k \left|\phi_n^{(k)}\right\rangle + \ldots\right), \\ &= \left(E_n^{(0)} + \lambda E_n^{(1)} + \ldots\right)\left(\left|\phi_n^0\right\rangle + \lambda \left|\phi_n^1\right\rangle + \ldots + \lambda^k \left|\phi_n^{(k)}\right\rangle + \ldots\right). \end{aligned} \tag{4.9}$$

It is worth noting that for $\lambda = 0$ equation (4.9) reduces to the unperturbed eigenvalue problem stated in equation (4.2). Since λ is an arbitrarily small parameter, it's necessary to match the coefficients of successive powers of λ on both sides of the equation (4.9).

- Zeroth term:

$$H_0 \left|\phi_n^{(0)}\right\rangle = E_n^{(0)} \left|\phi_n^{(0)}\right\rangle. \tag{4.10}$$

- First order correction:

$$H_0 \left|\phi_n^{(1)}\right\rangle + V \left|\phi_n^{(0)}\right\rangle = E_n^{(0)} \left|\phi_n^{(1)}\right\rangle + E_n^{(1)} \left|\phi_n^{(0)}\right\rangle. \tag{4.11}$$

- Second order correction:

$$H_0 \left|\phi_n^{(2)}\right\rangle + V \left|\phi_n^{(1)}\right\rangle = E_n^{(0)} \left|\phi_n^{(2)}\right\rangle + E_n^{(1)} \left|\phi_n^{(1)}\right\rangle + E_n^{(2)} \left|\phi_n^{(0)}\right\rangle. \tag{4.12}$$

Zeroth-order correction

The zeroth-order correction term in λ is already verified by the initial assumption.

First-order correction

First, we multiply equation (4.11) with $\left\langle\phi_n^{(0)}\right|$ from the left side

$$\left\langle\phi_n^{(0)}\right| H_0 \left|\phi_n^{(1)}\right\rangle + \left\langle\phi_n^{(0)}\right| V \left|\phi_n^{(0)}\right\rangle = E_n^{(0)} \left\langle\phi_n^{(0)} \middle|\phi_n^{(1)}\right\rangle + E_n^{(1)} \left\langle\phi_n^{(0)} \middle|\phi_n^{(0)}\right\rangle. \tag{4.13}$$

Since H_0 is Hermitian, the first term on the left side cancels with the first term on the right side. Therefore, we get the first-order perturbed energy eigenvalue correction as follows:

$$E_n^{(1)} = \left\langle\phi_n^{(0)}\right| V \left|\phi_n^{(0)}\right\rangle. \tag{4.14}$$

Thus, we can express the eigenvalue E_n of the Hamiltonian H, associated with $E_n^{(0)}$, up to the first order perturbation with

$$E_n = E_n^{(0)} + \lambda \left\langle\phi_n^{(0)}\right| V \left|\phi_n^{(0)}\right\rangle. \tag{4.15}$$

Now, let us determine $\left|\phi_n^{(1)}\right\rangle$. To this end, we multiply equation (4.11) with $\left\langle\phi_k^{(0)}\right|$ where $k \neq n$. We get

$$\left\langle\phi_k^{(0)}\right| \left(H_0 - E_n^0\right) \left|\phi_n^{(1)}\right\rangle + \left\langle\phi_k^{(0)}\right| \left(V - E_n^{(1)}\right) \left|\phi_n^{(0)}\right\rangle = 0. \tag{4.16}$$

By using the zeroth-order equation, we obtain

$$\left(E_k^0 - E_n^0\right)\left\langle \phi_k^{(0)} \middle| \phi_n^{(1)} \right\rangle + \left\langle \phi_k^{(0)} \middle| V \middle| \phi_n^{(0)} \right\rangle = 0. \tag{4.17}$$

Therefore, we can write

$$\left\langle \phi_k^{(0)} \middle| \phi_n^{(1)} \right\rangle = \frac{\left\langle \phi_k^{(0)} \middle| V \middle| \phi_n^{(0)} \right\rangle}{E_n^0 - E_k^0}, \text{ with } k \neq n. \tag{4.18}$$

By multiplying equation (4.18) with $\left|\phi_k^{(0)}\right\rangle$, we find

$$\left|\phi_n^{(1)}\right\rangle = \sum_{k\neq n} \frac{\left\langle \phi_k^{(0)} \middle| V \middle| \phi_n^{(0)} \right\rangle}{E_n^0 - E_k^0} \left|\phi_k^{(0)}\right\rangle. \tag{4.19}$$

After we substitute equation (4.19) into equation (4.8), we can express the eigenfunction $|\Psi_n\rangle$ of H to first order in λ as follows:

$$|\Psi_n\rangle = \left|\phi_n^{(0)}\right\rangle + \lambda \sum_{k\neq n} \frac{\left\langle \phi_k^{(0)} \middle| V \middle| \phi_n^{(0)} \right\rangle}{E_n^{(0)} - E_k^{(0)}} \left|\phi_k^{(0)}\right\rangle. \tag{4.20}$$

Second order correction

To obtain the second order correction of the energy eigenvalue function, we multiply equation (4.12) with $\left\langle \phi_n^{(0)} \right|$ from the left. Then, taking into account the orthonormality condition, we find

$$E_n^{(2)} = \left\langle \phi_n^{(0)} \middle| V \middle| \phi_n^{(1)} \right\rangle. \tag{4.21}$$

We employ equation (4.19) in equation (4.21) and get

$$\begin{aligned} E_n^{(2)} &= \sum_{k\neq n} \frac{\left\langle \phi_k^{(0)} \middle| V \middle| \phi_n^{(0)} \right\rangle \left\langle \phi_n^{(0)} \middle| V \middle| \phi_k^{(0)} \right\rangle}{E_n^{(0)} - E_k^{(0)}}, \\ &= \sum_{k\neq n} \frac{\left| \left\langle \phi_k^{(0)} \middle| V \middle| \phi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_k^{(0)}}, \end{aligned} \tag{4.22}$$

To express the final form. we substitute equations (4.14) and (4.22) in equation(4.11). Then, the eigenvalue function, E_n, up to the second-order of the perturbation reads:

$$E_n = E_n^{(0)} + \lambda \left\langle \phi_n^{(0)} \middle| V \middle| \phi_n^{(0)} \right\rangle + \lambda^2 \sum_{k \neq n} \frac{\left| \left\langle \phi_k^{(0)} \middle| V \middle| \phi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_k^{(0)}}. \tag{4.23}$$

Similarly, one can systematically obtain all orders of corrections of energy eigenvalue and eigenfunctions.

4.1.4 Degenerate case

Now, let us employ the perturbation theory to derive a system's energy spectrum and eigenstates whose unperturbed Hamiltonian H_0 is degenerate. First, we consider a scenario where there exist two original states, $\left|\phi_{n,1}^{(0)}\right\rangle$ and $\left|\phi_{n,2}^{(0)}\right\rangle$, that share the same unperturbed energy

$$H_0 \left|\phi_{n,i}^{(0)}\right\rangle = E_n^{(0)} \left|\phi_{n,i}^{(0)}\right\rangle \quad \text{for} \quad i = 1,2. \tag{4.24}$$

Here, we assume that

$$\left\langle \phi_{n,i}^{(0)} \middle| \phi_{n,j}^{(0)} \right\rangle = \delta_{i,j}. \tag{4.25}$$

Because of the degeneracy, any linear combination of $\left|\phi_{n,1}^{(0)}\right\rangle$ and $\left|\phi_{n,2}^{(0)}\right\rangle$ would also serve as an eigenstate of the Hamiltonian, H_0, with the energy $E_n^{(0)}$

$$\left|\phi_n^{(0)}\right\rangle = \alpha_1 \left|\phi_{n,1}^{(0)}\right\rangle + \alpha_2 \left|\phi_{n,2}^{(0)}\right\rangle. \tag{4.26}$$

Here, α_1 and α_2 are constants. Substituting equation (4.26) into equation (4.11), we have

$$\left(H_0 - E_n^{(0)}\right) \sum_k c_k \left|\phi_k^{(0)}\right\rangle + \left(V - E_n^{(1)}\right) \left(\alpha_1 \left|\phi_{n,1}^{(0)}\right\rangle + \alpha_2 \left|\phi_{n,2}^{(0)}\right\rangle\right) = 0, \tag{4.27}$$

where

$$\left|\phi_n^{(1)}\right\rangle = \sum_k c_k \left|\phi_k^{(0)}\right\rangle.$$

Then, we multiply equation (4.27) on the left with the state $\left\langle \phi_{n,i}^{(0)} \right|$. We get

$$\begin{cases} \alpha_1 \left(V_{11} - E_n^{(1)} \right) + \alpha_2 V_{12} = 0 \\ \alpha_1 V_{21} + \alpha_2 \left(V_{22} - E_n^{(1)} \right) = 0 \end{cases}, \tag{4.28}$$

where

$$V_{ij} = \left\langle \phi_{n,i}^{(0)} \right| V \left| \phi_{n,j}^{(0)} \right\rangle. \tag{4.29}$$

This is a system of two homogeneous linear equations for the coefficients α_i ($i = 1,2$), which are non-zero only when the determinant $\left| V_{ij} - E_n^{(1)} \delta_{ij} \right|$ equals zero

$$\begin{vmatrix} V_{11} - E_n^{(1)} & V_{12} \\ V_{21} & V_{22} - E_n^{(1)} \end{vmatrix} = 0. \tag{4.30}$$

This expression sets a constraint as

$$E_n^{(1)^2} - (V_{11} + V_{22}) E_n^{(1)} + V_{11} V_{22} - |V_{12}|^2 = 0. \tag{4.31}$$

This second-order equation has two possible solutions

$$\begin{cases} E_n^{(1),+} = \frac{V_{11}+V_{22}}{2} + \frac{1}{2}\sqrt{(V_{11}-V_{22})^2 + 4|V_{12}|^2} \\ E_n^{(1),-} = \frac{V_{11}+V_{22}}{2} - \frac{1}{2}\sqrt{(V_{11}-V_{22})^2 + 4|V_{12}|^2} \end{cases}. \tag{4.32}$$

Generalization Here, we examined two-fold degeneracy, however, in general, it can be g_n-fold. Therefore, we better derive a more general expression. Let us consider the case

$$H_0 \left| \phi_{n,i}^{(0)} \right\rangle = E_n^{(0)} \left| \phi_{n,i}^{(0)} \right\rangle \quad \text{with} \quad i = 1,2,...g_n, \tag{4.33}$$

and assume that

$$\left| \phi_n^0 \right\rangle = \sum_{i=1}^{g_n} \alpha_i \left| \phi_{n,i}^{(0)} \right\rangle. \tag{4.34}$$

Substitution of this in equation (4.11) gives us

$$\left(H_0 - E_n^{(0)} \right) \sum_k c_k \left| \phi_k^{(0)} \right\rangle + \left(V - E_n^{(1)} \right) \sum_{i=1}^{g_n} \alpha_i \left| \phi_{n,i}^{(0)} \right\rangle = 0. \tag{4.35}$$

Then, we multiply it with $\left\langle \phi_{n,j}^{(0)} \right|$, from the left. We get

$$\sum_{i=1}^{g_n} \left(V_{i,j} - E_n^{(1)} \delta_{ij} \right) \alpha_i = 0, \tag{4.36}$$

which represents a system of g_n simultaneous linear equations in the coefficients α_i. A non-trivial solution for this set of equations exists if and only if the following determinant equals zero

$$\begin{vmatrix} V_{1,1} - E_n^{(1)} & V_{1,2} & . & . & V_{1,g_n} \\ . & V_{2,2} - E_n^{(1)} & . & . & . \\ . & . & . & . & . \\ . & . & . & . & . \\ V_{1,g_n} & . & . & . & V_{g_n,g_n} - E_n^{(1)} \end{vmatrix} = 0. \tag{4.37}$$

Please note that the solution of this equation produces correction on the energy eigenvalue function only according to the first-order perturbation.

4.1.5 Example: Spin-Orbit Coupling

The spin-orbit interaction in the hydrogen atom originates from the interaction between the spin magnetic moment, $\overrightarrow{\mu} = -\frac{e\hat{\mathbf{S}}}{m_e c}$, of the electron and the orbital magnetic field, $\overrightarrow{B}$, generated by the proton. In this case, the Hamiltonian of the system can be divided into two components,

$$H = H_0 + W, \tag{4.38}$$

where

$$H_0 = \frac{\overrightarrow{p}^2}{2m} - \frac{e^2}{r}, \tag{4.39}$$

is the unperturbed Hamiltonian, and the perturbed Hamiltonian is given by

$$W = \frac{1}{2m_e c} \frac{1}{r} \frac{d}{dr} V(r) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{e^2}{2m_e c} \frac{1}{r^3} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \tag{4.40}$$

Here m_e is the electron mass, and c is the speed of light. To incorporate the electron's spin in the context of the hydrogen atom, we can construct the total wave function of hydrogen by combining the spatial and spin components. In fact,

we can use either

- the joint eigenstates $|n,\ell,s,m_\ell,m_s\rangle$ of $\hat{\mathbf{L}}^2,\hat{\mathbf{S}}^2,\hat{L}_z,\hat{S}_z$,

or

- the joint eigenstates $|n,\ell,s,J,M\rangle$ of $\hat{\mathbf{L}}^2,\hat{\mathbf{S}}^2,\hat{\mathbf{J}}^2,\hat{J}_z$

We choose the second option and express the eigenvalue of the Hamiltonian to the first-order perturbation as

$$E_n = E_n^{(0)} + \langle n,\ell,s,J,M|\, W\,|n,\ell,s,J,M\rangle\,, \tag{4.41}$$

where

$$E_n^{(0)} = \frac{-13.6}{n^2} eV,$$

are the energy levels of hydrogen. Now, let us introduce the total angular momentum

$$\hat{\mathbf{L}}\cdot\hat{\mathbf{S}} = \frac{\hat{\mathbf{J}}^2-\hat{\mathbf{L}}^2-\hat{\mathbf{S}}^2}{2}. \tag{4.42}$$

By substituting equation (4.42) in equation (4.41), we obtain

$$\begin{aligned} E_n &= E_n^{(0)} + \frac{e^2}{2m_e c}\langle n,\ell,s,J,M|\,\frac{1}{r^3}\frac{\hat{\mathbf{J}}^2-\hat{\mathbf{L}}^2-\hat{\mathbf{S}}^2}{2}\,|n,\ell,s,J,M\rangle\,, \\ &= E_n^{(0)} + \frac{\hbar^2 e^2\left[J(J+1)-\ell(\ell+1)-\frac{3}{4}\right]}{4m_e c}\langle n,\ell|\,\frac{1}{r^3}\,|n,\ell\rangle\,. \end{aligned} \tag{4.43}$$

For $\left\langle \frac{1}{r^3}\right\rangle$, we have (see N. Zettili p.389).

$$\langle n,\ell|\,\frac{1}{r^3}\,|n,\ell\rangle = \frac{2m_e e^2}{n^3\ell(\ell+1)(2\ell+1)\hbar^2}. \tag{4.44}$$

Therefore, the Spin-orbit energy shift reads:

$$\langle n,\ell,s,J,M|\,W\,|n,\ell,s,J,M\rangle = \frac{e^4}{2c}\frac{J(J+1)-\ell(\ell+1)-\frac{3}{4}}{n^3\ell(\ell+1)(2\ell+1)}. \tag{4.45}$$

4.2 Variational Method

4.2.1 A property of the ground state energy of the system

Let us consider a one-dimensional quantum system characterized by a time-independent Hamiltonian, H, in which we know the exact non-degenerate bound state energy levels and their corresponding eigenstates,

$$H|\phi_n\rangle = E_n|\phi_n\rangle; \qquad \langle\phi_m|\phi_n\rangle = \delta_{nm}. \tag{4.46}$$

with the condition

$$E_0 < E_1 < E_2, ... \tag{4.47}$$

For any given ket, $|\Phi\rangle$, it is possible to compute energy expectation values,

$$\langle E(\Phi)\rangle = \frac{\langle\Phi|H|\Phi\rangle}{\langle\Phi|\Phi\rangle}. \tag{4.48}$$

Now, let us expand the kets in terms of the exact eigenket of the Hamiltonian

$$|\Phi\rangle = \sum_{n=0} a_n|\phi_n\rangle, \tag{4.49}$$

where $a_n = \langle\phi_n|\Phi\rangle$. After substituting $|\Phi\rangle$ with $\sum_{n=0}\langle\phi_n|\Phi\rangle|\phi_n\rangle$, we obtain

$$\langle\Phi|\Phi\rangle = \sum_{m=0}\sum_{n=0} a_m^* a_n\langle\phi_m|\phi_n\rangle = \sum_{m=0}\sum_{n=0} a_{mn}^*\delta_{nm} = \sum_{n=0}|a_n|^2, \tag{4.50}$$

and

$$\langle\Phi|H|\Phi\rangle = \sum_{m=0}\sum_{n=0} a_m^* a_n\langle\phi_m|H|\phi_n\rangle = \sum_{n=0} E_n|a_n|^2 \geq \sum_{n=0} E_0|a_n|^2, \tag{4.51}$$

which turns equation(4.48) to

$$\langle E(\Phi)\rangle = \frac{\langle\Phi|H|\Phi\rangle}{\langle\Phi|\Phi\rangle} \geq E_0. \tag{4.52}$$

This is quite a significant result since it implies that the average energy value is always greater than or equal to the energy of the ground state.

4.2.2 Ritz's Theorem

Theorem 3 *When the ket $|\Phi\rangle$ is varied $|\Phi+\delta\Phi\rangle$, then the average value of the Hamiltonian $\langle E(\Phi)\rangle$ is stationary when $|\Phi\rangle$ is close to an eigenvector of the Hamiltonian $|\Phi\rangle \sim |\phi_n\rangle$.*

Proof:

According to equation (4.48), we can write

$$\langle E\rangle \langle\Phi|\Phi\rangle = \langle\Phi|H|\Phi\rangle . \tag{4.53}$$

Now, let us vary $|\Phi\rangle$ infinitesimally

$$|\Phi\rangle \to |\Phi\rangle + |\delta\Phi\rangle . \tag{4.54}$$

Then, we consider the variation of the equation (4.53)

$$\delta\left(\langle\Phi|\Phi\rangle\langle E\rangle\right) = \langle\delta\Phi|\Phi\rangle\langle E\rangle + \langle\Phi|\delta\Phi\rangle\langle E\rangle + \langle\Phi|\Phi\rangle\delta\langle E\rangle , \tag{4.55}$$

with

$$\delta\langle\Phi|H|\Phi\rangle = \langle\delta\Phi|H|\Phi\rangle + \langle\Phi|H|\delta\Phi\rangle . \tag{4.56}$$

After we compare equations (4.55) and (4.56), we get

$$\langle\Phi|\Phi\rangle\delta\langle E\rangle = \langle\delta\Phi|\left(H-\langle E\rangle\right)|\Phi\rangle + \langle\Phi|\left(H-\langle E\rangle\right)|\delta\Phi\rangle . \tag{4.57}$$

$\langle E\rangle$ is stationary if $\delta\langle E\rangle = 0$. Hence,

$$\langle\delta\Phi|\left[H-\langle E\rangle\right]|\Phi\rangle + \langle\Phi|\left[H-\langle E\rangle\right]|\delta\Phi\rangle = 0. \tag{4.58}$$

Now, let us introduce the ket $|F\rangle$, that is defined by

$$\left[H-\langle E\rangle\right]|\Phi\rangle = |F\rangle . \tag{4.59}$$

Then, equation (4.58) reads:

$$\langle\delta\Phi|F\rangle + \langle F|\delta\Phi\rangle = 0. \tag{4.60}$$

The latter equation has to be true for any infinitesimal ket, $|\delta\Phi\rangle$. In particular, if we consider

$$|\delta\Phi\rangle = \delta\lambda\,|F\rangle\,, \quad \text{where} \quad \delta\lambda << 1 \text{ and real,} \tag{4.61}$$

then equation (4.60) transforms into

$$2\delta\lambda\,\langle F\,|F\rangle = 0 \Longrightarrow \langle F\,|F\rangle = 0 \Longrightarrow |F\rangle = 0. \tag{4.62}$$

Taken into account the definition of equation (4.59), we conclude that

$$H\,|\Phi\rangle = \langle E\rangle\,|\Phi\rangle\,. \tag{4.63}$$

This result shows that $|\Phi\rangle$ must be an eigenstate of H for its expectation value to be stationary. Moreover, this establishes that the expectation value of the Hamiltonian remains stationary in the vicinity of its eigenstates.

4.2.3 Variational Technique

The Ritz method consists of:

- We select a trial function $|\chi(\lambda)\rangle$ that takes into account all the physical characteristics of the ground state.
- Then, we calculate the energy's expectation value,

$$E_0(\lambda) = \frac{\langle\chi(\lambda)|H\,|\chi(\lambda)\rangle}{\langle\chi(\lambda)\,|\chi(\lambda)\rangle}. \tag{4.64}$$

- After that, we minimize the expectation value by finding the root λ_0 of

$$\frac{\partial}{\partial\lambda}E_0(\lambda)\bigg|_{\lambda=\lambda_0} = 0. \tag{4.65}$$

- Finally, we substitute the root value, λ_0, into equation (4.64) to derive an estimated energy value. The resultant value, $E_0(\lambda_0)$, provides an upper bound for the exact ground state energy E_0. Consequently, The reel ground state eigenstate $|\phi_0\rangle$ is approximated by the state $|\chi(\lambda_0)\rangle$.

It is worth noting that this procedure can be readily extended to scenarios involving multiple parameters $\lambda_i\,(i=1,2,..)$, for which we find the roots of $\frac{\partial}{\partial\lambda_i}E_0(\lambda_i)$. In addition, a critical point of the $E_0(\lambda)$ might not always correspond to a minimum. The nature of these critical points can be partly categorized by the second derivative $\frac{\partial^2 E_0(\lambda)}{\partial\lambda_i\partial\lambda_j}$, computed at the critical point.

4.2.4 Example: Helium Atom

Let us examine the Helium atom "He" as an example where its Hamilton operator reads:

$$H=\frac{p_1^2}{2m}+\frac{p_2^2}{2m}-\frac{2e^2}{r_1}-\frac{2e^2}{r_2}+\frac{2e^2}{|\overrightarrow{r}_1-\overrightarrow{r}_2|}. \tag{4.66}$$

We introduce the trial function

$$\psi(r_1,r_2)=\Phi_0(r_1)\,\Phi_0(r_2), \tag{4.67}$$

with an adjustable scale parameter α as

$$\psi(r_1,r_2)=\left(\frac{1}{\pi\alpha^3}\right)e^{-\frac{(r_1+r_2)}{\alpha}},\qquad \alpha>0. \tag{4.68}$$

At first, we have to calculate

$$\begin{aligned}\langle\psi(\alpha)\,|\psi(\alpha)\rangle &= \int d\overrightarrow{r_1}\Phi_0^*(r_1)\,\Phi_0(r_1)\int d\overrightarrow{r_2}\Phi_0^*(r_2)\,\Phi_0(r_2),\\ &= 16\pi^2\left(\frac{1}{\pi\alpha^3}\right)\int_0^{+\infty}r_1^2e^{-\frac{2r_1}{\alpha}}dr_1\int_0^{+\infty}r_2^2e^{-\frac{2r_2}{\alpha}}dr_2.\end{aligned} \tag{4.69}$$

Here, we use the basic integral

$$\int_0^{+\infty}x^ne^{-ax}dx=\frac{n!}{a^{n+1}}, \tag{4.70}$$

and thus, we obtain

$$\langle\psi(\alpha)\,|\psi(\alpha)\rangle=1. \tag{4.71}$$

Next, we calculate $\langle\psi(\alpha)|H|\psi(\alpha)\rangle$, which has to be evaluated in three different terms. The first integral is with the kinetic terms

$$\begin{aligned}\langle\psi(\alpha)|\frac{p_i^2}{2m}|\psi(\alpha)\rangle &= \frac{-\hbar^2}{2m}\left(\frac{1}{\pi\alpha^3}\right)^2 16\pi^2\int_0^{+\infty} r_i^2 e^{-\frac{r_i}{\alpha}}\left(\frac{d^2}{dr_i^2}+\frac{2}{r_i}\frac{d}{dr_i}\right)e^{-\frac{r_i}{\alpha}}dr_i\int_0^{+\infty} r_j^2 e^{-\frac{2r_j}{\alpha}}dr_j \\ &= \frac{-\hbar^2}{2m}\left(\frac{1}{\pi\alpha^3}\right)^2 16\pi^2\int_0^{+\infty} r_i^2\left(\frac{1}{\alpha^2}-\frac{2}{\alpha r_i}\right)e^{-\frac{2r_i}{\alpha}}dr_i\int_0^{+\infty} r_j^2 e^{-\frac{2r_j}{\alpha}}dr_j \\ &= \frac{\hbar^2}{2m\alpha^2}, \end{aligned} \tag{4.72}$$

where the second one is with the interactions of proton and electrons

$$\begin{aligned}\langle\psi(\alpha)|\frac{1}{r_i}|\psi(\alpha)\rangle &= \left(\frac{1}{\pi\alpha^3}\right)^2 16\pi^2\int_0^{+\infty} r_i e^{-\frac{2r_i}{\alpha}}dr_i\int_0^{+\infty} r_j^2 e^{-\frac{2r_j}{\alpha}}dr_j \\ &= \frac{1}{\alpha}, \end{aligned} \tag{4.73}$$

and the third one is with the interactions of electrons

$$\langle\psi(\alpha)|\frac{1}{|\overrightarrow{r}_1-\overrightarrow{r}_2|}|\psi(\alpha)\rangle = \left(\frac{1}{\pi\alpha^3}\right)^2\int\frac{e^{-\frac{2(r_1+r_2)}{\alpha}}}{|\overrightarrow{r}_1-\overrightarrow{r}_2|}d\overrightarrow{r}_1 d\overrightarrow{r}_2. \tag{4.74}$$

Here, we can apply the Fourier transform

$$\frac{1}{|\overrightarrow{r}_1-\overrightarrow{r}_2|} = \frac{1}{(2\pi)^3}\int\frac{4\pi}{k^2}e^{i\overrightarrow{k}(\overrightarrow{r}_1-\overrightarrow{r}_2)}d\overrightarrow{k}, \tag{4.75}$$

which allows us to evaluate it as

$$\begin{aligned}\langle\psi(\alpha)|\frac{1}{|\overrightarrow{r}_1-\overrightarrow{r}_2|}|\psi(\alpha)\rangle &= \frac{1}{\pi\alpha^3}\frac{1}{(2\pi)^3}\int\int\frac{4\pi}{k^2}e^{i\overrightarrow{k}(\overrightarrow{r}_1-\overrightarrow{r}_2)-\frac{2(r_1+r_2)}{\alpha}}d\overrightarrow{k}d\overrightarrow{r}_1 d\overrightarrow{r}_2, \\ &= \left(\frac{1}{\pi\alpha^3}\right)^2\frac{1}{(2\pi)^3}\int\frac{4\pi}{k^2}d\overrightarrow{k}\left|\int e^{i\overrightarrow{k}\overrightarrow{r}_1-\frac{2r_1}{\alpha}}d\overrightarrow{r}_1\right|^2, \\ &= \left(\frac{1}{\pi\alpha^3}\right)^2\frac{1}{(2\pi)^3}\left(\frac{16\pi}{a}\right)^2\int\frac{4\pi}{k^2}\frac{d\overrightarrow{k}}{\left[k^2+\left(\frac{2}{\alpha}\right)^2\right]^4}, \\ &= \frac{5}{8a}. \end{aligned} \tag{4.76}$$

After summing up these three results, we obtain the expectation value

$$E_0(\alpha) = \langle \psi(\alpha) | H | \psi(\alpha) \rangle = \frac{\hbar^2}{m\alpha^2} - \frac{27e^2}{8\alpha}. \tag{4.77}$$

that has a minimum value

$$\frac{\partial}{\partial \alpha} E_0(\alpha) = -\frac{2\hbar^2}{m\alpha^3} + \frac{27}{8\alpha^2} e^2 = 0, \tag{4.78}$$

at

$$\alpha_{\min} = \frac{16\hbar^2}{27me^2}. \tag{4.79}$$

For this value of the parameter, the Hamiltonian's expectation value yields

$$E_0(\alpha_{\min}) = 2\left(\frac{27}{16}\right)^2 E_H, \tag{4.80}$$

where

$$E_H = -\frac{me^4}{2\hbar^2}, \tag{4.81}$$

is the ground state energy of the Hydrogen atom.

4.3 WKB method

4.3.1 General formalism

The Wentzel-Kramers-Brillouin (WKB) formalism, published almost simultaneously with the publication of the Schrödinger equation in 1926, is a semiclassical technique of quantum mechanics, where the wave function is approximated as an exponential function having slowly changing amplitude and phase in comparison to the de-Broglie wavelength λ.

Precisely, in this approximation, we investigate the particle's motion in one dimension with a time-independent potential $V(x)$.

$$\left[\frac{d^2}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))\right] \psi = 0. \tag{4.82}$$

In a specific scenario, where the potential is just a constant $V(x) = V_0$, wave function

the solutions arise in the form of plane waves,

$$\psi = Ae^{\pm \frac{i}{\hbar} px}. \tag{4.83}$$

Here, A is a constant and λ is the de-Broglie wavelength of the particle via $\lambda = \frac{h}{p}$ and $p = \sqrt{2m(E - V_0)}$.

If the potential energy varies very slowly via the location, then the solution of the Schrödinger equation can be considered as

$$\psi(x) = A(x) e^{\frac{i}{\hbar} S(x)}. \tag{4.84}$$

where $S(x)$ an unknown complex function. Then, by substituting equation (4.84) into equation (4.82), we get

$$A" - \frac{1}{\hbar^2} \left(S'\right)^2 A + \frac{2m}{\hbar^2} (E - V(x)) A = 0, \tag{4.85}$$

$$2S'A' + S"A = 0, \tag{4.86}$$

which can be reduced to

$$\left(S'\right)^2 = \hbar^2 \frac{A"}{A} + 2m(E - V(x)), \tag{4.87}$$

$$\left(S'A^2\right)' = 0. \tag{4.88}$$

The integration of equation (4.88) yields:

$$A = \frac{C}{\sqrt{S}}, \tag{4.89}$$

where C is the integration constant. By substituting equation (4.89) into equation (4.87), we obtain:

$$\left(S'\right)^2 = \frac{\hbar^2}{2} \left[\frac{3}{2} \left(\frac{S"}{S'} \right)^2 - \frac{S^{(3)}}{S'} \right] + 2m(E - V(x)). \tag{4.90}$$

If we expand $S(x)$ in a power series in $\hbar$, i.e.,

$$S(x) = S_0 + \hbar S_1 + \hbar^2 S_2 + ... \tag{4.91}$$

then we get

$$\left(S_0'\right)^2 = 2m\left(E - V\left(x\right)\right). \tag{4.92}$$

after using the expansion in equation (4.89) and retaining only the zeroth order terms. Now, we can consider the integration in equation (4.92)

$$S_0\left(x\right) = \pm \int^x \sqrt{2m\left(E - V\left(u\right)\right)} du. \tag{4.93}$$

Here, we have to deal with two cases, $E > V\left(x\right)$ and $E < V\left(x\right)$ cases, respectively. To this end, let us define $p\left(x\right)$ in the following form for each cases:

$$p\left(x\right) = \sqrt{2m\left(E - V\left(x\right)\right)}, \quad \text{if} \quad E > V\left(x\right), \tag{4.94}$$

$$\tilde{p}\left(x\right) = \sqrt{2m\left(V\left(x\right) - E\right)}, \quad \text{if} \quad E < V\left(x\right). \tag{4.95}$$

In the allowed region, where $E > V\left(x\right)$, the general solution takes the form of a combination of two fundamental solutions with waves propagating in opposite directions:

$$\psi_{WKB} = \frac{A}{\sqrt{\left|p\left(x\right)\right|}} e^{\frac{i}{\hbar}\int^x p(u)du} + \frac{B}{\sqrt{\left|p\left(x\right)\right|}} e^{-\frac{i}{\hbar}\int^x p(u)du}. \tag{4.96}$$

On the other hand, in the forbidden region, where $V\left(x\right) > E$, the wave functions fade according to

$$\psi_{WKB} = \frac{\tilde{A}}{\sqrt{\left|\tilde{p}\left(x\right)\right|}} e^{\frac{1}{\hbar}\int^x \tilde{p}(u)du} + \frac{\tilde{B}}{\sqrt{\left|\tilde{p}\left(x\right)\right|}} e^{-\frac{1}{\hbar}\int^x \tilde{p}(u)du}. \tag{4.97}$$

4.3.2 Criterion for the validity of the approximation

The approximation leading to the wave function given in equation (4.96) is valid when the following condition is satisfied,

$$\left| \frac{\hbar S_0"}{\left(S_0'\right)^2} \right| << 1, \tag{4.98}$$

which can be written as

$$\left| \frac{d\left(\hbar / S_0'\right)}{dx} \right| << 1. \tag{4.99}$$

Since $S_0'(x) = \pm p(x)$, we can simplify the equation (4.99) to

$$\frac{1}{2\pi}\left|\frac{d\lambda}{dx}\right| << 1, \tag{4.100}$$

where

$$\lambda = \frac{\hbar}{p(x)}, \tag{4.101}$$

This condition implies that de-Broglie wavelength has to alter slightly. Therefore, it is clear that this approach is not valid at the classical turning points, $E = V(x_j)$ where $p(x) = 0$. Classically, the particle stops at the turning points and subsequently reverses its direction. When the magnitude of $p(x)$ becomes small, then the wavelength as given in equation (4.101) becomes large, and hence, the requirement is violated. As a summary, the WKB formalism is valid in both the permitted and forbidden regions, but not at the classical turning points.

4.3.3 Bound State

Let us consider a potential well that does not have rigid walls, as shown in figure (4.1).

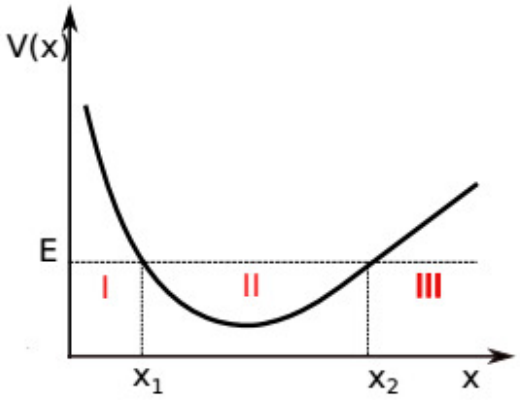

Figure 4.1: Potential with no rigid walls.

In the three regions, the wave function can be written as follows:

$$\psi_1 = \frac{C_1}{\sqrt{\tilde{p}(x)}} e^{\frac{-1}{\hbar}\int_x^{x_1}\tilde{p}(x)dx}, \quad x < x_1. \tag{4.102}$$

$$\psi_2 = \frac{C_1'}{\sqrt{p(x)}} e^{\frac{i}{\hbar}\int p(x)dx} + \frac{C_2''}{\sqrt{p(x)}} e^{-\frac{i}{\hbar}\int p(x)dx}, \quad x_1 < x < x_2. \tag{4.103}$$

$$\psi_3 = \frac{C_3}{\sqrt{\tilde{p}(x)}} e^{\frac{1}{\hbar}\int_x^{x_2}\tilde{p}(x)dx}, \quad x > x_2 \tag{4.104}$$

Now, let us emphasize several points:

- The WKB method is applicable except at the classical turning points $x = x_1$ and $x = x_2$.
- The wave function must decay exponentially in the first and third regions as $x \to \pm\infty$.
- The wave function must oscillate in the second region.

Connection of ψ_2 to ψ_3

The wave function can be re-written as

$$\psi_2 = \frac{\mathcal{D}}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_x^{x_2} p(u)\,du + \delta'\right). \tag{4.105}$$

Near the turning point $x = x_2$, we Taylor expand $V(x)$ to first order

$$V(x) = E + (x - x_2)F_0, \quad \text{where } F_0 = \frac{d}{dx}V(x)\bigg|_{x=x_2} \tag{4.106}$$

and then we substitute equation (4.106) into equation (4.82). We obtain

$$\left[\frac{d^2}{dy^2} - y\right]\psi = 0. \tag{4.107}$$

where $y = \left(\frac{2m}{\hbar^2}F_0\right)^{1/3}(x - x_2)$. The exact solution of the above equation can expressed in terms of Airy functions, $Ai(y)$:

$$\psi = A'\mathbf{Ai}(y). \tag{4.108}$$

Here, we have to recall the asymptotic forms of the Airy functions for large positive and negative values:

$$\begin{cases} \mathbf{Ai} \simeq \frac{\sin\left[\frac{2}{3}(-y)^{3/2}+\frac{\pi}{4}\right]}{\sqrt{-\pi}(-y)^{1/4}}, & y << 0 \\ \mathbf{Ai} \simeq \frac{e^{\frac{-2}{3}(-y)^{3/2}}}{2\pi(y)^{1/4}}, & y >> 0 \end{cases}. \tag{4.109}$$

With the help of equation (4.94), we write

$$p^2 = 2m\,(x-x_2)\,F_0 = -\,(2m\hbar F_0)^{2/3}\,y, \tag{4.110}$$

Thus,

$$\frac{1}{\hbar}\int_x^{x_2} p\,(u)\,du = \int_y^0 \sqrt{-y'}dy' = \frac{2}{3}\,(-y)^{3/2}. \tag{4.111}$$

By inserting this equation into equation (4.109), we obtain:

$$\psi = \begin{cases} A'\frac{(2m\hbar F_0)^{1/6}}{\sqrt{\pi}}\frac{\sin\left[\frac{1}{\hbar}\int_x^{x_2} p(u)du+\frac{\pi}{4}\right]}{\sqrt{p}}, & x << x_2 \\ A'\frac{(2m\hbar F_0)^{1/6}}{\sqrt{2\pi}}\frac{e^{-\frac{1}{\hbar}\int_x^{x_2}\tilde{p}(u)du}}{\sqrt{\tilde{p}}}, & x >> x_2 \end{cases}. \tag{4.112}$$

By the comparison of this equation with equation (4.105), we find the relations

$$\delta' = \frac{\pi}{4},\quad \mathcal{D} = A'\frac{(2m\hbar F_0)^{1/6}}{\sqrt{\pi}} \text{ and } \quad C_3 = A'\frac{(2m\hbar F_0)^{1/6}}{\sqrt{2\pi}}. \tag{4.113}$$

Consequently, equation (4.103) reads:

$$\psi_2 = \frac{\mathcal{D}}{\sqrt{p\,(x)}}\sin\left(\frac{1}{\hbar}\int_x^{x_2} p\,(u)\,du+\frac{\pi}{4}\right). \tag{4.114}$$

Connection of ψ_1 to ψ_2

The wave function of the second region can be written as

$$\psi_2 = \frac{D}{\sqrt{p\,(x)}}\sin\left(\frac{1}{\hbar}\int_{x_1}^{x} p\,(u)\,du+\delta\right). \tag{4.115}$$

Then, by using the same strategy, one can obtain the required relations:

$$\delta = \frac{\pi}{4}, \quad D = A' \frac{(2m\hbar F_0)^{1/6}}{\sqrt{\pi}} \text{ et } \quad C_1 = A' \frac{(2m\hbar F_0)^{1/6}}{\sqrt{2\pi}}. \tag{4.116}$$

to express the wave function

$$\psi_2 = \frac{D}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_{x_1}^{x} p(u)\,du + \frac{\pi}{4}\right). \tag{4.117}$$

Quantization condition

Since both solutions, namely equations (4.114) and (4.117), belong to the second region, they must be the same.

$$\frac{D}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_{x_1}^{x} p(u)\,du + \frac{\pi}{4}\right) = \frac{\mathcal{D}}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_{x}^{x_2} p(u)\,du + \frac{\pi}{4}\right), \tag{4.118}$$

In fact, these equations have the same form, $D\sin\theta = D\sin\vartheta$. This condition is fulfilled if we consider the following two relations:

$$D = (1)^n \mathcal{D}, \tag{4.119}$$

and

$$\frac{1}{\hbar}\int_{x_1}^{x} p(u)\,du + \frac{1}{\hbar}\int_{x}^{x_2} p(u)\,du + \frac{\pi}{2} = \pi n + \pi. \tag{4.120}$$

The latter equation can be rewritten as follows:

$$\int_{x_1}^{x_2} p(x)\,dx = \pi\hbar\left(n + \frac{1}{2}\right), \quad \text{with } n = 0, 1, \ldots \tag{4.121}$$

In conclusion, the general quantization condition of the WKB approximation reads:

$$\begin{cases} \int_{x_1}^{x_2} p(x)\,dx = \pi\hbar\left(n+\frac{1}{2}\right), & \text{for potential well with no rigid walls,} \\ \int_{x_1}^{x_2} p(x)\,dx = \pi\hbar\left(n+\frac{3}{4}\right), & \text{for potential well with one rigid wall,} \\ \int_{x_1}^{x_2} p(x)\,dx = \pi\hbar n, & \text{for potential well with two rigid walls.} \end{cases} \tag{4.122}$$

4.3.4 Example

Example 1:

Let us consider a particle in one dimension influenced by a potential $V(x) = a|x|$, and calculate the energy spectrum using the WKB method.

Solution:

This is a problem with no wall but with two turning points at $x_1 = -\frac{E}{a}$ and $x_2 = \frac{E}{a}$. First, we express the momentum of the particle with

$$p(x) = \sqrt{2m(E - a|x|)}. \tag{4.123}$$

Then, we substitute it in equation(4.121). We obtain:

$$\begin{aligned}
\int_{x_1}^{x_2} \sqrt{2m(E-a|x|)}dx &= \int_{-\frac{E}{a}}^{0} \sqrt{2m(E+ax)} + \int_{0}^{\frac{E}{a}} \sqrt{2m(E-ax)}dx = \hbar\left(n+\frac{1}{2}\right), \\
&= \sqrt{2ma}\left[\frac{2}{3}\left(\frac{E}{a}+x\right)^{3/2}\right]_{-\frac{E}{a}}^{0} + \sqrt{2ma}\left[-\frac{2}{3}\left(\frac{E}{a}-x\right)^{3/2}\right]_{0}^{\frac{E}{a}}, \\
&= \frac{4}{3}\sqrt{2ma}\left(\frac{E}{a}\right)^{3/2}.
\end{aligned} \tag{4.124}$$

After the simplification, we find the energy spectrum function

$$E_n = \left(\frac{3\hbar}{4\sqrt{2m}}a\left(n+\frac{1}{2}\right)\right)^{2/3}. \quad \text{where} \quad n = 0,1,2,3,\cdots. \tag{4.125}$$

Example 2:

Let us apply the WKB method to compute the energy eigenvalues of a massive particle confined in a one-dimensional box with walls located at $x = 0$ and $x = L$.

Solution:

This is a problem with two rigid walls $x = 0$ and $x = L$. First, let us express the momentum of the particle

$$p(x) = \sqrt{2mE}. \tag{4.126}$$

Then, according to equation (4.122) we obtain the energy spectrum

$$\int_{x_1}^{x_2} p(x)\,dx = \int_0^L \sqrt{2mE}dx = \pi\hbar n. \tag{4.127}$$

Thus,

$$\sqrt{2mE}L = \pi\hbar n, \tag{4.128}$$

After taking the square of the latter form, we get

$$E_n = \frac{\pi^2\hbar^2 n^2}{2mL^2}, \quad \text{where} \quad n = 1,2,3,\cdots. \tag{4.129}$$

4.4 Time-dependent Perturbation Theory

4.4.1 General theory

Time dependence forces the formalism to be constructed using the time-dependent Schrödinger equation. Therefore, with a very small real-valued perturbation parameter, $\lambda << 1$ and $\lambda \in R$, we consider

$$H|\psi(t)\rangle = [H_0 + \lambda V(t)]|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle. \tag{4.130}$$

Here, time-dependent potential, $V(t)$, represents an observable of the same order of magnitude H_0 which remains zero for $t < 0$. The Hamiltonian H_0 is a known and time-independent operator. Here, known means that its energy spectrum and corresponding eigenstates are determined via the following equation

$$H_0|\Phi_n\rangle = E_n|\Phi_n\rangle. \tag{4.131}$$

Here, E_n corresponds to the unperturbed energies, which are assumed to form a discrete spectrum. Moreover, $|\Phi_n\rangle$ are the unperturbed states associated with these energies. It is worth noting that the set of vectors, $|\Phi_k\rangle$, form a complete and orthonormal basis.

$$\langle\Phi_m|\Phi_n\rangle = \delta_{nm}, \quad \text{and} \quad \sum_n |\Phi_n\rangle\langle\Phi_n| = \mathbf{1}. \tag{4.132}$$

Let us suppose that the system is in the initial state, $|\psi(t=0)\rangle = |\Phi_i\rangle$.

On the other hand, $|\Phi_n\rangle$ are no longer eigenstates of H. Since they form a complete basis, we can expand $|\psi(t)\rangle$ in its basis

$$|\psi(t)\rangle = \sum_n c_n(t)\,|\Phi_n\rangle\,, \tag{4.133}$$

where

$$c_m(t) = \langle\Phi_m\,|\psi\rangle\,. \tag{4.134}$$

By substituting equation (4.133) into equation (4.130), we obtain

$$\sum_n c_n(t)\,H_0\,|\Phi_n\rangle + \sum_n c_n(t)\,W(t)\,|\Phi_n\rangle = i\hbar\sum_n \frac{\partial}{\partial t}c_n(t)\,|\Phi_n\rangle\,. \tag{4.135}$$

Then, we multiply it with $\langle\Phi_m|$ from the left. With the help of the orthogonality condition, we get

$$E_m c_m(t) + \lambda\sum_n c_n(t)\,V_{m,n}(t) = i\hbar\frac{\partial}{\partial t}c_m(t)\,, \tag{4.136}$$

where

$$V_{m,n}(t) = \langle\Phi_m|V(t)\,|\Phi_n\rangle\,. \tag{4.137}$$

Now, we introduce a perturbation parameter λ, analogous to the situation in time-independent perturbation theory, as follows:

$$c_n(t) = \sum_{j=0}\lambda^i a_n^{(i)}(t)\,e^{-\frac{i}{\hbar}E_n t} = e^{-\frac{i}{\hbar}E_n t}\left[c_n^{(0)}(t) + \lambda c_n^{(1)}(t) + \lambda^2 c_n^{(2)}(t) + \ldots\right]. \tag{4.138}$$

Substituting equation (4.138) into equation (4.136), we find

$$\sum_{n,j}\lambda^{j+1}e^{i\omega_{m,n}t}V_{m,n}(t)\,a_n^{(j)}(t) = i\hbar\sum_{j=0}\lambda^j\frac{\partial}{\partial t}a_m^{(j)}(t)\,, \tag{4.139}$$

where

$$\omega_{m,n} = \frac{E_m - E_n}{\hbar}.$$

When we match the coefficients of λ^j on both sides of the equation, we obtain

- Zeroth order correction

$$\frac{\partial}{\partial t}a_n^{(0)}(t) = 0, \tag{4.140}$$

thus,

$$a_n^{(0)}(t) = a_n^{(0)} = \text{Constant}. \tag{4.141}$$

Recalling that the system is initially in the state $|\Phi_i\rangle$, we conclude that

$$a_n^{(0)} = \delta_{i,n}. \tag{4.142}$$

- First order correction

$$\sum_n e^{i\omega_{m,n}t} V_{m,n}(t)\, a_n^{(0)}(t) = i\hbar \frac{\partial}{\partial t} a_m^{(1)}(t). \tag{4.143}$$

Substituting equation (4.142) into equation (4.143), we get

$$i\hbar \frac{\partial}{\partial t} a_m^{(1)}(t) = e^{i\omega_{m,i}t} V_{m,i}(t), \tag{4.144}$$

therefore,

$$a_n^{(1)}(t) = -\frac{i}{\hbar} \int_0^t e^{i\omega_{n,i}s} V_{n,i}(s)\, ds. \tag{4.145}$$

By incorporating equations (4.145) and (4.142) into equation (4.138), and subsequently inserting them into equation (4.133), we derive the state $|\psi(t)\rangle$ of the system at time t, up to the first order parameter as follows:

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}E_i t} |\Phi_i\rangle + \sum_{n\neq i} \frac{\lambda e^{-i\omega_n t}}{i\hbar} \left[\int_0^t e^{i\omega_{n,i}s} V_{n,i}(s)\, ds\right] |\Phi_n\rangle. \tag{4.146}$$

Utilizing the perturbation theory, we compute the transition probability, namely $P_{i\to f}$, from the initial state i at $t = 0$ to a different state f (where $i \neq f$) at time t. Keeping the definition of the transition probability in mind,

$$\mathcal{P}_{i\to f} = \left|\langle \Phi_f | \psi(t)\rangle\right|^2, \tag{4.147}$$

We substitute equation (4.146) into equation (4.147). We find

$$\mathcal{P}_{i\to f} = \frac{\lambda^2}{\hbar^2} \left| \int_0^t e^{i\omega_{f,i}s} V_{f,i}(s)\, ds \right|^2. \tag{4.148}$$

4.4.2 Special cases

Constant perturbation

Let us suppose that the time-dependent potential $W(t)$ takes the following form:

$$W(t) = \lambda V(t) = \begin{cases} 0 & \text{if } t < 0 \\ W(r) & \text{if } t \geq 0 \end{cases}. \tag{4.149}$$

By substituting equation (4.149) into equation (4.145), we find the transition amplitudes to first order in perturbation theory as

$$a_n^{(1)}(t) = -\frac{i\langle\Phi_n|V|\Phi_i\rangle}{\hbar}\int_0^t e^{i\omega_{n,i}s}ds, \tag{4.150}$$

or equivalently as

$$a_n^{(1)}(t) = \frac{\langle\Phi_n|V|\Phi_i\rangle}{\hbar\omega_{n,i}}\left(1 - e^{i\omega_{n,i}t}\right). \tag{4.151}$$

Therefore, the transition probability reads:

$$\begin{aligned} \mathcal{P}_{i\to f} &= \frac{\left|\langle\Phi_f|W|\Phi_i\rangle\right|^2}{\hbar^2\omega_{n,i}^2}\left|1 - e^{i\omega_{n,i}t}\right|^2\left(e^{-i\frac{\omega_{f,i}}{2}t} - e^{i\frac{\omega_{f,i}}{2}t}\right), \\ &= \frac{\left|\langle\Phi_f|W|\Phi_i\rangle\right|^2}{\hbar^2}\frac{\sin^2\left(\frac{\omega_{f,i}}{2}t\right)}{\frac{\omega_{n,i}^2}{4}}. \end{aligned} \tag{4.152}$$

Sinusoidal perturbation

Let us assume that the perturbation has a sinusoidal time dependence

$$V(t) = V(r)\cos\omega t = \frac{V(r)}{2}e^{i\omega t} + \frac{V(r)}{2}e^{-i\omega t}. \tag{4.153}$$

By employing this form in equation (4.26), we get

$$a_n^{(1)}(t) = -\frac{iV_{n,i}}{2\hbar}\left[\int_0^t e^{i(\omega_{n,i}+\omega)s}ds + \int_0^t e^{i(\omega_{n,i}-\omega)s}ds\right]. \tag{4.154}$$

After performing the integration, we obtain

$$a_n^{(1)}(t) = -\frac{V_{n,i}}{2\hbar}\left[\frac{e^{i(\omega_{n,i}+\omega)t}-1}{(\omega_{n,i}+\omega)} + \frac{e^{i(\omega_{n,i}-\omega)t}-1}{(\omega_{n,i}-\omega)}\right]. \tag{4.155}$$

Then, the transition probability reads:

$$\mathcal{P}_{i\to f} = \frac{|W_{f,i}|^2}{4\hbar^2}\left|\frac{e^{i(\omega_{n,f}+\omega)t}-1}{(\omega_{n,f}+\omega)} + \frac{e^{i(\omega_{n,f}-\omega)t}-1}{(\omega_{n,f}-\omega)}\right|^2. \tag{4.156}$$

If we suppose $\omega_{n,f} \simeq \omega$, then the transition probability takes the form of

$$\mathcal{P}_{i\to f} = \frac{|W_{f,i}|^2}{\hbar^2}\frac{\sin^2\left[(\omega_{n,f}-\omega)t/2\right]}{(\omega_{n,f}-\omega)^2}.$$

Here, we note that the transition probability reaches its peak value at $\omega_{n,f} = \omega$. The central peak has a height of $\frac{|W_{f,i}|^2}{4\hbar^2}$ and narrows over the time.

Interaction of atoms with electromagnetic radiation

The quantum-mechanical Hamiltonian describing a charged particle in the presence of magnetic radiation, characterized by a vector potential $\overrightarrow{A}(\overrightarrow{r},t)$, can be expressed as follows:

$$H = \frac{1}{2m}\left(\overrightarrow{p} + \frac{e}{c}\overrightarrow{A}\right)^2, \tag{4.157}$$

$$= \frac{\overrightarrow{p}^2}{2m} + \frac{e}{2mc}\overrightarrow{p}\cdot\overrightarrow{A} + \frac{e}{2mc}\overrightarrow{A}\cdot\overrightarrow{p} + \frac{e^2}{2mc^2}\overrightarrow{A}^2. \tag{4.158}$$

Neglecting the term $\overrightarrow{A}^2$ and imposing the Coulomb gauge condition on the vector potential

$$\overrightarrow{\nabla}\cdot\overrightarrow{A} = 0, \tag{4.159}$$

we re-write equation (4.157) as follows:

$$H = H_0 + V(t), \tag{4.160}$$

whereas the explicit forms of H_0 and $V(t)$ reads:

$$H_0 = \frac{\overrightarrow{p}^2}{2m}, \tag{4.161}$$

and

$$V(t) = \frac{e}{2mc}\overrightarrow{A}\cdot\overrightarrow{p}. \tag{4.162}$$

If we assume that the incident radiation takes the form of a plane wave with a specific polarization, $\overrightarrow{\varepsilon}$, and propagates along the direction $\overrightarrow{n}$, then the vector potential $\overrightarrow{A}$ can be represented by

$$\overrightarrow{A} = \sqrt{\frac{2\pi\hbar c^2}{\omega v}}\left(e^{i\left(\overrightarrow{k}\overrightarrow{r}-\omega t\right)} + e^{-i\left(\overrightarrow{k}\overrightarrow{r}-\omega t\right)}\right)\overrightarrow{\varepsilon}. \tag{4.163}$$

Using the vector potential in(4.162) leads to

$$V(t) = de^{-i\omega t} + d^{+}e^{i\omega t}, \tag{4.164}$$

where

$$d = \frac{e}{2mc}\sqrt{\frac{2\pi\hbar c^2}{\omega v}}e^{i\overrightarrow{k}\cdot\overrightarrow{r}}\overrightarrow{\varepsilon}\cdot\overrightarrow{p}, \tag{4.165}$$

$$d^{+} = \frac{e}{2mc}\sqrt{\frac{2\pi\hbar c^2}{\omega v}}e^{-i\overrightarrow{k}\cdot\overrightarrow{r}}\overrightarrow{\varepsilon}\cdot\overrightarrow{p}. \tag{4.166}$$

Then, the transition probability associated with this perturbation can be derived from (4.148),

$$\mathcal{P}_{i\to f} = \frac{1}{\hbar^2}\left|d_{f,i}\int_0^t e^{i(\omega_{f,i}-\omega)s}ds + d^{+}_{f,i}\int_0^t e^{i(\omega_{f,i}+\omega)s}ds\right|^2. \tag{4.167}$$

Successful integration yields to:

$$\mathcal{P}_{i\to f} = \frac{1}{\hbar^2}\left|\left\langle\Phi_f\right|d\left|\Phi_i\right\rangle\frac{e^{i(\omega_{f,i}-\omega)t}-1}{(\omega_{f,i}-\omega)} + \left\langle\Phi_f\right|d^{+}\left|\Phi_i\right\rangle\frac{e^{i(\omega_{f,i}+\omega)t}-1}{(\omega_{f,i}+\omega)}\right|^2. \tag{4.168}$$

By ignoring the cross terms, which are considered to be negligible in comparison to the other two terms, we rewrite the latter equation as

$$\mathcal{P}_{i\to f} = \frac{4}{\hbar^2}\left|\langle\Phi_f|\, d\,|\Phi_i\rangle\right|^2 \frac{\sin^2\left[\left(\omega_{f,i}-\omega\right)t/2\right]}{\left(\omega_{f,i}-\omega\right)^2} + \frac{4}{\hbar^2}\left|\langle\Phi_f|\, d^+\,|\Phi_i\rangle\right|^2 \frac{\sin^2\left[\left(\omega_{f,i}+\omega\right)t/2\right]^2}{\left(\omega_{f,i}+\omega\right)^2}\,. \tag{4.169}$$

We take the long times limit, $(t\to\infty)$, and make use the relation

$$\lim_{t\to\infty}\frac{\sin^2(xt)}{x^2 t} = \pi\delta(x)\,, \tag{4.170}$$

so that, the transmission probability reads:

$$\mathcal{P}_{i\to f} = \frac{2t}{\hbar}\left|\langle\Phi_f|\, d\,|\Phi_i\rangle\right|^2 \pi\delta\left(E_f-E_i-E\right) + \frac{2t}{\hbar^2}\left|\langle\Phi_f|\, d^+\,|\Phi_i\rangle\right|^2 2\pi\delta\left(E_f-E_i+E\right). \tag{4.171}$$

4.5 Exercises

Exercise 1

Consider the Hamiltonian

$$H = \frac{p^2}{2m} + \frac{k}{2}x^2 + \frac{\lambda}{2}x^2.$$

1 Find the exact energy of the n^{th} state of this Hamiltonian and expand it to order λ^2 assuming $|\lambda| < k$.

2 Use perturbation theory, treating $\frac{\lambda}{2}x^2$ as perturbation, and find the energy of n^{th} state to order λ^2.

Solution

1 Here

$$H = \frac{p^2}{2m} + \frac{k+\lambda}{2}x^2,$$

we define

$$\Omega^2 = \frac{k+\lambda}{m}; \omega^2 = \frac{k}{m}; \alpha^2 = \frac{\lambda}{m}.$$

The energy eigenvalue is given by

$$E_n = \hbar\Omega\left(n+\frac{1}{2}\right) = \hbar\sqrt{\omega^2+\alpha^2}\left(n+\frac{1}{2}\right).$$

we expand this in series in λ, we get

$$\begin{aligned} E_n &= \hbar\omega\left(n+\frac{1}{2}\right) + \frac{\hbar\alpha^2}{2\omega}\left(n+\frac{1}{2}\right) - \frac{1}{8}\frac{\hbar\alpha^4}{\omega^3}\left(n+\frac{1}{2}\right) + \ldots \\ &= \hbar\omega\left(n+\frac{1}{2}\right) + \frac{\hbar\lambda}{2m\omega}\left(n+\frac{1}{2}\right) - \frac{1}{8}\frac{\hbar\lambda^2}{m^2\omega^3}\left(n+\frac{1}{2}\right) + \ldots \end{aligned}$$

2 perturbation theory

First-Order correction:

$$\begin{aligned} E_n^{(1)} &= \lambda \langle n | H' | n \rangle, \\ &= \frac{\lambda}{2} \langle n | x^2 | n \rangle = \frac{\lambda\hbar}{4m\omega} \langle n | \left(a^{+2} + a^2 + 1 + 2a^+ a\right) | n \rangle, \\ &= \frac{\hbar\lambda}{2m\omega} \left(n + \frac{1}{2}\right). \end{aligned}$$

Second-Order Corrections

$$E_n^{(2)} = \lambda^2 \sum_{s \neq n} \frac{|\langle n | H' | s \rangle|^2}{E_n^{(0)} - E_s^{(0)}}.$$

$$\begin{aligned} \langle n | H' | s \rangle &= \frac{\hbar}{2m\omega} \langle n | \left(1 + a^{+2} + a^2 + 2a^+ a\right) | s \rangle, \\ &= \frac{\hbar}{2m\omega} \left(\sqrt{s(s-1)}\delta_{n,s-2} + \sqrt{(s+2)(s+1)}\delta_{n,s+2}\right), \end{aligned}$$

$$E_n^{(2)} = \frac{\hbar^2\lambda^2}{4m^2\omega^3} \left[\frac{s(s-1)\,\delta_{n,s-2}}{(n+1/2) - (s+1/2)} + \frac{(s+2)(s+1)\,\delta_{n,s+2}}{(n+1/2) - (s-3/2)}\right],$$

$$E_n^{(2)} = -\frac{\hbar^2\lambda^2}{8m^2\omega^3} \left(n + \frac{1}{2}\right).$$

Exercise 2

1 Determine the approximate ground state energy to second order for the Hamiltonian

$$H = \frac{p^2}{2m} + \frac{k}{2}x^2 + \frac{\lambda}{4}x^4,$$

using the perturbation theory.

2 Find the ground state correct to order λ

Solution

The unperturbed ground state energy is

$$E_0^{(0)} = \frac{\hbar\omega}{2}.$$

First-Order correction:

$$\begin{aligned} E_n^{(1)} &= \lambda \langle 0|H'|0\rangle = \frac{\lambda}{4}\langle 0|x^4|0\rangle = \frac{\lambda}{4}\left(\frac{\hbar}{2m\omega}\right)^2 \left\langle 0\left|\left(a+a^+\right)^4\right|0\right\rangle, \\ &= \frac{\lambda}{4}\left(\frac{\hbar}{2m\omega}\right)^2 \langle 0|\left(a^2a^{+2}+aa^+aa^+\right)|0\rangle = \frac{3\lambda}{16}\frac{\hbar^2}{m^2\omega^2}. \end{aligned}$$

Second-Order Corrections

$$E_n^{(2)} = \frac{\lambda^2}{16}\sum_{n\neq 0}\frac{\left|\langle n|x^4|0\rangle\right|^2}{E_n^{(0)}-E_0^{(0)}} = \frac{\lambda^2}{16}\left(\frac{\hbar}{2m\omega}\right)^4 \sum_{n\neq 0}\frac{\left|\left\langle n\left|\left(a+a^+\right)^4\right|0\right\rangle\right|^2}{E_n^{(0)}-E_0^{(0)}},$$

$$= \frac{\lambda^2}{16}\left(\frac{\hbar}{2m\omega}\right)^4 \sum_n \frac{\left|\sqrt{4!}\delta_{n,4}+6\sqrt{2}\delta_{n,2}\right|^2}{n} = -\frac{21}{8}\frac{1}{\hbar\omega}\left(\frac{\hbar\lambda}{2m\omega}\right)^4.$$

2 The wavefunction correct to order λ is

$$\begin{aligned} \left|\phi_0^{(1)}\right\rangle &= \frac{\lambda}{4}\sum_{k\neq 0}\frac{\langle k|x^4|0\rangle}{E_0^{(0)}-E_k^{(0)}}|k\rangle, \\ &= \frac{\lambda}{4}\left(\frac{\hbar}{2m\omega}\right)^4 \sum_{k\neq 0}\frac{\left\langle k\left|\left(a+a^+\right)^4\right|0\right\rangle}{E_0^{(0)}-E_k^{(0)}}|k\rangle, \end{aligned}$$

$$\left\langle k\left|\left(a+a^+\right)^4\right|0\right\rangle = \sqrt{4!}\delta_{k,4}+6\sqrt{2}\delta_{k,2}.$$

Therefore

$$\left|\phi_0^{(1)}\right\rangle = -\frac{\lambda}{4}\left(\frac{\hbar}{2m\omega}\right)^4\left[\frac{\sqrt{6}}{2\hbar\omega}|4\rangle+\frac{3\sqrt{2}}{\hbar\omega}|2\rangle\right].$$

Exercise 3

Utilize the variational approach to estimate the energy of the ground state of a one-dimensional harmonic oscillator. This can be achieved by employing two trial functions as follows:

a

$$\Psi = Ae^{-\alpha|x|},$$

b

$$\Phi = \frac{A}{x^2+\alpha},$$

where α is a positive real number and where A is the normalization constant.

Solution

a: normalization constant

$$\begin{aligned}\langle\Psi|\,\Psi\rangle &= \int dx\,|\Psi|^2 = 1,\\ &= |A|^2\int_{-\infty}^{0} e^{2\alpha x}dx + |A|^2\int_0^{\infty} e^{-2\alpha x}dx = \frac{|A|^2}{\alpha}.\end{aligned}$$

So, $A=\sqrt{\alpha}$. Next, we calculate $E(\alpha)=\langle\Psi|H|\Psi\rangle$,
The expectation value of the kinetic energy

$$\begin{aligned}\left\langle\Psi\left|p^2\right|\Psi\right\rangle &= -\hbar^2|A|^2\int_{-\infty}^{0} e^{\alpha x}\frac{d^2}{dx^2}e^{\alpha x}dx + |A|^2\int_0^{\infty} e^{-\alpha x}\frac{d^2}{dx^2}e^{-\alpha x}dx\\ &= \hbar^2\alpha^2.\end{aligned}$$

The expectation value of the potential

$$\langle\Psi|V(x)|\Psi\rangle = \frac{m\omega^2}{2}|A|^2\int_{-\infty}^{0} x^2e^{2\alpha x}dx + \frac{m\omega^2}{2}|A|^2\int_0^{\infty} x^2e^{-2\alpha x}dx.$$

Using the integral $\int_0^{\infty} x^n e^{-\alpha x}dx = \frac{n!}{\alpha^{n+1}}$, we find

$$\langle\Psi|V(x)|\Psi\rangle = \frac{m\omega^2}{4\alpha^2}.$$

$$E(\alpha) = \frac{\hbar^2\alpha^2}{2m} + \frac{m\omega^2}{4\alpha^2}.$$

The minimization of $E(\alpha)$

$$\frac{\partial}{\partial\alpha}E(\alpha) = \frac{\hbar^2\alpha}{m} - \frac{m\omega^2}{2\alpha^3} = 0 \Longrightarrow \alpha = \left(\frac{m^2\omega^2}{2\hbar^2}\right)^{1/4}$$

$\Longrightarrow$

$$E = 0.707\,11\hbar\omega.$$

b: normalization constant

$$\langle\Phi|\,\langle\Phi|\rangle = \int dx \frac{|A|^2}{\left(x^2+\alpha\right)^2} = |A|^2 \frac{\pi}{2\alpha^{3/2}} \Rightarrow A = \left(\frac{2\alpha^{3/2}}{\pi}\right)^{1/2}.$$

The ground state energy is given by

$$\begin{aligned} E(\alpha) &= \langle\Psi|H|\Psi\rangle \\ &= -\frac{\hbar^2}{2m}|A|^2 \int_{-\infty}^{+\infty} \frac{1}{x^2+\alpha}\frac{d^2}{dx^2}\frac{1}{x^2+\alpha}dx + \frac{m\omega^2}{2}|A|^2 \int_{-\infty}^{+\infty} \frac{x^2}{\left(x^2+\alpha\right)^2}dx, \end{aligned}$$

$$E(\alpha) = \frac{\hbar^2}{4\alpha m} + \frac{m\omega^2}{2}\alpha$$

minimization

$$-\frac{\hbar^2}{4\alpha^2 m} + \frac{m\omega^2}{2} = 0 \Longrightarrow \alpha = \frac{\hbar}{\sqrt{2}m\omega}.$$

$\Longrightarrow$

$$E = \frac{\sqrt{2}\hbar\omega}{2}.$$

Exercise 4

Consider the one-dimensional potential

$$V(x) = \frac{\lambda}{4}x^4 + \frac{\lambda a}{4}x^3 - \frac{\lambda a^2}{8}x^2.$$

Using the variational method, consider the trial wave function

$$\phi = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta(x+a)^2}.$$

Evaluate the expectation value of the energy for this wave function and find the equation defining the optimal values of the parameter β, in order to get an estimate of the ground-state energy. Now take a special, but reasonable, value of the coupling constant, $\lambda = \frac{\hbar^2}{ma^6}$, and obtain the corresponding estimate of the ground-state energy.

Solution

The expectation value of the kinetic energy

$$\langle T\rangle = -\frac{\hbar^2}{2m}\left(\frac{\beta}{\pi}\right)^{1/2}\int e^{-\beta(x+a)^2}\frac{d^2}{dx^2}e^{-\beta(x+a)^2} = \frac{\hbar^2\beta}{4m}.$$

The expectation value of the potential

$$\begin{aligned}\langle V\rangle &= \left(\frac{\beta}{\pi}\right)^{1/2}\int\left(\frac{\lambda}{4}x^4+\frac{\lambda a}{4}x^3-\frac{\lambda a^2}{8}x^2\right)e^{-2\beta(x+a)^2},\\ &= \frac{\lambda}{4}\left(\frac{3}{4\beta^2}+\frac{5a^2}{4\beta}-\frac{a^4}{2}\right).\end{aligned}$$

Thus we get

$$E(\beta) = \frac{\hbar^2}{4ma^2}\left[\beta a^2+\frac{\lambda ma^6}{\hbar^2}\left(\frac{3}{4a^4\beta^2}+\frac{5}{4a^2\beta}-\frac{1}{2}\right)\right].$$

Minimizing the energy with respect to $\theta = \beta a^2$, we get the equation

$$\theta^3-\frac{3\lambda ma^6}{2\hbar^2}-5\frac{\lambda ma^6}{4\hbar^2}\theta = 0,$$

for $\lambda = \frac{\hbar^2}{ma^6}$, there is a special exact solution, namely

$$\theta_0 = \frac{3}{2}\Longrightarrow E = \frac{13}{12}\frac{\hbar^2}{2ma^2}.$$

Exercise 5

A ball of mass m is acted on by uniform gravity g bouncing up and down an elastic floor. Take the floor to be the zero of the potential energy. Using WKB approximation obtain the quantized energy level of the system.

Solution

Suppose the ball is dropped from a height $z=a$ above the floor ($z=0$). The potential energy is $V=mgz$. We have one here, one, the floor and the other at $z=a$. If the energy is E, the turning point is E/mg. The quantization condition is

$$\int_0^{E/mg}\sqrt{2m\left(E-mgz\right)}dz=\int_0^{E/mg}\sqrt{2mE}\sqrt{1-\frac{mg}{E}z}dz=\pi\hbar\left(n+\frac{3}{4}\right).$$

Substituting $x=1-\frac{mg}{E}z\Longrightarrow dz=-\frac{E}{mg}dx$. The quantization condition then becomes

$$x=1-\frac{mg}{E}z$$

$$\begin{aligned}\int_0^{E/mg}\sqrt{2m\left(E-mgz\right)}dz &= \frac{\sqrt{\frac{2}{m}}E^{3/2}}{g}\int_0^1\sqrt{x}dx=\pi\hbar\left(n+\frac{3}{4}\right),\\ &= \left(\frac{8E^3}{9mg}\right)^{1/2}.\end{aligned}$$

The energy levels are

$$E=\left[\frac{9mg\pi^2\hbar^2}{8}\left(n+\frac{3}{4}\right)^2\right]^{1/3}.$$

Exercise 6

Calculate the energy levels of an electron in s- state bound to a nucleus by the potential $V\left(r\right)=\frac{-Ze^2}{r}$. The electron may be viewed as having a rigid wall as $r=a$ and $r=0$ where a is the turning point.

Solution

There is one turning point at $r=a$ where $E=-\frac{Ze^2}{a}\Longrightarrow a=-\frac{Ze^2}{E}$. In addition, there is a wall at $r=0$. The equation determining the energy is given by

$$\begin{aligned}\int_0^a p\left(r\right)dr &= \sqrt{2m}\int_0^a\sqrt{E+\frac{Ze^2}{r}}dr=\pi\hbar\left(n+\frac{3}{4}\right),\\ &= \sqrt{-2mE}\int_0^a\sqrt{\frac{a}{r}-1}dr,\\ &= \sqrt{-2mE}\frac{a\pi}{2}.\end{aligned}$$

Equating this to $\pi\hbar\left(n+\frac{3}{4}\right)$, we get

$$E_n = -\frac{mZ^2e^4}{2\hbar^2\left(n+\frac{3}{4}\right)^2}.$$

Exercise 7

A system of hydrogen atoms in the ground state is contained between the plates of a parallel-plate capacitor. A voltage pulse is applied to the capacitor so as to produce a homogeneous electric field

$$\mathcal{E} = 0 \qquad \text{for } t < 0,$$

and

$$\mathcal{E} = \mathcal{E}_0 e^{-\frac{t}{\tau}} \qquad \text{for } t < 0.$$

Show that, after a long time, the fraction of atoms in the $2p$ ($m = 0$) state is, to first order

$$\frac{2^{15}}{3^{10}} \frac{a_0^2 e^2 \mathcal{E}_0^2}{\hbar^2\left(\omega^2 + \frac{1}{\tau^2}\right)}$$

what is the fraction of atoms in the 2s state?

Solution

The probability that a transition has occurred to a state $|j\rangle$, with energy E_j at time t is $\left|c_j\right|^2$, where

$$c_j = \frac{1}{i\hbar}\int_0^t \langle j|V(t)|k\rangle e^{i\omega t'} dt'; \text{ with } \omega = \frac{E_j - E_k}{\hbar}.$$

In the present problem $V(t)$ is the potential of the electron in the applied electric field, whose direction we take as the $z-$axis, i.e.

$$V(t) = e\mathcal{E}z = e\mathcal{E}_0 z e^{-\frac{t}{\tau}}.$$

Fot $t \to \infty$, we have

$$c_j = \frac{e\mathcal{E}_0}{i\hbar}\langle j|z|k\rangle \int_0^\infty e^{\left(i\omega - \frac{1}{\tau}\right)t} dt.$$

The time integral is

$$\int_0^\infty e^{(i\omega-\frac{1}{\tau})t}dt = -\frac{1}{i\omega-\frac{1}{\tau}}.$$

Therefore

$$c_j = \frac{e\mathcal{E}_0}{\hbar}\frac{\langle j\,|z|\,k\rangle}{\omega+\frac{i}{\tau}}.$$

The initial state is the ground state of the hydrogen atom, I.e. the quantum numbers are $n=1,\ell=0,,m=0$ and the final state has $n=2,\ell=1,,m=0$. We evaluate the matrix element in spherical polar,

$$\langle j\,|z|\,k\rangle = \langle 2,1,0\,|z|\,1,0,0\rangle = \int d\overrightarrow{r}\,\psi^*_{2,1,0}(\overrightarrow{r})\,r\cos\theta\,\psi_{1,0,0}(\overrightarrow{r}),$$

where

$$\psi_{1,0,0}(\overrightarrow{r}) = \frac{2}{\sqrt{4\pi}}\frac{e^{-r/a_0}}{a_0^{3/2}},$$

$$\psi_{2,1,0}(\overrightarrow{r}) = \frac{1}{\sqrt{4\pi}}\frac{re^{-r/2a_0}}{a_0\left(2a_0\right)^{3/2}}\cos\theta.$$

Thus

$$\langle 2,1,0\,|z|\,1,0,0\rangle = \frac{1}{a_0^4 2^{3/2}}\int r^4 e^{-3r/2a_0}dr\int\cos^2\theta\sin\theta d\theta = \frac{4!}{2^{3/2}}\left(\frac{2}{3}\right)^6 a_0.$$

The probability of a transition is

$$\left|c_j\right|^2 = \frac{2^{15}}{3^{10}}\frac{a_0^2e^2\mathcal{E}_0^2}{\hbar^2\left(\omega^2+\frac{1}{\tau^2}\right)}.$$

The probability ofa transition to the state $n=2,\ell=0,m=0$ is zero. The wave functions $\psi_{1,0,0}$ and $\psi_{2,0,0}$ have positive parities, whereas the parity of the function z is negative. Consequently, the product's parity is negative as well, leading to a zero matrix element when integrated over all of space.

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