COURSE GUIDE

PHY 309
QUANTUM MECHANICS I

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INTRODUCTION

In Quantum Mechanics I (PHY 309), you learnt about the inadequacies of Classical Mechanics and the efforts made by Physicists to address the shortcomings on the platform of Quantum Mechanics. You have taken a look at the mathematical foundation necessary to understand that course. Once that was done, you learnt the application of quantum mechanics to the infinite as well as the finite potential well. The quantum treatment of the harmonic oscillator followed, culminating in Hermite's polynomials and the operator treatment of the harmonic oscillator.

PHY 409 is the second in the series of quantum mechanical courses. In the present course, you will start with further mathematics, laying a foundation of metric spaces and eventually, Hilbert spaces on which the inner product is defined. You will get to know that every Hilbert space has what we call a complete orthonormal basis, enabling us to handle a system which can be in a discrete set of states.

Later in the course, you will learn about the hydrogen-like atom, the spherically symmetric potential, leading to spherical harmonics and eventually, specific radial functions, completing the treatment of the simplest atom, that of hydrogen.

In the last module, further areas of quantum mechanics are discussed: perturbation and scattering. In perturbation theory, you will learn to handle small perturbations by modifying the more familiar related problem. Put another way, you will be able to deduce the energy levels and eigenfunctions of the perturbed system in terms of the eigenstates and eigenfunctions of the more familiar potential. You are already familiar with scattering in classical mechanics. Is there any difference in the case of quantum scattering, in which case, you have represented a particle by a wave?

You can see that you have a lot of interesting topics awaiting you in this course. Quantum mechanics is perhaps the most interesting part of Physics, and finds important applications of quantum theory include quantum chemistry, quantum optics, quantum computing, superconducting magnets, light-emitting diodes, and the laser, the transistor and semiconductors such as the microprocessor, medical and research imaging such as magnetic resonance imaging and electron microscopy. Explanations for many biological and physical phenomena are rooted in the nature of the chemical bond, most notably the macro-molecule DNA.

COURSE AIMS

The aim of the course is to equip you with the knowledge of fundamental aspects and derivations in the different areas of quantum mechanics especially inmathematical foundation,metric space, outer product, the projection operator and the completeness relation, angular momentum and spin of atomic and nuclear particles, three-dimensional spherically symmetric potentials and the polar angle equation, legendre polynomials.

COURSE OBJECTIVES

i. To introduce you to the concept of Convergence of a Sequence, Cauchy Sequence

   a. Banach Space, Hilbert Space Linear Map and Linear Functional.

ii. To define and give examples of a linear map, linear functional, explain and find the dual vector as well as to calculate the transition probability between one eigenstate and anotherLearners would be able to find the matrix elements of a linear operator, given the relevant basis vectors.

iii. To learn how to work with the spinors, find the Pauli spin matrices and calculate their eigenvectors and eigenvalues. In additionfind the solutions to the general Legendre equation, the associated Legendre functions.

iv. To evaluate integrals related to the hydrogen atom and expectation value of some physical observables in a given eigenstate of the hydrogen atom.

v. To show that radial wavefunction for a three-dimensional particle free to move inside a sphere satisfies the Bessel equation.

vi. To state the assumptions of the Born approximation and find the differential cross section for a given scattering potential in the Born approximation.

WORKING THROUGH THIS COURSE

The course is structured into four models. All the Modules consist of three unit each except .It is necessary that for the student to study and understand the content of all the units in the respective modules.

COURSE MATERIALS

You will be provided with the following materials:

1. Course Guide
2. Study Units

Module 1 The Mathematical Foundation

Unit 1	Metric Space, Hilbert Space
Unit 2	Linear Map, Linear Functional, Dual Vector Space
Unit 3	Commutator Algebra, Matrix Elements Of A Linear Operator
Unit 4	The Outer Product, The Projection Operator And The Completeness Relation

Module 2 Angular Momentum and Spin of Atomic and Nuclear Particles

Unit 1	Angular Momentum
Unit 2	Eigenfunctions of Angular Momentum I
Unit 3	Eigenfunctions of Angular Momentum II
Unit 4	Electron Spin I
Unit 5	Electron Spin II

Module 3

Unit 1	Three-Dimensional Spherically Symmetric Potentials
Unit 2	The Polar Angle Equation, Legendre Polynomials
Unit 3	Associated Legendre Functions, Angular Eigenfunctions
Unit 4	The Radial Equation
Unit 5	The Hydrogen Atom

Module 4 Perturbation Theory and Quantum Scattering

Unit 1	Perturbation Theory
Unit 2	Second Order Perturbation
Unit 3	Quantum Scattering I
Unit 4	Scattering II - The Born Approximation
Unit 5	Scattering III - Partial Wave Analysis

TEXTBOOKS

At the end of each unit of the course, there are reference materials to which you can refer in order to increase the depth of your knowledge on the course. Please take this seriously.

ASSIGNMENT FILES

A number of assignments have been prepared to help you succeed in this course. They will guide you to have understanding and good grasp of the course.

PRESENTATION SCHEDULE

The presentation schedule included in your course materials also have important dates of the year for the completion of tutor-marked assignments (TMAs) and your attendance at tutorials.
Remember, you are to submit all your assignments by the due date. You should guard against falling behind in your work.

ASSESSMENTS

There are two aspects to the assessment of the course: first are the tutor-marked assignments and a written examination.

In tackling the assignments, you are expected to apply information, knowledge and techniques gathered during the course. The assignments must be submitted to your tutor for formal assessment in accordance with the deadlines stated in the presentation schedule and the assignment file. The work you submitted to your tutor will count for 30 percent of your total course mark.

At the end of the course, you will need to sit for a final written examination of three hour duration. This examination will also count for 70 percent of your total coursework.

TUTOR-MARKED ASSIGNMENTS (TMAs)

Each of the units in the course material has a tutor-marked assignment (TMA) in this course. You only need to submit five of the eight assignments. You are to answer all the TMAs and compare your answers with those of your course mates. However, you should ensure that you collect four (TMAs) from the Study Centre. It is compulsory for you to answer four (4) TMAs from the Study Centre. Each TMA is allocated a total of 10 marks. However, the best three (3) of the four marks shall be used as your continuous assessment score.

You will be able to complete your assignment from the information and materials contained in your reading, references and study units. However, it is desirable in all degree level education to demonstrate that you have read and researched more widely than the required minimum.

Using other references will give you a broader viewpoint and may provide a deeper understanding of the subject.

FINAL EXAMINATION AND GRADING

The final examination for BFN721 will not be more than three hours' duration and has a value of 70 percent of the total course grade. The examination will consist of questions, which reflect the types of practice exercises and tutor-marked problems you have previously encountered. All areas of the course will be assessed.

When you have gone through the whole course, ensure you revise it again before sitting for the final examination. You may find it useful to review your tutor-marked assignments and comments on them before the examination. The final examination covers information from all parts of the course.

COURSE MARKING SCHEME

Table showing the total course marking scheme is shown below:

ASSESSMENT	MARKS
Assignment 4 (TMAs)	Best three marks of the 4 TMAs @ 10 marks is 30 marks of the course = 30%
Final Examination	70% of overall course marks
Total	**100% of course marks**

HOW TO GET THE MOST FROM THIS COURSE

In distance learning, the study units replace the university lecturer. This is one of the great advantages of distance education. You can read and work through the specially designed study materials at your own pace, and at a time and place that suits you best. Think of it as you read the lecture notes and that a lecturer might set you some readings to do.

The study unit will tell you when to read your other materials. Just as a lecturer might give you an in-class exercise, your study units also provide assignments for you to do at appropriate points.

Each of the study units follows a common format. The first item is an introduction to the subject matter of the unit, and how a particular unit is related with the other units and the course as a whole.

Next is a set of learning objectives. These objectives let you know what you should be able to do by the time you have completed the unit. You

should use these objectives to guide your study. When you have finished the unit, you must go back and check whether you have achieved the objectives set. If you make a habit of doing this, you will significantly improve your chances of passing the course.

The main body of the unit guides you through the required reading from other sources. This will usually be either from **Reading Section** or some other sources.

Self-tests/assignments are interspersed throughout the end of units. Working through these tests will help you to achieve the objectives of the unit and prepare you for the examinations. You should do each of the assignments as you come to it in the study unit. There will also be numerous examples given in the study units, work through these when you come to them too.

The following is a practical strategy for working through the course. If you run into any trouble, telephone your tutor. When you need help, don't hesitate to call and ask your tutor to provide it. In summary:

(1) Read this course guide.

(2) Organise a study schedule. Refer to the course overview for more details. Note the time you are expected to spend on each unit and how the assignments relate to the unit. Important information e.g. details of your tutorials and the date of the first day of the semester is available. You need to gather together all information in one place, such as your diary or a wall calendar. Whatever method you choose to use, you should decide on and write in your own dates for working on each unit.

(3) Once you have created your own study schedule, do everything you can to stick to it. The major reason that students fail is that they get behind with their coursework. If you get into difficulty with your schedule, please let your facilitator know before it is too late for help.

(4) Turn to unit 1 and read the introduction and the objectives for the unit.

(5) Assemble the study materials. Information about what you need for a unit is given in the 'Overview' at the beginning of each unit. You will always need both the study unit you are working on and one of your set books, on your desk at the same time.

(6) Work through the unit. The content of the unit itself has been arranged to provide a sequence for you to follow. As you work through this unit, you will be instructed to read sections from your set books or other articles. Use the unit to guide your reading.

(7) Well before the relevant due dates (about 4 weeks before the dates) access the Assignment file on the web and download your next required assignment. Keep in mind that you will learn a lot by doing the assignments carefully. They have been designed to help you meet the objectives of the course and, therefore, will help you pass the examination. Submit all assignments not later than the due dates.

(8) Review the objectives for each study unit to confirm that you have achieved them. If you feel unsure about any of the objectives, review the study material or consult your tutor.

(9) When you are confident that you have achieved a unit's objectives, you can then start on the next unit. Proceed unit by unit through the course and try to pace your study so that you keep yourself on schedule.

(10) When you have submitted an assignment to your tutor for marking, do not wait for its return before starting on the next unit. Keep to your schedule. When the assignment is returned, pay particular attention to your facilitator's comments. Consult your tutor as soon as possible if you have any questions or problems.

(11) After completing the last unit, review the course and prepare yourself for the final examination. Check that you have achieved the unit objectives and the course objectives.

TUTORS AND TUTORIALS

There are eight (8) hours of tutorials provided in support of this course. You will be notified of the dates, times and location of these tutorials, together with the names and phone number of your tutor, as soon as you are allocated a tutorial group.

Your tutor will mark and comment on your assignments, keep a close watch on your progress and on any difficulties you might encounter as they would provide assistance to you during the course. You must mail your tutor-marked assignments to your tutor well before the due date (at least two working days are required). They will be marked by your tutor and returned to you as soon as possible. Do not hesitate to contact your

tutor by telephone, e-mail, or discussion board if you need help. The following might be circumstances in which you would find help necessary.

Contact your tutor if you:

- do not understand any part of the study units or the assigned readings;
- have difficulty with the tutor-marked assignments;
- have a question or problem with an assignment or with your tutor's comments on an assignment or with the grading of an assignment.

You should try your possible best to attend the tutorials. This is the only chance to have face-to-face contact with your tutor and to ask questions which are answered instantly. You can raise any problem encountered in the course of your study during such contact. To gain the maximum benefit from course tutorials, prepare a question list before attending them. You will learn a lot from participating in discussions actively.

SUMMARY

On successful completion of the course, you would have gained immense knowledge on applications of quantum theory which include quantum chemistry, quantum optics, quantum computing, superconducting magnets, light-emitting diodes, and the laser, the transistor and semiconductors such as the microprocessor, medical and research imaging such as magnetic resonance imaging and electron microscopy. Explanations for many biological and physical phenomena are rooted in the nature of the chemical bond, most notably the macro-molecule DNA.

However, to gain a lot from the course please try to apply anything you learn in the course to term papers writing. We wish you success with the course and hope that you will find it fascinating and handy.

MAIN COURSE

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MODULE 1 THE MATHEMATICAL FOUNDATION

UNIT 1 METRIC SPACE, HILBERT SPACE

CONTENTS

1.0 INTRODUCTION

A vector space is one in which we can carry out the addition of two vectors and the scalar multiplication of a vector without worrying about whether the outcome of our operation falls outside the allowable possibilities, which in this case is the vector space itself. In the language of mathematics, this would mean that a vector space is closed under the two operations of vector addition and scalar multiplication. We have seen in PHY 309 that the idea of a vector has been generalised to include any mathematical structure on which we can define these two operations and have shown that the resulting space is closed under the two operations. We also gave some examples, including the space of the usual Euclidean vectors, the space of $m \times n$ matrices and the space of square integrable functions of x. We should be able to measure a form of 'distance' on a vector space. For this, we defined a norm, a function that assigns a positive length to each vector, apart from the zero vector, which has length zero, the distance of a point from itself. The norm can be visualised as the distance of a vector from the origin. In this Unit, you will get to know more about vector spaces and the additional

requirement a vector space should possess to be useful in the field of Quantum Mechanics. Having defined the distance of a vector from the origin, we could go on to define the distance between the endpoints of two vectors. For this, the term **metric** is defined. Once the metric is defined on a vector space, it becomes a metric space, and we are in a position to study the convergence of sequences in such a space. This naturally leads to the concept of completeness of a metric space. A complete normed vector space is a Banach space. If the norm is defined by the inner product, the complete normed space is a Hilbert space. Quantum Mechanics is done in a Hilbert space, or put another way, the Hilbert space is the space in which vectors in Quantum Mechanics live.

2.0 OBJECTIVES

At the end of this study session you will be able to:

- define metric space
- list and explain the properties of a metric space
- prove whether or not a given space is a metric space
- give examples of a metric space
- define and explain convergence of a sequence in a metric space
- explain what is meant by a Cauchy sequence
- explain what is meant by a complete metric space
- complete a given metric space
- define Banach space and Hilbert space
- discuss the relationship between Banach space and Hilbert space
- explain why Quantum Mechanics is done in a Hilbert space

3.0 MAIN CONTENT

3.1 Metric Space

3.1.1 Definition

A metric space is a non-empty set V such that for every x and y in V, there is a non-negative number, called the metric, a kind of 'distance,' which satisfies a certain set of axioms. Naturally, when such a concept of 'distance' involves three points, it should satisfy the law of triangle inequality, which stipulates that no single side of a triangle should be longer than the sum of the remaining two. The maximum possible value of the length of one side is equal to the sum of the remaining two. This is the case of a degenerate triangle in which all three vertices are collinear (along the same line). We would also expect the distance from point A to point B to be the same as the distance from point B to point A (symmetry). Finally, since a metric is a kind of 'distance,' it should be

such that the metric of a point from itself be zero, and zero metric imply the distance from the same point to itself (definiteness). These are outlined below in the language of Mathematics.

Mathematically, a metric is a function $d : V \times V \to R^+$, satisfying for all $f, g, h \in V$:

(i) $d(f,g) \le d(f,h) + d(h,g)$ (Triangle inequality)
1.1

(ii) $d(f,g) = d(g,f)$ (Symmetry)
1.2

(iii) $d(f,g) = 0$ if and only if $f = g$ (Definiteness)
1.3

An inner product induces a norm, and a norm induces a metric.

$$(a,b) \to \| a \| = \sqrt{(a,a)} \to \| a - b \|$$

Recall that we said that the norm is the 'distance' of a vector from the origin. You could see a metric as the 'distance' between the ends of two vectors, or equivalently, the distance between the two vectors.

We define a metric space as a vector space V equipped with a metric d, written as (V,d).

We take some examples:

(i) One of the simplest examples of a metric space is the real number line. An example of a metric on the vector space is the absolute value metric,
$$d(x,y) = | x - y |$$
1.4

(ii) Given the vector space *V*, we can define the metric
$$d(x,y) = \begin{cases} 0, & \text{if } x = y \\ 1, & \text{otherwise} \end{cases}$$

Thus, no pair of points are close. Every pair of points is apart. This is thus called a discrete metric.
You can easily see that if we replace 1 in the definition by *a*, the distance between two distinct pair of points is *a*.

(iii) In the case of the two-dimensional (Euclidean) vector space V_2, if the position vector of a is $a_x \mathbf{i} + a_y \mathbf{j}$ and that of b is $\mathbf{i} b_x + \mathbf{j} b_y$, we can define the metric

$$d(a,b) = \sqrt{(b_x - a_x)^2 + (b_y - a_y)^2} \qquad 1.5$$

This is called the usual metric on the two-dimensional Euclidean space. It is the distance between the two points *a* and *b* on the *x-y* plane. It is the usual metric because that is the concept of distance on a plane you have always been familiar with.

(iv) Consider the *x-y* plane $(\Re^2)$ as a vector space, together with the taxicab metric,

$$d((x_1, y_1),(x_2, y_2)) = | x_1 - x_2 | + | y_1 - y_2 | \qquad 1.6$$

As you can see, with the taxicab metric, the distance between two points is the sum of the absolute differences of their Cartesian coordinates, unlike the usual metric that is the square root of the sum of the squares of the difference between their Cartesian coordinates.

(iv) The metric induced by the supremum (at times shortened sup) norm on $\Re^2$,

$$d((x_1, y_1),(x_2, y_2)) = \max(| x_1 - x_2 | + | y_1 - y_2 |) \qquad 1.7$$

The sup norm is,

$$\| x \| = \max(| x_1 | + | x_2 |)$$

where $\mathbf{x} = (x_1, x_2)$ for $\mathbf{x} \in \Re^2$.

(v) For the space of continuous real-valued functions of *x* over the interval (a,b),

$$d(f, g) = \int_a^b | f(x) + g(x) | dx \qquad 1.8$$

Example 1.1

Given the metric space (X, d), show that $| d(x,z) - d(z,y) | \leq d(x,y)$.

Solution 1.1

$$d(x,z) \leq d(x,y) + d(y,z) \quad \text{(triangle inequality)} \quad 1.9$$

from which,

$$d(x,y) \geq d(x,z) - d(y,z) \qquad 1.10$$

Similarly, from triangle inequality,

$$d(y,z) \le d(y,x) + d(x,z) \qquad 1.11$$

or

$$d(y,z) - d(x,z) \le d(x,y) \qquad 1.12$$

Multiplying equation 1.12 by -1 reverses the inequality:

$$-d(y,z) + d(x,z) \ge -d(x,y)$$

Combining equations 1.10 and 1.12,

$$-d(x,y) \le d(x,z) - d(y,z) \le d(x,y) \qquad 1.13$$

Hence,

$$|\, d(x,z) - d(z,y) \,| \le d(x,y) \qquad 1.14$$

Self-Assessment Exercise 1

List and explain the properties of a metric space.

3.1.2 Convergence of a Sequence, Cauchy Sequence

Let $\{x_n\}$, where $n \in N$, be a sequence in a metric space (V,d). We say that x_n converges to x (that is, (x_n) converges to $x \in V$) or $x_n \to x$, if for $\varepsilon > 0$, there exists $N \in \aleph$ such that $d(x_n, x) < \varepsilon$ for all $n > N$. More loosely, we say x_n converges to x if $\lim_{n\to\infty} d(x_n, x) = 0$.

In a normed linear space (a vector or linear space on which a norm is defined), (x_n) converges to x implies $\lim_{n\to\infty} \| x_n - x \| = 0$.

A sequence (x_n) is said to be a **Cauchy sequence** when $d(x_n, x_m) \to 0$ when n, $m \to \infty$. Or more precisely, for a Cauchy sequence, for $\varepsilon > 0$, there exists $N \in \aleph$ such that $d(x_n, x_m) < \varepsilon$ for all $n, m > N$.

In more plain terms, a Cauchy sequence is one whose elements become arbitrarily close as the sequence progresses.

A convergent sequence is Cauchy, because, owing to the triangle inequality,

$$d(x_n, x_m) \le d(x_n, x) + d(x, x_m) < (\varepsilon/2) + (\varepsilon/2) = \varepsilon \qquad 1.15$$

since for a given $\varepsilon > 0$, there exists $N \in \aleph$ (a natural number *N*), such that $d(x_n, x) < \varepsilon/2$ and $d(x, x_m) < \varepsilon/2$, because the sequence is convergent. (Recall the triangle inequality which stipulates that no

single side of a triangle could be longer than the sum of the remaining two sides. The longest it can be is the sum of the other two sides.)

Thus, all convergent sequences are Cauchy, but not all Cauchy sequences converge. As an example, in the metric space (0, 1) with the absolute value metric $d(x, y) = |x - y|$, the sequence $x_n = 1/n$ does not converge in (0, 1). It does converge in [0, 1] however. Note that $1/n$ converges to 0, which is not included in (0, 1).

SELF-ASSESSMENT EXERCISE 2

Why is the definition of Cauchy convergence involving a small number ε considered more precise than that for which the metric $d(x_n, x_m) \to 0$?

3.2 Banach Space, Hilbert Space

We say a metric space (V, d) is **complete** if every Cauchy sequence converges to a point in the metric space.

Not all Cauchy sequences converge. For instance, the set of rational numbers is not complete, because $\sqrt{2}$, for example, is "missing" from it. Yet, we can construct a Cauchy sequence that converges to $\sqrt{2}$. The sequence, $1.4, 1.41, 1.414, 1.4142, 1.41421, \ldots$ which can be shown to be Cauchy, converges to $\sqrt{2}$, which is an irrational number. Hence, the set of rational numbers is not complete. However, we can "fill all the holes." That is, we can enlarge (complete) a metric space to contain the limit of any of its Cauchy sequences. If this metric is on a normed linear space, this gives us a **Banach space**. If we enlarge an inner product space to include the limit of any of its Cauchy sequences, we get a **Hilbert space**. Put another way, the Cauchy completion of a normed linear space is a Banach space, and the Cauchy completion of an inner product space is called a Hilbert space. A normed linear space is a space on which a norm is defined. An inner product space is a normed linear space in which the norm is induced by the inner product.

In the example in 1.1.2, on the real number line, (0, 1) is an open set (alternatively an open interval). As such, 0 and 1 are not elements of the set. [0, 1) is half-open, containing 0, but not 1. (0, 1] is also half-open, containing 1, but not zero. [0, 1] is a closed set, and is the closure of the open set (0, 1) or the half open sets [0, 1) and (0, 1]. The closure of a set is written by writing the symbol for the set and putting a bar on top. So, if $T = (0,1)$, $\overline{T} = [0,1]$. This is achieved by adding the limits of the set, in this case, the singletons (a set with only one element) $\{0\}$ and $\{1\}$. Thus, [0, 1] = $(0, 1) \cup \{0\} \cup \{1\}$. You can now see that the sequence in

question converges within the closed interval. Thus, we say that the closed interval [0, 1] is complete with the absolute value metric.

For any metric space M, we can equally construct a complete metric space $\overline{M}$, which contains M as a dense subspace. That is, for $x \in \overline{M}$, any neighbourhood of x contains at least one point from M. What does this mean? Let us take $x \in M \subset \overline{M}$, and there is nothing to prove, since any neighbourhood of x contains at least one point in *M*. We should therefore bother about a point on the boundary ∂M. In this case, we note that the smallest space that contains *M* as a proper subset is $\overline{M}$. Thus, for $x \in \partial M$, any neighbourhood of *x* contains at least one point in *M*. A subspace inherits all the properties of the space of which it is a subspace.

Fig. 1.1shows an open ball (Fig. 1.1a) and its closure (Fig. 1.1b). Point *x* on the boundary of the closed ball has neighbours both within and outside the open ball.

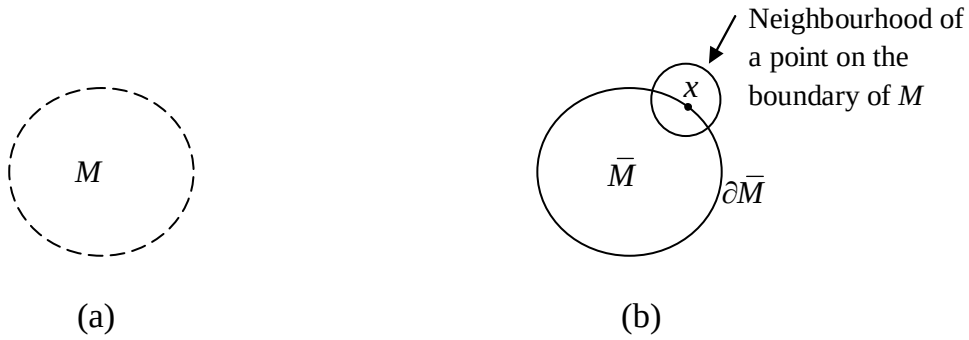

Fig. 1.1: Showing that the open ball (a) is dense in the closed ball (b)

Consequently, a Banach space is a complete normed space, that is, a normed space that is complete under the metric induced by the norm.

A Hilbert space is a Banach space in which the norm is induced by the inner product. Or a Hilbert space is a (Cauchy) complete inner product space. A Hilbert space is a Banach space, but not every Banach space is a Hilbert space. Hilbert $\subset$ Banach.

SELF-ASSESSMENT EXERCISE 3

State which of the following is an open or a closed set. If an open set, state the set needed to make it a closed set.

(i) (-1, 1)
(ii) [-1, 1]
(iii) [2, 9)
(iv) (3, 7]

Why Hilbert Spaces. For one, a Hilbert space is complete, meaning that we have no problem of convergence. Completeness in this case means that if a sequence of vectors is Cauchy, then it converges to a limit in the space. In effect, eigenvectors or eigenfunctions in Quantum mechanics live inside Hilbert space.

Moreover, Zorn's lemma (via the Hahn-Banach theorem in Functional Analysis) ensures that every non-empty Hilbert space has an orthonormal basis. Thus, we can expand any wavefunction as a linear combination of "elements" of the appropriate orthonormal basis.

In an inner product space, the inner product defines the norm of a vector $|\psi>$ in the vector space as $<\psi|\psi>=\|\psi\|^2$, and also enables us to write $<\psi, A\psi>$ or $<\psi|A\psi>$, the expectation value of the physical observable represented by the operator A in state $|\psi>$. The norm $<\psi|\psi>$ is a precursor to the normalisation of a vector (or wavefunction), which in turn leads to definition of probabilities in Quantum mechanics.

Note:
An element of a Hilbert space can be uniquely specified by its coordinates with respect to an orthonormal basis, in analogy with Cartesian coordinates. When the basis is countably infinite, this means that the Hilbert space can also be thought of in terms of infinite sequences that are square summable. You would recall from PHS 307 and PHS 302 that if $|\psi>$ is normalised, and $\{\phi_i\}_{i=1}^{\infty}$ is an orthonormal set, then,

$$<\psi|\psi>=\left(\sum_{i=1}^{\infty}c_i\phi_i,\sum_{j=1}^{\infty}c_j\phi_j\right)=\sum_{i=1}^{\infty}c_i^*\sum_{j=1}^{\infty}c_j(\phi_j,\phi_i)$$

$$=\sum_{i=1}^{\infty}c_i^*c_i=\sum_{i=1}^{\infty}|c_i|^2=1 \qquad 1.16$$

Examples of finite-dimensional Hilbert spaces include the real numbers with the dot product $<\mathbf{u},\mathbf{v}>=\mathbf{u}^T\mathbf{v}$ and the complex numbers with the vector dot product $<\mathbf{u},\mathbf{v}>=\mathbf{u}^+\mathbf{v}$. Examples of infinite-dimensional Hilbert space are, the set of all square integrable functions with the inner product defined as $<f,g>=\int_{-\infty}^{\infty} f(x)g(x)dx$ and the set of square integrable complex valued functions with the inner product defined as $<f,g>=\int_{-\infty}^{\infty} f^*(x)g(x)dx$. Square integrable in these cases is meant in the sense, respectively, $<f,f>=\int_{-\infty}^{\infty}[f(x)]^2dx<\infty$ and $<f,f>=\int_{-\infty}^{\infty}|f(x)|^2\,dx<\infty$.

4.0 CONCLUSION

In this Unit, you have learnt the background mathematical concepts that define the environment in which Quantum Mechanics operates. The word quantum itself implies a set of states in which a given physical system can exist. Each of the possible states is called a vector. You also learnt how to define a 'distance' on a vector space, so that you can find the distance between any two points on the vector space of interest. The vectors in Quantum Mechanics live in a Hilbert space, ensuring that we can expand any given state of the system as a linear combination of the possible states in which it can be found. This is possible because a Hilbert space is complete.

5.0 SUMMARY

In this Unit, you have learnt that:

- a metric space is complete if every Cauchy sequence converges to a point in the metric space
- a normed linear (vector) space is a space on which a norm is defined
- a complete normed linear space is a Banach space
- a complete normed linear space with the norm defined by the inner product is a Hilbert space
- every Hilbert space is a Banach space

Answer to Self-Assessment Exercise 1

A metric is a function $d:V\times V\rightarrow R^+$, satisfying for all $f,g,h\in V$:

(i) $d(f,g)\leq d(f,h)+d(h,g)$ (Triangle inequality)

The law of triangle inequality stipulates that no single side of a triangle can be longer than the sum of the remaining two sides. The endpoints of the vectors *f*, *g* and *h* form a triangle. As such the 'lines' joining the endpoints must form a triangle, obeying the triangle inequality.

(ii) $d(f,g) = d(g,f)$ (Symmetry)

The 'distance' from one point to another must be the same, irrespective of the start point and the end point.

(iii) $d(f,g) = 0$ if and only if $f = g$ (Definiteness)

The distance between a point must be zero, and if the distance between the endpoints of the vectors *f* and *g* is zero, they must be the same point.

Answer to Self-Assessment Exercise 2

A sequence (x_n) is said to be a **Cauchy sequence** when $d(x_n, x_m) \to 0$ when $n,\ m \to \infty$. Or more precisely, for a Cauchy sequence, for $\varepsilon > 0$, there exists $N \in \aleph$ such that $d(x_n, x_m) < \varepsilon$ for all $n, m > N$.

The case involving ε is stricter because we are able to find a finite natural number N such that the condition of Cauchy sequence is satisfied.

Answer to Self-Assessment Exercise 3

(i) (-1, 1) open set, {-1} and {1} needed to added to get the closed set [-1, 1]
(ii) [-1, 1] closed set
(iii) [2, 9) half-open set, {9} needed to be added to get the closed set [2, 0]
(iv) (3, 7] half-open set, {3} needed to be added to get the closed set [3, 7]

6.0 TUTOR-MARKED ASSIGNMENT

1. Justify whether or not each of the following is a metric space.

(a) $\Re^2$ with $d((x_1, x_2),(y_1, y_2)) = |x_1 - y_1|$.
(b) The real number line with $d(x_1, x_2) = |x_1^{\,2} - x_2^{\,2}|$
(c) $\Re^2$ with $d(a,b) = \sqrt{(a_x - b_x)^2 + (a_y - b_y)^2}$.

2 (a) When is a sequence said to be Cauchy?
(b) Give an example of a Cauchy sequence that does not converge.
(c) What is the relationship between a Hilbert space and a Banach space?

3. Consider a Hilbert space with a scalar product $(\cdot,\cdot)$. Prove the law of triangle inequality, $\| f+g \| \leq \| f \| + \| g \|$.
Hint: $(f,g) \leq |(f,g)|$ and Cauchy-Schwarz inequality, $|(f,g)| \leq \| f \| \times \| g \|$

4. Prove the Cauchy-Schwarz inequality, $|(\mathbf{u},\mathbf{v})| \leq \| \mathbf{u} \| \times \| \mathbf{v} \|$, for two vectors **u** and **v** in the 2-dimensional (complex) Hilbert space. Assume the complex number $\alpha = \frac{(\mathbf{v},\mathbf{u})}{\| \mathbf{v} \|^2}$ and the fact that $\| \mathbf{u} - \lambda \mathbf{v} \|^2 \geq 0$.

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UNIT 2 LINEAR MAP, LINEAR FUNCTIONAL, DUAL VECTOR SPACE

CONTENTS

1.0 INTRODUCTION

In PHY 309, you noticed that the concept of vector space is necessary in the description of a quantum-mechanical system as it can exist in a set of possible eigenstates. We often have to go from one vector space to another. A linear map is a ‘good’ function that enables us to take vectors from one vector space to another. If a linear function acts on the sum of two vectors in the first vector space, the result is the same as the linear function taking each vector into the other vector space and adding the two resulting functions in the new space. This means the function is additive. In addition, a linear function taking a linear multiple of a vector to another vector space is equivalent to that linear multiple (not a power of it different from 1) multiplied by the output of the function in the new vector space. A linear map is between two vector spaces. A linear functional is a linear map between a vector space and its underlying field. Recall that while defining a vector space, we referred to an underlying field, in which the scalar in the definition of the vector space resides.

In PHY 309, you noticed that we took the Hermitian conjugate of the first of two vectors involved in an inner product. In this unit, you will get to know that such a vector resides in what we call a dual vector space.

2.0 OBJECTIVES

At the end of this Unit, you should be able to:

- define and give examples of a linear map
- define and give examples of a linear functional
- explain the term dual vector space
- find the dual of a given vector
- work with the Dirac (bra and ket) notation
- calculate the transition probability between one eigenstate and another.

3.0 MAIN CONTENT

3.1 Linear Map

A linear map $f : X \to Y$ between vector spaces X and Y is a function which preserves vector addition and scalar multiplication, i.e.

$$f(x_1 + x_2) = f(x_1) + f(x_2) \qquad 2.1$$

$$f(\lambda x) = \lambda f(x) \text{ for } \lambda \in K \text{, a constant, and } x_1, x_2 \in X \qquad 2.2$$

We could lump these into a single requirement:

$$f(ax_1 + bx_2) = af(x_1) + bf(x_2) \qquad 2.3$$

3.1.1 Examples of Linear Maps

1. The zero map $f : X \to Y$, taking all vectors in vector space X to the zero vector in vector space Y.
2. The identity map $f : X \to Y$, taking each vector in vector space X to itself in the same vector space X.
3. The map $f : X \to Y$, such that $f(x) = 2x$.

$$f(ax_1 + bx_2) = 2(ax_1 + bx_2) = a(2x_1) + b(2x_2) = af(x_1) + bf(x_2)$$

3.2 Linear Functional

We could consider the underlying field, K, of the vector space as a vector space. In most problems in Physics, the underlying field is either the real number line or the complex plane. Each of these can be considered a linear space – a sum of any two vectors is also in the set, as well as a scalar multiplication.

A linear functional (or linear form or one-form or covector) $g : X \to K$ is a linear map (or linear function) from the vector space X to K, the underlying field of X, with K considered as a vector space, i.e.,

$$g(x_1 + x_2) = g(x_1) + g(x_2) \qquad 2.4$$

$$g(\lambda x) = \lambda g(x) \text{ for } \lambda \in K \text{, a constant, and } x_1, x_2 \in X \qquad 2.5$$

Equivalently,

$$g(ax_1 + bx_2) = ag(x_1) + bg(x_2) \qquad 2.6$$

Thus, a linear functional is a function from a vector space to its underlying field that is additive and homogeneous. Remember these are the two major characteristics of a vector space. Indeed, all the properties of a vector space are also the same for linear functionals.

3.3 Dual Vector Space

The set of all linear functionals from X to K is a vector space over K, called the dual vector space of X.

For example, if vectors in R^n are represented as column vectors,

$$\mathbf{x} = \begin{bmatrix} x_1 \\ . \\ . \\ x_n \end{bmatrix} \qquad 2.7$$

then any linear functional can be written in these coordinates as a sum of the form

$$f(\mathbf{x}) = a_1 x_1 + ... + a_n x_n \qquad 2.8$$

which is the matrix product of the row vector $[a_1 \quad . \quad . \quad a_n]$ and $\mathbf{x}$:

$$f(\mathbf{x}) = [a_1 \quad . \quad . \quad a_n] \begin{bmatrix} x_1 \\ . \\ . \\ x_n \end{bmatrix} \qquad 2.9$$

$[a_1 \quad . \quad . \quad a_n]$ is a matrix of constant elements and the right hand side of 2.9 gives a number in the underlying field.

As you can see in this expression, you need a dual vector (linear functional or covector) (from the dual vector space of the vector space) on the left and a vector (from the vector space) on the right to get an inner product. Thus, a linear functional $[a_1 \quad . \quad . \quad a_n]$ has taken a vector $\begin{bmatrix} x_1 \\ . \\ . \\ x_n \end{bmatrix}$ from the vector space to the underlying field. What you get out of this is a member of the underlying field. For a real vector space, you will get a real number; for a complex vector space, you will get a complex number in general. If you put the vector on the left and the dual vector on the right, you are not going to get a scalar. That indeed would be the outer product. The ket $|\psi>$ denotes the vector in a Hilbert space while the bra $<\psi|$ denotes a linear functional or covector in the dual vector space. This is why the dual vector space is also called the space of linear functionals over the vector space. Indeed, the dual of a Banach space is also a Banach space. The corollary is already implied: the dual of a Hilbert space is also a Hilbert space.

Let us take a direct example: The vectors $\begin{pmatrix} i \\ -1 \end{pmatrix}$ and $\begin{pmatrix} 1 \\ -1 \end{pmatrix}$ are in the vector space of column vectors over the field of complex numbers. Notice that the second vector might not have entries involving i. Nonetheless, it is still from the vector space of interest. It just so happens that the imaginary part of each component is zero. You might see the two vectors more generally in this way $\begin{pmatrix} 0+i \\ -1+0i \end{pmatrix}$ and $\begin{pmatrix} 1+0i \\ -1+0i \end{pmatrix}$.

To take the inner product, we write find the dual equivalent of the first vector, or in our present language, the equivalent linear functional:

$$\left(\begin{pmatrix} i \\ -1 \end{pmatrix}^T\right)^* = \begin{pmatrix} i & -1 \end{pmatrix}^* = \begin{pmatrix} i^* & -1^* \end{pmatrix} = \begin{pmatrix} -i & -1 \end{pmatrix}$$

The inner product is then

$$\begin{pmatrix} -i & -1 \end{pmatrix}\begin{pmatrix} 1 \\ -1 \end{pmatrix} = -i \times 1 + (-1) \times (-1) = -i + 1 = 1 - i$$

$1-i$ is in the complex plane, the field underlying our vector space. Thus, the linear functional $\begin{pmatrix} -i & -1 \end{pmatrix}$ (from the dual vector space over the complex numbers) has taken a vector from the vector space over the field of complex numbers $\begin{pmatrix} 1 \\ -1 \end{pmatrix}$ to the underlying field of complex numbers viewed as a vector space. Now, cast your mind back to PHY 309. How did you recover the coefficients of the expansion of a vector written as a linear combination of the vectors in the orthornormal basis?

That process is the same as the one described here. You expanded the vector as $\psi = \sum_i c_i \phi_i$, where $\{\phi_i\}$ is an orthornormal set. To get c_j, you took the inner product

$$(\phi_j, \psi) = (\phi_j, \sum_i c_i \phi_i) = \sum_i c_i (\phi_j, \phi_i) = \sum_i c_i \delta_{ij} = c_j$$

You took this a step further, finding the probability that the system under consideration is in any particular state. provided ψ is normalized,

$$(\psi, \psi) = (\sum_i c_i \phi_i, \sum_j c_j \phi_j) = \sum_i c_i \sum_j c_j (\phi_i, \phi_j) = \sum_i c_i^* \sum_j c_j \delta_{ij} = \sum_i c_i^* c_i = \sum_i |c_i|^2 = 1$$

In this case, the expression on the left is the norm of ψ, the output of which is always a real number. Nevertheless, the first member of the inner product is from the dual vector space.

You can now generalise what we have done so far to an $m \times n$ matrix. Let A and B be vectors in the vector space of $m \times n$ matrices over the complex plane. The inner product, $Tr(A^+ B)$ takes a vector B from the vector space to the field of complex numbers viewed as a vector space. Notice that A^+ is an $n \times m$ matrix. For example,

$$A = \begin{pmatrix} i & 2 & -2i \\ 2 & i & -1 \end{pmatrix}, B = \begin{pmatrix} 1 & -i & 1 \\ -2 & i & -2i \end{pmatrix}$$

The dual of A is,

$$A^+ = \begin{pmatrix} i* & 2* \\ 2* & i* \\ -2i* & -1* \end{pmatrix} = \begin{pmatrix} -i & 2 \\ 2 & -i \\ 2i & -1 \end{pmatrix}$$

$$Tr(A^+ B) = Tr\left(\begin{pmatrix} -i & 2 \\ 2 & -i \\ 2i & -1 \end{pmatrix} \begin{pmatrix} 1 & -i & 1 \\ -2 & i & -2i \end{pmatrix} \right) = Tr \begin{pmatrix} -i-4 & -1+2i & -i-4i \\ 2+2i & -2i+1 & 2-2 \\ 2i+2 & 2-i & -2i+2i \end{pmatrix}$$

$$= Tr \begin{pmatrix} -i-4 & -1+2i & -5i \\ 2+2i & -2i+1 & 0 \\ 2i+2 & 2-i & 0 \end{pmatrix} = -i-4+(-2i+1) = -i-4-2i+1 = -3-3i$$

$$= -3(1+i)$$

The functional above is defined with the product of two matrices.

As another example of a linear functional, let V be the vector space of $n \times n$ matrices over the field K, which could be the real number line or the complex plane. The scalars α and β are elements of the real number line or the complex plane as the case may be. The trace map, $T : V \to R$ is a linear map.

$$Tr(A+B) = (A_{11}+B_{11}) + (A_{22}+B_{22}) + ... + (A_{nn}+B_{nn})$$
$$= (A_{11}+A_{22}+...+A_{nn}) + (B_{11}+B_{22}+...+B_{nn}) = Tr(A) + Tr(B)$$

$$Tr(\alpha A) = \alpha A_{11} + \alpha A_{22} + ... + \alpha A_{nn} = \alpha(A_{11}+A_{22}+...+A_{nn}) = \alpha Tr(A)$$

Equivalently,

$$Tr(\alpha A+\beta B) = (\alpha A_{11}+\beta B_{11}) + (\alpha A_{22}+\beta B_{22}) + ... + (\alpha A_{nn}+\beta B_{nn})$$
$$= (\alpha A_{11}+\alpha A_{22}+...+\alpha A_{nn}) + (\beta B_{11}+\beta B_{22}+...+\beta B_{nn})$$
$$= \alpha(A_{11}+A_{22}+...+A_{nn}) + \beta(B_{11}+B_{22}+...+B_{nn})$$
$$= \alpha Tr(A) + \beta Tr(B)$$

Tr is an element in the dual space V^* of vector space *V*. The map *Tr* is the row containing the trace of all the matrices in the vector space. Any other linear functional defined on this space is also an element of V^*, the dual space of *V*. The trace in this case acts only on a matrix, unlike that in the previous example in which it acts on the product of two matrices.

For example, the map $T: V \to R$ taking the first element A_{11} of a matrix to the underlying field is also a linear functional on V^*. $T(A) = A_{11}$.

Self-Assessment Exercise 1

Explain the terms linear map, linear functional, vector space and dual space in a single paragraph.

3.4 The Dirac Notation (Bra and Ket Vectors)

To every vector $|\psi>$ in the vector space, there is exactly one dual vector $<\psi|$ in the dual vector space.

$(|\psi>)^+ = <\psi|$ (The dual of the ket vector is the bra covector)

$(<\psi|)^+ = |\psi>$ (The dual of the bra covector is the (initial) ket vector)

Put another way, the dual of the dual vector is again the vector itself.

For an operator A acting on the vector (eigenvector) $|\psi>$ in the vector space, we write $A|\psi>$. This is equivalent (since $(A|\psi>)^+ = (|\psi>)^+ A^+ = <\psi|A^+$) to $<\psi|A^+$ in the dual space. Moreover, since $(AB)^+ = B^+A^+$, $AB|\psi>$ is equivalent to $<\psi|B^+A^+$**.** ForHermitian operators *A* and *B*, this becomes $<\psi|BA$.

SELF-ASSESSMENT EXERCISE 2

In terms of vector spaces, dual vector spaces and matrices, what are bra and ket vectors? How can you form an inner product from the two kinds of vectors?

3.5 Transition Probability

In PHS 307, you expanded the wavefunction of a given quantum-mechanical system as a linear combination of the possible orthonormal eigenstates. There, you were able to (with the help of the inner product) recover the coefficient of the expansion and then deduce the probability of finding the system in any particular eigenstate. In just the same way, the inner product also defines the transition amplitude from state $|\psi>$ to state $<\phi|$, i.e., $<\varphi|\psi>$.

Therefore, in line with the Born interpretation of the wavefunction, the transition probability is,

$$P_{\phi\psi} = |<\phi|\psi>|^2 = \left|\int \phi^*(x)\psi(x)\,dx\right|^2 \qquad 2.10$$

This is the transition probability of the particle under consideration from state $|\psi>$ to state $<\phi|$.

You can see that the probability that the transition to the same state is unity (each eigenstate is normalised:

$$P_{\phi\phi} = |<\phi|\phi>|^2 = 1) \qquad 2.11$$

In the time-dependent case,

$$|\phi(x,t)>= e^{-\frac{iE_n t}{\hbar}} |\phi(x,0)> \qquad 2.12$$

$$|\psi(x,t')>= e^{-\frac{iE_n t'}{\hbar}} |\psi(x,0)> \qquad 2.13$$

and the transition probability from state $<\psi|$ to state$|\phi>$ is,

$$P_{\phi\psi} = \left|< \phi(x,t') \mid \psi(x,t) >\right|^2 = \left|< \phi(x,0) \mid e^{\frac{iE_m t}{\hbar}} e^{-\frac{iE_n t'}{\hbar}} \mid \psi(x,0) >\right|^2$$

2.14

$$= \left|< \phi(x) \mid e^{\frac{iE_m t - E_n t'}{\hbar}} \mid \psi(x) >\right|^2$$

2.15

SELF-ASSESSMENT EXERCISE 3

In terms of bra and ket vectors, what do you understand by 'transition probability?'

Example 2.1

A particle in a box of length L with infinite walls is in its ground state. What is the probability (transition probability) that the particle is in the ground state if one wall is suddenly moved outward, making the new box of length 3*L*?

Solution 2.1

Let us denote the ground state of the *L* length well $\psi_0^{(L)}$ and the ground state of the 3*L* length well $\psi_0^{(3L)}$. The allowable wavefunctions for the *L* length well are,

$$\psi_n^{(L)} = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

The eigenfunctions for the $3L$ well must be (transformation $L \to 3L$):

$$\psi_n^{(3L)} = \sqrt{\frac{2}{3L}} \sin \frac{n\pi x}{3L}$$

Therefore,

$$< \psi_0^{(3L)} \mid \psi_0^{(L)} >= \int_0^L \sqrt{\frac{2}{3L}} \sin \frac{\pi x}{3L} \times \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L} dx = \frac{2}{L\sqrt{3}} \int_0^L \sin \frac{\pi x}{3L} \sin \frac{\pi x}{L} dx$$

You can see this as the case where the time *t* is zero because the change occurred suddenly.

Note that the integral does not need to extend to 3*L*, because the wave function for the *L* well is zero outside the $0 \le x \le L$ range.

$$
\begin{aligned}
<\psi_0^{(3L)} \mid \psi_0^{(L)}> &= \frac{2}{L\sqrt{3}}\int_0^L \sin\frac{\pi x}{3L}\sin\frac{\pi x}{L}dx \\
&= \frac{2}{L\sqrt{3}}\int_0^L \frac{1}{2}\left\{\cos\left(\frac{\pi x}{3L}-\frac{\pi x}{L}\right)-\cos\left(\frac{\pi x}{3L}+\frac{\pi x}{L}\right)\right\}dx \\
&= \frac{1}{L\sqrt{3}}\int_0^L \left\{\cos\left(\frac{-2\pi x}{3L}\right)-\cos\left(\frac{4\pi x}{3L}\right)\right\}dx \\
&= \frac{1}{L\sqrt{3}}\int_0^L \left\{\cos\left(\frac{2\pi x}{3L}\right)-\cos\left(\frac{4\pi x}{3L}\right)\right\}dx \\
&= \frac{1}{L\sqrt{3}}\left(\frac{\sin\frac{2\pi x}{3L}}{\frac{2\pi}{3L}}-\frac{\sin\frac{4\pi x}{3L}}{\frac{4\pi}{3L}}\right)_0^L \\
&= \frac{1}{L\sqrt{3}}\left(\frac{\sin\frac{2\pi x}{3L}}{\frac{4\pi}{2\times 3L}}-\frac{\sin\frac{4\pi x}{3L}}{\frac{4\pi}{3L}}\right)_0^L \\
&= \frac{1}{L\sqrt{3}}\times\frac{3L}{4\pi}\left(2\times\frac{\sqrt{3}}{2}-\left[-\frac{\sqrt{3}}{2}\right]\right) \\
&= \frac{3}{4\pi\sqrt{3}}\left(\sqrt{3}-\left[-\frac{\sqrt{3}}{2}\right]\right) \\
&= \frac{3}{4\pi\sqrt{3}}\left(\sqrt{3}+\frac{\sqrt{3}}{2}\right) \\
&= \frac{3}{4\pi\sqrt{3}}\left(\frac{3}{2}\sqrt{3}\right) \\
&= \frac{9}{8\pi}
\end{aligned}
$$

Hence, the probability that the particle is in the ground state of the new box of length $3L$ is

$$P = \left|\frac{9}{8\pi}\right|^2 = \left(\frac{9}{8\pi}\right)^2 = \frac{81}{64\pi^2}$$

4.0 CONCLUSION

In this Unit, you learnt about linear maps, which are functions between two vector spaces, linear functionals which are functions from a vector space to the underlying field. You have also seen that the inner product of two vectors involves a vector from the space of dual vectors on the left and a vector from the vector space on the right. This ensures that the output of such an operation is in the field underlying the vector space.

You also learnt how to calculate the transition probability between a ket and a bra.

5.0 SUMMARY

In this Unit, you have learnt the following:

- a linear map is a function between two vector spaces which preserves vector addition and scalar multiplication
- a linear functional is a function from a vector space to the underlying field which preserves vector addition and scalar multiplication
- the set of all linear functionals of over a vector space is the dual space of the vector space
- the inner product of two vectors is between a vector in the dual space of the vector space as a bra on the left and a vector from the vector space on the right
- how to calculate the transition probability from a ket state to a bra state.

Answer to Self-Assessment Exercise 1

A linear map is a function between vector spaces that respects linearity and homogeneity. The codomain of a linear map is a vector space. A linear map therefore takes a vector space to a target space that is also a vector space. The output is a vector. A linear functional is a linear transformation whose target space (codomain) is the scalar field, which is a one-dimensional vector space or the complex plane (if from a complex vector space). The output is a scalar. A dual space of a vector space X is the set of all linear functionals from X to the underlying scalar field of X, from which the scalars for X are drawn. The dual space is also a vector space if we define addition and scalar multiplication componentwise.

Answer to Self-Assessment Exercise 2

Ket vectors are vectors from the vector space and are column vectors. Bra vectors are from the dual vector space and are column vectors.

An inner product is formed by having a row matrix on the left and a column matrix on the right. The resulting product gives a scalar.

Answer to Self-Assessment Exercise 3

The ket vector can be seen as the initial state in a transition. The bra represents the final state. The transition probability is the

probability that a system initially in the ket state is eventually found in the bra state. It is not sufficient to just take the inner product with the bra on the left and the ket on the right as the output might be complex. We take the square of the magnitude which must of necessity be a real number: $P_{\varphi\psi} = |<\varphi|\psi>|^2$.

6.0 TUTOR-MARKED ASSIGNMENT

1. Define the following terms:
   (a) Linear map (b) Linear functional

2. Show that the ordinary differential equation operator $L = \frac{d}{dx}$ is a linear operator.

3. Prove that the indefinite integral operator $f \mapsto \int f(x)dx$ is a linear operator.

4. Consider the space of functions. Show that the definite integral $f \mapsto \int_a^b f(x)dx$ is a linear functional from the vector space $C[a,b]$ of continuous functions on the interval $[a,b]$ to the space of real numbers.

5. A particle is confined in a one-dimensional box with dimensions $0 \le |a|$ and is known to be in the first excited state (n = 2). If suddenly, the width of the box is doubled without disturbing the state of the particle, and a measurement of the energy is made, find the probability that the system is in the ground state and the first excited state of the new well.

6. Given an orthonormal set $\{|\phi_j>\}_{j=1}^{\infty}$, Show that $\sum_{j=1}^{\infty} |\phi_j><\phi_j| = I$, the spectral representation of the identity operator.

7. The state of a system is given by
   $|\psi> = A[(1+i)|1> + \sqrt{2}e^{-i\pi/6}|2> -(2-i)|3>]$
(a) What is the associated bra vector?
(b) Normalise the vector.
(c) Calculate the probability amplitude and the probability of finding the system in each of the possible in each of the states $|1>, |2>$ and $|3>$.
(d) What is the most probable state the system can be found?
(e) Another state of the system is given by

$$|\varphi>=\frac{1}{\sqrt{12}}[2|1>+\sqrt{3}e^{-i\pi/6}|2>+(2-i)|3>]$$

Calculate the probability of observing the system in state $|\psi>$ if it was initially in state $|\varphi>$.

8. A molecule is composed of three atoms. An electron can attach to the molecule by attaching to any of the atoms. The electron can be in one of three possible eigenstates $|1>$, $|2>$ or $|3>$, where the state $|j>$ is the state in which the electron is attached to the j th atom.

(a) What is the dimension of the eigenspace of the system?

(b) The eigenstates $|1>$, $|2>$ or $|3>$ form a complete orthonormal basis for the system. Explain the term complete basis.

(c) What would have been the implication if the three eigenstates did not form a complete basis for the system?

(d) If the system is in state $|\psi>=\frac{1}{4}[3i|1>+2|2>-\sqrt{3}|3>]$, on which atom are you most likely to find the electron?

9. Show that the transformation $T:R^2\to R^3$, given by $(x,y)\to(y,x,2+x+y)$ is not a linear transformation.

7.0 REFERENCES/FURTHER READING

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UNIT 3 COMMUTATOR ALGEBRA, MATRIX ELEMENTS OF A LINEAR OPERATOR

CONTENTS

1.0 INTRODUCTION

In Quantum Mechanics, every physically observable is associated with a Hermitian operator. The physically observable properties include position, time, energy, angular momentum, etc. Quite unlike the case with Classical Mechanics, not all physically observable properties of a quantum-mechanical system can be measured precisely simultaneously. This is due to the Heisenberg uncertainty principle. If any two observable physical properties can be measured simultaneously with infinite accuracy, then their operators must commute. Indeed, you will get to know that two such observables can have the same eigenvectors. In this unit, you will also learn how to find the matrix elements of an operator in a given quantum-mechanical state. Thus, you will be able to calculate the expectation value of the physically observable property in such a state. In addition, you will learn about the outer product of two vectors as well as the projection operator.

2.0 OBJECTIVES

At the end of this study session, you will be able to:

- do commutator algebra
- write the matrix representation of a given linear operator
- show that two operators that commute can have the same eigenvectors
- find the outer product of two vectors
- work with projection operators.

3.0 MAIN CONTENT

3.1 The Commutator

Let two operators, corresponding to two physical observables be *A* and *B*, and let them have the same eigenvector ψ, with eigenvalues λ_a and λ_b respectively. Then, we can write

$$A\psi = \lambda_a\psi \qquad 3.1$$

and

$$B\psi = \lambda_b\psi \qquad 3.2$$

Multiplying equation 3.1 on the left by *B*,

$$BA\psi = B\lambda_a\psi = \lambda_a B\psi = \lambda_a\lambda_b\psi \qquad 3.3$$

Multiplying equation 3.1 on the left by *B*,

$$AB\psi = A\lambda_b\psi = \lambda_b A\psi = \lambda_b\lambda_a\psi \qquad 3.4$$

Subtracting equation (3.3 from equation 3.4),

$$AB\psi - BA\psi = \lambda_b\lambda_a\psi - \lambda_a\lambda_b\psi = 0 \qquad 3.5$$

$$(AB - BA)\psi = 0 \qquad 3.6$$

since the eigenvalues are just numbers.

Generally, $\psi \neq 0$. Hence, $AB - BA = 0$. This is written as $[A, B] = 0$, where $[A, B]$ is the commutator of A and B.

The commutator is anticommutative, that is,

$$[B, A] = -[A, B] \qquad 3.7$$

SELF-ASSESSMENT EXERCISE 1
Prove the relation 3.7.

Let the uncertainty in the measurement of physical observable *a* with a corresponding operator *A* be Δa and the uncertainty in the measurement of physical observable *b* with its corresponding operator *B* be Δb. Then, the uncertainty relation is

$$\Delta a \Delta b = \frac{i}{2}[\mathrm{A}, \mathrm{B}]$$

If the commutator $[A, B] = 0$, then the product of the uncertainties in the measurements of the corresponding physical observables is zero. It means the two physical observables can be measured simultaneously with infinite accuracy, $\Delta a = \Delta b = 0$. We then say *A* and *B* commute. Measuring one of the physical observables leaves the system undisturbed relative to a measurement of the other observable. We say the two observables are compatible.

If the commutator $[A, B] \neq 0$, *A* and *B* do not commute. Then the product of the uncertainties in the measurements of the corresponding physical observables is not zero. It means the two physical observables cannot be measured simultaneously with infinite accuracy, $\Delta a = 0$ would imply infinite error in the measurement of *b*. Measuring one of the observables disturbs the system, causing an error in the measurement of the other observable. We say the two observables are incompatible.

The commutator seems to ask, “What is the effect of measuring the physical quantity corresponding to operator A first, then the physical quantity corresponding to operator B, and measuring them in reverse order?” If the operators commute, it should not matter which physical quantity (corresponding to the operator) is measured first.

SELF-ASSESSMENT EXERCISE 2

What do you understand by commuting observables?

3.2 Commutator Algebra

Here are some properties of the commutator:

1. $[A, A] = AA - AA = 0$ 3.8
2. $[A, B] = AB - BA = -(BA - AB) = -[B, A]$ 3.9
3. $[AB, C] = ABC - CAB + ACB - ACB - CAB$
   $= ABC - ACB + ACB - CAB$
   $= A(BC - CB) + (AC - CA)B$
   $= A[B, C] + [A, C]B$ 3.10
4. $[A, BC] = ABC - BCA = ABC - BAC + BAC - BCA$
   $= (ABC - BAC) + (BAC - BCA)$
   $= (AB - BA)C + B(AC - CA)$
   $= [A, B]C + B[A, C]$ 3.11
5. $[A + B, C] = (A + B)C - C(A + B)$
   $= AC + BC - CA - CB$
   $= (AC - CA) + (BC - CB)$
   $= [A, C] + [B, C]$ 3.12
6. $[A, B + C] = A(B + C) - (B + C)A$
   $= AB + AC - BA - CA$
   $= AB - BA + AC - CA$
   $= [A, B] + [A, C]$ 3.13
7. $[A,[B, C]] = A[B, C] - [B, C]A$ 3.14

SELF-ASSESSMENT EXERCISE 3

Prove the Jacobi identity $[A,[B, C]] + [B,[C, A]] + [C,[A, B]] = 0$

3.3 Matrix Elements of a Linear Operator

Suppose operator A acting on ket $|\psi>$ results in the ket $|\chi>$, we write

$$|\chi> = A|\psi>$$

We can also expand $|\psi>$ in an orthonormal basis $\{|e_i>\}_{i=1}^{n}$,

$$|\psi> = \sum_{i=1}^{n} v_i |e_i>$$

On the other hand, we can expand $|\chi>$ directly in the same basis, using a different dummy index as the counter,

$$|\chi>=\sum_{j=1}^{n} v_j'|e_j>$$

so that we can recover $v_k'=<e_k|\chi>$.

$$\begin{aligned} v_k' = <e_k|\chi> = <e_k|A|\psi> = <e_k|A|\sum_{i=1}^{n} v_i|e_i> \\ = \sum_{i=1}^{n} v_i <e_k|A|e_i> \\ = \sum_{i=1}^{n} v_i A_{ki} \end{aligned}$$

Try to write out this sum, and what you get is,

$$v_k' = v_1 A_{k1} + v_2 A_{k2} + ... + v_n A_{kn}$$

Thus, we can write this as the *k*th row of a matrix *A* multiplying a column vector ***v***.

$$\begin{pmatrix} A_{11} & . & . & . & . & . & A_{1n} \\ . & & & & & & \\ . & & & & & & \\ A_{k1} & A_{k2} & . & . & . & . & A_{kn} \\ . & & & & & & \\ . & & & & & & \\ A_{n1} & . & . & . & . & . & A_{nn} \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \\ . \\ . \\ . \\ . \\ v_n \end{pmatrix}$$

Then,

$$\begin{pmatrix} v_1' \\ . \\ . \\ v_n' \end{pmatrix} = \begin{pmatrix} A_{11} & . & . & A_{1n} \\ . & . & . & . \\ . & . & . & . \\ A_{n1} & . & . & A_{nn} \end{pmatrix} \begin{pmatrix} v_1 \\ . \\ . \\ v_n \end{pmatrix}$$

3.15

So, we can represent any linear operator A by a square matrix $A_{ij}=<e_i|A|e_j>$.

More specifically, we can write,

$$A = \begin{pmatrix} <1|A|1> & <1|A|2> & . & . & . & <1|A|n> \\ <2|A|1> & <2|A|2> & . & . & . & <2|a|n> \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ <n|A|1> & <n|A|2> & . & . & . & <n|A|n> \end{pmatrix}$$

Take a look at each column or each row and you will see there is a pattern: The matrix is made up of a collection of *n* column vectors or we could see it as *n* row vectors:

$$\begin{pmatrix} <1|\psi_1> \\ <2|\psi_1> \\ . \\ . \\ . \\ <n|\psi_1> \end{pmatrix}, \begin{pmatrix} <1|\psi_2> \\ <2|\psi_2> \\ . \\ . \\ . \\ <n|\psi_2> \end{pmatrix}, \cdots \begin{pmatrix} <1|\psi_n> \\ <2|\psi_n> \\ . \\ . \\ . \\ <n|\psi_n> \end{pmatrix}$$

or

$$\begin{array}{l} (<\psi_1|1> \quad <\psi_1|2> \quad . \quad . \quad . \quad <\psi_1|n>) \\ (<\psi_2|1> \quad <\psi_2|2> \quad . \quad . \quad . \quad <\psi_2|n>) \\ \qquad\qquad\qquad\qquad . \\ \qquad\qquad\qquad\qquad . \\ \qquad\qquad\qquad\qquad . \\ (<\psi_n|1> \quad <\psi_n|2> \quad . \quad . \quad . \quad <\psi_n|n>) \end{array}$$

where $|\psi_1>=A|1>$, $|\psi_2>=A|2>$, etc., and $<\psi_1|=(|\psi_1>)^+ =<1|A^+$, etc.

Example 3.1

Find the matrix of representation of the identity operator.

Solution 3.1

For the identity operator I,

$$I|i>=|i>$$

$$I_{ji} =< j|I|i> = < j|i>= \delta_{ij}$$

Hence,

$$I = \begin{pmatrix} 1 & 0 & . & . & . & 0 \\ 0 & 1 & . & . & . & 0 \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ 0 & 0 & . & . & . & 1 \end{pmatrix}$$

3.16

SELF-ASSESSMENT EXERCISE 4

Find the matrix of representation of the linear transformation (in the usual basis in R^3),
$L : R^3 \to R^3$, such that $L(x_1, x_2, x_3) = (x_1 + x_2, x_1 - x_3, x_1 + x_3)$.

4.0 CONCLUSION

In this Unit, you learnt that two physical observables can be measured simultaneously and with infinite accuracy if their corresponding operators commute. If the operators do not commute, measuring one of the observables induces an error in the measurement of the other physical observable. Moreover, you have been able to find the matrix elements of a linear operator, given the relevant basis vectors.

5.0 SUMMARY

In this Unit, you have learnt the following:

- a commutator tells us if we can or cannot measure two physical observables simultaneously and with infinite accuracy
- if the commutator is zero, the two quantities corresponding to the operators can be measured simultaneously with infinite accuracy
- if the commutator is not zero, the two quantities corresponding to the operators cannot be measured simultaneously with infinite accuracy
- how to find the matrix elements of a linear operator

Answer to Self-Assessment Exercise 1

$[B, A] = BA - AB = -(AB - BA) = -[A, B]$

Answer to Self-Assessment Exercise 2
If the commutator $[A, B] = 0$, then the product of the uncertainties in the measurements of the corresponding physical observables is zero. It means the two physical observables can be measured simultaneously

with infinite accuracy, $\Delta a = \Delta b = 0$. We then say A and B commute. Measuring one of the physical observables leaves the system undisturbed relative to a measurement of the other observable. We say the two observables are compatible.

If the commutator $[A, B] \neq 0$, A and B do not commute. Then the product of the uncertainties in the measurements of the corresponding physical observables is not zero. It means the two physical observables cannot be measured simultaneously with infinite accuracy, $\Delta a = 0$ would imply infinite error in the measurement of b. Measuring one of the observables disturbs the system, causing an error in the measurement of the other observable. We say the two observables are incompatible.

Answer to Self-Assessment Exercise 3

$$\begin{aligned}
&[A,[B,C]]+[B,[C,A]]+[C,[A,B]] \\
&\quad = A[B,C]-[B,C]A+B[C,A]-[C,A]B+C[A,B]-[A,B]C \\
&\quad = ABC-ACB-BCA+CBA+BCA-BAC \\
&\qquad\qquad +ACB-CAB+CAB-CBA+BAC-ABC \\
&\quad = 0
\end{aligned}$$

Solution to Self-Assessment Exercise 4

$$\begin{aligned}
L(\mathbf{e}_1) &= L(1,0,0) = (1+0 \quad 1-0 \quad 1+0) = \begin{pmatrix} 1 & 1 & 1 \end{pmatrix} \\
L(\mathbf{e}_2) &= L(0,1,0) = (0+1 \quad 0-0 \quad 0+0) = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \\
L(\mathbf{e}_3) &= L(0,0,1) = (0+0 \quad 0-1 \quad 0+1) = \begin{pmatrix} 0 & -1 & 1 \end{pmatrix}
\end{aligned}$$

Hence, the matrix representing the linear transformation is,

$$L = \begin{pmatrix} < x_1 \mid L \mid x_1 > & < x_1 \mid L \mid x_2 > & < x_1 \mid L \mid x_3 > \\ < x_2 \mid L \mid x_1 > & < x_2 \mid L \mid x_2 > & < x_2 \mid L \mid x_3 > \\ < x_3 \mid L \mid x_1 > & < x_3 \mid L \mid x_2 > & < x_3 \mid L \mid x_3 > \end{pmatrix}$$

$$\begin{aligned}
&= \begin{pmatrix} (1\ 0\ 0)\cdot(1\ 1\ 1) & (1\ 0\ 0)\cdot(1\ 0\ 0) & (1\ 0\ 0)\cdot(0\ -1\ 1) \\ (0\ 1\ 0)\cdot(1\ 1\ 1) & (0\ 1\ 0)\cdot(1\ 0\ 0) & (0\ 1\ 0)\cdot(0\ -1\ 1) \\ (0\ 0\ 1)\cdot(1\ 1\ 1) & (0\ 0\ 1)\cdot(1\ 0\ 0) & (0\ 0\ 1)\cdot(0\ -1\ 1) \end{pmatrix} \\
&= \begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & -1 \\ 1 & 0 & 1 \end{pmatrix}
\end{aligned}$$

Notice that we might as well have arranged the matrix by writing out the three columns

$$L = \begin{pmatrix} L(\mathbf{e}_1) & L(\mathbf{e}_2) & L(\mathbf{e}_3) \end{pmatrix}$$

Alternatively,

$$L|1> = L(1,0,0) = (1+0)|1> +(1-0)|2>) + (1+0)|3> = |1> + |2> + |3>$$

$$L|2> = L(0,1,0) = (0+1)|1> +(0-0)|2> +(0+0)|3> = |1>$$
$$L|3> = L(0,0,1) = (0+0)|1> +(0-1)|2> +(0+1)|3> = -|2> + |3>$$

Hence,

$$L = \begin{pmatrix} <x_1|L|x_1> & <x_1|L|x_2> & <x_1|L|x_3> \\ <x_2|L|x_1> & <x_2|L|x_2> & <x_2|L|x_3> \\ <x_3|L|x_1> & <x_3|L|x_2> & <x_3|L|x_3> \end{pmatrix}$$

$$= \begin{pmatrix} <1|(|1> + |2> + |3>) & <1|1> & <1|(-|2> + |3>) \\ <2|(|1> + |2> + |3>) & <2|1> & <2|(-|2> + |3>) \\ <3|(|1> + |2> + |3>) & <3|1> & <3|(-|2> + |3>) \end{pmatrix}$$

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

Another approach:

$$\mathbf{e}_1 \cdot L(\mathbf{e}_1) = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \cdot \begin{pmatrix} 1 & 1 & 1 \end{pmatrix} = 1$$
$$\mathbf{e}_1 \cdot L(\mathbf{e}_2) = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} = 1$$
$$\mathbf{e}_1 \cdot L(\mathbf{e}_3) = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \cdot \begin{pmatrix} 0 & -1 & 1 \end{pmatrix} = 0$$
$$\mathbf{e}_2 \cdot L(\mathbf{e}_1) = \begin{pmatrix} 0 & 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} 1 & 1 & 1 \end{pmatrix} = 1$$
$$\mathbf{e}_2 \cdot L(\mathbf{e}_2) = \begin{pmatrix} 0 & 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} = 0$$
$$\mathbf{e}_2 \cdot L(\mathbf{e}_3) = \begin{pmatrix} 0 & 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} 0 & -1 & 1 \end{pmatrix} = -1$$
$$\mathbf{e}_3 \cdot L(\mathbf{e}_1) = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \cdot \begin{pmatrix} 1 & 1 & 1 \end{pmatrix} = 1$$
$$\mathbf{e}_3 \cdot L(\mathbf{e}_2) = \begin{pmatrix} 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} = 0$$
$$\mathbf{e}_3 \cdot L(\mathbf{e}_3) = \begin{pmatrix} 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} 0 & -1 & 1 \end{pmatrix} = 1$$

Arranging these in a matrix gives yet again,

$$L = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & -1 \\ 1 & 0 & 1 \end{pmatrix}$$

6.0 TUTOR-MARKED ASSIGNMENT

1. Show that $[A^n, B] = nA^{n-1}[A, B]$, provided $[[A, B], A] = 0$, for all $n \in \aleph$, the set of natural numbers.

2. The action on state $|n>$ of the lowering and the raising operators for the harmonic oscillator are, respectively, $a|n>=\sqrt{n}\,|n-1>$, $a^+|n>=\sqrt{n+1}\,|n+1>$.

a. Write out the matrix elements of a and that of a^+.

b. Find the two products of the matrices, aa^+ and a^+a.

c. Write the matrix form of the Hamiltonian operator for the harmonic oscillator, $H = \frac{\hbar\omega}{2}(aa^+ + a^+a)$.

3. (i) Find the eigenvectors of the matrices $\begin{pmatrix} 3 & 2 \\ 1 & 2 \end{pmatrix}$ and $\begin{pmatrix} 2 & 4 \\ 2 & 0 \end{pmatrix}$

(ii) Show that the matrices commute.

(iii) Comment on your findings in (i) and (ii).

4. Find an expression for the commutator $[AB, CD]$ in terms of the commutators of pairs of the operators.

5. The usual basis for a spin-half system is $|+>=\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $|->=\begin{pmatrix} 0 \\ 1 \end{pmatrix}$.

We can write the two vectors $|1>=\frac{1}{\sqrt{2}}(|->+i|+>)$ and $|2>=\frac{1}{\sqrt{2}}(|->-i|+>)$. Let the operator Q be defined by $Q|\pm>=\pm i\hbar|\mp>$

(a) Write the vectors as ket (column) vectors.

(b) Show that the vectors $|1>$ and $|2>$ are orthonormal.

(c) What is the matrix representation of the operator Q in the basis $\{|+>,|->\}$.

(d) Calculate $Q|1>$ and $Q|2>$.

(e) Calculate $<1|Q$, $<1|Q^+$.

6. The operator of a physical observable in the orthonormal states $|1>$, $|2>$ and $|3>$ which span the Hilbert space of a system is given by

$$Q|1>=2|1>-2i|2>+|3>$$
$$Q|2>=i|1>+2|2>-2i|3>$$
$$Q|3>=-2i|1>+i|2>-2|3>$$

(a) What is the matrix representation of Q in the $\{|1>,|2>,|3>\}$ basis?

(b) For the state $|\psi>=\frac{1}{\sqrt{6}}(|1>+2|2>+|3>)$, determine $Q|\psi>$ and $<\psi|Q$ in the representation of the vectors and operators in the $\{|1>,|2>,|3>\}$ basis.

7. In the isospin theory, the nucleons (proton and neutron) are assumed to be different states, denoted respectively by $|p>$ and $|n>$. If the state of the nucleon changes as a result of a collision between the nucleon and another particle, a change defined by

$$Q|p>=\frac{1}{\sqrt{2}}(|p>+i|n>)$$
$$Q|n>=\frac{1}{\sqrt{2}}(i|p>+|n>)$$

(a) Write the matrix representation of Q in the basis $\{|p>,|n>\}$.

(b) Assuming a proton undergoes such a collision, what is the probability that the nucleon could be observed to be a neutron after the collision?

(c) Normalise the state $|\psi>=|p>+3i|n>$ and hence, determine the new state of the system after the collision has occurred.

(d) Write the bra vector $|\psi>$ as a row vector. Hence, find the probability that the nucleon will be found in the state $|\psi>$ after the collision.

(e) Suppose the nucleon is in a state $|\psi>=c_1|p>+c_2|n>$ before a collision, find its state after the collision.

(f) Find, if possible, collisions in which the state does not change.

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UNIT 4 THE OUTER PRODUCT, THE PROJECTION OPERATOR AND THE COMPLETENESS RELATION

CONTENTS

1.0 INTRODUCTION

The inner product of two vectors is obtained by putting a bra vector, from the dual vector space on the left and a ket vector, from the vector space on the right. The outcome of this procedure is a scalar. In contrast, an outer product has a ket on the left and a bra on the right. The outcome is a matrix, not a scalar. A special case of the outer product is the projection operator, which …..

The completeness relation is a summation of all the outer products formed from each vector in the basis and its dual. This summation gives the identity matrix, meaning that the completeness relation expresses the physical situation where a measuring instrument placed in the path of the system under consideration, but making no measurement is the same as not having the instrument there in the first place.

In this study session, you will get to know the connection between completeness …..

2.0 OBJECTIVES

At the end of this unit, you will be able to:

- do commutator algebra (SAQ 6.1 and SAQ 6.2).
- write the matrix representation of a given linear operator (SAQ 6.3).

- show that two operators that commute can have the same eigenvectors (SAQ 6.4).
- find the outer product of two vectors (SAQ 6.5).
- work with projection operators (SAQ 6.6 and SAQ 6.7, SAQ 6.8).

3.0 MAIN CONTENT

3.1 The Outer Product

With the bra-vectors, $< \mathbf{v} |$, $< \mathbf{w} |$ and ket-vectors, $| \mathbf{v} >$ $| \mathbf{w} >$, the inner product of vectors **v** and **w** is written, $< \mathbf{v} | \mathbf{w} >$ and the **outer product** $| \mathbf{v} >< \mathbf{w} |$ which, is an operator A_{vw}.

$$A_{vw} | \mathbf{s} >= (| \mathbf{v} >< \mathbf{w} |) | \mathbf{s} >= | \mathbf{v} >< \mathbf{w} | \mathbf{s} >= \alpha | \mathbf{v} > \quad 4.1$$

where $< \mathbf{w} | \mathbf{s} >= \alpha$.

The adjoint of the outer product $| \mathbf{v} >< \mathbf{w} |$ is $(| \mathbf{v} >< \mathbf{w} |)^+ = (< \mathbf{w} |)^+ (| \mathbf{v} >)^+ = | \mathbf{w} >< \mathbf{v} |$, recalling that $(AB)^+ = B^+ A^+$ and noting that the adjoint operation turns a bra into a ket and vice versa.

Example 4.1
Find the inner product, $< \mathbf{v} | \mathbf{w} >$, and the outer product, $| \mathbf{v} >< \mathbf{w} |$, of the vectors

$$| \mathbf{v} >= \begin{bmatrix} v_1 \\ v_2 \\ v_3 \end{bmatrix} \text{ and } | \mathbf{w} >= \begin{bmatrix} w_1 \\ w_2 \\ w_3 \end{bmatrix}$$

in a real vector space. (A real vector space is such that the entries of the column or row vectors are all real.)

Solution 4.1

$$< \mathbf{v} | \mathbf{w} >= \mathbf{v}^T \mathbf{w} = \begin{bmatrix} v_1 & v_2 & v_3 \end{bmatrix} \begin{bmatrix} w_1 \\ w_2 \\ w_3 \end{bmatrix} = v_1 w_1 + v_2 w_2 + v_3 w_3$$

$$| \mathbf{v} >< \mathbf{w} | = \mathbf{v}\mathbf{w}^T = \begin{bmatrix} v_1 \\ v_2 \\ v_3 \end{bmatrix} \begin{bmatrix} w_1 & w_2 & w_3 \end{bmatrix} = \begin{bmatrix} v_1 w_1 & v_1 w_2 & v_1 w_3 \\ v_2 w_1 & v_2 w_2 & v_2 w_3 \\ v_3 w_1 & v_3 w_2 & v_3 w_3 \end{bmatrix}$$

More generally,

$$< \mathbf{a} | \mathbf{b} >= \mathbf{a}^+ \mathbf{b}, \text{ while } | \mathbf{a} >< \mathbf{b} | = \mathbf{a}\mathbf{b}^+$$

That is, the transpose is not the relevant operation, but the transpose and then the complex conjugation $\mathbf{a}^+ = (\mathbf{a}^T)^* = (\mathbf{a}^*)^T$, that is, Hermitian

conjugation. Note that the order can be reversed: you can first find the complex conjugate and then transpose the column vector.

Example 4.2

Find the inner product and the outer product of the vectors $< \mathbf{a} \mid \mathbf{b} >$, and the outer product, $\mid \mathbf{a} >< \mathbf{b} \mid$, given that,

$$\mathbf{a} = \begin{bmatrix} i \\ -2 \\ -i \end{bmatrix} \text{ and } \mathbf{b} = \begin{bmatrix} -2i \\ i \\ 2 \end{bmatrix}$$

Solution 4.2

$$< \mathbf{a} \mid \mathbf{b} >= \begin{bmatrix} i & -2 & -i \end{bmatrix}^* \begin{bmatrix} -2i \\ i \\ 2 \end{bmatrix} = \begin{bmatrix} -i & -2 & i \end{bmatrix}^* \begin{bmatrix} -2i \\ i \\ 2 \end{bmatrix} = -2 - 2i + 2i = -2$$

In general, this should be a complex number. In this case, the imaginary part is zero.

$$\mid \mathbf{a} >< \mathbf{b} \mid = \begin{bmatrix} i \\ -2 \\ -i \end{bmatrix} \begin{bmatrix} -2i & i & 2 \end{bmatrix}^* = \begin{bmatrix} i \\ -2 \\ -i \end{bmatrix} \begin{bmatrix} 2i & -i & 2 \end{bmatrix} = \begin{bmatrix} i \times 2i & i \times -i & i \times 2 \\ -2 \times 2i & -2 \times -i & -2 \times 2 \\ -i \times 2i & -i \times -i & -i \times 2 \end{bmatrix}$$

$$= \begin{bmatrix} -2 & 1 & 2i \\ -4i & -2 & -4 \\ 2 & -1 & -2i \end{bmatrix}$$

SELF-ASSESSMENT EXERCISE 1

Given that $\mid \psi >= \frac{1}{\sqrt{3}} \mid 1 > + \frac{1}{\sqrt{5}} \mid 2 > + A \mid 3 >$ is normalised, find *A*. Hence, calculate $P_3 \mid \psi >$.

3.2 The Projection Operator

Let us now take a special case of the operator $\mid \phi_j >< \phi_k \mid$, where $j = k$ in a given orthonormal basis, where any vector in the space can be written,

$$\mid \psi >= \sum_{i=1}^{\infty} c_i \mid \mathbf{v}_i >$$

4.2

$$|\phi_j><\phi_j|\psi>=|\phi_j><\phi_j|\sum_{i=1}^{\infty}c_i|\phi_i>=c_j|\phi_j>$$

4.3

We call

$$P_j=|\phi_j><\phi_j|$$

4.4

the projection operator as its effect on vector $|\psi>$ is to project it in only one 'direction,' that of $|\phi_j>$, that is in 'direction' *j*.

It also makes sense, that

$$P_jP_j|\psi>=P_j|\psi>$$

4.5

Indeed,

$$\begin{aligned}P_jP_j|\psi>&=|\phi_j><\phi_j|\phi_j><\phi_j|\psi>\\&=|\phi_j><\phi_j|c_j|\phi_j>\\&=c_j|\phi_j><\phi_j|\phi_j>\\&=c_j|\phi_j>\\&=P_j|\psi>\end{aligned}$$

Thus, to prove that a given operator is a projection operator, it is sufficient for it to satisfy,

$$P_j^{\,2}=P_j$$

4.6

3.3 The Completeness Relation

$$\sum_j|\varphi_j><\varphi_j|\psi>=\sum_j|\varphi_j><\varphi_j|\sum_i c_i|\varphi_i>=\sum_j|\varphi_j>\left(\sum_i c_i<\varphi_j|\phi_i>\right)=\sum_j c_j|\varphi_j>=|\psi>$$

since $\sum_i c_i<\varphi_j|\phi_i>=c_j$ (Recall from Quantum Mechanics I)

Hence, we can see that $\sum_j|\varphi_j><\varphi_j|$ is an identity operator. Therefore,

we can write $\sum_j|\varphi_j><\varphi_j|\psi>=I|\psi>=|\psi>$

4.7

Thus,

$$I = \sum_j |\varphi_j><\varphi_j| \qquad 4.8$$

This is the completeness relation for the orthonormal system $\{|\varphi_j>\}$. Equation 4.7 indicates that the completeness relation means all possible projections of the system have been taken into consideration. But this also means that the system can be in any of these states and in no other state outside the ones in the given basis vectors or states.

In the case of a continuous spectrum, the completeness relation takes the form of an integral:

$$|\psi>=\int_a^b |\varphi_j><\varphi_j|\psi> dx \qquad 4.9$$

Hence,

$$I = \int_a^b |\varphi_j><\varphi_j| dx \qquad 4.10$$

Now, is there any link between completeness as we discussed under Banach and Hilbert spaces? Of course, there we talked about 'filling holes.' With the 'holes' (if any) filled, we can safely lay out our vectors in such a way that a set of orthonormal basis vectors can be utilised in writing (or representing) any vector in the space. In Quantum Mechanics, that vector could be an energy vector, a position vector or an angular momentum vector. A vector space, you will also recall, is one that allows us to add vectors and multiply them by appropriate scalars (real or complex) and still be confident our result is still in the vector space. In addition, the idea of convergence implies there is an infinite number of vectors between any two points on a complete vector space (what we referred to as denseness). There is no hole. Thus, every Cauchy sequence converges within the vector space). Thus, for example, there is an infinite number of vectors between (1, 0, 0) and (2, 0, 0), such as (1.001, 0, 0), (1.01, 0, 0), (1.1,0,0), etc. Indeed, between any two of these, there is an infinite number of vectors. Does that ring a bell? Yes, the real number line itself is a Banach space as the irrationals that are the 'holes' have been plugged in. Thus, between 0.0 and 0.01, there is no open space and there is an infinite number of real numbers between them. The norm in this case is the absolute value norm. Likewise, the complex plane is a Banach space with the norm defined by the Euclidean norm $\sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2}$, where a vector in the space is represented by $z = x + iy$. It should also be clear from the foregoing, that the *n*-dimensional Euclidean space is also a complete metric space. Here, convergence should be seen in view of the metric defined on the

vector space. We recall that a metric space is a vector space equipped with a metric.

SELF-ASSESSMENT EXERCISE 1

What is the completeness relation? Outline the link, if any, between completeness of a complete normed linear space and the completeness relation.

4.0 CONCLUSION

In this Unit, you learnt about the outer product, the projection operator and the completeness relation. You learnt to distinguish between the inner product, the output of which is a scalar, and the outer product, the output of which is an operator. The projection is a special outer product that projects a vector in only one of the states in which it can possibly exist. Expectedly, applying the projection operator once more produces the same result, as the system is already in that state in which it has been projected. You learnt that the completeness relation means the system under consideration can only be in the set of prescribed eigenstates. This was also linked to completeness of a normed linear space as discussed under Banach and Hilbert space in Unit 2.

5.0 SUMMARY

In this study session, you have learnt:

- to distinguish between inner and outer products of vectors
- to find the outer product of two given vectors
- to work with projection operators
- about the completeness relation and its relationship to the completeness of a normed linear space

Solution to Self-Assessment Exercise 1

$$<\psi|\psi>=\sum_{i=1}^{3}|c_i|^2=1=\frac{1}{3}+\frac{1}{5}+A^2=\frac{8}{15}+A^2$$

$$A^2=1-\frac{8}{15}=\frac{7}{15}, \text{ and } A=\sqrt{\frac{7}{15}}$$

Therefore,

$$|\psi>=\frac{1}{\sqrt{3}}|1>+\frac{1}{\sqrt{5}}|2>+\sqrt{\frac{7}{15}}|3>$$

$$P_3|\psi>=c_3|3>=\sqrt{\frac{7}{15}}|3>$$

6.0 TUTOR-MARKED ASSIGNMENT

1. Find the inner product $<\mathbf{a}|\mathbf{b}>$ and the outer product $|\mathbf{a}><\mathbf{b}|$ of the vectors
$$\mathbf{a}=\begin{bmatrix}2\\-1\\1\end{bmatrix},\ \mathbf{b}=\begin{bmatrix}1\\-1\\3\end{bmatrix}$$

2. Given an orthonormal set $\{|\phi_j>\}_{j=1}^{\infty}$, Show that $\sum_{j=1}^{\infty}|\phi_j><\phi_j|=I$.

3. Show that the matrix $\begin{pmatrix}0&0&0\\0&1&0\\0&0&1\end{pmatrix}$ is a projector from R^3 to the $y-z$ plane.

4. Show that a linear operator P is a projection operator if and only if there exists another linear operator Q such that, $P+Q=I$.

5. What do you understand by 'the completeness relation?'

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MODULE 2 ANGULAR MOMENTUM AND SPIN OF ATOMIC AND NUCLEAR PARTICLES

UNIT 1 ANGULAR MOMENTUM

CONTENTS

1.0 INTRODUCTION

Angular momentum in quantum mechanics is equivalent to the same concept in classical mechanics. You will recall that in classical mechanics, the angular momentum of an isolated system is conserved. As usual, in quantum mechanics, the angular momentum operator is an operator. In quantum mechanics however, unlike the case of the classical analogy, the Cartesian components of the orbital angular momentum are operators which do not commute. This implies we cannot measure the different components of the angular momentum of a body simultaneously and with infinite accuracy.

2.0 OBJECTIVES

At the end of this Unit, you will be able to:

- find the expressions for the components of angular momentum
- find the commutator relationship between pairs of angular momentum operators

- calculate the eigenvalues of the magnitude of the angular momentum
- calculate the eigenvalues of the *z*-component of the angular momentum
- explain what is meant by angular momentum cones.

3.0 MAIN CONTENT

3.1 Angular Momentum Operators

The angular momentum of a body is the moment of its momentum about a given reference point. In Classical mechanics, the angular momentum of a body can take on any value. Is this the case in Quantum mechanics? To start with, as it is with all physical observables in Quantum mechanics, the angular momentum of a body is represented by an operator. We start our analysis by considering the angular momentum operator **L**.

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \qquad 1.1$$

In the Cartesian system, we can write this as

$$\mathbf{L} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

where $\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$ and $\mathbf{p} = p_x\mathbf{i} + p_y\mathbf{j} + p_z\mathbf{k}$ are respectively the position vector and the linear momentum of the body.

Thus,

$$\mathbf{L} = \mathbf{i}(yp_z - zp_y) + \mathbf{j}(zp_x - xp_z) + \mathbf{k}(xp_y - yp_x) \qquad 1.2$$

The commutation relations below hold:

$$\begin{aligned}[L_x, L_y] &= [yp_z - zp_y, zp_x - xp_z] \\ &= [yp_z, zp_x] - [y\,\mathrm{p}_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z] \\ &= yp_z zp_x - zp_x yp_z - (yp_z xp_z - xp_z yp_z) \\ &\quad -(zp_y zp_x - zp_x zp_y) + zp_y xp_z - xp_z zp_y \\ &= yp_z zp_x + zp_y xp_z - zp_x yp_z - xp_z zp_y \\ &\quad + zp_x zp_y - zp_y zp_x + xp_z yp_z - yp_z xp_z \text{ (this part is zero)}\end{aligned}$$

That part is zero because all the operators commute and it does not matter in which order they are written. Recall: $[q_i, p_j] = i\hbar\delta_{ij}$

Hence,

$$\begin{aligned}[L_y, L_z] = i\hbar L_x &= p_x y p_z z - p_x y z p_z + p_y x z p_z - p_y x p_z z \\ &= p_x y(p_z z - z p_z) + p_y x(z p_z - p_z z) \\ &= -p_x y(\mathrm{z}\, p_z - p_z\, \mathrm{z}) + p_y x(z p_z - p_z z) \\ &= -p_x y[z, p_z] + p_y x[z, p_z] \\ &= -i\hbar p_x y + i\hbar p_y x \\ &= -i\hbar(p_x y - p_y x) = i\hbar(y p_x - x p_y) = i\hbar L_z\end{aligned}$$

Thus,

$$[L_x, L_y] = i\hbar L_z \qquad 1.3$$

Similarly,

$$[L_y, L_z] = i\hbar L_x \qquad 1.4$$

and

$$[L_z, L_x] = i\hbar L_y \qquad 1.5$$

An alternative way of proving these commutation relations is in Appendix 2.

Equations 1.3-1.5 can all be summed up by Fig. 1.1. Clockwise rotation is reckoned positive, while counterclockwise rotation is reckoned negative. For instance, relation 1.3 gives a positive $i\hbar L_z$, while a counterclockwise $[L_z, L_y] = -i\hbar L_x$

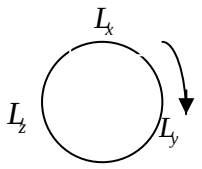

Fig. 1.1: Figure demonstrating the commutative relationship among the *x*, *y* and *z* components of the angular momentum

The relevant Hamiltonian (see Appendix 2), is

$$H = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{L^2}{r^2\hbar^2}\right] + V(r) \qquad 1.6$$

Using the relation $[q_i, p_j] = i\hbar\delta_{ij}$, $i, j = 1, 2, 3$, we can write

$$[L_z, H] = [p_z, H] = [L_z, p_z] = 0 \qquad \text{(Show)} \tag{1.7}$$

SELF-ASSESSMENT EXERCISE 1
Show each of the expressions in equation 1.6.

Since $[AB, C] = A[B, C] + [A, C]B$,

$$[L^2, L_z] = L[L, L_z] = L[L_x + L_y + L_z, L_z] = [L_x, L_z] + [L_x, L_z] + [L_x, L_z] = 0.$$

Indeed, L^2 commutes with each of the components of **L**, i.e., L_x, L_y and L_z. That is,

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0 \tag{1.8}$$

Since the three operators H, L_z and p_z commute with each other, it is possible to find states that are simultaneously eigenstates for all three operators.

The eigenvalue equation for L_z can be written as

$$L_z \mid m >= m\hbar \mid m > \tag{1.9}$$

where $m\hbar$ are the eigenvalues of L_z and the states have been labelled by m.
We conclude that the eigenvalues of L^2 are degenerate: to each eigenvalue $L^2 = l(l+1)\hbar^2$, there are $2l+1$ linearly independent eigenstates φ_{lm}, for values of m in the range $-l \le m \le l$. In other words, each L^2 eigenvalue is $2l+1$-fold degenerate.

The m in $m\hbar$ is called the magnetic quantum number, while l is called the orbital angular momentum (or azimuthal) quantum number.

3.2 The Angular Momentum Cones

The eigenvalues of the angular momentum L are $\sqrt{l(l+1)}\hbar$, meaning that a measurement of the magnitude of angular momentum will only find one of the discrete set of values,

$$| L | = \sqrt{l(l+1)}\hbar, \; l = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots \tag{1.10}$$

Also, a measurement of the component of angular momentum along a certain axis, e.g., the z-axis, would only find one of the possible values, one of the eigenvalues,

$$L_z = m\hbar\,,\ m \in \{-l,-l+1,-l+2,...,l-2,l-1,l\}$$
1.11

We now note the differences between angular momentum in classical and in quantum mechanics:
The angular momentum in any other direction, the *z*-direction say, is always smaller than the magnitude of the total (non-zero) angular momentum. Since $L_z = l\hbar$ is the largest possible value of L_z, and $l < \sqrt{l(l+1)}; l > 0$,

$$l\hbar < \sqrt{l(l+1)}\hbar$$
1.12

We conclude that the angular momentum can never be completely aligned in any particular direction. Indeed, if the angular momentum did point in any one definite direction, then all the components would be definite. However, we know corresponding operators do not commute; as such, these components cannot be measured accurately simultaneously.

We know in classical physics, that **L** is a vector in a definite direction. In quantum mechanics, in view of the Heisenberg uncertainty and non-commutativity of the operators involved, this cannot be the case. Hence, it is better to visualise the angular momentum associated with a given eigenstate φ_{lm} as a cone, the **angular momentum cone**.

Nevertheless, in an eigenstate we know that the magnitude of the angular momentum $|\mathbf{L}|$ and the z-component L_z are fixed,

$$|L| = \sqrt{l(l+1)}\hbar\,,\ L_z = m\hbar$$
1.13

While the values of L_x and L_y are indefinite, the squared expectation values must satisfy

$$< L_x^2 > + < L_y^2 > + < L_z^2 > = < L^2 >$$
1.14

Thus, due to non-commutativity of the components and the attendant uncertainty, an infinite number of allowable vectors form a cone that can have the same amplitude and *z*-component.

SELF-ASSESSMENT EXERCISE 2
What quantum-mechanical concept underlies angular momentum cones?

4.0 CONCLUSION

In Unit 1 of this Module, you learnt that the classical angular momentum has a quantum analogue. However, unlike the classical case, the components of the quantum-mechanical angular momentum do not commute. The implication of this is that it is not possible to measure all the components at the same time and with infinite accuracy. It also means that they cannot have the same eigenfunction. However, the z-component of the angular momentum commutes with the square of the magnitude of the angular momentum as well as with the Hamiltonian. All three operators can therefore have the same eigenfunction. In addition, with the non-commuting nature of the components of the angular momentum, it is impossible to measure any pair of components simultaneously with infinite accuracy due to the Heisenberg uncertainty principle. As such, the angular momentum associated with a given eigenvector is best visualised as a cone, the angular momentum cone.

5.0 SUMMARY

In this Unit, you have learnt:

- the quantum-mechanical angular momentum is the quantum equivalent of the classical angular momentum
- Unlike the classical angular momentum, the components of the quantum-mechanical angular momentum do not commute
- Non-commutativity implies the components of quantum-mechanical angular momentum cannot be measured simultaneously with infinite accuracy
- the Hamiltonian, as well as the square of the magnitude of the angular momentum commute with the z-component of the angular momentumall three can have the same eigenfunction
- the commutation relations for the Cartesian components of the angular momentum operator.
- the magnitude of the orbital angular momentum and its *z*-component are fixed; as such, due to non-commutativity of the components, an infinite number of vectors form a cone (angular momentum cone) that can have the same amplitude and *z*-component.

Answer to Self-Assessment Exercise 1

$[L_z, H] = 0$

This is because *H*(equation 1.6) involves a term in *r*, which commutes with L_z which has no term in *r*, and $[L_z, L^2] = 0$

$[p_z, H] = \left[\frac{\hbar}{i}\frac{\partial}{\partial z}, H\right] = 0$ because *H* has no explicit dependence on *z*.

$[L_z, p_z] = 0$ since $L_z = xp_y - yp_x$ and $[(xp_y - yp_x), p_z] = [xp_y - yp_x, p_z] = 0$ since all components of the linear momentum commute one with another.

Answer to Self-Assessment Exercise 2

Heizenberg's uncertainty principle.

6.0 TUTOR-MARKED ASSIGNMENT

1. Explain the term 'angular momentum cone.'

2. Prove the following identities:
   (i) $[L_x{}^2, L_y] = i\hbar L_x L_z + i\hbar L_z L_x$ (ii) $[L^2, L_y] = 0$

3. Find all the possible values (spectrum) L_x in the state $\frac{1}{\sqrt{6}}\begin{pmatrix}1\\1\\2\end{pmatrix}$.

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UNIT 2 EIGENFUNCTIONS OF ANGULAR MOMENTUM I

CONTENTS

1.0 INTRODUCTION

In Unit 1, we introduced the concept of quantum-mechanical angular momentum and were able to identify some commuting operators, two of which are the square of the magnitude of the angular momentum and the z-component of the angular momentum. As a result, the two operators can have the same eigenfunction. In this Unit, we explore this possibility. As in the case of the harmonic oscillator, we introduce the ladder operators, and starting with the 'highest' eigenfunction, we can then use the lowering operator to obtain all other eigenfunctions.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- showthe form of angular momentum eigenfunctions, the spherical harmonics
- identified all the wavefunctions for the square of a given orbital angular momentum and the z-component of the angular momentum
- determined the eigenvalues of the square of the magnitude of the angular momentum as well those of the z-component of angular momentum.

3.0 MAIN CONTENT

3.1 Angular Momentum in Spherical Coordinates

In the case of the harmonic oscillator as treated in PHY 319, the ground state wavefunction was found by solving the first order differential equation, $a\psi_0 = 0$, where a is the lowering operator for the harmonic oscillator, and all other eigenstates by applying the raising operator a^+.

In the case of angular momentum, we use a similar approach. Let l be given. Then, we solve the first order differential equations,

$$L_+\varphi_{ll}(x,y,z) = 0 \qquad 2.1$$

$$L_z\varphi_{ll}(x,y,z) = l\hbar\varphi_{ll} \qquad 2.2$$

and then obtain all other φ_{lm} wavefunctions in the multiplet by applying successively the lowering operator L_-.

In view of the spherical symmetry of the problem, it is much easier to solve these differential equations in spherical coordinates:radial r, polar θ, and azimuthal ϕ,

$$\left.\begin{aligned} z &= r\cos\theta \\ x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \end{aligned}\right\} \qquad 2.3$$

This is because in spherical coordinates, the r variable drops out of the angular momentum operators. The resulting angular momentum operators become (see Appendix for proof):

$$L_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \qquad 2.4$$

$$L_y = i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \qquad 2.5$$

$$L_z = -i\hbar\frac{\partial}{\partial\phi} \qquad 2.6$$

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\phi}\frac{\partial^2}{\partial\phi^2}\right] \qquad 2.7$$

SELF-ASSESSMENT EXERCISE 1

From the expression for L^2 in equation 2.7, show that $[L_z, L^2] = [L^2, H] = [L^2, p_z] = 0$

We shall encounter equation 2.7 while solving the angular part of the Schroedinger equation for a spherically symmetric potential. The eigenfunctions of L^2 are of the form

$$\varphi_{lm}(x, y, z) = f(r)Y_{lm}(\theta, \phi) \qquad 2.8$$

where $Y_{lm}(\theta, \varphi)$ are the spherical harmonics. We can therefore write the eigenvalue equation,

$$L^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi) \qquad 2.9$$

Thus the eigenvalues of L^2 are $l(l+1)\hbar^2$. A measurement of L^2 can only give a set of values $l(l+1)\hbar^2$.

Since L^2 and L_z commute, they can have the same eigenfunctions. So, we can also write

$$L_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi) \qquad 2.10$$

In like manner, the eigenvalues of L_z are $m\hbar$. A measurement of L_z can only give a set of values $m\hbar$.

$f(r)$ is any function such that the normalisation condition

$$1 = \int dxdydx\phi^*(x, y, z)\phi(x, y, z)$$

$$= \int_0^\infty r^2 dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi \, f^*(r) f(r) Y_{lm}^*(\theta, \phi) Y_{lm}(\theta, \phi)$$

is satisfied. Conventionally, we normalise the Y_{lm} such that the integral over angles is also equal to unity,

$$\int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi Y_{lm}^*(\theta, \phi) Y_{lm}(\theta, \phi) = 1$$

With this normalisation, the $Y_{lm}(\theta, \phi)$ are known as "spherical harmonics".

In spherical coordinates, the raising and lowering operators are

$$L_+ = L_x + iL_y \qquad 2.11$$

$$= \hbar e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right) \qquad 2.12$$

$$L_- = L_x - iL_y$$

2.13

Note that $L_- = (L_+)^+$.

$$= -\hbar e^{-i\phi}\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}\right)$$

2.14

We can then solve the first-order differential equations

$$L_+ Y_{ll} = 0,\ L_z Y_{lm} = l\hbar Y_{lm}$$

2.15

The first equation in equation 2.15 is a consequence of our inability to raise a state higher than the highest possible, which in this case is $m = l$.

SELF-ASSESSMENT EXERCISE 2

Using the raising and the lowering operators, respectively, $L_+ = L_x + iL_y$, $L_- = L_x - iL_y$, prove the following:

(i) $L_x = \frac{1}{2}(L_+ + L_-); L_y = \frac{1}{2}(L_+ - L_-)$

(ii) $L^2 = L_z{}^2 + \frac{1}{2}(L_+ L_- + L_- L_+)$

(iii) $[L_+, L_-] = 2\hbar L_z$

3.2 The Azimuthal Equation

By the method of separation of variables

$$Y_{lm}(\theta,\phi) = A(\theta)B(\phi)$$

2.16

The L_z eigenvalue equation (for any m) is,

$$-i\hbar\frac{dB}{d\phi} = m\hbar B$$

2.17

Hence,

$$\frac{dB}{B} = -\frac{1}{i}m\,d\phi = im\,d\phi$$

or

$$\ln B = im\phi + c$$

Taking the Napierian logarithm of both sides,

$$B(\phi) = De^{im\phi}$$

where $D = e^c$.

We can set D equal to unity since we are yet to normalise the function $Y_{lm}(\theta,\phi) = A(\theta)B(\phi)$. Then,

$$B(\phi) = e^{im\phi} \qquad 2.18$$

Since the angle $\phi = 0$ is the same as the angle $\phi = 2\pi$, so the wavefunctions must satisfy the periodicity condition

$$Y_{lm}(\theta, \phi + 2\pi) = Y_{lm}(\theta, \phi) \qquad 2.19$$

Since the periodicity condition must be satisfied, if ϕ increases by 2π, $B(\phi)$ must remain the same, i.e., $B(\phi) = e^{im\phi} = B(\phi + 2\pi) = e^{im(\phi+2\pi)}$.

$$e^{im\phi} = e^{im(\phi+2\pi)} = e^{im\phi} e^{2im\pi}$$

Then,

$$e^{2im\pi} = 1 = \cos 2m\pi + i \sin 2im\pi$$

Equating the real parts,

$$1 = \cos 2m\pi$$

This is possible only for integral (positive, negative and zero) values of *m*:

$$m = 0, \pm 1, \pm 2, \ldots, \qquad 2.20$$

(*m* is the magnetic quantum number)

As a result, since $-l \le m \le l$, the possible values for l are

$$l = 0, 1, 2, \ldots$$

So we have

$$Y_{lm}(\theta, \phi) = A(\theta) e^{im\phi} \qquad 2.21$$

and in particular, setting *m* equal to *l*, the largest possible value of *m*,

$$Y_{ll}(\theta, \phi) = A(\theta) e^{il\phi} \qquad 2.22$$

3.3 The Polar Equation

Applying the raising operator to the state given in equation 2.22, we must have (raising the highest state gives you zero, since no state is higher than the highest state):

$$\begin{aligned} 0 &= L_+ Y_{ll} \\ &= \hbar e^{i\phi} \left(i \cot\theta \frac{\partial}{\partial \phi} + \frac{\partial}{\partial \phi} \right) A(\theta) e^{il\phi} \\ &= \hbar e^{i\phi} \left(i \cot\theta \frac{\partial}{\partial \phi} (A(\theta) e^{il\phi}) + \frac{\partial}{\partial \theta} (A(\theta) e^{il\phi}) \right) \\ &= \hbar e^{i(l+1)\phi} \left(-l \cot\theta + \frac{\partial}{\partial \theta} \right) A(\theta) \end{aligned}$$

$$= \hbar e^{i(l+1)\phi}\left(-l\cot\theta + \frac{d}{d\theta}\right)A(\theta)$$

2.23

(The form of the differential changes from partial differential to ordinary differential, as $A(\theta)$ is a function only of θ)

or

$$\frac{d}{d\theta}A(\theta) = l\cot\theta\, A(\theta)$$

2.24

Hence,

$$\int \frac{dA(\theta)}{A(\theta)} = l\int \frac{\cos\theta}{\sin\theta}d\theta$$

The integral $\int \frac{f'(x)}{f(x)}dx = \ln f(x) + c.$

$$\ln A(\theta) = l(\ln\sin\theta) + c = \ln\sin^l\theta + c, \text{ since } \ln a^b = b\ln a$$

Taking the exponential of both sides,

$$e^{\ln A(\theta)} = e^{\ln\sin^l\theta + c} = e^c e^{\ln\sin^l\theta} = De^{\ln\sin^l\theta}$$

where $e^c = D$, a constant. We can therefore write (bearing in mind that $e^{\ln x} = x$)

$$A(\theta) = D\times\sin^l\theta$$

2.25

Then,

$$Y_{ll}(\theta,\phi) = A(\theta)B(\phi) = N\sin^l\theta e^{il\phi}$$

2.26

where N is a normalisation constant, which is determined from the normalisation condition

$$1 = \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi Y_{ll}^* Y_{ll}$$

$$= 2\pi N^2 \int_0^\pi \sin^{(2l+1)}\theta\, d\theta$$

$$= \frac{2\pi^{3/2} l!}{\Gamma\left(l+\frac{3}{2}\right)}N^2$$

2.27

The Γ-function is a special function with the property

$$\Gamma(x+1) = x\Gamma(x),\ \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$$

Equating equation 2.27 to 1, we get

$$N = \left[\frac{\Gamma\left(l + \frac{3}{2}\right)}{2\pi^{3/2} l!} \right]^{1/2}$$

2.28

$Y_{lm}(\theta,\phi)$ also depends on *l* in such a way that we choose $N = (-1)^l$ times the expression in 2.28 obtained from the normalisation.

From equation 7.41,

$$N = (-1)^l \left[\frac{\Gamma\left(l + \frac{3}{2}\right)}{2\pi^{3/2} l!} \right]^{1/2}$$

2.29

Therefore,

$$Y_{ll}(\theta,\phi) = (-1)^l \left[\frac{\Gamma\left(l + \frac{3}{2}\right)}{2\pi^{3/2} l!} \right]^{1/2} \sin^l \theta e^{il\phi}$$

2.30

Answer to Self-Assessment Exercise 1

L^2 is explicit only in the angles θ and ϕ and differentials with respect to these angles. The operator commutes with any operator that is not explicit in these angles and differentials having to do with the angles. All the other operators are not explicit in the angles or their differentials with respect to them. The periodicity condition on the azimuthal part of the spherical harmonics ensures that the eigenvalues of the z-component of the angular momentum are only 0, positive and negative integers. This also imposes a condition on the

Answer to Self-Assessment Exercise 2

$$L_+ = L_x + iL_y$$

$$L_- = L_x - iL_y$$

Adding and subtracting and dividing by 2, gives the desired expressions.

$L^2 = L_x{}^2 + L_y{}^2 + L_z{}^2$

But,

$$L_+L_- + L_-L_+ = (L_x + iL_y)(L_x - iL_y) + (L_x - iL_y)(L_x + iL_y)$$

$$= (L_x{}^2 - iL_xL_y + iL_yL_x + L_y{}^2) + (L_x{}^2 - iL_yL_x + iL_xL_y + L_y{}^2)$$

$$= 2L_x^{\,2} + 2L_y^{\,2}$$

$$L_x^{\,2} + L_y^{\,2} = \frac{1}{2}(L_+L_- + L_-L_+)$$

Hence,

$$L^2 = L_z^{\,2} + \frac{1}{2}(L_+L_- + L_-L_+)$$

$$[L_+, L_-] = L_+L_- - L_-L_+ = (L_x + iL_y)(L_x - iL_y) - (L_x - iL_y)(L_x + iL_y)$$

$$= (L_x^{\,2} - iL_xL_y + iL_yL_x + L_y^{\,2}) - (L_x^{\,2} + iL_xL_y - iL_yL_x + L_y^{\,2})$$

$$= 2i(L_yL_x - L_xL_y] = 2i[L_y, L_x] = 2i(-i\hbar L_z) = 2\hbar L_z$$

4.0 CONCLUSION

In this Unit, you learnt that the spherical harmonics are the eigenfunctions of both the square of the magnitude of the angular momentum operator and the *z*-component of the angular momentum. The periodicity condition on the azimuthal part of the wavefunction ensures that the magnetic quantum number can only take integral values, leading to a quantisation of the magnetic quantum numbers. This also implies that the azimuthal quantum number can also only be zero or a set of positive integers. By applying the raising and the lowering operators of angular momentum, you were able to obtain all the eigenfunctions (spherical harmonics) for a given value of the azimuthal or orbital angular momentum number *l*.

5.0 SUMMARY

In this Unit, you have learnt the following:

- the square of the magnitude of the angular momentum operator and the z-component of the angular momentum commute
- the spherical harmonics are the eigenfunctions of both the square of the magnitude of the angular momentum and the *z*-component of the angular momentum
- with the help of the ladder operators, we obtained all the eigenfunctions for a particular value of *l*
- the magnetic quantum number is quantised (only 0, and positive and negative integers)
- the orbital angular momentum quantum number is quantised (0, and positive integers only)
- expressions for the components of the angular momentum in spherical coordinates.
- expressions for the eigenvalues and the eigenfunctions of the square of the magnitude of theangular momentum and the z-component of the angular momentum.

6.0 TUTOR-MARKED ASSIGNMENT

1. Find the matrix of representation for the raising and the lowering operators of angular momentum.
2. Find the expectation values $<L_x>$, $<L_y>$, $<L_z>$, $<L_z^2>$ in the state $|l,l>$ and show that $<L_x^2> = <L_y^2>$.
3. Find the matrix representation for the raising and the lowering operators of angular momentum.

7.0 REFERENCES/FURTHER READING

Byron, F. W. Jr. & Fuller, R. W. (1992). *Mathematics of Classical and Quantum Physics*. NY: Dover Publications

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UNIT 3 EIGENFUNCTIONS OF ANGULAR MOMENTUM II

CONTENTS

1.0 INTRODUCTION

In Unit 2, we introduced the raising and the lowering operators of orbital angular momentum. In this Unit, we shall continue with our analysis of the eigenfunctions of angular momentum. We shall be writing a few of the spherical harmonics.

2.0 OBJECTIVES

At the end of this unit, you shouldbe able to:

- raise and lower the magnetic quantum number of spherical harmonics with the ladder operators
- calculate all the multiplets of a given orbital angular momentum quantum number

3.0 MAIN CONTENT

3.1 Raising and Lowering Operators of Orbital Angular Momentum

In the last Unit, we got the wavefunction (spherical harmonic)

$$Y_{ll}(\theta,\phi) = (-1)^l \left[\frac{\Gamma\left(l+\frac{3}{2}\right)}{2\pi^{3/2} l!} \right]^{1/2} \sin^l \theta e^{il\phi}$$

We can get the other Y_{lm} by applying the lowering operator, L_-,

$$L_{-}Y_{l,m}(\theta,\phi) = C_{lm}^{-}Y_{l,m-1}(\theta,\phi)$$
3.1

given the constant C_{lm}^{-}. Corresponding constants C_{lm}^{+} are defined from

$$L_{+}Y_{l,m}(\theta,\phi) = C_{lm}^{+}Y_{l,m+1}(\theta,\phi)$$
3.2

To get the C_{lm}^{-} constants, we do the following:

$$L_{-}L_{+} = L^2 - L_z^2 - \hbar L_z$$
3.3

$$L_{+}L_{-} = L^2 - L_z^2 + \hbar L_z$$
3.4

Then, making use of these values,

$$<\varphi_{lm}|L_{-}L_{+}|\varphi_{lm}> \quad = <\varphi_{lm}|(L^2 - L_z^2 - \hbar L_z)|\varphi_{lm}>$$
3.5

Therefore,

$$<\varphi_{lm}|L_{-}L_{+}|\varphi_{lm}> = <(L_{-})^{+}\phi_{lm}|L_{+}|\phi_{lm}>$$
$$= <L_{+}\varphi_{lm}|L_{+}\varphi_{lm}>$$
$$= \hbar^2[l(l+1) - m^2 - m) < \varphi_{lm}|\varphi_{lm}>$$
3.6

$$(C_{lm}^{+})^{*}(C_{lm}^{+}) \quad = \hbar^2(l-m)(l+m+1)$$
3.7

so that

$$C_{lm}^{+} = \hbar\sqrt{(l-m)(l+m+1)}e^{i\omega}$$
3.8

Note that for a complex number z, $z = re^{i\theta}$, and $|z|^2 = z^{*}z = r^2$. Notice that the phase disappears in the process of obtaining the magnitude of the number. We recover the original complex number by multiplying the magnitude by an arbitrary phase factor $e^{i\theta}$. You can then confirm that indeed, with this value of C_{lm}^{+} equation 3.7 holds.

Likewise,

$$<\varphi_{lm}|L_{+}L_{-}|\varphi_{lm}> \quad = <\varphi_{lm}|(L^2 - L_z^2 + \hbar L_z)|\varphi_{lm}>$$
3.9

$$<L_{-}\varphi_{lm}|L_{-}\varphi_{lm}> \quad = \hbar^2[l(l+1) - m^2 + m) < \varphi_{lm}|\varphi_{lm}>$$
3.10

$$(C^{-}_{lm})^{*}C^{-}_{lm} = \hbar^2(l-m)(l-m+1) \qquad 3.11$$

so that

$$C^{-}_{lm} = \hbar\sqrt{(l+m)(l-m+1)}e^{-i\omega} \qquad 3.12$$

In this case, ω is an arbitrary phase. This can always be absorbed into a rescaling of the wavefunction, i.e., $\varphi_{lm} \rightarrow e^{i\omega}\varphi_{lm}$, which does not affect the physical state. So we can always choose C^{-}_{lm} to be real. It can be shown that $C^{-}_{lm} = (C^{+}_{l,m-1})^{*}$. Hence, if the C^{-} coefficients are real, then the C^{+} coefficients are also real and

$$C^{-}_{lm} = \hbar\sqrt{(l+m)(l-m+1)} \qquad 3.13$$

$$C^{+}_{lm} = \hbar\sqrt{(l-m)(l+m+1)} \qquad 3.14$$

and we can now compute all the Y_{lm} using

$$Y_{ll}(\theta,\phi) = (-1)^{l}\left[\frac{\Gamma\left(l+\frac{3}{2}\right)}{2\pi^{3/2}l!}\right]^{1/2} \sin^{l}\theta\, e^{il\phi} \qquad 3.15$$

$$L_{-}Y_{lm} = \hbar\sqrt{(l+m)(l-m+1)}Y_{l,m-1} \qquad 3.16$$

$$L_{+}Y_{lm} = \hbar\sqrt{(l-m)(l+m+1)}Y_{l,m+1} \qquad 3.17$$

Since the Y_{ll} was normalised to 1, all of the Y_{lm} obtained by applying the lowering operator will also be normalised to 1.

Spherical harmonics corresponding to different values of l and/or m will be orthogonal:

$$\int_0^{\pi}\sin\theta\, d\theta\int_0^{2\pi} d\phi Y^{*}_{lm}(\theta,\phi)Y^{*}_{l'm'}(\theta,\phi) = \delta_{ll'}\delta_{mm'} \qquad 3.18$$

Example 3.1

Given that $Y_{11} = (-1)\left[\frac{\Gamma(5/2)}{2\pi^{3/2}}\right]^{1/2}\sin\theta\, e^{i\phi} = -\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi}$, compute two of the $l=1$ multiplet of spherical harmonics, i.e., Y_{11}, Y_{10} and $Y_{1,-1}$

Solution 3.1

$$Y_{11} = (-1)\left[\frac{\Gamma(5/2)}{2\pi^{3/2}}\right]^{1/2} \sin\theta\, e^{i\phi} \quad 3.19$$

$$= -\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi} \quad 3.20$$

then

$$L_{-}Y_{11} = -\sqrt{\frac{3}{8\pi}}\hbar e^{-i\phi}\left(i\cot\theta\frac{\partial}{\partial\phi} - \frac{\partial}{\partial\theta}\right)\sin\theta\, e^{i\phi} \quad 3.21$$

$$\hbar\sqrt{2}Y_{10} = \sqrt{\frac{3}{8\pi}}\hbar(\cot\theta\sin\theta + \cos\theta) \quad 3.22$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta \quad 3.23$$

Applying the lowering operator again,

$$L_{-}Y_{10} = \sqrt{\frac{3}{4\pi}}\hbar e^{-i\phi}\left(i\cot\theta\frac{\partial}{\partial\phi} - \frac{\partial}{\partial\theta}\right)\cos\theta \quad 3.24$$

$$\hbar\sqrt{2}Y_{1,-1} = \sqrt{\frac{3}{4\pi}}\hbar e^{-i\phi}\sin\theta \quad 3.25$$

$$Y_{1,-1} = \sqrt{\frac{3}{8\pi}}e^{-i\phi}\sin\theta \quad 3.26$$

SELF-ASSESSMENT EXERCISE 1

Show that $C^{-}_{lm} = (C^{+}_{l,m-1})^{*}$

SELF-ASSESSMENT EXERCISE 2

The Hamiltonian of a rigid rotator of angular momentum *L* and moment of inertia *I* immersed in a uniform magnetic field aligned with the *z*-axis can be written as

$$H = \frac{L^2}{2I} + \omega_0 L_z$$

where ω_0 is a constant. If $|\psi(t=0)>=\sqrt{\frac{48}{2\pi}}\sin\theta\cos\phi+\sqrt{\frac{27}{16\pi}}\cos\theta$, find

(a) the possible values a measurement of L_z will give, and with what probability.

(b) $|\psi(t)>$ for any arbitrary time *t*.

(c) the expectation value of L_y at time *t*.

4.0 CONCLUSION

In this Unit, you have learnt to make use of the raising and lowering operators to calculate all the multiplets of a given orbital angular momentum.

5.0 SUMMARY

In this Unit, you have learnt to:

- raise and lower the spherical harmonics with the ladder operators
- calculate the multiplets of a given orbital angular momentum number.

Answer to Self-Assessment Exercise 1

$$C^{+}_{lm}=\hbar\sqrt{(l-m)(l+m+1)}e^{i\omega}$$
$$C^{-}_{lm}=\hbar\sqrt{(l+m)(l-m+1)}e^{-i\omega}$$

$$C^{-}_{lm}=(C^{+}_{l,m-1})^{*}$$

Substituting $m-1$ for *m* in the expression for $C^{+}_{l,m}$,

$$(C^{+}_{l,m-1})^{*}=(\hbar\sqrt{(l-[m-1)][l+[m-1]+1)}e^{i\omega})^{*}$$
$$(C^{+}_{l,m-1})^{*}=\hbar\sqrt{(l-[m-1)][l+[m-1]+1)}e^{-i\omega}$$
$$(C^{+}_{l,m-1})^{*}=\hbar\sqrt{(l-m+1)(l+m)}e^{-i\omega}$$

Answer to Self-Assessment Exercise 2

(a) $$\sqrt{\frac{48}{2\pi}}\sin\theta\cos\phi+\sqrt{\frac{27}{4\pi}}\cos\theta=\sqrt{\frac{4\times3}{2\pi}}\sin\theta\cos\phi+\sqrt{\frac{9\times3}{4\pi}}\cos\theta$$
$$=2\sqrt{\frac{3}{2\pi}}\sin\theta\cos\phi+\frac{3}{2}\sqrt{\frac{3}{\pi}}\cos\theta$$

$$= 2\sqrt{\frac{3}{2\pi}}\sin\theta(\frac{e^{i\phi}+e^{-i\phi}}{2})+\frac{3}{2}\sqrt{\frac{3}{\pi}}\cos\theta\,.$$
$$= \sqrt{\frac{3}{2\pi}}\sin\theta(e^{i\phi}+e^{-i\phi})+\frac{3}{2}\sqrt{\frac{3}{\pi}}\cos\theta$$

$$= 2\times\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{i\phi}+2\times\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{-i\phi}+3\times\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$$
$$= -2Y_{1,1}+2Y_{1,-1}+3Y_{1,0}$$

Hence,

$$|\psi>=-2\,|1,1>+2\,|1,-1>+3\,|1,0>$$

Normalising,

$$|\psi>=\frac{1}{\sqrt{17}}(-2|1,1>+2|1,-1>+3|1,0>)$$

You can easily see that the possible outcome of a measurement of the z-component of the angular momentum would be $-\hbar, 0, \hbar$, with probability respectively $\frac{4}{17}, \frac{9}{17}, \frac{4}{17}$.

(b) $$|\psi(0)>=\frac{1}{\sqrt{17}}(-2|1,1>+2|1,-1>+3|1,0>)$$

We write, rightaway,

$$|\psi(t)>=\frac{1}{\sqrt{17}}(-2|1,1>e^{-iE_{1,1}t/\hbar}+2|1,-1>e^{-iE_{1,-1}t/\hbar}+3|1,0>e^{-iE_{1,0}t/\hbar})$$

Hence, $< L_y >= \frac{1}{2i} < \psi(t)\,|\,(L_+ - L_-)\,|\,\psi(t) >$

$$= \frac{1}{17}\frac{1}{2i}(<-2\,|1,1|\,e^{-iE_{1,1}t/\hbar}+2<1,-1|\,e^{-iE_{1,-1}t/\hbar}+3<1,0|\,e^{-iE_{1,0}t/\hbar})$$
$$(\mathrm{L}_+ - L_-)\,|\frac{1}{\sqrt{17}}(-2|1,1>e^{-iE_{1,1}t/\hbar}+2|1,-1>e^{-iE_{1,-1}t/\hbar}+3|1,0>e^{-iE_{1,0}t/\hbar})$$

$$\mathrm{L}_+\,|\,l,m>=\sqrt{(l-m)(l+m+1)}\,|\,l,m+1>$$
$$\mathrm{L}_-\,|\,l,m>=\sqrt{(l+m)(l-m+1)}\,|\,l,m-1>$$

For $m = l$, $\mathrm{L}_+\,|\,l,l>=0$ Why?

For $m = -l$, $\mathrm{L}_+\,|\,l,-l>=0$ Why?

$$\mathrm{L}_+\,|\,1,-1>=\sqrt{(1-(-1))(1-1+1)}\,|\,l,-1+1>=\sqrt{2}\,|\,l,0>$$
$$\mathrm{L}_+\,|\,1,0>=\sqrt{(1-0)(1+0+1)}\,|\,l,0+1>=\sqrt{2}\,|\,l,1>$$
$$\mathrm{L}_-\,|\,1,1>=\sqrt{(1+1)(1-1+1)}\,|\,1,1-1>=\sqrt{2}\,|\,l,0>$$
$$\mathrm{L}_-\,|\,1,0>=\sqrt{(1+0)(1-0+1)}\,|\,l,0-1>=\sqrt{2}\,|\,1,-1>$$

Hence,

$$< L_y >= \frac{1}{2i} < \psi(t) | (L_+ - L_-) | \psi(t) >$$

$$= \frac{1}{17}\frac{1}{2i}(< -2 | 1,1 | e^{-iE_{1,1}t/\hbar} + 2 < 1,-1 | e^{-iE_{1,-1}t/\hbar} + 3 < 1,0 | e^{-iE_{1,0}t/\hbar})$$

$$\mathrm{L}_+ | (-2 | 1,1 > e^{-iE_{1,1}t/\hbar} + 2 | 1,-1 > e^{-iE_{1,-1}t/\hbar} + 3 | 1,0 > e^{-iE_{1,0}t/\hbar})$$

$$+ \frac{1}{17}\frac{1}{2i}(< -2 | 1,1 | e^{-iE_{1,1}t/\hbar} + 2 < 1,-1 | e^{-iE_{1,-1}t/\hbar} + 3 < 1,0 | e^{-iE_{1,0}t/\hbar})$$

$$-L_- | \frac{1}{\sqrt{17}}(-2 | 1,1 > e^{-iE_{1,1}t/\hbar} + 2 | 1,-1 > e^{-iE_{1,-1}t/\hbar} + 3 | 1,0 > e^{-iE_{1,0}t/\hbar})$$

$$< L_y >= \frac{1}{2i} < \psi(t) | (L_+ - L_-) | \psi(t) >$$

$$= \frac{1}{17}\frac{1}{2i}(< -2 | 1,1 | e^{-iE_{1,1}t/\hbar} + 2 < 1,-1 | e^{-iE_{1,-1}t/\hbar} + 3 < 1,0 | e^{-iE_{1,0}t/\hbar})$$

$$| \frac{1}{\sqrt{17}}(2\sqrt{2} | 1,0 > e^{-iE_{1,-1}t/\hbar} + 3\sqrt{2} | 1,1 > e^{-iE_{1,0}t/\hbar})$$

$$+ \frac{1}{17}\frac{1}{2i}(< -2 | 1,1 | e^{-iE_{1,1}t/\hbar} + 2 < 1,-1 | e^{-iE_{1,-1}t/\hbar} + 3 < 1,0 | e^{-iE_{1,0}t/\hbar})$$

$$- | \frac{1}{\sqrt{17}}(-2\sqrt{2} | 1,0 > e^{-iE_{1,1}t/\hbar} + 3\sqrt{2} | 1,-1 > e^{-iE_{1,0}t/\hbar})$$

$$< L_y >= \frac{1}{2i} < \psi(t) | (L_+ - L_-) | \psi(t) >$$

$$= \frac{1}{17}\frac{1}{2i}(< -2 | 1,1 | e^{-iE_{1,1}t/\hbar} + 2 < 1,-1 | e^{-iE_{1,-1}t/\hbar} + 3 < 1,0 | e^{-iE_{1,0}t/\hbar})$$

$$| (2\sqrt{2} | 1,0 > e^{-iE_{1,-1}t/\hbar} + 3\sqrt{2} | 1,1 > e^{-iE_{1,0}t/\hbar})$$

$$- \frac{1}{17}\frac{1}{2i}(< -2 | 1,1 | e^{-iE_{1,1}t/\hbar} + 2 < 1,-1 | e^{-iE_{1,-1}t/\hbar} + 3 < 1,0 | e^{-iE_{1,0}t/\hbar})$$

$$| (-2\sqrt{2} | 1,0 > e^{-iE_{1,1}t/\hbar} + 3\sqrt{2} | 1,-1 > e^{-iE_{1,0}t/\hbar})$$

$$= \frac{1}{\sqrt{17}} \times \frac{1}{2i} \times 6\sqrt{2} - 6\sqrt{2} - 6\sqrt{2} + 6\sqrt{2} = 0$$

6.0 TUTOR-MARKED ASSIGNMENT

1. In the standard basis $\left\{ | 1\,1 >= \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, | 1\,0 >= \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, | 1\,-1 >= \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \right\}$, find the matrix representation of the operators L_x, L_y, L_z and L^2.

2. Show that $Y_{2,2}(\theta,\phi) = \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{2i\phi}$. Hence, find $Y_{2,1}$.

3. Find the expectation values $<L_x>$, $<L_y>$, $<L_z>$, $<L_z^{\,2}>$ in the state $|l,l>$ and show that $<L_x^{\,2}> = <L_y^{\,2}>$.

4. In the standard basis $\left\{|1\,1>=\begin{bmatrix}1\\0\\0\end{bmatrix},|1\,0>=\begin{bmatrix}0\\1\\0\end{bmatrix},|1\,-1>=\begin{bmatrix}0\\0\\1\end{bmatrix}\right\}$, find the matrix representation of the operators L_x, L_y, L_z and L^2.

5. Given the eigenstate $|l,m>=|2,m>$, what measurements are possible for L^2 and L_z?
The only possible value of L_2 is $|\psi>=l(l+1)\hbar^2=2(2+1)\hbar^2=6\hbar^2$
The possible values of L_z are, $-l\hbar,(-l+1)\hbar,...,0,\hbar,l\hbar$, which in this case, are, $-2\hbar$, $-\hbar$, 0, $\hbar$, $2\hbar$. What values would you get by operating on the eigenvector $|3,-2>$ with the angular momentum ladder operators L_+ and L_-?

6. If a system is found in the state $Y(\theta,\phi)=\sqrt{\frac{15}{8\pi}}\cos\theta\sin\theta\sin\phi$,
Find the possible values a measurement of L_z will give, and with what probability.

7.0 REFERENCES/FURTHER READING

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UNIT 4 ELECTRON SPIN I

CONTENTS

1.0 INTRODUCTION

Fine structure, the splitting of hydrogen spectral lines and the results of the Stern-Gerlach experiment suggest that an individual electron should possess an intrinsic angular momentum and a magnetic moment independent of the orbital angular momentum. Unlike orbital angular momentum which has as its analogy the classical concept of angular momentum, electron spin has no classical analogy. In this Study Session, you will learn how electron spin arises, the electron spin operators, as well as the eigenfunctions and the corresponding eigenvalues of the operators.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- show that unlike orbital angular momentum which has as its analogy the classical concept of angular momentum, spin has no classical analogy
- indicate that an individual electron possesses an intrinsic angular momentum and a magnetic moment
- depict that the intrinsic angular momentum is quantised
- point out that an electron has a spin equal to $\frac{1}{2}$
- reveal that the z-component of the spin angular momentum is quantised
- prove that when an atomic electron is placed in a magnetic field aligned with the *z*-axis, the *z*-component of the spin is either $\frac{1}{2}$ or $-\frac{1}{2}$, respectively spin-up or spin-down.

3.0 MAIN CONTENT

3.1 Electron Spin

An electron orbiting the nucleus possesses an orbital angular momentum, resulting in the orbital angular momentum quantum number *l*. Related to the orbital angular momentum is the magnetic quantum number *m*. $-l \le m \le l$. There are $2l+1$ values of *m* for a given *l*. The magnetic quantum number becomes relevant when the atom is placed in an external magnetic field.

In addition, a charge moving in a circle constitutes a current loop, the magnitude of the magnetic moment of which is given in Classical Physics as

$$\mu = \frac{IA}{c} \qquad 4.1$$

I is the current, A is the area enclosed by the circular orbit and *c* is the speed of light in vacuo. The current is

$$I = -\frac{e}{2\pi r}v \qquad 4.2$$

that is, the charge per unit length of the loop, times the velocity,

The velocity,

$$v = \frac{p}{m} = \frac{L}{mr} \quad (\text{since } \mathbf{L} = \mathbf{r} \times \mathbf{p} = pr \text{ in this case}) \qquad 4.3$$

$$A = \pi r^2$$

Since both vectors **μ** and **L** are normal to the loop,

$$\boldsymbol{\mu} = -\frac{e}{2mc}\mathbf{L} \qquad 4.4$$

In an external magnetic field **B**, the interaction energy between the magnetic dipole and the field is given by

$$E_{mag} = -\mathbf{B}\cdot\boldsymbol{\mu} \qquad 4.5$$

$$= \frac{e}{2mc}\mathbf{B}\cdot\mathbf{L} \qquad 4.6$$

For a hydrogen atom in an external constant magnetic field directed along the *z*-axis, the Hamiltonian relevant for the motion of the electron is

$$H = H_0 + \frac{e}{2mc} B_z L_z$$

4.7

where H_0 is the Hydrogen atom Hamiltonian in the absence of an external field

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{r}$$

4.8

The first term on the right hand side is the kinetic energy while the second term is the potential energy.

H_0 and L_z, in the case of quantum theory, become operators which commute with each other, implying that H_0 and L_z could have the same eigenstates φ_{nlm}. In particular, since we can write

$$L_z \varphi_{nlm} = m\hbar \varphi_{nlm}$$

4.9

Following from equation 4.7 and the fact that the eigenvalues of L_z are $m\hbar$,

$$H\varphi_{nlm} = \left(E_n^0 + mB_z \frac{e\hbar}{2mc} \right) \varphi_{nlm}$$

4.10

with the energy eigenvalues,

$$E_{nlm} = E_n^0 + mB_z \frac{e\hbar}{2mc}$$

4.11

where E_n^0 are the energy eigenvalues of the electron when there is no external field.

When placed in a strong magnetic field, this makes available many spectral lines (depending on the values of *m*, or equivalently, *n*, as the *m*'s depend on the *n*'s). This makes it possible for transitions to occur between the quantum numbers m_1 and m_2 corresponding, respectively, to the principal quantum numbers n_1 and n_2 split into many spectral lines, corresponding to transitions between states with different values of the L_z quantum numbers m_1 and m_2. There are certain selection rules governing which transitions are possible. The splitting of spectral lines in an external magnetic field is known as the strong field Zeeman effect. Indeed, for each pair of quantum numbers n and l, there are twice as many energy levels as one would expect. Indeed, instead of the expected $2l+1$ levels, there are two sets of $2l+1$ levels, with energies

$$E^{+}_{nlm} \approx E^{0}_{n} + (m+1)B_z \frac{e\hbar}{2mc} \quad 4.12$$

$$E^{-}_{nlm} \approx E^{0}_{n} + (m-1)B_z \frac{e\hbar}{2mc} \quad 4.13$$

From the foregoing, we conclude that an electron also has an intrinsic magnetic moment, associated with an intrinsic spin angular momentum. This is in addition to the magnetic moment due to its orbital angular momentum. Let the intrinsic magnetic moment of the electron be (in line with our analysis of $\mathbf{L}$),

$$\boldsymbol{\mu}_S = \frac{eg}{2mc}\mathbf{S} \quad 4.14$$

g being the constant called the gyromagnetic ratio. Every observable is represented by a Hermitian operator in quantum theory. Recall we said that Hermitian operators have real eigenvalues, because the values a measurement of the observable can possibly take must be real. Thus, *S* is a Hermitian operator. Further, we assume it satisfies the same commutation relations as orbital angular momentum:

$$[S_x, S_y] = i\hbar S_z \quad 4.15$$

$$[S_y, S_z] = i\hbar S_x \quad 4.16$$

$$[S_z, S_x] = i\hbar S_y \quad 4.17$$

We conclude the possible eigenvalues of S^2 and S_z are

$$S^2 = s(s+1)\hbar^2,\ s = 0,\ \frac{1}{2},\ 1,\ \frac{3}{2},\ \ldots \quad 4.18$$

$$S_z = s_z\hbar,\ -s \le s_z \le s \quad 4.19$$

Just as we had it in the case of orbital angular momentum, the eigenvalues of *S* are,

$$S = \hbar\sqrt{s(s+1)} \quad 4.20$$

Notice that the notation in orbital angular momentum are similar, with *S* replacing *L* and *s* replacing *l*.

Taking the electron magnetic moment into account, the total Hamiltonian is then

$$H = H_0 + \frac{e}{2mc} B_z L_z - (\mu_e)_z B_z$$

4.21

$$H = H_0 + \frac{e}{2mc} B_z L_z + (\mu_e)_z B_z$$

4.22

Electron spin is independent of the electron position and its angular momentum. We can therefore assume that

$$[H_0, S_z] = 0$$

4.23

and

$$[L_z, S_z] = 0$$

4.24

This means that H_0, L_z and S_z have a common set of eigenstates, say $|nlms_z>$.

This means we can write the eigenvalue equation,

$$H|nlms_z> = E_{nms_z}|nlms_z>$$

4.25

If we compare with the expressions for E^+_{nlm} and E^-_{nlm}, we get agreement if the electron has an intrinsic spin

$$s = \frac{1}{2} \quad \Rightarrow \quad s_z = \pm\frac{1}{2}$$

4.26

with the gyromagnetic ratio

$$g \approx 2$$

4.27

so that E^+ corresponds to $s_z = \frac{1}{2}$ and E^- to $s_z = -\frac{1}{2}$.

The experimental proof is provided by the Stern-Gerlach Experiment, which confirms the double-valued character of the electron magnetic moment when a beam of electrons is sent through a non-uniform magnetic field, oriented in the z-direction. A measurement of the deflection of the electron beam gives only two possibilities, $s_z = \pm\frac{1}{2}$, and the z-component of the force on a dipole μ in a non-uniform magnetic field, $\mathbf{F} = \nabla(\mu \cdot \mathbf{B})$, that is, $F_z = \frac{\partial B_z}{\partial z}\mu_z = \frac{eg}{2mc}\frac{\partial B_z}{\partial z}S_z$ is either oriented up or down along the z-axis. The magnitudes are, however, equal. $S_z = +\frac{1}{2}\hbar$ for spin-up eigenstate and $S_z = -\frac{1}{2}\hbar$ for spin-down eigenstate.

SELF-ASSESSMENT EXERCISE 1

What conclusion was drawn from the Stern-Gerlach experiment?

SELF-ASSESSMENT EXERCISE 2

An electron is in a uniform magnetic field along the *z*-direction. A measurement of the spin is initially (at $t = 0$) along the positive *x*-direction.

(i) What is the Schroedinger state vector for the spin. The relevant Hamiltonian is $H = -\mu \cdot \mathbf{B} = \mu_e \sigma \cdot \mathbf{B} = \hbar\omega\sigma_z = \hbar\omega B\sigma_z$

(ii) At time $t > 0$, calculate the expectation value of s_y, along the *y* direction. Note that this is the polarization along the *y* direction.

4.0 CONCLUSION

In this Unit, you learnt about the intrinsic angular momentum or spin. In analogy with the orbital angular momentum, the spin is also quantised, taking on 0 and positive multiples of half. It follows that some particles have integral spin (Bosons, e.g., photons) and others half-integral spin (Fermions, e.g., electrons). Just as in the case of orbital angular momentum the component (or projection) of spin in any direction is also quantised.

5.0 SUMMARY

In this Unit, you have learnt that:

- unlike orbital angular momentum which has as its analogy the classical concept of angular momentum, electron spin has no classical analogy
- an electron has a spin equal to $\frac{1}{2}$
- an individual electron possesses an intrinsic angular momentum and a magnetic moment
- the intrinsic angular momentum is quantised,
- the z-component of the spin angular momentum is quantised
- when an atomic electron is placed in a magnetic field aligned with the *z*-axis, the *z*-component of the spin is either $\frac{1}{2}$ or $-\frac{1}{2}$, respectively spin-up or spin-down.

Answer to Self-Assessment Exercise 1
In the text.

Answer to Self-Assessment Exercise 3

(i) $H = -\mu \cdot \mathbf{B} = \mu_e \sigma \cdot \mathbf{B} = \hbar\omega\sigma_z = \hbar\omega\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

(ii) $|\psi(t=0)> = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \begin{pmatrix} \psi_{10} \\ \psi_{20} \end{pmatrix}$

Applying the time-dependent Schroedinger equation,

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi$$

$$i\hbar\frac{\partial\psi}{\partial t} = \hbar\omega\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\psi$$

$$i\begin{pmatrix} \psi_1' \\ \psi_2' \end{pmatrix} = \omega\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

Therefore,

$$\psi_1' = -i\omega\psi_1$$

$$\psi_2' = i\omega\psi_2$$

Integrating,

$$\psi_1 = \psi_{10}e^{-i\omega t}$$

$$\psi_2 = \psi_{20}e^{i\omega t}$$

Hence,

$$\psi(t) = \begin{pmatrix} \psi_1(t) \\ \psi_1(t) \end{pmatrix} = \begin{pmatrix} \psi_{10}e^{-i\omega t} \\ \psi_{20}e^{i\omega t} \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} e^{-i\omega t} \\ e^{i\omega t} \end{pmatrix}$$

The expectation value of s_y is

$$<\psi(t)|s_y|\psi(\mathrm{t})> = \frac{\hbar}{2}\times\frac{1}{2}\begin{pmatrix} e^{i\omega t} & e^{-i\omega t} \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} e^{-i\omega t} \\ e^{i\omega t} \end{pmatrix}$$

$$= \frac{\hbar}{4}\begin{pmatrix} e^{i\omega t} & e^{-i\omega t} \end{pmatrix}\begin{pmatrix} -ie^{-i\omega t} \\ ie^{i\omega t} \end{pmatrix}$$

$$= \frac{\hbar}{4}(-i+i) = 0$$

6.0 TUTOR-MARKED ASSIGNMENT

1. What is the strong Zeeman Effect?

2. Show that S^2 is diagonalised in the basis of eigenvectors of S_z. Take the eigenvectors of S_z as $|\frac{1}{2}>$ and $|-\frac{1}{2}>$.

3. In the case of spin $s = 1$, three values of m_s are possible, so that the S_i are represented by 3×3 matrices. It follows that $s_+ |-1>= \sqrt{2}\,|0>$; $s_+ |0>= \sqrt{2}\,|+1>$; $s_- |+1>= \sqrt{2}\,|0>$; $s_- |0>= \sqrt{2}\,|-1>$. Find the matrix elements $(S_x)_{21}$, $(S_x)_{12}$ and $(S_x)_{23}$ of S_x.

4. Given that the operators for the three components of the spin of a spin-1/2 particle are $s_x = \frac{\hbar}{2}\sigma_x = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}$, $s_y = \frac{\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}$, $s_z = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$, confirm the commutation relation of the components, i.e., $[s_x, s_y] = i\hbar s_z$, etc.

7.0 REFERENCES/FURTHER READING

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UNIT 5 ELECTRON SPIN II

CONTENTS

1.0 INTRODUCTION

In Unit 4, we started our study of electron spin, its origin, and concluded that an electron also has an intrinsic magnetic moment, associated with an intrinsic spin angular momentum. This is in addition to the magnetic moment due to its orbital angular momentum. We also saw that the electron could either have a spin-up or a spin-down along the *z*-axis. We shall discuss the wavefunctions associated with electron spin. With the help of these wavefunctions, we shall find the matrices associated with the operators that are relevant to the theory of electron spin.

2.0 OBJECTIVES

At the end of this study session, you shouldbe able to:

- express the spin wavefunction as a column vector of 2 components, known as **spinor**
- find the matrix representation of the spin operators
- derive the Pauli spin matrices and relate them to the spin operators
- calculate the probability of a spin-up or down given a spin state.

3.0 MAIN CONTENT

3.1 Spin Wave functions

Let

$$|s=\frac{1}{2},s_z=\frac{1}{2}> \text{ and } |s=\frac{1}{2},s_z=-\frac{1}{2}>$$

5.1

be the two orthonormal ket eigenstates of S^2 and S_z vectors.

$$S^2 |\frac{1}{2}\frac{1}{2}> = \frac{3}{4}\hbar^2 |\frac{1}{2}\frac{1}{2}>$$
5.2

$$S_z |\frac{1}{2}\frac{1}{2}> = \frac{1}{2}\hbar |\frac{1}{2}\frac{1}{2}>$$
5.3

$$S^2 |\frac{1}{2}-\frac{1}{2}> = \frac{3}{4}\hbar^2 |\frac{1}{2}-\frac{1}{2}>$$
5.4

$$S_z |\frac{1}{2}-\frac{1}{2}> = -\frac{1}{2}\hbar |\frac{1}{2}-\frac{1}{2}>$$
5.5

Any $s= \frac{1}{2}$ state can be represented as a superposition (just the way you would write any vector in any space as a linear sum of the appropriate basis vectors),

$$|\psi> = a|\frac{1}{2}\frac{1}{2}> + b|\frac{1}{2}-\frac{1}{2}>$$
5.6

The transformation matrix above becomes

$$\begin{pmatrix} v_1' \\ v_2' \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix}$$
5.7

Hence, we can express the spin wavefunction as a column vector of 2 components, known as **spinor**, and express the spin operator as 2×2 matrices. Let the bases be

$$|e_1> = |\frac{1}{2}\frac{1}{2}> \quad |e_2> = |\frac{1}{2}-\frac{1}{2}>$$
5.8

The eigenstates can then be written as the column vectors (spinors)

$$|\frac{1}{2}\frac{1}{2}> \leftrightarrow \chi_+ \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad |\frac{1}{2}-\frac{1}{2}> \leftrightarrow \chi_- \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$
5.9

and any spin-$\frac{1}{2}$ state can be written as a superposition, in ket notation

$$|u> = u_+ |e_1> + u_- |e_2>$$
5.10

or in column vector notation

$$|u> = \begin{pmatrix} u_+ \\ u_- \end{pmatrix}$$
5.11

We can then write

$$S^2 \mid ss_z >= s(s+1)\hbar^2 \mid ss_z >$$

5.12

$$S_z \mid ss_z >= s_z\hbar \mid ss_z >$$

5.13

$$S_- \mid ss_z >= \sqrt{(s+s_z)(s-s_z+1)}\hbar \mid s, s_z - 1>$$

5.14

$$S_+ \mid ss_z >= \sqrt{(s-s_z)(s+s_z+1)}\hbar \mid s, s_z + 1>$$

5.15

$$S_x = \frac{1}{2}(S_+ + S_-)$$

5.16

$$S_y = \frac{1}{2i}(S_+ - S_-)$$

5.17

We have used S instead of L, s instead of l and s_z instead of m. For the electron, $s = \frac{1}{2}$ and $s_z = \frac{1}{2}, -\frac{1}{2}$. From these relations, we can obtain all the matrix elements.

Example 5.1

Calculate the element $(S_x)_{12}$ of the spin operator $(S_x)_{12}$.

Solution 5.1

$$(S_x)_{12} = <e_1 \mid S_x \mid e_2>$$

$$= <\frac{1}{2}\frac{1}{2} \mid S_x \mid \frac{1}{2} - \frac{1}{2}>$$

$$= \frac{1}{2}\left[<\frac{1}{2}\frac{1}{2} \mid S_+ \mid \frac{1}{2} - \frac{1}{2}> + <\frac{1}{2}\frac{1}{2} \mid S_- \mid \frac{1}{2} - \frac{1}{2}>\right]$$

$$= \frac{1}{2}\left[<\frac{1}{2}\frac{1}{2} \mid \hbar \mid \frac{1}{2}\frac{1}{2}> + 0\right]$$

$$= \frac{1}{2}\hbar$$

Eventually, we arrive at the following matrix form of the spin operators for $s = \frac{1}{2}$:

$$S^2 = \frac{3}{4}\hbar^2\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix},\ S_x = \frac{1}{2}\hbar\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix},\ S_y = \frac{1}{2}\hbar\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix},\ S_z = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

5.18

If we factor out $\frac{\hbar}{2}$, we can write

$$S_x = \frac{\hbar}{2}\sigma_x,\ S_y = \frac{\hbar}{2}\sigma_y,\ S_z = \frac{\hbar}{2}\sigma_z \qquad 5.19$$

where the matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},\ \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix},\ \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad 5.20$$

are the Pauli Spin Matrices. They are all traceless. That is, the trace of each of the matrices is zero.

SELF-ASSESSMENT EXERCISE 1

Find the eigenvalues (possible values the spin of an electron in the *x*-direction can take) of the operator

$$S_x = \frac{1}{2}\hbar\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

SELF-ASSESSMENT EXERCISE 2

Show that $S^2 = S_z{}^2 + \frac{1}{2}(S_+S_- + S_-S_+)$.

4.0 CONCLUSION

In Unit 4, you learnt how to work with the spinors. You were able to find the Pauli spin matrices and calculate their eigenvectors and eigenvalues. In addition, you were able to write each of the eigenvectors of any spin state in terms of the spinors. You also learnt to find the matrix element of a spin operator with the aid of the spinors.

5.0 SUMMARY

In this Unit, you learnt the following:

- the spinors
- expressing a given spin state in terms of the spinors
- calculating the matrix elements of a spin operator with the help of the spinors
- working with the Pauli spin matrices
- expressing the spin operators in terms of the Pauli spin matrices.

Answer to Self-Assessment Exercise 1

The indicial equation is given by,

$$\begin{vmatrix} 0-\lambda & \hbar/2 \\ \hbar/2 & 0-\lambda \end{vmatrix} = \begin{vmatrix} -\lambda & \hbar/2 \\ \hbar/2 & -\lambda \end{vmatrix} = 0$$

$$\lambda^2 - (\hbar/2)^2 = 0$$

Hence,

$$\lambda = \pm\frac{\hbar}{2}$$

Therefore, the eigenvalues are $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$.

These are the possible values of the spin in the *x*-direction.

Answer to Self-Assessment Exercise 2

$$S_+ = S_x + iS_y$$

$$S_- = S_x - iS_y$$

$$S^2 = S_x{}^2 + S_y{}^2 + S_z{}^2$$

But,

$$S_+S_- + S_-S_+ = (S_x + iS_y)(S_x - iS_y) + (S_x - iS_y)(S_x + iS_y)$$

$$= (S_x{}^2 - iS_xS_y + iS_yS_x + S_y{}^2) + (S_x{}^2 - iS_yS_x + iS_xS_y + S_y{}^2)$$

$$= 2S_x{}^2 + 2S_y{}^2$$

$$S_x{}^2 + S_y{}^2 = \frac{1}{2}(S_+S_- + S_-S_+)$$

Hence,

$$S^2 = S_z{}^2 + \frac{1}{2}(S_+S_- + S_-S_+)$$

6.0 TUTOR-MARKED ASSIGNMENT

1. What do you understand by the term spinor?
2. Find the eigenvalues of S_y. Write the eigenvectors in terms of the spin-1/2 spinors.

$$S_y = \frac{1}{2}\hbar\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

3. A particle is in the state $|\psi> = \frac{1}{\sqrt{5}}\begin{pmatrix} 2i \\ 1 \end{pmatrix}$.

(a) Find the probability of measuring spin-up or spin-down in the *z* direction.

(b) Find the probability of measuring spin-up or spin-down in the *y* direction.

4. An electron is in state with z-component of spin angular momentum $\hbar/2$. An observation designed to measure the component of spin angular momentum along an arbitrary direction $\hat{\mathbf{n}}$ is made.

(i) Prove that the operator corresponding to this observable $s_n = \mathbf{s}\cdot\mathbf{n}$ is

$$s_n = \frac{\hbar}{2}\begin{bmatrix} \cos\theta & \sin\theta\, e^{-i\phi} \\ \sin\theta\, e^{i\phi} & -\cos\theta \end{bmatrix}$$

(ii) Find the eigenvalues and the eigenvectors of the operator s_n. Hence, write the eigenvectors of s_n in terms of the spin-up and the spin-down eigenvectors.

(iii) What are the probabilities of observing a component of spin angular momentum $\pm\hbar/2$ along $\hat{\mathbf{n}}$? Interpret your answer in line with Classical Physics.
Hint: Let $\hat{\mathbf{n}} = \hat{\mathbf{n}}(\theta,\phi)$.

5. Find the eigenvalues and the eigenvectors of the Pauli spin matrices:

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

6. Given the matrix forms of the spin angular momentum operator as,

$$s_x = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, s_y = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}, s_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Calculate (i) s_y^2, (ii) $(s_x + is_y)^2$ and (iii) $(s_x - is_y)^3$

7. For the Pauli spin matrices, find expressions for the commutators: $[\sigma_x,\sigma_y]$, $[\sigma_y,\sigma_z]$ and $[\sigma_x,\sigma_z]$ in terms of the matrices themselves.

8. Using the expressions in equation 5.18, prove the following:
$[S^2,S_x]=0$, $[S^2,S_y]=0$, $[S^2,S_z]=0$

7.0 REFERENCES/FURTHER READING

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MODULE 3

UNIT 1 THREE-DIMENSIONAL SPHERICALLY SYMMETRIC POTENTIALS

CONTENTS

1.0 INTRODUCTION

Three-dimensional symmetric potentials are ubiquitous in Physics, from the sun-earth system in classical mechanics to the point charge in spherically symmetric three-dimensional space to the electron in the hydrogen atom. Advantage is taken of the symmetry of the problem, such as all such problems having the same solution called spherical harmonics. In this Unit, you will learn how to find the series solution to the problem, which has two parts, the azimuthal part as well as the polar equation part. Further, you will learn about the azimuthal equation and its solution. The physical interpretation of the solution of the azimuthal equation will certainly pique your interest.

2.0 OBJECTIVES

At the end of this study session, you will be able to:

- solve the time-independent Schroedinger equation for a spherically symmetric potential with the variable-separable method
- write the solution of the angular part as a product of azimuthal and polar solutions

- link up the azimuthal part with the magnetic quantum numbers.

3.0 MAIN CONTENT

3.1 Three-Dimensional Spherically Symmetric Potentials

In this chapter, we study the motion of a quantum-mechanical particle in a three-dimensional spherically symmetric potential. We say a potential is spherically symmetric if it is a function only of the radial distance from the origin, appropriately chosen to be at $r = 0$. Put in another form, the potential can be written as $V(r,\theta,\phi) = V(r)$.

For this reason, you will see that the results we shall obtain will have the spherical part $Y(\theta,\phi)$ behaving in the same way in whatever problem a spherical symmetry applies. The following …. come to mind: the earth-moon system, the sun-earth system.

It is obvious that r,θ,ϕ, the spherical coordinates are the natural coordinate system for a symmetrically symmetric potential. The usual Cartesian coordinate system fails to take advantage of spherical symmetry of the problem, making it impossible to take advantage of the symmetry.

Naturally, we go from the more hitherto familiar Cartesian coordinate system to the spherical coordinate system.

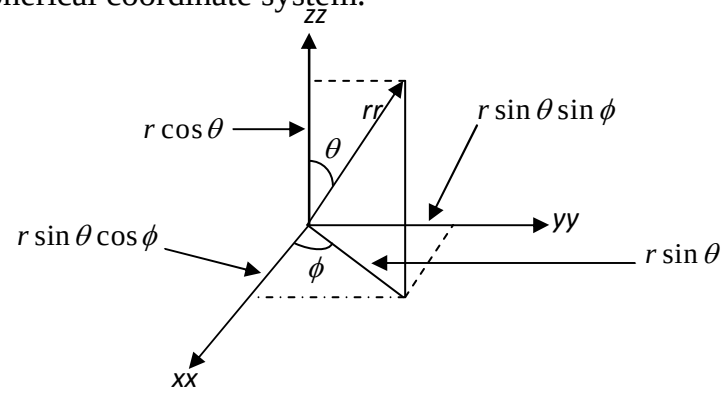

Fig. 9.1: Spherical polar coordinates

$x = r\sin\theta\cos\phi$
$y = r\sin\theta\sin\phi$
$z = r\cos\theta$

The resulting Laplacian is (see Appendix 1),

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$
1.1

Let us now apply the Laplacian to the wavefunction $\psi(r,\theta,\phi)$ via the time-independent Schroedinger equation.

$$\nabla^2\psi(r,\theta,\phi) = \frac{2m}{\hbar}(E-V(r))\psi(r,\theta,\phi)$$

$$\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)\psi(r,\theta,\phi) =$$

$$\frac{2m}{\hbar^2}(E-V(r))\psi(r,\theta,\phi)$$ 1.2

We assume that the solution $\psi(r,\theta,\phi)$ is variable-separable, meaning we can write it in the form,

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$$
1.3

We shall have cause to write

$$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$
1.4

popularly called the spherical harmonics.

We now write the left side of equation 1.2:

$$\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)R(r)\Theta(\theta)\Phi(\phi) =$$

$$\frac{\Theta(\theta)\Phi(\phi)}{r^2}\frac{d}{dr}r^2\frac{d}{dr}R(r)+\frac{R(r)\Phi(\phi)}{r^2\sin^2\theta}\frac{d^2\Theta(\theta)}{d\phi^2}+\frac{R(r)\Theta(\theta)}{r^2\sin^2\theta}\frac{d}{d\theta}\sin\theta\frac{d\Phi(\phi)}{d\theta}$$

Dividing through by $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$, we get,

$$\frac{1}{R(r)}\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}R(r)+\frac{1}{\Theta(\theta)}\frac{1}{r^2\sin^2\theta}\frac{d^2\Theta(\theta)}{d\phi^2}+\frac{1}{\Phi(\phi)}\frac{1}{r^2\sin^2\theta}\frac{d}{d\theta}\sin\theta\frac{d\Phi(\phi)}{d\theta}$$

Multiplying through by r^2 leaves the last two terms free of *r*.

$$\frac{1}{R(r)}\frac{d}{dr}r^2\frac{d}{dr}R(r)+\frac{1}{\Theta(\theta)}\frac{1}{\sin^2\theta}\frac{d^2\Theta(\theta)}{d\phi^2}+\frac{1}{\Phi(\phi)}\frac{1}{\sin^2\theta}\frac{d}{d\theta}\sin\theta\frac{d\Phi(\phi)}{d\theta}$$

We can then put the last two terms together:

$$\frac{1}{R(r)}\frac{d}{dr}r^2\frac{d}{dr}R(r)+\left[\frac{1}{\Theta(\theta)}\frac{1}{\sin^2\theta}\frac{d^2\Theta(\theta)}{d\phi^2}+\frac{1}{\Phi(\phi)}\frac{1}{\sin^2\theta}\frac{d}{d\theta}\sin\theta\frac{d\Phi(\phi)}{d\theta}\right]$$

Equation 1.2 can now be written as,

$$\frac{1}{R(r)}\frac{d}{dr}r^2\frac{d}{dr}R(r)+\left[\frac{1}{\Theta(\theta)}\frac{1}{\sin^2\theta}\frac{d^2\Theta(\theta)}{d\phi^2}+\frac{1}{\Phi(\phi)}\frac{1}{\sin^2\theta}\frac{d}{d\theta}\sin\theta\frac{d\Phi(\phi)}{d\theta}\right]$$
$$=\frac{2mr^2}{\hbar^2}(E-V(r))$$

(Recall we already divided the left side by $\psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\phi)$)

or

$$\left[\frac{1}{R(r)}\frac{d}{dr}r^2\frac{d}{dr}R(r)-\frac{2mr^2}{\hbar^2}(E-V(r))\right]+\left[\frac{1}{\Theta(\theta)}\frac{1}{\sin^2\theta}\frac{d^2\Theta(\theta)}{d\phi^2}+\frac{1}{\Phi(\phi)}\frac{1}{\sin^2\theta}\frac{d}{d\theta}\sin\theta\frac{d\Phi(\phi)}{d\theta}\right]=0$$

The first term in the sum depends only on *r* and the second only on the angles θ and ϕ. Each term must be equal to a constant, and the two constants must sum to zero.

We write

$$\frac{r^2}{Rr}\frac{d^2}{dr^2}[rR]+\frac{2mr^2}{\hbar^2}(E-V(r))=k \qquad 1.5$$

$$\frac{1}{\Phi\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Phi+\frac{1}{\Theta\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\Theta\right)=-k \qquad 1.6$$

Equations (1.5) and (1.6) are respectively the radial and the angular part of the Schroedinger equation in spherical coordinates.

We shall now consider the angular part.

Swapping the terms on the left in equation 1.6 and multiplying through by $\sin^2\theta$,

$$\left[\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta}+\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}\right]+k\sin^2\theta=0 \qquad 1.7$$

Notice that we do not need partial differentials anymore. The terms in the bracket have been separated into differentials only involving a function of a single variable.

Rearranging,

$$\left[\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta}+k\sin^2\theta\right]+\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=0 \qquad 1.8$$

The first two terms on the left are a function only of θ, while the last term is a function only of ϕ. If the sum is zero, then, each of them must be a constant, and the constants must sum up to zero.

3.2 The Azimuthal Equation

If we set

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2 \qquad 1.9$$

then,

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} + k\sin^2\theta = m^2 \qquad 1.10$$

Rearranging equation 9.11, we get

$$\frac{d^2\Phi}{d\phi^2} + m^2\Phi = 0 \qquad 1.11$$

Equation 1.11 is the azimuthal equation. This we solved earlier in Module 3, Unit 2. We concluded that $\Phi = Ae^{im\phi}$, implying that *m* must be an integer, $m = 0, \pm 1, \pm 2, \ldots$

SELF-ASSESSMENT EXERCISE 1

Show by direct substitution, that $Ae^{im\phi}$ is a solution of equation 1.11.

3.2.1 The physical meaning of *m*

m is the magnetic quantum number. It determines the orientation of the angular momentum of an electron in an external magnetic field along a specific axis. Thus, imposing the condition of periodicity on the azimuthal part of the wave function ensures that only a set of directions are possible for the orientation of the angular momentum vector.

SELF-ASSESSMENT EXERCISE 2

What is the physical significance of the magnetic quantum number?

4.0 CONCLUSION

In this Unit, you learnt to solve the Schroedinger equation for a spherically symmetric potential. The spherical symmetry allowed us to separate the solution into an angular part, the solution of which are the spherical harmonics. Further, we separated the spherical harmonics into a function of the azimuthal angle and the polar angle. Imposing the periodicity condition on the azimuthal solution gave rise to the magnetic quantum numbers.

5.0 SUMMARY

In this Unit, you were able to:

- solve the Schroedinger equation for a spherically symmetric potential by the variable-separable method
- write the solution as a product of a radial part and an angular part
- write the angular part as a product of the azimuthal part and the polar part
- link the azimuthal solution to the magnetic quantum numbers

Answer to Self-Assessment Exercise 1

$$\frac{d^2\Phi}{d\phi^2} + m^2\Phi = 0$$

$$\Phi = Ae^{im\phi}$$

$$\frac{d\Phi}{d\phi} = imAe^{im\phi}$$

$$\frac{d^2\Phi}{d\phi^2} = i^2m^2Ae^{im\phi} = -m^2Ae^{im\phi} = -m^2\Phi$$

Hence,

$$\frac{d^2\Phi}{d\phi^2} + m^2\Phi = 0$$

Answer to Self-Assessment Exercise 2

m is the magnetic quantum number. It determines the orientation of the angular momentum of an electron in an external magnetic field along a specific axis. Thus, imposing the condition of periodicity on the azimuthal part of the wave function ensures that only a set of directions are possible for the orientation of the angular momentum vector.

6.0 TUTOR-MARKED ASSIGNMENT

1. From $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$ and $z = r\cos\theta$, find an expression for *r*, θ and ϕ

2. Find the spherical coordinates of the point $(x, y, z) = (-1, 1, 2)$ in the Cartesian coordinate system.

3. Calculate the Cartesian coordinates of a point whose spherical coordinates are $(r, \theta, \phi) = (\sqrt{6}, 45^0, 135^0)$

4. Solve with the method of separation of variables the Laplace equation,

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Phi = 0$$

7.0 REFERENCES/FURTHER READING

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UNIT 2 THE POLAR ANGLE EQUATION, LEGENDRE POLYNOMIALS

CONTENTS

1.0 INTRODUCTION

In Unit 1 of this Module, we studied the three-dimensional symmetric potential, culminating in a two-part solution, the azimuthal and the polar angle parts. In this Unit, we look for a solution to the polar angle part of the equation. With appropriate assumptions, we shall reduce this equation to the Legendre equation. The solution of the Legendre equation is a set of polynomials called the Legendre polynomials.

2.0 OBJECTIVES

At the end of this study session, you will be able to:

- solve the polar part of the Schroedinger equation
- derive the Legendre equation
- solve the Legendre equation by the series solution method
- write some Legendre polynomials using the Rodriguez formula.

3.0 MAIN CONTENT

3.1 The Polar Angle Equation, the Legendre Equation

The polar angle equation involving θ only (equation 1.8), must be equal to m^2 so that the sum in equation 1.8 be zero as we have already discussed.

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta}+k\sin^2\theta=m^2 \qquad 2.1$$

We make the substitution

$$x = \cos\theta$$

2.2

Then,

$$\frac{dx}{d\theta} = -\sin\theta$$

2.3

Applying the chain rule,

$$\frac{d}{d\theta} = \frac{d}{dx}\frac{dx}{d\theta} = -\sin\theta\frac{d}{dx} = -\sqrt{1-\cos^2\theta}\,\frac{d}{dx} = -\sqrt{1-x^2}\,\frac{d}{dx}$$

and equation 2.1 becomes,

$$-\frac{\sqrt{1-x^2}}{\Theta}\sqrt{1-x^2}\,\frac{d}{dx}\left[-\sqrt{1-x^2}\sqrt{1-x^2}\,\frac{d\Theta}{dx}\right] + k(1-x^2) = m^2$$

2.4

or,

$$\frac{1-x^2}{\Theta}\frac{d}{dx}\left[(1-x^2)\frac{d\Theta}{dx}\right] + k\,(1-x^2) - m^2 = 0$$

2.5

If we divide through by $\frac{1-x^2}{\Theta}$,

$$\frac{d}{dx}\left[(1-x^2)\frac{d\Theta}{dx}\right] + \left(k - \frac{m^2}{1-x^2}\right)\Theta = 0$$

2.6

This is the generalized Legendre equation.

Notice that this equation remains invariant with respect to the transformation $x \to -x$. This implies that the solutions of the generalized Legendre equation must be either symmetric or antisymmetric in *x*.

Let $\Theta = P$. Then,

$$\frac{d}{dx}\left[(1-x^2)\frac{dP}{dx}\right] + \left(k - \frac{m^2}{1-x^2}\right)P = 0$$

2.7

We set

$$k = l(l+1)$$

2.8

$$\frac{d}{dx}\left[(1-x^2)\frac{dP}{dx}\right] + \left(l(l+1) - \frac{m^2}{1-x^2}\right)P = 0$$

2.9

The solutions of this equation are the associated Legendre functions, $P(x) = P(\cos\theta)$, that is, we set *x* equal to $\cos\theta$.

We shall first find the solutions of the simpler equation obtained by setting $m=0$:

$$\frac{d}{dx}\left[(1-x^2)\frac{dP}{dx}\right]+l(l+1)P=0$$

2.10

Let us assume the series solution,

$$P(x)=\sum_{j=0}^{\infty}a_j x^j$$

2.11

Then,

$$\frac{dP}{dx}=\sum_{j=0}^{\infty}ja_j x^{j-1}$$

2.12

$$(1-x^2)\frac{dP}{dx}=\sum_{j=0}^{\infty}ja_j x^{j-1}-\sum_{j=0}^{\infty}ja_j x^{j+1}$$

2.13

$$\frac{d}{dx}\left[(1-x^2)\frac{dP}{dx}\right]=\sum_{j=0}^{\infty}j(j-1)a_j x^{j-1}-\sum_{j=0}^{\infty}j(j+1)a_j x^{j+1}$$

2.14

Therefore,

$$\frac{d}{dx}\left[(1-x^2)\frac{dP}{dx}\right]+l(l+1)P=\sum_{j=0}^{\infty}j(j-1)a_j x^{j-2}$$
$$-\sum_{j=0}^{\infty}j(j+1)a_j x^j+l(l+1)\sum_{j=0}^{\infty}a_j x^j=0$$

2.15

If we rewrite the right hand side of equation 2.15 in such a way as to sum over the same powers of x:

$$\sum_{j=0}^{\infty}(j+2)(j+1)a_{j+2}x^j-\sum_{j=0}^{\infty}j(j+1)a_j x^j+l(l+1)\sum_{j=0}^{\infty}a_j x^j=0$$

2.16

we then obtain the recursive formula:

$$a_{j+2}=\frac{j(j+1)-l(l+1)}{(j+2)(j+1)}a_j$$

2.17

The recursive formula predicts a_{j+2} from a_j. We would therefore need two initial values of a: a_0 and a_1.

Since $x = \cos\theta$, then $-1 \le x \le 1$. If the series is to be infinite, then for sufficiently large j, $\frac{j(j+1)+l(l+1)}{(j+2)(j+1)} \approx \frac{j(j+1)}{(j+2)(j+1)} \approx \frac{j^2}{j^2} = 1$, and $a_{j+2} \approx a_j$, so that in this limit,

$$P = \sum_{j=0}^{\infty} a_j x^j \approx a \sum_{j=0}^{\infty} x^j \qquad 2.18$$

This is a geometric series, the sum of which is,

$$a \sum_{j=0}^{n} x^j = a \frac{1}{1-x} \qquad 2.19$$

with the proviso that $|x| < 1$. The series has to converge in the interval $[1,-1]$, so we need to terminate it. This we can do by setting $a_j = 0$ for all j greater than a certain finite value of j, say $j_{\max}$. This can be achieved in equation 9.31 if we set $j_{\max}(j_{\max}+1) = l(l+1)$. This means we can set $j_{\max} = l$. We also know that $j_{\max}$ cannot be negative. We get two sequences:

l odd:

$$a_0, a_2, \ldots, a_l$$

or

l even:

$$a_1, a_3, \ldots, a_l$$

However, if l is odd, the highest power for which the sequence must be zero must be odd. Likewise for l even, the highest power for which the sequence is zero must be even. We then see that if l is odd, we must set $a_0 = 0$ and if l is even, we set $a_1 = 0$.

From our discussion, $P = P_l$, that is, the solutions are dependent on l.

From equation 9.31,

$$a_{j+2} = \frac{j(j+1) - l(l+1)}{(j+2)(j+1)} a_j \qquad 2.20$$

Let $a_0 = 1$; then $a_1 = a_3 = \ldots = 0$.

For $l = 1$, $j = 0$. We choose $a_1 = 1$.

Then,

$$P_1(x) = a_1 x = x \qquad 2.21$$

For $l = 2$, $j = 1$.

Then, for $j = 1$, so that

$$a_2 = \frac{0(0+1) - 2(2+1)}{(0+2)(0+1)} a_0 = \frac{-6}{2} \times 1 = -3$$

Hence,

$$P_2 = a_0 + a_2 x^2 = 1 - 3x^2 \qquad 2.22$$

For $l = 3$, $j = 1$.

We know $a_1 = 1$. Then,

$$a_3 = \frac{1(1+1) - 3(3+1)}{(1+2)(1+1)} a_1 = -\frac{10}{6} \times 1 = -\frac{5}{3}$$

$$P_3(x) = a_1 x + a_3 x^3 = x - \frac{5}{3} x^3 \qquad 2.23$$

Thus, the first four Legendre polynomials and the corresponding normalised polynomials are:

$P_0 = 1$	$P_0 = 1$
$P_1 = x$	$P_1 = x$
$P_2 = 1 - 3x^2$	$P_2 = \frac{1}{2}(3x^2 - 1)$
$P_3 = x - \frac{5}{3} x^3$	$P_3 = \frac{1}{2}(5x^3 - 3x)$

The Legendre polynomials are defined by the Rodrigues formula:

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l \qquad 2.24$$

From this formula, it is obvious that l can only take positive integers. $P_l(x)$ is polynomial of degree l.

$$P_0(x) = \frac{1}{2^0 0!} \frac{d^0}{dx^0} (x^2 - 1)^0 = 1$$

$$P_1(x) = \frac{1}{2^1 1!} \frac{d}{dx} (x^2 - 1) = \frac{1}{2} 2x = x$$

$$P_2(x) = \frac{1}{2^2 2!} \frac{d^2}{dx^2} (x^2 - 1)^2 = \frac{4}{8} \frac{d}{dx} [(x^2 - 1)(x)] = \frac{1}{2} \frac{d}{dx} (x^3 - x)$$

$$= \frac{1}{2}(3x^2 - 1)$$

Example 2.1

With the aid of the Rodrigues formula, find $P_3(x)$.

Solution 2.1

$$P_3(x) = \frac{1}{2^3 3!}\frac{d^3}{dx^3}(x^2-1)^3 = \frac{1}{8}\frac{d^2}{dx^2}[(x^2-1)^2(x)]$$

$$= \frac{1}{8}\frac{d}{dx}[2(x^2-1)(2x^2) + (x^2-1)^2]$$

$$= \frac{1}{8}\frac{d}{dx}[4(x^4 - x^2) + (x^2-1)^2]$$

$$= \frac{1}{8}\frac{d}{dx}[4x^4 - 4x^2 + x^4 + 1 - 2x^2]$$

$$= \frac{1}{8}\frac{d}{dx}[5x^4 - 6x^2 + 1]$$

$$= \frac{1}{8}(20x^3 - 12x)$$

$$= \frac{1}{2}(5x^3 - 3x)$$

SELF-ASSESSMENT EXERCISE 1

Show that $\int_0^1 P_l(x)\,dx = \frac{(2k)!}{2^{2k+1}(2k+1)!}\binom{2k+1}{k}(-1)^{2k+1-k}$

4.0 CONCLUSION

In this Unit, you transformed the polar part by making a substitution, leading to the general Legendre equation. You solved the simplified Legendre equation (for the case $m = 0$) by the Frobenius series solution method, and found that the solutions are the Legendre polynomials. You were also able to write the Legendre polynomials using the Rodriguez formula.

5.0 SUMMARY

In this Unit, you learnt how to:

- solve the polar part of the Schroedinger equation
- derive the Legendre equation
- solve the Legendre equation by the series solution method
- write some Legendre polynomials using the Rodriguez formula

Answer to Self-Assessment Exercise 1

$$\int_0^1 P_l(x)\,dx = \int_0^1 \frac{1}{2^l\, l!}\frac{d^l}{dx^l}(x^2-1)^l\,dx = \frac{1}{2^l\, l!}\frac{d^{l-1}}{dx^{l-1}}(x^2-1)^l\Big|_0^1$$

The l – 1 derivatives do not exhaust all the l factors of (x^2-1), and the integral is zero at the upper limit x = 1.

If l is even, then, every term in the (l – 1)th differential of $(x^2-1)^l$ will contain a term in x. The last surviving term is the term involving $x^{l-(l-1)}$ or x. The expression therefore, vanishes at the lower limit.

$$(x^2-1)^l = \sum_{m=0}^{l}\binom{l}{m}(-1)^{l-m}x^{2m} \text{ (Binomial expansion)}$$

If l is odd, let $l = 2k+1$.
Then,

$$\int_0^1 P_l(x)\,dx = \left[\frac{1}{2^{2k+1}(2k+1)!}\frac{d^{2k}}{dx^{2k}}(x^2-1)^{2k+1}\right]_{x=0}$$

$$= \left[\frac{1}{2^{2k+1}(2k+1)!}\frac{d^{2k}}{dx^{2k}}\sum_{m=0}^{2k+1}\binom{2k+1}{m}(-1)^{2k+1-m}x^{2m}\right]_{x=0}$$

Hence,

$$\int_0^1 P_l(x)\,dx = \frac{(2k)!}{2^{2k+1}(2k+1)!}\binom{2k+1}{k}(-1)^{2k+1-k}$$

Why is it that only integral values of *l* are allowed in equation 2.24?

6.0 TUTOR-MARKED ASSIGNMENT

1. Solve the equation of simple harmonic motion, $\frac{d^2y}{dx^2}+\omega^2 y=0$, using the Frobenius (series solution) method.

2. Show that the Legendre polynomials are the solutions of the polar part of the Schroedinger equation for the hydrogen atom

3. With the aid of the Rodrigues formula, find $P_4(x)$.

4. Using the Rodrigues formula, prove the orthonormality condition for Legendre polynomials.

7.0 REFERENCES/FURTHER READING

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UNIT 3 ASSOCIATED LEGENDRE FUNCTIONS, ANGULAR EIGENFUNCTIONS

CONTENTS

1.0 INTRODUCTION

In Unit 2 of this Module, we simplified the general Legendre equation by setting *m* equal to zero. This led to the Legendre polynomials. In this unit, we solve the general Legendre equation to obtain the associated Legendre polynomials. Setting *m* equal to zero in the associated Legendre polynomials naturally gives us the Legendre polynomials. The solutions of the general Legendre equation are the associated Legendre functions. Thus, the associated Legendre functions are the solutions of the polar part of the time-independent Schroedinger equation for the spherically symmetric potential. The functions are polynomials only for even values of *m*.

2.0 OBJECTIVES

At the end of this unit, you shouldbe able to:

- find the solutions to the general Legendre equation, the associated Legendre functions
- find the associated Legendre function from a given Legendre polynomial
- deduce that the associated Legendre functions are the solutions of the polar part of the time-independent Schroedinger equation
- write the spherical harmonics as a product of associated Legendre functions and the solution of the azimuthal equation.

3.1 Associated Legendre functions, Angular Eigenfunctions and the Laguerre Equation

Let us differentiate the equation for $m = 0$, equation 2.10, m times. We repeat equation 2.10:

$$\frac{d}{dx}\left[(1-x^2)\frac{dP}{dx}\right]+l(l+1)P=0$$

Differentiating term by term once, m =1,

$$\left[(1-x^2)P_l''\right]^{(1)} = (1-x^2)P_l'''-2xP_l''$$

3.1

Differentiating one more time, m = 2,

$$\left[(1-x^2)P_l''\right]^{(2)} = (1-x^2)P_l^{(4)} - 2xP_l^{(3)} - 2xP_l^{(3)} - 2P_l''$$

$$= (1-x^2)P_l^{(2+2)} - 2(2)xP_l^{(2+1)} - 2(2-1)P_l$$

Hence, differentiating m times,

$$\left[(1-x^2)P_l''\right]^{(m)} = (1-x^2)P_l^{(m+2)} - 2mxP_l^{(m+1)} - m(m-1)P_l$$

$$\left[-2xP_l'\right]^{(m)} = -2xP_l^{(m+1)} - 2mP_l^{(m)}$$

$$\left[l(l+1)P_l\right]^{(m)} = l(l+1)P_l^{(m)}$$

Adding,

$$\left[(1-x^2)P_l''\right]^{(m)} + \left[-2xP_l'\right]^{(m)} + \left[l(l+1)P_l\right]^{(m)}$$

$$= (1-x^2)P_l^{(m+2)} - 2mxP_l^{(m+1)} - m(m-1)P_l - 2xP_l^{(m+1)} - 2mP_l^{(m)}$$

$$+ l(l+1)P_l^{(m)}$$

$$= (1-x^2)P_l^{(m+2)} - 2x(m+1)P_l^{(m+1)} + [l(l+1) - m^2 - m]P_l = 0$$

Let the solution of this ordinary differential equation be P_l^m, since it now involves m.

Let

$$P_l^{(m)} = u(1-x^2)^{-m/2}$$

3.2

Then, differentiating with respect to x,

$$P_l^{(m)}{}' = u'(1-x^2)^{-m/2} + mxu(1-x^2)^{-(m+2)/2}$$

$$= \left(u' + \frac{mxu}{1-x^2}\right)(1-x^2)^{-m/2}$$

$$P_l^{(m)\,''} = \left(u'' + \frac{mu}{1-x^2} + \frac{2mx^2u}{(1-x^2)^2}\right)(1-x^2)^{-m/2} + \frac{2xm}{2}\left(u' + \frac{mxu}{1-x^2}\right)(1-x^2)^{-(m+2)/2}$$

$$(1-x^2)\left[\left(u'' + \frac{mu}{1-x^2} + \frac{2mx^2u}{(1-x^2)^2}\right)(1-x^2)^{-m/2} + \frac{2xm}{2}\left(u' + \frac{mxu}{1-x^2}\right)(1-x^2)^{-(m+2)/2}\right]$$

$$-2x(m+1)\left(u' + \frac{mxu}{1-x^2}\right)(1-x^2)^{-m/2} + [l(l+1) - m^2 - m]u(1-x^2)^{-m/2} = 0$$

$$(1-x^2)u'' + mu + \frac{2mx^2u}{1-x^2} + xm\left(u' + \frac{mxu}{1-x^2}\right)$$

$$-2x(m+1)\left(u' + \frac{mxu}{1-x^2}\right) + [l(l+1) - m^2 - m] = 0$$

$$(1-x^2)u'' - 2xu' + mu + \frac{2mx^2u}{1-x^2} + \frac{m^2x^2u}{1-x^2}$$

$$-2x(m+1)\left(\frac{mxu}{1-x^2}\right) + [l(l+1) - m^2 - m]u = 0$$

$$(1-x^2)u'' - 2xu' + mu + \frac{2mx^2u}{1-x^2} + \frac{m^2x^2u}{1-x^2} - 2x(m+1)\left(\frac{mxu}{1-x^2}\right)$$

$$+[l(l+1) - m^2 - m]u = 0$$

$$(1-x^2)u'' - 2xu' + mu + \frac{2mx^2u}{1-x^2} + \frac{m^2x^2u}{1-x^2} - \frac{2x(m+1)mxu}{1-x^2}$$

$$+[l(l+1) - m^2 - m]u = 0$$

$$(1-x^2)u'' - 2xu' + mu + \frac{2mx^2u + m^2x^2u - 2x(m+1)mxu}{1-x^2}$$

$$+[l(l+1) - m^2 - m]u = 0$$

$$(1-x^2)u'' - 2xu' + mu + \frac{(2m + m^2 - 2m^2 - 2m)x^2u}{1-x^2} + [l(l+1) - m^2 - m]u = 0$$

$$(1-x^2)u'' - 2xu' + mu - \frac{m^2x^2u}{1-x^2} + l(l+1)u - m^2\frac{1-x^2}{1-x^2}u - mu = 0$$

$$(1-x^2)u'' - 2xu' + mu - \frac{m^2x^2u}{1-x^2} + l(l+1)u + \frac{m^2x^2u}{1-x^2} - \frac{m^2}{1-x^2}u = 0$$

$$(1-x^2)u'' - 2xu' + l(l+1)u - \frac{m^2}{1-x^2}u = 0$$

3.3

But,

$$\frac{d}{dx}((1-x^2)u') = (1-x^2)u''-2xu' \quad (3.4)$$

Hence, equation 10.3 becomes

$$\frac{d}{dx}((1-x^2)u') + l(l+1)u - \frac{m^2}{1-x^2}u = 0$$

which is the general Legendre equation in which *m* is arbitrary. This implies that $u(x)$ is a solution of the general Legendre equation. The solutions are the associated Legendre functions.

From equation 10.2,

$$P_l^{(m)}(x) = u(1-x)^{-m/2}$$

Hence,

$$u(x) = (1-x)^{m/2} P_l^{(m)}(x) = (1-x^2)^{m/2} \frac{d^m P_l}{dx^m} \quad (3.5)$$

We usually denote the associated Legendre function $u(x)$ by $P_l^m(x)$. Please note that this is different from $P_l^{(m)}(x)$ which is the *m*th differential of $P_l(x)$, the Legendre polynomial, with respect to *x* (recall that $x = \cos\theta$).

$$P_l^m(x) = (1-x^2)^{m/2} \frac{d^m}{dx^m} P_l(x) \quad (3.6)$$

In equation 3.6, it does not matter whether m is positive or negative. Therefore,

$$P_l^{-m}(x) = P_l^m \quad (3.7)$$

We can therefore write,

$$P_l^m(x) = (1-x^2)^{|m|/2} \frac{d^{|m|}}{dx^{|m|}} P_l(x) \quad (3.8)$$

SELF-ASSESSMENT EXERCISE 1

Generate the first five associated Legendre functions.

We recall that the Legendre polynomials are defined by the Rodrigues formula:

$$P_l(x) = \frac{1}{2^l l!} \frac{d}{dx}^l (x^2-1)^l \quad (3.9)$$

3.2 Angular Eigenfunctions

We can now write the spherical harmonics as,

$$Y_l^m(\theta,\phi) = \Theta(\theta)\Phi(\phi) = AP_l^m(\cos\theta)e^{im\phi} \quad 3.10$$

where A is a normalization constant. With normalization,

$$A = \left[\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{1/2} \quad 3.11$$

Hence,

$$Y_l^m(\theta,\phi) = (-1)^m\left[\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{1/2} P_l^m(\cos\theta)e^{im\phi};\ m \geq 0 \quad 3.12$$

Confirm that for l = 1, we obtain the multiplets of $l=1$ as we did in Module 3, Unit 3 (equations 3.20, 3.23 and 3.26).

For $m<0$, we use the formula,

$$Y_l^{-m} = (-1)^m(Y_l^m)^* \quad 3.13$$

4.0 CONCLUSION

In this Unit, you showed that the general associated Legendre functions are the solutions of the general Legendre equation. The solutions of the polar part of the time-independent Schroedinger equation for the spherically symmetric potential are the associated Legendre functions, polynomials only when *m* is even. The solution for the angular part of the solution for the Schroedinger equation in this case is a product of the associated Legendre functions and the azimuthal solution.

5.0 SUMMARY

In this Unit, you learnt how to:

- find the solutions to the general Legendre equation, the associated Legendre functions
- find the associated Legendre function from a given Legendre polynomial
- deduce that the associated Legendre functions are the solutions of the polar part of the time-independent Schroedinger equation
- write the spherical harmonics as a product of associated Legendre functions and the solution of the azimuthal equation

Answer to Self-Assessment Exercise 1

$$P_l^m = (1-x^2)^{m/2}\frac{d^m P_l}{dx^m}$$

$$P_0^0 = (1-x^2)^0\frac{d^0 P_0}{dx^0} = P_0 = 1$$

$$P_1^0 = (1-x^2)^0\frac{d^0 P_l}{dx^0} = P_1 = x = \cos\theta$$

$$P_1^1 = (1-x^2)^{1/2}\frac{dP_1}{dx} = (1-x^2)^{1/2}\frac{d}{dx}x = (1-x^2)^{1/2} = \sqrt{1-\cos^2\theta} = \sin\theta$$

$$P_2^1 = (1-x^2)^{1/2}\frac{dP_2}{dx} = (1-x^2)^{1/2}\frac{d}{dx}\frac{1}{2}\left(3x^2-1\right) = (1-x^2)^{1/2}\times 3x = 3\sin\theta\cos\theta$$

$$P_2^2 = (1-x^2)\frac{dP_2}{dx} = (1-x^2)\frac{d^2}{dx^2}\frac{1}{2}\left(3x^2-1\right) = (1-x^2)\times 3x = 3\sin^2\theta$$

6.0 TUTOR-MARKED ASSIGNMENT

1. Show that the associated Legendre function is a polynomial only for *m* even.

2. Starting from $\frac{d}{dx}\left[(1-x^2)\frac{dP}{dx}\right]+l(l+1)P=0$, derive the general Legendre equation.

3. Given the Legendre polynomial $P_3(x) = 48x^3 + 72(x^2-1)x$, find the associated Legendre polynomials P_3^0, P_3^1.

4. With the aid of $Y_l^m(\theta,\phi) = (-1)^m\left[\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{1/2}P_l^m(\cos\theta)e^{im\phi}$; $m \geq 0$, show that:
$Y_{2\pm1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$

5. Given that $Y_l^l(\theta,\phi) = C_l^l\sin^l\theta e^{il\phi}$, find the explicit form of the spherical harmonics $Y_3^0(\theta,\phi)$ and $Y_3^3(\theta,\phi)$.

6. Calculate the explicit form of the spherical harmonics $Y_4^0(\theta,\phi)$ and $Y_4^4(\theta,\phi)$.

7.0 REFERENCES/FURTHER READING

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UNIT 4 THE RADIAL EQUATION

CONTENTS

1.0 INTRODUCTION

So far, we have discussed the spherically symmetric potential. This can be seen as the potential energy part of the Shroedinger equation. Adding the kinetic part of the Hamiltonian gives the Schroedinger equation of a body in a spherically symmetric potential. This is the object of our discussion in this Unit. The Equation consists of two parts, the angular part (which we have discussed), which is the same for all spherically symmetric problems and the radial part, which varies from one problem to another. For the electron in the hydrogen atom, the resulting equation is the Laguerre equation, the solution of which depends on the nature of the problem under discussion.

2.0 OBJECTIVES

At the end of this study session, you shouldbe able to:

- write the radial part of the Schroedinger equation and identify the expression for the effective potential
- show that the radial equation of the Schroedinger equation in spherically polar coordinates results in the Laguerre equation.

3.0 MAIN CONTENT

3.1 The Radial Equation

The electron in the hydrogen atom is under the electrostatic potential

$$V(r) = -\frac{e^2}{r} \qquad 4.1$$

where r is the distance between the proton and the electron.

$$-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}[r\psi(r,\theta,\phi)]+\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\psi(r,\theta,\phi)\right)$$
$$+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\psi(r,\theta,\phi)+(V(r)-E)\psi(r,\theta,\phi)=0$$

4.2

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}(r)+\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(r,\theta,\phi)$$
$$=[E-V(r)]\psi(r,\theta,\phi)$$

4.3

With the aid of equations 1.3 and 3.10,

$$\psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\phi)=R(r)Y_{lm}(\theta,\phi)$$

We can then write

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}(r)+\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]R(r)Y(\theta,\phi)$$
$$=[E-V(r)]R(r)Y(\theta,\phi)$$

4.4

We repeat equation 1.5 and make use of equation 2.8:

$$\frac{r^2}{Rr}\frac{d^2}{dr^2}[rR]+\frac{2mr^2}{\hbar^2}(E-V(r))=k=l(l+1)$$

4.5

Multiplying through by $\frac{Rr}{r^2}\times\frac{\hbar^2}{2m}$ and rearranging,

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}(rR)+\frac{l(l+1)\hbar^2}{2mr^2}(Rr)=[E-V(r)]Rr$$

4.6

Hence, with the help of equation 4.1,

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}(rR)+\frac{l(l+1)\hbar^2}{2mr^2}(Rr)=\left[E+\frac{e^2}{r}\right]Rr$$

4.7

Let $U=rR(r)=rR$.

$R(r)$ just shows the dependence of R on r.

Then,

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+\frac{l(l+1)\hbar^2}{2mr^2}-\frac{e^2}{r}\right]U(r)=EU(r)$$

4.8

Let $\rho = r/a_0$, and $\lambda = \sqrt{\frac{-E}{E_1}}$, where a_0 is the Bohr radius $(=\frac{\hbar^2}{me^2})$ and E_1 is the ionization energy $(=\frac{me^4}{2\hbar^2})$ of the electron.

Then,

$$dr = a_0 d\rho, \text{ and } dr^2 = {a_0}^2 d\rho, \ \frac{d^2}{dr^2} = {a_0}^2 \frac{d^2}{d\rho^2}$$

Putting this in equation 4.8 and rearranging gives,

$$\left[-\frac{d^2}{{a_0}^2 d\rho^2} + \frac{l(l+1)}{{a_0}^2 \rho^2} - \frac{2me^2}{a_0 \hbar^2 \rho} - \frac{2m}{\hbar^2} E \right] U(\rho) = 0$$

4.9

or

$$\left[-\frac{d^2}{{a_0}^2 d\rho^2} + \frac{l(l+1)}{{a_0}^2 \rho^2} - \frac{2ma_0 e^2}{{a_0}^2 \hbar^2 \rho} - \frac{2m{a_0}^2}{{a_0}^2 \hbar^2} E \right] U(\rho) = 0$$

4.10

$$\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{ma_0 e^2}{\hbar^2} \frac{2}{\rho} + \frac{2m{a_0}^2}{\hbar^2} E \right] U(\rho) = 0$$

4.11

Finally, since $a_0 = \hbar^2/me^2$ and $\frac{2m{a_0}^2}{\hbar^2} = 2m\frac{\hbar^4}{\hbar^2 m^2 e^4} = \frac{2\hbar^2}{me^4} = \frac{1}{E_1}$

$$\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{2}{\rho} + \frac{E}{E_1} \right] U(\rho) = 0$$

4.12

Let us rewrite this equation as,

$$\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{2}{\rho} - \left(\sqrt{\frac{-E}{E_1}} \right)^2 \right] U(\rho) = 0$$

4.13

and set $\sqrt{-E/E_1} = \lambda$, then,

$$\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{2}{\rho} - \lambda^2 \right] U(\rho) = 0$$

4.14

This is now in the form of the Laguerre equation.

Until we know the specific form of $U(\rho)$, we cannot continue with our analysis.

SELF-ASSESSMENT EXERCISE 1

A three-dimensional particle is free to move inside a sphere of radius *A*, i.e.,

$$V(r) = \begin{cases} 0, & 0 < r < A \\ \infty, & r > A \end{cases}$$

Starting from the radial equation,

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - l(l+1) + \frac{2mr^2}{\hbar^2}E = 0,$$

and making the substitution $\eta = kr$, where $k = \frac{2mE}{\hbar^2}$, show that R satisfies the Bessel equation,

$$\eta^2\frac{d^2R}{d\eta^2} + 2\eta\frac{dR}{d\eta} + [\eta^2 - l(l+1)]R = 0$$

4.0 CONCLUSION

In this Unit, by making the appropriate substitution, we have reduced the radial part of the Schroedinger equation for a spherically symmetric potential to the Laguerre equation.

5.0 SUMMARY

In this Unit, you have learnt how to:

- write the radial part of the Schroedinger equation and identify the expression for the effective potential
- show that the radial equation of the Schroedinger equation in spherically polar coordinates results in the Laguerre equation

Answer to Self-Assessment Exercise 1

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - l(l+1) + \frac{2mr^2}{\hbar^2}E = 0$$

Multiplying through by Rr^2,

$$r^2\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - Rl(l+1) + \frac{2mRr^2}{\hbar^2}E = 0$$

Let $\eta = kr$. Then, $d\eta = kdr$ and $d\eta^2 = k^2dr^2$.

$$\frac{dR}{dr} = k\frac{dR}{d\eta}$$

$$\frac{d^2R}{dr^2} = k^2 \frac{d^2R}{d\eta^2}$$

$$\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) - Rl(l+1) + \frac{2mr^2R}{\hbar^2}E = 0$$

$$r^2 \frac{d^2R}{dr^2} + 2r\frac{dR}{dr} - Rl(l+1) + \frac{2mr^2R}{\hbar^2}E = 0$$

$$\frac{\eta^2}{k^2}k^2 \frac{d^2R}{d\eta^2} + 2\frac{\eta}{k}k\frac{dR}{d\eta} - Rl(l+1) + \frac{2mr^2R}{\hbar^2}E = 0$$

$$\eta^2 \frac{d^2R}{d\eta^2} + 2\eta\frac{dR}{d\eta} - Rl(l+1) + \frac{2mr^2R}{\hbar^2}E = 0$$

But $\frac{2mE}{\hbar^2} = k^2$. Hence, $\frac{2mE}{\hbar^2}r^2R = k^2r^2R = \eta^2R$

Therefore,

$$\eta^2 \frac{d^2R}{d\eta^2} + 2\eta\frac{dR}{d\eta} + [\eta^2 - l(l+1)]R = 0$$

6.0 TUTOR-MARKED ASSIGNMENT

1. With the change of variables $U(r) = rR(r)$, where $R(r)$ simply shows the functional dependence of the radial part R on r (the radial distance from the nucleus)

(a) Write the radial part of the Schroedinger equation (equation 10.20) in
spherical coordinates in terms of $U(r)$.

(b) Show that the effective potential is $\frac{l(l+1)\hbar^2}{2mr^2} + V(r)$. What is the physical significance of each term?

2. Show that the mass of the proton can be neglected in the treatment of the motion of the electron inside the hydrogen atom.

3. Find the normalised ground state (n = 0) wavefunction $R(r) = X(r)/r$ such that $\frac{d^2X(r)}{dr^2} + \left\{\frac{2m}{\hbar^2} - \frac{l(l+1)}{r^2}\right\}X(r) = 0$. Take $X\big|_{r=a} = X\big|_{r=b} = 0$.

7.0 REFERENCES/FURTHER READING

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UNIT 5 THE HYDROGEN ATOM

CONTENTS

1.0 INTRODUCTION

In Unit 4, we studied the radial part of the angular part of the Schroedinger equation for a particle in a spherically symmetric potential well. As a result, we obtained the Laguerre equation. In this study session, we consider specific forms of the radial part of the Schroedinger equation. In particular, we shall consider the hydrogen potential. Consequently, we shall write the complete solution for the Schroedinger equation for the hydrogen atom.

2.0 OBJECTIVES

At the end of this Unit, you should be able to:

- evaluate integrals related to the hydrogen atom
- find the expectation value of some physical observables in a given eigenstate of the hydrogen atom
- find the probability of finding an electron at a given distance from the nucleus of the hydrogen atom
- show that radial wavefunction for a three-dimensional particle free to move inside a sphere satisfies the Bessel equation.

3.0 MAIN CONTENT

3.1 The Hydrogen Atom

We shall pick a specific function $U(\rho)$:
Let

$$U(\rho) = e^{-\lambda\rho}\chi(\rho) \qquad 5.1$$

Then,

$$\frac{dU}{d\rho} = -\lambda e^{-\lambda\rho}\chi + e^{-\lambda\rho}\frac{d\chi}{d\rho}$$

5.2

$$\frac{d^2U}{d\rho^2} = \lambda^2 e^{-\lambda\rho}\chi - \lambda e^{-\lambda\rho}\frac{d\chi}{d\rho} - \lambda e^{-\lambda\rho}\frac{d\chi}{d\rho} + e^{-\lambda\rho}\frac{d^2\chi}{d\rho^2}$$

$$= \lambda^2 e^{-\lambda\rho}\chi - 2\lambda e^{-\lambda\rho}\frac{d\chi}{d\rho} + e^{-\lambda\rho}\frac{d^2\chi}{d\rho^2}$$

5.3

$$\left[\lambda^2 e^{-\lambda\rho}\chi - 2\lambda e^{-\lambda\rho}\frac{d\chi}{d\rho} + e^{-\lambda\rho}\frac{d^2\chi}{d\rho^2}\right] - \frac{l(l+1)}{\rho^2}e^{-\lambda\rho}\chi + \frac{2}{\rho}e^{-\lambda\rho}\chi - \lambda^2 e^{-\lambda\rho}\chi = 0$$

$$\left[-2\lambda\frac{d}{d\rho} + \frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{2}{\rho}\right]\chi = 0$$

$$\left[\frac{d^2}{d\rho^2} - 2\lambda\frac{d}{d\rho} + \left(\frac{2}{\rho} - \frac{l(l+1)}{\rho^2}\right)\right]\chi = 0$$

5.4

We seek a series solution for equation 11.4 in the form,

$$\chi(\rho) = \sum_{j=0}^{\infty} c_j \rho^{j+s}$$

5.5

Then,

$$\frac{d\chi}{d\rho} = \sum_{j=0}^{\infty}(j+s)c_j\rho^{j+s-1}$$

5.6

$$\frac{d^2\chi}{d\rho^2} = \sum_{j=0}^{\infty}(j+s)(j+s-1)c_j\rho^{j+s-2}$$

5.7

Substituting in equation 5.4,

$$\sum_{j=0}^{\infty}(j+s)(j+s-1)c_j\rho^{j+s-2} - 2\lambda\sum_{j=0}^{\infty}(j+s)c_j\rho^{j+s-1}$$
$$+\left(\frac{2}{\rho} - \frac{l(l+1)}{\rho^2}\right)\sum_{j=0}^{\infty}c_j\rho^{j+s} = 0$$

5.8

$$\sum_{j=0}^{\infty}(j+s)(j+s-1)c_j\rho^{j+s-2} - 2\lambda\sum_{j=0}^{\infty}(j+s)c_j\rho^{j+s-1}$$
$$+2\sum_{j=0}^{\infty}c_j\rho^{j+s-1} - l(l+1)\sum_{j=0}^{\infty}c_j\rho^{j+s-2} = 0$$

5.9

The lowest term (with $j = 0$) is then (coefficients of ρ^{s-2}):

$$s(s-1)c_0 - l(l+1)c_0 = 0$$

5.10

or

$$[s(s-1) - l(l+1)]c_0 = 0$$

5.11

Since $c_0 \neq 0$, this can only imply that $s(s-1) - l(l+1) = 0$.

But,

$$s^2 - s - l^2 - l = s^2 - sl - s + sl - l^2 - l = (s+l)(s-l-1) = 0$$

Hence, $s = -l$ or $s = l+1$

The general term ρ^{j+s-2} is given by setting $j = j-1$ in the terms involving ρ^{j+s-1},

$$(j+s)(j+s-1)c_j\rho^{j+s-2} - 2\lambda([j-1]+s)c_{j-1}\rho^{(j-1)+s-1} + 2c_{j-1}\rho^{(j-1)+s-1} - l(l+1)c_j\rho^{j+s-2} = 0$$

5.12

Hence,

$$(j+s)(j+s-1)c_j - 2\lambda([j-1]+s)c_{j-1} + 2c_{j-1} - l(l+1)c_j = 0$$

5.13

Set $s = l+1$:

$$(j+l+1)(j+l+1-1)c_j - 2\lambda([j-1]+l+1)c_{j-1} + 2c_{j-1} - l(l+1)c_j = 0$$

$$(j+l+1)(j+l)c_j - 2\lambda(j+l)c_{j-1} + 2c_{j-1} - l(l+1)c_j = 0$$

$$[(j^2 + jl + j + jl + l^2 + l) - l(l+1)]c_j - [2\lambda(j+l) - 2]c_{j-1} = 0$$

$$(j^2 + 2jl + j)c_j - 2[\lambda(j+l) - 1]c_{j-1} = 0$$

$$j(j+2l+1)c_j - 2[\lambda(j+l) - 1]c_{j-1} = 0$$

5.14

The recursion relation is,

$$c_j = \frac{2[\lambda(j+l) - 1]}{j(j+2l+1)}c_{j-1}$$

5.15

In general, the recursion relation can be distilled into [$(\lambda = \lambda_{kl}; n = k+1)$ hydrogen atom]

$$c_j = (-1)^j\left(\frac{2}{k+1}\right)^j \frac{(k-1)!}{(k-q-1)!}\frac{(2l+1)!}{q!(q+2l+1)!}c_0$$

Then,

$$R_{nl}(\rho) = -\sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho)$$

5.16

where $L_p^q(\rho)$ are the associated Laguerre polynomials,

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} \frac{(-1)^{k+1}[(n+l)!]^2 \rho^k}{(n-l-1-k)!(2l+1+k)!k!}$$

5.17

Some of the first few associated Laguerre polynomials are:

$$L_0^0 = 1 \qquad L_0^2 = 2$$
$$L_1^0 = 1 - x \qquad L_1^2 = 18 - 6x$$
$$L_2^0 = 2 - 4x + x^2 \qquad L_2^2 = 144 - 96x + 12x^2$$

The Laguerre polynomials are defined as,

$$L_n(x) = e^x \frac{d^n}{dx^n}(x^n e^{-x})$$

5.18

and the associated Laguerre polynomials,

$$L_{n-l}^l = (-1)^l \frac{d^l}{dx^l} L_n(x)$$

5.19

Example 5.1
From equations 5.18 and 5.19, find the Laguerre as well as all the associated Laguerre polynomials for *n* = 2.

Solution 5.1

$$L_2(x) = e^x \frac{d^2}{dx^2}(x^2 e^{-x}) = e^x \frac{d}{dx}(2xe^{-x} - x^2 e^{-x}) = e^x(2e^{-x} - 2xe^{-x} - 2xe^{-x} + x^2 e^{-x})$$
$$= 2 - 4x + x^2$$
$$L_{2-0}^0 = L_2^0 = (-1)^0 \frac{d^0}{dx^0} L_2(x) = L_2(x) = x^2 - 4x + 2$$
$$L_{2-1}^1 = L_1^1 = (-1)^1 \frac{d}{dx} L_2(x) = -\frac{d}{dx}(x^2 - 4x + 2) = -(2x - 4) = -2(x - 2)$$
$$L_{2-2}^2 = L_0^2 = (-1)^2 \frac{d^2}{dx^2} L_2(x) = \frac{d^2}{dx^2}(x^2 - 4x + 2) = \frac{d}{dx}[2(x-2)]$$
$= 2$ (not relevant to our treatment of the hydrogen atom, why?)

SELF-ASSESSMENT EXERCISE 1

From equations 5.18 and 5.19, find the Laguerre as well as all the associated Laguerre polynomials for $n = 3$.

From equation 5.16, the first three of the radial functions, R_{nl} , are,

$$R_{10}(\rho) = -\sqrt{\left(\frac{2}{(1)a_0}\right)^3 \frac{(1-0-1)!}{2(1)[(1+0)!]^3}} e^{-\rho/n} \rho^0 L_1^1(\rho)$$

$$= -\sqrt{\left(\frac{2}{a_0}\right)^3 \frac{1}{2}} e^{-\rho/1}(-1)$$

$$= -2(a_0)^{-3/2} e^{-r/a_0} \qquad (\text{since } \rho = r/a_0)$$

$$R_{20}(\rho) = -\sqrt{\left(\frac{2}{2a_0}\right)^3 \frac{(2-0-1)!}{2(2)[(2+0)!]^3}} e^{-\rho/2} \rho^0 L_{2+0}^{2(0)+1}(\rho)$$

$$= -\sqrt{\left(\frac{1}{a_0}\right)^3 \frac{1}{4\times 8}} e^{-\rho/2} \rho^0 L_2^1(\rho)$$

$$= -\sqrt{\left(\frac{1}{2a_0}\right)^3} e^{-\rho/2} \frac{2}{2}(2-\rho) = -2\sqrt{\left(\frac{1}{2a_0}\right)^3} e^{-\rho/2}\left(1-\frac{\rho}{2}\right)$$

$$= -2(2a_0)^{-3/2}\left(1-\frac{r}{2a_0}\right) e^{-r/2a_0}$$

$$R_{21} = -\frac{1}{\sqrt{24}}(a_0)^{-3/2}\left(\frac{r}{a_0}\right) e^{-r/2a_0}$$

These functions are sketched in Fig. 5.1.

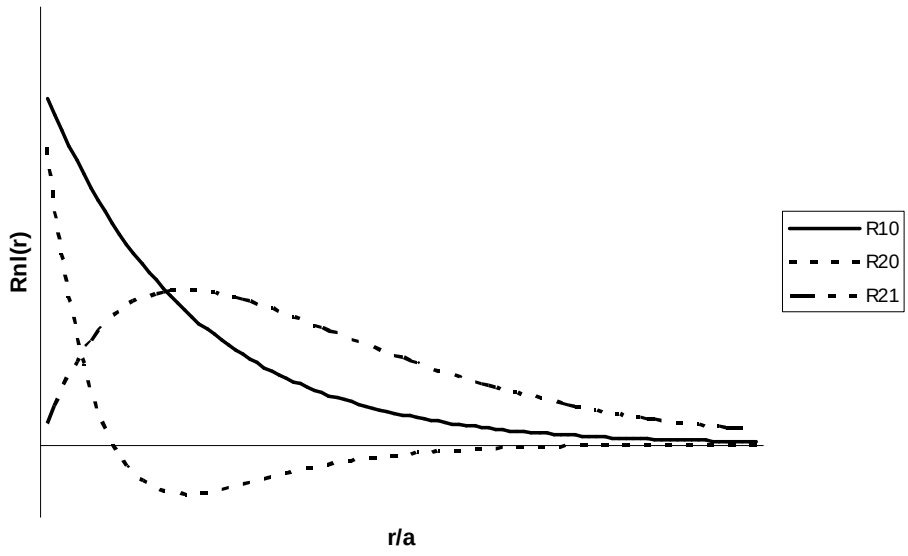

Fig. 5.1: Graphs of R_{10}, R_{20} and R_{21}

The corresponding wave functions for the hydrogen atom are,

$$\psi_{nlm} = R_{nl} Y_{lm}$$

$$\psi_{100} = R_{10} Y_0^0 =$$

$$R_{10}(\rho) Y_0^0(\theta,\phi) = -\sqrt{\left(\frac{2}{(1)a_0}\right)^3 \frac{(1-0-1)!}{2(1)[(1+0)!]^3}} e^{-\rho/2} \rho^0 L_1^1(\rho)$$

$$\times (-1)^0 \left[\frac{2(0)+1}{4\pi}\frac{(0-0)!}{(0+0)!}\right]^{1/2} P_0^0(\cos\theta) e^{i(0)\phi}$$

$$= -\sqrt{\left(\frac{2}{a_0}\right)^3 \frac{1}{2}} e^{-\rho/2}(-1) \times \sqrt{\frac{1}{4\pi}}(1)$$

$$= \sqrt{\frac{1}{\pi\, {a_0}^3}} e^{-\rho/2}$$

But $\rho = r/a_0$. Hence,

$$\psi_{100} = \frac{1}{\sqrt{\pi\, {a_0}^3}} e^{-r/a_0}$$

It should be easy for you to show that:

$$\psi_{200} = \frac{1}{\sqrt{32 {a_0}^3 \pi}} \left(2 - \frac{r}{{a_0}^3}\right) e^{-r/2a_0}$$

$$\psi_{210} = \frac{1}{\sqrt{32\, {a_0}^3 \pi}} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$$

$$\psi_{211} = \frac{1}{\sqrt{64 {a_0}^3 \pi}} \frac{r}{a_0} e^{-r/2a_0} \sin\theta\, e^{i\phi}$$

$$\psi_{21(-1)} = \frac{1}{\sqrt{64 {a_0}^3 \pi}} \frac{r}{a_0} e^{-r/2a_0} \sin\theta\, e^{-i\phi}$$

Different quantum numbers *n*, *l*, and *m* denote different stationary states. (In three dimensions we need three quantum numbers.) Since the corresponding operators commute, the eigenstates of the energy operator are also eigenstates of the square of the angular momentum operator, L^2, and of the *z*-component of the angular momentum operator, L_z. We recall that the quantum number *l* characterizes the eigenvalues $l(l+1)\hbar^2$ of L^2, and the quantum number *m* characterizes the eigenvalues $m\hbar$ of L_z. This implies that *E*, L^2 and L_z can be measured simultaneously (they all commute in pairs) for a particle with potential energy *U(r)*, we can know all three eigenvalues exactly at the same time. However, the energy of a stationary state never depends on *m* in a spherically symmetric potential. All states with the same *n* and *l* but different *m* are

degenerate, as the different eigenstates all correspond to the same energy.

We note that the functions $R_{nl}(r)$ depend on the exact form of the spherically symmetric potential U(r) (recall that we had to specify the form of U), but the spherical harmonics, $Y_{lm}(\theta,\phi)$, are the same for all spherically symmetric potentials. They are the eigenfunctions of L^2 and L_z, operators; they do not operate on the radial coordinate r (because of spherical symmetricity). $|Y_{lm}(\theta,\phi)|^2$ is the probability density of finding the particle at angles (θ,ϕ). Some of the normalized spherical harmonics are given below.

$$Y_{00} = \frac{1}{\sqrt{4\pi}},\ Y_{1\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi},\ Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_{2\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\phi}$$

SELF-ASSESSMENT EXERCISE 2

What is the average radius (expectation value of r) of the orbit of the electron for the radial wavefunction R_{20}? Take $\int_0^\infty r^n e^{-kr} dr = \frac{n!}{k^{1+n}}$.

4.0 CONCLUSION

In this Unit, you found the solution to the radial part of the Schroedinger equation for a specific form of the radial function, leading to the associated Laguerre polynomials. The solution to the radial equation is a function of the principal quantum number, n, and the orbital angular momentum, l. Hence, the solution of the Schroedinger equation for the hydrogen atom is the product of the radial solution and the spherical harmonics.

5.0 SUMMARY

In this study session, you have learnt how to:

- solve the Laguerre equation and hence obtain the radial wavefunction for a given principal quantum number and the orbital quantum number.
- write the Laguerre and the associated Laguerre polynomials for a given principal quantum number

- write the full solution of the Schroedinger equation for the hydrogen atom as a product of the radial solution and the appropriate spherical harmonic.

Answer to Self-Assessment Exercise 1

$$R_{20} = -2(2a_0)^{-3/2}\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}$$

$$< R_{20} >= \int_0^\infty (r^2 dr)\, r \mid R_{20} \mid^2$$

$$= \int_0^\infty r^3\left(-2(2a_0)^{-3/2}\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}\right)^2 dr$$

$$= 4(2a_0)^{-3}\int_0^\infty r^3 e^{-r/a_0}\left(1-\frac{r}{a_0}+\frac{r^2}{4a_0{}^2}\right)dr$$

$$= 4(2a_0)^{-3}\int_0^\infty e^{-r/a_0}\left(r^3-\frac{r^4}{a_0}+\frac{r^5}{4a_0{}^2}\right)dr$$

$$= 4(2a_0)^{-3}\left[\int_0^\infty r^3 e^{-r/a_0}dr - \int_0^\infty \frac{r^4}{a_0}e^{-r/a_0}dr \int_0^\infty \frac{r^5}{4a_0{}^2}e^{-r/a_0}dr\right]$$

$$= 4(2a_0)^{-3}\left[\int_0^\infty r^3 e^{-r/a_0}dr - \frac{1}{a_0}\int_0^\infty r^4 e^{-r/a_0}dr + \frac{1}{4a_0{}^2}\int_0^\infty r^5 e^{-r/a_0}dr\right]$$

$\int_0^\infty r^n e^{-kr}dr = \frac{n!}{k^{1+n}}$. Here, $k = 1/a_0$.

$$\int_0^\infty r^3 e^{-r/a_0}dr = \frac{3!}{(1/a_0)^{1+3}} = 6a_0{}^4$$

$$\int_0^\infty r^4 e^{-r/a_0}dr = \frac{4!}{(1/a_0)^{1+4}} = 24a_0{}^5$$

$$\int_0^\infty r^5 e^{-r/a_0}dr = \frac{5!}{(1/a_0)^{1+5}} = 120a_0{}^6$$

Hence,

$$< r >= 4(2a_0)^{-3}\left[6a_0{}^4 - \frac{24a_0{}^5}{a_0} + \frac{120}{4a_0{}^2}a_0{}^6\right]$$

$$= 4(2a_0)^{-3}[6a_0{}^4 - 24a_0{}^4 + 30a_0{}^4]$$

$$= 4(2a_0)^{-3}[12a_0{}^4]$$

$$= 6a_0$$

Answer to Self-Assessment Exercise 2

$$L_3(x) = e^x\frac{d^3}{dx^3}(x^3e^{-x}) = e^x\frac{d^2}{dx^2}(3x^2e^{-x} - x^3e^{-x})$$

$= e^x \frac{d}{dx}(6xe^{-x} - 6x^2e^{-x} + x^3e^{-x})$

$= e^x(6e^{-x} - 6xe^{-x} - 12xe^{-x} + 6x^2e^{-x} + 3x^2e^{-x} - x^3e^{-x})$

$= e^x(6e^{-x} - 18xe^{-x} + 9x^2e^{-x} - x^3e^{-x})$

$= 6 - 18x + 9x^2 - x^3$

$L^0_{3-0} = L^0_3 = L_3(x) = 6 - 18x + 9x^2 - x^3$

$L^1_{3-1} = L^1_2 = -\frac{d}{dx}L_3(x) = -\frac{d}{dx}(6 - 18x + 9x^2 - x^3) = -(-18 + 18x - 3x^2)$

$= 3(6 - 6x + x^2)$

$L^2_{3-2} = L^2_1 = (-1)^2\frac{d^2}{dx^2}L_3(x) = \frac{d^2}{dx^2}(6 - 18x + 9x^2 - x^3) = \frac{d}{dx}(-18 + 18x - 3x^2)$

$= 18 - 6x$

$L^3_{3-3} = L^3_0 = (-1)^3\frac{d^3}{dx^3}L_3(x) = -\frac{d}{dx}(18 - 6x) = 6$ (L^3_0 is of no relevance to us).

6.0 TUTOR-MARKED ASSIGNMENT

1. Evaluate the integral $\int_0^\infty r^n e^{-kr}dr$, where *n* is an integer greater than 1.

2. Find the expectation value of *r* and r^2 in the ground state of the hydrogen atom.

3. At what distance *r*, in terms of the Bohr radius a_0, from the nucleus does the probability distribution function of the wavefunction $\psi_{100}(r) = \frac{1}{\pi a_0^3}e^{-r/a_0}$ become less than five percent of its value at the Bohr radius?

4. The wavefunction of a hydrogen-like atom is $\psi(r) = Ae^{-r/a}$, where $a = a_0/Z$, a_0 is the Bohr radius, typically 0.5 Angstrom, and the charge on the nucleus is Ze. If the atom contains only one electron,

(a) Find the normalization constant.

(b) If the mass number is 150 and the atomic number is 72, what is the probability that it is not in the nucleus? Take the radius of the nucleus as $1.1A^{1/3} \times 10^{-5}$ Angstrom.

Assume the wavefunction is constant inside the nucleus since its dimensions are small compared to a_0/Z. Comment on your result.

5. At time $t = 0$, the wave function for a hydrogen atom is given as,

$$\psi(\mathbf{r},0) = \frac{1}{\sqrt{15}}(3\psi_{100} + 2\psi_{210} + \psi_{211} + \psi_{21-1})$$

where the subscripts are n, l, m.

(a) Calculate the expectation value for the energy of the system?

(b) Calculate the probability of finding the system with $l = 1$, $m = 0$ as a function of time.

7.0 REFERENCES/FURTHER READING

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MODULE 4 PERTURBATION THEORY AND QUANTUM SCATTERING

UNIT 1 PERTURBATION THEORY

CONTENTS

1.0 INTRODUCTION

In the case in which the Hamiltonian is no longer of a simple form, it might be impossible to find an exact solution for the Schroedinger equation. In such a situation, we may resort to perturbation method. In Quantum Mechanics, the energy of a body in an infinite potential well is quantised. Thus, the electron in an atom can only have a set of discrete energies (bound states). For a finite potential, the energy for a particle inside the potential, $E<V$, the energy is quantised. For $E>V$, the energy is one of a continuum. In this case, the energy is mixed, quantised and continuous, depending on the value of the energy of the particle. For a constant potential and for $E\geq V$, the energy is continuous. Without a loss of generality, as the reference for such a potential is arbitrary, we can redefine the zero of the potential, such that we can set it to zero, giving the case of a free particle. Thus, if an electron is no longer inside the atom, that is no longer inside a potential well, it can have any value in a continuum of energies. In addition, another electron can also have a continuum of energies. The difference in energy of such electrons can also take up any value of a continuum of energies. Perturbation theory relies on the known eigenstates of the unperturbed Hamiltonian. It follows that the theory applies only to bound states. The idea is that if the deviation from the simple Hamiltonian is ‘small,’ the solution may

be obtained by adding a small term to the energy and the wavefunction associated with the simple Hamiltonian. In this Unit, we shall consider Hamiltonians that are a little bit deviated from the simple Hamiltonians we are already familiar with.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- find the first order correction to the energy of a slightly perturbed system in terms of the known unperturbed energy
- find the first order correction to the wave function of a slightly perturbed system in terms of the known wave function.

3.0 MAIN CONTENT

3.1 Perturbation Theory

We shall assume that the Hamiltonian of the particle under discussion is a little different from a "simple" unperturbed Hamiltonian H_0 acting on the Hilbert space Ή, so we can write

$$H_0 |u_j> = E_j |u_j> \quad (1.1)$$

is known so that the known orthornormal basis $|u_j>$ in the analysis of the undisturbed Hamiltonian can still be used as a basis. We write the perturbed Hamiltonian, *H* as a sum of the unperturbed Hamiltonian and the 'small' perturbation λH_1,

$$H = H_0 + \lambda H_1, \ \lambda \in [0,1] \quad (1.2)$$

such that

$$|H_1| << |H_0| \quad (1.3)$$

λ in equation 1.2 is useful in keeping track of the order of order of perturbation.

λ

Let the eigenvalues-eigenvectors of the perturbed Hamiltonian H be such that

$$H|\psi_n> = E_n|\psi_n> \quad (1.4)$$

We shall seek solution at the *k*th level, with energy E, and wavefunction ψ so we can write

$$H\,|\psi> = E\,|\psi>$$

1.5

Assume E and ψ can be expanded in terms of $\{u_j\}$, $\{E_j\}$ and that

$$E_n = \lambda^0 E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \ldots$$

1.6

$$|\psi_n> = \lambda^0 |\psi_n^0> + \lambda |\psi_n^1> + \lambda^2 |\psi_n^2> + \ldots$$

1.7

Then,

$$H|\psi_n> = (H^0 + \lambda H_1)(|\psi_n^0> + \lambda|\psi_n^1> + \lambda^2|\psi_n^2> + \ldots)$$ (LHS of equation (1.4)

$$= (\lambda^0 E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \ldots)(|\psi_n^0> + \lambda|\psi_n^1> + \lambda^2|\psi_n^2> + \ldots) = E|\psi_n>$$

1.8

(RHS of equation (1.4)

$$H^0|\psi_n^0> + \lambda H^0|\psi_n^1> + \lambda^2 H^0|\psi_n^2> + \ldots$$
$$+\lambda H_1|\psi_n^0> + \lambda^2 H_1|\psi_n^1> + \lambda^3 H_1|\psi_n^2> + \ldots$$
$$= E_n^0|\psi_n^0> + \lambda E_n^0|\psi_n^1> + \lambda^2 E_n^0|\psi_n^2> + \ldots$$
$$+\lambda E_n^1|\psi_n^0> + \lambda^2 E_n^1|\psi_n^1> + \lambda^3 E_n^1|\psi_n^2> + \ldots$$
$$+\lambda^2 E_n^2|\psi_n^0> + \lambda^3 E_n^2|\psi_n^1> + \lambda^4 E_n^2|\psi_n^2> + \ldots$$

Equating coefficients of λ^k,

λ^0: $H^0|\psi_n^0> = E_n^0|\psi_n^0>$

1.9

λ^1: $H^0|\psi_n^1> + H^1|\psi_n^0> = E_n^0|\psi_n^1> + E_n^1|\psi_n^0>$

1.10

λ^2: $H^0|\psi_n^2> + H^1|\psi_n^1> = E_n^0|\psi_n^2> + E_n^1|\psi_n^1> + E_n^2|\psi_n^0>$

1.11

and so on.

Note that equation 1.9 is just stating the obvious, for the unperturbed system.

3.1.1 First-Order Perturbation

We multiply equation 1.10 by $<\psi_n^0|$ on the left:

$$<\psi_n^0|H^0|\psi_n^1> + <\psi_n^0|H^1|\psi_n^1> = E_n^0<\psi_n^0|\psi_n^1> + E_n^1<\psi_n^0|\psi_n^0>$$

1.12

The first term:

$$<\psi_n^0 | H^0 | \psi_n^1 >=<H^0\psi_n^0 | \psi_n^1 >=E_n^0 <\psi_n^0 | \psi_n^1 >$$ since H^0 is Hermitian.

Clearly, the first term on either side cancel out.

The second term on the right hand side, $E_n^1 <\psi_n^0 | \psi_n^0 >=E_n^1$. Hence, equation 1.12 reduces to,

$$E_n^1 =<\psi_n^0 | H^1 | \psi_n^0 >$$

1.13

This is the **1st order correction to the energy**, and as you can see, it is the expectation value of the perturbation H^1 over $|\psi_n^0>$, the unperturbed state.

Again, from equation 1.10,

$$H^0 | \psi_n^1 > -E_n^0 | \psi_n^1 >= E_n^1 | \psi_n^0 > -H^1 | \psi_n^0 >$$

We can rearrange this into

$$(H^0 - E_n^0) | \psi_n^1 >= (E_n^1 - H^1) | \psi_n^0 >$$

1.14

Expanding $|\psi_n^1>$ in terms of the orthonormal basis for the unperturbed system,

$$|\psi_n^1 >= \sum_{j\neq n} c_j^{(n)} | \psi_j^0 >$$

1.15

where $j = n$ has been omitted because from equation 1.7, any $|\psi_n^0>$ term in $|\psi_n^1>$ could have been pulled out and combined with the first term on the right.

$$|\psi_n >= \lambda^0 | \psi_n^0 > +\lambda | \psi_n^1 > +\lambda^2 | \psi_n^2 > +...$$

Let us put equation 1.15 into equation 1.14:

$$(H^0 - E_n^0)\sum_{j\neq n} c_j^{(n)} | \psi_j^0 >= (E_n^1 - H^1) | \psi_n^0 >$$

1.16

But $H^0 | \psi_j^0 >= E_j^0 | \psi_j^0 >$.

Therefore, equation 1.16 becomes,

$$\sum_{j\neq n} (E_j^0 - E_n^0) c_j^{(n)} | \psi_j^0 >= (E_n^1 - H^1) | \psi_n^0 >$$

1.17

Multiplying by $<\psi_k^0|$,

$$\sum_{j\neq n}(E_j^0-E_n^0)c_j^{(n)}<\psi_k^0|\psi_j^0>=<\psi_k^0|E_n^1|\psi_n^0>-<\psi_k^0|H^1|\psi_n^0>$$

or

$$\sum_{j\neq n}(E_j^0-E_n^0)c_j^{(n)}<\psi_k^0|\psi_j^0>=E_n^1<\psi_k^0|\psi_n^0>-<\psi_k^0|H^1|\psi_n^0>$$

1.18

If $k=n$, $<\psi_k^0|\psi_j^0>=<\psi_n^0|\psi_j^0>=0$ (see explanation after equation 1.15 the left side of equation 1.18 becomes zero, giving yet again, equation 1.13.

For $k\neq n$,

$$\sum_{j\neq n}(E_j^0-E_n^0)c_j^{(n)}\delta_{kj}=(E_k^0-E_n^0)c_k^{(n)}=E_n^1\times 0-<\psi_k^0|H^1|\psi_n^0>$$

Finally,

$$c_k^{(n)}=\frac{-<\psi_k^0|H^1|\psi_n^0>}{E_k^0-E_n^0}=\frac{<\psi_k^0|H^1|\psi_n^0>}{E_n^0-E_k^0}$$

Therefore,

$$c_j^{(n)}=\frac{<\psi_j^0|H^1|\psi_n^0>}{E_n^0-E_j^0}$$

1.19

And equation 1.15 becomes,

$$|\psi_n^1>=\sum_{j\neq n}\frac{<\psi_j^0|H^1|\psi_n^0>}{E_n^0-E_j^0}|\psi_j^0>$$

1.20

For first-order approximation and setting $\lambda=1$,

$$E_n=E_n^0+E_n^1=E_0+<\psi_n^0|H_1|\psi_n^0>$$

1.21

$$|\psi_n>=|\psi_n^0>+|\psi_n^1>=|\psi_n^0>+\sum_{j\neq n}\frac{<\psi_j^0|H^1|\psi_n^0>}{E_n^0-E_j^0}|\psi_j^0>$$

1.22

Example 1

A particle is in a box slanted such that we may write the Hamiltonian $H=H^{(0)}+H^{(1)}$, where $H^{(0)}=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ and $H^{(1)}=\frac{V}{a}x$. $\psi_n^0=\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}$ and $E_n^0=\frac{n^2h^2}{8ma^2}$. What are the first order corrections to the zeroth order (unperturbed) energies?

Solution 1

$H = H^{(0)} + H^{(1)}$

where $H^{(0)} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$, $H^{(1)} = \frac{V}{a}x$

The solution to $H^{(0)}\psi^{(0)} + E^{(0)}\psi^{(0)}$ are:

$$\psi_n^{(0)} = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a} \text{ and } E_n^{(0)} = \frac{n^2h^2}{8ma^2}$$

The first order corrections to the zeroth order (unperturbed) energies are:

$$E_n^{(1)} = <\psi_n^{(0)} \mid H^{(1)} \mid \psi_n^{(0)}>$$

$$= \int \left(\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\right)^* \left(\frac{V}{a}x\right)\left(\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\right)dx$$

$$= \frac{2V}{a^2}\int x\sin\frac{n\pi x}{a}dx$$

$$= \frac{V}{a^2}\int\left(x - x\cos\frac{2n\pi x}{a}\right)dx$$

$$= \frac{V}{a^2}\left[\frac{x^2}{2}\Big|_0^a - \int_0^a x\cos\frac{2n\pi x}{a}dx\right]$$

$$= \frac{V}{a^2}\frac{a^2}{2} - \frac{V}{a^2}\int_0^a x\cos\frac{2n\pi x}{a}dx$$

$$= \frac{V}{2} - \frac{V}{a^2}\left[\frac{a}{2n\pi}x\sin\frac{2n\pi x}{a}\Big|_0^a - \frac{a}{2n\pi}\int_0^a\sin\frac{2n\pi x}{a}dx\right]$$

$$= \frac{V}{2} + \frac{V}{2n\pi a}\int_0^a\sin\frac{2n\pi x}{a}dx$$

$$= \frac{V}{2} - \frac{V}{2n\pi a}\frac{a}{2n\pi}\cos\frac{2n\pi x}{a}\Big|_0^a$$

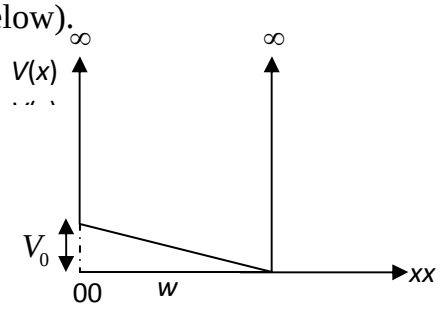
$$= \frac{V}{2} - \frac{V}{(2n\pi)^2}(1-1)$$

$$= \frac{V}{2}$$

Hence, the first order correction to the energies is $E^{(1)} = \frac{V}{2}$.

SELF-ASSESSMENT EXERCISE 1

Calculate the energy of the first two states for an infinite square well potential of width *d* (Figure below).



4.0 CONCLUSION

Starting with the energy and the wavefunction of the unperturbed quantum-mechanical system, you have learnt how to find the first order correction to the energy and the wavefunction of a quantum-mechanical system under a very small perturbation.

5.0 SUMMARY

In this Unit, you have learnt to:

- find 1st order correction to the energy of a slightly perturbed system
- find 1st order correction to the wavefunction of a slightly perturbed system

Answer to Self-Assessment Exercise 1

The modification to the Hamiltonian is $H' = V_0(1-\frac{x}{w})$, which can be considered a perturbation. The function you can easily prove by recognising that the slope is $-V_0 / w$, and the intercept on the V axis is V_0. Hence, $H'(x) = -\frac{V_0}{w}x + V_0 = V_0(1-\frac{x}{w})$.

The unperturbed eigenstates and the corresponding eigenvalues are,

$$\phi_1 = \sqrt{\frac{2}{w}}\sin\frac{\pi x}{w},\ E_1^0 = \frac{\pi^2\hbar^2}{2mw^2}$$

$$\phi_2 = \sqrt{\frac{2}{w}}\sin\frac{2\pi x}{w},\ E_1^0 = \frac{2^2\pi^2\hbar^2}{2mw^2}$$

Recall that

$$\int \sin^2 kxdx = \frac{x}{2} - \frac{1}{4k}\sin 2kx + \mathrm{c}$$

$$\int x\sin^2 kxdx = \frac{x^2}{4} - \frac{x}{4k}\sin 2kx - \frac{1}{8k^2}\cos 2kx + \mathrm{c}$$

In our own case, $k = \frac{\pi}{w}$

$$\int \sin^2 \frac{\pi}{w} x dx = \frac{x}{2} - \frac{w}{4\pi} \sin 2\frac{\pi}{w} x + \mathrm{c}$$

$$\int x \sin^2 \frac{\pi}{w} x dx = \frac{x^2}{4} - \frac{x\pi}{4w} \sin 2\frac{\pi}{w} x - \frac{w^2}{8\pi^2} \cos 2\frac{\pi}{w} x + \mathrm{c}$$

$$\int_0^w \sin^2 \frac{\pi}{w} x dx = \frac{w}{2}$$

$$\int_0^w x \sin^2 \frac{\pi}{w} x dx = \left(\frac{w^2}{4} - \frac{w\pi}{4w} \sin 2\pi - \frac{w^2}{8\pi^2} \cos 2\pi \right) - \left(\frac{0^2}{4} - \frac{0 \times \pi}{4w} \sin 2\frac{\pi}{w} x - \frac{w^2}{8\pi^2} \cos 0 \right)$$

$$= \left(\frac{w^2}{4} - \frac{w^2}{8\pi^2} \right) - \left(-\frac{w^2}{8\pi^2} \right) = \frac{w^2}{4}$$

Hence, the first order energy corrections are,

$$< \phi_1^0 \mid H' \mid \phi_1^0 > = < \phi_1^0 \mid \mathrm{V}_0 (1 - \frac{x}{w}) \mid \phi_1^0 >$$

$$= \frac{2}{w} \int_0^w dx V_0 (1 - \frac{x}{w}) \sin^2 \frac{\pi}{w} x = \frac{2V_0}{w} \int_0^w dx \sin^2 \frac{\pi}{w} x - \frac{2V_0}{w^2} \int_0^w x dx \sin^2 \frac{\pi}{w} x$$

$$= \frac{2V_0}{w} \times \frac{w}{2} - \frac{2V_0}{w^2} \left(\frac{w^2}{4} \right) = \frac{1}{2} V_0$$

Notice that the definite integral has nothing to do with the value of *n*. Hence, the first order correction is the same for all values of *n*. It is $\frac{1}{2} V_0$

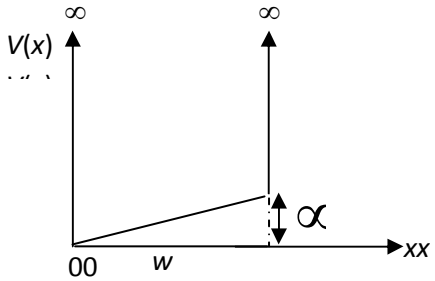
6.0 TUTOR-MARKED ASSIGNMENT

1. The Hamiltonian for anharmonic system in 1-dimensional oscillation is given by $H = \frac{p^2}{2m} + \frac{1}{2} kx^2 + bx^4$. Find the energy of this system up to the first order correction and obtain the total energy. (Assume that the ground state wave function of a simple harmonic oscillator is $\psi_0 = (\frac{k}{\pi\hbar\omega})^{\frac{1}{4}} e^{(-\frac{kx^2}{2\hbar\omega})}$,and $E_0 = \frac{\hbar\omega}{2}$) . Take $\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}$.

2. Consider a particle of mass μ and charge *e* in the central potential $V(r) = -\frac{e^2}{r}$, when $0 < r < R$ and $V(r) = -\frac{e^2}{r} e^{-\lambda(r-R)}$ when $R < r < \infty$. If the difference in potential is considered as a

perturbation, obtain the first order correction to the energy of the ground state.
(Assume that the ground state wave function of a simple harmonic oscillator is $\Psi_0 = (\pi a_0^3)^{-\frac{1}{2}} e^{(-\frac{r}{a_0})} = \Psi_0 * = \Psi_{100} *$ is the unperturbed ground state)

3. Calculate the energy of the first two states for an infinite square well potential of width *d* (Figure below).



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UNIT 2 SECOND ORDER PERTURBATION

CONTENTS

1.0 INTRODUCTION

In Unit 1, we took a look at the first order correction to a quantum-mechanical system with a very small perturbation. In this Unit, we shall be considering second-order corrections to the energy of the system. In addition to that, we consider the case of degeneracy, that is, a case where two different eigenfunctions have the same energy. In such a situation, the denominator of the expression for correcting the energy and the wavefunction becomes zero, meaning that the equations are no longer valid.

2.0 OBJECTIVES

At the end of this unit, you shouldbe able to:

- calculate second-order correction to the energy of a quantum-mechanical system with a very small perturbation
- split or separate degenerate energy levels.

3.0 MAIN CONTENT

3.1 Second Order Perturbation

We recall equation 1.11:

$$H^0|\psi_n^2>+H^1|\psi_n^1>=E_n^0|\psi_n^2>+E_n^1|\psi_n^1>+E_n^2|\psi_n^0>$$

Multiplying on the left by $<\psi_n^0|$,

$$<\psi_n^0|H^0|\psi_n^2>+<\psi_n^0|H^1|\psi_n^1>=E_n^0<\psi_n^0|\psi_n^2>+E_n^1<\psi_n^0|\psi_n^1>+E_n^2<\psi_n^0|\psi_n^0>$$

For the same reason as for the first order perturbation, the first term on the left is equal to the first term on the right. Also, the last term is E_n^2

since the basis vectors are orthonormal. The second term on the right is zero since we said that $|\psi_n^1>$ has no $|\psi_n^0>$ term.

Then,

$$E_n^2 = <\psi_n^0 | H^1 | \psi_n^1> \qquad 2.1$$

$$= \sum_{j\neq n} <\psi_n^0 | H^1 | \frac{<\psi_j^0 | H^1 | \psi_n^0>}{E_n^0 - E_j^0} | \psi_j^0> \qquad \text{[using eq. (1.20)]}$$

$$= \sum_{j\neq n} \frac{<\psi_j^0 | H^1 | \psi_n^0><\psi_n^0 | H^1 | \psi_j^0>}{E_n^0 - E_j^0}$$

$$= \sum_{j\neq n} \frac{|<\psi_j^0 | H^1 | \psi_n^0>|^2}{E_n^0 - E_j^0} \qquad 2.2$$

This is the **2nd order correction to the energy**.

Example 1

A charged particle is in simple harmonic motion such that $V(x) = \frac{1}{2} m\omega^2 x^2$, subjected to a constant electric field $H_1 = qEx$. With the aid of the raising and lowering operators, calculate the energy shift in the nth level to first and second order in qE.

Solution 1

$$a \equiv \sqrt{\frac{m\omega}{2\hbar}}\left(x + \frac{ip}{m\omega}\right), \; a^+ = \sqrt{\frac{m\omega}{2\hbar}}\left(x - \frac{ip}{m\omega}\right)$$

$$a + a^+ = 2x\sqrt{\frac{m\omega}{2\hbar}}$$

Hence,

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a + a^+)$$

Therefore,

$$H^1 = qEx = qE\sqrt{\frac{\hbar}{2m\omega}}(a + a^+)$$

To a first order,

$$E_1 = <\psi_n^0 | H^1 | \psi_n^0> = \sqrt{\frac{\hbar}{2m\omega}} <n | a + a^+ | n>$$

$$= \sqrt{\frac{\hbar}{2m\omega}}\left[<n | a | n> + <n | a^+ | n>\right]$$

$$= \sqrt{\frac{\hbar}{2m\omega}}\left[<n | \sqrt{n} | n-1> + <n | \sqrt{n+1} | n+1>\right]$$

$$= \sqrt{\frac{\hbar}{2m\omega}}\left[\sqrt{n} < n \mid n-1 > + \sqrt{n+1} < n \mid n+1 >\right]$$
$$= 0$$

To a second order (recall that $E_m^0 = m\hbar\omega$),

$$E_2 = \sum_{k \neq n} \frac{|< k \mid qEx \mid n >|^2}{\hbar\omega(n-k)} =$$

$$q^2E^2 \sum_{k \neq n} \frac{|< k \mid x \mid n >|^2}{\hbar\omega(n-k)} = \frac{q^2E^2}{\hbar\omega} \frac{\hbar}{2m\omega} \sum_{k \neq n} \frac{|< k \mid a + a^+ \mid n >|^2}{n-k}$$

Since only $k = n-1$ and $k = n+1$ contribute to the second order term,

$$\frac{q^2E^2}{\hbar\omega} \frac{\hbar}{2m\omega} \sum_{k \neq n} \frac{|< k \mid a + a^+ \mid n >|^2}{n-k}$$

$$= \frac{q^2E^2}{\hbar\omega} \frac{\hbar}{2m\omega} \left(\frac{|< n-1 \mid a + a^+ \mid n >|^2}{n-k} + \frac{|< n+1 \mid a + a^+ \mid n >|^2}{n-k} \right)$$

$$= \frac{q^2E^2}{\hbar\omega} \frac{\hbar}{2m\omega} \left(\frac{|< n-1 \mid a \mid n >|^2}{n-(n-1)} + \frac{|< n-1 \mid a^+ \mid n >|^2}{n-(n-1)} \right)$$

$$+ \frac{q^2E^2}{\hbar\omega} \frac{\hbar}{2m\omega} \left(\frac{|< n+1 \mid a \mid n >|^2}{n-(n+1)} + \frac{|< n+1 \mid a^+ \mid n >|^2}{n-(n+1)} \right)$$

$$= \frac{q^2E^2}{\hbar\omega} \frac{\hbar}{2m\omega} \left(\frac{|\sqrt{n}|^2 |< n-1 \mid n-1 >|^2}{1} + \frac{|\sqrt{n+1}|^2 |< n-1 \mid n+1 >|^2}{1} \right)$$

$$+ \frac{q^2E^2}{\hbar\omega} \frac{\hbar}{2m\omega} \left(\frac{|\sqrt{n}|^2 |< n+1 \mid n-1 >|^2}{-1} + \frac{|\sqrt{n+1}|^2 |< n+1 \mid n+1 >|^2}{-1} \right)$$

$$= \frac{q^2E^2}{\hbar\omega} \frac{\hbar}{2m\omega} \left(\frac{|\sqrt{n}|^2}{1} + 0 \right) + \frac{q^2E^2}{\hbar\omega} \frac{\hbar}{2m\omega} \left(0 + \frac{|\sqrt{n+1}|^2}{-1} \right)$$

$$= \frac{q^2E^2}{2m\omega^2} \left(|\sqrt{n}|^2 - |\sqrt{n+1}|^2 \right) = -\frac{q^2E^2}{2m\omega^2}$$

3.2 Degeneracy

We have assumed that the state energy E_n^k is distinct from those of other states. That is, $|\psi_n^k>$ is non-degenerate, otherwise, the denominator in equations 1.19, 1.20, 1.22 and 2.2 would vanish.

Suppose $|\psi_n^k>$ is m-degenerate, that is, there are m states, v_1, v_2, …, v_m with same energy, $m \geq 2$.

$$<v_r | v_s> = \delta_{rs}$$

2.3

That is, they are orthogonal but have same energy. We redefine the m states

$$\psi = \alpha_1 v_1 + \alpha_2 v_2 + ... + \alpha_m v_m$$

2.4

subject to

$$\sum_{r=1}^{m} | \alpha_r |^2 = 1$$

2.5

The simplest case, $m = 2$:

$$\psi^0 = \alpha v_1 + \beta v_2$$

2.6

$$|\alpha|^2 + |\beta|^2 = 1$$

2.7

Let $v_1 = u$ and $v_2 = v$. Then,

$$H = H_0 + H_1$$

2.8

$$H^0 | u> = E^0 | u>$$

2.9

$$H^0 | v> = E^0 | v>$$

2.10

$$< u | v >= 0 , \; < u | u >= 1 , \; < v | v >= 1$$

Let $| w > = \alpha | u > + \beta | v > = | \psi^0 >$

2.11

$$\begin{aligned} E_1 &= <\psi_0 | H_1 | \psi_0> \\ &= < w | H_1 | w > \\ &= < \alpha u + \beta v | H_1 | \alpha u + \beta v > \end{aligned}$$

Hence,

$$\begin{aligned} E_1(\alpha, \beta) = \; & \alpha^* \alpha < u | H_1 | u > \\ & + \alpha^* \beta < u | H_1 | v > \\ & + \beta^* \alpha < v | H_1 | u > \\ & + \beta^* \beta < v | H_1 | v > \end{aligned}$$

2.12

Let us represent the inner products above, respectively by M_{11}, M_{12}, M_{21}, M_{22}, with the matrix

$$M = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix}$$

2.13

Then, we can write

$$E_1(\alpha,\beta) = M_{11}\alpha^*\alpha + M_{12}\alpha^*\beta + M_{21}\beta^*\alpha + M_{22}\beta^*\beta \quad 2.14$$

Similarly, for $E_1(\alpha^*,\beta^*)$, $\alpha\alpha^* + \beta\beta^* = 1$, otherwise, α, β are arbitrary.

The eigenvalues of *M* are the first-order corrections to the energy. Different eigenvalues splits the energies, $E_0+\lambda_1, E_0+\lambda_2$, removing the degeneracy. The eigenvalues of the matrix equation 2.13 is obtained from

$$\begin{vmatrix} M_{11}-\lambda & M_{12} \\ M_{21} & M_{22}-\lambda \end{vmatrix} = 0 \quad 2.15$$

SELF-ASSESSMENT EXERCISE 1

Show that $\lambda_{\pm} = \dfrac{(M_{11}+M_{22}) \pm \sqrt{(M_{11}-M_{22})^2 + 4(M_{12})^2}}{2}$, M_{12} real, and

$$\lambda_{\pm} = \frac{(M_{11}+M_{22}) \pm \sqrt{(M_{11}-M_{22})^2 + 4|M_{12}|^2}}{2},\ M_{12} \text{ complex}$$

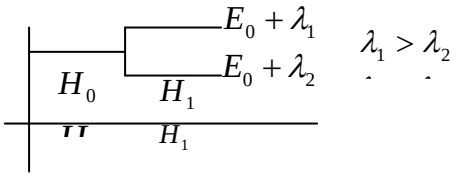

Fig. 12.1: The splitting of the degenerate energy levels by perturbation

If $\lambda_1 \neq \lambda_2$, then perturbation H_1 removes the degeneracy. If $\lambda_1 = \lambda_2$, then H_1 does not remove the degeneracy. One has to repeat the process by applying some perturbation in order to make distinct spectral lines. If there is still degeneracy, apply more perturbation until all the levels are distinct. Example: magnetic field applied to create distinction in spins.

SELF-ASSESSMENT EXERCISE 2

a. When is a quantum-mechanical state said to be degenerate?

b. The first excited state of the one-dimensional harmonic oscillator is found to be two-fold degenerate. The matrix associated with the perturbation of the oscillator is given as

$$\frac{1}{2\beta^2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

Find the two energy levels that result from the perturbation, given that the energy of the state is E_{10}.

4.0 CONCLUSION

In this Unit, you have learnt how to calculate the second-order correction to the energy of a quantum-mechanical system with a very small perturbation. You also learnt that applying perturbation lifts degeneracy, splitting up a line in the spectrum into distinct lines.

5.0 SUMMARY

In this Unit, you have learnt to:

- calculate the second-order correction to slightly perturbed system
- apply perturbation to remove degeneracy.

Answer to Self-Assessment Exercise 1

$$\begin{vmatrix} M_{11}-\lambda & M_{12} \\ M_{21} & M_{22}-\lambda \end{vmatrix} = 0$$

$$(M_{11}-\lambda)(M_{22}-\lambda)-M_{12}M_{21}=0$$

Expanding,

$$\lambda^2-(M_{11}+M_{12})\lambda+M_{11}M_{22}-M_{12}M_{21}=0$$

We solve this using the quadratic formula.

$$\lambda_{\pm}=\frac{(M_{11}+M_{22})\pm\sqrt{(M_{11}+M_{22})^2-4(\mathrm{M}_{11}M_{22}-M_{12}M_{21})}}{2}$$

$$=\frac{(M_{11}+M_{22})\pm\sqrt{M_{11}{}^2+M_{22}{}^2+2M_{11}M_{22}-4M_{11}M_{12}+4M_{12}M_{21}}}{2}$$

$$=\frac{(M_{11}+M_{22})\pm\sqrt{M_{11}{}^2+M_{22}{}^2-2M_{11}M_{22}+4M_{12}M_{21}}}{2}$$

$$=\frac{(M_{11}+M_{22})\pm\sqrt{(M_{11}-M_{22})^2+4M_{12}M_{21}}}{2}$$

Since $M_{21}=M_{12}^*, M_{12}M_{21}=|M_{12}|^2$, so we can write

$$\lambda_{\pm}=\frac{(M_{11}+M_{22})\pm\sqrt{(M_{11}-M_{22})^2+4|M_{12}|^2}}{2}$$

Answer to Self-Assessment Exercise 2

a. A quantum-mechanical system is said to be degenerate if different eigenstates correspond to the same energy.

b. The eigenvalue equation is

$$\begin{vmatrix} 0-\lambda & 2\beta^2 \\ 2\beta^2 & 0-\lambda \end{vmatrix} = 0$$

or

$$\lambda^2 - \left(\frac{1}{2\beta^2}\right)^2 = 0$$

Therefore,

$$\lambda = \pm\frac{1}{2\beta^2}$$

The two energy levels are $E_{10} + \frac{\lambda}{2\beta^2}$ and $E_{10} - \frac{\lambda}{2\beta^2}$

Summary of Study Session 12

In this study session, you have learnt how to:

- calculate the second order correction to a Hamiltonian subjected to a small perturbation.
- apply perturbation in order to remove degeneracy, making a single spectral line to split into distinct spectral lines.

6.0 TUTOR-MARKED ASSIGNMENT

1. The first energy correction term in the 2-degenerate perturbation of a Hamiltonian $H^{(0)}$ by a Hamiltonian $H^{(1)}$ ($H^{(1)} << H^{(0)}$) is $3\alpha * \alpha - 2\beta * \beta - \beta * \alpha + 2\alpha * \beta$, where $\psi = \alpha \mathbf{u} + \beta \mathbf{v}$ is the redefinition of the 2 states, subject to $\alpha^2 + \beta^2 = 1$. Show that $H^{(1)}$ removes the degeneracy.

2. A charged particle of mass *m* and charge *q* is sitting in a harmonic potential $V_0 = \frac{1}{2}m\omega^2 x^2$. A weak constant electric field *E* is applied in the z-direction, so that the potential is perturbed by $V_1 = -qEx$.
   (a) Show that there is no change in the energy levels to first order in *E*.
   (b) Calculate the second-order change in the energy levels.
   (c) Solve this problem exactly, by changing variables to $x' = x - \frac{q\varepsilon}{m\omega^2}$

3. Consider the Hamiltonian $H = E_0\begin{pmatrix} 1-\varepsilon & 0 & 0 \\ 0 & 1 & -\varepsilon \\ 0 & -\varepsilon & 0 \end{pmatrix}$, such that $|\varepsilon| << 1$ and E_0 is a constant.

a. Find the eigenvalues and the eigenvectors of the unperturbed $\varepsilon = 0$.
b. Find the eigenvalues and the eigenvectors of the Hamiltonian H and expand each to a second order in ε.
c. Find the approximate eigenvalue for the eigenvector corresponding to the non-degenerate eigenvector of the unperturbed Hamiltonian.
d. Find the first-order correction to the degenerate eigenvalues using the degenerate perturbation theory. Comment on your results.

7.0 REFERENCES/FURTHER READING

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UNIT 3 QUANTUM SCATTERING I

CONTENTS

1.0 INTRODUCTION

The basic idea behind scattering in classical mechanics is that a beam of particles of definite momentum are scattered from a target. In Quantum Mechanics, the incident particle as well as the scattering source istreated as waves, in line with the nature of the theory that matter behaves as a wave. Examples include a plane wave incident on a localised potential, or an alpha particle impinging on a nucleus. A flux of particles is incident on the target, scattered by the target and collected by detectors that measure the angle of deflection. The time-dependent Schroedinger equation should be solved to find the probability amplitudes for the scattered waves. However, if steady state conditions apply, it suffices to solve the time-independent Schroedinger equation.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- distinguish between quantum scattering and scattering in classical physics
- find an expression for the quantum scattering differential cross section.

3.1 Quantum Scattering

We start our analysis by considering a Hamiltonian of the form,

$$H = H_0 + H_1 \qquad 3.1$$

where H_0 is the Hamiltonian of a free particle of mass *m*,

$$H_0 = \frac{p^2}{2m}$$

3.2

H_1 is due to a source of scattering.

Assuming $|\phi>$ is an eigenstate of H_0, we can write,

$$H_0|\phi> = E|\phi>$$

3.3

If the eigenstate of the system described by *H* (scattering of the particle) is written as $|\psi>$, then, we can write the Schroedinger equation as,

$$H|\psi> = (H_0 + H_1)|\psi> = E|\psi>$$

3.4

Then, we can write

$$|\psi> = |\phi> + \frac{1}{E - H_0} H_1 |\psi>$$

3.5

We notice that $|\psi> \to |\phi>$ as $H_1 \to 0$.

The operator $\frac{1}{E - H_0}$ is singular when H_0 corresponds to E.

To take care of the singularity, we make *E* a little bit complex, by making the transformation $E - H_0 \to E - H_0 \pm i\varepsilon$. Hence, we arrive at the Lipmann-Schwinger equation:

$$|\psi^{\pm}> = |\phi> + \frac{1}{E - H_0 \pm i\varepsilon} H_1 |\psi^{\pm}>$$

3.6

where ε is a small positive real number.

We can convert equation 3.6 into an integral equation. To achieve this, let us multiply equation 3.6 on the left by $<\mathbf{r}|$. Then,

$$<\mathbf{r}|\psi^{\pm}> = <\mathbf{r}|\phi> + <\mathbf{r}|\frac{1}{E - H_0 \pm i\varepsilon} H_1 |\psi^{\pm}>$$

The left hand side is the projection of the wavefunction $|\psi^{\pm}>$ in the direction of the vector **r**. Recall that $<\mathbf{a}|\mathbf{b}> = ab\cos\theta = a(b\cos\theta)$ can be seen as the component of **b** in the direction of **a**, multiplied by the magnitude of **a**. Hence, $<\mathbf{r}|\psi^{\pm}> = \psi^{\pm}(\mathbf{r})>$ and $<\mathbf{r}|\varphi> = \phi(\mathbf{r})$. We insert the completeness relation in three dimensions (refer to equation 4.10, Module 1, Unit 4, the relation for 1-dimension) $\int d^3r' |\mathbf{r}'><\mathbf{r}'| = 1$. The resulting expression is an integral equation,

$$\psi^{\pm}(\mathbf{r}) = \phi(\mathbf{r}) + \int < \mathbf{r} \left| \frac{1}{E - H_0 \pm i\varepsilon} \right| \mathbf{r}' >< \mathbf{r}' | H_1 | \psi^{\pm} > d^3\mathbf{r}'$$

3.7

The integrand has two matrix elements and the wavefunction itself.

We can write the Schroedinger equation (scattering) as,

$$(\nabla^2 + k^2)\psi(\mathbf{r}) = \frac{2m}{\hbar^2} < \mathbf{r} | H_1 | \psi >$$

3.8

This is the inhomogeneous Helmholtz's equation, which can be inverted to,

$$\psi(\mathbf{r}) = \phi(\mathbf{r}) + \frac{2m}{\hbar^2} \int G(\mathbf{r}, \mathbf{r}') < \mathbf{r}' | H_1 | \psi > d^3\mathbf{r}'$$

3.9

with $(\nabla^2 + k^2)G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$. $G(\mathbf{r}, \mathbf{r}')$ is the Green's function.

For the Helmholtz problem, the Green's function is,

$$G(\mathbf{r}, \mathbf{r}') = -\frac{\exp(\pm ik|\mathbf{r} - \mathbf{r}'|)}{4\pi|\mathbf{r} - \mathbf{r}'|}$$

3.10

Inserting equation ( ) into equation 3.9,

$$\psi^{\pm}(\mathbf{r}) = \phi(\mathbf{r}) - \frac{2m}{\hbar^2} \int \frac{\exp(\pm ik|\mathbf{r} - \mathbf{r}'|)}{4\pi|\mathbf{r} - \mathbf{r}'|} < \mathbf{r}' | H_1 | \psi > d^3\mathbf{r}'$$

3.11

Comparing equations 3.7 and 3.11,

$$\left\langle \mathbf{r} \left| \frac{1}{E - H_0 \pm i\varepsilon} \right| \mathbf{r}' \right\rangle = -\frac{2m}{\hbar^2} \frac{\exp(\pm ik|\mathbf{r} - \mathbf{r}'|}{4\pi|\mathbf{r} - \mathbf{r}'|}$$

3.12

In the case where H_1 is a function of the position operators,

$$< \mathbf{r}' | H_1 | \mathbf{r} >= V(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$$

3.13

($V = V(\mathbf{r})$ implies a central potential)

Again, making use of the completeness relation $\int d^3r'' | \mathbf{r}'' >< \mathbf{r}'' | = 1$,

$$< \mathbf{r}' | H_1 | \psi^{\pm} >= \int < \mathbf{r}' | H_1 | \mathbf{r}'' >< \mathbf{r}'' | \psi^{\pm} > d^3\mathbf{r}$$

3.14

Then, equation 13.11 becomes,

$$\psi^{\pm}(\mathbf{r}) = \phi(\mathbf{r}) - \frac{2m}{\hbar^2} \int \frac{\exp(\pm ik|\mathbf{r} - \mathbf{r}'|}{4\pi|\mathbf{r} - \mathbf{r}'|} V(\mathbf{r}')\psi^{\pm}(\mathbf{r}')d^3\mathbf{r}'$$

3.15

Let the $|\phi>$ be a plane wave of wave (representing a free particle) vector **k**, then, the ket representing this state is $|\mathbf{k}>$, such that,

$$\psi_k(\mathbf{r}) = <\mathbf{r}|\mathbf{k}> = \frac{\exp(i\mathbf{k}\cdot\mathbf{r})}{(2\pi)^{3/2}}$$

3.16

where the normalisation is possible by taking the free particle in three dimensions to be a three-dimensional wave packet (understandably so in quantum mechanics). The normalisation constant is $(2\pi)^{3/2}$.

Hence,

$$<\mathbf{k}|\mathbf{k}'> = \int <\mathbf{k}|\mathbf{r}><\mathbf{r}|\mathbf{k}'> d^3\mathbf{r} = (2\pi)^{-3}\int \exp(-i\mathbf{r}\cdot[\mathbf{k}-\mathbf{k}'])d^3\mathbf{r}$$

$$= \delta(\mathbf{k}-\mathbf{k}')$$

3.17

$$(\mathbf{r}-\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}') = \mathbf{r}\cdot\mathbf{r} - 2\mathbf{r}\cdot\mathbf{r}' + \mathbf{r}'\cdot\mathbf{r}'$$

$$= r^2 - 2\mathbf{r}\cdot\mathbf{r}' + 2r'^2$$

$$(\mathbf{r}-\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}') = r^2\left(1 - 2\frac{\mathbf{r}}{r^2}\cdot\mathbf{r}' + \left[\frac{r'}{r}\right]^2\right) \approx r^2\left(1 - 2\frac{\mathbf{r}}{r^2}\cdot\mathbf{r}'\right) \qquad r >> r'$$

The approximation holds because the square of the ratio *r'*/*r* tends to zero.

$$|\mathbf{r}-\mathbf{r}'| = [(\mathbf{r}-\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}')]^{1/2} \approx r\left(1 - 2\frac{\mathbf{r}}{r^2}\cdot\mathbf{r}'\right)^{1/2} \approx r\left(1 - \frac{\mathbf{r}}{r^2}\cdot\mathbf{r}'\right) = r - \frac{\mathbf{r}}{r}\cdot\mathbf{r}'$$

Thus, for $r >> r'$, i.e., at a point far away from the scattering region, to a first order approximation,

$$|\mathbf{r}-\mathbf{r}'| \approx r - \frac{\mathbf{r}}{|\mathbf{r}|}\cdot\mathbf{r}'$$

3.18

If we define $\mathbf{k}'$ such that the particles whose motion is defined by this vector have the same energy as the incoming particle, propagating from the scattering region to the point of observation.

$$\mathbf{k}' = k\mathbf{r}/r$$

where **r**/*r* is a unit vector in the direction of **r**, that is, directed from the scattering region to the observation point.

With the approximation, in equation (3.15),

$$\exp(\pm ik|\mathbf{r}-\mathbf{r}'|) \approx \exp(\pm ik(r - \mathbf{r}\cdot\mathbf{r}'/r)) = \exp(\pm ikr - (\pm)\,\mathrm{i}\,k\mathbf{r}\cdot\mathbf{r}'/r))$$

$$= \exp(\pm ikr \mp i\mathbf{k}'\cdot\mathbf{r}')) = \exp(\pm ikr)\exp(\mp i\mathbf{k}'\cdot\mathbf{r}')$$

With

$$\exp(\pm ik|\mathbf{r}-\mathbf{r}'|) \approx \exp(\pm ikr)\exp(\mp i\mathbf{k}'\cdot\mathbf{r}')$$

3.19

Equation 3.15 in the limit $r >> r'$ becomes,

$$\psi^{\pm}(\mathbf{r}) = \frac{\exp(i\mathbf{k}\cdot\mathbf{r})}{(2\pi)^{3/2}} - \frac{m}{2\pi\hbar^2}\frac{\exp(\pm ikr)}{r}\int \exp(\mp i\mathbf{k}'\cdot\mathbf{r}')V(\mathbf{r}')\psi^{\pm}(\mathbf{r}')d^3\mathbf{r}' \quad 3.20$$

The first term is the incident wave, and the second a spherical wave with the source the scattering region. ψ^{+} is the wave propagating away from the scattering region. ψ^{-} propagates towards the scattering region and is therefore, not physically realisable. We conclude, therefore, that, far from the scattering region,

$$\psi(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}}\left[\exp(i\mathbf{k}\cdot\mathbf{r}) + \frac{\exp(ikr)}{r} f(\mathbf{k}',\mathbf{k})\right] \quad 3.21$$

with

$$f(\mathbf{k}',\mathbf{k}) = -\frac{(2\pi)^2 m}{\hbar^2}\int \frac{\exp(-i\mathbf{k}'\cdot\mathbf{r}')}{(2\pi)^{3/2}}V(\mathbf{r}')\psi(\mathbf{r}')d^3\mathbf{r}'$$

$$= -\frac{(2\pi)^2 m}{\hbar^2} < \mathbf{k}'|\, H_1 \,|\psi > \quad 3.22$$

The **differential cross-section**, $d\sigma/d\Omega$, is the fraction of the number of incident particles to the number scattered into an element of solid angle $d\Omega$.

The **total cross-section**, σ, corresponds to scatterings through any scattering angle, $\sigma = \int \frac{d\sigma}{d\Omega} d\Omega$, where differential cross-section = $d\sigma/d\Omega$.

The particle flux associated with ψ is,

$$\mathbf{j} = \frac{\hbar}{m}\mathrm{Im}(\psi^* \nabla \psi)$$

For the incident wavefunction,

$$\psi_i = \frac{\exp(i\mathbf{k}\cdot\mathbf{r})}{(2\pi)^{3/2}}$$

and $\mathbf{j}_{inc} = \frac{\hbar}{m}\mathrm{Im}\left(\frac{\exp(-i\mathbf{k}\cdot\mathbf{r})}{(2\pi)^{3/2}}\nabla\left(\frac{\exp(i\mathbf{k}\cdot\mathbf{r})}{(2\pi)^{3/2}}\right)\right)$

$$= \mathrm{Im}\left(\frac{\exp(-i\mathbf{k}\cdot\mathbf{r})}{(2\pi)^3} i\mathbf{k}\exp(i\mathbf{k}\cdot\mathbf{r})\right) = \mathrm{Im}\left(\frac{\hbar\, i}{(2\pi)^3}\mathbf{k}\right) = \frac{\hbar}{(2\pi)^3}\mathbf{k}$$

Similarly, for the scattered wavefunction,

$$\psi_{scat} = \frac{\exp(ikr)}{(2\pi)^{3/2}} \frac{f(\mathbf{k}', \mathbf{k})}{r}$$

and

$$\mathbf{j}_{scat} = \frac{\hbar}{(2\pi)^3} \frac{f(\mathbf{k}', \mathbf{k})}{r^3} k\mathbf{r}$$

$$\frac{d\sigma}{d\Omega} d\Omega = r^2 d\Omega \frac{|\mathbf{j}_{scat}|}{|\mathbf{j}_{inc}|}$$

Thus, the differential cross section is,

$$\frac{d\sigma}{d\Omega} = \frac{r^2 \frac{|f(\mathbf{k}', \mathbf{k})|}{r^2} k}{k} = |f(\mathbf{k}', \mathbf{k})|$$

4.0 CONCLUSION

In this Unit, you learnt the theory of quantum scattering. In this case, the incident particle as well as the scattering source istreated as waves. You were able to identify the differential cross-section, which is the fraction of the number of incident particles to the number scattered into an element of solid angle as well as the total cross-section, corresponding to scatterings through any scattering angle.

5.0 SUMMARY

In this unit, you have learnt how to:

- find an expression for the scattered wave function due to a given incident wave function.
- find the expressions for the differential cross-section and the total cross-section corresponds to scatterings through any scattering angle.

SELF-ASSESSMENT EXERCISE 1

How is the completeness relation in Module 1, Unit 4 related to the one you encountered in this unit?

Answer to Self-Assessment Exercise 1

The summation in the expression in Module 1, Unit 4 becomes an integral in this Unit as we are dealing with a continuous function, very much as inner product for continuous functions is an integral.

6.0 TUTOR-MARKED ASSIGNMENT

1. In the theory of quantum scattering, what do you understand about differential cross-section and total cross section?
2. Why is it that you cannot normalise a free particle?
3. The operator $\frac{1}{E-H_0}$ is singular when H_0 corresponds to E. How do you take care of the singularity?
4. Define the terms (a) differential cross-section (b) total cross-section.
5. Find an expression for the differential scattering cross-section in the scattering of particles by a central potential $V(r)$.

7.0 REFERENCES/FURTHER READING

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UNIT 4 SCATTERING II - THE BORN APPROXIMATION

CONTENTS

1.0 INTRODUCTION

In Born approximation, instead of taking the total field as the incident field, we take the incident field. This approximation then works when the scattered field is small compared to the incident field in the scatterer. In other words, the scattering is weak, and hence, the total wavefunction is not substantially different from the incident wavefront. In addition, the outgoing flux is observed sufficiently far away from the scatterer.

2.0 OBJECTIVES

At the end of this Unit, you will be able to:

- state the assumptions of the Born approximation
- find the differential cross section for a given scattering potential in the Born approximation.

3.0 MAIN CONTENT

3.1 The Born Approximation

You must have noticed that $f(\mathbf{k}',\mathbf{k})$, (equation 3.22), depends on the wavefunction $\psi(\mathbf{r})$, which is not yet determined. However, if the scattering is weak, we may take the total wavefunction $\psi(\mathbf{r})$as being almost the same as the incident wavefunction, that is,

$$\psi(\mathbf{r}) \approx \phi(\mathbf{r}) = \frac{\exp(i\mathbf{k}\cdot\mathbf{r})}{(2\pi)^{3/2}}$$

4.1

or

$$\psi(\mathbf{r}') \approx \frac{\exp(i\mathbf{k}\cdot\mathbf{r}')}{(2\pi)^{3/2}}$$

4.2

In the large r limit, we recall equation ( )

$$\psi(\mathbf{r}) = \phi(\mathbf{r}) - \frac{m}{2\pi\hbar^2}\frac{\exp(ikr)}{r}\int \exp(-i\mathbf{k}'\cdot\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}')d^3\mathbf{r}'$$

which becomes

$$\psi(\mathbf{r}) = \frac{\exp(i\mathbf{k}\cdot\mathbf{r})}{(2\pi)^{3/2}} - \frac{m}{2\pi\hbar^2}\frac{\exp(ikr)}{r}\int \exp(-i\mathbf{k}'\cdot\mathbf{r}')V(\mathbf{r}')\frac{\exp(i\mathbf{k}\cdot\mathbf{r}')}{(2\pi)^{3/2}}d^3\mathbf{r}'$$

4.3

and

$$f(\mathbf{k}',\mathbf{k}) = -\frac{(2\pi)^2 m}{\hbar^2}\int \frac{\exp(-i\mathbf{k}'\cdot\mathbf{r}')}{(2\pi)^{3/2}}V(\mathbf{r}')\frac{\exp(i\mathbf{k}\cdot\mathbf{r}')}{(2\pi)^{3/2}}d^3\mathbf{r}'$$

$$\approx -\frac{m}{2\pi\hbar}\int \exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}']V(\mathbf{r}')d^3\mathbf{r}'$$

4.4

Observe that this is the Fourier transform of the scattering potential $V(\mathbf{r})$ with respect to the wave vector $\mathbf{k}-\mathbf{k}'$.

Let this wave vector be $\mathbf{k}''$.

For a spherically symmetric potential,

$$f(\mathbf{k}',\mathbf{k}) \approx -\frac{m}{2\pi\hbar^2}\int_0^\infty\int_0^\pi\int_0^{2\pi}\exp[ik''r'\cos\theta']V(\mathbf{r}')r'^2\sin\theta' dr' d\theta' d\phi''$$

$$= -\frac{2\pi m}{2\pi\hbar^2}\int_0^\infty\int_0^\pi\left[\exp[ik''r'\cos\theta']r'\sin\theta\, d\theta\right]V(\mathbf{r}')r'^2\, dr'$$

having integrated over ϕ', with $r^2\sin\theta dr d\theta d\phi$ being the volume element in spherical-polar coordinates.

If $f(\theta) = \exp(ik''r'\cos\theta')$, $f'(\theta) = -ik''r'\sin\theta\exp(ik''r'\cos\theta')$

$$f(\mathbf{k}',\mathbf{k}) = \frac{m}{\hbar^2}\frac{1}{ik''}\int_0^\infty\int_0^\pi\left[\exp[ik''r'\cos\theta']ik''r'\sin\theta\, d\theta\right]V(\mathbf{r}')r'\, dr'$$

$$= -\frac{m}{\hbar^2}\frac{1}{ik''}\int_0^\infty\int_0^\pi\left[\exp[ik''r'\cos\theta'](-ik''r'\sin\theta\, d\theta)\right]V(\mathbf{r}')r'\, dr'$$

$$f(\mathbf{k}',\mathbf{k}) = -\frac{m}{\hbar^2}\frac{1}{ik''}\int_0^\infty\left[\exp[ik''r'\cos\theta']\right]_0^\pi\int_0^\pi V(\mathbf{r}')r'\, dr'$$

$$f(\mathbf{k}',\mathbf{k}) = -\frac{m}{\hbar^2}\frac{1}{ik''}\int_0^\infty\left[\exp[-ik''r'\cos\pi - \exp[-ik''r'\cos 0]\right]V(\mathbf{r}')r'\, dr'$$

$$= -\frac{m}{\hbar^2}\frac{1}{ik''}\int_0^\infty [\exp[ik''r' - \exp[-ik''r']]V(\mathbf{r}')r'dr'$$

$$= -\frac{m}{\hbar^2}\frac{2i}{ik''}\int_0^\infty \sin(k''r')V(\mathbf{r}')r'dr'$$

$$= -\frac{2m}{\hbar^2 k''}\int_0^\infty \sin(k''r')V(\mathbf{r}')r'dr'$$

But $k'' = |\mathbf{k}''| = |\mathbf{k} - \mathbf{k}'|$

$k = k'$ since the energy is conserved. When two vectors of equal length are added, the sum is equal to $2k\cos(\theta/2)$. Their difference is $2k\sin(\theta/2)$.

Therefore,

$$k'' = 2k\sin(\theta/2)$$

This is referred to as the **momentum transfer**, which is the amount of momentum one particle gives to another.

Example 1

Find the differential cross section for the Yukawa potential $V(r) = \frac{V_0 \exp(-\mu r)}{\mu r}$.

Solution 1

$$f(\theta) = -\frac{2m}{\hbar^2 k''}\int_0^\infty \sin(k''r')V(\mathbf{r}')r'dr'$$

$$= -\frac{2mV_0}{\hbar^2 k''\mu}\int_0^\infty \exp(-\mu r')\sin(k''r')\,dr'$$

$$= -\frac{2mV_0}{\hbar^2 k''\mu}\int_0^\infty \exp(-\mu r')\frac{1}{2i}[\exp(ik''r') - \exp(-ik''r')]r'dr'$$

$$= -\frac{2mV_0}{2i\hbar^2 k''\mu}\int_0^\infty \exp(-\mu r')[\exp(ik''r') - \exp(-ik''r')]r'dr'$$

$$= -\frac{mV_0}{i\hbar^2 k''\mu}\left[\frac{\exp[(-\mu + ik'')r']}{-\mu + ik''} - \frac{\exp[(-\mu - ik'')r']}{-\mu - ik''}\right]_0^\infty$$

$$= -\frac{mV_0}{i\hbar^2 k''\mu}\left[\frac{-1}{-\mu + ik''} - \frac{-1}{-\mu - ik''}\right]_0^\infty$$

$$= \frac{mV_0}{i\hbar^2 k''\mu}\left[\frac{1}{-\mu + ik''} - \frac{1}{-\mu - ik''}\right]_0^\infty = \frac{mV_0}{i\hbar^2 k''\mu}\left[\frac{-\mu - ik'' + \mu - ik''}{k''^2 + \mu^2}\right]$$

$$= \frac{mV_0}{i\hbar^2 k''\mu}\left[\frac{-2ik''}{k''^2 + \mu^2}\right]$$

$$= -\frac{2mV_0}{\hbar^2 \mu}\left[\frac{1}{k''^2 + \mu^2}\right]$$

Therefore,

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 = \left(\frac{2mV_0}{\hbar^2\mu}\right)^2\left[\frac{1}{k''^2+\mu^2}\right]^2$$

$$= \left(\frac{2mV_0}{\hbar^2\mu}\right)^2 \frac{1}{[4k^2\sin^2(\theta/2)+\mu^2]^2}$$

4.0 CONCLUSION

In this unit, you have learnt the condition under which the Born approximation holds, that is, if the scattering is weak, we may take the total wavefunction $\psi(\mathbf{r})$ as being almost the same as the incident wavefunction You have also learnt how to find the expression for the differential cross-section for a given potential.

5.0 SUMMARY

In this Unit, you have learnt the following:

- in what limit the Born approximation is valid
- how to find the differential cross section for a given potential

SELF-ASSESSMENT EXERCISE 1

Find the differential cross-section for the Coulomb Potential.

Solution of Self-Assessment Exercise 1

If we allow the $\mu \to 0$, but such that $\frac{V_0}{\mu} \to \frac{Q_1Q_2}{4\pi\varepsilon_0}$ then, the Yukawa potential $V(r) = \frac{V_0\exp(-\mu r)}{\mu r}$ becomes $V(r) = -\frac{Q_1Q_2}{4\pi\varepsilon_0 r}$ which is the Coulomb potential. Then, the Bohr differential cross-section is

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 \approx \left(\frac{2mQ_1Q_2}{4\pi\varepsilon_0\hbar^2}\right)^2 \frac{1}{16k^4\sin^4(\theta/2)}$$

6.0 TUTOR-MARKED ASSIGNMENT

1. Define the term momentum transfer.
2. What are the assumptions made in the derivation of the Born Approximation?

3. A spherically-symmetric potential takes the constant value V_0 for $0 < r < a$, and zero elsewhere. Find the differential cross section for this potential in the Born Approximation.

4. Using the Born approximation approach for the potential, $V(r) = \frac{2V_0 e^{ar}}{r}$,

   a. Write down the expression for the scattering amplitude and show that

   $$f(\theta) = -\frac{4mV_0}{\hbar^2(a^2 + q^2)}$$

   (Hint: note that the standard integral $\int_0^\infty e^{ar} \sin qr dr = \frac{q}{a^2 + q^2}$ and $q = 2k\sin(\theta/2)$)

   b. Establish that the total cross-section $\sigma_{tot} = \frac{32\pi m^2 V_0^2}{a^2\hbar^4(a^2 + 4k^2)}$

5. With the aid of the Born Approximation, find the scattering amplitude $f(\theta)$ for the truncated Coulomb potential, $V(r) = C\left(\frac{1}{a} - \frac{1}{r}\right)$; $r < a$ and $V(r) = 0$ for $r \geq a$. Find an expression for the scattering amplitude at very small values of θ and hence, deduce the approximate value of $\sin\frac{\theta}{2}$ at which the differential cross-section has fallen to one-third of its forward value. Take $f(\theta) = -\frac{2m}{\hbar^2 q}\int_0^\infty r\sin(qr)V(r)dr$.

7.0 REFERENCES/FURTHER READING

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UNIT 5 SCATTERING III - PARTIAL WAVE ANALYSIS

CONTENTS

1.0 INTRODUCTION

In Quantum Mechanics, every physically observable is associated with a Hermitian operator. The physically observable properties include position, time, energy, angular momentum, etc. Quite unlike the case with Classical Mechanics, not all physically observable properties of a quantum-mechanical system can be measured precisely simultaneously. This is due to the Heisenberg uncertainty principle. If any two observable physical properties can be measured simultaneously with infinite accuracy, then their operators must commute. Indeed, you will get to know that the two such observables can have the same eigenvectors. In this unit, you will also learn how to find the matrix elements of an operator in a given quantum-mechanical state. Thus, you will be able to calculate the expectation value of the physically observable property in such a state. In addition, you will learn about outer product of two vectors as well as the projection operator.

In Born approximation we assume the scattering is weak, and hence, the total wavefunction does not substantially differ from the incident wavefront. Put another way, the outgoing flux is sufficiently far away from the scatterer. As such, instead of the exact wavefunction, the Schroedinger equation is solved by a Green's function approach, excluding the possibility of double or multiple scattering. In partial wave analysis, we obtain the cross section without imposing any limitation on the strength of the scattering. We shall assume that the potential is spherically symmetric, ensuring the conservation of the angular momentum of the incident particle. The angular momentum of the incoming particle is the same before and after scattering. The problem is essentially that of a central potential, and the spherical harmonics come in useful once again.

2.0 OBJECTIVES

At the end of this unit, you shouldbe able to:

- write the partial wave amplitudes for a given scattering problem
- calculate the scattering amplitude for a given scattering problem
- obtain the differential cross-section for a given scattering problem
- find the total cross-section for a given scattering process
- write the partial-wave amplitudes in terms of the phase-shifts
- calculate the phase shift for a given scatterer.

3.0 MAIN CONTENT

3.1 Partial Wave Analysis

Spherical harmonics are of the form, $Y_l^m(\theta)$. We recall that the solution of the Schroedinger equation in spherical-polar coordinates, $\psi(r,\theta,\phi)$ is,

$$\psi(r,\theta,\phi) = R(r)Y_l^m(\theta,\phi)$$

We have seen that,

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]U(r) = EU(r)$$

As we often do in Quantum Mechanics, we first consider *r* very large. Then, $V(r) \to 0$ in this limit, and,

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}U(r) \approx EU(r) \qquad 5.1$$

or,

$$\frac{d^2}{dr^2}U(r) \approx \frac{2m}{\hbar^2}EU(r) = k^2U(r) \qquad 5.2$$

where $k = \sqrt{2mE/\hbar^2}$.

Therefore,

$$U(r) = Ce^{ikr} + De^{-ikr} \qquad 5.3$$

We set *D* equal to zero as the second term on the right represents an incoming spherical wave. Therefore,

$$U(r) \sim \frac{e^{ikr}}{r}$$

5.4

an outgoing spherical wave.

Let us now consider the intermediate region in which $1/r^2$ is important, but $V(r)$ is still effectively zero.

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} \right] U(r) = EU(r)$$

5.5

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} \right] U(r) = -\frac{2mE}{\hbar^2} U(r) = -k^2 U(r)$$

5.6

This equation can easily be transformed to:

$$r^2 \frac{d^2R}{dr^2} + 2r\frac{dR}{dr} + [k^2r^2 - l(l+1)]R = 0$$

5.7

The solution of this equation is of the form,

$$U(r) = Arj(kr) + Br\eta_l(kr)$$

5.8

where j_l and η_l are the spherical Bessel functions, generalized sine and cosine functions:

$$j_l(x) = x^l \left(-\frac{1}{x}\frac{d}{dx} \right)^l \frac{\sin x}{x};\ \eta_l(x) = -x^l \left(-\frac{1}{x}\frac{d}{dx} \right)^l \frac{\cos x}{x}$$

5.9

In the limit $x \to 0$, $j_l(x)$ exists, as the limit $\frac{\sin x}{x}$ exists, but $\eta_l(x)$ becomes inadmissible.

In the limit $x \to \infty$,

$$j_l(x) \to \frac{\sin(x - l\pi/2)}{x}$$

5.10

$$\eta_l(x) = \frac{\cos(x - l\pi/2)}{x}$$

5.11

We can also write,

$$h_l^{(1)}(x) = j_l(x) + i\eta_l(x)$$

5.12

and

$$h_l^{(2)}(x) = j_l(x) - i\eta_l(x)$$

5.13

which are the spherical Hankel functions. Respectively, they represent outgoing and incoming wave; generalized e^{ikr} and e^{-ikr} waves. Yet again, we drop the incoming wave and therefore conclude that,

$$\psi(r,\theta,\phi) = A\left[e^{ikz} + \sum_{lm} c_{lm} h_l^{(1)}(kr) Y_l^m(\theta,\phi) \right]$$

5.14

If we align the incident ray with the *z*-axis, $e^{i\mathbf{k}\cdot\mathbf{r}} = e^{ikz}$ is the incoming wave.

In the case where $V(\mathbf{r}) = V(r)$, that is, the spherically symmetric case, the dependence on ϕ becomes trivial (recall that the ϕ part of $Y_l^m(\theta,\phi)$ involves *m* ($\Phi(\phi) \sim e^{im\phi}$), and

$$\psi(r,\theta) = A\left[e^{ikz} + k\sum_{l=0}^{\infty} a^l\, i^{(l+1)} (2l+1) h_l^{(1)}(kr) P_l(\cos\theta) \right]$$

5.15

In this case, *m* = 0, and $Y_l^{m=0}(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta)$, and we have set $c_{l0} = i^{(l+1)} k\sqrt{4\pi(2l+1)}\, a_l$

Hence, since $h_l^{(1)}$ is a function of r,

$$f(\theta) = \sum_{l=0}^{\infty} (2l+1) a_l P_l(\cos\theta)$$

5.16

Then we only need to calculate the a_l's.

If we also write the incoming wavefunction as,

$$e^{ikz} = \sum_{l=0}^{\infty} i^l (2l+1)\, j_l(kr) P_l(\cos\theta)$$

5.17

Equation 5.15 becomes,

$$\psi(r,\theta) = A\sum_{l=0}^{\infty} i^l (2l+1)\left\{ j_l(kr) + ika_l h_l^{(1)}(kr) \right\} P_l(\cos\theta)$$

5.18

There is no need to include η_l in the expansion for the incoming wavefunction as it tends to infinity as r tends to zero.

a_l, the complex parameter is needed in the partial wave method. In one-dimension, when there is a reflection at an infinite potential, the incident wave suffers a phase shift as it is reflected, so that if the incident wave ~ e^{ikx} then the reflected wave ~ $e^{i(2\delta - kx)}$, where the factor 2 in the phase shift is out of convention.

In the case of three-dimensional scattering, and where the potential is spherically symmetric, the change due to scattering is a phase shift of δ_l .

The *l*-component is

$$\psi = Ai^l(2l+1)j_l(kr)P_l(\cos\theta) \qquad 5.20$$

For large x ,

$$j_l(x) = \frac{1}{2x}\left[(-i)^{l+1}e^{ix} + i^{l+1}e^{-ix})\right] \qquad 5.21$$

and

$$\psi = A\frac{2l+1}{2ikr}\left[e^{ikr} - (-1)^l e^{-ikr}\right]P_l(\cos\theta) \qquad 5.22$$

$$a_l = \frac{1}{k}e^{i\delta_l}\sin\delta_l = \frac{1}{k}e^{i\delta_l}\frac{e^{i\delta_l} - e^{i\delta_l}}{2i} = \frac{e^{2i\delta_l} - 1}{2ik} = \frac{S_l(k) - 1}{2ik}$$

where

$$S_l(k) = e^{2i\delta_l} \qquad 5.23$$

and

$$f(\theta) = \sum_{l=0}^{\infty}(2l+1)a_l P_l(\cos\theta) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)e^{i\delta_l}\sin\delta_l P_l(\cos\theta) \qquad 5.24$$

In the case where there is no flux loss, $|S_l(k)| = |e^{2i\delta_l}| = 1$. If there is flux loss due to absorption of the incident beam, then,

$$S_l(k) = \eta_l(k)e^{2i\delta_l} \qquad 5.25$$

with $0 < \eta_l(k) \leq 1$. In the no-flux loss case, all the η_l are equal to unity.

In case you find in the literature, $f(\theta) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)a_l P_l(\cos\theta)$, the partial wave amplitude is correspondingly defined as,

$$a_l = e^{i\delta_l}\sin\delta_l = e^{i\delta_l}\frac{e^{i\delta_l} - e^{i\delta_l}}{2i} = \frac{e^{2i\delta_l} - 1}{2i} = \frac{S_l(k) - 1}{2i} \qquad 5.26$$

Example 1

In a purely elastic scattering process, only the s- and p-waves are involved. Both pure s-wave and p-wave scattering are symmetric, is it possible to for the scattering to be unsymmetric between the forward and the backward hemispheres? Under what condition will the differential

cross-section in the forward direction be less than in the backward direction? Define

$$f(\theta) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)a_l P_l(\cos\theta).$$

Solution 1

We know that,

$$\frac{d\sigma}{d\Omega} = \left|f(\theta)\right|^2$$

and

$$f(\theta) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)a_l P_l(\cos\theta)$$

If only s- and p-waves contribute, then, the

$$f(\theta) = \frac{1}{k}\left\{\left[(2\times 0+1)a_0 \times 1\right] + \left[(2\times 1+1)a_1 \times \cos\theta\right]\right\}$$

$$= \frac{1}{k}(a_0 + 3a_1\cos\theta)$$

Then,

$$|\ f(\theta)|^2 = f^*(\theta)f(\theta) = \frac{1}{k^2}\left\{|\ a_0\ |^2 + 9|\ a_1\ |^2\ \cos^2\theta + 3(a_0^* a_1 + a_0 a_1^*)\cos\theta\right\}$$

Since the s-wave which has $a_1 = 0$ is isotropic (does not depend on θ) and pure p-wave has $a_0 = 0$ depends only on $(\cos\theta)^2$, both are symmetric. But the interference term depends on $\cos\theta$, and this is introduces asymmetry.

The forward $(\theta = 0)$ cross-section is,

$$\frac{d\sigma}{d\Omega} = \frac{1}{k}\left\{|\ a_0\ |^2 + 9|\ a_1\ |^2 + 3(a_0^* a_1 + a_0 a_1^*)\right\}$$

The backward $(\theta = \pi)$ cross-section is,

$$\frac{d\sigma}{d\Omega} = \frac{1}{k}\left\{|\ a_0\ |^2 + 9|\ a_1\ |^2 - 3(a_0^* a_1 + a_0 a_1^*)\right\}$$

For the backward cross-section to be larger than the forward cross-section,

$$a_0^* a_1 + a_0 a_1^* < 0$$

4.0 CONCLUSION

In this Unit, you have learnt we assumed that the potential is spherically symmetric, ensuring the conservation of the angular momentum of the incident particle. The angular momentum of the incoming particle is the same before and after scattering. Now a central potential problem, we

were able to take advantage of spherical harmonics once again. You were able to calculate the scattering amplitude for a given scattering problem, obtain the differential cross-section for a given scattering process.

5.0 SUMMARY

In this study session, you have learnt how to:

- write the partial wave amplitudes for a given scattering problem.
- calculate the scattering amplitude for a given scattering problem.
- obtain the differential cross-section for a given scattering problem.
- find the total cross-section for a given scattering process.
- write the partial-wave amplitudes in terms of the phase-shifts.
- calculate the phase shift for a given scatterer.

SELF-ASSESSMENT EXERCISE 1

What do you understand by partial-wave amplitude?

Solution to Self-Assessment Exercise 1

This is the complex number which multiplies the Legendre polynomial $P_l(\cos\theta)$, and $2l+1$ in the expansion of the scattering amplitude over the angular number *l*.

6.0 TUTOR-MARKED ASSIGNMENT

1. State the meanings of all the symbols in the expression for the partial-wave expansion,

$$f(\theta)=\frac{1}{k}\sum_{l=0}^{1}(2l+1)a_l P_l(\cos\theta)$$

2. At a certain energy in a scattering process there is a resonance in the s-wave while the p-wave phase-shift is $\pi/6$. Assuming the scattering is purely elastic ($\eta_l=1$ for all l) and that there is no significant scattering in any other partial wave,

(a) Write the $s-$ and $p-$wave partial wave amplitudes.
(b) Find the scattering amplitude.
(c) Obtain the elastic cross-section by integrating over solid angle.
(d) Find the total cross-section.

Take $f(\theta) = \frac{1}{k}\sum_{l=0}^{1}(2l+1)a_l P_l(\cos\theta)$.

3. In a scattering process, it is observed that there is significant scattering only in the s-wave and one other partial wave, *l*. Assuming that there is no scattering in any other partial wave and that there is no loss of flux,

(a) Write down, in terms of the partial wave amplitudes a_0 and a_l, an expression for the differential cross-section as a function of θ .

(b) Find the extrema of the differential cross-section, such that $\frac{d}{d(\cos\theta)}P_l$ remains unevaluated. Show that these occur at the turning points of $P_l(\cos\theta)$ and at angles such that,

$$\{2(2l+1)a_l * a_l P_l(\cos\theta) + (a_0 * a_l + a_0 a_l *)\} = 0 \quad \text{(i)}$$

(c) Write the partial-wave amplitudes in terms of the phase-shifts and prove that at the turning points satisfying equation (i),

$$P_l(\cos\theta) = -\frac{\cos(\delta_0 - \delta_l)\sin\delta_0}{(2l+1)\sin\delta_l}$$

Take $f(\theta) = \frac{1}{k}\sum_{l=0}^{1}(2l+1)a_l P_l(\cos\theta)$.

4. Particles of a given energy scatter on an infinitely hard sphere of radius *a*

(a) Calculate the phase shift $\delta_\ell(k)$.

(b) For s-waves (ℓ=0), obtain the expression for the total cross-section.

(c) Consider the case of low energies (ka<<1), show that the cross – section is four times the geometrical cross – section of the rigid sphere.

7.0 REFERENCES/FURTHER READING

Griffiths, D. J. (2005) *Introduction to Quantum Mechanics*. Upper Saddle River, NJ: Pearson Prentice Hall.

Mulders, P. J. (2011) *Advanced Quantum Mechanics*, Retrieved from http://master.particles.nl/LectureNotes/2011-QFT.pdf

Schiff, L. I. (1949). *Quantum Mechanics*. NY: McGraw-Hill

Appendix 1

$$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$= -i\hbar\left[r\sin\theta\sin\phi\left(\cos\theta\frac{\partial}{\partial r} - \frac{1}{r}\sin\theta\frac{\partial}{\partial\theta}\right)\right.$$

$$\left. -r\cos\theta\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\phi\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\right]$$

$$= -i\hbar\left[r\sin\theta\sin\phi\cos\theta\frac{\partial}{\partial r} - \sin^2\theta\sin\phi\frac{\partial}{\partial\theta} - r\sin\theta\sin\phi\cos\theta\frac{\partial}{\partial r}\right.$$

$$\left. -\cos^2\theta\sin\phi\frac{\partial}{\partial\theta} - \frac{\cos\theta\cos\phi}{\sin\theta}\frac{\partial}{\partial\phi}\right]$$

$$= -i\hbar\left[-\sin^2\theta\sin\phi\frac{\partial}{\partial\theta} - \cos^2\theta\sin\phi\frac{\partial}{\partial\theta} - \frac{\cos\theta\cos\phi}{\sin\theta}\frac{\partial}{\partial\phi}\right]$$

$$= -i\hbar\left[-\sin\phi\frac{\partial}{\partial\theta}(\sin^2\theta + \cos^2\theta) - \frac{\cos\theta\cos\phi}{\sin\theta}\frac{\partial}{\partial\phi}\right]$$

$$= -i\hbar\left[-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right]$$

$$L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$= -i\hbar\left[r\cos\theta\left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\right.$$

$$\left. -r\sin\theta\cos\phi\left(\cos\theta\frac{\partial}{\partial r} - \frac{1}{r}\sin\theta\frac{\partial}{\partial\theta}\right)\right]$$

$$= -i\hbar\left[r\cos\theta\sin\theta\cos\phi\frac{\partial}{\partial r} + \cos^2\theta\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right.$$

$$\left. -r\sin\theta\cos\theta\cos\phi + \sin^2\theta\cos\phi\frac{\partial}{\partial\theta}\right]$$

$$= -i\hbar\left[\left(\cos^2\theta + \sin^2\theta\right)\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right]$$

$$= -i\hbar\left[\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right]$$

$$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$= \sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}$$

$$= \sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\phi\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}$$

$$= -i\hbar\left[r\sin\theta\cos\phi\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\phi + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi} \right) \right.$$

$$\left. -r\sin\theta\sin\phi\left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi} \right) \right]$$

$$= -i\hbar\left(\cos^2\phi\frac{\partial}{\partial\phi} + \sin^2\phi\frac{\partial}{\partial\phi} \right) = -i\hbar\frac{\partial}{\partial\phi}(\cos^2\phi + \sin^2\phi)$$

$$= -i\hbar\frac{\partial}{\partial\phi}$$

$$L_x = -i\hbar\left[-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi} \right],$$

$$L_y = -i\hbar\left[\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi} \right],$$

$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

$$L^2 = {L_x}^2 + {L_y}^2 + {L_z}^2$$

$$= \left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi} \right)^2 + \left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi} \right)^2 + \frac{\partial^2}{\partial\phi^2}$$

$$\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi} \right)^2 = \left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi} \right)\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi} \right)$$

$$-\sin\phi\frac{\partial}{\partial\theta}\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi} \right)$$

$$= (-\sin\phi)^2\frac{\partial^2}{\partial\theta^2} + \cot\theta\sin\phi\cos\phi\frac{\partial^2}{\partial\theta\partial\phi} + \sin\phi\frac{\partial}{\partial\theta}(\sin\phi)\frac{\partial}{\partial\theta} + \sin\phi\frac{\partial}{\partial\theta}(\cot\theta\cos\phi)\frac{\partial}{\partial\phi}$$

$$= (-\sin\phi)^2\frac{\partial^2}{\partial\theta^2} + \cot\theta\sin\phi\cos\phi\frac{\partial^2}{\partial\theta\partial\phi} + 0 + \sin\phi\cos\phi\frac{\partial}{\partial\theta}(\cot\theta)\frac{\partial}{\partial\phi}$$

$$= \sin^2\phi\frac{\partial^2}{\partial\theta^2} + \cot\theta\sin\phi\cos\phi\frac{\partial^2}{\partial\theta\partial\phi} + \sin\phi\cos\phi\frac{\partial}{\partial\theta}(\cot\theta)\frac{\partial}{\partial\phi}$$

$$-\cot\theta\cos\phi\frac{\partial}{\partial\phi}\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi} \right)$$

$$= \cot\theta\sin\phi\cos\phi\frac{\partial^2}{\partial\phi\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}(\sin\phi)\frac{\partial}{\partial\theta} + \cot^2\theta\cos^2\phi\frac{\partial^2}{\partial\phi^2} + \cot^2\theta\cos\phi\frac{\partial}{\partial\phi}(\cos\phi)\frac{\partial}{\partial}$$

$$= \cot\theta\sin\phi\cos\phi\frac{\partial^2}{\partial\phi\partial\theta} + \cot\theta\cos^2\phi\frac{\partial}{\partial\theta} + \cot^2\theta\cos^2\phi\frac{\partial^2}{\partial\phi^2} - \cot^2\theta\sin\phi\cos\phi\frac{\partial}{\partial\phi}$$

$$\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi} \right)\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi} \right)$$

$$\cos\phi\frac{\partial}{\partial\theta}\left(\cos\phi\frac{\partial}{\partial\theta}-\cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$=\cos^2\phi\frac{\partial^2}{\partial\theta^2}+\cos\phi\frac{\partial}{\partial\theta}(\cos\phi)\frac{\partial}{\partial\theta}-\cot\theta\sin\phi\cos\phi\frac{\partial^2}{\partial\theta\partial\phi}-\cos\phi\frac{\partial}{\partial\theta}(\cot\theta\sin\phi)\frac{\partial}{\partial\phi}$$

$$=\cos^2\phi\frac{\partial^2}{\partial\theta^2}-0-\cot\theta\sin\phi\cos\phi\frac{\partial^2}{\partial\theta\partial\phi}-\sin\phi\cos\phi\frac{\partial}{\partial\theta}(\cot\theta)\frac{\partial}{\partial\phi}$$

$$=\cos^2\phi\frac{\partial^2}{\partial\theta^2}-\cot\theta\sin\phi\cos\phi\frac{\partial^2}{\partial\theta\partial\phi}-\sin\phi\cos\phi\frac{\partial}{\partial\theta}(\cot\theta)\frac{\partial}{\partial\phi}$$

$$-\cot\theta\sin\phi\frac{\partial}{\partial\phi}\left(\cos\phi\frac{\partial}{\partial\theta}-\cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$=-\cot\theta\sin\phi\cos\phi\frac{\partial^2}{\partial\phi\partial\theta}-\cot\theta\sin\phi\frac{\partial}{\partial\phi}(\cos\phi)\frac{\partial}{\partial\phi}+\cot^2\theta\sin^2\phi\frac{\partial^2}{\partial\phi^2}+\cot\theta\sin\phi\frac{\partial}{\partial\phi}(\cot\theta\sin\phi)\frac{\partial}{\partial\phi}$$

$$=-\cot\theta\sin\phi\cos\phi\frac{\partial^2}{\partial\phi\partial\theta}-\cot\theta\sin\phi\frac{\partial}{\partial\phi}(\cos\phi)\frac{\partial}{\partial\phi}+\cot^2\theta\sin^2\phi\frac{\partial^2}{\partial\phi^2}+\cot\theta\sin\phi\frac{\partial}{\partial\phi}(\cot\theta\sin\phi)\frac{\partial}{\partial\phi}$$

$$=-\cot\theta\sin\phi\cos\phi\frac{\partial^2}{\partial\phi\partial\theta}+\cot\theta\sin^2\phi\frac{\partial}{\partial\phi}+\cot^2\theta\sin^2\phi\frac{\partial^2}{\partial\phi^2}+\cot^2\theta\sin\phi\cos\phi\frac{\partial}{\partial\phi}$$

Adding all,

$$=\sin^2\phi\frac{\partial^2}{\partial\theta^2}+\cot\theta\sin\phi\cos\phi\frac{\partial^2}{\partial\theta\partial\phi}+\sin\phi\cos\phi\frac{\partial}{\partial\theta}(\cot\theta)\frac{\partial}{\partial\phi}$$

$$+\cot\theta\sin\phi\cos\phi\frac{\partial^2}{\partial\phi\partial\theta}+\cot\theta\cos^2\phi\frac{\partial}{\partial\theta}+\cot^2\theta\cos^2\phi\frac{\partial^2}{\partial\phi^2}-\cot^2\theta\sin\phi\cos\phi\frac{\partial}{\partial\phi}$$

$$+\cos^2\phi\frac{\partial^2}{\partial\theta^2}-\cot\theta\sin\phi\cos\phi\frac{\partial^2}{\partial\theta\partial\phi}-\sin\phi\cos\phi\frac{\partial}{\partial\theta}(\cot\theta)\frac{\partial}{\partial\phi}$$

$$-\cot\theta\sin\phi\cos\phi\frac{\partial^2}{\partial\phi\partial\theta}+\cot\theta\sin^2\phi\frac{\partial}{\partial\phi}+\cot^2\theta\sin^2\phi\frac{\partial^2}{\partial\phi^2}+\cot^2\theta\sin\phi\cos\phi\frac{\partial}{\partial\phi}$$

$$=\sin^2\phi\frac{\partial^2}{\partial\theta^2}+\cot\theta\cos^2\phi\frac{\partial}{\partial\theta}+\cot^2\theta\cos^2\phi\frac{\partial^2}{\partial\phi^2}+\cos^2\phi\frac{\partial^2}{\partial\theta^2}$$

$$+\cot\theta\sin^2\phi\frac{\partial}{\partial\phi}+\cot^2\theta\sin^2\phi\frac{\partial^2}{\partial\phi^2}$$

$$=\sin^2\phi\frac{\partial^2}{\partial\theta^2}+\cos^2\phi\frac{\partial^2}{\partial\theta^2}+\cot\theta\cos^2\phi\frac{\partial}{\partial\theta}+\cot\theta\sin^2\phi\frac{\partial}{\partial\phi}$$

$$+\cot^2\theta\sin^2\phi\frac{\partial^2}{\partial\phi^2}+\cot^2\theta\cos^2\phi\frac{\partial^2}{\partial\phi^2}$$

$$=(\sin^2\phi+\cos^2\phi)\frac{\partial^2}{\partial\theta^2}+(\cos^2\phi+\sin^2\phi)\cot\theta\frac{\partial}{\partial\theta}+(\sin^2\phi+\cos^2\phi)\cot^2\theta\frac{\partial^2}{\partial\phi^2}$$

$$=\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}+\cot^2\theta\frac{\partial^2}{\partial\phi^2}$$

Adding $\frac{\partial}{\partial\phi}\left(\frac{\partial}{\partial\phi}\right)=\frac{\partial^2}{\partial\phi^2}$,

$$\left(-\sin\phi\frac{\partial}{\partial\theta}-\cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)^2+\left(\cos\phi\frac{\partial}{\partial\theta}-\cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)^2+\frac{\partial^2}{\partial\phi^2}$$

$$=\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}+(\cot^2\theta+1)\frac{\partial^2}{\partial\phi^2}$$

$$L^2=L_x{}^2+L_y{}^2+L_z{}^2=(-i\hbar)^2\left(\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}+(\cot^2\theta+1)\frac{\partial^2}{\partial\phi^2}\right)$$

$$=-\hbar^2\left(\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}+\sec^2\theta\frac{\partial^2}{\partial\phi^2}\right)$$

$$=-\hbar^2\left(\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

Note that

$$\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}=\sin\theta\frac{\partial^2}{\partial\theta^2}+\frac{\partial}{\partial\theta}(\sin\theta)\frac{\partial}{\partial\theta}=\sin\theta\frac{\partial^2}{\partial\theta^2}+\cos\theta\frac{\partial}{\partial\theta}$$

Hence,

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}=\frac{\partial^2}{\partial\theta^2}+\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\theta}=\frac{\partial^2}{\partial\theta^2}+\cot\frac{\partial}{\partial\theta}$$

Finally, we can write

$$L^2=-\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

$$r=\sqrt{x^2+y^2+z^2}$$

$$\theta=\tan^{-1}\left(\frac{x^2+y^2}{z^2}\right)$$

$$\phi=\tan^{-1}\frac{y}{x}$$

$$\frac{\partial r}{\partial x}=\frac{\partial}{\partial x}\sqrt{x^2+y^2+z^2}=\frac{\partial}{\partial x}(x^2+y^2+z^2)^{1/2}=\frac{1}{2}(x^2+y^2+z^2)^{-1/2}\times 2x$$

$$=\frac{x}{(x^2+y^2+z^2)^{1/2}}=\frac{x}{r}=\frac{r\sin\theta\cos\phi}{r}=\sin\theta\cos\phi$$

Hence,

$$\frac{\partial x}{\partial r}=\sin\theta\cos\phi$$

Similarly,

$$\frac{\partial r}{\partial y}=\sin\theta\sin\phi$$

$$\frac{\partial r}{\partial z} = \cos\theta$$

$$\frac{\partial \theta}{\partial x} = \frac{\partial}{\partial x}\tan^{-1}\left(\frac{x^2+y^2}{z^2}\right)$$

Let $v = \frac{x^2+y^2}{z^2}$, so that $\frac{\partial v}{\partial x} = \frac{1}{2}\times\frac{2x}{z^2} = \frac{x}{z^2}$. Then, we can write

$$\frac{\partial \theta}{\partial x} = \frac{\partial}{\partial x}\tan^{-1}\frac{x^2+y^2}{z^2} = \frac{\partial}{\partial x}\tan^{-1} v = \frac{\partial}{\partial v}\tan^{-1} v\frac{\partial v}{\partial x}$$

$$= \frac{1}{1+v^2}\times\frac{x}{z^2\left(\frac{x^2+y^2}{z^2}\right)^{1/2}} = \frac{x}{z^2\left(1+\frac{x^2+y^2}{z^2}\right)\left(\frac{x^2+y^2}{z^2}\right)^{1/2}}$$

$$= \frac{1}{1+v^2}\times\frac{x}{z^2\left(\frac{x^2+y^2}{z^2}\right)^{1/2}} = \frac{x}{(x^2+y^2+z^2)\left(\frac{x^2+y^2}{z^2}\right)^{1/2}} = \frac{x}{r^2\tan\theta}$$

$$= \frac{r\sin\theta\cos\phi}{r^2\tan\theta} = \frac{\sin\theta\cos\phi}{\sin\theta/\cos\theta} = \frac{1}{r}\cos\theta\cos\phi$$

Hence,

$$\frac{\partial \theta}{\partial x} = \frac{1}{r}\cos\theta\cos\phi$$

You can also show that (bearing in mind that the expression is symmetric for *x* and *y*)

$$\frac{\partial \theta}{\partial y} = \frac{y}{r^2\tan\theta} = \frac{r\sin\theta\sin\phi}{r^2\sin\theta/\cos\theta} = \frac{1}{r}\cos\theta\sin\phi$$

$$\frac{\partial v}{\partial z} = \frac{\partial}{\partial z}\left(\frac{x^2+y^2}{z^2}\right)^{1/2} = \frac{\partial}{\partial z}z^{-1}(x^2+y^2)^{1/2} = -\frac{1}{z^2}(x^2+y^2)^{1/2} = -\frac{1}{z}\left(\frac{x^2+y^2}{z^2}\right)^{1/2}$$

$$\frac{\partial \theta}{\partial z} = \frac{\partial}{\partial z}\tan^{-1}\frac{x^2+y^2}{z^2} = \frac{\partial}{\partial z}\tan^{-1} v = \frac{\partial}{\partial v}\tan^{-1} v\frac{\partial v}{\partial z}$$

$$= \frac{1}{1+v^2}\times-\frac{1}{z}\left(\frac{x^2+y^2}{z^2}\right)^{1/2} = -\frac{\left(\frac{x^2+y^2}{z^2}\right)^{1/2}}{z\left(1+\frac{x^2+y^2}{z^2}\right)} = -\frac{\left(\frac{x^2+y^2}{z^2}\right)^{1/2}}{\frac{z}{z^2}(x^2+y^2+z^2)}$$

$$= -\frac{z\left(\frac{x^2+y^2}{z^2}\right)^{1/2}}{(x^2+y^2+z^2)} = -\frac{r\cos\theta\tan\theta}{r^2} = -\frac{1}{r}\cos\theta\times\sin\theta/\cos\theta = -\frac{1}{r}\sin\theta$$

$$\frac{\partial \theta}{\partial z} = -\frac{1}{r}\sin\theta$$

$$\frac{\partial\phi}{\partial x}=\frac{\partial}{\partial x}\tan^{-1}\frac{y}{x}=\frac{\partial}{\partial w}\tan^{-1}\frac{y}{x}\frac{\partial w}{\partial x}=\frac{1}{1+\left(\frac{y}{x}\right)^2}\times\left(-\frac{y}{x^2}\right)=\frac{1}{\frac{x^2+y^2}{x^2}}\frac{-y}{x^2}=\frac{-y}{x^2+y^2}$$

$$=\frac{-r\sin\theta\sin\phi}{r^2\sin^2\theta\cos^2\phi+r^2\sin^2\theta\sin^2\phi}=\frac{-r\sin\theta\sin\phi}{r^2\sin^2\theta(\cos^2\phi+\sin^2\phi)}$$

$$=\frac{-r\sin\theta\sin\phi}{r^2\sin^2\theta}=-\frac{1}{r}\frac{\sin\phi}{\sin\theta}$$

$$\frac{\partial\phi}{\partial x}=-\frac{1}{r}\frac{\sin\phi}{\sin\theta}$$

$$\frac{\partial\phi}{\partial y}=\frac{\partial}{\partial y}\tan^{-1}\frac{y}{x}=\frac{\partial}{\partial w}\tan^{-1}\frac{y}{x}\frac{\partial w}{\partial y}=\frac{1}{1+\left(\frac{y}{x}\right)^2}\times\left(\frac{1}{x}\right)=\frac{1}{\frac{x^2+y^2}{x^2}}\frac{1}{x}=\frac{x}{x^2+y^2}$$

$$=\frac{r\sin\theta\cos\phi}{r^2\sin^2\theta\cos^2\phi+r^2\sin^2\theta\sin^2\phi}=\frac{r\sin\theta\cos\phi}{r^2\sin^2\theta(\cos^2\phi+\sin^2\phi)}$$

$$=\frac{r\sin\theta\cos\phi}{r^2\sin^2\theta}=\frac{1}{r}\frac{\cos\phi}{\sin\theta}$$

$$\frac{\partial\phi}{\partial y}=\frac{1}{r}\frac{\cos\phi}{\sin\theta}$$

$$\frac{\partial\phi}{\partial z}=0$$

$$\frac{\partial}{\partial x}=\frac{\partial}{\partial r}\frac{\partial r}{\partial x}+\frac{\partial}{\partial\theta}\frac{\partial\theta}{\partial x}+\frac{\partial}{\partial\phi}\frac{\partial\phi}{\partial x}$$

$$=\sin\theta\cos\phi\frac{\partial}{\partial r}+\frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial\theta}-\frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}$$

$$\frac{\partial}{\partial y}=\frac{\partial}{\partial r}\frac{\partial r}{\partial y}+\frac{\partial}{\partial\theta}\frac{\partial\theta}{\partial y}+\frac{\partial}{\partial\phi}\frac{\partial\phi}{\partial y}$$

$$=\sin\theta\sin\phi\frac{\partial}{\partial r}+\frac{1}{r}\cos\theta\sin\phi\frac{\partial}{\partial\theta}+\frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}$$

$$\frac{\partial}{\partial z}=\cos\theta\frac{\partial}{\partial r}-\frac{1}{r}\sin\theta\frac{\partial}{\partial\theta}$$

$$\nabla=\left(\sin\theta\cos\phi\frac{\partial}{\partial r}+\frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial\theta}-\frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi},\sin\theta\sin\phi\frac{\partial}{\partial r}+\frac{1}{r}\cos\theta\sin\phi\frac{\partial}{\partial\theta}+\frac{\sin\phi}{r\sin\theta}\right.$$

$$\left.\cos\theta\frac{\partial}{\partial r}-\frac{1}{r}\sin\theta\frac{\partial}{\partial\theta}\right)$$

$$\nabla^2 = \left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)$$

+

$$\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\phi\frac{\partial}{\partial\theta} + \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\phi\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)$$

$$+\left(\cos\theta\frac{\partial}{\partial r} - \frac{1}{r}\sin\theta\frac{\partial}{\partial\theta}\right)\left(\cos\theta\frac{\partial}{\partial r} - \frac{1}{r}\sin\theta\frac{\partial}{\partial\theta}\right)$$

Expanding and rearranging, we arrive at,

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{\cot\theta}{r^2}\frac{\partial}{\partial\phi}$$

Rearranging,

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{\cot\theta}{r^2}\frac{\partial}{\partial\phi} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Appendix 2

$$L_x = yp_z - zp_y = y\left(-i\hbar\frac{\partial}{\partial z}\right) - z\left(-i\hbar\frac{\partial}{\partial y}\right) = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$L_y = zp_x - xp_z = z\left(-i\hbar\frac{\partial}{\partial x}\right) - x\left(-i\hbar\frac{\partial}{\partial z}\right) = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$L_xL_y = \left[-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right]\left[-i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\right]$$

$$= (-i\hbar)^2\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$= -\hbar^2\left[y\frac{\partial}{\partial z}\left(z\frac{\partial}{\partial x}\right) - xy\frac{\partial}{\partial z}\left(\frac{\partial}{\partial z}\right) - z^2\frac{\partial}{\partial y}\left(\frac{\partial}{\partial x}\right) + xz\frac{\partial}{\partial y}\left(\frac{\partial}{\partial z}\right)\right]$$

$$= -\hbar^2\left(y\frac{\partial}{\partial x} + yz\frac{\partial^2}{\partial z\partial x} - xy\frac{\partial^2}{\partial z^2} - z^2\frac{\partial^2}{\partial y\partial x} + xz\frac{\partial^2}{\partial y\partial z}\right)$$

$$= -\hbar^2\left(y\frac{\partial}{\partial x} + yz\frac{\partial^2}{\partial x\partial z} - xy\frac{\partial^2}{\partial z^2} - z^2\frac{\partial^2}{\partial x\partial y} + xz\frac{\partial^2}{\partial y\partial z}\right)$$

$$L_yL_x = \left[-i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\right]\left[-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right]$$

$$= (-i\hbar)^2\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$= -\hbar^2\left[z\frac{\partial}{\partial x}\left(y\frac{\partial}{\partial z}\right) - z^2\frac{\partial}{\partial x}\left(\frac{\partial}{\partial y}\right) - xy\frac{\partial}{\partial z}\left(\frac{\partial}{\partial z}\right) + x\frac{\partial}{\partial z}\left(z\frac{\partial}{\partial y}\right)\right]$$

$$= -\hbar^2\left(yz\frac{\partial^2}{\partial x\partial z} - z^2\frac{\partial^2}{\partial x\partial y} - xy\frac{\partial^2}{\partial z^2} + xz\frac{\partial^2}{\partial z\partial y} + x\frac{\partial}{\partial y}\right)$$

$$= -\hbar^2\left(yz\frac{\partial^2}{\partial x\partial z} - z^2\frac{\partial^2}{\partial x\partial y} - xy\frac{\partial^2}{\partial z^2} + xz\frac{\partial^2}{\partial y\partial z} + x\frac{\partial}{\partial y}\right)$$

$$-L_yL_x = -\hbar^2\left(-yz\frac{\partial^2}{\partial x\partial z} + z^2\frac{\partial^2}{\partial x\partial y} + xy\frac{\partial^2}{\partial z^2} - xz\frac{\partial^2}{\partial y\partial z} - x\frac{\partial}{\partial y}\right)$$

Rearranging,

$$-L_yL_x = -\hbar^2\left(-x\frac{\partial}{\partial y} - yz\frac{\partial^2}{\partial x\partial z} + xy\frac{\partial^2}{\partial z^2} + z^2\frac{\partial^2}{\partial x\partial y} - xz\frac{\partial^2}{\partial y\partial z}\right)$$

$$L_xL_y = -\hbar^2\left(y\frac{\partial}{\partial x} + yz\frac{\partial^2}{\partial x\partial z} - xy\frac{\partial^2}{\partial z^2} - z^2\frac{\partial^2}{\partial x\partial y} + xz\frac{\partial^2}{\partial y\partial z}\right)$$

$$-L_yL_x = -\hbar^2\left(-x\frac{\partial}{\partial y} - yz\frac{\partial^2}{\partial x\partial z} + xy\frac{\partial^2}{\partial z^2} + z^2\frac{\partial^2}{\partial x\partial y} - xz\frac{\partial^2}{\partial y\partial z}\right)$$

Adding equations ( ) and ( ),

$$[L_x, L_y] = L_x L_y - L_y L_x = -\hbar^2 \left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y} \right) = i\hbar \left[i\hbar \left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y} \right) \right]$$

$$= i\hbar \left[-i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) \right] = i\hbar L_z$$