

Lecture Notes
in
Quantum Mechanics

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Chapter 1

Review of Classical Mechanics

1.1 The Hamiltonian

We have seen the **Hamiltonian** function in classical mechanics; resembling the energy of the dynamical system in study.¹

$$H(\vec{p}, \vec{q}) \equiv \text{Energy of the system.} \quad (1.1)$$

Where, \vec{p} and \vec{q} are the generalised momentum and coordinates(configuration) for the system. We define the generalised/ canonical momentum as:²

$$p_i = \frac{\partial \mathcal{L}}{\partial \dot{q}^i}. \quad (1.2)$$

With \mathcal{L} being the Lagrangian function.³

1.1.1 Examples

1. The Hamiltonian for a free particle is given by:

$$H = \frac{p^2}{2m} \quad (1.3)$$

2. In a central potential, the Hamiltonian takes the form :

$$H = \frac{p^2}{2m} + g \frac{Q_1 Q_2}{r} \quad (1.4)$$

Where g is a constant, called *coupling constant*, and $Q_1 Q_2$ are charges/ masses. Depending on the type of interaction.

¹recall that $H = T + V$

²Note that \vec{p} here is not always $m\vec{v}$!

³recall that $\mathcal{L} = T - V$

3. A dipole in a magnetic field B has the following Hamiltonian:

$$H = \vec{\mu} \cdot \vec{B} \quad (1.5)$$

4. The Hamiltonian for a free rotating mass is: ⁴

$$H = \frac{L^2}{2I} \quad (1.6)$$

Here, L is the angular momentum of the system.

5. Lastly, a very important Hamiltonian, is the Hamiltonian for a simple harmonic oscillator (SHO).

$$H = \frac{P^2}{2m} + \frac{m\omega^2 q^2}{2}. \quad (1.7)$$

1.2 Hamilton's equations

For a dynamical system with a Hamiltonian. The evolution of that system obeys the set of equations, known as **Hamilton's equations**.⁵

$$\frac{\partial H}{\partial q^i} = -\dot{p}_i \quad (1.8)$$

$$\frac{\partial H}{\partial p_i} = \dot{q}^i \quad (1.9)$$

Some dynamical systems however, does not obey these equations. These systems are known as *Hamiltonian constraint* systems.

1.2.1 Poisson brackets

Let $f(\vec{q}, \vec{p})$, and $g(\vec{q}, \vec{p})$ be functions of both \vec{q} and \vec{p} . One may define the following operation :

$$\{f, g\} \equiv \sum_i \left(\frac{\partial f}{\partial q^i} \frac{\partial g}{\partial p_i} - \frac{\partial g}{\partial q^i} \frac{\partial f}{\partial p_i} \right) \quad (1.10)$$

This operation is called **Poisson brackets**, it shall prove importance in quantisation, and also in understanding conserved quantities (see homework).

⁴recall that $I = Mr^2$

⁵note that both \vec{p} and \vec{q} are functions of time

It is interesting to Poisson bracket the Hamiltonian with components of \vec{q} and \vec{p} , for example :

$$\begin{aligned}\{q^j, H\} &= \sum_i \frac{\partial q^j}{\partial q^i} \frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q^i} \underbrace{\frac{\partial q^j}{\partial p_i}}_{=0} \\ &= \sum_i \delta_i^j \underbrace{\frac{\partial H}{\partial p_i}}_{=\dot{q}^i} \\ &= \dot{q}^j\end{aligned}\tag{1.11}$$

Same goes for:

$$\{p_j, H\} = \dot{p}_j\tag{1.12}$$

This actually leads us to the general result, that for any function $f(\vec{q}, \vec{p})$, we have:

$$\{f(\vec{q}, \vec{p}), H\} = \frac{\partial f(\vec{q}, \vec{p})}{\partial t}\tag{1.13}$$

1.3 Phase space

Since one only needs the p 's and q 's ⁶ in order to fully describe the dynamical system. The **state** vector is defined in $2f$ dimensional space, called the phase space.

$$\vec{S}(t) \equiv (\vec{q}(t), \vec{p}(t))\tag{1.14}$$

1.3.1 Example: phase-space for SHO

This phase space for the SHO in 1-D is resembled by a circle: The circle resembles all the possible states the SHO can take, at any moment in time. In other words, this describes the full evolution of the system in time.

Since energy is conserved for the free SHO, the system will keep being in the circle. As for damped one, when energy is lost. The system will spiral until it comes to a halt.

1.4 Problems

1. Show that the Hamiltonian for a particle of mass m , orbiting a mass M , and they interact gravitationally is given by:

$$H = \frac{L^2}{2I} + G \frac{M m}{r}$$

⁶One needs as many of them as the number of degrees of freedom f for the system

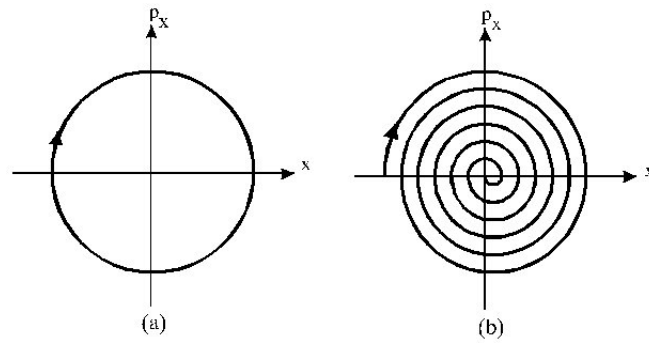


Figure 1.1: (a) The phase space for free SHO. (B) The phase space of a damped SHO

Then derive the equations of motion for this system, comment on your results.

2. Derive and solve the equation of motion for a 2-D SHO, with $m = 1$ and $\omega = 1$.
3. Show that :

$$\{p_j, H\} = \frac{\partial p_j}{\partial t}$$

4. Draw the shape of the phase space for a particle free-falling from altitude y_0
5. Discuss conserved quantities, and Neother's theorem in light of Hamiltonian dynamics.

Chapter 2

Mathematical preliminaries

2.1 Abstract vector spaces

In previous courses, the notion of a **vector** was introduced as being an n-tuple of ordered numbers (either real or complex). However, one can have a more general definition for a vector as being an element of a **vector space**. A vector space is a set that satisfies the following property

Let \mathcal{V} be a vector space, and $|\psi\rangle$ and $|\phi\rangle$ are elements of it . Then :

$$\alpha|\psi\rangle + \beta|\phi\rangle, \quad (2.1)$$

is also an element of that vector space, where α and β are complex or real numbers. The expression (2.1) is called the **superposition** of the vectors $|\psi\rangle$ and $|\phi\rangle$.

The dimension of \mathcal{V} could either be finite , countably infinite or uncountably infinite (see next section). For finite dimensional- or countably infinite- vector spaces. It is possible to represent a vector $|\psi\rangle$ as a column matrix :

$$|f\rangle \Leftrightarrow \begin{pmatrix} f_1 \\ f_2 \\ f_3 \\ \vdots \end{pmatrix} \quad (2.2)$$

We can represent the components of the above vector in what-so-called a **spike diagram** representing the magnitude of each component of the vector $|\psi\rangle$.

2.2 Functions as vectors

It may seem unfamiliar to most readers that functions could be considered as vectors of an uncountably infinite dimensional vector space. In order to see this,



Figure 2.1: Spike diagram of a vector in 3 dimensional vector space, and 30 dimensional one.

we use the spike diagrams discussed above. This time using a continuous parameter x taking real-number values instead of the discrete index i . The spike diagram for such vector would look like: In fact, this spike diagram looks familiar to the

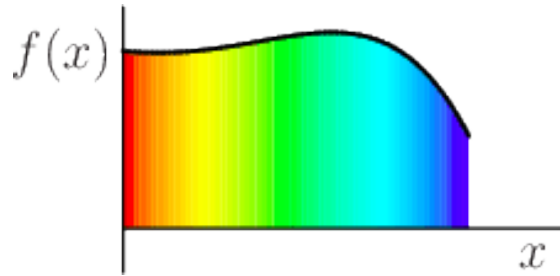


Figure 2.2: Spike diagram of a vector having infinite components

classical graph of a real-valued function $f(x)$: in this way, a function is just a

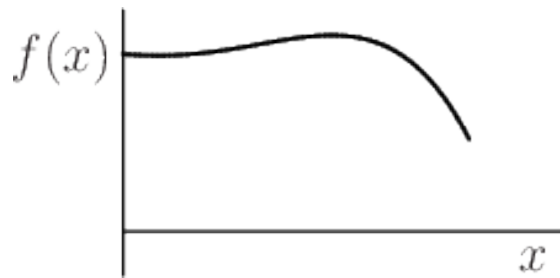


Figure 2.3: Classical graph of a function $f(x)$

single vector in an infinite dimensional space. It should be noted that to make the transition to infinite dimensions mathematically meaningful, you need to impose some smoothness constraints on the function. Typically, it is required that the function is continuous, or at least integrable in some sense. These details are not important for our purpose, thus we shall not discuss them further.

2.3 Dual spaces and inner product

One may define a map $\langle f|$ that sends a vector $|\phi\rangle$ in \mathcal{V} to the real or complex numbers. Defined as - for finite dimensional vector spaces or countably infinite ones:

$$\langle f|\phi\rangle = \sum_i f_i \phi_i \quad (2.3)$$

or for functions ¹:

$$\langle f|\phi\rangle = \int dx f(x)^* \phi(x) \quad (2.4)$$

We can easily show that the set of such maps form a vector space themselves, sometimes they which we call the **dual** vector space and denoted by \mathcal{V}^* . Moreover, the operation are called linear between a vector and a (dual) vector is called **inner product** . functionals

2.3.1 The Bra-Ket notation

Every vector space has its dual. In the notation adopted in quantum mechanics, and invented by Paul Dirac. A member of a vector space is called a **Ket** and denoted by $|\psi\rangle$, as we have seen, for discrete components it is represented as a column matrix .On the other hand, the elements of the dual space are denoted by a **Bra** $\langle f|$ in Dirac notation. And represented as a row matrix: ²

$$\langle f|\Leftrightarrow (f_1^* \ f_2^* \ f_3^* \ \dots) \quad (2.5)$$

The notation adopted is known as the **Bra-Ket notation** . Since for every vector space there is a dual space. One may turn a Ket vector into a Bra vector, by a one-to-one map. Hence defining the inner product in the vector space itself, calling it an **inner-product space**.

Two vectors $|\psi\rangle$ and $|\phi\rangle$ are called **orthogonal** if and only if :

$$\langle \phi|\psi\rangle = 0$$

2.3.2 Normed spaces

In a similar sense to the magnitude of a vector in the space (like velocity), we can extend this notion to *any* vector with the norm function. $\|\cdot\|$. There are many ways one can define the norm of a vector. However, we are only interested in the norm defined by the inner product:

$$\|\psi\| \equiv \sqrt{\langle \psi|\psi\rangle} \quad (2.6)$$

¹The star resembles the complex conjugation $f(x)^*$

²The inner product is carried like matrix multiplication between a row and a column

Note that the norm is always a **real number** . Vectors with a unit norm is called **normal vectors** .

2.4 Hilbert space

An inner product vector space \mathcal{H} , with a norm defined in (2.6), in addition to another property called *completeness* ³ is called a **Hilbert space**. Hilbert spaces are extremely important in quantum mechanics. They replace the phase spaces of classical mechanics. Hilbert spaces can be finite dimensional or infinite dimensional (both cases we call it **separable** Hilbert spaces), the latter infinite dimensional space might have either continuous and discrete *representations*.

2.4.1 Basis of a Hilbert space

We can express any vector in the Hilbert space as a linear superposition of $\dim \mathcal{H}$ other vectors. Hence, it is possible to construct orthonormal basis for a Hilbert space. You need as many of them as the dimension of the vector space itself. Given a vector $|\psi\rangle$ in the Hilbert space having a set of orthonormal basis $S = \{|e_i\rangle\}_i$, $|\psi\rangle$ is uniquely expressed in terms of the basis S :

$$|\psi\rangle = \sum_i \langle e_i | \psi \rangle |e_i\rangle \quad (2.7)$$

The coefficients $c_j = \langle e_j | \psi \rangle$ is sometimes called **Fourier coefficients**. We can have the same argument for the Bra-vectors:

$$\langle \psi | = \sum_i \langle \psi | e_i \rangle \langle e_i | \quad (2.8)$$

The basis satisfy⁴:

$$\langle e_i | e_j \rangle = \delta_{ij} \quad (2.9)$$

For function spaces, the basis have continuous parameter x instead of a discrete index the basis therefore are denoted by $|x\rangle$, for all x a real number. A function ϕ is written as :

$$\phi(x) = \langle x | \phi \rangle$$

³complete vector space is a space that all Cauchy sequences converge

⁴There is a fundamental difference by what we mean by basis here and the conventional basis tough in Classical mechanics The basis we use are called Schauder basis, whilst the latter is known as Hamel basis

Instead of using the Bra-Ket notation for functions, we shall only denote them by $\phi(x)$.

Note that we need some-sort of structure in the Hilbert space to insure that (2.7) converges if the sum is infinite. We call the Hilbert space in with the series of this type the ℓ^2 space, or the space of square-summable sequences. Moreover, the integrals used in this course - and in quantum mechanics in general- are known as the *Lebesgue integrals*, they are different from Riemann integrals defined in calculus courses.

Here, we have illustrated the most relevant properties of Hilbert spaces that concern us in the study of introductory quantum mechanics. A lot of mathematical details and rigour has been spared in this lecture. It is urged from the reader to conduct a further reading in the theory of Hilbert space; please consult: *Functional Analysis* by M. Reed and B. Simon.

2.5 The space L^2

Functions form a vector space, as we have seen previously, nevertheless, we need to imply an additional restriction on functions in order to form a Hilbert space. Let $\phi(x)$ be a function defined on the interval $[a, b]$, the norm of this function is defined to be - in accordance to the formal definition of the norm- :

$$\|\phi(x)\| = \sqrt{\int_a^b \phi(x)^* \phi(x) dx} \quad (2.10)$$

For the norm to exist, the function $\phi(x)$ needs to be **square integrable** on the interval $[a, b]$. It is not hard to show that the set of square-integrable functions on the same interval form a Hilbert space. This Hilbert space is known as the $L^2(R; d\mu)$ space. It reads; the space of square-integrable function on the interval/Region R ⁵, with respect to the measure $d\mu$. By measure we mean the volume element that we integrate over. In 1-D case $d\mu = dx$. Sometimes, one wishes to define a *weight* $w(x)$ for the space, but this is out of the scope of this course.

The space L^2 can have basis of orthogonal, and normalised functions $(u_1(x), u_2(x), \dots)$ depending on the interval of interest. For example the classical orthogonal polynomials including:

- Hermite polynomials:

$$H_n(x) = K_n^{-1} e^{x^2} \frac{d^n}{dx^n} \left(e^{-x^2} \right). \quad (2.11)$$

⁵Functions of L^2 could be of several variables, real or complex-valued

They could form basis for the space $L^2(-\infty, +\infty; dx)$.

- Legendre polynomials:

$$L_n^\nu = K_n^{-1} x^{-\nu} e^x \frac{d^n}{dx^n} (x^{\nu+1} e^x). \quad (2.12)$$

They could form basis for the space $L^2(0, +\infty; dx)$.

- Legendre polynomials (of the first kind):

$$P_n = K_n^{-1} \frac{d^n}{dx^n} (1 - x^2) \quad (2.13)$$

They could form basis for the space $L^2(0, 1; dx)$.

The second example of L^2 spaces, are the ones used in Fourier analysis. Where $\cos(nkx)$ and $\sin(nkx)$ form an orthonormal basis for a given L^2 space with an interval L . Recall that we can expand any function in a Fourier series :

$$f(x) = \sum_{n=0}^{\infty} A_n \cos\left(\frac{n\pi x}{L}\right) + B_n \sin\left(\frac{n\pi x}{L}\right) \quad (2.14)$$

Where :

$$A_n = \int_0^L f(x) \cos\left(\frac{n\pi x}{L}\right) dx \quad (2.15)$$

$$B_n = \int_0^L f(x) \sin\left(\frac{n\pi x}{L}\right) dx \quad (2.16)$$

Or expanding the function in a continuous basis (Fourier integral).

Note Advanced readers might not find the discussion in this lecture formal neither accurate enough, as discussing mathematical rigour of Hilbert spaces is very distant from the course aims.

2.6 Outer product

For a finite-dimensional vector space, the outer product can be understood as simple matrix multiplication:

$$|\phi\rangle \langle\psi| = \begin{pmatrix} \phi_1 \\ \phi_2 \\ \vdots \\ \phi_N \end{pmatrix} (\psi_1^* \quad \psi_2^* \quad \cdots \quad \psi_N^*) = \begin{pmatrix} \phi_1\psi_1^* & \phi_1\psi_2^* & \cdots & \phi_1\psi_N^* \\ \phi_2\psi_1^* & \phi_2\psi_2^* & \cdots & \phi_2\psi_N^* \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N\psi_1^* & \phi_N\psi_2^* & \cdots & \phi_N\psi_N^* \end{pmatrix}$$

The outer product is an $N \times N$ matrix.

2.7 Linear operators

The term 'linear operator' is used in many contexts, in quantum mechanics however, we are interested -mainly- in linear operators, acting on a Hilbert space. Linear operators are maps from a Hilbert space to itself (known mathematically as Endomorphisms). In simple words, they send 'kets' to 'kets'. Operators ⁶ are represented as square matrices (for finite dimensional or countably infinite dimensional Hilbert spaces). Hence, all the algebra of matrices will apply to operators. Such as :

2.7.1 The algebra of operators

1. Linearity:

Let \hat{A} and \hat{B} be operators acting on the Hilbert space \mathcal{H} , α and β are scalars, and $|\psi\rangle$ and $|\phi\rangle$ be vectors in \mathcal{H} . Then the following properties hold:

$$(\alpha\hat{A} + \beta\hat{B})|\psi\rangle = \alpha(\hat{A}|\psi\rangle) + \beta(\hat{B}|\psi\rangle) \quad (2.17)$$

Moreover:

$$\hat{A}(\alpha|\psi\rangle + \beta|\phi\rangle) = \alpha(\hat{A}|\psi\rangle) + \beta(\hat{A}|\phi\rangle) \quad (2.18)$$

A result from above :

$$\hat{A}|\psi\rangle = \sum_i \langle i|\psi\rangle (\hat{A}|i\rangle) \quad (2.19)$$

2. Eigenvalue:

A scalar λ is called an **eigenvalue** if it satisfied the equation:

$$\hat{A}|\psi\rangle = \lambda|\psi\rangle \quad (2.20)$$

Called the **eigenvalue equation**, and the vector $|\psi\rangle$ is called an **eigenket**/**eigenvector**. This equation is equivalent to :

$$\det(\hat{A} - \lambda\hat{I}) = 0 \quad (2.21)$$

For \hat{I} or just I being the identity operator. An important result from this property is the spectral decomposition, that we shall discuss later in this lecture.

3. Self-adjointness (Hermitian operators)

Let \hat{A} be an operator, then \hat{A}^\dagger is the **hermitian conjugate** of this operator. It is simply the hermitian matrix in the matrix representation of \hat{A} .

⁶we shall always mean linear operator when we use the term operator from now on

The hermitian conjugate acts on the dual space of \mathcal{H} (acts on the Bras). The following properties for the hermitian conjugation are listed below (for reminding)

- $\left(\hat{A}^\dagger\right)^\dagger = \hat{A}$ – involutiveness

- If an inverse for the operator exists then:

$$\left(\hat{A}^{-1}\right)^\dagger = \left(\hat{A}^\dagger\right)^{-1}$$

- Antilinearity:

$$\left(\alpha\hat{A} + \beta\hat{B}\right)^\dagger = \alpha^*\hat{A}^\dagger + \beta^*\hat{B}^\dagger$$

- $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$.

An operator is called **self-adjoint** , if it is equal to its hermitian conjugate:

$$\hat{A}^\dagger = \hat{A}$$

In other words, it acts both on the Kets and on the Bras. An important theorem for self-adjoint operators is stated below:

All the eigenvalues for a self-adjoint operator are real

Other properties of the matrices can be revised from a linear algebra book.

2.8 Spectral theorem

An important result from linear algebra is the spectral decomposition of an operator in terms of its eigenvalues and eigenvectors. If the set eigenvectors $\{|u_1\rangle, |u_2\rangle, |u_3\rangle \dots\}$ form a basis for the Hilbert space, and the set of eigenvalues $\{\lambda_i\}$ satisfying:

$$\hat{A}|u_j\rangle = \lambda_j|u_j\rangle \quad (2.22)$$

Then the operator \hat{A} is decomposed as follows:

$$\hat{A} = \sum_i \lambda_i |u_i\rangle\langle u_i| \quad (2.23)$$

Note that the outer product $|u_i\rangle\langle u_i|$ is gives the identity matrix / operator I .⁷ Hence, we may **diagonalise** the operator \hat{A} if we have found all of its eigenvalues.

⁷If two eigenkets have different eigenvalues they ought to be orthogonal

As for uncountably-infinite dimensional Hilbert spaces , which we refer to by: **inseparable** Hilbert spaces, the spectral theorem reads :

$$\hat{A} = \int d\mu(\lambda)\lambda \quad (2.24)$$

where, $d\mu(\lambda)$ is the integration measure that depends on the nature of spectrum for the measurement outcomes in the theory. We are not going to go further in the details, as they are beyond the scope of our course.

2.9 Projection operators

2.9.1 The identity operator

From the commutativity of Kets with (complex) scalars now follows that

$$\sum_{i \in \mathbb{N}} |e_i\rangle\langle e_i| = \hat{I} \quad (2.25)$$

must be the identity operator, which sends each vector to itself. This can be inserted in any expression without affecting its value, for example

$$\langle v|w\rangle = \langle v|\sum_{i \in \mathbb{N}} |e_i\rangle\langle e_i|w\rangle = \langle v|\sum_{i \in \mathbb{N}} |e_i\rangle\langle e_i|\sum_{j \in \mathbb{N}} |e_j\rangle\langle e_j|w\rangle = \langle v|e_i\rangle\langle e_i|e_j\rangle\langle e_j|w\rangle \quad (2.26)$$

2.9.2 Projection operators

We define the projection operator \hat{P}_α for a normalised vector $|\alpha\rangle$, as :

$$\hat{P}_\alpha \equiv |\alpha\rangle\langle\alpha| \quad (2.27)$$

. Observe that the projection operator is self-adjoint. and satisfies the identity:

$$\hat{P}_\alpha^2 = |\alpha\rangle\langle\alpha||\alpha\rangle\langle\alpha| = |\alpha\rangle\langle\alpha| = \hat{P}_\alpha \quad (2.28)$$

.

2.10 Unitary operators

An operator \hat{U} is called **unitary** if it preserves the inner product for two vectors, and thereby the norm . This also can be stated as:

$$\hat{U}^\dagger \hat{U} = \hat{U} \hat{U}^\dagger = \hat{I}. \quad (2.29)$$

Therefore, a unitary, self-adjoint operator is its own inverse .

2.11 Examples

2.11.1 Rotation in the Euclidean 2-D space

A vector in the 2-D plane is represented by :

$$|r\rangle = \begin{pmatrix} x \\ y \end{pmatrix} \quad (2.30)$$

The basis vectors are:

$$|e_x\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |e_y\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (2.31)$$

We can define a rotation operator $\hat{R}(\vartheta)$, that acts on the vector $|r\rangle$ by rotating it with an angle ϑ . This operator has a matrix representation:

$$\hat{R} = \begin{pmatrix} \cos \vartheta & -\sin \vartheta \\ \sin \vartheta & \cos \vartheta \end{pmatrix} \quad (2.32)$$

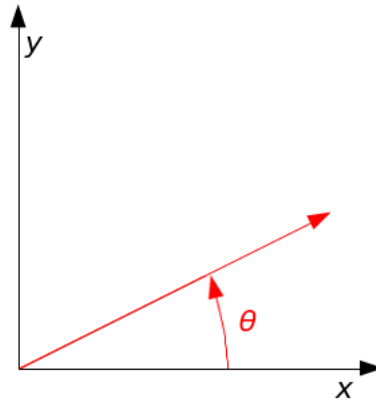


Figure 2.4: The rotation in 2-D space, carried put by the rotation operator.

2.11.2 The differential operator

There are operators also acting on function space, they have the same properties as the operators discussed above, but with slight modifications. For example, the operators acting on function space cannot have an *explicit* matrix representation.

The most famous operators which act on function space are the differential operators; denoted by \hat{L} . There are a variety of differential operators. They play an important rôle in the theory of differential equations. In fact, most of the problems in quantum mechanics are related to the analysis of the differential operators related to dynamical observables; as we shall see.

Take the function $f(x) = e^{\lambda x}$. It is the eigenfunction of the differential operator $\frac{d}{dx}$, with an eigenvalue λ . Hence, we conclude that $e^{\lambda x}$, is a solution to the differential equation:

$$\frac{d}{dx}(f(x)) = \lambda f(x) \quad (2.33)$$

The operator $\frac{d^2}{dx^2}$ has two eigenfunctions $e^{+\lambda x}$ and $e^{-\lambda x}$ they resemble solutions for the differential equation :

$$\frac{d^2}{dx^2}(f(x)) = \lambda f(x) \quad (2.34)$$

And by the superposition principle, a general solution would be:

$$f(x) = Ae^{+\lambda x} + Be^{-\lambda x} \quad (2.35)$$

2.12 Commutators

Just like ordinary matrix multiplication, the product between operators is generally non-commutative. In fact, this particular property of operator multiplication is behind the unfamiliar phenomena observed in quantum mechanics, thus generally we have :

$$\hat{A}\hat{B} \neq \hat{B}\hat{A} \quad (2.36)$$

We define the **commutator** between two operators as:

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \quad (2.37)$$

The commutator satisfies the following properties:

$$[\alpha A + \beta B, C] = \alpha[A, C] + \beta[B, C] \quad \text{linearity in both slots.}$$

$$[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0 \quad \text{Jacobi Identity} \quad \text{For the last prop-}$$

$$[AB, C] = [A, C]B + A[B, C] \quad \text{Product rule}$$

erty, it is a rule of thumb to think of the commutator as a kind of derivative $\mathcal{D}_C = [\cdot, C]$:

$$\mathcal{D}_C(AB) = \mathcal{D}_C(A)B + A\mathcal{D}_C(B)$$

2.13 Function of operator

Just like scalars, one can a function of an operator: $f(\hat{A})$ This is justified because, one can expand the function $f(\hat{A})$ as a series:

$$f(\hat{A}) \approx f_0 I + f_1 \hat{A} + \frac{f_2}{2!} \hat{A} \hat{A} + \dots \quad (2.38)$$

Since operator product is defined, the function itself is well-defined as well
Commutator of a function is given by :

$$[f(\hat{B}), \hat{A}] = \left(\frac{df(\hat{B})}{d\hat{B}} \right) [\hat{B}, \hat{A}] \quad (2.39)$$

Provided that

$$[[\hat{B}, \hat{A}], \hat{A}] = 0$$

Another important formula to learn is the Hadamard Lemma:

$$e^{\hat{A}} \hat{B} e^{-\hat{A}} = \hat{B} + [\hat{A}, \hat{B}] + \frac{1}{2!} [\hat{A}, [\hat{A}, \hat{B}]] + \dots \quad (2.40)$$

2.14 Commuting operators

For two commuting operators,

$$[\hat{A}, \hat{B}] = 0 \quad (2.41)$$

one can find a common set of eigenbasis :

$$\hat{A}|i\rangle = a_i|i\rangle \quad (2.42)$$

$$\hat{B}|i\rangle = b_i|i\rangle \quad (2.43)$$

The eigenkets form a mutual eigenbasis for the states $\hat{A}|\psi\rangle$ and $\hat{B}|\psi\rangle$. Hence one can simultaneously diagonalise both operators.

2.15 Problems

1. Find the eigenvalues of the operator :

$$\hat{A} = \begin{pmatrix} 1 & i & 0 \\ -i & 2 & -i \\ 0 & i & 1 \end{pmatrix}$$

Can we diagonalise it ?.

2. Is the operator d/dx acting on the L^2 Hilbert space hermitian ? How about $-id/dx$?
3. Show that for a Hermitian operator \hat{T} the operator $\hat{U} \equiv e^{i\hat{T}}$ is unitary.
4. Is the function $\cos kx$ an eigenfunction for the operator d/dx ? What about the operator d^2/dx^2 ?
5. Show that for an operator \hat{A} commuting with the **Hamiltonian operator** \hat{H} we can write its time evolution as:

$$e^{i\hat{H}t} \hat{A} e^{-i\hat{H}t}$$

Hint: use Hadmard lemma This is known as **Heisenberg equation**

6. We define the expected value - average value- of an operator with respect to a state vector $|\psi\rangle$ as:

$$\langle \hat{A} \rangle \equiv \langle \psi | \hat{A} | \psi \rangle$$

Show that if $|\psi\rangle$ is expanded in terms of the eigenbasis of \hat{A} , then the expected value is the sum of the eigenvalues of the operator a_n , i.e.

$$\langle \hat{A} \rangle = \sum_n c_n a_n$$

for some constants c_n .

7. Recall that we defined the identity operator as the outer product of the basis :

$$I = \sum_i |i\rangle \langle i|$$

Using this definition, show that this operator sends the ket $|\psi\rangle$ to itself (does not change the ket), then show this for the Bra vector $\langle \psi|$.

8. Discuss why if $[\hat{A}, \hat{B}]|\psi\rangle \neq 0$ one cannot find a mutual eigenbasis to expand $|\psi\rangle$ with ?

Chapter 3

Postulates of Quantum Mechanics

3.1 Introduction

In modern physics course and in modern physics lab, we have seen the clear motivation for using quantum mechanics in place of classical physics for the fundamental description of nature. Classical physics is merely an *approximation* for the real picture of the quantum world .

One of most important lessons learnt from quantum mechanics is the fact that measurement affects the system, no matter how hard ones tries to avoid such effect, it shall remain present (there are exceptions known as *weak measurements*). That implies that the *order* of measuring dynamical quantities of the system matters, hence **non-commutativity** is the heart and soul of quantum mechanics. Max Born tried to make an interpretation for these observable facts. His interpretation states that the quantum system is non-deterministic and each outcome of the measurement has its own probability. Moreover, the system before measurement takes a **superposition** of all of its possible states. The experimental motivation for these statements are assumed to be known by the reader.

3.2 The postulates of quantum mechanics

An axiomatic approach for quantum mechanics is followed in these lectures. The fundamental properties of quantum mechanics are derived from these postulates, as we shall see for the uncertainty principle for example. This approach is more modern and provides a deeper understanding of quantum mechanics. We start by having a classical system , that owns a Hamiltonian H and described by a phase space \mathcal{M} . We also can have a Poisson brackets $\{ \cdot, \cdot \}$. In order to make the quantum leap we have to make the following changes:

3.2.1 The first postulate

The phase space for the system is changed into a Hilbert space :

$$\mathcal{M} \longrightarrow \mathcal{H}$$

The state of the system becomes a ‘Ket’ $|\psi\rangle$ in \mathcal{H} instead of a vector in the phase space as we have seen in lecture (1). This abstract vector is unlike the state vector for the classical system *has no direct physical meaning* . As one can multiply this vector by *any* complex/real number and get the same state for physical system .¹ Hence if $|\psi\rangle$ describes the system , then $a|\psi\rangle$ for a a complex/real number describes the same state for the physics system, This however has rare exceptions (known as Berry phase). Therefore, one can normalise the state vector. such that it satisfies:

$$\langle\psi|\psi\rangle = 1 \quad (3.1)$$

In the probabilistic picture, this reads out as:

$$\begin{aligned} \langle\psi|\psi\rangle &= \sum_i |\psi_i|^2 = \sum_i P(i) \\ &\Leftrightarrow \sum_i P(i) = 1 \end{aligned} \quad (3.2)$$

Surely *the sum of all the probabilities of the possible measurable quantities for the system is ought to equal one.* This postulates implies what Max Born suggested for the statistical nature of quantum mechanics, or more generally the superposition principle (the quantum system takes all of its possible configurations when not measured). .

Recall
Schrödinger’s
cat!

3.2.2 The second postulate

Any dynamical **observable** for a classical system $\omega(p, q)$ is defined to be a **function on the phase space**. Upon quantisation, these observables will be resembled by a **linear self-adjoint (hermitian) operators** acting on the **Hilbert space** $\hat{\Omega}$. Measurement is expressed mathematically by acting the operator corresponding to the physical observable on the state vector. The possible values (outcomes) for a measurement is the set of eigenvalues for that operator. This a direct physical result from the spectral theorem.

¹In fact, the physical state is described by a **ray** in \mathcal{H} , not a one vector.

3.2.3 The third postulate

Because observables are linked to operators, this inherits non-commutativity in quantum mechanics. The third postulate of quantum mechanics is known as the **canonical quantisation postulate**. We replace the Poisson brackets with commutators.

$$[\cdot, \cdot] \longleftrightarrow i\hbar\{\cdot, \cdot\} \quad (3.3)$$

² In particular the for \hat{Q} and \hat{P} , the configuration space/ position and momentum operators will satisfy the **canonical commutation relation**:

$$[\hat{Q}^i, \hat{P}_j] = i\hbar\delta_j^i \hat{I} \quad (3.4)$$

We have learnt that if two operators do not commute, then one cannot have a mutual set of complete eigenbasis to simultaneously diagonalise them. This physically means that one cannot measure both observables with absolute accuracy. Leading to the **uncertainty principal**.

3.2.4 The forth postulate

The fourth postulate discusses the time evolution of a quantum system. The time evolution of a state is dictated by **Schrödinger's equation**.

$$\hat{H}|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}(|\psi(t)\rangle) \quad (3.5)$$

Note here we have the states being time-dependent, whilst operators are not. Sometimes the operators themselves are time-dependent not the states. The first 'picture' is known as Schrödinger's picture, and the second is Heisenberg picture. Both pictures are physically equivalent. The equation of motion for the operators - in Heisenberg picture- is known as Heisenberg equation. We have seen in the tutorials, that for an operator \hat{A} in Schrödinger's picture, we can write it in Heisenberg picture by Hadmard formula:

$$\hat{A}(t)_{\text{Hesenberg}} = e^{\frac{i}{\hbar}\hat{H}t} \hat{A}_{\text{Schrödinger}} e^{-\frac{i}{\hbar}\hat{H}t} \quad (3.6)$$

Using the correspondence between Poisson brackets, and quantum commutators (3.3). One can directly arrive to the **Heisenberg equation** by quantising Hamilton's equations:

$$\frac{d}{dt}\hat{A}(t) = \frac{i}{\hbar}[\hat{H}, \hat{A}(t)] + e^{iHt/\hbar} \left(\frac{\partial \hat{A}}{\partial t} \right) e^{-iHt/\hbar} \quad (3.7)$$

²note that every two operators would commute when $\hbar \rightarrow 0$

3.3 Measurement in quantum mechanics

We have used the word 'measurement' a lot in this lecture, it may be confusing for the reader what is really meant by it within the context of quantum mechanics. One may picture a 'physicist' in a lab who intend to measure a quantum system when thinking of the word measurement. However, measurement may not involve any experiment of actual *detectors*, rather simply it is any interaction between the quantum system and a classical object, which we call the *apparatus*.

In pure quantum mechanical view, there is no meaning for a path of a particle, as

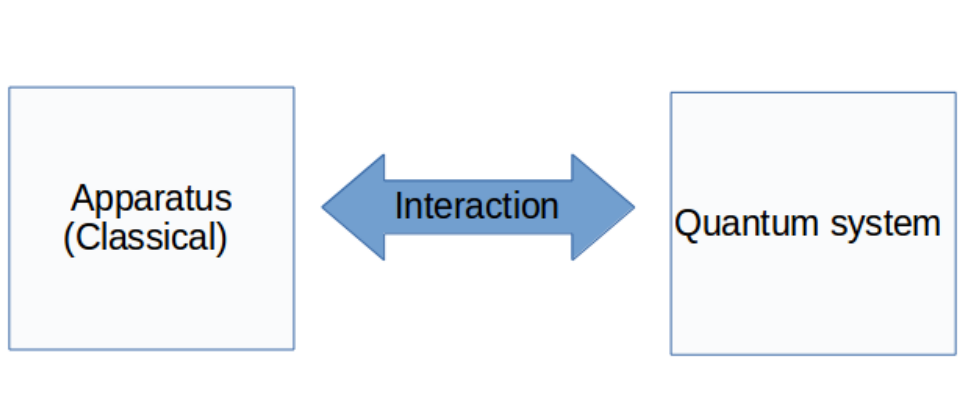


Figure 3.1: Measurement in quantum mechanics means any interaction between a quantum system and a classical object

defining a path requires an absolute knowledge of the momentum and position of that particle simultaneously. Surely this is impossible by the uncertainty principle. Moreover, there is no meaning for the speed in quantum mechanics, because - by definition- speed needs knowing the position of a particle exactly at each moment in time. This has no meaning in quantum mechanics, because of the measurement problem. Yet, one may define a velocity in a different perspective.

These reflections into the postulates of quantum mechanics lead us into the conclusion that in pure quantum mechanical world, there is no meaning for any dynamics we are familiar with from the classical physics. They appear in quantum mechanics merely due to measurement. Hence, we don not only need classical mechanics are the limit of quantum mechanics for macroscopic systems. Moreover, for the construction of quantum theory itself !

3.4 Example: Energy states

A bound electron is found to have discrete energies. The state for the electron is expanded in terms of the Hamiltonian eigen-energy states:

$$|\psi\rangle = \sum_{n=1}^{\infty} \alpha_n |E_n\rangle \quad (3.8)$$

Such that α_n is the probability amplitude for the n^{th} energy state and $|E_n\rangle$ satisfies the eigenvalue problem:

$$\hat{H}|E_n\rangle = E_n|E_n\rangle \quad (3.9)$$

which is -in fact- schrödinger's equation. We can write the Hamiltonian in matrix form :

$$\hat{H} = \begin{pmatrix} E_1 & 0 & 0 & \dots & 0 & \dots \\ 0 & E_2 & 0 & \dots & 0 & \dots \\ 0 & 0 & E_3 & 0 & 0 & \dots \\ 0 & 0 & \dots & E_n & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \dots \\ 0 & 0 & 0 & 0 & & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (3.10)$$

If the measurement resulted the particle having the energy state E_j . The state vector $|\psi\rangle$ is then projected into the eigenstate $|E_j\rangle$ causing of what-so-called the **wavefunction collapse** :

$$\langle E_j|\psi\rangle = \alpha_j \quad (3.11)$$

We may also calculate the expected-value for the energy:

$$\langle E \rangle = \langle \psi|\hat{H}|\psi\rangle \quad (3.12)$$

expanding this as we learnt:

$$\langle \psi|\hat{H}|\psi\rangle = \sum_{n=1}^{\infty} |\alpha_n|^2 E_n \quad (3.13)$$

3.5 Problems

1. Wilson's chamber is a sealed environment containing a supersaturated vapour, when a charged particle - like an electron or alpha particle- passes through the chamber. It leaves a track of cloud behind it. Discuss why we can 'see'

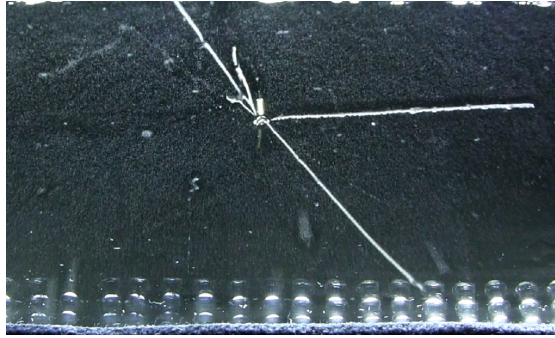


Figure 3.2: Alpha particles from a Radium source in a cloud chamber, notice the path of the particle

the quantum particle's path in this case although we have stated there is no path defined for quantum particles ?

2. If we let the position operator be a multiplicative one; i.e $\hat{Q}^i = q^i$; show that -in order to satisfy the commutation relation discussed in the lecture the momentum operator needs to be $\hat{P}_j = \frac{\hbar}{i} \frac{\partial}{\partial q^j}$.
3. From the previous problem, why we can't use $\hbar \frac{\partial}{\partial q_j}$. As a definition for the momentum operator, and $-iq^i$ as the position operator ?
4. Which is 'bigger' the phase space or the Hilbert space ? Provide a supporting argument for your answer .
5. In a *thought experiment* , imagine having a **quantum coin**. A coin which obeys the laws of quantum mechanics. Describe it mathematically
6. An electron can take 3 possible energy states $E_1 = 0.5eV$, $E_2 = 1.2eV$ and $E_3 = 1.6eV$. With probabilities: $P_1 = 0.8$, $P_2 = 0.13$ and $P_3 = 0.07$.
 - (a) Write the Hamiltonian in matrix form.
 - (b) Write the normalised eigenbasis
 - (c) Find $\langle E \rangle$ and $\sigma(E)$.
 - (d) What is the state ket after measuring the system and finding it taking the second energy state ?
 - (e) Show that $\langle \psi | \psi \rangle = 1$

³Remember that $|\alpha_n|^2 = P(E_n)$

Chapter 4

The Wavefunction

4.1 Position representation

We start naturally from the postulates of quantum mechanics, having the state ket $|\psi(t)\rangle$ (in Schrödinger's picture) that evolves in time by Schrödinger's equation:

$$\hat{H}|\psi(t)\rangle = i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle \quad (4.1)$$

What we are interested in knowing for a free particle is its position, we therefore project the state ket into the position space , and get the **wavefunction**:

$$\psi(x, t) = \langle x | \psi(t) \rangle \quad (4.2)$$

The Hilbert space is therefore : $\mathcal{H} \stackrel{\text{def}}{=} L^2(] - \infty, +\infty[; dx)$ ¹The position operator is simply a multiplicative operator :

$$\hat{X}\psi(x, t) = x\psi(x, t) \quad (4.3)$$

It has a continuous spectrum of eigenvalues being the position(s) of the quantum particle in the 1-dimensional space. Generalisation to 3-D space is straightforward - see homework- . The task now is to find the momentum operator in the position representation, this can be done from investigating the canonical commutation relation $[\hat{X}, \hat{p}_x] = i\hbar \hat{I}$, as following:

$$\begin{aligned} [\hat{X}, \hat{p}_x]\psi(x, t) &= i\hbar\psi(x, t) \\ x\hat{p}_x\psi(x, t) - \hat{p}_x(x\psi(x, t)) &= i\hbar\psi(x, t) \end{aligned} \quad (4.4)$$

¹This Hilbert space implies that the particle could be *anywhere* in the universe until measured; but the **propability vanishes at infinity points**

Rearranging the above equation :

$$\begin{aligned}\hat{p}_x(x\psi(x, t)) &= -i\hbar\psi(x, t) + x\hat{p}_x\psi(x, t) \\ \Leftrightarrow \hat{p}_x(x\psi(x, t)) &= \frac{\hbar}{i} \frac{\partial}{\partial x} (x\psi(x, t))\end{aligned}\quad (4.5)$$

Hence we conclude that the momentum operator in the position representation is given by :

$$\boxed{\hat{p}_x \stackrel{\text{def}}{=} \frac{\hbar}{i} \frac{\partial}{\partial x}} \quad (4.6)$$

4.2 Separation of variables in Schrödinger's equation

Now, we attempt to quantise the free particle system. This is done first by defining the wavefunction and the Hilbert space. Now what is left is to quantise the Hamiltonian; recall that the Hamiltonian for the free particle is given by:

$$H(p) = \frac{p^2}{2m} \quad (4.7)$$

The Hamiltonian operator that acts on the free-particle Hilbert space is $\hat{H} = \frac{\hat{p}^2}{2m}$, since we have the position representation for the momentum operator \hat{p} . We have the Hamiltonian operator:

$$\hat{H} \stackrel{\text{def}}{=} -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad (4.8)$$

Plunging it in the Schrödinger's equation; to obtain:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} = i\hbar \frac{\partial \psi(x, t)}{\partial t} \quad (4.9)$$

Observe the similarity between Schrödinger's equation and the classical wave equation. However, we have derived this equation from an axiomatic approach. In order to solve (4.9) we need to use a mathematical trick known as the **separation of variables**. Assume that we can write the wavefunction as the product of two functions:

$$\psi(x, t) = \varphi(x)h(t) \quad (4.10)$$

Substituting in (4.9), and rearranging, we obtain:

$$-\frac{\hbar^2}{2m} \frac{1}{\varphi(x)} \frac{d^2 \varphi(x)}{dx^2} = i\hbar \frac{1}{h(t)} \frac{dh(t)}{dt} \quad (4.11)$$

Each side of the equation (4.11) depends only on one variable, and since they equal each other. This implies :

$$-\frac{\hbar^2}{2m} \frac{1}{\varphi(x)} \frac{d^2\varphi(x)}{dx^2} = \text{Const.} \quad (4.12a)$$

$$i\hbar \frac{1}{h(t)} \frac{dh(t)}{dt} = \text{Const.} \quad (4.12b)$$

Evidently, the 'constant' is indeed the eigen-energy of the particle E . We start by solving the second equation (4.12b), the solution yields, what-so-called the **stationary states** time evolution:

$$h(t) = e^{-i\omega t}. \quad (4.13)$$

with $\omega = \frac{E}{\hbar}$. Observe this result can be obtained directly from the Heisenberg picture (Show how !) All systems of which we can separate their time dependence in this way is called stationary states. They shall be the main focus in these notes.

4.3 The free-particle solution

We now turn to the spacial part of Schrödinger's equation

$$-\frac{\hbar^2}{2m} \frac{d^2\varphi(x)}{dx^2} = E\varphi(x) \quad (4.14)$$

This has a particular solution of the form

$$u(x) = Ce^{ikx} \quad (4.15)$$

With $k^2 = \frac{2mE}{\hbar^2}$, having the dimension of inverse length; we recognise k being the wavenumber. The solution (4.15) can be written in terms of the momentum - by the relation $p = \hbar k$:-

$$u(x) = Ce^{\frac{i}{\hbar}px} \quad (4.16)$$

This solution is known as the plane wave solution. It represents a wave propagating in the $+x$ direction. This solution can be used to find $\varphi(x)$ by the superposition principle; the 'constant' of integration is not constant in fact. Rather, it is a function of p . In order to see this, recall that the eigen-energy of the free particle $E = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m}$ putting this in (4.9) we shall have a continuous spectrum of eigen-energies. Then use the spectral theorem we shall have therefore :

$$\varphi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \tilde{\varphi}(p) e^{\frac{i}{\hbar}px} dp \quad (4.17)$$

Which is simply the Fourier transform of the momentum wavefunctions $\tilde{\varphi}(p) = \langle p|\varphi \rangle$. We then identify the plane-wave solution as $\langle x|p \rangle = e^{\frac{i}{\hbar}px}$. We can use the wavefunctions to calculate the probability of finding the particle as a given position x' , $|\varphi(x')|^2$ or momentum p' , $|\tilde{\varphi}(p')|^2$.

Since momentum cannot be determined with absolute certainty; it then takes a Gaussian wavefunction. Of which its Fourier transform is a Gaussian function itself. The figure 4.3 is generated by a code we have made showing the time evolution of the wavefunction $\psi(x, t)$, given an initial width for the momentum wavefunction Gaussian : Observe how the wavefunction - indicating our certainty

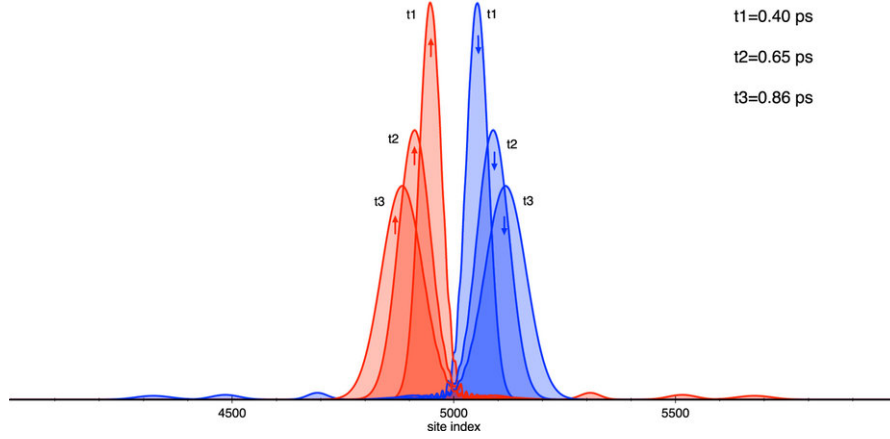


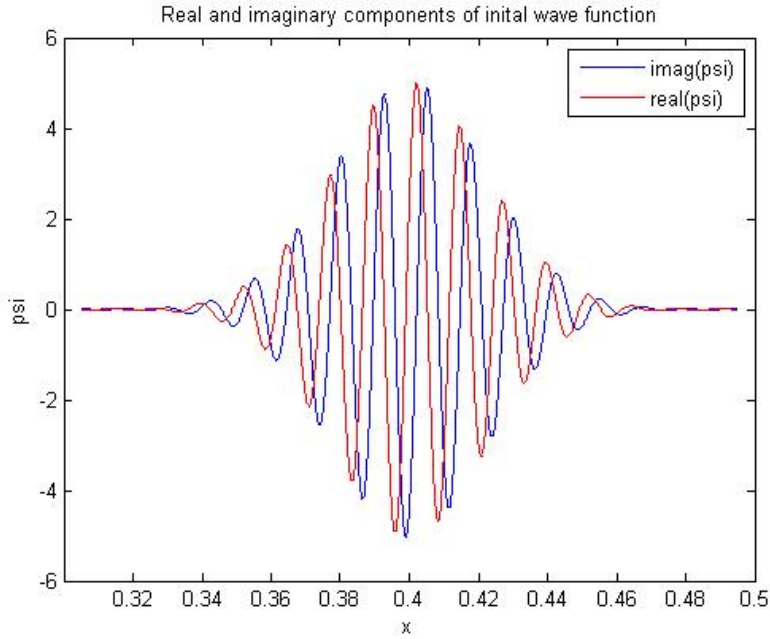
Figure 4.1: Simulated time evolution of a Gaussian wavefunction for the free particle, observe the dispersion of the wave as time progresses

of the particle's position- gets wider and wider as time progresses. The equation (4.17) indicates that the position wavefunction is composed of infinite number of momentum wavefunctions. The movement of the quantum particle is therefore expressed in terms of a **wavepacket** resulting from infinite number of waves interfering; we have run a computer code representing the wavepacket as seen in figure 4.3 :

4.4 Probability flux and density

Since $|\psi(x, t)|^2$ gives the probability of finding the particle at any point in space, at a given time. It defines a positive real-valued function of space. It is known as the **probability density function**:

$$\rho(x, t) = \psi^*(x, t)\psi(x, t) \quad (4.18)$$

Figure 4.2: The wavepacket of the free quantum particle $\psi(x, t)$

We also define the probability current density

$$j(x, t) = \frac{\hbar}{2mi} \left(-\frac{\partial \psi^*(x, t)}{\partial x} \psi(x, t) + \psi^*(x, t) \frac{\partial \psi(x, t)}{\partial x} \right) \quad (4.19)$$

let's now look at $\frac{\partial j(x, t)}{\partial x}$:

$$\begin{aligned} \frac{\partial j(x, t)}{\partial x} &= \frac{d}{dx} \left[\frac{\hbar}{2mi} \left(-\frac{\partial \psi^*(x, t)}{\partial x} \psi(x, t) + \psi^*(x, t) \frac{\partial \psi(x, t)}{\partial x} \right) \right] \\ &= \frac{\hbar}{2mi} \left(-\frac{\partial^2 \psi^*(x, t)}{\partial x^2} \psi(x, t) - \frac{\partial \psi^*(x, t)}{\partial x} \frac{\partial \psi(x, t)}{\partial x} + \right. \\ &\quad \left. \psi^*(x, t) \frac{\partial^2 \psi(x, t)}{\partial x^2} + \frac{\partial \psi^*(x, t)}{\partial x} \frac{\partial \psi(x, t)}{\partial x} \right) \\ &= \frac{\hbar}{2mi} \left(-\frac{\partial^2 \psi^*(x, t)}{\partial x^2} \psi(x, t) + \psi^*(x, t) \frac{\partial^2 \psi(x, t)}{\partial x^2} \right) \end{aligned} \quad (4.20)$$

We can also calculate $\dot{\rho}(x, t)$:

$$\begin{aligned} \dot{\rho}(x, t) &= \frac{\partial}{\partial t} (\psi^*(x, t) \psi(x, t)) \\ &= \frac{\partial \psi^*(x, t)}{\partial t} \psi(x, t) + \psi^*(x, t) \frac{\partial \psi(x, t)}{\partial t} \end{aligned} \quad (4.21)$$

But from Schrödinger's equation, we have $\frac{\partial \psi(x, t)}{\partial t} = \frac{-\hbar}{2mi} \left(\frac{\partial^2 \psi(x, t)}{\partial x^2} \right)$. Hence we incur:

$$\dot{\rho}(x, t) = \frac{\hbar}{2mi} \left(\frac{\partial^2 \psi^*(x, t)}{\partial x^2} \psi(x, t) - \psi^*(x, t) \frac{\partial^2 \psi(x, t)}{\partial x^2} \right) \quad (4.22)$$

$$\Leftrightarrow \frac{\partial j(x, t)}{\partial x} + \dot{\rho}(x, t) = 0 \quad (4.23)$$

This is the continuity equation in quantum mechanics, implying probability is conserved.

4.5 The Born conditions

Max Born's best known contribution to quantum mechanics was his proposal that the wave function, or rather its square modulus, should be interpreted as the probability density for finding the system in a given state at a given time. However, he also proposed four conditions on the wave function which are used in finding many solutions of the Schrödinger equation. As always, it's useful to take another look at the Schrödinger equation (in one dimension (4.14)) so we can see how Born's conditions fit in.

Born's conditions to be imposed on the wave function $\psi(x, t)$ are:

1. the wave function must be single valued. This means that for any given values of x and $\psi(x, t)$ must have a unique value. This is a way of guaranteeing that there is only a single value for the probability of the system being in a given state.
2. The wave function must be square-integrable. In other words, the integral of $|\psi|^2$ over all space must be finite. This is another way of saying that it must be possible to use $|\psi|^2$ as a probability density, since any probability density must integrate over all space to give a value of 1, which is clearly not possible if the integral of $|\psi|^2$ is infinite. One consequence of this proposal is that ψ must tend to 0 for infinite distances.
3. The wave function must be continuous everywhere. That is, there are no sudden jumps in the probability density when moving through space. If a function has a discontinuity such as a sharp step upwards or downwards, this can be seen as a limiting case of a very rapid change in the function. Such a rapid change would mean that the derivative of the function was very large (either a very large positive or negative number). In the limit of a step function, this would imply an infinite derivative. Since the momentum

of the system is found using the momentum operator, which is a first order derivative, this would imply an infinite momentum, which is not possible in a physically realistic system. Such an infinite derivative would also violate condition 4.

4. All first-order derivatives of the wave function must be continuous. Following the same reasoning as in condition 3, a discontinuous first derivative would imply an infinite second derivative, and since the energy of the system is found using the second derivative, a discontinuous first derivative would imply an infinite energy, which again is not physically realistic.

4.6 Problems

1. Calculate $\langle p \rangle$ and $\langle E \rangle$ for the free particle
2. We define the 'group velocity' v_g for a wavepacket as:

$$v_g = \frac{d\omega}{dk}$$

Show that this equals the 'classical velocity' for the particle.

3. We define the 'phase velocity' v_p as:

$$v_p = \frac{\omega}{k}$$

Show it equals half of the classical velocity.

4. If the momentum wavefunction $\tilde{\varphi}(p) \rightarrow \delta(p - p_0)$. Write down $\psi(x, t)$ explicitly. What do you observe ?
5. Show that in Heisenberg picture, we arrive to the same stationary states solution $e^{-i\frac{Et}{\hbar}}$
6. Show that the free particles could have both $k > 0$ and $k < 0$, i.e e^{-ikx} is also a solution to the free particle. What does that mean physically ?
7. Write Schrödinger's equation for the free particle in 3 dimensions.

Chapter 5

The Uncertainty Principle

5.1 The uncertainty principle for the free particle

In the previous lecture, we have derived the expression for the wavefunction of the free particle, for a Gaussian momentum wavefunction with width σ it is given by:

$$\psi(x, t) = \int_{-\infty}^{+\infty} dp e^{-\frac{p^2 t}{2m\hbar}} \frac{e^{-\frac{\sigma^2}{\hbar^2}(p-p_0)^2}}{\left(\frac{2\pi\hbar^2}{4\sigma^2}\right)^{1/2}} \frac{e^{ipx/\hbar}}{\sqrt{\hbar}} \quad (5.1)$$

This integral is a Gaussian itself. Nevertheless, the width of the position Gaussian is inversely proportional to the momentum one, in particular :

$$\sigma(x)\sigma(p) \sim \hbar \quad (5.2)$$

This is a form of the celebrated uncertainty relation for position and momentum, which is directly derived from solving the free particle problem. The physical meaning for this relation is that in order to have a well-defined position for the wave-packet (sharp width), we need to *superimpose* wide momentum wavefunctions ; and vice versa (figure 5.1). Implying the impossibility for having an absolute accurate measurement for either momentum and position regardless of the 'apparatus' used. Moreover, the increase in the accuracy in one implies the decrease in the other quantity.

¹ This principle is what -alone- explains the stability of atoms, counter to what the classical theory of electrodynamics predicts ². Because electrons are bound within the atomic radius $\sim 1 \text{ \AA}$ They have to possess a velocity uncertainty of

¹The uncertainty principle is a fundamental property in nature unrelated to our methods of measurement

²In classical electrodynamics, an accelerating charge emits electromagnetic radiation

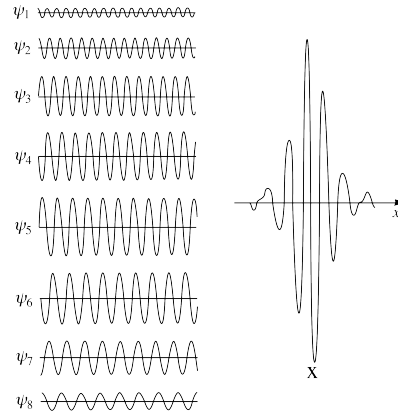


Figure 5.1: The position wavefunction is made from interference of infinite number of momentum wavefunctions

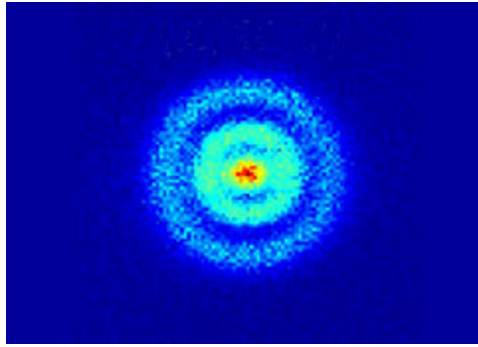


Figure 5.2: A real picture of Hydrogen atom; taken by special techniques. Indicating the probability of electron's position around the nucleus, in complete agreement with quantum theory. Reference: Stodolna, A. S., et al. Phys. Rev. Lett. 110.21 (2013)

about $\sim 3 \times 10^3$ m/s or few eV c^2 of energy. For the electron to fall into the nucleus, i.e. being bound by the nuclear radius $\sim 10^{-5}$ Å; it requires an enormous energy ~ 22 MeV or more. Thus, electrons are forbidden from falling into the nucleus. Figure 5.2 shows how the uncertainty principle, and Schrödinger's equation agrees completely with nature, the picture illustrates a real hydrogen atom's electron wavefunction indicating the probability of finding the electron in the vicinity of the atom.

5.2 General uncertainty principle

We can show - mathematically- a more general form of the uncertainty principle for position and momentum starting from the axioms of quantum mechanics; in particular the canonical commutation relation. We start by defining the variance of an operator $Var(A)$ ³, as :

$$Var(A) = |(A - \langle A \rangle)|^2 = \sigma(A)^2 \quad (5.3)$$

In the position representation this equals to $\int dx \psi^* \sigma(A)^2 \psi$. We define the **Schwartz inequality** :

$$|A|^2 |B|^2 \geq |AB|^2 \quad (5.4)$$

For $A = \sigma(X)$ and $B = \sigma(P)$; we have :

$$Var(X) Var(P) = |\langle X P \rangle|^2 \quad (5.5)$$

But the product XP can be expressed as :

$$XP = \frac{1}{2} [X, P] + \frac{1}{2} (XP + PX) \quad (5.6)$$

Proof :
Start by Writing :

$$XP = XP - \frac{1}{2}PX + \frac{1}{2}XP$$

Moreover :

$$XP = \frac{1}{2}PX + \frac{1}{2}XP - \frac{1}{2}PX + \frac{1}{2}XP$$

Gathering terms, we obtain :

$$XP = \frac{1}{2} [X, P] + \frac{1}{2} (XP + PX) \quad \square$$

Substituting this result in (5.5); and knowing $[X, P] = i\hbar$ we obtain:

$$Var(X) Var(P) \geq |\frac{1}{2}i\hbar|^2 + \frac{1}{4} |(\langle PX \rangle) + \langle XP \rangle|^2 \quad (5.7)$$

Since both $\langle PX \rangle$ and $\langle XP \rangle$ are equal, and the expression $\frac{1}{4} |(\langle PX \rangle) + \langle XP \rangle|^2$ is non-negative . We may write:

³We shall drop the 'hat' whenever it is understood we are talking about an operator

$$\text{Var}(X) \text{Var}(P) \geq \frac{\hbar^2}{4} \quad (5.8)$$

Taking the square root :

$$\boxed{\sigma(X)\sigma(P) \geq \frac{\hbar}{2}} \quad (5.9)$$

In fact, this result can be generalised for any two non-compatible observables A and B :

$$\boxed{\sigma(A)\sigma(B) \geq \frac{1}{2}|\langle[A, B]\rangle|} \quad (5.10)$$

This is the general form of uncertainty principle.

5.3 Uncertainty in time and energy

In modern physics, we were introduced to the **quantum harmonic oscillator**. Although we shall revisit it soon, but we may recall an import result. Which is the **zero-point energy**:

$$E_0 = \frac{1}{2}\hbar\omega \quad (5.11)$$

Although the harmonic oscillator is in its ground state, yet it has an amount of energy inversely proportional to its period of oscillation. If the period is dependent of measurement - like any quantum mechanical observable- to assign the period with accuracy, we need to measure time with precision. This implies a large ω of the oscillator that should be used for measurement since $T \propto \frac{1}{\omega}$. That implies adding a lot of energy to the system - even if it was in the ground state- by the above equation (5.11). In fact this translates to :

$$\boxed{\sigma(E)\sigma(t) \geq \frac{\hbar}{2}} \quad (5.12)$$

This principle holds for any quantum system, not just the harmonic oscillator. However, it is easier to see in this case.

The time-energy uncertainty principle has rather deep implications, in particular for the law of energy conservation. One can 'trade' energy with time, by adding energy -from nothing- to the system provided it is for short period of time. This is an important phenomena observed a lot in particle physics. For example the *weak interaction* which allow beta radiation (neutrons decaying into protons or vice versa). A particle called W- boson , having about 80 times the mass of proton is created from nothing, but for a very short time $\sim 10^{-18}$ sec. Just enough to allow the weak interaction to occur.

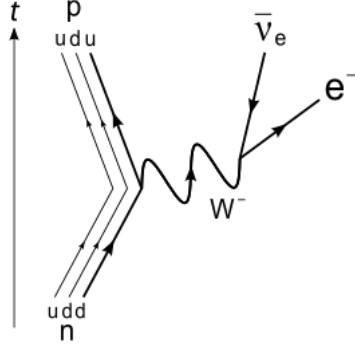


Figure 5.3: A diagram showing the weak interaction mediated by the W boson which is created from nothing by the uncertainty principle

5.4 Ehrenfest theorem

As we have seen, classical mechanics is obtained from averaging quantum mechanical results. For example the conservation of energy is an average result from the uncertainty principle discussed above. Therefore, we need to prove that from quantum mechanics we can arrive to classical equations of motion. This is **Ehrenfest theorem**.

The classical observable ω is the expected-value of the quantum mechanical operator $\hat{\Omega}$:

$$\omega = \langle \hat{\Omega} \rangle = \langle \psi | \hat{\Omega} | \psi \rangle \quad (5.13)$$

Let's take the time derivative of the expected-value $d/dt(\langle \hat{\Omega} \rangle)$:

$$\frac{d}{dt} \left(\langle \psi | \hat{\Omega} | \psi \rangle \right)$$

by the product rule:

$$\frac{\partial \langle \psi |}{\partial t} \hat{\Omega} | \psi \rangle + \langle \psi | \frac{\partial \hat{\Omega}}{\partial t} | \psi \rangle + \langle \psi | \hat{\Omega} \frac{\partial | \psi \rangle}{\partial t}$$

Now by substituting in Schrödinger's equation $\frac{1}{i\hbar} \hat{H} | \psi \rangle = \frac{\partial | \psi \rangle}{\partial t}$, and its complex conjugate. We obtain :

$$\frac{d}{dt} \left(\langle \psi | \hat{\Omega} | \psi \rangle \right) = -\frac{1}{i\hbar} \langle \psi | \hat{H} \hat{\Omega} | \psi \rangle + \langle \psi | \frac{\partial \hat{\Omega}}{\partial t} | \psi \rangle + \frac{1}{i\hbar} \langle \psi | \hat{\Omega} \hat{H} | \psi \rangle$$

This is equivalent to :

$$\boxed{\frac{d}{dt} \left(\langle \hat{\Omega} \rangle \right) = \frac{1}{i\hbar} \langle [\hat{\Omega}, \hat{H}] \rangle + \left\langle \frac{\partial \hat{\Omega}}{\partial t} \right\rangle} \quad (5.14)$$

This is the exact mathematical formula for Ehrenfest theorem. Now, we turn to applying this theorem to the operators p and X , in order to recover the classical equations of motion:

$$\langle \dot{p} \rangle = \frac{1}{i\hbar} \langle [p, V(x)] \rangle$$

since p is time-independent, and the Hamiltonian takes the form : $H = \frac{p^2}{2m} + V$. Working in the position representation, the above commutator is written explicitly as :

$$- \int dx \psi^* \frac{\partial}{\partial x} (V\psi) + \int dx \psi^* V \frac{\partial}{\partial x} (\psi)$$

Applying the product rule to the first expression :

$$- \int dx \psi^* \frac{\partial}{\partial x} (V) \psi - \int dx \psi^* V \frac{\partial}{\partial x} (\psi) + \int dx \psi^* V \frac{\partial}{\partial x} (\psi)$$

Thus we get:

$$\langle \dot{p} \rangle = - \left\langle \frac{\partial V}{\partial x} \right\rangle \quad (5.15)$$

Which is Newton's second law, or one of Hamilton's equations (recall that $F = -\frac{dV}{dx}$)

$$\boxed{\langle [p, H] \rangle = - \left\langle \frac{\partial V}{\partial x} \right\rangle} \quad (5.16)$$

Let's now apply Ehrenfest theorem. to the position operator X :

$$\langle \dot{X} \rangle = \frac{1}{i\hbar} \langle [X, \frac{p^2}{2m}] \rangle$$

since X is also time-independent, and the potential is only a function of position. We need to use the result from lecture (3), equation (22)

$$[A, f(B)] = [A, B] \frac{df(B)}{dB}$$

with $A = X$, $B = p$ and $f(p) = p^2$; we obtain:

$$\langle \dot{X} \rangle = \frac{1}{2im\hbar} \langle [X, p] \frac{d}{dp} (p^2) \rangle$$

\Leftrightarrow

$$= \frac{1}{2im\hbar} (i\hbar) (2\langle p \rangle)$$

Finally :

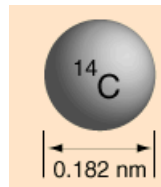
$$\langle \dot{X} \rangle = \frac{1}{m} \langle p \rangle \quad (5.17)$$

The definition for the classical velocity, or the second Hamilton's equation:

$$\boxed{\langle [X, H] \rangle = \frac{1}{m} \langle p \rangle} \quad (5.18)$$

5.5 Problems

1. We define the **first ionisation energy**, as the energy needed to free an electron from the vicinity of its atom. For Carbon 14, it is found; by detailed quantum mechanical calculations and experimental verification that the first ionisation energy is $E_{min} = 11.3 \text{ eV}$.
 - (a) Estimate using the uncertainty principle E_{min} , if you know the electron in the C(14) atom is confined to a box of $x = 0.182 \text{ nm}$. and $E = p^2/2m$
 - (b) Provide an explanation, from the uncertainty principle for not observing 'protons' being confined to atoms; use the last calculations on C(14) as a guide.

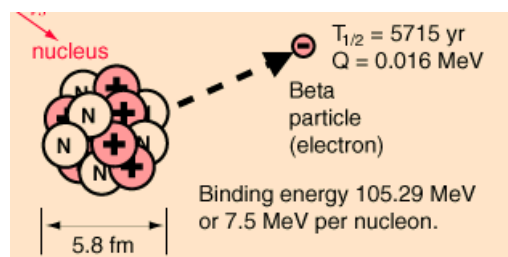


2. What is the origin of electrons in beta decay ?

Beta (β^-) decay is a nuclear decay process that turn a neutron into a proton. This happens when the number of neutrons are imbalanced, hence the nucleus decays by emitting an electron and another particle called the anti-neutrino in order to be stable.

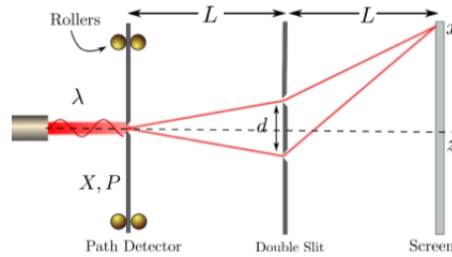
In the early days of nuclear physics, and because of the beta decay, it was argued that the nucleus is composed of electrons and protons. Thus electrons emitted in the beta decay are bound in the nucleus. This is known as the proton-electron hypothesis.

Provide an argument against this hypothesis from the uncertainty principle. Take the C(14) decay into N(14) as an example. The nuclear radius for C(14) is $5.8 \times 10^{-15} \text{ m}$ and the energy of the emitted electron is at maximum $E_{max} = 0.016 \text{ MeV}$.



3. Einstein's Recoiling Slit Experiment.

Einstein was known for his opposition against the quantum theory, although he admitted its validity. One of the arguments Einstein has made against the quantum theory - in particular the uncertainty principle- is a 'modified' version of the double-slit experiment . This full thought experiment is constructed as the figure shows. However, we shall take a simpler one. The



experiment goes as follows :

Imagine having a narrow slit, with small width d , a quantum particle passes through this slit . This let us *detect* its position by d , as a result, this causes a momentum uncertainty of $\sim \frac{h}{2d}$. However, Einstein suggested that we can measure the particle's momentum from the recoil of the screen of which the particle collides with after passing through the slit. If the screen is free to move in the x direction, by the laws of momentum conservation, the recoil of the screen is related to the incident particle momentum. In fact, the extended version of this thought experiment is done experimentally cf.(Nature Photonics 9, 120–125 (2015)).

Of course, Einstein has missed something in his thought experiment. Niels Böhr had provided an answer to Einstein's experiment defending the uncertainty principle. Can you guess what was that argument ?

4. Prove Ehrenfest theorem in Heisenberg picture.

(pictures are from Hyperphysics website, <http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html>)

Chapter 6

Basic Scattering Theory

6.1 Remarks on the quantum scattering theory

Scattering problem in quantum theory is a vast topic, it is the second problem in quantum mechanics along with bounded states one. There are two main cases for a an interacting quantum particle; the first is when it's **bounded to a potential**. The particle takes a **discrete energy spectrum** . The second case, is when the particle is **scattered of a potential**, and takes a **ccontinuous spectrum of energy**.

Hence, we inscribe the incident wavefunction $^o\psi(x, t)$ by a free particle wave-packet (as plane wave). The scatterer, is a stationary potential, that elastically scatter off the incident wave-packet (in our simplified problem), i.e. the energy is conserved. Then the scattered wave shall be a spherical wavefunction $^{out}\psi(\vec{r}, t)$, we care about

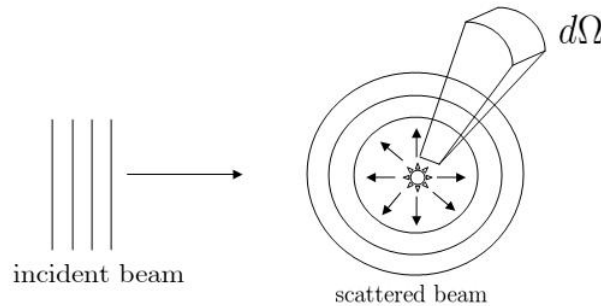


Figure 6.1: Sketch of the scattering problem in quantum mechanics. Notice that we use the wave nature of the quantum particles

the probability for a scattering with a certain solid angle Ω . This is calculated from

the **differential cross-section** see figure 6.1:

$$\frac{d\sigma}{d\Omega} \equiv \frac{N_{\phi,\theta}}{^o j} \quad (6.1)$$

Where $N_{\phi,\theta}$ is the probability of detecting the scattered particle by a detector placed at angles ϕ and θ . And $^o j$ is the incident probability flux current. i.e:

$$^o j = \frac{\hbar}{2mi} \left(^o \psi(x, t)^* \frac{\partial ^o \psi(x, t)}{\partial x} - ^o \psi(x, t) \frac{\partial ^o \psi(x, t)^*}{\partial x} \right) \quad (6.2)$$

However, we shall restrict ourselves to one dimensional scattering problems, where the differential cross section calculation is not the major problem. Rather we are interested in the probability of transmission and reflection of the incident flux.

6.2 Scattering/Reaction channels

In general, for two particles a and b interacting in a scattering problem. We have many possible **reaction channels**; listed as follows:

Reaction channel	Name
$a + b \longrightarrow a + b$	Elastic scattering
$a + b \longrightarrow a + b^*$	Inelastic scattering
$a + b \longrightarrow c + d$	Rearrangement collision
$a + b \longrightarrow c$	Absorption
$a \longrightarrow b + c$	Decay

Table 6.1: Classification of the reaction channels in a tow-particle scattering problem

6.3 Scattering by potentials in 1-D

A moving wave-packet with an energy E approaching some potential variations illustrated in figure . Will have the general solution for their time-independent Schrödinger equation (TISE):

$$\psi_L(x) = Ae^{+ikx} + Be^{-ikx} \quad (6.3a)$$

$$\psi_R(x) = Ce^{+ikx} + De^{-ikx} \quad (6.3b)$$

With:

$$k^2 = \frac{2mE}{\hbar^2}$$

The previous set of equations can be put in a vector form as follows:

$${}^{out}\Psi = S \cdot {}^o\Psi \quad \Leftrightarrow \begin{pmatrix} B \\ C \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} A \\ D \end{pmatrix}. \quad (6.4)$$

This equation resembles the scattering amplitude and S is known as the **S-matrix**, and it plays an important rôle in scattering problems. As the S-matrix elements characterises the full properties of the scattering process.

Recall the current density in (6.2) is conserved, i.e.:

$$j_R = j_L \quad (6.5)$$

That implies:

$$|A|^2 - |B|^2 = |C|^2 - |D|^2 \quad (6.6)$$

Since:

$$j_L = \frac{\hbar k}{m} (|A|^2 - |B|^2) \quad (6.7a)$$

$$j_R = \frac{\hbar k}{m} (|C|^2 - |D|^2) \quad (6.7b)$$

Since we have in our problem the incident flux is from the left only $\Rightarrow D = 0$. We have thereby:

$$T_L = \left| \frac{C}{A} \right|^2 = |S_{21}|^2 \quad R_L = \left| \frac{B}{A} \right|^2 = |S_{11}|^2$$

Or similarly for flux approaching from right $A = 0$:

$$T_R = \left| \frac{B}{D} \right|^2 = |S_{12}|^2 \quad R_R = \left| \frac{C}{D} \right|^2 = |S_{21}|^2$$

With T and R are the transmission and reflection probabilities respectively.

Note that:

$$T_{L(R)} + R_{L(R)} = 1 \quad (6.8)$$

6.4 The optical theorem in 1-D

Consider a free particle ($V = 0$), we can write the its S-matrix as:

$$S = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad (6.9)$$

taking the canonical form. When ($V \neq 0$), S should be written according to the continuity conditions. Let :

$$\psi(x)_L = e^{ikx} + re^{-ikx} \qquad \psi(x)_R = te^{ikx} \qquad (6.10)$$

Satisfying the conditions (V changes at $x = 0$):

$$\psi(x=0)_L = \psi(x=0)_R \qquad \frac{d\psi(x)_L}{dx}\bigg|_{x=0} = \frac{d\psi(x)_R}{dx}\bigg|_{x=0} \qquad (6.11)$$

We obtain the expression for the S-matrix:

$$S = \begin{pmatrix} 2ir & 1 + 2it \\ 1 + 2it & 2ir^* \frac{1+2it}{1-2it^*} \end{pmatrix}, \qquad (6.12)$$

Or:

$$\boxed{|r|^2 + |t|^2 = \Im(t)} \qquad (6.13)$$

Which is **the optical theorem** in one dimension.

Chapter 7

Stationary States

7.1 Particle in a box

We discuss here an application to the mathematical axioms of quantum mechanics studied earlier to a simple, yet important problem. The quantum particle in an infinite potential well, or a particle in a box see figure 7.1. This is an idealisation

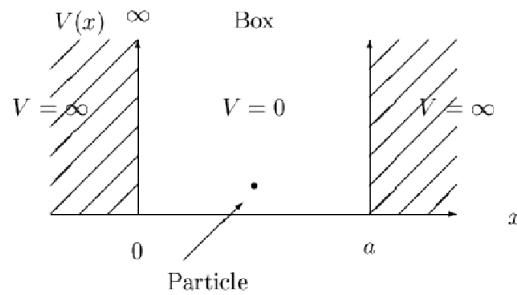


Figure 7.1: A diagram illustrating the particle in a box problem

for a large enough potential compared to the particle's energy. This problem is very important example to study discrete spectrum .

We start by a particle trapped in a potential well, of width a . The Schrödinger's equation for this particle is written as - in position representation-:

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t) + V(x) \psi(x, t) \quad (7.1)$$

With :

$$V(x) = \begin{cases} 0, & \text{for } 0 < x < a \\ \infty, & \text{otherwise} \end{cases} \quad (7.2)$$

Since the above equation is clearly separable, similar to the free particle. It resembles a stationary state. We then write the eigenvalue problem:

$$\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} u(x; E) + V(x)u(x; E) = Eu(x; E) \quad (7.3)$$

The energy eigenfunctions are then equal to $\psi(x, t; E) = u(x; E) e^{-i\hbar\omega t}$

7.1.1 Solution to Schrödinger's equation

We now attempt to solve (7.3) subject to the boundary conditions:

$$u(x = 0) = u(x = a) = 0 \quad (7.4)$$

Because there is a null probability of the particle being outside the box. And the second condition on the wavefunction :

$$\frac{du(x)}{dx} \Big|_{x=0} = \frac{du(x)}{dx} \Big|_{x=a} \quad (7.5)$$

This condition comes from naturally from the analysis of the problem. The first derivative of the wavefunction is proportional to the momentum of the particle, we expect the particle will 'bump' with both walls in the same manner. Although, this violates the *Born conditions* discussed in lecture 5, but keep in mind that the infinite well is an unphysical example!

Now, we rewrite Schrödinger's equation as:

$$\frac{d^2 u(x)}{dx^2} + k^2 u(x) = 0 \quad (7.6)$$

with $k = \sqrt{2mE}/\hbar$; this differential equation is solved by the substitution $u(x) = e^{Rx}$ Resulting:

$$u(x) = Ae^{ikx} + Be^{-ikx} \quad (7.7)$$

Where A and B are constants, we use the identity :

We observe that, using the boundary conditions we obtain :

$$\begin{aligned} ik(Ae^{ika} - Be^{-ika}) &= ik(A - B) \\ \Rightarrow u(x) &= C \sin(kx) \end{aligned} \quad (7.8)$$

$$\begin{aligned} u(a) &= C \sin(ka) = 0 \\ \Rightarrow k &= \frac{n\pi}{a} \end{aligned} \quad (7.9)$$

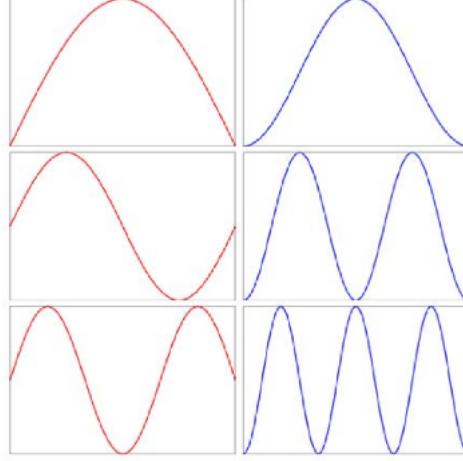


Figure 7.2: First, second, and third lowest-energy eigenfunctions (red) and associated probability densities (blue) for the infinite square well potential

But since $k = \sqrt{2mE}\hbar$, we conclude that energy takes discrete values :

$$\begin{aligned} E_n &= \frac{\hbar^2 n^2 \pi^2}{2ma^2} \\ &= E_0 n^2 \end{aligned} \quad (7.10)$$

With $E_0 = \frac{\hbar^2 \pi^2}{2ma^2}$, the ground energy. And n here denotes the **quantum number** for the excited states of the particle in the box. Now, we may write the energy-eigenfunctions, after calculating the normalisation factor $C = \sqrt{\frac{2}{a}} e^{i\varphi}$ ¹

$$\psi_n(x, t) = \sqrt{\frac{2}{a}} \left(\sin\left(\frac{n\pi x}{a}\right) \right) e^{i(\omega t + \phi)} \quad (7.11)$$

The total wavefunction is written as, by the superposition principle :

$$\psi(x, t) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} \left(\sin\left(\frac{n\pi x}{a}\right) \right) e^{i(\omega t + \phi)} \quad (7.12)$$

Which is a Fourier series (we could have obtained this solution immediately by Fourier analysis). The following figure demonstrates the eigenfunctions for various excitation states, and the probability density function ρ :

¹we can always add an arbitrary phase factor $e^{i\varphi}$

7.1.2 Momentum eigenfuctions

We now turn into calculation the Fourier transform of $u(x)$ in order to compute the momentum eigenfuctions $\phi(p, t)$:

$$v(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_0^a dx \underbrace{e^{\frac{i}{\hbar}px}}_{\langle p|x \rangle} \underbrace{u(x)}_{\langle x|u \rangle} \quad (7.13)$$

substituting with $u(x)$ we have:

$$v(p) = \frac{1}{\sqrt{\pi a \hbar}} \int_0^a dx e^{\frac{i}{\hbar}px} \sin(n\hbar px) \quad (7.14)$$

Evaluation of this integral gives: ²

$$v(p) = n\sqrt{\frac{a\pi}{\hbar}} \left(\frac{1 - (-1)^n e^{-\frac{i}{\hbar}pa}}{n^2\pi^2 - a^2\frac{p^2}{\hbar^2}} \right) \quad (7.15)$$

Plotting the momentum probability density function - for various excitations - : This calculation ends the basic analysis for a particle in a box.

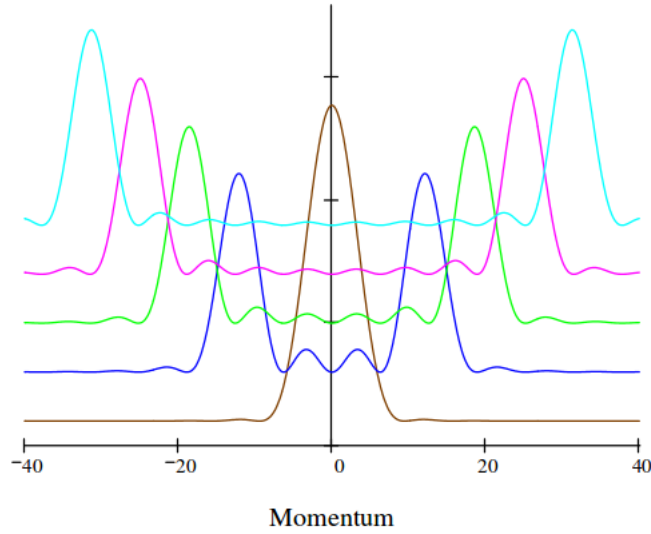


Figure 7.3: Momentum probability density function for the ground state and three more excitation states.

²The following identity was used :
 $\int e^{ax} \sin bx \, dx = \frac{e^{ax}}{a^2 + b^2} (a \sin bx + b \cos bx)$

7.2 Simple Harmonic Oscillator

7.2.1 Quantization of the SHO Hamiltonian

From lecture (1) we have the classical Hamiltonian for the simple harmonic oscillator (SHO) :

$$H(p, x) = \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2x^2 \quad (7.16)$$

Using the postulates of quantum mechanics discussed before, we obtain- upon quantization - the Hamiltonian operator

$$\hat{H} = \frac{1}{2m}\hat{P}^2 + \frac{1}{2}m\omega^2\hat{X}^2 \quad (7.17)$$

The Hilbert space of which \hat{X} and \hat{P} act on is

$$\mathcal{L}^2(-\infty, +\infty; dx)$$

We now introduce the dimensionless Hamiltonian

$$\hat{H}' = \frac{1}{2m\hbar\omega}\hat{P}^2 + \frac{1}{2}\frac{m\omega}{\hbar}\hat{X}^2 \quad (7.18)$$

This operator can be factorised and written in terms of 'creation' and 'inhilation' operators; a^\dagger and a respectively

$$\hat{H}' = a^\dagger a + \frac{1}{2}I \quad (7.19)$$

with:

$$a = \sqrt{\frac{m\omega}{2\hbar}}\hat{X} + i\sqrt{\frac{1}{2m\omega\hbar}}\hat{P} \quad (7.20a)$$

$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\hat{X} - i\sqrt{\frac{1}{2m\omega\hbar}}\hat{P} \quad (7.20b)$$

These operators, along with \hat{H}' , satisfy a well-known commutation relations. ³

$$[a, a^\dagger] = I \quad (7.21a)$$

$$[a, H'] = a \quad (7.21b)$$

$$[a^\dagger, H'] = -a^\dagger \quad (7.21c)$$

³The operators a , a^\dagger and H' along with the commutator operation $[\cdot, \cdot]$ satisfy the $su(1, 1)$ algebra.

We also define the **number operator** $N \equiv a^\dagger a$ that acts on the eigenstates $|n\rangle$ resulting an eigenvalue of n :

$$N|n\rangle = n|n\rangle$$

as a result we may conclude that

$$a|0\rangle = 0 \quad (7.22)$$

acting on the 'ground state' by the inhalation operator, kills it. Moreover

$$a|n\rangle = \sqrt{n}|n-1\rangle \quad (7.23)$$

$$a^\dagger|n\rangle = \sqrt{(n+1)}|n+1\rangle \quad (7.24)$$

Hence, The Hamiltonian acting on these states will result (the energy eigenvalue)

$$\hat{H}|n\rangle = \hbar\omega\left(n + \frac{1}{2}\right)|n\rangle \quad (7.25)$$

Implying that the 'number states' are the excitation states for the quantum harmonic oscillator. The creation and inhalation operators excite or deexcite it, and it has a discrete energy spectrum of :

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \quad (7.26)$$

Even in the ground state, the quantum harmonic oscillator has a non-vanishing energy. This is a direct result for the uncertainty principle in time and energy.

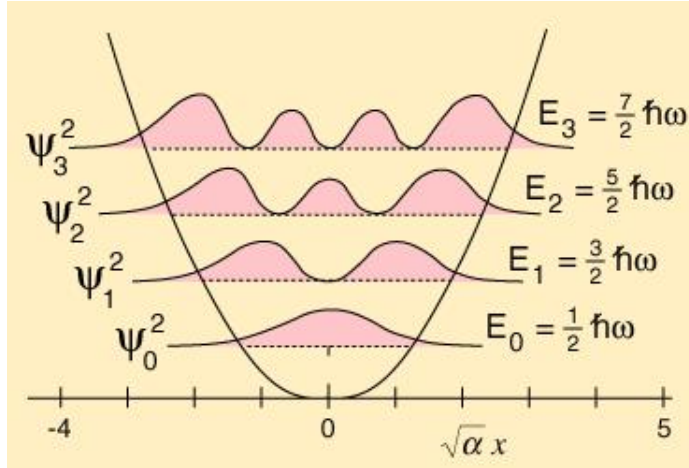


Figure 7.4: Energy-levels and wavefunctions of the quantum harmonic oscillator

7.2.2 The eigenfunctions

Since we introduced the eigenstates for the Hamiltonian (or the number operator equivalently). $|n\rangle$. We can use the ladder operator method to solve Schrödinger's equation in the position representation and find $\psi_n(x) = \langle x|n\rangle$.

we start from (7.22):

$$a\psi_0(x) = 0 \quad (7.27)$$

resulting the differential equation,

$$\left(x + \frac{\hbar}{m\omega} \frac{d}{dx}\right) \psi_0(x) = 0 \quad (7.28)$$

having the solution:

$$\psi_0(x) = Ae^{-\frac{m\omega}{2\hbar}x^2} \quad (7.29)$$

We can find the normalisation factor by:

$$\int_{-\infty}^{+\infty} e^{-\frac{m\omega}{2\hbar}x^2} dx = \frac{1}{|A|^2}. \quad (7.30)$$

Which is a typical Gaussian, hence A is found to be,

$$A = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \quad (7.31)$$

Now, in order to find the n th wavefunction $\psi_n(x)$, we first need to prove the following identity

$$|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle \quad (7.32)$$

Proof:

$$\frac{a^\dagger}{\sqrt{n}} |n-1\rangle = \frac{(a^\dagger)^2}{\sqrt{n(n-1)}} |n-2\rangle = \dots = \frac{(a^\dagger)^n}{\sqrt{n!}} |0\rangle.$$

Thereby,

$$\psi_n(x) = \frac{(a^\dagger)^n}{\sqrt{n!}} \psi_0(x) \quad (7.33)$$

Writing the expression explicitly , we obtain :

$$\psi_n(x) \equiv \langle x | n \rangle = \frac{1}{\sqrt{2^n n!}} \pi^{-1/4} \exp(-x^2/2) H_n(x) \quad (7.34)$$

Where $H_n(x)$ is the n th Hermit polynomial, that having the generating formula (Rodrigues's formula)

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2} \quad (7.35)$$

They are one of the classical orthogonal polynomials.

Note that this result can be obtained by solving immediately the Schrödinger's equation (using series solution, or Sturm-Liouville theorem).

7.2.3 Coherent states

Coherent states are a very important topic in quantum mechanics. Coherent states are quantum states that display an oscillatory behaviour similar to the one displayed in the simple harmonic oscillator. Formally, a coherent state is a state that has a minimum uncertainty, and takes the form (where a here is the annihilation operator) :

$$a|\alpha\rangle = \alpha|\alpha\rangle \quad (7.36)$$

The ground state $|0\rangle$ is a coherent state. Since it has the minimum uncertainty :

$$\langle\Delta X\rangle_0\langle\Delta P\rangle_0 = \frac{\hbar}{2} \quad (7.37)$$

This is not however the case for the stationary states $|n\rangle$, as we can show that:

$$\langle\Delta X\rangle_n\langle\Delta P\rangle_n = \frac{\hbar}{2}(2n+1) \quad (7.38)$$

Hence the states $|\alpha\rangle$, the coherent states of the Harmonic oscillator are not stationary states. Their time evolution is important in the classical limit, as it leads to Ehrenfest theorem, and one can obtain from them the Classical equations of motion for the Harmonic oscillator. Hence the classical harmonic oscillator is the limit for the coherent states $|\alpha\rangle$, not the states $|n\rangle$. However the detailed mathematical argument is beyond the scope of this course, the interested reader might want to refer to any Textbook in the references for details.

7.3 Problems

7.3.1 Particle in a box

1. Using the uncertainty principle for position and momentum, estimate the ground state energy for an infinite well of width a , compare the obtained result with the one found in the lecture.
2. Compute $\langle E \rangle$, $\langle p \rangle$ and $\langle x \rangle$ for the particle in a box.
3. Show that the normalisation factor for the particle in a box wavefunction is given by $\sqrt{\frac{2}{a}}$
4. Show that the eigenfunctions $u_n(x)$ are orthogonal .
5. What is the ground state, first excited and second excited states energies for an electron trapped in an infinite well of width 1 Å.

7.3.2 Simple Harmonic Oscillator

1. Express the position and momentum operators X and P in terms of a and a^\dagger
2. Verify the commutation relations of the triple H', a and a^\dagger stated in the lecture notes, recall the canonical commutation relation $[X, P] = i\hbar I$.
3. Find $\langle X \rangle$, $\langle P \rangle$, $\langle X^2 \rangle$ and $\langle P^2 \rangle$.
4. A quantum harmonic oscillator, in the 2nd excited state, having an energy of 2.45eV , find its angular frequency, and period.
5. Find the eigenfunction $\psi_1(x)$, and show that it is orthogonal to $\psi_0(x)$ seen in the lecture.
6. From problem (3), verify the uncertainty relation for position and momentum.
7. Verify that $a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$
8. Write the operators a and a^\dagger as matrices acting on the vector states :

$$|0\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix} \quad |1\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix} \quad |2\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ \vdots \end{pmatrix} \dots$$

Chapter 8

Angular Momentum

8.1 The Classical angular momentum

Recall that the angular momentum for a system is given by :

$$\vec{L} = \sum_i \vec{r}_i \wedge \vec{p}_i \quad (8.1)$$

With \wedge being the cross (wedge) product between the position \vec{r}_i and linear momentum \vec{p}_i of the i th degree of freedom in the system. For a single particle in 3 D we give a precise definition for the angular momentum :

$$\vec{L} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \quad (8.2)$$

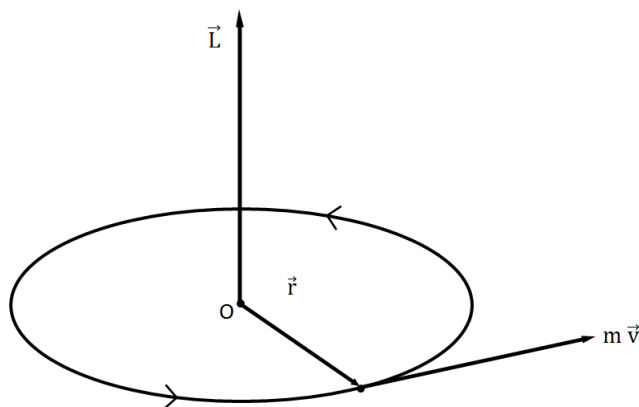


Figure 8.1: Illustration for the angular momentum of a classical rotating particle

8.2 Quantisation of the angular momentum

One can apply the canonical quantisation for the angular momentum observable and turn it into a vector operator, since it is defined -classically- by the coordinates and linear momenta :

$$[x^i, p_j] = i\hbar\delta_j^i \quad [x^i, x^j] = 0 \quad [p_i, p_j] = 0 \quad (8.3)$$

Hence the angular momentum operators are (dropping the hat) :

$$\begin{aligned} L_x &= -i\hbar(y\partial_z - z\partial_y) \\ L_y &= -i\hbar(z\partial_x - x\partial_z) \\ L_z &= -i\hbar(x\partial_y - y\partial_x) \end{aligned} \quad (8.4)$$

Or we may write them in the spherical coordinates (r, φ, θ) :

$$\begin{aligned} L_x &= i\hbar(\sin\varphi\partial_\theta + \cot\theta\cos\varphi\partial_\varphi) \\ L_y &= i\hbar(-\cos\varphi\partial_\theta + \cot\theta\sin\varphi\partial_\varphi) \\ L_z &= -i\hbar\partial_\varphi \end{aligned} \quad (8.5)$$

We also define the operator :

$$L^2 = L_x^2 + L_y^2 + L_z^2 \quad (8.6)$$

It is a formidable, yet straightforward task to prove the following commutation relations:

$$[L_x, L_y] = i\hbar L_z \quad [L_y, L_z] = i\hbar L_x \quad [L_z, L_x] = i\hbar L_y \quad (8.7a)$$

$$[L^2, L_i] = 0 \quad \text{For all } i = x, y, z \quad (8.7b)$$

We can also define the (rising and lowering) operators:

$$L_\pm = L_x \pm iL_y \quad (8.8)$$

Along with $L_z = L_3$ they satisfy a well-known commutation relations, known as the $su(2)$ algebra :

$$[L_+, L_-] = 2\hbar L_3 \quad (8.9a)$$

$$[L_\pm, L_3] = \mp\hbar L_\pm \quad (8.9b)$$

The rising and lowering operators are expressed in the coordinate representation as :

$$L_\pm = \pm e^{\pm i\varphi} (\partial_\theta \pm i \cot\theta \partial_\varphi) \quad (8.10)$$

8.3 The spherical harmonics

As we maintain in the coordinate representation, we wonder about the eigenfunction for the operator L_3 and their properties. The operator L_3 has a special importance over the other two angular momentum operators, as the latter ones compose the ladder(rising and lowering) operators. We start by assuming such wavefunction :

$$L_3 Y_\ell^m(\theta, \varphi) = m Y_\ell^m(\theta, \varphi). \quad (8.11)$$

With m and ℓ are eigenvalues, and m takes an integer values between ℓ and $-\ell$, this shall be made clear in the next lecture. However, at the meantime, we just accept these as given facts.

Therefore, we conclude that :

$$Y_\ell^m(\theta, \varphi) = e^{im\varphi} y_{\ell m} \quad (8.12)$$

Moreover, the fact that $L_\pm y_{\ell \pm \ell} = 0$ gives us the differential equation:

$$(\partial_\theta - \ell \cot \theta) y_{\ell \pm \ell} = 0 \quad (8.13)$$

Whose complete solution gives us the explicit expression of the functions Y_m^ℓ , which are known as the **Spherical Harmonics**

$$Y_\ell^m = (-1)^m \sqrt{\frac{2\ell+1}{4\pi} \frac{(\ell+m)!}{(\ell-m)!}} e^{im\varphi} P_m^\ell(\theta) \quad (8.14)$$

With $P_m^\ell(\theta)$ is the associated Legendre Polynomial.

The spherical harmonics form a complete orthonormal basis for the Hilbert space :

$$\mathcal{H} = \mathcal{L}^2(S^2, d\Omega)$$

With S^2 being the unit sphere, and $d\Omega = d\phi \sin \theta d\theta$, the solid angle element of the unit sphere.

8.4 Properties of the spherical harmonics

- Eigenvalue for L^2 :

$$L^2 Y_\ell^m(\theta, \varphi) = \ell(\ell+1) Y_\ell^m(\theta, \varphi). \quad (8.15)$$

- Orthonormality :

$$\int_{angles} Y_{\ell_1}^{m_1}(\theta, \varphi) Y_{\ell_2}^{*m_2}(\theta, \varphi) d\Omega = \delta_{m_1, m_2} \delta_{\ell_1, \ell_2} \quad (8.16)$$

- Since the spherical harmonics form an orthonormal basis, the product of two of them is again expressed in terms of spherical harmonics. Take the product $Y_{\ell_1}^{m_1}(\theta, \varphi) \cdot Y_{\ell_2}^{m_2}(\theta, \varphi)$, we can directly conclude that the resultant product is a multiple of the spherical harmonics having $M = m_1 + m_2$ since the term containing m is only an exponential, moreover, L taking the range $|\ell_1 - \ell_2| \leq L \leq |\ell_1 + \ell_2|$. The general rule for multiplication is given by Wigner 3j-symbols (or Clebsh-Gordon coefficients) $C(\ell_1, m_1; \ell_2, m_2; L, M)$ that shall be studied later in the addition of angular momenta.

$$Y_{\ell_1}^{m_1}(\theta, \varphi) \cdot Y_{\ell_2}^{m_2}(\theta, \varphi) = \sum_{M, L} \sqrt{\frac{(2\ell_1 + 1)(2\ell_2 + 1)(2L + 1)}{4\pi}} \times \begin{pmatrix} \ell_1 & \ell_2 & L \\ m_1 & m_2 & M \end{pmatrix} Y_L^{*M}(\theta, \varphi) \begin{pmatrix} \ell_1 & \ell_2 & L \\ 0 & 0 & 0 \end{pmatrix} \quad (8.17)$$

Where the Racah symbol is expressed in terms of 3j symbol

$$\begin{pmatrix} \ell_1 & \ell_2 & L \\ m_1 & m_2 & M \end{pmatrix} = (-1)^{\ell_1 - \ell_2 - M} \frac{1}{\sqrt{2L + 1}} C(\ell_1, m_1; \ell_2, m_2; L, -M) \quad (8.18)$$

These relations will prove useful as we discuss the addition of angular momenta.

- The Herglotz generating function
If the quantum mechanical convention is adopted for the Y_ℓ^m , then,

$$e^{v\mathbf{a} \cdot \mathbf{r}} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \sqrt{\frac{4\pi}{2\ell + 1}} \frac{r^\ell v^\ell \lambda^m}{\sqrt{(\ell + m)!(\ell - m)!}} Y_\ell^m. \quad (8.19)$$

with

$$\mathbf{a} = \hat{\mathbf{z}} - \frac{\lambda}{2}(\hat{\mathbf{x}} + i\hat{\mathbf{y}}) + \frac{1}{2\lambda}(\hat{\mathbf{x}} - i\hat{\mathbf{y}}) \quad (8.20)$$

λ here is a real parameter

More properties are found in the textbooks. We list here some of the spherical harmonics and their graphical representation:

$$Y_0^0(\theta, \varphi) = \frac{1}{2} \sqrt{\frac{1}{\pi}} \quad (8.21)$$

$$Y_1^{-1}(\theta, \varphi) = \frac{1}{2} \sqrt{\frac{3}{2\pi}} \cdot e^{-i\varphi} \cdot \sin \theta = \frac{1}{2} \sqrt{\frac{3}{2\pi}} \cdot \frac{(x - iy)}{r} \quad (8.22)$$

$$Y_1^0(\theta, \varphi) = \frac{1}{2} \sqrt{\frac{3}{\pi}} \cdot \cos \theta = \frac{1}{2} \sqrt{\frac{3}{\pi}} \cdot \frac{z}{r} \quad (8.23)$$

$$Y_1^1(\theta, \varphi) = -\frac{1}{2} \sqrt{\frac{3}{2\pi}} \cdot e^{i\varphi} \cdot \sin \theta = -\frac{1}{2} \sqrt{\frac{3}{2\pi}} \cdot \frac{(x + iy)}{r} \quad (8.24)$$

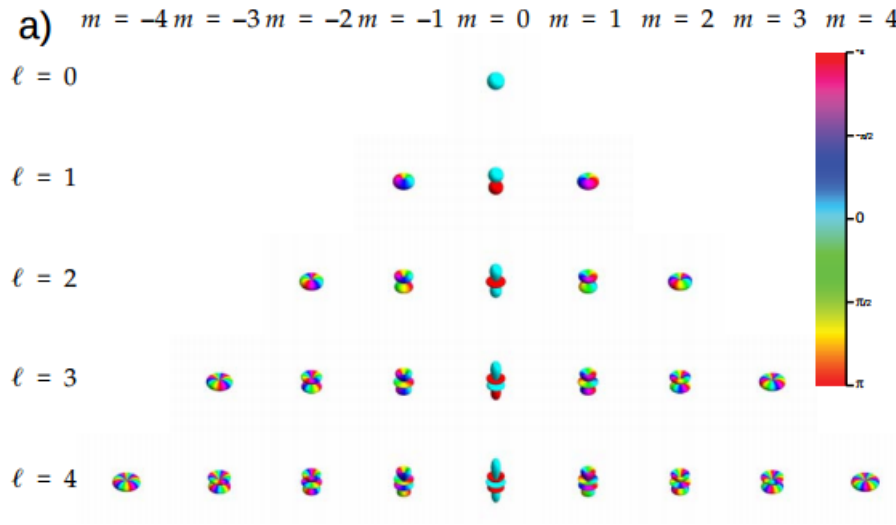


Figure 8.2: Graphical representation for some of the spherical harmonics, the colour coding represents the probability density calculated via $|Y_m^\ell(\theta, \varphi)|^2$

8.5 Angular momentum eigenstates

We now use more abstract method to analyse the angular momentum spectrum, by introducing the eigenstates for L^2 and L_3

$$|\beta, m\rangle \quad (8.25)$$

such that :

$$L^2|\beta, m\rangle = \beta|\beta, m\rangle \quad (8.26a)$$

$$L_3|\beta, m\rangle = m\hbar|\beta, m\rangle. \quad (8.26b)$$

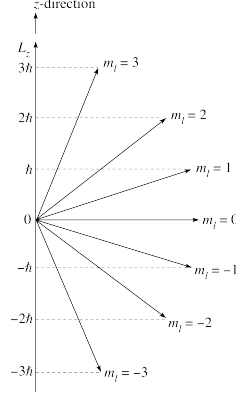


Figure 8.3: The z-component of the angular momentum is quantised

Now we look at the effect of the operators L_{\pm} on the eigenstates:

$$\begin{aligned}
 L_3 L_{\pm} |\beta, m\rangle &= L_{\pm} L_3 |\beta, m\rangle + [L_3, L_{\pm}] |\beta, m\rangle \\
 &= L_{\pm} (L_3 \pm \hbar) |\beta, m\rangle \\
 &= L_{\pm} (m\hbar \pm \hbar) |\beta, m\rangle \\
 \Rightarrow L_{\pm} |\beta, m\rangle &= |\beta, m \pm 1\rangle
 \end{aligned} \tag{8.27}$$

Therefore, the operators L_{\pm} acting on the eigenstates rise / lower the state, just like the creation and annihilation operators seen in the quantum harmonic oscillator. In fact, the operator L_+ rotates the angular momentum towards the z axis, whilst L_- rotates it away from the z axis towards the $-z$ axis.

8.6 The spectrum of angular momentum observable

Now consider the following expected values :

$$\langle L_3^2 \rangle = \hbar^2 m^2 \tag{8.28a}$$

$$\begin{aligned}
 \langle L^2 \rangle &= \langle L_1^2 \rangle + \langle L_2^2 \rangle + \langle L_3^2 \rangle \\
 \beta &= a^2 + b^2 + \hbar^2 m^2
 \end{aligned} \tag{8.28b}$$

For some numbers a and b . In order to find the explicit relation between β and m , we ought to investigate the spectrum of the angular momentum further.

We know, that for some value m_{max} and m_{min} :

$$L_+ |\beta, m_{max}\rangle = 0 \tag{8.29a}$$

$$L_- |\beta, m_{min}\rangle = 0 \tag{8.29b}$$

since the angular momentum will be totally aligned with the z or $z-$ after successive application of L_+ or L_- . If we let $\ell\hbar$ be the total angular momentum eigenvalue, then obviously $m_{max} = \ell$ and $m_{min} = -\ell$.

Now we analyse (5b) further :

$$\begin{aligned}
 \langle \beta, m_{max} | L_+^\dagger L_+ | \beta, m_{max} \rangle &= 0 \\
 \langle \beta, m_{max} | (L_1 - iL_2)(L_1 + iL_2) | \beta, m_{max} \rangle &= 0 \\
 \langle \beta, m_{max} | L_1^2 + L_2^2 + i[L_1, L_2] | \beta, m_{max} \rangle &= 0 \\
 \langle \beta, m_{max} | L^2 - L_3^2 - L_3 | \beta, m_{max} \rangle &= 0 \\
 \beta - \hbar^2 m_{max} - \hbar m_{max} &= 0 \\
 \Rightarrow \beta &= \hbar^2 \ell(\ell + 1)
 \end{aligned} \tag{8.30}$$

Hence, we may denote the eigenstates in terms of ℓ instead of β , which is more physically relevant :

$$|\beta, m\rangle \longleftrightarrow |\ell, m\rangle$$

Such that:

$$L^2 |\ell, m\rangle = \hbar^2 \ell(\ell + 1) |\ell, m\rangle \tag{8.31}$$

Hence the magnitude of the angular momentum observable :

$$\langle L \rangle = \hbar \sqrt{\ell(\ell + 1)} \tag{8.32}$$

We may now write a full description for the angular momentum spectrum:

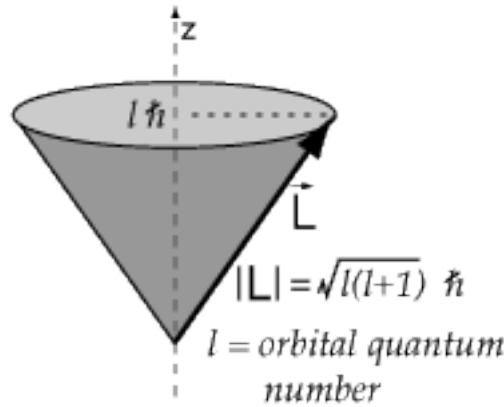


Figure 8.4: A vector model of the orbital quantum number

1. The **orbital** angular momentum eigenvalue is ℓ , it refers to the maximum positive or negative value the orbital angular momentum can take.

2. The z-component of the **orbital** angular momentum is m , sometimes , when other angular momenta are included we refer to it by m_ℓ takes the **integer** values between $+\ell$ and $-\ell$.
3. The length of the angular momentum is $\hbar\sqrt{\ell(\ell+1)}$.
4. We call ℓ the orbital / azimuthal quantum number and m_ℓ the magnetic quantum number.
5. There are other types of angular momenta, that shall be explored later, same analysis will be applied to them.

8.7 Problems

1. Verify that the operator L^2 commutes with all the angular momentum operator components L_z, L_x and L_y .
2. Verify the commutator algebra relations for L_\pm and L_z using the commutator relations between angular momentum operator components commutation relations.
3. Show that Y_1^0 and Y_1^1 are orthogonal.
4. Write the Hamiltonian operator for a system of two particles with reduced mass μ orbiting each other, in the position representation.
5. Calculate directly the product $Y_1^1 \cdot Y_1^0$.
6. Write all the eigenstates for the orbital quantum number $\ell = 3$
7. Draw the z components of the angular momentum states above
8. What is the minimal length of the momentum vector observable that carries the quantum number $m = -4\hbar$?
9. What is ℓ for the free particle ?
10. Show that we can write $\langle\varphi, \theta||\ell, m\rangle$ as $P_m(\varphi)F_\ell(\theta)$.

Chapter 9

The Hydrogen Atom

In classical mechanics, the Hamiltonian H for two bodies interacting via a - time independent- potential is given by :

$$(H = \sum_{i=1}^2 \frac{(p_i)^2}{2\mu} + V(r) \quad (9.1)$$

Where, $\mu = \frac{M+m}{Mm}$ is the reduced mass, and r is the radial separation between the bodies. p_i is the canonical momentum, that we may decompose into two parts :

$$p_r = \text{linear momentum} \quad p_t = \frac{L}{r} \quad \text{angular momentum} \quad (9.2)$$

Hence, we may write (9.1) as :

$$H = \frac{p^2}{2\mu} + \frac{L^2}{2\mu r^2} + V(r) \quad (9.3)$$

since we know that the moment of inertia $I = \mu r^2$ we can therefore write:

recall that $L = I\omega$

$$H = \frac{p^2}{2\mu} + \frac{L^2}{2I} + V(r) \quad (9.4)$$

The potential for the Hydrogen atom is the Coulomb potential, given by the formula:

$$V(r) = -\frac{ke^2}{r} \quad (9.5)$$

Hence we write the Hamiltonian function as :

$$H(p, r) = \frac{p^2}{2\mu} + \frac{L^2}{2\mu r^2} - \frac{ke^2}{r} \quad (9.6)$$

9.1 Canonical quantisation of the H-atom Hamiltonian

We have the state $|\Psi\rangle$ of the H-atom. We then define the Hamiltonian operator \hat{H} from quantising the Hamiltonian function in (9.6) that is :

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{\hat{L}^2}{2\mu\hat{r}^2} - \frac{ke^2}{\hat{r}} \quad (9.7)$$

Due to the spherical symmetry, it is logical to project the state $|\Psi\rangle$ into the configuration space in spherical polar coordinates, hereby the Hilbert space is :

$$\mathcal{H} : (\mathcal{L}, d\mu)$$

where $d\mu = dr d^2\phi \sin\phi^2 d\theta$, the volume element in the spherical polar coordinates and the wavefunction:

$$\psi(r, \phi, \theta) = \langle r, \phi, \theta | \psi \rangle$$

The H-atom is surely a stationary state $\Psi(r, \phi, \theta; t) = \psi(r, \phi, \theta)e^{-i\omega t}$. Hence the time-independent Schrödinger's equation is written as :

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(r, \phi, \theta) - \frac{ke^2}{r}\psi(r, \phi, \theta) = E\psi(r, \phi, \theta) \quad (9.8)$$

It was found -mathematically- that the wavefunction can be separated into three parts:

$$\psi(r, \phi, \theta) = R(r)P(\phi)F(\theta) \quad (9.9)$$

Where $R(r)$ is the radial function, and $P(\phi)F(\theta)$ make up the spherical Harmonics $Y(\phi, \theta)$.

9.2 Quantum numbers

Each of the functions above is an eigenfunction for some observable about the hydrogen atom with an associated quantum number:

$$\begin{aligned} R(r) &\longrightarrow n = 1, 2, 3 \dots && \text{Principle quantum number} \\ F(\theta) &\longrightarrow \ell = 0, 1, 2 \dots, n-1 && \text{orbital quantum number} \\ P(\phi) &\longrightarrow m_\ell = -\ell, -\ell+1, \dots, +\ell && \text{magnetic quantum number} \end{aligned}$$

9.3 Solution of the TISE for the Hydrogen

In fact, the H-atom is the only physical problem in quantum mechanics that can be solved exactly without using perturbation theory or other approximation methods. The TISE (9.8) can be written as three differential equations:

$$\frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \frac{2\mu}{\hbar^2} (Er^2 + ke^2) = \ell(\ell + 1) \quad (9.10a)$$

$$\frac{\sin \theta}{F(\theta)} \frac{d}{d\theta} \left(\sin \theta \frac{dF(\theta)}{d\theta} \right) + C_r \sin^2 \theta = -C_\phi \quad (9.10b)$$

$$\frac{1}{P(\phi)} \frac{d^2 P(\phi)}{d\phi^2} = C_\phi \quad (9.10c)$$

Solving the above equations to obtain the full expression for the wavefunction:

$$\psi_{n,\ell,m_\ell}(r, \phi, \theta) = A_{r\ell} e^{-r/a_0} r^\ell L_{n\ell}\left(\frac{r}{a_0}\right) \cdot Y_m^\ell(\phi, \theta) \quad (9.11)$$

Where:

- $A_{r\ell}$, a normalisation constant.
- a_0 , Bohr radius and it is equal to $\approx 0.53 \text{ \AA}$.
- $L_{n\ell}\left(\frac{r}{a_0}\right)$, the associated Laguerre polynomial.
- $Y_m^\ell(\phi, \theta)$, the associated spherical harmonics, the eigenfunction for the operators \hat{L} and \hat{L}_z .

We can find the energy spectrum for the Hydrogen atom from 9.11 :

$$E_n = - \left(\frac{\mu e^2}{8\epsilon_o^2 \hbar^2} \right) \frac{1}{n^2} = - \frac{13.6 \text{ eV}}{n^2} \quad (9.12)$$

With ϵ_o the vacuum permittivity.

As expected, the spectrum is discrete, but the spacing between the energy levels gets smaller and smaller as the principle quantum number increases, figure 9.3

If we wish to find the *ionisation energy* for hydrogen atom (i.e. the energy required to free the electron from the atom) we let $n \rightarrow \infty$ we obtain:

$$E_\infty = 13.606 \text{ eV} = Ry$$

it is equal to the Rydberg energy . For generality we can approximate the energy spectrum for any atom having Z electrons and μ reduced mass by:

$$E \sim -Z^2 \frac{\mu}{m_e} Ry \quad (9.13)$$

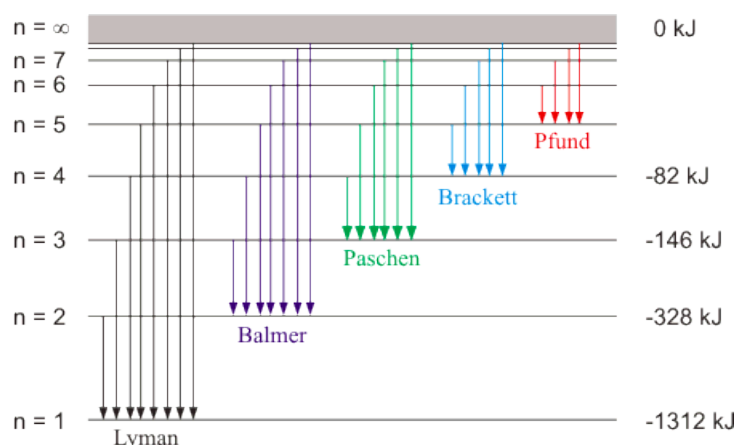


Figure 9.1: Energy levels of the idealised H-atom and the well-known spectral series associated with electron transitions

We ought to emphasise this is merely a hand-waving approximation ! The true energy spectrum for atoms (even the H-atom) is far more complicated, as we shall see later when we study the Real Hydrogen atom.

9.4 Degeneracies in the ideal H-atom

Since (9.11) depends on three quantum numbers , ℓ and m_ℓ , but the energy spectrum only depends on n , we have *degenerate states* in the idealised H-atom. Where we can have multiple wavefunctions having the same energy. For example, in the first excited state $n = 2$ we have the following wavefunctions:

$$\psi_{2,0,0} \quad \psi_{2,1,0} \quad \psi_{2,1,-1} \quad \psi_{2,1,1},$$

and so on . However, the number of electrons that can occupy each energy level is determined by **Pauli exclusion principle**: stating that no two electrons in the atom can have an overlapping wavefunctions. In other words each wavefunction can describe one electron only. Meaning no electrons in the atom can have all of their quantum numbers identical.

9.5 Spin quantum number

In addition to the quantum numbers (n, ℓ, m_ℓ) there is a fourth quantum number of the electron, corresponding to its **spin**, which is an internal degree of freedom electrons are found to possess. The spin quantum number m_s can take one of two values $\pm \frac{1}{2}$ of multiples of \hbar . So far, this new quantum number does not seem to

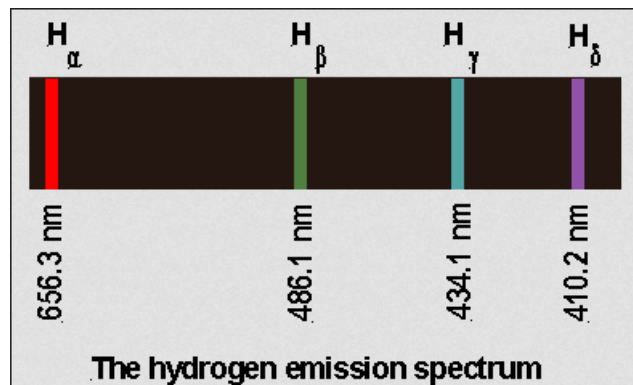
affect the energy spectrum. However, we shall see later that it plays a rôle in an interaction inside the H-atom affecting the energy spectrum.

9.6 Problems

1. If you know that the ground state radial function of the H-atom is given by:

$$R_{10} = e^{-r/a_0}$$

- (a) Normalize it .
 - (b) Construct ψ_{100} .
 - (c) Calculate $\langle r \rangle$, $\langle r^2 \rangle$, $\langle x \rangle$ and $\langle x^2 \rangle$, what do you observe?
2. Derive the Rydberg formula for the H-atom. Then obtain similar formulas for D-atom and positronium (electron orbiting its anti particle) .
 3. Having Pauli exclusion principle in mind, what is the maximum number of electrons one can have in each shell (for a given n) ?
 4. The H-atom emission spectrum is observed to be described in the picture below



- (a) If there is only one electron in the H-atom, how do you explain the existence of multiple emission lines ?
- (b) Explain the spectrum in detail, using the Rydberg formula.
- (c) Spectroscopy is used to distinguish between the isotopes of elements (H_2 and D_2 for example). Predict the D_2 spectrum and draw it, compare it the given H_2 spectrum.

5. Compare the energy spectrum of the H-atom, with the one in a 3-D box of dimension 1 Å.

6. Show that:

$$\left\langle \frac{\partial U}{\partial r} \right\rangle = \left\langle \frac{1}{r^2} \right\rangle$$

If U is the Coulomb potential.

7. Is it possible for electrons to exist in the nucleus ? Justify your answer using the calculation of probability for the electron to be detected within the nuclear radius $r_{nuclear} \sim 10^{-15}$ m.

- (a) Start by using the wavefunction ψ_{100} , and show it is valid for all values of r up to $r = 0$.
- (b) Assume that the wavefunction is constant over the small volume of the ‘spherical nucleus’ then calculate the probability $P \approx V_{nucleus} \times |\psi_{100}|^2$.
- (c) The previous step can be done in more ‘sophisticate way’ by expanding the wavefunction around the origin using the parameter $\epsilon = 2r_{nuclear}/a$
- (d) substitute for a_0 and $r_{nuclear}$ to estimate the probability.

8. The associated Laguerre polynomials are given by the following ‘generating formula’:

$$L(x)_{q-p}^p = (-1)^p \left(\frac{d}{dx} \right)^p L_q$$

With $L(x)_a$ is the Laguerre polynomials give by:

$$L(x)_q = e^x \left(\frac{d}{dx} \right)^q (e^{-x} x^q)$$

Use these equations to generate the first two associated polynomials. Are they orthonormal over the interval $[0, +\infty]$ and weighting function $w(x) = x^p e^{-x}$?

Chapter 10

Spin

10.1 Transformation of the wavefunction

Given a wavefunction defined at the point (in 1-D) x_0 , then we define the **infinitesimal translation** of the wave function as a transformation performed on it, by shifting the point x_0 by an infinitesimal parameter ϵ .

$$\psi(x_0) \longrightarrow \psi(x_0 + \epsilon)$$

Using the Taylor series expansion of the translated wavefunction around the point x_0 we can write :

$$\psi(x_0 + \epsilon) = \psi(x_0) + \epsilon \frac{d\psi}{dx} + \mathcal{O}(\epsilon^2). \quad (10.1)$$

since ϵ is an infinitesimal parameter , the order terms of ϵ^2 are considered vanishing, hence:

$$\psi(x_0 + \epsilon) \sim \psi(x_0) + \epsilon \frac{d\psi}{dx} \quad (10.2)$$

It won't affect the expansion if we multiplied and divided by $\frac{i}{\hbar}$:

$$\psi(x_0 + \epsilon) \sim \psi(x_0) + \epsilon \frac{i}{\hbar} \left(\frac{\hbar d\psi}{i dx} \right), \quad (10.3)$$

we hereby identify $\frac{\hbar}{i} \frac{d}{dx}$ as the m operator, \hat{P} . Thus,

$$\psi(x_0 + \epsilon) \sim \psi(x_0) + \epsilon \frac{i}{\hbar} \left(\hat{P}(\psi) \right). \quad (10.4)$$

This equation basically tells us that the translation is **generated** by the momentum operator , or the momentum operator is the **generator of translation**.

Same argument can be made for 3-D, in Cartesian coordinates $\vec{r} = (x, y, z)$, being translated by $\vec{\delta r}$. That is,

$$\psi(\vec{r}) \longrightarrow \psi(\vec{r} + \vec{\delta r})$$

By the same argument done before, the multivariate Tylor expansion :

$$\psi(\vec{r} + \vec{\delta r}) \sim \delta r \frac{i}{\hbar} \left(\frac{\hbar}{i} \nabla(\psi) \right). \quad (10.5)$$

We know that the 'linear momentum operator is defined by $\vec{P} \frac{\hbar}{i} \nabla$, where the gradient operator here is in the Cartesian coordinates .

Now, we can run the same argument for multi-particle system with f number of degrees of freedom in generalised coordinates : (q^1, q^2, \dots, q^f) , the transformation of generalised coordinates is not restricted translations, but also rotations (if some of the generalised coordinates correspond to angles for example.). But such transformation is written in the form : $\frac{\partial}{\partial q^i}$, that is, it depends on the derivatives of the coordinates - for a general configuration space - .

10.2 External and internal degrees of freedom for a system

The f degrees of freedom the system has, can be linked to a set of generalised coordinates of the configuration space. And the transformation of the wavefunction for that system's degrees of freedom is written in terms of (derivatives of the generalised coordinates), or we can say that such transformations are translations in space and time, in addition to 3-D rotations.

Examples : The linear and angular momentum, the velocity and energy... These degrees of freedom are called **external** degrees of freedom. The observables that are explicit functions of generalised coordinates are linked to these degrees of freedom. In other words, the operators corresponding to those observables act - effectively- on the same Hilbert space.

However, in quantum mechanics, there exist another type of degrees of freedom, that do not (explicitly) depend on space and time. (or configuration space). Rather they form a separate Hilbert space, with operators correspond to observables that are not an explicit functions of generalised coordinates, nor time. Although they can affect the external degrees of freedom observables, through physical process called **coupling**. But this is only when we consider the product of the two Hilbert spaces - the system as a whole-.

This is better understood via the transformations we have discussed earlier. As a space/ configuration space transformation is preformed, the internal degrees of

freedom of the system are not affected by themselves. This is the main difference between internal and external degrees of freedom of a system.

In fact, there is a theorem in mathematical physics called the *Coleman Mandula theorem*, that separates space and time translation symmetries and internal ones (one cannot be obtained from the other.) unless *supersymmetry* is used, this is beyond the scope of our study.

The distinction between, space and time (explicitly) dependent observables, and internal degrees of freedom is crucial in the understanding of elementary particle physics in one hand or quantum information in the other. There are many examples for observables originating from internal degrees of freedom of quantum particles. . Electric charge, magnetic dipole moment (from free electron), quantum numbers like: leptonic or baryonic quantum numbers, strangeness...etc

We should emphasise that they are degrees of freedom and not internal structure, as (elementary) particles are as far-as we know dimensionless.

10.3 Mathematical description for internal degrees of freedom

As we mentioned above, the internal degrees of freedom for a quantum system has an independent Hilbert space that we dealt with earlier (we can always go to L^2 for external ones). Now, we need to study how such space can be defined, or constructed.

We start by defining the state ket $|\psi\rangle$, decomposed into the basis for the Hilbert space $\{|\alpha_i\rangle\}$.

$$|\psi\rangle = \sum_{i=1}^{\dim \mathcal{H}} \alpha_i |\alpha_i\rangle \quad (10.6)$$

Such that, the dimension of the Hilbert space is the same as the number of the internal degrees of freedom described by that space. The coefficients α_i are the probability amplitudes of detecting the system having the state α_i , i.e. usually the quantum system is in a state of superposition, until it is measured. Identically to what is studied before.

We can picture a state space for these degrees of freedom and define transformations just like we have done in the external ones 10.3 Since the magnitude of $|\psi\rangle$ should be 1, i.e.

$$||\psi\rangle| = 1,$$

any transformation made upon this ket is ought to a rotation in the state space. If that space is quantised, the rotation is only possible in integer multiples, and via a ladder (raising and lowering) operators similar to what we have seen in the (orbital) angular momentum. Hence all these internal degrees of freedom are **physical realisations** of the same mathematical structure discussed earlier in the

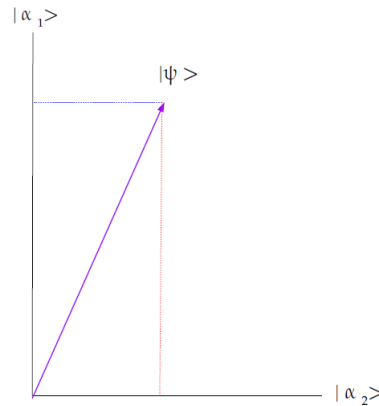


Figure 10.1: The quantum state can be abstractly represented as a vector in the state space

angular momentum.

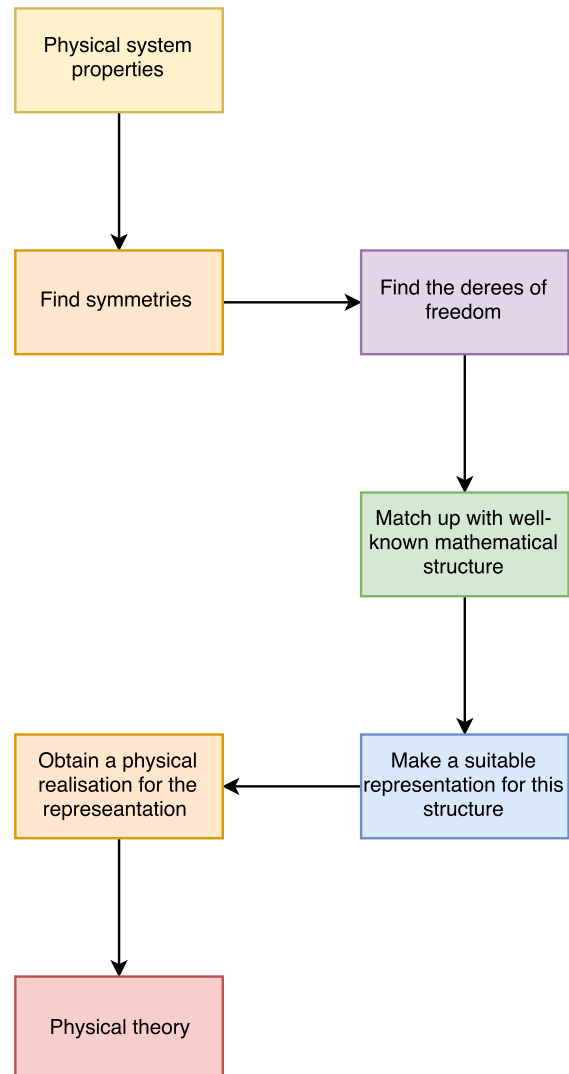
These facts are very powerful, because it allows us to apply the same techniques, and thought processes to many physical systems (with modifications that appears naturally). Depending on the nature of the physical problem (the symmetry, the number of degrees of freedom ..etc). To illustrate this power, this technique (which is known formally as **representation theory**) is used extensively in Fundamental physics. The whole standard model of particle physics is fundamentally built upon the same idea of *representation*, quantum electrodynamics and quantum chromodynamics ..etc

10.4 Discovery of electron's magnetic dipole moment

In 1925, the idea of 'spin' angular momentum for electron was first proposed George Uhlenbeck and Samuel Goudsmit to explain hyperfine splitting in atomic spectra. However, in 1922, Otto Stern and Walther Gerlach had shown that electrons act like tiny magnetic bars (they have a magnetic dipole moment), and that magnetic moment takes particular values only.

We are going to construct step-by-step the theory of quantum spin via the observations of S-G experiment, and discuss the mathematical properties of our construction. Following the lead of the philosophy developed above.

S-G apparatus is basically a magnetic field that is free to be in any direction, x, y, z . As a beam of electrons is passed through the S-G apparatus, the beam



splits either in the positive or negative direction (say the B field is aligned with the z axis). The split is due to a change of energy of the beam, because electron's have magnetic dipole moment, and it takes a \pm values or $1/2$ values only, otherwise ... If the electron has an integer multiples of some magnetic dipole moment, not $1/2$ the splitting would be at least in three ways, for \pm direction and renaming of the beam passing through unaffected. Quantitatively we write the change of the energy is given by :

$$\Delta H = \vec{\mu} \cdot \vec{B}. \quad (10.7)$$

Since $\vec{B} = B_z$ only the projection of the magnetic dipole moment in the z direction counts, we hence conclude that :

$$\mu_z = \pm \frac{1}{2} \cdot \text{const.} \quad (10.8)$$

Same effect is observed if the B field was aligned with any axis not just the z axis. Hence the observable of the dipole magnetic moment is associated with a vector operator $\vec{\mu}$ that has an eigenvalues of $1/2$ of some constant. This constant was found experimentally, and called the **Born magnetron** μ_B for the electron, but generally it is noted by γ the **gyromagnetic ratio**, being more careful, Born magnetron and the gyromagnetic ratio are not exactly equal, due to relativistic effects, and Thomas precession $\gamma = g_s \cdot \mu_B$ where g_s is **called Landé g-factor** . In fact we write :

$$\hat{\vec{\mu}} = -g_s \mu_B \frac{\hat{\vec{S}}}{\hbar} \quad (10.9)$$

We call the operator \hat{S} the spin operator .

10.5 Electron's spin

Although \hat{S} does not correspond to a direct observable (nobody can detect the spin directly separately from the magnetic dipole moment) But seems very natural to study the spin rather than the magnetic dipole moment directly. Although there is no classical analogy to the spin, as electrons do not spin around themselves (they are dimensionless points) but spin is a form of angular momentum corresponding to an internal degree of freedom for the electron.

So far, from S-G experiment, we can conclude that :

$$\langle \hat{S}_z \rangle = \pm \frac{1}{2} \hbar \quad (10.10)$$

We shall stick with z but any component gives as similar results as the S_z . And the \hbar is just to reserve the dimension of the spin, since it is an angular momentum. We let m_s for convenience denote :

$$\langle \hat{S}_z \rangle = m_s \hbar \quad m_s = -\frac{1}{2}, +\frac{1}{2} \quad (10.11)$$

Note how similarities in notation with the orbital angular momentum is appearing. Now, we turn into studying the spin operators more, via repeating the S-G experiment in the following way:

Start with S-G apparatus in the z direction, take the half of the initial beam that is aligned in the $+z$ direction (having $m_s = +1/2$) passed through another S-G apparatus but aligned in the x direction, it shall split the beam once again. This time in the $\pm x$ directions. One would expect that by these two apparatuses; we were able to measure two observables associated with \hat{S}_z and \hat{S}_x . Nevertheless, experiments have shown that this is not true, as taking the 1/4 of the beam that passed via the $+z$ first and $+x$ second, to a third S-G apparatus aligned in the z . We expect only one beam to pass in the $+z$ direction, but this does not happen. The beam splits into two a third time ! This does not happen if we passed it (initially) into three consecutive S-G apparatuses aligned in the z direction. Hence, we cannot measure the spin in two directions simultaneously. This is mathematically written as :

$$[\hat{S}_z, \hat{S}_x] \neq 0 \quad (10.12)$$

In fact the commutation relation for the spin operators take the form for the indices i, j, k taking the values x, y, z :

$$[\hat{S}_i, \hat{S}_j] = i\hbar \epsilon_{ij}^k \hat{S}_k \quad (10.13)$$

¹ Which is the same as for the \hat{L} 's that we studied before. We can therefore, adopting the philosophy of previous lectures define the following operators:

$$\hat{S}_{\pm} = \hat{S}_x \pm i\hat{S}_y \quad (10.14)$$

and:

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \quad (10.15)$$

With the eigenstates :

$$|s, m_s\rangle \quad (10.16)$$

But the eigenvalue s take one value only $s = \frac{1}{2}$ and m_s as we have seen takes the values $m_s = \pm \frac{1}{2}$:

$$\begin{aligned} \hat{S}_z |s, m_s\rangle &= m_s \hbar |s, m_s\rangle \\ \hat{S}_{\pm} |s, m_s\rangle &= \hbar \sqrt{s(s \pm 1)} |s, m_s \pm 1\rangle \end{aligned} \quad (10.17)$$

¹The symbol ϵ_{ij}^k is called the Levi-Civita symbol and it is equal to 0 if $i = j$ and ± 1 for even permutation and ∓ 1 for odd permutations of the indices

And the ladder operator ²:

$$\hat{S}_{\pm}|s, m_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s \pm 1)}|s, m_s \pm 1\rangle \quad (10.18)$$

The three operators \hat{S}_{\pm} and \hat{S}_z form the well-known $su(2)$ algebra commutation relations:

$$\begin{aligned} [\hat{S}_{\pm}, \hat{S}_z] &= \mp \hbar \hat{S}_{\pm} \\ [\hat{S}_+, \hat{S}_-] &= 2\hbar \hat{S}_z \end{aligned} \quad (10.19)$$

The Hilbert space for the spin is very simple, as it is 2-D only spanned by the basis $|\frac{1}{2}, +\frac{1}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle$ or denoted by $|\chi_+\rangle, |\chi_-\rangle$, respectively.

$$|\psi\rangle = \sum_{\lambda=\pm} \alpha_{\lambda} |\chi_{\lambda}\rangle \quad (10.20)$$

representing a superposition of the spin states.

10.6 Infel-van der Warden Symbols

Not always we can have the luxury of selecting the Cartesian coordinates in order to study the spin alignment, sometimes we need to work with any suitable set of coordinates (cylindrical, spherical ...) . Hence we need to link the spin operator vector to a more mathematically-rigorous argument other than the observations made from S-G experiment.

In fact, we may write the spin operator vector $\hat{\vec{S}}$ in terms of a set of symbols, known as **Infel-van der Warden Symbols** ($\sigma^1, \sigma^2, \sigma^3$):

$$\hat{\vec{S}} = \frac{\hbar}{2} \vec{\sigma} \quad (10.21)$$

Where, $\vec{\sigma} = (\sigma^1, \sigma^2, \sigma^3)$ is called the **Pauli vector** , and these symbols are known in the physics literature as **Pauli spin matrices** , Due to their relation - in this context- with the spin operator.

It goes without saying that the spin operators really have inherited the mathematical properties (commutation relations) from the Infel-van der Warden Symbols, or -as we shall call them from now on- the Pauli spin matrices. So, naturally there exist the two symbols:

$$\sigma^{\pm} = \sigma^1 \pm i\sigma^2 \quad (10.22)$$

That along with σ^3 form the $su(2)$ algebra commutation relations:

$$\begin{aligned} [\sigma^3, \sigma^{\pm}] &= \pm i\sigma^{\pm} \\ [\sigma^+, \sigma^-] &= i\sigma^3 \end{aligned} \quad (10.23)$$

²These operators are a direct result from the quantisation of the spin space

Usually Infel-van der Warden Symbols used in advanced texts differ from our notation by the factor of i , i.e. they usually call $i\sigma^i$ as the symbol

Also note that

$$[\sigma^i, \sigma^j] = 2i\varepsilon_k^{ij} \sigma^k$$

Moreover, the pauli spin matrices have an important mathematical property called the **Clifford algebra** relation:

$$\{\sigma^i, \sigma^j\} = \sigma^i \sigma^j + \sigma^j \sigma^i = 2\delta^{ij} \quad (10.24)$$

We call the operation $\{\cdot, \cdot\}$ the **anticommutator**. From this property we can easily prove that:

$$(\sigma^1)^2 = (\sigma^2)^2 = (\sigma^3)^2 = \delta^{ij} \quad (10.25)$$

So far, we only dealt with *abstract*, mathematical entities, and their properties (commutation relations), In order to use them in physical calculations, we need to find a proper **representation** for them in order to be realised in the physical world. We shall find that there are many possible representations for the Pauli spin matrices, that have a direct physical application and meaning. In fact, spin of the electron is only a simple application of the representations for the Pauli spin matrices, others go as deep as the *electroweak interaction* in the standard model of particle physics, and supersymmetry! However, there are other representations, that seems to be of an interest of mathematicians mainly like the quaternions (a higher form of complex numbers that has 3 imaginary units) .

10.7 Matrix representation of spin states

In the last sections, we have introduced the spin operators and their eigenstates. We discovered the algebra of spin operators, and derived the Pauli spin matrices. However, we only stated their properties abstractly without defining a particular representation for them, now we aim to realise the spin algebra in a simple representation.

Consider the eigenkets $|\chi_{-}\rangle$ and $|\chi_{+}\rangle$. They form a basis for a 2-D Hilbert space of the internal degree of freedom, we have called the ‘spin’. It is natural to introduce a canonical representation for these kets as the column vectors :

$$|\chi_{+}\rangle \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (10.26)$$

$$|\chi_{-}\rangle \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (10.27)$$

Now, the action of the spin operators $\hat{S}_1, \hat{S}_2, \hat{S}_3$ and the ladder spin operators \hat{S}_+, \hat{S}_- on the kets is :

$$\begin{aligned}\hat{S}_1|\chi_{\pm}\rangle &= \frac{\hbar}{2}|\chi_{\mp}\rangle & \hat{S}_2|\chi_{\pm}\rangle &= \pm i\frac{\hbar}{2}|\chi_{\mp}\rangle & \hat{S}_3|\chi_{\pm}\rangle &= \pm\frac{\hbar}{2}|\chi_{\pm}\rangle \\ \hat{S}_{\pm}|\chi_{\mp}\rangle &= \hbar|\chi_{\pm}\rangle & \hat{S}_{\pm}|\chi_{\pm}\rangle &= 0\end{aligned}\quad (10.28)$$

We can easily express the operators above as matrices, and with the help of the identity:

$$\vec{S} = \frac{\hbar}{2}\vec{\sigma} \quad (10.29)$$

We may write the explicit expression of the Pauli matrices:

$$\begin{aligned}\sigma_1 &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ \sigma_2 &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\ \sigma_3 &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} .\end{aligned}$$

And:

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

We shall only deal with the index-down matrices and drop the ket notion on the eigenstate, calling them. For convenience and consistency with quantum mechanics textbooks.

Sometimes, the states χ_+, χ_- are denoted by α and β , respectively. The spinor χ is defined as:

$$\chi = \begin{pmatrix} \chi_+ \\ \chi_- \end{pmatrix} \quad (10.30)$$

Moreover, we can define the Hermitian conjugate of the spinor:

$$\chi^\dagger = (\chi_+^* \quad \chi_-^*) \quad (10.31)$$

That satisfies:

$$\chi^\dagger \chi = 1 \quad (10.32)$$

We can calculate the expected value for an operator $\hat{\Omega}$ acting on the spin Hilbert space by:

$$\langle \hat{\Omega} \rangle = \chi^\dagger \hat{\Omega} \chi \quad (10.33)$$

10.8 Geometric representation

There is another representation for spin, connected to the ‘ spin vector ’ pointing in the 3-D space. In spherical polar coordinates, one may write the spin states as:

$$\chi_+ = e^{i(\delta-\varphi/2)} \cos \frac{1}{2}\theta \quad \chi_- = e^{i(\delta+\varphi/2)} \sin \frac{1}{2}\theta \quad (10.34)$$

Where φ, θ are the polar and azimuthal angles, respectively and δ is an arbitrary phase.

In order to see why this representation is correct, we start by evaluating the probability of detecting the particle spinning up, w.r.t. the z direction:

$$|\chi_+|^2 = \cos^2 \frac{1}{2}\theta \quad (10.35)$$

Similarly for the down direction:

$$|\chi_-|^2 = 1 - |\chi_+|^2 = 1 - \cos^2 \frac{1}{2}\theta = \sin^2 \frac{1}{2}\theta \quad (10.36)$$

It is clear now, what is the rôle of the magnitude of the spin states, in terms of θ . However, we need to discuss further the rôle that the phase plays.

Lets start by calculating the expected values of the spin operators:

$$\begin{aligned} \langle \hat{S}_x \rangle &= \frac{1}{2} \sin \theta \cos \varphi \\ \langle \hat{S}_y \rangle &= \frac{1}{2} \sin \theta \sin \varphi \\ \langle \hat{S}_z \rangle &= \frac{1}{2} \cos \theta \end{aligned} \quad (10.37)$$

Now, assume we wish to rotate the coordinates by an angle γ around z . We have the rotation matrix :

$$R(\gamma) = \begin{pmatrix} e^{i\gamma/2} & 0 \\ 0 & e^{-i\gamma/2} \end{pmatrix} \quad (10.38)$$

Applied to the spinor χ is equal to:

$$R(\gamma)\chi = \begin{pmatrix} e^{i(\delta-\frac{1}{2}(\varphi-\gamma))} \cos \frac{1}{2}\theta \\ e^{i(\delta+\frac{1}{2}(\varphi-\gamma))} \sin \frac{1}{2}\theta \end{pmatrix} \quad (10.39)$$

Notice that, in order for the spinor to return to its original state, before rotation, one needs not to make a 2ϕ rotation. Rather a rotation by 4π . This is the main characteristic of spinors, that makes them ‘ very ’ different from vectors, and manifesting itself in terms of the phase factor in the geometrical representation.

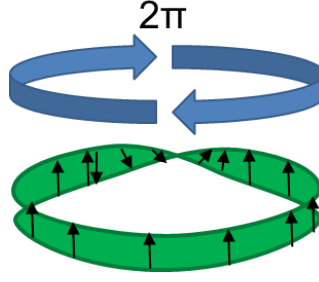


Figure 10.2: A spinor transformation can be thought of as a vector on a Möbius band.

Sometimes we denote this characteristic by saying that the ‘group’ of spin transformations **double covers** the ‘group’ of spatial transformations.

In order to picture this in a deeper way, one can think of the spinor’s internal space as a Möbius band - illustrated in the figure 1. A vector on the Möbius band needs to be transported along the band twice, in order to return to its initial state.

10.9 Spin in constant magnetic field

A particle with a spin - an electron- for example is put in a constant magnetic field, such that the direction of the field is parallel to the z -component of the spin. The Hamiltonian for such system is given by:

$$H = -\gamma \vec{B} \cdot \vec{S} \quad (10.40)$$

such that $\gamma = e/m$, the ratio between the electron’s charge and its mass. And $\vec{B} \cdot \vec{S} = BS_z$.

It is clear that:

$$[H, S_z] = 0 \quad (10.41)$$

Implying that there exist eigenstates for H and S simultaneously. Since we already know the eigenstates for S_z , and represented by the spinor χ . We then write :

$$H\chi = E\chi \quad (10.42)$$

or:

$$-\gamma B S_z \chi = E\chi. \quad (10.43)$$

Since, $S_z \chi = \pm \frac{1}{2} \hbar \chi$ The eigenenergies are:

$$E_{\pm} = \mp \mu_B B \quad (10.44)$$

The constant $\mu_B = \frac{e\hbar}{2m_e}$ is Born magneton. It is necessary to add another constant g_s as we have seen earlier to this equation, known as the Landé g-factor, because the electron *precesses* in the magnetic field. We then have:

$$E_{\pm} = \mp g_s \mu_B B \quad (10.45)$$

10.9.1 Stationary states

Since we have found the energy spectrum for an electron in magnetic field, we may now write the time evolution of the state χ , using the equation:

$$\chi(t) = e^{-i\omega t} \chi(0) \quad (10.46)$$

We have then, for A and B are normalisation constants:

$$\chi(t) = A e^{-i\omega t} \chi_+ + B e^{i\omega t} \chi_- \quad (10.47)$$

or:

$$\chi(t) = A e^{i\frac{1}{2}\gamma B t} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + B e^{-i\frac{1}{2}\gamma B t} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} A e^{i\frac{1}{2}\gamma B t} \\ B e^{-i\frac{1}{2}\gamma B t} \end{pmatrix} \quad (10.48)$$

10.10 Electron paramagnetic resonance EPR

From the above analysis, we have learnt that an electron in a magnetic field could occupy one of two energy states, depending on m_s :

$$E_{m_s} = m_s g_s \mu_B B \quad (10.49)$$

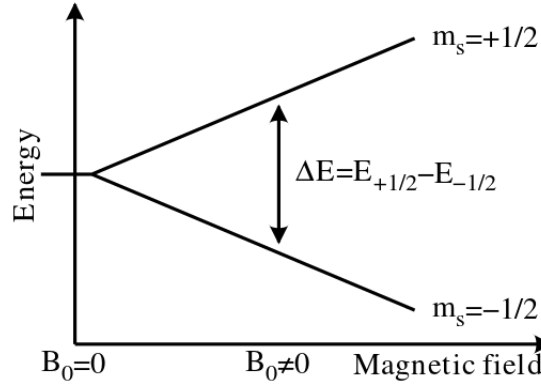
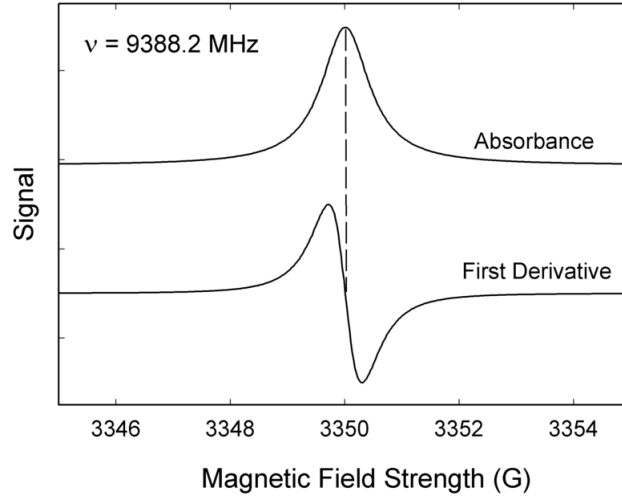
A transition from one energy state to another, is obtained by absorption / emission of photon of energy equal to $\Delta E = g_s \mu_B B$:

$$h\nu_r = g_s \mu_B B \quad (10.50)$$

If an ensemble of electrons in the magnetic field is exposed to photons of frequency $\nu = \nu_r$, then the electrons shall absorb them, otherwise no absorption will occur -only elastic scattering-. This peak of absorption is known as **electron paramagnetic resonance** or *EPR*. Moreover, ν_r is known as the resonance frequency.

This phenomena is very important in many areas, like measuring the value of the g factor, and detecting *free radicals* in biological systems.

In order to understand the reason for detecting absorption lines rather than the emission lines in EPR, we turn to calculating the population of electrons in the

Figure 10.3: Energy states of electron in a magnetic field B .Figure 10.4: EPR absorption resonance for $\nu = 9388.3 MHz$

upper energy level n_{upper} and the lower level n_{lower} , using Maxwell-Boltzmann statistics, under a thermodynamic temperature T :

$$\frac{n_{upper}}{n_{lower}} = \exp\left(-\frac{E_{upper} - E_{lower}}{kT}\right) = \exp\left(-\frac{\Delta E}{kT}\right) = \exp\left(-\frac{h\nu_r}{kT}\right) \quad (10.51)$$

Where k is Boltzmann constant .

We observe that at room temperature $T \sim 300K$ and typical microwave frequency $\nu_r \sim 9.7GHz$ the ratio is about $n_{upper}/n_{lower} \approx 0.998$. That means the upper population is slightly less than the lower one, implying transitions from the lower to upper energy states is more probable than the reverse transitions.

10.11 Problems

1. Show that for Spin vector \vec{S} , the vector product with itself is equal to

$$\vec{S} \wedge \vec{S} = i\hbar\vec{S}$$

hint: use the expression for the vector product $\vec{S} \wedge \vec{S} = \epsilon_{ij}^k S_i S_j \vec{e}_k$

2. prove that $(\sigma^i)^2 = \delta_{ij}$
3. We denote the hermitian Pauli matrix by σ_i , show that it is in fact equal to σ^i .

4. Show that,

$$\sigma^i \sigma^j = \delta^{ij} + i\epsilon_{ij}^k \sigma^k$$

. hint: use both the Clifford algebra and commutation relations the Pauli matrices obey.

5. Are Pauli matrices unitary ??
6. What is the action of σ^\pm, σ^3 of the states $|\chi_\pm\rangle$?
7. Use the definition of the spin vector in terms of the Pauli matrices to prove that

$$\langle \hat{S}^2 \rangle = \frac{3}{4}\hbar^2$$

8. Given a vector \vec{a} , find the dot product:

$$\vec{a} \cdot \vec{\sigma}$$

9. Prove that :

$$\det(\sigma^i) = 1$$

10. We define the Dirac gamma matrices as :

$$\gamma^k = \begin{pmatrix} 0 & -i\sigma^k \\ i\sigma^k & 0 \end{pmatrix}$$

Show that the Clifford algebra relation also holds for the gamma matrices :

$$\{\gamma^i, \gamma^j\} = 2\delta^{ij}I$$

11. Given the following 2×2 matrices :

$$\begin{aligned}\sigma_1 &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ \sigma_2 &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\ \sigma_3 &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} .\end{aligned}$$

Find their eigenvalues and eigenvectors. They form the matrix representation for the Pauli spin matrices, moreover, the results obtained will form the explicit expression of the eigenstates $|\chi_{\pm}\rangle$ in column form.

12. Given

$$\hat{\Omega} = \begin{pmatrix} -1 & -i \\ i & 2 \end{pmatrix}$$

an operator acting on the spin Hilbert space:

- (a) Show that it could correspond to an observable.
 - (b) Decompose it in terms of the Pauli spin matrices.
 - (c) Find its eigenvalues.
 - (d) Compute $\langle \Omega \rangle$.
13. Since the spin operator is a vector in the 3-D space. Show that if it is rotated by an angle γ around the z -axis, the commutation relations algebra remains invariant, for the rotated operator .
14. Calculate the EPR frequency for an experiment with $B = 100$ Gauß. where $\mu_B = 9.274 \times 10^{-24}$ Joule/Tesla. and the material used is Holmium with $g_s = 1.97$.

Appendix A

The Virial Theorem

Given a system having α particles, with associated position \vec{r}_α and momenta \vec{p}_α . We define the virial function as:

$$\varsigma = \sum_{\alpha} \vec{p}_\alpha \cdot \vec{r}_\alpha \quad (\text{A.1})$$

It would be interesting to look for the time derivative of this function:

$$\frac{d\varsigma}{dt} = \sum_{\alpha} \vec{p}_\alpha \cdot \vec{r}_\alpha + \vec{p}_\alpha \cdot \vec{r}_\alpha \quad (\text{A.2})$$

Since we are dealing with many-particle system. We can take the time average for the previous expression

$$\begin{aligned} \left\langle \frac{d\varsigma}{dt} \right\rangle &= \frac{\int_0^\tau \frac{d\varsigma}{dt} dt}{\int_0^\tau dt} \\ &= \frac{\varsigma(\tau) - \varsigma(0)}{\tau} \end{aligned} \quad (\text{A.3})$$

Now, if the system has a periodic motion of a period τ . The time average for the derivative of the virial function will vanish. even if the system does not admit a periodic motion, the virial function ought to be bounded, hence one can integrate over a sufficiently large interval such that the time average $\left\langle \frac{d\varsigma}{dt} \right\rangle$ will approach zero.

Hence, we have (at least as an approximation):

recall that $\vec{F} = \vec{p}$

$$\left\langle \sum_{\alpha} \vec{p}_\alpha \cdot \vec{r}_\alpha \right\rangle = - \left\langle \sum_{\alpha} \vec{p}_\alpha \cdot \vec{r}_\alpha \right\rangle \quad (\text{A.4})$$

We can now identify the LHS being twice the kinetic energy , the RHS is the force dotted with the position :

$$\langle T \rangle = -\frac{1}{2} \left\langle \sum_{\alpha} \vec{F}_{\alpha} \cdot \vec{r}_{\alpha} \right\rangle \quad (\text{A.5})$$

This is the **Virial theorem** , the expected value for the kinetic energy for a system is equal to its virial function.

It is interesting to look at forces that arise from central potential taking the form :

$$V = kr^{n+1} \quad (\text{A.6})$$

Hence, by the virial theorem eq (A.5):

$$\begin{aligned} \langle T \rangle &= \frac{1}{2} \left\langle r \cdot \frac{d}{dr} (kr^{n+1}) \right\rangle \\ &= \frac{1}{2} \langle (n+1)kr^{n+1} \rangle \\ &= \frac{n+1}{2} \langle V \rangle \end{aligned} \quad (\text{A.7})$$

For Columb and gravitational potentials, $n = -2$. Therefore we have :

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle \quad (\text{A.8})$$

Appendix B

Summery of Hilbert spaces

B.1 Representations of Hilbert space

We list a summery for the most basic properties of Hilbert spaces, in both representations. **Discrete** and **continuous**

The list goes as follows:

Continuous representation	Discrete representation
$ \psi\rangle = \int \psi(x) x\rangle dx$	$ \psi\rangle = \sum_n \psi_n e_n\rangle$
$\langle x' x\rangle = \int dx \delta(x' - x)$	$\langle e_m e_n\rangle = \delta_{mn}$
$\langle \psi \psi\rangle = \int \psi^*(x)\psi(x)dx = 1$	$\langle \psi \psi\rangle = \sum_n \psi_n ^2 = 1$
$\langle \phi \psi\rangle = \int \langle \phi x\rangle \langle x \psi\rangle dx = \int \phi^*(x)\psi(x)dx$	$\langle \phi \psi\rangle = \sum_n \langle \phi e_n\rangle \langle e_n \psi\rangle = \sum_n \phi_n^* \psi_n$

Note that we sometimes denote the basis $|e_i\rangle$ by $|i\rangle$. Here we consider the vector $|\psi\rangle$ to be normalised.

B.2 Operator properties

We start by defining the normalised ket :

$$|\psi\rangle = \sum_i \psi_i |i\rangle$$

With the property :

$$|\psi_j|^2 \equiv P(j)$$

Hence the square modulus of the component is equal to what-to-be considered as probability. Note that any of the following argument will also apply to continuous basis representation according to the list above. We can write an operator $\hat{\Omega}$ as :

$$\hat{\Omega} = \sum_i \omega_i |\omega_i\rangle \langle \omega_i|$$

This is known as the **spectral decomposition**, where ω_i and $|\omega_i\rangle$ are the eigenvalues and eigenbasis respectively. The expected-value for $\hat{\Omega}$ is written as:

$$\langle \hat{\Omega} \rangle = \langle \psi | \hat{\Omega} | \psi \rangle$$

Proof:

Expanding the above expression :

$$\begin{aligned} & \left(\sum_k \psi_k^* \langle \omega_k | \right) \left(\sum_j \omega_j |\omega_j\rangle \langle \omega_j| \right) \left(\sum_i \psi_i |\omega_i\rangle \right) = \\ & \Leftrightarrow \sum_k \sum_j \psi_k^* \omega_j \underbrace{\langle \omega_k | \langle \omega_j \rangle}_{=\delta_{kj}} \sum_j \sum_i \psi_i \underbrace{\langle \omega_j | \langle \omega_i \rangle}_{=\delta_{ij}} = \\ & \Leftrightarrow \sum_j \omega_j \underbrace{|\psi_j|^2}_{=\psi_j^* \psi_j} = \sum_j \omega_j P(j) \quad \square \end{aligned}$$

Similarly, we can define the standard deviation :

$$\sigma^2(\Omega) = \langle \hat{\Omega}^2 \rangle - \left(\langle \hat{\Omega} \rangle \right)^2$$

And the expected value for a function of $\hat{\Omega}$:

$$\langle f(\hat{\Omega}) \rangle = \sum_j f(\omega_j) P(j)$$

That implies that the eigenvalue of the function of the operator is the function of the eigenvalue itself.

We now attempt to find the matrix element for an operator $\hat{\Omega}$ not expressed in the eigenbasis. Starting by :

$$|\phi\rangle = \hat{\Omega} |\psi\rangle$$

expanding this expression:

$$\sum_k \phi_k |k\rangle = \hat{\Omega} \sum_i \psi_i |i\rangle$$

Taking the j th component of the LHS, by projecting on the basis $|j\rangle$:

$$\phi_j = \sum_i \psi_i \langle j | \hat{\Omega} | i \rangle$$

Moreover, the ket $|\phi\rangle$ is written as:

$$\sum_j \phi_j = \sum_j \sum_i \psi_i \langle j | \hat{\Omega} | i \rangle$$

We identify the matrix elements of the operator by

$$\Omega_{ji} = \sum_j \sum_i \langle j | \hat{\Omega} | i \rangle$$

We can simply make the transition to the eigenbasis :

$$\Omega_{ij} = \langle \omega_i | \hat{\Omega} | \omega_j \rangle$$

But $\hat{\Omega}|\omega_j\rangle = \omega_j|\omega_j\rangle$, then we have , by linearity:

$$\begin{aligned} \Omega_{ij} &= \omega_j \langle \omega_i | \omega_j \rangle = \\ &\Leftrightarrow \omega_j \delta_{ij} \end{aligned}$$

Hence the operator is diagonalised by the eigenbasis.

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