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Chapter 1

Preface

These lecture notes arose as a result of our need to fill the gap between the elementary textbooks in quantum mechanics and more advanced text addressed at professional physicists. We were seeking a compromise in the level of presentation that would be both acceptable for advanced undergraduate students and allow them to grasp certain difficult concepts of contemporary physics. It was our intention to enable the readers to reach a new, more abstract level of thinking, while at the same time provide them with theoretical tools needed for practical problem solving. (All that was supposed to be accomplished within one semester).

These notes owe a lot to various famous predecessors that have presented the subject matter in much greater depth than we did here. Therefore this text should rather not be treated as a substitute for the recommended list of books as included below, and is supposed to be rather a roadmap with a bit of personal guidance. We made some sacrifices, mostly in presenting the mathematics in a very non-mathematical way. We also borrowed heavily from several outstanding books and scientists. This text is influenced by a relatively recent book "Modern Quantum Mechanics" by Sakurai and to the book by Merzbacher, perhaps rewritten in a more contemporary language. The introductory part of these notes dealing with mathematical concepts does not have a published precedent at similar level, with some of these ideas are presented in greater depth in the book by Byron and Fuller but on a much more advanced level.

We have included below quite a few problems with solutions, hoping however, that the reader will work through them independently. In general, books containing advanced, modern problems in quantum mechanics are not particularly numerous but some older books such as that by Schiff are certainly worth reading.

We assume a certain level of knowledge in the reader, equivalent to having been through the elementary quantum mechanics course in excess of 20 hours and having covered issues such as the concept of wave function, the Schrödinger equation in position representation, the concept of spin and matrices. As far as the mathematics is concerned, the reader is assumed to be practically familiar with vector spaces. The following remark concerns our notation, namely all vectors are typed in boldface and all operators are denoted by hats.

This lecture course starts from recapping the Stern-Gerlach experiment and explaining the need for a new approach, based on treating quantum states as vectors, to explain its results. Then we introduce the main mathematical facts needed for further development.
The following chapter deals with postulates of quantum mechanics. These postulates are listed in a separate section. In this chapter we also study the time evolution of kets, address the problem of constants of the motion and the uncertainty relation. The next chapter deals with position and momentum representation, from practical rather than fundamental point of view, and (briefly) discusses translational invariance and parity. The next chapter is devoted to the quantum harmonic oscillator. Rotational symmetry is presented mostly from the orbital angular momentum viewpoint, but we do mention the role of spin. Further we catch up once again with mathematics in the context of tensor product of vector spaces. At this stage we leave the quantum mechanics of a single particle and move on to systems of many particles. The course continues with the perturbation theory and some of its applications. Then we move on to discuss the semiclassical treatment of electromagnetic field and field quantisation. This will ultimately allow to understand the concept of a photon.

While we are aware, how much of the important physics we have missed, we also believe that this course lays necessary foundations for further independent studies in quantum mechanics. The following roadmap (Fig 1.1) outlines the structure of the course.
Chapter 2

Introduction - Stern-Gerlach experiment

In the beginning of the 20th century scientists realised that the rules of the classical physics may not apply universally and the microscopic world - the phenomena that occur on a microscopic scale have to be described otherwise. Thus quantum mechanics was born with its key concept of the wavefunction, later interpreted in the probabilistic fashion, spectacularly succesful in describing such phenomena as for example quantized energy levels in atoms. In the nineteen thirties the discovery of electron spin shook the foundations of quantum mechanics. It turned out that the description of the particles in terms of their wavefunction is not sufficient, and obviously the classical description was not complete either. In these lectures we will present the formalism used to describe the spin-related phenomena, and thus develop the computational techniques that can be used in the context of spin. Spin is also the key example in many case studies that follow. Knowledge of these examples is the key to understanding the concept of spin. One of the assignment questions that we would like to foreshadow here is to present your understanding of spin phenomena.

The notion of electron spin has been proposed as a way of resolving the puzzling results of the Stern-Gerlach (S-G) experiment. For the complete description the reader is referred to the book by Sakurai. Below we recap the fundamentals.

In the S-G experiment the Ag atoms are released from an oven and after being collimated, they traverse the region of magnetic field that is nonuniform in the \( z \) direction (see Fig. 2.1). The atoms emerging from the magnetic field are counted by the detector which, in turn, is moving along \( z \). The result of the S-G experiment is shown in Fig. 2.2 that shows the graph of the number of atoms per unit time arriving at the detector as a function of detector position along \( z \). This graph shows two clearly resolved peaks. It is not possible to explain the results of the S-G experiments neither in the framework of the classical physics nor by the concept of the wavefunction. Below we present the classical analysis of the S-G experiment.

An Ag atom is composed of a nucleus and of 47 electrons, 46 of these form a spherically symmetric shell with zero angular momentum. The 47-th electron is placed on the 5s orbital and has the orbital momentum equal to zero as well. As Ag atoms do interact somehow with nonuniform magnetic field, let us assume that each of these atoms has a net classical magnetic moment \( \vec{\mu} \), as if it were a small magnet. When such classical
This arrangement is symbolised by S-Gz.

Figure 2.1: The Stern-Gerlach experiment (left), will be symbolically denoted as on the right.

Figure 2.2: The results of the Stern-Gerlach experiment.

Magnets are passing through the nonuniform magnetic field they interact with it. The energy of interaction is given by $-\vec{\mu} \cdot \vec{B}$. Then the $z$-component of the force acting on the atom is:

$$F_z = \frac{\partial}{\partial z} \vec{\mu} \cdot \vec{B} = \mu_z \frac{\partial B_z}{\partial z}$$

The atoms emerge from the oven with random orientation of their magnetic moment (Fig. 2.3). Classical gyroscopes with magnetic moment $\vec{\mu}$, proportional to the angular momentum $\vec{l}$, that is $\vec{\mu} = M \cdot \vec{l}$, when placed in magnetic field, carry out the precessional motion with the circular frequency of $\omega_L = M \cdot B$ (see Fig. 2.4). Hence the component $\mu_z$ of $\mu$ along the magnetic field remains constant, while $\mu_x$ and $\mu_y$ oscillate quickly about zero. This means that on the average the atoms have magnetic moment along $z$ - they get polarized. But $\mu_z$ can take all values between the maximum and minimum value of $|\vec{\mu}|$. Therefore the classical predictions would give the graph as in Fig. 2.5 in contrast with the observations. The actual experimental result is that the electron behaves as if it had an internal nonclassical magnetic moment of electron which can take only two values $S_z = +\hbar/2$ and $S_z = -\hbar/2$. However, as the classical explanation is not valid, we can not visualise this magnetic moment in classical terms, as for example due to the electron charge quickly spinning around - this idea is **wrong**.

The explanation of the S-G experiment in the language of wavefunctions is impossible - this concept does not give rise to any magnetic moment and the interaction with nonuniform magnetic field is impossible within this framework.

It is not our purpose here to offer a full explanation of the S-G experiment - this will be done later, after we go through some mathematics. However we would like to foreshadow that the explanation of the S-G experiment can be accomplished if electrons are described
Figure 2.3: Ag atoms emerging from the oven

Figure 2.4: Precession of classical magnetic moment around the magnetic field

Figure 2.5: Classical prediction of the Stern-Gerlach experiment
in terms of its state. The state is considered to be a vector, that is the element of a certain vector space. The discussion of spin phenomena requires the knowledge of the spin state, (other information is irrelevant, at least for the time being). Our knowledge about the spin state is derived from the S-G experiment only, but for some extra insight these experiments can be combined together, and then they are referred to as sequential S-G experiments. A single S-G experiment in which the nonuniform magnetic field is along z, denoted S-Gz, provides the following information:

As a result of the $S_z$ measurement - the measurement of the z component of the spin state we know that the z-component of the electron magnetic moment can take only two values of $+\hbar/2$ and $-\hbar/2$.

Similar statements can be formulated for $x$ and $y$ direction separately.

Now we will present experimental results of various S-G experiments performed sequentially. The results of these sequential experiments look surprising. First we consider the sequential S-G experiment as shown schematically in the Fig 2.6 A. Two S-Gz experiments are performed in close proximity, one another. One of the atom beams emerging from the first S-Gz experiment, characterised by the value of $+\hbar/2$ for the electron magnetic moment and symbolically marked as being in $|S_z^+\rangle$ state traverses the second S-Gz apparatus (the other beam $|S_z^-\rangle$ is blocked). When it emerges, the magnetic moment of all electrons is unchanged. This is (still) very intuitive and we can easily understand that the S-Gz apparatus effectively filters out the atoms with the magnetic moment of their 5s electron $=\hbar/2$. Therefore the second filtering process does not cause any further changes.

Now we consider a different sequential S-G experiment as shown in the Fig 2.6B in which the beam of atoms in the $|S_z^+\rangle$ state crosses the S-Gx apparatus. It turns out that half of the emerging atoms are in the $|S_z^+\rangle$ state with the $x$-component of the magnetic moment equal to $+\hbar/2$ and the other half is in the $|S_z^-\rangle$ state with the $x$-component of the magnetic moment equal to $-\hbar/2$. This is also quite intuitive: after all all electrons characterised by the $z$-component of $\hbar/2$ may have their $x$-component randomly distributed. But as there are only two possible values of the $x$ component of the magnetic moment, namely $\pm\hbar/2$, it is not surprising that half of all electrons show the positive and another half- the negative value.
The sequential S-G experiment shown in Fig 2.6C is the most puzzling of all three. The beam in the state $|S^+_z\rangle$, emerging from the first S-Gz apparatus goes through the S-Gx apparatus and is split into two. One of these emerging beams, which is in the state $|S^+_x\rangle$ is going through another S-Gz apparatus. To everyone’s surprise it turns out that two beams are again created, and therefore the beam that we have thought to be in the $|S^+_z\rangle$ state - as it has emerged from the S-Gz apparatus - after having gone through the S-Gx experiment has ”lost its identity”. By making the measurement of the $x$ component of spin we have destroyed the information about the $z$ spin component!!

In order to reconcile these surprising findings it has been postulated that:

**The quantum-mechanical states will be described as vectors in an abstract complex vector space called ket space. The ket space is specified according to the nature of a physical system under consideration.**

By doing so we emphasise practical aspect of quantum mechanics. We do not claim to know what spin really is (one wonders how this question can be answered at all). What is offered is a description - a set of rules, on what to do in order to explain or predict the results of experiments, such as for example the S-G experiments and numerous others. By the way if you wonder what kind of philosophy we are selling here try reading Popper

In the case if you are apprehensive of the idea of describing physical quantities in a very abstract fashion, that seems not to have anything in common with the real world, please be consoled by the fact that it was done many times in the past. Good examples here are: representation of mechanical quantities such as forces, positions, velocities etc by vectors: it is certainly not obvious that the force should be a vector, on the basis of the everyday experience of pushing and pulling. Another example is the configuration space used to describe the motion of N point masses (which is 6-dimensional, each mass contributes 3 components of position and 3 components of its momentum). Finally description of particles in terms of their wavefunction and its probabilistic interpretation belongs here too as well as many others - the list may never be complete.
Chapter 3

Mathematical formalism

3.1 Hilbert space formulation

In this lecture we will remind the reader a couple of basic mathematical facts and illustrate them with examples. As the concept of the vector space will have a leading role, we will start with the definition of the complex vector space.

The (complex) vector space is a set of vectors $V$ with the operation of addition (+) and the multiplication $\cdot$ by a scalar which is a complex number $\lambda \in \mathbb{C}$. This set fulfills the following:

- $(v_1 + v_2) + v_3 = v_1 + (v_2 + v_3)$ for all $v_1, v_2, v_3 \in V$
- There exist a vector $0 \in V$ such that for every $v_1 \in V$ we have $v_1 + 0 = v_1$
- For every $v_1 \in V$ there exists a vector $v_2 \in V$ such that $v_1 + v_2 = 0$; $v_2$ is called $-v_1$.
- For every $v_1, v_2$ we have $v_1 + v_2 = v_2 + v_1$
- For every $\lambda \in \mathbb{C}$ and for every $v_1, v_2$, $\lambda \cdot (v_1 + v_2) = \lambda \cdot v_1 + \lambda \cdot v_2$
- $(\lambda_1 + \lambda_2) \cdot v_1 = \lambda_1 \cdot v_1 + \lambda_2 \cdot v_1$ for every $\lambda_1, \lambda_2 \in \mathbb{C}, v_1 \in V$
- $\lambda_1 \cdot (\lambda_2 \cdot v_1) = (\lambda_1 \lambda_2) \cdot v_1$ for every $\lambda_1, \lambda_2 \in \mathbb{C}, v_1 \in V$.

This definition is a bit long, it is worthwhile to underline the key point: vectors can be added and they can also be multiplied by the (complex) numbers. In quantum mechanics vector spaces are "specified according to the nature of a physical system under consideration" This means that when you work on a particular problem this is you who decide which space is suitable. That is why we need to be familiar with a range of vector spaces. The following examples are supposed to illustrate the concept of a vector space.

**Example 3.1** The vector space of "arrows" attached to the fixed point. The following picture (Figure 3.1) shows how to add two such arrows and how to multiply them by a real number. This is a real (not a complex) vector space.

Many useful concepts can be introduced in the vector spaces. One such concept is the notion of the basis. In case of the space of "arrows" the basis is the minimum set of vectors (here-two) $\{e_1, e_2\}$, such that all vectors $v \in V$ can be expressed as their linear
Figure 3.1: Adding "arrows" and multiplying them by numbers

![Figure 3.1: Adding "arrows" and multiplying them by numbers](image)

Figure 3.2: Various bases in the space of "arrows"

![Figure 3.2: Various bases in the space of "arrows"](image)

combination. Here \( \mathbf{v} = a_1 \cdot \mathbf{e}_1 + a_2 \cdot \mathbf{e}_2 \). In the space of "arrows" one can identify a number of different bases as in the Fig 3.2. The third basis plays a prominent role as it is orthogonal.

Now we come to the key idea that will be appearing in the first part of this lectures in a number of different settings, the idea of the representation. Consider the space \( \mathbb{R}^2 \) of the columns of two real numbers:

\[
\mathbf{v} = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}.
\]

We are aware that \( \mathbb{R}^2 \) is a vector space - we know how to add such columns of two numbers and how to multiply them by a real number. Moreover these operations are much more convenient than similar operations on "arrows". For example adding arrows involves making a drawing with parallel lines. Therefore it is convenient to represent the "arrows" by the elements of \( \mathbb{R}^2 \), that is by columns of two numbers. To do that we need to specify a basis. Obviously the same vector in two different bases will have two different representations as illustrated in the Fig 3.3.

It is recommended to revise the details what happens to these columns when you change the basis. Below we illustrate the basic idea taking as an example the space of "arrows" and \( \mathbb{R}^2 \). We express the arrow \( \mathbf{v} \) in two bases \((\mathbf{e}_1, \mathbf{e}_2)\) and in the basis \((\mathbf{e}_3, \mathbf{e}_4)\) equal to

\[
\begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \begin{pmatrix} 1/2 \\ 0 \end{pmatrix}
\]

Figure 3.3: The same vector expressed in two different bases
Figure 3.4: The change of basis

\( (e_1, e_2) \) rotated by 90 degrees anticlockwise. In the first basis the vector \( v \) is almost

\[
v \approx \begin{pmatrix} 2 \\ 0 \end{pmatrix}.
\]

In the second basis the same vector is almost

\[
v \approx \begin{pmatrix} 0 \\ -2 \end{pmatrix}.
\]

Figure 3.4 shows that identical final result is obtained if the basis stayed where it was, but the vector were rotated by 90 degrees in the opposite direction \( U^{-1}v \) where \( U \) is the operation of rotation by 90 degrees anticlockwise. The formulas on how the coefficients \( a_1, a_2 \) change with the change of basis can be expressed as: "the coefficients of \( v \) in the new (here rotated) basis are equal to the coefficients of \( U^{-1}v \) in the old basis."

Coming back to the example of the space of "arrows" and \( \mathbb{R}^2 \) we can also say that the elements of \( \mathbb{R}^2 \) can be represented by "arrows". This illustrates that a vector is a different object than all its representations. A good analogy is the difference between a human being in general and individual people: John, Mary, you, me etc. All that we can say about a vector is that a vector is the element of the vector space.

A final remark here: the number of vectors in a basis is called its dimension.

Vector spaces can be constructed out of very diverse objects: it is sufficient to define the operation of addition and multiplication by scalars as shown in the following examples.

**Example 3.2** The set of all polynomials defined on \( \mathbb{R} \) forms a vector space. Its dimension is infinite, an example of a basis is \( 1, x, x^2, x^3, x^4 \ldots \) etc.

**Example 3.3** All functions \( f: \mathbb{R}^3 \rightarrow \mathbb{C} \) form a vector space.

The operation of addition \( \psi = \phi_1 + \phi_2 \) is defined as:

\[
\psi(\mathbf{r}) = (\phi_1 + \phi_2)(\mathbf{r}) = \phi_1(\mathbf{r}) + \phi_2(\mathbf{r})
\]
Figure 3.5: An example of a basis in the space of functions

\[ a \cdot b = |a| |b| \cos \alpha \]

Figure 3.6: The scalar product in the space of "arrows"

The multiplication \( \psi = a\phi_1 \) is defined as:

\[ \psi(r) = (a\phi)(r) = a[\phi_1(r)] \]

where \( a \) is a complex number. This space is also infinite dimensional. An example of its basis is illustrated in the Fig 3.5. The functions \( e_r \) defined by:

\[ e_r(r') = 1 \text{ when } r' = r \]
\[ e_r(r') = 0 \text{ when } r' \neq r \]

The elements of this basis are indexed with \( r \). This index runs continuously through all elements of \( \mathbb{R}^3 \).

Vector spaces have a very rich structure and it is possible to define for them a number of very useful concepts, such as for example the scalar or the dot product.

**Example 3.4** The scalar product in the space of "arrows" is illustrated in the Fig 3.6.

To evaluate \( a \cdot b \) we have to multiply the length of \( a \) by the length of \( b \) and by the cosine of the angle between the arrows. The same scalar product can be evaluated using representations of \( a \) and \( b \) in an orthogonal basis.

\[ a = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \]
\[ b = \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} \]

Then \( a \cdot b = a_1b_1 + a_2b_2 \).

**Example 3.5** The scalar product in the space of real polynomials on the interval \([1,2]\) can be defined as:

\[ P \cdot Q = \int_1^2 P(x)Q(x)dx \]
The scalar product has its formal definition. It is defined as an operation \( a \) on two vectors \( x, y \) that assigns to them a certain complex (or real) number \( a(x, y) \rightarrow \mathbb{C} \) or \( \mathbb{R} \). The operation \( a \) fullfills the conditions:

1. \( a(x_1 + x_2, y) = a(x_1, y) + a(x_2, y) \)
2. \( a(x, y) = [a(y, x)]^* \) (complex conjugate)
3. \( a(x, \lambda \cdot y) = \lambda a(x, y) \)
4. \( a(x, x) \in \mathbb{R} \)
5. \( a(x, x) \geq 0 \)
6. \( a(x, x) = 0 \) if and only if \( x = 0 \).

The first 0 is the complex number the second 0 is the element of the vector space and they are completely different objects.

Scalar product is very useful and for example can be used to define the length \( \| x \| \) of a vector \( x \) in agreement with a common meaning of length:

\[ \| x \| = \sqrt{x \cdot x} \]

When we know how to measure the length of vectors it makes sense to discuss the convergence of the vector sequences. Fig 3.7 shows an attempt to draw a convergent sequence of vectors. Hilbert space is defined as a vector space with a scalar product that contains limits of all sequences. A non-Hilbert space does not contain limits of all sequences, and we can intuitively visualise it as having "blurred edges" or "microscopic holes" in some quantities, (mind you a non-Hilbert space has to be infinite-dimensional). We can think of a Hilbert space as of a high quality vector space. Quantum mechanics assumes that ket spaces are complex Hilbert spaces whose dimensionality is specified according to the nature of physical system under consideration.

### 3.2 Bra and ket vectors

Throughout these lectures we will be using the Dirac notation. In this notation the state vectors or kets are denoted as \( |a\rangle \). We will define their "siblings" that are called "bras". A bra is denoted by the symbol \( \langle a| \) and it has a strict mathematical meaning. In this section we will define what they are.
First we will show that each ket space $K$ gives rise to another vector space, called a **dual** space.

Consider an object $b$ that acts on vectors $|k\rangle$ and assigns a complex number to each ket $b(a) = c \in \mathbb{C}$ in such a way that

$$b(\lambda_1 k_1 + \lambda_2 k_2) = \lambda_1 b(k_1) + \lambda_2 b(k_2), \lambda_1, \lambda_2 \in \mathbb{C}$$

Such object is called a functional on this ket space. It is evident that functionals are different objects than the vectors they act on. Functionals themselves form a vector space. It is left to the reader to propose how to add functionals and multiply them by scalars (numbers).

**Example 3.6** Here we present a a simple functional. Let us consider a certain ket $|b_0\rangle$. The functional $b_0$ can be defined as:

$$b_0(a) = \text{ scalar product of } |b_0\rangle \text{ and } |a\rangle \text{ for all } a.$$  

This example tells us how to assign a functional to each vector. It can be proved that in a Hilbert space all functionals are of this form.

**Theorem 3.1** When $K$ is a Hilbert space then all functionals $b$ on $K$ have a corresponding ("dual") ket $|b\rangle$ such that

$$b(a) = \text{ scalar product of } |b\rangle \text{ and } |a\rangle$$

Please note the difference between the above example and the above Theorem. All functionals from the dual space have a corresponding "dual" ket. Therefore the functionals $b$ from the dual space are denoted $\langle b |$. The ket dual to $\langle a |$ is denoted $|a\rangle$. Hence

$$b(a) = \langle b | a \rangle = \text{ scalar product of } |b\rangle \text{ and } |a\rangle.$$  

An important property of bras and kets follows from the properties of the scalar (dot) product.

$$\langle b | a \rangle^* = \langle a | b \rangle$$

At this stage you might recall how you used to evaluate the scalar product of two vectors in the orthonormal basis

$$k = \begin{pmatrix} k_1 \\ k_2 \\ k_3 \end{pmatrix},$$

$$a = (a_1, a_2, a_3).$$

Then you used to evaluate the scalar product as $k_1a_1 + k_2a_2 + k_3a_3$. This is good only for real and not for complex scalar product. In quantum mechanics the prescription is

$$\langle k | a \rangle = k_1^*a_1 + k_2^*a_2 + k_3^*a_3$$

Below we show a couple of examples on how to use bra and ket in practical calculations.
Example 3.7  a) Let us take a finite dimensional (3 dim) complex space. \( |k\rangle \) is represented by \[
\begin{pmatrix}
k_1 \\
k_2 \\
k_3
\end{pmatrix}, how to calculate the corresponding bra?
\]

Answer: In the finite dimensional space, say three dimensional \( \langle k| \) is represented by \( (k^*_1, k^*_2, k^*_3) \). To check, evaluate the following using conventional rules of matrix multiplication

\[
\langle k|a\rangle = (k^*_1, k^*_2, k^*_3) \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = k^*_1 a_1 + k^*_2 a_2 + k^*_3 a_3
\]

b) In the infinite dimensional space of functions (restricted to some extent). Let \( |\phi\rangle \) be represented by a function \( \phi(r) \) and \( |\psi\rangle \) be represented by a function \( \psi(r) \). Then

\[
\langle \psi|\phi \rangle = \int d^3r \psi^*(r) \phi(r)
\]

In this case the bra \( \langle \psi| \) is represented by \( \int d^3r \psi^*(r) \cdot \). The \( \cdot \) is supposed to mean "acting on something".

3.3 Operators

A linear operator is a prescription \( \hat{A} \) that assigns a vector \( y \) to each vector \( x \)

\[
\hat{A}(x) = y
\]

such that \( \hat{A}(a \cdot x + b \cdot y) = a \hat{A}(x) + b \hat{A}(y) \)

That means that this prescription is linear, \( a, b \in \mathbb{C} \) or \( \mathbb{R} \). Linear operators are important because physical quantities (observables) such as momentum, spin, position, energy etc will be described (represented) by them. Below we give examples of linear operators:

Example 3.8  Operator "multiply by 5", \( \hat{M}_5 \) is defined as: \( \hat{M}_5(x) = 5 \cdot x \) is a linear operator.

Example 3.9  This really is a counterexample to the previous one. Let \( x_0 \) be a fixed vector \( \neq 0 \). The operator denoted \( \hat{M}_{5+x_0} \) and defined as \( \hat{M}_{5+x_0}(x) = 5 \cdot x + x_0 \) is not a linear operator because of the addition of \( x_0 \).

Please note a couple of simple observations.

\( \hat{A} \) acts on vectors. \( \hat{A}(7) \) is not defined. The composition of \( \hat{A} \cdot \hat{M}_5 \) makes sense and is a linear operator, defined as:

\[
\hat{A} \cdot \hat{M}_5(x) = \hat{A} \cdot (5 \cdot x) = 5 \cdot \hat{A}(x)
\]

as \( \hat{A}(x) \) is a vector.
We can also add the linear operators provided they are defined on the same space, the sum is defined as:
\[ \forall \mathbf{x} (\hat{A} + \hat{B})(\mathbf{x}) = \hat{A}(\mathbf{x}) + \hat{B}(\mathbf{x}) \]

Please also note the difference between functionals and linear operators.

In the Dirac notation we will write operators acting on kets on the left side of a ket. On the other hand the operators acting on bra are written always on the right side of this bra.
\[ \langle \text{bra} | \text{Operator} = \langle \text{another bra} | \]

Any other sequence does not make sense and is illegal.

Now we introduce an important concept of an adjoint operator \( \hat{A}^\dagger \) to the operator \( \hat{A} \) which is defined as follows.

Let \( |a\rangle \) be an arbitrary ket. Consider the relationship between the bra \( \langle a | \) and a bra dual to the ket \( \hat{A}|a\rangle \). It can be easily shown that these two bras are related through a new linear operator called adjoint to the operator \( \hat{A} \) and written \( \hat{A}^\dagger \). In other words
\[ \langle a | \hat{A}^\dagger = \text{the bra dual to } \hat{A}|a\rangle \]

The operator is said to be Hermitean if \( \hat{A}^\dagger = \hat{A} \). You may wish to note that this definition makes sense in Hilbert spaces, where there is a one to one correspondence between the space itself and a dual space.

Adjoint operator enjoys the following property, that is sometimes used as a definition:
\[ \langle b | \hat{A}|a\rangle = \langle b | \hat{A}^\dagger |a\rangle^* \]

Now we will lead you through a couple of exercises.

**Exercise 3.1** Find the operator adjoint to \( \hat{A} = |b\rangle \langle a | \), where \( |a\rangle, |b\rangle \) are given kets.

Solution: Take two arbitrary states \( \mathbf{x} \) and \( \mathbf{y} \). Then
\[ \langle \mathbf{y} | \hat{A}| \mathbf{x}\rangle = \langle \mathbf{y} | b \rangle \langle a | \mathbf{x}\rangle = \langle \mathbf{x} | a \rangle \langle b | \mathbf{y}\rangle^* = [\langle \mathbf{x} | a \rangle \langle b | \mathbf{y}\rangle]^* \]

The last equation is a consequence of the rules for complex numbers \( A^*B^* = (AB)^* \).

Therefore \( \hat{A}^\dagger = |a\rangle \langle b | \)

**Exercise 3.2** The projection operator \( \hat{P} \) is defined as a Hermitean operator that fulfills \( \hat{P}^2 = \hat{P} \hat{P}^2 = \hat{P} \cdot \hat{P} \). The following Fig 3.8 illustrates that this property is fulfilled by the conventional 90 degrees projection from high school geometry.

Write down the projection operator onto the normalised state \( |\alpha\rangle \) using Dirac notation. Normalised means that \( \langle \alpha | \alpha \rangle = 1 \).
Solution: \( \hat{P}_\alpha = |\alpha\rangle \langle \alpha | \) is of course Hermitean. We check that \( \hat{P}_\alpha \hat{P}_\alpha = \hat{P}_\alpha \). For any arbitrary \( |\beta\rangle \)

\[ |\alpha\rangle \langle \alpha | \alpha\rangle \langle \alpha | = |\alpha\rangle \langle \alpha | \langle \alpha | \beta \rangle \] using normalisation.

**Exercise 3.3**  
*Normalise the vector* \( \left( \begin{array}{c} i \\ 2 \\ 3 \end{array} \right) \) *and write the projection operator* \( \hat{P} \) *that projects onto this vector.*

Solution: \( |\gamma\rangle \) is represented by

\[
\left( \begin{array}{c} i \\ 2 \\ 3 \end{array} \right),
\]

\( \langle \gamma | \) is represented by

\[
( -i \ 2 \ 3 ).
\]

The scalar product

\[
\langle \gamma | \gamma \rangle = ( -i \ 2 \ 3 ) \left( \begin{array}{c} i \\ 2 \\ 3 \end{array} \right) = 1 + 4 + 9 = 14.
\]

The normalised \( |\gamma\rangle \) denoted \( |\gamma'\rangle \) is represented by:

\[
\frac{1}{\sqrt{14}} \left( \begin{array}{c} i \\ 2 \\ 3 \end{array} \right),
\]

the normalised bra \( \langle \gamma' | \) is represented by:

\[
\frac{1}{\sqrt{14}} ( -i \ 2 \ 3 ),
\]

Therefore:

\[
|x'\rangle \langle x'| = \frac{1}{14} \left( \begin{array}{c} i \\ 2 \\ 3 \end{array} \right) ( -i \ 2 \ 3 ) = \frac{1}{14} \left( \begin{array}{c} 1 \\ 2i \\ 3i \end{array} \right).
\]

Now we will check that \( \hat{P}|\gamma'\rangle = |\gamma'\rangle \):

\[
\frac{1}{14} \frac{1}{\sqrt{14}} \left( \begin{array}{ccc} 1 & 2i & 3i \\ -2i & 4 & 6 \\ -3i & 6 & 9 \end{array} \right) \left( \begin{array}{c} i \\ 2 \\ 3 \end{array} \right) = \frac{1}{14} \left( \begin{array}{c} 14i \\ 28 \\ 42 \end{array} \right) \frac{1}{\sqrt{14}} = \frac{1}{\sqrt{14}} \left( \begin{array}{c} i \\ 2 \\ 3 \end{array} \right).
\]
Exercise 3.4 Write explicitly the projection operator onto a normalised function $\Phi(r)$.

Solution: The normalisation condition means that

$$\int d^3r \phi^*(r)\phi(r) = 1.$$  

$$\hat{P}_\phi = |\phi\rangle\langle\phi|,$$

$$\hat{P}_\phi(\cdot) = \phi(r) \int \phi^*(r') (\cdot) d^3r' = \int \phi(r)\phi^*(r') (\cdot) d^3r'.$$

For any function $f$

$$\hat{P}_\phi(f(r)) = \int \phi(r)\phi^*(r') f(r') d^3r'.$$

3.4 Eigenvectors and eigenvalues

Let $\hat{A}$ be a linear operator, $|\lambda\rangle$ is called an eigenvector (eigenket, or eigenstate) of $\hat{A}$ if

$$\hat{A}|\lambda\rangle = \lambda|\lambda\rangle, \quad \lambda \in \mathbb{C}$$

$\lambda$ is called an eigenvalue. A following important theorem tells more about the eigenvalues and eigenkets of a Hermitean operator.

**Theorem 3.2** The eigenvalues of a Hermitean operator $\hat{A}$ are real, the eigenkets corresponding to different eigenvalues are orthogonal.

(Orthogonal means that their scalar product is zero).

Proof:

Let $|a\rangle$ be an eigenket of $\hat{A}$. Then

$$\hat{A}|a\rangle = a|a\rangle \quad (1)$$

Let $\langle a'|$ be an eigenvector of $\hat{A}^\dagger$ with the eigenvalue $a'^*$. 

$$\langle a' | \hat{A}^\dagger = a'^* \langle a'|$$

$\hat{A}$ is hermitean, then

$$\langle a'| \hat{A} = a'^* \langle a'| \quad (2)$$

We take a scalar product of $\langle a'|$ with Equation (1) and get

$$\langle a'| \hat{A} = a' \langle a'|a\rangle \quad (3)$$

We take a scalar product of $|a\rangle$ with Equation (2), 

$$\langle a'| \hat{A} = a'^* \langle a'|a\rangle \quad (4)$$
We subtract the Equation 4 from the Equation 3.

\[ 0 = (a' - a'^*)\langle a''|a' \rangle \quad (5) \]

Two cases are possible

- If \(|a''\rangle = |a''\rangle\) (identical kets) then from (5) \(a'' = a'^*\). This means that the eigenvalues of a Hermitian operator are real.

- If the eigenkets are not the same then \(a'' \neq a'^*\) and from (5) \(\langle a''|a' \rangle = 0\). This means that the eigenvectors corresponding to different eigenvalues are orthogonal.

The problem arises how to calculate the eigenvalues and the eigenvectors of a given operator \(\hat{A}\). It is particularly easy for \(\hat{A}\) acting in a finite (\(n\)) dimensional space. Let \(|e_i\rangle, i = 1, \ldots, n\) be a basis. Then the matrix \(A\) given by:

\[
A = \begin{pmatrix}
\langle e_1|\hat{A}|e_1 \rangle & \cdots & \langle e_1|\hat{A}|e_n \rangle \\
\vdots & \ddots & \vdots \\
\langle e_n|\hat{A}|e_1 \rangle & \cdots & \langle e_n|\hat{A}|e_n \rangle
\end{pmatrix}
\]

has the same eigenvectors as the operator \(\hat{A}\). The reader is assumed to have mastered the technique of calculation those eigenvalues. The eigenvectors of this matrix represent the eigenkets of \(\hat{A}\). The matrix \(A\) is called the representation of the operator \(\hat{A}\) in a given basis. Obviously \(\hat{A}\) has \(n\) eigenvectors and \(n\) eigenvalues, but generally speaking some of these eigenvalues may be the same.

The eigenvectors of a Hermitian operator are said to form a complete set. This means that there is enough eigenvectors to express any other vector as their linear combination.

Let \(|a'\rangle\) be a normalised eigenvector of a Hermitian operator \(\hat{A}\). Then

\[
\sum_{a'} |a'\rangle\langle a'| = \hat{1}
\]

The symbol \(\hat{1}\) means the operator \(M_1\) that multiplies by 1. Then

\[
|\beta\rangle = \hat{1}|\beta\rangle = \sum_{a'} |a'\rangle\langle a'|\beta\rangle
\]

The following exercises help to gain some manual dexterity with kets and bras.

**Exercise 3.5** Prove that for arbitrary \(|z\rangle\),

\[
(a\langle x| + b\langle y|)z = a\langle x|z) + b\langle y|z
\]

In other words prove the linearity of bras.

Proof. Let \(\langle q| = a\langle x| + b\langle y|\). We have

\[
\langle q|z\rangle = \langle z|q\rangle^* = \langle z|a^*|x\rangle + b^*\langle z|y\rangle
\]

Taking the complex conjugate of both sides we have:

\[
\langle q|z\rangle = \langle z|q\rangle^* = a\langle x|z) + b\langle y|z
\]
**Exercise 3.6** Prove the property of the adjoint operator mentioned a couple of pages ago, that
\[\langle a|\hat{A}|b\rangle = \langle b|\hat{A}^\dagger|a\rangle^*\]
for any arbitrary \(|a\rangle, |b\rangle\)

Proof: Let us put \(|x\rangle = \hat{A}|b\rangle\) so that
\[\langle a|\hat{A}|b\rangle = \langle a|x\rangle\]
By properties of the scalar product
\[\langle a|x\rangle^* = \langle x|a\rangle\]
By definition of the adjoint operator \(\hat{A}^\dagger\)
\[\langle x| = \langle b|\hat{A}^\dagger\]
so that
\[\langle x|a\rangle = \langle b|\hat{A}^\dagger|a\rangle\]
Thus
\[\langle b|\hat{A}^\dagger|a\rangle = \langle x|a\rangle = \langle a|x\rangle^* = \langle a|\hat{A}|b\rangle^*\]
or
\[\langle a|\hat{A}|b\rangle = \langle b|\hat{A}^\dagger|a\rangle^*\]

**Exercise 3.7** Prove that the operator \(\hat{B}\) defined from the linear operator \(\hat{A}\) by the equation \(\langle p|\hat{A}|q\rangle = \langle q|\hat{B}|p\rangle\) is not a linear operator.

Solution: Consider \(\langle x|\hat{B}|(\lambda_1|q_1\rangle + \lambda_2|q_2\rangle)\) where \(|x\rangle\) is arbitrary. Then
\[\langle x|\hat{B}|(\lambda_1|q_1\rangle + \lambda_2|q_2\rangle)\]
\[= (\lambda_1^*\langle q_1| + \lambda_2^*\langle q_2|)\hat{A}|x\rangle = \lambda_1^*\langle q_1|\hat{A}|x\rangle + \lambda_2^*\langle q_2|\hat{A}|x\rangle\]
\[= \lambda_1^*\langle x|\hat{B}|q_1\rangle + \lambda_2^*\langle x|\hat{B}|q_2\rangle = \langle x|((\lambda_1^*\hat{B}|q_1\rangle + \lambda_2^*\hat{B}|q_2\rangle)\]
As \(|x\rangle\) is arbitrary, then
\[\hat{B}|(\lambda_1|q_1\rangle + \lambda_2|q_2\rangle) = \lambda_1^*\hat{B}|q_1\rangle + \lambda_2^*\hat{B}|q_2\rangle\]
\(\hat{B}\) is called **anti-linear**.

**Exercise 3.8** For \(\hat{A}|b_i\rangle = \sum_j b_{ij}|b_j\rangle\) where the \(|b_j\rangle\) form a complete orthonormal set, evaluate \(\langle b_i|\hat{A}\) by using the rule:
\[\langle b_i|\hat{A}|x\rangle = \langle b_i|\hat{A}|x\rangle\]
Solution: First we remind that

\[ b_{ij} = \langle b_i | \hat{A} | b_j \rangle \]

and

\[ \sum_j |b_j\rangle\langle b_j| = \hat{1} \]

We have

\[ \langle b_i | \hat{A} \cdot \hat{1} = \sum_j \langle b_i | \hat{A} | b_j \rangle \langle b_j | \]

\[ = \sum_{j} |b_i\rangle\langle b_j| = \sum_{j} \sum_{k} b_{jk} |b_k\rangle\langle b_j| \]

\[ = \sum_{jk} b_{jk} \langle b_i | b_k \rangle \langle b_j | = \sum_{j} \sum_{k} b_{jk} \delta_{ik} \langle b_j | \]

\[ = \sum_{j} b_{ji} \langle b_j | \]

3.5 Continuous eigenvalue spectra and the Dirac delta function

First we will make a distinction between the operators with discrete eigenvalues and the operators with continuous eigenvalues. An example of the operator with discrete eigenvalues is the following operator \( \hat{O}_1 \) with eigenvalues of 0.25, 1/3, 0.75, 1.0, 4/3, ..., 2.25, 7/3, ... etc. These eigenvalues can be indexed with integers. This is what is called a discrete spectrum of an operator. An example of the operator with the continuous spectrum is the operator \( \hat{O}_2 \) whose eigenvalue is any number between 3 and 17. This operator is said to have a continuous spectrum. Mixed cases are quite common, when for example negative eigenvalues are discrete and positive are continuous.

For (hermitean) operators with discrete spectrum we have:

\[ \hat{A}|a_n\rangle = a_n |a_n\rangle \]

\[ \langle a_n | a_{n'} \rangle = \delta_{nn'} \]

The symbol \( \delta_{nn'} \) is a Kronecker delta and is equal to 1 if \( n = n' \) and 0 otherwise. It is useful when for instance we want to evaluate the coefficients of expansion of a given state \(|q\rangle\) in the complete set \(|n\rangle\) of eigenstates of \( \hat{A} \). Then we have:

\[ |q\rangle = \sum_{n'} c_{n'} |a'_{n'}\rangle \]

\[ \langle a_n | q \rangle = \sum_{n'} \langle a_n | a'_{n'} \rangle = c_n \] \hspace{1cm} (*)

It would be very useful to have a formula similar to (*) for operators with continuous spectrum. Many physical quantities can take a continuous range of values, for example energy of a free particle, position, momentum and numerous others.
To be more specific let us take the momentum operator \( \hat{p} \) in one dimension. The momentum of a particle can take any real value, and this means that the eigenvalue of \( \hat{p} \) can be any real number.

\[
\hat{p}|p\rangle = p'|p\rangle, p' \in \mathbb{R}
\]

We express

\[
|q\rangle = \int_{-\infty}^{\infty} c_{p'}|p'\rangle dp'
\]

and we would like to retain

\[
\langle p|q \rangle = \int_{-\infty}^{\infty} \langle p|p' \rangle = C(p)
\]

Unfortunately \( \langle p|p' \rangle \) can not be simply replaced by the Kronecker delta. Obviously for \( p \neq p' \) the value of \( \langle p|p' \rangle \) has to be zero, but no number is suitable for \( p = p' \). Therefore \( \langle p|p' \rangle \) is not a function. (It is in fact a functional). \( \langle p|p' \rangle \) will be further called a Dirac delta and denoted \( \delta(p - p') \). You should manipulate it with some caution. A useful practical rule is to never let Dirac delta stand alone, always integrate it with some function, because then all quantities in your mathematics will have a well defined meaning as below.

\[
\int_{-\infty}^{\infty} f(p)\delta(p - p') dp' = f(p')
\]

Some innocent looking operations such as taking a square in case of Dirac delta are mathematically improper and usually indicate serious faults in your derivations. Beware. Dirac delta is a limit of numerous sequences of functions. Two of them is shown in the Figs 3.9 and 3.10 and given by:

\[
\delta(x) = \lim_{\alpha \to \infty} \sqrt{\frac{\alpha}{\pi}} \exp(-\alpha x^2)
\]

and also

\[
\delta(x) = \lim_{\alpha \to \infty} \frac{\sin(\alpha x)}{\pi x}
\]

The same reasoning as for the momentum operator can be repeated for the position operator. The results are summarised below.

\[
\langle x'|x'' \rangle = \delta(x' - x'')
\]

\[
\langle p'|p'' \rangle = \delta(p' - p'')
\]
Figure 3.10: $\frac{\sin(\alpha x)}{\pi x}$
Chapter 4

Basic postulates of quantum mechanics

4.1 Probability and observables

4.1.1 Measurement in quantum mechanics

Below we will briefly discuss the concept of measurements in quantum mechanics without too much detail. The quantities that can be measured in classical physics include the one that are related to a single particle, such as the position of a particle, its momentum or acceleration. Many other quantities can be measured such as for example the volume of gas, pressure, viscosity etc. In quantum mechanics the physical quantities that we will be concerned with, apply either to a single particle or to small systems. These measurable quantities include for example position, momentum, angular momentum, spin, etc. (It is to be noted that mass is not an observable as it is a proportionality coefficient between between force or the first derivative of momentum and acceleration).

In classical physics the measurement is supposed not to change the state of the system. For example in electrodynamics a concept of a "probe charge" is introduced, that is used to probe or to measure the electric field. A probe charge is so small that it does not perturb the electric field it is supposed to measure. This concept of noninterfering measurements can not be upheld in quantum mechanics - no probe is small enough to maintain existing experimental conditions in case of small particles. An example of such perturbation is an experiment in which we attempt to measure position of an electron by means of a single photon scattering. After the detection of this particular photon, we make a judgement about the position of our electron. This judgement, however refers to its position a while ago, during the event of scattering. In the act of scattering the electron has been knocked off its position and is now somewhere else. A somewhat extreme case is the photodetection. In photodetection a photon is annihilated or destroyed in the photodiode, giving rise to an electron-hole pair, and their current is further amplified and for example visualised on the CRO. The change of state in case of this photon is quite dramatic and quite properly has been described as "quantum demolition". Very recently it has been realised that the act of photon detection may not be accompanied by its destruction. Such experiments are called "quantum non-demolition" measurements. An example of such experiments, in which photons can be counted without being destroyed is based in the principle of an optical Kerr effect. In the optical Kerr effect electric field is applied perpendicularly to an electrooptic crystal. The crystal acts as an electric field dependent polariser for the light beam. The
change of polarisation between the incoming and the outgoing field is proportional to the electric field. In "quantum nondemolition" photon detection two photon beams intersect the crystal. One photon beam will be sensing changes in polarisation and is called the probe beam. The detected or counted beam provides electric field for the Kerr effect. Each passing photon provides (some) electric field in the crystal for a short while. This electric field changes the polarisation of the probe beam, which is further analysed using standard methods. Of course photons in the detected beam are not destroyed, detailed calculations show that they not emerge unscathed.

A key element of a correct methodology in physics involves experiments that can be reproduced. This feature is carried on to quantum mechanics, where experiments are understood to be performed a number of times in identical conditions on a number of identical systems called an ensemble. In order to ensure that we are dealing with identical systems the systems are subjected to the state preparation. An example of state preparation is demonstrated in the S-Gz experiment in which one of the beams, namely $S_z^-$ is blocked. The remaining beam is in the $S_z^+$ state, or we can say that it has been prepared in the $S_z^-$ state- we know with certainty or with probability 1 that the 5s electrons in Ag atoms have the magnetic moment of $\hbar/2$ and they will retain it till further interactions. This beam is said to be in a pure state. Such pure states are main object of our lectures. Being in a pure state means to be fully characterised by a state vector or a ket. There are some cases, however, when a physical system can not be described as a state vector. Such states are called mixed states. An example of a mixed state is a beam of Ag atoms just emerged from an oven. We do not know what are their spins like. Mixed states involve incomplete knowledge about the system. The formalism used in such cases takes advantage of the concept of the density operator, which is outside the scope of our lectures.

We will now briefly describe experiments that provide information about physical quantities for a single particle. It has to be noted that these are "demolition" experiments. The measurement of position is illustrated in the Fig 4.1 A. The particles are moving towards the slit of the width $\Delta z$ placed at $z$. A particle detector is placed behind the slit. The particles, having emerged from the slit have their $z$ component filtered - it is close to $z$ with the uncertainty of $\Delta z$. A particle registered in the detector is known to have had its $z$ component equal to $z$ and its uncertainty is $\Delta z$. A similar momentum measurement is illustrated in the Fig 4.1B. The (charged) particles emerging from a given point but with various momenta are moving in a constant magnetic field. Their trajectory will be circular with the radius of curvature related to the particle momentum. A slit placed in their path will select particles with a particular values of the momentum. A detector placed behind this slit registers particles with this particular value of momentum within the uncertainty given by the slit width, as in the previous case. Finally a S-Gz experiment can filter out electrons with a particular value of spin - either $\hbar/2$ or $-\hbar/2$, depending on which beam is blocked. Obviously these experiments can be performed in a sequential fashion in order to give information about various physical quantities of a given particle simultaneously, but as we remember from the sequential S-G experiments, this may result in changing the quantum state. Later we give conditions for such change not to occur. Finally in classical mechanics experiments conducted on identical systems in identical conditions are supposed to give exactly identical results. Some small experimental uncertainties are attributed to practical difficulty in maintaining these identical conditions. In quantum mechanics, however such experiments may give different individual results. A good example is the S-Gx experiment conducted on the $S_x^+$ state. In 50 % of cases the result is that the particle is in $S_x^+$ with the eigenvalue of $\hbar/2$ and in the remaining 50 % $S_x^-$ with the eigenvalue of $-\hbar/2$. However as we will discuss later quantum mechanical systems with classical analogue behave in a way that the quantum mechanical average coincides with
4.1.2 Postulates

The postulates of quantum mechanics to some extent resemble Newton’s laws in classical mechanics - they summarise the minimum necessary facts that allow to understand all more complex phenomena. The postulates are listed below and they are discussed later.

Postulate 1.
the state of a system is described in terms of its state vector or ket that belong to a certain Hilbert space.

Postulate 2.
physical quantities (dynamical variables) associated with a given system are represented by linear hermitean operators.

Postulate 3.
as a result of measurement of a given dynamical variable A only eigenvalues of the corresponding operator $\hat{A}$ can be observed.

Postulate 4.
the probability for the system being thrown into $|a'\rangle$ is equal to $|\langle a' | \alpha \rangle|^2$

As pointed out earlier it is postulated that the state of a system is described in terms of its state vector or ket that belong to a certain Hilbert space.

In quantum mechanics it is also postulated that physical quantities (dynamical variables) associated with a given system are represented by linear hermitean operators.
Some important operators that are associated with a single particle albeit not only are listed below. These include

- the position operator \( \hat{x} \)
- the momentum operator \( \hat{p} \)
- the spin operators \( \hat{S}_x, \hat{S}_y, \hat{S}_z \)
- the energy operator \( \hat{H} \)
- the angular momentum operator \( \hat{L} \)

It is postulated that as a result of measurement of a given dynamical variable \( A \) only eigenvalues of the corresponding operator \( \hat{A} \) can be observed.

It is easiest to see how it works for one of the S-G experiments. The measurements we are concerned with are "filtration" experiments they "filter out" or "throw" or "project" the system into one of the eigenstates of the operator \( \hat{A} \). In the case of the S-G experiment when the S-Gz experiment is performed, the system is thrown into one of the eigenstates of the \( \hat{S}_z \) operator. If we measure the \( x \)-component of spin doing the S-Gx experiment, the system will be thrown into one of the eigenstates of the \( \hat{S}_x \) operator.

Note that this postulate usually entails the change of state occurring during the measurement.

Assume that before the measurement the system was in one of its states \( |\alpha\rangle \). Then

\[
|\alpha\rangle = \sum_{a'} c_{a'} |a'\rangle = \sum_{a'} |a'\rangle \langle a'| \alpha\rangle
\]

where \( |a'\rangle \) is the eigenstate of the observable \( A \). After the measurement the system is in one of the states \( |a'\rangle \)

It is postulated that the probability for the system being thrown into \( |a'\rangle \) is equal to \( |\langle a'|\alpha\rangle|^2 \)

For example if we consider the system prepared in the state \( |S^+\rangle \) and consecutively measure the \( x \)-component of spin in this state by letting the particles pass through the S-Gx experiment, the probability of obtaining the value of the \( x \)-component of spin of \( +\hbar/2 \) is:

\[
|\langle S^+_x | S^+_z \rangle|^2 = 0.5
\]

and the probability of obtaining the value of the \( x \)-component of spin of \( -\hbar/2 \) is:

\[
|\langle S^+_x | S^-_z \rangle|^2 = 0.5
\]

We can write down all possible expressions such as the ones above for all possible combinations of S-G experiments, and they together with the condition of two eigenstates of the same spin operator being orthonormal give rise to the explicit expressions for the spin states \( |S^+_x\rangle, |S^+_y\rangle, |S^+_z\rangle \) in the following form:

\[
|S^+_x\rangle = \frac{1}{\sqrt{2}} |S^+_z\rangle + \frac{1}{\sqrt{2}} |S^-_z\rangle
\]

\[
|S^+_y\rangle = \frac{1}{\sqrt{2}} |S^+_z\rangle + \frac{i}{\sqrt{2}} |S^-_z\rangle
\]
Please note that $|S^\pm_x\rangle$ are NOT orthogonal to $|S^\pm_z\rangle$. We have to quickly dissociate ourselves from the notion of spin states being just components of a three dimensional spin vector, in which case the x-component is orthogonal to the z and y component. It will take us a while to identify this conventional three dimensional vector associated with spin and proportional to the magnetic moment and we are not there yet.

The above probabilities are instrumental when calculating the average value of a dynamical variable $A$ obtained in a given measurement of $A$. The averaged measured value of $A$ is given by the expectation value of $\hat{A}$ in a given state $|\alpha\rangle$. We remind here that in all considered measurements the system is supposed to be in a pure state.

The expectation value of an observable $A$ in the state $|\alpha\rangle$ is defined as:

$$\langle \hat{A} \rangle = \langle \alpha | \hat{A} | \alpha \rangle$$

and it is consistent with the notion of the averaged measured value.

$$\langle \hat{A} \rangle = \sum_{\alpha'} \sum_{\alpha''} \langle \alpha | \alpha'' \rangle \langle \alpha'' | \hat{A} | \alpha' \rangle \langle \alpha' | \alpha \rangle = \sum_{\alpha'} |\langle \alpha' | \alpha \rangle|^2 \alpha'$$

The expectation value of $A$ is the weighted average of the eigenvalues of $\hat{A}$. The weights are equal to the probability of obtaining the eigenvalue $\alpha'$ as a result of measurement.

These postulates and our knowledge of the results of all sequential S-G experiments allow us to find explicitly the spin operators as shown in the following example.

**Example 4.1** Spin states (kets) will be represented as two-dimensional complex vectors (why?). On the basis of results of all sequential S-G experiments determine the operators $\hat{S}_x, \hat{S}_y, \hat{S}_z$.

Solution: As presented above the results of sequential S-G experiments allow to determine the explicit expression for the states $|S^\pm_x\rangle$ and $|S^\pm_y\rangle$ in terms of $|S^\pm_z\rangle$, as follows:

$$|S^+_x\rangle = \frac{1}{\sqrt{2}}|S^+_z\rangle \pm \frac{1}{\sqrt{2}}|S^-_z\rangle$$

$$|S^+_y\rangle = \frac{1}{\sqrt{2}}|S^+_z\rangle \pm \frac{i}{\sqrt{2}}|S^-_z\rangle$$

The proposition for the operator $\hat{S}_x$ is the following:

$$\hat{S}_x^{proposed} = \frac{\hbar}{2}|S^+_x\rangle \langle S^+_x| + \frac{-\hbar}{2}|S^-_x\rangle \langle S^-_x|$$

It can easily be seen that this operator is linear. In order to check its correctness we will apply it to the spin eigenstates, that (hopefully) are its eigenvectors. In this case we should have:

$$\hat{S}_x|S^+_x\rangle = \frac{\hbar}{2}|S^+_x\rangle$$

$$\hat{S}_x|S^-_x\rangle = \frac{-\hbar}{2}|S^-_x\rangle$$

We evaluate the similar quantity for the proposed operator

$$\hat{S}_x^{proposed}|S^+_x\rangle = \frac{\hbar}{2}|S^+_x\rangle \langle S^+_x|S^+_x\rangle + \frac{-\hbar}{2}|S^-_x\rangle \langle S^-_x|S^+_x\rangle$$
Now we have to calculate the scalar products:

\[ \langle S_x^+ | S_x^+ \rangle = \left( \frac{1}{\sqrt{2}} | S_z^+ \rangle + \frac{1}{\sqrt{2}} | S_z^- \rangle \right) \left( \frac{1}{\sqrt{2}} | S_z^+ \rangle + \frac{1}{\sqrt{2}} | S_z^- \rangle \right) = 1 \]

\[ \langle S_x^+ | S_x^- \rangle = \left( \frac{1}{\sqrt{2}} | S_z^+ \rangle + \frac{1}{\sqrt{2}} | S_z^- \rangle \right) \left( \frac{1}{\sqrt{2}} | S_z^+ \rangle - \frac{1}{\sqrt{2}} | S_z^- \rangle \right) = 0 \]

A similar calculation has to be performed for the other eigenstate. This proves that

\[ \hat{S}_x^{\text{proposed}} | S_x^+ \rangle = \frac{\hbar}{2} | S_x^+ \rangle \]

and

\[ \hat{S}_x^{\text{proposed}} | S_x^- \rangle = -\frac{\hbar}{2} | S_x^- \rangle \]

thus confirming that our proposition was good. Similar expressions can be proposed and proven in identical fashion for the \( \hat{S}_y \) and the \( \hat{S}_z \) operators.

**Exercise 4.1** Evaluate the matrix of the operator \( \hat{S}_x \) in the basis \( |S_x^\pm\rangle \).

Solution: We remind ourselves how to construct a matrix representing a given operator (its elements are \( a_{ij} = \langle e_i | \hat{A} | e_j \rangle \)) and write the matrix directly as:

\[
\begin{pmatrix}
\langle S_z^+ | \hat{S}_x | S_z^+ \rangle & \langle S_z^+ | \hat{S}_x | S_z^- \rangle \\
\langle S_z^- | \hat{S}_x | S_z^+ \rangle & \langle S_z^- | \hat{S}_x | S_z^- \rangle
\end{pmatrix}
\]

The reader may wish to write down the matrices of the remaining spin operators in the same basis or in other bases, such as \( |S_x^\pm\rangle, |S_y^\pm\rangle \) and answer simple questions such as for example what is the average value of the operator \( \hat{S}_z \) in the state \( |S_z^\pm\rangle \). At this stage you should be able to completely understand the sequential S-G experiments.

### 4.2 The concept of a complete set of commuting (compatible) observables

This concept arose from the problem of interfering vs non-interfering measurements. When discussing the sequential S-G experiment S-Gz - S-Gx - S-Gz we noted that the S-Gx experiment somehow destroyed what we knew about the pure state having emerged from the first S-Gz experiment. S-Gz and S-Gx are therefore interfering with each other. This fact is quite easy to understand from the mathematical point of view. The measurement of a given physical observable \( A \) can be compared to applying a projection operator \( P_{a} \) (that project onto one of the eigenstates of \( \hat{A} \) to a given quantum state. The sequential measurement of A and B means that we apply two different projection operators \( P_{a} \) and \( P_{b} \) to a given state. After A has been measured with the result \( a \) the system is in the state \( |a\rangle \) with probability 1. When we apply the projection operator \( P_{b} \) to this state \( |a\rangle \) we have some chance of getting either the state \( |a\rangle \) with probability \( \langle b | a \rangle \) or any other state of \( \hat{B} \). Clearly this means that the pure state \( |a\rangle \) has been destroyed. Moreover if we consider making the measurements of A and B in two sequences A after B and B after A we will get different results. To understand that it is useful to see the Fig 4.2 where we illustrate these two sequences of measurements using geometric projections onto
Figure 4.2: The orthogonal projections onto two different vectors do not commute.
two different vectors. (We know that the projection operator has very much in common with the ordinary geometrical projection). It is easy to see that these two sequences of projections give different final results.

For some physical observables called compatible observables it does not have to be this way. Below we present the condition that two physical observables have to fulfill for non-interfering measurements. Such two quantities can be measured consecutively in any order with identical results. We will present the condition and its mathematical proof first, the geometrical interpretation and use later.

Definition: A and B are called compatible observables if

\[ \hat{A} \cdot \hat{B} - \hat{B} \cdot \hat{A} = 0 \]

This important quantity \( \hat{A} \cdot \hat{B} - \hat{B} \cdot \hat{A} \) is denoted \([\hat{A}, \hat{B}]\) and is called a **comutator** of \( \hat{A} \) and \( \hat{B} \). This condition gives rise to a very special relationship between the eigenstates of both observables presented in the Theorem below. Before we go any further we would like to remind the reader that sometimes two linearly independent eigenkets of an operator may share the same eigenvalue, in this case the eigenvalue is called **degenerate**.

**Theorem 4.1** Let \( A \) and \( B \) be compatible observables, that is the respective operators commute \([\hat{A}, \hat{B}] = 0\). Assume that all eigenvalues of \( \hat{A} \) are non-degenerate. Then the matrix elements of \( \hat{B} \), \( \langle a'' | \hat{B} | a' \rangle \) are diagonal. (That means they are 0 if \( a'' \neq a' \). Recall that \( \langle a'' | \hat{A} | a' \rangle \) already is diagonal). In other words if two operators commute then they can be diagonalised by the same set of kets.

Proof:

\[ 0 = \langle a'' | [\hat{A}, \hat{B}] | a' \rangle = (a'' - a') \langle a'' | \hat{B} | a' \rangle \]

Therefore \( \langle a'' | \hat{B} | a' \rangle = 0 \) unless \( a' = a'' \)

It is to be noted that this theorem still holds even if there is n-fold degeneracy, that is \( A | a^{(i)} \rangle = a' | a^{(i)} \rangle \) for \( i = 1, 2, \ldots, n \), although the above proof has to be changed.

Such simultaneous eigenkets of \( A \) and \( B \) will be denoted with both eigenvalues \( |a', b'\rangle \).

We can generalise the idea of compatible observables to more than two. Let us take several mutually compatible observables \( A, B, C \), such that

\[ [\hat{A}, \hat{B}] = [\hat{B}, \hat{C}] = [\hat{A}, \hat{C}], \cdots = 0 \quad (*) \]

Assume that the set \( \hat{A}, \hat{B}, \hat{C}, \ldots \) is maximal, so that we can not add more observables without violating (*). We will denote common eigenkets of all those operators by \( |a', b', c', \ldots \rangle \). Then it can be proved that this set of kets is complete. (big enough so that we can express every vector in terms of \( |a', b', c', \ldots \rangle \). In mathematical terms completeness is written as:

\[ \sum_{a'} \sum_{b'} \sum_{c'} \cdots |a', b', c', \ldots \rangle \langle a', b', c', \ldots | = \hat{1} \]
A useful remark here is that the eigenvalues of individual operators in the above may have degeneracies, but when we specify a combination of \( a', b', c' \ldots \) then the eigenket of \( \hat{A}, \hat{B}, \hat{C}, \ldots \) is uniquely specified.

A following problem illustrates the concept of a complete set of kets.

**Example 4.2** A series of experiments on a certain kind of elementary particle was performed in order to determine the observables that can be used to fully characterize the eigenstates in which this kind of particle can be found. The first observable identified was called flavour (associated operator \( \hat{F} \)) and was found to have six possible values represented by the letters \( u, d, s, c, t \) and \( b \). The second one identified was an observable called colour (\( \hat{C} \)) which had three values \( r, g \) and \( b \). The particles were found to have more familiar properties: the spin angular momentum \( \hat{S}_z \) was always found to have values \( \pm 1/2\hbar \), and the particles possessed ordinary electric charge \( \hat{Q} \). However whenever the flavour observables had the values of \( u, c, \) or \( t \) the charge was measured to be \( 2e/3 \), where \( e \) is the charge on an electron, while for the flavours \( d, s, b \) a charge \( -e/3 \) was always observed. Assuming that the operators \( \hat{F}, \hat{C}, \hat{S}_z, \hat{Q} \) form a complete set of commuting observables for this kind of particles (quarks), write down the corresponding complete set of eigenstates for quarks. (A table is a good idea).

Solution: The simultaneous eigenkets of the commuting set of operators \( \hat{F}, \hat{Q}, \hat{C} \) and \( \hat{S}_z \) can be labelled by their flavour eigenvalue (\( f \)), charge (\( q \)) eigenvalue, colour (\( c \)) eigenvalue and spin (\( m \)) eigenvalue. So the eigenvalue is of the form \( |f, q, c, m\rangle \) where \( f = u, d, s, c, t, b, q = 2e/3, -e/3 \), \( c = r, g, b, m = \pm \hbar/2 \). Not all combinations are permitted: \( f \) and \( q \) are correlated. Altogether there is \( 6 \times 3 \times 2 = 36 \) possible states.

Now we will discuss the relationship between the compatible observables and measurements. Let us assume that \( \hat{A}, \hat{B} \) are compatible. First we consider the case of nondegenerate eigenvalues. The system is assumed to be prepared in the state \( |\alpha\rangle \). Assume that the measurement of \( A \) gave the result \( a' \), that is one of the eigenvalues of \( \hat{A} \). From compatibility the system is thrown into the simultaneous eigenket of \( \hat{A} \) and \( \hat{B} \), that is \( |a', b\rangle \). The consecutive measurement of \( B \) will result in the value \( b' \), but the state remains the same. Therefore the following measurement of \( A \) will also give the value \( a' \). This means that \( A \) and \( B \) can be measured one after another in any sequence with no effect for the final result. These two measurements do not interfere.

Now we will consider the case of some degenerate eigenvalues. Let the eigenvalue \( a' \) of \( \hat{A} \) be degenerate. Then the measurement of \( a' \) is a projection onto a certain linear combination

\[
\sum_{i=1}^{n} c_{a'}^{(i)} |a', b^{(i)}\rangle
\]

If we measure \( B \) afterwards, then the measurement of \( B \) selects one of \( b^{(i)} \)-s. Let us say that \( b^{(j)} \) is selected. Then in the measurement of \( B \) the system is projected onto \( |a', b^{(j)}\rangle \). Nevertheless if \( A \) is again measured afterwards, the ket stays the same and the result is again \( a' \). Therefore even in the case of degenerate eigenvalues \( A \) and \( B \) can be measured in any sequence - those two measurements do not interfere.
4.3 Quantum dynamics - time evolution of kets

The question that will be addressed in this section is the following. Let us assume that the system at \( t = 0 \) was in the state \( |\alpha, 0\rangle = |\alpha\rangle \). What will happen to this state after time \( t \)?

It is therefore the question of time evolution of kets. First we will discuss general properties of this time evolution.

We will introduce the **time evolution operator** which relates the kets at \( t = 0 \) and at \( t \).

\[
|\alpha, t\rangle = \hat{U}(t, t_0)|\alpha, 0\rangle
\]

We postulate the following intuitive properties of this operator:

- It does not change the scalar product of kets (their"length" or "norm"). If \( \langle \alpha, t_0 | \alpha, t_0 \rangle = 1 \), then \( \langle \alpha, t | \alpha, t \rangle = 1 \)

- It has the composition property

  \[
  \hat{U}(t_2, t_0) = \hat{U}(t_2, t_1) \cdot \hat{U}(t_1, t_0); t_2 > t_1 > t_0
  \]

  The intuition of this composition property is that the evolution of a given ket from \( t_0 \) to \( t_2 \) can be considered as the evolution from \( t_0 \) to \( t_1 \) and consequently from \( t_1 \) to \( t_2 \).

- For very small time intervals \( \hat{U}(t_0 + dt, t_0) \) is not very different from \( \hat{1} \)

Those conditions are satisfied if we put

\[
\hat{U}(t_0 + dt, t_0) = \hat{1} - \frac{i\hat{H}dt}{\hbar}
\]

where \( \hat{H} \) is a certain (hermitean) operator called a Hamiltonian.

It is left as an exercise for the reader to show that the time evolution operator fullfills the **Schrödinger equation for the time evolution operator** in the following form:

\[
i\hbar \frac{\partial}{\partial t} \hat{U}(t, t_0) = \hat{H}\hat{U}(t, t_0)
\]

This equation leads directly to the **time dependent Schrödinger equation for the kets** :

\[
i\hbar \frac{\partial}{\partial t} \hat{U}(t, t_0)|\alpha, t_0\rangle = \hat{H}\hat{U}(t, t_0)|\alpha, t_0\rangle
\]

therefore

\[
i\hbar \frac{\partial}{\partial t}|\alpha, t\rangle = \hat{H}|\alpha, t\rangle
\]

Two approaches are therefore possible in order to find the time evolution of kets

- either to solve the time dependent Schrödinger equation for the kets for each \( t \). To do that you need to explicitly know \( \hat{H} \).

- or (provided we explicitly know \( \hat{U}(t, t_0) \) to take \( |\alpha, t_0\rangle \) and "evolve" it using \( \hat{U}(t, t_0) \).

The Hamiltonian can be time independent or explicitly time dependent, we will give those examples later when discussing where to take the Hamiltonian from for a given system. Before we do that we will evaluate the time evolution operator in the case of the time independent Hamiltonian.
Example 4.3 The time evolution operator $\hat{U}$ for time-independent Hamiltonian.

Solution: The approach is to solve the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \hat{U} = \hat{H} \hat{U}$$

This equation is in a strict analogy to a common variety differential equation

$$\frac{d}{dx} f(x) = cf(x)$$

An example of its solutions is a function

$$f(x) = exp(cx)$$

It is easy to agree that a good way of postulating the solution can be proposed as follows:

$$\hat{U}(t, t_0) = \exp(-i\hat{H}(t - t_0) / \hbar)$$

But we really should hesitate: $\hat{H}$ is an operator and we want to evaluate its exp. How we are supposed to do that? Below we give a prescription. There is more than one such prescription or rather a definition each with its own drawbacks. Those drawbacks will not intervene at your level.

General prescription how to calculate functions of operators

Let $\hat{A}$ be an operator. We want to calculate a certain function $f(\hat{A})$ of this operator, for example $\sqrt{A}, \sin(\hat{A}), \exp(\hat{A})$. Let $a'$ be the eigenvalue of $\hat{A}$, $|a'\rangle$ is the eigenket of $\hat{A}$ with the eigenvalue $a'$. Then the operator $\hat{A}$ can be expressed as:

$$\hat{A} = \sum_{a'} a' P_{a'} = \sum_{a'} a' |a'\rangle \langle a'|$$

In case of a continuous spectrum

$$\hat{A} = \int da' a' |a'\rangle \langle a'|$$

This formula is called the spectral theorem. Then $f(\hat{A})$ is defined as:

$$f(\hat{A}) = \sum_{a'} f(a) |a'\rangle \langle a'|$$

In the case of a continuous spectrum:

$$f(\hat{A}) = \int da' f(a') |a'\rangle \langle a'|$$

Coming back to our problem of evaluating the time evolution operator $\hat{U}$: in order to calculate the $\exp(-i\hat{H}(t - t_0) / \hbar)$ we should:

- find the eigenkets $|\Psi_i\rangle$ and the eigenvalues $E_i$ of the Hamiltonian.
- then evaluate

$$\exp(-i\hat{H}(t - t_0) / \hbar) = \sum_i \exp(-iE_i(t - t_0) / \hbar) |\Psi_i\rangle \langle \Psi_i|$$
Example 4.4 Spin precession

We consider a quantum spin 1/2 system (such as for example an electron) in a magnetic field $\mathbf{B}$ parallel to the $z$ axis. The Hamiltonian of such a system is given by:

$$\hat{H} = \frac{-g e B}{m_e c} \hat{S}_z = -\omega \hat{S}_z$$

where $m_e$ is the electron mass, $g \sim 2$. We will evaluate the following:

1) the time evolution operator $\hat{U}(t,0)$
2) the time evolution of the kets $|S_+^z\rangle$ and $|S_-^z\rangle$
3) the expectation value of $\hat{S}_x$, $\hat{S}_y$ in the state $|S_+^z, t\rangle$ and of $\hat{S}_z$ in the state $|S_+^z, t\rangle$

Further we will discuss the physical meaning of the results of the point 3 which describe a new phenomenon of spin precession.

Solution: Part a)

$$\hat{U}(t,0) = \exp\left(-\frac{i\hat{H}t}{\hat{h}}\right)$$

This means that the eigenstates of $\hat{H}$ are the same as the eigenstates of $\hat{S}_z$, that is $|S_+^z\rangle$ and $|S_-^z\rangle$. The eigenvalues of $\hat{H}$ are $\hbar/2 \cdot -\omega$ for $|S_+^z\rangle$ and $\hbar/2 \cdot \omega$ for $|S_-^z\rangle$, respectively. Now we can evaluate the exp using the previous definition.

$$f(\hat{A}) = \sum_{a'} f(a)|a'\rangle\langle a'|$$

This gives

$$\hat{U}(t,0) = \exp\left(\frac{i\omega t}{2\hbar}\right)|S_+^z\rangle\langle S_+^z| + \exp\left(-\frac{i\omega t}{2\hbar}\right)|S_-^z\rangle\langle S_-^z|$$

Part b)

We will find the time evolution of $|S_+^z, t = 0\rangle = |S_+^z\rangle$, that is we evaluate $|S_+^z, t\rangle$. We have

$$|S_+^z, t\rangle = \hat{U}(t,0)|S_+^z\rangle$$

We substitute the above expression for the time evolution operator and get:

$$\hat{U}(t,0)|S_+^z\rangle = \exp\left(\frac{i\omega t}{2}\right)|S_+^z\rangle\langle S_+^z| + \exp\left(-\frac{i\omega t}{2}\right)|S_-^z\rangle\langle S_-^z|$$

We know that

$$\langle S_-^z|S_+^z\rangle = 0$$

and

$$\langle S_+^z|S_+^z\rangle = 1$$

This gives

$$|S_+^z, t\rangle = \exp\left(\frac{i\omega t}{2}\right)|S_+^z\rangle$$
In order to find the time evolution of the ket $|S_x^+\rangle$ we have to recall that

$$|S_x^\pm\rangle = \frac{1}{\sqrt{2}}|S_x^+\rangle \pm \frac{1}{\sqrt{2}}|S_x^-\rangle$$

Now we can evaluate

$$|S_x^+, t\rangle = \hat{U}(t, 0)|S_x^+, 0\rangle = \hat{U}(t, 0)\frac{1}{\sqrt{2}}(|S_x^+\rangle + |S_x^-\rangle).$$

This can be further evaluated using the results obtained earlier. (Try to do it on your own). The answer is:

$$|S_x^+, t\rangle = \frac{1}{\sqrt{2}}\exp\left(\frac{i\omega t}{2}\right)|S_x^+\rangle + \frac{1}{\sqrt{2}}\exp\left(-\frac{i\omega t}{2}\right)|S_x^-\rangle$$

We can see that there is a distinct difference between the time evolution of $|S_x^+\rangle$ and $|S_x^+\rangle$. The state $|S_x^+, t\rangle$ differs from the state $|S_x^+\rangle$ only by the phase factor and an experiment to test what is the probability that the state $|S_x^+, t\rangle$ is in $|S_x^+\rangle$ would give the result $|\exp\left(\frac{i\omega t}{2}\right)||^2|\langle S_x^+|S_x^+\rangle|^2 = 1$ Such state is called stationary. On the other hand the state $|S_x^+, t\rangle$ keeps evolving between $|S_x^+,\rangle$ and $|S_x^-\rangle$ Such a state is called non-stationary.

Part c)

Now we will evaluate the expectation value of the operator $\hat{S}_x$ in the state $|S_x^+, t\rangle$. The expectation value of an operator $\hat{A}$ in the state $|\alpha\rangle$ is defined as:

$$\langle \hat{A} \rangle = \sum_{a'} a'|\langle a'|\alpha\rangle|^2$$

where $|\langle a'|\alpha\rangle|^2$ is interpreted as the probability of getting the eigenvalue $a'$ as a result of the measurement of $A$ for the system in the state$|\alpha\rangle$. In our case we replace

$$|\alpha\rangle = \frac{1}{\sqrt{2}}\exp\left(\frac{i\omega t}{2}\right)|S_x^+\rangle + \frac{1}{\sqrt{2}}\exp\left(-\frac{i\omega t}{2}\right)|S_x^-\rangle$$

For $|a'\rangle$ we should take the eigenstates of the $\hat{S}_x$, but because $|\alpha\rangle$ is expressed in terms of $|S_x^+\rangle$ and $|S_x^-\rangle$ it is convenient to express $|S_x^+\rangle$ and $|S_x^-\rangle$ in terms of the latter. Then we can evaluate

$$\langle \hat{A} \rangle = \sum_{a'} a'|\langle a'|\alpha\rangle|^2$$

After some tedious calculations we get:

$$\langle \hat{S}_x \rangle = \frac{\hbar}{2}\cos^2\left(\frac{\omega t}{2}\right) - \frac{\hbar}{2}\sin^2\left(\frac{\omega t}{2}\right) = \frac{\hbar}{2}\cos(\omega t)$$

Similar calculations for the expectation value of $\hat{S}_y$ result in:

$$\langle \hat{S}_y \rangle = \frac{\hbar}{2}\sin(\omega t)$$

while

$$\langle \hat{S}_z \rangle = 0$$

These two results physically mean the following: Assume that many copies of identical systems prepared in the state $|S_x^+\rangle$ are placed in a constant magnetic field parallel to $z$. Then we measure the $x$ component of spin (by projecting the evolving state onto
\[ E(t) = E_0 \cos(\omega t) \]

\[ \vec{\mu} - \text{dipole moment} \]

Figure 4.3: The ammonia molecule in an alternating electric field

\[ |S_x^+, S_y^-\rangle \] and do the same to the y component of spin (by projecting the evolving state onto \((|S_x^+, S_y^-\rangle)\). (Each experiment is performed on a different copy of the system). Then we take the average value of the x component of spin obtained as a result of all these measurements. We know that this average value is equal to the expectation value of \( \hat{S}_x \). We also take the average value of the x component of spin. This number is in turn equal to the expectation value of \( \hat{S}_y \). Our previous calculations show that these average values of the x and y component of spin behave as if they were the x and y component of a certain vector that rotates with the frequency \( \omega \) in the \( x - y \) plane. This phenomenon is called the \textbf{spin precession} and it has been confirmed experimentally. Further we will show another argument why these average values of \( S_x \), \( S_y \) and \( S_z \) in fact are three components of a real (should we rather say realistic) three dimensional vector in our space \( \mathbb{R}^3 \) associated with spin. The last part that is the evolution of the \( \langle S_z \rangle \) in the same state is left to the reader as an exercise. The answer is that it does not change in time and is zero. A good exercise is to discuss what happens if the evolution starts from \( |S_z^+\rangle \).

\textbf{Example 4.5} \textit{The ammonia molecule in alternating electric field.}

The ammonia molecule is placed in an alternating electric field as in the Fig 4.3. Find the evolution of its states.

Solution: This problem will be solved in two stages. In the Stage 1 we briefly remind the evolution of the ammonia molecule without electric field. In the second stage the electric field is turned on.

Stage I

The evolution of the ammonia molecule without the electric field. (see for example the book by Das and Melissinos [ref], page 155). The ammonia molecule can be found in two states \( |1\rangle \) and \( |2\rangle \) both characterised by the same energy \( E_0 \). These states are shown in the Fig 4.4.

Nitrogen atom is capable of tunelling through the hydrogen plane with a finite probability. This can be described as:

\[ \langle 2|\hat{H}|1\rangle = -A \]
Therefore the matrix $H$ that represents the Hamiltonian in the basis $|1\rangle$ and $|2\rangle$ is

$$H = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}$$

Its eigenstates are:

$$|E_1\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$$

$$|E_2\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$$

The respective eigenvalues are:

$$E_1 = E_0 - A$$

$$E_2 = E_0 + A$$

Now we discuss the time evolution of the ammonia molecule if it starts from $|1\rangle$.

The N atom oscillates between its two positions corresponding to the states $|1\rangle$ and $|2\rangle$ with the period $T = \pi \hbar / A$. The probabilities that the state can be found in each of the states $|1\rangle$ and $|2\rangle$ are illustrated in the Fig 4.5.
The characteristic frequency of oscillations lies in the microwave region, about 24GHz. These oscillations of the state for the ammonia molecule between $|1\rangle$ and $|2\rangle$ mean that $|1\rangle$ is a non-stationary state. If we consider the evolution starting from the state $|2\rangle$ we would get a very similar picture, as the state $|2\rangle$ is also non-stationary. The characteristic frequency of oscillations lies in the microwave region, about 24GHz.

On the other hand if the evolution starts from the state $|E_1\rangle$ then the molecule will not be found in $|E_2\rangle$, and the reverse. The states $|E_1\rangle$ and $|E_2\rangle$ are stationary.

Stage II

The evolution of the nitrogen molecule in the alternating electric field $\mathbf{E}(t) = \frac{1}{2} \mathbf{E}_0 [\exp(i\omega t) + \exp(-i\omega t)]$

The electrostatic energy in the state $|1\rangle$ that is for the electric dipole moment $\vec{\mu}$ in the direction of the electric field is equal to

$$\vec{\mu} \cdot \mathbf{E}(t) = \mu \cdot \mathbf{E}(t)$$

The electrostatic energy in the state $|2\rangle$ that is for the electric dipole moment $\vec{\mu}$ opposite to the direction of the electric field is equal to

$$\vec{\mu} \cdot \mathbf{E}(t) = -\mu \cdot \mathbf{E}(t)$$

The hamiltonian in the basis $|1\rangle$ and $|2\rangle$ is therefore represented by the following matrix:

$$H = \begin{pmatrix} E_0 + \mu \cdot \mathbf{E}(t) & -A \\ -A & E_0 - \mu \cdot \mathbf{E}(t) \end{pmatrix}$$

We would like to express this matrix in the basis of stationary states $|E_1\rangle$ and $|E_2\rangle$. To achieve that we split the Hamiltonian matrix into two parts:

$$H = H_0 + H_1 = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix} + \begin{pmatrix} \mu \cdot \mathbf{E}(t) & 0 \\ 0 & -\mu \cdot \mathbf{E}(t) \end{pmatrix}$$

The matrix of $H'_0$ in the basis $|E_1\rangle$ and $|E_2\rangle$ simply is diagonal

$$H'_0 = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

but for the $H'_1$ the transformation has to be performed explicitly. We will evaluate then the coefficients of the matrix $\tilde{H}'_1$ which in the basis $|1\rangle$ and $|2\rangle$ are given by:

$$\begin{pmatrix} \mu \cdot \mathbf{E}(t) & 0 \\ 0 & -\mu \cdot \mathbf{E}(t) \end{pmatrix}$$

in the new basis $|E_1\rangle$ and $|E_2\rangle$. This can be accomplished either through the transformation matrix $S$ such that

$$S|1\rangle = |E_1\rangle$$
$$S|2\rangle = |E_2\rangle$$

in which case the matrix $H'_1 = S \cdot \tilde{H}'_1 \cdot S^{-1}$ or directly. Here we will follow the second route. Let $\mathbf{1}$ denote the unit matrix.

$$\langle E_1|H_1|E_1\rangle = \langle E_1|\mathbf{1}|\tilde{H}_1|\mathbf{1}|E_1\rangle =$$
So the matrix of the entire Hamiltonian has the form:

\[
H' = \begin{pmatrix}
0 & \mu \cdot E(t) \\
\mu \cdot E(t) & 0
\end{pmatrix}
\]

When we have determined the Hamiltonian matrix we have in fact determined the operator itself as:

\[
\hat{H} = E_1|E_1\rangle\langle E_1| + \mu \cdot E(t)|E_1\rangle\langle E_2| + \mu \cdot E(t)|E_2\rangle\langle E_1| + E_2|E_2\rangle\langle E_2|
\]

Now we determine the evolution of the system using the Schrödinger equation: We express the state of the system \(|\Psi(t)\rangle\) in terms of basis states with the unknown, time dependent coefficients \(c_1(t), c_2(t)\) and solve with respect to them.

\[
|\Psi(t)\rangle = c_1(t)|E_1\rangle + c_2(t)|E_2\rangle
\]

\[
i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle
\]

\[
i\hbar \frac{\partial}{\partial t} (c_1(t)|E_1\rangle + c_2(t)|E_2\rangle) =
E_1c_1(t)|E_1\rangle + \mu \cdot E(t)c_2(t)|E_1\rangle + \mu \cdot E(t)c_1(t)|E_2\rangle + E_2c_2(t)|E_2\rangle
\]

Now we evaluate the scalar product of \(|E_1\rangle\) with both sides of the above equation and get

\[
i\hbar \frac{\partial}{\partial t} c_1(t) = E_1c_1(t) + \mu \cdot E(t)c_2(t)
\]

By repeating a similar operation, now with \(|E_2\rangle\) we get:

\[
i\hbar \frac{\partial}{\partial t} c_2(t) = \mu \cdot E(t)c_1(t) + E_2c_2(t)
\]
This is a pair of coupled differential equations. Our aim is to evaluate $c_1(t)$ and $c_2(t)$. In the absence of electric field the equations are decoupled and their respective solutions are:

\[ c_1(t) = a(t) \exp(-iE_1 t/\hbar) \]
\[ c_2(t) = b(t) \exp(-iE_2 t/\hbar) \]

where $a(t)$ and $b(t)$ are simply constants. For weak electric field we will use a certain approximation that consists of the following - we will write $c_i(t)$ as a product of a slowly varying function $a(t)$ and $b(t)$, compared to the quickly varying $\exp(-iE_1 t/\hbar)$ and the same exponential as before. Then we will try to calculate $a(t)$ and $b(t)$. If we succeed (and confirm, that they are indeed slowly varying) then we can evaluate $c_i$-s.

\[ c_1(t) = a(t) \exp(-iE_1 t/\hbar), \]
\[ c_2(t) = b(t) \exp(-iE_2 t/\hbar). \]

Similarly:

\[ ih \frac{\partial}{\partial t} c_1(t) = \{ih[\frac{\partial}{\partial t} a(t)] + iha(t) \frac{-i}{\hbar} E_1\} \exp(-iE_1 t/\hbar) \]
\[ = \{ih[\frac{\partial}{\partial t} a(t)] + a(t)E_1\} \exp(-iE_1 t/\hbar) = \]
\[ = ih \frac{\partial}{\partial t} a(t) \exp(-iE_1 t/\hbar) + E_1 c_1(t) = E_1 c_1(t) + \mu \cdot E(t)b(t) \exp(-iE_2 t/\hbar). \]

This gives:

\[ h \frac{\partial}{\partial t} a(t) = \mu \cdot E(t)b(t) \exp(-i(E_2 - E_1) t/\hbar) \] (4.1)

Similarly:

\[ ih \frac{\partial}{\partial t} c_2(t) = \{ih[\frac{\partial}{\partial t} b(t)] + ihb(t) \frac{-i}{\hbar} E_2\} \exp(-iE_2 t/\hbar) \]
\[ = \{ih[\frac{\partial}{\partial t} b(t)] + b(t)E_2\} \exp(-iE_2 t/\hbar) = \]
\[ = ih \frac{\partial}{\partial t} b(t) \exp(-iE_2 t/\hbar) + E_2 c_2(t) = E_2 c_2(t) + \mu \cdot E(t)a(t) \exp(-iE_1 t/\hbar) \]

This gives:

\[ h \frac{\partial}{\partial t} b(t) = \mu \cdot E(t)a(t) \exp(i(E_2 - E_1) t/\hbar) \] (4.2)

We will solve these equations for $a(t)$ and $b(t)$ for the sinusoidally varying electric field

\[ E(t) = E_0 \cos(\omega t) = \frac{1}{2} E_0 (\exp(i\omega t) + \exp(i\omega t)) \]

Let us denote $(E_2 - E_1)t/\hbar = \omega_0$ and substitute the electric field $E(t)$ into the equations 4.1 and 4.2. We get:

\[ \frac{d}{dt} a(t) = \frac{-i}{2\hbar} \mu \cdot E_0 (\exp(i(\omega - \omega_0)t) + \exp(-i(\omega + \omega_0)t)) b(t) \] (4.3)

\[ \frac{d}{dt} b(t) = \frac{-i}{2\hbar} \mu \cdot E_0 (\exp(i(\omega + \omega_0)t) + \exp(-i(\omega - \omega_0)t)) a(t) \] (4.4)
We can write the formal solution:

\[ a(t) = \frac{-i}{2\hbar} \mu \cdot E_0 \int_0^t (\exp(i(\omega - \omega_0)t')b(t')dt' + \int_0^t \exp(-i(\omega + \omega_0)t')) b(t') \]

and a similar one for \( b(t) \), though it does not seem constructive as we express one unknown function through another unknown one. However we can now use a certain trick. If \( b(t) \) varies slowly compared to \( \exp(i(\omega + \omega_0)t) \) then we can approximately write:

\[ \int_0^t b(t') \exp(i(\omega + \omega_0)t')dt' \approx b(t'') \int_0^t \exp(i(\omega + \omega_0)t')dt' \]

where \( 0 < t'' < t \). But, as we integrate the exponential over very many of its periods, the second integral gives approximately zero. This method is called a rotating wave approximation.

Therefore the terms in and that contain \( \exp(i(\omega + \omega_0)t) \) and \( \exp(i(\omega - \omega_0)t) \) do not contribute to the solution and can be neglected. Note that the same trick does not work for \( \int_0^t b(t') \exp(i(\omega - \omega_0)t')dt' \) because in case of \( \omega \approx \omega_0 \) the \( \exp(i(\omega - \omega_0)t) \) is NOT a quickly varying function any more. Thus simplified 4.1 and 4.2 take the form:

\[ \frac{d}{dt} a(t) = \frac{-i}{2\hbar} \mu E_0 \exp(i(\omega - \omega_0)t)b(t) \]
\[ \frac{d}{dt} b(t) = \frac{-i}{2\hbar} \mu E_0 \exp(i(\omega + \omega_0)t)a(t) \]

We will now solve the above equations at the resonance, that is for \( \omega = \omega_0 \) Substituting the resonance condition, differentiating the above equations and substituting one into the other we get:

\[ \frac{d^2}{dt^2} a(t) = -\left(\frac{\mu E_0}{2\hbar}\right)^2 a(t) \]
\[ \frac{d^2}{dt^2} b(t) = -\left(\frac{\mu E_0}{2\hbar}\right)^2 b(t) \]

The solutions are:

\[ a(t) = a_0 \cos\left(\frac{\mu E_0 t}{2\hbar}\right) + b_0 \sin\left(\frac{\mu E_0 t}{2\hbar}\right) \]
\[ b(t) = -ia_0 \sin\left(\frac{\mu E_0 t}{2\hbar}\right) + ib_0 \cos\left(\frac{\mu E_0 t}{2\hbar}\right) \]

Now it is time to check if \( a(t) \) and \( b(t) \) are slowly varying. Indeed for weak electric fields \( E_0 \) is small and \( a(t) \) and \( b(t) \) vary slowly.

The constants \( a_0, b_0 \) depend on the initial conditions. For example if at \( t = 0 \) our system was in the state \(|\Psi\rangle = |E_1\rangle\) then \( a_0 = 1, b_0 = 0 \). We can evaluate then the probability of finding the system in the state \(|E_2\rangle\) as:

\[ P_{E_2}(t) = |c_2(t)|^2 = |b(t)|^2 = \sin^2\left(\frac{\mu E_0 t}{2\hbar}\right) \]

and for finding it in \(|E_1\rangle\):

\[ P_{E_1}(t) = |c_1(t)|^2 = |a(t)|^2 = \cos^2\left(\frac{\mu E_0 t}{2\hbar}\right) \]

These probabilities are shown in the Fig 4.6.
Figure 4.6: The probabilities of the optical transition for the ammonia molecule starting from the stationary states of the molecule with no field

\[ E_2 \]

\[ f = 24 \text{ GHz} \]

\[ = E_2 - E_1 \]

\[ E_1 \]

Figure 4.7: The optical transition occurs when the frequency of electric field matches the energy difference between the two states

The meaning of this result is that in the presence of alternating (weak) electric field the states \( |E_1\rangle \) and \( |E_2\rangle \) are not stationary any more. The system evolves between \( |E_1\rangle \) and \( |E_2\rangle \). After the time \( t = \hbar \pi / \mu E_0 \) the system evolves from \( |E_1\rangle \) to \( |E_2\rangle \). This means that the time dependent electric field causes a transition between the states \( |E_1\rangle \) and \( |E_2\rangle \). For \( \mu E_0 t / 2 \hbar << 1 \), \( P_{E_2} \approx (\mu E_0 t / 2 \hbar)^2 \). This in turn means that the transition probability is proportional to the square of electric field amplitude. As the average intensity of an electromagnetic wave is

\[ \langle I \rangle = \left( \frac{\varepsilon_0}{4 \mu_0} \right)^{1/2} E_0^2 \]

the last observation means that the transition probability is proportional to the intensity of light. The Fig 4.7 illustrates the transition occurring between states \( E_1 \) and \( E_2 \) for the electric field frequency corresponding to the difference in energies between these two states.

### 4.4 The evolution of expectation values

In this section we analyse the evolution of the expectation values of an observable, that is the evolution of ”averages”. We take into consideration a system that evolves:

\[ |\alpha, 0\rangle \rightarrow |\alpha, t\rangle \]

and an observable \( \hat{X} \) which does not depend explicitly on time:

\[ \frac{\partial}{\partial t} \hat{X} = 0 \]
We would like to evaluate how does the expectation value of this observable evolves in time. We will do it by evaluating

\[
\frac{d}{dt} \langle \alpha, t | \hat{X} | \alpha, t \rangle = (\frac{d}{dt} \langle \alpha, t |) \hat{X} | \alpha, t \rangle + \langle \alpha, t | \hat{X} | (\frac{d}{dt} \alpha, t) \rangle
\]  

(@)

To proceed further we need to evaluate \( \frac{d}{dt} \langle \alpha, t |t \rangle \), which is equal to \( \frac{\partial}{\partial t} \langle \alpha, t |t \rangle \) - there is no implicit time dependence. We know that

\[
i\hbar \frac{\partial}{\partial t} |\alpha, t \rangle = \hat{H} |\alpha, t \rangle
\]

It follows that

\[
-i\hbar \frac{\partial}{\partial t} |\alpha, t \rangle = \langle \alpha, t |\hat{H}^\dagger = \langle \alpha, t |\hat{H}
\]

Now we can rewrite the equation (@) in the form:

\[
\frac{d}{dt} \langle \alpha, t | \hat{X} | \alpha, t \rangle = \frac{1}{i\hbar} \langle \alpha, t | - \hat{H} \cdot \hat{X} + \hat{X} \hat{H} | \alpha, t \rangle
\]

Therefore we can conclude that:

\[
\frac{d}{dt} \langle \hat{X} \rangle = \frac{1}{i\hbar} \langle [\hat{X}, \hat{H}] \rangle
\]

Note that if \([\hat{X}, \hat{H}]=0\) then \(\frac{d}{dt} \langle \hat{X} \rangle = 0\) for any state. This means that a dynamical variable is conserved.

Sometimes a dynamical variable can depend explicitly on time. Then we have

\[
\frac{d}{dt} \langle \hat{X} \rangle = \frac{1}{i\hbar} \langle [\hat{X}, \hat{H}] \rangle + \frac{\partial}{\partial t} \langle \hat{X} \rangle
\]

You probably may recall a clear analogue of this equation from classical mechanics. We recommend here to read the section ”Classical lagrangian and Hamiltonian equations of motion” of the book by Schiff [ref] page 174 to refresh the terminology. Here we just summarise the final result. Let us consider a dynamical variable \( F \) (such as for example the energy, the angular momentum, etc). To be more specific let us concentrate on energy when f point masses perform a complicated motion. Then \( F \) may change for a number of reasons. First \( F \) may change because external influences force it to change. Secondly it may change as a result of the motion of these point masses. \( F \) (say energy) depends on the (canonical) coordinates \( q_i \) of the masses and these will vary in time as a result of the motion. \( F \) may also depend on the canonical conjugates of \( q_i \), namely \( p_i \) (say momenta). These conjugates may also depend on time. All this is summarised in the equation:

\[
\frac{d}{dt} F(q_1, \ldots, q_f, p_1, \ldots, p_f, t) = \frac{\partial}{\partial t} F + \sum_{i=1}^{f} (\frac{\partial}{\partial q_i} F \frac{\partial}{\partial t} q_i + \frac{\partial}{\partial p_i} F \frac{\partial}{\partial t} p_i) = \frac{\partial}{\partial t} F + \{F, H\}
\]

The last symbol denotes Poisson brackets.

4.5 Canonical quantisation

Many systems considered in quantum mechanics have a clear classical analogue. For such systems we expect that in the limit of \( \hbar \to 0 \) the expectation values of operators behave like the corresponding classical quantities. This rule is known as a correspondence
principle. For example we know that a classical particle is located at some position $x$ but quantum mechanics predict that the same particle can easily be found elsewhere, most often in close vicinity of $x$. On the other hand the expectation value of the position operator evaluated in the (time-evolved) state of this particle coincides with the classical position.

The correspondence principle is satisfied if the description of a quantum system is derived from the classical one in the following fashion:

- The classical system has to be described within the framework of the canonical formalism: canonically conjugate variables and the Hamiltonian equation of motion.
- The canonical variables for the classical system $q_i, p_i$ and the Hamiltonian function $H$ are replaced by the operators $\hat{q}_i, \hat{p}_i, \hat{H}$ for the corresponding quantum system. (Some caution is needed - sometimes we need to symmetrise the classical Hamiltonian so that the $\hat{H}$ is hermitean.)
- Poisson brackets from classical mechanics are replaced by commutators of the relevant operators.

This procedure is called the canonical quantisation and it provides a partial answer where to get a quantum Hamiltonian from.

Now we have a good opportunity for an overview of the similarities and differences between the classical mechanics and quantum mechanics in the Schrödinger picture in which we are working. In this picture the states are evolving as we have just learned. (This picture is not unique and in the second part of this lectures we will learn of other”pictures”). In classical mechanics the system evolves by moving along a trajectory: \{$p_i(t), (i = 1, \ldots, f)$, $q_i(t), (i = 1, \ldots, f)$\}. Various dynamical variables $F$ can be followed along this trajectory and we just learned how to evaluate their time dependence. In quantum mechanics this concept of motion along the trajectory in the space \{$p_i, q_i$\} is replaced by the evolution of kets $|\alpha, t\rangle$ in Hilbert space. One can call it a ”trajectory” in some sense. The important difference is that the evolution of kets contains now all information about the motion: the operators $\hat{q}_i, \hat{p}_i$ are completely detached from the motion and do not evolve: The trajectory from classical mechanics \{$p_i(t), (i = 1, \ldots, f)$, $q_i(t), (i = 1, \ldots, f)$\} and the ”trajectory” $|\alpha, t\rangle$ in the Hilbert space are linked via the correspondence principle. That is

$$\langle \alpha, t | \hat{p}_i | \alpha, t \rangle$$

corresponds to $p_i(t)$

and

$$\langle \alpha, t | \hat{q}_i | \alpha, t \rangle$$

corresponds to $q_i(t)$.

4.6 Heisenberg uncertainty relation

From the basic quantum mechanics course we remember that

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

where $\Delta x$ is the uncertainty in the position measurement and $\Delta p$ is the uncertainty in the momentum measurement. A similar relationship is true for the energy and time measurement.

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$
Further we learned that the operators \( \hat{x} \) and \( \hat{p} \) are associated with the position and momentum. We also learned that

\[
[\hat{x}, \hat{p}] = i\hbar
\]

The question arises is it accidental that the same two quantities that appear in the uncertainty relationship correspond to non-commuting operators. Below we generalise the uncertainty relation and also tie it with commutators.

Let \( \hat{A} \) be an observable. We define \( \Delta \hat{A} \) as:

\[
\Delta \hat{A} = \hat{A} - \langle \hat{A} \rangle \hat{1} = \hat{A} - \langle \alpha | \hat{A} | \alpha \rangle \hat{1}
\]

The quantity

\[
\langle (\Delta \hat{A})^2 \rangle
\]

evaluated in the state \( |\alpha\rangle \) is called **dispersion** of \( \hat{A} \), or variance, or the mean square deviation. We can rearrange it to get:

\[
\langle (\Delta \hat{A})^2 \rangle = \langle (\hat{A}^2 - 2\hat{A}\langle \hat{A} \rangle + \langle \hat{A} \rangle^2) \rangle = \langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2
\]

An example how to use this definition in practice is shown below.

**Example 4.6** The spin \( 1/2 \) system is in \( |\alpha\rangle = |S_z^+\rangle \) state. Calculate the dispersion of \( \hat{S}_z \) and \( \hat{S}_x \).

Solution: Dispersion of \( \hat{S}_z \)

\[
\langle S_z^+ | (\hat{S}_z)^2 | S_z^+ \rangle = \frac{\hbar^2}{4} \langle S_z^+ | S_z^+ \rangle = \frac{\hbar^2}{4}
\]

\[
\langle S_z^+ | \hat{S}_z | S_z^+ \rangle = \frac{\hbar}{2}
\]

\[
\langle (\Delta \hat{S}_z)^2 \rangle = 0
\]

Dispersion of \( \hat{S}_x \)

\[
\hat{S}_x = \frac{\hbar}{2} (|S_x^+\rangle \langle S_x^-| + |S_x^-\rangle \langle S_x^+|)
\]

\[
\langle \hat{S}_x \rangle = 0
\]

\[
\hat{S}_x^2 = \frac{\hbar^2}{4} (|S_x^+\rangle \langle S_x^+| + |S_x^-\rangle \langle S_x^-|)
\]
\[
(\langle \hat{S}_x^2 \rangle) = \frac{\hbar^2}{4}
\]

\[
\langle (\Delta \hat{S}_x)^2 \rangle = \frac{\hbar^2}{4}
\]

**Example 4.7** Show, from the usual definition of the variance of a set of random results that the uncertainty \(\Delta \hat{A}\) in the results of experiments performed to measure the observable \(\hat{A}\) for a very large number of systems, all prepared in the same state \(|\Psi\rangle\) is given by:

\[
(\Delta \hat{A})^2 = \langle (\hat{A} - \langle \hat{A} \rangle)^2 \rangle = \langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2
\]

Assume that the eigenvalue spectrum of \(\hat{A}\) is discrete.

Solution: Let

\[
\hat{A}|a\rangle = a|a\rangle
\]

Take an arbitrary \(|\Psi\rangle\).

\[
\langle \hat{A} \rangle = \langle \Psi | \hat{A} | \Psi \rangle = \sum_a a |\langle a | \Psi \rangle|^2
\]

\[
(\Delta \hat{A})^2 = \sum_a (a - \langle \hat{A} \rangle)^2 |\langle a | \Psi \rangle|^2
\]

The meaning of individual terms is that a is the actual value obtained in the experiment, \(\langle \hat{A} \rangle\) is the mean value and \(|\langle a | \Psi \rangle|^2\) is the probability of obtaining a. The last formula is in fact equivalent to the standard prescription how to calculate the standard deviation (variance). It remains to show that

\[
\sum_a (a - \langle \hat{A} \rangle)^2 |\langle a | \Psi \rangle|^2 = 2 \langle (\hat{A} - \langle \hat{A} \rangle)^2 \rangle
\]

We have

\[
\sum_a (a - \langle \hat{A} \rangle)^2 |\langle a | \Psi \rangle|^2 = \sum_a \langle \Psi | a \rangle (a - \langle \hat{A} \rangle)^2 \langle a | \Psi \rangle = (*)
\]

But

\[
(\hat{A} - \langle \hat{A} \rangle)^2 |a\rangle = (a - \langle \hat{A} \rangle)^2 |a\rangle
\]

so

\[
(*) = \sum_a \langle \Psi | (\hat{A} - \langle \hat{A} \rangle)^2 |a\rangle \rangle |\langle a | \Psi \rangle|^2 \neq |\Psi | (\hat{A} - \langle \hat{A} \rangle)^2 |\Psi \rangle
\]
because $\sum_a |a\rangle\langle a| = \hat{1}$.

Now that we know how to practically calculate the dispersion and that its meaning is similar to the "spread" in the measured values we can introduce a generalised uncertainty relation. In fact it is now a mathematical equality with a mathematical proof (see ref [Sakurai]). It can be formulated as:

$$\langle(\Delta \hat{A})^2\rangle \langle(\Delta \hat{B})^2\rangle \geq \frac{1}{4} |\langle[\hat{A}, \hat{B}]\rangle|^2$$

In other words any two dynamical variables that do not commute can not be accurately measured at the same time. Now we are able to generate new uncertainty relations purely on the basis of the corresponding operators.

This approach works only in case of dynamical variables. We would like to underline here that time is not a dynamical variable - it is a parameter and the energy-time uncertainty has to be explained in a different fashion on the basis of the time evolution of kets, by answering the question how quickly the ket $|\alpha, t\rangle$ starts to be appreciably different from $|\alpha, 0\rangle$ (see Schiff).
Chapter 5

Symmetry operations on quantum systems

5.1 Translation - displacement in space

5.1.1 Operation of translation

We begin now an important new topic in which we will analyse the consequence of symmetry operations for quantum systems. Many systems in physics, both classical and quantum display varying degree of symmetry, and there are many various types of symmetries. For example a molecule such as benzene $\text{C}_6\text{H}_6$ where C atoms are placed regularly in a circle will look exactly the same when rotated around its center by $k \times 60$ degrees (see Fig 5.1).

This rotational symmetry has important consequences for physical properties of this molecule - in this case it determines the number of different frequencies of vibration that this molecule can accomplish. This is an important simplification when it comes to modelling - it tells us how many independent parameters we have to determine experimentally. In the following lectures we will discuss several basic symmetries of quantum systems (although not all of them). In this section we will concentrate on the translational symmetry.

The operation of translation performed on a system is illustrated in the Fig 5.2. The quantum system is placed in space with the reference frame. A selected point of a system
is placed at $r$. The operation of translation consist of moving the system from its old position to a new position as in the Fig 5.2. The selected pint is now placed at $r + \Delta R$. It has to be noted that the same final result can be accomplished by pulling the reference frame by $-\Delta R$. This is illustrated in the Fig 5.3. The reciprocal character of translation: we can either push a system or pull the reference frame with the same result is worth remembering as it will appear later in quantum mechanics.

When this operation of translation is performed on some systems they remain unchanged. This is called translational invariance. A system with (some) translational invariance is shown in the Fig 5.4. This system contains an infinite number of atoms regularly placed on a square lattice. When this system is translated by a lattice vector we can not distinguish it from the original system. The translational invariance is limited to the lattice vectors only: a translation by $1/2 \times$ the distance between adjacent atoms horizontally is not a symmetry operation.

There are numerous other examples of systems with translational invariance. A point mass in a free space is translationally invariant: it can be moved by any vector $\Delta R$ and nothing would change. Two point masses interacting via a potential that depends only on their respective distance is also translationally invariant: obviously it does not matter for
those two point masses where we place the reference frame. On the other hand a charged particle placed in a capacitor with the reference frame on one plate (see Fig 5.5) does not have the translational invariance in y direction.

An important consequence of the translational invariance is the conservation of the classical momentum. We illustrate this statement with an example: we will show how this conservation of the momentum is a consequence of the translational invariance for the system of two point masses interacting via a potential that depends only on their respective distance mentioned before.

The system is shown in the Fig 5.6, its Hamiltonian function is:

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(|r_1 - r_2|)$$

When the system is moved by $\Delta R$ ( or the reference frame moved by $-\Delta R$ then

$$r'_1 = r_1 + \Delta R; \quad r'_2 = r_2 + \Delta R$$

but

$$p'_1 = p_1; \quad p'_2 = p_2$$

The new Hamiltonian of the translated system is thus:

$$H = \frac{p_1'^2}{2m_1} + \frac{p_2'^2}{2m_2} + V(|r'_1 - r'_2|) = H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(|r_1 - r_2|)$$

Therefore the Hamiltonian remains unchanged by translation. We introduce now new variables: the position of the center of mass, $R$ and the relative position $r$:

$$R = \frac{m_1 r_1 + m_2 r_2}{m_1 + m_2},$$
Figure 5.6: Two point masses interacting via a central potential

\[ r = r_1 - r_1 \]

It can be shown that the respective (canonically conjugate) momenta are given by the center of mass momentum \( P \) and the relative momentum \( p \) given by:

\[ P = p_1 + p_2 \]
\[ p = m^* \frac{dr}{dt}; \quad m^* = \frac{m_1 m_2}{m_1 + m_2} \]

Obviously \( H \) does not depend on \( R \). From the Hamilton equations it follows that:

\[ \frac{dP}{dt} = -\frac{\partial H}{\partial R} = 0 \]

This in turn means that the center of mass momentum \( P \) is conserved.

5.1.2 Translation for quantum systems

Classical systems are described by their (canonically conjugate) coordinates \( p_i, q_i, i = 1, \ldots, f \). The translation does something to these coordinates: changes them into new coordinates \( p'_i, q'_i, i = 1, \ldots, f \). In a way described before. In quantum mechanics we describe system using states \( |\alpha, t\rangle \). The translation should do something to these states: change them into new states \( |\alpha', t\rangle \). Therefore mathematically speaking translation is a certain specific operator. First we will describe the operator of infinitesimal translation \( \hat{T}_{dx} \) that translates states by \( dx \). The infinitesimal translation operator is defined using the eigenstates of position operator as:

\[ \hat{T}_{dx} |x\rangle = |x + dx\rangle \]

As in the case of the infinitesimal time evolution operator we postulate that:

- \( \hat{T}_{dx} \) does not change the state norm: if \( \langle \alpha | \alpha \rangle = 1 \) then \( \langle \alpha | \hat{T}^\dagger_{dx} \hat{T}_{dx} | \alpha \rangle = 1 \). This means that the operator \( \hat{T}_{dx} \) is unitary.
- \( \hat{T}_{dx} \) has the composition property:

\[ \hat{T}_{dx} \cdot \hat{T}_{dx'} = \hat{T}_{dx+dx'} \]
\[ \hat{T}_{-dx} = \hat{T}_{dx}^{-1} \]
\[ \hat{T}_{dx} \approx \hat{1} \]

These properties are fullfilled by \( \hat{T}_{dx} \) of the following form:

\[ \hat{T}_{dx} = \hat{1} - i\hat{K}dx \]

where \( \hat{K} \) is a certain hermitean operator. We do not know yet the details of \( \hat{K} \), in order to learn more we will establish the relationship between \( \hat{K} \) and the position operator \( \hat{x} \). We have:

\[ \hat{x} \cdot \hat{T}_{dx} |x'\rangle = \hat{x} |x' + dx\rangle = (x' + dx') |x' + dx\rangle \]

On the other hand

\[ \hat{T}_{dx} \cdot \hat{x} |x'\rangle = x' \hat{T}_{dx} |x'\rangle = x'|x' + dx\rangle \]

Hence

\[ [\hat{x}, \hat{T}_{dx}] |x'\rangle = dx' |x' + dx\rangle \approx dx'|x'\rangle \]

This is true for any position eigenket and they form a complete set of kets. Therefore:

\[ -i\hat{x} \cdot \hat{K}dx' + i\hat{K}\hat{x}dx' = dx' \]

that is:

\[ [\hat{x}, \hat{K}] = i \cdot \hat{1} \]

In three dimensions the same relationship takes the form:

\[ [\hat{x}_i, \hat{K}_j] = i\delta_{ij} \hat{1} \]

Quite often the operator \( \hat{1} \) is simply omitted.

### 5.1.3 Formal analogies between translation and time evolution

Below we give the main results for the translation operator and the time evolution operator that will show a very close analogy between these two formalisms.

#### Time evolution

Infinitesimal time evolution operator is:

\[ \hat{U}(t_0 + dt, t_0) = \hat{1} - i\hat{H}dt/\hbar. \]

The differential equation fullfilled by the time evolution operator is:

\[ i\hbar \frac{\partial}{\partial t} \hat{U}(t, t_0) = \hat{H}\hat{U}(t, t_0) \]

Its solution is:

\[ \hat{U}(t, t_0) = \exp(-i\hat{H}(t - t_0)/\hbar) \]

#### Translation

The infinitesimal translation is:

\[ \hat{T}_{dx} = \hat{1} - i\hat{K}dx \]
The differential equation fulfilled by the finite translation $\hat{T}$ is the same as for $\hat{U}(t, t_0)$ as they both have an identical composition property.

$$i\frac{d}{dx}\hat{T} = \hat{K} \cdot \hat{T}$$

The solution is identical as before:

$$\hat{T}_a = e^{i\hat{K}a}$$

where

$$\hat{T}_a |x\rangle = |x + a\rangle$$

is the finite translation by the one dimensional translation vector $a$ in $x$ direction. In three dimensions the same formula is:

$$\hat{T}_a = e^{i(\hat{K}_x a_x + \hat{K}_ya_y + \hat{K}_za_z)}$$

where

$$\hat{T}_a |x\rangle = |x + a\rangle$$

### 5.1.4 Translational invariance for quantum systems: commutation of Hamiltonian with translation operator

We will concentrate on a translationally invariant system where we will establish the commutation rule (if any) of the finite translation operator with the Hamiltonian.

For any state $|\psi\rangle$ we have

$$ih\frac{d}{dt}|\psi\rangle = \hat{H}|\psi\rangle$$

We can apply the translation operator $\hat{T}$ to both sides of the above equation:

$$ih\hat{T}\frac{d}{dt}|\psi\rangle = \hat{T}\hat{H}|\psi\rangle$$

Let us now leave this for a while and consider the $\hat{T}|\psi\rangle$. Obviously it is also a state (from the Hilbert space) of the same system, therefore it fulfills:

$$ih\frac{d}{dt}(\hat{T}|\psi\rangle) = \hat{H}'(\hat{T}|\psi\rangle)$$

The question now is whether the Hamiltonian $\hat{H} = \hat{H}'$. For translationally invariant systems the answer is yes. The same was true for translationally invariant systems in classical mechanics as for example two masses interacting via central potential. Then since $\hat{T}$ is explicitly time independent:

$$\hat{T}\frac{d}{dt}|\psi\rangle = \frac{d}{dt}(\hat{T}|\psi\rangle)$$

and consequently

$$\hat{T} \cdot \hat{H}|\psi\rangle = \hat{H} \cdot \hat{T}|\psi\rangle$$

for any $|\psi\rangle$. This means that

$$[\hat{T}, \hat{H}] = 0$$
5.1.5 Identification of $\hat{K}$ with the momentum

In the previous section we have established that for any translation:

$$[\hat{T}, \hat{H}] = 0$$

Of course the same applies to the infinitesimal translation operator:

$$[\hat{T}_{dx}, \hat{H}] = 0$$

Using the explicit form of $\hat{T}_{dx}$ we have:

$$[\hat{K}, \hat{H}] = 0$$

Therefore $\hat{K}$ is a unique operator associated with all translations (that is by translations by any vector) for quantum systems that are translationally invariant. Moreover $\hat{K}$ is conserved. It is therefore postulated that $\hat{K}$ is proportional to the momentum operator $\hat{p}$.

$$\hat{K} = \hat{p}/\hbar$$

This gives:

$$\hat{T}_{dx} = \hat{1} - i\hat{p}dx/\hbar$$

This equation is expressed in words that the momentum is a generator of an infinitesimal translation.

Finally from the commutation rule of $\hat{T}$ with $\hat{x}$ an extremely important commutation rule for the position and momentum operator can be derived:

$$[\hat{x}, \hat{p}] = i\hbar$$

5.2 Position and momentum operators and representation

5.2.1 Position operator versus momentum operator

The idea of position operator and the momentum that appeared before needs some clarification. First the position eigenstate $|x\rangle$ describes a particle in a given position $x$. The position operator when applied to this position eigenstate, extracts this position. This position is a certain real number, the same as in the eigenstate:

$$\hat{x}|x'\rangle = x'|x'\rangle$$

or for example for the particle at $x' = 0.2333$ m from the origin (see Fig 5.7)

$$\hat{x}|0.2333\rangle = 0.2333|0.2333\rangle$$

The position operator can have any real number for its eigenvalue.

The same conditions are fullfilled by the momentum operator. Yet we denote it by a different letter:

$$\hat{p}|p'\rangle = p'|p'\rangle$$
This is because the position and momentum operator are not identical: the link (or the difference) between them is given by the commutation rule:

\[ [\hat{x}, \hat{p}] = i\hbar \]

It should be noted that these conditions do not uniquely define \( \hat{x} \) and \( \hat{p} \).

We have also postulated the orthogonality conditions:

\[
\langle x | x' \rangle = \delta(x - x') \\
\langle p | p' \rangle = \delta(p - p')
\]

We will further examined the consequences of these conditions and explicitly show what \( \hat{x} \) and \( \hat{p} \) are.

### 5.2.2 Position representation

In order to do that we first introduce the position representation. Let us consider a certain state \( |\psi\rangle \) and take all eigenstates of \( \hat{x} \). We would like to know what kind of mathematical object is \( \langle x' | \psi \rangle \). Clearly for each \( x' \) the quantity is a certain complex number, in principle different for every \( x' \). Such object is a function that maps \( \mathbb{R} \rightarrow \mathbb{C} \), that is it assigns to every \( x \in \mathbb{R} \) a certain number \( \langle x' | \psi \rangle \in \mathbb{C} \). We will denote this function \( \psi(x) \). An obvious question now is: we have identified a function that is associated with a given state \( |\psi\rangle \), is it a wavefunction. The answer will turn out to be positive, but it can be reached only by the way of experiment. The experiment consists of the measurement of a position of the particle by letting it pass through a slit of the small width \( \Delta x \approx dx \) and placed at \( x \) (see Fig 5.8).

Before the measurement the particle was in the state \( |\alpha\rangle \):

\[
|\alpha\rangle = \int_{-\infty}^{\infty} dx' \, x' \langle x'|\alpha\rangle
\]

After the measurement the particle is in the state \( |f\rangle \)

\[
|f\rangle = \int_{x-\Delta/2}^{x+\Delta/2} dx' |x'| \langle x'|\alpha\rangle \approx \Delta |x\rangle \langle x|\alpha\rangle \approx dx \langle x|\alpha\rangle |x\rangle
\]
The probability that the particle will emerge in the state $|x\rangle$ is then

$$P = |\langle x|\alpha\rangle|^2 \, dx$$

On the other hand, this probability is

$$P = |\psi(x)|^2 \, dx$$

on the basis of the probabilistic interpretation. Therefore $\langle x|\alpha\rangle$ is a wavefunction to within a phase factor $\exp(i\alpha)$.

Additionally it should be noted that in the above experiment the probability that the particle will have a certain value of position is 1 (the particle is somewhere). This can be expressed as:

$$\int_{-\infty}^{\infty} |\langle x|\alpha\rangle|^2 \, dx = 1$$

The same is true for the $|\psi(x)|^2$:

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = 1$$

The wavefunction $\psi(x)$ is called a representation of the state $|\psi\rangle$ in the position space. In complete analogy (just by changing symbols from $x$ to $p$ we get that:

$$\langle p|\psi\rangle = \psi(p)$$

Now we would like to underline formal similarities between the wavefunction and the coefficients of a finite-dimensional vector in a given basis in order to understand better why the wavefunctions were called "representations".

### DISCRETE

| $i = 1,\ldots,n$, $e_i$ - basis | $|x\rangle$ - complete set $x \in \mathbb{R}$ |
| --- | --- |
| $v = \sum_{i=1}^{n} a_i e_i$ or $v = \sum_{i=1}^{n} |e_i\rangle \langle e_i|v\rangle$ | $|\psi\rangle = \int_{-\infty}^{\infty} dx \, |x\rangle \langle x|\psi\rangle$ |
| $a_i = \langle e_i|v\rangle$ | $\langle x|\psi\rangle = \psi(x)$ |

$a_i$ - representation of $v$

in the basis $e_i \, i = 1,\ldots,n$

We take the second basis $g_i$

$$v = \sum_{i=1}^{n} b_i g_i = \sum_{i=1}^{n} |g_i\rangle \langle g_i|v\rangle$$

$b_i = \langle g_i|v\rangle$

$b_i$ - representation of $v$

in the basis $g_i \, i = 1,\ldots,n$

We take another complete set: eigenkets of $\hat{p}$ (momentum) operator $|p\rangle, \, p \in \mathbb{R}$

$$|\psi\rangle = \int_{-\infty}^{\infty} dp \, |p\rangle \langle p|\psi\rangle$$

$

\psi(x)$ - wavefunction of $|\psi\rangle$

in the position representation in the basis of eigenstates of the position operator $x \in \mathbb{R}$

$

\psi(x)$ - wavefunction of $|\psi\rangle$

in the momentum representation in the basis of eigenstates of the momentum operator $\hat{p}$
5.2.3 Relationship between $\psi(x)$ and $\psi(p)$

It is easy to see that

$$\psi(x) = \langle x | \psi \rangle = \int_{-\infty}^{\infty} dp \langle x | p \rangle \langle p | \psi \rangle = \int_{-\infty}^{\infty} \langle x | p \rangle \psi(p) dp$$

and conversely

$$\psi(p) = \langle p | \psi \rangle = \int_{-\infty}^{\infty} dx \langle p | x \rangle \langle x | \psi \rangle = \int_{-\infty}^{\infty} \langle p | x \rangle \psi(x) dx$$

though it is not helpful as we still do not know $\langle p | x \rangle$ and $\langle x | p \rangle$. The discrete analogy of $\langle p | x \rangle$ is $\langle g_i | e_j \rangle$. If the coefficients $\langle g_i | e_j \rangle$ are known then we know the operator $U$ of the transformation from the old to the new basis. This allows to calculate the coefficients of a given vector in the new basis. That is why $\langle p | x \rangle$ and $\langle x | p \rangle$ are important.

The calculation will be conducted in two steps:

Step 1. We find the differential equation for the $\langle x | p \rangle|\alpha\rangle$ for an arbitrary $\alpha$.

Let us take a small $\Delta x'$. Then

$$\hat{T}_{\Delta x'}|\alpha\rangle = \int_{-\infty}^{\infty} dx' \hat{T}_{\Delta x'}|x'\rangle|\alpha\rangle = \int_{-\infty}^{\infty} dx' |x'\rangle + \Delta x' \langle x'| \alpha \rangle =$$

(after the change of variables $x'' = x' + \Delta x'$):

$$= \int_{-\infty}^{\infty} dx'' |x''\rangle \langle x'' - \Delta x'| \alpha \rangle =$$

(now we rename $x'' = x'$ and use the Taylor expansion $f(x) \approx f(x_0) + (x - x_0)f'(x_0)$)

$$= \int_{-\infty}^{\infty} dx'|x'\rangle (\langle x'| \alpha \rangle - \Delta x'' \frac{\partial}{\partial x'} (\langle x'| \alpha \rangle))$$

Now we remind ourselves that

$$\hat{T}_{dx}|\alpha\rangle = (\hat{1} - i\hat{p}\Delta x'/\hbar)|\alpha\rangle$$

Since

$$\hat{1} = \int_{-\infty}^{\infty} dx'|x'\rangle \langle x'|$$

then

$$-i\hat{p}\Delta x'/\hbar|\alpha\rangle = \int_{-\infty}^{\infty} dx'|x'\rangle (-\Delta x') \frac{\partial}{\partial x'} \langle x'| \alpha \rangle$$
and we get
\[ \hat{p}|\alpha\rangle = \int_{-\infty}^{\infty} dx'|x'\rangle(-i\hbar \frac{\partial}{\partial x'}\langle x'|\alpha\rangle) \]

Further we apply \( \langle x| \) to both sides of the above equation and use the rule \( \langle x|x'\rangle = \delta(x-x') \) and also the fact that Dirac delta is even, that is \( \delta(\zeta) = \delta(-\zeta) \). We obtain:
\[ \langle x|\hat{p}|\alpha\rangle = \int_{-\infty}^{\infty} dx'\delta(x-x')(-i\hbar \frac{\partial}{\partial x'}\langle x'|\alpha\rangle) \]
or finally
\[ \langle x|\hat{p}|\alpha\rangle = -i\hbar \frac{\partial}{\partial x}\langle x|\alpha\rangle \]

Step 2. We solve the above equation and find \( \langle x|p\rangle \) and \( \langle p|x\rangle \) Let \( |\alpha\rangle \) be \( |p\rangle \). Then we have:
\[ \langle x|\hat{p}|p\rangle = -i\hbar \frac{\partial}{\partial x}\langle x|p\rangle \]
or
\[ p\langle x|p\rangle = -i\hbar \frac{\partial}{\partial x}\langle x|p\rangle \]

This is a differential equation for the function \( \langle x|p\rangle \) of the variable \( x \). The solution is:
\[ \langle x|p\rangle = Ne^{ipx/\hbar} \]

where \( N \) is the normalisation constant. It can be shown that
\[ N = \frac{1}{\sqrt{2\pi\hbar}} \]
in one dimension and
\[ N = \frac{1}{(\sqrt{2\pi\hbar})^3} \]
in three dimensions.

In summary the relationship between the \( \psi(x) \) and the \( \psi(p) \) is as follows:
\[ \psi(x) = \langle x|\psi\rangle = \int_{-\infty}^{\infty} dp\langle x|p\rangle\langle p|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} dp\exp(ipx/\hbar)\psi(p) \]

Conversely
\[ \psi(p) = \langle p|\psi\rangle = \int_{-\infty}^{\infty} dx\langle p|x\rangle\langle x|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} dx\exp(-ipx/\hbar)\psi(x) \]

This important fact should be remembered: \( \psi(x) \) and \( \psi(p) \) are related through the Fourier transform.

We are aware now that a state can be expressed in various representations - this is like writing a vector in various bases, and of course the results in various bases may be different. The same is true if we want to write the matrices of operators, their appearance depends on the choice of basis. Therefore we are not surprised that the representations of operators
(like the matrices) depend on a choice of the complete set. The table below spells out this analogy in more detail:

<table>
<thead>
<tr>
<th>DISCRETE</th>
<th>CONTINUOUS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>e_i\rangle$ - basis</td>
</tr>
<tr>
<td>$</td>
<td>e_i\rangle$ - representation of $\hat{Q}$</td>
</tr>
<tr>
<td>$\hat{Q}</td>
<td>x\rangle =</td>
</tr>
<tr>
<td>Insert $1 = \sum_j</td>
<td>e_j\rangle\langle e_j</td>
</tr>
<tr>
<td>Then apply $\langle e_i</td>
<td>$</td>
</tr>
<tr>
<td>$\sum_j \langle e_i</td>
<td>\hat{Q}</td>
</tr>
<tr>
<td>$Q_{ij}$ is the representation</td>
<td>$\int_{-\infty}^{\infty} x\delta(x' - x)\psi(x) dx$</td>
</tr>
<tr>
<td>of $\hat{Q}$ in the basis $</td>
<td>e_i\rangle$</td>
</tr>
<tr>
<td></td>
<td>$= x'\psi(x') = \langle x'</td>
</tr>
</tbody>
</table>

Concluding the result of the operator $\hat{x}$ on $|\psi\rangle$ is to multiply the wavefunction by the argument:

$$\phi(x') = x'\psi(x')$$

We will repeat the same procedure for the momentum operator:

$$\langle x'|\hat{p}|\psi\rangle = \int_{-\infty}^{\infty} dx \langle x'|\hat{p}|x\rangle \langle x|\psi\rangle$$

$$= -i\hbar \frac{\partial}{\partial x} \langle x|\psi\rangle = -i\hbar \frac{\partial}{\partial x} \psi(x)$$

The matrix element $\langle x'|\hat{p}|x\rangle$ is known from $\langle x|\hat{p}|\alpha\rangle$

Concluding the momentum operator in position representation differentiates the function.

We have to confess here: we have just stated what these two operators do in position representation to the wavefunction in position representation. We did not tell you what is the position representation of a position and momentum operator as it is just outside the scope of these lectures.

In this section we concentrated on the position representation, in the assignment problems we will lead you through the momentum representation in more detail. Many other representations are of course possible, such as for example an important energy representation in the eigenstates of the $\hat{H}$ and a wide choice of others.

5.2.4 Wavepackets

A "wavepacket" denotes a state $|\psi\rangle$ for which the wavefunction is localised in a certain region in space. A couple of examples are presented in Fig 5.9.

For the wavepacket in Fig 5.9 given by the formula

$$\Psi(x) = \text{normalised } e^{-\lambda|x|} \sin(kx)$$
one is tempted to determine the wavelength as the distance between the adjacent maxima, the problem is that different maxima give different values. This is a direct consequence of the wavepacket localisation - the wave is very small for large $x$. Another example of the wavepacket is presented in the Fig 5.10 and given by the expression:

$$\Psi(x) = \text{normalised } \exp\left(-\frac{x^2}{2\sigma^2}\right)$$

Such wavepackets are important for describing particles. We may for example ask the question: where is a given particle at a particular instance of time. The experimental answer is provided by the repetitive experiment performed on a large number of copies of particles prepared in an identical state. The answers in this experiment will be spread. They will also be fully described by the wavefunction: the $|\Psi(x)|^2$ gives the probability that the value $x$ of position is measured. By taking a weighted average of these positions (weighted with the respective probabilities) we can evaluate what is the average position, that means where the classical particle would be. One can also calculate or estimate from the graph what is the "spread" of those measured positions.

In case of a particle it is legitimate to ask what is its momentum. In case of the first wavepacket the momentum can be estimated on the basis of the wavelength, and we already know that it does not have a single value. Experimentally we get the answer by doing a repetitive experiment on many copies and the answer what values of the momentum will be measured are provided by the wavefunction in momentum representation

$$\langle p|\Psi\rangle = \Psi(p)$$

sometimes also called the spectral content of the wavepacket. The $|\Psi(p)|^2dp$ gives the probability that the value $p$ will be measured. In the previous section we learned that
Figure 5.11: The Fourier transform of the first wavepacket

Figure 5.12: The Fourier transform of the gaussian wavepacket

Ψ(p) is the Fourier transform of Ψ(r). In case of the first packet this gives:

Ψ₁(p) = ????

In case of the second one

Ψ₂(p) = ?? exp \left( \frac{-\sigma^2 p^2}{2} \right)

These two are sketched in the Fig 5.11 and 5.12. We immediatly see what values of the momentum will be measured, with what probabilities and what is the spread of the momentum.

Let us discuss what happens to the first packet when we try to localise it more and more in space by making it more and more narrow. When we do that the maximum has to grow, because of the normalisation. At the same time the corresponding momentum wavefunction will become more and more flat. In the limit of a particle localised in one point the momentum wavefunction is a plane wave. This is an important observation that can be express in the following way: the eigenstate of position (that describes a particle localised at a point) in the position representation is a Dirac delta. The eigenstate of position in the momentum representation is a plane wave.

A similar approach can be adopted in case of the particle having a well determined momentum. Such a particle is described by the momentum wavefunction that is extremely narrow. Then its wavefunction in position space can be calculated by means of an inverse
Fourier transform. This wavefunction is a plane wave, which physically means that it is not localised in space.

An interesting and easy question is what does the time evolution of such wavepackets is like: here we just present pictures.

Now we will solve an associated problem.

**Exercise 5.1** Find the probability of obtaining (as a result of a momentum measurement) the value $p_0$ of momentum for a particle in the first state of an infinite potential well. Also find the expectation value of momentum in this state.

Solution: Let $|\Psi\rangle$ be the eigenstate of the Hamiltonian, $|p'\rangle$ is the complete orthonormal set. We have:

$$\langle p'|p'' \rangle = \delta(p' - p'')$$

$$|\Psi\rangle = \int_{-\infty}^{\infty} dp' |p'\rangle\langle p'|\Psi\rangle$$

because

$$\hat{1} = \int_{-\infty}^{\infty} dp' |p'\rangle\langle p'|$$

The probability of obtaining the value $p$ of the momentum is $|\langle p|\Psi\rangle|^2 dp$. The wavefunction in position representation of this state is:

$$\langle x|\Psi\rangle = \Psi(x) = \sqrt{\frac{1}{a}} \cos \left(\frac{\pi x}{2a} \right)$$

Then we have:

$$\langle p|\Psi\rangle = \int_{-\infty}^{\infty} dx \langle p|x\rangle\langle x|\Psi\rangle$$

$$= \int_{-a}^{a} dx \frac{1}{\sqrt{2\pi h}} \exp \left(-\frac{ipx}{\hbar} \right) \sqrt{\frac{1}{a}} \cos \left(\frac{\pi x}{2a} \right)$$

Therefore

$$|\langle p|\Psi\rangle|^2 = \frac{8\pi}{h} \frac{1}{\left(\frac{4p^2a^2}{h^2} - \pi^2 \right)} \cos^2 \left(\frac{pa}{\hbar} \right)$$

The expectation value is:

$$\langle p \rangle = \int_{-\infty}^{\infty} dp \, p \, |\langle p|\Psi\rangle|^2 = 0$$

as the $|\langle p|\Psi\rangle|^2$ is even. This expectation value is zero for any energy eigenstate regardless of the potential!
5.3 Parity

In this section we will learn about another important symmetry, this time a discrete one, called inversion symmetry and the associated operator of parity. Some physicists visualise the inversion or the parity symmetry as the similarity between the physical experiment and its mirror image, to some extent (mathematically) it has some sense (inversion is not a mirror symmetry). More accurately parity is a characteristic feature of even and odd functions. In quantum mechanics we are describing quantum systems using states. The parity is defined to be an operator \( \hat{P} \) such that:

\[
\hat{P}|x\rangle = |-x\rangle
\]

Further we will learn that such definition although broader does embrace even and odd functions in some sense. In order to learn more about parity we will solve the following two problems:

**Exercise 5.2** Prove that \( \hat{P} \) is both hermitean and unitary. A unitary operator is the one that fulfills:

\[
\hat{P} \cdot \hat{P}^\dagger = \hat{P}^\dagger \cdot \hat{P} = \hat{1},
\]

for the hermitean operator \( \hat{P} = \hat{P}^\dagger \).

Solution: We make use of the completeness of the eigenstates of the position operator \( \hat{x} \):

\[
\int_{-\infty}^{\infty} dx \left| x \right\rangle \langle x | = \hat{1}
\]

Consider an arbitrary \( |\Psi\rangle, |\Phi\rangle \). We have:

\[
\langle \Phi | \hat{P} | \Psi \rangle = \int_{-\infty}^{\infty} dx \langle \Phi | \hat{P} | x \rangle \langle x | \Psi \rangle = \int_{-\infty}^{\infty} dx \langle \Phi | -x \rangle \langle x | \Psi \rangle
\]

\[
= \int_{-\infty}^{\infty} dx \langle -x | \Phi \rangle^* \Psi(x) = \int_{-\infty}^{\infty} dx \Phi^*(-x) \Psi(x)
\]

Now we change the variables taking \( x' = -x \) and get:

\[
\int_{-\infty}^{\infty} dx \Phi^*(-x) \Psi(x) = \int_{-\infty}^{\infty} dx' \Phi^*(x') \Psi(-x') = \int_{-\infty}^{\infty} \langle \Phi | x' \rangle \langle -x' | \Psi \rangle
\]

\[
= \int_{-\infty}^{\infty} dx' \langle \Phi | x' \rangle \left( \langle \Psi | -x' \rangle \right)^* = \int_{-\infty}^{\infty} dx' \langle \Phi | x' \rangle \left( \langle \Psi | \hat{P} | x' \rangle \right)^*
\]

\[
= \int_{-\infty}^{\infty} dx' \langle \Phi | x' \rangle \langle x' | \hat{P}^\dagger | \Psi \rangle = \langle \Phi | \hat{P}^\dagger | \Psi \rangle
\]
As $|\Psi\rangle, |\Phi\rangle$ were arbitrary, then $\hat{P} = \hat{P}^\dagger$, that is $\hat{P}$ is hermitean.

To show that $\hat{P}$ is unitary we show that $\hat{P}^2 = \hat{P} \cdot \hat{P}$ as follows:

$$
\langle \Phi | \hat{P}^2 | \Psi \rangle = \int_{-\infty}^{\infty} dx \langle \Phi | \hat{P}^2 | x \rangle \langle x | \Psi \rangle = \int_{-\infty}^{\infty} dx \langle \Phi | \hat{P} | x \rangle \langle x | \Psi \rangle =
$$

$$
= \int_{-\infty}^{\infty} dx \langle \Phi | x \rangle \langle x | \Psi \rangle = \langle \Phi | 1 | \Psi \rangle
$$

Therefore $\hat{P}^2 = 1$, but $\hat{P} = \hat{P}^\dagger$ so $\hat{P} \cdot \hat{P}^\dagger = \hat{P}^\dagger \cdot \hat{P} = 1$.

**Exercise 5.3** A particle is moving in an even potential $V(\hat{x}) = V(-\hat{x})$. What can we tell about parity of the eigenstates of $\hat{H}$? Assume that $\hat{H}$ has non-degenerate eigenvalues.

Solution: The Hamiltonian of this particle is of the form:

$$
\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})
$$

First we explore what we can say about the parity of the wavefunctions in the position representation. We know what does the parity operator do to position eigenstates: namely $\hat{P} | x \rangle = |-x \rangle$. We will determine what does parity do to an arbitrary state (but only in the position representation. Assume

$$
\hat{P} | \Psi \rangle = | \Phi \rangle
$$

$$
\langle x | \hat{P} | \Psi \rangle = \langle x | \Phi \rangle = \phi(x)
$$

$$
\int_{-\infty}^{\infty} dx' \langle x | \hat{P} | x' \rangle \langle x' | \Psi \rangle = \int_{-\infty}^{\infty} dx' \langle x | -x' \rangle \Psi(x') = \int_{-\infty}^{\infty} dx'' \langle x | x'' \rangle \Psi(-x'')
$$

$$
= \int_{-\infty}^{\infty} dx'' \langle x | x'' \rangle \Psi(-x'') = \int_{-\infty}^{\infty} dx'' \delta(x'' - x) \Psi(-x'') = \Psi(-x).
$$

This gives

$$
\Phi(x) = \Psi(-x)
$$

that is the parity acting on $\Psi(x)$ gives $\Psi(-x)$. We have learned some time ago that in position representation the momentum operator acting on the state $| \Psi \rangle$ is equivalent to taking $-i\hbar \frac{d\Psi(x)}{dx}$. It can be shown (with some effort) that in position representation the Hamiltonian acting on the state $| \Psi \rangle$ gives:

$$
\langle x | \hat{H} | \Psi \rangle = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x) + V(x) \Psi(x)
$$
Now we are ready to show that the parity operator commutes with the Hamiltonian, that is \([\hat{P}, \hat{H}] = 0\). This will be done in the position representation:

\[
\langle x | \hat{P} \cdot \hat{H} - \hat{H} \cdot \hat{P} | \Psi \rangle = 0
\]

\[
\langle x | \hat{P} \cdot \hat{H} | \Psi \rangle = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial^2(-x)} \psi(-x) + V(-x)\psi(-x)
\]

\[
\langle x | \hat{H} \cdot \hat{P} | \Psi \rangle = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial^2(x)} \psi(-x) + V(x)\psi(-x)
\]

Now \(\frac{\partial^2}{\partial^2(-x)} = \frac{\partial^2}{\partial^2(x)}\), and \(V(x) = V(-x)\). Therefore the commutator is zero for any \(\Psi\), hence \(\hat{P} \cdot \hat{H} = \hat{H} \cdot \hat{P}\). This in turn means that the eigenstates of \(\hat{H}\) will be the eigenstates of \(\hat{P}\). In order to see it better let \(|\Psi\rangle\) be the eigenstate of \(\hat{H}\) with the eigenvalue \(E\). We have:

\[
\hat{H} |\Psi\rangle = E |\Psi\rangle
\]

Let us apply \(\hat{P}\) to both sides:

\[
\hat{P} \cdot \hat{H} |\Psi\rangle = E \hat{P} |\Psi\rangle
\]

But as \(\hat{H}\) commutes with \(\hat{P}\) we have:

\[
\hat{H} \cdot (\hat{P} |\Psi\rangle) = E (\hat{P} |\Psi\rangle)
\]

So \(\hat{P} |\Psi\rangle\) is also an eigenstate of \(\hat{H}\) with the eigenvalue \(E\). But \(\hat{H}\) was assumed to have non-degenerate eigenvalues. This means that \(|\Psi\rangle\) and \(\hat{P} |\Psi\rangle\) are proportional, that is \(|\Psi\rangle\) is the eigenstate of \(\hat{P}\). The wavefunctions that correspond to eigenstates of parity are either even (parity eigenvalue = +1) or odd (with parity eigenvalue of -1).

**Exercise 5.4** A particle is moving in a symmetric potential but now the \(\hat{H}\) may have degenerate eigenvalues. Write down the even and odd wavefunctions corresponding to a given eigenvalue \(E\).

Solution: We have:

\[
-\frac{\hbar^2}{2m} \frac{d^2u(x)}{dx^2} + V(x)u(x) = Eu(x),
\]

where \(V(x) = V(-x)\). If \(E\) is degenerate then we should take the new function \(w(x) = u(-x)\). \(w(x)\) is also a wavefunction of this Hamiltonian with the eigenvalue \(E\):

\[
-\frac{\hbar^2}{2m} \frac{d^2w(x)}{dx^2} + V(x)w(x) = Ew(x)
\]

Then we take the following combinations: an even one:

\[
u_e(x) = \frac{1}{2}[u(x) + w(x)] = \frac{1}{2}[u(x) + u(-x)],
\]

and an odd one:

\[
u_o(x) = \frac{1}{2}[u(x) - w(x)] = \frac{1}{2}[u(x) - u(-x)]
\]
5.3.1 Nonconservation of parity in weak interactions

As pointed out before we would expect the laws of physics to be the same for the experiment and its reflected in the mirror counterpart, where the vectors $\mathbf{r}$ and $\mathbf{p}$ have their $x$-coordinates reversed. It turns out that the beta decay process is in open conflict with the principle of reflection symmetry if the charge of a particle is assumed to be unchanged under reflection. It was found that a magnetised sample of Co$_{60}$ emits more electrons in a direction opposite to the magnetic moment than along it. This observation is not in accord with reflection symmetry if the mirror image of the electron is again an electron. However the agreement is reached if upon reflection the particles are changed into the antiparticles. The need for the charge reversal in reflections appears only in weak interactions which cause the decay of elementary particles. If these interactions are neglected symmetry prevails and parity is conserved. More about this subject can be found in Merzbacher.

5.4 Symmetries - general

5.4.1 Symmetries of eigenstates of the Hamiltonian

We are familiar so far with two important examples of symmetries: the translational symmetry characterised by the translation vector and the parity symmetry. There are numerous other symmetries and two more will be presented in these lectures. Now we will consider general consequences of a system having some sort of symmetry.

First we remind, that for a Hermitian operator $\hat{Q}$ that does not depend explicitly on time for any $|\Psi\rangle$ we have:

$$\frac{d}{dt}\langle \Psi | \hat{Q} | \Psi \rangle = \frac{1}{i\hbar} \langle \Psi | [\hat{Q}, \hat{H}] | \Psi \rangle$$

If $[\hat{Q}, \hat{H}] = 0$ then $\hat{Q}$ is the constant of the motion.

Let now $\hat{T}$ be a symmetry operation, such that: ([ref Das-M], page 266)

$$\hat{T} | \Psi \rangle = | \Psi' \rangle$$

Let us take these two states at $t = t_1$

$$| \Psi'(t_1) \rangle = \hat{T} | \Psi(t_1) \rangle$$
Then:

\[ |\Psi(t_2)\rangle = \hat{U}(t_2 - t_1)|\Psi(t_1)\rangle \]

\[ |\Psi'(t_2)\rangle = \hat{U}(t_2 - t_1)|\Psi'(t_1)\rangle \]

If the two states are to evolve identically, then:

\[ |\Psi'(t_2)\rangle = \hat{T}|\Psi(t_2)\rangle \]

Therefore for any \(|\Psi\rangle\):

\[ |\Psi'(t_2)\rangle = \hat{T} \cdot \hat{U}(t_2 - t_1)|\Psi(t_1)\rangle = \hat{U}(t_2 - t_1) \cdot \hat{T}|\Psi(t_1)\rangle \]

This means that

\[ \hat{T} \cdot \hat{U} = \hat{U} \cdot \hat{T} \]

For small \(t_2 - t_1 = dt\)

\[ \hat{U} = \hat{1} - \frac{i}{\hbar} \hat{H} dt \]

Then from \([\hat{T}, \hat{U}] = 0\) we get:

\[ [\hat{T}, \hat{H}] = 0. \]

We can express this by saying, that if the quantum system possesses a certain symmetry \(\hat{T}\) then the corresponding symmetry operator commutes with the Hamiltonian. The reverse statement is also true.

The above statement can be used as a criterium whether a given system possesses the symmetry \(\hat{T}\). It is enough to check two things:

- whether \(\hat{T}\) is unitary (remember, parity and translations were unitary), this means that \(\hat{T}\) is a symmetry operation.
- whether \([\hat{T}, \hat{H}] = 0\)

If the answer is yes then the system possesses the symmetry \(\hat{T}\).

An obvious consequence of the above commutation rule is that \(\hat{T}\) and \(\hat{H}\) can be diagonalised simultaneously by the same set of kets (by the theorem derived in the chapter ??). This in turn means that the eigenstates of the \(\hat{H}\) are the eigenstates of \(\hat{T}\). (see Example ??). Therefore the study of the system symmetries can give information about the state vectors of the system.

### 5.4.2 Symmetry and the constants of the motion, the Stone theorem

Another important aspect of symmetries is their relationship with the constants of the motion. As an example we remind, that in the case of finite translations the translation operator was commuting with the Hamiltonian and we were able to identify the corresponding physical observable (the Hermitian operator), namely the momentum that was a constant of the motion. The same was true for parity: the parity of the wavefunction was the constant of the motion (see page ??). This can be generalised to all symmetry
operations by saying that for every symmetry operation there is a corresponding physical observable that is a constant of the motion. The last phrase in fact is a mathematical statement called the Stone theorem. It is associated with the fact that symmetries of a given type form a group: for example we have a group of translations $T_a$ indexed with the translation vector $a$. This group is called continuous because the index can take a continuous range of values. (You probably noticed that the postulates on page ?? for the infinitesimal translation were in fact the axioms of a group.) Another example is the group composed of two elements: identity operator $1$ and the parity operator $P$. This group is discrete. Stone theorem applies to the continuous groups only.

**Stone theorem**

Let $U_\xi$ be a group of unitary transformations, indexed with a continuous index $\xi$. The Stone theorem says that the elements of such group are of the form:

$$U_\xi = \exp(-i\hat{Q}\xi)$$

where $\hat{Q}$ is a certain Hermitean operator.

This purely mathematical theorem is the reason why in our treatment of time evolution and translations (and as we will see further, also for rotations) we end up with identical differential equation for $\hat{Q}$ (which is a consequence of the composition property for the unitary group elements) and as a result with the identical exponential form of the unitary transformation. It should not surprise us either that in each of these cases we are able to identify a Hermitean operator called the **group generator** $\hat{Q}$ being $\hat{H}/\hbar$ for the time evolution and $\hat{p}/\hbar$ for translations, further we will learn that $\hat{J}_i/\hbar$, $i = 1, 2, 3$ are generators of rotation. As $\hat{Q}$ is hermitean there is a dynamical variable or a physical quantity associated with it.

Assume now that the physical system is endowed with this particular symmetry $U_\xi$. Then as we have learned previously, the operator $U_\xi$ commutes with the Hamiltonian. For small values of the parameter $\xi$, namely $d\xi$ the "infinitesimal" symmetry operation $U_{d\xi}$ can be expressed as:

$$U_{d\xi} = 1 - i\hat{Q}d\xi$$

like in the case of infinitesimal translations and time evolution. Then from

$$[U_{d\xi}, \hat{H}] = 0$$

we deduce that:

$$[\hat{Q}, \hat{H}] = 0$$

which in terms implies that $\hat{Q}$ is the constant of the motion, that is a conserved quantity. This is an extremely useful fact, and it is very helpful in elementary particle physics, where by way of experiments we are able to find conserved quantities, but have no prior knowledge of the Hamiltonian.

**5.4.3 Symmetry and degeneracy**

Sometimes the symmetry can give rise to degeneracy of the eigenstates of the Hamiltonian. Let

$$\hat{H}|\alpha\rangle = E_\alpha|\alpha\rangle$$
and assume

\[ \{ \hat{Q}, \hat{H} \} = 0 \]

Then \( \hat{Q}|\alpha\rangle \) is the energy eigenstate of \( \hat{H} \) with the eigenvalue \( E_\alpha \). It may happen that \( \hat{Q}|\alpha\rangle \) is linearly independent of \( |\alpha\rangle \), then the eigenvalue \( E_\alpha \) is degenerate. An example of such behaviour is the energy degeneracy of momentum eigenstates, which can be easily checked in position representation. Energy degeneracy associated with geometrical symmetry is often easy to identify.

5.5 Time reversal

The reversal in time of a state represented by the ket \( |\alpha\rangle \) changes it into the ket \( |\alpha'\rangle \) that evolves in accordance with the opposite sense of progression of time. The time reversal changes \( t \) to \( -t \). In classical mechanics this correspond to reversing the signs of all linear and angular momenta, leaving position vectors and other unchanged. In fact a better name would be a "motion reversal". This feature is retained by quantum mechanics.

Time reversal is effected by a time independent operator \( \hat{T} \) such that

\[ \hat{T}|\alpha\rangle = |\alpha'\rangle \]

The fact that the time reversal does not change the position is expressed as:

\[ \hat{T}\hat{x}\hat{T}^{-1} = \hat{x}, \]

similarly for \( \hat{y} \) and \( \hat{z} \). The reversal of momentum is written as:

\[ \hat{T}\hat{p}_x\hat{T}^{-1} = -\hat{p}_x \]

similarly for \( \hat{p}_y, \hat{p}_z \). What follows is a little unexpected: \( \hat{T} \) turns out not to be linear but antilinear \( \hat{T}(a_1|\psi_1\rangle + a_2|\psi_2\rangle) = a_1^*\hat{T}|\psi_1\rangle + a_2^*\hat{T}|\psi_2\rangle \). To show that we take:

\[ \hat{x}\hat{p}_x - \hat{p}_x\hat{x} = i\hbar \]

and write all operators in a time - reversed frame of reference:

\[ \hat{T}\hat{x}\hat{T}^{-1}\hat{T}\hat{p}_x\hat{T}^{-1} - \hat{T}\hat{p}_x\hat{T}^{-1}\hat{T}\hat{x}\hat{T}^{-1} = \hat{T}i\hbar\hat{T}^{-1} \]

The right hand side should be equal to \(-i\hbar\), this can be true only if:

\[ \hat{T}i\hat{T}^{-1} = -i \]

This calculation was supposed to show that the time reversal is not quite like all previously discussed symmetry operations. Below we quote a several more of such unusual features: for a more formal presentation with algebraic proofs see for example Schiff [ref] p. 228. We might for example expect that the application of the time reversal twice will result in restoring the original time coordinate, that is \( \hat{T}^2 = 1 \). This is not true: the \( \hat{T}^2 \) when acting on the state with integer total angular momentum gives the same state (the eigenvalue is +1) and when acting on a state with half odd integer total angular momentum, for example a spin 1/2 state, gives the \(-1 \times \) the state. In the position representation the time reversal applied to the wavefunction converts it into its complex conjugate. Also \( \hat{T} \)
is not unitary as all other previously discussed symmetries, but antiunitary \((\hat{T}\hat{T}^\dagger = -\hat{1})\).

It is assumed that \(\hat{T}\) is a symmetry operation for closed isolated systems, that is

\[ [\hat{T}, \hat{H}] = 0 \]

However the invariance of the \(\hat{H}\) under time reversal does not produce conserved quantities, but may sometimes increase the degeneracy of the energy eigenstates. This occurs for example for a system composed of the odd number of spin 1/2 particles and is called the Kramers degeneracy.

5.6 More ”abstract” symmetries: isospin symmetry.

It is probably best to come back to this section once again after having studied the rotations, but nevertheless we include it here. Up to now we were discussing the symmetries of space and time, and will be further developing this topic in the chapter about rotations. In this section we will mention an example of another type of symmetry, more abstract in a sense, but on the other hand deduced directly from experiments and feeding into the theory. This short story allows to see why the study of symmetries can be very useful for example in elementary particle physics.

The story is about the proton and the neutron and the forces that bind them together in the nuclei. Nuclei are extremely small and extremely difficult to experimentally study, therefore for a long time the nature of their interaction (called strong interaction) was unclear. The observation of certain symmetries in the experiment allows to make some statements about the strong interaction and particularly about the Hamiltonian. [Ballantine p.228]. Protons and neutrons are distinguished by their electric charge, but when they are extremely close, it has been found experimentally that it does not matter much as the behaviour is dominated by the strong interaction. The experimental evidence includes:

- **the mirror nuclei.** There are many pairs of nuclei in which the number of protons in one is equal to the number of neutrons in the other and vice versa, for example the \(^3\)H (tritium), which contains one proton and two neutrons, and the halium isotope \(^3\)He, which contains two protons and one neutron. Other examples are \(^{19}\)F\(^{10}\), \(^{19}\)\(^{10}\)Ne\(^6\) and \(^{14}\)\(^6\)C\(^8\), \(^{14}\)\(^8\)O\(^6\)). It is found that in such pairs the structure of energy levels of the two nuclei are very similar, particularly after the differences in electrostatic potential energy are accounted for. If we assume that the Hamiltonian is the sum of several terms, one for each pair of particles in the nucleus, this suggests that the potential for two protons is the same as that for two neutrons. No conclusions can be drawn concerning the potential for a proton and a neutron, since the number of such pairs is the same in each of the two nuclei.

- **Scattering data** suggest that the n-p potential is the same as the n-n and p-p potentials. Scattering experiments determine the distribution of particles emerging from a collision, and are thus concerned with unbound states (whereas the states of a nucleus are bound states). It is found that the wave functions of these two states for two protons, after allowing for the electrostatic repulsion, are similar to those for a neutron and a proton, provides one compares states with the same spin and orbital angular momentum.

These facts can be accounted for by regarding the proton and the neutron as two states of a single particle, the **nucleon**, and supposing that the Hamiltonian of the strong interaction does not discriminate between these states. This means that the Hamiltonian \(\hat{H}_{\text{strong}}\)
commutes with the unitary operator $\hat{U}$ (describing the symmetry between the proton $|p\rangle$ and the neutron $|n\rangle$) defined by:

$$\hat{U}|p\rangle = \alpha|p\rangle + \beta|n\rangle$$

$$\hat{U}|n\rangle = \gamma|p\rangle + \delta|n\rangle$$

where the matrix of $\hat{U}$ in the $|p\rangle, |n\rangle$ basis:

$$\begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix}$$

is unitary. Now each $\hat{U}$ is associated with its unique set of $\alpha, \beta, \gamma, \delta$ that can take continuous complex values, (but only three of them are independent). Such transformations $\hat{U}$ form a continuous group of symmetries, identical with the group of rotations of a spin 1/2 system. Therefore

$$\hat{U} = \exp(i\hat{\mathbf{I}}\hat{\mathbf{n}}\phi)$$

where $\hat{I}_1, \hat{I}_2, \hat{I}_3$ operators act on the state space in the same way as the generators of rotation (the angular momentum operators of the spin 1/2) act on the spin space. The three operators $\hat{I}_1, \hat{I}_2, \hat{I}_3$ represented by the three matrices $\sigma_i/2$ ($\sigma_1$ are the Pauli matrices) are called the components of isospin. The proton and neutron are in eigenstates of the third component of isospin with eigenvalues of 1/2 and -1/2 respectively. It is easy to see that $\hat{I}_k$ represent the conserved observables. Namely $\hat{H}$ does not distinguish between the $|n\rangle, |p\rangle$ and their normalised mutually orthogonal combinations, and therefore

$$[\hat{H}, \hat{U}] = 0$$

$\hat{U}$ is not hermitean and can not be an observable, but we have:

$$[\hat{H}, \hat{I}_k] = 0$$

for hermitean $\hat{I}_k$ and this gives conserved quantity.

### 5.7 Types of symmetries

We would like to list here some symmetries important for quantum mechanics. We have for example:

- Symmetries of space - time forming continuous groups - translational symmetry of isolated systems in space with the associated conserved quantity - momentum (the group generator) $\hat{p}$.

- Rotational symmetry of isolated systems in space with the associated conserved quantity $\hat{L}$ or $\hat{J}$, orbital angular momentum or angular momentum.

- Symmetry with respect to Lorenz or Galilean transformations between the uniformly moving frame of reference.

- Other continuous symmetries
- isospin $\hat{I}_x, \hat{I}_y, \hat{I}_z$.

- Discrete symmetries
  - inversion (conserved parity $\hat{P}$)
  - exchange (permutation of identical particles) - conserved: symmetry of the wavefunction with respect to permutations - (fermions/bosons)

- Not exactly symmetries
  - time reversal

This table is not complete.

The importance of symmetries for quantum mechanics can not be underestimated. For many quantum systems there is a way to postulate the Hamiltonian through canonical quantisation, but in many cases there is no classical equivalent. It may happen that in those cases the experiments show that a certain quantity is conserved, i.e. is a constant of the motion. We may be able to reconstruct the symmetry group on the basis of this constant of the motion and make a judgement about the symmetry of the system. This may determine the form of the Hamiltonian.
Chapter 6

Simple harmonic oscillator

The simple harmonic oscillator is a quantum mechanical system of unprecedented importance.

The Hamiltonian function of a classical oscillator is of the form:

$$H = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}$$

where $\omega$ is the angular frequency of the oscillator related to the spring constant in the Hooke’s law

$$\omega = \sqrt{\frac{k}{m}}$$

The quantum Hamiltonian is:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2 \hat{x}^2}{2}.$$  

We will find the eigenstates and the eigenvalues of this Hamiltonian. It is possible to achieve that by writing the Schrödinger equation in position representation. This is a second order differential equation and not too difficult one. Below we adopt another approach which is very important in other areas of physics. We define two convenient operators called the creation operator $\hat{a}^\dagger$ and annihilation operator $\hat{a}$:

$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left( \hat{x} - i \frac{\hat{p}}{m\omega} \right),$$

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}} \left( \hat{x} + i \frac{\hat{p}}{m\omega} \right).$$

Note that these two operators are not hermitean and they do not represent any physical quantities. We establish their commutation rule:

$$[\hat{a}, \hat{a}^\dagger] = \frac{1}{2\hbar} (-i[\hat{x}, \hat{p}] + i[\hat{p}, \hat{x}]) = \hat{1}$$

$$[\hat{a}, \hat{a}^\dagger] = \hat{1}$$
This unity operator is often simply written as a number, to be understood just as a shorthand notation.

\[ [\hat{a}, \hat{a}^\dagger] = 1 \]

Now we define the operator \( \hat{N} \) that is called the **number operator**:

\[ \hat{N} = \hat{a}^\dagger \hat{a} \]

It turns out that this operator is closely related with the Hamiltonian:

\[
\hat{a}^\dagger \hat{a} = \frac{m \omega}{2 \hbar} \left( \hat{x}^2 + \frac{\hat{p}^2}{m^2 \omega^2} \right) + \frac{i}{2 \hbar} [\hat{x}, \hat{p}] = \frac{\hat{H}}{\hbar \omega} - \frac{1}{2}
\]

Therefore

\[
\hat{H} = \hbar \omega (\hat{a}^\dagger \hat{a} + \frac{1}{2}) = \hbar \omega (\hat{N} + \frac{1}{2}).
\]

Obviously \( \hat{N} \) can be diagonalised simultaneously with \( \hat{H} \) by the same set of kets. Let us denote the eigenket of \( \hat{N} \) by its value \( n \), so

\[ \hat{N}|n\rangle = n|n\rangle \]

Of course

\[ \hat{H}|n\rangle = (n + \frac{1}{2}) \hbar \omega |n\rangle \]

The energy eigenvalues are:

\[ E_n = (n + \frac{1}{2}) \hbar \omega \]

We still do not know though how much is \( n \). Now we will work that out. First we need two simple facts:

**Fact 1:**

\[
[\hat{N}, \hat{a}] = [\hat{a}^\dagger \hat{a}, \hat{a}] = \hat{a}^\dagger \hat{a} \hat{a} - \hat{a} \hat{a}^\dagger \hat{a} = [\hat{a}^\dagger, \hat{a}] \hat{a} = -\hat{a},
\]

that gives

\[ \hat{N} \hat{a} = \hat{a} \hat{N} - \hat{a} \]

**Fact 2:**

\[ [\hat{N}, \hat{a}^\dagger] = \hat{a}^\dagger, \]

in other words

\[ \hat{N} \hat{a}^\dagger = \hat{a}^\dagger \hat{N} + \hat{a}^\dagger \]
Now we evaluate
\[ \hat{N} \hat{a}^\dagger |n\rangle = (\hat{N} \hat{a}^\dagger + \hat{a}^\dagger \hat{N}) |n\rangle = (n + 1) \hat{a}^\dagger |n\rangle \]
and
\[ \hat{N} \hat{a} |n\rangle = (\hat{N} \hat{a} + \hat{a} \hat{N}) |n\rangle = (n - 1) \hat{a} |n\rangle \]
This shows that \( \hat{a}^\dagger |n\rangle \) (and \( \hat{a} |n\rangle \)) is also an eigenket of \( \hat{N} \) with the eigenvalue increased (decreased) by one. Hence \( \hat{a} |n\rangle \) and \( |n - 1\rangle \) are the same up to a multiplicative constant \( C \) to be determined from the normalisation conditions.
\[ \hat{a} |n\rangle = C |n - 1\rangle \]
\[ \langle n | \hat{a}^\dagger \hat{a} | n \rangle = |C|^2 \]
\[ n = |C|^2 \]
We take \( C \) to be real and positive:
\[ \hat{a} |n\rangle = \sqrt{n} |n - 1\rangle \tag{*} \]
Similarly
\[ \hat{a}^\dagger |n\rangle = \sqrt{n + 1} |n + 1\rangle \]
We keep on applying the annihilation operator \( \hat{a} \) to \( (*) \):
\[ \hat{a}^2 |n\rangle = \sqrt{n(n - 1)} |n - 2\rangle \]
\[ \hat{a}^3 |n\rangle = \sqrt{n(n - 1)(n - 2)} |n - 3\rangle \]
etc. Note that \( n = |C|^2 \geq 0 \). The following argument is quite subtle. On the one hand the above sequence can be continued to infinity. On the other hand the square root in front can not possibly become imaginary, because then the state \( \hat{a}^m |n\rangle \) for certain \( m \) would have a negative norm. The only way for these two conditions to be satisfied is for \( n \) to be a positive integer. Then we would have:
\[ \hat{a}^n |n\rangle = \sqrt{n(n - 1) \ldots (n - (n - 1))} |0\rangle \]
\[ \hat{a}^{(n + 1)} |n\rangle = 0 | - 1\rangle = |\varnothing\rangle \]
and of course for any further power of \( \hat{a} \) we would get
\[ \hat{a}^{n+m} |n\rangle = \hat{a}^m |\varnothing\rangle = |\varnothing\rangle \]
where \( |\varnothing\rangle \) denotes zero from the vector space and \( |0\rangle \) denotes the eigenstate of \( \hat{H} \) with \( n = 0 \). This state is sometimes called the vacuum state.
Applying the annihilation operator to $|n\rangle$ is like descending the stairs from the n-th step. Each application is like descending one step lower, and we can do that until we reach the ground. Then we can still be stepping down, but will not be going any further. The repeated application of the creation operator is like stepping up the infinite stairs.

Summarising this part we determined that allowed $n$ values are nonnegative integers. The states of the harmonic oscillator are characterised by their energies:

$$E_0 = \frac{1}{2} \hbar \omega$$

$$E_n = \hbar \omega (n + \frac{1}{2})$$

$$\hat{a}|0\rangle = |\varnothing\rangle$$

$$|1\rangle = \hat{a}^\dagger|0\rangle$$

$$|2\rangle = \frac{\hat{a}^\dagger}{\sqrt{2}}|1\rangle = \frac{(\hat{a}^\dagger)^2}{\sqrt{2}}|0\rangle$$

$$|3\rangle = \frac{(\hat{a}^\dagger)^3}{\sqrt{3!}}|0\rangle$$

$$|n\rangle = \left[ \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}} \right]|0\rangle$$

It is quite easy to obtain the energy eigenfunctions in position representation by solving (in position representation) the equation:

$$\hat{a}|0\rangle = |\varnothing\rangle$$

and then apply the creation operator in position representation to get the wavefunctions of the higher energy states. The approach presented for the quantum harmonic oscillator has found a range of applications. Below we present one of the more surprising ones.

**Example 6.1** A spinless particle of the charge $e$ and mass $m$ is moving in a constant magnetic field $B$ parallel to the $z$ axis. Find the energy levels of this particle.

Solution: Few comments before we start the proper solution. Classically this particle would be moving along a helix or a circle with the radius of

$$R = \frac{mv}{eB}$$

To solve the problem we need to know the scalar $\Phi$ and the vector $\mathbf{A}$ potential of the electromagnetic field. They are not unambiguous and can be modified without changes to
electric and magnetic field. This modification is called the **gauge transformation** and consists of:

\[ \Phi \rightarrow \Phi + \text{const} \]

\[ \mathbf{A} \rightarrow \mathbf{A} + \Delta \mathbf{A} \]

where \( \Lambda \) is the function of position. These modified potentials put into the Maxwell equations

\[ \mathbf{E} = -\nabla \Phi - \frac{1}{c} \frac{\partial}{\partial t} \mathbf{A}; \]

\[ \mathbf{B} = \nabla \times \mathbf{A} \]

give the same fields as the original ones, this is because of the mathematical identity

\[ \nabla \times (\nabla Q) = 0 \]

We have the freedom to choose the gauge we like, let us choose the following gauge for \( \mathbf{B} \) parallel to \( z \) (called Landau gauge):

\[
\begin{pmatrix}
0 \\
0 \\
B
\end{pmatrix},
\mathbf{A} = \begin{pmatrix}
-yB \\
0 \\
0
\end{pmatrix}
\]

The Hamiltonian for a particle with electric charge \( e \) in the electromagnetic field is:

\[ \hat{H} = \frac{1}{2m} \left( \hat{p} - \frac{eA}{c} \right)^2 + e\Phi, \]

where

\[
\mathbf{p} = \begin{pmatrix}
\hat{p}_x \\
\hat{p}_y \\
\hat{p}_z
\end{pmatrix},
\]

\( \Phi \) and \( \mathbf{A} \) are functions of position operator and they are operators themselves. Now we introduce new operators \( \hat{\pi}_i \) that will replace the operators \( \hat{p}_i \) as it is apparent from the following relationship

\[
\langle \frac{d\hat{x}_i}{dt} \rangle = \frac{1}{i\hbar} \langle [\hat{x}_i, \hat{H}] \rangle = \frac{1}{m} \langle \hat{p}_i - \frac{e\hat{A}_i}{c} \rangle
\]

Therefore in presence of electromagnetic field the operator \( \hat{\pi}_i = \hat{p}_i - \frac{e\hat{A}_i}{c} \) plays the same role as the operator \( \hat{p} \) without the field. Now we will find the commutation rules for these operators \( \hat{\pi}_i \).

\[
[\hat{\pi}_x, \hat{\pi}_y] = [\hat{p}_x + \frac{e\hat{B}y}{c}, \hat{p}_y] = \frac{e}{c} B \hat{y}, \hat{p}_y] = \frac{e}{c} B \hat{i}\hbar
\]

\[
[\hat{\pi}_z, \hat{\pi}_x] = 0
\]

\[
[\hat{\pi}_y, \hat{\pi}_z] = 0
\]
At the same time $\pi_y = \hat{p}_y$, $\pi_z = \hat{p}_z$. We can now express the Hamiltonian using these new operators $\pi_i$.

\[
\hat{H} = \frac{1}{2m} (\hat{\pi}_x^2 + \hat{\pi}_y^2 + \hat{\pi}_z^2) = \hat{H}_\perp + \hat{H}_\parallel
\]

where

\[
\hat{H}_\perp = \frac{1}{2m} (\hat{\pi}_x^2 + \hat{\pi}_y^2), \quad \hat{H}_\parallel = \frac{1}{2m} \hat{\pi}_z^2
\]

Of course

\[
[\hat{H}_\perp, \hat{H}_\parallel] = 0,
\]

therefore there exists a common set of eigenkets of both $\hat{H}_\perp$ and $\hat{H}_\parallel$:

\[
\hat{H}_\perp | h_\perp, h_\parallel \rangle = h_\perp | h_\perp, h_\parallel \rangle
\]

\[
\hat{H}_\parallel | h_\perp, h_\parallel \rangle = h_\parallel | h_\perp, h_\parallel \rangle.
\]

They are also eigenstates of the Hamiltonian:

\[
\hat{H} | h_\perp, h_\parallel \rangle = \hat{H}_\perp | h_\perp, h_\parallel \rangle + \hat{H}_\parallel | h_\perp, h_\parallel \rangle = (h_\perp + h_\parallel) | h_\perp, h_\parallel \rangle
\]

We will work out these eigenvalues $h_\perp$ and $h_\parallel$ separately. First note that:

\[
\hat{H}_\parallel = \frac{1}{2m} \hat{p}_z^2,
\]

Therefore the eigenvalues of $\hat{p}_z$ are also eigenvalues of $\hat{H}_\parallel$, and the eigenvalues of $\hat{H}_\parallel$ are simply $\frac{1}{2m} \hat{p}_z^2$. Now we will evaluate the eigenvalues of $\hat{H}_\perp$:

\[
\hat{H} = \frac{\hat{\pi}_x^2 + \hat{\pi}_y^2}{2m},
\]

We introduce two new operators $\hat{p}$ and $\hat{q}$. They are based on mostly the new momentum $\pi$ but one of them will algebraically play a role of the artificial ”position”.

\[
\hat{q} = \hat{\pi}_x \sqrt{\frac{c}{eB}},
\]

\[
\hat{p} = \hat{\pi}_y \sqrt{\frac{c}{eB}}.
\]

Now we will find their commutation rules:

\[
[\hat{q}, \hat{p}] = \frac{c}{eB} [\hat{\pi}_x, \hat{\pi}_y] = i\hbar
\]

Note that this commutation rule is identical as in the case of true position operator $\hat{x}$ and a true momentum operator $\hat{p}$.
Now we express the Hamiltonian in terms of $\hat{q}, \hat{p}$.

$$\hat{H}_\perp = \frac{eB}{c} \left( \frac{\hat{p}^2}{2m} + \frac{\hat{q}^2}{2m} \right) = \frac{1}{2m} \frac{eB}{c} (\hat{p}^2 + \hat{q}^2).$$

Now the $\hat{H}_\perp$ starts to resemble formally the Hamiltonian of the quantum harmonic oscillator with $\hat{q}$ playing the role of position operator $\hat{x}$. So the previously developed method of creation and annihilation operators can be applied. Let us define then, in full analogy to the case of a quantum harmonic oscillator the creation $\hat{a}^\dagger$ and annihilation operator $\hat{a}$ and the number operator. We postulate that:

$$\hat{a}^\dagger = \frac{1}{\sqrt{2\hbar}} (\hat{q} - i\hat{p}),$$

$$\hat{a} = \frac{1}{\sqrt{2\hbar}} (\hat{q} + i\hat{p}).$$

We check if their commutation rule is the same as in the case of an ordinary quantum oscillator:

$$[\hat{a}, \hat{a}^\dagger] = \frac{1}{2\hbar} [\hat{q} + i\hat{p}, \hat{q} - i\hat{p}] = \frac{1}{2\hbar} ([\hat{p}\hat{q}, \hat{q}] - [\hat{q}, -i\hat{p}])$$

$$= \frac{1}{2\hbar} (i\hat{p}\hat{q} - i\hat{q}\hat{p} - i\hat{q}\hat{p} + i\hat{q}\hat{p}) = -\frac{2i}{2\hbar} [\hat{q}, \hat{p}] = -\frac{2i}{2\hbar} \hbar = 1$$

Now

$$\hat{a}^\dagger \hat{a} = \frac{1}{2\hbar} (\hat{q} - i\hat{p})(\hat{q} + i\hat{p}) = \frac{1}{2\hbar} (\hat{q}^2 + \hat{p}^2 + i(\hat{q}\hat{p} - \hat{p}\hat{q})) = \frac{1}{2\hbar} (\hat{q}^2 + \hat{p}^2 - \hbar)$$

and then

$$\hat{a}^\dagger \hat{a} + \frac{1}{2} = \frac{1}{2\hbar} (\hat{q}^2 + \hat{p}^2)$$

Using this we have:

$$\hat{H}_\perp = \frac{\hbar eB}{mc} (\hat{a}^\dagger \hat{a} + \frac{1}{2})$$

The quantity $\frac{eB}{mc} = \omega_c$ is the cyclotron frequency. As the $\hat{a}^\dagger \hat{a}$ is the number operator its eigenvalues are non-negative integers and the eigenvalues of the $\hat{H}_\perp$ are $\hbar \omega_c (n + 1/2)$. The index $n$ denotes the consecutive Landau levels. The eigenvalues of the entire Hamiltonian $\hat{H}$ are

$$\hbar \omega_c (n + 1/2) + \frac{p_z^2}{2m}.$$

The motion of electrons is free along the $z$ axis but it is quantised in the $x - y$ plane. In some physical systems the electrons can be confined in a two-dimensional sheet by being placed in a very narrow potential well $V(z)$ with very high barriers. In such circumstances the electrons are free to move in the $x - y$ plane, but their movement is quantised in the $z$ direction, for example

$$\Psi(z) \approx \cos \left( \frac{2\pi z}{a} \right).$$

If the magnetic field is applied perpendicularly to this plane then the electron energy is completely quantised. This is illustrated in the Fig 6.1.
Figure 6.1: The full quantization of motion for two-dimensional electrons in magnetic field
Chapter 7

Angular momentum in quantum mechanics

7.1 Rotational symmetry

7.1.1 Operation of rotation

The operation of rotation performed on a system is presented in the Fig 7.1 and 7.2. Similarly as in the case of translations the rotation by the angle $\phi$ around a given axis is equivalent to rotating the reference frame by the angle $-\phi$ around the same axis. Rotation is fully characterised when both the angle $\phi$ and the axis is specified, it is accepted to combine this information in form of a vector $\vec{\phi}$.

7.1.2 Rotational invariance for classical systems - conservation of classical angular momentum

Let us consider an example similar to the one discussed in case of translational invariance, that is the classical system of two point mases interacting via a central potential. Its Hamiltonian function is given by:

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(|\mathbf{r}_1 - \mathbf{r}_2|).$$

Let us consider rotations by a small angle $d\phi$ around the axis of rotation pasing through the center of the system of coordinates. After this rotation the new values of position

Figure 7.1: The system is undergoing a rotation
Figure 7.2: This rotation is equivalent to a reverse rotation of the reference frame.

Figure 7.3: The change of a position vector upon an infinitesimal rotation

vectors are:

\[ \mathbf{r}'_1 = \mathbf{r}_1 + d\vec{\phi} \times \mathbf{r}_1 \]

\[ \mathbf{r}'_2 = \mathbf{r}_2 + d\vec{\phi} \times \mathbf{r}_2 \]

as in the Fig 7.3.

Note that the length of the vector does not change:

\[ |\mathbf{r}'_1| = |\mathbf{r}_1|, \]

\[ |\mathbf{r}'_1 - \mathbf{r}'_2| = |\mathbf{r}_1 - \mathbf{r}_2 + d\vec{\phi} \times (\mathbf{r}_1 - \mathbf{r}_2)| = |\mathbf{r}_1 - \mathbf{r}_2|, \]

therefore

\[ V(|\mathbf{r}'_1 - \mathbf{r}'_2|) = V(|\mathbf{r}_1 - \mathbf{r}_2|). \]

However, somewhat unexpectedly the velocities change!

\[ \mathbf{v} = \frac{\mathbf{r}(t + dt) - \mathbf{r}(t)}{dt}, \]

\[ \mathbf{v}' = \frac{\mathbf{r}'(t + dt) - \mathbf{r}'(t)}{dt} \]

\[ = \frac{\mathbf{r}(t + dt) + d\vec{\phi} \times \mathbf{r}(t + dt)}{dt} - \frac{\mathbf{r}(t) + d\vec{\phi} \times \mathbf{r}(t)}{dt} = \mathbf{v} + d\vec{\phi} \times \mathbf{v}. \]

So the velocity vector is different, but fortunately

\[ |\mathbf{v}'| = |\mathbf{v}|, \]
Figure 7.4: The two point masses interacting via central forces

Therefore

\[ p_1' = p_1, \quad \text{and} \quad p_2' = p_2. \]

As a consequence the Hamiltonian \( H' \) after rotation is equal to the Hamiltonian before rotation.

\[ H' = H. \]

Now we will show that the classical angular momentum is conserved. No external forces are acting in this system, only internal ones and these are shown in the Fig 7.4 as \( f_{12} \) and \( f_{21} \).

The angular momentum is:

\[ L = r_1 \times m_1 v_1 + r_2 \times m_2 v_2, \]

and its time derivative:

\[ \frac{dL}{dt} = v_1 \times m_1 v_1 + v_2 \times m_2 v_2 + r_1 \times m_1 a_1 + r_2 \times m_2 a_2. \]

Now

\[ m_1 a_1 = f_{12}, \quad m_2 a_2 = f_{21}. \]

\[ f_{12} = -\nabla V \text{ with respect to } r_1, \]

\[ f_{21} = -\nabla V \text{ with respect to } r_2 \]

\[ f_{12} = -f_{21}. \]

Then

\[ \frac{dL}{dt} = r_1 \times f_{12} + r_2 \times f_{21} \]

As it is shown in the Fig 7.5 the first vector product is equal to the length of the OA interval and the value of force \( f_{12} \), while the second vector product is equal to minus the length of OA times the value of \( f_{12} \). This gives:

\[ \frac{dL}{dt} = 0 \]

that is the conservation of the classical angular momentum.
7.1.3 Rotation for quantum systems with a classical analogue

We have learned how do the vectors change upon rotation:

$$r' = r + d\vec{\phi} \times r,$$

which can be denoted in short

$$\hat{R}(r) = r'$$

Now we analyse what happens to kets when the system is rotated. We denote the ket in a rotated system as $|\Psi\rangle_R$ and it should be somehow related to the original ket $|\Psi\rangle$:

$$|\Psi\rangle_R = \hat{D}_R(d\vec{\phi}) |\Psi\rangle.$$

It requires faith at this stage to accept that the relationship is through a linear operator, but we will prove this later.

A short comment why the ket should be affected by rotation at all: it is easy to see it in a position representation:

$$\Psi(\hat{R}^{-1}r) = \hat{D}_R(d\vec{\phi}) \Psi(r)$$

$$\Psi(\hat{R}^{-1}r) = \Psi(r - d\vec{\phi} \times r) \approx \Psi(r) - d\vec{\phi} \times r \cdot \nabla \Psi(r)$$

The last formula follows from the Taylor expansion and that $\hat{p}$ can be replaced by $-i\hbar \nabla$. Then we get:

$$\Psi(r) - d\vec{\phi} \times r \cdot \nabla \Psi(r) = \Psi(r) - \frac{i}{\hbar} (d\vec{\phi} \times r) \cdot \hat{p} \Psi(r)$$

Now we use the identity:

$$(a \times b) \cdot c = a \cdot (b \times c)$$

and get that

$$\hat{D}_R(d\vec{\phi}) = \hat{1} - \frac{i}{\hbar} d\vec{\phi} \cdot \hat{L}.$$
7.1.4 The finite rotations

First we note a certain fact from everyday geometry: that rotations about different axes may not commute. This is illustrated in the Fig 7.6 that shows a brick being rotated about the $z$ axis and afterwards about the $x$ axis (top row), This means it is subject to $\hat{R}_x \cdot \hat{R}_z$. The bottom row shows the same brick being rotated about $x$ first, and about $z$ later, that means it is undergoing $\hat{R}_z \cdot \hat{R}_x$. As we can see in the Fig 7.6 the final results are different: the brick ends up in different position in the top row and in the bottom row, although it started the same. This means that finite rotations do not commute:

$$[\hat{R}_x, \hat{R}_z] \neq 0$$

We might have expected something of that nature, the other operators that are associated with rotations, namely $\hat{L}_i$ also do not commute. We can easily find their commutation rule by substituting the explicit form $\hat{L} = \hat{r} \times \hat{p}$. We get:

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

where

$$\epsilon_{ijk} = 1 \text{ for } ijk = xyz, yzx, zxy$$

$$\epsilon_{ijk} = -1 \text{ otherwise}.$$  

Now we will evaluate the explicit form of the operator $\hat{D}(\Theta)$ of the finite rotation by the angle $\Theta$ around the $z$ axis. As in the case of infinitesimal translations the infinitesimal rotations can be composed together resulting in rotations. If very many of such infinitesimal rotations are composed together the result is a finite rotation. This intuitive reasoning can be formalised as follows:
We would like to determine the operator \( \hat{D}(\Theta) \) on the basis of \( \hat{D}_R(d\phi) \). where \( d\phi \) is a very small angle. Let us denote

\[
n = \frac{\Theta}{d\phi}
\]

\( \hat{D}(\Theta) \) is composed of \( n \) consecutive infinitesimal rotations:

\[
\hat{D}(\Theta) = \left( \hat{1} - \frac{i}{\hbar} d\phi \hat{L}_z \right)
\]

Now we evaluate its explicit form. Let \( |\lambda\rangle \) be the eigenstate of \( \hat{L}_z \). We have:

\[
\left( \hat{1} - \frac{i}{\hbar} d\phi \hat{L}_z \right)^n = \sum_{\lambda} \left( 1 - \frac{i}{\hbar} d\phi \lambda \right)^n |\lambda\rangle \langle \lambda|
\]

where as we remember \( |\lambda\rangle \langle \lambda| \) is the projection operator onto the eigenstate \( |\lambda\rangle \). The spectral theorem allows us now to work using numbers.

\[
\left( 1 - \frac{i}{\hbar} d\phi \lambda \right)^n = \left( 1 - \frac{i}{\hbar} \frac{\Theta}{n} \lambda \right)^n
\]

We will now prove that:

\[
\lim_{n \to \infty} \left( 1 - \frac{i}{\hbar} \frac{\Theta}{n} \lambda \right)^n = e^{-i \frac{\Theta}{\hbar} \lambda}.
\]

Proof:

\[
\left( 1 - \frac{i}{\hbar} \frac{\Theta}{n} \lambda \right)^n = \exp \left( n \ln \left( 1 - \frac{i}{\hbar} \frac{\Theta}{n} \lambda \right) \right),
\]

Now

\[
\ln(1 - x) \approx -x + \ldots
\]

This gives

\[
\left( 1 - \frac{i}{\hbar} \frac{\Theta}{n} \lambda \right)^n \approx \exp \left( n \left( \frac{-i}{\hbar} \frac{\Theta}{n} \lambda \right) + n \left( \frac{-i}{\hbar} \frac{\Theta}{n} \lambda \right)^2 + \ldots \right)
\]

\[
\approx_{n \to \infty} \exp \left( \frac{-i}{\hbar} \Theta \lambda \right).
\]

So

\[
\lim_{n \to \infty} \left( \hat{1} - \frac{i}{\hbar} d\phi \hat{L}_z \right)^n = \sum_{\lambda} \lim_{n \to \infty} \left( 1 - \frac{i}{\hbar} d\phi \lambda \right)^n |\lambda\rangle \langle \lambda|
\]

\[
= \sum_{\lambda} \exp \left( \frac{-i}{\hbar} \Theta \lambda \right) |\lambda\rangle \langle \lambda| = \exp \left( \frac{-i}{\hbar} \Theta \hat{L}_z \right).
\]

Therefore

\[
\hat{D}(\Theta \text{ about } z) = \exp \left( \frac{-i}{\hbar} \Theta \hat{L}_z \right).
\]
7.1.5 Rotation for quantum systems with partial or no classical analogue

The approach presented in previous sections is applicable for the systems with a classical analogue. Other systems though such as for example the spin 1/2 system have states that are also affected by the rotations. There is a need for a more general approach to rotation that would not hinge on the operator $\hat{L}$.

In analogy to the rotations of wavefunctions we define the three operators $\hat{J}_x, \hat{J}_y, \hat{J}_z$ such that they are generators of the infinitesimal rotation in the ket space:

$$\hat{D}(d\phi) = 1 - \frac{i\hbar}{\hbar} (\hat{J}_x n_x + \hat{J}_y n_y + \hat{J}_z n_z),$$

where

$$\mathbf{n} = \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} = \frac{d\vec{\phi}}{|d\phi|}.$$

It is also postulated that the three new operators have identical commutation properties as $\hat{L}_i$-s.

$$[\hat{J}_i, \hat{J}_j] = i\hbar \epsilon_{ijk} \hat{J}_k$$

The operators $\hat{J}_i$ ($i = x, y, z$) are called the angular momentum operators, while the operators $\hat{L}_i$ are called the orbital angular momentum operators.

$\hat{J}_i$-s are more general than $\hat{L}_i$-s. $\hat{L}_i$-s are more specific examples of $\hat{J}_i$-s, when the spin is zero. Another example of the $\hat{J}_i$-s are the three spin operators $\hat{S}_i$, ($i = x, y, z$). These operators rotate spin states in two-dimensional spin space.

In order to gain some familiarity how to use these new operators and how to accomplish these rotations in practice we will examine the following example.

**Example 7.1** The three operators

$$\hat{S}_x = \frac{\hbar}{2} (|S^+_z \rangle \langle S^-_z| + |S^-_z \rangle \langle S^+_z|)$$

$$\hat{S}_y = \frac{i\hbar}{2} (-|S^+_z \rangle \langle S^-_z| + |S^-_z \rangle \langle S^+_z|)$$

$$\hat{S}_z = \frac{\hbar}{2} (|S^+_z \rangle \langle S^+_z| - |S^-_z \rangle \langle S^-_z|)$$

after being divided by $\hbar$ obey the same commutation rules as the operators $\hat{J}_i$.

Let $\hat{R}(\vec{\phi})$ be a rotation by a finite angle $\phi$ about the $z$ axis. Evaluate:

- the $\hat{D}_R$ - the rotation operator in the spin space.
- the rotated ket $\hat{D}_R |\alpha\rangle$ in two cases: for $|\alpha\rangle = |S^+_z\rangle$ and for $|\alpha\rangle = |S^-_z\rangle$.
- the effect of this rotation on the expectation value of $\hat{S}_x$. 
Solution: We calculate the rotation operator:

\[
\hat{D}_R = \exp \left( -\frac{i\hat{S}_z \phi}{\hbar} \right).
\]

\[
\hat{D}_R = \exp \left( -\frac{i\phi}{2} \right) |S_z^+\rangle \langle S_z^+| + \exp \left( \frac{i\phi}{2} \right) |S_z^-\rangle \langle S_z^-|
\]

Now we calculate the rotated kets:

\[
|\alpha\rangle = |S_z^+\rangle
\]

\[
|\alpha\rangle_R = \hat{D}_R |\alpha\rangle = \exp \left( -\frac{i\phi}{2} \right) |S_z^+\rangle
\]

\[
|\alpha\rangle = |S_z^+\rangle = \frac{1}{\sqrt{2}} |S_z^+\rangle + \frac{1}{\sqrt{2}} |S_z^-\rangle
\]

\[
|\alpha\rangle_R = \frac{1}{\sqrt{2}} \exp \left( -\frac{i\phi}{2} \right) |S_z^+\rangle + \frac{1}{\sqrt{2}} \exp \left( \frac{i\phi}{2} \right) |S_z^-\rangle
\]

Now we calculate the expectation value of the spin operator \(\hat{S}_x\) in an arbitrary state \(|\alpha\rangle\) (before rotation) and in \(|\alpha\rangle_R\) - after rotation.

\[
|\alpha\rangle_R = \exp \left( -\frac{i\hat{S}_z \phi}{\hbar} \right) |\alpha\rangle
\]

\[
\langle \alpha|R \hat{S}_x|\alpha\rangle_R = \langle \alpha| \exp \left( \frac{i\hat{S}_z \phi}{\hbar} \right) \hat{S}_x \exp \left( -\frac{i\hat{S}_z \phi}{\hbar} \right) |\alpha\rangle.
\]

After rotation the \(\langle \alpha|R \hat{S}_x|\alpha\rangle\) becomes

\[
\langle \alpha|R \hat{S}_x|\alpha\rangle_R = \langle \alpha| \exp \left( \frac{i\hat{S}_z \phi}{\hbar} \right) \hat{S}_x \exp \left( -\frac{i\hat{S}_z \phi}{\hbar} \right) |\alpha\rangle.
\]

Now

\[
\hat{S}_x = \frac{\hbar}{2} \left( |S_z^+\rangle \langle S_z^-| + |S_z^-\rangle \langle S_z^+| \right),
\]

\[
\exp \left( \frac{i\hat{S}_z \phi}{\hbar} \right) \hat{S}_x \exp \left( -\frac{i\hat{S}_z \phi}{\hbar} \right) = \frac{\hbar}{2} \left( \exp \left( \frac{i\phi}{2} \right) |S_z^+\rangle \langle S_z^+| + \exp \left( -\frac{i\phi}{2} \right) |S_z^-\rangle \langle S_z^-| \right)
\]

\[
\times \left( |S_z^+\rangle \langle S_z^-| + |S_z^-\rangle \langle S_z^+| \right) \times \left( \exp \left( -\frac{i\phi}{2} \right) |S_z^+\rangle \langle S_z^+| + \exp \left( \frac{i\phi}{2} \right) |S_z^-\rangle \langle S_z^-| \right)
\]

\[
= \frac{\hbar}{2} \left( \exp \left( \frac{i\phi}{2} \right) |S_z^+\rangle \langle S_z^+| + \exp \left( -\frac{i\phi}{2} \right) |S_z^-\rangle \langle S_z^+| \right)
\]
\[
\frac{\hbar}{2} \left\{ (|S_x^+\rangle\langle S_x^-| + |S_x^-\rangle\langle S_x^+|) \cos(\phi) + i \left( |S_x^+\rangle\langle S_x^-| - |S_x^-\rangle\langle S_x^+| \right) \sin(\phi) \right\} \\
= \hat{S}_x \cos(\phi) - \hat{S}_y \sin(\phi).
\]

In summary the expectation value of \( \hat{S}_x \) before rotation is:

\[
\langle \hat{S}_x \rangle = \langle \alpha | \hat{S}_x | \alpha \rangle,
\]

and after the rotation about \( z \) by the angle \( \phi \) it becomes:

\[
\langle \alpha | R \hat{S}_x | \alpha \rangle_R = \langle \alpha | \hat{S}_x | \alpha \rangle \cos(\phi) - \langle \alpha | \hat{S}_y | \alpha \rangle \sin(\phi)
\]

that is

\[
\langle \hat{S}_x \rangle \rightarrow \langle \hat{S}_x \rangle \cos(\phi) - \langle \hat{S}_y \rangle \sin(\phi) = \langle \hat{S}_x \rangle',
\]

Similarly it can be shown that:

\[
\langle \hat{S}_y \rangle \rightarrow \langle \hat{S}_y \rangle \cos(\phi) + \langle \hat{S}_x \rangle \sin(\phi) = \langle \hat{S}_y \rangle'.
\]

\( \langle \hat{S}_z \rangle \) does not change, \( \langle \hat{S}_z \rangle \rightarrow \langle \hat{S}_z \rangle' \).

Now we will demonstrate that these expressions for the new expectation values have a very simple geometrical interpretation. Namely if we consider the three numbers \( \langle \hat{S}_x \rangle, \langle \hat{S}_y \rangle, \langle \hat{S}_z \rangle \) to be the coordinates of a three dimensional vector:

\[
s = \begin{pmatrix}
\langle \hat{S}_x \rangle \\
\langle \hat{S}_y \rangle \\
\langle \hat{S}_z \rangle
\end{pmatrix}
\]

then the three new numbers \( \langle \hat{S}_x \rangle', \langle \hat{S}_y \rangle', \langle \hat{S}_z \rangle' \) are the coordinates of the vector \( s' \) which is equal to \( s \) rotated by \( \phi \) about \( z \). This is quite an important statement as it allows to identify a "proper" three dimensional vector that is associated with spin. To prove it we check that \( s \) and \( s' \) have the property of ordinary vectors \( a = \begin{pmatrix} a_x \\ a_y \end{pmatrix}, \ a' = \begin{pmatrix} a'_x \\ a'_y \end{pmatrix} \) shown in the Fig 7.7, derived from two equivalent ways of calculating the scalar (dot) product, namely

\[
\begin{pmatrix} a_x & a_y \end{pmatrix} \begin{pmatrix} a'_x \\ a'_y \end{pmatrix} = \sqrt{a_x^2 + a_y^2} \sqrt{a'_x^2 + a'_y^2} \cos(\alpha)
\]

This means that the coordinates of vectors have to obey special transformation rules upon rotation, that is the new coordinates in a rotated system are completely determined by the old coordinates and the angle and the axis of rotation. We will check now that the coordinates of \( s \) and of \( s' \) obey this relationship.

\[
s \cdot s' = \langle \hat{S}_x \rangle \left( \langle \hat{S}_x \rangle \cos(\phi) - \langle \hat{S}_y \rangle \sin(\phi) \right) + \langle \hat{S}_y \rangle \left( \langle \hat{S}_y \rangle \cos(\phi) + \langle \hat{S}_x \rangle \sin(\phi) \right)
\]

\[
= \left( \langle \hat{S}_x \rangle^2 + \langle \hat{S}_y \rangle^2 \right) \cos(\phi)
\]

The length of \( s' \) is the same as the length of \( s \), therefore we see that \( s' \) is indeed equal to the rotated \( s \).
7.1.6 The Pauli spin matrices

There is no new physics in this section, only some terminology. When we take the three operators:

\[ \frac{2}{\hbar} \hat{S}_x, \frac{2}{\hbar} \hat{S}_y, \frac{2}{\hbar} \hat{S}_z \]

and write their matrices in the \(|S^+_z\), \(|S^-_z\) basis we get the three matrices that are called **Pauli spin matrices** \(\sigma_x, \sigma_y, \sigma_z\):

\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}
\]

\[
\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}
\]

\[
\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\]

They are used sometimes for the rotation of kets in the spin space but this is exactly equivalent to using the spin operators.

7.1.7 More about the \(\hat{J}_i\) operators: \(\hat{J}^2\), the eigenvalues of \(\hat{J}^2\) and \(\hat{J}_z\)

We learned that kets are rotated by means of the operator \(\exp\left(-i \Theta \hat{J}_n / \hbar\right)\), where the three operators \(\hat{J}_i\) have certain commutation properties. It turns out that these commutation properties enable us to get a very precise picture of these operators, including their eigenvalues. In this section we demonstrate how this can be achieved.

Let us define the operator \(\hat{J}^2 = \hat{J}_x \cdot \hat{J}_x + \hat{J}_y \cdot \hat{J}_y + \hat{J}_z \cdot \hat{J}_z\). We show the following commutation rule:

\[ [\hat{J}^2, \hat{J}_k] = 0, \ k = x, y, z. \]

Proof:

We will conduct the calculation for \(z\) only.

\[ [\hat{J}^2, \hat{J}_z] = 0 \]
Now we introduce the ladder operators $\hat{J}_+$ and $\hat{J}_-$ common eigenkets by the eigenket of $\hat{J}_z$ obvious.

This means that if $|a, b\rangle$ is the eigenket of $\hat{J}_z$ with the eigenvalue $b$ then the $\hat{J}_\pm|a, b\rangle$ is also the eigenket of $\hat{J}_z$ but with the eigenvalue increased (decreased) by $\hbar$. At the same time if $\hat{J}^2|a, b\rangle = a|a, b\rangle$ then:

$$\hat{J}_\pm \left( \hat{J}_\pm|a, b\rangle \right) = \hat{J}_\pm \left( \hat{J}^2|a, b\rangle \right) = \hat{J}_\pm a|a, b\rangle = a \left( \hat{J}_\pm|a, b\rangle \right)$$

Adding these we get $[\hat{J}^2, \hat{J}_z] = 0$. $\hat{J}^2$ and $\hat{J}_z$ can then be diagonalised simultaneously by the same set of kets. Let us denote the eigenvalues of $\hat{J}^2$ by $a$, the eigenvalues of $\hat{J}_z$ by $b$, and common eigenkets by $|a, b\rangle$:

$$\hat{J}^2|a, b\rangle = a|a, b\rangle$$

$$\hat{J}_z|a, b\rangle = b|a, b\rangle$$

Now we introduce the ladder operators $\hat{J}_+$ and $\hat{J}_-$ using identical strategy as in the case of the quantum harmonic oscillator (and with the same purpose)

$$\hat{J}_+ = \hat{J}_x + i\hat{J}_y$$

$$\hat{J}_- = \hat{J}_x - i\hat{J}_y$$

They fulfill the following commutation rules:

$$[\hat{J}^2, \hat{J}_\pm] = 0$$

which is very easy to see and

$$[\hat{J}_z, \hat{J}_\pm] = \pm \hbar \hat{J}_\pm$$

We will prove the last one.

$$[\hat{J}_z, \hat{J}_x \pm i\hat{J}_y] = [\hat{J}_z, \hat{J}_x] \pm i[\hat{J}_z, \hat{J}_y] = i\hbar \hat{J}_y \pm i \left( -i\hbar \hat{J}_x \right)$$

$$= \hbar \left( \hat{J}_x \pm i\hat{J}_y \right) = \pm \hbar \hat{J}_\pm.$$
This means that \( \hat{J}_\pm \) does not change \( a \). In summary we have shown that:

\[
\hat{J}_\pm |a, b\rangle = c_\pm |a, b \pm h\rangle
\]

Upon consecutive application of \( \hat{J}_+ \) the eigenvalue of \( \hat{J}_z \) in the ket \( |a, b\rangle \) is increased. Now we would like to analyse whether such increase can continue forever, that is can we reach an arbitrarily large \( b \) for a given \( a \)? The answer is negative as shown by the following calculation. We will prove that

\[
a \geq b^2
\]

Proof:

Note that

\[
\hat{J}^2 - \hat{J}_z^2 = \frac{1}{2} \left( \hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+ \right) = \frac{1}{2} \left( \hat{J}_+ \hat{J}_+^\dagger + \hat{J}_+^\dagger \hat{J}_+ \right)
\]

Such pairs of operators \( \hat{Q} \hat{Q}^\dagger \) have nonnegative expectation values, which is easy to see. That means:

\[
\langle a, b | \hat{J}^2 - J_z^2 | a, b \rangle \geq 0,
\]

which is equivalent to

\[
a - b^2 \geq 0
\]

Now the same idea comes in as in case of a quantum harmonic oscillator. On the one hand upon repeated application of \( \hat{J}_+ \) to \( |a, b\rangle \) the second eigenvalue can be increased (seemingly) indefinitely. On the other hand \( a - b^2 \geq 0 \). The only way this contradiction can be resolved is when at some stage the application of \( \hat{J}_+ \) to the \( |a, b\rangle \) results in reaching the zero of the ket space \( |\varnothing\rangle \). That is there has to be a \( b_{\text{max}} \) such that:

\[
\hat{J}_+ |a, b_{\text{max}}\rangle = |\varnothing\rangle
\]

\[
\hat{J}_- \hat{J}_+ |a, b_{\text{max}}\rangle = |\varnothing\rangle
\]

But

\[
\hat{J}_- \hat{J}_+ = \hat{J}_x^2 + \hat{J}_y^2 - i \left( \hat{J}_y \hat{J}_x - \hat{J}_x \hat{J}_y \right) = \hat{J}^2 - \hat{J}_z^2 - \hbar \hat{J}_z
\]

then

\[
\left( \hat{J}^2 - \hat{J}_z^2 - \hbar \hat{J}_z \right) |a, b_{\text{max}}\rangle = |\varnothing\rangle
\]

But \( |a, b_{\text{max}}\rangle \neq |\varnothing\rangle \), this means then that:

\[
a - b_{\text{max}}^2 - \hbar b_{\text{max}} = 0
\]

Similarly there is \( b_{\text{min}} \) such that \( \hat{J}_- |a, b_{\text{min}}\rangle = |\varnothing\rangle \)

\[
\hat{J}_+ \hat{J}_- = \hat{J}^2 - \hat{J}_z^2 + \hbar \hat{J}_z
\]

and

\[
a - b_{\text{min}}^2 + \hbar b_{\text{min}} = 0
\]
By comparison we see that

\[ b_{max} = -b_{min} \]

The possible values of \( b \) are found between these two limiting values and the adjacent \( b \)-s are separated by \( \hbar \). We get:

\[ b_{max} = b_{min} + n\hbar \]

\[ b_{max} = \frac{n\hbar}{2} \]

It follows that:

\[ a = \frac{n\hbar}{2} \left( \frac{n\hbar}{2} + \hbar \right) \]

It is accepted to denote \( j = \frac{n}{2} \). Then the maximum eigenvalue of \( \hat{J}_z \) is \( j\hbar \), and the eigenvalue of \( \hat{J}^2 \) is \( h^2 j(j + 1) \). We also usually call \( b = mh \). The allowed values of \( m \) are:

\[ m = -j, -j + 1, \ldots, j - 1, j \]

and there are \( 2j + 1 \) of such values.

In summary we have found the eigenvalues of the \( \hat{J}^2 \) and the \( \hat{J}_z \) operator:

\[ \hat{J}^2 |j, m\rangle = h^2 j(j + 1) |j, m\rangle \]

\[ \hat{J}_z |j, m\rangle = m\hbar |j, m\rangle \]

where \( j \) is an integer or a half-integer and \( m \) can take \( 2j + 1 \) values \( m = -j, -j + 1, \ldots, j \). We underline here once again, that this result was obtained on the basis of the commutation rules only.

### 7.1.8 More about the orbital angular momentum

The orbital angular momentum operator \( \hat{L} \) components are:

\[ \hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \]

\[ \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \]

\[ \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \]

and their commutation rule is:

\[ [\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk} \hat{L}_k \]

We check it in the case of \( \hat{L}_x \) and \( \hat{L}_y \).

\[ [\hat{L}_x, \hat{L}_y] = [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] = [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] \]
Figure 7.8: The spherical polar coordinates

\[ \hat{L}_z |l, m\rangle = m \hbar |l, m\rangle \]

\[ \hat{L}_z^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \]

\[ \hat{L}_z^2 |l, m\rangle = \hbar^2 l(l + 1) |l, m\rangle \]

where \( l \) is a nonnegative integer only.

\[ m \in (-l, -l + 1, \ldots, l - 1, l) \]

It is sometimes helpful to use the operator \( \hat{L} \) in the position representation. We will show below what does it do to a wavefunction:

\[ \langle \mathbf{r} | \hat{L}_x | \Psi \rangle = -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \Psi(\mathbf{r}) \]

\[ \langle \mathbf{r} | \hat{L}_y | \Psi \rangle = -i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \Psi(\mathbf{r}) \]

\[ \langle \mathbf{r} | \hat{L}_z | \Psi \rangle = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \Psi(\mathbf{r}) \]

In spherical polar coordinates (see Fig 7.8) we have:

\[ x = r \sin(\Theta) \cos(\phi) \]

\[ y = r \sin(\Theta) \sin(\phi) \]

\[ z = r \cos(\Theta) \]
the operators $\hat{L}_i$ act as if they were replaced by the following:

$$\hat{L}_x \rightarrow i\hbar \left( \sin(\phi) \frac{\partial}{\partial \Theta} + \cot(\Theta) \cos(\phi) \frac{\partial}{\partial \phi} \right),$$

$$\hat{L}_y \rightarrow i\hbar \left( -\cos(\phi) \frac{\partial}{\partial \Theta} + \cot(\Theta) \sin(\phi) \frac{\partial}{\partial \phi} \right),$$

$$\hat{L}_z \rightarrow -i\hbar \frac{\partial}{\partial \phi}.$$

The total orbital angular momentum $\hat{L}^2$ is replaced by:

$$\hat{L}^2 \rightarrow -\hbar^2 \left( \frac{1}{\sin^2(\Theta)} \frac{\partial^2}{\partial \Theta^2} \left( \sin(\Theta) \frac{\partial}{\partial \Theta} \right) + \frac{1}{\sin^2(\Theta)} \frac{\partial^2}{\partial \phi^2} \right).$$

To get this form one has to change variables from the cartesian to the spherical polar ones. The partial derivatives change as illustrated below:

$$z = r \cos(\Theta)$$

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z} \frac{\partial}{\partial r} + \frac{\partial \Theta}{\partial z} \frac{\partial}{\partial \Theta} = \frac{1}{r \sin(\Theta)} \frac{\partial}{\partial r} + \frac{1}{r \sin(\Theta)} \frac{\partial}{\partial \Theta}.$$  

## 7.1.9 Spherically symmetric potential in three dimensions

The orbital angular momentum allows to simplify the Schrödinger equation in three dimensions in case of the spherically symmetric potential $V(r)$. The Schrödinger equation in position representation takes the form:

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right) \Psi(r) = E \Psi(r)$$

In spherical polar coordinates:

$$-\frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin(\Theta)} \frac{\partial}{\partial \Theta} \left( \sin(\Theta) \frac{\partial}{\partial \Theta} \right) + \frac{1}{r^2 \sin^2(\Theta)} \frac{\partial^2}{\partial \phi^2} \right] \Psi(r, \Theta, \phi) + V(r) \Psi(r, \Theta, \phi) = E \Psi(r, \Theta, \phi).$$

The radial and angular part of this equation can be separated. We substitute

$$\Psi(r, \Theta, \phi) = R(r) Y(\Theta, \phi)$$

into the Schrödinger equation and divide its both sides by $\Psi(r, \Theta, \phi)$ : The angular part is an eigenvalue problem for the operator $\hat{L}^2$.

The eigenstates of $\hat{L}^2$ and $\hat{L}_z$ are called the spherical harmonics: $Y_{lm}(\Theta, \phi)$. They fulfill:

$$\hat{L}_z \Psi_{lm}(\Theta, \phi) = \hbar m \Psi_{lm}(\Theta, \phi)$$
which means that $Y_{lm}(\Theta, \phi) \propto \exp(im\phi)$, and
\[
\hat{L}^2 \Psi_{lm}(\Theta, \phi) = \hbar^2 l(l + 1)Y_{lm}(\Theta, \phi)
\]

Since for the rotations in real space we expect
\[
\Psi_{lm}(\Theta, \phi + 2\pi) = \Psi_{lm}(\Theta, \phi)
\]
then $m$ can be an \textbf{integer only}. No half integers are allowed. The explicit form of the spherical harmonics are:
\[
Y_{lm}(\Theta, \phi) = \epsilon \left[ \frac{2l + 1 (l - m)!}{4\pi (l + m)!} \right] P_l^m(\cos(\Theta)) \exp(i m \phi)
\]
where $\epsilon = (-1)^m$ if $m = 0$ and $\epsilon = 1$ otherwise. The $P_l^m$ are the associated Legendre polynomials (you can look them up if you ever need them) The first few normalised spherical harmonics are:

\[
Y_{00} = \frac{1}{\sqrt{4\pi}}
\]

\[
Y_{1\pm 1} = \pm \sqrt{\frac{3}{8\pi}} \sin(\Theta) \exp(\pm i \phi)
\]

\[
Y_{10} = \sqrt{\frac{1}{4\pi}} \cos(\Theta)
\]

\[
Y_{2\pm 2} = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2(\Theta) \exp(\pm 2i \phi)
\]

\[
Y_{2\pm 1} = \pm \sqrt{\frac{15}{8\pi}} \sin(\Theta) \cos(\Theta) \exp(\pm i \phi)
\]

\[
Y_{20} = \sqrt{\frac{5}{4\pi}} \left( \frac{3}{2} \cos^2(\Theta) - \frac{1}{2} \right)
\]

and they are presented in the Fig 7.9.

Spherical harmonics are also eigenstates of the parity operator with eigenvalues $(-1)^l$. To check note that the inversion, that is the replacement $\mathbf{r} \rightarrow -\mathbf{r}$ means that $\Theta \rightarrow \pi - \Theta$, $\phi \rightarrow \phi + \pi$ and substitute those into the above expression for $Y_{lm}$. Finally using
\[
\cos(\Theta) = \frac{z}{r}, \quad \sin(\Theta) \cos(\phi) = \frac{x}{r}, \quad \sin(\Theta) \sin(\phi) = \frac{y}{r}
\]
we can see that:

\[
Y_{10} = \sqrt{\frac{3}{4\pi r}} z, \\
Y_{11} = -\sqrt{\frac{3}{8\pi r}} \frac{x + iy}{r}, \\
Y_{1-1} = \sqrt{\frac{3}{8\pi r}} \frac{x - iy}{r}.
\]

Now we will do a couple of exercises.
Figure 7.9: The spherical harmonics

**Exercise 7.1** Prove that for the particle moving in a spherically symmetric potential the orbital angular momentum $\hat{L}$ is the constant of the motion.

Solution: We need to prove that:

$$\frac{d}{dt} \langle \hat{L} \rangle = 0$$

We know that

$$\frac{d\langle \hat{L} \rangle}{dt} = \langle [\hat{L}, \hat{H}] \rangle,$$

this means

$$\frac{d\langle \hat{L}_i \rangle}{dt} = \langle [\hat{L}_i, \hat{H}] \rangle, \ i = x, y, z.$$

The Hamiltonian in the spherical polar coordinates has a form:

$$\hat{H} = \hat{D}_r + \frac{1}{r^2} \hat{L}^2$$

where $\hat{D}_r$ is a certain differential operator acting on the $r$ coordinate only. (The reader is asked to write it explicitly) and $\hat{L}^2$ is a we know a differential operator acting on $\Theta, \phi$ only. Obviously

$$[\hat{L}_i, \hat{D}_r] = 0$$

because the operators $\hat{L}_i$ are independent of $r$. Hence:

$$[\hat{L}_i, \hat{H}] = [\hat{L}_i, \hat{L}^2] = 0.$$

**Exercise 7.2** (Vibrational - Rotational Spectra of Molecules) In a diatomic $H_2$ molecule the atoms are free to vibrate around their equilibrium positions $r_0$ along their common axis and the molecule is free to rotate around its center of mass. Find the allowed energy levels of the molecule. In the solution ignore the orbital angular momentum of electrons and their spin.
Solution: We first examine the oscillatory motion (in the reference frame that rotates with the molecule). The kinetic energy in this rotating reference frame is (see Fig 7.10):

\[ E_{k,osc} = 2 \times \frac{1}{2} m_H v_u^2 + 2 m_H \omega^2 (u - r_0)^2 \]

\[ = \frac{p_u^2}{m_H} + m_H \omega^2 (u - r_0)^2 \]

Note that in our reference frame where \( r \) is the distance to the center:

\[ u = r \]

Therefore in our reference frame we have:

\[ E_{T,osc} = \frac{p_r^2}{m_H} + m_H \omega^2 (r - r_0)^2 \]

where \( p_r \) is the radial component of the momentum.

Now we examine the rotational motion, as shown in the Fig 7.11.

Let \( p \) be the momentum of the first atom. Then the total angular momentum of the system about its center of mass is:

\[ L = r_0 \times p + (-r_0) \times (-p) = 2r_0 \times p \]

\[ L^2 = 4r_0^2 p^2 \]

The total rotational energy of the molecule is then:

\[ E_{rot} = 2 \times \frac{p^2}{2m_H} = \frac{p_r^2}{m_H} = \frac{L^2}{4m_H r_0^2} \]
Now we examine the total Hamiltonian for the quantum system

\[ \hat{H} = \frac{\hat{p}_r^2}{m_H} + m_H \omega^2 (\hat{r} - r_0)^2 + \frac{\hat{L}_r^2}{4m_H r_0^2} \]

in which we identify two parts:

\[ \hat{H} = \hat{H}_{\text{radial}} + \hat{H}_{\text{angular}} \]

We want to prove that

\[ [\hat{H}_{\text{radial}}, \hat{H}_{\text{angular}}] = 0 \]

which is obvious as \( \hat{H}_{\text{radial}} \) is independent of \( \Theta, \phi \) and \( \hat{H}_{\text{angular}} \) is independent of \( r \). Therefore \( \hat{H}_{\text{radial}} \) and \( \hat{H}_{\text{angular}} \) can be diagonalised simultaneously by the same set of kets. These kets are also eigenkets of the total Hamiltonian and the eigenvalues of the \( \hat{H} \) are sums of the corresponding eigenvalues of \( \hat{H}_{\text{radial}} \) and \( \hat{H}_{\text{angular}} \). Now \( \hat{H}_{\text{radial}} \) is the Hamiltonian of the quantum harmonic oscillator, its eigenvalues are \((n + 1/2) \hbar \omega \) and its eigenstates are \( |n\rangle \). \( \hat{H}_{\text{angular}} \) has eigenvalues \( \frac{1}{4m_H r_0^2} \hbar^2 l(l + 1) \) and its eigenstates are \( |l, m\rangle \). Therefore the eigenstate of \( \hat{H} \) is labelled \( |n, l, m\rangle \) and its eigenvalue is

\[ E_{nlm} = (n + 1/2) \hbar \omega + \frac{1}{4m_H r_0^2} \hbar^2 l(l + 1) \]

Each of these eigenvalues has the \( 2l + 1 \) degeneracy (with respect to \( m \)). The included Figs from Eisberg show the rotational states (visible in absorption) and vibrational-rotational states in transmission. The last figure shows the realistic case in which not only oscillations and rotations of the molecule result in energy levels, but also the electronic energy is included. The electronic levels are coupled to oscillations as evidenced in a different equilibrium position for the lower and the higher electronic state. The ladder of quantum harmonic oscillator states is visible, each of its levels is decorated by an additional sequence of rotational states. This picture is a bit idealised. In a realistic situation there may be some complications such as for example:

- the masses of the nuclei may be unequal (different isotopes),
- spin may not be zero,
- the molecule may be in an excited electron state, then the electron orbital angular momentum may be non-zero,
- the moment of inertia \( I \) is affected by the oscillatory motion - (longer spring means larger \( I \) ) hence oscillations are coupled with rotations,
- in some molecules such as \( \text{H}_2 \) or \( \text{N}_2 \) additional conditions are imposed by the exchange symmetry.

**Exercise 7.3** Find the energy levels and the wavefunction of the particle of mass \( \mu \) moving with orbital angular momentum zero in infinitely deep spherical potential well

\[ V(r) = 0 \quad \text{for} \quad r \leq R \]

\[ V(r) = \infty \quad \text{otherwise.} \]
Solution: Since the symmetry of this problem is spherical it is convenient to solve it in spherical polar coordinates, for which the Schrödinger equation takes the form:

\[-\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin(\Theta)} \frac{\partial}{\partial \Theta} \left( \sin(\Theta) \frac{\partial}{\partial \Theta} \right) + \frac{1}{r^2 \sin^2(\Theta)} \frac{\partial^2}{\partial \phi^2} \right) \Psi + V(r)\Psi = E\Psi\]

Now we separate the radial and the angular part of the Schrödinger equation assuming that \(\Psi(r)\) can be expressed as a product of the radial and the angular part. This is an Ansatz and in some cases it may not work.

\(\Psi(r) = \Psi(r, \Theta, \phi) = P(r)U(\Theta, \phi)\)

Before we substitute this form to the equation both sides are multiplied by \(r^2\). We get:

\[-\frac{\hbar^2}{2m} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \right) P(r)U(\Theta, \phi) + \frac{1}{\sin(\Theta)} \frac{\partial}{\partial \Theta} \left( \sin(\Theta) \frac{\partial}{\partial \Theta} \right) U(\Theta, \phi)P(r) + \frac{1}{\sin^2(\Theta)} \frac{\partial^2}{\partial \phi^2} U(\Theta, \phi)P(r) \right] + [r^2V(r) - Er^2] U(\Theta, \phi)P(r) = 0\]

We divide both sides of the above equation by \(U(\Theta, \phi)P(r)\) and get:

\[-\frac{\hbar^2}{2m} \left[ \frac{1}{P(r)} \frac{1}{\partial r} \left( r \frac{\partial}{\partial r} \right) P(r) \right] + r^2(V(r) - E) + \frac{1}{U(\Theta, \phi)} \frac{1}{2m} \left[ \frac{1}{\sin(\Theta)} \frac{\partial}{\partial \Theta} \left( \sin(\Theta) \frac{\partial}{\partial \Theta} \right) + \frac{1}{\sin^2(\Theta)} \frac{\partial^2}{\partial \phi^2} \right] U(\Theta, \phi) = 0\]

On this basis we have in fact two equations:

\[-\frac{\hbar^2}{2m} \left[ \frac{1}{P(r)} \frac{1}{\partial r} \left( r \frac{\partial}{\partial r} \right) P(r) \right] + r^2(V(r) - E) = -\lambda\]

\[\frac{1}{U(\Theta, \phi)} \left[ \frac{1}{\sin(\Theta)} \frac{\partial}{\partial \Theta} \left( \sin(\Theta) \frac{\partial}{\partial \Theta} \right) + \frac{1}{\sin^2(\Theta)} \frac{\partial^2}{\partial \phi^2} \right] U(\Theta, \phi) = \frac{2m}{\hbar^2} \lambda\]

In the second equation we recognise the eigenvalue problem for the \(\hat{L}^2\). This allows us to identify \(\frac{2m}{\hbar^2} \lambda = \hbar^2(l + 1)\) and \(U(\Theta, \phi) = Y_m(\Theta, \phi)\), where \(l, m\) are integers. Now we can focus on the radial part:

\[-\frac{\hbar^2}{2m} \left[ \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \right) P(r) \right] + r^2(V(r) - E) P(r) = \frac{\hbar^2}{2m} l(l + 1) P(r)\]

In our problem the angular momentum is zero, then we have to solve a simpler equation:

\[\left[ \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \right) P(r) \right] + \frac{2m}{\hbar^2} r^2 (E - V(r)) P(r) = 0\]

which within the well is further simplified to:
\[
\left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) P(r) \right] + \frac{2m}{\hbar^2} r^2 E P(r) = 0
\]

In order to solve this equation we substitute:

\[
P(r) = \frac{\chi(r)}{r},
\]

\[
\frac{dP(r)}{dr} = \frac{1}{r} \frac{d\chi(r)}{dr} - \frac{1}{r^2} \chi(r),
\]

\[
\frac{d}{dr} \left( r^2 \frac{dP(r)}{dr} \right) = \frac{d}{dr} \left( r \frac{d\chi(r)}{dr} - \chi(r) \right) = \frac{d\chi(r)}{dr} + r \frac{d^2\chi(r)}{dr^2} - \frac{d\chi(r)}{dr}
\]

\[
= r \frac{d^2\chi(r)}{dr^2}.
\]

This gives:

\[
\frac{d^2\chi(r)}{dr^2} + \frac{2mE}{\hbar^2} \chi(r) = 0,
\]

that in conjunction with the boundary conditions results in:

\[
\chi(r) = \sin \left( \sqrt{\frac{2mE}{\hbar^2}} r \right), \text{ where } \sqrt{\frac{2mE}{\hbar^2}} R = 2n\pi.
\]

### 7.2 The tensor product of Hilbert spaces

We are able to treat a range of problems related to the electron wavefunction such as the orbital motion. Simultaneously we are able to solve some problems that relate to the electron spin, but if the wavefunction part of our problem interferes with the spin part we would be in a difficulty.

Below we show how to define the appropriate ket space for the combined system on the basis of the infinite dimensional space \(|\Psi\rangle\) that gave us the wavefunctions and the two-dimensional spin space. We will do that through a sequence of examples.

**Example 7.2** We are solving a problem concerning two spin 1/2 particles. The ket space for each particle is two-dimensional. What is the ket space of the combined system?

Solution: For a system made up of two parts \(S_1\) and \(S_2\) each of which can be considered a system on its own, every state can be expressed as:

\[
|\Psi\rangle = \sum_{i,j} c_{ij} |\Psi_i\rangle \otimes |\Psi\rangle = \sum_{i,j} c_{ij} |\Psi_i\rangle |\Psi\rangle
\]
where $\otimes$ is to be read "a tensor product". Here $|\Psi_i\rangle$ represents possible basis states of $S_i$ and $|\Psi_j\rangle$ are basis states of $S_j$. The ket state of the combined system $S$ is a tensor product of the ket space of $S_1$ and the ket space of $S_2$. Basis states in the tensor product space are tensor products of basis states in $S_1, (|\Psi_i\rangle)$, and in $S_2, (|\Psi_j\rangle)$. $|\Psi_i\rangle \otimes |\Psi_j\rangle$ is an ordered pair $(|\Psi_i\rangle, |\Psi_j\rangle)$. Such pairs span a certain vector space (tensor product space) that is composed of all possible pairs $(|\Psi\rangle, |\Phi\rangle)$. In vector spaces one should have a prescription how to add its elements and multiply them by scalars (numbers), that is how to take a linear combination. Below we show how to define a linear combination for our prescription how to add its elements and multiply them by scalars (numbers), that is how to take a linear combination. Below we show how to define a linear combination for our pairs, thus confirming that we have a vector space. We postulate that:

$$c_1|\Phi\rangle \otimes |\Psi_1\rangle + c_2|\Phi\rangle \otimes |\Psi_2\rangle = |\Phi\rangle \otimes (c_1|\Psi_1\rangle + c_2|\Psi_2\rangle)$$

$$c_1|\Phi_1\rangle \otimes |\Psi\rangle + c_2|\Phi_2\rangle \otimes |\Psi\rangle = (c_1|\Phi_1\rangle + c_2|\Phi_2\rangle) \otimes |\Phi\rangle$$

The ket spaces of $S_1$ and $S_2$ are Hilbert spaces and we need to have a scalar (dot) product in the tensor product space. We postulate:

$$(|\Phi_1\rangle \otimes \langle\Psi_1\rangle)(|\Phi_2\rangle \otimes \langle\Psi_2\rangle) = \langle\Phi_1|\Phi_2\rangle\langle\Psi_1|\Psi_2\rangle.$$  

We will not include any proofs here as well as we leave out the closure of the Hilbert space.

**Example 7.3** *The basis states for two spin 1/2 particle system.*

Solution: The basis states of the first particle are: $|S_{z}^{+}(1)\rangle, |S_{z}^{-}(1)\rangle$. The basis states of the second particle are $|S_{z}^{+}(2)\rangle, |S_{z}^{-}(2)\rangle$. The basis states in the tensor product space are $|e_1\rangle, |e_2\rangle, |e_3\rangle, |e_4\rangle$:

$$|e_1\rangle = |S_{z}^{+}(1)\rangle|S_{z}^{+}(2)\rangle$$

$$|e_2\rangle = |S_{z}^{+}(1)\rangle|S_{z}^{-}(2)\rangle$$

$$|e_3\rangle = |S_{z}^{-}(1)\rangle|S_{z}^{+}(2)\rangle$$

$$|e_4\rangle = |S_{z}^{-}(1)\rangle|S_{z}^{-}(2)\rangle$$

The same basis states in the $|e_1\rangle, |e_2\rangle, |e_3\rangle, |e_4\rangle$ representation are:

$$\begin{pmatrix}
\langle e_1| e_1 \rangle \\
\langle e_2| e_1 \rangle \\
\langle e_3| e_1 \rangle \\
\langle e_4| e_1 \rangle
\end{pmatrix} = \begin{pmatrix} 1 \\
0 \\
0 \\
0 \end{pmatrix}$$

$$\begin{pmatrix}
\langle e_1| e_2 \rangle \\
\langle e_2| e_2 \rangle \\
\langle e_3| e_2 \rangle \\
\langle e_4| e_2 \rangle
\end{pmatrix} = \begin{pmatrix} 0 \\
1 \\
0 \\
0 \end{pmatrix}$$

Now we would like to address the issue of operators acting in tensor spaces.

Let $\hat{A}$ act in one ket space $|\Psi\rangle$ and $\hat{B}$ act in another $|\Phi\rangle$. We can define two new operators $\hat{A} \otimes \hat{1}$ and $\hat{1} \otimes \hat{B}$ in the following way:

- The operator $\hat{A} \otimes \hat{1}$ acts in the tensor product space of $|\Psi\rangle|\Phi\rangle$ and acts as an equivalent of $\hat{A}$ in this tensor space:

$$\hat{A} \otimes \hat{1}(|\Psi\rangle|\Phi\rangle) = (\hat{A}|\Psi\rangle)|\Phi\rangle$$
The operator $\hat{1} \otimes \hat{B}$ acts in the tensor product space of $|\Psi\rangle|\Phi\rangle$ and acts as an equivalent of $\hat{B}$ in this tensor space:

$$\hat{1} \otimes \hat{B}(|\Psi\rangle|\Phi\rangle) = |\Psi\rangle(\hat{B}|\Phi\rangle)$$

$\hat{A} \otimes \hat{1}$ and $\hat{1} \otimes \hat{B}$ act in the same space and they can be added.

Example 7.4 We would like to evaluate the matrix of the operator $\hat{1} \otimes \hat{B}$ in the particular case of $\hat{B} = \hat{S}_z$. The basis states are from the tensor product space.

Solution: The matrix is composed of the elements $\langle e_i | \hat{1} \otimes \hat{B} | e_j \rangle$ and is equal to:

$$\begin{pmatrix}
\frac{\hbar}{2} & 0 & 0 & 0 \\
0 & -\frac{\hbar}{2} & 0 & 0 \\
0 & 0 & \frac{\hbar}{2} & 0 \\
0 & 0 & 0 & -\frac{\hbar}{2}
\end{pmatrix} = \begin{pmatrix} 1 & 0 \end{pmatrix} \otimes \begin{pmatrix} \frac{\hbar}{2} & 0 \\
0 & -\frac{\hbar}{2} \end{pmatrix}.$$

Example 7.5 Similar as above, but now we evaluate the matrix of $\hat{A} \otimes \hat{1}$ for $\hat{A} = \hat{S}_z$.

Solution:

$$\begin{pmatrix}
\frac{\hbar}{2} & 0 & 0 & 0 \\
0 & \frac{\hbar}{2} & 0 & 0 \\
0 & 0 & -\frac{\hbar}{2} & 0 \\
0 & 0 & 0 & -\frac{\hbar}{2}
\end{pmatrix} = \begin{pmatrix} \frac{\hbar}{2} & 0 \\
0 & -\frac{\hbar}{2} \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \end{pmatrix}.$$

Now we define the tensor product of two operators. The operator $\hat{A} \otimes \hat{B}$ is called the tensor product of two operators $\hat{A}$ and $\hat{B}$ when it acts in the tensor space in the following way:

$$(\hat{A} \otimes \hat{B})|\Psi\rangle|\Phi\rangle = (\hat{A}|\Psi\rangle)(\hat{B}|\Phi\rangle).$$

7.3 Addition of angular momentum

Just as in classical mechanics, the concept of angular momentum arises quantum-mechanically as the generator of rotations in the sense that if we rotate a physical system through an angle $\phi$ around the axis $n$, then the state vector of the system is transformed according to

$$|\psi\rangle_R = \exp \left(-i\hat{J}n\phi/\hbar\right) |\psi\rangle$$

or equivalently $|\psi\rangle_R$ is the new state vector with respect to a new set of spatial coordinates rotated an angle $-\phi$ about $n$ relative to their former orientation.
The operator \( \hat{J} \) which generates the rotation is identified as the total angular momentum operator for the system. The components of \( \hat{J} \) have the properties

\[
[\hat{J}_i, \hat{J}_j] = \epsilon_{ijk} \hbar \hat{J}_k
\]

from which it can be derived what are the eigenvalues and the eigenstates of \( \hat{J}_z \) and \( \hat{J}^2 \), namely

\[
\hat{J}^2 |j, m_j\rangle = \hbar^2 j(j+1) |j, m_j\rangle
\]

\[
\hat{J}_z |j, m_j\rangle = \hbar m_j |j, m_j\rangle
\]

where \( j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots ; m_j = -j, -j+1, \ldots, j-1, j \). It must be borne in mind that this is a very general result: the system can consist of one or many particles, that may or may not interact with one another. How do we understand this result? To do so let us consider the case of a single particle system.

### 7.3.1 Single Particle System: Orbital and Spin Angular Momentum

Classically we know that for a single particle, the angular momentum of that particle is given by:

\[
\mathbf{L} = \mathbf{r} \times \mathbf{p}
\]

this is the angular momentum associated with the motion of the particle through space. If we then define the quantum version of angular momentum by making \( \mathbf{r} \) and \( \mathbf{p} \) the position and momentum operators \( \hat{r} \) and \( \hat{p} \) respectively of a particle, i.e.

\[
\hat{L} = \hat{r} \times \hat{p}
\]

then we find that

\[
[\hat{L}_i, \hat{L}_j] = \epsilon_{ijk} \hat{L}_k
\]

that is exactly the same rule as for the \( \hat{J} \) operator, and if we work out the eigenstates and eigenvalues of \( \hat{L}^2 \) and \( \hat{L}_z \) we end up with:

\[
\hat{L}^2 |l, m_l\rangle = \hbar^2 l(l+1) |l, m_l\rangle
\]

\[
\hat{L}_z |l, m_l\rangle = \hbar m_l |l, m_l\rangle
\]

where \( l = 0, 1, 2, \ldots; m_l = -l, -l+1, \ldots, l-1, l \). i.e we end up with integer values only. Thus the angular momentum associated with the motion of the particle through space is quantized in the integer multiples of \( \hbar \). This angular momentum is known as orbital angular momentum and it is almost always represented by the symbol \( \hat{L} \).

However the more general operator \( \hat{J} \) is defined without reference to the position and momentum of anything, so it is a much more general quantity than \( \hat{L} \). So what is to be made of the half integer eigenvalues of \( \hat{J} \). Experiment provided the clue: it is associated with the intrinsic angular momentum or spin, of what is, in principle a point particle. Such a property is not possible classically - a classical point particle cannot possess spin, so that it is a purely quantum phenomenon.
It turns out, that particles exist in nature, that possess integer spin: indeed half integer and integer particles are known to have vastly different statistical properties, and are identified by different names - fermions and bosons respectively. But particle spin is an intrinsic property of a particle quite distinct from the orbital angular momentum and is almost always represented by the symbol $\hat{S}$.

Continuing with a single particle example, we now arrive at the picture of a system with two contributions to its angular momentum: its orbital angular momentum $\hat{L}$ associated with the motion of the particle through space, and $\hat{S}$, the intrinsic spin of the particle. It is reasonable to expect, that for our single particle system, the total angular momentum $\hat{J}$ is given by:

$$\hat{J} = \hat{L} + \hat{S} = \hat{r} \times \hat{p} + \hat{S}$$

At this point we have to recognise that $\hat{L} = \hat{r} \times \hat{p}$ is an operator acting on an infinite dimensional vector space associated with the motion in space of the particle, while for example if the particle has spin $\frac{1}{2}$, then we know that the spin space is two-dimensional. Two operators acting in two different vector spaces cannot be simply added. This is the kind of situation that is handled mathematically by introducing the notion of a tensor product, i.e.

$$\hat{J} = \hat{L} \otimes I_s + I_L \otimes \hat{S}$$

where $\hat{L}$ acts on vectors on the infinite dimensional Hilbert space $H_L$ associated with the motion of the particle, and $I_L$ is the associated identity operator, while $\hat{S}$ acts on vectors in the finite dimensional Hilbert space, $H_S$ associated with the intrinsic spin of the particle, with $I_S$ the identity operator on $H_S$. The total angular momentum operator then acts on the combined (tensor product) Hilbert space

$$H = H_L \otimes H_S$$

as do $\hat{L} \otimes I$ and $I \otimes \hat{S}$. The Hilbert space is spanned by the states:

$$|r\rangle \otimes |s, m_s\rangle$$

with $s = \frac{1}{2}$ and $m_s = \pm \frac{1}{2}$, for the electron spin (the nuclear spin and nuclear motion have been ignored here).

These states are therefore simultaneous eigenstates of $\hat{L}_z^2$, $\hat{S}_z^2$, $\hat{S}_z$ and serve as a useful set of basis states for the system. However we also know the eigenstates (and eigenvalues) associated with $\hat{J}$, via the $|j, m_j\rangle$. The natural question then is what the relationship between the two sets of basis states happens to be. It is the aim here to investigate this relationship and how it can be made use of.

Before proceeding, there is a subsidiary matter to be addressed. In the above we have more or less taken for granted that $\hat{L} + \hat{S}$ in its tensor product form is equal to the generator $\hat{J}$ of rotations. Actually proving that is not an easy task, though the result seems to be physically obvious. Moreover it is not necessarily obvious that the result $\hat{L} + \hat{S}$ is an angular momentum operator. We are not in a position to address the first difficulty, but we can actually tackle the latter and in doing so we will gain some practice at handling the tensor product formalism.
Example 7.6 We wish to prove that $\hat{J}$ defined as $\hat{L} + \hat{S}$ (in a tensor product sense) fulfills the commutation rule:

$$[\hat{J}_i, \hat{J}_j] = \epsilon_{ijk} \hbar \hat{J}_k$$

which follows from the commutation rules for the components $\hat{L}$ and $\hat{S}$.

Solution: We write out the rigorous expressions for $\hat{J}$:

$$\hat{J} = \hat{L} \otimes \hat{1}_s + \hat{1}_L \otimes \hat{S}$$

so that

$$\hat{J}_i = \hat{L}_i \otimes \hat{1}_s + \hat{1}_L \otimes \hat{S}_i$$

We will evaluate a typical commutator, that is $[\hat{J}_x, \hat{J}_y]$, which will be evaluated by determining its action on an arbitrary basis state $|l, m_l \rangle \otimes |s, m_s \rangle$.

$$[\hat{J}_x, \hat{J}_y]|l, m_l \rangle \otimes |s, m_s \rangle =$$

$$= \hat{J}_x \hat{J}_y |l, m_l \rangle \otimes |s, m_s \rangle - \hat{J}_y \hat{J}_x |l, m_l \rangle \otimes |s, m_s \rangle$$

Working out the first term only, and then only starting with the action of $\hat{J}_y$ we have:

$$\hat{J}_y |l, m_l \rangle \otimes |s, m_s \rangle = [\hat{L}_y \otimes \hat{1}_s + \hat{1}_L \otimes \hat{S}_y]|l, m_l \rangle \otimes |s, m_s \rangle =$$

$$= \hat{L}_y |l, m_l \rangle \otimes \hat{1}_s |s, m_s \rangle + \hat{1}_L |l, m_l \rangle \otimes \hat{S}_y |s, m_s \rangle =$$

$$= \hat{L}_y |l, m_l \rangle \otimes |s, m_s \rangle + |l, m_l \rangle \otimes \hat{S}_y |s, m_s \rangle$$

Next acting on this with $\hat{J}_x$ gives:

$$[\hat{L}_x \otimes \hat{1}_s + \hat{1}_L \otimes \hat{S}_x] \hat{L}_y |l, m_l \rangle \otimes |s, m_s \rangle + |l, m_l \rangle \otimes \hat{S}_y |s, m_s \rangle =$$

$$= \hat{L}_x \hat{L}_y |l, m_l \rangle \otimes |s, m_s \rangle + \hat{L}_x |l, m_l \rangle \otimes \hat{S}_y |s, m_s \rangle +$$

$$+ \hat{L}_y |l, m_l \rangle \otimes \hat{S}_x |s, m_s \rangle + |l, m_l \rangle \otimes \hat{S}_x \hat{S}_y |s, m_s \rangle.$$
\[ \hat{J}_z = i\hbar \hat{J}_z. \]

Since \( |l, m_l \rangle \otimes |s, m_s \rangle \) is an arbitrary basis state, we conclude that:

\[ [\hat{J}_z, \hat{J}_y] = i\hbar \hat{J}_z. \]

and similarly for other components. Thus indeed we see that such defined \( \hat{J} \) fulfills the commutation rules of the angular momentum operator.

This result can be easily generalised in case of the sum of two angular momentum operators, which turns out also to be an angular momentum operator. It will be of some value later.

Later we will abandon the tensor product notation altogether, but before showing how we go about doing so (we will do it in general context) we will look at another physical situation which leads to summing the angular momentum operators.

### 7.3.2 Many particle systems

Here we have:

\[ \hat{J} = \sum_i \hat{L}_i + \sum_i \hat{S}_i \]

where \( \hat{L}_i \) and \( \hat{S}_i \) are the orbital and spin angular momentum operators for the i-th particle.

Of course this is understood in terms of the appropriate tensor product. Thus for two particles the Hilbert space is

\[ H = H_{L1} \otimes H_{S1} \otimes H_{L2} \otimes H_{S2} \]

where the indices \( L_i, S_i \) refer to the i-th particle, and for instance

\[ \hat{L}_1 = \hat{L}_1 \otimes \hat{S}_{1} \otimes \hat{L}_{2} \otimes \hat{S}_{2} \]

obviously a cumbersome notation, though it does emphasise that \( \hat{L}_1 \otimes \hat{S}_{1} \otimes \hat{L}_{2} \otimes \hat{S}_{2} \) is an operator acting on a combined Hilbert space. Often this expression is written

\[ \hat{J} = \hat{L} + \hat{S} \]

where

\[ \hat{L} = \sum_i \hat{L}_i, \quad \hat{S} = \sum_i \hat{S}_i. \]

From the result obtained earlier, it is clear that \( \hat{L} \) and \( \hat{S} \) defined in this manner are also angular momentum operators - the total orbital angular momentum and spin angular momentum operators respectively. Of course \( \hat{L} + \hat{S} = \hat{J} \) is also an angular momentum operator.

Thus we recover, mathematically at least the same problem we had before with two angular momentum operators \( \hat{L} \) and \( \hat{S} \) combining to give a third, \( \hat{J} \). Moreover we also have the same mathematics contained for instance

\[ \hat{S} = \hat{S}_1 + \hat{S}_2 \]
in which we are combining the spin or orbital angular momentum operators for the whole
system. Once again this is mathematically the same kind of situation though of course
physically there is considerable difference. This then leads to the essential nature of the
problem that we are dealing with.

7.4 The Nature of the Problem

In all the cases considered above, we find that they amount to dealing with
\[ \hat{J} = \hat{J}_1 + \hat{J}_2 \]
where \( \hat{J}_1 \) and \( \hat{J}_2 \) would be the orbital or spin angular momentum of one or more particles
in the various combinations considered above. In general this expression should be written:
\[ \hat{J} = \hat{J}_1 \otimes \hat{1}_2 + \hat{1}_1 \otimes \hat{J}_2 \]
and the tensor product space \( H = H_1 \otimes H_2 \) will be spanned by the set of basis states:
\[ |j_1, m_1 \rangle \otimes |j_2, m_2 \rangle \]
It is at this point that we would like to move away from the tensor product notation and
write these basis states as:
\[ |j_1, j_2, m_1, m_2 \rangle \]
We also remind how we write down operators and operator ordering. Namely we have:
\[ (\hat{A}_1 \otimes \hat{1}_2)|j_1, m_1 \rangle \otimes |j_2, m_2 \rangle = \hat{A}_1|j_1, m_1 \rangle \otimes |j_2, m_2 \rangle = \hat{A}_1|j_1, j_2, m_1, m_2 \rangle \]
where \( \hat{A}_1 \) is any operator acting on vectors in \( H_1 \), and similarly:
\[ (\hat{1}_1 \otimes \hat{A}_2)|j_1, m_1 \rangle \otimes |j_2, m_2 \rangle = \hat{A}_2|j_1, j_2, m_1, m_2 \rangle = |j_1, m_1 \rangle \otimes \hat{A}_2|j_2, m_2 \rangle \]
Finally
\[ \hat{A}_1 \hat{A}_2|j_1, j_2, m_1, m_2 \rangle = (\hat{A}_1 \otimes \hat{1}_2)(\hat{1}_1 \otimes \hat{A}_2)|j_1, m_1 \rangle \otimes |j_2, m_2 \rangle = \hat{A}_1|j_1, m_1 \rangle \otimes \hat{A}_2|j_2, m_2 \rangle = (\hat{1}_1 \otimes \hat{A}_2)(\hat{A}_1 \otimes 1)|j_1, m_1 \rangle \otimes |j_2, m_2 \rangle = \]
\[ \hat{A}_2 \hat{A}_1|j_1, j_2, m_1, m_2 \rangle \]
This gives:
\[ \hat{A}_1 \hat{A}_2|j_1, j_2, m_1, m_2 \rangle = \hat{A}_2 \hat{A}_1|j_1, j_2, m_1, m_2 \rangle \]
or
\[ [\hat{A}_1, \hat{A}_2] = 0 \]
so in the tensor product free notation, the operators acting on different Hilbert spaces commute. Thus we have our set of rules that free us from the tyranny of the $\otimes$. Of course if in doubt we return to the usual notation to make clear what is being done.

With these rules in place, we can restate all that we know at present:

- The operators $\hat{J}^2_1, \hat{J}_{1z}, \hat{J}^2_2, \hat{J}_{2z}$ all commute with one another. Thus these operators have a common complete set of kets labelled $|j_1, j_2, m_1, m_2\rangle$. They fullfill

  $$\hat{J}^2_1 |j_1, j_2, m_1, m_2\rangle = \hbar^2 j_1(j_1 + 1)|j_1, j_2, m_1, m_2\rangle$$

  $$\hat{J}_{1z} |j_1, j_2, m_1, m_2\rangle = \hbar m_1 |j_1, j_2, m_1, m_2\rangle$$

  where $j_1 = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$; $m_1 = -j_1, -j_1 + 1, \ldots, j_1 - 1, j_1$ and similarly for $\hat{J}^2_2$ and $\hat{J}^2_2$.

- The total angular momentum operator $\hat{J}$ is also associated with eigenstates $|j, m\rangle$ of $\hat{J}^2$ and $\hat{J}_z$, but this operator is an observable of the same system described by the basis states $|j_1, j_2, m_1, m_2\rangle$ which contain four quantum numbers. It is therefore reasonable to expect that there are two more operators which commute with $\hat{J}^2$ and $\hat{J}_z$. It is not hard to show that these are $\hat{J}^2_1$ and $\hat{J}_{1z}$, i.e. $[\hat{J}^2_1, \hat{J}^2] = [\hat{J}^2_1, \hat{J}_z] = [\hat{J}^2_2, \hat{J}^2_2] = 0$

  and similarly with the index 1 interchanged with 2. Therefore there exists a complete set of eigenstates of the four operators $\hat{J}^2_1, \hat{J}^2_2, \hat{J}_z$, and $\hat{J}_z$ given by $|j_1, j_2, j, m\rangle$ with the properties:

  $$\hat{J}^2_1 |j_1, j_2, j, m\rangle = \hbar^2 j_1(j_1 + 1) |j_1, j_2, j, m\rangle$$

  $$\hat{J}^2_2 |j_1, j_2, j, m\rangle = \hbar^2 j_2(j_2 + 1) |j_1, j_2, j, m\rangle$$

  $$\hat{J}^2_2 |j_1, j_2, j, m\rangle = \hbar^2 j(j + 1) |j_1, j_2, j, m\rangle$$

  $$\hat{J}_z |j_1, j_2, j, m\rangle = \hbar m_1 |j_1, j_2, j, m\rangle$$

  These states then represent an alternate set of basis states for our system. Consequently we can write

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

  where we have used the completeness relation

  $$\sum_{m_1, m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2 | = \hat{1}$$

  though note that we are confining ourselves to those states with fixed $j_1$ and $j_2$ i.e. we are not summing over $j_1$ and $j_2$.

  The coefficients $\langle j_1, j_2, m_1, m_2| j_1, j_2, j, m\rangle$ are known as Clebsch- Gordon coefficients, and it is the aim to determine what these coefficients are. In that way, given the magnetic
quantum numbers $m_1$ and $m_2$ we can determine what possible angular momenta $j$ and $m$
quantum numbers the whole system may possess.

In doing so we will need to make use of the idea of ladder operators defined by

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

and similarly for $\hat{J}_1\pm$ and $\hat{J}_2\pm$. These operators have the property that

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

i.e. it increases or decreases the magnetic quantum number by unity.

To illustrate the whole idea we will make use of a simple but nevertheless important
example, that of two spin half particles.

### 7.4.1 Two Spin Half Particles

This situation is of some importance as it arises in a number of significant physical systems. These include the hydrogen atom in which the electron and proton each have spin half, the deuteron, consisting of a proton and neutron, the helium atom in which the two electrons each have spin half, elementary particles called mesons each consisting of two spin half quarks and so on. What we are after are the possible angular momentum states of the combined system, given that the constituents each have spin half. Here we have, with $\hat{J} \longrightarrow \hat{S}$:

$$\hat{S} = \hat{S}_1 + \hat{S}_2.$$ 

the relevant $|s_1, s_2, m_1, m_2\rangle$ states are then:

$$|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\rangle \equiv |m_1 = \frac{1}{2}, m_2 = \frac{1}{2}\rangle$$

where we have dropped $s_1 = s_2 = \frac{1}{2}$ as these values do not change, and to remind us what basis states we are using, we have retained $m_1 = \ldots, m_2 = \ldots$ in the ket.

We want to construct the state $|s_1, s_2, s, m\rangle$ as a linear combination of these four states. To do this, and to check our result we need to express $\hat{S}^2$ in terms of $\hat{S}_1^2$ and $\hat{S}_2^2$:

$$\hat{S}^2 = (\hat{S}_1 + \hat{S}_2)^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1\hat{S}_2 =$$

$$\hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_{1z}\hat{S}_{2z} + \hat{S}_{1-}\hat{S}_{2+} + \hat{S}_{1+}\hat{S}_{2-}$$

the last line following by substituting for $\hat{S}_{1x}$ etc the terms of $\hat{S}_{1\pm}$ etc.

To start with, we need to guess a possible eigenstate of $\hat{S}^2$ and $\hat{S}_z$ which can act as a "seed" out of which we can construct, by use of ladder operators, the remaining eigenstates. The starting point, the most obvious, is the "top of the ladder" state $|m_1 = \frac{1}{2}, m_2 = \frac{1}{2}\rangle$

We can check that this is indeed an eigenstate of $\hat{S}^2$ and $\hat{S}_z$ by direct calculation. Thus:

$$\hat{S}_z |m_1 = \frac{1}{2}, m_2 = \frac{1}{2}\rangle = (\hat{S}_{1z} + \hat{S}_{2z}) |m_1 = \frac{1}{2}, m_2 = \frac{1}{2}\rangle =$$
\[ |m_1 = \frac{1}{2}, m_2 = \frac{1}{2} \rangle = \hat{h} \]

Further

\[ \hat{S}^2 |m_1 = \frac{1}{2}, m_2 = \frac{1}{2} \rangle = \]

\[ = (\hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1\hat{S}_2_+ + \hat{S}_1\hat{S}_2_-) |m_1 = \frac{1}{2}, m_2 = \frac{1}{2} \rangle = \]

\[ = (\frac{1}{2}(\frac{1}{2} + 1)\hat{h}^2 + \frac{1}{2}(\frac{1}{2} + 1)\hat{h}^2 + 2 \times \frac{\hat{h}^2}{2} \times \frac{\hat{h}^2}{2} + 0 + 0) |m_1 = \frac{1}{2}, m_2 = \frac{1}{2} \rangle = \]

\[ = 2\hat{h}^2 |m_1 = \frac{1}{2}, m_2 = \frac{1}{2} \rangle = \hat{h}^2(1 + 1) |m_1 = \frac{1}{2}, m_2 = \frac{1}{2} \rangle \]

This means that

\[ \hat{S}_z |m_1 = \frac{1}{2}, m_2 = \frac{1}{2} \rangle = \hat{m}\hat{h} |m_1 = \frac{1}{2}, m_2 = \frac{1}{2} \rangle, \text{ where } m = 1 \]

\[ \hat{S}_+ |m_1 = \frac{1}{2}, m_2 = \frac{1}{2} \rangle = \hat{h}^2 j(j + 1) |m_1 = \frac{1}{2}, m_2 = \frac{1}{2} \rangle, \text{ where } j = 1 \]

or in other words:

\[ |m_1 = \frac{1}{2}, m_2 = \frac{1}{2} \rangle = |j = 1, m = 1 \rangle \]

So the state \( |m_1 = \frac{1}{2}, m_2 = \frac{1}{2} \rangle \) is the same as the state \( |j, m \rangle \) with \( j = 1, m = 1 \). If we now apply the ladder operator \( \hat{J}_- \) to \( |j = 1, m = 1 \rangle \) we will get:

\[ \hat{J}_- |j = 1, m = 1 \rangle = \sqrt{2} |j = 1, m = 0 \rangle \]

but since

\[ \hat{J}_- = \hat{J}_1_- + \hat{J}_2_- \]

we also get

\[ (\hat{J}_1_- + \hat{J}_2_-) |m_1 = \frac{1}{2}, m_2 = \frac{1}{2} \rangle = \sqrt{\left(\frac{1}{2} + \frac{1}{2}\right)} \hat{h} |m_1 = \frac{1}{2}, m_2 = \frac{1}{2} \rangle + \]

\[ + \sqrt{\cdot} |m_1 = \frac{1}{2}, m_2 = -\frac{1}{2} \rangle \]

Doing this again gives:

\[ \sqrt{1(2)} |s = 1, m = -1 \rangle = \frac{1}{\sqrt{2}} \left[ |m_1 = -\frac{1}{2}, m_2 = -\frac{1}{2} \rangle + |m_1 = -\frac{1}{2}, m_2 = -\frac{1}{2} \rangle \right] = \]

\[ = \sqrt{2} |m_1 = -\frac{1}{2}, m_2 = -\frac{1}{2} \rangle \]

or \( |s = 1, m = 1 \rangle = |m_1 = -\frac{1}{2}, m_2 = -\frac{1}{2} \rangle \). At this point the process stops, but we have only uncovered three states. The fourth will follow by requiring that it be orthogonal to the three just uncovered. This leads to:

\[ \frac{1}{\sqrt{2}} \left[ |m_1 = \frac{1}{2}, m_2 = -\frac{1}{2} \rangle - |m_1 = -\frac{1}{2}, m_2 = \frac{1}{2} \rangle \right] \]

which can also be shown to be the state

\[ |s = 0, m = 0 \rangle \]

i.e. as expected we get three state \( s = 1, m = -1, 0, 1 \), also known as spin triplet, and the state \( s = 0, m = 0 \), also known as spin singlet. In essence the above is the analysis follows in a more involved general case.
7.5 The General Case

It is not straightforward to carry through the above procedure in the general case. One method is described below: not the shortest, but probably the easiest to apply.

First of all we can start with:

\[ |j_1, j_2, j, m\rangle = \sum_{m_1, m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2|j_1, j_2, j, m\rangle \]

Applying \( \hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z} \) to both sides of this equation gives

\[ m\hbar |j_1, j_2, j, m\rangle = \sum_{m_1, m_2} (m_1 + m_2) \hbar |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2|j_1, j_2, j, m\rangle \]

But the left hand side can be expanded as above to give

\[ \sum_{m_1, m_2} m\hbar |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2|j_1, j_2, j, m\rangle \]

so comparing the two expansions we get:

\[ m = m_1 + m_2 \]

which means nothing more than that the total \( z \) component of angular momentum is the sum of the \( z \) components of the subsystems (contributing \( \hat{J}_1 \) and \( \hat{J}_2 \) to \( \hat{J} \)).

We can now use this result to determine the limits on the values of \( j \).

We know that

\[ -j \leq m \leq j \]

\[ -j_1 \leq m_1 \leq j_1 \]

\[ -j_2 \leq m_2 \leq j_2 \]

so putting \( m = j \) and \( j_1 = m_1 \) we have

\[ m_2 = m - m_1 = j - j_1 \]

so that

\[ -j_2 \leq j - j_1 \leq j_2 \]

i.e.

\[ j_1 - j_2 \leq j \leq j_1 + j_2 \]

Similarly putting \( m = j \) and \( m_2 = j_2 \) we end up with

\[ j_2 - j_1 \leq j \leq j_1 + j_2 \]

Combining these two equations we conclude that

\[ |j_1 - j_2| \leq j \leq j_1 + j_2 \]
Figure 7.12: Addition of angular momenta

\[ j = |j_1 - j_2|, |j_1 - j_2| + 1, \ldots, j_1 + j_2 - 1, j_1 + j_2. \]

This last result is known as the *triangle condition*. The three numbers \( j, j_1, j_2 \) must be such, that they could constitute the three sides of a triangle, see Fig 7.12.

We now combine there two last results, plus the ladder operator property

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

and similarly for \( \hat{J}_1- \) and \( \hat{J}_2- \), plus the fact that all the states \( |j, m\rangle \) are orthonormal:

\[ \langle j', m'|j, m\rangle = \delta_{jj'} \delta_{mm'} \]

and similarly for the states \( |m_1, m_2\rangle \)

\[ \langle m_1', m_2'|m_1, m_2\rangle = \delta_{m_1'm_1} \delta_{m_2'm_2} \]

The procedure is then as follows:

(i) Start with \( j = j_1 + j_2; m = j = j_1 + j_2 \) i.e. both \( j \) and \( m \) have their maximum possible values. Then using

\[ |j, m\rangle = \sum_{m_1, m_2} |m_1, m_2\rangle \langle m_1, m_2|j, m\rangle \]

(dropping \( j, j_2 \) for convenience) we have only one term in the sum, since \( m_1 + m_2 = m \):

\[ |j = j_1 + j_2, m = j_1 + j_2\rangle = |m_1 = j, m_2 = j_2\rangle A \]

Here \( A \) is the Clebsch-Gordon coefficient. But all states are normalised to unity, so \( A = 1 \) and we get:

\[ |j = j_1 + j_2, m = j_1 + j_2\rangle = |m_1 = j, m_2 = j_2\rangle \]

Now apply \( \hat{J}_- = \hat{J}_1- + \hat{J}_2- \) to this equation: \( \{1\} \)

\[ \sqrt{\cdots}|j = j_1 + j_2; m = j_1 + j_2 - 1\rangle = \sqrt{\cdots}|m_1 = j_1 - 1, m_2 = j_2\rangle + \]

\[ + \sqrt{\cdots}|m_1 = j_1, m_2 = j_2 + 1\rangle \]
where the $\sqrt{\ldots}$ comes from the property above of $\hat{J}_-$. Now apply $\hat{J}_-$ again: \{2\}

\[ \sqrt{\ldots}|j = j_1 + j_2, m = j_1 + j_2 - 2\rangle = \sqrt{\ldots}|m_1 = j_1 - 2, m_2 = j_2\rangle + \]

\[ + \sqrt{\ldots}|m_1 = j_1 - 1, m_2 = j_2 - 1\rangle + \]

\[ + \sqrt{\ldots}|m_1 = j_1 - 1, m_2 = j_2 - 1\rangle + \]

\[ + \sqrt{\ldots}|m_1 = j_1, m_2 = j_2 - 2\rangle \]

and so on until the whole thing stops, since we can only decrease as far as its minimum value $-(j_1 + j_2)$.

(ii) Now we start the whole thing over again, but starting with the state in which $j = j_1 + j_2 - 1, m = j_1 + j_2 - 1$ i.e. one less than the previous starting point. The Clebsch-Gordon expansion is \{3\}

\[ |j = j_1 + j_2 - 1, m = j_1 + j_2 - 1\rangle = \sum_{m_1, m_2} |m_1, m_2\rangle \langle m_1, m_2|j = j_1 + j_2 - 1, m = j_1 + j_2 - 1\rangle \]

The restriction that we must leave $m_1 + m_2 = m$ leads to:

\[ |j = j_1 + j_2 - 1, m = j_1 + j_2 - 1\rangle = B_1|m_1 = j_1, m_2 = j_2 - 1\rangle + B_2|m_1 = j_1 - 1, m_2 = j - 2\rangle \]

here $B_1$ and $B_2$ are unknown Clebsch- Gordon coefficients. Normalization then implies that

\[ |B_1|^2 + |B_2|^2 = 1 \]

which is not enough to fix $B_1$ and $B_2$. But the state $|j = j_1 + j_2 - 1, m = j_1 + j_2 - 1\rangle$ defined in \{3\} is orthogonal to the state $|j = j_1 + j_2, m = j_1 + j_2 - 1\rangle$ defined in \{1\} and \{1\} and \{3\} are linear combinations of the same orthonormal states $|m_1 = j_1 - 1, m_2 = j_2\rangle$ and $|m_1 = j, m_2 = j_2 - 1\rangle$. Thus if we take the inner product of \{1\} and \{3\} we will end up with the equation:

\[ \sqrt{\ldots}B_1 + \sqrt{\ldots}B_2 = 0 \]

so we can now solve for $B_1$ and $B_2$ up to an arbitrary phase factor, which we can choose to suit ourselves. The convention here is to choose the phase factor so that $B_1$ is real and positive. In this way $B_1$ and $B_2$ are fixed and we can proceed down the ladder by applying $\hat{J}_-$ as in \{1\}. For instance we get: \{4\}

\[ \sqrt{\ldots}|j_1 + j_2 - 1, m = j_1 + j_2 - 2\rangle = B_1\sqrt{\ldots}|m_1 = j_1 - 1, m_2 = j_2 - 1\rangle + \]

\[ + B_1\sqrt{\ldots}|m_1 = j_1, m_2 = j_2 - 2\rangle + \]

\[ + B_2\sqrt{\ldots}|m_1 = j_1 - 2, m_2 = j_2\rangle + \]

\[ + B_2\sqrt{\ldots}|m_1 = j_1 - 1, m_2 = j_2 - 1\rangle \]

and so on until the sequence stops.
(iii) Now put \( j = j_1 + j_2 - 2, m = j_1 + j_2 - 2 \). The Clebsch-Gordon expansion is:

\[
|j = j_1 + j_2 - 2, m = j_1 + j_2 - 2) = C_1|m_1 = j_1, m_2 = j_2 - 2) + \\
+C_2|m_1 = j_1 - 1, m_2 = j_2 - 1) + \\
+C_3|m_1 = j_1 - 2, m_2 = j_2). 
\]

We now normalise to unity to give

\[
|C_1|^2 + |C_2|^2 + |C_3|^2 = 1 
\]

and note that \( \{5\} \) is orthogonal to \( \{4\} \) leading to an equation:

\[
\sqrt{\ldots} C_1 + \sqrt{\ldots} C_2 + \sqrt{\ldots} C_3 = 0 
\]

which is still not enough (three unknowns but only two equations.) so we have to go back to step (i) equation \( \{2\} \) and use orthogonality yet again to give another equation for \( C_1, C_2 \) and \( C_3 \). Then we can solve for \( C_1, C_2 \) and \( C_3 \). Choose \( C_1 \) to be real and positive and we have fixed equation \( \{5\} \). Then apply \( \hat{J}_- \) to equation \( \{5\} \) and so on.

(iii) Put \( j = j_1 + j_2 - 3, m = j_1 + j_2 - 3 \) etc. There are four unknowns, so four equations are needed. Using orthonormality etc etc until we reach minimum \( j = |j_1 - j_2| \).

Given the complexity of the above procedure, it should be clear that it becomes an increasingly tedious calculation for anything but low angular momentum states. Typically the Clebsch-Gordon coefficients are tabulated once and for all.

We can illustrate the procedure for the system in which \( j_1 = 1, j_2 = \frac{1}{2} \).

(i) \( |j = \frac{3}{2}, m = \frac{3}{2} \rangle = |m_1 = 1, m_2 = \frac{1}{2} \rangle \) Applying \( \hat{J}_- \) creates

\[
\sqrt{\ldots} j = \frac{3}{2}, m = \frac{1}{2} \rangle = \sqrt{\ldots} m_1 = 0, m_2 = \frac{1}{2} \rangle + \sqrt{\ldots} m_1 = 1, m_2 = -\frac{1}{2} \rangle 
\]

and again creates

\[
\ldots |j = \frac{3}{2}, m = -\frac{1}{2} \rangle = \ldots m_1 = -1, m_2 = \frac{1}{2} \rangle + \ldots m_1 = 0, m_2 = -\frac{1}{2} \rangle 
\]

and again creates

\[
\ldots |j = \frac{3}{2}, m = -\frac{3}{2} \rangle = \ldots m_1 = -1, m_2 = -\frac{1}{2} \rangle 
\]

and stops at this point as a further application of \( \hat{J}_- \) will give zero on both sides.

(ii) \( |j = \frac{1}{2}, m = \frac{1}{2} \rangle = B_1|m_1 = 1, m_2 = -\frac{1}{2} \rangle + B_2|m_1 = 0, m_2 = \frac{1}{2} \rangle \), therefore \( |B_1|^2 + |B_2|^2 = 1 \). This state is orthogonal to \( |j = \frac{3}{2}, m = \frac{1}{2} \rangle \) above which gives

\[
B_1 \sqrt{\ldots} + B_2 \sqrt{\ldots} = 0 
\]

so that \( B_1 \) and \( B_2 \) can be solved for. Now apply \( \hat{J}_- \) to \( |j = \frac{1}{2}, m = \frac{1}{2} \rangle \) which will give

\[
|j = \frac{1}{2}, m = -\frac{1}{2} \rangle = \ldots |m_1 = 0, m_2 = -\frac{1}{2} \rangle + \ldots |m_1 = -1, m_2 = \frac{1}{2} \rangle 
\]
and one more time will create nothing more that $\hat{J}_- |j = \frac{1}{2}, m = -\frac{1}{2} \rangle = 0$ as $m$ cannot be less than $-\frac{1}{2}$.

(iii) Cannot decrease $j$ any further as its smallest value is $|j_1 - j_2| = \frac{1}{2}$ which we have already reached. Then we have generated the states of the form $|jm\rangle$:

$$|j = \frac{3}{2}, m = \frac{3}{2}\rangle; \ |j = \frac{3}{2}, m = \frac{1}{2}\rangle; \ |j = \frac{3}{2}, m = -\frac{1}{2}\rangle;$$

$$|j = \frac{3}{2}, m = -\frac{3}{2}\rangle; \ |j = \frac{1}{2}, m = \frac{1}{2}\rangle; \ |j = \frac{1}{2}, m = -\frac{1}{2}\rangle;$$

i.e. six in number, the same number of basis states of the form $|m_1, m_2\rangle$ that were:

$$|m_1 = 1, m_2 = \frac{1}{2}\rangle; \ |m_1 = 0, m_2 = \frac{1}{2}\rangle; \ |m_1 = -1, m_2 = \frac{1}{2}\rangle;$$

$$|m_1 = 1, m_2 = -\frac{1}{2}\rangle; \ |m_1 = 0, m_2 = -\frac{1}{2}\rangle; \ |m_1 = -1, m_2 = -\frac{1}{2}\rangle.$$

Once the expansions of the $|jm\rangle$ in terms of the $|m_1, m_2\rangle$ states are written out, the various Clebsch-Gordon coefficients can be read off.

Note also that the coefficients in the expansion have an arbitrary phase factor so chosen that the coefficient of the term with the largest $m_1$ value in each expansion is real and positive. This is only one of the many conventions in the literature.

Example 7.7 Spin-orbit coupling:

Solution: Consider a hydrogen atom for simplicity assumed to be one in which the nucleus is assumed to be fixed and stationary. (see adjacent Figure)

By virtue of its spin, the electron possesses a magnetic moment operator

$$\hat{\mu} = -\frac{e}{m_e c} \hat{S}$$
and by virtue of its motion through the Coulomb field produced by the nucleus, experiences the magnetic field \( \mathbf{B} \). The energy associated with the electron in this field is then:

\[
H_{so} = -\frac{e}{m_e c} \hat{\mathbf{S}} \mathbf{B}
\]

This field \( \mathbf{B} \) can be shown to be proportional to the orbital angular momentum of the electron, i.e. \( \hat{\mathbf{L}} \) so that

\[
H_{so} \propto \hat{\mathbf{S}} \hat{\mathbf{L}}
\]

The effect of this interaction is to shift the energy levels of the \( \text{H} \) atom giving them so called fine structure splitting.

Due to the presence of this term in the interaction neither \( \hat{\mathbf{J}} \) nor \( \hat{\mathbf{S}} \) are the constants of the motion for the system. However it turns out, since the system is isolated, that \( \hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}} \) is a constant of the motion, i.e.

\[
[\hat{\mathbf{J}}, \hat{H}] = 0
\]

where \( \hat{H} \) denotes the total Hamiltonian including \( H_{so} \). In that way \( \hat{H} \) and \( \hat{\mathbf{J}} \) have simultaneous eigenstates which turn out to be the best states with which the corrected energy levels of the atom can be most readily calculated.

**Example 7.8 The Helium Atom**

Solution: In calculating the energy levels of the \( \text{He} \) atom (or in a more complex fashion any multilevel atom), it turns out to be useful to write the state of the atom as:

\[
|\psi_1, \psi_2\rangle \otimes |\chi_1, \chi_2\rangle
\]

where \( |\psi_i\rangle \) are the state vectors for electron motion and \( |\chi_i\rangle \) are spin states for electrons. i.e. we work with the eigenstates of \( \hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2 \) the total spin angular momentum for the two electrons.
Chapter 8

Identical Particles

According to classical physics, the properties of a collection of identical particles are in no way affected by the fact that the particles are physically identical. The point of view adopted in classical physics is that it is always possible, in principle, to label each particle and keep track of each particle in the same way as if they were distinguishable in the first place.

Thus, for example, in the collision of two classical identical particles, there is in principle no difficulty in monitoring each particle as the collision progresses. Such a collision cannot be represented by a totally unambiguous diagram:

However, quantum mechanics introduces an extra twist which turns out to be of paramount significance. This is the uncertainty principle, which effectively states that the position of a particle cannot be known with total precision (except at the cost of having no knowledge of the momentum of the particle). As a consequence, it is not possible, according to the quantum mechanics, to keep track of the individual behaviour of identical particles because, if they get too close, it is not possible, even in principle, to be sure which one is which. This can be illustrated by the following diagram:

Here the spread out paths indicate the uncertainty in the position of the two particles. This is of no consequence while the particles are well separated. However, eventually, as the particles close in, the regions in space where the particles are likely to be found will overlap. If we were to perform a particle detection experiment in this region, then there will be a non-zero probability of our detection picking up one or the other of the particles. However, since the particles are identical, we will have no way of knowing which of the two particles we actually detect. It is this indistinguishability that we have to take into account.
account of when describing the quantum-mechanical state of the system, and in doing so we find that the states are restricted to being of two different kinds, each associated with distinct kinds of particles (bosons and fermions).

Here we will be concerned only with the case of two identical particles. This is sufficient to illustrate the kinds of behaviour that is found to occur. With more than two particles, a difficult mathematical formalism to that which we will use here proves to be much more powerful, but as it involves introducing a new Hilbert spaces and new classes of operators, we will not be going down that path.

The states we are interested in are built out of single particle states, which we will consider first.

### 8.1 Single Particle States

Suppose we have a single particle moving under the influence of some potential, e.g. an electron moving in the Coulomb potential associated with a fixed nucleus. We will then have as the system Hamiltonian:

\[
\hat{H}^{(1)} = \frac{p^2}{2m} + V(\hat{r}) = \hat{H}
\]  

where possible examples of \( V(\hat{r}) \) include (i) walls of a box, (ii) periodic potential in crystals, (iii) particles in Coulomb well of an atom. The superscript \(^{(1)}\) on \( \hat{H}^{(1)} \) serves to indicate that this is a single particle Hamiltonian.

The states we are going to work with are obviously eigenstates of \( \hat{H}^{(1)} \). But these states will in all likelihood be degenerate so we should be a little more specific so as to how to describe these eigenstates. To this end, recall that in order to unambiguously specify a complete set of states for a system, we need to select a complete set of states for a system, we need to select a complete set of commuting observables, this set including the Hamiltonian \( \hat{H}^{(1)} \). The rest of numbers of this set will depend on the nature of the system. Suppose the set is

\[
\{ \hat{H}^{(1)}, \hat{A}, \hat{B}, \hat{C}, ... \}
\]

where any pair of operators from this set will commute. In that case these operators will have a complete set of eigenstates in common, which we will write as:

\[
|E, a, b, c, ... \rangle
\]
such that:

$$\hat{H}^{(1)}|E, a, b, c, ...\rangle = E|E, a, b, c, ...\rangle,$$

$$\hat{A}|E, a, b, c, ...\rangle = a|E, a, b, c, ...\rangle,$$

and so on. The completeness relation is:

$$\sum_{E} \sum_{a} \sum_{b} \ldots |E, a, b, c, ...\rangle \langle E, a, b, c, ...| = 1.$$  

We will summarise the list of eigenvalues labelling the eigenstates by writing

$$|k\rangle = |E, a, b, c, ...\rangle,$$

and the completeness relation as

$$\sum_{k} |k\rangle \langle k| = 1.$$  

As an example, we could suppose that \(V(\hat{r}) \) is an attractive Coulomb potential, so that \(\hat{H}^{(1)}\) is essentially the Hamiltonian for the hydrogen atom. Then the complete set is, neglecting spin

$$\{\hat{H}^{(1)}, \hat{L}^2, \hat{L}_z\}$$

and the eigenstates are usually written as \(|n \ell m\rangle\), where

$$\hat{H}^{(1)}|n \ell m\rangle = -\frac{E_0}{n^2}|n \ell m\rangle,$$

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

$$\hat{L}_z|n \ell m\rangle = m\hbar|n \ell m\rangle.$$  

8.2 Two Non-Interacting Particles

Now suppose that we have a two particle system for which the Hamiltonian is:

$$\hat{H}^{(2)} = \hat{H}_1^{(1)} + \hat{H}_2^{(1)} =$$

$$\hat{p}_1^2 2m + V(\hat{r}_1) + \frac{\hat{p}_2^2}{2m} + V(\hat{r}_2),$$

Note that in this Hamiltonian we are assuming that there is no interaction between the particles; the particles move independently of each other, though both are moving in the same potential \(V(\hat{r})\).

We should also note that, the two operators \(\hat{H}_1^{(1)}\) and \(\hat{H}_2^{(1)}\) act on vectors belonging to two distinct Hilbert spaces: \(\mathcal{H}_1\), the Hilbert space of particle 1, and \(\mathcal{H}_2\), the Hilbert space of particle 2. So it is more correct to write the above two particle Hamiltonian as:

$$\hat{H}^{(2)} = \hat{H}_1^{(1)} \otimes \hat{1}_2 + \hat{1}_1 \otimes \hat{H}_2^{(1)},$$

so that the Hamiltonian \(\hat{H}^{(2)}\) is an operator acting on vectors belonging to the tensor product Hilbert space \(\mathcal{H}_1 \otimes \mathcal{H}_2\).

This latter Hilbert space will be spanned by basis states (eigenstates of \(\hat{H}^{(2)}\) of the form:

$$|E, a, b, c, ...\rangle \otimes |E', a', b', c', ...\rangle,$$
where the first ket refers to the particle 1 and the second refers to the particle 2. We will be denoting these kets as $|K\rangle \otimes |K'\rangle$, or alternatively as $|K\rangle|K'\rangle$. Then we have for instance

$$\hat{H}^{(2)}|K\rangle \otimes |K'\rangle = \left[ H^{(1)}_1 \otimes \hat{1}_2 + \hat{1}_1 \otimes H^{(1)}_2 \right] |K\rangle \otimes |K'\rangle$$

$$= \left( \hat{H}^{(1)}_1 \otimes \hat{1}_2 \right) |K\rangle \otimes |K'\rangle + \left( \hat{1}_1 \otimes \hat{H}^{(1)}_2 \right) |K\rangle \otimes |K'\rangle$$

$$= \hat{H}_1 |K\rangle \otimes |K'\rangle + \hat{1}_1 |K\rangle \otimes \hat{H}^{(1)}_2 |K'\rangle$$

$$= E_K |K\rangle \otimes |K'\rangle + E_K' |K\rangle \otimes |K'\rangle = (E_K + E_K') |K\rangle \otimes |K'\rangle.$$ 

Thus confirming that $|K\rangle \otimes |K'\rangle$ is indeed an eigenstate of $\hat{H}^{(2)}$. Note also that the state $|K\rangle \otimes |K'\rangle$ is also an eigenstate of $\hat{H}^{(2)}$ with eigenvalue $E_K + E_K'$. The states $|K\rangle \otimes |K'\rangle$ and $|K'\rangle \otimes |K\rangle$ are thus degenerate, this being known as exchange degeneracy as one state is obtained from the other by exchanging the state labels.

We note here that the bra vector corresponding to $|K\rangle \otimes |K'\rangle$ is $\langle K'\rangle \otimes \langle K\rangle$. Thus the fact that these states form a complete set i.e. they form a basis for $\mathcal{H}_1 \otimes \mathcal{H}_2$, can be written as:

$$\sum_K \sum_{K'} (\langle K\rangle \langle K\rangle) \otimes (\langle K'\rangle \langle K'\rangle) = \hat{1}$$

It is actually a good exercise in the use of the $\otimes$ notation to prove this i.e. the left hand side is:

$$\sum_K \sum_{K'} (\langle K\rangle \langle K\rangle) \otimes (\langle K'\rangle \langle K'\rangle) =$$

$$= \left( \sum_K |K\rangle \langle K| \right) \otimes \left( \sum_{K'} |K'\rangle \langle K'| \right) =$$

$$\hat{1}_1 \otimes \hat{1}_2 = \hat{1}.$$ 

As then states from a complete set, any two particle state can be written as a linear combination:

$$|\Psi\rangle = \sum_{KK'} a_{KK'} |K\rangle \otimes |K'\rangle.$$ 

From now on, the tensor product notation will be dropped.

### 8.3 Symmetric and Antisymmetric States of Two Identical Particles

So far we have not made use of the fact, that the particles are identical, so the above arguments and notation applies to a pair of non-identical particles (though of identical mass $m$). However, we now want to look at the consequences of imposing the condition that the particles are supposed to be identical.

In imposing this condition we recognise that if the two particles are identical, it should not matter which particle we call particle 1, and which we call particle 2. In other words, if we were to impose some means of naming the particles in the description of the state of the two particle system, and if we were to then exchange the names, then the result
should be no change in the physical properties of the system as determined from the state vector.

In order to implement this idea, let us suppose that the two particle system is in some arbitrary state
\[ |\Psi\rangle = \sum_{KK'} a_{KK'} |K\rangle |K'\rangle. \]
and we proceed to construct a new state by "exchanging" particles. This is achieved mathematically by introducing a linear Hermitean operator \( \hat{P} \) (not to be confused with parity operator, having been denoted by the same symbol), the particle exchange operator, which fulfills
\[ \hat{P} |K\rangle |K'\rangle = |K'\rangle |K\rangle, \]
i.e. particle 1 is now in the state formerly of particle 2, and particle 2 is now in the state formerly of particle 1.

Applying this operator to the general state \( |\Psi\rangle \) gives:
\[ |\Psi\rangle' = \hat{P} |\Psi\rangle = \sum_{KK'} a_{KK'} \hat{P} |K\rangle |K'\rangle = \sum_{KK'} a_{KK'} |K'\rangle |K\rangle. \]

What we now argue is that the new state \( |\Psi\rangle' \) must predict exactly the same physical properties for our two particle system as would the original state \( |\Psi\rangle \). We claim this because the particles are identical, and no performing the exchange as above cannot produce any change in the physics.

Consequently we conclude that if \( |\Psi\rangle \) is a legitimate state of two identical particles, then the transformed state \( |\Psi\rangle' \) can differ from state \( |\Psi\rangle \) by no more than a phase factor, i.e.
\[ |\Psi\rangle = \exp(i\Theta) |\Psi\rangle, \]
as this is the only way possible, in quantum mechanics for two different state vectors to yield the same physical results: the factor \( \exp(i\Theta) \) always cancels out when calculating any expectation value, probability etc. Thus we have:
\[ \hat{P} |\Psi\rangle = \exp(i\Theta) |\Psi\rangle. \]

If we then repeat the procedure, i.e.
\[ \hat{P}^2 |\Psi\rangle = \hat{P} \exp(i\Theta) |\Psi\rangle = (\exp(i\Theta))^2 |\Psi\rangle, \]
we must recover the original state \( |\Psi\rangle \), i.e.
\[ (\exp(i\Theta))^2 |\Psi\rangle = |\Psi\rangle \]
or
\[ \exp(i\Theta) = \pm 1. \]

Thus we conclude that the only allowed states of two identical particles are those for which either (i)
\[ \hat{P} |\Psi\rangle = |\Psi\rangle \]
i.e. there is no change in sign under particle exchange. Such states are said to be symmetric. Alternatively (ii)
\[ \hat{P} |\Psi\rangle = -|\Psi\rangle \]
i.e. the state changes sign when the particles are exchanged. Such states are said to be anti-symmetric.
8.4 Symmetrized Energy Eigenstates

In order to see what these states look like, we will determine the energy eigenststes of $\hat{H}^{(2)}$ that have the correct symmetry properties. That this is necessary can be seen by noting that:

$$\hat{P}|k\rangle|K\rangle = |K\rangle|k\rangle \neq \pm |K\rangle|k\rangle$$

i.e. the state $|K\rangle|K\rangle$ is not, in general, an acceptable state. However we note that

$$[\hat{P}, \hat{H}^{(2)}] = 0$$

since

$$\hat{P}\hat{H}^{(2)}|K\rangle|K\rangle = (E + E') \hat{P}|K\rangle|K\rangle = (E + E') |K\rangle|K\rangle$$

$$= \hat{H}^{(2)}|K\rangle|K\rangle = \hat{H}^{(2)} \hat{P}|K\rangle|K\rangle.$$ 

Thus $\hat{P}$ and $\hat{H}^{(2)}$ have a common set of eigenstates which can be readily shown to be:

- **symmetric eigenstates**

  $$|K, K\rangle_+ = \frac{1}{\sqrt{2}} \left(|K\rangle|K\rangle' + |K\rangle'|K\rangle\right)$$

  for $K \neq K'$ and

  $$|K\rangle|K\rangle' = |K\rangle|K\rangle$$

  for $K = K'$. This state is an eigenstate of $\hat{P}$ with the eigenvalue of $+1$.

  $$\hat{P}|K, K\rangle_+ = +1|K, K\rangle_+$$

  $$\hat{H}^{(2)}|K, K\rangle_+ = (E + E')|K, K\rangle_+.$$

  We note that it is possible for both particles to be in the same state.

- **antisymmetric eigenstates**

  $$|K, K\rangle_- = \frac{1}{\sqrt{2}} \left(|K\rangle|K\rangle' - |K\rangle'|K\rangle\right)$$

  for $K \neq K'$ and

  $$|K\rangle|K\rangle' = |K\rangle|K\rangle$$

  for $K = K'$. This state is an eigenstate of $\hat{P}$ with the eigenvalue of $-1$.

  $$\hat{P}|K, K\rangle_- = -1|K, K\rangle_-$$

  $$\hat{H}^{(2)}|K, K\rangle_- = (E + E')|K, K\rangle_-.$$

  Note that the antisymmetric state vanishes if the two particles are in the same state, or better: we cannot have two particles in the same state if this state vector is antisymmetric. This result is known and the Pauli exclusion principle, about which we will say more a little later.
8.5 More Than Two Particles

The above arguments when applied to systems consisting of more than two identical particles do not lead to an unambiguous classification of states of identical particles as being symmetric or antisymmetric with respect to the exchange of any pair of particles - i.e. the possibility of states with mixed symmetry appears to exist. However experimentally this is never found to occur, so it is adopted as a quantum postulate that the state vector of a system of identical particles must be either totally symmetric or totally antisymmetric with respect to the exchange of any pair of particles.

The problem that remains is how to determine whether or not the state vector for any given system of identical particles is symmetric or antisymmetric i.e. what is physically, that determines the symmetry of the state vector?

8.6 Bosons and Fermions

Relativistic quantum field theory predicts and it is observed experimentally that there are two kinds of particles found in nature, antisymmetric and symmetric by the symmetry of their collective state vector, and by their spin. These two kinds of particles are known as fermions and bosons, and they play substantially different roles in determining the make up of the physical world.

8.6.1 Bosons

The state vector of a system of identical particles having integer spin (i.e. integer multiples of $\hbar$) is always symmetric. Such particles are known as bosons. Any number of bosons can be found in the same state. In fact, all interactions in nature: i.e. electromagnetic, strong, weak and gravitational can be understood as being due to, or at least be said to be carried by, particles that arise from the quantum nature of the associated force fields (gauge fields). For instance the photon (spin $\pm 1$) is the carrier of the electromagnetic force.

8.6.2 Fermions

The state vector of a system of identical particles having half integer spin is always antisymmetric. Such particles are known as fermions. No more than one fermion can be found in a given state as stated by the Pauli exclusion principle. Fermions constitute the hard bits of matter and are the matter on which forces are exerted by gauge fields. The exclusion principle plays a significant role in determining the distribution of electrons in atoms, with enormous consequences for the chemical properties of the elements.

8.7 Completeness of Symmetrized Eigenstates $|K, K'\rangle_\pm$

Suppose

$$|\Psi\rangle = \sum_{KK'} a_{KK'} |K\rangle |K'\rangle$$

Suppose
is an arbitrary (allowed) state of a system of two identical particles. We then know that

\[ \hat{P}\langle \Psi | = \pm |\Psi \rangle = \sum_{KK'} a_{KK'} \hat{P} |K| \langle K'| = \sum_{KK'} a_{KK'} |K'| \langle K|, \]

i.e.

\[ |\Psi\rangle = \pm \sum_{KK'} a_{KK'} |K'| \langle K| = \sum_{KK'} a_{KK'} |K'| \langle K|, \]

Adding these two expressions together:

\[ 2|\Psi\rangle = \sum_{KK'} a_{KK'} [|K\rangle \langle K'| \pm |K'| \langle K|] \]

or

\[ |\Psi\rangle = \frac{1}{2} \sum_{KK'} \left( \frac{1}{\sqrt{2}} a_{KK'} \right) |K, K'\rangle \pm = \frac{1}{2} \sum_{KK'} b_{KK'} |K, K'\rangle \pm. \]

Further we also have

\[ |\Psi\rangle = \sum_{KK'} a_{KK'} |K\rangle \langle K'| = \sum_{KK'} a_{K'K} |K\rangle \langle K'| = \pm \sum_{KK'} a_{KK'} |K'| \langle K|, \]

so that

\[ a_{KK'} = \pm a_{K'K} \]

therefore

\[ b_{KK'} = \sqrt{2} a_{KK'} + a_{K'K} \]

\[ = \frac{a_{KK'} + a_{K'K}}{\sqrt{2}}. \]

Thus, for bosons we have for an arbitrary state |\Psi\rangle :

\[ |\Psi\rangle = \frac{1}{2} \sum_{KK'} b_{KK'} |K, K'\rangle_\pm; \quad b_{KK'} = b_{K'K} \]

while for fermions:

\[ |\Psi\rangle = \frac{1}{2} \sum_{KK'} b_{KK'} |K, K'\rangle_\pm; \quad b_{KK'} = -b_{K'K} \]

Thus the symmetric or antisymmetric eigenstates |K, K'\rangle_\pm are basis states for an arbitrary state of a system of two identical particles.

In many applications, particularly in atomic and molecular physics, it is usually, or at least often the practice, that the wave function of the two-particle system is preferentially used. However, as the state vector includes particle spin, the wave function will contain contributions due to both the position and the spin of the particle. So, before dealing with the two-particle case, we will look at the single particle wave function first.

### 8.7.1 Wave Function of Single Particle

First, we recognise that the state |K\rangle can be written:

\[ |K\rangle = |k\rangle |m_s\rangle \quad (\equiv |k, m_s\rangle) \]

where \( m_s \) is the magnetic quantum number for a particle of spin \( s \), i.e.

\[ m_s = -s, -s + 1, \ldots, s - 1, s. \]
The label $k$ represents all the other quantum numbers associated with the spatial motion of the particle. Thus, for instance, for an electron moving in an attractive Coulomb potential, we would have:

$$|k⟩ = |nlm_l⟩|m_s⟩$$

where the first ket refers to the orbital motion and the second one to electron spin.

What we are now after is the wave function associated with this state vector $|K⟩$. Before we do this, we will review what is meant by the wave function in the simple case of a spinless particle.

### 8.7.2 Wave Function for a Spinless Particle

In this case there is only orbital motion, i.e. motion in space. If such a particle is in an arbitrary state $|Ψ⟩$, then we arrive at the idea of a wave function in the following way.

First we note that amongst the possible observables for the particle is its position, represented by the position operator $\hat{r}$. This operator will have a complete set of eigenstates $|r⟩$ i.e. such that

$$\hat{r}|r⟩ = r|r⟩$$

Moreover, as these eigenstates are complete, they form a basis for the Hilbert space of the particle, and we can determine the components of $|Ψ⟩$ relative to these basis states. These components are

$$⟨r|Ψ⟩ \equiv \Psi(r)$$

which can be understood, as suggested by the functional notation, as being a complex valued function of the continuous variable $r$. This quantity $\Psi(r)$ is what we mean by the wave function, or at least the spatial wavefunction of the particle when in the state $|Ψ⟩$.

Its meaning, in probabilistic terms, is that $|Ψ(r)|^2d^3r$ gives the probability of observing the particle in the volume $d^3r$ surrounding the point $r$.

If $|Ψ⟩$ happens to be some particular state, e.g. an eigenstate $|k⟩$, then the notation is to write

$$⟨r|k⟩ = \Psi_k(r)$$

for the associated wave function.

We now turn to the problem of attempting to use the states $|m_s⟩$ to be our basis states, and define the spin wave function of an arbitrary spin state $|χ⟩$ to be the quantity

$$⟨m_s|χ⟩ = χ(m_s).$$

In particular we note that

$$⟨m_s|m_s'⟩ = χ_{m_s}(m_s) = δ_{m_s,m_s'}$$

which is analogous to the notation $\Psi_k(r)$ for the spatial wave function of the specific state $k$. For example, we have, if $s = 1/2$, the $m_s = \pm 1/2$ and so, for the state $|\frac{1}{2}⟩$:

$$⟨m_s|\frac{1}{2}⟩ = χ_{\frac{1}{2}}(m_s)$$

$$= 1 \quad m_s = \frac{1}{2}$$
\[ m_s = -\frac{1}{2} \]

For an arbitrary state \( |\chi\rangle \) where
\[ |\chi\rangle = a \left| \frac{1}{2} \right\rangle + b \left| -\frac{1}{2} \right\rangle \]
then
\[ \chi(m_s) = \langle m_s | \chi \rangle = a \chi_{\frac{1}{2}}(m_s) + b \chi_{-\frac{1}{2}}(m_s) \]

We can now readily evaluate the spin wavefunction:
\[ \chi \left( \frac{1}{2} \right) = a \]
\[ \chi \left( -\frac{1}{2} \right) = b \]

Finally, as regards the interpretation of \( \chi(m_s) \), we use that
\[ |\chi(m_s)|^2 \]
is the probability, if the particle is in spin state \( |\chi\rangle \), or observing the \( z \) component of spin to be \( m_s \hbar \).

Having thus defined what we mean by the spatial and spin wave function, we can now put the two together to give a combined wavefunction.

Thus if the particle is in the state \( |K\rangle \) where \( |K\rangle \equiv |k\rangle |m_s\rangle \), we can pull out the spatial wave function and write
\[ \langle r' | k \rangle = \langle r' | k \rangle |m_s\rangle = \Psi_k(r') |m_s\rangle \]
which we often as far as it goes - part wavefunction and part spin state vector. However, to conclude the story, we write
\[ \Psi(r', m_s) = \langle m'_s | \langle r' | k \rangle |k\rangle = \langle r' | k \rangle \langle m'_s | m_s \rangle = \Psi_k(r') \chi_{m_s}(m'_s). \]

### 8.7.3 The Two Particle Wave Function

The above discussion is now generalised to two particle states \( |K\rangle |K'\rangle \). It is useful here to review what this state represents. Thus \( |K\rangle = \text{ket vector belonging to Hilbert space of particle 1, viz } \mathcal{H}_1 \), \( |K'\rangle = \text{ket vector belonging to Hilbert space of particle 2, viz } \mathcal{H}_2 \).

We note that \( \mathcal{H}_1 \) will be spanned by the basis states \( |r_1\rangle |m_{s_1}\rangle \), while \( \mathcal{H}_2 \) will be spanned by \( |r_2\rangle |m_{s_2}\rangle \). The combined Hilbert space
\[ \mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2 \]
is then spanned by the states
\[ |r_1\rangle |m_{s_1}\rangle \otimes |r_2\rangle |m_{s_2}\rangle \equiv |r_2\rangle |m_{s_2}\rangle |r_2\rangle |m_{s_2}\rangle \]
which will then constitute the basis states for our two particle system in terms of which we can define the two-particle wave function.
So the wavefunction associated with $|k\rangle|k'\rangle$ is:

$$
\langle m_{s_2}|\langle r_2|\langle m_{s_1}|\langle r_1|K\rangle|K'\rangle =
$$

$$
= \langle m_{s_2}|\langle r_2|\langle m_{s_1}|\langle r_1|K\rangle|K'\rangle =
$$

$$
= \psi_{K'}(r_2)\chi_{m'_s}(m_{s_2}) \times \psi_K(r_1)\chi_{m_s}(m_{s_1}).
$$

where $|K\rangle = |k\rangle|m_{s_1}\rangle,|K'\rangle = |k'\rangle|m_{s_2}\rangle$.

For symmetrized states $|K, K'\rangle_{\pm}$ we therefore have:

$$
\psi_{K,K'}^{(+)}(r_1, m_{s_1}, r_2, m_{s_2}) = \langle r_2|\langle m_{s_2}|\langle r_1|\langle m_{s_1}|K\rangle|K'\rangle_{\pm} =
$$

$$
= \frac{1}{\sqrt{2}} [\langle r_2|\langle m_{s_2}|\langle r_1|\langle m_{s_1}|K\rangle|K'\rangle_{\pm} + \langle r_2|\langle m_{s_2}|\langle r_1|\langle m_{s_1}|K'\rangle|K\rangle_{\pm}]
$$

$$
= \frac{1}{\sqrt{2}} [\psi_K(r_1, m_{s_1})\psi_{K'}(r_2, m_{s_2}) \pm \psi_{K'}(r_1, m_{s_1})\psi_K(r_2, m_{s_2})],
$$

which can be further expanded in terms of the spatial and spin wave functions:

$$
\psi_{K,K'}^{(+)}(r_1, m_{s_1}, r_2, m_{s_2}) =
$$

$$
= \frac{1}{\sqrt{2}} [\psi_K(r_1)\psi_{K'}(r_2)\chi_{m_s}(m_{s_1})\chi_{m'_s}(m_{s_2}) \pm \psi_{K'}(r_1)\psi_K(r_2)\chi_{m'_s}(m_{s_1})\chi_{m_s}(m_{s_2})]
$$

As an example, suppose we have two electrons in the state where both $m_s = m_{s'}$, then since $\psi$ has to be antisymmetric, we choose the $\psi_{K,K'}^{(-)}$ state above and write:

$$
\psi_{K,K'}^{(-)}(r_1, m_{s_1}, r_2, m_{s_2}) =
$$

$$
= \frac{1}{\sqrt{2}} [\psi_K(r_1)\psi_{K'}(r_2)\chi_{m_s}(m_{s_1})\chi_{m'_s}(m_{s_2}) - \psi_{K'}(r_1)\psi_K(r_2)\chi_{m'_s}(m_{s_1})\chi_{m_s}(m_{s_2})]
$$

or in terms of ket vectors only

$$
|K,K'\rangle_{-} = \frac{1}{\sqrt{2}} [|K\rangle|K'\rangle - |K'\rangle|K\rangle] \frac{1}{\sqrt{2}} [\frac{1}{2}, \frac{1}{2}]
$$

Here we note that the overall wave function (or the state vector) factorises into two parts - a purely spatial factor which is antisymmetric under particle exchange, and a purely spin part which is symmetric under particle exchange - thus guaranteeing that the overall state is antisymmetric as required for two spin 1/2 particles. This factorization assumes a more central role when we look at states with definite angular momentum.

### 8.8 Singlet and Triplet States

We have just seen that, at least for a pair of spin 1/2 particles, that we can construct a correct symmetrized state in which there appears the spin state $|\frac{1}{2}\rangle|\frac{1}{2}\rangle$. This state can be recognised, from the earlier work an addition of angular momentum, to be just the total angular momentum state $|s = 1, m = 1\rangle$, the joint state of $\hat{S}^2$ and $\hat{S}_z$, where $\hat{S} = \hat{S}_1 + \hat{S}_2$ is the total angular momentum operator of the two identical particles. In fact it turns out to be possible to construct completely symmetrical states, in which the spin states are the eigenstates of $\hat{S}^2$ and $\hat{S}_z$. That this can be done follows from the fact that the eigenstates
of $\hat{S}^2$ are either symmetric or antisymmetric under particle exchange. We shall not prove this here, but simply illustrate that it is in fact the case for a pair of spin half particles. This is also a case e.g. for electrons, of substantial significance in many applications. We have shown in our discussion of the addition of angular momentum, that the eigenstates of $\hat{S}^2$ and $\hat{S}_z$ are:

$$|s = 1, m = 1\rangle = |m_{s_1} = \frac{1}{2}\rangle|m_{s_2} = \frac{1}{2}\rangle \text{ symmetric,}$$

$$|s = 1, m = 0\rangle = \frac{1}{\sqrt{2}} \left[|m_{s_1} = \frac{1}{2}\rangle|m_{s_2} = -\frac{1}{2}\rangle + |m_{s_1} = -\frac{1}{2}\rangle|m_{s_2} = \frac{1}{2}\rangle\right]$$

symmetric,

$$|s = 1, m = -1\rangle = |m_{s_1} = -\frac{1}{2}\rangle|m_{s_2} = -\frac{1}{2}\rangle \text{ symmetric,}$$

and

$$|s = 0, m = 0\rangle = \frac{1}{\sqrt{2}} \left[|m_{s_1} = \frac{1}{2}\rangle|m_{s_2} = -\frac{1}{2}\rangle - |m_{s_1} = -\frac{1}{2}\rangle|m_{s_2} = \frac{1}{2}\rangle\right]$$

antisymmetric

The correctly symmetrized states, including the spatial part are then:

$$\frac{1}{\sqrt{2}} \left[|K\rangle|K'\rangle - |K'\rangle|K\rangle\right]|\frac{1}{2}\rangle|\frac{1}{2}\rangle,$$

$$\frac{1}{\sqrt{2}} \left[|K\rangle|K'\rangle - |K'\rangle|K\rangle\right] \times \frac{1}{\sqrt{2}} \left[\frac{1}{2}\rangle - \frac{1}{2}\rangle + | - \frac{1}{2}\rangle| \frac{1}{2}\rangle\right],$$

$$\frac{1}{\sqrt{2}} \left[|K\rangle|K'\rangle - |K'\rangle|K\rangle\right] = | - \frac{1}{2}\rangle| - \frac{1}{2}\rangle,$$

which all have antisymmetric spatial parts. These three states are known as triplet states. The remaining state is

$$\frac{1}{\sqrt{2}} \left[|K\rangle|K'\rangle + |K'\rangle|K\rangle\right] \times \frac{1}{\sqrt{2}} \left[\frac{1}{2}\rangle - \frac{1}{2}\rangle - | - \frac{1}{2}\rangle| \frac{1}{2}\rangle\right],$$

in which the spatial part is symmetric. This state is known as a singlet state.

The important difference between these states lies in the spatial part. The two particle wavefunction will be:

$$\Psi_{\pm}(r_1, r_2) = \frac{1}{\sqrt{2}} (r_1| |K\rangle|K'\rangle \pm |K'\rangle|K\rangle) =$$

$$\frac{1}{\sqrt{2}} \left[\Psi_K(r_1)\Psi_{K'}(r_2) \pm \Psi_{K'}(r_1)\Psi_K(r_2)\right],$$

with the plus sign for the singlet state, the minus sign for a triplet state.

### 8.9 Probability Distribution for Symmetrized Wave Functions

The presence of spin requires the spatial part of the state vector to take on the symmetric or an antisymmetric forms given above. This in turn leads to different probability distributions for where e.g. electrons are likely to be found, with enormous consequences for
atomic structure, but more particularly for molecular structure. As might be expected $|\Psi_\pm(r_1, r_2)|^2 \, d^3r_1 \, d^3r_2$ is the probability of detecting a particle in $d^3r_1$ and a particle in $d^3r_2$. The normalization condition is easily shown to be:

$$\int d^3r_1 \int d^3r_2 |\Psi_\pm(r_1, r_2)|^2 = 1.$$  

In applying this result, it is necessary to be quite clear about which probability is actually being calculated. To make it precise, we shall suppose that we have two (macroscopic) particle detectors, quite distinguishable. We can then suppose that detector 1 is placed at $r_1$ in space, detector 2 at $r_2$. Each detector has a detecting volume $dV$ i.e. if a particle should be present in $dV_1$, then the detector will go off. Then, if the particle detector 1 is at $r_1 = r$ and detector 2 at $r_2 = r'$, then the probability of both detectors going off is:

$$|\Psi_\pm(r, r')|^2 \, (dV)^2$$

A different experiment is to place detector 1 at $r_1 = r'$ and detector $r_2 = r$. The probability of both detectors going off in this case is then:

$$|\Psi_\pm(r', r)|^2 \, (dV)^2 = |\Psi_\pm(r, r')|^2 \, (dV)^2$$

i.e. exactly the same, as it has to be as the particles are identical. Nevertheless, the two experiments are considered to be distinguishable, independent experiments.

We can also look more closely at the probability density $|\Psi_\pm(r_1, r_2)|^2$, given by:

$$\frac{1}{2} \left\{ |\Psi_k(r_1)|^2 |\Psi_{k'}(r_2)|^2 + |\Psi_{k'}(r_1)|^2 |\Psi_k(r_2)|^2 \pm 2 \text{Re} \left[ \Psi_k(r_1) \Psi_{k'}(r_2) \Psi_{k'}(r_1) \Psi_k^*(r_2) \right] \right\}$$

The last term is known as the exchange density. This result immediately tells us that if the particles (electrons) are in a triplet state, then for $r_1 \rightarrow r_2$ this probability density vanishes i.e. the electrons avoid one another.

By contrast, if the electrons are in the singlet state, then for $r_1 \rightarrow r_2$, the exchange density enhances the probability of finding them at the same point. Thus the electrons tend to be found together.

Finally, if $\Psi_k(r)$ is non-zero only where $\Psi_{k'}(r)$ vanishes, and vice versa i.e. the probability distribution $|\Psi_k(r)|^2$ and $|\Psi_{k'}(r)|^2$ do not overlap, then the exchange density term vanishes and we end up with

$$|\Psi_k(r_1)|^2 |\Psi_k(r_2)|^2$$

which is what we would have expected if the particles were distinguishable in the first place. Thus, having $|\Psi_k(r)|^2$ and $|\Psi_{k'}(r)|^2$ non-zero in different regions in space automatically means that even though they are identical, the particles are still distinguishable by virtue of their position in space. Thus there is no need to use antisymmetric state vectors if the particles are well separated in space.
Chapter 9

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