Notes on Quantum Mechanics

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Abstract

Quantum Mechanics is introduced using state vectors, linear operators and canonical quantisation rules. Spectra of some operators are calculated algebraically. The Schrödinger Equation, is introduced and applied to problems of a single particle in a potential field and then to some three dimensional problems.

Contents

*These notes are an edited version of notes kindly provided by D.J.Smith, who in turn based them on the notes of R.C. Johnson and on the notes I gave him.

Useful Books

- Classic Texts:

L I Schiff, *Quantum Mechanics*, McGraw-Hill (3rd edition 1968)

L D Landau and E M Lifshitz, *Quantum Mechanics*, Pergamon (2nd edition 1965)

A Messiah, *Quantum Mechanics*, Vols I & II, North-Holland (1961)

- Modern Texts:

L E Ballentine, *Quantum Mechanics*, Prentice Hall (1990)

F Mandl, *Quantum Mechanics*, John Wiley (1992)

A Sudbery, *Quantum Mechanics and the Particles of Nature*, CUP (1986)

- Standard Monograph:

P A M Dirac, *The Principles of Quantum Mechanics*, OUP (4th edition 1958)

- Background:

J D Jackson, *Mathematics for Quantum Mechanics*, Benjamin (1962)

R P Feynman, *Lectures on Physics*, Vol III, Addison-Wesley (1965)

A J G Hey & P Walters, *The Quantum Universe*, CUP (1987)

P V Landshoff & A Metherell, *Simple Quantum Physics*, CUP (1979)

J C Polkinghorne, *The Quantum World*, Longman (1984)

There are very many more.

1 Introduction

1.1 Prerequisites

This lecture course will depend very strongly on the linear algebra courses from your first two years and parts of the second year Analysis in Many Variables module. You will also need some knowledge of Hamiltonian dynamics (but we will revise what is needed.) But please, do **revise** the **linear algebra** courses from the first two years (vector spaces, bases, expansions of vectors, linear operators, eigenvectors, eigenvalues *etc.*)

1.2 Quantum Mechanics and its place

Familiar classical mechanics applies to the everyday world of moderate-sized objects. Very small things like atoms and molecules, *i.e.* objects of size of 10^{-8}m or smaller, need quantum mechanics, and the scale is set by the (reduced) Planck constant $\hbar \approx 10^{-34}$ Js (Joule seconds – SI units of energy $\times$ time.) It appears that quantum mechanics describes the world of atomic and subatomic scales probably at least down to 10^{-34}m. At scales smaller than this, strings and other objects of elementary particle physics, may be relevant and they may require a modification of standard quantum mechanics but such questions have not been resolved yet and are subjects of current research.

Classical mechanics and quantum mechanics are examples of *mathematical models* of what we (aided by measuring instruments) see around us. A mathematical model identifies measurable quantities with abstract mathematical objects that are manipulated according to certain axioms or postulates and then interpreted to make predictions. For instance in the simplest form of classical mechanics positions, momenta, forces *etc.* are identified as vectors and Newton's Laws taken as axioms that determine them. Ideally, models are accepted or rejected strictly according to the success or otherwise of their predictions. But consistency with models of neighbouring sectors of the world is important and, because models using mathematics seem always to work so well, mathematical elegance exerts a strong influence too.

Classical mechanics, in its proper domain, succeeds beautifully. Design of tables and chairs, planes and space ships depends on it crucially. But modern life depends also on the success of quantum mechanics. Quantum Mechanics describes how atoms are put together and why they are stable; is responsible for magnetism and chemistry. Apart from its high aesthetic value it has practical applications. Lasers, superconductors, atom bombs, and the ubiquitous silicon chip all work because they're designed with the help of quantum mechanics. Moreover the two models are both elegant and mutually consistent. In the limit $\hbar \to 0$ quantum mechanics gives classical results.

In addition, Quantum Mechanics is probably the most original (challenging) theory of physical phenomena. Its description is very different from that of classical mechanics and some of its predictions may appear very counter-intuitive.

In advanced classical mechanics the basic variables are the generalised coordinates and their conjugate momenta, *i.e.* the q, p coordinates in phase space. Measurable quantities like energy, force, velocity *etc.* are constructed from them. These are assumed observable to any necessary precision, simply by looking carefully enough. The equations of motion are Hamilton's equations, which are differential equations for the p's and q's as functions of time. In another, completely equivalent formulation, one uses Lagrangians, which are functions of generalised coordinates and their time derivatives (generalised velocities) and the equations of motion are the second order equations for those generalised coordinates.

In quantum mechanics the fundamental entity is the 'state vector', an element of a linear vector space. Measurements are explicitly modelled through properties of certain linear operators in the space. The equation of motion can be written as a differential equation for the state vector, the Schrödinger Equation.

It's a reasonable assumption based on everyday experience that classical measurements are possible to arbitrary accuracy. But in the quantum world of atoms and molecules normal intuition fails. In general no matter how delicate and skillful the observer, a disturbance of the observed system is inevitable. To some extent this is understandable, for looking at an atom means bouncing light off it and the atom is so small that the collision is bound to upset it. All is not lost, however, for quantum theory predicts the probabilities of alternative possible results of individual measurements. In the large-scale limit averages are observed and classical mechanics is recovered.

The linear-space structure of the theory — the superposition principle — is the key to uncertainty, for a state vector composed of other state vectors will allow a measurement to realise any of the corresponding physical configurations. Of course the superposition principle is a familiar feature of classical waves, *e.g.* sound and light. In quantum mechanics we see 'wave-particle duality' for microscopic systems.

1.3 Crisis in Classical Mechanics - Quantum Phenomena

The quantum era may be dated from Becquerel's discovery of radioactivity in 1896. But explanation as a quantum tunnelling effect did not come until Gamow, Gurney and Condon in 1928.

Planck in 1901 produced the first satisfactory theory of blackbody radiation with the revolutionary idea that matter and electromagnetic radiation interchange energy in packets ('quanta') with energy E proportional to frequency ν. The constant of proportionality is Planck's constant, h. Einstein used Planck's idea to explain features of the photoelectric effect (1905) (for which he got his Nobel prize) and to solve problems with specific heats (1907).

In 1897 Thomson discovered the electron. Its charge was difficult to measure but in experiments involving metals that were heated electrons were given off. Thomson concluded that the electron had a specific value of charge (i.e. charge was quantised) and that its mass was a very tiny fraction of the mass of the hydrogen atom. Then the question arose; if electrons are given off, where do they come from? What do atoms look like? Hence Thomson proposed a "plum pudding" model of the atoms - involving a cloud of positively charged material with negatively charged electrons stuck in it. However, in 1911 Rutherford showed that this is wrong. His scattering experiments suggested that the atom consists of a cloud some 10^{-8}cm across of electrons bound by Coulomb attraction to a relatively massive central nucleus about 10^{-13}cm across. But according to classical notions this system is completely unstable, since the bound charges are accelerated and therefore radiate electromagnetic waves. So they rapidly lose energy and the atom collapses. Classical mechanics *inevitably* predicts unstable matter with a lifetime of typically 10^{-10} seconds! This is even before understanding how such apparently insubstantial things, mostly empty space, can be arranged into solids, liquids and gases.

Bohr (1913) introduced stability at the atomic level with the *ad hoc* postulate that atomic electrons can have angular momentum equal only to an integral multiple of $\hbar \equiv h/2\pi$. Transitions between two of the resulting discrete electronic energy-levels separated by E then conserve energy by emitting or absorbing radiation quanta of definite frequency $\nu = E/h$. This model agrees with the main features of the line spectra of light emitted from simple atoms.

Explanation of finer structure in atomic spectra came after the discovery of electron spin and magnetic moment, following the Stern-Gerlach experiments (1921). The electron behaves like a spinning charge with angular momentum $\frac{1}{2}\hbar$. Subtleties stemming from this (Fermi-Dirac Statistics) led to successful models of multi-electron atoms and eventually (in the 50s) to understanding the stability of bulk matter.

But meanwhile Compton (1923) found that X-rays (wavelength $\lambda \sim 10^{-11}$cm) scatter from atomic electrons like particles ('photons') moving at the speed of light c with momentum $p = h/\lambda$ and energy $E = hc/\lambda = h\nu$. In 1925 de Broglie proposed that also electrons and other particles might show wave-like behaviour, with wavelength and momentum related by $\lambda = h/p$. For atomic electrons, if they occupy only circular orbits with a standing de Broglie wave, the Bohr quantisation rule follows since in such an orbit of circumference $2\pi r$ there is a whole number of wavelengths h/p. Davisson and Germer (1927) confirmed diffraction and interference of electrons scattered by metals for de Broglie wavelengths of the order of atomic size and spacing.

During the 20s Heisenberg, Born and Jordan were introducing matrix mechanics, Schrödinger was developing wave mechanics from de Broglie's idea, and Dirac (1926) discovered that both are manifestations of a new linear theory. Schrödinger's theory of the hydrogen atom (the simplest) agreed remarkably with the Bohr model.

In quantum mechanics wave-particle duality and quantisation of energy and angular momentum come directly from non-commutativity of linear operators that model observations. Another consequence is the Uncertainty Principle and statistical scatter of individual observations.

2 Theory of Quantum Mechanics

2.1 States

The configuration of a classical system at any time is specified by a point in $2n$ dimensional phase space — *i.e.* by its coordinates, the set of q's and p's. Equivalent description is in terms of a point (and its velocity) in configuration space. The mathematical objects of the theory are these coordinates as functions of time. Other observables are constructed from them. Of course, some quantities, do not play a role; *i.e.* colour of a falling ball or its internal structure. Thus they not appear in the description.

For a quantum system the q's and p's are not all simultaneously measurable with precision ('compatible'), as will appear. A configuration is instead specified by a set of measurements that *are* mutually compatible. The results of these are used as labels for a 'state vector'. A state is thus described as an *undisturbed motion* that is restricted by as many conditions as are theoretically possible without mutual interference.

The state vector (or state for short) is the central mathematical object and contains all information about the system. It is written $|\alpha\rangle$ in the Dirac notation, where α stands for the set of labels needed for unambiguous specification in the current context.

In classical mechanics the basic quantities are functions of time which thus belong to a (vector) space of functions. Similarly, the quantum mechanical state vector also belongs to a vector space which, as we will see, is a complex Hilbert space (a complete vector space with an inner (scalar) product).

> **Examples:** $|\mathbf{p}\rangle$ could be a state of a particle of momentum $\mathbf{p}$; $|E, \mathbf{p}\rangle$ could be a state of a free particle of definite energy and momentum; $|\mathbf{r}_1, \mathbf{r}_2\rangle$ could be a state of two particles at positions $\mathbf{r}_{1,2}$; $|E, j, m\rangle$ could be a state of an atom with definite energy, angular momentum and z-component of angular momentum; $|E_n\rangle$ or just $|n\rangle$ could be the state of a system with energy E_n, the n^{th} of a discrete set of possibilities.

> **Examples:** Other, more homely, mathematical theories may be formulated with state vectors, and operators. For instance, models of:- travel round networks; stochastic (Markov) processes.

State vectors $|\alpha\rangle$ belong to a linear vector space over $\mathbf{C}$, comprising all possible states of the system. The axioms of a linear vector space involve the existence of a zero element and commutativity with numbers. The superposition principle is very important: if $|\alpha\rangle$ and $|\beta\rangle$ are in the space then so is $c_1|\alpha\rangle + c_2|\beta\rangle$ for all complex $c_{1,2}$.

Superposition in quantum mechanics embodies uncertainty, for a state may be linearly composed of other states, each corresponding to a different possible outcome of a measurement.

> **Example:** If an atom may be observed to have energies E_1 or E_2, with corresponding states (state vectors) $|E_1\rangle$ and $|E_2\rangle$, then another possible state of the atom is described by the state (vector) $|\psi\rangle = |E_1\rangle + |E_2\rangle$, say. (Here the ψ sign is just a convenient state label. It *doesn't* mean that $|\psi\rangle$ has energy $E_1 + E_2$ nor that its energy$=\psi$. As will become clear, an energy measurement made on state $|\psi\rangle$ may realise either outcome, E_1 or E_2, with equal probability.

The theory gives the same significance to $|\alpha\rangle$ and $c|\alpha\rangle$ for any non-zero complex number c. Such an equivalence corresponds to considering **rays** in the space of states. Often one exploits this equivalence and considers normalised states of the original space. However, for this to be made precise one needs to define the norm.

• With each state vector $|\alpha\rangle$ is associated a dual vector $\langle\alpha|$. Then the inner or scalar product of two states is defined as the complex number $\langle\alpha|\beta\rangle$ with the property that

$$\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle^*$$

where * means complex conjugate. Note that this implies that the dual to the state vector $c|\alpha\rangle$ is $c^*\langle\alpha|$ and that $\langle\alpha|\alpha\rangle$ is a real number.

In Dirac's terminology $|\alpha\rangle$ is called a 'ket vector' and its dual $\langle\alpha|$ is called a 'bra vector'.

As usual the inner product is distributive over linear combination of states and obeys

$$\langle\alpha|\alpha\rangle \geq 0$$

with equality iff $|\alpha\rangle = 0$. Then the Schwarz Inequality

$$\langle\alpha|\alpha\rangle\langle\beta|\beta\rangle \geq |\langle\alpha|\beta\rangle|^2$$

follows from $\langle\gamma|\gamma\rangle \geq 0$ for all complex c where $|\gamma\rangle = |\alpha\rangle + c|\beta\rangle$. Also the convention is to normalise states to

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

whenever possible. This fixes any multiplicative complex constant up to a phase (and in fact corresponds to standard normalisation of probability density functions, as will appear).

> **Examples:**
> (i) If $|\alpha\rangle$ *etc.* are represented by complex-valued functions $\psi_\alpha(x)$ *etc.* of the real variable $x \in (0,1)$ then a suitable inner product $\langle\alpha|\beta\rangle$ is
>
> $$\int_0^1 \psi_\alpha^*(x)\psi_\beta(x)\,dx.$$
>
> (ii) With states represented by column vectors α_i *etc.* then an appropriate inner product is $\alpha^+\beta$, where α^+ is the Hermitian conjugate of α — that is, its transpose with complex conjugate elements.

Examples (i) and (ii) illustrate several ideas — normalisation for instance: in (i) $\psi_\alpha = \sqrt{2}\sin\pi x$ is normalised by the factor $\sqrt{2}$. An unnormalised state $|\alpha\rangle$ can always be normalised by dividing by $\langle\alpha|\alpha\rangle^{1/2}$. Note that an additional factor $e^{i\theta}$ for any real θ does not change the normalisation.

Two states are mutually orthogonal if their inner product is zero; the only state orthogonal to all others is the zero vector. Examples in cases (i) and (ii) are easy to find.

• Recall the idea of linear independence of a set of vectors, remember that a spanning set can be used to express any vector in the space as a linear combination, and recall that a basis for a linear vector space is a linearly-independent spanning set.

In quantum mechanics it is assumed that the state space is spanned by a set of states corresponding to all the different possible outcomes of measurements of relevant observable quantities — momentum, energy, angular momentum, position, or whatever — *i.e.* physical completeness corresponds to mathematical completeness. These spanning states turn out to be mutually orthogonal (or can be made so by the Gram-Schmidt procedure), hence they are linearly independent, and so basis sets. They may be finite or infinite in number, depending on the system and on the observable. Of course because some measurements are mutually incompatible their corresponding bases are alternatives. The usual basis is that corresponding to a maximal set of mutually compatible measurements. This is less vague than it sounds for the simplest quantum systems.

Note that if an orthogonal basis $\{|i\rangle; i = 1, \ldots; \langle i|j\rangle = 0, i \neq j\}$ is normalised: $\langle i|i\rangle = 1$, then in the basis expansion

$$|\alpha\rangle = \sum_i c_{i,\alpha}|i\rangle$$

the coefficients $c_{i,\alpha}$ are simply given by

$$c_{i,\alpha} = \langle i|\alpha\rangle.$$

If moreover $|\alpha\rangle$ is normalised then

$$\sum_i |c_{i,\alpha}|^2 = 1.$$

Examples: In case (i) recall Fourier Series; in case (ii) there is the standard basis $\{u_i\}$ where u_i has 1 as its i'th element and zero elsewhere.

We assume at present that the basis is discrete (countable). Infinite-dimensional inner-product spaces over **C** like this are called Hilbert Spaces. Comment: note, however, that the condition of countability of the set of basis vectors is sometimes relaxed.

2.2 Operators

All physical information contained in a system's state vector is extracted by certain **linear operators** acting in the state space. Any operator $\widehat{A}$ in the space maps states to states:

$$|\alpha\rangle \to |\beta\rangle = \widehat{A}|\alpha\rangle.$$

A *linear* operator commutes with complex numbers and its operation is distributive over vector addition.

Examples: A simple linear operator is the identity $\widehat{I}$ that maps every vector to itself. Another is the 'back-to-back' pairing of a vector and a dual vector

$$\widehat{A} = |\alpha\rangle\langle\beta|$$

that maps $c_1|\gamma\rangle + c_2|\delta\rangle$ to the state $|\alpha\rangle$ multiplied by the complex number $c_1\langle\beta|\gamma\rangle + c_2\langle\beta|\delta\rangle$. In example (i) there are differential operators d/dx, d^2/dx^2 etc; and in (ii) linear operators are (complex) square matrices.

- The sum of two operators is an operator. Writing the expansion of an arbitrary vector

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

in terms of any complete orthonormal (basis) set $\{|i\rangle; \langle i|j\rangle = \delta_{ij}\}$ we deduce a representation of the identity operator;

$$\widehat{I} = \sum_i |i\rangle\langle i|.$$

Each term $|i\rangle\langle i|$ is an example of a projection operator.

- The product $\widehat{A}\widehat{B}$ is an operator defined by

$$\widehat{A}\widehat{B}|\alpha\rangle = \widehat{A}(\widehat{B}|\alpha\rangle)$$

for all states $|\alpha\rangle$.

Examples: For any $\widehat{A}$ we have $\widehat{A}\widehat{I} = \widehat{I}\widehat{A} = \widehat{A}$. For projectors $\widehat{P}_i = |i\rangle\langle i|$ we have $\widehat{P}_i \widehat{P}_j = \delta_{ij}\widehat{P}_j$.

Operator multiplication is generally not commutative, as illustrated by operators $|\alpha\rangle\langle\beta|$ and $|\gamma\rangle\langle\delta|$. Non-commutativity is significant in discussion of compatibility of measurements, when it is useful to define the 'commutator'

$$[\widehat{A}, \widehat{B}] \equiv \widehat{A}\widehat{B} - \widehat{B}\widehat{A}.$$

We will appreciate the true significance of the commutator later, when we discuss the compatibility of measurements.

Note that the commutator has properties similar to those of the Poisson Bracket of classical mechanics:

$$[\widehat{A}, \widehat{B}] = -[\widehat{B}, \widehat{A}]$$

$$[\widehat{A} + \widehat{B}, \widehat{C}] = [\widehat{A}, \widehat{C}] + [\widehat{B}, \widehat{C}]$$

$$[c\widehat{A}, \widehat{B}] = c[\widehat{A}, \widehat{B}]$$

$$[\widehat{AB}, \widehat{C}] = \widehat{A}[\widehat{B}, \widehat{C}] + [\widehat{A}, \widehat{C}]\widehat{B}$$

$$[\widehat{A}, [\widehat{B}, \widehat{C}]] + [\widehat{C}, [\widehat{A}, \widehat{B}]] + [\widehat{B}, [\widehat{C}, \widehat{A}]] = 0.$$

The last of these is the 'Jacobi Identity'.

- Positive integer powers of operators are defined by $\widehat{A}^n = \widehat{A}(\widehat{A}^{n-1})$ with $\widehat{A}^0 = \widehat{I}$. The usual index laws apply and the unique inverse $\widehat{A}^{-1}$ obeys

$$\widehat{A}\widehat{A}^{-1} = \widehat{A}^{-1}\widehat{A} = \widehat{I}$$

if it exists. The inverse of a product of operators is easily seen to be the product of inverses in reverse order.

- Functions of operators, like $\exp \widehat{A}$, can be defined by *e.g.* power-series expansion. Then *e.g.* $(\exp \widehat{A})^{-1} = \exp -\widehat{A}$, but some convention is needed to deal with expressions like $\exp(\widehat{A} + \widehat{B})$ if $[\widehat{A}, \widehat{B}] \neq 0$. Clearly functions of operators commute iff the operators themselves commute.

- The inner product $\langle\alpha|(\widehat{A}|\beta\rangle)$ is written symmetrically as

$$\langle\alpha|\widehat{A}|\beta\rangle$$

and called a matrix element of $\widehat{A}$. The matrix elements of $\widehat{A}$ define its action in the dual space by defining the bra vector $\langle\alpha|\widehat{A}$ for arbitrary $|\beta\rangle$.

> **Examples:** The dual-space action of $\widehat{A} = |\gamma\rangle\langle\delta|$ is clear. In the space of example (ii) of column vectors u_α, with duals the rows u_α^+ and where the operators are square matrices M, the result is just the matrix product $u_\alpha^+ M$. In the function space (i) for differential operators where the inner product is an integral the corresponding dual space operation is defined by integration by parts, with homogeneous conditions specified to make boundary terms vanish.

- The vector dual to the ket $\widehat{A}|\alpha\rangle$ is the bra $\langle\alpha|\widehat{A}^\dagger$. Therefore the definition of the adjoint operator $\widehat{A}^\dagger$ uses the complex inner product property, *i.e.*

$$\langle\alpha|\widehat{A}^\dagger|\beta\rangle = \langle\beta|\widehat{A}|\alpha\rangle^*$$

for all states.

> **Examples:** If $\widehat{A} = |\gamma\rangle\langle\delta|$ then $\widehat{A}^\dagger = |\delta\rangle\langle\gamma|$. In (ii) the adjoint of square matrix M is its Hermitian conjugate M^+. In function space (i), for a differential operator, integrate by parts.

It is easily seen that $(\widehat{A}^\dagger)^\dagger = \widehat{A}$, that the adjoint of a product is the product of adjoints in reverse order and that $(c\widehat{A})^\dagger = c^*\widehat{A}^\dagger$.

- The eigenvalue problem for an operator: if

$$\widehat{A}|a\rangle = a|a\rangle$$

for some complex number a and non-zero vector $|a\rangle$, then $|a\rangle$ is an eigenvector of $\widehat{A}$ belonging to eigenvalue a. (Using a as state label is actually consistent with labelling by possible results of observation, as we will see later, the latter turn out to be just eigenvalues).

Note that the equation defining an eigenvector is homogeneous so normalisation is arbitrary and can be chosen for convenience.

The set of eigenvalues and eigenvectors of $\widehat{A}$ is called its **spectrum**. The spectrum of $\widehat{A}$ can be empty, finite, countably infinite, or continuous. Some operators in quantum mechanics have an infinite spectrum, part countable and part continuous.

> **Examples:** If $\widehat{A} = |\alpha\rangle\langle\beta|$ then its spectrum consists of eigenvector $|\alpha\rangle$ with eigenvalue $\langle\beta|\alpha\rangle$, plus any non-zero states orthogonal to $|\beta\rangle$, each with eigenvalue zero. The projector $|i\rangle\langle i|$ is a particular case. This illustrates the possibility of 'degeneracy', when two or more linearly independent eigenvectors belong to the same eigenvalue. For instance the entire spectrum of $\widehat{I}$ is degenerate, as any non-zero state is an eigenvector with eigenvalue unity. If the vectors in space (ii) have n components we have the familiar $n \times n$ matrix eigenvalue problem, where besides degeneracy a defective spectrum is common. In a space (i) of functions $\psi(x)$ on [0,1] the operator d/dx has an empty spectrum if the space is restricted by the boundary condition $\psi(0) = \psi(1) = 0$. However with these boundary conditions the operator d^2/dx^2 has eigenvectors $\sin n\pi x$ with eigenvalues $-(n\pi)^2$ for $n = 1, 2 \ldots$. If there are no boundary conditions the spectrum of d/dx is $\psi_a(x) = \exp(ax)$ for any complex eigenvalue a, and that of d^2/dx^2 is $\psi_a(x) = \exp(\pm iax)$ with eigenvalue $-a^2$ for any a; twofold degeneracy. Note the illustration of possible dangers in too carelessly asserting that if $\widehat{A}|a\rangle = a|a\rangle$ then $\widehat{f}(\widehat{A})|a\rangle = f(a)|a\rangle$, although this is usually true.

> **Theorem:** If both operators $\widehat{A}$ and $\widehat{B}$ have non-empty spectra then they have a common set of eigenvectors if $[\widehat{A}, \widehat{B}] = 0$. The converse is true if the eigenvectors are complete in the space.

Proof: Let $\widehat{A}\widehat{B} = \widehat{B}\widehat{A}$ and $\widehat{A}|a\rangle = a|a\rangle$. Then

$$\widehat{A}\left(\widehat{B}|a\rangle\right) = \widehat{B}\widehat{A}|a\rangle = a\left(\widehat{B}|a\rangle\right).$$

The inference is that either $\left(\widehat{B}|a\rangle\right)$ is zero or, since it obeys the same eigenvalue equation as $|a\rangle$, it must actually *be* $|a\rangle$ — up to a factor anyway — *i.e.* $\widehat{B}|a\rangle = b|a\rangle$. The inference made here is a crucial step appearing repeatedly. It is clearly true if the eigenvalue a is unique (non-degenerate). Otherwise $\widehat{B}|a\rangle$ is some linear combination of degenerate states with eigenvalue a. However the degenerate subspace may be diagonalised with respect to $\widehat{B}$ and so simultaneous eigenvectors constructed. Thus the first part is proved. To establish the converse, if both $\widehat{A}|a,b\rangle = a|a,b\rangle$ and $\widehat{B}|a,b\rangle = b|a,b\rangle$ then $\widehat{A}\widehat{B}|a,b\rangle = ab|a,b\rangle = \widehat{B}\widehat{A}|a,b\rangle$. This holds for any linear combination of eigenvectors $|a,b\rangle$ and so we deduce that $[\widehat{A}, \widehat{B}] = 0$ if the set $\{|a,b\rangle\}$ is complete. Completeness is assumed in quantum mechanics for operators identified with observables.

• It's important to realise, and worth repeating, that even if $[\widehat{A}, \widehat{B}] = 0$ then an eigenstate of $\widehat{A}$ is not *automatically* an eigenstate of $\widehat{B}$ *unless* the spectrum of $\widehat{A}$ is non-degenerate!

> **Example:** Commuting pairs with common eigenvectors include $\widehat{A}$ and $\widehat{f}(\widehat{A})$, but then degeneracy may appear. For instance when $\widehat{A} = \frac{1}{2}\widehat{p}^2$ and $\widehat{B} = \widehat{p}$ then eigenstates of $\widehat{A}$ are generally linear combinations of two eigenstates of $\widehat{B}$ with eigenvalues $\pm p$. See also the examples of d/dx and d^2/dx^2 above. Some operators apply to separate spaces and commute for this reason — the momentum and spin observables of a particle for instance.

• Two very important special types of operator are **self-adjoint** operators and **unitary** operators. Operator $\widehat{S}$ is **self-adjoint** (or Hermitian) if $\widehat{S} = \widehat{S}^\dagger$, *i.e.* if

$$\langle\alpha|\widehat{S}|\beta\rangle = \langle\beta|\widehat{S}|\alpha\rangle^*$$

for all states $|\alpha\rangle, |\beta\rangle, \ldots$ in a complete set.

Examples: Both $\widehat{I}$ and $\widehat{P}_i = |i\rangle\langle i|$ are clearly self-adjoint; for (ii) with square matrices M the property is $M = M^+$, *i.e.* M is an Hermitian matrix. In space (i) with $\psi(0) = \psi(1) = 0$, operator d/dx is not self-adjoint while id/dx and d^2/dx^2 are. (Integrate by parts).

Preceding examples illustrate the following:

Theorem: The eigenvalues of a self-adjoint operator (if it has any!) are real and the eigenvectors belonging to different eigenvalues are orthogonal.

Firstly observe that if $\widehat{S}|s\rangle = s|s\rangle$ the dual equation is $\langle s|\widehat{S} = s^*\langle s|$, giving two results for $\langle s|\widehat{S}|s\rangle$ that imply $s = s^*$ since $\langle s|s\rangle \neq 0$. Secondly, if $\widehat{S}|s_i\rangle = s_i|s_i\rangle$ for $i = 1, 2$ then the case $i = 1$ and the dual of the case $i = 2$ give two calculations of $\langle s_2|\widehat{S}|s_1\rangle$ — which leads at once to $(s_1 - s_2)\langle s_2|s_1\rangle = 0$ and if $s_1 \neq s_2$ orthogonality is established. In fact this applies to the whole spectrum since degenerate eigenvectors can be orthogonalised by the Gram-Schmidt method.

A useful spectral representation of $\widehat{S} = \widehat{S}^\dagger$ (of which the resolution of $\widehat{I}$ into projectors is a special case) is found by using its (assumed) complete set of orthonormal eigenvectors. *i.e.* Since $\widehat{S}|\alpha\rangle = \sum_s \widehat{S}|s\rangle\langle s|\alpha\rangle$ we can write $\widehat{S} = \sum_s |s\rangle s\langle s|$.

- Operator $\widehat{U}$ is **unitary** if $\widehat{U}^{-1} = \widehat{U}^\dagger$. Then $\widehat{U}\widehat{U}^\dagger = \widehat{U}^\dagger\widehat{U} = \widehat{I}$ so that if $|\alpha\rangle = \widehat{U}|\beta\rangle$ then $\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle$ *i.e.* have the same norm; thus $\widehat{U}$ is norm preserving. If further $|\alpha\rangle = c|\beta\rangle$ then we see that all (complex) eigenvalues c of $\widehat{U}$ have modulus unity.

Clearly $\widehat{I}$ is unitary; so is any operator $\widehat{U}(\theta) = \exp(i\theta\widehat{S})$ where θ is real and $\widehat{S} = \widehat{S}^\dagger$. This parametrisation is useful when $\widehat{U}$ is connected continuously to the identity $\widehat{I} = \widehat{U}(0)$. Then the connection between unitary (norm-preserving) operators and self-adjoint (observable) operators is of great significance.

2.3 Measurements: Physical Assumptions

We make two basic assumptions which connect the mathematical formulation of the theory to the observations (*i.e.* measurements) of physical quantities.

The first postulate (**connection with physics**) states:

To every physically observable quantity *i.e.* an observable A corresponds a self-adjoint linear operator $\widehat{A}$ in the state space with a complete set of eigenvectors $\{|a\rangle\}$ (and conversely).

The second postulate (**the measurement postulate**) states:

A single measurement of A on a system in state $|\alpha\rangle$ gives one of the (real) eigenvalues a of $\widehat{A}$ with probability $|\langle a|\alpha\rangle|^2$. After the measurement the state is $\sim |a\rangle$.

Note that results of observations are real numbers, and this statement assumes for now that the spectrum of $\widehat{A}$ is discrete and that state $|\alpha\rangle$ and (orthogonal) eigenstates $\{|a\rangle; \widehat{A}|a\rangle = a|a\rangle\}$ are normalised to unity. Otherwise $|\langle a|\alpha\rangle|^2$ is a *relative* probability.

The set of 'observables' includes (usually) the basic degrees of freedom of the system — the classical p's and q's — and quantities derived from them.

Examples: For a particle, observables include position $\mathbf{r}$, linear momentum $\mathbf{p}$, plus *e.g.* kinetic energy $T(\mathbf{p})$, potential energy $V(\mathbf{r})$, angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, as well as any intrinsic properties like spin, electric charge, *etc.*

The measurement postulate refers to a result of an observation merely having a probability of realisation. It's goodbye to classical determinism — results of measurements on quantum systems are generally uncertain even when the state vector is known.

At the heart of this is the basis expansion of a state in terms of eigenstates of the observable $\widehat{A}$: if $|\alpha\rangle = \sum_a c_{a,\alpha}|a\rangle$ then the size of the coefficient $c_{a,\alpha} = \langle a|\alpha\rangle$ determines the 'amount of $|a\rangle$ present'. In fact the squared moduli are the probabilities of getting the a's — and normalisation of the states makes their sum equal to 1.

If it happens that $|\alpha\rangle = |a\rangle$, an eigenstate of $\widehat{A}$, then measurement of A is certain (probability=1) to give result a (from normalisation) and never (probability=0) gives any other outcome (from orthogonality). The system is 'in a state of definite A'.

However, when the system is **not** in a state of definitive A the measurement changes the state:

$$|\alpha\rangle \to \lambda|a\rangle,$$

where $|a\rangle$ is an eigenstate of $\widehat{A}$. The factor λ is there to indicate that after the measurement the vector is not normalised. However, as the states correspond to rays - the resultant vector can be normalised by multiplication by an appropriate λ.

Note that the process of measurement is very "acausal"; one way to think of it is to put

$$|\alpha\rangle = \sum_a c_{a,\alpha}|a\rangle \;\to\; |a\rangle$$

and we have "the reduction of the wave function" or "the collapse of the state vector" onto (just one) eigenvector of $\widehat{A}$.

Note that as after the measurement of $\widehat{A}$ which gave the value a the state vector is an eigenstate of $\widehat{A}$ the successive remeasurements of the same observable (*i.e.* of $\widehat{A}$) will give the same answer *i.e.* a. This is how the theory describes the sudden change in the observer's state of knowledge and the "preparation" of a system to being in a definite state.

Exactly how a non-deterministic collapse of the state vector takes place, especially when the 'observer' should in principle be described by quantum mechanics too, is a feature that provokes discussion.

- Making a measurement of A on each of a large number of identically-prepared copies of a system generally gives a distribution of results, for which the ordinary mean or mathematical expectation $\langle A\rangle$ is given by $\sum_a(\text{result})_a(\text{probability})_a$. Each copy of the system has by definition the same state vector $|\alpha\rangle$ so we have:

$$\langle A\rangle = \sum_a a\,|\langle a|\alpha\rangle|^2 = \sum_a \langle\alpha|a\rangle a\langle a|\alpha\rangle$$

and, recognising the spectral representation of $\widehat{A}$, we obtain the important formula

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

for an expectation value in quantum mechanics.

If A is observed on many identical systems then its expectation value is $\langle A\rangle$ and the standard deviation ΔA is a familiar measure of scatter of results defined by $(\Delta A)^2 \equiv \langle(A-\langle A\rangle)^2\rangle \equiv \langle A^2\rangle - \langle A\rangle^2$. Note that with the formula $\langle A\rangle = \langle\alpha|\widehat{A}|\alpha\rangle$ we have $\Delta A = 0$ iff $|\alpha\rangle$ is an eigenvector of $\widehat{A}$.

- Observables are simultaneously measurable with precision (compatible) if their corresponding operators commute, for as seen above, a state can then be an eigenstate of them all. The common eigenstates of a complete set of mutually commuting observables form an orthonormal basis for the state space — they include all possible outcomes of measurement of all compatible A's and physical completeness is equated to mathematical completeness. What constitutes the former is a physical judgement and usually includes at least those observables from which is built the system's most important operator — the Hamiltonian operator, controlling its time-dependence (as described below).

- Observables that are not compatible have non-commuting operators and the degree of the mutual interference of their measurement is given precise meaning in terms of their commutator, as shown in the following theorem

> **Theorem:** Let A and B be observables with self-adjoint operators $\widehat{A}$ and $\widehat{B}$. Then for a quantum system in state $|\alpha\rangle$ at a given instant
>
> $$\Delta A \Delta B \geq \tfrac{1}{2}\left|\langle\alpha|[\widehat{A},\widehat{B}]|\alpha\rangle\right|.$$

Proof: Let $\widehat{A}' = \widehat{A} - \langle\alpha|\widehat{A}|\alpha\rangle\widehat{I}$, similarly $\widehat{B}'$. Then both $\widehat{A}'$ and $\widehat{B}'$ are self-adjoint (expectation values of self-adjoint operators are real) and their commutator is identical to $[\widehat{A}, \widehat{B}]$. Therefore

$$\langle\alpha|[\widehat{A}, \widehat{B}]|\alpha\rangle = \langle\alpha|\widehat{A}'\widehat{B}'|\alpha\rangle - \langle\alpha|\widehat{B}'\widehat{A}'|\alpha\rangle = 2i\mathrm{Im}\langle\alpha|\widehat{A}'\widehat{B}'|\alpha\rangle.$$

Note that the product of two self-adjoint operators is not self-adjoint unless they commute, so its expectation value is not real. We now have

$$\tfrac{1}{2}\left|\langle\alpha|[\widehat{A}, \widehat{B}]|\alpha\rangle\right| \leq \left|\langle\alpha|\widehat{A}'\widehat{B}'|\alpha\rangle\right| \leq \sqrt{\langle\alpha|(\widehat{A}')^2|\alpha\rangle\langle\alpha|(\widehat{B}')^2|\alpha\rangle}.$$

The last step uses the Schwarz inequality and the square root is just $\Delta A\Delta B$. So the result is proved.

The conclusion is that incompatible measurements carried out simultaneously on copies of a system always give a scatter of results. This is a manifestation of uncertainty in quantum mechanics.

Thus, after measurement of A, a measurement of quantity B on the same system will give an uncertain result if $[\widehat{A}, \widehat{B}] \neq 0$, for the system cannot now be in an eigenstate of $\widehat{B}$, even if it was originally. The mutual interference of incompatible observations on the same system is thus clear. This is another aspect of quantum mechanical uncertainty.

2.4 Revision of Classical Mechanics

Newton's second law for a particle of mass m at position $\mathbf{r}$ and experiencing force $\mathbf{F}$ is

$$\frac{d\mathbf{p}}{dt} = \mathbf{F},$$

where $\mathbf{p} = m\dot{\mathbf{r}}$. Taking the vector product with $\mathbf{r}$ leads to introduction of angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, which is conserved for central forces. Taking the scalar product with $\dot{\mathbf{r}}$ and integrating with respect to time t leads to discussion of work and of energy and its conservation, and for conservative forces to the introduction of a potential $V(\mathbf{r})$ where $\mathbf{F}(\mathbf{r}) = -\nabla V$. Extended systems are treated as assemblies of interacting particles.

Advanced formulations use energy. Generalised coordinates $q_i(t)$ in an N-dimensional abstract 'configuration space' are used to eliminate constraint forces that do no work. They coincide with coordinates in ordinary space only in simple cases. N counts the system's 'degrees of freedom'. The Lagrangian $\mathcal{L}$ is defined in terms of kinetic energy $T(q_i, \dot{q}_j)$ and potential energy V as

$$\mathcal{L}(q_i, \dot{q}_j) = T - V.$$

The N second-order Lagrangian equations of motion

$$\frac{d}{dt}\left(\frac{\partial\mathcal{L}}{\partial\dot{q}_i}\right) = \frac{\partial\mathcal{L}}{\partial q_i}$$

then follow as necessary conditions for the 'action'

$$S = \int \mathcal{L}\, dt$$

(which measures mean energy interchange in the motion) to be stationary against variations in each trajectory $q_i(t)$ independently.

Comments:

- 1. The principle of least action is equivalent to Newton's second law.
- 2. The principle involves certain acausality. How does the particle know which way to go? Does it try all possibilities? In fact Quantum Mechanics solves this problem. All trajectories are used but classically we observe only those of least action. (This leads us to Feynman's path integral formulation of Quantum Mechanics.)

Generalised momentum

$$p_i \equiv \frac{\partial \mathcal{L}}{\partial \dot{q}_i}$$

conjugate to q_i is conserved if $\partial\mathcal{L}/\partial q_i = 0$. Linear momentum is conjugate to linear displacement; angular momentum is conjugate to angular displacement.

The Hamiltonian is

$$H(q_i, p_j) = -\mathcal{L}(q_i, \dot{q}_j) + \sum_{k=1}^{N} p_k \dot{q}_k$$

with $\dot{q}$'s eliminated in favour of p's. If (as is usual) T is bilinear in $\dot{q}$'s the Hamiltonian is total energy $T+V$ expressed in the p, q variables. The p's and q's are independent dynamical variables; a configuration of the system is a point in the $2N$-dimensional $p-q$ 'phase space'. Its time development is a path traced out according to the $2N$ first-order Hamilton equations of motion

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}, \qquad \dot{q}_i = \frac{\partial H}{\partial p_i}.$$

Observables like position, velocity, momentum, angle, angular momentum, energy *etc.* are constructed from the phase-space coordinates q, p. Any observable A depends on time t through these coordinates, as well as possibly explicitly. Then using the chain rule and Hamilton's equations we have

$$\frac{dA}{dt} = \frac{\partial A}{\partial t} + \{A, H\}$$

where the **Poisson Bracket** of A and H appears. This is defined for any two functions A, B of the p's and q's as

$$\{A, B\} \equiv \sum_{k=1}^{N} \left(\frac{\partial A}{\partial q_k}\frac{\partial B}{\partial p_k} - \frac{\partial A}{\partial p_k}\frac{\partial B}{\partial q_k} \right)$$

and is an invariant of canonical transformations, *i.e.* changes of variables that leave the form of Hamilton's equations intact. The Poisson Bracket has properties:

$$\{A, B\} = -\{B, A\}$$
$$\{A + B, C\} = \{A, C\} + \{B, C\}$$
$$\{cA, B\} = c\{A, B\}$$
$$\{AB, C\} = A\{B, C\} + \{A, C\}B$$
$$\{A, \{B, C\}\} + \{C, \{A, B\}\} + \{B, \{C, A\}\} = 0.$$

Comments:

- 1. This is another equivalent formulation of Classical Mechanics.
- 2. Poisson Bracket of A and B has the same properties as the commutator of $\widehat{A}$ and $\widehat{B}$.
- 3. The basic Poisson Bracket is
$$\{q_j, p_k\} = \delta_{jk}.$$
- 4. An observable A is conserved (a constant of the motion) if both $\partial A/\partial t = 0$ and $\{A, H\} = 0$. So for instance energy is conserved if H is not explicitly t-dependent.

  Example: The simple pendulum, which is a mass-point on a light inextensible string making *small* oscillations in a plane about equilibrium under gravity alone, has one degree of freedom and is an example of a (one-dimensional) simple-harmonic oscillator. If mass is m and linear displacement is q, then kinetic energy is $T = \frac{1}{2}m\dot{q}^2$ and potential energy is $V = \frac{1}{2}m\omega^2 q^2$. Here ω is angular frequency of oscillation, related to the length of the string and the acceleration of gravity. Conjugate momentum is $p = m\dot{q}$ and the Hamiltonian is $H = \frac{1}{2}((p^2/m) + m\omega^2 q^2)$. Total energy is identical to H and is conserved. The classical oscillator is important because quite general systems near equilibrium can be decoupled into normal modes undergoing simple harmonic motions. And in quantum mechanics the quadratic Hamiltonian is one of the few completely soluble examples.

2.5 Quantum Conditions

The theory gets some content by the specification of commutators of operators. This allows the computation of their spectra and so of the actual results of measurements. This is also the place where Planck's constant $\hbar$ enters.

The 'canonical' quantisation postulate (**the correspondence principle**) states that for any two observables

$$[\widehat{A}, \widehat{B}] = i\hbar\{A, B\},$$

i.e. that the commutator of two self-adjoint operators is equal to $i\hbar\times$(the result of calculating the Poisson Bracket of the corresponding classical quantities), where the result is interpreted as an operator. Plainly this is not inconsistent with the properties of self-adjoint operators, commutators and Poisson Brackets. But, most importantly, the resulting theory agrees with the experiment. It also has the correct classical limit.

An immediate application is to the degrees of freedom q and p themselves. While $[\widehat{q}_i, \widehat{q}_j] = [\widehat{p}_i, \widehat{p}_j] = 0$ we have

$$[\widehat{q}_j, \widehat{p}_k] = i\hbar\delta_{jk}\widehat{I}.$$

That is, a generalised coordinate and its conjugate momentum are always incompatible.

At the same time, from the result for the dispersions **the Heisenberg Uncertainty Relation** follows:

$$\Delta A\Delta B \geq \tfrac{1}{2}\hbar\left|\{A, B\}\right|,$$

which for the p,q coordinates reads

$$\Delta q_j\Delta p_k \geq \tfrac{1}{2}\hbar\delta_{jk}.$$

So for a quantum system like an electron or atom or molecule with position $\mathbf{r}$ and linear momentum $\mathbf{p}$ the x-components (say) cannot be precisely determined together and many measurements on identically prepared systems have dispersions constrained by

$$\Delta x\Delta p_x \geq \tfrac{1}{2}\hbar.$$

Planck's constant sets a fundamental limit of smallness. Note however that *e.g.* y and p_x are compatible and can be measured together exactly.

As will be elucidated, to a particle with definite momentum p corresponds a plane wave of wavelength $\lambda = 2\pi\hbar/p$ uniformly filling space and the particle is equally likely to be found anywhere. And to a particle with definite position corresponds a uniform Fourier superposition of plane waves of all wavelengths and so its momentum is completely indeterminate.

Also, to see things smaller than δx one needs radiation of wavelength $\lambda < \delta x$. This inevitably means transfer of momentum $\delta p \approx 2\pi\hbar/\lambda > 2\pi\hbar/\delta x$, consistent with the Uncertainty Principle. Schiff *pps.* 9 – 11 and Polkinghorne *pps.* 44 – 50 discuss the 'gamma-ray microscope'.

Confinement of a particle to a finite region inevitably means that its momentum and so its kinetic energy is non-zero.

- Direct from the quantisation rule we get for instance that $[\widehat{p}_j, \widehat{A}] = -i\hbar\partial\widehat{A}/\partial\widehat{q}_j$, and likewise with p and q interchanged and opposite sign on the right. So *e.g.* $[\widehat{p}_x, \widehat{x}^2] = -2i\hbar\widehat{x}$, which also follows easily from the x, p_x commutator, using the basic properties of $[\widehat{A}, \widehat{B}]$. Indeed, often it's simplest to express observables explicitly as functions of the p's and q's (using the classical relations) and then compute commutators from $[\widehat{q}, \widehat{p}] = i\hbar$. A warning: problems could arise if ordering of non-commuting operators can't be fixed by the need for self-adjointness, or if the system has no classical analogue.

Examples: For a particle of mass m, position $\mathbf{r}$ and linear momentum $\mathbf{p}$, the kinetic energy $T = \frac{1}{2}\mathbf{p}\cdot\mathbf{p}/m$ and potential energy $V(\mathbf{r})$ are made quantum operators by replacing components $x\ldots$ and $p_x\ldots$ by $\widehat{x}\ldots$ and $\widehat{p}_x\ldots$. Angular momentum $\mathbf{L} = \mathbf{r}\times\mathbf{p}$ is quantised likewise. *e.g.* A free particle has $\widehat{V} = 0$ and a one-dimensional simple harmonic oscillator of angular frequency ω has $\widehat{V} = \frac{1}{2}m\omega^2\widehat{x}^2$. Total energy is $\widehat{E} = \widehat{T} + \widehat{V}$. Then $[\widehat{p}, \widehat{T}] = [\widehat{r}, \widehat{V}] = 0$ for any components and *e.g.*

$$[\widehat{x}, \widehat{E}] = [\widehat{x}, \widehat{T}] = \frac{i\hbar}{m}\widehat{p}_x.$$

A free particle can be described by states $|E, \mathbf{p}\rangle$ of definite energy and momentum and for a given E there is degeneracy with respect to direction of momentum $\mathbf{p}$.

2.6 Simple Applications

Commutators determine spectra. Here are 3 cases, including discrete ('quantised') spectra of two observables (energy, angular momentum) that classically take continuous values. Planck's constant sets the scale of discreteness.

Each calculation incorporates a similar logical step, namely if $\widehat{A}|?\rangle = a|?\rangle$ then $|?\rangle \equiv c|a\rangle$, where $|a\rangle$ is *the* eigenvector of $\widehat{A}$ belonging to eigenvalue a, and c could be zero. The possibility of degeneracy of $\widehat{A}$'s spectrum is ignored in these simple cases because it's irrelevant. In each example there's no other observable or operator that can distinguish degenerate states.

2.6.1 Position and Momentum

Suppose $[\widehat{x}, \widehat{p}] = i\hbar\widehat{I}$ where $\widehat{x} = \widehat{x}^\dagger$, $\widehat{p} = \widehat{p}^\dagger$ and $\widehat{x}|x\rangle = x|x\rangle$, and let

$$|?\rangle = (\widehat{I} - \frac{i}{\hbar}\epsilon\widehat{p})|x\rangle$$

for real ϵ where $|\epsilon| \ll 1$. Then

$$\widehat{x}|?\rangle = (\widehat{I}\widehat{x} - \frac{i}{\hbar}\epsilon\widehat{x}\widehat{p})|x\rangle = ((\widehat{I} - \frac{i}{\hbar}\epsilon\widehat{p})\widehat{x} + \epsilon\widehat{I})|x\rangle,$$

using the $x,\ p$ commutator. So we have

$$\widehat{x}|?\rangle = (x + \epsilon)|?\rangle + \mathcal{O}(\epsilon^2)$$

for any small number ϵ, implying that (no degeneracy!)

$$|?\rangle = c|x + \epsilon\rangle$$

to first order. Now to the same approximation $|c| = 1$, since

$$\langle ?|?\rangle = \langle x|(\widehat{I} + \frac{i}{\hbar}\epsilon\widehat{p})(\widehat{I} - \frac{i}{\hbar}\epsilon\widehat{p})|x\rangle = \langle x|x\rangle + \mathcal{O}(\epsilon^2),$$

and we choose $c = 1$. The normalisation of states $|x\rangle$ is not specified.

An arbitrary finite displacement $x \to x + \Delta$ can be composed of a large number n of small displacements Δ/n:

$$|x + \Delta\rangle \approx (I - \frac{i}{\hbar}\frac{\Delta}{n}\widehat{p})^n|x\rangle,$$

which in the limit $n \to \infty$ gives the unitary transformation

$$|x + \Delta\rangle = \exp(-\frac{i\Delta}{\hbar}\widehat{p})|x\rangle.$$

Thus, as Δ is arbitrary, without any other constraints we have that the spectrum of a configuration-space position operator is continuous and that unitary transformations $|x\rangle \to |x + \Delta\rangle$ are 'generated' by the canonically conjugate self-adjoint momentum $\widehat{p}$. Translations in y and z are generated by $\widehat{p}_y$ and $\widehat{p}_z$ and commute with those in x since *e.g.* $[\widehat{p}_x, \widehat{p}_y] = 0$.

Interchanging position and momentum gives independent translations in components of momentum:

$$|p + k\rangle = \exp(\frac{ik}{\hbar}\widehat{x})|p\rangle$$

where k is arbitrary unless other conditions apply.

Comments:

- 1. The sign is different due to the asymmetry of the commutator.

- 2. Similar results hold for any canonically conjugate q, p pair where $[\widehat{q}, \widehat{p}] = i\hbar$. In particular continuous angular displacements (rotations) about an axis are generated by the conjugate angular momentum. (Replace $\widehat{x}$ by an angle and $\widehat{p}$ by the operator for the component of angular momentum about the rotation axis).
- 3. However, the fundamental fact that rotations about different axes in three dimensions don't commute implies that components of angular momentum in quantum mechanics don't commute. Then, because of these extra conditions, *continuous* changes in angular momentum cannot be generated by an angular position operator.

2.6.2 Angular Momentum

Classically $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ and quantising by writing each Cartesian component of $\mathbf{r}$ and $\mathbf{p}$ as a self-adjoint operator we have

$$\widehat{L}_j = \epsilon_{jkl} \widehat{r}_k \widehat{p}_l,$$

i.e. $\widehat{L}_x = \widehat{y}\widehat{p}_z - \widehat{z}\widehat{p}_y$ and so on. Now $\widehat{L}_j = \widehat{L}_j^\dagger$ since $[\widehat{r}_k, \widehat{p}_l] = 0$ for $k \neq l$; there is no operator-ordering ambiguity. With the commutation rules for position and linear momentum or direct from Poisson brackets we find

$$[\widehat{r}^2, \widehat{L}_j] = [\widehat{p}^2, \widehat{L}_j] = 0,$$

consistent with lengths of vectors being unaffected by rotations. At the same time we find the fundamental commutator for angular momentum operators:

$$[\widehat{L}_j, \widehat{L}_k] = i\hbar\epsilon_{jkl} \widehat{L}_l,$$

or $[\widehat{L}_x, \widehat{L}_y] = i\hbar \widehat{L}_z$ and so on.

Definition: any self-adjoint operators, $\widehat{J}_{1,2,3}$ say, that obey these commutators are called **angular momentum operators**. Then as

$$[\widehat{J}^2, \widehat{J}_k] = 0$$

where $\widehat{J}^2 = \widehat{J}_1^2 + \widehat{J}_2^2 + \widehat{J}_3^2 = (\widehat{J}^2)^\dagger$ the length of $\mathbf{J}$ and just one of its components (say $\widehat{J}_z \equiv \widehat{J}_3$) can be sharply defined together. This is in contrast to classical mechanics where all components of the vector can be determined completely.

So there is a set of orthonormal states $|a, b\rangle$ where simultaneously

$$\widehat{J}^2|a, b\rangle = a|a, b\rangle \quad \widehat{J}_z|a, b\rangle = b|a, b\rangle$$

for real a,b. To find them, first observe that $a \geq b^2 \geq 0$, because $a - b^2 = \langle a, b|(\widehat{J}^2 - \widehat{J}_z^2)|a, b\rangle$ and this is a sum of terms of the form $\left\| \widehat{A}|\alpha\rangle \right\|^2$, where $\widehat{A} \equiv \widehat{J}_{x,y} = \widehat{A}^\dagger$.

To deal with $\widehat{J}_x^2 + \widehat{J}_y^2$ define

$$\widehat{J}_\pm = \widehat{J}_x \pm i\widehat{J}_y = (\widehat{J}_\mp)^\dagger,$$

and calculate

$$\widehat{J}_\mp \widehat{J}_\pm = \widehat{J}_x^2 + \widehat{J}_y^2 \pm i[\widehat{J}_x, \widehat{J}_y] = \widehat{J}^2 - \widehat{J}_z^2 \mp \hbar \widehat{J}_z.$$

So

$$\langle a, b|\widehat{J}_\mp \widehat{J}_\pm|a, b\rangle = a - b^2 \mp b\hbar \geq 0$$

since this is $\left\| \widehat{J}_\pm|a, b\rangle \right\|^2$. Now since

$$[\widehat{J}_z, \widehat{J}_\pm] = [\widehat{J}_z, \widehat{J}_x] \pm i[\widehat{J}_z, \widehat{J}_y] = \pm\hbar \widehat{J}_\pm$$

we find that

$$\widehat{J}_z(\widehat{J}_\pm|a, b\rangle) = (\widehat{J}_\pm \widehat{J}_z \pm \qquad \text{and} \qquad \hbar \widehat{J}_\pm)|a, b\rangle = (b \pm \hbar)(\widehat{J}_\pm|a, b\rangle)$$

and conclude that either $\widehat{J}_\pm|a,b\rangle = 0$ or $\widehat{J}_\pm|a,b\rangle = c_\pm|a,b\pm\hbar\rangle$ where from above $|c_\pm|^2 = a - b^2 \mp b\hbar$. Since $[\widehat{J}^2, \widehat{J}_\pm] = 0$ the eigenvalue a is unaffected by $\widehat{J}_\pm$ and keeps an upper limit on b^2.

Thus from a given $|a,b\rangle$ with $b^2 \le a$ successive applications of $\widehat{J}_+$ yield eigenvectors of $\widehat{J}_z$ with b increasing in steps of $\hbar$ until $b = b'$ where $\widehat{J}_+|a,b'\rangle = 0$, when $c_+ = 0$ and $a = b'(b'+\hbar)$. Likewise, successive applications of $\widehat{J}_-$ step down in b until $c_- = 0$, or $b = b''$ where $a = b''(b''-\hbar)$. Clearly $(b'-b'')/\hbar = n$, an integer, so solving:

$$b' = -b'' = \frac{n}{2}\hbar \qquad \text{and} \qquad a = \frac{n}{2}(\frac{n}{2}+1)\hbar^2.$$

The spectra are discrete; length and z-projection of angular momentum are quantised in units of $\hbar$.

Introduce angular momentum 'quantum numbers' j and m as labels for the state $|j,m\rangle$ where

$$\widehat{J}^2|j,m\rangle = j(j+1)\hbar^2|j,m\rangle \qquad \text{and} \qquad \widehat{J}_z|j,m\rangle = m\hbar|j,m\rangle$$

for $j = n/2 = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots$ with $m = -j, -j+1, -j+2, \ldots j-1, j$; *i.e.* $(2j+1)$ values and where $\langle j,m|j',m'\rangle = \delta_{jj'}\delta_{mm'}$. The usual phase choice is $c_\pm$ real and positive, giving for the 'ladder operators'

$$\widehat{J}_\pm|j,m\rangle = \sqrt{(j\mp m)(j\pm m+1)}\hbar|j,m\pm 1\rangle.$$

Since $\widehat{J}_x = (\widehat{J}_+ + \widehat{J}_-)/2$ and $\widehat{J}_y = (\widehat{J}_+ - \widehat{J}_-)/2i$, although the x- and y-components of angular momentum are not sharply defined in an eigenstate $|j,m\rangle$ we still have $\langle J_{x,y}\rangle = 0$.

Comments:

- 1. For ordinary ('orbital') angular momentum of a particle $\mathbf{L} = \mathbf{r}\times\mathbf{p}$ only integer values of $l \equiv j$ are realised; all possibilities are encountered for 'spin' angular momentum, an internal degree of freedom of a quantum particle.
- 2.
  - a. For $j = \frac{1}{2}$ two values $m = \pm\frac{1}{2}$ are possible; the a.m. vector of length $\frac{1}{2}\sqrt{3}\hbar$ is either nearly parallel ($m = \frac{1}{2}$) or antiparallel ($m = -\frac{1}{2}$) to the z-axis.
  - b. For $j = 1$ the values $m = 1, 0, -1$ correspond to a vector of length $\sqrt{2}\hbar$ nearly parallel, perpendicular, nearly antiparallel, to the z-axis. And so on. In each case the projection on the $x-y$ plane is not simultaneously measurable but its average is zero.

2.6.3 Energy of a Simple-Harmonic Oscillator (one dimension)

For a particle of mass m executing SHM on the x-axis about the origin with angular frequency ω we have the Hamiltonian (which is the same as the total energy operator)

$$\widehat{H} = \frac{1}{2m}\widehat{p}^2 + \frac{m\omega^2}{2}\widehat{x}^2 = \widehat{H}^\dagger$$

where $[\widehat{x},\widehat{p}] = i\hbar$ and $\widehat{x} = \widehat{x}^\dagger$ and $\widehat{p} = \widehat{p}^\dagger$, and we wish to solve $\widehat{H}|E\rangle = E|E\rangle$. Firstly we have $E = E^*$ and, because $\widehat{H}$ is a sum of squares of self-adjoint operators, $E \ge 0$. For the previous sum of squares a 'factorisation' into what proved to be ladder operators did the trick. So define

$$\widehat{a} = (\widehat{p} + im\omega\widehat{x})/\sqrt{2m}, \qquad \widehat{a}^\dagger = (\widehat{p} - im\omega\widehat{x})/\sqrt{2m}.$$

Then

$$\widehat{a}\widehat{a}^\dagger = \widehat{H} + \frac{i\omega}{2}[\widehat{x},\widehat{p}] = \widehat{H} - \tfrac{1}{2}\hbar\omega\widehat{I} \qquad \widehat{a}^\dagger\widehat{a} = \widehat{H} + \tfrac{1}{2}\hbar\omega\widehat{I}.$$

Thus

$$\widehat{H}\widehat{a} = (\widehat{a}\widehat{a}^\dagger + \tfrac{1}{2}\hbar\omega)\widehat{a} = \widehat{a}(\widehat{a}^\dagger\widehat{a} + \tfrac{1}{2}\hbar\omega) = \widehat{a}(\widehat{H} + \hbar\omega),$$

or $[\widehat{H},\widehat{a}] = \hbar\omega\widehat{a}$. Likewise $\widehat{H}\widehat{a}^\dagger = \widehat{a}^\dagger\widehat{H} - \hbar\omega\widehat{a}^\dagger$.

The similarity with the $J_z, J_\pm$ commutator is clear and indeed

$$\widehat{H}(\widehat{a}|E\rangle) = (\widehat{a}\widehat{H} + \hbar\omega\widehat{a})|E\rangle = (E + \hbar\omega)(\widehat{a}|E\rangle),$$

so unless $\widehat{a}|E\rangle = 0$ we infer that

$$\widehat{a}|E\rangle = c_+|E + \hbar\omega\rangle.$$

Similarly either $\widehat{a}^\dagger|E\rangle = 0$ or

$$\widehat{a}^\dagger|E\rangle = c_-|E - \hbar\omega\rangle.$$

Using the formulae for $\widehat{a}\widehat{a}^\dagger$ and $\widehat{a}^\dagger\widehat{a}$ and with normalised states $|E\rangle$ we have

$$|c_+|^2 = \langle E|\widehat{a}^\dagger\widehat{a}|E\rangle = E + \tfrac{1}{2}\hbar\omega \geq 0,$$

$$|c_-|^2 = \langle E|\widehat{a}\widehat{a}^\dagger|E\rangle = E - \tfrac{1}{2}\hbar\omega \geq 0.$$

So from given $|E'\rangle$ with $E = E' \geq 0$ successive uses of of $\widehat{a}^\dagger$ step E down by $\hbar\omega$ at a time until $E = E_0$ where $\widehat{a}^\dagger|E_0\rangle = 0$. Evidently this happens at $E_0 = \frac{1}{2}\hbar\omega$, when $c_- = 0$. To avoid negative $|c_-|$ only starting values $E' = \frac{1}{2}\hbar\omega, \frac{3}{2}\hbar\omega, \frac{5}{2}\hbar\omega, \ldots$ are possible. Clearly $\widehat{a}$ steps up this sequence indefinitely.

Summary: The one-dimensional simple-harmonic oscillator has a discrete energy spectrum, with eigenstates of $\widehat{H}$ labelled by quantum number n:

$$\{|n\rangle; \quad \langle n|n'\rangle = \delta_{nn'}\}$$

and eigenvalues

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

where

$$\widehat{H} = \tfrac{1}{2}(\widehat{a}\widehat{a}^\dagger + \widehat{a}^\dagger\widehat{a}),$$

$$\widehat{a}|n\rangle = \sqrt{(n+1)\hbar\omega}|n+1\rangle, \qquad \widehat{a}^\dagger|n\rangle = \sqrt{n\hbar\omega}|n-1\rangle$$

for $n = 0, 1, 2, 3, \ldots$. The 'ground state' $|0\rangle$ obeys $\widehat{a}^\dagger|0\rangle = 0$ and

$$|n\rangle = \frac{1}{\sqrt{n!\,(\hbar\omega)^n}}(\widehat{a})^n|0\rangle.$$

Observables $\widehat{p}$ and $\widehat{x}$ are proportional to $\widehat{a} \pm \widehat{a}^\dagger$ where the 'annihilation' and 'creation' operators obey

$$[\widehat{a}^\dagger, \widehat{a}] = \hbar\omega\widehat{I}.$$

Comments:

- The quantum oscillator is never at 'rest' for its ground-state energy has 'zero-point' value $\frac{1}{2}\hbar\omega$.
- Note the appearance of a relation of form $Energy = \hbar \times (angular \quad frequency)$, which has general significance in discussion of time-dependence.

3 Representation Theory

3.1 Position Representation

3.1.1 Wave function

Consider a system which classically has N degrees of freedom. Then $\widehat{q}_1, ..\widehat{q}_N$ form a complete set of commuting operators and we have

$$[\widehat{q}_i,\, \widehat{q}_j] = 0, \quad [\widehat{p}_i,\, \widehat{p}_j] = 0, \quad [\widehat{q}_i,\, \widehat{p}_j] = i\hbar\delta_{ij}.$$

Hence we can take as a basis in the space of states of the system the basis formed by all eigenstates of $\widehat{q}_i$ *i.e.*

$$|q_1, ..q_N\rangle = |\mathbf{q}\rangle,$$

where

$$\widehat{q}_i|\mathbf{q}\rangle = q_i|\mathbf{q}\rangle$$

As we already know these eigenvalues are continuous; they generalise the concept of position of a particle. To see this consider one particle and the self-adjoint operator $\widehat{\mathbf{r}}$ that measures its position components as generalised variables, coinciding with its coordinates in ordinary three-dimensional space. An eigenstate $|\mathbf{r}\rangle$ of $\widehat{\mathbf{r}}$ is labelled by the continuously-variable real vector eigenvalue $\mathbf{r}$. Orthonormality must be generalised from the discrete case that uses the Kronecker delta, and completeness (resolution of the identity) from a simple sum over eigenvalues.

Proceed by generalising the completeness relation. Define

$$\widehat{I} = \int d^3r\, |\mathbf{r}\rangle\langle\mathbf{r}|,$$

where d^3r stands for $dx\,dy\,dz$ and the integral extends over all space. Then the basis expansion is

$$|\alpha\rangle = \int d^3r|\mathbf{r}\rangle\langle\mathbf{r}|\alpha\rangle$$

and from considering $\langle\mathbf{r}'|\alpha\rangle$ we find

$$\langle\mathbf{r}'|\mathbf{r}\rangle = \delta(\mathbf{r}' - \mathbf{r}).$$

So the presence of operators with continuous spectra necessarily leads to state vectors with 'delta-function normalisation', *i.e.* orthogonal but with a certain type of infinite norm. We will see later that this is equally so if the basis of $\mathbf{r}$ is replaced by another continuous basis, *e.g.* momentum.

In our N dimensional space we have as normalisation

$$\langle\mathbf{q}'|\mathbf{q}\rangle = \langle q_1'...q_N'|q_1...q_N\rangle = \prod_{i=1,N} \delta(q_i' - q_i) = \delta^N(\mathbf{q}' - \mathbf{q})$$

and in this basis

$$1 = \int d^Nq|\mathbf{q}\rangle\langle\mathbf{q}|.$$

Moreover,

$$|\alpha\rangle = \int d^Nq|\mathbf{q}\rangle\langle\mathbf{q}|\alpha\rangle$$

The representative of $|\alpha\rangle$ is the complex number $\langle\mathbf{q}|\alpha\rangle$ that depends continuously on the real (N dimensional) vector $\mathbf{q}$. This is a complex function of $\mathbf{q}$, which we can denote by wavefunction $\psi_\alpha(\mathbf{q})$. This function is called the **wavefunction** of the state $|\alpha\rangle$ in the basis $\{|q\rangle\}$. Note that in many texts and we adopt this convention too this function is denoted, simply, as $\alpha(\mathbf{q})$.

The inner product is

$$\langle\alpha|\beta\rangle = \int d^Nq\, \psi_\alpha^*(\mathbf{q})\psi_\beta(\mathbf{q})$$

and for normalisable states $|\alpha\rangle$ the wavefunction is square-integrable:

$$\langle\alpha|\alpha\rangle = \int d^Nq\, |\psi_\alpha(\mathbf{q})|^2 = 1.$$

This implies that the wavefunction decreases faster than $|\mathbf{q}|^{-N/2}$ as $|\mathbf{q}| \to \infty$.

When labels α, $\beta, \ldots$ are themselves continuous eigenvalues then evidently the eigenfunctions are not square-integrable but:

$$\langle\alpha|\alpha'\rangle = \int d^Nq\, \psi_\alpha^*(\mathbf{q})\psi_{\alpha'}(\mathbf{q}) = C(\alpha)\delta(\alpha - \alpha'),$$

if $\widehat{I} = \int d\alpha\, C^{-1}|\alpha\rangle\langle\alpha|$. The converse implication in fact holds too: eigenfunctions that are not square-integrable but have δ-function norm imply continuous eigenvalues (and normalisable eigenfunctions imply a discrete spectrum).

Comment:

- Note that
$$|\alpha\rangle \;\to\; \psi_\alpha(\mathbf{q})$$
defines an isomorphism between the 'abstract' Hilbert space of states $|\alpha\rangle$ and $\mathcal{L}_2(R^N)$, the Hilbert space of functions, square integrable on R^N.

How does any operator $\widehat{\xi}(\widehat{\mathbf{q}})$ act on $\psi_\alpha(\mathbf{q})$? Clearly

$$\widehat{\xi}(\widehat{\mathbf{q}})|\mathbf{q}\rangle = \xi(\mathbf{q})|\mathbf{q}\rangle.$$

So

$$\widehat{\xi}(\widehat{\mathbf{q}})|\alpha\rangle = \widehat{\xi}(\widehat{\mathbf{q}}) \int d^N q \psi_\alpha(\mathbf{q})|\mathbf{q}\rangle = \int d^N q \psi_\alpha(\mathbf{q})\xi(\mathbf{q})|\mathbf{q}\rangle$$

so the wavefunction of $\widehat{\xi}(\widehat{\mathbf{q}})|\alpha\rangle$ is $\xi(\widehat{\mathbf{q}})\psi_\alpha(\mathbf{q})$ and so the action of $\widehat{\xi}(\widehat{\mathbf{q}})$ is the multiplication by $\xi(\mathbf{q})$.

Definition: The basis $\{|\mathbf{q}\rangle\}$ is said to be a **position representation** of the Hilbert space of states in which $\psi_\alpha(\mathbf{q})$ is the wavefunction of $|\alpha\rangle$.

3.1.2 Change of basis

Note that the equation

$$\widehat{q}_i|\mathbf{q}\rangle = q_i|\mathbf{q}\rangle$$

defines the eigenstates up to a factor; normalisation condition defines the eigenvectors up to a factor of modulus 1. Thus we can replace the basis $\{|\mathbf{q}\rangle\}$ by a new basis

$$|\mathbf{q}, *\rangle = e^{i\xi(\mathbf{q})}|\mathbf{q}\rangle.$$

In this basis $|\alpha\rangle$ will be represented by $\psi_{\alpha *}(\mathbf{q})$, where

$$\psi_{\alpha *}(\mathbf{q}) = \langle \mathbf{q}, *|\alpha\rangle = e^{-i\xi(\mathbf{q})}\psi_\alpha(\mathbf{q})$$

and

$$|\alpha\rangle = \int d^N q \psi_{\alpha *}(\mathbf{q})|\mathbf{q}, *\rangle.$$

3.1.3 Finding the action of the $\widehat{\mathbf{p}}$ operator (setting up the Schrödinger representation)

Next we have to decide how the operators $\widehat{\mathbf{p}}$ act in the space of wave functions. We will argue that we can represent their action by

$$\widehat{p}_i = -i\hbar \frac{\partial}{\partial q_i}$$

in the sense that

$$\widehat{\mathbf{p}}_i \psi(\mathbf{q}) = -i\hbar \frac{\partial}{\partial q_i}\psi(\mathbf{q}).$$

First define

$$\widehat{\partial}_i|\psi\rangle \equiv \int d^N q \frac{\partial \psi}{\partial q_i}(\mathbf{q})|\mathbf{q}\rangle$$

and then we will show that $-i\hbar\widehat{\partial}_i$ behaves as $\widehat{p}_i$. Note that here we are using the convention that $\psi(\mathbf{q}) = \langle \mathbf{q}|\psi\rangle$.

Next we calculate

$$
\begin{aligned}
\langle\phi|\widehat{\partial}_i|\psi\rangle &= \int d^N q\, \phi^\star(\mathbf{q}) \tfrac{\partial\psi}{\partial q_i}(\mathbf{q}) = \\
= \int d^N q\, \tfrac{\partial}{\partial q_i}\left[\phi^\star(\mathbf{q})\psi(\mathbf{q})\right] &- \int d^N q\, \psi(\mathbf{q}) \tfrac{\partial}{\partial q_i}\phi^\star(\mathbf{q}) = \\
= \int d^{N-1} q\, \phi^\star(\mathbf{q})\psi(\mathbf{q}) \,|_{-\infty}^{\infty} &- \left[\int d^N q\, \psi^\star(\mathbf{q}) \tfrac{\partial\phi}{\partial q_i}(\mathbf{q})\right]^\star ,
\end{aligned}
$$

where in going from the first line to the second we have integrated by parts. Assuming that the functions vanish *at infinity* the first term in the last line vanishes and we have

$$\langle\phi|\widehat{\partial}_i|\psi\rangle = -(\langle\psi|\widehat{\partial}_i|\phi\rangle)^\star$$

and so

$$\langle\phi| - i\hbar\widehat{\partial}_i|\psi\rangle = (\langle\psi| - i\hbar\widehat{\partial}_i|\phi\rangle)^\star$$

and so we see that $-i\hbar\widehat{\partial}_i$ is Hermitian in the space of functions which *vanish at infinity*.

Next we consider the commutator $[-i\hbar\widehat{\partial}_i,\, -i\hbar\widehat{\partial}_j]$. We have

$$(-i\hbar\widehat{\partial}_i)(-i\hbar\widehat{\partial}_j)|\psi\rangle = -\hbar^2 \int d^N q \tfrac{\partial^2\psi}{\partial q_i \partial q_j}|\mathbf{q}\rangle = (-i\hbar\widehat{\partial}_j)(-i\hbar\widehat{\partial}_i)|\psi\rangle$$

thus showing that

$$[-i\hbar\widehat{\partial}_i,\, -i\hbar\widehat{\partial}_j] = 0 = [\widehat{p}_i,\, \widehat{p}_j].$$

Next we consider $[-i\hbar\widehat{\partial}_i,\, \widehat{q}_j]$ or, more generally, $[-i\hbar\widehat{\partial}_i,\, \widehat{\gamma}(\widehat{\mathbf{q}})]$. We have

$$
\begin{aligned}
(-i\hbar\widehat{\partial}_i)\widehat{\gamma}(\widehat{\mathbf{q}})|\psi\rangle &= -i\hbar\widehat{\partial}_i\, \widehat{\gamma}(\widehat{\mathbf{q}}) \int d^N q\, \psi(\mathbf{q})|\mathbf{q}\rangle \\
= -i\hbar\widehat{\partial}_i \int d^N q \psi(\mathbf{q})\gamma(\mathbf{q})|\mathbf{q}\rangle &= -i\hbar \int d^N q \tfrac{\partial}{\partial q_i}\left\{\psi(\mathbf{q})\gamma(\mathbf{q})\right\}|\mathbf{q}\rangle \\
= -ih \int d^N q[\gamma(\mathbf{q})\tfrac{\partial\psi}{\partial q_i} + \tfrac{\partial\gamma}{\partial q_i}\psi(\mathbf{q})]|\mathbf{q}\rangle &= [-i\hbar\widehat{\gamma}(\widehat{\mathbf{q}})\widehat{\partial}_i - i\hbar\tfrac{\partial\gamma}{\partial q_i}(\widehat{\mathbf{q}})]|\psi\rangle.
\end{aligned}
$$

So we see that

$$[-i\hbar\widehat{\partial}_i,\, \widehat{\gamma}(\widehat{\mathbf{q}})] = -i\hbar\frac{\partial\gamma}{\partial q_i}(\widehat{\mathbf{q}}).$$

In particular

$$[\widehat{q}_i,\, -i\hbar\widehat{\partial}_j] = i\hbar\delta_{ij} = [\widehat{q}_i,\, \widehat{p}_j]$$

and so we see that

$$[\widehat{q}_i,\, \widehat{p}_j + i\hbar\widehat{\partial}_j] = 0.$$

Thus $\widehat{p}_j + i\hbar\widehat{\partial}_j$ commutes with a complete commuting set of observables $(\widehat{q}_i)$ and so must be a function of them. So

$$\widehat{p}_j + i\hbar\widehat{\partial}_j = Z_j(\widehat{\mathbf{q}}).$$

However, as $[\widehat{p}_i,\, \widehat{p}_j] = 0$ we have

$$[Z_i(\widehat{\mathbf{q}}) - i\hbar\widehat{\partial}_i,\, Z_j(\widehat{\mathbf{q}}) - i\hbar\widehat{\partial}_j] \;=\; [Z_i,\, Z_j] + [-i\hbar\widehat{\partial}_i, Z_j] - [-i\hbar\widehat{\partial}_j, Z_i] + [-i\hbar\widehat{\partial}_i,\, -i\hbar\widehat{\partial}_j] = 0.$$

Thus

$$0 = [-i\hbar\widehat{\partial}_i, Z_j] - [-i\hbar\widehat{\partial}_j, Z_i] = -i\hbar\left(\tfrac{\partial Z_j}{\partial q_i} - \tfrac{\partial Z_i}{\partial q_j}\right)$$

and so we see that

$$Z_i = \tfrac{\partial Z}{\partial q_i}$$

for some Z. Thus

$$\widehat{p}_i = -i\hbar\widehat{\partial}_i + \tfrac{\partial Z}{\partial q_i}.$$

Finally, we now change the basis and use $[|\mathbf{q},\star\rangle\}$ and $\psi_\star(\mathbf{q})$. This leads to a new $\widehat{\partial}_i$ which we denote by $\widehat{\partial}_i^{\,\star}$. Its action is given by

$$\begin{aligned}\widehat{\partial}_i^{\,\star}|\psi\rangle &\equiv \textstyle\int d^N q \frac{\partial\psi_\star}{\partial q_i}|\mathbf{q},\star\rangle = \int d^N q \frac{\partial}{\partial q_i}\left(e^{-i\xi}\psi\right)e^{i\xi}|\mathbf{q}\rangle \\ &= \textstyle\int d^N q \left(\frac{\partial\psi}{\partial q_i} - i\frac{\partial\xi}{\partial q_i}\psi\right)|\mathbf{q}\rangle = \left(\widehat{\partial}_i - i\frac{\partial\xi}{\partial q_i}\right)|\psi\rangle.\end{aligned}$$

So choosing $\xi = -\frac{Z}{\hbar}$ we have $\widehat{p}_i = -i\hbar\widehat{\partial}_i^{\,\star}$. Thus, dropping $\star$ we see that we can take

$$\widehat{p}_i = -i\hbar\widehat{\partial}_i.$$

The representation in which this is the case is called the **Schrödinger representation** and $\psi(\mathbf{q})$ is called the **Schrödinger wave function**.

3.1.4 Example

Operators that are functions of $\widehat{\mathbf{p}}$ are differential operators in wave mechanics; *e.g.* kinetic energy of a particle in 3 dimensions $\widehat{T} = \widehat{\mathbf{p}}^2/2m$ becomes $-(\hbar^2/2m)\nabla^2$ and its angular momentum operator is $-i\hbar\mathbf{r}\times\nabla$. Matrix elements are calculated as

$$\langle\alpha|\widehat{A}(\widehat{\mathbf{q}},\widehat{\mathbf{p}})|\beta\rangle = \int d^3q\,\psi_\alpha^*(\mathbf{q})A(\mathbf{q},-i\hbar\nabla)\psi_\beta(\mathbf{q}).$$

As an example let us consider a simple harmonic oscillator in 1 dimension.

With energy eigenfunctions $\phi_n(x) \equiv \langle x|n\rangle$, $n = 0,1,2,\ldots$ and $\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle$ the differential equation

$$-\frac{\hbar^2}{2m}\frac{d^2\phi_n}{dx^2} + \tfrac{1}{2}m\omega^2x^2\phi_n = E_n\phi_n, \quad \langle x|\widehat{H}|\phi_n\rangle = E_n\langle x|\phi_n\rangle$$

determines eigenvalues $E_n = (n+\frac{1}{2})\hbar\omega$ if the solution is required to be normalisable — *i.e.* to vanish as $|x|\to\infty$. The textbook procedure of series solution (Schiff, *p.* 66 and see later) gives ϕ_n as the product of a factor $\exp(-\frac{1}{2}(x/x_0)^2)$ and a Hermite polynomial in x/x_0, where $x_0^2 \equiv \hbar/m\omega$ (x_0 is the amplitude of a classical oscillator of energy $\frac{1}{2}\hbar\omega$). In fact instead we can find the energy eigenfunctions starting from the definition of the ground-state, $\widehat{a}^\dagger|0\rangle = 0$, which for the wavefunction $\phi_0(x)\equiv\langle x|0\rangle$ is the differential equation

$$\hbar\frac{d\phi_0}{dx} + m\omega x\phi_0 = 0.$$

The solution, normalised using $\int_{-\infty}^{\infty}\exp(-x^2)\,dx = \sqrt{\pi}$, is easily found:

$$\phi_0(x) = (\frac{m\omega}{\pi\hbar})^{1/4}\exp(-\tfrac{1}{2}m\omega x^2/\hbar) = \pi^{-1/4}x_0^{-1/2}\exp(-\tfrac{1}{2}(x/x_0)^2).$$

Then n applications of $\widehat{a} = (-i\hbar\,d/dx + im\omega x)/\sqrt{2m}$ gives the (normalised) eigenfunction

$$\langle x|n\rangle \equiv \phi_n(x) = \frac{1}{\sqrt{n!}}\left(\frac{-i}{\sqrt{2}}\right)^n\left(x_0\frac{d}{dx} - \frac{x}{x_0}\right)^n\phi_0(x),$$

showing the origin of the Hermite polynomial. Also note that $\phi_n(-x) = (-1)^n\phi_n(x)$.

3.2 Probabilistic Interpretation

Let us consider first one particle in 3 dimensions and as $\mathbf{q}$ use Cartesian coordinates x, y, z. The expectation value of observable A in state $|\alpha(t)\rangle$ of a particle is

$$\langle A\rangle = \langle\alpha(t)|\widehat{A}|\alpha(t)\rangle = \int dV\, \psi_\alpha^*(\mathbf{r},t)\widehat{A}(\mathbf{r},-i\hbar\nabla)\psi_\alpha(\mathbf{r},t),$$

where $dV = dx\,dy\,dz$. For a quantity A independent of momentum is

$$\langle A\rangle = \int dV\, \widehat{A}(\mathbf{r})\,|\psi|^2\,.$$

Recalling the formalism of elementary probability theory makes clear the standard interpretation of the wavefunction, namely that

$$|\psi_\alpha|^2\ \delta V \quad\equiv\quad |\langle\mathbf{r}|\alpha(t)\rangle|^2\ \delta V$$

is the relative probability of a measurement showing the particle to be in volume $\delta V = \delta x\,\delta y\,\delta z$ at position $\mathbf{r}$ at time t.

For a system with N degrees of freedom and generalised coordinates

$$\mathbf{q} = (q_1, \ldots q_N),$$

which by virtue of their commutators with canonically-conjugate variables have continuous spectra, $|\langle q|\alpha\rangle|^2\, dq^N$ is interpreted as a relative probability of observing the system in a state described by a point in a small volume $d^N q$ at q in the abstract N-dimensional configuration space.

Compare with the discrete case where $|\langle a|\alpha(t)\rangle|^2$ is the relative probability of a measurement of A at time t giving as outcome the eigenvalue a.

So for a single particle in a potential $\rho(\mathbf{r},t) \equiv |\psi|^2$ can be viewed as a 'density of the particle' in ordinary space.

3.3 Harmonic Oscillator Revisited

Previously we discussed the eigenstates of the harmonic oscillator using algebraic methods. Now we discuss this problem using the wave functions and then show the relation between the two approaches.

$$V = \frac{1}{2}m\omega^2 x^2 \qquad \text{hence} \quad \hat{H} = \frac{1}{2}\frac{\hat{p}^2}{m} + \frac{1}{2}m\omega^2\hat{x}^2.$$

So, the wavefunction satisfies

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}m\omega^2x^2\psi(x) \ =\ E\psi(x).$$

To get bound states (*ie* normalisable states) we require that $\psi(x) \to 0$ as $x \to \infty$ (as $V \to \infty$).

To do this we rewrite

$$-\Big(\frac{\hbar}{m\omega}\frac{d^2}{dx^2} - \frac{m\omega}{\hbar}x^2\Big)\psi \ =\ \frac{2E}{\hbar\omega}\psi$$

and change the variable $x \to y = \sqrt{\frac{m\omega}{\hbar}}x$ and introduce $\lambda = \frac{2E}{\hbar\omega}$. Then our equation becomes

$$\frac{d^2\psi}{dy^2} + (\lambda - y^2)\psi \ =\ 0.$$

When $y \to \infty$ the equation becomes $\frac{d^2\psi}{dy^2} - y^2\psi = 0$ and its solutions are

$$\psi \sim e^{\pm\frac{1}{2}y^2}$$

to order $O(\frac{1}{y^2})$.

So to satisfy our boundary condition we take $e^{-\frac{1}{2}y^2}$. Thus we put

$$\psi = e^{-\frac{1}{2}y^2} H(y)$$

and derive the equation for $H(y)$. As $\frac{d\psi}{dy} = e^{-\frac{1}{2}y^2}\dot{H} - ye^{-\frac{1}{2}y^2}H$ we see that

$$\frac{d^2\psi}{dy^2} = e^{-\frac{1}{2}y^2}\ddot{H} - 2ye^{-\frac{1}{2}y^2}\dot{H} + (y^2-1)e^{-\frac{1}{2}y^2}H$$

and we find that H satisfies

$$\frac{d^2H}{dy^2} - 2y\frac{dH}{dy} + (\lambda - 1)H = 0$$

This equation (**Hermite's** equation) appears harder to solve. We seek its solutions by a power series expansion around $y = 0$. We put

$$H \ = \ y^\sigma \sum_{r=0}^{\infty} a_r \, y^r,$$

where $a_0 \neq 0$ and then we try to determine σ and all the coefficients a_r $r \neq 0$. The left hand side of Hermite's equation is now

$$\begin{aligned} &\textstyle\sum_{r=0}^{\infty} a_r y^\sigma [(r+\sigma)(r+\sigma-1)y^{r-2} - 2(r+\sigma)y^r + (\lambda-1)y^r] \\ &= y^{\sigma-2}a_0\sigma(\sigma-1) + y^{\sigma-1}a_1\sigma(\sigma+1) + \textstyle\sum_{r=0}^{\infty} y^{r+\sigma}[(r+\sigma+2)(r+\sigma+1)a_{r+2} - (2r+2\sigma+1-\lambda)a_r] = 0 \end{aligned}$$

So comparing powers of y we see that we have to require

$$\begin{gathered} a_0\sigma(\sigma-1) = 0 \\ a_1\sigma(\sigma+1) = 0 \\ (\sigma+r+2)(\sigma+r+1)a_{r+2} = [2r+2\sigma+1-\lambda]a_r. \end{gathered}$$

As $a_0 \neq 0$ we have either $\sigma = 0$ or $\sigma = 1$. If $\sigma = 0$ a_1 is arbitrary, but if $\sigma = 1$ then $a_1 = 0$. So, we take $\sigma = 0$ and have a_0 (times a function of y^2) + a_1 (times an odd function of y).

Note that the behaviour of $H(y)$ as $y \to \infty$ is determined by

$$\frac{a_{r+2}}{a_r} \ \to \ \frac{2}{r} \qquad \text{as} \quad r \to \infty,$$

which, unless series terminates, gives

$$H(y) \ \sim \ y^\sigma \sum \frac{1}{r!}y^{2r} \ \sim \ y^\sigma e^{y^2}$$

thus leading to a **non-normalisable** ψ which goes as $\psi \ \sim \ y^\sigma e^{\frac{1}{2}y^2}$. Hence to have a normalisable wave function ψ we have to require that the series terminates; *i.e.* that

$$a_{2r+2} = 0$$

for some $r = m$, say. Then

$$(2(m+\sigma) + 1 - \lambda = 0 \qquad i.e. \quad \lambda = 2(m+\sigma) + 1.$$

Then $H(y)$ is a polynomial of degree $m + \sigma$ and parity $(-1)^\sigma$.

Call $m + \sigma = n$. This polynomial is $H_n(y)$ - the Hermite polynomial.

Thus

$$\psi_n = \psi_n(y) = H_n(y)e^{-\frac{1}{2}y^2} \quad \sim \quad y^n e^{-\frac{1}{2}y^2}$$

as $y \to \infty$. The corresponding energy eigenvalue is $\lambda = 2n + 1$ which gives us

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

Comments

- As ψ_m correspond to different eigenvalues they are orthogonal.

$$\int_{-\infty}^{\infty} \psi_m^\star(y)\psi_n(y)dy = \int_{-\infty}^{\infty} e^{-y^2} H_m(y)H_n(y)dy = K_n\delta_{nm}.$$

- The normalisation constant K_n is chosen so that $\int_{-\infty}^{\infty} \psi_n^2\, dx = 1$ *i.e.* $\psi_n = \frac{1}{\pi}\frac{1}{4}\frac{1}{\sqrt{n!2^n}} H_n(y)e^{-\frac{1}{2}y^2}$.

3.4 Relation to the Algebraic Approach

In our algebraic approach we used

$$\begin{aligned}\hat{a} &= (\hat{p} + im\omega\hat{x})\tfrac{1}{\sqrt{2m}} \\ \hat{a}^\dagger &= (\hat{p} - im\omega\hat{x})\tfrac{1}{\sqrt{2m}}\end{aligned}$$

and $|0\rangle$ was the ground energy state, *i.e.* it satisfied $\hat{a}^\dagger|0\rangle = 0$. In the Schrödinger representation

$$\begin{aligned}\hat{a}^\dagger = (\hat{p} - im\omega\hat{x})\frac{1}{\sqrt{2m}} &= \quad (-i\hbar\tfrac{\partial}{\partial x} - im\omega x)\tfrac{1}{\sqrt{2m}} \\ = -i(\hbar\frac{\partial}{\partial x} + m\omega x)\frac{1}{\sqrt{2m}} &= \qquad -i\sqrt{\tfrac{\omega\hbar}{2}}(y + \tfrac{\partial}{\partial y}).\end{aligned}$$

So the Schrödinger wave function for the lowest state

$$\langle y|0\rangle = \psi_0(y) \qquad \text{satisfies} \qquad -i\sqrt{\frac{\omega\hbar}{2}}\left(y + \frac{\partial}{\partial y}\right)\psi_0(y) = 0$$

and so is given by $\psi \;\sim\; A\, e^{-\frac{1}{2}y^2}$.

Higher states $|n\rangle \;\sim\; (a)^n|0\rangle$ and so $\sim (..)^n(y - \frac{\partial}{\partial y})^n\psi_0(y)$ and so

$$\psi_n(y) \;\sim\; A_n\left(y - \frac{\partial}{\partial y}\right)^n \psi_0(y).$$

But note that

$$e^{\frac{1}{2}y^2}\frac{\partial}{\partial y}\left(e^{-\frac{1}{2}y^2} f\right) = \frac{\partial f}{\partial y} - yf = \left(\frac{\partial}{\partial y} - y\right) f$$

and so we have

$$\begin{aligned}y - \frac{\partial}{\partial y} &= e^{\frac{1}{2}y^2}(-\frac{\partial}{\partial y})e^{-\frac{1}{2}y^2} \\ (y - \frac{\partial}{\partial y})^n &= e^{\frac{1}{2}y^2}(-\frac{\partial}{\partial y})^n e^{-\frac{1}{2}y^2}.\end{aligned}$$

So

$$\psi_n \;\sim\; \text{const}\, e^{\frac{1}{2}y^2}(-\frac{\partial}{\partial y})^n e^{-y^2} \;=\; \text{const}\, e^{-\frac{1}{2}y^2} H_n(y)$$

as $H_n(y) = e^{y^2}(-\frac{\partial}{\partial y})^n e^{-y^2}$.

The last result can be derived from the generating function for $H_n(y)$. Recall that this function is given by

$$e^{-\eta^2+2\eta\xi} = \sum_{n=0}^{\infty}\frac{H_n(\xi)}{n!}\eta^n.$$

But as $e^{-\eta^2+2\eta\xi} = e^{\xi^2-(\eta-\xi)^2}$ we see that $H_n(\xi)$ is related to the coefficient of η^n in the expansion of $e^{-(\eta-\xi)^2}$. This coefficient is given by

$$\frac{1}{n!}(\frac{\partial}{\partial\eta})^n e^{-(\xi-\eta)^2}|_{\eta=0} = \frac{1}{n!}(\frac{-\partial}{\partial\xi})^n e^{-\xi^2}$$

and so

$$H_n(\xi) = e^{\xi^2}(-\frac{\partial}{\partial \xi})^n e^{-\xi^2}$$

as required.

So the two methods give the same spectrum of the Hamiltonian.

Comments:

- This time, as we saw earlier, we have $\frac{1}{2}\hbar\omega$ as the zero point energy.
- In many theories we can treat fields as sets of harmonic oscillators (when resolved into normal modes). Then each mode has its own zero point energy.

3.5 Momentum Representation

The commutation relations

$$[\widehat{q}_i,\, \widehat{q}_j] =\; 0\; = [\widehat{p}_i,\, \widehat{p}_j], \quad [\widehat{q}_i,\, \widehat{p}_j] = i\hbar\delta_{ij}$$

have a symmetry

$$\widehat{q}_i \to \widehat{p}_i, \quad \widehat{p}_j \to -\widehat{q}_j$$

(corresponding to a canonical transformation in phase space) and so we can take a representation in which $\widehat{p}_i$ acts by a multiplication and $\widehat{q}_i$ acts as $i\hbar\frac{\partial}{\partial p_i}$. This corresponds to choosing as our basis momentum eigenstates $\{|p_i\rangle\}$ with

$$|\psi\rangle \;=\; \int d^N p\, \tilde{\psi}(\mathbf{p})|\mathbf{p}\rangle.$$

Then

$$\widehat{q}_i|\psi\rangle = i\hbar \int d^N p\, \tfrac{\partial\psi}{\partial p_i}|\mathbf{p}\rangle.$$

Note that the function $\tilde{\psi(\mathbf{p})}$ is the momentum representation analogue of the wave function, called momentum wave function.

What is $\langle \mathbf{q}|\mathbf{p}\rangle$, *i.e.* an eigenstate on $\widehat{\mathbf{p}}$ in the position representation $\{|\mathbf{q}\rangle\}$?

To answer this question let us restrict our attention to one dimension. Then we have $\widehat{q}$ and $\widehat{p}$ which satisfy

$$\widehat{q}\widehat{p} - \widehat{p}\widehat{q} = i\hbar.$$

Then we observe that

$$\langle q|\widehat{q}\widehat{p}|q'\rangle - \langle q|\widehat{p}\widehat{q}|q'\rangle = i\hbar\langle q|q'\rangle = i\hbar\delta(q-q').$$

Thus

$$(q-q')\langle q|\widehat{p}|q'\rangle = i\hbar\delta(q-q').$$

However we can use the following property of the Dirac delta function:

$$x\delta'(x) = -\delta(x), \qquad x\delta(x) = 0$$

and so we see that

$$\langle q|\widehat{p}|q'\rangle = \tfrac{\hbar}{i}\delta'(q-q')$$

and

$$p\langle q|p\rangle = \int dq'\langle q|\widehat{p}|q'\rangle\langle q'|p\rangle = \tfrac{\hbar}{i}\int dq'\delta'_q(q-q')\langle q'|p\rangle = -\tfrac{\hbar}{i}\int dq'\delta'_{q'}(q-q')\langle q'|p\rangle = \tfrac{\hbar}{i}\tfrac{\partial}{\partial q}\left(\langle q|p\rangle\right)$$

and so

$$\langle q|p\rangle \;=\; A\, e^{\frac{ipq}{\hbar}},$$

where A is a normalisation factor.

Note that $\langle q|p\rangle$ is a wave function of a state with a well defined momentum. Naively, we may expect this function, like any wavefunction to be normalised *i.e.* to satisfy

$$\int dq\psi(q)^\star\psi(q) = 1$$

but from the above we get

$$|A|^2\int dq\, e^{\frac{ipq}{\hbar}}e^{\frac{-ipq}{\hbar}} = |A|^2\int dq = 1$$

and so we see that $|A|^2 = \frac{1}{V}$ where V is the range of integration (*i.e.* ∞).

Thus we have run into the well known problem of normalisation. There are three ways of dealing with this problem:

- consider only wave packets (*i.e.* always have some spread in momentum)
- normalise in a "box" of finite dimensions and later take these dimensions to ∞.
- *practical* - not worry about normalisation (but keep it at the back of our mind).

Returning to the case of N degrees of freedom we see that in the momentum representation

$$\begin{aligned}|\psi\rangle &= \int d^Np\,|\mathbf{p}\rangle\langle\mathbf{p}|\psi\rangle \,=\, \int d^Np\,|\mathbf{p}\rangle\tilde{\psi}(\mathbf{p}) \\ &= \int d^Nq\,|\mathbf{q}\rangle\langle\mathbf{q}|\psi\rangle \,=\, \int d^Nq\,|\mathbf{q}\rangle\psi(\mathbf{q}).\end{aligned}$$

Thus

$$\begin{aligned}\psi(\mathbf{q}) &= \langle\mathbf{q}|\psi\rangle \,=\, \int d^Np\,\langle\mathbf{q}|\mathbf{p}\rangle\langle\mathbf{p}|\psi\rangle \\ &= \int d^Np\,\langle\mathbf{q}|\mathbf{p}\rangle\tilde{\psi}(\mathbf{p}).\end{aligned}$$

So

$$\psi(\mathbf{q}) \,=\, A\int d^Np\,e^{\frac{i\mathbf{qp}}{\hbar}}\,\tilde{\psi}(\mathbf{p})$$

and

$$\tilde{\psi}(\mathbf{p}) \,=\, A\int d^Nq\,e^{\frac{-i\mathbf{qp}}{\hbar}}\,\psi(\mathbf{q}).$$

Note that if we choose

$$A = \left(\frac{1}{\sqrt{2\pi\hbar}}\right)^N$$

we have

$$\langle\psi|\psi\rangle \,=\, \int d^Nq\,|\psi(\mathbf{q})|^2 \,=\, \int d^Np\left|\tilde{\psi}(\mathbf{p})\right|^2$$

Then the interpretation of $\tilde{\psi}(p)$ is analogous to the interpretation of $\psi(\mathbf{q})$ and we see that going from the momentum to the position representation wave functions involves taking Fourier transforms.

Comments:

- 1. Note that $\psi(\mathbf{q}) = \int d^Np\,e^{\frac{1\mathbf{qp}}{\hbar}}\tilde{\psi}(\mathbf{p})$ has a meaning of a superposition of plane waves of momentum $\mathbf{p}$ with weights provided by the function $\tilde{\psi}(\mathbf{p})$. Thus we have a **wave packet**.
- 2. If $\tilde{\psi}(\mathbf{p}) \neq B\delta(\mathbf{p}-\mathbf{p_0})$ then the momentum of the system is not uniquely defined and we have a spread in momentum.

4 Equation of Motion - Dynamics

4.1 Introduction

In classical mechanics, as we have said earlier, the time evolution (the dynamics) can be described in terms of Hamilton's equations

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

or, equivalently, in terms of Poisson's brackets

$$\frac{dA}{dt} = \frac{\partial A}{\partial t} + \{A,\, H\}$$

etc. In Quantum Mechanics there are, similarly, also several equivalent ways of describing the dynamics. Such descriptions are called **pictures**.

4.2 The Schrödinger picture

The theory involves both state vectors and certain operators that extract the information they encode. As times progresses either or both could change. It is perhaps more "natural" to associate this change with the the state vector. The observables correspond to fixed operators - although the results of their action on the state depend on time as the state changes with time. This way of describing the development of the system is called the **Schrödinger picture**. Then as long as the system is left undisturbed it evolves causally and its evolution is described by the equation of motion.

But **warning**; when any measurement is performed the system is perturbed and during this measurement its change is acausal.

So what is this causal evolution?

Let us assume that at time t the state is $|\psi_t\rangle$ and at $t = t_0$ it is $|\psi_{t_0}\rangle$. We expect that there is an unitary operator $\widehat{U}(t, t_0)$ which connects these two states of the system. *i.e.* which acts as

$$|\psi_t\rangle = \widehat{U}(t, t_0)|\psi_{t_0}\rangle.$$

Why? In classical mechanics the time evolution can be thought of as a continuous unfolding of canonical transformations which preserve Hamilton's equations and Poisson's brackets. So we may even expect that the operator U has "something to do" with the Hamiltonian of the system.

Let us **assume** that the operator $\widehat{U}(t, t_0)$ is linear, *i.e.* that it satisfies

$$\mu|\psi_t\rangle + \lambda|\phi_t\rangle \;=\; \widehat{U}(t, t_0)\,[\mu|\psi_{t_0}\rangle + \lambda|\phi_{t_0}\rangle]$$

and that the operator $\widehat{U}$ is independent of the state vector $|\psi\rangle$. Let us assume further that

$$\langle\psi_t|\psi_t\rangle = \langle\psi_{t_0}|\psi_{t_0}\rangle,$$

although, this may appear less clearly motivated (this is equivalent to the statement that $\widehat{U}$ is unitary, *i.e.* $\widehat{U}^\dagger\widehat{U} = \widehat{1}$) and

$$\widehat{U}(t_1, t_2)\,\widehat{U}(t_2, t_3) \;=\; \widehat{U}(t_1, t_3).$$

This last requirement tells us that as $\widehat{U}(t_0, t_1)\widehat{U}(t_1, t_0) = \widehat{1}$, $\widehat{U}(t_0, t_1) = \widehat{U}^{-1}(t_1, t_0)$ and so that

$$\widehat{U}^\dagger(t_0, t_1) = \widehat{U}^{-1}(t_0, t_1) = \widehat{U}(t_1, t_0).$$

Let us now derive the equation of motion in a differential form. To do this define

$$\begin{aligned}
\frac{d}{dt}|\psi_t\rangle &= \lim_{\epsilon\to 0}\frac{1}{\epsilon}\left(|\psi_{t+\epsilon}\rangle - |\psi_t\rangle\right) = \lim_{\epsilon\to 0}\frac{1}{\epsilon}\left(\widehat{U}(t+\epsilon, t_0) - \widehat{U}(t, t_0)\right)|\psi_{t_0}\rangle \\
&= \frac{d\widehat{U}(t, t_0)}{dt}|\psi_{t_0}\rangle = \frac{d\widehat{U}(t, t_0)}{dt}\widehat{U}^\dagger(t, t_0)|\psi_t\rangle.
\end{aligned}$$

So

$$\frac{d}{dt} = \frac{d\widehat{U}(t,t_0)}{dt}\widehat{U}^\dagger(t,t_0).$$

Defining $U_t \equiv \widehat{U}(t,t_0)$ we see that

$$\frac{d}{dt}\left(U_t U_t^\dagger\right) = 0$$

gives

$$\frac{dU_t}{dt}U_t^\dagger + U_t\frac{dU_t^\dagger}{dt} = 0$$

which shows that the operator

$$\frac{dU_t}{dt}U_t^\dagger$$

is anti-Hermitian. So putting in $i\hbar$ we have

$$\left[i\hbar\frac{dU_t}{dt}U_t^\dagger\right] = i\hbar\frac{dU_t}{dt}U_t^\dagger \equiv \widehat{H}(t),$$

where $\widehat{H}$ is a Hermitian operator. Thus our equation becomes

$$i\hbar\frac{d}{dt}|\psi_t\rangle \; = \; \widehat{H}(t)|\psi_t\rangle.$$

This equation, called the **Schrödinger equation** specifies the dynamics in the Schrödinger picture.

What is $\widehat{H}(t)$? This will become clearer after we have introduced an alternative formulation of the dynamics - in terms of the **Heisenberg picture**.

At the moment let us note that if $\widehat{H} \neq \widehat{H}(t)$, *i.e.* $\widehat{H}$=const then we can solve

$$i\hbar\frac{dU_t}{dt}U_t^\dagger = \widehat{H}$$

as then

$$i\hbar\frac{dU_t}{dt} \; = \; \widehat{H}U_t$$

and so we see that

$$U_t = \widehat{U}(t,t_0) = exp\left(-\frac{i\widehat{H}(t-t_0)}{\hbar}\right)$$

where we have determined the constant of integration from $\widehat{U}(t_0,t_0) = \widehat{1}$.

4.3 The Heisenberg Picture

In the Schrödinger picture we had

$$|\psi_t\rangle = \widehat{U}(t,t_0)|\psi_{t_0}\rangle$$

and all the operators were fixed $\widehat{A}$. However, we can perform an unitary transformation

$$|\psi_t\rangle \; \rightarrow \; \widehat{U}(t_0,t)|\psi_t\rangle = |\psi_{t_0}\rangle.$$

and transform the operators

$$\widehat{A} \; \rightarrow \; \widehat{A}_t = \widehat{U}(t_0,t)\widehat{A}\widehat{U}(t,t_0)$$

and then we will have an equivalent description of the dynamics of the system as all matrix elements

$$\langle\psi_t|\widehat{A}|\phi_t\rangle = \langle\psi_{t_0}|\widehat{A}_t|\phi_{t_0}\rangle$$

are unchanged (we have defined the transformation of $\widehat{A}$ so that this is the case!).

This way we have a second description of the dynamics - the **Heisenberg picture**, in which the states are fixed (coinciding with the states in the Schrödinger picture at $t = t_0$, *i.e.* $|\psi_{t_0}\rangle$) but all observables are represented by time dependent operators $\widehat{A}_t$.

What is the equation of motion? Now this is the equation governing the time evolution of $\widehat{A}_t$.

To find it let us assume, for simplicity, that $\widehat{H} \neq \widehat{H}(t)$. Then $\widehat{U}(t,t_0) = exp\left(-\frac{i\widehat{H}(t-t_0)}{\hbar}\right)$ and

$$\begin{aligned} i\hbar\frac{d\widehat{A}_t}{dt} &= i\hbar\frac{d}{dt}\left(e^{\frac{i\widehat{H}(t-t_0)}{\hbar}}\widehat{A}e^{\frac{-i\widehat{H}(t-t_0)}{\hbar}}\right) \\ &= -\widehat{H}\left(e^{\frac{i\widehat{H}(t-t_0)}{\hbar}}\widehat{A}e^{\frac{-i\widehat{H}(t-t_0)}{\hbar}}\right) + \left(e^{\frac{i\widehat{H}(t-t_0)}{\hbar}}\widehat{A}e^{\frac{-i\widehat{H}(t-t_0)}{\hbar}}\right)\widehat{H} = [\widehat{A}_t,\,\widehat{H}]. \end{aligned}$$

This equation

$$i\hbar\frac{d\widehat{A}_t}{dt} = [\widehat{A}_t,\,\widehat{H}]$$

is called the Heisenberg's equation of motion; or the equation of motion in Heisenberg's picture.

By comparing it with

$$\frac{dA}{dt} = \{A,\,H\}$$

in classical mechanics and the quantisation condition

$$\{A,H\} \to \frac{[\widehat{A},\,\widehat{H}]}{i\hbar}$$

we see that it is natural to identify $\widehat{H}$ with the Hamiltonian.

Notes:

- 1 If $\widehat{H} = \widehat{H}(t)$ then

  $$i\hbar\frac{d}{dt}\widehat{A}_t = [\widehat{A}_t,\,\widehat{H}_t(t)]$$

  where $\widehat{H}_t(t) = \widehat{U}^\dagger(t,t_0)\widehat{H}(t)\widehat{U}(t,t_0)$ *i.e.* has the same expression as $\widehat{A}_t$.

- 2 If $\widehat{A} = \widehat{A}(t)$ then

  $$i\hbar\frac{d\widehat{A}_t}{dt} = [\widehat{A}_t,\,\widehat{H}_t] + i\hbar\frac{\partial}{\partial t}\widehat{A}_t,$$

  where $\frac{\partial}{\partial t}\widehat{A}_t \equiv \widehat{U}^\dagger(t,t_0)\frac{d\widehat{A}}{dt}(t)\widehat{U}(t,t_0)$. Note that $H_t = H$ if $H \neq H(t)$.

4.4 Conserved quantities; constants of motion

So which picture is the most convenient? In practice, it is the Schrödinger picture. However, the Heisenberg picture is very useful as it tells us how to find constants of motion. To see this note that for any operator $\widehat{A}$ its Heisenberg equation of motion is

$$i\hbar\frac{d}{dt}\widehat{A}_t = i\hbar\frac{\partial}{\partial t}\widehat{A}_t + [\widehat{A}_t,\,\widehat{H}_t].$$

So if $\frac{\partial}{\partial t}\widehat{A}_t = 0$, *i.e.* $\widehat{A} = \widehat{A}(p,q)$ only, and if

$$[\widehat{A}_t,\,\widehat{H}_t] = 0, \qquad \text{then} \qquad \widehat{A}_t = \text{const.}$$

However,

$$[\widehat{A}_t,\widehat{H}_t] = 0, \qquad \rightleftharpoons \qquad [\widehat{A},\,\widehat{H}] = 0$$

and so we see that this result is true in any picture. Thus, the observables, which in the Schrödinger picture do **not** depend explicitly on time are conserved if they commute with the Hamiltonian. The constants of motion are represented by time independent observables which commute with the Hamiltonian.

4.5 Stationary states. Time independent Schrödinger equation

4.5.1 Stationary states

Consider

$$i\hbar\frac{d}{dt}|\psi(t)\rangle = \widehat{H}|\psi(t)\rangle.$$

Then, if $\widehat{H} \neq \widehat{H}(t)$

$$|\psi(t)\rangle = \exp(-i\frac{t}{\hbar}\widehat{H})|\psi(0)\rangle.$$

Next insert $\widehat{I} = \sum_E |E\rangle\langle E|$ (the identity resolved into energy eigenstates) immediately to the right of $\exp(-i\frac{t}{\hbar}\widehat{H})$ giving

$$|\psi(t)\rangle = \sum_E \langle E|\psi(0)\rangle \exp(-i\frac{Et}{\hbar})|E\rangle.$$

Time dependence is exhibited in a phase factor for each component and is harmonic with angular frequency $E/\hbar$.

Note that if $|\psi(0)\rangle = |E\rangle$, where

$$\widehat{H}|E\rangle = E|E\rangle$$

i.e. the system starts in an energy eigenstate, then

$$|\psi(t)\rangle = |E(t)\rangle = \exp(-i\frac{Et}{\hbar})|E\rangle$$

and the energy-value remains sharp — always $\Delta E = 0$. Also for any $\widehat{A}$

$$\langle E(t)|[\widehat{A}, \widehat{H}]|E(t)\rangle = 0$$

and so for all observables A where $\partial\widehat{A}/\partial t = 0$ we have $\langle A\rangle =$ constant. An energy eigenstate $\exp(-i\frac{Et}{\hbar})|E\rangle$ or just simply $|E\rangle$ is called a **stationary state**. An isolated atom in a stationary state is stable. However, 'isolation' is an idealisation and real atoms in excited states (energy eigenstates above the ground state) usually decay quickly.

Thus in general, we have all terms in the expression above. If the Hamiltonian $\widehat{H}$ has both continuous and discrete parts of the spectrum, then

$$|\psi(0)\rangle = \sum_i a_i|E_i\rangle \; + \int dE' a(E')|E'\rangle$$

and so

$$|\psi(t)\rangle = \sum_i a_i \exp(-i\frac{E_i t}{\hbar})|E_i\rangle \; + \int dE' a(E') \exp(-i\frac{E' t}{\hbar})|E'\rangle.$$

We see that the problem of determining the dynamics reduces to that of finding solutions of the eigenvalue equation for $\widehat{H}$ *i.e.*

$$\widehat{H}|E\rangle = E|E\rangle.$$

This equation is called the **time independent Schrödinger equation**.

4.5.2 Schrödinger wave equation

Consider one particle of mass m in a potential field $V(\mathbf{r})$. The Schrödinger Equation

$$i\hbar\frac{d}{dt}|\psi_t\rangle = \widehat{H}|\psi_t\rangle$$

where $\widehat{H} = \widehat{\mathbf{p}}^2/2m + \widehat{V}(\widehat{\mathbf{r}})$ becomes the Schrödinger Wave Equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(\mathbf{r})\psi = i\hbar\frac{\partial\psi}{\partial t}$$

for the wavefunction $\psi(\mathbf{r},t)$. We can think of this equation as having come from the equation above by acting on it, from the left, with the bra vector $\langle\mathbf{r}|$. Then exploiting the fact that the potential V is a function of $\mathbf{r}$ only we get the Schrödinger Wave Equation. Its solution, using the energy eigenbasis

$$|\psi(t)\rangle = \sum_E \langle E|\psi(0)\rangle \exp(-i\frac{Et}{\hbar})|E\rangle,$$

becomes the separation-of-variables solution

$$\psi(\mathbf{r},t) = \sum_E c_E \exp(-i\frac{Et}{\hbar})\phi_E(\mathbf{r})$$

where $\phi_E(\mathbf{r}) = \langle\mathbf{r}|E\rangle$ is a normalised energy eigenfunction obeying

$$-\frac{\hbar^2}{2m}\nabla^2\phi + V(\mathbf{r})\phi = E\phi$$

(often called the 'time-independent Schrödinger Wave Equation' — this was actually the first form guessed by Schrödinger, in June 1926). Here $c_E = \langle E|\psi(0) = \int dV\, \phi_E^*(\mathbf{r})\psi(\mathbf{r},0)$. The eigenfunctions ϕ_E also obey the eigenvalue differential equations corresponding to mutually compatible conserved quantities such as momentum or angular momentum.

If the spectrum of $\widehat{H}$ is continuous (or has a continuous sector) then the $\sum_E$ becomes an integral over (part of) E and the energy eigenfunctions have Dirac δ-function normalisation. Otherwise the solutions are square-integrable and ψ and ϕ vanish quickly at large $|\mathbf{r}|$.

4.5.3 Example - Free particle

For a particle experiencing no force we define $V(\mathbf{r}) = 0$, (adding a constant to $\widehat{H}$ adds only an overall phase to solutions of the Schrödinger Equation). A free particle of mass m then has $\widehat{H} = \widehat{\mathbf{p}}^2/2m$. Since $[\widehat{H}, \widehat{\mathbf{p}}] = 0$, momentum $\mathbf{p}$ is conserved and eigenstates $|E, \mathbf{p}\rangle$ of $\widehat{\mathbf{p}}$ are eigenstates of $\widehat{H}$ with eigenvalues related by $E = \mathbf{p}\cdot\mathbf{p}/2m$. Note that angular momentum is conserved too, $[\widehat{H}, \widehat{L}] = 0$, but $\mathbf{L}$ and $\mathbf{P}$ are incompatible, $[\widehat{P}, \widehat{L}] \neq 0$.

In wave mechanics a momentum eigenfunction $\phi_{\mathbf{p}}(\mathbf{r})$ obeys

$$-i\hbar\nabla\phi = \mathbf{p}\phi,$$

which, as we have said earlier, is satisfied by

$$\phi = \phi_{\mathbf{p}}(\mathbf{r}) \equiv \langle\mathbf{r}|\mathbf{p}\rangle = C\exp(\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}).$$

Here C is a constant and in the absence of other constraints components of $\mathbf{p}$ take any (real) values.

With continuous $\mathbf{p}$ the wavefunctions ϕ are unnormalisable with inner product

$$\int d^3r\, \phi_{\mathbf{p}}^*(\mathbf{r})\phi_{\mathbf{p}'}(\mathbf{r}) = |C|^2 \int dx\,dy\,dz\, \exp(\frac{i}{\hbar}(\mathbf{p}'-\mathbf{p})\cdot\mathbf{r}) = |C|^2\,(2\pi\hbar)^3\delta(\mathbf{p}'-\mathbf{p}).$$

Choose $C = 1$ so that

$$\langle\mathbf{p}|\mathbf{p}'\rangle = (2\pi\hbar)^3\delta(\mathbf{p}-\mathbf{p}') \qquad \text{and} \qquad \widehat{I} = \int \frac{d^3p}{(2\pi\hbar)^3}|\mathbf{p}\rangle\langle\mathbf{p}|,$$

where the momentum-space volume element d^3p is $dp_x\,dp_y\,dp_z$ in Cartesian coordinates.

Box Normalisation: While δ-function normalisation is generally no problem, there are some difficulties: *e.g.* in the proof that $\widehat{\mathbf{r}}$ has a continuous spectrum and in the handling of the parity operator, as we will see later, where infinite factors are cancelled! Also simply checking self-adjointness of $\widehat{\mathbf{p}} = -i\hbar\nabla$ is a puzzle if wavefunctions do not vanish at ∞. One escape device is to use 'box normalisation' where space is given torus topology by putting the particle into a cube of edge-length L and identifying parallel faces. Then the wavefunction $\phi_{\mathbf{p}}(\mathbf{r})$ (for instance) obeys periodic boundary conditions which imply that Cartesian components p_i of $\mathbf{p}$ are quantised by $p_iL = 2\pi n_i\hbar$ for $n_i = 0, \pm 1, \ldots$ and which ensure that $\widehat{\mathbf{p}}$ is self-adjoint. Choosing $C = L^{-3/2}$ integration over the box gives $\langle \mathbf{p}|\mathbf{p}'\rangle$ as a product of Kronecker deltas on integers n_i and $\widehat{I} = \sum_{n_i} |\mathbf{p}\rangle\!\langle\mathbf{p}|$. Factors of L cancel from results of observation. For more details see Schiff, *p.* 48.

Momentum eigenstates obey the free-particle energy eigenvalue equation

$$-\frac{\hbar^2}{2m}\nabla^2\phi = E\phi$$

provided $|\mathbf{p}|^2 = 2mE$ and with this relation understood we have

$$\phi \equiv \langle \mathbf{r}|E(\mathbf{p}), \mathbf{p}\rangle = \exp(\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}).$$

For each E there is degeneracy with respect to direction of $\mathbf{p}$ and all directions must be counted in summing over the complete set of energies to construct the wavefunction $\psi(\mathbf{r}, t)$.

So with continuous momentum eigenstates instead of discrete energy eigenstates the sum solution to the Schrödinger Wave Equation for a free particle becomes the Fourier Integral expression

$$\psi(\mathbf{r}, t) = \int \frac{d^3p}{(2\pi\hbar)^3}\tilde{\psi}(\mathbf{p})\exp(\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{r} - \frac{\mathbf{p}^2}{2m}t)),$$

where

$$\tilde{\psi}(\mathbf{p}) \equiv \langle E, \mathbf{p}|\psi\rangle = \int d^3r\ \exp(-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r})\psi(\mathbf{r}, 0)$$

is the Fourier Transform of the initial data, its 'momentum-space wavefunction'. This form of $\psi(\mathbf{r}, t)$ is a 'wavepacket' solution to the Schrödinger Wave Equation.

For a particle with definite momentum $\mathbf{p}_0$ at $t = 0$ we have

$$\tilde{\psi}(\mathbf{p}) = \langle E, \mathbf{p}|\mathbf{p}_0\rangle = (2\pi\hbar)^3\delta(\mathbf{p} - \mathbf{p}_0)$$

and the Schrödinger Wave Equation has plane-wave solution

$$\psi(\mathbf{r}, t) = \exp(i(\mathbf{k}\cdot\mathbf{r} - \omega t))$$

with wave-vector $\mathbf{k} \equiv \mathbf{p}_0/\hbar$ and angular frequency $\omega \equiv E/\hbar$ connected by the 'dispersion relation' $\omega(\mathbf{k}) = \hbar\mathbf{k}\cdot\mathbf{k}/2m$. This is the particle's de Broglie wave, just as experiment observes, with group velocity

$$\frac{d\omega}{d\mathbf{k}} = \frac{\mathbf{p}_0}{m},$$

which is the classical particle velocity.

Example: The 'Two-slit Experiment'. This is discussed as a thought experiment in textbooks (*e.g.* Schiff *pps.* 12–14; Feynman Ch. 1) but certainly has been performed in the lab). Here a stream of electrons of definite momentum $\mathbf{p}$ falls normally on a screen with two narrow slits, parallel and close-spaced, and the point of arrival of each particle on a parallel screen behind is recorded. The electrons fall in bands, forming the diffraction pattern appropriate to the wavevector $\mathbf{p}/\hbar$. The stream 'looks like a wave'. But the pattern builds up even if the intensity is so low that only a single electron is in transit at any time. The wave is usually pictured like a water wave, propagating from source to screen each time an electron travels. But it must be recalled that in fact the wave is a solution of the Schrödinger Wave Equation with boundary conditions appropriate to the physical circumstances; here an arrangement of source, screens and slits, and it is a complex-valued function defined in an entirely abstract configuration space for the electron. The position of arrival of each electron (its configuration at the that instant) is a random event with probability density given by the wavefunction's squared modulus. The wave serves to describe the possible outcomes of observation in the quantum model, just as a set of p, q coordinates obeying Hamilton's equations would do (albeit with greater certainty!) in a classical model. The quantum particle *is* no more a wave than the classical particle *is* a point in phase space. If a slit is closed the diffraction pattern disappears, for the boundary conditions on the Schrödinger Wave Equation are changed and the wavefunction changes. In fact then the position of the electron is known as it passes the first screen. The same is true if any observation determines the particle's position in transit. A position measurement changes its wavefunction to a position eigenfunction. With all this in mind it's instructive to read accounts of the two-slit experiment in Feynman, Secs. 1-4 to 1-11; Polkinghorne, Chap. 4.

4.6 Spreading of a wave packet

Let us how that a wave packet always spreads as time evolves. To see this let us take a (one dimensional) wave packet which at $t = 0$ is centred at $x = 0$ with a spread a_0. For this we can take a Gaussian

$$\psi_{a_0}(x,0) = \frac{1}{(a_0\sqrt{\pi})^{\frac{1}{2}}}\, e^{-\frac{x^2}{2a_0^2}}.$$

Notice that this wave function happens to be real (this does not matter) and that the normalisation has been so chosen that $\int_{-\infty}^{\infty} dx\, |\psi|^2 = 1$.

Then

$$\tilde{\psi}_{a_0}(p,0) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx\, e^{-\frac{ixp}{\hbar}}\, \psi_{a_0}(x,0) = \frac{1}{\sqrt{2\pi\hbar}} \frac{1}{(a_0\sqrt{\pi})^{\frac{1}{2}}} \int_{-\infty}^{\infty} dx\, e^{-\frac{ixp}{\hbar}}\, e^{-\frac{x^2}{2a_0^2}} =$$

$$\frac{1}{\sqrt{2\pi\hbar}} \frac{1}{(a_0\sqrt{\pi})^{\frac{1}{2}}} \int_{-\infty}^{\infty} dx\, e^{-\left(\frac{x}{\sqrt{2}a_0} + \frac{ia_0 p}{\sqrt{2}\hbar}\right)^2} e^{-\frac{a_0^2 p^2}{2\hbar^2}} = \frac{\sqrt{2}a_0}{\sqrt{2\pi\hbar}\sqrt{a_0\sqrt{\pi}}} e^{-\frac{a_0^2 p^2}{2\hbar^2}} \int dx e^{-x^2} = \frac{\sqrt{2a_0\sqrt{\pi}}}{\sqrt{2\pi\hbar}} e^{-\frac{a_0^2 p^2}{2\hbar^2}}.$$

In this calculation we have used $\int_{-\infty}^{\infty} dx\, e^{-x^2} = \sqrt{\pi}$ and assumed that we can alter the path of the integration from the real line (in x) to the line (parallel to the real axis) in the complex x plane .

If the particle is free then $E = \frac{p^2}{2m}$ and

$$\tilde{\psi}_{a_0}(p,t) = \tilde{\psi}_{a_0}(p,0)\, e^{-i\frac{p^2 t}{2m\hbar}}.$$

Thus

$$\begin{aligned}\psi(x,t) &= \tfrac{1}{\sqrt{2\pi\hbar}} \textstyle\int_{-\infty}^{\infty} dp\, e^{\frac{ixp}{\hbar}}\, \tilde{\psi}_{a_0}(p,t) = \tfrac{\sqrt{2a_0\sqrt{\pi}}}{2\pi\hbar} \textstyle\int_{-\infty}^{\infty} dp\, e^{-\frac{ip^2 t}{2m\hbar} + \frac{ixp}{\hbar} - \frac{a_0^2 p^2}{2\hbar^2}} \\ &= \tfrac{\sqrt{2a_0\sqrt{\pi}}}{2\pi\hbar} \textstyle\int_{-\infty}^{\infty} dp\, e^{-z(p+Rx)^2} e^{zR^2x^2},\end{aligned}$$

where $z = \frac{a_0^2}{2\hbar^2} + \frac{it}{2m\hbar}$ and $R = -\frac{i}{2z\hbar}$.

Again, we change the integration variable from p to $(p + Rz)\sqrt{z}$ and, distorting the contour, obtain

$$\frac{\sqrt{2a_0\sqrt{\pi}}\sqrt{\pi}}{2\pi\hbar\sqrt{\left(\frac{a_0^2}{2\hbar^2} + \frac{it}{2m\hbar}\right)}} e^{-\frac{x^2}{4\hbar^2 z}} = \frac{1}{(\pi)^{\frac{1}{4}}\sqrt{a_0 + \frac{it\hbar}{ma_0}}} e^{-\frac{x^2}{2\left(a_0^2 + \frac{it\hbar}{m}\right)}}.$$

Note that

$$|\psi_{a_0}(x,t)| = |\psi_a(x,0)|$$

where

$$a^2 = a_0^2 + \frac{\hbar^2 t^2}{m^2 a_0^2}.$$

So we see that our Gaussian wave packet is spreading; its width grows as $a(t)$. This effect is called the **spreading of the wave function**. To prevent this from happening you need some non-linearity in ψ - such phenomena, (non-linear Schrödinger equation *etc.*) are discussed in a course on solitons.

4.7 Ehrenfest's theorems; Energy-time uncertainty principle

4.7.1 Ehrenfest's theorems

Ehrenfest showed that the mean values of observables $\langle\widehat{A}\rangle$ behave like classical quantities; they satisfy equations of classical mechanics.

To see this assume that $\widehat{A} \neq \widehat{A}(t)$. Then

$$\begin{aligned}\frac{d}{dt}\langle\widehat{A}\rangle = \quad & \frac{d}{dt}\langle\psi|\widehat{A}|\psi\rangle = \left(\frac{d}{dt}\langle\psi|\right)\widehat{A}|\psi\rangle + \langle\psi|\widehat{A}\left(\frac{d}{dt}|\psi\rangle\right)\\ = \quad & \frac{1}{i\hbar}\langle\psi|[\widehat{A},\widehat{H}]|\psi\rangle = \frac{1}{i\hbar}\langle[\widehat{A},\widehat{H}]\rangle.\end{aligned}$$

Recall that in classical mechanics we had (Poisson brackets)

$$\frac{d}{dt}A = \{A,\, H\}.$$

Thus, for a particle of mass m in one dimension, we have

$$\frac{d}{dt}\langle\widehat{x}\rangle \;=\; \frac{1}{i\hbar}\langle[\widehat{x},\, \frac{p^2}{2m}]\rangle \;=\; \frac{\langle\widehat{p}\rangle}{m}.$$

If

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

and if $\widehat{F}(\widehat{x}) = -\frac{\partial}{\partial x}\widehat{V}$ then

$$\frac{d}{dt}\langle\mathbf{p}\rangle \;=\; \frac{1}{i\hbar}\langle[\widehat{p},\, \widehat{V}(\widehat{x})]\rangle = -\langle\frac{\partial\mathbf{V}}{\partial x}\rangle = \langle\widehat{F}\rangle.$$

This last equation looks very much like the Newton law. But **note** that we have $\langle\frac{\partial V}{\partial x}\rangle$ and not

$$\frac{\partial V}{\partial x}(\langle x\rangle)$$

and so we cannot talk about the centre of the packet as moving classically; moreover, as we already know, we have also some additional effects due to the spreading out of the packet.

4.7.2 Time-energy uncertainty principle

Recall that

$$\frac{d}{dt}\langle\widehat{A}\rangle = \frac{1}{i\hbar}\langle[\widehat{A},\, \widehat{H}]\rangle$$

But,

$$\Delta A = \left(\langle\widehat{A}^2\rangle - \langle\widehat{A}\rangle^2\right)^{\frac{1}{2}}$$

so

$$\Delta A \Delta B \geq \tfrac{1}{2}\left|\langle[\widehat{A},\, \widehat{B}]\rangle\right|.$$

So applying this to $\widehat{A}$ and $\widehat{H}$ we have

$$\Delta A \Delta H \geq \tfrac{1}{2}\left|\langle[\widehat{A},\, \widehat{H}]\rangle\right| = \tfrac{\hbar}{2}\left|\tfrac{d}{dt}\langle\widehat{A}\rangle\right|.$$

But $\Delta\widehat{H} = \Delta E$ so

$$\tau_A \, \Delta E \geq \frac{\hbar}{2},$$

where

$$\tau_A = \frac{\Delta\widehat{A}}{\left|\frac{d}{dt}\langle\widehat{A}\rangle\right|}.$$

Here τ_A is the time characteristic of the statistical evolution of the system as seen via its effects on the observable $\widehat{A}$; *i.e.* the time required for the centre $\langle\widehat{A}\rangle$ of this distribution to be displaced by an amount equal to its width; *i.e.* time necessary for the statistical distribution to be appreciably altered.

Take $\tau = \min_A \tau_A$. Then

$$\tau \Delta E \geq \frac{\hbar}{2}.$$

which is the **Time-Energy uncertainty principle**.

Comments:

- If a system is in a stationary state then $\frac{d\langle\widehat{A}\rangle}{dt} = 0$ (as then $\langle\psi|[\widehat{A},\, \widehat{H}]|\psi\rangle = 0$) and so $\tau = \infty$ but then energy is well defined and so $\Delta E = 0$.
- Note that the origin of the time-energy uncertainty principle is different from $\Delta q \Delta p \geq \hbar/2$. There's no self-adjoint 'time' operator but instead an operator for 'evolution time as measured by A' has been introduced as $\widehat{A}/\left|\partial\langle A\rangle/\partial t\right|$. It's clear that the less well-defined is energy, the more frequencies $E/\hbar$ contribute to the series solution of the Schrödinger Equation and the faster the system may appear to evolve in terms of any measurable A. Conversely a sharper definition of energy forces slower evolution. The time-energy uncertainty relation is often invoked in picturing, say, an electromagnetic interaction of two charged particles as exchange of a photon. It is said that violation of energy conservation in emission and absorption can be allowed if it occurs quickly enough. Similar statements are often made in connection with 'tunnelling', *e.g.* Polkinghorne *pps.* 50 – 52.

Examples:

- 1. Decay of nuclear matter (energy not well defined).
- 2. Superposition of 2 stationary states. Take a superposition of 2 stationary states of energies E_1 and E_2.

  $$\psi(\mathbf{r}, t) = \psi_1(\mathbf{r})e^{-\frac{iE_1 t}{\hbar}} + \psi_2(\mathbf{r})e^{-\frac{iE_2 t}{\hbar}}.$$

  Then

  $$P(\mathbf{r}, t) = |\psi_1(\mathbf{r})|^2 + |\psi_2(\mathbf{r})|^2 + 2Re\left(\psi_1^{\star}\psi_2\, e^{\frac{i(E_1-E_2)t}{\hbar}}\right).$$

  This quantity oscillates in time between 2 extreme values $(|\psi_1| - |\psi_2|)^2$ and $(|\psi| + |\psi_2|)^2$ with the period of the oscillation given by $\tau = \frac{h}{(E_1 - E_2)}$.

  Thus the statistical distribution of the results of measurements made at t_1 and t_2 will be practically identical if $\Delta t = |t_1 - t_2|$ is small compared to τ.

  Thus, in order that the properties of the system be significantly modified over the time period Δt, $\Delta t \, \Delta E$ must be at least $\sim \hbar$.

4.8 Probability current; Conservation of probability

Recall that $|\psi(\mathbf{r},t)|^2\, d^3x$ gives the probability (when ψ is properly normalised) of finding the particle within $\mathbf{r}$ and $\mathbf{r}+d\mathbf{r}$ at time t. Thus

$$P_\Omega = \int_\Omega d^3x\; |\psi(\mathbf{r},t)|^2 = \int_\Omega d^3x \rho(\mathbf{r},t)$$

is the probability of finding the particle in Ω. Note that $P_\Omega \to 1$ as $Vol(\Omega) \to \infty$ and $\Omega \to \mathbf{R}^3$.

But $P_\Omega = P_\Omega(t)$. So calculate

$$\frac{dP_\Omega}{dt} = \frac{d}{dt}\int_\Omega d^3x\,\psi^\star\psi = \int_\Omega d^3x\,\frac{\partial\psi^\star}{\partial t}\psi + \int_\Omega d^3x\,\psi^\star\frac{\partial\psi}{\partial t},$$

if $\Omega \neq \Omega(t)$.

Using Schrödinger equation this is equal to

$$\frac{i\hbar}{2m}\int_\Omega d^3x\,\nabla\left[\psi^\star\nabla\psi - \psi\nabla\psi^\star\right] = \frac{i\hbar}{2m}\int_S d\mathbf{S}(\psi^\star\nabla\psi - \psi\nabla\psi^\star),$$

where $\mathbf{S}$ is the surface bounding Ω.

Then define

$$\mathbf{j}(\mathbf{r},t) = -\frac{i\hbar}{2m}(\psi^\star\nabla\psi - \psi\nabla\psi^\star) = -\frac{i\hbar}{m}Im(\psi^\star\nabla\psi) = -Re(\frac{i\hbar}{m}\psi^\star\nabla\psi),$$

the **probability current** and we see that we have

$$\frac{\partial\rho}{\partial t}(\mathbf{r},t)\; +\; \nabla\cdot\mathbf{j}(\mathbf{r},t) = 0.$$

i.e. a continuity equation.

This has similar status to the local conservation laws that apply in fluid mechanics, electromagnetism, heat, *etc.* The ‘density of the particle’ is not created or destroyed, it just moves about. Indeed in a normalisable state $\int d\tau\,\rho(\mathbf{r},t) = 1$ independent of t, (the Schrödinger Wave Equation preserves norms).

Note: if the particle is in a stationary state then $P_\Omega \neq P_\Omega(t)$ as $\rho(\mathbf{r},t) = \rho(\mathbf{r})$ and $\nabla(\psi^\star\nabla\psi) = 0$ thus

$$\nabla[\psi^\star(\mathbf{r})\,\nabla\psi(\mathbf{r})] = 0$$

as the time dependent factors cancel out. This helps us to determine the boundary conditions on $\psi(\mathbf{r})$ when we consider it in a given region Ω.

$$[-\tfrac{\hbar^2}{2m}\nabla^2\psi + V(\mathbf{r})\psi] = i\hbar\tfrac{\partial\psi}{\partial t}, \qquad \text{or} \quad = E\psi.$$

Boundary conditions (as this is a second order equation for $\psi(\mathbf{r},t)$ or $\psi(\mathbf{r})$):

- 1. Conditions at $|\mathbf{r}| \to \infty$

  $$\langle\psi|\psi\rangle = \int d^3x\,|\psi|^2 = 1$$

  so

  $$\psi(\mathbf{r}) \;\to\; 0 \quad \text{as} \quad |\mathbf{r}| \to \infty$$

  sufficiently fast.

  Comment: Sometimes we use generalised eigenstates, *i.e.* use replace wave packets by plane waves $e^{i\mathbf{pr}}$. Such states are not realisable physically but they simplify the calculations, For such states $|\psi| \sim$ const as $|\mathbf{r}| \to \infty$)

- 2. Points of discontinuity of $V(\mathbf{r})$. We patch solutions in each region in which V is continuous. At the discontinuity surfaces we demand that ρ and $\mathbf{j}$ are continuous. This implies that ψ and $\nabla\psi\cdot\mathbf{n}$, where $\mathbf{n}$ is a unit vector normal to the boundary of the region, have to be continuous.

- 3. Points where $V(\mathbf{r}) = \pm\infty$. At such points it may happen that$\psi = 0$ and $\nabla\psi$ has a discontinuity. (This will be discussed in the next chapter)

5 One-Dimensional Systems

5.1 Preliminary (recall also 4.9)

Justification: We study wave mechanics first in one dimension for practice and to discover generalities (*e.g.* tunnelling) without needing to deal with angular momentum. This is just like classical mechanics and, just as there, in (important) circumstances where angular momentum is conserved three-dimensional problems can be reduced to equivalent one-dimensional form.

Problem: A quantum particle of mass m moves on the x-axis in a potential field $V(x)$. Discuss boundary conditions on the wavefunction.

Solution: The wavefunction $\psi(x,t)$ obeying the one-dimensional Schrödinger Wave Equation is a sum or integral over E involving the energy eigenfunction $\phi_E(x)$ which solves

$$\phi'' = \frac{2m}{\hbar^2}(V(x)-E)\phi.$$

Localised or bound solutions with discrete E-values occur for $E < \min\{V_\pm\}$ where $V_\pm \equiv V(x \to \pm\infty)$ and have $\phi(x \to \pm\infty) \sim \exp(-K_\pm |x|)$ where $K_\pm^2 = 2m(V_\pm - E)/\hbar^2$. If $V(|x| \to \infty) \to \infty$ then $\phi_E \to 0$ faster at ∞.

Scattering solutions $\phi_E(|x| \to \infty) \sim \exp(\pm ikx)$ where $k^2 = -K_\pm^2$ occur for $E > \min\{V_\pm\}$, have continuous E-values and correspond to leftward (-) and rightward (+) motion, being asymptotically eigenfunctions of $\widehat{p} = -i\hbar d/dx$ with momentum eigenvalues $\pm\hbar k$ ($k > 0$ by definition).

Integrating the energy-eigenvalue equation we have

$$\phi_E'(x_1) - \phi_E'(x_2) = \frac{2m}{\hbar^2}\int_{x_1}^{x_2}(V(x)-E)\phi_E(x)\,dx$$

and so, using the continuity of ϕ,

$$\phi_E'(x+\epsilon) - \phi_E'(x-\epsilon) \approx \frac{2m}{\hbar^2}\phi_E(x)\int_{x-\epsilon}^{x+\epsilon}V(x)\,dx$$

for very small $|\epsilon|$. The right-hand side vanishes as $\epsilon \to 0$ whenever $V(x)$ is continuous or, we note, whenever $V(x)$ is piecewise continuous. So at a finite jump in $V(x)$ both $\phi_E(x)$ and $\phi_E'(x)$ are continuous. This ensures continuity of the one dimensional probability current $j = (\hbar/m)\mathrm{Im}(\psi^*\partial\psi/\partial x)$.

As examples will illustrate, in the limit of an infinite jump in $V(x)$ where the integral on the right-hand side diverges consistency demands that ϕ_E vanishes. Then generally ϕ_E' has a finite discontinuity, and j is continuous and zero. A wavefunction that penetrates a region of very large V is exponentially damped and an infinite jump in V is an impenetrable barrier; the particle bounces back.

If, bizarrely, $V(x)$ has an infinite jump of zero width, *i.e.* $V(x) = g\delta(x-a)+\ldots$, then ϕ' has a discontinuity at $x = a$:

$$\phi_E'(a_+) - \phi_E'(a_-) = \frac{2m}{\hbar^2}g\phi_E(a)$$

where ϕ_E is continuous and not necessarily zero at $x = a$.

5.2 Examples

5.2.1 Free Particle

For a 'free particle' define $V = 0$. A particle of mass m and energy $E > 0$ moving freely on the x-axis has wavefunction $\psi(x,t) = \exp(-iEt/\hbar)\phi_E(x)$ and everywhere the energy eigenfunction $\phi_E(x)$ obeys $\phi'' + k^2\phi = 0$ where $k = +\sqrt{2mE}/\hbar$ for any $E > 0$. The solution

$$\phi_E(x) = c_1\exp(ikx) + c_2\exp(-ikx)$$

is a superposition of right- and left-moving parts, eigenstates of $\widehat{p} = -i\hbar d/dx$ with eigenvalues $\pm\hbar k$. Energy eigenstates are two-fold degenerate. The discussion of wavepackets in Sec. 3.5 simplifies: $\mathbf{r} \to x$, $\mathbf{p} \to p$, $(2\pi\hbar)^3 \to 2\pi\hbar$.

5.2.2 One Dimensional Step Potential

Consider the stationary problem; *i.e.* the time independent Schrödinger equation corresponding to the potential

$$V(x) = \begin{cases} 0, & x < 0 \\ V_0 > 0 & x > 0 \end{cases}$$

and consider the case of $E < V_0$. Classically the particle can be anywhere for $x < 0$ and the region $x > 0$ is not accessible.

Quantum mechanically, we study the wave function in each region and then use the continuity conditions to relate the functions in each region.

So we put $\psi(x) = \psi_>(\psi_<)$ for $x > 0 \quad (x < 0)$. So $\widehat{H}\psi = E\psi$ gives

$$\begin{array}{llll} x < 0 & -\frac{\hbar^2}{2m}\frac{d^2\psi_<}{dx^2} = E\psi_< & \rightarrow & \psi_< = A\sin(kx) + B\cos(kx) \\ x > 0 & -\frac{\hbar^2}{2m}\frac{d^2\psi_>}{dx^2} = (E - V_0)\psi_> & \rightarrow & \psi_> = C\exp(-\alpha x) + D\exp(\alpha x), \end{array}$$

where $k = \sqrt{\frac{2mE}{\hbar^2}}$, $\alpha = \sqrt{\frac{2m(V_0-E)}{\hbar^2}}$.

Next we impose our boundary conditions. At $x = \infty$ the function is not infinite so $D = 0$.

At $x = 0$ we have

$$\begin{array}{llll} \psi_> = \psi_< & \rightarrow & B = C & \\ \dot{\psi}_> = \dot{\psi}_< & \rightarrow & Ak = -C\alpha & \rightarrow C = -\frac{kA}{\alpha}. \end{array}$$

So $\psi_>(x) = \frac{-kA}{\alpha}e^{-\alpha x}$ and $\psi_<(x) = A(\sin kx - \frac{k}{\alpha}\cos kx)$.

Note that as $V_0 \rightarrow \infty$ then $\alpha \rightarrow \infty$ and $\psi_>(x) \rightarrow \infty$ (due to the exponential) and $\psi_<(x) \rightarrow A\sin kx$, as mentioned before.

Note that our wavefunction cannot be normalised as $\int_{-\infty}^{0} \psi_<^*(x)\psi_<(x) < 0$ is impossible to satisfy as $\int_{-\infty}^{0} \sin^2(kx)\,dx = \infty$. So we interpret this situation as describing a beam of particles (we will come back to this case later when we will discuss transmission and reflection phenomena).

Comment: Note that quantum mechanically there is a non-zero probability of finding our particles in the region of $x > 0$.

5.2.3 One Dimensional Potential with Rigid Walls

A surface for which $V = \infty$ is called rigid. Hence transition from $V \neq \infty$ to $V = \infty$ due to $\mathbf{F} = -\bigtriangledown V$ involves very strong forces. This would be the case if we had, say, very strong reaction forces preventing the particle from entering such a region.

To study such a case we consider

$$V = \begin{cases} 0, & |x| < a \\ \infty, & |x| > a \end{cases}$$

So for $|x| > a$ $\psi = 0$ and for $|x| < a$ we have

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

which has as solutions $\psi(x) = A\sin(kx) + B\cos(kx)$ with k as before.

The continuity at $|x| = a$ gives us

$$A\sin(ka) + B\cos(ka) = 0$$
$$-A\sin(ka) + B\cos(ka) = 0.$$

Its solutions are $A = B = 0$ (*i.e.* no state) or $\sin(ka) = 0$ and $B = 0$ or $\cos(ka) = 0$ and $A = 0$.

The two choices give us $k = \frac{n\pi}{a}$ or $k = \frac{2n+1}{2}\frac{\pi}{a}$ so we see that

$$k = \frac{n\pi}{2a}, \qquad n = 1, 2, 3...$$

and so the possible values of energy are

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{\pi^2 \hbar^2 n^2}{8ma^2}.$$

Comments:

- We have a completely discrete spectrum of E. This is characteristic of potentials which go to ∞ as $|x| \to \infty$.
- $E_n \to \infty$ as $n \to \infty$
- $E_1 = \frac{\pi^2\hbar^2}{8ma^2}$. The lowest energy $\neq 0$. (The particle is **never at rest**; this phenomenon is called **zero point energy**).

Note; we can understand why $E_1 \neq 0$ (from the uncertainty principle). As $|\Delta x| \leq a$ we have that $\Delta p \geq \frac{\hbar}{2\Delta x}$. So

$$E = \frac{1}{2m}\langle p^2 \rangle \sim \frac{1}{2m}(\Delta p)^2 = \frac{\hbar^2}{8ma^2}.$$

If you plot a few lowest energy wave functions (say, $\psi_1(x), \psi_2(x)$ and $\psi_3(x)$) we see that ψ_1 has no **nodes**; ψ_2 has one node, ψ_3 has 2 nodes etc.

The larger the number of nodes - the higher the energy. This can be understood as follows; more nodes corresponds the larger variation of the wave function and, in consequence, the larger energy and momentum.

5.3 Parity

Bound-state wavefunctions of the square well and, as we will see later, of the simple-harmonic oscillator have definite symmetry under the 'parity' operation $x \to -x$. This is reflection through the origin; in three dimensions $\mathbf{r} \to -\mathbf{r}$.

In quantum mechanics a parity operator $\widehat{\mathcal{P}}$ for one particle can be defined by its effect on elements of the Schrödinger basis, eigenstates of $\widehat{\mathbf{r}}$:

$$\widehat{\mathcal{P}}|\mathbf{r}\rangle = c|-\mathbf{r}\rangle$$

or in position representation as

$$\widehat{\mathcal{P}}\psi(\mathbf{r}) = c\psi(-\mathbf{r}).$$

Requiring that two reflections return to the start, $\widehat{\mathcal{P}}^2 = \widehat{I}$ and hence $c^2 = 1$. Choose $c = 1$. Since $\langle \mathbf{r}|\widehat{\mathcal{P}}^\dagger\widehat{\mathcal{P}}|\mathbf{r}\rangle = \langle -\mathbf{r}|-\mathbf{r}\rangle = \langle \mathbf{r}|\mathbf{r}\rangle$ then $\widehat{\mathcal{P}}$ is unitary (skating over normalisation!) So both $\widehat{\mathcal{P}} = \widehat{\mathcal{P}}^{-1}$ and $\widehat{\mathcal{P}}^{-1} = \widehat{\mathcal{P}}^\dagger$. Hence $\widehat{\mathcal{P}}$ is self-adjoint, with (by inspection) eigenvectors $(|\mathbf{r}\rangle \pm |-\mathbf{r}\rangle)/\sqrt{2}$ for any $\mathbf{r}$ and eigenvalues ± 1.

In the position representations the eigenfunctions of $\widehat{\mathcal{P}}$ are $(1 \pm \widehat{\mathcal{P}})\psi$ for any ψ as

$$\widehat{\mathcal{P}}(1 \pm \widehat{\mathcal{P}})\psi = (\widehat{\mathcal{P}} \pm 1)\psi = \pm(1 \pm \widehat{\mathcal{P}})\psi.$$

Note that $\widehat{\mathcal{P}}$ does not have unique eigenvectors but simply partitions the $\mathbf{r}$-basis into two parts. The spectrum is complete, so $\widehat{\mathcal{P}}$ is observable, even though it cannot be constructed from basic degrees of freedom. (It is not a rotation because left- and right-handed Cartesian axes transform to each other).

Note that

$$(1 \pm \widehat{\mathcal{P}})\psi(\mathbf{r}) = \psi(\mathbf{r}) \pm \psi(-\mathbf{r})$$

so the eigenfunctions are even and odd functions of $\mathbf{r}$ with corresponding eigenvalues +1 and -1.

Now $\widehat{\mathcal{P}}\widehat{\mathbf{r}}\widehat{\mathcal{P}}|\mathbf{r}\rangle = -\mathbf{r}|\mathbf{r}\rangle = -\widehat{\mathbf{r}}|\mathbf{r}\rangle$ for any $|\mathbf{r}\rangle$ and so $\widehat{\mathbf{r}}\widehat{\mathcal{P}} = -\widehat{\mathcal{P}}\widehat{\mathbf{r}}$. Thus, since $[\widehat{\mathbf{r}}, \widehat{\mathbf{p}}] = i\hbar$, we also have $\widehat{\mathbf{p}}\widehat{\mathcal{P}} = -\widehat{\mathcal{P}}\widehat{\mathbf{p}}$. (Note that this means $\widehat{\mathcal{P}}|\mathbf{p}\rangle = c'|-\mathbf{p}\rangle$ with $c'^2 = 1$, which can be an alternative definition of $\widehat{\mathcal{P}}$). Therefore it follows that $[\widehat{\mathbf{r}}^2, \widehat{\mathcal{P}}] = [\widehat{\mathbf{p}}^2, \widehat{\mathcal{P}}] = 0$.

Indeed, under parity the self-adjoint operator corresponding to any observable $A(\mathbf{r}, \mathbf{p})$ transforms as

$$\widehat{A}(\widehat{\mathbf{r}}, \widehat{\mathbf{p}}) \to \widehat{\mathcal{P}}\widehat{A}\widehat{\mathcal{P}} = \widehat{A}(-\widehat{\mathbf{r}}, -\widehat{\mathbf{p}}).$$

If $\widehat{A}$ is unchanged (invariant) then $[\widehat{\mathcal{P}}, \widehat{A}] = 0$ and $\widehat{A}$ and parity are compatible.

> **Examples:** Kinetic energy $T = \mathbf{p}\cdot\mathbf{p}/2m$ and angular momentum $\mathbf{L} = \mathbf{r}\times\mathbf{p}$ of a particle are parity-invariant. Intrinsic spin is also parity-invariant.

For one particle, mass m, in a potential we have Hamiltonian $\widehat{H} = \widehat{\mathbf{p}}^2/2m + \widehat{V}(\widehat{\mathbf{r}})$ and so if $[\widehat{V}, \widehat{\mathcal{P}}] = 0$ we have $[\widehat{H}, \widehat{\mathcal{P}}] = 0$ and parity is conserved. The condition on $\widehat{V}$ is equivalent to $\widehat{V}(\widehat{\mathbf{r}}) = \widehat{V}(-\widehat{\mathbf{r}})$ — *i.e.* that $\widehat{V}$ depends only on $\widehat{\mathbf{r}}^2$.

If parity is conserved, energy eigenstates can also be also eigenstates of $\widehat{\mathcal{P}}$ — indeed they *must* have definite parity if the spectrum of $\widehat{H}$ is non-degenerate.

> **Examples:** For a free particle ($V = 0$) momentum eigenstates $|E, \mathbf{p}\rangle$ can be partitioned into parity eigenstates $(|E, \mathbf{p}\rangle \pm |E, -\mathbf{p}\rangle)/\sqrt{2}$ with parity ± 1. For a central potential, where $V = V(|\mathbf{r}|)$, parity is conserved alongside angular momentum.

In wave mechanics for a particle in a symmetrical potential $V(\mathbf{r}) = V(-\mathbf{r})$, and when $\widehat{H}$ has non-degenerate spectrum, for the wavefunction we have

$$\phi_E(\mathbf{r}) \equiv \langle \mathbf{r}|E\rangle = \langle \mathbf{r}|\widehat{\mathcal{P}}^\dagger \widehat{\mathcal{P}}|E\rangle = \langle -\mathbf{r}|(\pm|E\rangle) = \pm\phi_E(-\mathbf{r}),$$

i.e. definite symmetry under $\mathbf{r} \to -\mathbf{r}$. If there is degeneracy then energy eigenfunctions *may* have definite parity, but it must be checked explicitly. For bound states of a central potential (see Chap 6), where parity is conserved, there is angular-momentum degeneracy. But even so, the wavefunctions turn out to have definite parity, for $[\widehat{L}, \widehat{\mathcal{P}}] = 0$ and $\widehat{L}$ has a non-degenerate spectrum.

In one-dimensional wave mechanics parity is conserved iff $V(-x) = V(x)$, which is true, as we have seen, for the symmetrical square-well potential and for the simple harmonic oscillator. There is no degeneracy for bound states (as shown in the next Section) and so the energy eigenfunctions are necessarily eigenfunctions of parity. Thus in the case of the square well our wavefunctions are eigenfunctions of $\widehat{\mathcal{P}}$. Note that

$$\widehat{\mathcal{P}}\psi_n(x) = (-1)^{n+1}\psi_n(x)$$

and so $\psi_n(x)$ has parity $(-1)^{n+1}$. Note that the ground state wavefunction has parity $+1$, *i.e.* is an even function of x). This is the case for all "reasonable" potentials (which are even).

Note that if ψ is even then $\psi(x) = \psi(-x)$. Then $\dot{\psi}(x) = -\dot{\psi}(-x)$ and so $\dot{\psi}(0) = 0$. And if ψ is odd we have $\psi(-x) = -\psi(-x)$ and so $\psi(0) = 0$.

We can exploit this observation as follows. If $\psi(x)$ is a solution of $\widehat{H}\psi = E\psi$ (with $V(-x) = V(x)$) for $x > 0$ then if

$$\dot{\psi}(0) = 0 \qquad \psi(-x) = \psi(x)$$

is a solution for $x < 0$ and if

$$\psi(0) = 0 \qquad \text{then} \quad \psi(-x) = -\psi(x)$$

is a solution for $x < 0$.

Message For even potentials we may look for eigenstates of definitive parity. We do this by solving

$$\widehat{H}\psi = E\psi$$

in $x > 0$ subject to $\psi(0) = 0$ or $\dot{\psi}(0) = 0$ and extend as above.

For scattering from a symmetrical potential the asymptotic energy eigenfunctions are degenerate with respect to momentum direction and there is no automatic even/odd symmetry of energy eigenfunctions. Indeed incoming- or outgoing-wave boundary conditions generally exclude it.

5.4 Finite Square Well

Next we consider a finite square well potential, *i.e.* a system with $V(x)$ given by

$$V(x) = \begin{cases} 0, & |x| < a \\ V_0, & |x| \geq a \end{cases}.$$

Classically, if $E > V_0$ the particle can move off to ∞ and so is not bound, but when $E < V_0$ - the particle must remain in the hole and we have a bound state. This aspect of the problem is preserved in Quantum Mechanics but is modified.

First look at bound states (*i.e.* consider $E < V_0$). Then

$$x < a \qquad -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \qquad \to \qquad \psi(x) = B\sin(kx) + A\cos(kx), \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

$$x \geq a \qquad -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = (E - V_0)\psi \qquad \to \qquad \psi(x) = Ce^{-\alpha x} + De^{\alpha x}, \qquad \alpha = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

and to stop ψ from $|\psi| \to \infty$ as $|x| \to \infty$ we have to put $D = 0$

Hence for **even parity** states we take $\dot{\psi}(0) = 0$ and so $B = 0$ and the continuity of ψ and $\dot{\psi}$ at $x = a$ gives us

$$\begin{aligned} A\cos(ka) &= Ce^{-\alpha a} \\ -Ak\sin(ka) &= -C\alpha e^{-\alpha a} \end{aligned}$$

and so

$$k\,\tan(ka) \;=\; \alpha$$

is our condition for a non-zero wavefunction. This is our eigenvalue equation for E.

For **odd parity** states we put

$$\psi(0) \;=\; 0 \qquad \to \qquad A = 0$$

and so continuity of ψ and $\dot{\psi}$ at $x = a$ gives us

$$\begin{aligned} B\sin(ka) &= Ce^{-\alpha a} \\ Bk\cos(ka) &= -C\alpha e^{-\alpha a} \end{aligned}$$

and so

$$k\,\cot(ka) \;=\; -\alpha.$$

The equations for E *i.e.* for k can be solved only numerically or graphically.

graphical analysis

Change variables to $x1 = ka$ and $y1 = \alpha a$. Then

$$x1^2 + y1^2 = (k^2 + \alpha^2)a^2 = \frac{2mV_0}{\hbar^2}a^2 = R^2a^2$$

and so we see that the solutions of our equations lie on the intersection of this circle with $x1\tan(x1) = y1$ (for even states) and $x1\cot(x1) = -y1$ for odd states.

We see that the number of states is **finite** and that there is always **at least one state**.

If V_0 is such that $R^2 \sim R_1^2$ (where $R_1 < \frac{\pi}{2}$) we have only one (positive parity) state. If $R \sim R_2$, where $\frac{\pi}{2} < R_2 < \pi$ we have two states (one odd, one even); if $R \sim R_3$, where $\pi < R_3 < \frac{3\pi}{2}$ we have three states (two even, one odd).

In general, if

$$\sqrt{\frac{2mV_0a^2}{\hbar^2}} \in [n\pi,\,(n + \frac{1}{2})\pi]$$

we have $n + 1$ even and n odd states while if

$$\sqrt{\frac{2mV_0a^2}{\hbar^2}} \in [(n + \frac{1}{2})\pi,\,(n + 1)\pi]$$

we have $(n + 1)$ odd and $(n + 1)$ even states.

Notes

- If $V_0 \to \infty$ the momenta $ka \to \frac{n\pi}{2}$ and so $E \to \frac{\pi^2\hbar^2 n^2}{8ma^2}$ as before.
- Even when the particle is bound there is a small probability that the particle is outside the well. This probability is proportional to $exp(-2\alpha x)$.

It is easy to sketch the wave functions for a few lowest states.

Next consider the **continuous** part of the spectrum, For this we need $E > V_0$. Then

$$\psi = A\sin(kx) + B\cos(kx), \qquad -a < x < a$$

and

$$\text{for } x > a \quad \psi = Ce^{i\gamma(x-a)} + De^{-i\gamma(x-a)},$$

where $\gamma = \sqrt{\frac{(E-V_0)2m}{\hbar^2}} = i\alpha$.

Now the condition of $x \to \infty$ gives no restriction on C and D and the states cannot be normalised.

We can still take eigenstates of definitive parity (even or odd). For even states $A = 0$ and $B\cos(ka) = C + D$ and $-kB\sin(ka) = (C - D)i\gamma$. These can be solved for any E thus the spectrum is continuous. Similarly for odd states. Thus we have **two** eigenstates (not normalised), one of each parity, for every value of $E > V_0$.

5.5 Reflection and Transmission Phenomena

Consider the step potential as before ($V = 0$, $x < 0$; $V = V_0$ for $x > 0$). We have found eigenstates for $0 < E < V_0$. Let us now show that this problem has also eigenstates for $E > V_0$. Moreover, there are no states for $E < 0$ so the spectrum satisfies $0 < E < \infty$.

Return to the case of $E < V_0$. Then for $x < 0$ the wave function satisfies

$$\begin{aligned}\psi(x) = \psi_<(x) &= A(\sin(kx) - \tfrac{\alpha}{k}\cos(kx)) \\ &= \tfrac{A}{2i}(1 - \tfrac{ik}{\alpha})e^{ikx} - \tfrac{A}{2i}(1 + \tfrac{ik}{\alpha})e^{-ikx},\end{aligned}$$

where $k = \sqrt{\frac{2mE}{\hbar^2}}$ and $\alpha = \sqrt{\frac{2m(V_0-E)}{\hbar^2}}$.

For $x > 0$

$$\psi(x) = \psi_>(x) = -\frac{k}{\alpha}A\,e^{-\alpha x}.$$

Thus in $x < 0$ the wavefunction is a superposition of e^{ikx} and e^{-ikx}. But

$$\hat{p}(e^{\pm ikx}) = -\hbar i\frac{\partial}{\partial x}(e^{\pm ikx}) = -\hbar i(\pm ikx)e^{\pm ikx} = \pm\hbar k e^{\pm ikx}.$$

So $e^{\pm ikx}$ is an eigenfunction of momentum with $\pm\hbar k$ as its eigenvalue.

But $e^{\pm ikx}$ is not normalisable. So it cannot represent a single particle of exact momentum $\pm\hbar k$. As $\left|e^{\pm ikx}\right|^2 = 1$ we would have probability 1 of finding the particle in a unit interval. Thus we interpret $e^{\pm ikx}$ as representing a **beam of particles, of density 1 per unit length, each of momentum** $\pm\hbar k$.

Similarly Ae^{ikx} gives density $|A|^2$ per unit length. Thus $e^{ikx}(e^{-ikx})$ describes particles moving to the **right** (left).

The flux of particles is density$\times$ velocity so for Ae^{ikx} the flux is $|A|^2\,\frac{\hbar k}{m}$.

Thus, in our case, the flux moving to the right is

$$\frac{|A|^2}{4}(1 + \frac{k^2}{\alpha^2})\frac{\hbar k}{m}, \qquad x < 0$$

and to the left also

$$\frac{|A|^2}{4}(1 + \frac{k^2}{\alpha^2})\frac{\hbar k}{m}, \qquad x < 0.$$

In the region of $x > 0$ the wave is exponentially decreasing and so no particles get to $x = \infty$. This explains why the flux to the left is the same as the flux to the right - we have complete reflection.

We can relate these observations to the continuity equation.

As ψ is stationary $\nabla \mathbf{j} = 0$ so in one dimension $\frac{d}{dx}j = 0$ and so $j(a) = j(b)$ where, in one dimension

$$j = -\frac{i\hbar}{2m}\left(\psi^\star \frac{d\psi}{dx} - \psi \frac{d\psi^\star}{dx}\right).$$

So for $\psi = A\,e^{ikx}$ we see that $j = \frac{\hbar k}{m}|A|^2$ confirming our observations.

For a more general case

$$\psi_< = A\,e^{ikx} + B\,e^{-ikx}, \qquad \psi_> = C\,e^{-\alpha x}$$

Then, it is easy to check that

$$j(x<0) = \frac{\hbar k}{m}[|A|^2 - |B|^2], \qquad j(x>0) = 0$$

So, as we have already verified, there is no flux to the right and $|A| = |B|$.

Note; this is exactly like in the classical case. There, if $E < V_0$ the particles would be stopped by the potential at some point x' where $V(x') = E$, $T(x') = 0$. Their motion is then reversed by the action of the force resulting in the complete reflection of the beam.

If $E > V_0$ the situation is different. Classically, the particles emerge with kinetic energy T_1 and momentum p_1 such that

$$T_1 = \frac{p_1^2}{2m} = E - V_0 > 0.$$

And in Quantum mechanics? We have, for $x < 0$

$$\psi = \psi_<, \quad \frac{d^2\psi_<}{dx^2} + k^2\psi_< = 0, \quad k = \sqrt{\frac{2mE}{\hbar^2}} \quad \to \quad \psi_< = Ae^{ikx} + Be^{-ikx}$$

while for $x > 0$

$$\psi = \psi_>, \quad \frac{d^2\psi_>}{dx^2} + \beta^2\psi_> = 0, \quad \beta = \sqrt{\frac{2m(E-V_0)}{\hbar^2}} \quad \to \quad \psi_> = Ce^{i\beta x} + De^{-i\beta x}.$$

The conditions on ψ and $\dot\psi$ are not sufficient to determine 3 constants (the overall constant is irrelevant as it is related to the density of the beam).

Having $A \neq 0$ and $D \neq 0$ means that we have beams incident from both $x = -\infty$ and $x = \infty$.

Physically we expect some reflection *etc* so if the incoming beam is from the left (*i.e.* from $-\infty$) then we do not expect any beam from ∞ so $D = 0$. By this requirement we specify that **the beam is fired at the barrier from $-\infty$.**

Then the continuity conditions give us

$$\psi_>(0) = \psi_<(0) \quad \to \quad A + B = C$$
$$\dot\psi_>(0) = \dot\psi_<(0) \quad \to \quad k(A - B) = \beta C$$

giving

$$C = \frac{2k}{k+\beta}A, \qquad B = \frac{k-\beta}{k+\beta}A.$$

So the incident flux is $\frac{\hbar k}{m}|A|^2$, reflected flux is

$$\frac{\hbar k}{m}|B|^2 = \frac{\hbar k}{m}\left|\frac{k-\beta}{k+\beta}\right|^2 |A|^2$$

and the transmitted flux is

$$\frac{\hbar \beta}{m}|C|^2 = \frac{\hbar\beta}{m}\frac{4k^2}{|k+\beta|^2}|A|^2$$

So

$$j(x<0)=\tfrac{\hbar k}{m}(|A|^2-|B|^2)$$
$$j(x>0)=\tfrac{\hbar\beta}{m}|C|^2\,.$$

Due to $j(x>0)=j(x<0)$ we see that the incident flux is a sum of the reflected and transmitted fluxes. We define R - the reflection coefficient

$$R=\frac{\text{reflected flux}}{\text{incident flux}}=\frac{(k-\beta)^2}{(k+\beta)^2}$$

and T- the transmission coefficient

$$T=\frac{\text{transmitted flux}}{\text{incident flux}}=\frac{4\beta k}{(k+\beta)^2}$$

and we see that $T+R=1$.

5.6 The Tunnelling Effect

Consider V as indicated

$$V(x)=\begin{cases}0, & x<0\\ V_0>0, & a>x>0\\ 0, & x>a\end{cases}.$$

Then let us study what happens when a beam of particles, of unit density is incident from $-\infty$ with some particular energy E. Classically, if $E<V_0$ the beam will be reflected and if $E>V_0$ it will be transmitted. In Quantum mechanics we have reflection and transmission in each case.

Study first $E<V_0$. Then

$$x<0\quad -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}=E\psi,\qquad\rightarrow\quad \psi=e^{ikx}+Be^{-ikx},\quad k=\sqrt{\frac{2mE}{\hbar^2}}$$

$$0<x<a\quad -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}=(E-V_0)\psi,\qquad\rightarrow\quad \psi=Ce^{\alpha x}+De^{-\alpha x},\quad \alpha=\sqrt{\frac{2m(V_0-E)}{\hbar^2}}$$

$$x>a\quad -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}=E\psi,\qquad\rightarrow\quad \psi=\tilde{E}e^{ikx}$$

(we have set $A=1$ for simplicity). We relate B, C, D and $\tilde{E}$ by the continuity of ψ and $\dot{\psi}$ at $x=0$ and $x=a$. The conditions at $x=0$ give us

$$1+B=C+D,\qquad ik-ikB=\alpha(C-D)$$
$$\rightarrow\quad 2ik=(\alpha+ik)C-(\alpha-ik)D.$$

and at $x=a$ we get

$$Ce^{\alpha a}+D^{-\alpha a}=\tilde{E}e^{ika},\qquad \alpha Ce^{\alpha a}-\alpha De^{-\alpha a}=ik\tilde{E}e^{ika}$$
$$\rightarrow\quad (-ik+\alpha)Ce^{\alpha a}=(\alpha+ik)De^{-\alpha a}.$$

To solve them we put $C=\lambda(\alpha+ik)e^{-\alpha a}$ and $D=\lambda(\alpha-ik)e^{\alpha a}$, which solves the last condition, and find

$$\frac{2ik}{\lambda}=(\alpha+ik)^2e^{-\alpha a}-(\alpha-ik)^2e^{\alpha a}.$$

So

$$\lambda=\tfrac{2ik}{(\alpha+ik)^2e^{-\alpha a}-(\alpha-ik)^2e^{\alpha a}}=\tfrac{2ik}{(\alpha^2-k^2)(e^{-\alpha a}-e^{\alpha a})+2ik\alpha(e^{-\alpha a}+e^{\alpha a})}$$
$$=\tfrac{ik}{(k^2-\alpha^2)sh(\alpha a)+2ik\alpha ch(\alpha a)}.$$

Then

$$\tilde{E} = (Ce^{\alpha a} + De^{-\alpha a})e^{-ika} = 2\lambda\alpha e^{-ika} = \frac{2ik\alpha e^{-ika}}{(k^2-\alpha^2)sh(\alpha a) + 2ik\alpha ch(\alpha a)}$$

And

$$B = C + D - 1 = \lambda(\alpha + ik)e^{-\alpha a} + \lambda(\alpha - ik)e^{\alpha a} - 1 = 2\lambda\alpha ch(\alpha a)$$
$$-1 - 2ik\lambda sh(\alpha a) = \tfrac{(k^2+\alpha^2)sh(\alpha a)}{(k^2-\alpha^2)sh(\alpha a)+2ik\alpha ch(\alpha a)}.$$

Then $R = |B|^2$ and $T = \left|\tilde{E}\right|^2$ and

$$\left|\tilde{E}\right|^2 + |B|^2 = \frac{4k^2\alpha^2}{(k^2-\alpha^2)^2 sh^2(\alpha a) + 4k^2\alpha^2 ch^2(\alpha a)} + \frac{(k^2+\alpha^2)^2 sh^2(\alpha a)}{(k^2-\alpha^2)^2 sh^2(\alpha a) + 4k^2\alpha^2 ch^2(\alpha a)} = 1$$

as required. The fact that we have a transmitted wave in the region that is not accessible classically is called the **tunnelling effect**.

Note that if the barrier is very narrow *i.e.* a is small we have $\alpha a \sim 0$ and so $B \sim 0$, $\tilde{E} \sim 1$ and the whole wave is transmitted.

This effect plays a very important role in nuclear physics, in the description of the α decay of nuclei.

5.7 Lessons

If $V(\infty)$ is finite the spectrum of $\widehat{H}$ has two sectors, scattering and bound-state. Scattering energy-values are continuous with asymptotic double degeneracy with respect to momentum (in, out). The square-well example shows that the linear and homogeneous continuity conditions are consistent with all E-values if both in and out asymptotic components of the wavefunction are present, but that they restrict allowed E-values to just a discrete set when the asymptotic form is a single decaying exponential.

Scattered particles may reflect from sudden changes in $V(x)$ and the 'tunnelling' may occur. Confined, localised, or bound particles have zero-point energy (a non-trivial wavefunction vanishing at both $\pm\infty$ must be curved, so that $\langle p^2\rangle > 0$).

Discrete energy levels are bound states, with square-integrable wavefunctions. They are always non-degenerate in one dimension. This is easily seen by supposing otherwise when both $\phi_1(x)$ and $\phi_2(x)$ obey

$$\phi'' = \frac{2m}{\hbar^2}(V(x) - E)\phi$$

with the same E and, multiplying each equation by the other ϕ and subtracting, we have

$$\phi_1\phi_2'' - \phi_1''\phi_2 = 0.$$

Integrating, the Wronskian of the two supposedly independent functions is a constant. But the constant is zero, evaluating at $x = \pm\infty$ where the (bound-state) ϕ's vanish, so they are in fact linearly dependent.

With a symmetric potential parity is a good quantum number. The ground state is always symmetrical (theorem) and eigenfunctions have zeroes increasing by one going up the spectrum (theorem) and interleaving (theorem). Refer to Messiah, Vol I, *pps.* 98 to 113 for proofs of these theorems, which follow from the Sturm-Liouville nature of the Hamiltonian operator.

6 Three-Dimensional Systems

6.1 Square well with rigid walls

Now we look at more "physical" cases *i.e.* particles in 3 dimensions. We start with problems that can be solved with the knowledge of 1-dim results.

Let us look at the stationary Schrödinger equation.

$$[-\frac{\hbar^2}{2m}\nabla^2 + V(r)]\psi(\mathbf{r}) = E\psi(\mathbf{r}).$$

Usually we can make progress by exploiting some symmetry of the problem or by separating the equation in some set of coordinates.

Here we look at case of the potential

$$V(\mathbf{r}) = \begin{cases} 0 & |x| < a, \quad |y| < b, \quad |z| < c, \\ \infty & \text{otherwise} \end{cases}$$

In this case it is convenient to use Cartesian coordinates.

Clearly $\psi(\mathbf{r}) = 0$ for $|x| > a$ or $|y| > b$ or $|z| > c$ so the particle is confined to a box.

We seek a solution of the Schrödinger equation in the form $\psi(\mathbf{r}) = \psi_1(x)\psi_2(y)\psi_3(z)$. Then

$$-\frac{\hbar^2}{2m}\left(\frac{\ddot{\psi}_1}{\psi_1} + \frac{\ddot{\psi}_2}{\psi_2} + \frac{\ddot{\psi}_3}{\psi_3}\right) = E.$$

Thus

$$-\frac{\hbar^2}{2m}\frac{\ddot{\psi}_i}{\psi_i} = E_i,$$

where $\sum_i E_i = E$ and

$$\psi_1(\pm a) = 0, \qquad \psi_2(\pm b) = 0, \qquad \psi_3(\pm c) = 0$$

and so we have 3 one dimensional problems whose solutions are known.

As possible values of E_1 are $\frac{n_1^2\pi^2\hbar^2}{8a^2m}$ we see that

$$E = \frac{\pi^2\hbar^2}{8m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right)$$

The corresponding eigenfunctions are

$$\psi(\mathbf{r}) = A\,\sin\big(\frac{n_1\pi}{2a}x + \frac{n_1\pi}{2}\big)\,\sin\big(\frac{n_2\pi}{2b}y + \frac{n_2\pi}{2}\big)\,\sin\big(\frac{n_3\pi}{2c}z + \frac{n_3\pi}{2}\big),$$

which are complete ($n_1, n_2, n_3 = 1, 2, 3, ..$).

Note that if $a^2 = b^2 = c^2 = d^2$ then

$$E = \frac{\pi^2\hbar^2}{8md^2}[n_1^2 + n_2^2 + n_3^2]$$

so states like (1,2,2), (2,1,2,) and (2,2,1) have the same energy. There must be operators which allow us to distinguish between these states; they are $\widehat{p}_i$.

6.2 3 Dimensional Harmonic Oscillator

For the 3 dimensional Harmonic oscillator we take

$$\widehat{H} = \frac{\widehat{\mathbf{p}}^2}{2m} + \frac{1}{2}m\omega^2\widehat{\mathbf{r}}^2,$$

where $\widehat{\mathbf{r}}^2 = \widehat{x}^2 + \widehat{y}^2 + \widehat{z}^2$. We solve it as a problem in wave mechanics *i.e.* in position representation. Then

$$\widehat{\mathbf{p}}^2 = -\hbar^2\nabla^2 = -\hbar^2(\partial_x^2 + \partial_y^2 + \partial_z^2)$$

and we put

$$\psi(\mathbf{r}) = \psi_1(x)\psi_2(y)\psi_3(z).$$

We get 3 equations

$$(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}m\omega^2x^2)\psi_1(x)=E_1\psi_1(x)$$

and similar equations for $\psi_2(y)$ and $\psi_3(z)$.

$$E=E_1+E_2+E_3.$$

We use our previous knowledge to discuss their solutions. As one dim. SHO has eigenvalues $E_1 = (n_1+\frac{1}{2})\hbar\omega$, $n_1 = 0, 1, 2...$ with eigenfunctions

$$\psi_{n_1}(x)=H_{n_1}(x')e^{-\frac{1}{2}x'^2}, \qquad x'=\sqrt{\frac{m\omega}{\hbar}}x$$

we see that

$$E=\left(n_1+n_2+n_3+\frac{3}{2}\right)\hbar\omega$$

with eigenfunctions

$$\psi(\mathbf{r})=\psi_{n_1}(x)\psi_{n_2}(y)\psi_{n_3}(z).$$

To put it differently, we set

$$\widehat{H}=\sum_{i=x,y,z}\widehat{H}_i$$

where

$$\widehat{H}_x=\frac{\widehat{p}_x^2}{2m}+\frac{1}{2}m\omega^2\widehat{x}^2, \quad etc.$$

As $\widehat{H}_i$ commute and are Hermitian we can find a basis of simultaneous eigenstates of all $\widehat{H}_i$ and $\widehat{H}$. So we take $|n_1,n_2,n_3\rangle$ where

$$\begin{aligned}
\widehat{H}_x|n_1,n_2,n_3\rangle &= \hbar\omega\left(n_1+\frac{1}{2}\right)|n_1,n_2,n_3\rangle\\
\widehat{H}_y|n_1,n_2,n_3\rangle &= \hbar\omega\left(n_2+\frac{1}{2}\right)|n_1,n_2,n_3\rangle\\
\widehat{H}_z|n_1,n_2,n_3\rangle &= \hbar\omega\left(n_3+\frac{1}{2}\right)|n_1,n_2,n_3\rangle
\end{aligned}$$

and so

$$\widehat{H}|n_1,n_2,n_3\rangle=\hbar\omega\left(n_1+n_2+n_3+\frac{3}{2}\right)|n_1,n_2,n_3\rangle.$$

Thus we see that our theorem about commuting operators is closely related to the separation of variables; in fact, the separation of variables is really just our usage of this theorem.

6.3 Central Potentials

In three-dimensional wave mechanics the wavefunction $\psi(\mathbf{r},t)$ of a particle of mass M in a potential $V(\mathbf{r})$ obeys the Schrödinger Wave Equation

$$\frac{-\hbar^2}{2M}\nabla^2\psi+V(\mathbf{r})\psi=i\hbar\frac{\partial\psi}{\partial t}$$

and may be expressed as a superposition of energy eigenfunctions $\phi_E(\mathbf{r})$ satisfying

$$\frac{-\hbar^2}{2M}\nabla^2\phi+V(\mathbf{r})\phi=E\phi.$$

Each eigenfunction may be chosen to be simultaneously an eigenfunction of all the mutually compatible conserved quantities.

Examples: Free-particle energy eigenfunctions ψ may be eigenstates of $-i\hbar\nabla$ with momentum $\mathbf{p}$ in any direction so long as $E = \frac{1}{2}|\mathbf{p}|^2/M$. Alternatively they may be eigenstates of parity or of angular momentum, or of both.

With a central potential $V(\mathbf{r}) = V(r)$, where $r = |\mathbf{r}| = \sqrt{\mathbf{r}\cdot\mathbf{r}}$, all components of angular momentum $\widehat{L}$ commute with $\widehat{H}$ since they commute with both $\widehat{\mathbf{p}}^2$ and $\widehat{\mathbf{r}}^2$. So angular momentum is conserved, as in classical mechanics (and note that parity is conserved too). Then $\phi = \phi_{E\ell m}(\mathbf{r})$ obeys simultaneously

$$\frac{-\hbar^2}{2M}\nabla^2\phi + V(r)\phi = E\phi,$$

$$\widehat{L}^2\phi = \ell(\ell+1)\hbar^2\phi, \qquad \widehat{L}_z\phi = m\hbar\phi,$$

where $\widehat{L}^2 = \widehat{L}_x^2 + \widehat{L}_y^2 + \widehat{L}_z^2$ and

$$\widehat{L}_x = \widehat{y}\widehat{p}_z - \widehat{z}\widehat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \qquad \text{etc.}$$

The commutators of angular momentum alone permit $\ell = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$ and constrain $m = -\ell, -\ell+1, \ldots, \ell$.

Because V depends only on radial distance r, spherical polar coordinates (r, θ, φ) are better than Cartesians. Then the angular momentum operators that commute with $V(r)$ can depend only on angular derivatives. So the angular-momentum equations fix the (θ, φ)-dependence of $\phi_{E\ell m}(r, \theta, \varphi)$ for any central V. Its remaining r-dependence is determined by the energy eigenvalue equation and depends on details of $V(r)$. This is an effective one-dimensional problem.

6.4 Separation of Variables

Standard spherical polar coordinates (r, θ, φ) are related to right-handed Cartesians by

$$(x, y, z) = r(\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$$

and all space is covered by $0 \le r < \infty$, $0 \le \theta \le \pi$ (or $-1 \le \cos\theta \le 1$) and $0 \le \varphi < 2\pi$. The volume element is

$$d\tau = dx\,dy\,dz = r^2\sin\theta\,dr\,d\theta\,d\varphi = r^2 dr\,d\Omega$$

where the solid-angle element is $d\Omega = d(\cos\theta)\,d\varphi$ and $\int d\Omega = 4\pi$.

Simple calculation of derivatives $(\partial/\partial x, \partial/\partial y, \partial/\partial z)$ leads to angular momentum operators in spherical polars:

$$\widehat{L}_\pm = i\hbar e^{\pm i\varphi}\left\{\cot\theta\frac{\partial}{\partial\varphi} \mp i\frac{\partial}{\partial\theta}\right\},$$

$$\widehat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$$

and so

$$\widehat{L}^2 = -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}.$$

Note that

$$\widehat{L}_\mp\widehat{L}_\pm = \widehat{L}^2 - \widehat{L}_z^2 \mp \hbar\widehat{L}_z.$$

The form of $\widehat{L}_z$ is just as expected for the generator of rotations about the z-axis. Note that

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left(-\frac{1}{\hbar^2}\widehat{L}^2\right).$$

(This suggests decomposition of $\widehat{\mathbf{p}}^2 = -\hbar^2\nabla^2$ into radial and angular components as in classical mechanics: $\mathbf{P}^2 = P_r^2 + L^2/r^2$. But the radial part of ∇^2 is not simply the square of the radial component of ∇. Messiah (*p.* 346) shows how to define a self-adjoint $\widehat{\mathbf{p}}_r$ obeying $[\widehat{r}, \widehat{P}_r] = -i\hbar$ with wavefunctions bounded at $r = 0$).

Thus in spherical polars $\phi = \phi_{E\ell m}(r,\theta,\varphi)$ obeys

$$\frac{\partial\phi}{\partial\varphi} = im\phi,$$

$$-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\phi}{\partial\theta}\right) + \frac{m^2}{\sin^2\theta}\phi = \ell(\ell+1)\phi$$

and

$$\frac{-\hbar^2}{2Mr^2}\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial\phi}{\partial r}\right) - \ell(\ell+1)\phi\right\} + V(r)\phi = E\phi.$$

These are eigenvalue equations for $\widehat{L}_z$, $\widehat{L}^2$ and $\widehat{H}$ respectively with each simplified using its predecessor. Hence this process corresponds to the separation of variables. Thus effectively we are putting

$$\phi(r,\theta,\varphi) \;=\; f(r)\chi(\theta)h(\varphi).$$

The L_z equation gives

$$\phi_{E\ell m}(r,\theta,\varphi) = \chi_{E\ell m}(r,\theta)e^{im\varphi}$$

and, since φ and $\varphi + 2n\pi$ are identified for all integer n, we have $m = 0, 1, 2, \ldots$ if ϕ is to be single-valued. This implies $\ell = 0, 1, 2, \ldots$ only. That is, 'orbital' angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ of a quantum particle can be only integer multiples of $\hbar$.

6.5 The Legendre Equation

Next we look at the equation for χ (neglecting for the moment the fact that χ depends also on r as here it still means $\chi(r,\theta) = f(r)\chi(\theta)$):

$$\frac{1}{\sin(\theta)}\frac{d}{d\theta}\left(\sin(\theta)\frac{d\chi}{d\theta}\right) - \frac{m^2\chi}{\sin^2(\theta)} + k\chi = 0,$$

where $k = l(l+1)$,

To solve this equation it is convenient to change variables and introduce $x = \cos(\theta)$ (**do not confuse it with the original** x). Then

$$\frac{d\chi}{d\theta} \;=\; \frac{d\chi}{dx}\frac{dx}{d\theta} \;=\; -\frac{d\chi}{dx}\sin(\theta) \quad\rightarrow\quad \frac{1}{\sin(\theta)}\frac{d}{d\theta} \;=\; -\frac{d}{dx}$$

and so

$$\frac{d}{dx}\left(\sin^2(\theta)\,\frac{d\chi}{dx}\right) \;-\; \frac{m^2}{\sin^2(\theta)}\chi \;+\; k\chi \;=\; 0$$

ie

$$\frac{d}{dx}\left((1-x^2)\frac{d\chi}{dx}\right) \;-\; \frac{m^2}{1-x^2}\chi \;+\; k\chi \;=\; 0$$

or

$$(1-x^2)\frac{d^2\chi}{dx^2} - 2x\frac{d\chi}{dx} \;+\; k\chi \;=\; \frac{m^2}{1-x^2}\chi.$$

This is clearly a very complicated equation.

Let us consider first the case when $m - 0$. Then this equation becomes

$$(1-x^2)\frac{d^2\chi}{dx^2} - 2x\frac{d\chi}{dx} \;+\; k\chi \;=\; 0$$

and is called the **Legendre equation**. Its solutions are called Legendre functions.

Let us solve our equation for χ by a power series expansion around $x = 0$ (note that $x = 0$ corresponds to $\theta = \frac{\pi}{2}$ *i.e.* the equator).

So put

$$\chi(x) \;=\; \sum_{n=0}^{\infty} a_n\, x^{n+\alpha}.$$

Actually, we do not need α in this expression (*ie* we can put $\alpha = 0$ but ... it does not hurt to put it there either).

Then

$$\sum_{r=0}^{\infty} \left[(r+\alpha)(r+\alpha-1)a_r(1-x^2)x^{r+\alpha-2} \;-\; 2a_r(r+\alpha)x^{r+\alpha} \;+\; ka_r x^{r+\alpha}\right] \;=\; 0$$

ie

$$\sum_{r=0}^{\infty}(r+\alpha)(r+\alpha-1)a_r x^{r+\alpha-2} \;-\; \sum_{r=0}^{\infty}\left[(r+\alpha)(r+\alpha+1)-k\right] a_r x^{r+\alpha} \;=\; 0.$$

Look at the powers of x. The two lowest ones are x^β where $\beta = (\alpha-2)$ and $\beta = (\alpha-1)$. Their coefficients are respectively

$$\alpha(\alpha-1)\, a_0 \;=\; 0$$
$$(\alpha+1)\alpha\, a_1 \;=\; 0$$

Then when $\beta = \alpha$ we have

$$(\alpha+2)(\alpha+1)\, a_2 \;-\; [\alpha(\alpha+1)-k]\, a_0 \;=\; 0$$

and in general (for $\beta = \alpha + n$)

$$(\alpha+n+2)(\alpha+n+1)\, a_{n+2} \;-\; [(n+\alpha)(n+\alpha+1)-k]\, a_n \;=\; 0.$$

So we see that if we satisfy the first two equations the remaining ones can be satisfied recurrsively; *ie* we can use them to define a_{n+2} given a_n. So we treat the last expression as the recurrence relation for a_n.

To satisfy the first two equations we note that if $\alpha = 0$ both a_0 and a_1 are arbitrary and the equations are satisfied. Then, as the recurrence relation involves only a_k with k differing by 2, a_2 can be expressed in terms of a_0, a_3 in terms of a_1, a_4 in terms of a_2 and thus in terms of a_0 *etc.* Thus all the a_n for n even are expressible in terms of a_0 and all the ones with n odd, in terms of a_1.

In both cases the recurrence relation is given by

$$a_{n+2} \;=\; \frac{n(n+1)-k}{(n+1)(n+2)}\, a_n.$$

Let us calculate a_n for n even. We have

$$a_2 = -\frac{k}{2}a_0, \qquad a_4 \;=\; \tfrac{2\times 3-k}{4\times 3}a_2 \;=\; -\tfrac{k(6-k)}{2\times 3\times 4}a_0$$
$$a_6 = \frac{4\times 5-k}{6\times 5}a_4 \qquad = \tfrac{-k(6-k)(20-k)}{2\times 3\times 4\times 5\times 6}a_0 \qquad etc$$

So if $a_1 = 0$ the solution is given by the a_0 series and is of the form

$$\chi \;=\; \chi_1 \;=\; a_0\left[1 \;-\; \frac{k}{2!}x^2 \;-\; \frac{k(2\times 3-k)}{4!}x^4 \;-\; \frac{k(2\times 3-k)(4\times 5-k)}{6!}x^6 \;-\; ...\right].$$

The coefficients of the odd series (*ie* the series starting with a_1) take the form:

$$a_3 \;=\; \frac{1\times 2-k}{2\times 3}a_1, \quad a_5 \;=\; \frac{3\times 4-k}{4\times 5}a_3 \;=\; \frac{(1\times 2-k)(3\times 4-k)}{5!}a_1 \quad itc$$

and so this series is given by

$$\chi \;=\; \chi_2 \;=\; a_1 x\left[1 \;+\; \frac{1\times 2-k}{3!}x^2 \;+\; \frac{(1\times 2-k)(3\times 4-k)}{5!}x^4 \;+\; ...\right].$$

The total solution is given by

$$\chi = \chi_1 + \chi_2,$$

where $x = \cos\theta$, and so is characterised by two arbitrary constants a_0 and a_1.

Note:

- A possible way of solving the first two equations would involve $\alpha = 1$ and $a_1 = 0$. However, a little thought shows that the resultant series gives again function χ_2.

6.6 Convergence Problems - Legendre Polynomials

Look at the recurrence relations

$$\frac{a_{n+2}}{a_n} = \frac{(n+\alpha)(n+\alpha+1)-k}{(n+\alpha+2)(n+\alpha+1)}$$

so for large n

$$\frac{a_{n+2}}{a_n} \quad \rightarrow 1$$

Hence the series becomes (for large $n > N$, for some N)

$$\chi \sim ..... \quad + a_N(x^N + x^{N+2} + x^{N+4} + ...)$$

This series diverges at $x^2 = 1$ *ie* for $x = \pm 1$.

However, $x = \cos(\theta)$ so $x = 1 \quad \rightarrow \quad \theta = 0$ and $x = -1$ corresponds to $\theta = \pi$.

So if we want $\chi(r, \theta) = \chi(\theta)f(r)$ to be **finite** when $\theta = 0$ or π (*ie* on the z axis) we have to impose the conditions that

$$\lim_{\theta\rightarrow 0, \theta\rightarrow\pi} \chi(\theta) = \lim_{x\rightarrow\pm 1} \chi(x) = \text{finite}.$$

However, we recall that $k = l(l+1)$, and so we see that for each value of α one solution is a polynomial and the other one diverges. So what are these polynomials? (they are polynomials as they involve only finite series)

For $\alpha = 0$ (n even and the series starting with a_0, or n odd and the series starting with a_1) we have

$$a_{n+2} = \frac{n(n+1) - l(l+1)}{(n+2)(n+1)} a_n$$

so $a_{l+2} = 0$ and we have a polynomial of degree l.

Such (polynomial) solutions of our equation are called **Legendre polynomials**. They are either odd or even in x as they involve either odd (or even) powers of x.

Examples

$$\begin{aligned}
l = 0 \qquad \chi_0(x) &= a_0 \\
l = 1 \qquad \chi_1(x) &= a_1 x \\
l = 2 \qquad \chi_2(x) &= a_0(1 - 3x^2) \\
l = 3 \qquad \chi_3(x) &= a_1 x(1 - \frac{5}{3}x^2)
\end{aligned}$$

We can choose a convenient normalisation - the conventional choice is $\chi_l(1) = 1$; this normalisation fixes the values of a_0 and a_1 in the expressions above. With this normalisation the polynomials are called **Legendre polynomials** and are denoted by $P_l(x)$.

The lowest Legendre polynomials are therefore

$$\begin{aligned}
P_0(x) &= 1 \\
P_1(x) &= x \\
P_2(x) &= \frac{1}{2}(3x^2 - 1)
\end{aligned}$$

$$\begin{aligned}
P_3(x) &= \frac{1}{2}(5x^3 - 3x) \\
P_4(x) &= \frac{1}{8}(35x^4 - 30x^2 + 3) \\
P_5(x) &= \frac{1}{8}(63x^5 - 70x^3 + 15x)
\end{aligned}$$

Recall, however, that χ is really also a function of r. Hence we can have (for $m = 0$)

$$\chi_{E\ell 0} = f_{E\ell 0}(r) P_\ell(\cos\theta),$$

where $P_\ell(x = \cos\theta)$ is the familiar Legendre Polynomial of degree ℓ. (The other solution, $Q_\ell(x)$, as we have argued, is singular at $x = \pm 1$, or $\theta = 0, \pi$ and so can be ignored).

6.7 Spherical Harmonics

Our previous results were obtained when we put $m = 0$ in our equation for χ:

$$(1 - x^2)\frac{d^2\chi}{dx^2} - 2x\frac{d\chi}{dx} + k\chi = \frac{m^2}{1 - x^2}\chi$$

Then when we put $m = 0$, we eliminated dependence of χ on φ and our equation for χ became the Legendre equation.

Let us now look at the case when $m \neq 0$.

To solve this equation let us recall that $k = l(l + 1)$ and set

$$\chi = (1 - x^2)^{\frac{m}{2}} u.$$

Then

$$\frac{d\chi}{dx} = (1 - x^2)^{\frac{m}{2}}\frac{du}{dx} - mx(1 - x^2)^{\frac{m-2}{2}} u$$

and

$$\begin{aligned}
\frac{d^2\chi}{dx^2} &= (1 - x^2)^{\frac{m}{2}}\frac{d^2u}{dx^2} - 2mx(1 - x^2)^{\frac{m-2}{2}}\frac{du}{dx} \\
&-m(1 - x^2)^{\frac{m-2}{2}} u + m(m - 2)x^2(1 - x^2)^{\frac{m-4}{2}} u
\end{aligned}$$

So

$$\begin{aligned}
&(1 - x^2)\tfrac{d^2u}{dx^2} - 2mx\tfrac{du}{dx} - mu + \tfrac{m(m-2)x^2}{1-x^2}u \\
&-2x\tfrac{du}{dx} + 2mx^2\tfrac{u}{1-x^2} + l(l + 1)u - \tfrac{m^2u}{1-x^2} = 0.
\end{aligned}$$

ie

$$(1 - x^2)\ddot{u} - 2(m + 1)x\dot{u} + [l(l + 1) - m(m + 1)]u = 0.$$

But $P_l(x)$ satisfies

$$(1 - x^2)\ddot{P}_l - 2x\dot{P}_l + l(l + 1)P_l = 0.$$

Differentiate this equation once and obtain

$$-2x\frac{d^2P_l}{dx^2} + (1 - x^2)\frac{d^3P_l}{dx^3} - 2\frac{dP_l}{dx} - 2x\frac{d^2P_l}{dx^2} + l(l + 1)\frac{dP_l}{dx} = 0.$$

ie

$$(1 - x^2)\frac{d^3P_l}{dx^3} - 4x\frac{d^2P_l}{dx^2} + [l(l + 1) - 2]\frac{dP_l}{dx} = 0.$$

So we note that $\frac{dP_l}{dx}$ solves the equation for $m = 1$.

It is easy to check that $\frac{d^2P_l}{dx^2}$ solves the equation for $m = 2$ and, in general, χ is given by

$$\chi \; = \; A_l(1-x^2)^{\frac{m}{2}} \left(\frac{d}{dx}\right)^m P_l(x) \; = \; A_l \, P_l^m(x),$$

where A_l are some functions of r. These functions (for $A_l = 1$) are called **associated Legendre functions**.

Special cases of associated Legendre functions:

As $P_l^m(x) = (1-x^2)^{\frac{m}{2}} \frac{d^m}{dx^m} P_l(x)$ we have

- $P_l^0(x) = P_l(x)$
- $P_1^1(x) = (1-x^2)^{\frac{1}{2}} = sin(\theta)$
- $P_2^1(x) = 3x(1-x^2)^{\frac{1}{2}} = 3\cos(\theta)\sin(\theta)$

so P_l^m are polynomials in $\sin(\theta)$ and $\cos(\theta)$.

Moreover, choosing a normalisation constants of χ when $A_l = 1$, appropriately, we have

$$Y_n^m(\theta,\varphi) \; = \; \sqrt{\frac{2n+1}{4\pi}\frac{(n-m)!}{(n+m)!}}\, P_n^m(\cos(\theta))e^{im\varphi}$$

which are called **spherical harmonics**. They form a complete set of functions on (θ, φ), satisfy the orthogonality condition

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin(\theta)\, d\theta \, Y_{n_1}^{m_1\star}(\theta,\varphi)\, Y_{n_2}^{m_2}(\theta,\varphi) \; = \; \delta_{n_1 n_2}\, \delta_{m_1 m_2}$$

and any function on (θ, φ) can be expanded

$$f(\theta,\varphi) \; = \; \sum_{n,m} a_{nm}\, Y_n^m(\theta,\varphi)$$

with the coefficients of the expansion found from the orthogonality relations.

Returning to our problem we see that calling our $A(r) = f_{E\ell m}(r)$

$$\phi_{E\ell m}(r,\theta,\varphi) = f_{E\ell m}(r) P_\ell^m(\cos\theta) e^{im\varphi}.$$

Then f obeys the radial (energy) equation.

Writing $f(r) = u(r)/r$ the radial equation simplifies and $u = u_{E\ell}(r)$ satisfies

$$\frac{-\hbar^2}{2M}\frac{d^2u}{dr^2} + \left(V(r) + \frac{\ell(\ell+1)\hbar^2}{2Mr^2}\right) u = Eu.$$

This is in the form of a one-dimensional problem with effective potential

$$V_1 = \infty \quad (r<0) \qquad \text{and} \qquad V_1 = V(r) + \frac{\ell(\ell+1)\hbar^2}{2Mr^2} \quad (r>0),$$

which includes the boundary condition $u(0) = 0$ needed for finiteness of $\phi_{E\ell m}$ at the origin. Notice the ‘additional” centrifugal potential term.

The radial equation is independent of m so there is always $(2\ell + 1)$-fold degeneracy for given E and ℓ. For a central potential the eigenfunctions of energy and angular momentum are then

$$\phi_{E\ell m}(r,\theta,\varphi) = \frac{u_{E\ell}(r)}{r} Y_{\ell m}(\theta,\varphi),$$

where the angular-momentum wavefunctions are the spherical harmonics defined before

$$Y_{\ell m}(\theta,\varphi) \propto P_\ell^m(\cos\theta)\, e^{im\varphi}.$$

Note that $Y_{\ell m}$ satisfy

$$\widehat{L}_{\pm} Y_{\ell m} = \sqrt{(\ell \mp m)(\ell \pm m + 1)} \hbar Y_{\ell, m\pm 1}$$

as well as both

$$\widehat{L}^2 Y_{\ell m} = \ell(\ell+1)\hbar^2 Y_{\ell m} \qquad \text{and} \qquad \widehat{L}_z Y_{\ell m} = m\hbar Y_{\ell m}.$$

With $P_\ell^0 \equiv P_\ell(\cos\theta)$ and conventional phase we have

$$Y_{\ell 0} = \sqrt{\frac{2\ell+1}{4\pi}} P_\ell(\cos\theta),$$

involving an ordinary Legendre Polynomial. Then $Y_{\ell m}$ for $m \neq 0$ can be found by application of the differential operators $\widehat{L}_{\pm} = i\hbar e^{\pm i\varphi}(\cot\theta\, \partial/\partial\varphi \mp i\partial/\partial\theta)$.

Clearly $Y_{00} = 1/\sqrt{4\pi}$ and states with $\ell = 0$ are spherically symmetric. Then from $P_1(\cos\theta) = \cos\theta$ it follows at once that

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta \qquad \text{and} \qquad Y_{11} = -Y^*_{1,-1} = -\sqrt{\frac{3}{8\pi}} \sin\theta\, e^{i\varphi}.$$

Likewise from $P_2(\cos\theta) = (3\cos^2\theta - 1)/2$ we have $Y_{20} = \sqrt{5/16\pi}(3\cos^2\theta - 1)$, from which $\widehat{L}_{\pm}$ and $\widehat{L}^2_{\pm}$ give

$$Y_{21} = -Y^*_{2,-1} = -\sqrt{\frac{15}{8\pi}} \sin\theta\cos\theta\, e^{i\varphi} \qquad \text{and} \qquad Y_{22} = Y^*_{2,-2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta\, e^{2i\varphi}.$$

Generally

$$Y_{\ell m}(\theta,\varphi) = \sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}} P_\ell^m(\cos\theta)\, e^{im\varphi}.$$

Moreover, it can be shown that

$$P_\ell^m = P_\ell^{-m}.$$

Note also that for a given value of l the possible values of m are $m = -\ell, -\ell+1, ...\ell-1, \ell$ as for $m > \ell$ $\frac{d^{\ell+m}}{dx^{\ell+m}}(x^2-1)^\ell = 0$.

The $\ell = 1, 2$ examples above illustrate that $Y_{\ell,-m} = (-1)^m Y^*_{\ell m}$. Note that Messiah (*p.* 495) and Schiff (*p.* 80) have unusual (and different) phase conventions, apparently clashing with that adopted for the ladder operators.

The spherical harmonics are complete on the sphere; also it is useful to note the existence of a relation

$$\cos\theta\, Y_{\ell m}(\theta,\varphi) = A_{\ell m} Y_{\ell+1,m}(\theta,\varphi) + B_{\ell m} Y_{\ell-1,m}(\theta,\varphi)$$

where A and B are independent of (θ, φ). For $m = 0$ this is just the recurrence formula for Legendre polynomials.

Comment on **Jargon**;

- ℓ is called the angular quantum number
- **m** is called the magnetic quantum number (due to the coupling **HL** $\sim L_z$)
- **n**; when we have discrete values of energy they can be ordered using an integer - normally denoted by **n** which is then referred to as the principal quantum number.

More jargon:

The states corresponding to $\ell = 0, 1, 2, 3, 4, 5...$ are called **s, p, d, f, g, h,.. wave** states. The term $\frac{\hbar^2}{2M}\frac{\ell(\ell+1)}{r^2}$ is called the centrifugal potential.

Under parity, $\mathbf{r} \to -\mathbf{r}$, angles go $\theta \to \pi - \theta$ and $\varphi \to \pi + \varphi$. So $\cos\theta$ changes sign and $\sin\theta$ is unaffected, implying $P_\ell^m \to (-1)^{\ell-m} P_\ell^m$. With $e^{im\varphi} \to (-1)^m e^{im\varphi}$ then we have simply $Y_{\ell m} \to (-1)^\ell Y_{\ell m}$, confirming that angular momentum eigenstates have definite parity, equal to $(-1)^\ell$. Therefore, since r is unaffected,

$$\phi_{E\ell m}(\mathbf{r}) = (-1)^\ell \phi_{E\ell m}(-\mathbf{r}).$$

6.8 An Algebraic Approach to Angular Momentum

Previously we analysed the spectrum of angular momentum algebraically. We took $\widehat{L}_i = \epsilon_{ijk}\widehat{x}_j\widehat{p}_k$ and showed that

$$[\widehat{L}_i,\, \widehat{L}_j] \;=\; i\hbar\epsilon_{ijk}\widehat{L}_k$$

and then having found that $[\widehat{L}^2,\, \widehat{L}_k] = 0$ we decided to use simultaneous eigenstates of $\widehat{L}^2$ and $\widehat{L}_z$

$$\widehat{L}^2|\lambda, m\rangle = \hbar^2\lambda|\lambda, m\rangle$$
$$\widehat{L}_z|\lambda, m\rangle = \hbar m|\lambda, m\rangle.$$

By analysing various properties of such states we have found that $\lambda = \ell(\ell+1)$, $m = -\ell, ..\ell$ where 2ℓ is an integer. So we have found more possibilities than we have here.

Clearly our cases $\ell = 0, 1, 2, ...$ $\quad m = -\ell, -\ell+1, ..0..\ell$ are the ones we have found before. So $|\ell, m\rangle$ are represented, in the position representation, by our spherical harmonics $Y_{\ell m}$.

But what about the others?; those that correspond to half odd integer values of l? *e.g.* $\ell = \frac{1}{2},\ m = -\frac{1}{2}$, $m = \frac{1}{2}$ or $\ell = \frac{3}{2}$, $m = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}$ or $\frac{3}{2}$?

The non-integer values of m would make the wave function $\phi_{E\ell m}$ not single valued so for our **orbital** angular momentum we have only integer values of ℓ. But the general theory allows for the existence of another angular momentum - called **spin**. This new angular momentum is realised in nature; in fact, many elementary particles, such as electron and proton, have it. This extra degree of freedom is not described in terms of orbital wave functions $Y_{\ell,m}(\theta,\varphi)$ but is described by the purely quantum mechanical spin operators $\widehat{S}_x$, $\widehat{S}_y$ and $\widehat{S}_z$ which satisfy

$$[\widehat{S}_i,\, \widehat{S}_j] \;=\; i\hbar\, \epsilon_{ijk}\, \widehat{S}_k.$$

For electron, proton, neutron $\widehat{S}^2 = s(s+1)\hbar^2$ where $s = \frac{1}{2}$. Thus the eigenvalues of $\widehat{S}_z$ have two values $\pm\frac{1}{2}\hbar$; we have two spin states of each electron. For an electron a complete set of commuting observables involves its position operators $\widehat{x}$, $\widehat{y}$, $\widehat{z}$ and $\widehat{S}_z$ ($\widehat{S}^2$ is fixed). Its total angular momentum is $\widehat{J}_i = \widehat{S}_i + \widehat{L}_i$.

6.9 Radial Equation

With $\phi_{E\ell m}(r,\theta,\varphi) = u_{E\ell}(r)Y_{\ell m}(\theta,\varphi)/r$ the radial function $u = u_{E\ell}$ obeys

$$\frac{-\hbar^2}{2ME}\frac{d^2u}{dr^2} + \left(\frac{V(r)}{E} + \frac{\ell(\ell+1)\hbar^2}{2MEr^2}\right)u = u$$

for $r \geq 0$. The boundary condition $u(0) = 0$ applies and, with normalised spherical harmonics, we have

$$\int_0^\infty dr\, u^*_{E\ell}(r)\, u_{E'\ell'}(r) = \delta_{EE'}\delta_{\ell\ell'}$$

to ensure that

$$\int d\tau\, \phi^*_{E\ell m}\phi_{E'\ell' m'} = \delta_{EE'}\delta_{\ell\ell'}\delta_{mm'}.$$

For continuous eigenvalues E replace $\delta_{EE'} \to \delta(E - E')$.

The division by $E \neq 0$ makes plain the dimensionless variable kr where $k \equiv \sqrt{2M\,|E|}/\hbar$. For 'non-singular potentials' where $r^2V(r) \to 0$ as $r \to 0$ the 'centrifugal' term dominates as $r \to 0$ and then

$$\frac{d^2u}{d(kr)^2} \approx \frac{\ell(\ell+1)}{(kr)^2}u$$

with solutions $u \sim (kr)^{\ell+1}, (kr)^{-\ell}$. Since $\ell = 0, 1, 2, \ldots$ only the former is acceptable if $u(0) = 0$.

6.9.1 Free Particle

Here $V = 0$ and $E > 0$. The radial equation is

$$\frac{d^2u}{d(kr)^2} + \left(1 - \frac{\ell(\ell+1)}{(kr)^2}\right) u = 0.$$

For $\ell = 0$ we have $u_{E0}(r) \propto \sin kr$, rejecting the cosine that isn't zero at $r = 0$. For general ℓ the non-singular solution is $kr\, j_\ell(kr)$, where j_ℓ is the (first kind of) 'spherical Bessel function'.

These functions can be shown to be given by:

$$j_\ell(x) = x^\ell \left(-\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\sin x}{x}.$$

Clearly $j_0(x) = \sin x/x$ and we can prove by induction that xj_l, for $l \neq 0$, satisfies the equation above:

To see this define

$$u_l = x^{l+1} \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\sin x}{x}.$$

Then

$$u_{l+1} = \frac{du_l}{dx} - \frac{(l+1)}{x} u_l.$$

So

$$\frac{du_{l+1}}{dx} = -\frac{(l+1)}{x}\frac{du_l}{dx} + \frac{(l+1)}{x^2} u_l + \frac{d^2u_l}{dx^2}$$

and

$$\frac{d^2u_{l+1}}{dx^2} = \frac{d^3u_l}{dx^3} - \frac{(l+1)}{x}\frac{d^2u_l}{dx^2} + 2\frac{(l+1)}{x^2}\frac{du_l}{dx} - 2\frac{(l+1)}{x^3} u_l.$$

Putting all this into the equation we find that

$$\frac{d^3u_l}{dx^3} + \left[1 - \frac{l(l+1)}{x^2}\right]\frac{du_l}{dx} + 2\frac{l(l+1)}{x^3} u_l$$

However this expression vanishes as can be seen from differentiating the equation for u_l.

See Jackson (*pps.* 84-87) for more details.

A free-particle solution with definite momentum $\mathbf{p} = \hbar\mathbf{k}$ is (Sec 2.4) $\phi_{E,\mathbf{p}}(\mathbf{r}) = \exp i\mathbf{k}\cdot\mathbf{r}$, which must be expressible as a superposition of free angular-momentum eigenstates $\phi_{E\ell m}(r,\theta,\varphi) = j_\ell(kr)Y_{\ell m}(\theta,\varphi)$. Choosing z-axis along $\mathbf{k}$ there is no φ dependence and the link is through the well-known formula

$$\exp(ikr\cos\theta) = \sum_{\ell=0}^{\infty}(2\ell+1)i^\ell j_\ell(kr)P_\ell(\cos\theta).$$

6.9.2 Spherical Square Well

Here $V = V_0\theta(r-a)$.

The radial equation now takes the form

$$\frac{-\hbar^2}{2M}\frac{d^2u}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2Mr^2}u = Eu \qquad 0 < r < a$$

and

$$\frac{-\hbar^2}{2M}\frac{d^2u}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2Mr^2}u = (E - V_0)u \qquad r > a$$

The boundary conditions

- $u \to 0 \qquad r \to 0$

1. $u \to 0 \qquad r \to \infty$ for bound states
2. $u \to$ const $r \to \infty$ for cont. states

Consider first the **s** wave states; *i.e.* $\ell = 0$. For $E < V_0$ we have for $0 < r < a$

$$(\frac{d^2}{dr^2} + \alpha^2)u \;=\; 0, \qquad \alpha = \sqrt{\frac{2ME}{\hbar^2}}$$

i.e.

$$u = A\cos(\alpha r) \;+\; B\sin(\alpha r)$$

while for $r > a$ we have

$$(\frac{d^2}{dr^2} - \beta^2)u = 0, \qquad \beta = \sqrt{\frac{2M(V_0 - E)}{\hbar^2}}$$

and so

$$u = Ce^{-\beta r} + De^{\beta r}.$$

The boundary conditions impose $D = 0$ and $A = 0$ and we see that we have only **odd** solutions of the corresponding one dimensional problem (where we had odd and even solutions).

Comments:

- Of course $r > 0$ so the fact that we have odd solutions (for $r < 0$) is irrelevant
- Recall that the number of bound states depends on $\frac{2MV_0a^2}{\hbar^2}$. Since we are permitting only odd states there need not be any bound states (if V_0 is small enough) in contradistinction to the one-dimensional case where there is **always** at least one state. For $E > V_0$ we have the continuous spectrum as in the one dimensional case).

Next we look at the case of general ℓ. We put $\rho = \alpha r$ and note that our equation becomes

$$\frac{d^2}{d\rho^2}(\rho f) + [1 - \frac{\ell(\ell+1)}{\rho^2}]\rho f = 0,$$

where $0 < \rho < \frac{a}{\alpha}$ and, as before, $\alpha = \sqrt{\frac{2ME}{\hbar^2}}$.

However, this is exactly like the free case discussed before; and its solutions are the spherical Bessel's functions $j_\ell(\rho)$ and $n_\ell(\rho)$. The function $j_\ell(\rho)$ was defined in the free case; $n_\ell(\rho)$ is singular at the origin and is more complicated. So the boundary condition at $\rho = 0$ gives us

$$f = A\,j_\ell(\alpha r) \qquad \text{for} \quad 0 < r < a$$

and for $r > a$ we have

$$f = C\,j_\ell(i\beta r) \;+\; D\,n_\ell(i\beta r) \quad \text{for} \quad r > a,$$

where the constants C and D are related by the requirement that $f \not\to \infty$ as $r \to \infty$. This gives us one condition between C and D. The continuity of f and its derivative at $r = a$ gives us two further conditions which together not only fix C and D but also determine the energy levels. Thus in particular, it can be shown that there is at least one **p wave** bound state if

$$\pi \leq \sqrt{\frac{2MV_0a^2}{\hbar^2}} < 2\pi$$

and two if

$$2\pi \leq \sqrt{\frac{2MV_0a^2}{\hbar^2}} < 3\pi. \quad \text{etc}$$

Comparing this result with the condition for an **s wave** we see that the minimum value of $\frac{2MV_0a^2}{\hbar^2}$ for the **p wave** is higher. This is because of the additional **repulsion** present due to the angular momentum barrier $\frac{\ell(\ell+1)}{r^2}$. As ℓ increases V_0a^2 has to get larger for the system to have bound states for angular momentum ℓ.

6.10 Two Particle Systems

So far we have been looking at systems involving only one particle under the influence of a fixed potential. However, our discussion generalises to two particles moving under the influence of mutual forces.

A system of two particle can be described by two position vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ and momenta $\mathbf{p}_1$ and $\mathbf{p}_2$. Let us assume that the particles have masses m_1 and m_2, respectively. So

$$H = \frac{1}{2m_1}(\mathbf{p}_1)^2 + \frac{1}{2m_2}(\mathbf{p}_2)^2 + V(\mathbf{r}_1 - \mathbf{r}_2).$$

Such a system is invariant under translations:

$$\mathbf{r}_i \quad \rightarrow \quad \mathbf{r}_i + \mathbf{a}$$

and also under rotations, if $V(\mathbf{r}_1 - \mathbf{r}_2) = V(|\mathbf{r}_1 - \mathbf{r}_2|)$. In classical mechanics we can treat such a system as corresponding to a one particle in a fixed potential. We do this by introducing centre of mass, and relative coordinates. To do this we define

$$\begin{aligned} \mathbf{r} &= \mathbf{r}_1 - \mathbf{r}_2 \\ M\mathbf{R} &= m_1\mathbf{r}_1 + m_2\mathbf{r}_2, \qquad M = m_1 + m_2 \end{aligned}$$

We can introduce similar variables in quantum mechanics.

We have

$$\{-\frac{\hbar^2}{2m_1}(\nabla_1)^2 - \frac{\hbar^2}{2m_2}(\nabla_2)^2 + V(|\mathbf{r}_1 - \mathbf{r}_2)|)\}\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2),$$

in the Schrödinger representation. Here, $(\nabla_i)^2 = \frac{\partial^2}{\partial x_k^{(i)} \partial x_k^{(i)}}$ summed over k.

But

$$\begin{aligned} \frac{\partial}{\partial x_i^{(1)}} &= \frac{m_1}{M}\frac{\partial}{\partial R_i} + \frac{\partial}{\partial x_i} \\ \frac{\partial}{\partial x_i^{(2)}} &= \frac{m_2}{M}\frac{\partial}{\partial R_i} - \frac{\partial}{\partial x_i} \end{aligned}$$

we see that

$$\begin{aligned} \frac{1}{m_1}(\nabla_1)^2 + \frac{1}{m_2}(\nabla_2)^2 &= \frac{1}{m_1}(\frac{m_1}{M}\frac{\partial}{\partial R_i} + \frac{\partial}{\partial x_i})^2 + \frac{1}{m_2}(\frac{m_2}{M}\frac{\partial}{\partial R_i} - \frac{\partial}{\partial x_i})^2 \\ &= \frac{1}{M}(\nabla_c)^2 + \frac{1}{\mu}\nabla^2 \end{aligned}$$

where $(\nabla_c)^2 = \frac{\partial^2}{\partial R_i \partial R_i}$, $(\nabla^2) = \frac{\partial^2}{\partial x_i \partial x_i}$ and $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass.

So the Schrödinger equation becomes

$$\left[-\frac{\hbar^2}{2M}(\nabla_c)^2 - \frac{\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r})\right]\Psi = E\Psi$$

and so it is convenient to separate in $\mathbf{R}$ and $\mathbf{r}$.

We write $\Psi = \Psi_c(\mathbf{R})\psi(\mathbf{r})$ and obtain

$$-\frac{\hbar^2}{2M}\nabla_c^2\Psi_c(\mathbf{R}) = E_c\Psi_c(\mathbf{R})$$

i.e. like the equation of a free particle of mass $M = m_1 + m_2$ and

$$[-\frac{\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r})]\psi(\mathbf{r}) = E'\psi(\mathbf{r})$$

like a particle of reduced mass in a fixed potential.

Note that the solutions of the free equation are

$$\Psi_c = Ae^{i\frac{\mathbf{PR}}{\hbar}}$$

of energy $E_c = \frac{\mathbf{P}^2}{2M}$ and we are left with having to solve the relative position problem and then the total energy is the sum of the two.

Comment: Our procedure (of separating variables), once again, can be regarded as choosing an appropriate set of commuting observables. For if we define $\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2$ and $\mathbf{p} = \frac{m_1}{M}\mathbf{p}_1 - \frac{m_2}{M}\mathbf{p}_2$ we have

$$[x_i, P_j] = 0, \quad [x_i, p_j] = i\hbar\delta_{ij}$$
$$[R_i, p_j] = 0, \quad [R_i, P_j] = i\hbar\delta_{ij}$$

and so we can choose as our basis the simultaneous eigenstates of $\widehat{\mathbf{P}}$ and $-\frac{\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r})$.

6.10.1 Isotropic Simple-Harmonic Oscillator - once again

Here $V = \frac{1}{2}M\omega^2 r^2$. The spectrum is of bound states for $E > 0$ and the radial function $u_{E\ell}(r)$ obeys

$$-\frac{d^2u}{d(kr)^2} + \left\{ \left(\frac{kr}{\lambda}\right)^2 + \frac{\ell(\ell+1)}{(kr)^2} \right\} u = u,$$

where $\lambda^2 \equiv 2Ek^2/M\omega^2$, *i.e.* $E = \lambda\hbar\omega/2$. We seek a solution

$$u = (kr)^{\ell+1}\exp(-\frac{(kr)^2}{2\lambda})F(kr),$$

where acceptable behaviour as $r \to 0$ and $r \to \infty$ is made explicit. A solution with F a polynomial (and therefore harmless at $0, \infty$) is found by the usual series method when $\lambda = 2n + 3$ for 'principal quantum number' $n = 0, 1, 2, \ldots$. The degree of F is $0, 2, 4, \ldots$, and is equal to $n - \ell$. So energy levels are $E = E_n = (n + \frac{3}{2})\hbar\omega$ and there is degeneracy with respect to ℓ.

For $n = 0$ only $\ell = 0$ is allowed and for $n = 1$ only $\ell = 1$; in each case $F =$ constant. For $n = 2$ the possibilities are $\ell = 0$ (F is quadratic) and $\ell = 2$ ($F =$ constant), and for $n = 3$ there is $\ell = 1$ (F quadratic) and $\ell = 3$ ($F =$ constant). Remembering m, the $n = 0, 1, 2, 3$ levels have degeneracy $1, 3, 6, 10$ respectively; for general n degeneracy is $\frac{1}{2}(n + 1)(n + 2)$.

This oscillator is 'isotropic' because $r^2 = x^2 + y^2 + z^2$ and so in Cartesians $\widehat{H} = -(\hbar^2/2M)\nabla^2 + V$ is a sum of terms for three independent one-dimensional simple-harmonic oscillators with the same frequency. Each contributes $(n_i + \frac{1}{2})\hbar\omega$ to E and $n = n_x + n_y + n_z$. Counting degeneracy is straightforward: $n = 0$ is all $n_i = 0$; $n = 1 = 1 + 0 + 0$ (3 ways); $n = 2$ is $2 + 0 + 0$ (3 ways) and $1 + 1 + 0$ (3 ways); $n = 3$ is $3 + 0 + 0$ (3) and $2 + 1 + 0$ (6) and $1 + 1 + 1$ (1) in complete agreement with our discussion at the beginning of this chapter.

6.11 Hydrogen Atom

The simplest model of a one-electron atom is a point electron of charge $-e$ and mass M moving non-relativistically in the inverse-square electrostatic (Coulomb) attraction of a point nucleus of charge $+Ze$ fixed at the origin. Hydrogen has atomic number $Z = 1$ and so we have a three-dimensional potential problem with $V(r) = -e^2/r$. There is a scattering sector to the energy spectrum for $E > 0$ and a bound-state sector when $E < 0$. Here we deal with the latter.

With $E = -|E|$ and $k^2 = 2M|E|/\hbar^2$ the radial wavefunction $u = u_{E\ell}(r)$ obeys

$$\frac{d^2u}{d(kr)^2} + \left(\frac{\alpha}{kr} - \frac{\ell(\ell+1)}{(kr)^2}\right) u = u,$$

where

$$\alpha \equiv \frac{e^2 k}{|E|} = \frac{e^2}{\hbar}\sqrt{\frac{2M}{|E|}}.$$

Writing

$$u(r) = (kr)^{\ell+1} e^{-kr} F(kr),$$

with required behaviour as $r \to 0$ and $r \to \infty$ extracted (note $u'' \approx u$ for large r), we find that $F(x)$ obeys

$$x\frac{d^2F}{dx^2} + 2[(\ell+1) - x]\frac{dF}{dx} + [\alpha - 2(\ell+1)]F = 0.$$

A routine series expansion finds (Laguerre) polynomial solutions (harmless as $r \to 0$ and $r \to \infty$) of degree $N = 0, 1, 2, \ldots$ if $\alpha = 2(N + \ell + 1)$. Therefore the bound-state energies for this model of the hydrogen atom are

$$E_n = -\frac{Me^4}{2\hbar^2 n^2},$$

labelled by 'principal quantum number' $n = N + \ell + 1 = 1, 2, 3, \ldots$. The ground state is at $E_1 \approx -13.6$ eV and the infinite set of levels packs closer as n increases, blending into the continuum at $E = 0$.

The unique ground state is $n = 1$, where $N = \ell = m = 0$. All higher ('excited') states are degenerate. For $n = 2$ there is $N = 1$, $\ell = m = 0$ plus $N = 0$, $\ell = 1$ with $m = -1, 0, +1$. Indeed for every n degeneracy is $1 + 3 + 5 + \ldots + (2n - 1) = n^2$. This high degree of 'accidental' or 'dynamic' degeneracy is special to the Coulomb potential, although the isotropic simple-harmonic oscillator shows something similar. It is symptomatic of conserved quantities beyond angular momentum and parity so far identified. For the inverse-square force law there is the (Laplace-)Runge-Lenz vector, as described by H. Goldstein, *Classical Mechanics*, Addison Wesley, 2nd Ed., 1980, *p.* 102 *etc.*

The lowest few wavefunctions $\phi_{n\ell m}(r,\theta,\varphi) = u_{n\ell}(r)Y_{\ell m}(\theta,\varphi)/r$ are

$$\phi_{100} = \frac{1}{\sqrt{\pi a_0^3}}\exp(-\frac{r}{a_0}),$$

$$\phi_{200} = \frac{1}{\sqrt{8\pi a_0^3}}\left(2 - \frac{r}{a_0}\right)\exp(-\frac{r}{2a_0})$$

and

$$\phi_{21m} = \frac{1}{\sqrt{8\pi a_0^3}}\frac{r}{a_0}\exp(-\frac{r}{2a_0}) \times \begin{cases} \frac{1}{\sqrt{2}}\sin\theta e^{-i\varphi} \\ \cos\theta \\ -\frac{1}{\sqrt{2}}\sin\theta e^{i\varphi} \end{cases}$$

with $m = -1, 0, +1$ respectively, and where $a_0 = \hbar^2/Me^2$ is the Bohr radius.

The formula for the energy levels agrees quite well with experiment, being the same as that given by the Bohr model. However n, the principal quantum number, is no longer the electron's orbital angular momentum in units of $\hbar$ and has nothing to do with fitting de Broglie waves into a circle. And while a_0 is the radius of the lowest orbit of the Bohr atom, now we have $\langle r \rangle = \frac{3}{2}a_0$ in the ground state.

Transitions $E \to E'$ conserve energy by absorption and emission of radiation of characteristic frequency $\nu = |E - E'|/2\pi\hbar$ and wavelength $\lambda_{nn'}^{-1} = R_\infty \left|n^{-2} - n'^{-2}\right|$. The latter formula was discovered empirically by spectroscopists before 1900. The 'Rydberg Constant' is

$$R_\infty \equiv \frac{Me^4}{4\pi\hbar^3 c} = 10973731.571\text{m}^{-1},$$

according to recent measurements of fundamental constants (see *Physics Letters B*, vol. 239, 12 Apr 1990, page III.1).

A simple refinement of this model treats the atom as two moving and interacting bodies. Then $\mathbf{r}$ is a relative coordinate and otherwise results are identical except that M is replaced by 'reduced mass' $Mm_0/(M + m_0)$ where m_0 is the mass of the nucleus. (See *e.g.* Schiff *pps.* 88-90). For hydrogen corrections are order $M/m_0 \sim 1/2000$.

Another refinement recognises the intrinsic spin angular momentum $\frac{1}{2}\hbar$ of the electron. As a classical spinning charge $-e$ its consequent magnetic moment is $-e\hbar/2Mc$. This interacts with magnetic fields, adding terms to $\widehat{H}$ that tend to lift the degeneracy of its eigenvalues. Magnetic fields are provided by the spatial motion of the charged nucleus relative to the electron (giving 'fine structure' to the spectrum) and may be provided by any intrinsic spin of the charged nucleus ('hyperfine structure'). Hydrogen, with one proton of spin $\frac{1}{2}$, shows both effects.

External static magnetic fields couple to the effective electric current of the orbital electron (producing the '(normal) Zeeman effect') and couple to its intrinsic magnetic moment to give the 'anomalous Zeeman effect'.

Relatively small effects can be treated perturbatively.

7 Conclusion

7.1 Summary

Observable quantities are associated with (self-adjoint) operators that work in a linear state space with inner product. A measurement gives a (real) eigenvalue of the appropriate operator. State vectors are linear combinations of its (orthogonal, complete) eigenvectors. A measurement is a random realisation of an outcome (eigenvalue) and the relative probability of each is the squared modulus of the coefficient of the corresponding eigenvector in the basis expansion. After a measurement the state vector is changed to the eigenvector belonging to the eigenvalue realised.

Quantisation is discreteness of eigenvalues and is a consequence of commutation rules for operators, where $\hbar$ enters. Commutation rules and positivity also lead to the Uncertainty Principle, constraining statistical scatter of results of mutually incompatible measurements on systems with identical state vectors.

Time-dependence of state vectors between measurements is determined by the Schrödinger Equation as a unitary transformation. Again $\hbar$ enters and unitarity keeps consistency with measurement axioms. The Schrödinger Equation and commutation rules give Ehrenfest's theorems, which ensure the proper classical limit.

States of definite energy are stable and external time-dependent perturbations cause transitions, with energy interchange. Transitions between quantised atomic and molecular levels involve emission and absorption of energy as electromagnetic radiation of characteristic frequencies.

Wave mechanics represents a state vector in a basis of eigenstates of an operator measuring the system's configuration-space coordinates. The Schrödinger Equation becomes the Schrödinger Wave Equation and the squared modulus of its solution (wavefunction) gives a probability density for measurements of configuration-space coordinates. For one particle these may coincide with coordinates of ordinary spatial position; this is 'wave-particle duality'.

The formalism gives predictions that agree with experiment although important questions of principle remain, connected with measurement and the collapse of the state vector.

7.2 Measurement

Measurement gives an eigenvalue of a self-adjoint operator at random according to a certain probability density and involves thereupon changing the state vector used to describe a quantum system from a general superposition of eigenvectors to the single eigenvector belonging to the eigenvalue realised. In the 2-slit experiment when one slit is closed or when an electron arrives at the detecting screen its position is recorded and the state vector becomes a position eigenstate. This is called 'collapse of the state vector' and is a change not described by the electron's Schrödinger Equation.

But the electron's detection involves its interaction with a detector, colliding with constituent atoms which are excited and then decay, emitting photons which typically travel to and interact with atoms of a camera film. Later this is developed and fixed by chemicals, then later still photons bounce off the film and into your eye, where they interact with the retina to cause electrical impulses to travel via optic nerve to brain. You 'see' the electron's position.

We think at first of the 'quantum system' as just the electron and the 'detector' as being a separate classical recording device. But the chain of events involved in the observation of the electron's position is clearly, from the description above, a set of physical processes at the microscopic level, each of which should (if we had the computational power) be described by quantum mechanics.

So perhaps, more correctly, part at least of the chain of detection apparatus should be included in a vastly more complicated Schrödinger Equation for the experiment, when the borderline between quantum and classical, and so the wavefunction collapse, occurs at a much later stage.

But where? At the camera? When the film is developed? When light bounces off it? When it enters your eye? When you're conscious of it? When you tell me about it? The answer is not obvious.

The dilemma is sharpened by the 'Schrödinger's Cat' thought experiment. A cat is shut in a box for a set time with a radioactive nucleus which has exactly a 50:50 chance of decaying during that period. If (and only if) it does decay then a bulb of cyanide is broken and the cat dies. When you open the box you see with equal probability either 'a cooling corpse or a frisking feline' (Polkinghorne, *p.* 62).

The state vector of the unobserved quantum system is an equal mixture of two eigenstates— decayed and undecayed, or equivalently dead and alive. When the box is opened uncertainty has gone. But surely the cat alone is competent to tell at least whether it's dead or alive? Surely without being seen the bulb is either broken or intact? Just where in the chain of events does 'observation' occur and collapse of the state vector happen?

One possible answer is that collapse occurs at a point where the system becomes so complex that irreversible phenomena become important. This tries to identify the quantum/classical interface and is fashionable now that deterministic chaos and properties of cellular automata have come to the fore.

But this is so far only a vague idea, and doesn't answer other questions that we think have some meaning: What's the electron really doing before it hits the screen? How is it determined which position eigenstate it collapses to? How is it fixed when the nucleus decays? *What's happening in the world while we're not looking?*

We assume that an objective world indeed exists — that's the simplest hypothesis consistent with everyday experience, after all, and it seems to work in everyday affairs. But it may be that at a submicroscopic level things are arranged so that with the tools we can make from the physical processes available we simply can't resolve whatever mechanism may guide state vector collapse, any more than without a microscope you can see the cells of the skin on your hand. Maybe down there effectively there's no 'real world' to be seen because there's no way of seeing it!

There are substantial issues here. Einstein talked of 'God playing dice' and these questions are in focus again with technological advances that allow clear-cut experiments. Aspect has done a version of the EPR thought experiment (Phys. Rev. Letters **49**, 91 & 1804(1982)) and for example Nagourney *et al.* (Phys. Rev. Letters **56**, 2797(1986)) have watched a single calcium ion making quantum jumps.

More modern texts like Ballentine, and Sudbery, give some attention to these issues, and the book by Polkinghorne and those he cites on his *p.* 97 explain more and describe alternative theories for whatever may underlie the 'fall of the dice'.

7.3 And There's More . . .

Only the simplest atom (hydrogen) has been treated, in the simplest model. But the theory clearly predicts that such typical atoms, in their ground state, are stable. The most obvious classical catastrophe of the Rutherford atom is avoided.

But most atoms have many electrons around their tiny nucleus, and would seem to be mostly empty space. The next step is to understand how multiple-electron atoms are arranged and how aggregates of atoms in bulk matter keep themselves apart — why don't they interpenetrate and collapse? To answer this needs development of the quantum mechanics of many-body systems and in particular Fermi-Dirac Statistics and the Exclusion Principle. And if you want to learn more about this and other related concepts do come to the course on Advanced Quantum Theory.