PH2201

Basic Quantum Mechanics

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Contents

1   Introduction

The quantum world differs from the classical world in many aspects, most of which we seldom encounter in our daily lives and are hence unintuitive.

- The physical world is not deterministic; uncertainty is intrinsic to the quantum world. This is sometimes illustrated by the Schrödinger's cat thought experiment.

- Both light and matter exhibit characteristics of waves as well as those of particles. However, a single object cannot exhibit both of these properties simultaneously.

- Physical quantities may be quantized – they may be constrained to have discrete values rather than vary continuously.

2   Duality of light

2.1   Blackbody radiation

A blackbody is an object which absorbs all radiation incident on it, and reflects none. It also emits radiation of all frequencies.

Kirchoff's Law says that the rates of emission and absorption of radiation of a body in thermal equilibrium will be equal. By thermal equilibrium, we mean that the temperatures of the body and its surroundings are equal.

Proposition 2.1 (Stefan-Boltzmann Law)**.** *The power emitted by a blackbody is given by*

$$P = \sigma A T^4.$$

Here, $\sigma \approx 5.67 \times 10^{-8}\,\mathrm{Js^{-1}m^{-2}K^{-4}}$ is called the Stefan-Boltzmann constant.

We may break down the total energy density $\rho \propto T^4$ in terms of the contributions from each frequency, so

$$\rho = \int_0^\infty \rho(\nu)\,d\nu.$$

It turns out that $\rho(\nu)$ is non-monotonic. This cannot be explained by classical mechanics (Rayleigh-Jean's Law), which predicts that $\rho(\nu)$ is unbounded with increasing frequency – the famous ultraviolet catastrophe.

Proposition 2.2 (Wien's Law)**.** *The positions of the peaks in $\rho(\nu)$ are described by*

$$\lambda_{peak} = \frac{w}{T}.$$

Here, $w \approx 2.9 \times 10^{-3}\,\mathrm{mK}$.

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Note that at $T \approx 300\,\mathrm{K}$, the peak wavelength λ_{peak} is in the infrared range: this is why night vision googles are useful.

Consider a collection of electromagnetic waves in a blackbody cavity, with temperature T. This can be seen as the superposition of normal modes. The classical approach to the blackbody problem is to suppose that the energy density at a particular frequency is given by

$$\rho(\nu) = \langle E \rangle n(\nu),$$

where $n(\nu)$ is the number density of wave modes with frequency ν, and E is the average energy of the radiation.

The classical law of equipartition of energy gives

$$\langle E \rangle = k_B T,$$

where k_B is the Boltzmann constant.

The wavenumber of for modes within the cavity is given by

$$\boldsymbol{k} = \frac{2\pi}{L}\boldsymbol{n},$$

where $\boldsymbol{n} = (n_x, n_y, n_z)$ with integral components. Now,

$$\nu = \frac{c}{\lambda} = \frac{c}{L}n.$$

Treating n as a continuous variable and using $dV = 4\pi n^2 dn$, we write

$$n(\nu)\,d\nu = \frac{8\pi}{c^3}\nu^2\,d\nu.$$

This leads to the Rayleigh-Jean Law,

$$\rho(\nu)\,d\nu = \langle E \rangle n(\nu)\,d\nu = \frac{8\pi k_B T}{c^3}\nu^2\,d\nu.$$

Planck looked at the probability distribution for the energy,

$$P(E) = \frac{1}{k_B T}e^{-E/k_B T}.$$

This is the Boltzmann distribution. It can be shown that

$$\langle E \rangle = \frac{\int_0^\infty EP(E)\,dE}{\int_0^\infty P(E)\,dE} = k_B T,$$

which recovers the Rayleigh-Jean Law.

Planck's idea was to restrict E to discrete values; integral multiples of the frequency ν. This leads to

$$\langle E \rangle = \frac{\sum EP(E)}{\sum P(E)} = \frac{h\nu}{e^{h\nu/k_B T} - 1}.$$

This gives us the Planck distribution.

Proposition 2.3 (Planck's Law)**.** *The spectral energy density of radiation emitted by a blackbody in thermal equilibrium is described by the distribution*

$$\rho(\nu)\,d\nu = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/k_B T}-1}\,d\nu.$$

Here, $h \approx 6.626 \times 10^{-34}\,\mathrm{J\,s}$ is called Planck's constant.

When $h\nu \ll 1$, we recover the Rayleigh-Jean limit. When $h\nu \gg 1$, we get the Wien limit.

Now we calculate,

$$\rho = \int_0^\infty \rho(\nu)\,d\nu = \frac{8\pi^5 k_B^4}{15c^3 h^3}T^4,$$

which recovers the Stefan-Boltzmann Law with

$$\sigma = \frac{2\pi^5 k_B^4}{15c^2 h^3}.$$

Also, the maxima of the Planck distribution recovers Wien's Law, with

$$\nu_{max} \approx 2.8\frac{k_B T}{h}.$$

2.2   Photoelectric effect

This reveals the dual nature of light. Classical optics relies on the wave nature of light, thus explaining phenomena such as interference and diffraction. This culminates in Maxwell's equations, which predict the wave nature of light as the propagation of oscillating electric and magnetic fields.

The photoelectric effect in the phenomenon in which light shining on a metal surface ejects electrons from it, thus producing a current. Suppose that the incident light has frequency ν, intensity I and this produces a current i. We can calculate the maximum kinetic energy of the emitted electrons $E_{max} = eV_0$ by adjusting an opposing potential V.

It turns out that for a constant intensity I, the photocurrent saturates at the same value. However, different frequencies ν produces different stopping potentials V_0; the greater the frequency, the greater the magnitude of the stopping potential. This turns out to have a linear relationship, with

$$E_{max} = eV_0 = h(\nu - \nu_0) = h\nu - \phi.$$

The slope h is universal for all metals, while $\phi = h\nu_0$ varies between different metals. This shows that below a certain frequency ν_0, we obtain no photocurrent, regardless of the intensity! This appears strange from a classical perspective, where the energy delivered by an electromagnetic wave is related to its intensity, not its frequency.

Einstein proposed that light strikes the metal in bundles of energy, all integral multiples of $h\nu$. There is also a minimum binding energy which must be overcome to liberate electrons from the metal surface – this cannot be paid in a continuous manner, since any partial energy given to an electron will be lost before the arrival of the next energy bundle. Thus, each energy bundle must carry a minimum energy $h\nu_0$ in order to liberate electrons and produce a photocurrent.

This establishes a particle-like mature of light. Each energy bundle, or particle of light, is called a photon.

3   Duality of matter

3.1   Matter waves

Louis de Broglie further hypothesised that matter also has a wave nature, with an associated wavelength of

$$\lambda_{matter} = \frac{h}{p}.$$

This has been demonstrated by Davisson and Germer, where a stream of electrons exhibits diffraction.

This has some amazing implications. In the classical world, knowledge of a particle's position and momentum is enough to pinpoint its trajectory with arbitrary precision. However, the wavelike nature of matter would imply that we can no longer talk of a definite, localized position when we have knowledge of the particle's momentum! This uncertainty is inherent to quantum mechanics.

Another consequence is the phenomenon of quantum tunnelling.

3.2   Double slit experiment with pellets

Consider Young's double slit experiment, this time with pellets sprayed from a gun at a wall with two slits. The other sides has a collector, which is moveable. Assume that the pellets do not break, and that they arrive in groups independent of the rate of firing. We want to find the probability that a pellet lands at a distance x from the centre of the screen.

Now, this just means that we have to count the number of pellets which reach the detector in a given time interval. Also, we expect that the probability distribution for two slits ought to be the sum of the distributions for the individual slits, obtained by closing one slit at a time. The distribution for a single slit looks something like a Gaussian, so their combination should also look like a broad Gaussian.

Note that this says nothing about phenomena such as interference.

3.3   Double slit experiment with electrons

Instead of using pellets, we now use electrons. These can be fired by heating a tungsten wire inside a box with a pinhole. Suppose that the detector at the other side produces a 'click' whenever an electron strikes it; all such clicks are identical and random. The electrons are also fired very slowly, so that there is only one electron passing through the slits and hitting the screen at a given time. This means that we hear distinct, separate clicks at random intervals, which means that an electron must have passed through one of the slits at random before impacting the screen.

What we observe is that over a long time, the probability distribution of the electrons is in the form of an interference pattern, just like with light waves. The strange thing is that if each electron passes through one slit at a time, the other slit ought to be 'closed' from its perspective, which means that we ought to have obtained the superposition of two Gaussians!

An attempt to explain this might be that the electrons follow some complex pathways incorporating both slits. On the other hand, the probability observed at the centre is greater than the sum of the probabilities for the single slits, and there are regions of zero probability on the screen where the single slit probabilities would suggest finite values. This would imply that closing a slit somehow increases the probabilities in one region and decreases that in another.

Thus, the electrons arrive at the screen as particles, but their distribution on the screen shows interference patterns just like those of a wave!

This suggests that a simple sum of the probabilities P_1 and P_2 from each of the slits is not enough. Analogous to the double slit experiment with light, we must assign complex probability amplitudes A_1 and A_2, which we then add up.

$$P_1 = |A_1|^2, \qquad P_2 = |A_2|^2, \qquad P_{12} = |A_1 + A_2|^2.$$

3.3.1 Spying on the electrons

Suppose that we repeat this experiment, but this time we place a detector on the slits. Thus, we can be sure which slit a given electron passes through. One way to do this is to place a light source in between the slits and the screen. When an electron passes through a slit, it will scatter some light which we see as a flash in the neighbourhood of the slit.

What happens is that the interference pattern disappears! The distribution now has two peaks, just like a classical particle would behave, i.e. we now have $P_1 + P_2$. We do indeed observe a single flash corresponding to each click, so we can pinpoint which slit a given electron on the screen corresponds to.

To see whether the light source is somehow disturbing the paths of the electrons, we make it dimmer and dimmer. Note that this merely changes the number of photons hanging around the slits, not their energy (which is $\propto h\nu$), so we do not expect the brightness of the flashes to change. Now, some clicks do not have a corresponding flash; some electrons are reaching the screen unnoticed by our detector at the slits. The interference pattern at the screen gradually reappears, in the form P_{12}!

Now, the momentum imparted by the light photons obeys $p = h/\lambda$. By choosing a very large λ, we can have $p \to 0$, which ought to disturb the electrons to a lesser extent. When we do this, we still observe the classical pattern. However, when λ exceeds the order of the slit separation, we lose the ability to resolve which slit the electron passed through, i.e. the flashes cannot be identified with the correct slit. At this point, we get back the interference pattern.

Thus, there is no way to answer which slit each electron passed through while retaining the interference pattern! This is intrinsic to the quantum system, in the form of the Heisenberg uncertainty principle.

4 Bohr's atomic model

Recall Rutherford's experiment where he fired α particles at a gold foil, which established the existence of a very small region of positive charge in the centre of every atom (the nucleus), surrounded by negatively charged electrons. This raises the problem of the stability of the electron orbits – an accelerating charge must radiate energy, that too over a wide range of frequencies. On the other hand, radiation emitted by an atom is always observed at discrete frequencies. For example, the wavelengths emitted by hydrogen are given by the Rydberg constant.

$$\frac{1}{\lambda} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right).$$

Bohr's idea was that the angular momenta of the electrons are quantized. We set

$$L = pr = mvr = n\hbar.$$

In a sense, an electron forms a standing wave in its orbit, with a circumference of $n\lambda$. By balancing the Coulomb and centripetal forces, we can write

$$r = \frac{4\pi\epsilon_0\hbar^2}{me^2}n^2 = a_0 n^2.$$

Here, $a_0 \approx 5.29 \times 10^{-11}$ m is called the Bohr radius. As a result,

$$E_n = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r} \approx -13.6\frac{1}{n^2}\text{ eV}.$$

The energies emitted by electrons are now restricted to differences of these energy levels, so

$$h\nu = E_m - E_n.$$

5   Postulates of quantum mechanics

1. Associated with each classical outcome of a quantum experiment is a probability amplitude, Ψ, which is not directly observable.

2. The probability distribution is given by $P = |\Psi|^2$, which is observable. For any physically interpretable wavefunction Ψ, we demand that $|\Psi|^2$ is normalizable. Thus,

$$\int |\Psi|^2 \, dV = 1.$$

   As a consequence, we require $\Psi \to 0$ as we move away from the origin. We also demand Ψ be continuous, and Ψ' be continuous almost everywhere.

3. For a system with many classical outcomes, we write

$$\Psi = \sum_{i=1}^{\infty} \Psi_i.$$

   Thus, the probability distribution P carries signatures of the probabilities $P_i = |\Psi_i|^2$. For example when we have $n = 2$ outcomes,

$$P = |\Psi_1 + \Psi_2|^2 = P_1 + P_2 + 2\sqrt{P_1 P_2}\cos\delta.$$

5.1   The Schrödinger Equation

Proposition 5.1. *The wavefunction Ψ must obey the differential equation*

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r}, t)\right]\Psi(\boldsymbol{r}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\boldsymbol{r}, t).$$

Consider the simpler case where $V(\boldsymbol{r})$ has no time dependence. To solve this equation, we often perform separation of variables,

$$\Psi(\boldsymbol{r}, t) = \psi(\boldsymbol{r})\,T(t).$$

As a result, we observe that

$$-\frac{1}{\psi}\frac{\hbar^2}{2m}\nabla^2\psi + V = \frac{i\hbar}{T}\frac{dT}{dt} = \text{constant}.$$

The time part is solved by $T(t) = e^{-iEt/\hbar}$, where the constant is denoted as E. Note that we have shown $\Psi(\boldsymbol{r}, t) = \psi(\boldsymbol{r})e^{-iEt/\hbar}$, so

$$|\Psi|^2 = \Psi^*\Psi = \psi^*\psi = |\psi^2|,$$

The spatial part must now satisfy

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$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi.$$

which is called the time independent Schrödinger equation. The Hamiltonian operator is defined as

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V,$$

so the spatial part of the equation says $\hat{H}\psi = E\psi$. In other words, the wavefunction Ψ here is an eigenfunction of the Hamiltonian. The full solution can be written as a linear superposition of all such eigenfunctions Ψ_i. For convenience, we deal with only one spatial dimension here on.

5.2 Observables and operators

Definition 5.1 (Expectation value)**.** The expectation value of any linear operator $\hat{A}$ is defined as

$$\langle\hat{A}\rangle = \int_{-\infty}^{+\infty} \psi^*\hat{A}\psi \, dx.$$

Example. For example, the position, momentum, and energy operators are given by

$$\hat{x} = x, \qquad \hat{p}_x = -i\hbar\frac{\partial}{\partial x}, \qquad \hat{E} = i\hbar\frac{\partial}{\partial t}.$$

This covers all physically observable quantities, and are thus called observables. Note that these are all linear operators.

What happens if ψ is an eigenstate of $\hat{A}$, with eigenvalue λ? Note that $\hat{A}\psi = \lambda\psi$, so

$$\langle\hat{A}\rangle = \int_{-\infty}^{+\infty} \lambda\psi^*\psi \, dx = \lambda.$$

Proposition 5.2 (Ehrenfest's Theorem)**.** *The expectation values obey classical laws. For instance,*

$$\frac{d}{dt}\langle p\rangle = \langle-\frac{\partial}{\partial x}V\rangle.$$

Proof. We start by calculating

$$
\begin{aligned}
\hat{p}\hat{H} - \hat{H}\hat{p} &= \left(-i\hbar\frac{\partial}{\partial x}\right)\left(\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right) - \left(\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right)\left(-i\hbar\frac{\partial}{\partial x}\right) \\
&= -\frac{i\hbar^3}{2m}\frac{\partial^3}{\partial x^3} - i\hbar\frac{\partial}{\partial x}V + \frac{i\hbar^3}{2m}\frac{\partial^3}{\partial x^3} + i\hbar V\frac{\partial}{\partial x} \\
&= -i\hbar\frac{\partial}{\partial x}V + i\hbar V\frac{\partial}{\partial x} \\
&= -i\hbar\frac{\partial V}{\partial x}.
\end{aligned}
$$

Now,

$$\frac{d\langle p\rangle}{dt} = \int \frac{\partial\psi^*}{\partial t}\hat{p}\psi \, dx + \int \psi^*\frac{\partial\hat{p}}{\partial t}\psi \, dx + \int \psi^*\hat{p}\frac{\partial\psi}{\partial t} \, dx.$$

The central term is just $\langle \partial \hat{p} / \partial t \rangle$, which is zero. From the Schrödinger equation, we can write

$$\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}, \qquad (\hat{H}\psi)^* = \psi^* \hat{H} = -i\hbar \frac{\partial \psi^*}{\partial t}.$$

Thus,

$$\frac{d\langle p \rangle}{dt} = \frac{1}{i\hbar} \int \psi^*(\hat{p}\hat{H} - \hat{H}\hat{p})\psi \, dx = \langle -\frac{\partial V}{\partial x} \rangle. \qquad \square$$

Definition 5.2 (Commutator)**.** The commutator of two linear operators $\hat{A}$ and $\hat{B}$ is defined as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}.$$

In a statistical distribution, the first, second, third and fourth moments deal with the mean, standard deviation, skew and kurtosis. Skew is a measure of symmetry, and kurtosis is a measure of peakedness.

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5.3   The uncertainty principle

Proposition 5.3 (Heisenberg's Uncertainty Principle). *The standard deviations of the position and momentum are related as*

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}.$$

More generally, for any two Hermitian operators,

$$\sigma_A \sigma_B \geq \frac{1}{2}|\langle [\hat{A}, \hat{B}] \rangle|.$$

Proof. We evaluate the following expression using integration by parts.

$$i\hbar \int \frac{d\psi^*}{dx}\psi x \, dx = -i\hbar \int \psi^* \psi \, dx - i\hbar \int \frac{d\psi}{dx}\psi^* x \, dx = -i\hbar + \left[i\hbar \int \frac{d\psi^*}{dx}\psi x \, dx \right]^*$$

Thus,

$$2i \operatorname{Im} \int i\hbar \frac{d\psi^*}{dx}\psi x \, dx = -i\hbar.$$

Since $z^* z \geq b^2$, where $z = a + ib$, we must have

$$4 \left[\int i\hbar \frac{d\psi^*}{dx}\psi x \, dx \right]^2 \geq \hbar^2.$$

Cauchy Schwarz gives

$$\int x\psi^* \, x\psi \, dx \int \left(i\hbar \frac{\partial \psi^*}{\partial x} \right) \left(-i\hbar \frac{\partial \psi}{\partial x} \right) \, dx \geq \left[\int i\hbar \frac{d\psi^*}{dx}\psi x \, dx \right]^2 \geq \frac{\hbar^2}{4}.$$

In other words,

$$\langle x^2 \rangle \langle p^2 \rangle \geq \frac{\hbar^2}{4}.$$

By writing $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$ and $\sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2$, and by choosing $\langle x \rangle = \langle p \rangle = 0$, we arrive at the Heisenberg uncertainty principle,

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}. \qquad \qquad \square$$

Another uncertainty relation is the energy-time uncertainty,

$$\sigma_E \sigma_t \geq \frac{\hbar}{2}.$$

5.4   Eigenstates and eigenvalues

Recall that the time independent Schrödinger equation is given by $\hat{H}\psi = E\psi$, which means that we seek eigenfunctions (or eigenstates) ψ_n of the Hamiltonian, and their associated eigenvalues E_n. The eigenvalue E_n captures the time evolution of the associated eigenstate, since $\Psi_n = \psi_n e^{-iE_n t/\hbar}$.

Definition 5.3 (Degenerate eigenstates). If two eigenstates ψ_1 and ψ_2 have the same energy eigenvalue, they are said to be degenerate with respect to one another.

Proposition 5.4. *The energy eigenvalues of the Hamiltonian are real.*

Proof. This follows from the fact that the Hamiltonian is Hermitian, i.e. $\hat{H}^* = \hat{H}$. Thus, if E is an eigenvalue of $\hat{H}$ with the eigenstate ψ, then

$$\hat{H}\psi = E\psi, \qquad \langle \hat{H} \rangle = \int \psi^* \hat{H}\psi \, dx = E.$$

Now,

$$E^* = \int (\psi^* \hat{H}\psi)^* \, dx = \int \psi^* \hat{H}^* \psi \, dx = E,$$

which forces $E \in \mathbb{R}$. $\qquad\square$

Proposition 5.5. *Non-degenerate eigenstates of the Hamiltonian are orthonormal.*

Proof. Suppose that ψ_1 and ψ_2 are two non-degenerate eigenstates, with distinct eigenvalues E_1 and E_2. Then,

$$\hat{H}\psi_1 = E_1\psi_1, \qquad \hat{H}\psi_2 = E_2\psi_2.$$

Observe that

$$\int \psi_1^* \hat{H}\psi_2 \, dx = \int (\hat{H}^* \psi_1)^* \psi_2 \, dx.$$

Since the energy eigenvalues are real, we conclude that

$$E_2 \int \psi_1^* \psi_2 \, dx = E_1 \int \psi_1^* \psi_2 \, dx.$$

Since $E_1 \neq E_2$, the inner product must be zero. $\qquad\square$

Remark. If $\{\psi_i\}$ are degenerate, note that all linear combinations also form degenerate eigenstates.

$$\hat{H} \sum c_i \psi_i = E \sum c_i \psi_i.$$

Thus, although $\{\psi_i\}$ may not be orthonormal, we can apply the Gram-Schmidt process to obtain an orthonormal basis of that eigenspace.

Proposition 5.6. *If $[\hat{A}, \hat{B}] = 0$, then $\hat{A}$ and $\hat{B}$ share non-degenerate eigenstates.*

Proof. Let ψ be a non-degenerate eigenstate of $\hat{A}$, so $\hat{A}\psi = \lambda\psi$. Since $\hat{A}$ and $\hat{B}$ commute,

$$\lambda \hat{B}\psi = \hat{B}\hat{A}\psi = \hat{A}\hat{B}\psi,$$

so $\hat{B}\psi$ is also an eigenstate of $\hat{A}$ with eigenvalue λ. From the non-degeneracy of ψ, we must have $\hat{B}\psi = \mu\psi$ for some non-zero scalar μ. $\qquad\square$

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Proposition 5.7. *The eigenstates of the time independent Schrödinger equation form a complete set of states, i.e. they form a basis of the set of all solutions.*

$$\Psi(x,t) = \sum c_n \psi_n(x) e^{-iE_n t/\hbar}.$$

In order to obtain the coefficients c_n, we simply take inner products

$$\int \Psi_n^* \Psi \, dx = c_n.$$

Proof. The first statement can be regarded as a postulate. The second follows from the orthonormality of the eigenstates,

$$\int \psi_n^* \psi_m \, dx = \delta_{nm}.$$

This means that with $\Psi_n = \psi_n e^{-iE_n t/\hbar}$, we have

$$\int \psi_n^* \left[\sum c_m \psi_m e^{-iE_m t/\hbar} \right] e^{iE_n t/\hbar} \, dx = \sum c_m e^{-i(E_m - E_n)t/\hbar} \int \psi_n^* \psi_m \, dx = c_n. \qquad \square$$

6   Bound state problems

Here, we wish to solve the Schrdinger equation in one dimension with a time independent potential $V(x)$.

6.1   Piecewise constant potentials

If $V(x)$ is a constant over some interval, then we can write

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + (V - E)\psi = 0.$$

Plugging in the Ansatz $\psi(x) = Ae^{kx}$, we obtain

$$k = \pm\sqrt{\frac{2m}{\hbar^2}(V - E)}.$$

Thus, our solution looks like

$$\psi(x) = Ae^{kx} + Be^{-kx}, \qquad \psi(x) = C\cos\bar{k}x + D\sin\bar{k}x$$

depending on whether $V > E$ or $V < E$. We can stitch together these solutions over all such intervals by demanding the continuity of ψ and $d\psi/dx$.

6.2   Infinite square well (particle in a box)

Consider a potential of the form

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

Note that this forces $\psi(x) = 0$ outside the well where the potential is infinite. Now, setting $k = \sqrt{2mE}/\hbar$, we have the solution inside the well given by

$$\psi(x) = A\cos kx + B\sin kx.$$

We further demand $\psi(0) = \psi(a) = 0$, which forces $A = 0$ and $k = n\pi/a$ for integral values of n. Thus, we have

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}, \qquad E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}.$$

The factor of $\sqrt{2/a}$ is required to normalize ψ_n.

6.3 Quantum harmonic oscillator

For any smooth potential $V(x)$ with a local minima at x_0, we can expand this as a Taylor series to write

$$V(x) = V(x_0) + V'(x_0)(x - x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + O(x^3).$$

Noting that $V'(x_0) = 0$ and setting $V''(x_0) = m\omega^2$, we have

$$V(x) \approx \frac{1}{2}m\omega^2 x^2,$$

which is the potential of a simple harmonic oscillator. This means that if we want to solve the Schrödinger equation about a local minimum x_0 of the potential $V(x)$, we can solve

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

6.3.1 Algebraic method

Rewrite the equation as follows.

$$\frac{1}{2m}(p^2 + (m\omega x)^2)\psi = E\psi.$$

This can be 'factorized' in the following way.

$$p^2 + (m\omega x)^2 = (ip + m\omega x)(-ip + m\omega x) + im[x, p].$$

Note that $[x, p] = i\hbar$. We thus define the raising and lowering operators a_+ and a_- as follows.

$$a_\pm = \frac{1}{\sqrt{2m\omega\hbar}}(\mp ip + m\omega x).$$

Their commutator can be calculated as

$$[a_+, a_-] = \frac{1}{2m\omega\hbar}((-ip + m\omega x)(ip + m\omega x) - (ip + m\omega x)(-ip + m\omega x)) = -1.$$

Note that a_+ and a_- are not Hermitian, instead $a_+^* = a_-$. Now,

$$a_- a_+ = \frac{1}{\hbar\omega}\hat{H} + \frac{1}{2}, \qquad \hat{H} = \hbar\omega\left(a_- a_+ - \frac{1}{2}\right) = \hbar\omega\left(a_+ a_- + \frac{1}{2}\right).$$

Proposition 6.1. *If ψ is an eigenstate of the Hamiltonian, with eigenvalue E, then $a_+\psi$ is also an eigenstate with eigenvalue $E + \hbar\omega$, and $a_-\psi$ is an eigenstate with eigenvalue $E - \hbar\omega$.*

Proof. If $\hat{H}\psi = E\psi$, then

$$
\begin{aligned}
\hat{H}(a_+\psi) &= \hbar\omega \left(a_+a_- + \frac{1}{2} \right) a_+\psi \\
&= \hbar\omega \left(a_+a_-a_+ + \frac{1}{2}a_+ \right) \psi \\
&= \hbar\omega a_+ \left(a_-a_+ + \frac{1}{2} \right) \psi \\
&= \hbar\omega a_+ \left(a_-a_+ - \frac{1}{2} + 1 \right) \psi \\
&= a_+(\hat{H} + \hbar\omega)\psi \\
&= (E + \hbar\omega)(a_+\psi).
\end{aligned}
$$

An analogous process shows that $\hat{H}(a_-\psi) = (E - \hbar\omega)(a_-\psi)$. $\square$

For the existence of a ground state, we demand $a_-\psi_0 = 0$. This is because we want ψ_0 to be the state with the lowest possible energy, with no other states below it. Thus, the lowering operator must cause ψ_0 to vanish. It can be shown that

$$
\psi_0(x) = A_0 e^{-m\omega x^2/2\hbar}.
$$

Plugging this into the Schrödinger equation, we see that this state has the energy eigenvalue

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

which must be the lowest possible energy for the system. Thus, we get a set of solutions by repeatedly applying the raising operator.

$$
\psi_n(x) = A_n(a_+)^n e^{-m\omega x^2/2\hbar}, \qquad E_n = \left(n + \frac{1}{2} \right) \hbar\omega.
$$

To compute the normalisation coefficients, suppose that

$$
a_+\psi_n = c_n\psi_{n+1}, \qquad a_-\psi_n = d_n\psi_{n-1}.
$$

Now,

$$
\int (a_+\psi_n)^*(a_+\psi_n) \, dx = \int \psi_n^*(a_-a_+)\psi_n \, dx = \int \psi_n^* \left(\frac{1}{\hbar\omega}\hat{H} + \frac{1}{2} \right) \psi_n \, dx.
$$

Due to normalisation, the first term is $|c_n|^2$. Expanding the final term, we have

$$
|c_n|^2 = \frac{1}{\hbar\omega} \int \psi_n^*\hat{H}\psi_n \, dx + \frac{1}{2} \int \psi_n^*\psi_n \, dx = \frac{1}{\hbar\omega}E_n + \frac{1}{2} = n + 1.
$$

Thus, we can choose $c_n = \sqrt{n+1}$. Similarly, we can show that $d_n = \sqrt{n}$. This means that

$$
A_n = \frac{1}{\sqrt{n!}}A_0.
$$

We can also show that ψ_i are orthogonal.

$$
\int \psi_m^*\psi_n \, dx = \delta_{mn}.
$$

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6.3.2   Analytic method

We obtain a power series solution. Set $\xi = \sqrt{m\omega/\hbar}x$, $K = 2E/\hbar\omega$. The Schrödinger equation now reads

$$\frac{d^2\psi}{d\xi^2} = (\xi^2 - K)\psi.$$

Note that when $\xi \gg K$, our equation has the approximate solution

$$\psi(\xi) = Ae^{-\xi^2/2}.$$

We drop the $e^{+\xi^2/2}$ term to ensure $\psi \to 0$ as $\xi \to \infty$. Now, we use the Ansatz

$$\psi(\xi) = f(\xi)\,e^{-\xi^2/2},$$

which when plugged into the differential equation demands

$$f'' - 2\xi f' + (K - 1)f = 0.$$

Writing f as a power series,

$$f(\xi) = \sum_{n=0}^{\infty} a_n \xi^n, \quad f'(\xi) = \sum_{n=0}^{\infty} n a_n \xi^{n-1}, \quad f''(\xi) = \sum_{n=0}^{\infty} (n+1)(n+2)a_{n+2}\xi^n.$$

Thus,

$$\sum_{n=0}^{\infty} \left[(n+1)(n+2)a_{n+2} - 2na_n + (K-1)a_n\right]\xi^n = 0,$$

whence we obtain the recurrence relation

$$a_{n+2} = \frac{2n + 1 - K}{(n+1)(n+2)}a_n.$$

Note that this gives two chains of even and odd coefficients, completely determined once we fix a_0 and a_1. When $n \gg K$, we have the approximation

$$a_{n+2} \approx \frac{2}{n}a_n, \qquad a_n \approx \frac{C}{(n/2)!}.$$

This means that $f(\xi)$ grows roughly as

$$\sum \frac{C}{(n/2)!}\xi^n = \sum \frac{C}{n!}\xi^{2n} = Ce^{\xi^2}.$$

This would cause ψ to diverge at infinity. To fix this, we demand that $a_{m+2} = 0$ for some $m \in \mathbb{N}$ and also kill the other chain, which would force the power series to terminate. Thus, $2m + 1 = K$, so

$$a_{n+2} = \frac{2(n - m)}{(n+1)(n+2)}a_n, \qquad E_m = \left(m + \frac{1}{2}\right)\hbar\omega.$$

This gives us our solutions ψ_m. For ψ_0, set $a_1 = 0$, which gives

$$\psi_0(\xi) = a_0 e^{-\xi^2/2}, \qquad E_0 = \frac{1}{2}\hbar\omega.$$

For ψ_1, set $a_1 = 0$, which gives

$$\psi_1(\xi) = a_1 \xi e^{-\xi^2/2}, \qquad E_0 = \frac{3}{2}\hbar\omega.$$

In this manner, we can obtain all ψ_m by using our recurrence relation.

$$\psi_n(\xi) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{2^n n!}}H_n(\xi)\,e^{-\xi^2/2}, \qquad E_n = \left(n + \frac{1}{2}\right)\hbar\omega.$$

Here, $H_n(\xi)$ are the Hermite polynomials.

7   Free particles

Consider a free particle, which entails $V(x) = 0$. Now,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi, \qquad \psi'' = -k^2\psi$$

where $k^2 = 2mE/\hbar$. This gives the solutions

$$\Psi(x,t) = Ae^{ik(x-\hbar kt/2m)} + Be^{-ik(x+\hbar kt/2m)}.$$

This looks like the superposition of two waves moving left and right with speeds $v = \hbar k/2m - \sqrt{E/2m}$, and momenta $p = \hbar k$. This is not normalizable. To do this, we take the superposition of many such waves with different velocities, thus localizing the resultant 'wave packet'. This gives

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}}\int \phi(k)\,e^{ix(x-vt)}\,dk,$$

for appropriate choice of $\phi(k)$. Initially, at $t = 0$, note that

$$\psi(x,0) = \frac{1}{\sqrt{2\pi}}\int \phi(k)\,e^{ikx}\,dk.$$

The inverse Fourier transform directly gives ϕ as

$$\phi(k) = \frac{1}{\sqrt{2\pi}}\int \psi(x,0)\,e^{-ikx}\,dx.$$

The phase velocity of a wave packet is defined as $v_p = \omega/k$, while the group velocity is $v_g = d\omega/dk$. We see that

$$v_g = \frac{\hbar k}{m} = 2v_p.$$

This resolves a discrepancy with the classical wave velocity and energy of $\sqrt{2E/m}$.

8   Scattering problems and quantum tunnelling

8.1   Step function potential

Consider a potential of the form

$$V(x) = V_0\,u(x) = \begin{cases} 0, & \text{if } x < 0 \\ V_0, & \text{if } x \geq 0 \end{cases}$$

Classically, we expect that a particle of energy E moving from left to right will bounce back when $E < V_0$ and pass when $E > V_0$.

We have already solved the Schrödinger equation for constant potentials. The boundary conditions at $x = 0$ demand

$$\psi(x \to 0^-) = \psi(x \to 0^+), \qquad \psi'(x \to 0^-) = \psi'(x \to 0^+).$$

When $E > V_0$, the solutions are those of a free particle everywhere, with

$$\psi(x) = \begin{cases} Ae^{ik_1 x} + Be^{-ik_1 x}, & x < 0, \quad k_1 = \sqrt{2mE/\hbar^2}, \\ Ce^{ik_2 x} + De^{-ik_2 x}, & x \geq 0, \quad k_2 = \sqrt{2m(E-V_0)/\hbar^2}. \end{cases}$$

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We choose $D = 0$ on physical grounds, since we have a free particle coming in from the left. The boundary conditions give $A + B = C$ and $k_1(A - B) = k_2 C$. With the choice $A = 1$,

$$B = \frac{k_1 - k_2}{k_1 + k_2}, \qquad C = \frac{2k_1}{k_1 + k_2}.$$

We call these the reflection and transmission amplitudes, which are the probability amplitudes for the reflection and transmission of the particle at the boundary. Note the analogy with Fresnel coefficients in optics. The reflection and transmission coefficients R and T can be set to B^2 and C^2. See that

$$R + \frac{k_2}{k_1}T = 1.$$

When $E < V_0$, we have

$$\psi(x) = \begin{cases} Ae^{ik_1 x} + Be^{-ik_1 x}, & x < 0, \quad k_1 = \sqrt{2mE/\hbar^2}, \\ Ce^{k_2 x} + De^{-k_2 x}, & x \geq 0, \quad k_2 = \sqrt{2m(V_0 - E)/\hbar^2}. \end{cases}$$

This time, we set $C = 0$ and $A = 1$. The boundary conditions $1 + B = D$ and $ik_1(1 - B) = -k_2 D$ give

$$B = \frac{k_1 - ik_2}{k_1 + ik_2}, \qquad D = \frac{2k_1}{k_1 + ik_2}.$$

With $R = |B|^2$, we now have

$$R = 1, \qquad T = \frac{k_1}{k_2}(1 - R) = 0.$$

Thus, even though $T = 0$, we still have $\psi(x) \neq 0$ for $x \geq 0$! This phenomenon is called *quantum tunnelling*. There is an analogy here with evanescent waves during total internal reflection.

8.2   Finite potential barrier

Consider a potential of the form

$$V(x) = \begin{cases} 0, & \text{if } x < 0 \\ V_0, & \text{if } 0 \leq x \leq a \\ 0, & \text{if } a < x \end{cases}$$

We solve this as

$$\psi(x) = \begin{cases} e^{ik_1 x} + re^{-ik_1 x}, & x < 0, & k_1 = \sqrt{2mE/\hbar^2}, \\ Ae^{ik_2 x} + Be^{-ik_2 x}, & 0 \leq x \leq a, & k_2 = \sqrt{2m(E - V_0)/\hbar^2}, \\ te^{ik_1 x}, & a < x. \end{cases}$$

Applying our boundary conditions,

$$1 + r = A + B, \qquad k_1(1 - r) = k_2(A - B),$$

$$te^{ik_1 a} = Ae^{ik_2 a} + Be^{-ik_2 a}, \qquad k_1 te^{ik_1 a} = k_2(Ae^{ik_2 a} - Be^{-ik_2 a}).$$

Set $\mu = k_2/k_1 = \sqrt{1 - V_0/E}$, and $\mathcal{A} = (1 + \mu^2)\sin k_2 a + 2\mu i \cos k_2 a$. We can show that

$$r = (1 - \mu^2)\sin k_2 a/\mathcal{A}, \qquad t = 2\mu i e^{-ik_1 a}/\mathcal{A},$$

$$A = i(1 + \mu)e^{-ik_2 a}/\mathcal{A}, \qquad B = -i(1 - \mu)e^{ik_2 a}/\mathcal{A}.$$

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When $E > 0$ and $E \geq V_0$, the transmission coefficient $T = |t|^2$ is given by

$$T = \frac{4\mu^2}{(1+\mu^2)^2 \sin^2 k_2 a + 4\mu^2 \cos^2 k_2 a} = \frac{1}{1 + \frac{1}{4}\left(\frac{1-\mu^2}{\mu}\right)^2 \sin^2 k_2 a}.$$

Note that $T \leq 1$, and $R = 1 - T$. Whenever $k_2 a = n\pi$, the system is in resonance and we get perfect transmission. Also,

$$E_n = V_0 + \frac{n^2\pi^2\hbar^2}{2ma^2}.$$

Note the similarities with the 'particle in a box' system, and a Fabry-Perot interferometer cavity. Thus, we have standing waves formed in the region $[0, a]$ at such resonance energies.

On the other hand, in the limit $E \to V_0^+$ and for very small a, we have

$$T \approx 1 - \frac{mV_0 a^2}{2\hbar^2}.$$

When $E < V_0$, the quantity k_2 is imaginary, say $k_2 = iK$. With $\mu' = k_1/K$,

$$T = \frac{4\mu'^2}{(1 - \mu'^2)\sinh^2 Ka + 4\mu'^2 \cosh^2 Ka}.$$

As $E \to 0^+$, we have $T \to 0$ and $R \to 1$. This is another case of quantum tunnelling.

9 The Schrödinger equation in 3D

9.1 Particle in a 3D box

Consider a potential of the form

$$V(\boldsymbol{r}) = \begin{cases} 0, & \text{if } 0 < x < a,\ 0 < y < b,\ 0 < z < c \\ \infty, & \text{otherwise} \end{cases}$$

We perform separation of variables

$$\psi(\boldsymbol{r}) = \psi_x(x)\,\psi_y(y)\,\psi_z(z),$$

and plug this into the time independent Schrödinger equation inside the box

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

This gives

$$\sum \frac{1}{\psi_i}\frac{\partial^2 \psi_i}{\partial x_i{}^2} = -\frac{2mE}{\hbar^2}.$$

We can thus write

$$\frac{1}{\psi_x}\frac{\partial^2 \psi_x}{\partial x^2} = -\frac{2mE_x}{\hbar^2}, \qquad \frac{1}{\psi_y}\frac{\partial^2 \psi_y}{\partial y^2} = -\frac{2mE_y}{\hbar^2}, \qquad \frac{1}{\psi_z}\frac{\partial^2 \psi_z}{\partial z^2} = -\frac{2mE_z}{\hbar^2}.$$

We know how to solve these equations; these just give the one dimensional 'particle in a box' solutions. Thus,

$$\psi(\boldsymbol{r}) = A \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi x}{b} \sin\frac{n_z \pi x}{c}, \qquad E = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right).$$

Note that the ground state corresponds to $n_x = n_y = n_z = 1$.

9.2   Angular momentum

We write
$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} = L_x \hat{i} + L_y \hat{j} + L_z \hat{k}, \qquad L_i = x_j p_k - x_k p_j.$$
It can be shown that $\boldsymbol{L}$ is Hermitian. Furthermore, the commutators are of the form
$$[L_x, L_y] = i\hbar L_z, \qquad [L_y, L_z] = i\hbar L_x, \qquad [L_z, L_x] = i\hbar L_y.$$
This immediately gives us uncertainty relations between the different components of the angular momentum. In other words, simultaneous eigenstates of any pair of L_x, L_y, L_z do not exist. However, note that
$$[L^2, L_i] = 0, \qquad L^2 = L_x^2 + L_y^2 + L_z^2.$$
Thus, we can get simultaneous eigenfunctions of L^2 and any one component, say L_z.

The total angular momentum $\boldsymbol{J}$ of an atomic system is given as the sum of the orbital and spin angular momenta.
$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}.$$
We get back the commutation relations exactly the same as for $\boldsymbol{L}$. Now, we define the ladder operators
$$J_+ = J_x + iJ_y, \qquad J_- = J_x - iJ_y, \qquad [J_x, J_y] = 2\hbar J_z.$$
Again, $J_+^* = J_-$, which means that the ladder operators are not Hermitian. Now, let ψ be a simultaneous eigenstate of J^2 and J_z, with $J^2\psi = \alpha\psi$ and $J_z\psi = \beta\psi$. Setting $\varphi = J_+\psi$, we have
$$J^2\varphi = \alpha\varphi.$$
Thus, J_+ does not change the eigenvalues of eigenstates of J^2. However, note that the commutator $[J_z, J_+]$ is non-zero, with
$$[J_z, J_+] = i\hbar J_y + \hbar J_x = \hbar J_+.$$
Similarly,
$$[J_z, J_-] = \hbar J_-.$$
Thus, we calculate
$$J_z\varphi = J_z J_+\psi = (\beta + \hbar)\varphi.$$
This shows that the raising operator gives another eigenstate with eigenvalue incremented by $\hbar$. Similarly,
$$J_z J_-\psi = (\beta - \hbar)(J_-\psi),$$
so the lowering operator lowers the eigenvalue by $\hbar$. On the other hand, this cannot proceed indefinitely, since the eigenvalues must be bounded as $\beta^2 \leq \alpha$, since $J_z^2 \leq J^2$. This means that we have two states,
$$J_+\psi_{max} = 0, \qquad J_-\psi_{min} = 0.$$
Write
$$J^2 = J_- J_+ + J_z^2 + \hbar J_z = J_+ J_- + J_z^2 - \hbar J_z.$$
Now,
$$J^2\psi_{max} = (\beta_{max}^2 + \hbar\beta_{max})\psi_{max} = \alpha\psi_{max}, \qquad J^2\psi_{min} = (\beta_{min}^2 - \hbar\beta_{min})\psi_{min} = \alpha\psi_{min}.$$
This gives $\beta_{max} = -\beta_{min}$ and $\beta_{max} = \beta_{min} + n\hbar$. Thus,
$$\beta_{max} = \frac{1}{2}n\hbar.$$
Writing $j = n/2$, we have
$$\alpha = \hbar^2 j(j+1), \qquad \beta = m_j\hbar, \qquad m_j = -j, -j+1, \ldots, j-1, j.$$
These are the eigenvalues of ψ with respect to J^2 and J_z. Note that fermions (matter particles) correspond to odd n, and bosons (force particles) correspond to even n.

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9.3   Orbital angular momentum

Recall that using spherical polar coordinates, we can write

$$\boldsymbol{\nabla} = \hat{\boldsymbol{e}}_r \frac{\partial}{\partial r} + \hat{\boldsymbol{e}}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\boldsymbol{e}}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}.$$

With this, we write

$$L_x = i\hbar \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right), \quad L_y = i\hbar \left(-\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right), \quad L_z = -i\hbar \frac{\partial}{\partial \phi}.$$

Also,

$$L^2 = -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right), \qquad L_\pm = \hbar e^{\pm i\phi} \left(\pm \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right).$$

We want to have

$$L^2 \psi_{lm} = \hbar^2 l(l+1) \psi_{lm}, \qquad L_z \psi_{lm} = m\hbar \psi_{lm}.$$

To solve these eigenvalue equations, we separate variables as $\psi(\theta, \phi) = \Theta(\theta)\Phi(\phi)$. The second equation thus gives

$$\Phi(\phi) = e^{im\phi}, \qquad \psi_{lm} = \Theta e^{im\phi}.$$

Note that ψ_{lm} must be periodic in ϕ with period 2π, which forces m to be an integer. Plugging this into the first equation gives

$$\left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) - \frac{m^2}{\sin^2 \theta} + l(l+1) \right] \Theta(\theta) = 0.$$

This is called a Legendre differential equation, whose solutions are the Legendre polynomials. The solutions $\psi_{lm} = Y_{lm}$ are called spherical harmonics. Each of the Legendre functions $P_{lm}(\xi)$ has $l - m$ roots within $|\xi| < 1$. The Legendre polynomials P_l satisfy the recurrence

$$(l+1)P_{l+1}(\xi) = (2l+1)\xi P_l(\xi) - lP_{l-1}(\xi).$$

The Legendre functions satisfy

$$P_{lm}(-\xi) = (-1)^{l+m} P_{lm}(\xi),$$

$$\int_{-1}^{+1} P_{lm}(\xi) P_{l'm}(\xi) \, d\xi = \frac{2}{2l+1} \cdot \frac{(l-m)!}{(l+m)!} \delta_{ll'}.$$

It can also be shown that all Y_{lm} are orthogonal and complete. Note that Y_{lm} is even for even l and odd for odd l.

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