Principles of Quantum Mechanics

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09/01/2023

Contents

2 Time Independent Schrödingerś Equation

2.1 Stationary States

We need to solve the Schrödinger equation,

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V \tag{2.1}$$

Assuming that V is independent of t, we can look for the solutions: $\Psi(x,t) = \psi(x)\phi(t)$.

For separable solutions we have

$$\frac{\partial\Psi}{\partial t} = \psi\frac{\partial\phi}{\partial t}, \quad \frac{\partial^2\Psi}{\partial x^2} = \frac{\mathrm{d}\phi}{\mathrm{d}x}\phi \tag{2.2}$$

and substituting this, the Schrödingerś equation reads

$$i\hbar\psi\frac{\mathrm{d}\phi}{\mathrm{d}t} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}\phi + V\psi\phi \tag{2.3}$$

$$i\hbar\frac{1}{\phi}\frac{\mathrm{d}\phi}{\mathrm{d}t} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V. \tag{2.4}$$

Now, the left hand side is a function of t alone, and the right hand side is a function of x alone. This is ONLY true if both sides are constant. Lets call this constant E. Then

$$i\hbar\frac{1}{\phi}\frac{\mathrm{d}\phi}{\mathrm{d}t} = E \tag{2.5}$$

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = -\frac{iE}{\hbar}\phi \tag{2.6}$$

and

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V = E \tag{2.7}$$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V\psi = E\psi \tag{2.8}$$

The solution to equation 2.6 is simply $\phi(t) = e^{-iEt/\hbar}$. The solution to equation 2.8 is the time-independent Schrödinger equation and it cannot be solved without specifying the potential V.
The wave function is obtained using

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n\psi_n(x)e^{-iE_nt/\hbar} \tag{2.9}$$

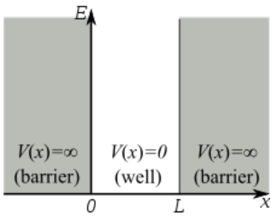
where the set $\{\psi_n\}$ is obtained by solving the time-independent Schrödinger equation and $|c_n|^2$ is the *probability* that a measurement of energy would return the value E_n. This leads to:

$$\sum_{n=1}^{\infty} |c_n|^2 = 1 \tag{2.10}$$

$$\langle H|H\rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n \tag{2.11}$$

2.2 The Infinite Square Well

Suppose we have the potential:



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

Inside the well, the time-independent Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi \tag{2.12}$$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -k^2\psi, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}. \tag{2.13}$$

The general solution becomes $\psi(x) = A\sin kx + B\cos kx$, and applying the boundary condition $\psi(0) = 0$, we get $\psi(x) = A\sin kx$. Now applying $\psi(a) = 0$, we get $k_n = \frac{n\pi}{a}$, with $n \in \mathbb{N}$.
This leads to

$$E_n = \frac{\hbar k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2} \tag{2.14}$$

and

$$\psi_n = \sqrt{\frac{2}{a}}\sin\Big(\frac{n\pi}{a}x\Big). \tag{2.15}$$

Note that two different states are orthonormal:

$$\int \psi_m(x)^*\psi_n(x)\,\mathrm{d}x = \delta_{nm} \tag{2.16}$$

These states are also complete - any other function $f(x)$ can be expressed as a linear combination of them:

$$f(x) = \sum_{n=1}^{\infty} c_n\psi_n(x) \tag{2.17}$$

To find the coefficients c_n, we use Fourier's trick. Multiply both sides of equation 2.17 by $\psi_m(x)^*$, and integrate.

$$\int \psi_m(x)^* f(x)\,\mathrm{d}x = \sum_{n=1}^{\infty} c_n \int \psi_m(x)^*\psi_n(x)\,\mathrm{d}x = \sum_{n=1}^{\infty} c_n\delta_{mn} = c_m. \tag{2.18}$$

Combining everything together, the stationary states for the infinite potential well becomes:

$$\Psi_n(x,t) = \psi_n(x)e^{-iE_nt/\hbar} \tag{2.19}$$

$$= \sqrt{\frac{2}{a}}\sin\Big(\frac{n\pi}{a}x\Big)e^{-i(n^2\pi^2\hbar/2ma^2)t} \tag{2.20}$$

The wave function of this potential is then

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n\sqrt{\frac{2}{a}}\sin\Big(\frac{n\pi}{a}x\Big)e^{-i(n^2\pi^2\hbar/2ma^2)t} \tag{2.21}$$

where $c_n = \int_0^a \sin\big(\frac{n\pi}{a}x\big)\Psi(x,0)\,\mathrm{d}x$, using Fourier's trick.

2.3 The Harmonic Oscillator

In classical mechanics, oscillatory motion is governed by Hooke's law,

$$F = -kx = m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} \tag{2.22}$$

with solution $x(t) = A\sin(\omega t) + B\cos(\omega t)$ where the angular frequency is $\omega = \sqrt{\frac{k}{m}}$.
The potential energy is $V(x) = \frac{1}{2}kx^2$. If we expand $V(x)$ around the local minimum x_0 we get

$$V(x) = V(x_0) + V'(x_0)(x - x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + ..., \tag{2.23}$$

We can subtract the $V(x_0)$ since adding a constant doesn't change the force, also recognise $V(x_0) = 0$ and drop higher order terms, we get

$$\begin{aligned} V(x) &\approx \frac{1}{2}V''(x_0)(x - x_0)^2 && (2.24)\\ &\approx \frac{1}{2}m\omega^2(x - x_0)^2. && (2.25)\end{aligned}$$

The quantum problem requires us to solve the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi. \tag{2.26}$$

2.3.1 Algebraic Method

$$\frac{1}{2m}\left[\hat{p}^2 + (m\omega x)^2\right]\psi = E\psi \tag{2.27}$$

We cannot factor the brackets using complex numbers because operators do not necessarily commute. This motivates the quantities

$$\hat{a}_\pm \equiv \frac{1}{\sqrt{2\hbar m\omega}}(\mp i\hat{p} + m\omega x) \tag{2.28}$$

The product $\hat{a}_-\hat{a}_+$ becomes

$$\begin{aligned} \hat{a}_-\hat{a}_+ &= \frac{1}{2\hbar m\omega}(i\hat{p} + m\omega x)(-i\hat{p} + m\omega x) && (2.29)\\ &= \frac{1}{2\hbar m\omega}\left[\hat{p}^2 + (m\omega x)^2 - im\omega(x\hat{p} - \hat{p}x)\right] && (2.30)\\ &= \frac{1}{2\hbar m\omega}\left[\hat{p}^2 + (m\omega x)^2\right] - \frac{i}{2\hbar}[x, \hat{p}] && (2.31)\\ &= \frac{1}{\hbar\omega}\hat{H} + \frac{1}{2}. && (2.32)\end{aligned}$$

Similarly,

$$\hat{a}_+\hat{a}_- = \frac{1}{\hbar}\omega\hat{H} - \frac{1}{2}. \tag{2.33}$$

In particular, $[\hat{a}_-, \hat{a}_+] = 1$. Meanwhile, the Schrödinger equation takes the form

$$\hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)\psi = E\psi \tag{2.34}$$

It can be shown that if ψ satisfies the Schrödinger equation with energy E, then $\hat{a}_+\psi$ satisfies the equation with energy $(E + \hbar\omega)$. Similarly, $\hat{a}_-\psi$ satisfies the equation with energy $(E - \hbar\omega)$.

There occurs a "lowest rung" such that $\hat{a}_-\psi_0 = 0$:

$$\frac{1}{\sqrt{2\hbar m\omega}}\left(\hbar\frac{\mathrm{d}}{\mathrm{d}x} + m\omega x\right)\psi_0 = 0 \tag{2.35}$$

or

$$\frac{\mathrm{d}\psi_0}{\mathrm{d}x} = -\frac{m\omega}{\hbar}x\psi_0. \tag{2.36}$$

Whose solution becomes

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}. \tag{2.37}$$

To determine the energy of this state we plug it into the Schrödinger equation (2.34) to obtain

$$E_0 = \frac{1}{2}\hbar\omega. \tag{2.38}$$

Now that we have defined the ground state of the quantum oscillator, we simply apply the raising operator repeatedly to generate the excited states while increasing the energy by $\hbar\omega$ each step:

$$\psi_n(x) = A_n(\hat{a}_+)^n\psi_0(x), \quad \text{with } E_n = \left(n + \frac{1}{2}\right)\hbar\omega. \tag{2.39}$$

Now we need to find an expression for the coefficients so we are not required to normalise the wave function each time. We begin by noting that $\hat{a}_\pm$ is the hermitian conjugate of $\hat{a}_\mp$

$$\int_{-\infty}^{\infty} f * (\hat{a}_\pm g)\,\mathrm{d}x = \int_{-\infty}^{\infty} (\hat{a}_\mp f) * g\,\mathrm{d}x \tag{2.40}$$

so that

$$\int_{-\infty}^{\infty} (\hat{a}_\pm\psi_n)^*(\hat{a}_\pm\psi_n)\,\mathrm{d}x = \int_{-\infty}^{\infty} (\hat{a}_\mp\hat{a}_\pm\psi_n) * \psi_n\,\mathrm{d}x\,. \tag{2.41}$$

Using equation 2.34, we get

$$\hat{a}_+\psi_n = \sqrt{n+1}\psi_{n+1}, \quad \hat{a}_-\psi_n = \sqrt{n}\psi_{n-1}. \tag{2.42}$$

Thus

$$\psi_1 = \frac{1}{\sqrt{1!}}\hat{a}_+\psi_0, \qquad \psi_2 = \frac{1}{\sqrt{2}}\hat{a}_+\psi_1 = \frac{1}{\sqrt{2\cdot 1}}(\hat{a}_+)^2\psi_0, \qquad \psi_3 = \frac{1}{\sqrt{3}}\hat{a}_+\psi_2 = \frac{1}{\sqrt{3\cdot 2\cdot 1}}(\hat{a}_+)^3\psi_0$$

and we have

$$\begin{aligned} \psi_n &= \frac{1}{\sqrt{n!}}(\hat{a}_+)^n\psi_0 && (2.43)\\ &= \frac{1}{\sqrt{n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}(\hat{a}_+)^n e^{-\frac{m\omega}{2\hbar}x^2} && (2.44) \end{aligned}$$

which is the general wave function of the quantum harmonic oscillator with energy level $E_n = \hbar\omega(n + \frac{1}{2})$.

2.4 The Free Particle

The free particle has $V = 0$ everywhere. The time-independent Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi \tag{2.45}$$

or

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -k^2\psi, \quad \textit{where } k \equiv \frac{\sqrt{2mE}}{\hbar} \tag{2.46}$$

This is the same as the infinite square well, however we prefer to write the general solution in exponential form:

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \tag{2.47}$$

Unlike the infinite square well, there are no boundary conditions to restrict the possible values of k (and hence E). We can attach the standard time dependence $e^{-iEt/\hbar}$.

$$\Psi(x) = Ae^{ik(x-\frac{\hbar k}{2m}t)} + Be^{-ik(x+\frac{\hbar k}{2m}t)} \tag{2.48}$$

In the first term, we have the argument $x - vt$ so this represents a wave travelling to the right. Similarly the second term represents a wave travelling to the left. Now since these terms only differ by the sign in front of k, we can write

$$\Psi_k(x,t) = Ae^{i\left(kx-\frac{\hbar k^2}{2m}t\right)}, \quad \textit{where } k \equiv \pm\frac{\sqrt{2mE}}{\hbar}, \quad \textit{with} \begin{cases} k > 0 \Longrightarrow \text{ travelling to the right.} \\ k < 0 \Longrightarrow \text{ travelling to the left.} \end{cases} \tag{2.49}$$

This wave function is not normalisable. This means a free particle cannot exist in a stationary state; or, to put it another way, there is no such thing as a free particle with a definite energy. Instead of using separable solutions, we use the solution of the time-dependent Schrödinger equation which is still a linear combination of the separable solutions, but only this time it's an integral over the continuous variable k

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k)e^{i(kx-\frac{\hbar k^2}{2m}t)}\,\mathrm{d}k \tag{2.50}$$

This wave function can be normalised for an appropriate choice of $\phi(k)$. But it carries a range of ks, and hence a range of energies and speeds. We call it a **wave packet**. It is a superposition of sinusoidal functions whose amplitudes are modulated by ϕ.

If we have the initial wave function

$$\Psi(x,0) = \frac{1}{\sqrt{2m}}\int_{-\infty}^{\infty}\phi(k)e^{ikx}\,\mathrm{d}k\,, \tag{2.51}$$

We can find $\phi(k)$ by using the Fourier transform:

$$\phi(k) = \frac{1}{\sqrt{2m}}\int_{-\infty}^{\infty}\Phi(x,0)e^{-ikx}\,\mathrm{d}x \tag{2.52}$$

Given equation 2.63, and assuming $\phi(k)$ has is narrowly peaked about some particular value k_0, we can Taylor-expand the function

$$\omega(k) \approx \omega_0 + \omega_0'(k-k_0) \tag{2.53}$$

Now changing variables $s \equiv k - k_0$

$$\Psi(x,t) \approx \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k_0+s)e^{i[(k_0+s)x-(w_0+w_0's)t]}\,\mathrm{d}x \tag{2.54}$$

$$= \frac{1}{\sqrt{2\pi}}e^{i(k_0x-\omega_0t)}\int_{-\infty}^{\infty}\phi(k_0+s)e^{is(x-w_0't)}ds \tag{2.55}$$

The term in front of the integral is the sinusoidal wave travelling at speed $\frac{\omega_0}{k_0}$. It is modulated by the envelope which is propagating at the speed w_0'. Thus we have

$$v_{phase} = \frac{\omega}{k} \tag{2.56}$$

$$v_{group} = \frac{\mathrm{d}\omega}{\mathrm{d}k} \tag{2.57}$$

Now, using $\omega = \frac{\hbar k^2}{2m}$, we conclude that $v_{classical} = v_{group} = \frac{\hbar k}{m} = 2v_{phase}$.

2.5 Delta-Function Potential

Both the infinite square well and harmonic oscillators admit bound states only ($E < 0$), since potentials go to infinity as $x \to \pm\infty$. Whereas the free particle potential is zero everywhere, it only allows scattering states ($E > 0$). Note that it is a scattering state if $E > 0$ for a finite potential due to quantum tunnelling.

Consider the potential of the form $V(x) = -\alpha\delta(x)$. The Schrödinger equation takes the form:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - \alpha\delta(x)\psi = E\psi \tag{2.58}$$

which yields both bound states ($E < 0$) and scattering states ($E > 0$).

2.5.1 Bound States

In region $x < 0$, $V(x) = 0$, so

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{2mE}{\hbar^2}\psi = \kappa^2\psi, \quad \textit{where } \kappa \equiv \frac{\sqrt{-2mE}}{\hbar} \tag{2.59}$$

remembering that $E < 0$ so k is real and positive. The general solution to equation 2.59 is

$$\psi(x) = Ae^{-\kappa x} + Be^{\kappa x}, \tag{2.60}$$

since the first term blows up, the solution becomes

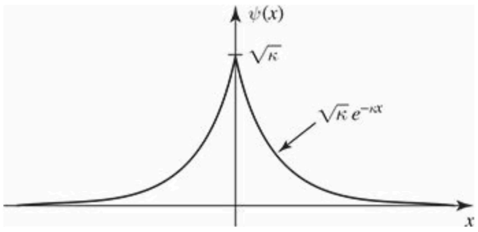
$$\psi(x) = Be^{\kappa x}. \tag{2.61}$$

Similarly in the region $x > 0$, the solution is

$$\psi(x) = Fe^{\kappa x}. \tag{2.62}$$

Now since $\psi(x)$ is always continuous, we have $F = B$, so

$$\psi(x) = \begin{cases} Be^{\kappa x}, & x \le 0 \\ Be^{-\kappa x}, & x \ge 0 \end{cases} \tag{2.63}$$



Integrating the Schrödinger equation from $-\epsilon$ to ϵ, and then take the limit as $\epsilon \to 0$:

$$\frac{\hbar^2}{2m}\int_{-\epsilon}^{+\epsilon}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}\,\mathrm{d}x + \int_{-\epsilon}^{+\epsilon} V(x)\psi(x)\,\mathrm{d}x = E\int_{-\epsilon}^{+\epsilon}\psi(x)\,\mathrm{d}x \tag{2.64}$$

The first integral is just $\frac{\mathrm{d}\psi}{\mathrm{d}x}$, evaluated at the two endpoints, while the last integral is zero, in the limit $\epsilon \to 0$. Thus

$$\Delta\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) = \lim_{\epsilon\to 0}\left(\frac{\partial\psi}{\partial x}\bigg|_{+\epsilon} - \frac{\partial\psi}{\partial x}\bigg|_{-\epsilon}\right) = \frac{2m}{\hbar^2}\lim_{\epsilon\to 0}\int_{-\epsilon}^{+\epsilon} V(x)\psi(x)\,\mathrm{d}x \tag{2.65}$$

$$= \frac{-2m\alpha}{\hbar^2}\psi(0) \tag{2.66}$$

For the cases in equation 2.63, we have

$$\begin{cases} \frac{\mathrm{d}\psi}{\mathrm{d}x} = -B\kappa e^{-\kappa x}, \quad \textit{for } (x > 0), \quad \textit{so } \frac{\mathrm{d}\psi}{\mathrm{d}x}\Big|_{+} = -B\kappa, \\ \frac{\mathrm{d}\psi}{\mathrm{d}x} = +B\kappa e^{+\kappa x}, \quad \textit{for } (x < 0), \quad \textit{so } \frac{\mathrm{d}\psi}{\mathrm{d}x}\Big|_{-} = +B\kappa \end{cases} \tag{2.67}$$

Hence $\Delta(\frac{\mathrm{d}\psi}{\mathrm{d}x}) = -2B\kappa$ and $\psi(0) = B$. So equation 2.66 becomes

$$\kappa = \frac{m\alpha}{\hbar^2} \tag{2.68}$$

and from equation 2.13, the allowed energies and the wave function is

$$\psi(x) = \frac{\sqrt{m\alpha}}{\hbar}e^{-m\alpha|x|/\hbar^2}; \quad E = -\frac{m\alpha^2}{2\hbar^2} \tag{2.69}$$

2.5.2 Scattering States

Schrödinger equation takes the form

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi, \quad where\ k \equiv \frac{\sqrt{2mE}}{\hbar} \tag{2.70}$$

The general solution for $x < 0$:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \tag{2.71}$$

and similarly for $x > 0$:

$$\psi(x) = Fe^{ikx} + Ge^{-ikx}, \tag{2.72}$$

The continuity at x=0 requires that $A + B = F + G$. The derivatives are

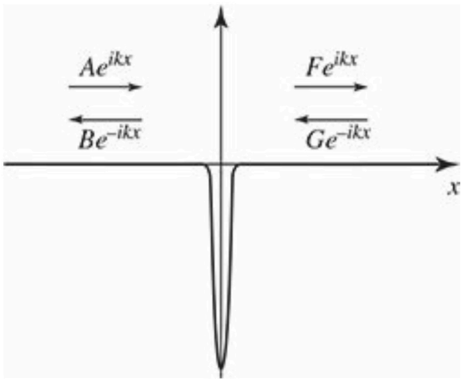
$$\begin{cases} \frac{\mathrm{d}\psi}{\mathrm{d}x} = ik(Fe^{ikx} + Ge^{-ikx}), & for\ (x > 0), \quad so\ \left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{+} = ik(F - G), \\ \frac{\mathrm{d}\psi}{\mathrm{d}x} = ik(Ae^{ikx} + Be^{-ikx}), & for\ (x < 0), \quad so\ \left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{-} = ik(A - B), \end{cases} \tag{2.73}$$

and hence $\Delta(\frac{\mathrm{d}\psi}{\mathrm{d}x}) = ik(F - G - A + B)$. Meanwhile, $\psi(0) = A + B$. So from equation 2.66

$$ik(F - G - A + B) = -\frac{2m\alpha}{\hbar^2}(A + B),$$

or more compactly,

$$F - G = A(1 + 2i\beta) - B(1 - 2i\beta), \quad where\ \beta \equiv \frac{m\alpha}{\hbar^2 k^2}$$



In typical scattering experiments, particles are fired in from one direction, lets say from the left. This means that $G = 0$. Solving equation 2.74 with the constraint equation gives

$$B = \frac{i\beta}{1 - i\beta}A, \quad F = \frac{1}{1 - i\beta}A \tag{2.74}$$

Now, the fraction of the incoming number that will bounce back is called the *reflection coefficient*:

$$R \equiv \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1 + \beta^2}. \tag{2.75}$$

Meanwhile, the fraction of particles that will continue through is called the *transmission coefficient*:

$$T \equiv \frac{|F|^2}{|A|^2} = \frac{1}{1 + \beta^2} \tag{2.76}$$

In terms of energy,

$$R = \frac{1}{1 + (2\hbar^2 E/m\alpha^2)}, \quad T = \frac{1}{1 + (m\alpha^2/2\hbar^2 E)}. \tag{2.77}$$

The higher the energy, the greater the probability of transmission. We have covered the delta-function well, if we want to have a look at the delta-function barrier, we just need to swap $\alpha \to -\alpha$. Note this doesn't change R and T. This means that both the barrier AND well have some probability of reflection! Note that transmission is still possible even when $E > V_{max}$. We call this phenomenon **tunnelling**.

2.6 Finite Square Well

The finite square well has potential

$$V(x) = \begin{cases} -V_0, & -a \leq x \leq a, \\ 0, & |x| > a \end{cases} \tag{2.78}$$

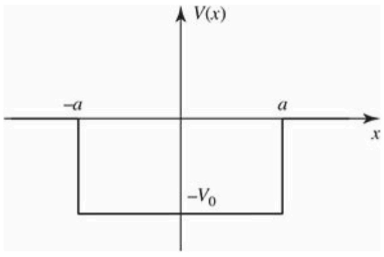


Figure 1: Finite square well potential

2.6.1 Bound States

In the region $x < -a$ the Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi, \quad \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \kappa^2\psi, \quad \textit{where } \kappa \equiv \frac{\sqrt{-2mE}}{\hbar} \tag{2.79}$$

The general solution is $\psi(x) = Ae^{-\kappa x} + Be^{\kappa x}$, but the first term blows up so we are left with

$$\psi(x) = Be^{\kappa x}, \quad (x > a). \tag{2.80}$$

In the region $-a < x < a$, $V(x) = -V_0$, and the Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - V_0\psi = E\psi, \text{ or } \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -l^2\psi \tag{2.81}$$

where

$$l \equiv \frac{\sqrt{2m(E+V_0)}}{\hbar} \tag{2.82}$$

Although $E < 0$, it must be greater than $-V_0$ because of the theorem $E > V_{min}$.
The general solution is

$$\psi(x) = C\sin(lx) + D\cos(lx), \quad (-a < x < a) \tag{2.83}$$

Finally in region $x > a$ the potential is zero and the general solution is $\psi(x) = Fe^{-\kappa x} + Ge^{\kappa x}$ and removing the divergent term, the solution becomes

$$\psi(x) = Fe^{-\kappa x}, \quad (x > a) \tag{2.84}$$

Since the potential is even, the solutions are either even or odd. Lets first do the evens

$$\psi(x) = \begin{cases} Fe^{\kappa x}, & (x > a) \\ D\cos(lx), & (0 < x < a), \\ \psi(-x), & (x < 0). \end{cases} \tag{2.85}$$

The continuity of $\psi(x)$ and $\frac{\mathrm{d}\psi}{\mathrm{d}x}$ at $x = a$ says

$$Fe^{-\kappa a} = D\cos(la) \quad \textit{and} \quad -\kappa Fe^{-\kappa a} = -lD\sin(la) \tag{2.86}$$

Dividing the two equations we get

$$\kappa = l\tan(la), \tag{2.87}$$

which is a formula for the allowed energies, since κ and l are both functions of E. We now adopt nicer notation:

$$z \equiv la, \quad \textit{and } z_0 \equiv \frac{a}{\hbar}\sqrt{2mV_0} \tag{2.88}$$

and according to the definitions of κ and l, we can derive $\kappa^2 + l^2 = \frac{2mV_0}{\hbar^2}$, so $\kappa a = \sqrt{z_0^2 - z^2}$ and equation 2.87 reads

$$\tan z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1} \tag{2.89}$$

This equation can be solved by plotting $\tan z$ and $\sqrt{(z_0/z)^2 - 1}$ and looking for points of intersection.

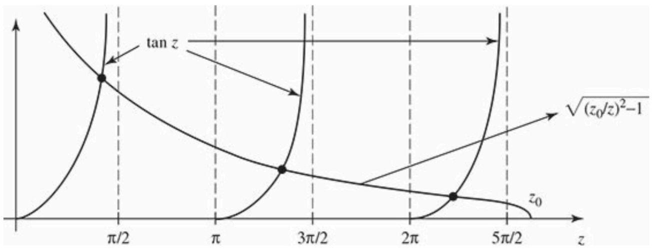


Figure 2: Graphical solution to equation 2.89

There are two limiting cases of special interest:

Wide, deep well :

if z_0 is very large, the intersections occur slightly below $z_n = n\pi/2$ with n odd. Rewriting this equation, it follows that

$$E_n + V_0 \approx \frac{n^2\pi^2\hbar^2}{2m(2a)^2}, \quad (n = 1, 3, 5, ...) \tag{2.90}$$

$E + V_0$ is the energy *above* the bottom of the well, and on the right hand side we have the infinite square well energies, but for a well of width $2a$ (rather, half of them because this n is odd). The number of bound states correspond to the number of intersections on the graph.

Shallow. narrow well :

As z_0 decreases, there are fewer and fewer bound states, until for $z_0 < \pi/2$, only one state remains. There is always this one bound state, no matter how low the potential (z_0) becomes.

2.6.2 Scattering States

We now consider $E > 0$. To the left, where $V(x) = 0$, we have

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad (x < -a), \quad k \equiv \frac{\sqrt{2mE}}{\hbar} \tag{2.91}$$

Inside the well, where $V(x) = -V_0$,

$$\psi(x) = C\sin(lx) + D\cos(lx), \quad (-a < x < a), \quad l \equiv \frac{\sqrt{2m(E+V_0)}}{\hbar} \tag{2.92}$$

To the right, assuming no incoming wave

$$\psi(x) = Fe^{ikx}. \tag{2.93}$$

From the continuity of $\psi(x)$ and its derivative at $-a$ and a, we can eliminate C and D to obtain

$$B = i\frac{\sin(2la)}{2kl}(l^2 - k^2)F, \tag{2.94}$$

$$F = \frac{e^{-2ika}A}{\cos(2la) - i\frac{(k^2+l^2)}{2kl}\sin(2la)}. \tag{2.95}$$

The transmission coefficient ($T = |F|^2/|A|^2$), expressed as the original variables is given by

$$T^{-1} = 1 + \frac{V_0^2}{4E(E+V_0)}\sin^2\left(\frac{2a}{\hbar}\sqrt{2m(E+V_0)}\right) \tag{2.96}$$

When the sine is zero, the well becomes transparent, that is

$$\frac{2a}{\hbar}\sqrt{2m(E_n+V_0)} = n\pi \tag{2.97}$$

Rearranging this equation gives the energies for perfect transmission

$$E_n + V_0 = \frac{n^2\pi^2\hbar^2}{2m(2a)^2} \tag{2.98}$$

which will occur at precisely the allowed energies for the *infinite* square well.

3 Formalism of Quantum Mechanics

3.1 Determinant States

Ordinarily, when you measure an observable Q on an ensemble of identically prepared systems, all in the same state Ψ, you do not get the same result of each time. However, is it possible to prepare a state such that every measurement of Q is certain to return the same value q?
For this to occur, the standard deviation of Q would be zero:

$$\sigma^2 = \langle (Q - \langle Q \rangle)^2 \rangle = \left\langle \Psi \middle| (\hat{Q} - q)^2 \Psi \right\rangle = \left\langle (\hat{Q} - q)\Psi \middle| (\hat{Q} - q)\Psi \right\rangle = 0 \tag{3.1}$$

Now the only vector whose inner product with itself vanishes is 0, so

$$\hat{Q}\Psi = q\Psi \tag{3.2}$$

which is the eigenvalue equation for the operator $\hat{Q}$. Thus

Determinant states of Q are eigenfunctions of $\hat{Q}$

3.2 Discrete Spectra

Hermitian operators have the following properties

1. Their eigenvalues are real
2. Eigenfunctions belonging to distinct eigenvalues are orthogonal
3. If two or more eigenfunctions share the same eigenvalue, any linear combination of them is itself and eigenfunction, with the same eigenvalue.
4. The eigenfunctions of an observable operator are *complete*: Any function in a Hilbert space can be expressed as a linear combination of them.

3.3 Statistical Interpretation

If you measure an observable Q on a particle in the state Ψ, you are certain to get one of the eigenvalues of the hermitian operator $\hat{Q}$.

Discrete: The probability of getting the particular eigenvalue q_n associated with the eigenfunction $f_n(x)$ is $|c_n|^2$, where $c_n = \langle f_n | \Psi \rangle$.

Continuous: The probability of getting a particular eigenvalue $q(z)$ associated with the eigenfunction $f_z(x)$ in the range dz is $|c(z)|^2 dz$ where $c(z) = \langle f_z | \Psi \rangle$.

The eigenfunctions of an observable operator are complete, so the wave function can be written as a linear combination of them:

$$\Psi(x,t) = \sum_n c_n(t) f_n(x) \tag{3.3}$$

and using Fourier's trick:

$$c_n(t) = \langle f_n | \Psi \rangle = \int f_n(x)^* \Psi(x,t)\, \mathrm{d}x\,. \tag{3.4}$$

Qualitatively, c_n tells you how much f_n is contained in Ψ and $|c_n|^2$ is the probability of the measurement being the eigenstate f_n when you measure Ψ. It's a common misconception that $|c_n|^2$ is the probability of the system being in the state f_n. This is not true because the system is in the state Ψ, period. It is rather the probability of a measurement yielding f_n and hence collapsing the wave function to f_n.

3.4 Heisenberg's Uncertainty Principle

From equation 3.1, we have

$$\sigma_A^2 = \left\langle (\hat{A} - \langle A \rangle)\Psi \middle| (\hat{A} - \langle A \rangle)\Psi \right\rangle = \langle f|f \rangle, \quad \textit{where } f \equiv \left(\hat{A} - \langle A \rangle\right)\Psi. \tag{3.5}$$

Likewise, for any other observable B:

$$\sigma_B^2 = \langle g|g \rangle, \quad \textit{where } g \equiv \left(\hat{B} - \langle B \rangle\right)\Psi. \tag{3.6}$$

Invoking the Schwarz inequality,

$$\sigma_A^2 \sigma_B^2 = \langle f|f \rangle \langle g|g \rangle \geq | \langle f|g \rangle |^2, \tag{3.7}$$

Now, for any complex number z,

$$|z|^2 = [\mathrm{Re}(z)]^2 + [\mathrm{Im}(z)]^2 \geq [\mathrm{Im}(z)]^2 = \left[\frac{1}{2i}(z - z^*)\right]^2. \tag{3.8}$$

Now, letting $z = \langle f|g \rangle$,

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i}[\langle f|g \rangle - \langle g|f \rangle]\right)^2. \tag{3.9}$$

Meanwhile, we can exploit the hermiticity of $\left(\hat{A} - \langle A \rangle\right)$ from equation 3.5:

$$\begin{aligned}
\langle f|g \rangle &= \left\langle \left(\hat{A} - \langle A \rangle\right)\Psi \middle| \left(\hat{B} - \langle B \rangle\right)\Psi \right\rangle && (3.10)\\
&= \left\langle \Psi \middle| \left(\hat{A} - \langle A \rangle\right)\left(\hat{B} - \langle B \rangle\right)\Psi \right\rangle && (3.11)\\
&= \left\langle \Psi \middle| \left(\hat{A}\hat{B} - \hat{A}\langle B \rangle - \hat{B}\langle A \rangle + \langle A \rangle \langle B \rangle\right)\Psi \right\rangle && (3.12)\\
&= \left\langle \Psi \middle| \hat{A}\hat{B}\Psi \right\rangle - \langle B \rangle \left\langle \Psi \middle| \hat{A}\Psi \right\rangle - \langle A \rangle \left\langle \Psi \middle| \hat{B}\Psi \right\rangle + \langle A \rangle \langle B \rangle \langle \Psi|\Psi \rangle && (3.13)\\
&= \left\langle \hat{A}\hat{B} \right\rangle - \langle A \rangle \langle B \rangle && (3.14)
\end{aligned}$$

Similarly,

$$\langle g|f \rangle = \left\langle \hat{B}\hat{A} \right\rangle - \langle A \rangle \langle B \rangle \tag{3.15}$$

so

$$\langle f|g \rangle - \langle g|f \rangle = \langle [A, B] \rangle \tag{3.16}$$

and finally

$$\boxed{\sigma_A \sigma_B \geq \frac{1}{2i} \langle [A, B] \rangle}. \tag{3.17}$$

If we plug in our parameters for position and momentum,

$$\begin{aligned}
\sigma_x \sigma_p &\geq \frac{1}{2i} \langle [\hat{x}, \hat{p}] \rangle && (3.18)\\
&\geq \frac{1}{2i} \langle i\hbar \rangle && (3.19)\\
&\geq \frac{\hbar}{2} && (3.20)
\end{aligned}$$

we get the original Heisenberg uncertainty principle. In fact, there is an uncertainty principle for every pair of observables whose operators do not commute, these are incompatible observables. Incompatible observables do not have shared eigenfunctions.

In the laboratory, the act of measuring a particle's position collapses the wave function to a narrow spike, which carries a broad range of wavelengths in its Fourier decomposition. If we now measure the momentum, the state will collapse to a long sinusoidal wave and the particle no longer has position you got in the first measurement. The problem is that the second measurement renders the outcome of the first measurement obsolete. Only if the wave function were simultaneously an eigenstate of both observables would it be possible to make the second measurement without disturbing the state of the particle. This is only possible if the two observables are compatible.

3.4.1 The Limit of Minimum Uncertainty

To have the minimum uncertainty, we require the generalised uncertainty principle to have equality:

$$\sigma_A\sigma_B = \frac{1}{2i}\left\langle [A,B]\right\rangle . \tag{3.21}$$

The Schwarz inequality becomes equality when one function is a multiple of the other: $g(x) = cf(x)$, for some complex number c. The inequality in equation 3.8 become equality when $\mathrm{Re}(z) = 0$, that is, $\mathrm{Re}(\langle f|g\rangle) = \mathrm{Re}(c\langle f|g\rangle) = 0$. We know $\langle f|f\rangle$ is real, is this means c must be purely imaginary. Using $c = ia$, we get

$$g(x) = iaf(x). \tag{3.22}$$

For the position-momentum uncertainty this becomes:

$$\left(-i\hbar\frac{\mathrm{d}}{\mathrm{d}x} - \langle p\rangle\right)\Psi = ia(x - \langle x\rangle)\Psi \tag{3.23}$$

which is a differential equation with the general solution:

$$\Psi(x) = Ae^{-a(x-\langle x\rangle)^2/2\hbar}e^{i\langle p\rangle x/\hbar}. \tag{3.24}$$

Evidently, the minimum-uncertainty wave packet is a gaussian. This means that since the ground state of the harmonic oscillator and free particle are gaussians, they are the wave functions of minimum uncertainty.

3.4.2 Energy-Time Uncertainty Principle

Since time is a parameter and not a observable, we can't use the generalised uncertainty principle. As a measure of how fast a system is changing, we compute the time derivative of the expectation value of some observable, $Q(x,p,t)$:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle Q\rangle = \frac{\mathrm{d}}{\mathrm{d}t}\left\langle \Psi\middle|\hat{Q}\Psi\right\rangle = \left\langle \frac{\mathrm{d}\Psi}{\mathrm{d}t}\middle|\hat{Q}\Psi\right\rangle + \left\langle \Psi\middle|\frac{\partial\hat{Q}}{\partial t}\Psi\right\rangle + \left\langle \Psi\middle|\hat{Q}\frac{\mathrm{d}\Psi}{\mathrm{d}t}\right\rangle . \tag{3.25}$$

Now, from the Schrödinger equation,

$$i\hbar\frac{\mathrm{d}\Psi}{\mathrm{d}t} = \hat{H}\Psi \tag{3.26}$$

we get

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\langle Q\rangle &= -\frac{1}{i\hbar}\left\langle \hat{H}\Psi\middle|\hat{Q}\Psi\right\rangle + \left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle + \frac{1}{i\hbar}\left\langle\Psi\middle|\hat{Q}\hat{H}\Psi\right\rangle && (3.27)\\
&= -\frac{1}{i\hbar}\left\langle \Psi\middle|\hat{H}\hat{Q}\Psi\right\rangle + \left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle + \frac{1}{i\hbar}\left\langle\Psi\middle|\hat{Q}\hat{H}\Psi\right\rangle \quad \text{since } \hat{H} \text{ is hermitian} && (3.28)\\
&= \frac{i}{\hbar}\left\langle\left[\hat{H},\hat{Q}\right]\right\rangle + \left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle && (3.29)
\end{aligned}$$

This is called the generalised Ehrenfest theorem. In the case where the operator does not depend explicitly on time $\left(\frac{\partial\hat{Q}}{\partial t} = 0\right)$, it tells us that the rate of change of the expectation value is determined by the commutator of the operator with the Hamiltonian. In particular, if $\hat{Q}$ commutes with $\hat{H}$, the $\langle Q\rangle$ is constant, and therefore Q is a conserved quantity.

From the generalised uncertainty principle,

$$\begin{aligned}
\sigma_H^2\sigma_Q^2 &\geq \left(\frac{1}{2i}\left\langle\left[\hat{H},\hat{Q}\right]\right\rangle\right)^2 = \left(\frac{1}{2i}\frac{\hbar}{i}\frac{\mathrm{d}\langle Q\rangle}{\mathrm{d}t}\right)^2 \quad \text{from the Ehrenfest theorem} && (3.30)\\
\sigma_H\sigma_Q &\geq \frac{\hbar}{2}\left|\frac{\mathrm{d}\langle Q\rangle}{\mathrm{d}t}\right|. && (3.31)
\end{aligned}$$

If we define $\Delta E \equiv \sigma_H$ and $\Delta t \equiv \frac{\sigma_Q}{\left|\frac{\mathrm{d}\langle Q\rangle}{\mathrm{d}t}\right|}$, we get $\Delta E\Delta t \geq \frac{\hbar}{2}$.

Since $\sigma_Q = \left|\frac{\mathrm{d}\langle Q\rangle}{\mathrm{d}t}\right|\Delta t$, we can see that Δt is the amount of time it takes the expectation value of Q to change by one standard deviation. If E is known precisely, then the rate of change of the observable must be very gradual and vice versa.

To get an intuitive understanding of this, lets consider the initial state of our system is an eigenstate of our hamiltonian:

$$|\Psi(t_0)\rangle = |u_n\rangle \implies \Delta E = 0, \quad \text{since we only have a single eigenvalue } E \text{ for that state.} \tag{3.32}$$

From the Schrödinger equation, the wave function at a later time t is given by

$$|\Psi(t)\rangle = e^{-iE_n(t-t_0)\hbar} |u_n\rangle = e^{-iE_n(t-t_0)\hbar} |\Psi(t_0)\rangle \,. \tag{3.33}$$

For the observable Q:

$$\begin{aligned}
\langle \hat{Q} \rangle (t) &= \left\langle \Psi(t) \middle| \hat{Q} \middle| \Psi(t) \right\rangle && (3.34)\\
&= \left\langle \Psi(t_0) \middle| e^{iE_n(t-t_0)/\hbar} \hat{Q} e^{-iE_n(t-t_0)/\hbar} \middle| \Psi(t_0) \right\rangle && (3.35)\\
&= \left\langle \Psi(t_0) \middle| \hat{Q} \middle| \Psi(t_0) \right\rangle && (3.36)\\
&= \langle \hat{Q} \rangle (t_0) && (3.37)\\
\implies \frac{\mathrm{d} \langle \hat{Q} \rangle}{\mathrm{d}t} &= 0 && (3.38)
\end{aligned}$$

Now from the definition of Δt, we have:

$$\Delta t = \frac{\Delta \hat{Q}}{\left| \frac{\mathrm{d}\langle \hat{Q} \rangle}{\mathrm{d}t} \right|} \longrightarrow \infty \tag{3.39}$$

which makes sense because the time taken to change state is infinite for a stationary state that is independent of time.

The implications of this is that particles with a very short lifespan doesn't have a well defined mass. If we attempt to measure the mass repeatedly, we get a bell shaped curve with a large uncertainty.
A common misconception is that if the energy is uncertain by ΔE, then conservation of energy can be violated by ΔE for a time Δt. However, this is not the case because the uncertainty relation deals with the *precision* of our measurements, not the actual values themselves.

4 Quantum Mechanics in Three Dimensions

4.1 Spherical Harmonics

This section aims to investigate the physics behind the shape of atoms and their properties. Note that in spherical coordinates, the expectation value takes the form:

$$\langle Q\rangle = \int \psi^* Q\psi \,\mathrm{d}^3r \quad \textit{where } \mathrm{d}^3r = r^3 \sin\theta \,\mathrm{d}\phi \,\mathrm{d}\theta \,\mathrm{d}r\,. \tag{4.1}$$

4.1.1 Spherical Coordinates

The Schrödinger equation in cartesian coordinates takes the form

$$i\hbar\frac{\mathrm{d}\Psi}{\mathrm{d}t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \tag{4.2}$$

and the time-independent Schrödinger takes the form

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi. \tag{4.3}$$

To convert to spherical coordinates, we simply convert the laplacian

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right] + V\psi = E\psi. \tag{4.4}$$

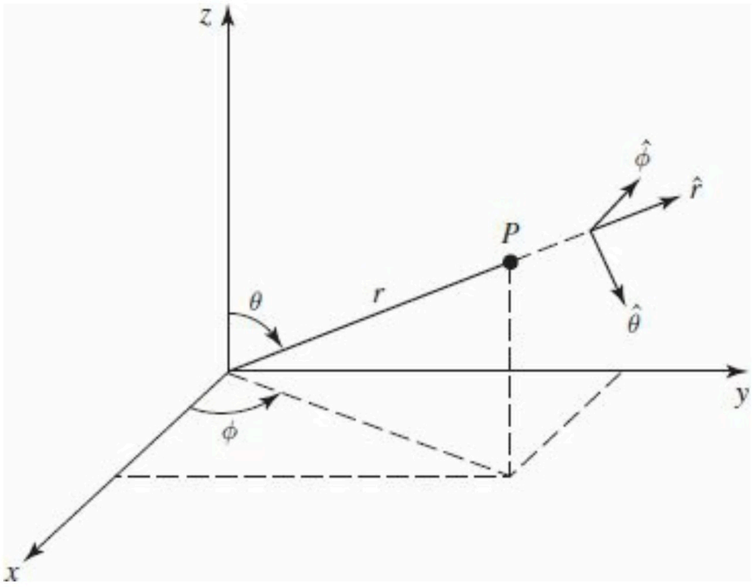


Figure 3: Spherical coordinates: radius r, polar angle θ, and azimuthal angle ϕ.

We begin by looking for solutions that are separable into products

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi). \tag{4.5}$$

Substituting this into equation 4.4, dividing by YR and multiplying by $-2mr^2/\hbar^2$:

$$\left\{\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) - \frac{2mr^2}{\hbar^2}[V(r)-E]\right\} + \frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} = 0. \tag{4.6}$$

Since the first term depends only on r, and the second depends only on the angles, they both must be opposite constants. We write the constants as

$$\left\{\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) - \frac{2mr^2}{\hbar^2}[V(r)-E]\right\} = l(l+1); \tag{4.7}$$

$$\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} = -l(l+1). \tag{4.8}$$

4.1.2 The Angular Equation

Multiplying equation 4.8 by $Y \sin^2\theta$ gets us

$$\sin\theta \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\phi^2} = -l(l+1)Y\sin^2\theta. \tag{4.9}$$

Using separation of variables, we substitute

$$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi) \tag{4.10}$$

into equation 4.9 to get

$$\left\{\frac{1}{\Theta}\left[\sin\theta \frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta \frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)\right] + l(l+1)\sin^2\theta\right\} + \frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = 0. \tag{4.11}$$

Again, we notice that the first and second terms must be constant, lets call this m^2:

$$\frac{1}{\Theta}\left[\sin\theta \frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta \frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)\right] + l(l+1)\sin^2\theta = m^2 \tag{4.12}$$

$$\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -m^2. \tag{4.13}$$

The solution to equation 4.13 is simply $\Phi(\phi) = e^{im\phi}$, the term with the negative exponent is covered by allowing m to be both positive and negative. We have also absorbed the constant A into Φ. Now, by the periodicity of the Φ, we have

$$\Phi(\phi + 2\pi) = \Phi(\phi). \tag{4.14}$$

In other words, $e^{im(\phi+2\pi)} = e^{im\phi} \implies e^{2\pi im} = 1$, so $m \in \mathbb{Z}$.

Meanwhile, the solution to equation 4.12 is

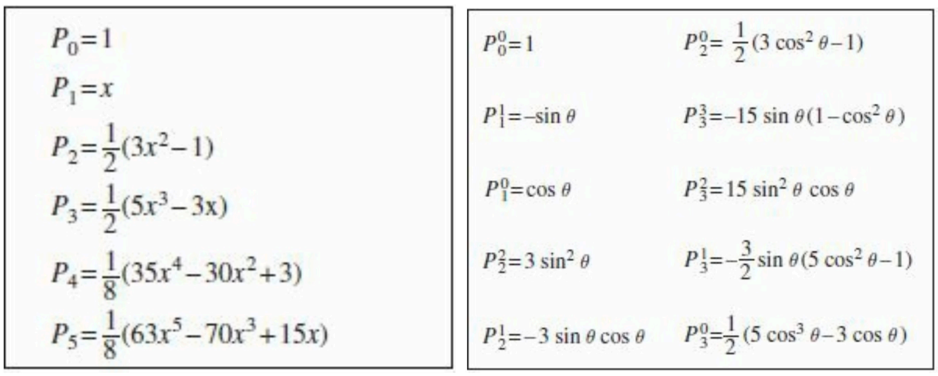
$$\Theta(\theta) = AP_l^m(\cos\theta) \tag{4.15}$$

where P_l^m is the associated Legendre function, defined by

$$P_l^m(x) \equiv (-1)^m\left(1-x^2\right)^{m/2}\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^m P_l(x). \tag{4.16}$$

and $P_l(x)$ is the lth Legendre polynomial, defined by the Rodrigues formula:

$$P_l(x) \equiv \frac{1}{2^l l!}\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^l \left(x^2-1\right)^l. \tag{4.17}$$



$P_0=1$

$P_1=x$

$P_2=\frac{1}{2}(3x^2-1)$

$P_3=\frac{1}{2}(5x^3-3x)$

$P_4=\frac{1}{8}(35x^4-30x^2+3)$

$P_5=\frac{1}{8}(63x^5-70x^3+15x)$

$P_0^0=1$

$P_1^1=-\sin\theta$

$P_1^0=\cos\theta$

$P_2^2=3\sin^2\theta$

$P_2^1=-3\sin\theta\cos\theta$

$P_2^0=\frac{1}{2}(3\cos^2\theta-1)$

$P_3^3=-15\sin\theta(1-\cos^2\theta)$

$P_3^2=15\sin^2\theta\cos\theta$

$P_3^1=-\frac{3}{2}\sin\theta(5\cos^2\theta-1)$

$P_3^0=\frac{1}{2}(5\cos^3\theta-3\cos\theta)$

Figure 4: Legendre polynomials and functions

Note l must be a non-negative integer for the derivative and factorial in equation 4.17 to make sense. Moreover, if $m > l$, then equation 4.16 says that $P_l^m = 0$. So for any given l, there are $(2l+1)$ possible values for m:

$$l = 0,\ 1,\ 2,\ ...;\quad m = -l,\ -l+1,\ ...,-1,\ 0,\ 1,\ ...,\ l-1,\ l. \tag{4.18}$$

Now, the normalisation condition is

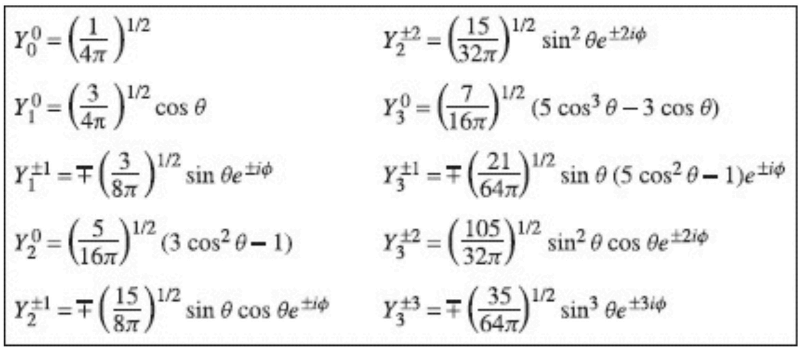
$$\int |\psi|^2 r^2 \sin\theta \,\mathrm{d}r \,\mathrm{d}\theta \,\mathrm{d}\phi = \int |R|^2 r^2 \,\mathrm{d}r \int |Y|^2 \,\mathrm{d}\Omega = 1. \tag{4.19}$$

It is convenient to normalise separately

$$\int_0^\infty |R|^2 r^2 \,\mathrm{d}r = 1 \quad \textit{and} \quad \int_0^\pi \int_0^{2\pi} |Y|^2 \sin\theta \,\mathrm{d}\theta \,\mathrm{d}\phi = 1. \tag{4.20}$$

Now if we normalise the angular wave function $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi) = AP_l^m(\cos\theta)\Phi(\phi)$, we obtain the spherical harmonics:

$$\boxed{Y_l^m(\theta, \phi) = \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}} e^{im\phi} P_l^m(\cos\theta)}. \tag{4.21}$$



$$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$

$$Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta \cos\theta e^{\pm i\phi}$$

$$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$$

$$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$$

$$Y_3^{\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta\,(5\cos^2\theta - 1) e^{\pm i\phi}$$

$$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta \cos\theta e^{\pm 2i\phi}$$

$$Y_3^{\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$$

Figure 5: The first few spherical harmonics

4.1.3 The Radial Equation

The angular part of the wave function, $Y(\theta, \phi)$, is the same for all spherically symmetric potentials since it doesn't depend on $V(r)$. The potential only affects the radial part of the wave function, $R(r)$, which is given by equation 4.7:

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2 \frac{\mathrm{d}R}{\mathrm{d}r}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E] = l(l+1)R. \tag{4.22}$$

This simplifies if we change variables to

$$u(r) \equiv rR(r), \tag{4.23}$$

so that

$$\boxed{-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} + \left[V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right] u = Eu}. \tag{4.24}$$

This is called the radial equation; it is identical in form to the one-dimensional Schrödinger equation, except that the effective potential,

$$V_{\text{eff}} = V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}, \tag{4.25}$$

contains the extra centrifugal term. It tends to through the particle outward (away from the origin). Meanwhile, the normalisation condition becomes

$$\int_0^\infty |u|^2 \,\mathrm{d}r = 1. \tag{4.26}$$

That's as far as we can go until a specific potential $V(r)$ is provided.

4.2 The Hydrogen Atom

The potential energy of the electron can be obtained from Coulomb's Law:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \tag{4.27}$$

and the radial equation 4.24 says

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu. \tag{4.28}$$

Since $V_{centrifugal}$ is proportional to $1/r^2$ and $V_{Coulomb}$ is proportional to $1/r$, for $r \to 0$, the $V_{centrifugal}$ dominates the total potential and when $r \to \infty$, the $V_{Coulomb}$ dominates the total potential.

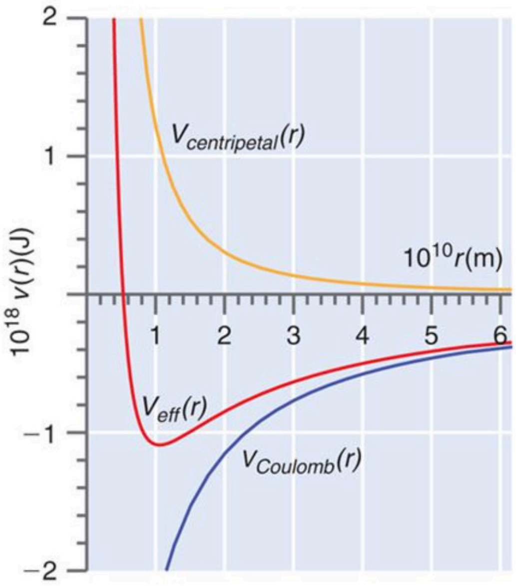


Figure 6: The effective potential for hydrogen if $l > 0$

4.2.1 The Radial Wave Equation

Lets tidy up the notation. Let

$$\kappa \equiv \frac{\sqrt{-2m_e E}}{\hbar}. \tag{4.29}$$

For bound states, $E < 0$ so κ is real. Dividing equation 4.28 by E, we have

$$\frac{1}{\kappa^2}\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} = \left[1 - \frac{m_e e^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{(\kappa r)} + \frac{l(l+1)}{(\kappa r)^2}\right]u. \tag{4.30}$$

This motivates the introduction of

$$\rho \equiv \kappa r, \quad \text{and} \quad \rho_0 \equiv \frac{m_e e^2}{2\pi\epsilon_0\hbar^2\kappa}. \tag{4.31}$$

so that

$$\frac{\mathrm{d}^2 u}{\mathrm{d}\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u. \tag{4.32}$$

next, we examine the asymptotic form of the solutions. As $\rho \to \infty$, the constant term in the brackets dominates so

$$\frac{\mathrm{d}^2 u}{\mathrm{d}\rho^2} = u. \tag{4.33}$$

The general solution for large ρ is

$$u(\rho) \approx Ae^{-\rho}, \tag{4.34}$$

after removing the term that explodes.

On the other hand, as $\rho \to 0$ the centrifugal term dominates; then:

$$\frac{\mathrm{d}^2 u}{\mathrm{d}\rho^2} = \frac{l(l+1)}{\rho^2} u. \tag{4.35}$$

The general solution for small ρ is therefore

$$u(\rho) \approx C\rho^{l+1} \tag{4.36}$$

after removing the term that explodes. The next step is to peel off the asymptotic behaviour, introducing a new function $v(\rho)$: $u(\rho) = \rho^{l+1} e^{-\rho} v(\rho)$ in the hopes that $v(\rho)$ will turn out to be simpler than $u(\rho)$. Differentiating repeatedly gives us

$$\frac{\mathrm{d}u}{\mathrm{d}\rho} = \rho^l e^{-\rho}\left[(l+1-\rho)v + \rho\frac{\mathrm{d}v}{\mathrm{d}\rho}\right], \tag{4.37}$$

and

$$\frac{\mathrm{d}^2 u}{\mathrm{d}\rho^2} = \rho^l e^{-\rho}\left\{\left[-2l+2+\rho+\frac{l(l+1)}{\rho}\right]v + 2(l+1-\rho)\frac{\mathrm{d}v}{\mathrm{d}\rho} + \rho\frac{\mathrm{d}^2 v}{\mathrm{d}\rho^2}\right\}. \tag{4.38}$$

Substituting these new expressions with $v(\rho)$ into equation 4.32 gives us

$$\rho\frac{\mathrm{d}^2 v}{\mathrm{d}\rho^2} + 2(l+1-\rho)\frac{\mathrm{d}v}{\mathrm{d}\rho} + [\rho_0 - 2(l+1)]v = 0. \tag{4.39}$$

Finally, we assume the solution $v(\rho)$, can be expressed as a power series in ρ:

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j. \tag{4.40}$$

The goal is to determine the coefficients. Differentiating term by term:

$$\frac{\mathrm{d}v}{\mathrm{d}\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j. \tag{4.41}$$

Differentiating again,

$$\frac{\mathrm{d}^2 v}{\mathrm{d}\rho^2} = \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j-1}. \tag{4.42}$$

Inserting these into equation 4.39,

$$\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^j + 2(l+1)\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^j - 2\sum_{j=0}^{\infty} jc_j\rho^j + [\rho_0 - 2(l+1)]\sum_{j=0}^{\infty} c_j\rho^j = 0 \tag{4.43}$$

Since these terms all have ρ^j, we can equate coefficients

$$j(j+1)c_{j+1} + 2(l+1)(j+1)c_{j+1} - 2jc_j + [\rho_0 - 2(l+1)]c_j, \tag{4.44}$$

or:

$$c_{j+1} = \left\{\frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)}\right\} c_j. \tag{4.45}$$

This recursion formula determines the coefficients. We start with c_0 since it is eventually determined by normalisation

$$c_{j+1} \approx \frac{2j}{j(j+1)} c_j \tag{4.46}$$

$$\approx \frac{2}{j+1} c_j \tag{4.47}$$

so

$$c_j \approx \frac{2^j}{j!} c_0. \tag{4.48}$$

Suppose for a moment this was the exact result. Then

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{1}{j!}(2\rho)^j = c_0 e^{2\rho}. \tag{4.49}$$

and hence

$$u(\rho) = c_0 \rho^{l+1} e^{\rho}, \tag{4.50}$$

which explodes at large ρ. This solution to the radial equation is not normalisable. There is only one escape from this dilemma: *The series must terminate.* There must occur some integer N such that $c_{N-1} \neq 0$ but $c_N = 0$. In that case, equation 4.45 says that

$$2(N + l) - \rho_0 = 0. \tag{4.51}$$

Defining $n \equiv N + l$, we have

$$\rho_0 = 2n. \tag{4.52}$$

But ρ_0 determines E (equations 4.29) and 4.31):

$$E = -\frac{\hbar^2 \kappa^2}{2m} = \frac{m_e e^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2}, \tag{4.53}$$

so the allowed energies are

$$\boxed{E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, ...} \tag{4.54}$$

This is the famous Bohr formula - the most important result in all of quantum mechanics. From equation 4.31, we find that

$$\kappa = \left(\frac{m_e e^2}{4\pi\epsilon_0 \hbar^2}\right)\frac{1}{n} = \frac{1}{an}, \tag{4.55}$$

where

$$\boxed{a \equiv \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = 0.529 \times 10^{-10} \text{ m}} \tag{4.56}$$

is the Bohr radius. The spatial wave functions are labeled by three quantum numbers (n, l, and m):

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi), \tag{4.57}$$

where (referring back to equations 4.50 and 4.23),

$$R_{nl}(r) = \frac{1}{r}\rho^{l+1} e^{-\rho} v(\rho). \tag{4.58}$$

and $v(\rho)$ is a polynomial of degree $n - l - 1$ in ρ, whose coefficients are determined (up to a normalisation factor) by the recursion formula:

$$c_{j+1} = \frac{2(j + l + 1 - n)}{(j + 1)(j + 2l + 2)} c_j. \tag{4.59}$$

Thee ground state is the case $n = 1$ putting in the accepted values for the physical constants, we get:

$$\boxed{E_1 = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right] = -13.6\text{eV}.} \tag{4.60}$$

The binding energy of hydrogen (the amount of energy you would have to impart to the electron in ground state in order to ionise the atom) is 13.6 eV.

Lets now find

$$\psi_{100}(r,\theta,\phi) = R_{10}(r)Y_0^0(\theta,\phi). \tag{4.61}$$

The recursion formula truncades after the first term so $v(\rho)$ is a constant (c_0), and

$$R_{10}(r) = \frac{c_0}{a}e^{-r/a}. \tag{4.62}$$

and after normalisation and the computation of Y_0^0, the ground state of hydrogen is

$$\boxed{\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}}e^{-r/a} \quad and\ E_n = -\frac{13.6\text{eV}}{n^2}} \tag{4.63}$$

For arbitrary n, the possible values of l can be found using $n = N + l$ and adjusting N:

$$l = 0, 1, 2, ..., n-1, \tag{4.64}$$

and for each l there are $(2l+1)$ possible values for m, so the total degeneracy of the energy level E_n is

$$d(n) = \sum_{l=0}^{n-1}(2l+1) = n^2. \tag{4.65}$$

The polynomial $v(\rho)$ can be written as

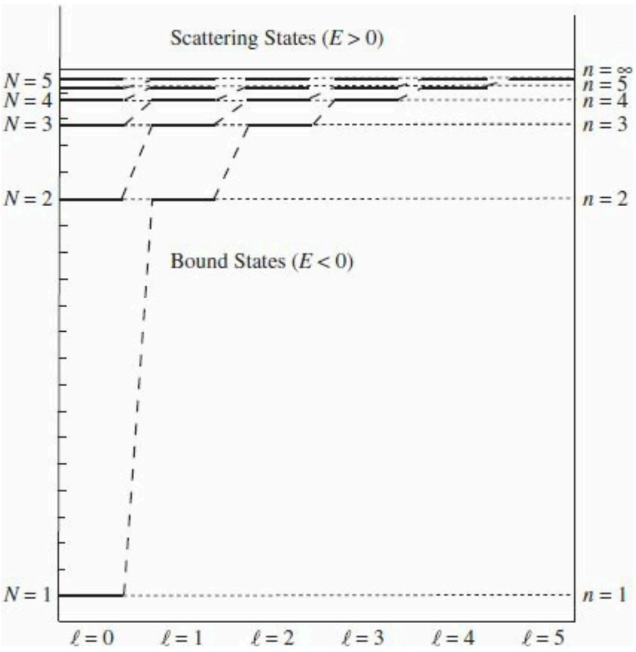


Figure 7: Energy levels for hydrogen

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho), \tag{4.66}$$

where

$$L_q^p(x) \equiv (-1)^p\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^p L_{p+q}(x) \tag{4.67}$$

is an associated Laguerre polynomial, and

$$L_q(x) \equiv \frac{e^x}{q!}\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^2\left(e^{-x}x^q\right) \tag{4.68}$$

is the qth Laguerre polynomial. The normalised hydrogen wave functions are

$$\boxed{\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n(n+l)!}}e^{-r/na}\left(\frac{2r}{na}\right)^l\left[L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)\right]Y_l^m(\theta,\phi).} \tag{4.69}$$

4.2.2 The Hydrogen Spectrum

If the hydrogen atom is perturbed by processes such as the collision with another atom or by shining light on it, the atom may undergo a transition to some other stationary state - either by absorbing energy, and moving up to a higher energy state, or by giving off energy typically in the form of electromagnetic radiation. The emitted photon's energy corresponds to the difference in energy between the initial and final states:

$$E_\gamma = E_i - E_f = -13.6\text{eV}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right). \tag{4.70}$$

Now from the Planck formula, $E_\gamma = h\nu$, so

$$\frac{1}{\lambda} = \frac{\nu}{c} = \frac{E_\gamma}{hc} = \frac{-13.6\text{eV}}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = \mathcal{R}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{4.71}$$

where $\mathcal{R} = 1.097 \times 10^7\text{m}^{-1}$ is known as the Rydberg constant. At room temperature, most hydrogen atoms are in the ground state; to obtain the emission spectrum you must first populate the various excited states; typically this is done by passing an electric spark through the gas.

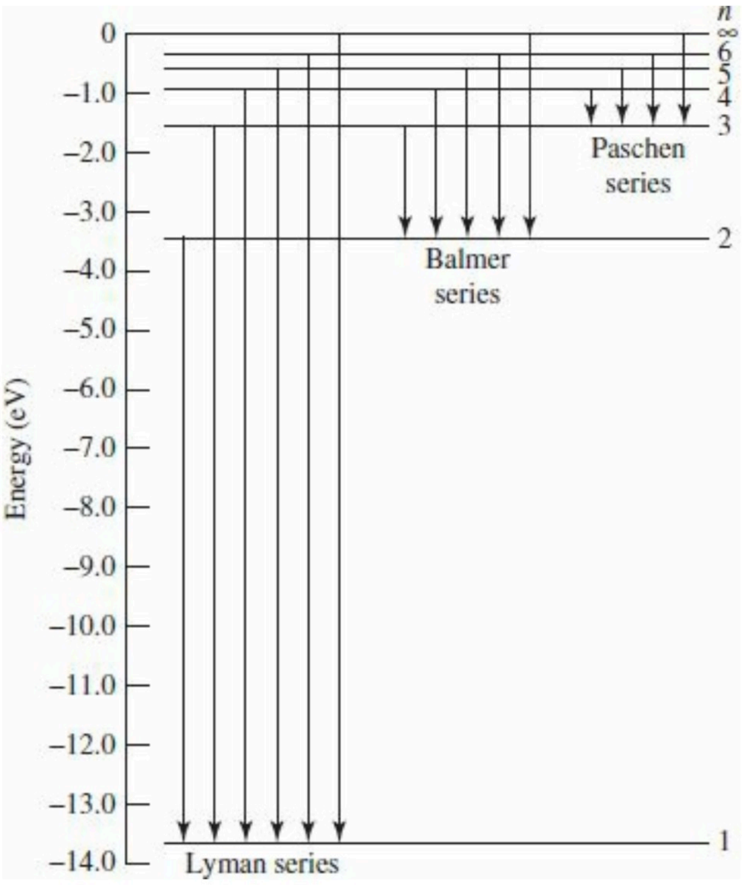


Figure 8: Energy Levels and transitions in the hydrogen spectrum

4.3 Angular Momentum

Classically, the angular momentum of a particle is given by the formula

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}, \tag{4.72}$$

which is to say,

$$L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x. \tag{4.73}$$

To transition to quantum mechanics, we simply replace the classical momenta with their operator form.

4.3.1 Eigenvalues

Let us start by noting down important commutation relations:

$$[r_i, p_j] = i\hbar\delta_{ij}, \quad [r_i, r_j] = [p_i, p_j] = 0. \tag{4.74}$$

Now, we begin by calculating the commutators:

$$\begin{aligned}
[L_x, L_y] &= [yp_z - zp_y, zp_x - xp_z] && (4.75)\\
&= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z] && (4.76)\\
&= yp_x[p_z, z] + p_y x[z, p_z] && (4.77)\\
&= i\hbar(xp_y - yp_z) && (4.78)\\
&= i\hbar L_z && (4.79)
\end{aligned}$$

So we have the commutators

$$\boxed{[L_x, L_y] = i\hbar L_z; \qquad [L_y, L_z] = i\hbar L_x; \qquad [L_z, L_x] = i\hbar L_y} \tag{4.80}$$

which are incompatible observables. It would be futile to look for states that are simultaneously eigenfunctions of L_x and L_y. On the other hand, the square of the total angular momentum

$$L^2 \equiv L_x^2 + L_y^2 + L_z^2, \tag{4.81}$$

does commute with L_x:

$$\begin{aligned}
\left[L^2, L_x\right] &= \left[L_x^2, L_x\right] + \left[L_y^2, L_x\right] + \left[L_z^2, L_x\right] && (4.82)\\
&= L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z && (4.83)\\
&= L_y(-i\hbar L_z) + (-i\hbar L_z)L_y + L_z(i\hbar L_y) + (i\hbar L_y)L_z && (4.84)\\
&= 0. && (4.85)
\end{aligned}$$

So L^2 also commutes with L_y and L_z:

$$\left[L^2, L_x\right] = 0, \quad \left[L^2, L_y\right] = 0, \quad \left[L^2, L_z\right] = 0. \tag{4.86}$$

or, more compactly,

$$\left[L^2, \mathbf{L}\right] = 0. \tag{4.87}$$

Since L^2 is compatible with each component of $\mathbf{L}$, we can find simultaneous eigenstates of L^2 and L_z:

$$L^2 f = \lambda f \quad \textit{and} \quad L_z f = \mu f. \tag{4.88}$$

Using the ladder operator technique, let

$$L_\pm \equiv L_x \pm iL_y. \tag{4.89}$$

The commutator with L_z is

$$[L_z, L_\pm] = [L_z, L_x] \pm i[L_z, L_y] = i\hbar L_y \pm i(-i\hbar L_x) = \hbar(\pm L_x + iL_y) = \pm\hbar(L_x \pm iL_y), \tag{4.90}$$

so

$$[L_z, L_\pm] = \pm\hbar L_\pm, \tag{4.91}$$

and it follows that

$$\left[L^2, L_\pm\right] = 0. \tag{4.92}$$

If f is an eigenfunction of L^2 and L_z, so also is $L_\pm f$

$$L^2(L_\pm f) = L_\pm(L^2 f) = L_\pm(\lambda f) = \lambda(L_\pm f) \tag{4.93}$$

so $L_\pm f$ is an eigenfunction of L^2, with the same eigenvalue λ,

$$L_z(L_\pm f) = (L_z L_\pm - L_\pm L_z)f + L_\pm L_z f = \pm\hbar L_\pm f + L_\pm(\mu f) = (\mu \pm \hbar)(L_\pm f) \tag{4.94}$$

so $L_\pm f$ is an eigenfunction of L_z with the new eigenvalue $\mu \pm \hbar$. For a given value of λ, we obtain a ladder of states, with each "rung" separated from its neighbours by one unit of $\hbar$ in the in the eigenvalue of L_z. To ascend the ladder we apply the raising operator, and to descend, the lowering operator. However, there must be a top rung f_t such that $L_+ f_t = 0$. Let $\hbar l$ be the eigenvalue of L_z at the top rung:

$$L_z f_t = \hbar l f_t; \qquad L^2 f_t = \lambda f_t. \tag{4.95}$$

Now,

$$L_\pm L_\mp = (L_x \pm iL_y)(L_x \mp iL_y) = L_x^2 + L_y^2 \mp i(L_x L_y - L_y L_x) = L^2 - L_z^2 \mp i(i\hbar L_z), \tag{4.96}$$

and rearranging,

$$L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z \tag{4.97}$$

It follows that

$$L^2 f_t = (L_- L_+ + L_z^2 + \hbar L_z) f_t = (0 + \hbar^2 l^2 + \hbar^2 l) f_t = \hbar^2 l(l+1) f_t, \tag{4.98}$$

and hence

$$\lambda = \hbar^2 l(l+1). \tag{4.99}$$

This tells us the eigenvalue of L^2 in terms of the maximum eigenvalue of L_z. Meanwhile, there is also a bottom rung, f_b, such that $L_- f_b = 0$. Let $\hbar\bar{l}$ be the eigenvalue of L_z at this bottom rung:

$$L_z f_b = \hbar\bar{l} f_b; \qquad L^2 f_b = \lambda f_b. \tag{4.100}$$

Now, finding the eigenvalues for L^2:

$$L^2 f_b = (L_+ L_- + L_z^2 - \hbar L_z) f_b = (0 + \hbar^2\bar{l} - \hbar^2\bar{l}) f_b = \hbar^2\bar{l}(\bar{l} - 1) f_b, \tag{4.101}$$

and therefore

$$\lambda = \hbar^2\bar{l}(\bar{l} - 1). \tag{4.102}$$

Since λ is the same for all lowered/raised states, we have $l(l+1) = \bar{l}(\bar{l} - 1)$ so either $\bar{l} = l + 1$ (which is incorrect because the bottom rung can't be higher than the top rung) or else $\bar{l} = -l$. So the eigenvalues of L_z are $m\hbar$ where m goes from $-l$ to $+l$, in N integer steps. In particular, it follows that $l = -l + N$, and hence $l = N/2$, so l must be an *integer* or *half-integer*. The eigenfunctions are therefore characterised by the numbers l and m in the form:

$$\boxed{L^2 f_l^m = \hbar^2 l(l+1) f_l^m; \quad L_z f_l^m = \hbar m f_l^m; \quad l = 0,\ 1/2,\ 1,\ 3/2\ ...; \quad m = -l,\ -l+1,\ ...,\ l.} \tag{4.103}$$

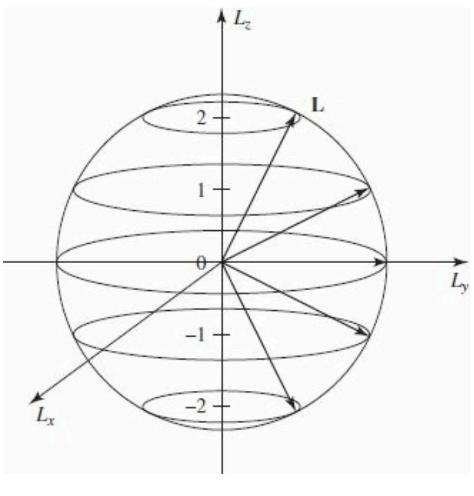


Figure 9: Angular momentum states for $l = 2$

4.3.2 Eigenfunctions

First of all we need to rewrite L_x, L_y, and L_z in spherical coordinates. Now, $\mathbf{L} = -i\hbar(\mathbf{r} \times \boldsymbol{\nabla})$, so:

$$\mathbf{L} = -i\hbar\left[r(\hat{\mathbf{r}} \times \hat{\mathbf{r}})\frac{\partial}{\partial r} + (\hat{\mathbf{r}} \times \hat{\theta})\frac{\partial}{\partial \theta} + (\hat{\mathbf{r}} \times \hat{\phi})\frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\right]. \tag{4.104}$$

$$= -i\hbar\left(\hat{\phi}\frac{\partial}{\partial \theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\right) \tag{4.105}$$

The unit vectors $\hat{\theta}$ and $\hat{\phi}$ can be resolved into their cartesian components:

$$\hat{\theta} = (\cos\theta\cos\phi)\hat{\mathbf{i}} + (\cos\theta\sin\phi)\hat{\mathbf{j}} - (\sin\theta)\hat{\mathbf{k}} \tag{4.106}$$

$$\hat{\phi} = -(\sin\phi)\hat{\mathbf{i}} + (\cos\phi)\hat{\mathbf{j}}. \tag{4.107}$$

Thus

$$\hat{\mathbf{L}} = -i\hbar\left[\left(-\sin\phi\hat{\mathbf{i}} + \cos\phi\hat{\mathbf{j}}\right)\frac{\partial}{\partial \theta} - \left(\cos\theta\cos\phi\hat{\mathbf{i}} + \cos\theta\sin\phi\hat{\mathbf{j}} - \sin\theta\hat{\mathbf{k}}\right)\frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\right]. \tag{4.108}$$

So

$$L_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial \theta} - \cos\phi\cot\theta\frac{\partial}{\partial \phi}\right), \tag{4.109}$$

$$L_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial \theta} - \sin\phi\cot\theta\frac{\partial}{\partial \phi}\right), \tag{4.110}$$

$$L_z = -i\hbar\frac{\partial}{\partial \phi}. \tag{4.111}$$

We shall need the raising and lowering operators:

$$L_\pm = L_x \pm iL_y = -i\hbar\left[(-\sin\phi \pm i\cos\phi)\frac{\partial}{\partial \theta} - (\cos\phi \pm i\sin\phi)\cot\theta\frac{\partial}{\partial \phi}\right]. \tag{4.112}$$

$$= \pm\hbar e^{\pm i\phi}\left(\frac{\partial}{\partial \theta} \pm i\cot\theta\frac{\partial}{\partial \phi}\right) \tag{4.113}$$

From this, we can derive

$$L_+L_- = -\hbar^2\left(\frac{\partial^2}{\partial \theta^2} + \cot\theta\frac{\partial}{\partial \theta} + \cot^2\theta\frac{\partial^2}{\partial \phi^2} + i\frac{\partial}{\partial \phi}\right), \tag{4.114}$$

and hence, from equation 4.97, we have

$$\boxed{L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right].} \tag{4.115}$$

We can now determine $f_l^m(\theta, \phi)$. It's an eigenfunction of L^2, with eigenvalue $\hbar^2 l(l+1)$:

$$L^2 f_l^m = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right]f_l^m = \hbar^2 l(l+1)f_l^m. \tag{4.116}$$

This is actually the angular equation 4.9. And it's also an eigenfunction of L_z, with the eigenvalue $m\hbar$:

$$L_z f_l^m = -i\hbar\frac{\partial}{\partial \phi}f_l^m = \hbar m f_l^m, \tag{4.117}$$

but this is equivalent to the azimuthal equation 4.13. Since we have both the solutions to the azimuthal and angular equations, we know that the eigenfunctions of L^2 and L_z are nothing but the old spherical harmonics! Incidentally, we can use equation 4.115 to represent the spherical Schrödinger equation 4.4 more compactly as:

$$\frac{1}{2mr^2}\left[-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + L^2\right]\psi + V\psi = E\psi. \tag{4.118}$$

There is one final point worth mentioning, the algebraic method using raising/lowering operators permits l and m to take on *half*-integer values (Equation 4.103), whereas the separation of variables method yielded eigenfunctions only for integer values (Equation 4.18). It may seem like half integer angular momentum is pointless but they have profound importance in the spin theory of quantum mechanics.

4.4 Quantum Spin

Elementary particles carry intrinsic angular momentum called spin and extrinsic orbital angular momentum. The algebraic theory of spin is identical to the theory of orbital angular momentum:

$$[S_x, S_y] = i\hbar S_z, \qquad [S_y, S_z] = i\hbar S_x, \qquad [S_z, S_x] = i\hbar S_y. \tag{4.119}$$

It follows as before that the eigenvectors of S^2 and S_z satisfy

$$S^2 \left|s, m\right\rangle = \hbar^2 s(s+1) \left|s, m\right\rangle; \qquad S_z \left|s, m\right\rangle = \hbar m \left|s, m\right\rangle; \tag{4.120}$$

and

$$S_\pm \left|s, m\right\rangle = \hbar\sqrt{s(s+1) - m(m \pm 1)} \left|s, (m \pm 1)\right\rangle, \tag{4.121}$$

where $S_\pm \equiv S_x \pm iS_y$. Note that we have switched to Dirac notation since the eigenstates of spin are not functions. But this time these eigenfunctions are not spherical harmonics since they're not functions of θ and ϕ at all., and there's no reason to exclude the half-integer values of s and m:

$$s = 0,\ \frac{1}{2},\ 1,\ \frac{3}{2}, ...; \qquad m = -s,\ -s+1, ...,\ s-1,\ s. \tag{4.122}$$

Every particle has a specific and unchangeable value of s. By contrast, the orbital angular momentum quantum number l can take on any integer value, and will change from one to another when the system is perturbed.

4.4.1 Spin 1/2

This is the most important case because particles that make up ordinary matter (protons, neutrons, and electrons), as well as all quarks and all leptons. There are just two eigenstates: spin up, $\left|\uparrow\right\rangle = \left|\frac{1}{2}, \frac{1}{2}\right\rangle$, and spin down, $\left|\downarrow\right\rangle = \left|\frac{1}{2}, -\frac{1}{2}\right\rangle$. Using these as basis vectors, the general spin state of a spin-1/2 particle can be represented by a two-element column matrix called a **spinor**:

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_-, \tag{4.123}$$

with $\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ representing spin up and $\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ for spin down. With respect to this basis the spin operators become 2 × 2 matrices, which we can work out by noting their effect on χ_+ and χ_-:

$$S^2\chi_+ = \frac{3}{4}\hbar^2\chi_+ \quad \text{and} \quad S^2\chi_- = \frac{3}{4}\hbar^2\chi_-. \tag{4.124}$$

If we write S^2 as a matrix:

$$S^2 = \begin{pmatrix} c & d \\ e & f \end{pmatrix}, \tag{4.125}$$

then Equation 4.124 says that

$$\begin{pmatrix} c \\ e \end{pmatrix} = \begin{pmatrix} \frac{3}{4}\hbar^2 \\ 0 \end{pmatrix}, \tag{4.126}$$

$$\begin{pmatrix} d \\ f \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{3}{4}\hbar^2 \end{pmatrix}, \tag{4.127}$$

so

$$S^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{4.128}$$

Meanwhile, from

$$S_z\chi_+ = \frac{\hbar}{2}\chi_+, \quad S_z\chi_- = -\frac{\hbar}{2}\chi_-, \tag{4.129}$$

from which it follows that

$$S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{4.130}$$

Meanwhile, from Equation 4.121, says

$$S_+\chi_- = \hbar\chi_+, \quad S_-\chi_+ = \hbar\chi_-, \quad S_+\chi_+ = S_-\chi_- = 0, \tag{4.131}$$

so

$$S_+ = \hbar\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}, \quad S_- = \hbar\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}. \tag{4.132}$$

Now $S_\pm = S_x \pm iS_y$, so $S_x = (1/2)(S_+ + S_-)$ and $S_y = (1/2i)(S_+ - S_-)$, and hence

$$S_x = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}, \quad S_y = \frac{\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}. \tag{4.133}$$

Now S_x, S_y, and S_z carry a factor of $\hbar/2$, it is tidier to write $S = (\hbar/2)\sigma$, where

$$\boxed{\sigma_x \equiv \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}, \quad \sigma_y \equiv \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}, \quad \sigma_z \equiv \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}.} \tag{4.134}$$

These are the **Pauli spin matrices**. Note that S_x, S_y, S_z, and S^2 are all hermitian matrices since the represent observables whereas $S_\pm$ are not - evidently they are not observable.

If you measure S_z on a particle in the general state χ, according to Equation 4.129, you could get $+\hbar/2$ with probability $|a|^2$, or $-\hbar/2$ with probability $|b|^2$, where $|a|^2 + |b|^2 = 1$ (spinor must be normalised). What if instead, you chose to measure S_x? Lets work out the eigenvalues and eigenspinors of S_x:

$$\begin{vmatrix}-\lambda & \hbar/2\\ \hbar/2 & -\lambda\end{vmatrix} = 0 \Longrightarrow \lambda = \pm\frac{\hbar}{2}. \tag{4.135}$$

Now finding the eigenspinors:

$$\pm\frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}\alpha\\ \beta\end{pmatrix} = \pm\frac{\hbar}{2}\begin{pmatrix}\alpha\\ \beta\end{pmatrix} \Longrightarrow \begin{pmatrix}\beta\\ \alpha\end{pmatrix} = \pm\begin{pmatrix}\alpha\\ \beta\end{pmatrix}, \tag{4.136}$$

so $\beta = \pm\alpha$. Evidently the normalised eigenspinors of S_x are

$$\chi_+^{(x)} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ 1\end{pmatrix}, \quad \left(eigenvalue: +\frac{\hbar}{2}\right); \qquad \chi_-^{(x)} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ -1\end{pmatrix}, \quad \left(eigenvalue: -\frac{\hbar}{2}\right). \tag{4.137}$$

As the eigenspinors of a hermitian matrix, they span the space; the generic spinor χ can be expressed as a linear combination of them:

$$\chi = \left(\frac{a+b}{\sqrt{2}}\right)\chi_+^{(x)} + \left(\frac{a-b}{\sqrt{2}}\right)\chi_-^{(x)}. \tag{4.138}$$

If you measure S_x, the probability of getting $+\hbar/2$ is $1/2|a+b|^2$, and the probability of getting $-\hbar/2$ is $1/2|a-b|^2$.

Now we want to construct a matrix S_r, representing the component of spin along an arbitrary direction $\hat{r}$. In spherical coordinates:

$$S_r = S\cdot\hat{r} = S_x\sin\theta\cos\phi + S_y\sin\theta\sin\phi + S_z\cos\theta \tag{4.139}$$

$$= \frac{\hbar}{2}\begin{pmatrix}\cos\theta & e^{-i\phi}\sin\theta\\ e^{i\phi}\sin\theta & -\cos\theta\end{pmatrix} \tag{4.140}$$

The eigenvalues and eigenspinors to this matrix are:

$$\chi_+^{(r)} = \begin{pmatrix}\cos\frac{\theta}{2}\\ e^{i\phi}\sin\frac{\theta}{2}\end{pmatrix}, \quad \left(eigenvalue: +\frac{\hbar}{2}\right); \qquad \chi_-^{(r)} = \begin{pmatrix}e^{-i\phi}\sin\frac{\theta}{2}\\ -\cos\frac{\theta}{2}\end{pmatrix}, \quad \left(eigenvalue: -\frac{\hbar}{2}\right). \tag{4.141}$$

Note $\chi_+^{(z)} = \begin{pmatrix}1\\ 0\end{pmatrix}$, so

$$P_+^{(z)} = |c_+^{(z)}|^2 = \left|\begin{pmatrix}1 & 0\end{pmatrix}\begin{pmatrix}\cos\frac{\theta}{2}\\ e^{i\phi}\sin\frac{\theta}{2}\end{pmatrix}\right|^2 = \cos^2\frac{\theta}{2}. \tag{4.142}$$

4.4.2 Electron in a Magnetic Field

A spinning charged particle constitutes a magnetic dipole which is proportional to its spin, $\mu = \gamma \mathbf{S}$. The proportionality constant, γ, is called the gyromagnetic ratio. When a magnetic dipole is placed within a magnetic field $\mathbf{B}$, it experiences a torque, $\boldsymbol{\mu} \times \mathbf{B}$, which tends to line it up parallel to the field. The energy associated with this torque is:

$$H = -\boldsymbol{\mu} \cdot \mathbf{B}, \tag{4.143}$$

so the Hamiltonian matrix for a spinning charged particle

$$H = -\gamma \mathbf{B} \cdot \mathbf{S}. \tag{4.144}$$

4.4.3 Larmor Precession

Imagine a spin-1/2 particle at rest in a uniform magnetic field, which points in the z-direction, $\mathbf{B} = B_0 \hat{\mathbf{k}}$:

$$H = -\gamma B_0 S_z = -\frac{\gamma B_0 \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{4.145}$$

The eigenstates of H are the same as those of S_z:

$$\chi_+, \quad \text{with energy } E_+ = -(\gamma B_0 \hbar)/2, \tag{4.146}$$

$$\chi_-, \quad \text{with energy } E_- = +(\gamma B_0 \hbar)/2. \tag{4.147}$$

Note that we have defined zero potential energy when the dipole is perpendicular to the magnetic field. Now since the Hamiltonian is time independent, the general solution to the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial \chi}{\partial t} = H\chi, \tag{4.148}$$

can be expressed in terms of the stationary states:

$$\chi(t) = a\chi_+ e^{-iE_+ t/\hbar} + b\chi_- e^{-iE_- t/\hbar} = \begin{pmatrix} a e^{i\gamma B_0 t/2} \\ b e^{-i\gamma B_0 t/2} \end{pmatrix}. \tag{4.149}$$

The constants a and b are determined by the initial condition: $\chi(0) = \begin{pmatrix} a \\ b \end{pmatrix}$.
Lets write $a = \cos(\alpha/2)$ and $b = \sin(\alpha/2)$. Thus

$$\chi(t) = \begin{pmatrix} \cos(\alpha/2) e^{i\gamma B_0 t/2} \\ \sin(\alpha/2) e^{-i\gamma B_0 t/2} \end{pmatrix}. \tag{4.150}$$

To get a feel for what is happening, lets calculate the expectation value of $\mathbf{S} = \chi(t)^\dagger \mathbf{S} \chi(t)$:

$$\langle S_x \rangle = \frac{\hbar}{2} \sin\alpha \cos(\gamma B_0 t), \tag{4.151}$$

$$\langle S_y \rangle = -\frac{\hbar}{2} \sin\alpha \sin(\gamma B_0 t), \tag{4.152}$$

$$\langle S_z \rangle = \frac{\hbar}{2} \cos\alpha. \tag{4.153}$$

Thus $\langle \mathbf{S} \rangle$ is tilted at a constant angle α to the z-axis, and precesses about the field at the Larmor frequency $\omega = \gamma B_0$, just as it would classically (as we expect since expectation values behave classically).

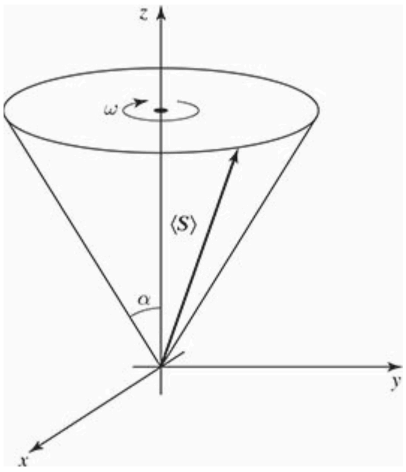


Figure 10: Precession of $\langle \mathbf{S} \rangle$ in a uniform magnetic field.

4.4.4 The Stern-Gerlach Experiment

In an inhomogeneous magnetic field, there is not only a torque, but also a force, on a magnetic dipole:

$$\mathbf{F} = \boldsymbol{\nabla}(\boldsymbol{\mu} \cdot \mathbf{B}). \tag{4.154}$$

This force can be used to separate out particles with a particular spin orientation. We will use a beam of heavy neutral silver atoms: neutral to avoid the Lorentz force and heavy to construct localised wave packets and treat them as classical. The silver atoms are travelling in the y-direction, which passes through a region of static but inhomogeneous magnetic field - say

$$\mathbf{B}(x, y, z) = -\alpha x\hat{\mathbf{i}} + (B_0 + \alpha z)\hat{\mathbf{k}}, \tag{4.155}$$

where B_0 is a strong uniform field and α describes a small deviation from homogeneity. We actually prefer just the z-component of this field but $\boldsymbol{\nabla} \cdot \mathbf{B} = 0$ prevents us from doing so. The force on the atoms is:

$$\mathbf{F} = \gamma\alpha(-S_x\hat{\mathbf{i}} + S_z\hat{\mathbf{k}}). \tag{4.156}$$

But because the Larmor precession about $\mathbf{B_0}$, S_x oscillates rapidly, and averages to zero; the net force is in the z-direction:

$$F_z = \gamma\alpha S_z, \tag{4.157}$$

and the beam is deflected up or down. Classically we'd expect a smear because S_z would not be quantised, but in fact the beam splits into $m = 2s{+}1 = 2$ seperate streams, demonstrating the quantisation of angular momentum. The inner electrons of the silver atom are paired, in such way that their angular momenta cancel. The net spin is simply that of the outermost - unpaired - electron.

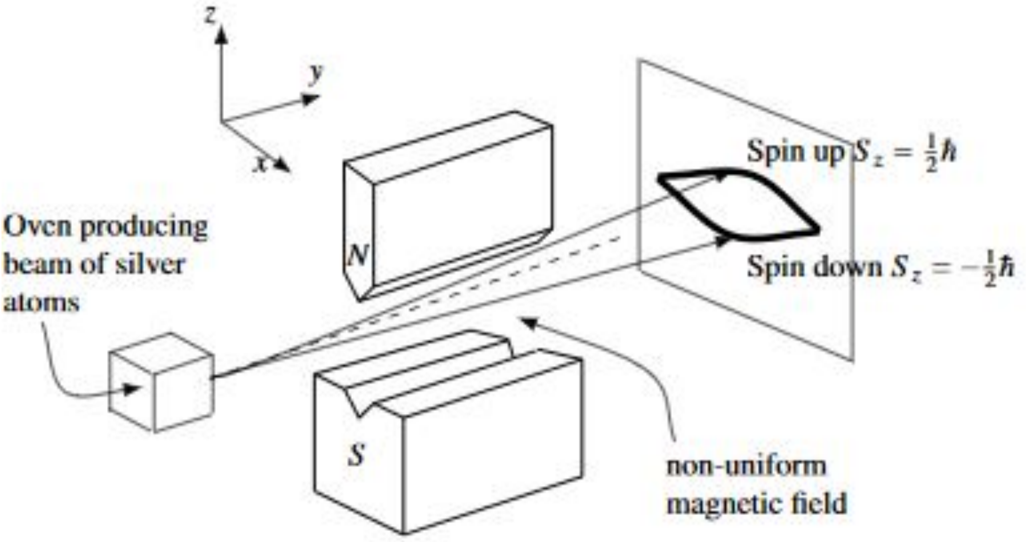


Figure 11: The Stern-Gerlach apparatus

Note that due to the atomic beam being wider than the magnetic field, an elongated shape is produced. If you want to prepare a beam of atoms in a given spin configuration, you pass an unpolarised beam through a Stern-Gerlach magnet, and select the outgoing stream you are interested in. Conversely if you measure the z-component of an atom's spin, you send it through a Stern-Gerlach apparatus, and record which bin it lands in.

4.4.5 Addition of Angular Momenta

Suppose now that we have two particles, with spins s_1 and s_2. Say, the first is in the state $|s_1, m_1\rangle$ and the second in the state $|s_2, m_2\rangle$. We denote the composite state by $|s_1, s_2, m_1, m_2\rangle$:

$$S^{2(1)}\,|s_1, s_2, m_1, m_2\rangle = s_1(s_1+1)\hbar^2\,|s_1, s_2, m_1, m_2\rangle\,, \tag{4.158}$$

$$S^{2(2)}\,|s_1, s_2, m_1, m_2\rangle = s_2(s_2+1)\hbar^2\,|s_1, s_2, m_1, m_2\rangle \tag{4.159}$$

$$S_z^{(1)}\,|s_1, s_2, m_1, m_2\rangle = m_1\hbar\,|s_1, s_2, m_1, m_2\rangle \tag{4.160}$$

$$S_z^{(2)}\,|s_1, s_2, m_1, m_2\rangle = m_2\hbar\,|s_1, s_2, m_1, m_2\rangle\,. \tag{4.161}$$

We need to now find the total angular momentum $\mathbf{S} = \mathbf{S}^{(1)} + \mathbf{S}^{(2)}$, of this system. I.e. the net spin of the combination, s, and the z-component m. The z-component is easy:

$$\begin{aligned} S_z\,|s_1, s_2, m_1, m_2\rangle &= S_z^{(1)}\,|s_1, s_2, m_1, m_2\rangle + S_z^{(2)}\,|s_1, s_2, m_1, m_2\rangle && (4.162)\\ &= \hbar(m_1+m_2)\,|s_1, s_2, m_1, m_2\rangle && (4.163)\\ &= \hbar m\,|s_1, s_2, m_1, m_2\rangle\,, \text{ where } m = m_1+m_2 && (4.164) \end{aligned}$$

But s is much more subtle, consider the case of two spin-1/2 particles - say, the electron and the proton in the ground state of hydrogen. Each can have spin up or spin down, so there are four possibilities:

$$|\uparrow\uparrow\rangle = \left|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right\rangle, \qquad m = 1 \tag{4.165}$$

$$|\uparrow\downarrow\rangle = \left|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}\right\rangle, \qquad m = 0 \tag{4.166}$$

$$|\downarrow\uparrow\rangle = \left|\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}\right\rangle, \qquad m = 0 \tag{4.167}$$

$$|\downarrow\downarrow\rangle = \left|\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}\right\rangle, \qquad m = -1 \tag{4.168}$$

However, this doesn't look right: m is supposed to advance in integer steps, from $-s$ to s, but there is an extra state with $m = 0$. To untangle this problem, we can apply the lowering operator, $S_- = S_-^{(1)} + S_-^{(2)}$ to the state $|\uparrow\uparrow\rangle$ using Equation 4.132:

$$\begin{aligned} S_-\,|\uparrow\uparrow\rangle &= \left(S_-^{(1)}\,|\uparrow\rangle\right)|\uparrow\rangle + |\uparrow\rangle\left(S_-^{(2)}\,|\uparrow\rangle\right) && (4.169)\\ &= (\hbar\,|\downarrow\rangle)\,|\uparrow\rangle + |\uparrow\rangle\,(\hbar\,|\downarrow\rangle) = \hbar(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle) && (4.170) \end{aligned}$$

Evidently, the three states with $s = 1$ (in the notation $|s, m\rangle$) are:

$$s = 1 \quad \text{(triplet)} \quad \begin{cases} |1,1\rangle = |\uparrow\uparrow\rangle \\ |1,0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |1,-1\rangle = |\downarrow\downarrow\rangle \end{cases} \tag{4.171}$$

Meanwhile, the orthogonal state with $m = 0$ carries $s = 0$:

$$s = 0 \quad \text{(singlet)} \quad \Big\{ |0,0\rangle = \tfrac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \tag{4.172}$$

The combination of two spin-1/2 particles can carry a total spin of 1 or 0, depending on whether they occupy the triplet or the singlet configuration. It can be shown that triplet states are eigenvectors of S^2 with eigenvalue $2\hbar^2$, and the singlet is an eigenvector of S^2 with an eigenvalue of 0.

If you combine spins s_1 and s_2, is that you get every spin from $(s_1 + s_2)$ down to $|(s_1 - s_2)|$ in integer steps:

$$\boxed{s = (s_1+s_2),\ (s_1+s_2-1),\ (s_1+s_2-2), ...,\ |s_1-s_2|.} \tag{4.173}$$

The highest spin occurs when the individual spins are parallel to each other, and the lowest occurs when they are antiparallel. For example, if you package together a particle with spin-3/2 with a particle of spin-2, you could get a total spin of 7/2, 5/2, 3/2 or 1/2, depending on the configurations. Another example: If a hydrogen atom is in the state ψ_{nlm}, the net angular momentum of the electron (spin plus orbital) is $l + 1/2$ or $l - 1/2$; if you now throw in spin of the proton, the atom's total angular momentum quantum number is $l + 1$, l, or $l - 1$ where l can be achieved in two distinct ways.

The combined state $|s,m\rangle$ will be some linear combination of the composite states $|s_1,s_2,m_1,m_2\rangle$:

$$|s,m\rangle = \sum_{m_1+m_2=m} C^{s_1,s_2,s}_{m_1,m_2,m} |s_1,s_2,m_1,m_2\rangle \,. \tag{4.174}$$

Since z-components add, the only states that contribute are those for which $m_1+m_2=m$. The constants $C^{s_1,s_2,s}_{m_1,m_2,m}$ are called **Clebsch-Gordan coefficients**.

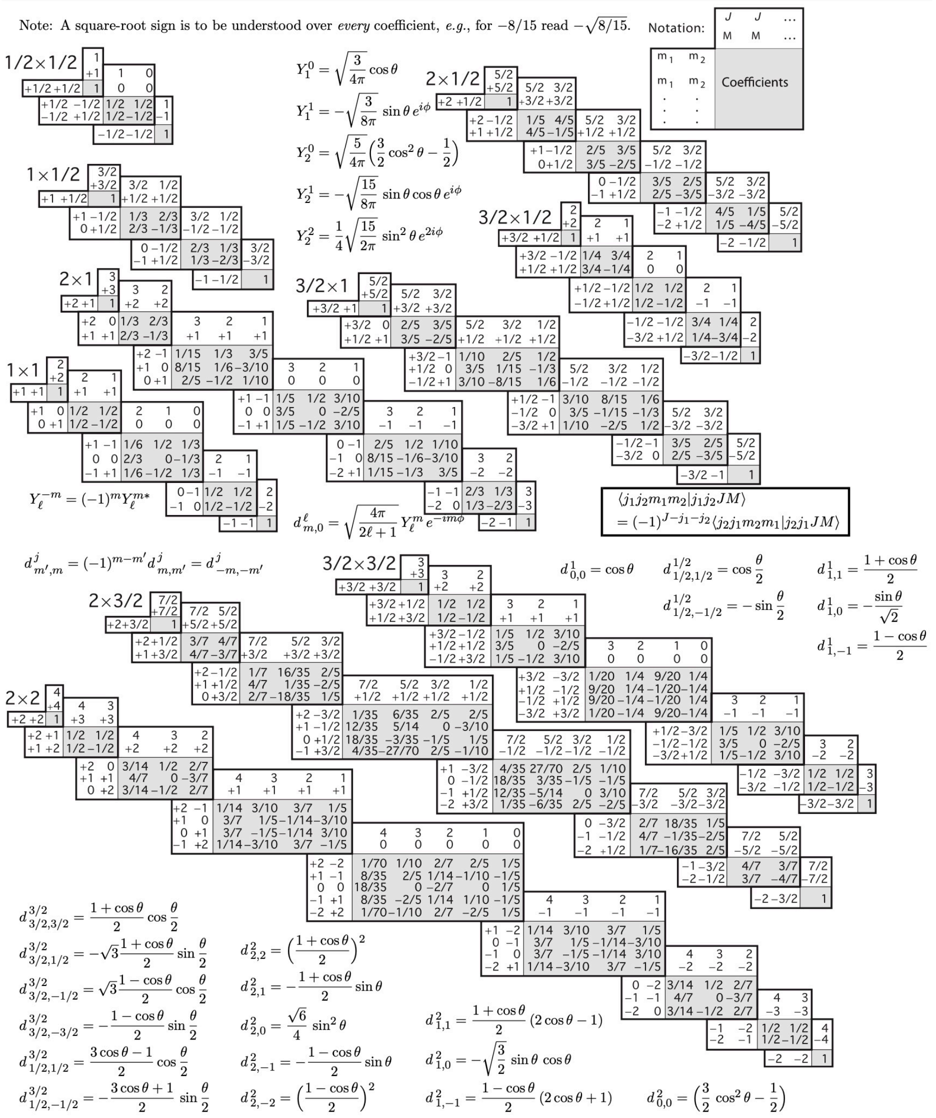


Figure 12: Clebsch-Gordan coefficients

A square root sign is implied for every entry and a minus sign, if present, goes outside the radical. For example, the 2×1 table tells us that

$$|3,0\rangle = \frac{1}{\sqrt{5}}\,|2,1\rangle\,|1,-1\rangle + \sqrt{\frac{3}{5}}\,|2,0\rangle\,|1,0\rangle + \frac{1}{\sqrt{5}}\,|2,-1\rangle\,|1,1\rangle \,. \tag{4.175}$$

$$= \frac{1}{\sqrt{5}}\,|2,1,1,-1\rangle + \sqrt{\frac{3}{5}}\,|2,1,0,0\rangle + \frac{1}{\sqrt{5}}\,|2,1,-1,1\rangle \tag{4.176}$$

This says that if two particles of spin-2 and spin-1 are at rest in a box, and the total spin component is 3, and total z-component is 0, then from Equation 4.120, a measurement of $S_z^{(1)}$ could return the value of $\hbar$ (with probability 1/5), or 0 (with probability 3/5), or $-\hbar$ (with probability 1/5). These tables work the other way around:

$$|s_1,s_2,m_1,m_2\rangle = \sum_s C^{s_1,s_2,s}_{m_1,m_2,m} |s,m\rangle\,, \quad (m=m_1+m_2). \tag{4.177}$$

For example the $3/2\times 1$ tells us that

$$\left|\frac{3}{2},1,\frac{1}{2},0\right\rangle = \sqrt{\frac{3}{5}}\left|\frac{5}{2},\frac{1}{2}\right\rangle + \frac{1}{\sqrt{15}}\left|\frac{3}{2},\frac{1}{2}\right\rangle - \frac{1}{\sqrt{3}}\left|\frac{1}{2},\frac{1}{2}\right\rangle. \tag{4.178}$$

If you put particles of spin-3/2 and spin-1 in the box, and you know that the first has $m_1 = 1/2$ and the second has $m_2 = 0$ (so $m = 1/2$), and you measure the total spin, s, you could get 5/2 (with probability 3/5), or 3/2 (with probability 1/15), or 1/2 (with probability 1/3).

4.5 Electromagnetic Interactions

4.5.1 Minimal Coupling

In classical electrodynamics, the force on a particle of charge q moving with a velocity v through electric and magnetic fields E and B is given by the **Lorentz force law**:

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}). \tag{4.179}$$

Lorentz force cannot be expressed as the gradient of a scalar potential energy function because it is velocity dependent. For this reason, the Schrödinger equation in it's original form (Equation 2.1) cannot accommodate it. But in a more sophisticated form:

$$i\hbar\frac{\partial \Psi}{\partial t} = \hat{H}\Psi, \tag{4.180}$$

there is no problem. The classical Hamiltonian for a particle of charge q and momentum $\mathbf{p}$, in the presence of electromagnetic fields is

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\phi, \tag{4.181}$$

where $\mathbf{A}$ is the vector potential and ϕ is the scalar potential:

$$\mathbf{E} = -\boldsymbol{\nabla}\phi - \frac{\partial \mathbf{A}}{\partial t}, \qquad \mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}. \tag{4.182}$$

Making the standard substitution for momentum, we obtain the Hamiltonian operator

$$\hat{H} = \frac{1}{2m}(-i\hbar\boldsymbol{\nabla} - q\mathbf{A})^2 + q\phi, \tag{4.183}$$

and the Schrödinger equation becomes

$$\boxed{i\hbar\frac{\partial \Psi}{\partial t} = \left[\frac{1}{2m}(-i\hbar\boldsymbol{\nabla} - q\mathbf{A})^2 + q\phi\right]\Psi.} \tag{4.184}$$

This is the quantum implementation of the Lorentz force law; it is sometimes called the minimal coupling rule.

4.5.2 The Aharonov-Bohm Effect

Classical electrodynamics is invariant under gauge transformations:

$$\phi' \equiv \phi - \frac{\partial \Lambda}{\partial t}, \qquad \mathbf{A}' \equiv \mathbf{A} + \boldsymbol{\nabla}\Lambda. \tag{4.185}$$

In quantum mechanics the potentials play a more direct role, and it is of interest to ask whether quantum mechanics remains gauge invariant. The Schrödinger equation (Equation 4.184) remains invariant under the transformation

$$\Psi' \equiv e^{iq\Lambda/\hbar}\Psi \tag{4.186}$$

with the gauge-transformed potentials ϕ' and $\mathbf{A}'$. Since Ψ' only differs by a phase factor, it represents the same physical state, and in this sense quantum mechanics is gauge-invariant. For a long time it was taken for granted that there could be no electromagnetic influences in regions where E and B are zero any more than there can be in the classical theory. But in 1959 Aharonov and Bohm showed that the vector potential can affect the quantum behaviour of a charged particle, even when the particle is confined to a region where the field itself is zero.

Imagine a particle constrained to move in a circle of radius b. Along the axis runs a solenoid of radius $a < b$, carrying a steady electric current I. If the solenoid is extremely long, the magnetic field inside it is uniform, and the field outside is zero.

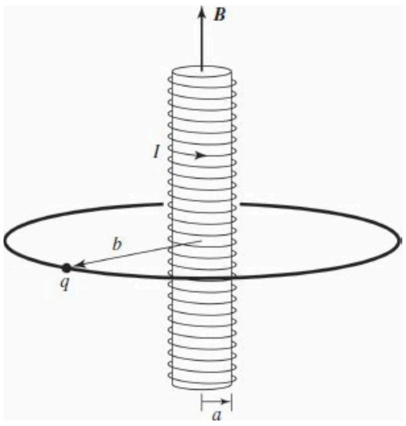


Figure 13: Charged bead on a circular ring through which a solenoid passes.

The vector potential outside the solenoid is not zero; in fact, using $\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$ and integrating with respect to d$\mathbf{a}$, we can show that

$$\mathbf{A} = \frac{\Phi}{2\pi r}\hat{\phi}, \quad (r > a), \tag{4.187}$$

where $\Phi = \pi a^2 B$ is the magnetic flux through the solenoid. Meanwhile, the solenoid itself is uncharged, so the scalar potential ϕ is zero. From Equation 4.183, we have

$$\hat{H} = \frac{1}{2m}\left[-\hbar^2\boldsymbol{\nabla}^2 + q^2A^2 + 2i\hbar q\mathbf{A}\cdot\boldsymbol{\nabla}\right], \tag{4.188}$$

and since the wave function is constrained to move along the wire, we can use the substitutions $\theta = \pi/2$, $r = b$, so $\boldsymbol{\nabla} \to \left(\hat{\phi}/b\right)(\mathrm{d}/\mathrm{d}\phi)$ using cylindrical coordinates. Therefore

$$\frac{1}{2m}\left[-\frac{\hbar^2}{b^2}\frac{\mathrm{d}^2}{\mathrm{d}\phi^2} + \left(\frac{q\Phi}{2\pi b}\right)^2 + i\frac{\hbar q\Phi}{\pi b^2}\frac{\mathrm{d}}{\mathrm{d}\phi}\right]\psi(\phi) = E\psi(\phi). \tag{4.189}$$

This is a linear differential equation with constant coefficients:

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\phi^2} - 2i\beta\frac{\mathrm{d}\psi}{\mathrm{d}\phi} + \epsilon\psi = 0, \tag{4.190}$$

where

$$\beta \equiv \frac{q\Phi}{2\pi\hbar} \quad \text{and} \quad \epsilon \equiv \frac{2mb^2E}{\hbar^2} - \beta^2. \tag{4.191}$$

Solutions are of the form

$$\psi = Ae^{i\lambda\phi}, \tag{4.192}$$

with

$$\lambda = \beta \pm \sqrt{\beta^2 + \epsilon} = \beta \pm \frac{b}{\hbar}\sqrt{2mE}. \tag{4.193}$$

Continuity of $\psi(\phi)$, at $\phi = 2\pi$, requires that λ be an integer:

$$\beta \pm \frac{b}{\hbar}\sqrt{2mE} = n, \tag{4.194}$$

and it follows that

$$E_n = \frac{\hbar^2}{2mb^2}\left(n - \frac{q\Phi}{2\pi\hbar}\right)^2 = \frac{\hbar^2}{2mb^2}\left(n - \frac{qa^2B}{2\hbar}\right)^2, \quad n \in \mathbb{Z}. \tag{4.195}$$

Positive n, representing a particle traveling in the same direction as the current in the solenoid, has a somewhat lower energy (assuming $q > 0$) than negative n, describing a particle travelling in the opposite direction. More importantly, the allowed energies for the particle clearly depend on the field inside the solenoid, even though the field at the location of the particle is zero!

More generally, suppose a particle is moving through a region where $\mathbf{B} = 0$ (so $\boldsymbol{\nabla} \times \mathbf{A} = 0$), but $\mathbf{A}$ itself is not. The Schrödinger equation,

$$\left[\frac{1}{2m}(-i\hbar\boldsymbol{\nabla} - q\mathbf{A})^2\right]\Psi = i\hbar\frac{\partial\Psi}{\partial t}, \tag{4.196}$$

can be simplified by writing

$$\Psi = e^{ig}\Psi', \tag{4.197}$$

where

$$g(\mathbf{r}) \equiv \frac{q}{\hbar}\int_O^{\mathbf{r}} \mathbf{A}(\mathbf{r}') \cdot \mathrm{d}\mathbf{r}', \tag{4.198}$$

and O is some arbitrarily chosen reference point. (Note that this definition makes sense only when $\boldsymbol{\nabla} \times \mathbf{A} = 0$ throughout the region in question - otherwise the line integral would depend on the path taken from O to $\mathbf{r}$, and hence would not define a function of $\mathbf{r}$.) In terms of Ψ', the gradient of Ψ is

$$\boldsymbol{\nabla}\Psi = e^{ig}(i\boldsymbol{\nabla}g)\Psi' + e^{ig}\big(\boldsymbol{\nabla}\Psi'\big), \tag{4.199}$$

but $\boldsymbol{\nabla}g = (q/\hbar)\mathbf{A}$, so

$$(-i\hbar\boldsymbol{\nabla} - q\mathbf{A})\Psi = -i\hbar e^{ig}\boldsymbol{\nabla}\Psi', \tag{4.200}$$

and it follows that

$$(-i\hbar\boldsymbol{\nabla} - q\mathbf{A})^2\Psi = -\hbar^2 e^{ig}\nabla^2\Psi'. \tag{4.201}$$

Putting this into Equation 4.196, and cancelling the common factor of e^{ig}, we are left with

$$-\frac{\hbar^2}{2m}\nabla^2\Psi' = i\hbar\frac{\partial\Psi'}{\partial t}. \tag{4.202}$$

Evidently Ψ' solves the Schrödinger equation without $\mathbf{A}$. If we want to correct for the presence of the curl-free vector potential, we just add on the phase factor e^{ig}. Aharonov and Bohm proposed an experiment in which a beam of electrons is split in two, and they pass either side of a long solenoid before recombining.

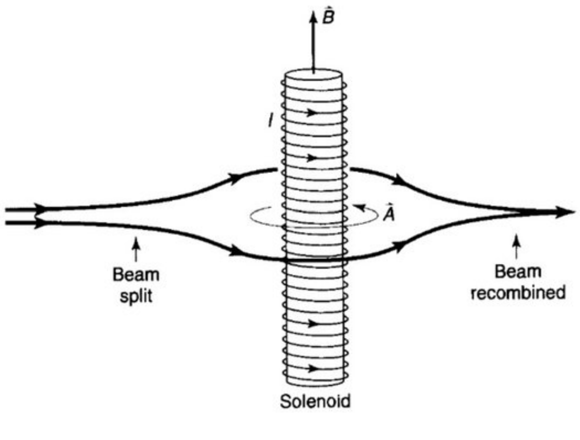


Figure 14: The Aharonov-Bohm effect: Electron beam splits around solenoid.

The electron beam experiences $\mathbf{B} = 0$, but $\mathbf{A}$ is not zero, and the two beams arrive with different phases:

$$g = \frac{q}{\hbar}\int \mathbf{A} \cdot \mathrm{d}\mathbf{r} = \frac{q\Phi}{2\pi\hbar}\int \left(\frac{1}{r}\hat{\phi}\right) \cdot \left(r\hat{\phi}\,\mathrm{d}\phi\right) = \pm\frac{q\Phi}{2\hbar}. \tag{4.203}$$

The plus sign applies to the electrons travelling in the same direction as $\mathbf{A}$ - the same direction of current in the solenoid. The phase shift is proportional to the magnetic field inside of the solenoid.

$$\text{phase difference} = \frac{q\Phi}{\hbar} = \frac{q\pi a^2 B}{\hbar}. \tag{4.204}$$

The phase shift can be measured using the interference pattern on a screen. Note, however, this does not make $\mathbf{A}$ itself measurable. Only the enclosed flux comes into the final answer, and quantum mechanics remains gauge invariant. Unlike classical mechanics, the vector potential is of physical significance in quantum mechanics.

5 Identical Particles

5.1 Two Particle Systems

The state for a two-particle system is a function of the coordinates of particle one ($\mathbf{r_1}$), the coordinates of particle two ($\mathbf{r_2}$), and the time, t:

$$\Psi(\mathbf{r_1}, \mathbf{r_2}, t). \tag{5.1}$$

Its time evolution is determined by the Schrödinger equation:

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi, \tag{5.2}$$

where H is the Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\mathbf{r_1}, \mathbf{r_2}, t). \tag{5.3}$$

The statistical interpretation carries over:

$$|\Psi(\mathbf{r_1}, \mathbf{r_2}, t)|^2 \, \mathrm{d}^3\mathbf{r_1} \, \mathrm{d}^3\mathbf{r_2} \, , \tag{5.4}$$

is the probability of finding particle 1 in the volume $\mathrm{d}^3\mathbf{r_1}$ and particle 2 in the volume $\mathrm{d}^3\mathbf{r_2}$. As always, this needs to be normalised:

$$\int |\Psi(\mathbf{r_1}, \mathbf{r_2}, t)|^2 \, \mathrm{d}^3\mathbf{r_1} \, \mathrm{d}^3\mathbf{r_2} = 1. \tag{5.5}$$

For time-independent potentials, we obtain a complete set of solutions by separation of variables:

$$\Psi(\mathbf{r_1}, \mathbf{r_2}, t) = \psi(\mathbf{r_1}, \mathbf{r_2})e^{-iEt/\hbar}, \tag{5.6}$$

where the spatial wave function (ψ) satisfies the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi - \frac{\hbar^2}{2m_2}\nabla_2^2\psi + V\psi = E\psi, \tag{5.7}$$

and E is the total energy of the system. In general, solving this equation is difficult, but two special cases can be reduced to one-particle problems:

1. **Noninteracting particles**. Consider two noninteracting particles that are each subject to some external force. E.g. attached to two different springs.

   $$V(\mathbf{r_1}, \mathbf{r_2}) = V_1(\mathbf{r_1}) + V_2(\mathbf{r_2}), \tag{5.8}$$

   In that case Equation 5.7 can be solved using separation of variables:

   $$\psi(\mathbf{r_1}, \mathbf{r_2}) = \psi_a(\mathbf{r_1})\psi_b(\mathbf{r_2}). \tag{5.9}$$

   Plugging this equation into Equation 5.7, we find two equations that tell us ψ_a and ψ_b each satisfy the one-particle Schrödinger equation:

   $$-\frac{\hbar^2}{2m_{1,2}}\nabla_{1,2}^2\psi_{a,b}(\mathbf{r_{1,2}}) + V_{1,2}(\mathbf{r_{1,2}})\psi_{a,b}(\mathbf{r_{1,2}}) = E_{a,b}\psi_{a,b}(\mathbf{r_{1,2}}). \tag{5.10}$$

   In this case the two-particle wave function is:

   $$\begin{aligned} \Psi(\mathbf{r_1}, \mathbf{r_2}, t) &= \psi_a(\mathbf{r_1})\psi_b(\mathbf{r_2})e^{-i(E_a+E_b)t/\hbar} && (5.11) \\ &= \left(\psi_a(\mathbf{r_1})e^{-iE_at/\hbar}\right)\left(\psi_b(\mathbf{r_2})e^{-iE_bt/\hbar}\right) = \Psi_a(\mathbf{r_1}, t)\Psi_b(\mathbf{r_2}, t), && (5.12) \end{aligned}$$

   we can say that particle 1 is in state a, and particle 2 is in state b. Any linear combination of such solutions will also satisfy the (time-dependent) Schrödinger equation:

   $$\Psi(\mathbf{r_1}, \mathbf{r_2}, t) = \frac{3}{5}\Psi_a(\mathbf{r_1}, t)\Psi_b(\mathbf{r_2}, t) + \frac{4}{5}\Psi_c(\mathbf{r_1}, t)\Psi_d(\mathbf{r_2}, t). \tag{5.13}$$

   In this case each particle's state depends on the other. If you measured the energy of particle 1, you might get E_a (with probability 9/25), in which case the energy of particle 2 is definitely E_b. These two particles are **entangled**. An entangled state is one that cannot be written as a product of single-particle states.

2. **Central potentials**. Suppose the particles only interact via a potential that depends on their separation: $V(\mathbf{r_1},\mathbf{r_2}) \to V(|\mathbf{r_1}-\mathbf{r_2}|)$. The hydrogen atom would be an example, if you include the motion of the proton. In this case the two-body problem reduces to an equivalent one-body problem. In general, two particles will be subjected to both external forces and to mutual interactions which makes analysis more complicated. E.g. think of the two electrons in a helium atom: each feels the Coulomb attraction of the nucleus (charge $2e$), and at the same time they repel each other:

$$V(\mathbf{r_1},\mathbf{r_2}) = \frac{1}{4\pi\epsilon_0}\left(-\frac{2e^2}{|\mathbf{r_1}|}-\frac{2e^2}{|\mathbf{r_2}|}+\frac{e^2}{|\mathbf{r_1}-\mathbf{r_2}|}\right). \tag{5.14}$$

5.1.1 Bosons and Fermions

Suppose we have two noninteracting particles, particle 1 is in state ψ_a and particle 2 is in ψ_b. The wave function describing this system would be

$$\psi(\mathbf{r_1},\mathbf{r_2}) = \psi_a(\mathbf{r_1})\psi_b(\mathbf{r_2}). \tag{5.15}$$

This assumes that the particles are distinguishable because otherwise it wouldn't make sense to claim that particle 1 is in state ψ_a and particle 2 is in ψ_b. Quantum mechanics neatly accommodates the existence of particles that are indistinguishable in principle: We simply construct a wave function that is noncommittal as to which particle is in which state. There are two ways to do this:

$$\psi_\pm(\mathbf{r_1},\mathbf{r_2}) = A[\psi_a(\mathbf{r_1})\psi_b(\mathbf{r_2}) \pm \psi_b(\mathbf{r_1})\psi_a(\mathbf{r_2})], \tag{5.16}$$

the theory admits two kinds of identical particles: **bosons** (the plus sign), and **fermions** (the minus sign). Boson states are symmetric under the interchange $\psi_+(\mathbf{r_1},\mathbf{r_2}) = \psi_+(\mathbf{r_2},\mathbf{r_1})$; fermion states are antisymmetric under this interchange, $\psi_-(\mathbf{r_1},\mathbf{r_2}) = -\psi_-(\mathbf{r_2},\mathbf{r_1})$. It so happens that

$$\begin{cases}\text{all particles with integer spin are bosons, and}\\ \text{all particles with half integer spin are fermions.}\end{cases} \tag{5.17}$$

It follows that two identical fermions (e.g. two electrons) cannot occupy the same state. If $\psi_a = \psi_b$, then

$$\psi_-(\mathbf{r_1},\mathbf{r_2}) = A[\psi_a(\mathbf{r_1})\psi_a(\mathbf{r_2}) - \psi_a(\mathbf{r_1})\psi_a(\mathbf{r_2})] = 0, \tag{5.18}$$

and we are left with no wave function at all. This is the famous **Pauli exclusion principle**. Note that we are neglecting the spin, for example if the two fermions were in the same spin state.

Suppose we have two non-interacting particles, both of mass m, in the infinite square well. The one-particle states are

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right), \qquad E_n = n^2K \tag{5.19}$$

where $K \equiv \pi^2\hbar^2/2ma^2$. If the particles are distinguishable, with particle 1 in state n_1 and particle 2 in state n_2, the composite wave function is a simple product:

$$\psi_{n_1,n_2}(x_1,x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2), \qquad E_{n_1,n_2} = \left(n_1^2+n_2^2\right)K. \tag{5.20}$$

For example, the ground state is

$$\psi_{1,1} = \frac{2}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right), \qquad E_{1,1} = 2K; \tag{5.21}$$

the first excited state is doubly degenerate:

$$\psi_{1,2} = \frac{2}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{2\pi x_2}{a}\right), \qquad E_{1,2} = 5K; \tag{5.22}$$

$$\psi_{2,1} = \frac{2}{a}\sin\left(\frac{2\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right), \qquad E_{2,1} = 5K; \tag{5.23}$$

and so on. If the two particles are identical bosons, the ground state is unchanged, but the first excited state is nondegenerate:

$$\psi = \frac{\sqrt{2}}{a}\left[\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{2\pi x_2}{a}\right)+\sin\left(\frac{2\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right)\right], \qquad E = 5K. \tag{5.24}$$

And if the particles are identical fermions, there is no state with energy $2K$; the ground state is

$$\psi = \frac{\sqrt{2}}{a}\left[\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{2\pi x_2}{a}\right)-\sin\left(\frac{2\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right)\right], \qquad E = 5K. \tag{5.25}$$

5.1.2 Exchange Forces

Lets investigate what the symmetrisation requirement (Equation 5.16) actually does. Consider particle 1 is in state $\psi_a(x)$, and the other is in state $\psi_b(x)$, and these two states are orthogonal and normalised. If the two particles are distinguishable, then the combined wave function is

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2); \tag{5.26}$$

if they are identical bosons, the composite wave function is

$$\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)]; \tag{5.27}$$

and if they are identical fermions, it is

$$\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)] \tag{5.28}$$

Lets calculate the expectation value of the square of the separation distance between the two particles,

$$\left\langle (x_1 - x_2)^2 \right\rangle = \left\langle x_1^2 \right\rangle + \left\langle x_2^2 \right\rangle - 2\left\langle x_1 x_2 \right\rangle. \tag{5.29}$$

1. **Case 1: Distinguishable particles.** For the wave function in Equation 5.26,

$$\left\langle x_1^2 \right\rangle = \int x_1^2 |\psi_a(x_1)|^2 \, \mathrm{d}x_1 \int |\psi_b(x_2)|^2 \, \mathrm{d}x_2 = \left\langle x^2 \right\rangle_a, \tag{5.30}$$

$$\left\langle x_2^2 \right\rangle = \int |\psi_a(x_1)|^2 \, \mathrm{d}x_1 \int x_2^2 |\psi_b(x_2)|^2 \, \mathrm{d}x_2 = \left\langle x^2 \right\rangle_b, \tag{5.31}$$

$$\left\langle x_1 x_2 \right\rangle = \int x_1^2 |\psi_a(x_1)|^2 \, \mathrm{d}x_1 \int x_2^2 |\psi_b(x_2)|^2 \, \mathrm{d}x_2 = \left\langle x \right\rangle_a \left\langle x \right\rangle_b, \tag{5.32}$$

Therefore, from Equation 5.29,

$$\left\langle (x_1 - x_2)^2 \right\rangle_d = \left\langle x^2 \right\rangle_a + \left\langle x^2 \right\rangle_b - 2\left\langle x \right\rangle_a \left\langle x \right\rangle_b. \tag{5.33}$$

2. **Case 2: Identical particles.** For the wave function in Equation 5.16, we have

$$\left\langle x_1^2 \right\rangle = \int \psi_\pm^*(x_1, x_2) x_1^2 \psi_\pm(x_1, x_2) \, \mathrm{d}x_1 \, \mathrm{d}x_2 \tag{5.34}$$

$$= \frac{1}{2}\left[\int x_1^2 |\psi_a(x_1)^2| \, \mathrm{d}x_1 \int |\psi_b(x_2)|^2 \, \mathrm{d}x_2\right] \tag{5.35}$$

$$+ \int x_1^2 |\psi_b(x_1)|^2 \, \mathrm{d}x_1 \int |\psi_a(x_2)|^2 \, \mathrm{d}x_2 \tag{5.36}$$

$$\pm \int x_1^2 \psi_a(x_1)^* \psi_b(x_1) \, \mathrm{d}x_1 \int \psi_b(x_2)^* \psi_a(x_2) \, \mathrm{d}x_2 \tag{5.37}$$

$$\pm \int x_1^2 \psi_b(x_1)^* \psi_a(x_1) \, \mathrm{d}x_1 \int \psi_a(x_2)^* \psi_b(x_2) \, \mathrm{d}x_2 \tag{5.38}$$

$$= \frac{1}{2}\left[\left\langle x^2 \right\rangle_a + \left\langle x^2 \right\rangle_b \pm 0 \pm 0\right] = \frac{1}{2}\left(\left\langle x^2 \right\rangle_a + \left\langle x^2 \right\rangle_b\right). \tag{5.39}$$

Similarly,

$$\left\langle x_2^2 \right\rangle = \frac{1}{2}\left(\left\langle x^2 \right\rangle_b + \left\langle x^2 \right\rangle_a\right), \tag{5.40}$$

so $\left\langle x_1^2 \right\rangle = \left\langle x_2^2 \right\rangle$ which makes sense because the particles are identical. Now

$$\left\langle x_1 x_2 \right\rangle = \int \psi_\pm^*(x_1, x_2) x_1 x_2 \psi_\pm(x_1, x_2) \, \mathrm{d}x_1 \, \mathrm{d}x_2 \tag{5.41}$$

$$= \frac{1}{2}\left[\int x_1 |\psi_a(x_1)^2| \, \mathrm{d}x_1 \int x_2 |\psi_b(x_2)|^2 \, \mathrm{d}x_2\right] \tag{5.42}$$

$$+ \int x_1 |\psi_b(x_1)|^2 \, \mathrm{d}x_1 \int x_2 |\psi_a(x_2)|^2 \, \mathrm{d}x_2 \tag{5.43}$$

$$\pm \int x_1^2 \psi_a(x_1)^* \psi_b(x_1) \, \mathrm{d}x_1 \int \psi_b(x_2)^* \psi_a(x_2) \, \mathrm{d}x_2 \tag{5.44}$$

$$\pm \int x_1 \psi_b(x_1)^* \psi_a(x_1) \, \mathrm{d}x_1 \int x_2 \psi_a(x_2)^* \psi_b(x_2) \, \mathrm{d}x_2 \tag{5.45}$$

$$= \frac{1}{2}\left(\left\langle x \right\rangle_a \left\langle x \right\rangle_b + \left\langle x \right\rangle_b \left\langle x \right\rangle_a \pm \left\langle x \right\rangle_{ab} \left\langle x \right\rangle_{ba} \pm \left\langle x \right\rangle_{ba} \left\langle x \right\rangle_{ab}\right) \tag{5.46}$$

$$= \left\langle x \right\rangle_a \left\langle x \right\rangle_b \pm |\left\langle x \right\rangle_{ab}|^2, \tag{5.47}$$

where

$$\langle x \rangle_{ab} \equiv \int x\psi_a(x)^*\psi_b(x)\,\mathrm{d}x\,. \tag{5.48}$$

Therefore, from equation 5.29:

$$\left\langle (x_1 - x_2)^2 \right\rangle_{\pm} = \left\langle x^2 \right\rangle_A + \left\langle x^2 \right\rangle_b - 2\left\langle x \right\rangle_a \left\langle x \right\rangle_b \mp 2|\langle x \rangle_{ab}|^2. \tag{5.49}$$

Comparing the equations for the distinguishable particles and identical particles, we see that the difference resides in the additional final term:

$$\left\langle (\Delta x)^2 \right\rangle_{\pm} = \left\langle (\Delta x)^2 \right\rangle_{d} \mp 2|\langle x \rangle_{ab}|^2; \tag{5.50}$$

identical bosons tend to be closer together, and identical fermions are further apart, than distinguishable particles in the same two states. Notice that $\langle x \rangle_{ab}$ (Equation 5.48) vanishes in regions where the two wave functions do not overlap. In these regions, it's not necessary to antisymmetrise the wave function. Therefore, it is okay to pretend that electrons with non-overlapping wave functions are distinguishable.

In the case of overlapping wave functions, $\langle x \rangle_{ab} \neq 0$. According to Equation 5.50, the system behaves as though there were a ”force of attraction” between identical bosons, and a ”force of repulsion” between identical fermions. We call this an **exchange force**, although it's not really a force at all - no physical agency is pushing on the particles; rather, it is a purely geometrical consequence of the symmetrisation requirement. It is also a strictly quantum mechanical phenomenon with no classical counterpart.

5.1.3 Spin

The complete state of an electron includes not only its position wave function, but also a spinor, describing the orientation of its spin:

$$\psi(\mathbf{r})\chi. \tag{5.51}$$

In a two-particle state,

$$\psi(\mathbf{r_1}, \mathbf{r_2})\chi(1, 2) \tag{5.52}$$

it is the whole thing, not just the spatial part, that needs to be antisymmetric with respect to exchange

$$\psi(\mathbf{r_1}, \mathbf{r_2})\chi(1, 2) = -\psi(\mathbf{r_2}, \mathbf{r_1})\chi(2, 1). \tag{5.53}$$

Now, looking back at the composite spin states (Equations 4.171 and 4.172) reveals that the singlet combination is antisymmetric (and hence would need to be joined with a symmetric spatial function), whereas the three triplet states are all symmetric (and would require an antisymmetric spatial function). Thus the Pauli principle actually allows two electrons in a given position state, as long as their spins are in the singlet configuration (but not in the same position state and in the same spin state).

5.2 Atoms

A neutral atom, of atomic number Z, consists of a heavy nucleus, with electric charge Ze, surrounded by Z electrons. The Hamiltonian for this system is

$$\hat{H} = \sum_{j=1}^{Z} \left\{ -\frac{\hbar^2}{2m}\nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0}\right)\frac{Ze^2}{r_j} \right\} + \frac{1}{2}\left(\frac{1}{4\pi\epsilon_0}\right)\sum_{j\neq k}^{Z} \frac{e^2}{|\mathbf{r_j} - \mathbf{r_k}|}. \tag{5.54}$$

The first term represents the kinetic plus potential energy of the jth electron in the electric field of the nucleus; the second sum is the potential energy associated with the mutual repulsion of the electrons (the factor of 1/2 avoids double counting). The problem now is to solve the Schrödinger equation,

$$\hat{H}\psi = E\psi, \tag{5.55}$$

for the wave function $\psi(\mathbf{r_1}, \mathbf{r_2}, ..., \mathbf{r_z})$. Unfortunately, the Schrödinger equation with this Hamiltonian cannot be solved exactly, except for the simplest case, $Z = 1$. In practice, one must resort to approximation methods. For now we're going to sketch out the qualitative features of the solutions, obtained by neglecting electron repulsion.

5.2.1 Helium

The Hamiltonian for helium is

$$\hat{H} = \left\{ -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r_1} - \mathbf{r_2}|}, \tag{5.56}$$

which consists of two hydrogenic Hamiltonians (with nuclear charge $2e$), one for electron 1 and one for electron 2. If we ignore the term regarding the repulsion of the electrons, then the Schrödinger equation separates, and the solutions can be written as products of hydrogen wave functions:

$$\psi(\mathbf{r_1}, \mathbf{r_2}) = \psi_{nlm}(\mathbf{r_1})\psi_{n'l'm'}(\mathbf{r_2}), \tag{5.57}$$

with only half the Bohr radius, and four times the Bohr energies. The total energy would be

$$E = 4(E_n + E_{n'}), \tag{5.58}$$

where $E_n = -13.6/n^2$ eV. In particular, the ground state would be

$$\psi_0(\mathbf{r_1}, \mathbf{r_2}) = \psi_{100}(\mathbf{r_1})\psi_{100}(\mathbf{r_2}) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}, \tag{5.59}$$

where the extra factors come from the adjustments mentioned previously. The energy of the grounds state would be

$$E_0 = 8(-13.6\text{eV}) = -109\text{eV}. \tag{5.60}$$

Because ψ_0 is a symmetric function, the spin state has to be antisymmetric, so the ground state of helium should be a singlet configuration, with spins oppositely aligned. The excited states of helium consist of one electron in the hydrogenic ground state, and the other in an excited state:

$$\psi_{nlm}\psi_{100}. \tag{5.61}$$

If you try put both electrons in excited states, one immediately drops to the ground state, releasing enough energy to knock the other one into the continuum ($E > 0$), leaving you with a helium ion and a free electron.

$$C = \left[\frac{(1-r)^n - 1}{r} \right] \tag{5.62}$$