

Quantum Mechanics Review Sheet

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Physical background

Photoelectric effect. Electrons in atoms and line spectra. Particle diffraction. [1]

Schrödinger equation and solutions

De Broglie waves. Schrödinger equation. Superposition principle. Probability interpretation, density and current. [2]

Stationary states. Free particle, Gaussian wave packet. Motion in 1-dimensional potentials, parity. Potential step, square well and barrier. Harmonic oscillator. [4]

Observables and expectation values

Position and momentum operators and expectation values. Canonical commutation relations. Uncertainty principle. [2]

Observables and Hermitian operators. Eigenvalues and eigenfunctions. Formula for expectation value. [2]

Hydrogen atom

Spherically symmetric wave functions for spherical well and hydrogen atom.

Orbital angular momentum operators. General solution of hydrogen atom. [5]

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1 Schrödinger Equation and Wavefunctions

Biggest difference between classical and quantum physics: You can't be sure of anything at any time. Everything is formulated in probability. The probability of a particle being in $[a, b]$ is $\int_a^b |\psi(x)|^2 dx$, where $\psi(x)$ is its *wavefunction*. Here is a non-exhaustive list of basic principles that are good to know:

- To calculate the probability, we need to normalize the wavefunctions so that the square of it is actually a probability distribution. But we wouldn't do it otherwise because it just involves fiddling with constants. However, we would like to work for *normalizable* wavefunctions, or those that satisfy:

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx < \infty.$$

Because if they don't, we are in normalization trouble.

- Equations in quantum mechanics are linear, so any linear combination of solutions is a solution.
- In quantum Mechanics, we conduct everything in operators that operate on the wavefunction, which contain all the information. Important ones are:

position	$\hat{x} = x$	$\hat{x}\psi = x\psi(x)$
momentum	$\hat{p} = -i\hbar \frac{\partial}{\partial x}$	$\hat{p}\psi = -i\hbar\psi'(x)$
energy	$H = \frac{\hat{p}^2}{2m} + V(\hat{x})$	$H\psi = -\hbar^2 \frac{\partial^2}{\partial x^2} \psi + V(x)\psi(x)$

- An observable corresponding to an operator is *definite* if and only if it is an eigenvalue of the operator. For example, the particle has energy E is and only if $H\psi = E\psi$. Otherwise, it follows a probability distribution.

Now we introduce the time independent/dependent Schrödinger equation:

Definition (Schrödinger equation). The *time-independent Schrödinger equation* (T-ID SE) is the energy eigenvalue equation

$$H\psi = E\psi \quad \Leftrightarrow \quad -\frac{\hbar^2}{2m}\psi'' + V(x)\psi = E\psi.$$

The time-dependent Schrödinger equation (T-D SE) is:

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

Where we have written the wavefunction as Ψ .

Then we can use separation technique to find a special class of time-dependent wavefunctions, namely $\Psi(x, t) = \psi(x)T(t)$ where $\psi(x)$ satisfy the T-ID SE, which are called stationary states:

Definition (Stationary state). A *stationary state* is a state of the form

$$\Psi(x, t) = \psi(x) \exp\left(-\frac{iEt}{\hbar}\right).$$

where $\psi(x)$ is an eigenfunction of the Hamiltonian with eigenvalue E . This term is also sometimes applied to ψ instead.

We have the following proposition:

Proposition. The probability density $P(x, t) = |\Psi(x, t)|^2$ obeys

$$\frac{\partial P}{\partial t} = -\frac{\partial j}{\partial x},$$

where $j(x, t) = -\frac{i\hbar}{2m} \left(\Psi^* \frac{d\Psi}{dx} - \frac{d\Psi^*}{dx} \Psi \right)$ is the *probability current*.

Proof.

$$\frac{\partial P}{\partial t} = \Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t} \Psi = \Psi^* \frac{i\hbar}{2m} \Psi'' - \frac{i\hbar}{2m} \Psi''^* \Psi = -\frac{\partial j}{\partial x}.$$

□

Note that this is expressed in a space derivative, so the change in probability of finding the particle in $[a, b]$ is just $j(a, t) - j(b, t)$, or the current entering at a and leaving at b .

2 One Dimensional Examples

Before we enter examples, we first illustrate a concept:

2.1 Parity

Consider the Schrödinger equation for a particle of mass m

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

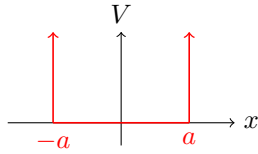
with potential $V(x) = V(-x)$. By changing variables $x \rightarrow -x$, we see that $\psi(x)$ is an eigenfunction of H with energy E if and only if $\psi(-x)$ is an eigenfunction of H with energy E . There are two possibilities:

- (i) If $\psi(x)$ and $\psi(-x)$ is the same quantum state, this can only happen if $\psi(-x) = \eta\psi(x)$ for some constant η . Then we get that $\eta = \pm 1$ and $\psi(-x) = \pm\psi(x)$. We call η the *parity*, and say ψ has even/odd parity if η is $+1/-1$ respectively.
- (ii) If $\psi(x)$ and $\psi(-x)$ are different quantum states, then we take linear combinations $\psi_{\pm}(x) = \alpha(\psi(x) \pm \psi(-x))$, and these are eigenstates with energy eigenvalue E , where α is for normalization. Then by construction, $\psi_{\pm}(-x) = \pm\psi_{\pm}(x)$ and have parity $\eta = \pm 1$.

Hence, if we are given a potential with reflective symmetry $V(-x) = V(x)$, then we can restrict our attention and just look for solutions with ± 1 parity. Now we go for examples.

3 Examples

Infinite Well The simplest case to consider is the infinite well. Here the potential is infinite outside the region $[-a, a]$, so for $|x| > a$, we must have $\psi(x) = 0$, or else $V(x)\psi(x)$ would be infinite.



We require $\psi = 0$ for $|x| > a$ and ψ continuous at $x = \pm a$. Within $|x| < a$, the Schrödinger equation is

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

We simplify this to become

$$\psi'' + k^2\psi = 0,$$

where $E = \frac{\hbar^2 k^2}{2m}$. Here, instead of working with the complex exponentials, we use sin and cos since we know well when these vanish. The general solution is thus

$$\psi = A \cos kx + B \sin kx.$$

Now we solve for the boundary conditions, so that ψ vanishes at $\pm a$. This turns out to give

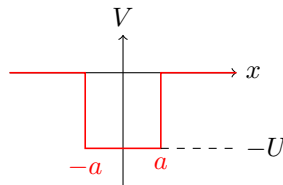
$$E_n = \frac{\hbar^2 \pi^2}{8ma^2} n^2,$$

where $n = 1, 2, \dots$, and the wavefunctions are

$$\psi_n(x) = \left(\frac{1}{a}\right)^{\frac{1}{2}} \begin{cases} \cos \frac{n\pi x}{2a} & n \text{ odd} \\ \sin \frac{n\pi x}{2a} & n \text{ even} \end{cases}.$$

If you stare at this long enough, you can realize they are just standing waves.

Potential Well We consider a potential:



The potential is given by some constant $U > 0$. We want to seek energy levels for a particle of mass m , defined by the Schrödinger equation

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

For energies in the range $-U < E < 0$, we set

$$U + E = \frac{\hbar^2 k^2}{2m} > 0, \quad E = -\frac{\hbar^2 \kappa^2}{2m},$$

where $k, \kappa > 0$ are new real constants. Note they must satisfy

$$k^2 + \kappa^2 = \frac{2mU}{\hbar^2}.$$

Using these constants, the Schrödinger equation becomes

$$\begin{cases} \psi'' + k^2\psi = 0 & |x| < a \\ \psi'' - \kappa^2\psi = 0 & |x| > a. \end{cases}$$

We first consider the even parity solutions $\psi(-x) = \psi(x)$. We can write our solution as

$$\psi = \begin{cases} A \cos kx & |x| < a \\ B e^{-\kappa|x|} & |x| > a \end{cases}$$

We now match ψ and ψ' at $x = a$ to make it continuous. So we need

$$\begin{aligned} A \cos ka &= B e^{-\kappa a} \\ -Ak \sin ka &= -\kappa B e^{-\kappa a}. \end{aligned}$$

By parity, there is no additional information from $x = -a$. We can divide the equations to obtain

$$k \tan ka = \kappa.$$

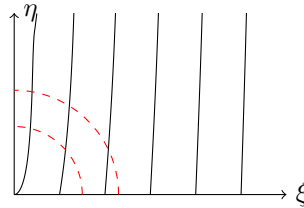
this is still not something we can solve easily. To find when solutions exist, it is convenient to introduce

$$\xi = ka, \quad \eta = \kappa a,$$

Hence the solution we need are solutions to

$$\eta = \xi \tan \xi. \quad \text{and} \quad \xi^2 + \eta^2 = \frac{2ma^2U}{\hbar^2}.$$

Where the second equation comes from our initial relation. We can look for solutions by plotting these two equations.

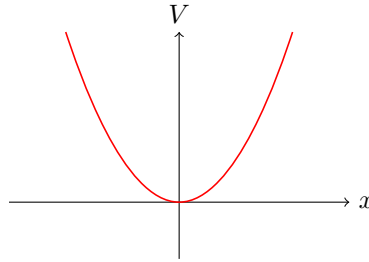


So there will be a different number of solutions depending on the value of $2ma^2U/\hbar^2$. In particular, if

$$(n-1)\pi < \left(\frac{2mUa^2}{\hbar^2}\right)^{1/2} < n\pi,$$

then we have exactly n even parity solutions (for $n \geq 1$). If $E > 0$ or $E < -U$, we have non-normalizable solutions.

The odd parity case, not shown here, can be done similarly. It can be shown that there are no bound states (normalizable energy eigenfunctions) if $a^2U < \frac{(\pi\hbar)^2}{8m}$.



Harmonic Oscillator

This is a harmonic oscillator of mass m with

$$V(x) = \frac{1}{2}m\omega^2 x^2.$$

Note the similarity with this to the second term in a Taylor expansion. And assuming x_0 is an equilibrium, the first term is zero so this is the first non-zero approximation term! That's why people say physics is just increasingly complicated harmonic oscillators.

We seek all normalizable solutions to the time-independent Schrödinger equation

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

So simplify constants, we define $y = \left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}} x$ and $\mathcal{E} = \frac{2E}{\hbar\omega}$ both of which is dimensionless. Then we are left with

$$-\frac{d^2\psi}{dy^2} + y^2\psi = \mathcal{E}\psi.$$

Now we try

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

Why? Well, we want to offset the y^2 factor in the differential equation here. Then the Schrödinger equation gives

$$\frac{d^2f}{dy^2} - 2y\frac{df}{dy} + (\mathcal{E} - 1)f = 0.$$

This is known as *Hermite's equation*. We try a series solution $f(y) = \sum_{r \geq 0} a_r y^r$, and substitute in to get

$$\sum_{r \geq 0} ((r+2)(r+1)a_{r+2} + (\mathcal{E} - 1 - 2r)a_r)y^r = 0.$$

This holds if and only if

$$a_{r+2} = \frac{2r+1-\mathcal{E}}{(r+2)(r+1)}a_r, \quad r \geq 0.$$

We have independent in a_0 and a_1 so they give 2 solutions. But we want normalizable solutions. We can observe that the coefficients obey:

$$a_p/a_{p-2} \sim \frac{1}{p}.$$

So we are getting something like a series expansion of e^{y^2} , which is bad, as ψ would not be normalizable. So we need to terminate the series. This occurs iff $\mathcal{E} = 2n + 1$ for some n . Note that for each n , only one of the two independent solutions is normalizable. So for each \mathcal{E} , we get exactly one solution.

For n even, we have

$$a_{r+2} = \frac{2r - 2n}{(r+2)(r+1)} a_r$$

for r even, and $a_r = 0$ for r odd, and the other way round when n is odd.

The solutions are thus $f(y) = h_n(y)$, where h_n is a polynomial of degree n with $h_n(-y) = (-1)^n h_n(y)$. For example, we have

$$h_1(y) = a_1 y \quad h_2(y) = a_0(1 - 2y^2)$$

With constants fixed by normalization. These are known as the *Hermite polynomials*. Thus, we have:

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

for $n = 0, 1, 2, \dots$.

The wavefunctions are

$$\psi_n(x) = h_n \left(\left(\frac{m\omega}{\hbar} \right)^{\frac{1}{2}} x \right) \exp \left(-\frac{1}{2} \frac{m\omega}{\hbar} x^2 \right),$$

4 Expectation and Uncertainty

This is the section for theory behind quantum mechanics. Wait. Didn't we just solve like the Schrödinger equations? Well, we did... But there is much more.

4.1 Definitions

First up, notations and some definitions:

Definition (Inner product). Let $\psi(x)$ and $\phi(x)$ be normalizable wavefunctions at some fixed time. We define the complex *inner product* by

$$(\phi, \psi) = \int_{-\infty}^{\infty} \phi(x)^* \psi(x) dx.$$

Definition (Norm). The *norm* of a wavefunction ψ , written, $\|\psi\|$ is defined by

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

Definition (Expectation value). The *expectation value* of any observable H on the state ψ is

$$\langle H \rangle_\psi = (\psi, H\psi).$$

Definition (Uncertainty, or Variance). The *uncertainty* in position $(\Delta x)_\psi$ and momentum $(\Delta p)_\psi$ are defined by

$$(\Delta x)_\psi^2 = \langle (\hat{x} - \langle \hat{x} \rangle_\psi)^2 \rangle_\psi = \langle \hat{x}^2 \rangle_\psi - \langle \hat{x} \rangle_\psi^2,$$

with exactly the same expression for momentum:

$$(\Delta p)_\psi^2 = \langle (\hat{p} - \langle \hat{p} \rangle_\psi)^2 \rangle_\psi = \langle \hat{p}^2 \rangle_\psi - \langle \hat{p} \rangle_\psi^2,$$

Definition (Hermitian operator). An operator Q is *Hermitian* iff for all normalizable ϕ, ψ , we have

$$(\phi, Q\psi) = (Q\phi, \psi) \Leftrightarrow \int \phi^* Q\psi \, dx = \int (Q\phi)^* \psi \, dx.$$

\hat{x} , \hat{p} and H are all Hermitian (From definition, just use integration by parts).

4.2 Ehrenfest's Theorem and the Uncertainty Principle

The two theorems are to show you that quantum mechanics is kind of similar (Ehrenfest) to classical mechanics, but not really (Uncertainty Principle).

Theorem (Ehrenfest's theorem).

$$\begin{aligned} \frac{d}{dt} \langle \hat{x} \rangle_\Psi &= \frac{1}{m} \langle \hat{p} \rangle_\Psi \\ \frac{d}{dt} \langle \hat{p} \rangle_\Psi &= -\langle V'(\hat{x}) \rangle_\Psi. \end{aligned}$$

Proof. We have

$$\begin{aligned} \frac{d}{dt} \langle \hat{x} \rangle_\Psi &= (\dot{\Psi}, \hat{x}\Psi) + (\Psi, \hat{x}\dot{\Psi}) \\ &= \left(\frac{1}{i\hbar} H\Psi, \hat{x}\Psi \right) + \left(\Psi, \hat{x} \left(\frac{1}{i\hbar} H \right) \Psi \right) \end{aligned}$$

Since H is Hermitian, we can move it around and get

$$= -\frac{1}{i\hbar} (\Psi, H(\hat{x}\Psi)) + \frac{1}{i\hbar} (\Psi, \hat{x}(H\Psi)) = \frac{1}{i\hbar} (\Psi, (\hat{x}H - H\hat{x})\Psi).$$

But we know

$$\hat{x}H - H\hat{x}\Psi = -\frac{\hbar^2}{2m}(x\Psi'' - (x\Psi)'') + (xV\Psi - Vx\Psi) = -\frac{\hbar^2}{m}\Psi' = \frac{i\hbar}{m}\hat{p}\Psi.$$

So done. The second part is similar. So we have:

$$\frac{d}{dt} \langle \hat{p} \rangle_\Psi = (\dot{\Psi}, \hat{p}\Psi) + (\Psi, \hat{p}\dot{\Psi}) = \frac{1}{i\hbar} (\Psi, (\hat{p}H - H\hat{p})\Psi)$$

Then of course, we have

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

So done. □

Theorem (Heisenberg's uncertainty principle). If ψ is any normalized state (at any fixed time), then

$$(\Delta x)_\psi (\Delta p)_\psi \geq \frac{\hbar}{2}.$$

Yes, this is the famed theorem that we cannot know anything exactly. To prove this we need the following:

Definition (Commutator). Let Q and S be operators. Then the *commutator* is denoted and defined by

$$[Q, S] = QS - SQ.$$

This is a measure of the lack of commutativity of the two operators.

In particular, the commutator of position and momentum is

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

Now we prove the Uncertainty principle:

Proof. Choose $\alpha = \langle \hat{x} \rangle_\psi$ and $\beta = \langle \hat{p} \rangle_\psi$, and define

$$X = \hat{x} - \alpha, \quad P = \hat{p} - \beta.$$

Then we have

$$\begin{aligned} (\Delta x)_\psi^2 &= (\psi, X^2\psi) = (X\psi, X\psi) = \|X\psi\|^2 \\ (\Delta p)_\psi^2 &= (\psi, P^2\psi) = (P\psi, P\psi) = \|P\psi\|^2 \end{aligned}$$

Then we have

$$\begin{aligned} (\Delta x)_\psi (\Delta p)_\psi &= \|X\psi\| \|P\psi\| \\ &\geq |(X\psi, P\psi)| \\ &\geq |\operatorname{Im}(X\psi, P\psi)| \\ &\geq \left| \frac{1}{2i} [(X\psi, P\psi) - (P\psi, X\psi)] \right| \\ &= \left| \frac{1}{2i} [(\psi, XP\psi) - (\psi, PX\psi)] \right| = \left| \frac{1}{2i} (\psi, [X, P]\psi) \right| = \left| \frac{\hbar}{2} (\psi, \psi) \right| = \frac{\hbar}{2}. \end{aligned}$$

□

5 More One Dimension Results

5.1 Gaussian Wavepackets

A wavepacket is some wavefunction that is localized in space, but this is really not well defined. But we do have a good definition of this:

Definition (Gaussian wavepacket). A *Gaussian wavepacket* is given by

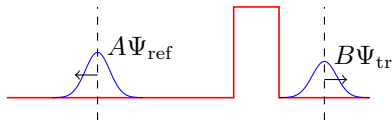
$$\Psi_0(x, t) = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{1}{\gamma(t)^{1/2}} e^{-x^2/2\gamma(t)},$$

for some $\gamma(t)$.

Now we will use these functions later. First, we have:

5.2 Scattering

Consider the time-dependent Schrödinger equation with a potential barrier. We send a wavepacket to a barrier, and in quantum mechanics, we would expect some part to pass it, and some part to be reflected:



Here Ψ , Ψ_{ref} and Ψ_{tr} are normalized wavefunctions, and

$$P_{\text{ref}} = |A|^2, \quad P_{\text{tr}} = |B|^2.$$

are the probabilities of reflection and transmission respectively.

Now generally these are hard problems, but we can use the following trick: We allow $\Psi(x, t)$ to represent *beams* of infinitely many particles, with $|\Psi(x, t)|^2$ being the density of the number of particles (per unit length) at x, t . When we do this, instead of having one particle and watching it evolve, we constantly send in particles so that the system does not appear to change with time. This allows us to find *steady states*. Therefore, to determine, say, the probability of reflection, we kind of just look at the proportion of particles moving left compared to the proportion of particles moving right in this steady state.

For these particle beams, $\Psi(x, t)$ is bounded, but no longer normalizable. Recall that for a single particle, the probability current was defined as

$$j(x, t) = -\frac{i\hbar}{2m}(\Psi^*\Psi' - \Psi\Psi'^*).$$

If we have a particle beam instead of a particle, and Ψ is the particle density instead of the probability distribution, j now represents the *flux* of particles at x, t , ie. the number of particles passing the point x in unit time.

Often, when solving a scattering problem, the solution will involve sums of momentum eigenstates. So it helps to understand these better. Our momentum eigenstates are

$$\psi(x) = Ce^{ikx},$$

which are solutions to the time-independent Schrödinger equation with $V = 0$ with $E = \frac{\hbar^2 k^2}{2m}$.

Applying the momentum operator, we find that $p = \hbar k$ is the momentum of each particle in the beam, and $|\psi(x)|^2 = |C|^2$ is the density of particles in the beam. We can also evaluate the current to be

$$j = \frac{\hbar k}{m}|C|^2.$$

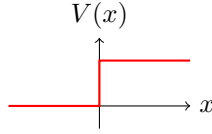
This makes sense. $\frac{\hbar k}{m} = \frac{p}{m}$ is the velocity of the particles, and $|C|^2$ is how many particles we have. So this still roughly corresponds to what we used to have classically.

In scattering problems, we will seek the transmitted and reflected flux j_{tr} , j_{ref} in terms of the incident flux j_{inc} , and the probabilities for transmission and reflection are then given by

$$P_{\text{tr}} = \frac{|j_{\text{tr}}|}{|j_{\text{inc}}|}, \quad P_{\text{ref}} = \frac{|j_{\text{ref}}|}{|j_{\text{inc}}|}.$$

Now we would illustrate this using two examples:

Potential Step We consider a wavepacket going into this:



$E < U$ We apply the standard method, introducing constants $k, \kappa > 0$ such that

$$E = \frac{\hbar^2 k^2}{2m}, \quad U - E = \frac{\hbar^2 \kappa^2}{2m}.$$

Then the Schrödinger equation becomes

$$\begin{cases} \psi'' + k^2\psi = 0 & x < 0 \\ \psi'' - \kappa^2\psi = 0 & x > 0 \end{cases}$$

The solutions are $\psi = Ie^{ikx} + Re^{-ikx}$ for $x < 0$, and $\psi = Ce^{-\kappa x}$ for $x > 0$ (since ψ has to be bounded).

Since ψ and ψ' are continuous at $x = 0$, we have the equations

$$\begin{cases} I + R = C \\ ikI - ikR = -\kappa C \end{cases}.$$

So we have

$$R = \frac{k - i\kappa}{k + i\kappa} I, \quad C = \frac{2k}{k + i\kappa} I.$$

If $x < 0$, $\psi(x)$ is a superposition of beams (momentum eigenstates) with $|I|^2$ particles per unit length in the incident part, and $|R|^2$ particles per unit length in the reflected part, with $p = \pm\hbar k$. The current is

$$j = j_{\text{inc}} + j_{\text{ref}} = |I|^2 \frac{\hbar k}{m} - |R|^2 \frac{\hbar k}{m},$$

The probability of reflection is

$$P_{\text{ref}} = \frac{|j_{\text{ref}}|}{|j_{\text{inc}}|} = \frac{|R|^2}{|I|^2} = 1,$$

On the right hand side, we have $j = 0$. So $P_{\text{tr}} = 0$.

$E > U$ This is really similar, except we have

$$E = \frac{\hbar^2 k^2}{2m}, \quad E - U = \frac{\hbar^2 \kappa^2}{2m},$$

We then match the two solutions again (skipping some steps to show you the important part):

$$\begin{cases} I + R = T \\ ikI - ikR = ikT. \end{cases}$$

We can solve these to obtain

$$R = \frac{k - \kappa}{k + \kappa} I, \quad T = \frac{2k}{k + \kappa} I.$$

Our flux on the left is now

$$j = j_{\text{inc}} + j_{\text{ref}} = |I|^2 \frac{\hbar k}{m} - |R|^2 \frac{\hbar k}{m},$$

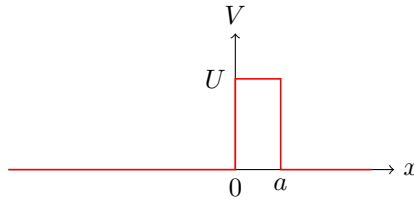
while the flux on the right is

$$j = j_{\text{tr}} |T|^2 \frac{\hbar \kappa}{m}.$$

The probability of reflection and transmission is

$$P_{\text{ref}} = \frac{|j_{\text{ref}}|}{|j_{\text{inc}}|} = \frac{|R|^2}{|I|^2} = \left(\frac{k - \kappa}{k + \kappa} \right)^2, \quad P_{\text{tr}} = \frac{|j_{\text{tr}}|}{|j_{\text{inc}}|} = \frac{|T|^2 \kappa}{|I|^2 k} = \frac{4k\kappa}{(k + \kappa)^2}.$$

Potential Barrier Consider the following potential:



Now consider a stationary state with energy E with $0 < E < U$. We set the constants

$$E = \frac{\hbar^2 k^2}{2m}, \quad U - E = \frac{\hbar^2 \kappa^2}{2m}.$$

Then the Schrödinger equations become

$$\begin{aligned} \psi'' + k^2 \psi &= 0 & x < 0 \\ \psi'' - \kappa^2 \psi &= 0 & 0 < x < a \\ \psi'' + k^2 \psi &= 0 & x > a \end{aligned}$$

So we get

$$\begin{aligned} \psi &= Ie^{ikx} + Re^{-ikx} & x < 0 \\ \psi &= Ae^{\kappa x} + Be^{-\kappa x} & 0 < x < a \\ \psi &= Te^{ikx} & x > a \end{aligned}$$

Matching ψ and ψ' at $x = 0$ and a gives the equations

$$\begin{aligned} I + R &= A + B \\ ik(I - R) &= \kappa(A - B) \\ Ae^{\kappa a} + Be^{-\kappa a} &= Te^{ika} \\ \kappa(Ae^{\kappa a} - Be^{-\kappa a}) &= ikTe^{ika}. \end{aligned}$$

We can work out the *boring* algebra to obtain:

$$T = I e^{-ika} \left(\cosh \kappa a - i \frac{k^2 - \kappa^2}{2k\kappa} \sinh \kappa a \right)^{-1}$$

Therefore we can use these to find the transmission probability, and it turns out to be

$$P_{\text{tr}} = \frac{|j_{\text{tr}}|}{|j_{\text{inc}}|} = \frac{|T|^2}{|I|^2} = \left[1 + \frac{U^2}{4E(U-E)} \sinh^2 \kappa a \right]^{-1}.$$

This demonstrates *quantum tunneling*. There is a non-zero probability that the particles can pass through the potential barrier even though it classically does not have enough energy.

5.3 Bound vs Scattering States

As $|x| \rightarrow \infty$ the T-ID SE gives:

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

Which give solutions like:

$$\psi \sim \begin{cases} Ae^{ikx} + Be^{-ikx} & E = \frac{\hbar^2 k^2}{2m} > 0 \\ Ae^{\kappa x} + Be^{-\kappa x} & E = -\frac{\hbar^2 \kappa^2}{2m} < 0. \end{cases}$$

For it to be bound, we need $E < 0$. Thus we need to have

$$\psi \sim \begin{cases} Ae^{\kappa x} & x \rightarrow -\infty \\ Be^{-\kappa x} & x \rightarrow +\infty \end{cases}$$

Which is overdetermined. That's why bound state energy levels are quantized.

If it is not bounded, then we have:

$$\psi \sim \begin{cases} Ie^{ikx} + Re^{-ikx} & x \rightarrow -\infty \\ Te^{ikx} & x \rightarrow +\infty \end{cases}$$

So we have:

$$P_{\text{ref}} = |A_{\text{ref}}|^2 = \frac{|j_{\text{ref}}|}{|j_{\text{inc}}|}$$

$$P_{\text{tr}} = |A_{\text{tr}}|^2 = \frac{|j_{\text{tr}}|}{|j_{\text{inc}}|},$$

where $A_{\text{ref}}(k) = \frac{R}{I}$ and $A_{\text{tr}}(k) = \frac{T}{I}$.

Note. In quantum mechanics, Amplitude squared generally gives probability.

6 Axioms for Quantum Mechanics

Note. This section is in the notes but honestly I fail to see how they can test this. But still read through it. It will help a lot when (if) you do PQM next year.

Now we would list the axioms, and some useful results:

- States of a quantum system correspond to non-zero elements of a complex vector space V (which has nothing to do with the potential), with ψ and $\alpha\psi$ physically equivalent for all $\alpha \in \mathbb{C} \setminus \{0\}$.
- There is also a complex inner product on V .
- A measurable quantity, named *observable* is a Hermitian operator.
- A Hermitian operator has orthogonal eigenvectors with respect to different eigenvalues, and the eigenvalues of it are real. (cf. Vectors and Matrices)
- Any state can be written as a (maybe infinite) linear combination of eigenstates of \mathbb{Q} . We say the set of eigenstates is *complete*. We would not prove this.
- Let a state be written as $\psi = \sum_n \alpha_n \chi_n$. Then
 - o The outcome of a measurement is some eigenvalue of \mathbb{Q} .
 - o The probability of having λ_n is $|\alpha_n|^2$.
 - o The measurement forces the state into χ_n and is instantaneous.

Note. The last one is really because measuring it means knowing it at a certain state, and in some given small period of time, you can't let it be very far away from the state you just measured.

- Now the expectation and uncertainty of Q in state ψ can be reformulated to be:

$$\langle Q \rangle_\psi = (\psi, Q\psi) = \sum \lambda_n P_n$$

$$(\Delta Q)_\psi^2 = \langle (Q - \langle Q \rangle_\psi)^2 \rangle_\psi = \langle Q^2 \rangle_\psi - \langle Q \rangle_\psi^2 = \sum_n (\lambda_n - \langle Q \rangle_\psi)^2 P_n$$

- The state of a quantum system $\Psi(t)$ obeys the Schrödinger equation

$$i\hbar\dot{\Psi} = H\Psi,$$

where H is a Hermitian operator, the *Hamiltonian*; this holds at all times except at the instant a measurement is made. This is called the wavefunction collapse. Why? Well.....You just asked a million dollar question.

- For any observable Q , the number of linearly independent eigenstates with eigenvalue λ is the *degeneracy* of the eigenvalue. In other words, the degeneracy is the dimension of the eigenspace

$$V_\lambda = \{\psi : Q\psi = \lambda\psi\}.$$

An eigenvalue is *non-degenerate* if the degeneracy is exactly 1, and is *degenerate* if the degeneracy is more than 1.

Not an Axiom What if we wanted to distinguish degenerate states? Then we need two observables A and B , and the state needs to be an eigenstate for both of them. From linear algebra, we can know that this is possible if A and B commutes.

Not an Axiom

Theorem (Ehrenfest's theorem in General). If Q is any operator with no explicit time dependence, then

$$i\hbar \frac{d}{dt} \langle Q \rangle_{\Psi} = \langle [Q, H] \rangle_{\Psi},$$

where $[Q, H] = QH - HQ$ is the commutator. The proof is done by expanding out the definition and replacing $-i\hbar \dot{\Psi}$ with $H\Psi$.

Not an Axiom For a state at time 0 written as $\Psi(0) = \sum_n \alpha_n \psi_n$, then using stationary states, we can write the general form as:

$$\Psi(t) = \sum_n \alpha_n e^{-iE_n t/\hbar} \psi_n.$$

7 Quantum Mechanics. Now in 3D™

Now we go into 3D. Everything we have learned pretty much just follows directly, and commutator relations such as $[\hat{x}_i, \hat{p}_j] = -i\hbar \delta_{ij}$, $[\hat{x}_i, \hat{x}_j] = [\hat{p}_i, \hat{p}_j] = 0$ don't really change except that indices are added. Now we define the following:

Definition (Structureless particle). A *structureless particle* is one for which all observables can be written in terms of position and momentum.

In reality, this is mostly not true but we don't care. The method of solving this is simply by separation of variables where we look for solutions in one dimension and multiply them together. I know. It is not exciting. Let's get to the more exciting stuff:

7.1 Angular momentum

This is the important stuff.

Definition (Angular momentum). The *angular momentum* is a vector of operators

$$\mathbf{L} = \hat{\mathbf{x}} \wedge \hat{\mathbf{p}} = -i\hbar \mathbf{x} \wedge \nabla.$$

In components, this is given by

$$L_i = \varepsilon_{ijk} \hat{x}_j \hat{p}_k = -i\hbar \varepsilon_{ijk} x_j \frac{\partial}{\partial x_k}.$$

For example, we have

$$L_3 = \hat{x}_1 \hat{p}_2 - \hat{x}_2 \hat{p}_1 = -i\hbar \left(x_1 \frac{\partial}{\partial x_2} - x_2 \frac{\partial}{\partial x_1} \right).$$

Definition. The *total angular momentum operator* is

$$\mathbf{L}^2 = L_i L_i = L_1^2 + L_2^2 + L_3^2.$$

Of course, everything defined above is Hermitian and thus an observable. We have the following commutator relations:

$$[L_i, L_j] = i\hbar\varepsilon_{ijk}L_k \quad [L_i, \hat{x}_j] = i\hbar\varepsilon_{ijk}\hat{x}_k, \quad [L_i, \hat{p}_j] = i\hbar\varepsilon_{ijk}\hat{p}_k$$

And also the following:

$$[\mathbf{L}^2, L_i] = 0$$

All of this can be proven easily using indices operations. Now we introduce a lemma that comes in handy:

Lemma (Leibnitz's Property). We have, for any three operators A, B, C :

$$[AB, C] = [A, C]B + A[B, C] \quad [A, BC] = [A, B]C + B[A, C]$$

This lemma allows us to deal with products effectively. Very. Effectively.

7.2 Spherical Polars

Now we can rewrite the angular momentum in spherical polars. The formula for L_3 will be rather simple, since x_3 is our axis of rotation. However, those for L_1 and L_2 will be much more complicated. Instead of writing them out directly, we instead write down the formula for $L_{\pm} = L_1 \pm iL_2$. A routine application of the chain rule gives

$$\begin{aligned} L_3 &= -i\hbar \frac{\partial}{\partial \phi} \\ L_{\pm} &= L_1 \pm iL_2 = \pm\hbar e^{\pm i\phi} \left(\frac{\partial}{\partial \theta} \pm i \cot \theta \frac{\partial}{\partial \phi} \right) \\ \mathbf{L}^2 &= -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right). \end{aligned}$$

From above, we can see that we can measure L_3 and \mathbf{L}^2 simultaneously, so there are simultaneous eigenfunctions of these operators, which we call $Y_{\ell m}(\theta, \varphi)$, with $\ell = 0, 1, 2, \dots$ and $m = 0, \pm 1, \pm 2, \dots, \pm \ell$. These have eigenvalues $\hbar m$ for L_3 and $\hbar^2 \ell(\ell + 1)$ for \mathbf{L}^2 .

In spherical polars, we have:

$$H = -\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{2\mu} \frac{1}{r^2} \mathbf{L}^2 + V(r).$$

We can check that

$$[L_i, H] = [\mathbf{L}^2, H] = 0.$$

This implies we can use the eigenvalues of H, \mathbf{L}^2 and L_3 to label our solutions to the equation. Therefore, we can simultaneously measure them, so the joint eigenstates must be:

$$\psi(\mathbf{x}) = R(r)Y_{\ell m}(\theta, \varphi),$$

Now we then try to solve the Schrodinger equation, which gives:

$$-\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{d^2}{dr^2}(rR) + \frac{\hbar^2}{2\mu r^2} \ell(\ell+1)R + VR = ER.$$

Now $R(r)$ is called the radial part of the wavefunction, and we will work with $\chi(r) = rR(r)$, often called the *radial wavefunction*. Then the equation turns into:

$$-\frac{\hbar^2}{2\mu} \chi'' + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} \chi + V\chi = E\chi.$$

The *radial Schrödinger Equation*. NOW since we would like R to be finite as $r \rightarrow 0$, so $\chi = 0$ at $r = 0$. The normalization conditions turns into:

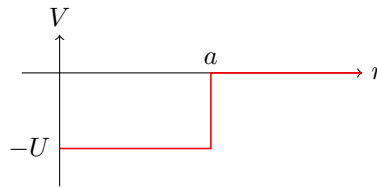
$$\int_0^\infty |R(r)|^2 r^2 dr < \infty.$$

Alternatively, this requires

$$\int_0^\infty |\chi(r)|^2 dr < \infty.$$

Now we look at an example:

Example (Three-dimensional well). We now plot our potential as a function of r :



We now look for bound state solutions to the Schrödinger equation with $-U < E < 0$, with total angular momentum quantum number ℓ .

For $r < a$, our radial wavefunction χ obeys

$$\chi'' - \frac{\ell(\ell+1)}{r^2} \chi + k^2 \chi = 0,$$

where k is a new constant obeying

$$U + E = \frac{\hbar^2 k^2}{2\mu}.$$

For $r \geq a$, we have

$$\chi'' - \frac{\ell(\ell+1)}{r^2} \chi - \kappa^2 \chi = 0,$$

with κ obeying

$$E = -\frac{\hbar^2 \kappa^2}{2\mu}.$$

We can solve in each region and match χ, χ' at $r = a$, with boundary condition $\chi(0) = 0$. Note that given this boundary condition, solving this is equivalent to solving it for the whole \mathbb{R} but requiring the solution to be odd.

Solving this for general ℓ is slightly complicated (would be taught in Applied Quantum Mechanics course). So we shall look at some particular examples.

For $\ell = 0$, we have no angular term, and we have done this before. The general solution is

$$\chi(r) = \begin{cases} A \sin kr & r < a \\ B e^{-\kappa r} & r > a \end{cases}$$

Matching the values at $x = a$ determines the values of k, κ and hence E .

For $\ell = 1$, it turns out the solution is just

$$\chi(r) = \begin{cases} A \left(\cos kr - \frac{1}{kr} \sin kr \right) & r < a \\ B \left(1 + \frac{1}{kr} \right) e^{-\kappa r} & r > a \end{cases}.$$

After matching, the solution is

$$\psi(r) = R(r)Y_{1m}(\theta, \varphi) = \frac{\chi(r)}{r} Y_{1m}(\theta, \varphi),$$

where m can take values $m = 0, \pm 1$.

8 The Hydrogen Atom

After developing so much theory, we now have the tools to describe....the Hydrogen Atom! Isn't that exciting?

Note. Note we are not going to *actually* solve this, because electrons have spin, so they behave slightly more weirdly. Although this doesn't really affect the hydrogen atom, it does add complexity to the equations. See PQM for the actual solution.

8.1 Introduction

Consider an electron moving in a Coulomb potential

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

This potential is due to a proton stationary at $r = 0$. We follow results from the last section of the last chapter, and set the mass $\mu = m_e$, the electron mass. The joint energy eigenstates of H, \mathbf{L}^2 and L_3 are of the form

$$\phi(\mathbf{x}) = R(r)Y_{\ell m}(\theta, \varphi)$$

for $\ell = 0, 1, \dots$ and $m = 0, \pm 1, \dots, \pm \ell$.

The radial part of the Schrödinger equation can be written

$$R'' + \frac{2}{r}R' - \frac{\ell(\ell+1)}{r^2}R + \frac{2\lambda}{r}R = \kappa^2 R, \quad (*)$$

with

$$\lambda = \frac{m^2}{4\pi\epsilon_0\hbar^2}, \quad E = \frac{-\hbar^2\kappa^2}{2m_e}.$$

Note that here we work directly with R instead of χ , as this turns out to be easier later on.

The goal of this chapter is to understand *all* the (normalizable) solutions to this equation (*).

Now we start by guessing. For large r , we get

$$R'' \sim \kappa^2 R.$$

This implies $R \sim e^{-\kappa r}$ for large R .

For small r , we by assumption know that R is finite, while R' and R'' could potentially go crazy. So we multiply by r^2 and discard the rR and r^2R terms to get

$$r^2 R'' + 2rR' - \ell(\ell + 1)R \sim 0.$$

This gives the solution $R \sim r^\ell$.

We'll be bold and try a solution of the form

$$R(r) = Cr^\ell e^{-\kappa r}.$$

When we substitute this in, we will get three kinds of terms. The $r^\ell e^{-\kappa r}$ terms match, and so do the terms of the form $r^{\ell-2} e^{-\kappa r}$. Finally, we see the $r^{\ell-1} e^{-\kappa r}$ terms match if and only if

$$2(\ell r^{\ell-1})(-\kappa e^{-\kappa r}) + 2(r^{\ell-1})(-\kappa e^{-\kappa r}) + 2\lambda r^{\ell-1} e^{-\kappa r} = 0.$$

When we simplify this mess, we see this holds if and only if

$$(\ell + 1)\kappa = \lambda.$$

Hence, for any integer $n = \ell + 1 = 1, 2, 3, \dots$, there are bound states with energies

$$E_n = -\frac{\hbar^2 \lambda^2}{2m_e n^2} = -\frac{1}{2} m_e \left(\frac{e^2}{4\pi\epsilon_0 \hbar} \right)^2 \frac{1}{n^2}.$$

In our model, the total angular momentum eigenvalue is thus

$$\hbar^2 \ell(\ell + 1) = \hbar^2 n(n - 1),$$

But this is only one solution as for each energy level, there are many possible angular momentums.

8.2 General solution

We guessed our solution $r^\ell e^{-\kappa r}$ above by looking at the asymptotic behaviour at large and small r . We then managed to show that this is *one* solution of the hydrogen atom. But we want all of them. So we continue guessing:

$$R(r) = e^{-\kappa r} f(r).$$

Putting it in, we obtain

$$f'' + \frac{2}{r} f' - \frac{\ell(\ell + 1)}{r^2} f = 2 \left(\kappa f' + (\kappa - \lambda) \frac{f}{r} \right).$$

Now each side of the equality is equidimensional, which is great for series solutions. This equation is regular singular at $r = 0$, so we guess a solution of the form

$$f(r) = \sum_{p=0}^{\infty} a_p r^{p+\sigma}, \quad a_0 \neq 0.$$

Then substitution gives

$$\sum_{p \geq 0} ((p+\sigma)(p+\sigma-1) - \ell(\ell+1)) a_p r^{p+\sigma-2} = \sum_{p \geq 0} 2(\kappa(p+\sigma+1) - \lambda) a_p r^{p+\sigma-1}.$$

The lowest term gives us the indicial equation

$$\sigma(\sigma+1) - \ell(\ell+1) = (\sigma - \ell)(\sigma + \ell + 1) = 0.$$

So either $\sigma = \ell$ or $\sigma = -(\ell + 1)$. We discard the $\sigma = -(\ell + 1)$ solution since this would make f and hence R singular at $r = 0$. So we have $\sigma = \ell$.

Given this, the coefficients are then determined by

$$a_p = \frac{2(\kappa(p+\ell) - \lambda)}{p(p+2\ell+1)} a_{p-1}, \quad p \geq 1.$$

Similar to the harmonic oscillator, we now observe that, unless the series terminates, we have

$$\frac{a_p}{a_{p-1}} \sim \frac{2\kappa}{p}$$

as $p \rightarrow \infty$, which matches the behaviour of $r^\alpha e^{2\kappa r}$ (for some α). So $R(r)$ is normalizable only if the series terminates. Hence the possible values of λ are

$$\kappa n = \lambda$$

for some $n \geq \ell + 1$. So the resulting energy levels are exactly those we found before:

$$E_n = -\frac{\hbar^2}{2m_e} \kappa^2 = -\frac{\hbar^2}{2m_e} \frac{\lambda^2}{n^2} = -\frac{1}{2} m_e \left(\frac{e^2}{4\pi\epsilon_0 \hbar} \right)^2 \frac{1}{n^2}.$$

for $n = 1, 2, 3, \dots$. This n is called the *principle quantum number*.

For any given n , the possible angular momentum quantum numbers are

$$\begin{aligned} \ell &= 0, 1, 2, 3, \dots, n-1 \\ m &= 0, \pm 1, \pm 2, \dots, \pm \ell. \end{aligned}$$

The simultaneous eigenstates are then

$$\psi_{n\ell m}(\mathbf{x}) = R_{n\ell}(r) Y_{\ell m}(\theta, \varphi),$$

with

$$R_{n\ell r} = r^\ell g_{n\ell}(r) e^{-\lambda r/n},$$

where $g_{n\ell}(r)$ are (proportional to) the *associated Laguerre polynomials*.

In general, the “shape” of probability distribution for any electron state depends on r and θ, φ mostly through $Y_{\ell m}$. For $\ell = 0$, we have a spherically symmetric solutions

$$\psi_{n00}(\mathbf{x}) = g_{n0}(r) e^{-\lambda r/n}.$$

The degeneracy of each energy level E_n is

$$\sum_{\ell=0}^{n-1} \sum_{m=-\ell}^{\ell} 1 = \sum_{\ell=0}^{n-1} (2\ell + 1) = n^2.$$

So. We solved the hydrogen atom. Kind of. By guessing. But hey, we solved it.