

I. GENERAL THINGS

Schrödinger Equation

Time-dependent

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

Time-independent

If the potential is time-independent we can use separation of variables to split the PDE into a time dependent ($T(t)$) and time-independent ($X(x)$) part:

$$\Psi(x, t) = T(t)X(x)$$

Thus

$$\hat{H}\Psi - i\hbar \frac{\partial \Psi}{\partial t} = 0$$

can be separated into

$$\frac{dT(t)}{dt} = -\left(\frac{iE}{\hbar}\right)T(t)$$

and

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

Thus the general solution to the Schrödinger equation can be written as

$$\Psi(x, t) = \sum_n c_n \psi_n(x) \exp\left(-\frac{iE_n t}{\hbar}\right)$$

Normalisation

The solution to the Schrödinger equation must be normalised, such that

$$\langle \Psi | \Psi \rangle = \int_{-\infty}^{\infty} \Psi^* \Psi dx = \int_{-\infty}^{\infty} |\Psi|^2 dx = 1$$

Operators

$$\hat{x} = x \quad \rightarrow \quad \hat{\mathbf{r}} = (x, y, z)$$

$$\hat{p} = -i\hbar \frac{\partial}{\partial x} \quad \rightarrow \quad \hat{\mathbf{p}} = -i\hbar \nabla$$

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) = \hat{T} + \hat{V}$$

$$\rightarrow \quad \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r})$$

Expectation values/ averages

$$\langle Q \rangle = \int_{-\infty}^{\infty} \Psi^*(x) \hat{Q} \Psi(x) dx$$

Commutator

The commutator of two operators \hat{A}, \hat{B} is defined as:

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

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

Here are some examples of some useful commutation relations:

$$[\hat{r}_i, \hat{p}_j] = -[\hat{p}_i, \hat{r}_j] = i\hbar \delta_{ij}$$

$$[\mathbf{r}_i, \mathbf{r}_j] = [\mathbf{p}_i, \mathbf{p}_j] = 0$$

Spin and Angular momentum:

$$[L_i, L_j] = i\hbar \varepsilon_{ijk} L_k$$

$$[S_i, S_j] = i\hbar \varepsilon_{ijk} S_k$$

where ε_{ijk} is the Levi-Civita symbol. Or, written in a way, that one actually can understand:

$$[L_x, L_y] = i\hbar L_z$$

$$[L_y, L_z] = i\hbar L_x$$

$$[L_z, L_x] = i\hbar L_y$$

$$[L_i, L_i] = 0$$

And similar for the spin operators

$$[S_x, S_y] = i\hbar S_z$$

$$[S_y, S_z] = i\hbar S_x$$

$$[S_z, S_x] = i\hbar S_y$$

$$[S_i, S_i] = 0$$

For systems that can have **half-spin** $[-\hbar/2$ or $\hbar/2$ (in z -direction)] the \hat{S} matrices are given by the Pauli matrices:

$$\hat{S}_x = \frac{\hbar}{2} \sigma_x, \quad \hat{S}_y = \frac{\hbar}{2} \sigma_y, \quad \hat{S}_z = \frac{\hbar}{2} \sigma_z$$

The Pauli matrices are:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

For systems that can have integer spins ($-\hbar$, 0 or \hbar), the \hat{S} matrices become a bit uglier:

$$S_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$S_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

$$S_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Otherwise one can also use the following identities:

$$S_x = \frac{1}{2}(S_+ + S_-)$$

$$S_y = \frac{1}{2i}(S_+ - S_-)$$

Remembering that

$$\hat{S}_+ |s, m\rangle = A_s^m |s, m+1\rangle$$

$$\hat{S}_- |s, m\rangle = B_s^m |s, m-1\rangle$$

where

$$A_s^m = \hbar \sqrt{s(s+1) - m(m+1)}$$

$$B_s^m = \hbar \sqrt{s(s+1) - m(m-1)}$$

We can do the same thing for the \hat{L} operators, by letting $s \rightarrow \ell$ (and $\hat{S} \rightarrow \hat{L}$).

Uncertainty Principle

Once we have the commutators, we can define a generalised uncertainty principle:

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2$$

Conservation laws

Additionally we can define conservation laws, using the commutators:

$$\frac{d}{dt} \langle Q \rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{Q}] \rangle + \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle$$

Numerical calculations

$$E_c = \frac{\hbar^2}{m x_0^2}$$

How to find eigenvectors and -values:

An eigenvector, \mathbf{v} , to a matrix, A is defined as follows:

$$A\mathbf{v} = \lambda\mathbf{v} \quad \text{for } \mathbf{v} \neq \mathbf{0}, \quad \lambda \in \mathbb{F}$$

where \mathbb{F} can either be \mathbb{R} or \mathbb{C} . The value λ is the eigenvalue that corresponds to the eigenvector, \mathbf{v} . A convenient way of calculating the eigenvalues is using the characteristic equation:

$$\det(A - \lambda I) = 0$$

where I is the identity matrix. Once we have found λ we can calculate the corresponding eigenvectors:

$$(A - \lambda I)\mathbf{v} = \mathbf{0}$$

This will give you a system of equations for v_x, v_y etc., however, it doesn't matter which line of equations we use, because per definition of the eigenvalue each line in $(A - \lambda I)$ is linearly dependent (that means each line holds the same information) – therefore just use the line that gives you the easiest equation for v_x, v_y etc. The equation will give you a ratio between v_x and v_y , which is because any vector that has this ratio is an eigenvector (but it's usually helpful to chose an eigenvector that has magnitude one.)

Operators

Let us suppose we have an operator, \hat{Q} , that can be represented by a matrix, Q . Usually we know what the operator does to different states, so we usually also know what the eigenstates are:

$$\hat{Q} |q\rangle = \lambda_q |q\rangle$$

We can always use the following definition to calculate the matrix representation of \hat{Q} , in the basis $\{|b_j\rangle\}$:

$$Q_{mn} = \langle b_m | \hat{Q} | b_n \rangle$$

If we choose the basis for Q that consists of its eigenvectors, it will be a diagonal matrix, with the eigenvalues on the diagonal:

$$Q = \begin{pmatrix} \lambda_1 & 0 & 0 & \dots \\ 0 & \lambda_2 & 0 & \dots \\ 0 & 0 & \lambda_3 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

Measurements

Again let's consider an operator \hat{Q} , with matrix representation Q . The possible measurement outcomes for the measurement represented by the operator \hat{Q} are its eigenvalues, λ_q . If we are measuring \hat{Q} of an arbitrary state, χ , it's convenient to express χ as a linear combination of the eigenvectors of \hat{Q} , $|q\rangle$:

$$\chi = \sum_q c_q |q\rangle$$

The coefficients, c_q , are:

$$c_q = \langle q|\chi\rangle$$

Then the probability of measuring λ_q will be $|c_q|^2$. If we, for example measure λ_q , then the wave function will *collapse* to the eigenstate, $|q\rangle$, that corresponds to the λ_q .

For example. We start in the following state:

$$\Psi = \begin{pmatrix} a \\ b \end{pmatrix}$$

It's important that the state is normalised, thus we require that $|a|^2 + |b|^2 = 1$

And we take a measurement using the following operator:

$$H = \begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix}$$

H has eigenvalues $\lambda_1 = 1$ and $\lambda_2 = 2$, with corresponding eigenvectors:

$$|v_1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |v_2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Now we express our state, Ψ , in terms of H 's eigenvectors:

$$\begin{aligned} \Psi &= \langle v_1|\Psi\rangle \cdot |v_1\rangle + \langle v_2|\Psi\rangle \cdot |v_2\rangle \\ &= a |v_1\rangle + b |v_2\rangle \end{aligned}$$

The probability of measuring λ_1 is defined as:

$$P(\lambda_1) = \langle \Psi|v_1\rangle \langle v_1|\Psi\rangle = a^* a = |a|^2$$

Let's say we *do* measure λ_1 , then we *know* that the new state of the system as

$$\Psi_{new} = |v_1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

Which therefore affects the probability of the outcomes of any following measurements.

Other useful formulae

De Broglie wavelength:

$$\lambda = \frac{2\pi\hbar}{p} = \frac{h}{p}$$

Energy's relation to wavelength (λ) and frequency (ν):

$$E = h\nu = \frac{hc}{\lambda}$$

II. DIFFERENT POTENTIALS

Harmonic Oscillator

The potential:

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

The raising and lowering operators:

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

Normalisation after having used \hat{a}_{\pm} :

$$\psi_n = \frac{1}{\sqrt{n!}} (\hat{a}_+)^n \psi_0$$

Here are some useful identities:

$$\begin{aligned} \hat{a}_+ \psi_{n-1} &= \sqrt{n} \psi_n \\ \hat{a}_- \psi_{n+1} &= \sqrt{n+1} \psi_n \\ \hat{a}_+ \hat{a}_- \psi_n &= n \psi_n \\ \hat{a}_- \hat{a}_+ \psi_n &= (n+1) \psi_n \end{aligned}$$

Additionally

$$\begin{aligned} \hat{a}_+^2 \psi_{n-2} &= \sqrt{n(n-1)} \psi_n \\ \hat{a}_-^2 \psi_{n+2} &= \sqrt{(n+1)(n+2)} \psi_n \end{aligned}$$

Their commutators are

$$[\hat{a}_-, \hat{a}_+] = \hat{a}_- \hat{a}_+ - \hat{a}_+ \hat{a}_- = 1$$

The operators can be reformulated:

$$\begin{aligned} \hat{x} &= \sqrt{\frac{\hbar}{2m\omega}} (\hat{a}_+ + \hat{a}_-) \\ \hat{p} &= i\sqrt{\frac{\hbar m\omega}{2}} (\hat{a}_+ - \hat{a}_-) \end{aligned}$$

Allowed energy levels:

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

The groundstate:

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

The first excited state:

$$\psi_1(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \sqrt{\frac{2m\omega}{\hbar}} x \exp\left(-\frac{m\omega}{2\hbar} x^2 \right)$$

The n -th eigenstate, can be written using the Hermite polynomials:

$$\psi_n(\xi) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) \exp\left(-\frac{\xi^2}{2} \right)$$

where:

$$\xi \equiv \sqrt{\frac{m\omega}{\hbar}} x$$

Here is a table with the first few Hermite polynomials:

$H_0(\xi) = 1$
$H_1(\xi) = 2\xi$
$H_2(\xi) = 4\xi^2 - 2$
$H_3(\xi) = 8\xi^3 - 12\xi$
$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$
$H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi$

Table I: Hermite polynomials

Infinite Square Well

The infinite square well's potential is given by:

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

The (normalised) n -th eigenstate is given by, where a is the width of the well:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a} \right)$$

And the energy of the n -th eigenstate:

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

Delta Function Potential:

The potential is:

$$V(x) = -\alpha \delta(x)$$

for some $\alpha > 0$. There is exactly *one* bound state:

$$\psi(x) = \frac{\sqrt{m\alpha}}{\hbar} \exp\left(-\frac{m\alpha|x|}{\hbar^2}\right)$$

Which has the following energy:

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

Finite Square Well:

The finite square well has the following potential:

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

There was an exercise where we had to show that the eigenfunctions to an even potential ($V(-x) = V(x)$), then each eigenstate is either even or odd (thus there do not exist any eigenstates that are neither even nor odd!).

Even eigenstates:

Griffiths tells us that the energy of the bound, *even* eigenstates can be found with:

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

where $z = \ell a$ and $z_0 = \frac{a}{\hbar} \sqrt{2mV_0}$. This is usually done graphically, but by inspecting the graphs of $\tan z$ and of $\sqrt{\left(\frac{z_0}{z}\right)^2 - 1}$ we can conclude that the number, n , of bound, *even* eigenstates is given by:

$$n = \left\lfloor \frac{z_0}{\pi} + 1 \right\rfloor$$

Odd eigenstates:

In our assignment we showed that the energy of the bound, *odd* eigenstates is found using:

$$\cot z = -\sqrt{\frac{z_0^2}{z^2} - 1}$$

where $z_0 = \sqrt{\tilde{V}_0}$ and $z = \sqrt{2(\tilde{E} + \tilde{V}_0)}$. Then we concluded that the number of bound, *odd* eigenstates is

$$n = \left\lfloor \frac{z_0}{\pi} + \frac{1}{2} \right\rfloor$$

Hydrogen Atom:

The potential for a hydrogen atom is:

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

This is spherically symmetric, therefore we can split the solution into

$$\Psi_{n\ell m} = R_{n\ell}(r)Y_{\ell}^m(\theta, \phi)$$

Where Y_{ℓ}^m are spherical harmonics, that always can be used, for spherically symmetric potentials. $R_{n\ell}$ depends on the potential, therefore the radial part can only be used for potentials that are proportional to r^{-1} . Possible values for n, ℓ and m :

$$\begin{aligned} \ell &= 0, 1, \dots, n-1 \\ m &= -\ell, -\ell+1, \dots, \ell-1, \ell \end{aligned}$$

Angular part

The angular part of the (separable) solution is given by the spherical harmonics:

$$Y_{\ell}^m(\theta, \phi) = \sqrt{\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}} e^{im\phi} P_{\ell}^m(\cos\theta)$$

Where P_{ℓ}^m are the associated Legendre polynomials.

First a table of the associated Legendre polynomials:

$P_0^0 = 1$	$P_2^2 = 3 \sin^2 \theta$
$P_1^0 = \cos \theta$	$P_3^0 = \frac{1}{2} (5 \cos^3 \theta - 3 \cos \theta)$
$P_1^1 = -\sin \theta$	$P_3^1 = -\frac{3}{2} \sin \theta (5 \cos^2 \theta - 1)$
$P_2^0 = \frac{1}{2} (3 \cos^2 \theta - 1)$	$P_3^2 = 15 \sin^2 \theta \cos \theta$
$P_2^1 = -3 \sin \theta \cos \theta$	$P_3^3 = -15 \sin^3 \theta$

Table II: Associated Legendre polynomials. Also on page 137 in Griffiths

And now a table for the spherical harmonics:

$Y_0^0 = \left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$
$Y_1^0 = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos \theta$
$Y_1^{\pm 1} = \mp \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin \theta e^{\pm i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{\frac{1}{2}} (3 \cos^2 \theta - 1)$
$Y_2^{\pm 1} = \mp \left(\frac{15}{8\pi}\right)^{\frac{1}{2}} \sin \theta \cos \theta e^{\pm i\phi}$
$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{\frac{1}{2}} \sin^2 \theta e^{\pm 2i\phi}$
$Y_3^0 = \left(\frac{7}{16\pi}\right)^{\frac{1}{2}} (5 \cos^3 \theta - 3 \cos \theta)$
$Y_3^{\pm 1} = \mp \left(\frac{21}{64\pi}\right)^{\frac{1}{2}} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$
$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{\frac{1}{2}} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$
$Y_3^{\pm 3} = \mp \left(\frac{35}{64\pi}\right)^{\frac{1}{2}} \sin^3 \theta e^{\pm 3i\phi}$

Table III: Spherical Harmonics. Also on page 137 in Griffiths

Radial Part

The radial part $R_{n\ell}$ can be written in the following form:

$$R_{n\ell} \propto \frac{1}{r} \left(\frac{r}{an}\right)^{\ell+1} e^{-r/an} L_{n-\ell-1}^{2\ell+1}(2r/an)$$

Where

$$L_q^p(x) = (-1)^p \left(\frac{d}{dx}\right)^p L_{p+q}(x)$$

So here are the first few $R_{n\ell}$:

But what does it mean!

Often we write the state $\Psi_{n\ell m}$ as $|n\ell m\rangle$. A measurement of the energy is accomplished with the Hamiltonian operator:

$$\hat{H} |n\ell m\rangle = E_n |n\ell m\rangle$$

Where

$$\begin{aligned} E_n &= - \left[\frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} \\ &= - \frac{13.6 \text{ eV}}{n^2} = \frac{E_1}{n^2} \end{aligned}$$

Here is a table of the first few energies of the hydrogen atom:

$R_{10} = 2a^{-3/2} \exp(-r/a)$
$R_{20} = \frac{a^{-3/2}}{\sqrt{2}} \left(1 - \frac{r}{2a}\right) \exp(-r/2a)$
$R_{21} = \frac{a^{-3/2}}{2\sqrt{6}} \left(\frac{r}{a}\right) \exp(-r/2a)$
$R_{30} = \frac{2a^{-3/2}}{3\sqrt{3}} \left(1 - \frac{2r}{3a} + \frac{2}{27} \left(\frac{r}{a}\right)^2\right) \exp(-r/3a)$
$R_{31} = \frac{8a^{-3/2}}{27\sqrt{6}} \left(1 - \frac{1}{6} \frac{r}{a}\right) \left(\frac{r}{a}\right) \exp(-r/3a)$
$R_{32} = \frac{4a^{-3/2}}{81\sqrt{30}} \left(\frac{r}{a}\right)^2 \exp(-r/3a)$
$R_{40} = \frac{a^{-3/2}}{4} \left(1 - \frac{3r}{4a} + \frac{1}{8} \left(\frac{r}{a}\right)^2 - \frac{1}{192} \left(\frac{r}{a}\right)^3\right) e^{-r/4a}$
$R_{41} = \frac{5}{16\sqrt{15}} a^{-3/2} \left(1 - \frac{r}{4a} + \frac{1}{80} \left(\frac{r}{a}\right)^2\right) \left(\frac{r}{a}\right) e^{-r/4a}$
$R_{42} = \frac{1}{64\sqrt{5}} a^{-3/2} \left(1 - \frac{r}{12a}\right) \left(\frac{r}{a}\right)^2 \exp(-r/4a)$
$R_{43} = \frac{a^{-3/2}}{768\sqrt{35}} \left(\frac{r}{a}\right)^3 \exp(-r/4a)$

Table IV: Spherical Harmonics. Also on page 151 Griffiths

E_1	-13.6 eV
E_2	-3.4 eV
E_3	-1.5 eV
E_4	-0.85 eV
E_5	-0.54 eV
E_6	-0.38 eV

A measurement of the angular momentum is rather weird, due to the fact that \hat{L}_x , \hat{L}_y and \hat{L}_z don't commute. Therefore one often measures the length of the angular momentum vector \hat{L}^2 , as well as *one* of the components, for example \hat{L}_z . When we measure these, we get the following:

$$\begin{aligned} \hat{L}^2 |n\ell m\rangle &= \hbar^2 \ell(\ell+1) |n\ell m\rangle \\ \hat{L}_z |n\ell m\rangle &= \hbar m |n\ell m\rangle \end{aligned}$$

Thus the quantum number ℓ tells us something about the length of the angular momentum, and the quantum number m tells us about the component of angular momentum along the z -axis.

$$\begin{aligned} \hbar &= 1.0545718 \times 10^{-34} \text{Js} \\ h &= 6.62607015 \times 10^{-34} \text{Js} \end{aligned}$$

III. MATHEMATICS

Spherical Coordinates:

$$\begin{aligned} x &= r \cos \phi \sin \theta \\ y &= r \sin \phi \sin \theta \\ z &= r \cos \theta \end{aligned}$$

The (determinant of the) Jacobian for the transformation from cartesian to spherical coordinates is $r^2 \sin \theta$,

therefore every spherical integral will look like this:

$$\int_0^{2\pi} \int_0^\pi \int_0^\infty (\dots) r^2 \sin \theta \, dr d\theta d\phi$$

Exponential integrals:

$$\int_0^\infty x^n \exp\left(-\frac{x}{a}\right) dx = n! a^{n+1}$$

Gaussian integrals:

$$\begin{aligned} \int_0^\infty x^{2n} \exp\left(-\frac{x^2}{a^2}\right) dx &= \sqrt{\pi} \frac{(2n)!}{n!} \left(\frac{a}{2}\right)^{2n+1} \\ \int_0^\infty x^{2n+1} \exp\left(-\frac{x^2}{a^2}\right) dx &= \frac{n!}{2} a^{2n+2} \end{aligned}$$

IV. CONSTANTS