PX2132: Introductory Quantum Mechanics

F. Flicker

October 21, 2020

1 Introduction

Lecture: 10am on 5/10/20.

Office hours: 11am on 5/10/20.

Videos: V1.0, V1.1, V1.2, V1.3, V1.4, V1.5

These notes accompany the course videos; details of derivations will appear here, but the videos should also be watched for surrounding explanation.

1.1 The Schrödinger equation

The time-dependent Schrödinger equation (TDSE) is

$$\boxed{i\hbar\partial_t\psi\left(\boldsymbol{x},t\right)=\hat{H}\psi\left(\boldsymbol{x},t\right)} \tag{1}$$

where

$$\partial_t\psi\left(\boldsymbol{x},t\right)=\left(\frac{\partial\psi\left(\boldsymbol{x},t\right)}{\partial t}\right)_{\boldsymbol{x}} \tag{2}$$

and $(\cdot)_x$ indicates that x is held constant. The Hamiltonian operator, which has dimensions of energy, is defined to be

$$\hat{H}\psi\left(\boldsymbol{x},t\right)=\left(-\frac{\hbar^2}{2m}\nabla^2+V\left(\boldsymbol{x}\right)\right)\psi\left(\boldsymbol{x},t\right). \tag{3}$$

The TDSE is a second-order partial differential equation. The equation is separable using the substitution $\psi\left(\boldsymbol{x},t\right)=\phi\left(\boldsymbol{x}\right)T\left(t\right)$:

$$\begin{gathered} i\hbar\phi\left(\boldsymbol{x}\right)\frac{\mathrm{d}T\left(t\right)}{\mathrm{d}t}=T\left(t\right)\hat{H}\phi\left(\boldsymbol{x}\right) \\ \downarrow \\ i\hbar\frac{1}{T\left(t\right)}\frac{\mathrm{d}T\left(t\right)}{\mathrm{d}t}=\frac{1}{\phi\left(\boldsymbol{x}\right)}\hat{H}\phi\left(\boldsymbol{x}\right) \end{gathered} \tag{4}$$

where the derivatives are now total derivatives. Since the relation holds for all $\boldsymbol{x}$ and t both sides must be equal to a constant which we will suggestively call E. We can assume E is real for now; we will prove this later. This gives two equations. The first is **the time-independent Schrödinger equation (TISE)**:

$$\begin{gathered} \frac{1}{\phi\left(\boldsymbol{x}\right)}\hat{H}\phi\left(\boldsymbol{x}\right)=E \\ \downarrow \end{gathered}$$

$$\boxed{\hat{H}\phi(\boldsymbol{x}) = E\phi(\boldsymbol{x})} \tag{5}$$

and the second gives the time evolution of the wavefunction:

$$\begin{aligned} i\hbar\frac{1}{T(t)}\frac{\mathrm{d}T(t)}{\mathrm{d}t} &= E \\ &\downarrow \\ T(t) &= \exp(-iEt/\hbar)\,T(0) \\ &\downarrow \\ \psi(\boldsymbol{x},t) &= \exp(-iEt/\hbar)\,\psi(\boldsymbol{x},0)\,. \end{aligned} \tag{6}$$

We will focus on the 1D case in which $\nabla = \partial/\partial x = \partial_x$ unless otherwise stated, but the generalisation is straightforward.

1.2 General boundary conditions

The following boundary conditions apply to all the cases of physical interest in the TISE:

$$\boxed{\begin{array}{c} \text{(i)} \quad \phi(\boldsymbol{x}) \text{ is continuous} \\ \\ \text{(ii)} \quad \nabla\phi(\boldsymbol{x}) \text{ is continuous except possibly at infinite discontinuities in } V(\boldsymbol{x})\,. \end{array}} \tag{7}$$

These follow from the fact that the TISE is second-order in spatial derivatives, and we never consider potentials which are too pathological (we can have infinite potentials and discontinuous potentials, and even derivatives of discontinuities, but nothing worse). A useful condition for cases when (ii) does not apply is that $\psi = 0$ in regions where $V = \infty$.

1.3 Probability density

The meaning of the wavefunction ψ is debated. What can be said for certain is that $|\psi(x,t)|^2\,\mathrm{d}x$ gives the probability to find the particle between x and $x + \mathrm{d}x$ at time t. This is called the Born rule. The quantity

$$\boxed{\rho(x,t) = |\psi(x,t)|^2} \tag{8}$$

is called the probability density.

1.4 Probability current density

Consider how the probability density $\rho(\boldsymbol{x}, t)$ changes with respect to time (it's no harder to consider three dimensions, so we will for generality):

$$\begin{aligned}
\partial_t \rho(x,t) = \partial_t |\psi|^2 &= \psi^* \partial_t \psi + \psi \partial_t \psi^* \\
&= \frac{1}{i\hbar} \left\{ \psi^* \left(i\hbar \partial_t \psi \right) - \psi \left(-i\hbar \partial_t \psi^* \right) \right\} \\
&\downarrow \text{TDSE} \\
&= \frac{i\hbar}{2m} \left\{ \psi^* \nabla^2 \psi - \psi \nabla^2 \psi^* \right\} \\
&= \frac{i\hbar}{2m} \nabla \cdot \left\{ \psi^* \nabla \psi - \psi \nabla \psi^* \right\}.
\end{aligned}$$

This gives us a **continuity equation for conservation of probability**:

$$\boxed{\partial_t \rho(\boldsymbol{x}, t) = -\nabla \cdot \boldsymbol{j}(\boldsymbol{x}, t)} \tag{9}$$

where

$$\boxed{\boldsymbol{j}(\boldsymbol{x}, t) = \frac{i\hbar}{2m} \left\{ \psi \nabla \psi^* - \psi^* \nabla \psi \right\}} \tag{10}$$

is the **probability current density**.

2 Scattering and tunnelling

Lecture: 10am on 12/10/20.

Office hours: 11am on 12/10/20.

Videos: V2.1a, V2.1b, V2.1c, V2.1d, V2.2, V2.3

2.1 TISE: solutions in regions of constant potential

In regions of constant potential there are three forms of solution, all of which have counterparts in classical waves:

$$\text{travelling waves (plane waves):} \phi(x) = a\exp(ikx) + b\exp(-ikx) \tag{11}$$

$$\text{standing waves:} \phi(x) = a\cos(kx) + b\sin(kx) \tag{12}$$

$$\text{evanescent waves:} \phi(x) = a\exp(\kappa x) + b\exp(-\kappa x)\,. \tag{13}$$

The coefficients a and b can be complex in general. In fact the travelling wave solution is already completely general (allowing for complex wavevectors for evanescent waves). Nevertheless, it is often simpler to choose the appropriate form of solution using physical intuition. Standing waves are relevant if leftgoing and rightgoing travelling waves appear in the region with equal amplitude (useful for bound states); evanescent waves are relevant if the particle's energy is less than the potential in the region.

2.2 Plane waves

A trivial example is given by $V(x) = 0$. Here we find the general solutions

$$\begin{aligned} \phi(x) &= a_\pm \exp(\pm ikx) \\ T(t) &= T(0)\exp(-iEt/\hbar) \end{aligned} \tag{14}$$

for real k. The time dependent wave function is

$$\psi(x,t) = \phi(x)\,T(t) = a_\pm \exp(\pm ikx - iEt/\hbar) \tag{15}$$

for a possibly complex $a_\pm$. These correspond to plane waves propagating in the $\pm x$ directions. Comparing to the general form of a plane wave solution

$$\psi(x,t) = a_\pm \exp(i(\pm kx - \omega t)) \tag{16}$$

we see that

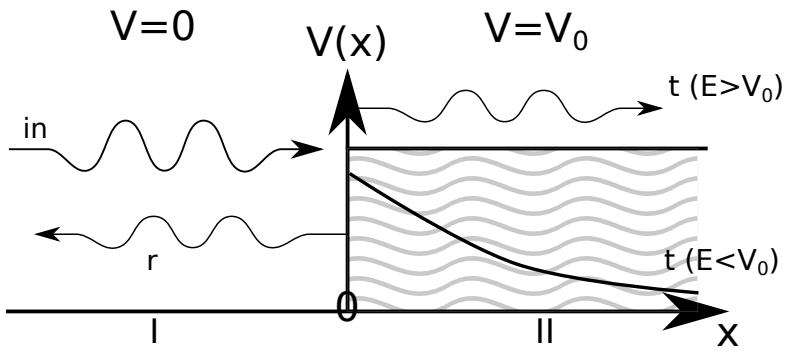

Figure 1: The potential step defined in Eq. 21, with schematic solutions indicated.

$$E = \hbar\omega \tag{17}$$

(the Einstein relation). Substituting into the TISE, Eq. 5, we find that

$$E = \frac{\hbar^2 k^2}{2m}. \tag{18}$$

Equating this to the non-relativistic expression for the kinetic energy

$$E = \frac{p^2}{2m} \tag{19}$$

we find the de Broglie relation

$$p = \hbar k. \tag{20}$$

2.3 Scattering from a potential step

Consider the potential

$$V(x) = \begin{cases} 0, & x < 0 \text{ (region } I\text{)} \\ V_0, & x \geq 0 \text{ (region } II\text{)}. \end{cases} \tag{21}$$

This is shown schematically in Fig. 21. Assume a particle is incident from the left.
We can solve the TISE in both regions and match them using the the general boundary conditions of Eq. 7. From the solution of the TISE we can always obtain the time-dependent solutions without extra work.

2.3.1 Region I

For $x < 0$ we have the general solution

$$\phi_{_I}(x) = a_{_I}\exp(ik_{_I}x) + b_{_I}\exp(-ik_{_I}x)$$
$$E = \frac{\hbar^2 k_{_I}^2}{2m}. \tag{22}$$

where $a_{_I}$ corresponds to the rightmoving ingoing wave, and $b_{_I}$ the leftmoving reflected wave. This wavefunction is unphysical as it cannot be normalised; a more physical solution would involve summing up plane waves to form a wave packet of finite extent. Without loss of generality set $a_{_I} = 1$ and $b_{_I} = r$, the reflection amplitude:

$$\phi_{_I}(x) = \exp(ik_{_I}x) + r\exp(-ik_{_I}x). \tag{23}$$

2.3.2 Region II: $E > V_0$

Assuming $E > V_0$ we have the general solution

$$\phi_{_{II}}(x,t) = a_{_{II}}\exp(ik_{_{II}}x) + b_{_{II}}\exp(-ik_{_{II}}x)$$
$$E - V_0 = \frac{\hbar^2 k_{_{II}}^2}{2m} \tag{24}$$

Therefore

$$k_{_I}^2 = k_{_{II}}^2 + \frac{2mV_0}{\hbar^2}. \tag{25}$$

Physically we know that $b_{_{II}} = 0$, and therefore rename $a_{_{II}} = t$ the transmission amplitude:

$$\phi_{_{II}}(x) = t\exp(ik_{_{II}}x). \tag{26}$$

Boundary condition (i):

$$\phi_{_I}(0) = \phi_{_{II}}(0)$$
$$\downarrow$$
$$1 + r = t. \tag{27}$$

Boundary condition (ii):

$$\phi_{I}'(0) = \phi_{II}'(0)$$
$$\downarrow$$
$$k_{I}(1-r) = k_{II}t. \tag{28}$$

Therefore combining with Eq. 27 we have:

$$r = \frac{k_{I} - k_{II}}{k_{I} + k_{II}} \tag{29}$$
$$t = \frac{2k_{I}}{k_{I} + k_{II}}. \tag{30}$$

2.3.3 Region II: $E < V_0$

Assuming $E > V_0$ we instead have the solution

$$\phi_{II}(x) = a_{II}\exp(\kappa x) + b_{II}\exp(-\kappa x)$$
$$E - V_0 = -\frac{\hbar^2\kappa^2}{2m}. \tag{31}$$

We know on physical grounds that $a_{II} = 0$. We can rename $b_{II} = t$.

$$\phi_{II}(x) = t\exp(-\kappa x). \tag{32}$$

Boundary condition (i):

$$\phi_{I}(0) = \phi_{II}(0)$$
$$\downarrow$$
$$1 + r = t \tag{33}$$

as before (Eq. 27). From Eqs. 22, 31

$$k_{I}^2 = -\kappa^2 + \frac{2mV_0}{\hbar^2}. \tag{34}$$

Boundary condition (ii):

$$\phi_{I}'(0) = \phi_{II}'(0)$$

$$\downarrow$$

$$ik_{I}(1-r) = -\kappa t. \tag{35}$$

Therefore combining with Eq. 33 we have:

$$r = \frac{k_{I} - i\kappa}{k_{I} + i\kappa} \tag{36}$$

$$t = \frac{2k_{I}}{k_{I} + i\kappa}. \tag{37}$$

Note that the same result can be achieved more simply by substituting $k_{II} \rightarrow i\kappa$ into the results for $E > V_0$.

2.3.4 Probability fluxes

The probability that the particle is reflected by the step, R, is given by the ratio of reflected probability current density j_R to incident probability current density j_{in}:

$$R = \left|\frac{j_R}{j_{in}}\right| \tag{38}$$

where the probability current density is defined in Eq. 10. Similarly the probability that the particle is transmitted by the step, T, is given by the ratio of transmitted probability current density j_T to incident probability current density j_{in}:

$$T = \left|\frac{j_T}{j_{in}}\right|. \tag{39}$$

For $E > V_0$ we have

$$\psi_{in}(x,t') = \exp(-iEt'/\hbar)\exp(ik_{I}x) \tag{40}$$

$$\psi_{R}(x,t') = r\exp(-iEt'/\hbar)\exp(-ik_{I}x) \tag{41}$$

$$\psi_{T}(x,t') = t\exp(-iEt'/\hbar)\exp(-ik_{II}x) \tag{42}$$

where t' has been used to indicate time in order to avoid confusion with the transmission probability amplitude t. Therefore

$$j_{in} = \frac{\hbar k_{_I}}{m} \tag{43}$$

$$j_R = \frac{\hbar\left(-k_{_I}\right)}{m}\left|r\right|^2 \tag{44}$$

$$j_T = \frac{\hbar k_{_{II}}}{m}\left|t\right|^2 \tag{45}$$

where the negative sign in j_R is because j is a vector quantity. The probability of reflection and transmission is

$$R = \left|r\right|^2 \tag{46}$$

$$T = \frac{k_{_{II}}}{k_{_I}}\left|t\right|^2 \tag{47}$$

meaning that

$$R + T = 1 \tag{48}$$

in accordance with conservation of probability.

For $E < V_0$ we have

$$\psi_{in}\left(x, t'\right) = \exp\left(-iEt'/\hbar\right)\exp\left(ik_{_I}x\right) \tag{49}$$

$$\psi_R\left(x, t'\right) = r\exp\left(-iEt'/\hbar\right)\exp\left(-ik_{_I}x\right) \tag{50}$$

$$\psi_T\left(x, t'\right) = t\exp\left(-iEt'/\hbar\right)\exp\left(-\kappa x\right) \tag{51}$$

and so

$$j_{in} = \frac{\hbar k_{_I}}{m} \tag{52}$$

$$j_R = \frac{\hbar\left(-k_{_I}\right)}{m}\left|r\right|^2 \tag{53}$$

$$j_T = 0. \tag{54}$$

The probability of reflection and transmission is now

$$R = 1 \tag{55}$$

$$T = 0. \tag{56}$$

The particle is reflected with certainty. It nevertheless has an amplitude to be detected within the barrier. If a measurement were to locate the particle in the barrier, the additional energy would

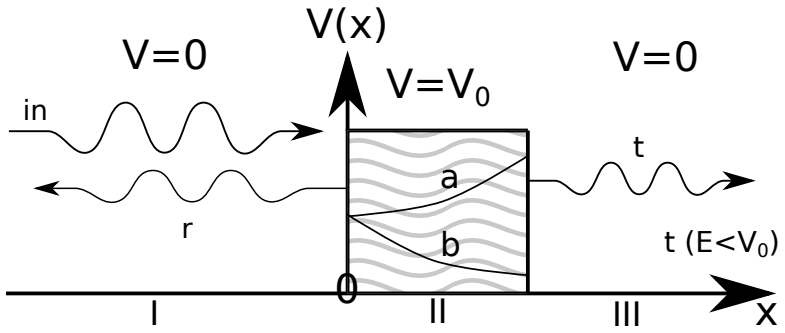

Figure 2: The potential barrier of Eq. 57. Schematic solutions; those in region II assume $E < V_0$.

have to be provided by the measurement itself. You can think of it as the measurement device changing the potential so that the potential step has a finite width, beyond which $E < V_0$ again. We will consider this situation next.

2.4 Quantum tunnelling

Now consider the potential

$$V(x) = \begin{cases} 0, & x < 0 \,(\text{region } I) \\ V_0, & 0 \leq x < L \,(\text{region } II) \\ 0, & x \geq L \,(\text{region } III). \end{cases} \tag{57}$$

This is shown in Fig. 2.

We can no longer neglect the increasing solution in region II. While we therefore have two extra unknowns, we also have two extra boundary conditions, giving four in total:

$$(i) \quad \phi_{I}(0) = \phi_{II}(0) \tag{58}$$

$$(ii) \quad \phi'_{I}(0) = \phi'_{II}(0) \tag{59}$$

$$(iii) \quad \phi_{II}(L) = \phi_{III}(L) \tag{60}$$

$$(iv) \quad \phi'_{II}(L) = \phi'_{III}(L). \tag{61}$$

We know that $k_{I} = k_{III}$ from symmetry:

$$k_{I} = k_{III} \triangleq k \tag{62}$$

and

$$k = \frac{\sqrt{2mE}}{\hbar}. \tag{63}$$

As before, we must treat the cases $E > V_0$ and $E < V_0$ separately.

2.4.1 $E > V_0$

The wavefunctions in the various regions are:

$$\phi_{I}(x) = \exp(ikx) + r\exp(-ikx) \tag{64}$$

$$\phi_{II}(x) = a\exp(ik'x) + b\exp(-ik'x) \tag{65}$$

$$\phi_{III}(x) = t\exp(ikx). \tag{66}$$

where the wavevector in region II is defined to be k':

$$k_{II} \triangleq k' \tag{67}$$

$$k' = \frac{\sqrt{2m(E-V_0)}}{\hbar}. \tag{68}$$

Applying the boundary conditions we have

$$(i) \quad 1 + r = a + b \tag{69}$$

$$(ii) \quad 1 - r = \frac{k'}{k}(a - b) \tag{70}$$

$$(iii) \quad a\exp(ik'L) + b\exp(-ik'L) = t\exp(ikL) \tag{71}$$

$$(iv) \quad \frac{k'}{k}(a\exp(ik'L) - b\exp(-ik'L)) = t\exp(ikL). \tag{72}$$

These are four coupled linear equations in four unknowns, and can be solved by standard methods. There is no especially elegant way to do so. Defining

$$\theta \triangleq \frac{k'}{k} \tag{73}$$

we can write the equations in matrix form:

$$\begin{pmatrix} -1 & 1 & 1 & 0 \\ 1 & \theta & -\theta & 0 \\ 0 & e^{ik'L} & e^{-ik'L} & -1 \\ 0 & \theta e^{ik'L} & -\theta e^{-ik'L} & -1 \end{pmatrix} \begin{pmatrix} r \\ a \\ b \\ t\exp(ikL) \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \\ 0 \\ 0 \end{pmatrix}. \tag{74}$$

Defining the matrix to be M we have that

$$\begin{pmatrix} r \\ a \\ b \\ t\exp(ikL) \end{pmatrix} = M^{-1} \begin{pmatrix} 1 \\ 1 \\ 0 \\ 0 \end{pmatrix}. \tag{75}$$

Let's look at the transmission amplitude. Multiplying out gives

$$t\exp(ikL) = M^{-1}_{41} + M^{-1}_{42}. \tag{76}$$

The general result for matrix inversion tells us that

$$M^{-1}_{ij} = \frac{1}{\det(M)} C_{ji} \tag{77}$$

where C_{ji} is the signed cofactor of element M_{ij}, *i.e.* the determinant of the matrix formed by removing row i and column j from the transpose of M, multiplied by $(-1)^{i+j}$. Therefore

$$t\exp(ikL) = \frac{C_{14} + C_{24}}{\det(M)} \tag{78}$$

and in this case

$$C_{24} = \begin{vmatrix} -1 & 1 & 1 \\ 0 & e^{ik'L} & e^{-ik'L} \\ 0 & \theta e^{ik'L} & -\theta e^{-ik'L} \end{vmatrix} = 2\theta \tag{79}$$

$$C_{14} = -\begin{vmatrix} 1 & \theta & -\theta \\ 0 & e^{ik'L} & e^{-ik'L} \\ 0 & \theta e^{ik'L} & -\theta e^{-ik'L} \end{vmatrix} = 2\theta \tag{80}$$

$$\begin{aligned} \det(M) &= -\begin{vmatrix} \theta & -\theta & 0 \\ e^{ik'L} & e^{-ik'L} & -1 \\ \theta e^{ik'L} & -\theta e^{-ik'L} & -1 \end{vmatrix} - \begin{vmatrix} 1 & 1 & 0 \\ e^{ik'L} & e^{-ik'L} & -1 \\ \theta e^{ik'L} & -\theta e^{-ik'L} & -1 \end{vmatrix} \\ &= 4\theta\cos(k'L) - 2i\left(1+\theta^2\right)\sin(k'L) \end{aligned}$$

where the rules of determinants can be used to simplify the problem significantly. This gives

$$t = \frac{2\theta\exp(-ikL)}{2\theta\cos(k'L) - i\left(1+\theta^2\right)\sin(k'L)} \tag{81}$$

and

$$T = \frac{j_{III}}{j_{in}} = |t|^2 = \frac{4\theta^2}{4\theta^2 \cos^2(k'L) + (1+\theta^2)^2 \sin^2(k'L)} = \frac{1}{1 + \left(\frac{\theta^2-1}{2\theta}\right)^2 \sin^2(k'L)}$$

or, substituting Eqs. 63, 68, and 73:

$$T = \frac{4E(E-V_0)}{4E(E-V_0) + V_0^2 \sin^2\left(L\sqrt{2m(E-V_0)}/\hbar\right)}. \tag{82}$$

Note that when $k'L = n\pi$ for integer n, there is perfect 'resonant transmission', $T = 1$, $R = 0$.

2.4.2 $E < V_0$

The wavefunction regions I, III are unchanged, and that in region II is:

$$\phi_{II}(x) = a\exp(\kappa x) + b\exp(-\kappa x). \tag{83}$$

We can simply take the results of the $E > V_0$ case and substitute $k' \to -i\kappa$. This changes $\theta \to -i\kappa/k$, which we can call $-i\theta$. We find

$$T = \frac{1}{1 + \left(\frac{\theta^2+1}{2\theta}\right)^2 \sinh^2(\kappa L)} \tag{84}$$

or, substituting the expressions for k and κ:

$$T = \frac{4E(V_0-E)}{4E(V_0-E) + V_0^2 \sinh^2\left(L\sqrt{2m(V_0-E)}/\hbar\right)}. \tag{85}$$

2.4.3 $E = V_0$

In the special case that $E = V_0$, the TISE in the barrier takes the form

$$-\frac{\hbar^2}{2m}\phi''_{II}(x) = 0 \tag{86}$$

i.e.

$$\phi_{II}(x) = ax/L + b \tag{87}$$

where the L is included so that all coefficients have the same dimensions. Since k_I is now the only wavevector in the problem rename it k. Applying the boundary conditions gives

$$1 + r = b \tag{88}$$

$$ik\,(1 - r) = a/L \tag{89}$$

$$a + b = t \exp(ikL) \tag{90}$$

$$a/L = ikt \exp(ikL)\,. \tag{91}$$

We can eliminate a and b to give

$$1 + r = t \exp(ikL)\,(1 - ikL) \tag{92}$$

$$1 - r = t \exp(ikL) \tag{93}$$

so that

$$t = \frac{2 \exp(-ikL)}{2 - ikL} \tag{94}$$

and

$$T = |t|^2 = \frac{4}{4 + k^2 L^2}. \tag{95}$$

Substituting

$$\frac{\hbar^2 k^2}{2m} = E = V_0 \tag{96}$$

gives

$$T = \frac{1}{1 + \frac{mV_0 L^2}{2\hbar^2}}. \tag{97}$$

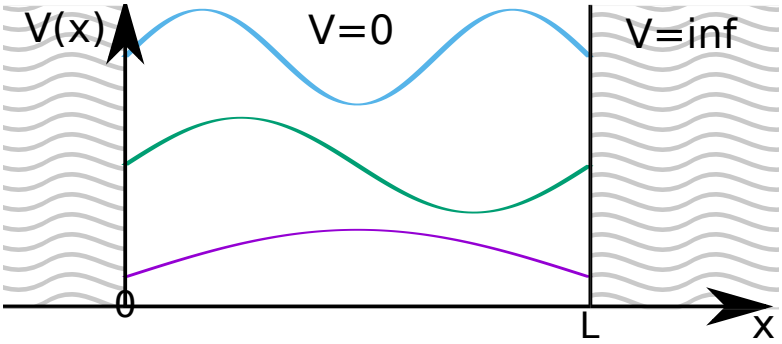

Figure 3: The infinite potential well. Snapshots of the real parts of the first few energy eigenfunctions are shown, offset vertically for clarity (see video V3.1).

3 Bound states (I)

Lecture: 10am on 19/10/20.

Office hours: 11am on 19/10/20.

Videos: V3.1, V3.2, V3.3, V3.4, V3.5

3.1 The 1D infinite potential well

Consider the following potential:

$$V(x) = \begin{cases} 0, & 0 < x < L \\ \infty, & \text{otherwise.} \end{cases} \tag{98}$$

This is shown in Fig. 3. Inside the well the TISE is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\phi(x)}{\mathrm{d}x^2} = E\phi(x)\,. \tag{99}$$

The general solutions are now standing waves:

$$\phi(x) = a\cos(kx) + b\sin(kx)\,. \tag{100}$$

The infinite potential acts as a boundary condition enforcing

$$\text{(i) } \phi(0) = 0 \tag{101}$$

$$\text{(ii) } \phi(L) = 0. \tag{102}$$

Applying the conditions gives

$$\text{(i) } a = 0 \tag{103}$$

$$\text{(ii) } \sin(kx) = 0 \ \therefore \ k = \frac{n\pi}{L}, \ n \in \mathbb{Z}. \tag{104}$$

There are an infinite number of solutions:

$$\phi_n(x) = b_n \sin(k_n x) \tag{105}$$

where

$$k_n = \frac{n\pi}{L} \tag{106}$$

and substituting into the TISE gives the corresponding energy eigenvalues

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mL^2}. \tag{107}$$

with n any positive integer. The first few are shown in Fig. 3. The solutions ϕ_n are called energy eigenstates: $\phi_1$is called the ground state wavefunction, ϕ_2 the first excited state, and so on. They are states of definite energy: if the energy of ϕ_n is measured, E_n will be found with probability 1.

3.2 Normalisation

While the position of the particle cannot be predicted with certainty, we know that the particle must exist somewhere, and so the probability density integrated over all of space must be one. In general, in 1D, we therefore have that

$$\boxed{1 = \int_{-\infty}^{\infty} |\psi(x,t)|^2 \, \mathrm{d}x} \tag{108}$$

the normalization of the wavefunction. In the specific case of the infinite well we have that

$$1 = \int_0^L |\psi|^2 \, \mathrm{d}x. \tag{109}$$

This condition allows us to find the coefficient C in Eq. 105:

$$1 = \int_0^L \left| b_n \sin\left(\frac{n\pi x}{L}\right) \right|^2 \mathrm{d}x$$

$$\downarrow$$

$$|b_n| = \sqrt{\frac{2}{L}}. \tag{110}$$

Therefore the normalised eigenfunctions are

$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \tag{111}$$

up to an arbitrary complex prefactor of magnitude 1. This arbitrary prefactor is called the global phase of the wavefunction, and is meaningless by itself as it can never be observed. The differences in phases between two wavefunctions can, however, be detected, as we saw in the two-slit experiment.

3.3 Stationary states

Recall that we can always reconstruct the time dependence of the wavefunction from the time-independent solution using Eq. 6. In the case of the infinite well we have

$$\psi_n(x,t) = \exp(iE_n t/\hbar)\,\phi_n(x) = \sqrt{\frac{2}{L}} \exp\left(\frac{i\hbar n^2\pi^2 t}{2mL^2}\right) \sin\left(\frac{n\pi x}{L}\right). \tag{112}$$

In the specific case that $\phi_n(x)$ is an energy eigenfunction, the time evolution only affects the complex phase, not the magnitude of the solution. Energy eigenfunctions are called stationary states, as the observable probability density $|\psi|^2$ does not vary with time:

$$|\psi_n(x,t)|^2 = |\phi_n(x)|^2 = \frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right). \tag{113}$$

3.4 Expectation values

Using the probability density we can find the expectation values $\langle\mathcal{O}\rangle$, *i.e.* the average values, of observables $\mathcal{O}$:

$$\boxed{\left\langle\hat{\mathcal{O}}\right\rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\,\mathcal{O}(x)\,\psi(x,t)\,\mathrm{d}x.} \tag{114}$$

For example, the expected value of positon is

$$\langle x\rangle = \int_{-\infty}^{\infty} x\,|\psi(x)|^2\,\mathrm{d}x \tag{115}$$

and

$$\left\langle x^2\right\rangle = \int_{-\infty}^{\infty} x^2\,|\psi(x)|^2\,\mathrm{d}x. \tag{116}$$

The expected position of the particle in the ground state of the infinite potential well is given by

$$\begin{aligned}\langle x\rangle &= \int_0^L x\,|\psi_1(x,t)|^2\,\mathrm{d}x \\ &= \int_0^L x\,|\phi_1(x)|^2\,\mathrm{d}x \\ &= \frac{2}{L}\int_0^L x\sin^2\left(\frac{\pi x}{L}\right)\mathrm{d}x \\ &= 0.\end{aligned}$$

4 Bound states (II)

Lecture: 10am on 26/10/20.

Office hours: 11am on 26/10/20.

Videos: V4.1, V4.2

4.1 Quantum superposition

Quantum mechanics is linear. As a corollory, if two wavefunctions each individually solve the Schrödinger equation, any linear combination of them also solves the Schrödinger equation. While energy eigenfunctions are stationary states, the sum of two eigenfunctions is not, in general. Consider for example the sum of the first two eigenfunctions of the infinite well:

$$\left|\psi_1(x,t)+\psi_2(x,t)\right|^2=\frac{2}{L}\left(\sin^2\left(\frac{\pi x}{L}\right)+\sin^2\left(\frac{2\pi x}{L}\right)+2\cos\left(\frac{3\hbar\pi^2 t}{2mL^2}\right)\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi x}{L}\right)\right). \tag{117}$$

which is time dependent. Note that the combined state $\psi_1(x,t)+\psi_2(x,t)$ is also no longer correctly normalized. If a measurement of energy is performed on a superposition of energy eigenstates

$$\varphi(x)=\sum_n a_n\phi_n(x) \tag{118}$$

one of the energies E_n will be found. After this measurement the wavefunction will be changed to the corresponding eigenstate ϕ_n. This process is termed the collapse of the wavefunction. The probability of finding state ϕ_n is given by $|a_n|^2$ before the measurement; after the measurement it is 1. These statements are well-tested experimentally; their philosophical interpretation is debated. Understanding what happens when measurements are performed on quantum systems is called the measurement problem, and is a major open problem in physics and philosophy.

4.2 Complete orthonormal basis

In general, the set of normalised energy eigenfunctions form a complete orthonormal basis. Mathematically, this means that

$$\int_{-\infty}^{\infty}\phi_n^*(x)\,\phi_m(x)\,\mathrm{d}x=\delta_{nm} \tag{119}$$

where the Kronecker delta is defined through

$$\delta_{nm}=\begin{cases}1, & n=m\\ 0, & n\neq m\end{cases}. \tag{120}$$

This means that any function can be constructed from them using Fourier decomposition:

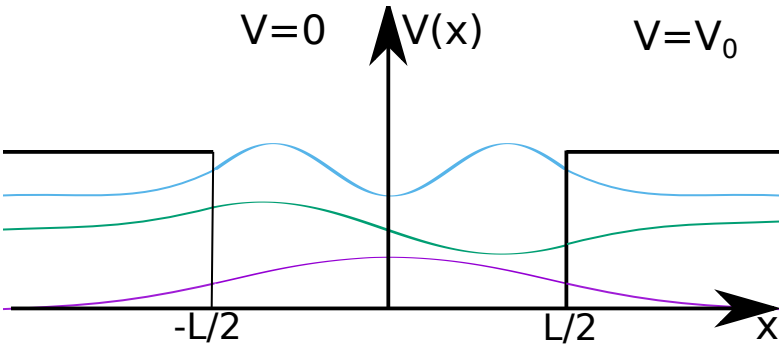

Figure 4: The finite potential well. In this case the potential V_0 is such that three bound states exist. The real parts of the wavefunctions are sketched offset in energy.

$$\varphi(x) = \sum_n a_n \phi_n(x) \tag{121}$$

where the complex coefficients can be found using

$$a_n = \int_{-\infty}^{\infty} \phi_n^*(x)\, \varphi(x)\, \mathrm{d}x. \tag{122}$$

We can, as always, include the time dependence:

$$\varphi(x) = \sum_n a_n \phi_n(x) \tag{123}$$

$$\downarrow \tag{124}$$

$$\psi(x,t) = \sum_n a_n \phi_n(x) \exp(-iE_n t/\hbar). \tag{125}$$

4.3 The finite potential well

Consider the potential:

$$V(x) = \begin{cases} V_0, & x < -L/2 \text{ (region } I) \\ 0, & -L/2 \leq x \leq L/2 \text{ (region } II) \\ V_0, & x > L/2 \text{ (region } III). \end{cases} \tag{126}$$

The particle now has a probability to exist within the boundary region, and only a finite number of energy eigenstates will exist within the well (bound states with $E < V_0$). We must solve the TISE in each region then match the solutions using the boundary conditions of Eqns.

Region II

Within the well the general solution is the same as that of the infinite well before boundary conditions are applied. As the edges of the well are now symmetrical about the origin it is convenient to write the general solution in terms of odd and even functions:

$$\phi_{II}(x) = a\sin(kx) + b\cos(kx) \tag{127}$$

$$E = \frac{\hbar^2 k^2}{2m}. \tag{128}$$

Regions I, III

Assuming $E < V_0$ we have the general solution

$$\phi(x) = c\exp(\kappa x) + d\exp(-\kappa x) \tag{129}$$

$$E - V_0 = -\frac{\hbar^2\kappa^2}{2m} \tag{130}$$

for real κ. Normalizability requires that the wavefunction tend to zero at $x = \pm\infty$, which means only the solutions which decay away from the well are relevant:

$$\phi_I(x) = c\exp(\kappa x) \tag{131}$$

$$\phi_{III}(x) = d\exp(-\kappa x). \tag{132}$$

Solution

We have four unknown quantities and four boundary conditions, but the problem is underdetermined:

$$(i) \quad \phi_I(-L/2) = \phi_{II}(-L/2) \tag{133}$$

$$(ii) \quad \phi'_I(-L/2) = \phi'_{II}(-L/2) \tag{134}$$

$$(iii) \quad \phi_{II}(L/2) = \phi_{III}(L/2) \tag{135}$$

$$(iv) \quad \phi'_{II}(L/2) = \phi'_{III}(L/2). \tag{136}$$

It is convenient to consider the even and odd solutions separately. Inspired by the solutions for the infinite well, we see that:

$$\text{even } \phi\text{:} \quad a = 0 \tag{137}$$

$$d = c \tag{138}$$

$$\text{odd } \phi\text{:} \quad b = 0 \tag{139}$$

$$d = -c. \tag{140}$$

Figure 5: Graphical solutions for the bound state energies in Eq. 144.

The relative size of the two coefficients is easily fixed with one of the boundary conditions, and the overall normalisation fixed in the usual way. As in the infinite well, only discrete energy eigenvalues exist at certain values of E. Unlike the infinite well, there are now a finite number of eigenvalues, and the eigenfunctions are not orthogonal to one another and do not form a complete set of states.

$$\text{even } \phi\text{:} \quad \left.\begin{array}{ll} (i) & c\exp\left(-\kappa L/2\right) = b\cos\left(kL/2\right) \\ (ii) & \kappa c\exp\left(-\kappa L/2\right) = kb\sin\left(kL/2\right) \end{array}\right\} \quad \frac{\kappa}{k} = \tan\left(kL/2\right) \tag{141}$$

$$\text{odd } \phi\text{:} \quad \left.\begin{array}{ll} (i) & c\exp\left(-L/2\right) = -a\sin\left(kL/2\right) \\ (ii) & \kappa c\exp\left(-L/2\right) = ka\cos\left(kL/2\right) \end{array}\right\} \quad \frac{\kappa}{k} = -\cot\left(kL/2\right). \tag{142}$$

These are transcendental equations and cannot be solved analytically. Using the expressions for k and κ in terms of E (Eqs. 128 and 130) reveals solutions for

$$\sqrt{\frac{V_0 - E}{E}} = \begin{cases} \tan\left(\frac{L}{\hbar}\sqrt{\frac{mE}{2}}\right), & \text{even } \phi \\ -\cot\left(\frac{L}{\hbar}\sqrt{\frac{mE}{2}}\right), & \text{odd } \phi \end{cases} \tag{143}$$

squaring both sides and rearranging gives

$$E = \begin{cases} V_0\cos^2\left(\frac{L}{\hbar}\sqrt{\frac{mE}{2}}\right), & \text{even } \phi \\ V_0\sin^2\left(\frac{L}{\hbar}\sqrt{\frac{mE}{2}}\right), & \text{odd } \phi. \end{cases} \tag{144}$$

some solutions are shown graphically in Fig. 5. There is always at least one even solution even for arbitrarily weak V_0.

5 Finite-dimensional Hilbert spaces

Lecture: 10am on 2/11/20.

Office hours: 11am on 2/11/20.

Videos: V5.1, V5.2, V5.3a, V5.3b, V5.3c, V5.4

For the purposes of this course we can define a Hilbert space to be a linear vector space equipped with an inner product, in which all vectors are square-integrable. We will see in lecture 7 wavefunctions obey these properties: functions obey all the axioms of linear vector spaces. They can be thought of as infinite-dimensional vectors, since their value must be specified for an infinite number of points in space. They obey a simple inner product, and wavefunctions are always square integrable as the integral over all space of the square modulus of a wavefunction is one. Therefore wavefunctions can be thought of as living in a complex Hilbert space.

In fact Hilbert spaces need not be infinite dimensional. The simplest example of a finite-dimensional Hilbert space is the set of states associated with the spin of a spin-1/2 particle such as an electron. Measuring the spin of an electron along a chosen direction always returns the value either $+\hbar/2$ or $-\hbar/2$. The fact that the results take quantized values rather than a continuous range of values is perhaps the simplest example of a quantum system.

The description of finite-dimensional Hilbert spaces is in terms of complex vectors and matrices. This approach to quantum mechanics, 'matrix mechanics', was developed by Werner Heisenberg and others simultaneously with Schrodinger's development of wave mechanics. The two are equivalent as we will see.

Before looking at spin-1/2 in more detail it will be necessary to look at some properties of (finite-dimensional) complex vectors and matrices.

5.1 Complex vectors and matrices

Quantum mechanics is linear algebra: vectors and matrices, but also functions, which can be thought of as infinite-dimensional vectors. Specifically, the vectors live in a complex vector space equipped with an inner product, and the square modulus of the vectors is one (the normalisation property). This defines it to be a 'Hilbert space' $\mathcal{H}$. A convenient notation for complex vectors, formerly denoted $\boldsymbol{v}$, has them written $|v\rangle$:

$$\boldsymbol{v} = |v\rangle = \begin{pmatrix} v_1 \\ v_2 \\ v_3 \\ \vdots \\ v_N \end{pmatrix} \tag{145}$$

where v_i are the complex scalar elements of the N-dimensional vector $|v\rangle$. The Hermitian conjugate (complex conjugate transpose) of the vector is then written $\langle v|$:

$$\boldsymbol{v}^\dagger = (|v\rangle)^\dagger = (|v\rangle)^{*T} = \langle v| = \begin{pmatrix} v_1^*, & v_2^*, & v_3^*, & \ldots, & v_N^* \end{pmatrix}. \tag{146}$$

We generally refer to this as Dirac notation, after its inventor Paul Dirac. Dirac himself referred to it as bra-ket notation, where vectors $|\psi\rangle$ are referred to as 'kets' and their Hermitian conjugates $\langle\psi|$ are referred to as 'bras'. The notation implies the existence of the inner product (dot product), so that

$$\boldsymbol{u}^\dagger \boldsymbol{v} = \langle u|v\rangle = \begin{pmatrix} u_1^*, & u_2^*, & u_3^*, & \ldots, & u_N^* \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \\ v_3 \\ \vdots \\ v_N \end{pmatrix} = \sum_i^N u_i^* v_i. \tag{147}$$

This is then a bra-ket, *i.e.* bracket. It is a complex scalar, because a $1 \times N$ matrix (row vector) multiplied by an $N \times 1$ matrix (column vector) is a 1×1 matrix (scalar). From Eq. 147 it can be seen that another convenience of the notation follows:

$$\boxed{\langle v|u\rangle = (\langle u|v\rangle)^*} \tag{148}$$

sometimes written

$$(\langle u|v\rangle)^* = \overline{\langle u|v\rangle}. \tag{149}$$

Similarly, we can define the outer product (tensor product) as a ket-bra:

$$\boldsymbol{v}\boldsymbol{u}^\dagger = |v\rangle\langle u| = \begin{pmatrix} v_1 \\ v_2 \\ v_3 \\ \vdots \\ v_N \end{pmatrix} \begin{pmatrix} u_1^*, & u_2^*, & u_3^*, & \ldots, & u_N^* \end{pmatrix} = \begin{pmatrix} v_1u_1^* & v_1u_2^* & v_1u_3^* & \ldots & v_1u_N^* \\ v_2u_1^* & & & & \\ v_3u_1^* & & & & \\ \vdots & & & \ddots & \\ v_Nu_1^* & & & & v_Nu_N^* \end{pmatrix} \tag{150}$$

this is an $N \times N$ complex matrix. For this reason it is also an operator, capable of acting on other vectors:

$$(|v\rangle\langle u|)\,|w\rangle = |v\rangle\langle u|w\rangle = \langle u|w\rangle|v\rangle \tag{151}$$

i.e. the matrix $|v\rangle\langle u|$ acts on vector $|w\rangle$ to give vector $|v\rangle$ multiplied by scalar $\langle u|w\rangle$. A useful identity which holds for any complete set of orthonormal vectors $|e_i\rangle$ is the **resolution of the identity**:

$$\boxed{\mathbb{I} = \sum_i |e_i\rangle\langle e_i|} \tag{152}$$

where $\mathbb{I}$ is the identity matrix. This allows us to write any vector into the basis $|e_i\rangle$:

$$|v\rangle = \mathbb{I}|v\rangle = \sum_i |e_i\rangle\langle e_i|v\rangle = \sum_i \left(\langle e_i|v\rangle\right)|e_i\rangle. \tag{153}$$

For example, since

$$|e_1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \; |e_2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{154}$$

span the space of two-dimensional vectors, we can write any two-dimensional vector as

$$|v\rangle = \sum_{i=1}^{2} \left(\langle e_i|v\rangle\right)|e_i\rangle = v_1|e_1\rangle + v_2|e_2\rangle, \tag{155}$$

and the resolution of the identity holds:

$$\sum_{i=1}^{2} |e_i\rangle\langle e_i| = |e_1\rangle\langle e_1| + |e_2\rangle\langle e_2| \tag{156}$$

$$= \begin{pmatrix} 1, & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \begin{pmatrix} 0, & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{157}$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \tag{158}$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \checkmark \tag{159}$$

5.2 Hermitian matrices

Important for quantum mechanics are **Hermitian matrices**, those matrices equal to their Hermitian conjugates:

$$\boxed{M = M^\dagger.} \tag{160}$$

These have many important and physically-relevant properties.

Hermitian operators have real eigenvalues:

Denote the eigenvector with eigenvalue λ_n by the convenient notation $|n\rangle$:

$$M|v_n\rangle = \lambda_n|v_n\rangle. \tag{161}$$

Taking the Hermitian conjugate we have

$$(M|v_n\rangle)^\dagger = (\lambda_n|v_n\rangle)^\dagger$$
$$\downarrow$$
$$\langle v_n|M^\dagger = \langle v_n|\lambda_n^*. \tag{162}$$

Therefore

$$\langle v_n|M - M^\dagger|v_n\rangle = (\lambda_n - \lambda_n^*)\langle v_n|v_n\rangle \tag{163}$$

because we can act right with M using Eq. 161 and left with $M^\dagger$ using Eq. 162. Since

$$\langle v_n|v_n\rangle = ||n\rangle|^2 > 0 \tag{164}$$

(*i.e.* the square modulus of a vector is always strictly greater than zero) we see that

$$M = M^\dagger \Rightarrow \lambda = \lambda^* \tag{165}$$

i.e. Hermitian operators have real eigenvalues □

The normalised eigenvectors of Hermitian matrices are orthonormal:

Begin again with Eq. 161. Consider this object:

$$\langle v_m|M - M^\dagger|v_n\rangle = (\lambda_n - \lambda_m)\langle v_m|v_n\rangle \tag{166}$$

where the equality follows from acting M to the right and $M^\dagger$ to the left as before. Assuming no two eigenvalues are degenerate, i.e. $\lambda_n \neq \lambda_m \forall m \neq n$, we have that

$$M = M^\dagger \Rightarrow \langle v_m|v_n\rangle = 0. \tag{167}$$

Furthermore, assuming we always normalise our eigenvectors correctly,

$$\langle v_n|v_n\rangle = 1 \tag{168}$$

and so we have the stronger condition

$$\boxed{\langle v_n|v_m\rangle = \delta_{nm}} \tag{169}$$

with δ_{nm} the Kronecker delta. □

In fact the eigenvectors of a Hermitian matrix form a complete orthonormal basis for the vector space (Hilbert space) in which they live. This means that we can use them to resolve the identity:

$$\boxed{\mathbb{I} = \sum_n |v_n\rangle\langle v_n|} \,. \tag{170}$$

Acting on this expression with M shows that any Hermitian operator can be written as the sum of its eigenvalues multiplied by outer products formed from their respective eigenvectors:

$$\boxed{M = \sum_n \lambda_n |v_n\rangle\langle v_n|} \,. \tag{171}$$

In fact, you can look at the resolution of the identity as a special case of this, since the identity matrix is Hermitian with eigenvalue 1 for every vector. Therefore any complete orthonormal basis can be used to construct the identity.

5.3 Spin-1/2

Reference: Feynman III Chapter 5

5.3.1 Mathematical structure

A simple example of matrices in action in quantum mechanics is provided by spin-1/2 particles (of which electrons are an example). Spin is intrinsic angular momentum. Classically you might think of it as analogous to the angular momentum of the Earth spinning about its axis, but it is inherently quantum in nature and has no good classical analogue. In the classic Stern Gerlach experiment a beam of spin-1/2 silver atoms was directed through a magnetic field gradient (directed along z) which accelerated the atoms according to the z-projection of their spins (silver atoms were used as these have spin but are charge-neutral; electrons would receive an additional unhelpful redirection owing to their charges). Whereas classically we would expect a continuous range of deflections. Measuring the Earth's intrinsic angular momentum along a continuous range of directions will return a continuous range of values, with a maximum when measuring parallel to the axis of rotation and zero when measuring perpendicular to this axis. The silver atoms were instead found to deflect in one of two directions, a clear demonstration of quantization. For spin-n particles there are $2n + 1$ directions.
Some key observations are these:

- measurement of spin along any chosen direction yields either $+\hbar/2$ or $-\hbar/2$
- subsequent measurements along the same direction, without other measurements in between, will consistently return the same result
- if the spin is known along z, a measurement along any perpendicular direction is completely ambiguous, with 50% probability for each of $\pm\hbar/2$
- therefore, even though repeated measurements along z yield the same result, if a measurement along x is performed, a subsequent re-measurement of z will give a 50% probability of either

result $\pm\hbar/2$.

This suggests the following mathematical structure. The state of the spin-1/2 particle should be represented by vectors with two eigenvalues, $\pm\hbar/2$. Since there are two eigenvalues there should be two eigenvectors which span a two-dimensional complex vector space. The observable quantities associated with spin measurements should be 2×2 Hermitian matrices with these eigenvalues. Defining $\hat{S}_i$ to be the operator corresponding to the observable spin along direction i, we have:

$$\hat{S}_i|\uparrow\rangle_i = +\frac{\hbar}{2}|\uparrow_i\rangle, \;\; i \in \{x, y, z\} \tag{172}$$

$$\hat{S}_i|\downarrow\rangle_i = -\frac{\hbar}{2}|\downarrow_i\rangle. \tag{173}$$

There should be three such matrices, one for each perpendicular direction, and they should not commute. Their lack of commutation should be such that an eigenvector of one operator should have equal amplitudes to be either eigenvector of either other operator. For example:

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}}\exp(i\alpha)\left(|\uparrow_z\rangle + \exp(i\beta)\,|\downarrow_z\rangle\right) \tag{174}$$

where α is a real number corresponding to an unmeasurable global phase, and β is a real number corresponding to an unspecified relative phase. Similar relations must hold between the other eigenvectors. A consistent choice is as follows:

$$\hat{S}_i = \frac{\hbar}{2}\sigma_i \tag{175}$$

with

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{176}$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \tag{177}$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{178}$$

These are called the Pauli matrices. For this choice we have

$$|\uparrow_z\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{179}$$

$$|\downarrow_z\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{180}$$

and, for example,

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}}\left(|\uparrow_z\rangle + |\downarrow_z\rangle\right). \tag{181}$$

The different matrices do not commute, as required:

$$\left[\hat{S}_i, \hat{S}_j\right] = i\hbar\epsilon_{ijk}\hat{S}_k \tag{182}$$

where Einstein summation notation has been assumed (*i.e.* there is an implicit sum over index k) and ϵ_{ijk} is the Levi-Civita symbol defined by

$$\epsilon_{ijk} = \begin{cases} 0, \text{ any of } i,j,k \text{ equal} \\ 1,\ ijk = 123 \text{ or cyclic permutations} \\ -1,\ ijk = 321 \text{ or cyclic permutations.} \end{cases} \tag{183}$$

5.3.2 Measurements

To work out what happens when a state is prepared with a definite state of spin in one direction but is then measured in a different direction, we have to decompose the vector into the relevant basis. For example, say a state is prepared with spin up along x:

$$|\psi\rangle = |\uparrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}. \tag{184}$$

This state is then measured in the z direction. To work out the possible outcomes and their relative amplitudes we should write the state in the z-basis:

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}}\left(|\uparrow_z\rangle + |\downarrow_z\rangle\right). \tag{185}$$

The probability for measuring $|\uparrow_z\rangle$ is given by the square magnitude of the coefficient of $|\uparrow_z\rangle$: $1/2$. Mathematically, the probability amplitude for finding the state $|\uparrow_z\rangle$ upon performing a measurement in the z direction for a state $|\uparrow_x\rangle$ is

$$\langle\uparrow_z | \uparrow_x\rangle. \tag{186}$$

In this case,

$$\langle \uparrow_z \mid \uparrow_x \rangle = \langle \uparrow_z \mid \cdot \frac{1}{\sqrt{2}} \left(\mid \uparrow_z \rangle + \mid \downarrow_z \rangle \right) \tag{187}$$

$$= \frac{1}{\sqrt{2}} \left(\langle \uparrow_z \mid \uparrow_z \rangle + \langle \uparrow_z \mid \downarrow_z \rangle \right) \tag{188}$$

$$= \frac{1}{\sqrt{2}} (1 + 0) \tag{189}$$

and the corresponding probability for measuring $\mid \uparrow_z \rangle$ in a z-measurement of state $\mid \uparrow_x \rangle$ is

$$|\langle \uparrow_z \mid \uparrow_x \rangle|^2 = 1/2. \tag{190}$$

In general we can say that:

the amplitude for measuring state $\|\varphi\rangle$ when a state is prepared as $\|\psi\rangle$ is $\langle \varphi \| \psi \rangle$ (191) and the corresponding probability is $\|\langle \varphi \| \psi \rangle\|^2$. (192)

We can also consider repeated measurements by passing the particle along multiple Stern Gerlach apparatuses with different orientations. To find the amplitude for a state initially prepared spin-up-in-z to pass a filter for spin-down-in-y then spin-up-in-x, and to finally be measured spin-down-in-z, we need to evaluate

$$\begin{array}{ccccc} (\text{amplitude for } \downarrow_z \text{ given initially } \uparrow_x) & \cdot & (\text{amplitude for } \uparrow_x \text{ given initially } \downarrow_y) & \cdot & (\text{amplitude for } \downarrow_y \text{ given initially } \uparrow_z) \\ \langle \downarrow_z \mid \uparrow_x \rangle & \cdot & \langle \uparrow_x \mid \downarrow_y \rangle & \cdot & \langle \downarrow_y \mid \uparrow_z \rangle \end{array} \tag{193}$$

and so on. Each condition is required to be true independently so we multiply the probability amplitudes. Probability amplitudes in quantum mechanics play the role of probabilities in classical probability theory: it is the amplitudes which are multiplied or added rather than the probabilities. Consider a state initially spin up along z which is then passed through an x-oriented Stern Gerlach apparatus, but the two possible beams are recombined before measuring along z again. Then we must add the amplitudes for the two possibilities in the intermediate x state, because both are accepted:

$$\langle \uparrow_z \mid \uparrow_x \rangle \cdot \langle \uparrow_x \mid \uparrow_z \rangle + \langle \uparrow_z \mid \downarrow_x \rangle \cdot \langle \downarrow_x \mid \uparrow_z \rangle. \tag{194}$$

But if we accept both intermediate states we haven't made an intermediate measurement, so we don't expect the state to be changed and the overall amplitude should be 1 (the amplitude for a

state prepared spin-up-in-z to be measured spin-up-in-z). This is born out mathematically, as we can rewrite the expression as:

$$\langle\uparrow_z|(|\uparrow_x\rangle\langle\uparrow_x|+|\downarrow_x\rangle\langle\downarrow_x|)|\uparrow_z\rangle \tag{195}$$

$$=\langle\uparrow_z|\mathbb{I}|\uparrow_z\rangle \tag{196}$$

$$=\langle\uparrow_z|\uparrow_z\rangle = 1. \tag{197}$$

The second line follows because $|\uparrow_x\rangle$ and $|\downarrow_x\rangle$ together form a complete orthonormal basis for the set of 2D complex vectors (allowing them to have complex coefficients), which must be true because they are the full set of non-degenerate eigenvectors of a Hermitian matrix $\hat{S}_x$. You can also check this explicitly:

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix},\ |\downarrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix} \tag{198}$$

$$|\uparrow_x\rangle\langle\uparrow_x|+|\downarrow_x\rangle\langle\downarrow_x| = \frac{1}{2}\begin{pmatrix}1\\1\end{pmatrix}(1,1)+\frac{1}{2}\begin{pmatrix}1\\-1\end{pmatrix}(1,-1) \tag{199}$$

$$=\frac{1}{2}\begin{pmatrix}1&1\\1&1\end{pmatrix}+\frac{1}{2}\begin{pmatrix}1&-1\\-1&1\end{pmatrix} \tag{200}$$

$$=\begin{pmatrix}1&0\\0&1\end{pmatrix}. \tag{201}$$

While a simple mathematical result, the physical interpretation is quite profound. Preparing a state of definite spin-up-in-z we pass the particle through an intermediate x-oriented Stern Gerlach apparatus which measures the spin in the x-direction. The two possible paths followed by the particle are separated macroscopically; you could put your finger in the gap between them. A measurement along x would randomise the result of a measurement along z. But because we erase the information about the x-measurement before measuring along z (by recombining the possible beams), the initial z information remains intact. This is even though a classical particle would take one beam or the other. This is an example of a quantum eraser experiment. It shows that there is a fundamental difference between a quantum superposition with two possible outcomes, versus a classical probability with two known outcomes (such as tossing a coin).

5.3.3 Expectation values

The expected value of a given observable for a given state is simply given by the expectation value of the corresponding operator in that state. For example, the expected value of the spin in the i direction, of state $|\psi\rangle$, is

$$\langle \hat{S}_i \rangle = \langle \psi | \hat{S}_i | \psi \rangle. \tag{202}$$

For example, if we prepare a state of spin up in z, the expectation value of the $\hat{S}_z$ operator is

$$\langle \uparrow_z | \hat{S}_z | \uparrow_z \rangle = \langle \uparrow_z | \frac{\hbar}{2} | \uparrow_z \rangle = \frac{\hbar}{2} \tag{203}$$

as expected since it is an eigenstate. We could have found this using matrices:

$$\langle \uparrow_z | \hat{S}_z | \uparrow_z \rangle = (1,0) \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}.$$

On the other hand,

$$\langle \uparrow_z | \hat{S}_x | \uparrow_z \rangle = (1,0) \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0. \tag{204}$$

This makes sense as a measurement of the spin in the x-direction of an eigenstate of spin in the z-direction has an equal probability of coming out $+\hbar/2$ or $-\hbar/2$.

6 Matrix mechanics (II): the Heisenberg picture

Lecture: 10am on 9/11/20.

Office hours: 11am on 9/11/20.

Videos: V6.1, V6.2, V6.3, V6.4

6.1 Operators and observables

Observable quantities are represented in quantum mechanics by Hermitian operators. Operators are denoted with hats $\hat{\mathcal{O}}$. For finite-dimensional Hilbert spaces operators are just Hermitian matrices. For infinite-dimensional Hilbert spaces they are differential operators such as $-i\hbar\nabla$. This mathematical structure was chosen by Heisenberg based on experimental observations. First, real eigenvalues are required because we measure real numbers in experiment, and Hermitian operators have real eigenvalues. Second, different Hermitian matrices need not commute; if two matrices commute it is possible to find simultaneous eigenvectors for them, and the observables corresponding to both operators can be known simultaneously. But this need not be the case in quantum mechanics. For example, we have the position operator $\hat{x}$, which has an infinite number of orthonormal eigenvectors $|x\rangle$, with eigenvalues x the possible positions of the particle:

$$\hat{x}|x\rangle = x|x\rangle. \tag{205}$$

We have the momentum operator $\hat{p}$ with eigenvectors $|p\rangle$:

$$\hat{p}|p\rangle = p|p\rangle. \tag{206}$$

These operators do not commute. In fact we have the **canonical commutation relation**

$$\boxed{[\hat{x}, \hat{p}] = i\hbar\hat{\mathbb{I}}} \tag{207}$$

where $\hat{\mathbb{I}}$ is the identity operator which has eigenvalue 1 for any state. Because these operators do not commute, no state is able to simultaneously be an eigenstate of both: it is not possible to have simultaneous knowledge of a particle's position and momentum.

The energy operator is already familiar. It is the Hamiltonian appearing in the Schrödinger equation:

$$\hat{H}|n\rangle = E_n|n\rangle. \tag{208}$$

The energy receives contributions from the kinetic $\hat{T}$ and potential $\hat{V}$ terms:

$$\hat{H} = \hat{T} + \hat{V} = \frac{\hat{p}^2}{2m} + \hat{V}. \tag{209}$$

In the special case of a free particle we can drop the potential term. In this case we have that

$$\hat{H} = \frac{\hat{p}^2}{2m} \tag{210}$$

and in this case the Hamiltonian commutes with the momentum operator:

$$\text{free particle:} \quad \left[\hat{H}, \hat{p}\right] = 0. \tag{211}$$

When two operators commute it is possible to find simultaneous eigenvectors for them. Dirac notation is very convenient for such cases, allowing us to write things such as

$$\hat{H}|p, n\rangle = E_n|p, n\rangle \tag{212}$$

$$\hat{p}|p, n\rangle = p|p, n\rangle. \tag{213}$$

6.2 The Heisenberg Uncertainty Principle

Proof: Griffiths 3.5.1

Define the uncertainty $\sigma_{\hat{A}}$ in an observable $\hat{A}$ as the standard deviation:

$$\sigma_{\hat{A}} = \sqrt{\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2}. \tag{214}$$

For any two operators $\hat{A}$ and $\hat{B}$ we have the (generalized) **Heisenberg Uncertainty Principle**:

$$\boxed{\sigma_{\hat{A}}\sigma_{\hat{B}} \geq \frac{1}{2}\left|\left\langle\left[\hat{A}, \hat{B}\right]\right\rangle\right|.} \tag{215}$$

For example, from Eq. 207 we have the uncertainty relation between $\hat{x}$ and $\hat{p}$:

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}. \tag{216}$$

6.3 The Heisenberg and Schrödinger pictures

Until now we have been working in the **Schrödinger picture**: time-independent operators $\hat{A}_{\mathrm{S}}$ (S for Schrödinger) and time-dependent states $|\psi_{\mathrm{S}}(t)\rangle$, where

$$|\psi_{\mathrm{S}}(t)\rangle = \exp\left(-i\hat{H}t/\hbar\right)|\psi_{\mathrm{S}}(0)\rangle. \tag{217}$$

Here the state $|\psi\rangle$ has not been assumed to be an energy eigenstate; if it is, the expression reduces to the usual form

$$|\psi_{\mathrm{S}}(t)\rangle = \exp\left(-iEt/\hbar\right)|\psi_{\mathrm{S}}(0)\rangle. \tag{218}$$

The **Heisenberg picture** takes the opposite approach: time-independent states $|\psi_{\mathrm{H}}\rangle$ (H for Heisenberg) are acted on by time-dependent operators $\hat{A}_{\mathrm{H}}(t)$, where

$$\hat{A}_{\mathrm{H}}(t) = \exp\left(i\hat{H}t/\hbar\right)\hat{A}_{\mathrm{S}}\exp\left(-i\hat{H}t/\hbar\right). \tag{219}$$

While Schrödinger operators can have their own explicit time dependence, for example if the potential is changing with time, we will not consider such cases in this course. The Schrödinger and Heisenberg pictures are completely equivalent and make all the same predictions. They are equivalent to active and passive transformations: operators map between states $|\psi\rangle$ in the Hilbert space, and the question of time dependence is simply whether the states or operators are changing. In particular, amplitudes are the same:

$$\begin{aligned}\langle\varphi_{\mathrm{S}}(t)|\hat{A}_{\mathrm{S}}|\psi_{\mathrm{S}}(t)\rangle &= \langle\varphi_{\mathrm{S}}(0)|\exp\left(i\hat{H}t/\hbar\right)\hat{A}_{\mathrm{S}}\exp\left(-i\hat{H}t/\hbar\right)|\psi_{\mathrm{S}}(0)\rangle \\ &= \langle\varphi_{\mathrm{H}}|\exp\left(i\hat{H}t/\hbar\right)\hat{A}_{\mathrm{S}}\exp\left(-i\hat{H}t/\hbar\right)|\psi_{\mathrm{H}}\rangle \\ &= \langle\varphi_{\mathrm{H}}|\hat{A}_{\mathrm{H}}(t)|\psi_{\mathrm{H}}\rangle. \end{aligned}\tag{220}$$

where we made the arbitrary choice

$$|\psi_{\mathrm{H}}\rangle = |\psi_{\mathrm{S}}(0)\rangle. \tag{221}$$

6.4 The Heisenberg equation of motion

Taking the derivative of Eq. 219 with respect to time gives the Heisenberg equation of motion

$$\boxed{i\hbar\frac{\mathrm{d}\hat{A}_{\mathrm{H}}(t)}{\mathrm{d}t} = \left[\hat{A}_{\mathrm{H}}(t), \hat{H}\right]} \tag{222}$$

This equation fulfils the role of the TDSE in the Heisenberg picture.

6.5 Conserved quantities

The observable quantity A associated with operator $\hat{A}$ is conserved if and only if

$$A \text{ conserved iff } \frac{\mathrm{d}\langle\psi|\hat{A}|\psi\rangle}{\mathrm{d}t} = 0 \ \forall|\psi\rangle. \tag{223}$$

Note that this statement is independent of picture. It therefore follows that

$$\boxed{A \text{ conserved iff } \left[\hat{A}, \hat{H}\right] = 0.} \tag{224}$$

Take the trivial but important example of $\hat{A} = \hat{\mathbb{I}}$:

$$\left[\hat{\mathbb{I}}, \hat{H}\right] = 0 \tag{225}$$

$$\therefore \quad \frac{\mathrm{d}\langle\psi|\psi\rangle}{\mathrm{d}t} = 0 \tag{226}$$

the conservation of probability. This was used in Eq. 10 to define the probability current.

6.6 Quantum numbers

Two Hermitian matrices can share a set of eigenvectors if and only if they commute. Therefore the observable quantities associated with different operators can be known simultaneously if and only if the corresponding operators commute. We call a set of observables which can be known simultaneously 'quantum numbers'. In general the observable properties we wish to refer to are those independent of time; since time-independent expectation values require the operator to commute with the Hamiltonian, it is usual to take the energy as one of the observables, and therefore the quantum numbers of a particle are the observable properties associated with the set of operators which commute with the Hamiltonian.
For example, the quantum numbers of the electron in the Hydrogen atom (see lecture 10):

$$\text{energy: } \hat{H}|n\rangle = E_n|n\rangle \tag{227}$$

$$\text{squared total angular momentum: } \hat{L}^2|l\rangle = \hbar^2 l\,(l+1)\,|l\rangle \tag{228}$$

$$z\text{-projection of angular momentum: } \hat{L}_z|m\rangle = \hbar m|m\rangle \tag{229}$$

$$\text{spin: } \hat{S}|s=\pm\rangle = \pm\frac{\hbar}{2}|s=\pm\rangle \tag{230}$$

and therefore we can write the states of the electron in the Hydrogen atom, unambiguously, as $|n, l, m, s\rangle$ where the letters label the quantum numbers. We have, for example,

$$\hat{H}\hat{L}_z|n,l,m,s\rangle = \hat{L}_z\hat{H}|n,l,m,s\rangle = E_n\hbar m|n,l,m,s\rangle. \tag{231}$$

6.7 Ehrenfest's theorem

In the Heisenberg picture states $|\psi_{\mathrm{H}}\rangle$ are time independent, so sandwiching Eq. 222 between states gives

$$i\hbar\langle\psi_{\mathrm{H}}|\frac{\mathrm{d}\hat{A}_{\mathrm{H}}(t)}{\mathrm{d}t}|\psi_{\mathrm{H}}\rangle = \langle\psi_{\mathrm{H}}|\left[\hat{A}_{\mathrm{H}}(t), \hat{H}\right]|\psi_{\mathrm{H}}\rangle$$

$$\downarrow$$

$$i\hbar\frac{\mathrm{d}\langle\psi_{\mathrm{H}}|\hat{A}_{\mathrm{H}}(t)|\psi_{\mathrm{H}}\rangle}{\mathrm{d}t} = \langle\psi_{\mathrm{H}}|\left[\hat{A}_{\mathrm{H}}(t), \hat{H}\right]|\psi_{\mathrm{H}}\rangle$$

noting that both sides of the expression are again independent of picture, we have Ehrenfest's theorem:

$$\boxed{i\hbar\frac{\mathrm{d}\langle\hat{A}\rangle}{\mathrm{d}t} = \langle\left[\hat{A},\hat{H}\right]\rangle}. \tag{232}$$

This is key in demonstrating that quantum mechanics matches classical predictions on average, meaning that classical quantities relate to expectation values. In particular, we have

$$m\frac{\mathrm{d}\langle\hat{x}\rangle}{\mathrm{d}t} = \langle\hat{p}\rangle \tag{233}$$

which shows that the classical equation $p = mv$ is obeyed by quantum systems when classical p and x are replaced by the expectation values of their quantum operators, and

$$\frac{\mathrm{d}\langle\hat{p}\rangle}{\mathrm{d}t} = -\langle\nabla V\left(\hat{x}\right)\rangle. \tag{234}$$

This resembles Newton's second law, but not quite: the expectation value is taken over all $\langle\nabla V\left(\hat{x}\right)\rangle$, while the expression would need to read $\nabla V\left(\langle\hat{x}\rangle\right)$ for Newton's second law to be obeyed by the expectation values of position and momentum. Nevertheless, Ehrenfest's theorem lends weight to the 'correspondence principle', that classical mechanics is returned in the limit of large quantum numbers: if the standard deviation $\sqrt{\langle\hat{x}^2\rangle - \langle\hat{x}\rangle^2}$ around the mean $\langle\hat{x}\rangle$ is small, i.e. the particle is sharply localised, the approximation $\langle\nabla V\left(\hat{x}\right)\rangle \approx \nabla V\left(\langle\hat{x}\rangle\right)$ is better, and classical mechanics is approximately returned by expectations values. Since $\hat{x}$ and $\hat{H}$ do not commute, a wavepacket well-localised in $\hat{x}$ necessarily requires more contribution from higher energy levels in the superposition of energy eigenstates.

7 Quantum mechanics

Lecture: 10am on 16/11/20.

Office hours: 11am on 16/11/20.

Videos: V7.1, V7.2, V7.3, V7.4, V7.5

7.1 Infinite-dimensional Hilbert spaces

Functions $f(x)$, including complex functions, obey all the axioms of linear vector spaces, and can be thought of as infinite-dimensional vectors. Recall Eq. 152, the resolution of the identity, which tells us that for a complete set of orthonormal vectors $\{|e_i\rangle\}$ we have:

$$\mathbb{I} = \sum_i |e_i\rangle\langle e_i|.$$

The position eigenstates $\{|x\rangle\}$ form a complete orthonormal basis for an infinite-dimensional vector space. The resolution of the identity can be written

$$\boxed{\mathbb{I} = \int_{-\infty}^{\infty} |x\rangle\langle x| \mathrm{d}x} \tag{235}$$

or in three dimensions

$$\mathbb{I} = \iiint_{-\infty}^{\infty} |\boldsymbol{x}\rangle\langle\boldsymbol{x}| \mathrm{d}^3\boldsymbol{x}. \tag{236}$$

This is consistent with the Born rule for the probability $P(x)$:

$$P(x) = |\langle x|\psi\rangle|^2 \tag{237}$$

and the fact that the total proability to find the particle is 1:

$$\mathbb{I} = \int_{-\infty}^{\infty} |x\rangle\langle x| \mathrm{d}x \tag{238}$$

$$\downarrow$$

$$\langle\psi|\mathbb{I}|\psi\rangle = \int_{-\infty}^{\infty} \langle\psi|x\rangle\langle x|\psi\rangle \mathrm{d}x \tag{239}$$

$$\downarrow$$

$$\langle\psi|\psi\rangle = 1 = \int_{-\infty}^{\infty} P(x)\, \mathrm{d}x. \tag{240}$$

A useful trick, the infinite-dimensional generalisation of Eq. 171, is to act the $\hat{x}$ operator on Eq. 235, using

$$\hat{x}|x\rangle = x|x\rangle \tag{241}$$

to give the representation of the operator in the position basis:

$$\boxed{\hat{x} = \int_{-\infty}^{\infty} x|x\rangle\langle x|\mathrm{d}x.} \tag{242}$$

The momentum eigenstates $\{|p\rangle\}$ also form a complete orthonormal basis for the same space, and we also have

$$\boxed{\mathbb{I} = \int_{-\infty}^{\infty} |p\rangle\langle p|\mathrm{d}p} \tag{243}$$

and

$$\boxed{\hat{p} = \int_{-\infty}^{\infty} p|p\rangle\langle p|\mathrm{d}p.}$$

The energy eigenstates solving the TISE form complete orthonormal bases:

$$\hat{H}|n\rangle = E_n|n\rangle \tag{244}$$

and we can similarly define

$$\mathbb{I} = \sum_n |n\rangle\langle n| \tag{245}$$

and

$$\hat{H} = \sum_n E_n|n\rangle\langle n|.$$

Just as we can project a vector into the basis $\{|e_i\rangle\}$ using Eq. 152, we can project an infinite dimensional vector $|f\rangle$ into the position basis:

$$|f\rangle = \mathbb{I}|f\rangle = \int_{-\infty}^{\infty} |x\rangle\langle x|f\rangle\mathrm{d}x = \int_{-\infty}^{\infty} \left(\langle x|f\rangle\right)|x\rangle\mathrm{d}x \tag{246}$$

where

$$\boxed{\langle x|f\rangle = f\left(x\right).} \tag{247}$$

This returns a complex scalar for each position x, and is simply the complex function $f\left(x\right)$ as the notation suggests. The space of functions is equipped with an inner product:

$$\boxed{\langle f|g\rangle = \int_{-\infty}^{\infty} f\left(x\right)^* g\left(x\right)\mathrm{d}x} \tag{248}$$

proven using the resolution of the identity, Eq. 235:

$$\langle f|g\rangle = \langle f|\mathbb{I}|g\rangle = \int_{-\infty}^{\infty} \langle f|x\rangle\langle x|g\rangle \mathrm{d}x = \int_{-\infty}^{\infty} f(x)^* g(x)\,\mathrm{d}x. \tag{249}$$

Functions plus this inner product are therefore equipped to form a Hilbert space.

Just as we are free to choose any orthonormal basis for our finite-dimensional vector spaces, we are free to do so with our infinite-dimensional spaces. For example, we can equally-well project our kets into the momentum basis:

$$\langle p|f\rangle = f(p). \tag{250}$$

To convert a function written in the position basis, $f(x)$, to the same function written in the momentum basis, $f(p)$, we would usually use the Fourier transform. This gives us a consistency condition. Starting from Eq. 250 and inserting a complete set of position states:

$$f(p) = \langle p|f\rangle \tag{251}$$

$$= \int_{-\infty}^{\infty} \langle p|x\rangle\langle x|f\rangle \mathrm{d}x \tag{252}$$

$$= \int_{-\infty}^{\infty} \langle p|x\rangle f(x)\,\mathrm{d}x \tag{253}$$

and therefore

$$f(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \exp(-ipx/\hbar) f(x)\,\mathrm{d}x \tag{254}$$

where we see

$$\boxed{\langle p|x\rangle = \frac{1}{\sqrt{2\pi\hbar}} \exp(-ipx/\hbar).} \tag{255}$$

The inverse Fourier transform follows naturally:

$$f(x) = \langle x|f\rangle \tag{256}$$

$$= \int_{-\infty}^{\infty} \langle x|p\rangle\langle p|f\rangle \mathrm{d}p \tag{257}$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \exp(ipx/\hbar) f(p)\,\mathrm{d}p \tag{258}$$

with

$$\langle x|p\rangle = (\langle p|x\rangle)^* \tag{259}$$

where the general result of Eq. 148 has been used.

7.2 Operators in the position basis

The non-commuting operators in Heisenberg's matrix mechanics all have equivalents in Schrodinger's wave mechanics. Working in the position basis they become differential operators. Writing them in three dimensional space for generality:

$$\hat{\boldsymbol{x}} \rightarrow \boldsymbol{x} \tag{260}$$

$$\hat{\boldsymbol{p}} \rightarrow -i\hbar\nabla \tag{261}$$

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + \hat{V} \rightarrow -\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x}). \tag{262}$$

For example, the canonical commutation relation of Eq. 207 becomes:

$$\begin{aligned}
[\hat{x}, \hat{p}]\,\psi(x) &= [x, -i\hbar\partial_x]\,\psi(x) \\
&= -i\hbar\left(x\frac{\partial\psi(x)}{\partial x} - \frac{\partial}{\partial x}(x\psi(x))\right) \\
&= -i\hbar\left(\cancel{x\frac{\partial\psi(x)}{\partial x}} - \psi(x) - \cancel{x\frac{\partial\psi(x)}{\partial x}}\right) \\
&= i\hbar\psi(x)
\end{aligned}$$

as required.

7.3 Expectation values of operators

The expectation value of operator $\hat{A}$, denoted$\langle\hat{A}\rangle$, in state $|\psi\rangle$ is given by

$$\boxed{\langle\hat{A}\rangle = \langle\psi|\hat{A}|\psi\rangle} \tag{263}$$

which is another convenience of Dirac notation. For example, we can evaluate the expectation value of the position operator using

$$\hat{x} = \int x|x\rangle\langle x|\mathrm{d}x \tag{264}$$

to give

$$\langle\hat{x}\rangle = \langle\psi|\hat{x}|\psi\rangle \tag{265}$$

$$= \langle\psi|\left(\int x|x\rangle\langle x|\mathrm{d}x\right)|\psi\rangle \tag{266}$$

$$= \int x\langle\psi|x\rangle\langle x|\psi\rangle\mathrm{d}x \tag{267}$$

$$= \int x\,|\psi(x)|^2\,\mathrm{d}x \tag{268}$$

which agrees with the wave mechanics expression of Eq. 114 (in that earlier expression, operators were assumed projected into the position basis). Similarly, by acting $\hat{x}$ on Eq. 264 we find

$$\hat{x}^2 = \int x^2 |x\rangle\langle x| \mathrm{d}x \tag{269}$$

and so

$$\left\langle \hat{x}^2 \right\rangle = \int x^2 \left|\psi\left(x\right)\right|^2 \mathrm{d}x. \tag{270}$$

7.4 Hermiticity of differential operators

Hermiticity is obvious in the matrix representation; for example,

$$\hat{p} = \int p|p\rangle\langle p| \mathrm{d}p = \hat{p}^\dagger. \tag{271}$$

However, some care has to be taken when working in a particular basis, because, naively, we might think that $\left(-i\hbar\partial_x\right)^\dagger = i\hbar\partial_x \neq -i\hbar\partial_x$, which is not true. Instead, working in the position basis, the Hermitian conjugate of an operator $\hat{A}$ is defined as:

$$\int_{-\infty}^{\infty} \varphi\left(x\right)^* \left(\hat{A}^\dagger \psi\left(x\right)\right) \mathrm{d}x \triangleq \int_{-\infty}^{\infty} \left(\hat{A}\varphi\left(x\right)\right)^* \psi\left(x\right) \mathrm{d}x \tag{272}$$

for arbitrary $\varphi\left(x\right)$, $\psi\left(x\right)$. Therefore the condition for Hermiticity is:

$$\boxed{\text{Hermiticity: } \int_{-\infty}^{\infty} \varphi\left(x\right)^* \left(\hat{A}\psi\left(x\right)\right) \mathrm{d}x = \int_{-\infty}^{\infty} \left(\hat{A}\varphi\left(x\right)\right)^* \psi\left(x\right) \mathrm{d}x} \tag{273}$$

where $\varphi\left(x\right)$, $\psi\left(x\right)$ are normalisable, requiring them to vanish at $x = \pm\infty$. For example, the position operator trivially satisfies this:

$$\int_{-\infty}^{\infty} \varphi\left(x\right)^* \left(x\psi\left(x\right)\right) \mathrm{d}x = \int_{-\infty}^{\infty} \left(x\varphi\left(x\right)\right)^* \psi\left(x\right) \mathrm{d}x. \tag{274}$$

The momentum operator is also Hermitian:

$$\begin{aligned}\int_{-\infty}^{\infty} \varphi\left(x\right)^* \left(-i\hbar\partial_x\psi\left(x\right)\right) \mathrm{d}x &= \left[\varphi\left(x\right)^* \left(-i\hbar\psi\left(x\right)\right)\right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \left(-i\hbar\partial_x\varphi\left(x\right)^*\right) \psi\left(x\right) \mathrm{d}x \\ &= \int_{-\infty}^{\infty} \left(-i\hbar\partial_x\varphi\left(x\right)\right)^* \psi\left(x\right) \mathrm{d}x\end{aligned}$$

where integration by parts was used, and the boundary terms disappear because $\varphi\left(x\right)$ and $\psi\left(x\right)$ are required to vanish at $x = \pm\infty$.

7.5 Basis-indepdendent TDSE

The **time dependent Schrödinger equation in its most general form** is

$$\boxed{i\hbar\partial_t|\psi\,(t)\rangle = \hat{H}|\psi\,(t)\rangle} \tag{275}$$

which avoids specifying a basis for the ket $|\psi\,(t)\rangle$. The usual position-dependent wavefunction is then given by projecting into the position basis:

$$\boxed{\psi\,(x,t) = \langle x|\psi\,(t)\rangle.} \tag{276}$$

Note that while we must project into the position basis, or the momentum basis, we do not need to perform a similar operation for time: $|\psi\,(t)\rangle$ is simply labelled by its time. Quantum mechanics which is non-relativistic, and treats time as priveliged. To treat position and time on an equal footing, a necessary condition for including relativistic effects, we must use quantum field theory, which is beyond the scope of this course.

7.6 The Postulates of Quantum Mechanics

1. States of a system are represented by normalized kets $|\psi\rangle$ in a complex Hilbert space $\mathcal{H}$.
2. Observable quantities are represented by Hermitian operators in $\mathcal{H}$.
3. All such Hermitian operators $\hat{A}$ are assumed to possess a complete set of orthogonal eigenstates: $\hat{A}|a_n\rangle = a_n|a_n\rangle$.
4. The fundamental probability postulate for measurement is:
   (a) the possible results of a measurement of $\hat{A}$ are a_n;
   (b) after measurement of $\hat{A}$ on state $|\psi\rangle$ with result a_n the resulting state is $|a_n\rangle$;
   (c) the probability for this to happen is $|\langle a_n|\psi\rangle|^2$ (the Born rule).
5. In the absence of measurement states evolve unitarily in time according to the TDSE: $i\hbar\partial_t|\psi\,(t)\rangle = \hat{H}|\psi\,(t)\rangle$.

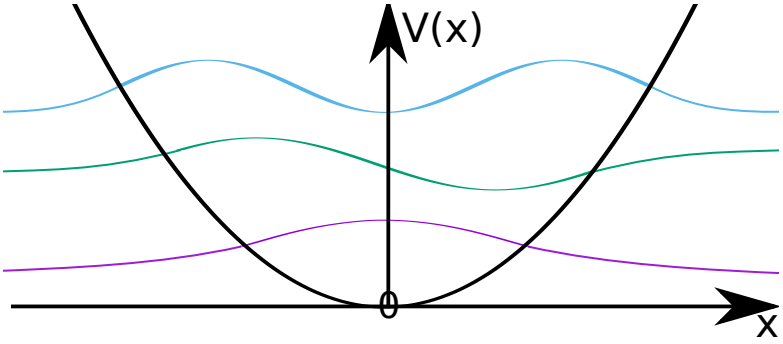

Figure 6: The quantum harmonic oscillator potential $V(x) = \frac{1}{2}m\omega^2 x^2$ and first few eigenstates.

8 The quantum harmonic oscillator

Lecture: 10am on 23/11/20.

Office hours: 11am on 23/11/20.

Videos: V8.1, V8.2, V8.3, V8.4

A very important problem is the quantum harmonic oscillator:

$$\hat{V} = \frac{1}{2}m\omega^2\hat{x}^2. \tag{277}$$

This is the quantum version of the simple harmonic oscillator in 1D. The TISE reads:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\phi_n(x)}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2\phi_n(x) = E_n\phi_n(x). \tag{278}$$

The potential is shown in Fig. 6.

8.1 Hermite polynomials

It is convenient to rescale using $x = \alpha y$:

$$-\frac{\hbar^2}{2m\alpha^2}\frac{\mathrm{d}^2\phi_n(y)}{\mathrm{d}y^2} + \frac{1}{2}m\omega^2\alpha^2 y^2\phi_n(y) = E_n\phi_n(y) \tag{279}$$

and selecting

$$\alpha^2 = \frac{\hbar}{m\omega} \tag{280}$$

gives

$$-\frac{\mathrm{d}^2\phi_n(y)}{\mathrm{d}y^2} + y^2\phi_n(y) = \epsilon_n\phi_n(y) \tag{281}$$

where

$$\epsilon_n \triangleq \frac{2E_n}{\hbar\omega}. \tag{282}$$

Eq. 281 is a second order ODE. Substitute

$$\phi_n(y) = H_n(y) \exp\left(-\frac{y^2}{2}\right) \tag{283}$$

to reduce Eq. 281 to

$$H_n(y)'' - 2yH_n(y)' + (\epsilon - 1) H_n(y) = 0. \tag{284}$$

This is known as Hermite's equation. It can be solved with Frobenius series to yield $H_n(y)$, the Hermite polynomials:

$$H_n(y) = (-1)^n \exp\left(y^2\right) \frac{\mathrm{d}^n}{\mathrm{d}y^n} \exp\left(-y^2\right) \tag{285}$$

with energy eigenvalues

$$\epsilon_n = 2n + 1 \tag{286}$$

for integer $n \geq 0$. Returning to the original scaling we have

$$E_n = \hbar\omega \left(n + \frac{1}{2}\right). \tag{287}$$

8.2 Ladder operators

However, there is a far more elegant method. Returning to the original scaling of the TISE

$$\hat{H}|n\rangle = \left(\frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2\right)|n\rangle = E_n|n\rangle \tag{288}$$

define non-Hermitian operators

$$\boxed{\hat{a}^\dagger \triangleq \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i}{m\omega}\hat{p}\right)} \tag{289}$$

implying

$$\boxed{\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i}{m\omega}\hat{p}\right).} \tag{290}$$

This gives

$$\hat{a}^\dagger\hat{a} = \frac{m\omega}{2\hbar}\left(\hat{x}^2 + \frac{\hat{p}^2}{m^2\omega^2} + \frac{i}{m\omega}\left(\hat{x}\hat{p} - \hat{p}\hat{x}\right)\right). \tag{291}$$

The term in nested parentheses is just the commutator

$$[\hat{x}, \hat{p}] = i\hbar\hat{\mathbb{I}} \tag{292}$$

giving

$$\hat{a}^\dagger\hat{a} = \frac{m\omega}{2\hbar}\hat{x}^2 + \frac{\hat{p}^2}{2\hbar m\omega} - \frac{1}{2}\hat{\mathbb{I}}$$

and so

$$\hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\hat{\mathbb{I}}\right) = \hat{H}. \tag{293}$$

Therefore the TISE can be written

$$\boxed{\hat{H}|n\rangle = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)|n\rangle = E_n|n\rangle.} \tag{294}$$

8.2.1 Commutation relations

The commutator of the operators is

$$\left[\hat{a}, \hat{a}^\dagger\right] = \frac{m\omega}{2\hbar}\left[\hat{x} + \frac{i}{m\omega}\hat{p}, \hat{x} - \frac{i}{m\omega}\hat{p}\right] \tag{295}$$

$$= -\frac{i}{\hbar}\left[\hat{x}, \hat{p}\right] \tag{296}$$

and so

$$\boxed{\left[\hat{a}, \hat{a}^\dagger\right] = 1} \tag{297}$$

The commutator of the operators with the Hamiltonian is therefore:

$$\left[\hat{H}, \hat{a}^\dagger\right] = \left[\hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\mathbb{I}\right), \hat{a}^\dagger\right] \tag{298}$$

$$= \hbar\omega\left(\hat{a}^\dagger\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}^\dagger\hat{a}\right) \tag{299}$$

$$= \hbar\omega\hat{a}^\dagger\left[\hat{a}, \hat{a}^\dagger\right] \tag{300}$$

giving

$$\boxed{\left[\hat{H}, \hat{a}^\dagger\right] = \hbar\omega\hat{a}^\dagger.} \tag{301}$$

and similarly

$$\left[\hat{H}, \hat{a}\right] = -\hbar\omega\hat{a}. \tag{302}$$

8.2.2 Energy eigenstates and eigenvalues

Using Eq. 301 we can see the effect of $\hat{a}^\dagger$ on the TISE of Eq. 294:

$$\hat{H}|n\rangle = E_n|n\rangle \tag{303}$$

$$\downarrow$$

$$\hat{a}^\dagger\hat{H}|n\rangle = E_n\hat{a}^\dagger|n\rangle \tag{304}$$

$$\downarrow$$

$$\left(\hat{H}\hat{a}^\dagger - \left[\hat{H},\hat{a}^\dagger\right]\right)|n\rangle = E_n\hat{a}^\dagger|n\rangle \tag{305}$$

$$\downarrow$$

$$\left(\hat{H}\hat{a}^\dagger - \hbar\omega\hat{a}^\dagger\right)|n\rangle = E_n\hat{a}^\dagger|n\rangle \tag{306}$$

and the final result

$$\boxed{\hat{H}\left(\hat{a}^\dagger|n\rangle\right) = \left(E_n + \hbar\omega\right)\left(\hat{a}^\dagger|n\rangle\right).} \tag{307}$$

That is, if $|n\rangle$ is an eigenstate of the harmonic oscillator with eigenvalue E_n, then $\hat{a}^\dagger|n\rangle$ is an eigenstate with eigenvalue $E_n + \hbar\omega$. Repeating the process m times we find

$$\hat{H}\left(\left(\hat{a}^\dagger\right)^m|n\rangle\right) = \left(E_n + m\hbar\omega\right)\left(\left(\hat{a}^\dagger\right)^m|n\rangle\right). \tag{308}$$

This tells us that the energy levels are evenly-spaced, and that

$$\left(\hat{a}^\dagger\right)^m|n\rangle \propto |n+m\rangle. \tag{309}$$

Similarly, we find

$$\hat{H}\left(\hat{a}|n\rangle\right) = \left(E_n - \hbar\omega\right)\left(\hat{a}|n\rangle\right). \tag{310}$$

We call $\hat{a}^\dagger$ the raising operator, and $\hat{a}$ the lowering operator; collectively we call them ladder operators, as they move the state up or down the rungs of an energy ladder with evenly-spaced rungs. While there exist an infinite number of rungs, the energies do not stretch down to negative energies. We know this because

$$|\hat{a}|n\rangle|^2 \geq 0 \tag{311}$$

by the definition of the norm, and so

$$\langle n|\hat{a}^\dagger\hat{a}|n\rangle \geq 0 \tag{312}$$

$$\langle n|\frac{1}{\hbar\omega}\hat{H} - \frac{1}{2}|n\rangle \geq 0 \tag{313}$$

$$\langle n|\frac{1}{\hbar\omega}E_n - \frac{1}{2}|n\rangle \geq 0 \tag{314}$$

$$E_n \geq \frac{\hbar\omega}{2}. \tag{315}$$

Therefore there is a lowest-energy state, the ground state which we denote $|0\rangle$. This has the property that

$$\boxed{\hat{a}|0\rangle = 0} \tag{316}$$

where the right hand side is just the number 0, so that any further action of lowering operators continues to return 0. To find the energy of the ground state we can work in the position basis using the definition of the lowering operator from Eq. 290:

$$\sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i}{m\omega}\hat{p}\right)|0\rangle = 0 \tag{317}$$

$$\downarrow$$

$$\left(x + \frac{\hbar}{m\omega}\frac{\mathrm{d}}{\mathrm{d}x}\right)\phi_0(x) = 0 \tag{318}$$

a first order linear ODE which has the solution

$$\phi_0(x) \propto \exp\left(-\frac{m\omega}{2\hbar}x^2\right). \tag{319}$$

Inserting this into the TISE of Eq. 278 gives

$$E_0 = \frac{\hbar\omega}{2}. \tag{320}$$

This is the ground state energy, also called the zero-point energy.
Combining the results, we see that

$$\hat{H}|n\rangle = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)|n\rangle = \hbar\omega\left(n + \frac{1}{2}\right)|n\rangle$$

for integer n. Defining the 'number operator'

$$\hat{n} \triangleq \hat{a}^\dagger\hat{a} \tag{321}$$

we see that

$$\hat{n}|n\rangle = n|n\rangle. \tag{322}$$

8.2.3 Normalization

We have that

$$\langle n|\hat{n}|n\rangle = n \tag{323}$$

$$\downarrow$$

$$\langle n|\hat{a}^\dagger\hat{a}|n\rangle = n \tag{324}$$

$$\downarrow$$

$$\|\hat{a}|n\rangle\|^2 = n \tag{325}$$

$$\downarrow$$

$$\|\hat{a}|n\rangle\| = \sqrt{n}. \tag{326}$$

Therefore, since

$$\hat{a}|n\rangle \propto |n-1\rangle$$

and

$$\langle n-1|n-1\rangle = 1 \tag{327}$$

we have

$$\boxed{\hat{a}|n\rangle = \sqrt{n}|n-1\rangle.} \tag{328}$$

Similarly,

$$\left|\hat{a}^\dagger|n\rangle\right|^2 = \langle n|\hat{a}\hat{a}^\dagger|n\rangle = \langle n|\hat{n} + \left[\hat{a}, \hat{a}^\dagger\right]|n\rangle = n+1 \tag{329}$$

and so

$$\boxed{\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle}. \tag{330}$$

By induction we can also see that

$$\boxed{\frac{1}{\sqrt{n!}}\left(\hat{a}^\dagger\right)^n|0\rangle = |n\rangle.} \tag{331}$$

8.3 Second quantization

- Equation 331 tells us we can create the n^{th} excited state of the harmonic oscillator by acting n raising operators on the ground state.
- Since all rungs of the ladder are evenly spaced with spacing $\hbar\omega$, we can also interpret the n^{th} excited state as the presence of n identical particles each of energy $\hbar\omega$.
- Solving the TDSE for the wavefunction of a quantum system we call 'first quantization'. It is the realisation that classical particles gain wave-like properties in a quantum description. We call the process of rewriting a problem in terms of ladder operators 'second quantization'. It is the realisation that classical waves gain particle-like properties in a quantum description. The descriptions are equivalent.
- It turns out that in order to consistently include relativistic effects into quantum mechanics, you must allow the number of particles to vary. The result is quantum field theory. This treats particles as excitations of quantum fields which permeate all of space; to create a particle at position x you act a raising operator $\hat{a}_x^\dagger$ on the vacuum state of no particles.
- For this reason we also call the raising and lowering operators the creation and annihilation operators.
- The fact that we can fit multiple particles into the same state identifies $\hat{a}^\dagger$ as the creation operator of a bosonic particle.

9 The Schrödinger equation in three dimensions

Lecture: 10am on 30/11/20.

Office hours: 11am on 30/11/20.

Videos: V9.1, V9.2, V9.3, V9.4

9.1 TISE in three dimensions

9.1.1 Cubic box

Consider the infinite potential well in three dimensions where

$$\boldsymbol{r} = (x, y, z) \tag{332}$$

$$V(\boldsymbol{r}) = \begin{cases} 0, & 0 < \{x, y, z\} < a \\ \infty, & \text{otherwise.} \end{cases} \tag{333}$$

Inside the box the TISE reads

$$-\frac{\hbar^2 \nabla^2}{2m} \phi_{\boldsymbol{n}}(\boldsymbol{r}) = E_n \phi_{\boldsymbol{n}}(\boldsymbol{r}) \tag{334}$$

$$-\frac{\hbar^2}{2m} \left(\partial_x^2 + \partial_y^2 + \partial_z^2\right) \phi_{\boldsymbol{n}}(\boldsymbol{r}) = E_{\boldsymbol{n}} \phi_{\boldsymbol{n}}(\boldsymbol{r}) \tag{335}$$

where $\boldsymbol{n} = (n_x, n_y, n_z)$ just assigns an independent integer to each direction. This is separable into three second order ODEs using

$$\phi_{\boldsymbol{n}}(\boldsymbol{r}) \triangleq X_{n_x}(x)\, Y_{n_y}(y)\, Z_{n_z}(z) \tag{336}$$

$$E_{\boldsymbol{n}} \triangleq E^x_{n_x} + E^y_{n_y} + E^z_{n_z} \tag{337}$$

giving

$$-\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{\mathrm{d}^2 X}{\mathrm{d}x^2} + \frac{1}{Y}\frac{\mathrm{d}^2 Y}{\mathrm{d}y^2} + \frac{1}{Z}\frac{\mathrm{d}^2 Z}{\mathrm{d}z^2}\right) = E^x_{n_x} + E^y_{n_y} + E^z_{n_z}. \tag{338}$$

we simply have three independent copies of the 1D infinite potential well. We can define three separate TISEs:

$$\hat{H}^x X_{n_x}(x) \triangleq \left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right) X_{n_x}(x) = E^x_{n_x} X_{n_x}(x) \tag{339}$$

and the same for y and z. Solving as before we find

$$X_{n_x}(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi x}{a}\right) \tag{340}$$

$$E^x_{n_x} = \frac{\hbar^2 n_x^2 \pi^2}{2ma^2} \tag{341}$$

and overall we have

$$\phi_{\boldsymbol{n}}(\boldsymbol{r}) = \sqrt{\frac{8}{a^3}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right) \tag{342}$$

$$E_{\boldsymbol{n}} = \frac{\hbar^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right). \tag{343}$$

Since the Hamiltonians in each direction commute:

$$\left[\hat{H}^i, \hat{H}^j\right] = 0, \ \{i, j\} \in \{x, y, z\} \tag{344}$$

we can define a set of time-independent quantum numbers

$$\hat{H}|n_x, n_y, n_z\rangle = E_{\boldsymbol{n}}|n_x, n_y, n_z\rangle \tag{345}$$

where

$$\langle \boldsymbol{x}|n_x, n_y, n_z\rangle = \phi_{\boldsymbol{n}}(\boldsymbol{r}). \tag{346}$$

The ket is labelled by the three independent integers. While the ground state $|1,1,1\rangle$ is unique, with energy $E_{(1,1,1)} = 3\hbar^2/2ma^2$, higher excited states are degenerate, with $E_{1,1,2} = E_{1,2,1} = E_{2,1,1}$. However, the eigenkets still form an orthonormal basis:

$$\langle m_x, m_y, m_z|n_x, n_y, n_z\rangle = \delta_{n_x m_x}\delta_{n_y m_y}\delta_{n_z m_z} \tag{347}$$

which can be seen explicitly, for example, by inserting a complete set of position states:

$$\langle m_x, m_y, m_z|n_x, n_y, n_z\rangle = \iiint \langle m_x, m_y, m_z|\boldsymbol{x}\rangle\langle \boldsymbol{x}|n_x, n_y, n_z\rangle \mathrm{d}x\mathrm{d}y\mathrm{d}z \tag{348}$$

$$= \frac{8}{a^3}\iiint \sin\left(\frac{m_x \pi x}{a}\right)\sin\left(\frac{m_y \pi y}{a}\right)\sin\left(\frac{m_z \pi z}{a}\right)\sin\left(\frac{n_x \pi x}{a}\right)\sin\left(\frac{n_y \pi y}{a}\right)\sin\left(\frac{n_z \pi z}{a}\right)\mathrm{d}x\mathrm{d}y\mathrm{d}z \tag{349}$$

$$= \left(\frac{2}{a}\int \sin\left(\frac{m_x \pi x}{a}\right)\sin\left(\frac{n_x \pi x}{a}\right)\mathrm{d}x\right)\cdot(x \to y)\cdot(x \to z) \tag{350}$$

$$= \delta_{n_x m_x}\delta_{n_y m_y}\delta_{n_z m_z}. \tag{351}$$

9.1.2 3D Harmonic oscillator

In precisely the same manner, the 3D harmonic oscillator can be separated into three 1D harmonic oscillators:

$$\hat{H}\phi_{\boldsymbol{n}}(\boldsymbol{r}) = \left(-\frac{\hbar^2\nabla^2}{2m} + \frac{1}{2}m\omega^2\hat{\boldsymbol{r}}^2\right)\phi_{\boldsymbol{n}}(\boldsymbol{r}) = E_{\boldsymbol{n}}\phi_{\boldsymbol{n}}(\boldsymbol{r}) \tag{352}$$

with energy eigenvalues

$$E_{\boldsymbol{n}} = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right). \tag{353}$$

We can define ladder operators in each cartesian direction separately:

$$\hat{a}_x^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i}{m\omega}\hat{p}_x\right) \tag{354}$$

$$\hat{a}_y^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{y} - \frac{i}{m\omega}\hat{p}_y\right) \tag{355}$$

$$\hat{a}_z^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{z} - \frac{i}{m\omega}\hat{p}_z\right) \tag{356}$$

and number operators

$$\hat{n}_x = \hat{a}_x^\dagger\hat{a}_x \tag{357}$$

etc. so that

$$\hat{H}|n_x, n_y, n_z\rangle = \hbar\omega\left(\hat{n}_x + \hat{n}_y + \hat{n}_z + \frac{3}{2}\right)|n_x, n_y, n_z\rangle. \tag{358}$$

9.2 Angular momentum

9.2.1 Cartesian co-ordinates

Classically angular momentum is defined to be

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} \tag{359}$$

and quantum mechanically we promote observables to operators as usual, so that

$$\hat{\boldsymbol{L}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}} \tag{360}$$

or in the position basis

$$\boxed{\hat{\boldsymbol{L}} = -i\hbar\hat{\boldsymbol{r}} \times \nabla.} \tag{361}$$

Note that angular momentum has the same dimensions as $\hbar$. In cartesian co-ordinates we have

$$\hat{\boldsymbol{L}} = -i\hbar \begin{pmatrix} \hat{y}\partial_z - \hat{z}\partial_y \\ \hat{z}\partial_x - \hat{x}\partial_z \\ \hat{x}\partial_y - \hat{y}\partial_x \end{pmatrix}. \tag{362}$$

Checking the commutation relations we find

$$\boxed{\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\epsilon_{ijk}\hat{L}_k} \tag{363}$$

where ϵ_{ijk} is the Levi-Civita symbol and Einstein summation notation is assumed (*i.e.* there is an implicit sum over $k \in \{1, 2, 3\}$). Since no two operators commute, it is not possible to have simultaneous knowledge of the angular momentum along any two directions. From the Heisenberg uncertainty principle of Eq. 215 we see that

$$\sigma_{\hat{L}_i}\sigma_{\hat{L}_i} \geq \frac{\hbar}{2}\left|\left\langle \hat{L}_k \right\rangle\right|.$$

However, the squared angular momentum

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{364}$$

commutes with all three:

$$\left[\hat{L}_i, \hat{L}^2\right] = 0. \tag{365}$$

The maximal set of commuting operators is $\hat{L}^2$ and one of $\hat{L}_i$. The physical observable associated with the operator $\hat{L}^2$ is the square of the angular momentum.

9.2.2 Spherical polar co-ordinates

In spherical polar co-ordinates

$$\boldsymbol{r} = (r, \theta, \phi) \tag{366}$$

we have that

$$\hat{L}_z = -i\hbar\partial_\phi.$$

This is particularly simply compared to $\hat{L}_x$ and $\hat{L}_y$. For this reason we choose our co-ordinates so that $\hat{z}$ lies along whatever direction is of interest, and use $\hat{L}^2$ and $\hat{L}_z$ as our maximal commuting set.

Re-expressing ∇^2 gives the TISE:

$$\hat{H}\psi\left(\boldsymbol{r},t\right)=\left(-\frac{\hbar^{2}}{2mr^{2}}\partial_{r}\left(r^{2}\partial_{r}\right)+\frac{1}{2mr^{2}}\hat{L}^{2}+V\left(r,\theta,\phi\right)\right)\psi\left(\boldsymbol{r},t\right)=E\psi\left(\boldsymbol{r},t\right) \tag{367}$$

where the squared angular momentum operator is

$$\hat{L}^{2}\psi\left(\boldsymbol{r},t\right)=-\hbar^{2}\left(\frac{1}{\sin\left(\theta\right)}\partial_{\theta}\left(\sin\left(\theta\right)\partial_{\theta}\right)+\frac{1}{\sin^{2}\left(\theta\right)}\partial_{\phi}^{2}\right)\psi\left(\boldsymbol{r},t\right). \tag{368}$$

This can also be found from Eq. 361.

9.2.3 Ladder operators

Consider the operators

$$\hat{L}_{\pm}=\hat{L}_{x}\pm i\hat{L}_{y}. \tag{369}$$

Using Equation 363 the commutator with $\hat{L}_z$ can be seen to be

$$\left[\hat{L}_{\pm},\hat{L}_{z}\right]=\mp\hbar\hat{L}_{\pm}. \tag{370}$$

By the reasoning applied to the energy raising and lowering operators of the harmonic oscillator, we see that $\hat{L}_{\pm}$ are raising and lowering (ladder) operators for the z-projection of angular momentum. It is conventional to denote the eigenstates of $\hat{L}_z$ as $|m\rangle$, where m is an integer unrelated to the mass of the particle:

$$\hat{L}_{z}|m\rangle=\hbar m|m\rangle. \tag{371}$$

The fact that the eigenvalues of $\hat{L}_z$ take integer values will be derived explicitly in Section 10. Assuming it for now, we find that

$$\hat{L}_{\pm}\hat{L}_{z}|m\rangle=\hbar m\hat{L}_{\pm}|m\rangle \tag{372}$$

$$\left(\hat{L}_{z}\hat{L}_{\pm}+\left[\hat{L}_{\pm},\hat{L}_{z}\right]\right)|m\rangle=\hbar m\hat{L}_{\pm}|m\rangle \tag{373}$$

$$\left(\hat{L}_{z}\hat{L}_{\pm}\mp\hbar\hat{L}_{\pm}\right)|m\rangle=\hbar m\hat{L}_{\pm}|m\rangle \tag{374}$$

$$\hat{L}_{z}\left(\hat{L}_{\pm}|m\rangle\right)=\hbar\left(m\pm1\right)\left(\hat{L}_{\pm}|m\rangle\right) \tag{375}$$

that is, if $|m\rangle$ is an eigenstate of $\hat{L}_z$ with eigenvalue $\hbar m$, then $\hat{L}_{\pm}|m\rangle$ is an eigenstate with eigenvalue $\hbar\left(m\pm1\right)$, as required. Since

$$\left[\hat{L}_{i},\hat{L}^{2}\right]=0 \tag{376}$$

we also have that

$$\left[\hat{L}_{\pm}, \hat{L}^2\right] = 0 \tag{377}$$

and the operators do not affect the total angular momentum, only its protection along a given direction. Thinking physically we see that there must therefore be both a top and bottom rung to the ladder of eigenvalues $\hbar m$, and that

$$-l \leq m \leq l. \tag{378}$$

10 The hydrogen atom

Lecture: 10am on 7/12/20.

Office hours: 11am on 7/12/20.

Videos: V10.1, V10.2, V10.3

10.1 Spherically-symmetric potentials

The TDSE is always separable into time and space co-ordinates. In the special case of a spherically-symmetric potential $V = V(r)$ it additionally becomes separable into ODEs for the radial part, and the angular parts:

$$\psi(\boldsymbol{r}, t) \triangleq T(t)\,\varphi(\boldsymbol{r}) \tag{379}$$

$$\varphi(\boldsymbol{r}) \triangleq T(t)\,R(r)\,Y(\theta, \phi)\,. \tag{380}$$

Inserting into Eq. 367 gives

$$\frac{1}{Y(\theta,\phi)}\hat{L}^2 Y(\theta,\phi) = 2mr^2\left(E - V(r)\right) + \frac{\hbar^2}{R(r)}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right)R(r)\,. \tag{381}$$

Both sides are therefore equal to a constant which we choose to be $\hbar^2 k^2$, giving:

$$\text{radial equation: } \frac{\hbar^2}{R(r)}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right)R(r) + 2mr^2\left(E - V(r)\right) = \hbar^2 k^2 \tag{382}$$

$$\text{angular equation: } \hat{L}^2 Y(\theta,\phi) = \hbar^2 k^2 Y(\theta,\phi)\,. \tag{383}$$

10.1.1 Angular part

The angular equation reads:

$$-\hbar^2\left(\frac{1}{\sin(\theta)}\partial_\theta\left(\sin(\theta)\,\partial_\theta\right) + \frac{1}{\sin^2(\theta)}\partial_\phi^2\right)Y(\theta,\phi) = \hbar^2 k^2 Y(\theta,\phi) \tag{384}$$

re-arranging,

$$-\partial_\phi^2 Y(\theta,\phi) = k^2\sin^2(\theta)\,Y(\theta,\phi) + \sin(\theta)\,\partial_\theta\left(\sin(\theta)\,\partial_\theta\right)Y(\theta,\phi)\,. \tag{385}$$

This is again separable: substituting

$$Y(\theta,\phi) = P(\theta)\,F(\phi) \tag{386}$$

gives

$$\frac{\sin(\theta)}{P(\theta)}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin(\theta)\frac{\mathrm{d}P(\theta)}{\mathrm{d}\theta}\right)+k^2\sin^2(\theta)=-\frac{1}{F(\phi)}\frac{\mathrm{d}^2F(\phi)}{\mathrm{d}\phi^2}. \tag{387}$$

We again set both sides equal to a constant. It is traditional to name this constant m^2 which causes an unfortunate confusion with the mass m.

Polar part

The polar part is solved by

$$F(\phi)=\exp(\pm im\phi). \tag{388}$$

The observable probability density $|F|^2$ should be single-valued, requiring

$$F(\phi+2\pi)=F(\phi) \tag{389}$$

and so

$$\exp(2\pi im)=1. \tag{390}$$

This requires m to be an integer. Note that $F_m(\phi)$ is an eigenstate of $\hat{L}_z$:

$$\hat{L}_zF_m(\phi)=-i\hbar\partial_\phi F_m(\phi)=\hbar mF_m(\phi). \tag{391}$$

The integer m is called the 'magnetic quantum number'; it is the observable corresponding to the measurement of the angular momentum projected along the z-axis.

Azimuthal part

The azimuthal equation

$$\sin(\theta)\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin(\theta)\frac{\mathrm{d}P(\theta)}{\mathrm{d}\theta}\right)+k^2\sin^2(\theta)P(\theta)=m^2P(\theta) \tag{392}$$

is known as the associated Legendre equation. It is solved by the 'associated Legendre polynomials' $P_l^m(\cos(\theta))$ where $k^2=l(l+1)$ for l any positive integer: it is called the 'orbital quantum number', or 'azimuthal quantum number'. The values of m are limited to the range

$$-l\leq m\leq l,\ l\in\mathbb{Z}. \tag{393}$$

Solution to angular equation

Overall we have that

	$m=-2$	-1	0	1	2
$l=0$			$\frac{1}{2\sqrt{\pi}}$		
1		$\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin(\theta)\exp(-i\phi)$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos(\theta)$	$-Y_1^{-1*}$	
2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2(\theta)\exp(-2i\phi)$	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin(2\theta)\exp(-i\phi)$	$\frac{1}{4}\sqrt{\frac{5}{\pi}}\left(3\cos^2(\theta)-1\right)$	$-Y_2^{-1*}$	Y_2^{-2*}

Table 1: The first few spherical harmonics $Y_l^m(\theta,\phi)$.

$$\hat{L}^2 Y_l^m(\theta,\phi) = \hbar^2 l(l+1) Y_l^m(\theta,\phi) \tag{394}$$

$$\hat{L}_z Y_l^m(\theta,\phi) = \hbar m Y_l^m(\theta,\phi) \tag{395}$$

where

$$Y_l^m(\theta,\phi) = \mathcal{N} P_l^m(\cos(\theta))\exp(\pm im\phi) \tag{396}$$

are the 'spherical harmonics' ($\mathcal{N}$ is a normalization). They are orthonormal:

$$\int_0^\pi \mathrm{d}\theta \sin(\theta) \int_0^{2\pi} \mathrm{d}\phi Y_{l'}^{m'*}(\theta,\phi) Y_l^m(\theta,\phi) = \delta_{ll'}\delta_{mm'} \tag{397}$$

and form a complete orthonormal basis for functions on the surface of a sphere:

$$f(\theta,\phi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} f_{lm} Y_l^m(\theta,\phi) \tag{398}$$

for complex scalars f_{lm}. The first few spherical harmonics are given in Table 1.

Note that we can write this using Dirac notation:

$$\hat{L}^2|l,m\rangle = \hbar^2 l(l+1)|l,m\rangle \tag{399}$$

$$\hat{L}_z|l,m\rangle = \hbar m|l,m\rangle \tag{400}$$

where

$$\langle\theta,\phi|l,m\rangle = Y_l^m(\theta,\phi). \tag{401}$$

10.1.2 Radial part

Substituting Eq. 394 into the radial equation of Eq. 382 gives

$$\left(-\frac{\hbar^2}{2mr^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right) + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right) R_l(r) = E R_l(r). \tag{402}$$

It is conventent to define

$$R(r) \triangleq \frac{\chi(r)}{r} \tag{403}$$

which gives

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\chi(r)}{\mathrm{d}r^2} + V_{eff}(r)\chi(r) = E\chi(r) \tag{404}$$

where

$$V_{eff}(r) \triangleq V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}. \tag{405}$$

Eq. 404 is simply the 1D TISE with a modified potential term given in Eq. 405. The additional contribution built into V_{eff} is called the centrifugal barrier term.

10.1.3 Solution and normalization

Substituting Eq. 394 back into Eq. 367 we find that, **for spherically-symmetric potentials, the TISE reduces to:**

$$\boxed{\hat{H}\varphi_{l,m}(\boldsymbol{r}) = \left(-\frac{\hbar^2}{2mr^2}\partial_r\left(r^2\partial_r\right) + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right)\varphi_{l,m}(\boldsymbol{r}) = E\varphi_{l,m}(\boldsymbol{r})} \tag{406}$$

with

$$\varphi_{l,m}(\boldsymbol{r}) = R_l(r)\,Y_l^m(\theta,\phi). \tag{407}$$

In spherical polars we have the Jacobian $r^2\sin(\theta)$; given that

$$\iiint |\varphi(\boldsymbol{r})|^2\,\mathrm{d}^3\boldsymbol{r} = 1 \tag{408}$$

$$\downarrow \tag{409}$$

$$\int_0^\infty r^2\,|R(r)|^2\,\mathrm{d}r \int_0^\pi \sin(\theta)\,|P_l^m(\theta)|^2\,\mathrm{d}\theta \int_0^{2\pi} |F_m(\phi)|^2\,\mathrm{d}\phi = 1 \tag{410}$$

it is convenient to chose a normalization such that

$$\int_0^\infty r^2\,|R(r)|^2\,\mathrm{d}r = 1 \tag{411}$$

$$2\pi\int_0^\pi \sin(\theta)\,|P_l^m(\theta)|^2\,\mathrm{d}\theta = 1. \tag{412}$$

10.2 The hydrogen atom

The TISE governing the electron in the Hydrogen atom is

$$\hat{H}\varphi\left(\boldsymbol{r}\right)=\left(-\frac{\hbar^{2}\nabla^{2}}{2m}-\frac{e^{2}}{4\pi\epsilon_{0}r}\right)\varphi\left(\boldsymbol{r}\right). \tag{413}$$

Note that the potential is negative, giving an infinite ladder of negative energy bound states. The potential is spherically symmetric, and so we can use the separable form

$$\varphi_{l,m}\left(\boldsymbol{r}\right)=r^{-1}\chi\left(r\right)Y_{l}^{m}\left(\theta,\phi\right). \tag{414}$$

From Eq. 404 the radial equation is then

$$-\frac{\hbar^{2}}{2m}\frac{\mathrm{d}^{2}\chi\left(r\right)}{\mathrm{d}r^{2}}-\frac{e^{2}}{4\pi\epsilon_{0}r}\chi\left(r\right)+\frac{\hbar^{2}l\left(l+1\right)}{2mr^{2}}\chi\left(r\right)=E\chi\left(r\right).$$

Defining the quantities

$$a_{0}\triangleq\frac{4\pi\epsilon_{0}\hbar^{2}}{me^{2}}\text{ (the Bohr radius)} \tag{415}$$

$$\rho\triangleq\frac{r}{a_{0}} \tag{416}$$

$$\lambda^{2}\triangleq-\frac{2mEa_{0}^{2}}{\hbar^{2}} \tag{417}$$

and redefining $\chi\left(a_{0}\rho\right)\rightarrow\chi\left(\rho\right)$ since χ is not yet known, the equation reduces to

$$\frac{\mathrm{d}^{2}\chi\left(\rho\right)}{\mathrm{d}\rho^{2}}-\left(\lambda^{2}-\frac{2}{\rho}+\frac{l\left(l+1\right)}{\rho^{2}}\right)\chi\left(\rho\right)=0. \tag{418}$$

For $\rho\gg1$ the normalizable solution is

$$\chi\left(\rho\right)\underset{\lim\rho\rightarrow\infty}{\propto}\exp\left(-\lambda\rho\right) \tag{419}$$

and for $\rho\ll1$

$$\chi\left(\rho\right)\underset{\lim\rho\rightarrow0}{\propto}\rho^{l+1}. \tag{420}$$

This motivates the substitution

$$\chi\left(\rho\right)=\rho^{l+1}\exp\left(-\lambda\rho\right)F\left(2\lambda\rho\right) \tag{421}$$

for a function $F\left(2\lambda\rho\right)$ to be found. Substituting into Eq. 418 along with

$$y=2\lambda\rho \tag{422}$$

gives

$$yF''\left(y\right)+F'\left(y\right)\left(2\left(l+1\right)-y\right)-\left(l+1-\frac{1}{\lambda}\right)F\left(y\right)=0 \tag{423}$$

which is LaGuerre's equation, whose solutions are LaGuerre polynomials $L_{n-l-1}^{2l+1}(y)$ (which again form a complete orthonormal basis), with $n \geq 0$ an integer called the 'principal quantum number'. The energy eigenvalues, substituting back into Eq. 413, are

$$E_n = \frac{-\hbar^2}{2ma_0^2 n^2}. \tag{424}$$

Overall the solutions are

$$\varphi_{n,l,m}(r,\theta,\phi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \exp\left(-\frac{r}{na_0}\right)\left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) Y_l^m(\theta,\phi). \tag{425}$$

Note that the result is labelled by three integers: these form a set of quantum numbers which can be known simultaneously. It is convenient to define the ket $|n,l,m\rangle$ such that

$$\langle r,\theta,\phi|n,l,m\rangle = \varphi_{n,l,m}(r,\theta,\phi) \tag{426}$$

in which case we have the following results:

$$\hat{H}|n,l,m\rangle = E_n|n,l,m\rangle \tag{427}$$

$$\hat{L}^2|n,l,m\rangle = \hbar^2 l(l+1)|n,l,m\rangle \tag{428}$$

$$\hat{L}_z|n,l,m\rangle = \hbar m|n,l,m\rangle \tag{429}$$

where

$n > 0$ the principal quantum number

$0 \leq l < n$ the azimuthal quantum number, or orbital quantum number

$-l \leq m \leq l$ the magnetic quantum number (z-projection of orbital angular momentum).

The set of quantum numbers is completed by the spin quantum number $s = \pm 1/2$ which we saw in section 5.

10.2.1 The Bohr model

Eq. 424 accurately predicts the energy levels of the Hydrogen atom. Niels Bohr earlier arrived at the same result through a simpler but incorrect model based on the quantization of angular momentum: $mvr = n\hbar$ with n the principal quantum number. This condition can be useful in obtaining rough estimates for the energy levels of Hydrogen-like systems.