Notes on Physical Chemistry

Notes I took based loosely on the Natural Sciences curriculum, and then some

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Part I

Quantum mechanics and applications

Chapter 1

Quantum Mechanics

1.1 INTRODUCTION

The 1-D Schrödinger equation is given by

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi \tag{1.1.1}$$

1.1.1 Normalisation

Theorem 1.1.1.1 (Preservation of normalisation)**.** Solutions to the Schrödinger equation automatically preserves normalisation.

Proof. We need to show that

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\infty}^{+\infty} |\Psi(x,t)|^2 dx = 0. \tag{1.1.2}$$

We do so by directly evaluating using integration by parts.

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{+\infty} |\Psi(x,t)|^2 \,\mathrm{d}x \tag{1.1.3a}$$

$$= \int_{-\infty}^{+\infty} \frac{\partial}{\partial t}(\Psi^*\Psi)\,\mathrm{d}x \tag{1.1.3b}$$

$$= \int_{-\infty}^{+\infty} \left(\Psi^*\frac{\partial \Psi}{\partial t} + \Psi\frac{\partial \Psi^*}{\partial t}\right)\mathrm{d}x, \tag{1.1.3c}$$

$$\because \frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m}\frac{\partial^2\Psi}{\partial t^2} - \frac{i}{\hbar}V\Psi \tag{1.1.3d}$$

$$\therefore \frac{\partial \Psi^*}{\partial t} = \frac{-i\hbar}{2m}\frac{\partial^2\Psi^*}{\partial t^2} + \frac{i}{\hbar}V\Psi^* \tag{1.1.3e}$$

$$\Rightarrow \text{integrand} = \Psi^*\left(\frac{i\hbar}{2m}\frac{\partial^2\Psi}{\partial x^2} - \frac{i}{\hbar}V\Psi\right) + \Psi\left(\frac{-i\hbar}{2m}\frac{\partial^2\Psi^*}{\partial t^2} + \frac{i}{\hbar}V\Psi^*\right) \tag{1.1.3f}$$

$$= \frac{i\hbar}{2m}\left(\Psi^*\frac{\partial^2\Psi}{\partial x^2} - \Psi\frac{\partial^2\Psi^*}{\partial x^2}\right) \tag{1.1.3g}$$

$$= \frac{\partial}{\partial x}\left[\frac{i\hbar}{2m}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right)\right] \tag{1.1.3h}$$

$$\Rightarrow \frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{+\infty} |\Psi(x,t)|^2 \,\mathrm{d}x \tag{1.1.3i}$$

$$= \frac{i\hbar}{2m}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right)\Big|_{-\infty}^{+\infty}, \tag{1.1.3j}$$

where Equation 1.1.3j results from the foundamental theorem of calculus. For all normalisable wavefunctions, $\Psi \to 0$ as $|x| \to \infty$, this implies

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{+\infty} |\Psi(x,t)|^2 \,\mathrm{d}x = 0. \tag{1.1.4}$$

□

Worked example 1.1.1.1. Consider the wave function

$$\Psi(x,t) = Ae^{-\lambda|x|}e^{-i\omega t}, \tag{1.1.5}$$

where A, λ and ω are positive real constants.
(a) Nomalise Ψ.
The time dependence cancels out in

$$\int_{-\infty}^{+\infty} \Psi^*\Psi\,\mathrm{d}x, \tag{1.1.6}$$

leaving us with

$$\begin{aligned}&2A^2 \int_0^{\infty} e^{-2\lambda x}\,\mathrm{d}x\\ =&\frac{A^2}{\lambda}\\ =&1\\ \Rightarrow& A=\sqrt{\lambda}\end{aligned} \tag{1.1.7}$$

We therefore have the normalised wavefunction as

$$\Psi(x,t)=\sqrt{\lambda}e^{-\lambda|x|}e^{-i\omega t}. \tag{1.1.8}$$

(b) Determine the standard deviation of x and calculate the probability that x falls in the range of $\langle x\rangle \pm \sigma$.
As the wavefunction is an even function, $\langle x\rangle = 0$.
We still need to calculate $\langle x^2\rangle$:

$$\begin{aligned}&2\lambda \int_0^{\infty} x^2 e^{-2\lambda x}\,\mathrm{d}x\\ =&\frac{1}{2\lambda^2}\\ \because&\sigma^2=\langle x^2\rangle-\langle x\rangle^2\\ \Rightarrow&\sigma=\frac{1}{\sqrt{2}\lambda}\end{aligned} \tag{1.1.9}$$

The required probability is then calculated by

$$\begin{aligned}&\lambda \int_{-1/\sqrt{2}\lambda}^{1/\sqrt{2}\lambda} e^{-2\lambda x}\,\mathrm{d}x\\ =&1-e^{-\sqrt{2}}\\ =&0.7569.\end{aligned} \tag{1.1.10}$$

1.1.2 Momentum

Postulate 1.1.2.1. *All* classical dynamical variables can be expressed in terms of postition and momentum.

We already know the *postion operator*, $\boldsymbol{X}=x$, and now we will find the momentum operator. We know that

$$\langle x\rangle = \int_{-\infty}^{+\infty} x|\Psi(x,t)|^2\,\mathrm{d}x. \tag{1.1.11}$$

We postulate that

$$\langle v\rangle = \frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \int_{-\infty}^{+\infty} x\frac{\partial}{\partial x}|\Psi(x,t)|^2\,\mathrm{d}x = \frac{i\hbar}{2m}\int_{-\infty}^{+\infty} x\frac{\partial}{\partial x}\left[\frac{i\hbar}{2m}\left(\Psi^*\frac{\partial\Psi}{\partial x}-\Psi\frac{\partial\Psi^*}{\partial x}\right)\right]\mathrm{d}x \tag{1.1.12a}$$

$$= -\frac{i\hbar}{2m}\int_{-\infty}^{+\infty}\left(\Psi^*\frac{\partial\Psi}{\partial x}-\Psi\frac{\partial\Psi^*}{\partial x}\right) \tag{1.1.12b}$$

$$= -\frac{i\hbar}{m}\int_{-\infty}^{+\infty}\Psi^*\frac{\partial\Psi}{\partial x}, \tag{1.1.12c}$$

where Equations 1.1.12b and 1.1.12c are the results of integration by parts.

Definition 1.1.2.1 (Momentum operator)**.** We can now extract the definition of the momentum operator, $\boldsymbol{P}$, from Equation 1.1.12c:

$$\boldsymbol{P} \equiv \frac{\hbar}{i}\frac{\partial}{\partial x}. \tag{1.1.13}$$

Theorem 1.1.2.1 (Ehrenfest theorem)**.** The Ehrenfest theorem states that

$$m\frac{\mathrm{d}}{\mathrm{d}t}\langle x\rangle = \langle p\rangle, \text{ and} \tag{1.1.14a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle p\rangle = -\langle V'(x)\rangle. \tag{1.1.14b}$$

Equation 1.1.14a is already proven, and we give a proof to Equation 1.1.14b below.

Proof.

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle p\rangle = \frac{\mathrm{d}}{\mathrm{d}t}\left(-i\hbar\int_{-\infty}^{+\infty}\Psi^*\frac{\partial\Psi}{\partial x}\,\mathrm{d}x\right) \tag{1.1.15a}$$

$$= -i\hbar\int_{-\infty}^{+\infty}\frac{\partial}{\partial t}\left(\Psi^*\frac{\partial\Psi}{\partial x}\right)\mathrm{d}x \tag{1.1.15b}$$

$$= -i\hbar\int_{-\infty}^{+\infty}\Psi_t^*\Psi_x + \Psi^*\Psi_{xt}\,\mathrm{d}x \tag{1.1.15c}$$

$$= -i\hbar\int_{-\infty}^{+\infty}\frac{-i\hbar}{2m}\Psi_{xx}^*\Psi_x + \frac{i}{\hbar}V\Psi^*\Psi_x + \Psi^*\frac{\partial}{\partial x}\left(\frac{i\hbar}{2m}\Psi_{xx}-\frac{i}{\hbar}V\Psi\right)\mathrm{d}x \tag{1.1.15d}$$

$$= -i\hbar\int_{-\infty}^{+\infty}\frac{-i\hbar}{2m}\Psi_{xx}^*\Psi_x + \frac{i}{\hbar}V\Psi^*\Psi_x + \Psi^*\left(\frac{i\hbar}{2m}\Psi_{xxx}-\frac{i}{\hbar}V_x\Psi-\frac{i}{\hbar}V\Psi_x\right)\mathrm{d}x \tag{1.1.15e}$$

$$= -i\hbar\int_{-\infty}^{+\infty}\frac{-i\hbar}{2m}\Psi_{xx}^*\Psi_x + \Psi^*\frac{i\hbar}{2m}\Psi_{xxx} - \frac{i}{\hbar}V_x\Psi\Psi^*\,\mathrm{d}x \tag{1.1.15f}$$

We attempt to reduce the expression by evaluating $\int_{-\infty}^{+\infty} \Psi_{xx}^* \Psi_x \, \mathrm{d}x$ by parts twice:

$$\int_{-\infty}^{+\infty} \Psi_{xx}^* \Psi_x \, \mathrm{d}x = \Psi_x^* \Psi_x \Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \Psi_x^* \Psi_{xx} \, \mathrm{d}x \tag{1.1.16a}$$

$$= 0 - \Psi^* \Psi_{xx} \Big|_{-\infty}^{+\infty} + \int_{-\infty}^{+\infty} \Psi^* \Psi_{xxx} \, \mathrm{d}x \tag{1.1.16b}$$

$$= \int_{-\infty}^{+\infty} \Psi^* \Psi_{xxx} \, \mathrm{d}x. \tag{1.1.16c}$$

This leads to the cancellation of the first two terms in the integrand in Equation 1.1.15f and we are left with the desired result:

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle p \rangle = - \int_{-\infty}^{+\infty} \Psi^* V_x \Psi \, \mathrm{d}x = -\langle V'(x) \rangle. \tag{1.1.17}$$

□

1.1.3 The uncertainty principle

Theorem 1.1.3.1 (The uncertainty principle)**.** The uncertainty principle relates the error in position and momentum by

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}, \tag{1.1.18}$$

a result we will prove only later.

Worked example 1.1.3.1.

A particle of mass m is in the state

$$\Psi(x,t) = Ae^{-a[(mx^2/\hbar)+it]}, \tag{1.1.19}$$

where A and a are positive real constants.

(a) Find A.

$$A^2 \int_{-\infty}^{+\infty} \psi\psi^* \, \mathrm{d}x = 1 \tag{1.1.20a}$$

$$A^2 \int_{-\infty}^{+\infty} e^{-2a(mx^2/\hbar)} \, \mathrm{d}x = 1 \tag{1.1.20b}$$

$$A^2 \sqrt{\frac{\pi\hbar}{2ma}} = 1 \tag{1.1.20c}$$

$$A = \left(\frac{2ma}{\pi\hbar}\right)^{1/4}. \tag{1.1.20d}$$

(b) For what potential energy function $V(x)$ does Ψ satisfy the Schrödinger equation ?
We have the spatial wave function

$$\psi(x) = \left(\frac{2ma}{\pi\hbar}\right)^{1/4} e^{-max^2/\hbar}, \tag{1.1.21}$$

which when differentiated twice gives

$$\left(\frac{2ma}{\pi\hbar}\right)^{1/4} \left(\frac{4m^2a^2}{\hbar^2}x^2 - \frac{2ma}{\hbar}\right) e^{-max^2/\hbar} = \left(\frac{4m^2a^2}{\hbar^2}x^2 - \frac{2ma}{\hbar}\right)\psi, \tag{1.1.22}$$

and the Schrödinger equation gives

$$\left[\left(\hbar a - 2ma^2x^2\right) + V\right]\psi = E\psi \tag{1.1.23}$$

The energy is found by

$$i\hbar\frac{\mathrm{d}\phi}{\mathrm{d}t} = E\phi \tag{1.1.24a}$$

$$E = \hbar a, \tag{1.1.24b}$$

with $\phi = e^{-iat}$. The potential must then be

$$V(x) = 2ma^2x^2, \tag{1.1.25}$$

the harmonic oscillator potential.
(c) Calculate the expectation values of x, x^2, p, and p^2.
$x\phi$ and $\frac{\partial\phi}{\partial x}$ are odd functions and as such

$$\langle x\rangle = \langle p\rangle = 0. \tag{1.1.26}$$

Letting $k = ma/\hbar$

$$\begin{aligned}
\langle x^2 \rangle &= \int_{-\infty}^{+\infty} x^2 \psi^2 \,\mathrm{d}x && (1.1.27\text{a})\\
&= \left(\frac{2ma}{\pi\hbar}\right)^{1/2} \int_{-\infty}^{+\infty} x^2 e^{-kx^2} && (1.1.27\text{b})\\
&= -\frac{x}{2k} e^{-kx^2} \Big|_{-\infty}^{+\infty} + \int_{-\infty}^{+\infty} \frac{1}{2k} e^{-kx^2} \,\mathrm{d}x && (1.1.27\text{c})\\
&= 0 + \frac{1}{2k}\sqrt{\frac{\pi}{k}} \cdot \left(\frac{2ma}{\pi\hbar}\right)^{1/2} && (1.1.27\text{d})\\
&= \frac{\hbar}{4ma}. && (1.1.27\text{e})
\end{aligned}$$

$$\begin{aligned}
\langle p^2 \rangle &= -\hbar^2 \int_{-\infty}^{+\infty} \psi \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} \,\mathrm{d}x && (1.1.28\text{a})\\
&= -\hbar^2 \int_{-\infty}^{+\infty} \left(\frac{4m^2a^2}{\hbar^2} x^2 - \frac{2ma}{\hbar}\right) \psi^2 && (1.1.28\text{b})\\
&= -4m^2a^2 \langle x^2 \rangle + 2\hbar ma \int_{-\infty}^{+\infty} \psi^2 && (1.1.28\text{c})\\
&= \hbar ma. && (1.1.28\text{d})
\end{aligned}$$

Standard deviations are given by

$$\begin{aligned}
\sigma_x &= \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \frac{1}{2}\sqrt{\frac{\hbar}{ma}} && (1.1.29\text{a})\\
\sigma_p &= \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \sqrt{\hbar ma}, && (1.1.29\text{b})
\end{aligned}$$

with the product of uncertainties

$$\sigma_x \sigma_p = \frac{\hbar}{2}. \tag{1.1.30}$$

In this case, the uncertainty is as small as possible.

1.2 TIME-INDEPENDENT SCHRÖDINGER EQUATION

1.2.1 Stationary states

We solve the Schrödinger equation of the form

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi \tag{1.2.1}$$

For a general potential $V(x)$, independent of t. We solve the partial differential equation by separation of variables:

$$\Psi(x,t) = \psi(x)\phi(t). \tag{1.2.2}$$

Substituting into the original equation we have

$$i\hbar\frac{1}{\phi}\frac{\mathrm{d}\phi}{\mathrm{d}t} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V. \tag{1.2.3}$$

So we have

$$i\hbar\frac{1}{\phi}\frac{\mathrm{d}\phi}{\mathrm{d}t} = E \tag{1.2.4a}$$

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V\psi = E, \tag{1.2.4b}$$

or,

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = -\frac{iE}{\hbar}\phi \tag{1.2.5a}$$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V\psi = E\psi. \tag{1.2.5b}$$

Solving Equation 1.2.5a gives

$$\phi(t) = e^{-iEt/\hbar}. \tag{1.2.6}$$

Equation 1.2.5b is the *time-independent Schrödinger equation* and solving it requires that $V(x)$ be specified.

Property 1.2.1.1 (Stationary states)**.** Stationary states have the following properties:

- *All expectation value is constant.* This means that, from Equation 1.1.14a,

$$\langle p \rangle = 0. \tag{1.2.7}$$

- *Total energy is definite.* Proof follows.

Proof.

$$H(x,p) = \frac{p^2}{2m} + V(x). \tag{1.2.8}$$

The corresponding quantum mechanical Hamiltonian operator is given by canonical substitution $p \to (\hbar/i)(\partial/\partial x)$:

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x). \tag{1.2.9}$$

We can then write the Schrödinger equation as

$$H\psi = E\psi, \tag{1.2.10}$$

So the expectation value of the total energy is

$$\langle H \rangle = \int_{-\infty}^{+\infty} \psi^* H \psi \, \mathrm{d}x = E \int_{-\infty}^{+\infty} \psi^2 \, \mathrm{d}x = E, \tag{1.2.11}$$

and

$$\langle H^2 \rangle = \int_{-\infty}^{+\infty} \psi^* H^2 \psi \, \mathrm{d}x = E^2 \int_{-\infty}^{+\infty} \psi^2 \, \mathrm{d}x = E^2. \tag{1.2.12}$$

The variance of H is calculated by

$$\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = 0 \tag{1.2.13}$$

Hence, every measurement of the total energy is certain to return the value E. □

Corollary 1.2.1.1. As a result of the second property above, we can simplify the calculation of $\langle H \rangle$ by using the *intial wavefunction* $\Psi(x,0)$ which usually have a simpler form than the complete wavefunction.

Theorem 1.2.1.1 (Particle-in-a-box general solution)**.**
The general solution is a linear combination of separable solutions:

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n e^{-iE_n t/\hbar}, \tag{1.2.14}$$

which is a *Fourier series*, whose coefficients can be determined by initial condition.
It is worth stressing that Property 1.2.1.1 *does not* apply to the general solution, becasue the exponential time dependences do not cancel out due to different energies, but rather individual summation terms, the stationary states.

Worked example 1.2.1.1. Suppose a particle starts out in a linear combination of junst two *real* stationary states, *i.e.*, all other c_n's are 0:

$$\Psi(x,0) = c_1\psi_1 + c_2\psi_2. \tag{1.2.15}$$

What is the complete wavefunction $\Psi(x,t)$ at subsequent times? Find the probability denstiy function and describe its motion.
Solution: The first part is trivial: just stick the time dependence onto the spatial wavefunction:

$$\Psi(x,t) = c_1\psi_1 e^{-iE_1 t/\hbar} + c_2\psi_2 e^{-iE_2 t/\hbar}. \tag{1.2.16}$$

So

$$|\Psi(x,t)|^2 = \Psi\Psi^* \tag{1.2.17a}$$
$$= c_1^2\psi_1^2 + c_2^2\psi_2^2 + 2c_1c_2\psi_1\psi_2\cos[(E_2 - E_1)t/\hbar]. \tag{1.2.17b}$$

It oscillates sinusoidally at $\omega = (E_2 - E_1)/\hbar$, so clearly the complete solution is *not* a stationary state.

We now introduce three seemingly trivial but oft-invoked theorems.

Theorem 1.2.1.2 (Energy must be real)**.**
For all normalisable solutions, the separation constant E must be real.

Proof. Suppose $E = E_0 + i\Gamma$ in

$$\Psi = \psi e^{-iEt/\hbar} \tag{1.2.18}$$

The normalisablity criterion requires that

$$1 = \int_{-\infty}^{+\infty} \mathbf{\Psi}^* \mathbf{\Psi} \, \mathrm{d}x \tag{1.2.19a}$$

$$= \int_{-\infty}^{+\infty} \psi^2 e^{(iE^* - iE)t/\hbar} \, \mathrm{d}x \tag{1.2.19b}$$

which means that

$$iE^* - iE = 0 \tag{1.2.20a}$$

$$i(E_0 - i\Gamma) - i(E_0 + i\Gamma) = 0 \tag{1.2.20b}$$

$$2\Gamma = 0 \tag{1.2.20c}$$

$$\Gamma = 0. \tag{1.2.20d}$$

☐

Theorem 1.2.1.3 (ψ can always be taken to be real)**.**
The time-independent wavefunction ψ, even if complex, can always be expressed as a linear combination of solutions with the same energy that are real (with complex coefficients).

Proof. For any ψ that satisfies

$$H\psi = E\psi, \tag{1.2.21}$$

ψ^* will also satisfy it. Therefore a linear combination of the two, *i.e.*, the real and the imaginary parts, will also separately satisfy the equation:

$$\begin{aligned} H(\psi + \psi^*) &= E(\psi + \psi^*) \\ Hi(\psi - \psi^*) &= Ei(\psi - \psi^*). \end{aligned} \tag{1.2.22}$$

Therefore, we can always take ψ's to be real when working with them. ☐

Theorem 1.2.1.4 (Even potentials)**.**
If $V(x)$ is an even function, then ψ can always be taken to be either even or odd.

Proof. For any $\psi(x)$ that satisfies

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)\psi(x) &= E\psi(x) \\ H\psi(x) &= E\psi(x) \end{aligned} \tag{1.2.23}$$

with $V(x) = V(-x)$. $\psi(-x)$ can also satisfy the same equation:

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(-x)}{\mathrm{d}x^2} + V(x)\psi(-x) &= E\psi(-x) \\ H\psi(-x) &= E\psi(-x), \end{aligned} \tag{1.2.24}$$

Therefore in the same vein as the previous proof, two linear combinations $\psi_{even} = \psi(x) + \psi(-x)$ amd $\psi_{odd} = \psi(x) - \psi(-x)$ can both satisfy the equation. ☐

Theorem 1.2.1.5 (E must exceed minimum value of V)**.**
E must exceed minimum value of V for every normalisable solution to the time-independent Schrödinger equation .

Proof. The time-independent Schrödinger equation can be rewritten as

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \frac{2m}{\hbar^2}(V - E)\psi. \tag{1.2.25}$$

If $E < V_{min}$, ψ and ψ_{xx} will have the same sign, therefore maxima must occur when $\psi < 0$ amd minima when $\psi > 0$, *i.e.*, it always curves away from the x-axis, hence it will not tend to 0 as $|x| \to \infty$. The classical analogue is that $T \equiv K + V \geq V$. ☐

1.2.2 The infinite square well

We now specify a potential:

$$V(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq a, \\ \infty & \text{otherwise.} \end{cases} \tag{1.2.26}$$

We first solve the time-independent Schrödinger equation :

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} &= E\psi \\ \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} &= -k^2\psi, \text{ where } k \equiv \frac{\sqrt{2mE}}{\hbar}. \end{aligned} \tag{1.2.27}$$

We arrive at the general SHM solution of

$$\psi(x) = A\sin kx + B\cos kx. \tag{1.2.28}$$

We impose the boundary condition

$$\psi(0) = \psi(a) = 0 \tag{1.2.29}$$

to yield

$$B = 0 \text{ and } k_n = \frac{n\pi}{a}. \tag{1.2.30}$$

Therefore from Equation 1.2.27 we have permitted values of E:

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}. \tag{1.2.31}$$

We then find A_n by normalising ψ:

$$\int_0^a |A|^2 \sin^2(kx)\,\mathrm{d}x = |A|^2 \cdot \frac{2}{a} = 1,\ A = \sqrt{\frac{2}{a}}. \tag{1.2.32}$$

The second equality comes from the fact that $k = n\pi/a$, and the third is due to that the phase of A bears no physical significance. We now have

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right), \text{ and } E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}. \tag{1.2.33}$$

Property 1.2.2.1 (Particle-in-a-box solutions)**.** The solutions have the following properties:

1. The are *alternately even and odd* wrt the centre of the well: ψ_1 is even, ψ_2 is odd an so on.
2. Going up in energy, each successive state has one more node with ψ_1 having none.
3. They are *mutually orthogonal*:

$$\int_{-\infty}^{+\infty} \psi_m^* \psi_n \,\mathrm{d}x = \delta_{mn}. \tag{1.2.34}$$

4. They are *complete* in that they are terms of an (odd) Fourier series and as such their linear combination can represent any (odd) function with the same period. The coefficients can be evaluated as follows

$$c_n = \int_{-\infty}^{+\infty} \psi_n^*(x) f(x)\,\mathrm{d}x. \tag{1.2.35}$$

The most general solution is then

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar^2/2ma^2)t}, \tag{1.2.36}$$

where c_n can be appropriately chosen to fit any initial wavefunction $\Psi(x,0)$:

$$c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \Psi(x,0)\,\mathrm{d}x. \tag{1.2.37}$$

Worked example 1.2.2.1. A particle in the infinite square well has the initial wavefunction

$$\Psi(x,0) = Ax(a-x).\ (0 \le x \le a) \tag{1.2.38}$$

Find $\Psi(x,t)$.

Solution: We normalise the boundary conditions first:

$$\begin{aligned} A &= \frac{1}{\sqrt{\int_0^a x^2(a-x)^2\,\mathrm{d}x}} \\ &= \sqrt{\frac{30}{a^5}}. \end{aligned} \tag{1.2.39}$$

The Fourier coefficients are

$$\begin{aligned} c_n &= \frac{2\sqrt{15}}{a^3} \int_0^a \sin\left(\frac{n\pi}{a}x\right) x(a-x)\,\mathrm{d}x && \text{(1.2.40a)} \\ &= \frac{2\sqrt{15}}{a^2} \int_0^a x \sin\left(\frac{n\pi}{a}x\right) \mathrm{d}x - \frac{2\sqrt{15}}{a^3} \int_0^a x^2 \sin\left(\frac{n\pi}{a}x\right) \mathrm{d}x && \text{(1.2.40b)} \\ &= \frac{2\sqrt{15}}{a^2} \left[\frac{-a^2}{n\pi}(-1)^n\right] - \frac{2\sqrt{15}}{a^3} \left[\frac{-a^3}{n\pi}(-1)^n - \frac{2a^3}{n^3\pi^3}[(-1)^n - 1]\right] && \text{(1.2.40c)} \\ &= \frac{4\sqrt{15}}{(n\pi)^3}\left[(-1)^n - 1\right], && \text{(1.2.40d)} \end{aligned}$$

which is equal to

$$\begin{cases} 0, & \text{if } n \text{ is even} \\ 8\sqrt{15}/(n\pi)^3. & \text{if } n \text{ is odd} \end{cases} \tag{1.2.41}$$

Therefore the complete wavefunction is

$$\Psi(x,t) = \sqrt{\frac{30}{a}} \left(\frac{2}{\pi}\right)^3 \sum_{\text{odd } n} \frac{1}{n^3} \sin\left(\frac{n\pi}{x}\right) e^{-iEt}. \tag{1.2.42}$$

Theorem 1.2.2.1 (Coefficient squared sums to 1)**.**

$$\sum_{n=1}^{\infty} |c_n|^2 = 1. \tag{1.2.43}$$

Proof.

$$\begin{aligned}
1 &= \int_{-\infty}^{+\infty} |\Psi(x,0)|^2 \, \mathrm{d}x && (1.2.44a)\\
&= \int_{-\infty}^{+\infty} \left(\sum_{m=1}^{\infty} c_m \psi_m(x) \right)^* \left(\sum_{n=1}^{\infty} c_n \psi_n(x) \right) \mathrm{d}x && (1.2.44b)\\
&= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_m^* c_n \delta_{mn} && (1.2.44c)\\
&= \sum_{n=1}^{\infty} |c_n|^2 && (1.2.44d)
\end{aligned}$$

□

Theorem 1.2.2.2 (Energy expectation in terms of coefficients)**.**

$$\langle H \rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n. \tag{1.2.45}$$

Proof. We know that

$$H\psi_n = E_n \psi_n. \tag{1.2.46}$$

Therefore we can write

$$\begin{aligned}
\langle H \rangle &= \int_{-\infty}^{+\infty} \Psi^* H \Psi \, \mathrm{d}x && (1.2.47a)\\
&= \int_{-\infty}^{+\infty} \left(\sum c_m \psi_m \right) * H \left(\sum c_n \psi_n \right) \mathrm{d}x && (1.2.47b)\\
&= \sum \sum c_m^* c_n E_n \int_{-\infty}^{+\infty} \psi_m^* \psi_n \, \mathrm{d}x = \sum |c_n|^2 E_n. && (1.2.47c)
\end{aligned}$$

□

Worked example 1.2.2.2. Calculate $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p \rangle$, $\langle p^2 \rangle$, σ_x and σ_p.
A tedious excercise in integration, we will simply list the results

- $\langle x \rangle = a/2$

- $\langle x^2 \rangle = a^2(1/3 - 1/2n^2\pi^2)$
- $\langle p \rangle = 0$
- $\langle p^2 \rangle = n^2\pi^2\hbar^2/a^2$
- $\sigma_x^2 = (n^2\pi^2 - 6)a^2/12n^2\pi^2$
- $\sigma_p^2 = n^2\pi^2\hbar^2/a^2$
- $\sigma_x\sigma_p = \hbar\sqrt{(\pi^2 n^2 - 6)/12}$
- Smallest uncertainty occurs when $n = 1$ at $\approx 0.568\hbar$.

Worked example 1.2.2.3. A particle in the infinite square well has as its initial wavefunction an even mixture of the first two stationary states:

$$\boldsymbol{\Psi}(x,0) = A[\psi_1(x) + \psi_2(x)]. \tag{1.2.48}$$

(a) Normalise $\boldsymbol{\Psi}(x,0)$.

$$\begin{aligned} 1 &= \int_0^a \boldsymbol{\Psi}^*\boldsymbol{\Psi}\,\mathrm{d}x && \text{(1.2.49a)} \\ &= \int_0^a A^2(\psi_1^2 + \psi_2^2 + 2\psi_1\psi_2)\,\mathrm{d}x && \text{(1.2.49b)} \\ &= 2A^2, && \text{(1.2.49c)} \end{aligned}$$

which implies $A = 1/\sqrt{2}$. We invoke Theorem 1.1.1.1 to be assured that we only need to normalise the wavefunction this one time.
(b) Find $\boldsymbol{\Psi}(x,t)$ and $|\boldsymbol{\Psi}(x,t)|^2$.
By properties of Fourier series we arrive immediately at

$$\begin{aligned} \boldsymbol{\Psi}(x,t) &= \frac{1}{\sqrt{2}}\left[\psi_1 e^{-i\omega t} + \psi_2 e^{-4i\omega t}\right] \\ &= \frac{\sqrt{a}}{2}\left[\sin(\pi x/a)e^{-i\omega t} + \sin(2\pi x/a)e^{-4i\omega t}\right], \end{aligned} \tag{1.2.50}$$

where we have set $\omega \equiv \pi^2\hbar/2ma^2$. Then

$$|\boldsymbol{\Psi}(x,t)|^2 = \frac{1}{2}[\psi_1^2 + \psi_2^2 + 2\psi_1\psi_2\cos(3\omega t)] \tag{1.2.51}$$

(c) Compute $\langle x \rangle$ and $\langle p \rangle$.

The integral to evaluate is

$$\begin{aligned}&\frac{1}{a}\int_0^a x\sin^2(\pi x/a)+x\sin^2(2\pi x/a)+2x\sin(\pi x/a)\sin(2\pi x/a)\cos(3\omega t)\,\mathrm{d}x\\ =&\frac{1}{a}\int_0^a x\sin^2(\pi x/a)+x\sin^2(2\pi x/a)+2x\sin^2(\pi x/a)\cos(\pi x/a)\cos(3\omega t)\,\mathrm{d}x\end{aligned} \tag{1.2.52}$$

Tedious again, we evaluate the integrals separately, using double angle and trigo power expansion formulae in the second integral:

$$\int_0^a x\sin\left(\frac{n\pi}{a}\right)\mathrm{d}x=\frac{a^2}{4} \tag{1.2.53a}$$

$$\int_0^a 2x\sin^2\left(\frac{\pi x}{a}\right)\cos\left(\frac{\pi x}{a}\right)\cos(3\omega t)\,\mathrm{d}x=-\frac{8a}{9\pi^2}\cos(3\omega t) \tag{1.2.53b}$$

So,

$$\langle x\rangle=\frac{2}{a}-\frac{16a}{9\pi^2}\cos(3\omega t). \tag{1.2.54}$$

$\langle p\rangle$ can easily be evaluated by Ehrenfest theorem (eq. 1.1.14a):

$$\langle p\rangle=\frac{16m\omega a}{3\pi^2}\sin(3\omega t)=\frac{8\hbar}{3a}\sin(3\omega t). \tag{1.2.55}$$

(d) If you measured the energy of this particle, what values might you get and what's the probability of getting each of them? Find $\langle H\rangle$.
We might get $E_1=\pi^2\hbar^2/2ma^2$ and $E_2=2\pi^2\hbar^2/ma^2$ each with 0.5 probability, and $\langle H\rangle=1.25\pi^2\hbar^2/ma^2$.

Worked example 1.2.2.4. A oarticle in the infinite square well has the initial wavefunction

$$\Psi(x,0)=\begin{cases}Ax, & 0\le x\le a/2\\ A(a-x). & a/2\le x\le a\end{cases} \tag{1.2.56}$$

Find $\Psi(x,t)$

Solution: We normalise the initial wavefunction first:

$$1=\int_0^a \Psi^*\Psi\,\mathrm{d}x \tag{1.2.57a}$$

$$=\frac{a^3A^2}{24}+\frac{a^3A^2}{24}=\frac{a^3A^2}{12}, \tag{1.2.57b}$$

which means that $A = \sqrt{12}/a^{3/2}$ The coefficients are obtained by

$$c_n = \int_0^{a/2} Ax \cdot \sqrt{\frac{2}{a}} \sin(n\pi x/a)\, \mathrm{d}x + \int_{a/2}^{a} A(a-x)\sqrt{\frac{2}{a}} \sin(n\pi x/a)\, \mathrm{d}x \tag{1.2.58a}$$

$$= \frac{2\sqrt{6}}{a^2}\left[\int_0^{a/2} x\sin(n\pi x/a)\,\mathrm{d}x - \int_{a/2}^{a} x\sin(n\pi x/a)\,\mathrm{d}x + \int_{a/2}^{a} a\sin(n\pi x/a)\,\mathrm{d}x\right] \tag{1.2.58b}$$

$$= \frac{2\sqrt{6}}{a^2}\left[\frac{a^2}{n^2\pi^2}\sin(n\pi/2) + \frac{a^2}{n\pi}\cos(n\pi/2) + \frac{a^2}{n^2\pi^2}\sin(n\pi/2) - \frac{a^2}{n\pi}\cos(n\pi/2)\right] \tag{1.2.58c}$$

$$= \frac{4\sqrt{6}}{n^2\pi^2}\sin(n\pi/2). \tag{1.2.58d}$$

We write the initial conditions as a linear combination of the stationary states:

$$\Psi(x,0) = \frac{4\sqrt{6}}{\pi^2}\left[\sum_{n=1} \frac{\psi_n}{(4n-3)^2} - \frac{\psi_n}{(4n-1)^2}\right]. \tag{1.2.59}$$

Full solution can be written out:

$$\Psi(x,t) = \frac{4\sqrt{6}}{\pi^2}\left[\sum_{n=1} \frac{\psi_n}{(4n-3)^2}e^{-iE_{4n-3}t/\hbar} - \frac{\psi_n}{(4n-1)^2}e^{-iE_{4n-1}t/\hbar}\right]. \tag{1.2.60}$$

The probability of energy turning out to be E_1 is

$$|c_1|^2 = \frac{96}{\pi^4} \approx 0.9855. \tag{1.2.61}$$

And

$$\langle H\rangle = \sum_{n=1}|c_n|^2E_n = \frac{48\hbar^2}{2\pi^2ma^2}\sum_{\text{odd } n}\frac{1}{n^2} = \frac{48\hbar^2}{2\pi^2ma^2}\frac{\pi^2}{8} = \frac{6\hbar^2}{ma^2} \approx 1.216E_1. \tag{1.2.62}$$

This example illustrates that the initial wavefunction does *not* need to have continuous first or second derivative or, for that matter, be continuous.

1.2.3 The harmonic oscillator

The harmonic potential is a very important class of potentials due to the ubiquitous presence of it as a result of Taylor expansion of many more complex potentials. It is given as

$$V(x) = \frac{1}{2}m\omega^2 x^2, \tag{1.2.63}$$

where we can replace m with μ when we are dealing with heteronuclear diatomics. The corresponding time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2\psi = E\psi. \tag{1.2.64}$$

Two methods at solving are available, we discuss the algebraic 'ladder operator' solution first.

1.2.3.1 Ladder operator

We can rewrite Equation 1.2.64 in a more suggestive form

$$\frac{1}{2m}[p^2 + (m\omega x)^2]\psi = E\psi, \tag{1.2.65}$$

where we have rewritten the Hamiltonian operator in terms of momentum and position operators.
We are therefore inspired to decompose it into two operators of the form

$$q_\pm \equiv \mp ip + m\omega x. \tag{1.2.66}$$

Aside: we do not write $q_\pm \equiv p \pm im\omega x$ because we want to obtain real ψ's (Theorem 1.2.1.3) and the i in front of p operator does that for us by getting rid of the i in the momentum operator.
The two operators should ideally be such that

$$q_+ q_- \overset{?}{=} p^2 + (m\omega x)^2. \tag{1.2.67}$$

But we cannot do this as p and x commutes, and we should calculate the commutator $[x, p]$ first.

$$[x, p]f(x) = \left[x\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}(f) - \frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}(xf)\right] \tag{1.2.68a}$$

$$= \frac{\hbar}{i}\left(x\frac{\mathrm{d}f}{\mathrm{d}x} - f - x\frac{\mathrm{d}f}{\mathrm{d}x}\right) \tag{1.2.68b}$$

$$= i\hbar f(x) \tag{1.2.68c}$$

Property 1.2.3.1. This gives the **canonical commutation relation**

$$[x,p] = i\hbar \tag{1.2.68d}$$

We re-examine q_+q_-:

$$q_+q_- = (-ip + m\omega x)(ip + m\omega x) = p^2 + (m\omega x)^2 + im\omega[x,p] = 2mH - m\omega\hbar. \tag{1.2.68e}$$

This means that

$$H \equiv \hbar\omega\left(\frac{q_+q_-}{2m\hbar\omega} + \frac{1}{2}\right) \tag{1.2.69}$$

For simplicity's sake we redefine

Definition 1.2.3.1 (Ladder operators)**.**

$$a_\pm \equiv \frac{1}{\sqrt{2m\hbar\omega}}(\mp ip + m\omega x), \tag{1.2.70}$$

So now we have

$$H = \hbar\omega\left(a_+a_- + \frac{1}{2}\right) = \hbar\omega\left(a_-a_+ - \frac{1}{2}\right) = \hbar\omega\left(a_\pm a_\mp \pm \frac{1}{2}\right). \tag{1.2.71}$$

Property 1.2.3.2 (Ladder operator commutator)**.** Additionally, the commutator

$$[a_-, a_+] = 1 \tag{1.2.72}$$

will come in handy.

We now introduce the important theorem

Theorem 1.2.3.1 (Ladder operator theorem)**.** If ψ satisfies the Schrödinger equation with energy E then $a_+\psi$ satisfies the Schrödinger equation with energy $E + \hbar\omega$.

Proof.

$$H(a_+\psi) = \hbar\omega\left(a_+a_- + \frac{1}{2}\right)(a_+\psi) = \hbar\omega\left(a_+a_-a_+ + \frac{1}{2}a_+\right)\psi \tag{1.2.73a}$$

$$= \hbar\omega a_+\left(a_-a_+ + \frac{1}{2}\right)\psi = a_+\left[\hbar\omega\left(a_+a_- + 1 + \frac{1}{2}\right)\psi\right] \tag{1.2.73b}$$

$$= a_+(H + \hbar\omega)\psi = a_+(E + \hbar\omega)\psi = (E + \hbar\omega)(a_+\psi). \tag{1.2.73c}$$

Similarly,

$$H(a_-\psi) = (E - \hbar\omega)(a_-\psi). \tag{1.2.74}$$

□

Corollary 1.2.3.1 (Ground state of harmonic potential)**.** The normalised ground state is

$$\psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar}. \tag{1.2.75}$$

with energy

$$E_0 = \frac{1}{2}\hbar\omega. \tag{1.2.76}$$

Proof. The ground state occurs when the lowering operator fails to produce a normalisable wavefunction, *i.e.*,

$$\begin{aligned} 0 &= a_-\psi_0 && (1.2.77a)\\ &= \frac{1}{\sqrt{2\hbar m\omega}}\left(\hbar\frac{\mathrm{d}}{\mathrm{d}x} + m\omega x\right)\psi_0, && (1.2.77b) \end{aligned}$$

or,

$$\frac{\mathrm{d}\psi_0}{\mathrm{d}x} = -\frac{m\omega}{\hbar}x\psi_0. \tag{1.2.78}$$

Solutions is obtained immediately as

$$\psi_0 = Ae^{-\frac{m\omega}{2\hbar}x^2}. \tag{1.2.79}$$

To normalise,

$$A = \frac{1}{\sqrt{\int_{-\infty}^{+\infty} e^{-\frac{m\omega}{\hbar}x^2}}} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}. \tag{1.2.80}$$

Therefore the ground state wavefunction is

$$\psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar}. \tag{1.2.81}$$

The energy of the ground state can be found as follows

$$\begin{aligned} \hbar\omega\left(a_+a_- + \frac{1}{2}\right)\psi_0 &= E_0\psi_0 && (1.2.82a)\\ \frac{1}{2}\hbar\omega\psi_0 + \hbar\omega a_+a_-\psi_0 &= E_0\psi_0 && (1.2.82b)\\ E_0 &= \frac{1}{2}\hbar\omega. && (1.2.82c) \end{aligned}$$

□

We can therefore now write[1]

$$\psi_n(x) = A_n(a_+)^n\psi_0(x), \text{ with } E_n = \left(n+\frac{1}{2}\right)\hbar\omega, \tag{1.2.83}$$

where A_n is the normalisation factor (on top of the normalisation factor that is included in the ground state wavefunction), and we will determine it in Theorem 1.2.3.2. But to do so we first need to introduce a lemma:

Lemma 1.2.3.1 (Hermitian conjugate)**.** For any well-behaved, *i.e.*, goes to zero at $\pm\infty$, functions $f(x)$ and $g(x)$, we have, where $a_\pm$ and $a_\mp$ can be any pair of hermitian conjugates,

$$\int_{-\infty}^{+\infty} f^*(a_\pm g)\,\mathrm{d}x = \int_{-\infty}^{+\infty}(a_\mp f)^* g\,\mathrm{d}x. \tag{1.2.84}$$

Proof. We show this result by explicit evaluation of the integral:

$$\begin{aligned}\int_{-\infty}^{+\infty} f^*(a_\pm g)\,\mathrm{d}x &= \frac{1}{\sqrt{2\hbar m\omega}}\int_{-\infty}^{+\infty} f^*\left(\mp\hbar\frac{\mathrm{d}}{\mathrm{d}x}+m\omega x\right)g\,\mathrm{d}x && \text{(1.2.85a)}\\ &= \frac{1}{\sqrt{2\hbar m\omega}}\int_{-\infty}^{+\infty}\left[\left(\pm\hbar\frac{\mathrm{d}}{\mathrm{d}x}+m\omega x\right)f\right]^* g\,\mathrm{d}x && \text{(1.2.85b)}\\ &= \int_{-\infty}^{+\infty}(a_\mp f)^* g\,\mathrm{d}x. && \text{(1.2.85c)}\end{aligned}$$

Where the second last equality comes from integration by parts with the boundary terms vanishing for well-behaved functions. □

Theorem 1.2.3.2 (Normalisation of harmonic potential wavefunctions)**.**

$$\psi_n = \frac{1}{\sqrt{n!}}(a_+)^n\psi_0. \tag{1.2.86}$$

Proof. We know that $a_\pm\psi_n$ is proportional to $\psi_{n\pm1}$, with all three of the wavefunctions normalised, so we have

$$a_+\psi_n = c_n\psi_{n+1},\quad a_-\psi_n = d_n\psi_{n-1}. \tag{1.2.87}$$

---

[1] Many sources prefer the use of v as the index here to distinguish between the vibrational quantum number and the principal quantum number of hydrogen atom. We will adopt this notation in later chapters.

From Lemma 1.2.3.1 we can write that

$$\int_{-\infty}^{+\infty} (a_\pm \psi_n)^* (a_\pm \psi_n)\,\mathrm{d}x = \int_{-\infty}^{+\infty} (a_\mp a_\pm \psi_n)^* \psi_n \,\mathrm{d}x. \tag{1.2.88}$$

We then invoke Equations 1.2.71 and 1.2.83 and write

$$H\psi_n = E_n \psi_n \tag{1.2.89a}$$

$$\hbar\omega \left(a_+ a_- + \frac{1}{2}\right) \psi_n = \hbar\omega \left(n + \frac{1}{2}\right) \psi_n \tag{1.2.89b}$$

$$a_+ a_- \psi_n = n\psi_n. \tag{1.2.89c}$$

The commutator relation further gives us that

$$a_- a_+ \psi_n = (n+1)\psi_n. \tag{1.2.90}$$

So it follows that

$$\int_{-\infty}^{+\infty} (a_+\psi_n)^*(a_+\psi_n)\,\mathrm{d}x = |c_n|^2 \int_{-\infty}^{+\infty} |\psi_{n+1}|^2 \,\mathrm{d}x = (n+1) \int_{-\infty}^{+\infty} |\psi_n|^2 \,\mathrm{d}x \tag{1.2.91a}$$

$$\int_{-\infty}^{+\infty} (a_-\psi_n)^*(a_-\psi_n)\,\mathrm{d}x = |d_n|^2 \int_{-\infty}^{+\infty} |\psi_{n-1}|^2 \,\mathrm{d}x = n \int_{-\infty}^{+\infty} |\psi_n|^2 \,\mathrm{d}x. \tag{1.2.91b}$$

Because we know that all three wavefunctions are normalised, it must follow that $|c_n|^2 = n+1$ and that $|d_n|^2 = n$, and hence we obtain the recurrence relation

$$a_+\psi_n = \sqrt{n+1}\psi_{n+1}, \;\; a_-\psi_n = \sqrt{n}\psi_{n-1}. \tag{1.2.92}$$

Finally,

$$\psi_n = \frac{1}{\sqrt{n!}}(a_+)^n \psi_0. \tag{1.2.93}$$

□

Theorem 1.2.3.3 (Orthonormality)**.** Stationary states of the harmonic oscillator are orthogonal:

$$\int_{-\infty}^{+\infty} \psi_m^* \psi_n \,\mathrm{d}x = \delta_{mn}. \tag{1.2.94}$$

Proof.

$$\begin{aligned}\int_{-\infty}^{+\infty}\psi_m^*(a_+a_-)\psi_n\,\mathrm{d}x &= n\int_{-\infty}^{+\infty}\psi_m^*\psi_n\,\mathrm{d}x \qquad (1.2.95\text{a})\\ &= \int_{-\infty}^{+\infty}(a_-\psi_m)^*(a_-\psi_n)\,\mathrm{d}x \qquad (1.2.95\text{b})\\ &= \int_{-\infty}^{+\infty}(a_+a_-\psi_m)^*\psi_n\,\mathrm{d}x \qquad (1.2.95\text{c})\\ &= m\int_{-\infty}^{+\infty}\psi_m^*\psi_n\,\mathrm{d}x, \qquad (1.2.95\text{d})\end{aligned}$$

where the first equality comes from Equation 1.2.89c, and the second and third from Equation 1.2.84. Unless $m = n$ the integral must vanish.

Orthonormality means that we can again use the Fourier series method to evaluate the coefficients of $\Psi(x, 0)$ when it is written as a linear combination of stationary states, and $|c_n|^2$ is again the probablity that a measurement of the energy would yield the value E_n. □

Worked example 1.2.3.1. Find the expectation value of the potential energy in the n-th state of the harmonic oscillator.

Solution:

We need to evaluate

$$\langle V\rangle = \left\langle \frac{1}{2}m\omega^2x^2\right\rangle = \frac{1}{2}m\omega^2\int_{-\infty}^{+\infty}\psi_n^*x^2\psi_n\,\mathrm{d}x. \qquad (1.2.96)$$

The ladder operators again comes in very handy as we can use them to evaluate integrals involving powers of x and p:

$$\begin{aligned}x &= \sqrt{\frac{h}{2m\omega}}(a_+ + a_-) \qquad (1.2.97\text{a})\\ p &= i\sqrt{\frac{hm\omega}{2}}(a_+ - a_-). \qquad (1.2.97\text{b})\end{aligned}$$

So

$$x^2 = \frac{h}{2m\omega}\left[(a_+)^2 + (a_+a_-) + (a_-a_+) + (a_-)^2\right], \qquad (1.2.98)$$

and so

$$\langle V\rangle = \frac{\hbar\omega}{4}\int_{-\infty}^{+\infty}\psi_n^*\left[(a_+)^2 + (a_+a_-) + (a_-a_+) + (a_-)^2\right]\psi_n\,\mathrm{d}x. \qquad (1.2.99)$$

The squares of raising and lowering operators will result in $\psi_{n\pm2}$ and as such will drop out due to the orthonormality condition. The middle two terms can be evaluated by Equations 1.2.90 and 1.2.89c to get

$$\langle V\rangle = \frac{\hbar\omega}{4}(n+n+1) = \frac{1}{2}\hbar\omega\left(n+\frac{1}{2}\right), \tag{1.2.100}$$

exactly half of $\langle E\rangle$.

Worked example 1.2.3.2. Construct $\psi_2(x)$.
Solution:
We just have two apply the raising operator twice:
We have

$$\psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar}. \tag{1.2.101}$$

So,

$$\psi_1 = \frac{1}{\sqrt{1!}}\frac{1}{\sqrt{2m\hbar\omega}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\left(-\hbar\frac{\mathrm{d}}{\mathrm{d}x}+m\omega x\right)e^{-m\omega x^2/2\hbar} \tag{1.2.102a}$$

$$= \frac{2m\omega}{\sqrt{2m\hbar\omega}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} xe^{-m\omega x^2/2\hbar} \tag{1.2.102b}$$

$$= \frac{\sqrt{2}}{\pi^{1/4}}\left(\frac{m\omega}{\hbar}\right)^{3/4} xe^{-m\omega x^2/2\hbar}. \tag{1.2.102c}$$

Applying the raising operator again (ugh) we get

$$\psi_2 = \frac{1}{\sqrt{2}}\frac{1}{\sqrt{2m\hbar\omega}}\left(\hbar\frac{\mathrm{d}}{\mathrm{d}x}+m\omega x\right)xe^{-m\omega x^2/2\hbar} \tag{1.2.103a}$$

$$= \left(\frac{m\omega}{4\pi\hbar}\right)^{\frac{1}{4}}\left(2\frac{m\omega}{\hbar}x^2-1\right)e^{-m\omega x^2/2\hbar}. \tag{1.2.103b}$$

Property 1.2.3.3 (Symmetry)**.** The stationary states of the harmonic oscillator is alternately even and odd, with ψ_0 even.

Property 1.2.3.4 (Substitutions)**.** We can introduce the following substitutions to simplify calculations. We will see that these substitutions also arise from the power series solution discussed below.

$$\xi \equiv \sqrt{\frac{m\omega}{\hbar}}x \tag{1.2.104a}$$

$$\alpha \equiv \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}. \tag{1.2.104b}$$

For example, ψ_0 now becomes

$$\psi_0 = \alpha e^{-\xi^2/2}. \tag{1.2.105}$$

Property 1.2.3.5 (Integrals containing exponentials)**.** We give some common integrals, all of the integrals involving x^n, where n is a positive integer, can be proven by induction:

$$\int_0^\infty x^n e^{-ax}\,\mathrm{d}x = \frac{n!}{a^{n+1}} \tag{1.2.106a}$$

$$\int_0^\infty e^{-ax^2}\,\mathrm{d}x = \left(\frac{\pi}{4a}\right)^{1/2} \tag{1.2.106b}$$

$$\int_0^\infty x^{2n} e^{-ax^2}\,\mathrm{d}x = \frac{\prod_{\text{odd } r, r=1}^{2n-1}(r)}{(2a)^n}\left(\frac{\pi}{4a}\right)^{1/2} \tag{1.2.106c}$$

$$\int_0^\infty x^{2n+1} e^{-ax^2}\,\mathrm{d}x = \frac{n!}{2a^{n+1}}. \tag{1.2.106d}$$

Worked example 1.2.3.3. Find $\langle x\rangle$, $\langle p\rangle$, $\langle x^2\rangle$, $\langle p^2\rangle$ and $\langle T\rangle$ for ψ_0 and ψ_1 by explicit integration.

Solution:

For ψ_0, an even function, we have

$$\langle x\rangle = \langle p\rangle = 0. \tag{1.2.107}$$

And

$$\langle x^2\rangle = \int_{-\infty}^{+\infty} \psi_0^* x^2 \psi_0\,\mathrm{d}x \tag{1.2.108a}$$

$$= \alpha^2\left(\frac{\hbar}{m\omega}\right)^{\frac{3}{2}}\int_{-\infty}^{+\infty} \xi^2 e^{-\xi^2}\,\mathrm{d}\xi \tag{1.2.108b}$$

$$= \alpha^2\left(\frac{\hbar}{m\omega}\right)^{\frac{3}{2}}\frac{\sqrt{\pi}}{2} \tag{1.2.108c}$$

$$= \frac{\hbar}{2m\omega}, \tag{1.2.108d}$$

where we used the standard result that $\int_{-\infty}^{+\infty}\xi^2 e^{-\xi^2}\,\mathrm{d}\xi = \sqrt{\pi}/2$. For momentum, we first note that the momentum operator under our substitutions is

$$p = -i\hbar\sqrt{\frac{m\omega}{\hbar}}\frac{\mathrm{d}}{\mathrm{d}\xi} \tag{1.2.109a}$$

$$p^2 = -m\omega\hbar\frac{\mathrm{d}^2}{\mathrm{d}\xi^2}. \tag{1.2.109b}$$

We therefore have

$$\langle p^2\rangle = -m\omega\hbar\alpha^2\sqrt{\frac{\hbar}{m\omega}}\int_{-\infty}^{+\infty} e^{-\xi^2/2}\frac{\mathrm{d}^2}{\mathrm{d}\xi^2}e^{-\xi^2/2}\,\mathrm{d}\xi \tag{1.2.110a}$$

$$= m\omega\hbar\pi^{-\frac{1}{2}}\int_{-\infty}^{+\infty}\left(\xi^2e^{-\xi^2} - e^{-\xi^2}\right)\mathrm{d}\xi \tag{1.2.110b}$$

$$= \frac{1}{2}m\omega\hbar. \tag{1.2.110c}$$

Therefore the uncertainty principle for ψ_0 is

$$\sigma_x\sigma_p = \frac{\hbar}{2}, \tag{1.2.111}$$

the smallest possible uncertainty. Now, for ψ_1, an odd function, we immediately know that $x\psi_1^2$ is odd. The derivative of an odd function is even, and as such $\psi_1 p\psi_1$ is odd, and so

$$\langle x\rangle = \langle p\rangle = 0. \tag{1.2.112}$$

Moving on to the squares, we have the wavefunction

$$\psi_1 = \sqrt{\frac{2\pi\hbar}{m\omega}}\alpha^3\xi e^{-\xi^2/2}. \tag{1.2.113}$$

So,

$$\langle x^2\rangle = 2\pi\left(\frac{\hbar}{m\omega}\right)^{5/2}\alpha^6\int_{-\infty}^{+\infty}\xi^4e^{-\xi^2}\,\mathrm{d}\xi \tag{1.2.114a}$$

$$= 2\pi\left(\frac{\hbar}{m\omega}\right)^{5/2}\alpha^6\frac{1\cdot 3}{2^2}\sqrt{\pi} \tag{1.2.114b}$$

$$= \frac{3}{2}\frac{\hbar}{m\omega}. \tag{1.2.114c}$$

And,

$$\langle p^2\rangle = -2\pi\hbar^2\left(\frac{\hbar}{m\omega}\right)^{3/2}\alpha^6\int_{-\infty}^{+\infty}(\xi^4 - 3\xi^2)e^{-\xi^2}\,\mathrm{d}\xi \tag{1.2.115a}$$

$$= \frac{3}{2}m\omega\hbar. \tag{1.2.115b}$$

And therefore the uncertainty principle is

$$\sigma_x\sigma_p = \frac{3\hbar}{2}. \tag{1.2.116}$$

Finally we note that

$$\langle T\rangle = \frac{\langle p^2\rangle}{2m} \tag{1.2.117a}$$
$$\langle V\rangle = \frac{k\langle x^2\rangle}{2} \tag{1.2.117b}$$

So we have

$$\langle T\rangle_0 = \langle V\rangle_0 = \frac{\hbar\omega}{4} \tag{1.2.118a}$$
$$\langle T\rangle_1 = \langle T\rangle_1 = \frac{3\hbar\omega}{4}, \tag{1.2.118b}$$

as expected.

Worked example 1.2.3.4. Now calulate the same quantities for ψ_n.
Solution:
We use the method developed in Worked example 1.2.3.1 (Equations 1.2.97a and 1.2.97b). As x and p only contains $a_\pm$ terms, by orthonormality conditions,

$$\langle x\rangle_n = \langle p\rangle_n = 0. \tag{1.2.119}$$

And

$$\langle x^2\rangle_n = \frac{\hbar}{2m\omega}\int_{-\infty}^{+\infty} \psi_n^* \left[(a_+a_-) + (a_-a_+)\right] \psi_n \,\mathrm{d}x \tag{1.2.120a}$$
$$= \frac{\hbar}{m\omega}\left(n+\frac{1}{2}\right), \tag{1.2.120b}$$

$$\langle p^2\rangle_n = \frac{-\hbar m\omega}{2}\int_{-\infty}^{+\infty} \psi_n^* \left[-(a_+a_-) - (a_-a_+)\right] \psi_n \,\mathrm{d}x \tag{1.2.121a}$$
$$= \hbar m\omega\left(n+\frac{1}{2}\right). \tag{1.2.121b}$$

The uncertainty principle is then

$$(\sigma_x)_n(\sigma_p)_n = \hbar\left(n+\frac{1}{2}\right). \tag{1.2.121c}$$

Energies are

$$\langle T\rangle = \langle V\rangle = \frac{1}{2}\hbar\omega\left(n+\frac{1}{2}\right). \tag{1.2.121d}$$

Another thing that ladder operator can do is to derive the selection rule for harmonic oscillators. This will be derived in Section 2.2.3.

1.2.3.2 Analytic Method

The Schrödinger equation for the harmonic oscillator is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+\frac{1}{2}m\omega^2x^2\psi=E\psi. \tag{1.2.122}$$

We now want to solve it directly via the power series method. We first non-dimensionalise the equation [24], because doing so will

- simplify the form of the equation greatly;
- reveal charateristic quantities of the equation;
- reduce the number of coefficients which may depend on other variables, and hence simplify the process of solving the equation numerically, if so required.

Non-dimensionalisation

To nondimensionalise ψ, the unknown to be solved, we proceed as follows:
First we note that, since

$$1=\int_{-\infty}^{+\infty}|\psi(x)|^2\,\mathrm{d}x, \tag{1.2.123}$$

we can conclude that $|\psi(x)|^2$ has the unit of inverse length, we must write it in terms of a dimensionless variable. To do this, we introduce substitution

$$\xi\equiv\frac{x}{x_c}, \tag{1.2.124}$$

where x_c is some characteristic length of the system. This gives us the dimensionless wavefunction:

$$\psi(x)=\psi(\xi x_c)=\psi(x(x_c))\equiv\widetilde{\psi}(\xi), \tag{1.2.125}$$

where $\widetilde{\psi}$ is the non-dimensionalised wavefunction that takes as its argument ξ and outputs the same value of ψ at corresponding x, hence the defined equivalence sign.
Now the Schrödinger equation becomes

$$\left(-\frac{\hbar^2}{2m}\frac{1}{x_c^2}\frac{\mathrm{d}^2}{\mathrm{d}\xi^2}+\frac{1}{2}m\omega^2x_c^2\xi^2\right)\widetilde{\psi}=E\widetilde{\psi} \tag{1.2.126a}$$

$$\Rightarrow\left(-\frac{\mathrm{d}^2}{\mathrm{d}\xi^2}+\frac{m^2\omega^2x_c^4}{\hbar^2}\xi^2\right)\widetilde{\psi}=\frac{2mx_c^2E}{\hbar^2}\widetilde{\psi}. \tag{1.2.126b}$$

To make the coeffients of ξ^2 dimensionless as well, we set

$$\frac{m^2\omega^2 x_c^4}{\hbar^2} = 1 \;\Rightarrow\; x_c = \sqrt{\frac{\hbar}{m\omega}}. \tag{1.2.127}$$

Non-dimensionalising E as well:

$$K \equiv \frac{2E}{\hbar\omega}, \tag{1.2.128}$$

we arrive at the fully dimensionless equation

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} = (\xi^2 - K)\psi, \tag{1.2.129}$$

where we have written $\widetilde{\psi}$ as ψ for simplicity of notation, but it is important that we remember to revert it back after solving the equation.

An almost identical alternative nondimensionalisation scheme uses $\hbar\omega$ (instead of $\hbar\omega/2$ of K, that's the only difference) as the natural unit of energy and arrives at

$$\left(-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}q^2} + \frac{1}{2}q^2\right)\psi = E\psi, \tag{1.2.130}$$

where q is the scaled position coordinate, and is identically defined as ξ.

Asymptotic analysis

At large $|\xi|$, ξ^2 dominates over the constant K, so in this regime

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} \approx \xi^2\psi, \tag{1.2.131}$$

which gives

$$\psi(\xi) \approx Ae^{-\xi^2/2} + Be^{\xi^2/2}. \tag{1.2.132}$$

To get a normalisable wavefunction, we must have that $B = 0$.

Frobenius method

We try the solution of the form

$$\psi(\xi) = h(\xi)e^{-\xi^2/2}. \tag{1.2.133}$$

Substituting Equation 1.2.133 into Equation 1.2.129, we first differentiate it twice:

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} = \left(\frac{\mathrm{d}^2 h}{\mathrm{d}\xi^2} - 2\xi\frac{\mathrm{d}h}{\mathrm{d}\xi} + (\xi^2 - 1)h\right)e^{-\xi^2/2}, \tag{1.2.134}$$

which enables us to write

$$\frac{\mathrm{d}^2h}{\mathrm{d}\xi^2} - 2\xi\frac{\mathrm{d}h}{\mathrm{d}\xi} + (K-1)h = 0. \tag{1.2.135}$$

Performing a series expansion in ξ,

$$h(\xi) = \sum_{j=0}^{\infty} a_j\xi^j, \tag{1.2.136}$$

plugging this into Equation 1.2.129 we get

$$0 = \sum_{j=0}^{\infty} j(j-1)a_j\xi^{j-2} - \sum_{j=0}^{\infty} 2ja_j\xi^j + \sum_{j=0}^{\infty}(K-1)a_j\xi^j \tag{1.2.137a}$$

$$= \sum_{j=0}^{\infty} \left[(j+2)(j+1)a_{j+2} - 2ja_j + (K-1)a_j\right]\xi^j \tag{1.2.137b}$$

$$\Rightarrow (j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j = 0. \tag{1.2.137c}$$

We get

$$a_{j+2} = \frac{2j+1-K}{(j+1)(j+2)}a_j, \tag{1.2.138}$$

a *recursion formula* with two arbitrary constants, a_0 and a_1, which are fixed by

$$a_0 = h(0) \tag{1.2.139a}$$

$$a_1 = h'(0). \tag{1.2.139b}$$

It is entirely equivalent to the Schrödinger equation we started with.
We write the complete solution as

$$h(\xi) = h_{\text{even}}(\xi) + h_{\text{odd}}(\xi), \tag{1.2.140}$$

where

$$h_{\text{even}}(\xi) \equiv a_0 + a_2\xi^2 + a_4\xi^4 + \cdots \tag{1.2.141}$$

and likewise for $h_{\text{odd}}(\xi)$.

Truncation

Up till now we have not checked if our solution is normalisable, *i.e.*, physical. We inspect the behaviour of recursion formula for suspicious behaviour at large j, when the recursion formula becomes

$$a_{j+2} \approx \frac{2}{j}a_j, \tag{1.2.142}$$

which means

$$a_j = \frac{2}{j-2} \cdot \frac{2}{j-4} \cdot \frac{2}{j-6} \cdots \approx \frac{C}{(j/2)!}. \tag{1.2.143}$$

This yields at large ξ where higher powers dominate

$$h(\xi) \approx C \sum \frac{1}{(j/2)!} \xi^j. \tag{1.2.144}$$

Relabelling, we get

$$h(\xi) \approx C \sum \frac{1}{j!} \xi^{2j} = Ce^{\xi^2}. \tag{1.2.145}$$

This is not good as

$$\psi(\xi) = h(\xi) e^{-\xi^2} \approx e^{\xi^2}, \tag{1.2.146}$$

and as such is not normalisable. However we note that we assumed large j to get here, so we should terminate the series before it can reach large j. This will truncate either the even or odd series and the other one must be *set* to 0 from the start. Say the highest $j \equiv n$ is now set, and we see from Equation 1.2.138 that

$$K = 2n + 1. \tag{1.2.147}$$

So energy must be

$$E = \left(n + \frac{1}{2}\right) \hbar\omega \tag{1.2.148}$$

for integer n's. For allowed values of K, the recursion formula in Equation 1.2.138 becomes

$$a_{j+2} = \frac{-2(n-j)}{(j+1)(j+2)} a_j. \tag{1.2.149}$$

There are a few features to this formula:

- For even n we must fix a definite non-zero value for a_0, for odd n, a_1.
- For even n a_1 must be fixed at 0 because the n value is unable to terminate the odd series, and vice versa for odd n.
- For each value of n the power series coefficients are different and are subject to normalisation.

Normalisation

The polynomials generated by this recursion formula are named **Hermite polynomials**, $H(\xi)$, and conventionally the a_i's are chosen such that the highest power of ξ is 2^n. We demonstrate the generation of a few such polynomials:

For $n = 0$ we must pick $a_1 = 0$ and so

$$H_0(\xi) = 1. \tag{1.2.150}$$

For $n = 1$ we set $a_0 = 0$ so

$$H_1(\xi) = 2\xi. \tag{1.2.151}$$

For $n = 2$, $a_1 = 0$, $a_2 = -2a_0$, therefore,

$$H_2(\xi) = 4\xi^2 - 2, \tag{1.2.152}$$

and so on. Now the wavefunction is

$$\psi_n(x) = A_n H_n(\xi) e^{-\xi^2/2}, \tag{1.2.153}$$

and we need to find out the normalisation constant. This process is by no means straightforward and very often omitted by textbooks. The following outline of proof is adapted from p.69-72 in [14], Section 2.7 of [21] and [9]:
The Hermite equation is obtained when $K = 2n + 1$ in Equation 1.2.135:

$$H_n'' - 2\xi H_n' + 2nH_n = 0. \tag{1.2.154}$$

We introduce the generating function for Hermite polynomials, $S(\xi, s)$:

$$S(\xi, s) = e^{\xi^2 - (s-\xi)^2} = e^{-s^2 + 2s\xi}. \tag{1.2.155}$$

We perform a Taylor series expansion on the second expression about $\xi = 0$:

$$F(\xi, s) \equiv \frac{S(\xi, s)}{e^{\xi^2}} = e^{-(s-\xi)^2} = e^{-(\xi-s)^2} \tag{1.2.156a}$$

$$= \sum_{n=0}^{\infty} (-1)^n \frac{s^n}{n!} (e^{-\xi^2})^{(n)}, \tag{1.2.156b}$$

and so we define

$$S(\xi, s) = \sum_{n=0}^{\infty} H_n \xi \frac{s^n}{n!}, \tag{1.2.157}$$

with

$$H_n(\xi) = \frac{(-1)^n}{n!} e^{\xi^2} \frac{\mathrm{d}^n}{\mathrm{d}\xi^n} (e^{-\xi^2}), \tag{1.2.158}$$

which is the **Rodrigue's formula** for Hermite polynomials, but we do not know that yet and will need to show that it satisfies the equation. We proceed as follows:

$$\frac{\partial S}{\partial \xi} = 2se^{-s^2+2s\xi} = \sum \frac{2s^{n+1}}{n!} H_n, \tag{1.2.159}$$

but it is also equal to, based on Equation 1.2.157

$$\sum \frac{s^n}{n!} H_n'. \tag{1.2.160}$$

We do the same wrt s:

$$\frac{\partial S}{\partial s} = (-2s+2\xi)e^{-s^2+2s\xi} = \sum \frac{(-2s+2\xi)s^n}{n!} H_n = \sum \frac{s^{n-1}}{(n-1)!} H_n, \tag{1.2.161}$$

where the last equality is from Equation 1.2.157. Equating equal powers of s in the sums of $\partial S/\partial \xi$ and $\partial S/\partial s$ respectively, we have

$$H_n' = 2nH_{n-1} \tag{1.2.162a}$$

$$H_{n+1} = 2\xi H_n - 2nH_{n-1}. \tag{1.2.162b}$$

From Equations 1.2.162a and 1.2.162b we can construct:

$$H_n' = 2\xi H_n - H_{n+1} \tag{1.2.163a}$$

$$H_n'' = 2H_n + 2\xi H_n' - H_{n+1}' \tag{1.2.163b}$$

$$H_n'' = 2H_n + 2\xi H_n' - 2(n+1)H_n \tag{1.2.163c}$$

$$H_n'' - 2\xi H_n' + 2nH_n = 0, \tag{1.2.163d}$$

the Hermite equation exactly. This shows that our definition in the forms of the generating function Equation 1.2.157 or the Rodrigue's formula Equation 1.2.158 do indeed correspond to Hermite polynomials.

We now pause and give a summary of the foregoing:

Definition 1.2.3.2 (Hermite polynomial)**.** The Hermite polynomial of degree n is defined either by the generating function

$$\begin{aligned} S(\xi, s) = S(\xi, s) = e^{\xi^2-(s-\xi)^2} &= e^{-s^2+2s\xi} \\ &\equiv \sum_{n=0}^{\infty} H_n \xi \frac{s^n}{n!}, \end{aligned} \tag{1.2.164}$$

which is not very useful, so the equivalent definition that is a result of a Taylor series expansion on the generating function is

$$H_n(\xi) = \frac{(-1)^n}{n!} e^{\xi^2} \frac{\mathrm{d}^n}{\mathrm{d}\xi^n}(e^{-\xi^2}). \tag{1.2.165}$$

Property 1.2.3.6 (Recurrence relation of Hermite polynomials)**.**

$$H_n' = 2nH_{n-1} \tag{1.2.166a}$$

$$H_{n+1} = 2\xi H_n - 2nH_{n-1}. \tag{1.2.166b}$$

Now, on to the normalisation constant. We have

$$1 = \int_{-\infty}^{+\infty} |\psi|^2 \, \mathrm{d}x = x_c|A_n|^2 \int_{-\infty}^{+\infty} H_n^2(\xi)e^{-\xi^2} \, \mathrm{d}\xi. \tag{1.2.167}$$

The generating function now comes in handy as we can write the integral containing two generating functions:

$$\int_{-\infty}^{+\infty} S(\xi,s)S(\xi,t)e^{-\xi^2} \, \mathrm{d}\xi = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \frac{s^n t^m}{n!m!} \int_{-\infty}^{+\infty} H_n(\xi)H_m(\xi)e^{-\xi^2} \, \mathrm{d}\xi, \tag{1.2.168}$$

where we can evaluate the LHS:

$$\int_{-\infty}^{+\infty} S(\xi,s)S(\xi,t)e^{-\xi^2} \, \mathrm{d}\xi \tag{1.2.169a}$$

$$= \int_{-\infty}^{+\infty} e^{-s^2+2s\xi}e^{-t^2+2t\xi}e^{-\xi^2} \, \mathrm{d}\xi \tag{1.2.169b}$$

$$= e^{-s^2-t^2} \int_{-\infty}^{+\infty} e^{-\xi^2+2\xi(s+t)} \, \mathrm{d}\xi \tag{1.2.169c}$$

$$= e^{-s^2-t^2+(s+t)^2} \int_{-\infty}^{+\infty} e^{-[\xi-(s+t)]^2} \, \mathrm{d}\xi \tag{1.2.169d}$$

$$= e^{2st}\pi^{\frac{1}{2}} \tag{1.2.169e}$$

$$= \pi^{\frac{1}{2}} \sum_{n=0}^{\infty} \frac{(2st)^n}{n!}. \tag{1.2.169f}$$

This implies

$$\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \frac{s^n t^m}{n!m!} \int_{-\infty}^{+\infty} H_n(\xi)H_m(\xi)e^{-\xi^2} \, \mathrm{d}\xi = \pi^{\frac{1}{2}} \sum_{k=0}^{\infty} \frac{(2st)^k}{k!}. \tag{1.2.169g}$$

Equating equal powers of s and t we get

$$\int_{-\infty}^{+\infty} H_n^2(\xi)e^{-\xi^2} \, \mathrm{d}\xi = 2^n n!\sqrt{\pi} \tag{1.2.170a}$$

$$\int_{-\infty}^{+\infty} H_n(\xi)H_m(\xi)e^{-\xi^2} \, \mathrm{d}\xi = 0. \tag{1.2.170b}$$

Beautiful. Now Equation 1.2.170a tells us we should choose, within an arbitrary complex phase factor, the normalisation constant to be

$$A_n = \left(\frac{1}{x_c \pi^{\frac{1}{2}} 2^n n!}\right)^{\frac{1}{2}} = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}}. \tag{1.2.171}$$

Finally, reverting back to dimensionful $\psi(x)$, we have the complete stationary state wavefunction:

$$\psi(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) e^{-m\omega x^2/2\hbar}. \tag{1.2.172}$$

That wasn't too bad.

1.2.3.3 The Morse potential

The morse potential is a more exact potential than the Hookeian potential, and it includes explicitly the effect of bond breaking: it approaches an asymptotic value, also known as the dissociation energy, D_e. As a result it admits scattering states.

Definition 1.2.3.3 (The Morse potential)**.** The potential is given by

$$V_M(r) = D_e\left[1 - e^{-\beta(r-r_e)}\right]^2, \tag{1.2.173}$$

where r_e is the equilibirum bond length, and D_e is the dissociation energy, **not** bond strength as we will see soon.

Now if we expand the potential about $r = r_e$, to simply we rewrite

$$t \equiv \beta(r - r_e) \;\Rightarrow\; V_M = D_e(1 - e^{-t})^2. \tag{1.2.174}$$

So we have

$$\begin{aligned} V_M(r) &= D_e\left[1 - \left(1 - t + \frac{1}{2}t^2 - \frac{1}{6}t^3 + \cdots\right)\right]^2 \\ &= D_e\left(t - \frac{1}{2}t^2 + \frac{1}{6}t^3 - \cdots\right)^2 \\ &= D_e\left(t^2 - t^3 + \frac{7}{12}t^2 - \cdots\right) \\ &= D_e\left[\beta^2(r - r_e)^2 - \beta^3(r - r_e)^3 + \cdots\right]. \end{aligned} \tag{1.2.175}$$

So we can see from the quadratic term that, k_e, the force constant near equilibrium, *i.e.*, at small r about r_e where the quadratic term dominates, is given by

$$k_e = 2\beta^2 D_e. \tag{1.2.176}$$

Or it's to say that, β, the heretofore unspecified constant is

$$\beta = \sqrt{\frac{k_e}{2D_e}} \tag{1.2.177}$$

The Schrödinger equation is rather messy to solve:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + V(r)\right]\psi_n = E_n\psi_n \tag{1.2.178}$$

we can introduce some new variables to simplify the equation:

$$x \equiv ar,\ x_e \equiv ar_e,\ \lambda \equiv \frac{\sqrt{2mD_e}}{a\hbar},\ \epsilon_n \equiv \frac{2m}{a^2\hbar^2}E_n. \tag{1.2.179}$$

The Schrödinger equation now becomes

$$\left[-\frac{\partial^2}{\partial x^2} + V(x)\right]\psi_n(x) = \epsilon_n\psi_n(x), \tag{1.2.180}$$

where

$$V(x) = \lambda^2\left[e^{-2(x-x_e)} - 2e^{-(x-x_e)}\right]. \tag{1.2.181}$$

todo: solve this or at least outline steps, priority:low.

An important result is very neat however: the eigenvalues, *i.e.*, allowed energies turn out to be

Property 1.2.3.7 (Eigenvalues of Morse potential)**.**

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega - \left(n + \frac{1}{2}\right)^2\hbar\omega x_e, \tag{1.2.182}$$

where $\omega = \sqrt{k_e/m}$ and

$$x_e = \frac{\hbar\beta^2}{2m\omega} = \frac{\hbar\omega}{4D_e} \tag{1.2.183}$$

is the **anharmonicity constant**.

Property 1.2.3.8 (Bond energy)**.** The bond energy is the *difference* between the dissociation energy and the ground state energy:

$$E_B = D_e - E_0 = D_e - \frac{1}{2}\hbar\omega + \frac{1}{4}\hbar\omega x_e. \tag{1.2.184}$$

1.2.4 The free particle

This subsection deals with the case where

$$V(x) = 0. \tag{1.2.185}$$

Superficially this should be the simplest case of all, as the classical analogue is just constant velocity. However the case is not quite as straightforward as we shall see.
The Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi, \tag{1.2.186}$$

or

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -k^2\psi, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}. \tag{1.2.187}$$

We get the complex solution

$$\psi(x) = Ae^{ikx} + Be^{-ikx}. \tag{1.2.188}$$

Unlike the infinite square well, there are *no boundary conditions* - the free particle can carry any energy. The time-dependent solution is just

$$\Psi(x,t) = Ae^{ik(x-\hbar kt/2m)} + Be^{-ik(x+\hbar kt/2m)}, \tag{1.2.189}$$

which reminds us to write

$$\Psi(x,t) = \Psi(x \pm vt), \tag{1.2.190}$$

which describes a wave of fixed profile. We might as well write

$$\Psi_k(x,t) = Ae^{i(kx-\hbar k^2 t/2m)}, \quad \text{with } k \equiv \pm\frac{\sqrt{2mE}}{\hbar} \tag{1.2.191}$$

. The 'stationary states' have wavelengths

$$\lambda = \frac{2\pi}{|k|}, \tag{1.2.192}$$

and by de Broglie formula they carry momentum

$$p = \hbar k, \tag{1.2.193}$$

and velocity

$$v_q = \frac{\hbar|k|}{2m} = \sqrt{\frac{E}{2m}}. \tag{1.2.194}$$

However, classically, if we have energy E,

$$v_c = \sqrt{\frac{2E}{m}} = 2v_q. \tag{1.2.195}$$

Not too good. But something way worse is here: these 'stationary states' are not normalisable:

$$\int_{-\infty}^{+\infty} \Psi_k^* \Psi_k \, \mathrm{d}x = |A|^2 \int_{-\infty}^{+\infty} \mathrm{d}x = |A|^2(\infty). \tag{1.2.196}$$

This means that there is no such thing as a free particle with a definite energy.

But wait, the complete time-dependent solution can be written, with a continuous variable coefficient $\phi(k)$:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{i(kx - \hbar k^2 t/2m)} \, \mathrm{d}k, \tag{1.2.197}$$

where the factor $1/\sqrt{2\pi}$ is factored out of $\phi(k)$ for convenience. This solution can be normalisable for appropriate choice of $\phi(k)$, but it necessarily carries a range of k's, and hence a range of energies and speeds. We term it a **wave packet**.

Returning to the generic quantum problem where we are given $\Psi(x,0)$ and we need to find $\Psi(x,t)$, and we do so by determining the coefficient function $\phi(k)$:

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{ikx} \, \mathrm{d}k, \tag{1.2.198}$$

where the integrand is just the continuous version of the linear combination of stationary states, which is e^{ikx} in this problem.

But how to determine $\phi(k)$? We introduce

Theorem 1.2.4.1 (Plancherel's theorem)**.** Plancherel's theorem states that

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(k) e^{ikx} \, \mathrm{d}k \;\leftrightarrow\; F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) e^{-ikx} \, \mathrm{d}x. \tag{1.2.199}$$

$F(k)$ is called the **Fourier transform** of $f(x)$ and $f(x)$ is the **inverse Fourier transform** of $F(k)$, provided that the integrals exist.

Proof. Dirichlet's theorem states that for any well behaved function $f(x)$ on the interval $[-a, +a]$,

$$f(x) = \sum_{n=0}^{\infty} [a_n \sin(n\pi x/a) + b_n \cos(n\pi x/a)]. \tag{1.2.200}$$

This can be written as a complex series

$$f(x) = \sum_{n=-\infty}^{\infty} c_n e^{in\pi x/a}, \tag{1.2.201}$$

expanding we have

$$\begin{aligned} f(x) &= \sum_{n=-\infty}^{\infty} c_n e^{in\pi x/a} && (1.2.202a) \\ &= c_0 + \sum_{n=1}^{\infty} (c_n + c_{-n}) \cos(n\pi x/a) + \sum_{n=1}^{\infty} i(c_n - c_{-n}) \sin(n\pi x/a) && (1.2.202b) \\ &\equiv \sum_{n=0}^{\infty} [a_n \sin(n\pi x/a) + b_n \cos(n\pi x/a)]. && (1.2.202c) \end{aligned}$$

So we have

$$\begin{aligned} c_n &= \frac{1}{2}(b_n - ia_n) && (1.2.203a) \\ c_{-n} &= \frac{1}{2}(b_n + ia_n). && (1.2.203b) \end{aligned}$$

We can obtain the coefficients by

$$c_n = \frac{1}{2a} \int_{-a}^{+a} f(x) e^{-in\pi x/a} \, \mathrm{d}x. \tag{1.2.204}$$

This is due to the orthogonality of $e^{-in\pi x/a}$:

$$\int_{-a}^{+a} e^{-in\pi x/a} e^{-im\pi x/a} \, \mathrm{d}x = \frac{\delta_{nm}}{2a}. \tag{1.2.205}$$

We now introduce new variable

$$k \equiv \frac{n\pi}{a} \tag{1.2.206}$$

so

$$c_n(k) = \frac{1}{2a} \int_{-a}^{+a} f(x) e^{-ikx} \, \mathrm{d}x. \tag{1.2.207}$$

We also introduce

$$F(k) \equiv \sqrt{\frac{2}{\pi}} a c_n(k), \tag{1.2.208}$$

such that

$$f(x) = \sum_{n=-\infty}^{\infty} c_n e^{in\pi x/a} \tag{1.2.209a}$$

$$= \sum_{n=-\infty}^{\infty} c_n \Delta n e^{ikx} \tag{1.2.209b}$$

$$= \sum_{k=-\infty}^{\infty} \frac{F(k)}{a}\sqrt{\frac{\pi}{2}}\frac{a\Delta k}{\pi} e^{ikx} \tag{1.2.209c}$$

$$= \frac{1}{\sqrt{2\pi}} \sum_{k=-\infty}^{\infty} F(k) e^{ikx} \Delta k, \tag{1.2.209d}$$

and

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-a}^{+a} f(x) e^{-ikx} \, \mathrm{d}x. \tag{1.2.210}$$

In the limit that $a \to \infty$, $k \to 0$, we obtain

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(k) e^{ikx} \, \mathrm{d}k \tag{1.2.211a}$$

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) e^{-ikx} \, \mathrm{d}x. \tag{1.2.211b}$$

□

With Plancherel's theorem we can conclude that

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \Psi(x,0) e^{-ikx} \, \mathrm{d}x, \tag{1.2.212}$$

and we now see why a factor of $1/\sqrt{2\pi}$ was taken out.

Worked example 1.2.4.1. A free particle, which is initially localised in the range $-a < x < a$, is released at time $t = 0$:

$$\Psi(x,0) = \begin{cases} A, & \text{if } -a < x < a, \\ 0, & \text{otherwise.} \end{cases} \tag{1.2.213}$$

Find $\Psi(x,t)$.

Solution:

First we normalsied $\Psi(x,0)$ to get

$$\Psi(x,0) = \frac{1}{\sqrt{2a}}. \tag{1.2.214}$$

And then we calculate $\phi(k)$:

$$\begin{aligned}\phi(k) &= \frac{1}{\sqrt{2a}}\frac{1}{\sqrt{2\pi}}\int_{-a}^{+a} e^{-ikx}\,\mathrm{d}x && (1.2.215a)\\ &= \frac{1}{2\sqrt{\pi a}}\left[\frac{e^{-ikx}}{-ik}\right]_{-a}^{+a} && (1.2.215b)\\ &= \frac{1}{k\sqrt{\pi a}}\left(\frac{e^{ika}-e^{-ika}}{2i}\right) && (1.2.215c)\\ &= \frac{1}{\sqrt{\pi a}}\frac{\sin(ka)}{k} && (1.2.215d)\\ &= \sqrt{\frac{a}{\pi}}\mathrm{sinc}(ka). && (1.2.215e)\end{aligned}$$

Therefore we get the time-dependent solution

$$\begin{aligned}\Psi(x,t) &= \frac{1}{\pi\sqrt{2a}}\int_{-\infty}^{+\infty}\frac{\sin(ka)}{k}e^{i(kx-\hbar k^2t/2m)}\,\mathrm{d}k\\ &= \frac{\sqrt{a/2}}{\pi}\int_{-\infty}^{+\infty}\mathrm{sinc}(ka)e^{i(kx-\hbar k^2t/2m)}\,\mathrm{d}k.\end{aligned} \qquad (1.2.216)$$

This integral can't be generally solved except for a few cases. However we can observe some limiting behaviour:
At small a: The starting wavefunction is a localised spike, in fact, the Dirac delta function. Under small angle approximation, $\mathrm{sinc}(\theta) = 1$

$$\phi(k) = \sqrt{\frac{a}{\pi}}. \qquad (1.2.217)$$

It has no k dependence and is flat for all k. This means for an infinetissimally localised particle, the spread of momentum / velocity is infinite upon release.
At large a: The starting wavefunction is now a flat distribution and $\phi(k)$ is just a very sharp sinc function. This is exactly the reverse situation as above and illustrates again the uncertainty principle.

We now return to the problem of the quantum velocity being half the classical velocity. We introduce the following theorem

Theorem 1.2.4.2 (Group velocity)**.** For a wave packet made of waves of many different frequencies, the group velocity, describing how fast the interference pattern, *i.e.*, *modulation* or *envelope* of the wave, moves, is given by

$$v_g = \frac{\partial \omega}{\partial k}, \tag{1.2.218}$$

where $\omega(k, \cdots)$ is called the **dispersion relation**.

Proof. We need to determine the group velocity of a wave packet of the form

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{i(kx-\omega t)} \, \mathrm{d}k. \tag{1.2.219}$$

In this specific case,

$$\omega = \frac{\hbar k^2}{2m}, \tag{1.2.220}$$

but this proof is generally applicable.
Let's assume that $\phi(k)$ is narrowly peaked about k_0, for it to have a narrow spread of speeds, *i.e.*, almost monochromatic, such that the shape of the packet does not change too rapidly. Since the integrand is negligible except around k_0, we Taylor expand $\omega(k)$ about that point:

$$\omega(k) = \omega_0 + \omega_0'(k - k_0) + O(k^2). \tag{1.2.221}$$

We perform a change of variable

$$s \equiv k - k_0 \tag{1.2.222}$$

to give

$$\Psi(x,t) \approx \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k_0 + s) e^{i[(k_0+s)x + (\omega_0 + \omega_0' s)t]} \, \mathrm{d}s \tag{1.2.223a}$$

$$= \frac{1}{\sqrt{2\pi}} e^{i(-\omega_0 t + k_0 \omega_0' t)} \int_{-\infty}^{+\infty} \phi(k_0 + s) e^{i(k_0+s)(x - \omega_0' t)} \, \mathrm{d}s. \tag{1.2.223b}$$

Nothing fancy there, just pure algebra. We can also see that when $t = 0$, we have

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k_0 + s) e^{i(k_0+s)x} \, \mathrm{d}s. \tag{1.2.224}$$

The integrands in Equations 1.2.224 and 1.2.223b are the same except for the shift from x to $(x - \omega_0' t)$, so

$$\Psi(x,t) \approx e^{i(-\omega_0 t + k_0 \omega_0' t)} \Psi\big((x - \omega_0' t), 0\big). \tag{1.2.225}$$

The complex factor in front is just a phase factor and will not affect $|\Psi|^2$, and from the form of the function we see clearly that the wave packet moves at speed ω_0', which is to say

$$v_g = \frac{\partial \omega}{\partial k}. \tag{1.2.226}$$

This is in contrast with the phase velocity, of a specific component wave, given as

$$v_p = \frac{\omega}{k}. \tag{1.2.227}$$

□

1.2.5 The delta-function potential

1.2.5.1 Bound states and scattering states

Definition 1.2.5.1 (Bound and scattering states)**.** In quantum mechanics, all the potentials we deal with go to 0 at $|\infty|$, the distinction between bound and scattering states is

$$\begin{cases} E < 0 \;\Rightarrow & \text{bound state,} \\ E > 0 \;\Rightarrow & \text{scattering state.} \end{cases} \tag{1.2.228}$$

Property 1.2.5.1. Bound states give rise to normalisable and quantised solutions whereas scattering states give unphysical and non-normalisable solutions.

1.2.5.2 The Dirac delta function

From this section onwards we explore potentials that give rise to both bound and scattering states.

The **Dirac delta function** is defined as

Definition 1.2.5.2 (Dirac delta fucntion)**.**

$$\delta(x) \equiv \begin{cases} 0, & \text{if } x \neq 0 \\ \infty, & \text{if } x = 0 \end{cases} \quad \text{with} \quad \int_{-\infty}^{+\infty} \delta(x)\, \mathrm{d}x = 1. \tag{1.2.229}$$

Property 1.2.5.2 (Extracting value under integral)**.** We can write

$$f(x)\delta(x-a) = f(a)\delta(x-a), \tag{1.2.230}$$

so under integral,

$$\int_{-\infty}^{+\infty} f(x)\delta(x-a)\,\mathrm{d}x = f(a)\int_{-\infty}^{+\infty} \delta(x-a)\,\mathrm{d}x = f(a). \tag{1.2.231}$$

The following properties we prove will need this equality for two equivalent expressions D_1 and D_2 involving delta functions:

$$\int_{-\infty}^{+\infty} f(x)D_1(x)\,\mathrm{d}x = \int_{-\infty}^{+\infty} f(x)D_2(x)\,\mathrm{d}x. \tag{1.2.232}$$

Property 1.2.5.3 ('Wider' deltas)**.**

$$\delta(cx) = \frac{1}{|c|}\delta(x). \tag{1.2.233}$$

Proof. We make the substitution

$$\alpha \equiv cx. \tag{1.2.234}$$

So we have

$$\int_{-\infty}^{+\infty} f(x)\delta(cx)\,\mathrm{d}x = \frac{1}{c}\int_{-\infty}^{+\infty} f(\alpha/c)\delta(\alpha)\,\mathrm{d}\alpha = \frac{1}{c}f(x) = \int_{-\infty}^{+\infty} f(x)\frac{1}{c}\delta(x)\,\mathrm{d}x, \tag{1.2.235}$$

for $c > 0$, and for $c < 0$ we have

$$\int_{-\infty}^{+\infty} f(x)\delta(cx)\,\mathrm{d}x = \frac{1}{c}\int_{+\infty}^{-\infty} f(\alpha/c)\delta(\alpha)\,\mathrm{d}\alpha = -\frac{1}{c}f(x) = \int_{-\infty}^{+\infty} f(x)\frac{-1}{c}\delta(x)\,\mathrm{d}x, \tag{1.2.236}$$

so we have by way of Equation 1.2.232 that

$$\delta(cx) = \frac{1}{|c|}\delta(x). \tag{1.2.237}$$

This is seemingly confusing but we have to realised that the 'scaled' delta gives a smaller but wider peak. □

Property 1.2.5.4 (Derivative of Heaviside)**.** The derivative of the Heaviside step function is the Dirac delta function.

Proof.

$$\int_{-\infty}^{+\infty} f(x)\frac{\mathrm{d}H(x)}{\mathrm{d}x}\,\mathrm{d}x = f(0)\int_{-\infty}^{+\infty}\frac{\mathrm{d}H(x)}{\mathrm{d}x}\,\mathrm{d}x = f(0)(1-0) = f(0), \tag{1.2.238}$$

which is the same behaviour as $\delta(x)$. □

Property 1.2.5.5 (Fourier transform)**.** This is not a rigorous mathematical result but only used for expediency in quantum mechanics:

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{ik(x'-x)}\,\mathrm{d}k = \delta(x'-x). \tag{1.2.239}$$

Proof. Because we have that

$$\int_{-\infty}^{+\infty} \delta(x-x')f(x')\,\mathrm{d}x' = f(x), \tag{1.2.240}$$

and from Theorem 1.2.4.1 we can also write

$$f(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} e^{-ikx}f(x)\,\mathrm{d}x \tag{1.2.241a}$$

$$f(x') = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} e^{ikx'}f(k)\,\mathrm{d}x, \tag{1.2.241b}$$

substituting the top equation into the bottom one we have

$$f(x') = \int_{-\infty}^{+\infty}\left(\frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{ik(x'-x)}\,\mathrm{d}k\right)f(k)\,\mathrm{d}x. \tag{1.2.242}$$

So we can identify

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{ik(x'-x)}\,\mathrm{d}k = \delta(x'-x). \tag{1.2.243}$$

□

1.2.5.3 Delta potential: bound states

Let's consider a potential of the form

$$V(x) = -\alpha\delta(x), \tag{1.2.244}$$

where $\alpha > 0$. The Schrödinger equation now reads

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - \alpha\delta(x)\psi = E\psi. \tag{1.2.245}$$

We can see soon that this potential admits both bound and scattering states, *i.e.*, the energy can be both positive and negative in different parts of the solution.
We look for bound states first. In the region $x < 0$, $V(x) = 0$, so

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \kappa^2\psi, \text{ where } k \equiv \frac{\sqrt{-2mE}}{\hbar}, \tag{1.2.246}$$

where, as we are looking for bound states, $E < 0$. The solution is

$$\psi(x) = Ae^{-\kappa x} + Be^{\kappa x},\ (x < 0) \tag{1.2.247}$$

and we must have that $A = 0$ as the term will blow up as $x \to -\infty$ as we are concerned with the negative part of the potential. Now, for the positive part we similarly have

$$\psi(x) = Fe^{-\kappa x}.\ (x < 0) \tag{1.2.248}$$

Now we just need to use the boundary conditions to 'stitch' the two solutions together. Continuity of wavefunction requires that

$$F = B. \tag{1.2.249}$$

So we get

$$\psi(x) = \begin{cases} Be^{\kappa x}, & (x \leq 0) \\ Be^{-\kappa x}. & (x \geq 0) \end{cases} \tag{1.2.250}$$

However, as the potential is infinite at $x = 0$ the continuity of first derivative does not need to be fulfilled. But the delta function has not come into the picture at all so far, and we need it to determine the discontinuity in the derivative. We do so by integrating the Schrödinger equation from $-\epsilon$ to $+\epsilon$ and take the limit as $\epsilon \to 0$:

$$-\frac{\hbar^2}{2m}\int_{-\epsilon}^{+\epsilon}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}\,\mathrm{d}x + \int_{-\epsilon}^{+\epsilon} V(x)\psi(x)\,\mathrm{d}x = E\int_{-\epsilon}^{+\epsilon}\psi(x)\,\mathrm{d}x \tag{1.2.251a}$$

$$\frac{2m}{\hbar^2}\lim_{\epsilon\to 0}\int_{-\epsilon}^{+\epsilon} V(x)\psi(x)\,\mathrm{d}x = \lim_{\epsilon\to 0}\left(\left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{+\epsilon} - \left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{-\epsilon}\right) \equiv \Delta\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right). \tag{1.2.251b}$$

This gives

$$\Delta\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) = -\frac{2m\alpha}{\hbar^2}\psi(0), \tag{1.2.252}$$

and for the present case we can readily evaluate $\Delta\left(\mathrm{d}\psi/\mathrm{d}x\right) = -2B\kappa$, so

$$\kappa = \frac{m\alpha}{\hbar^2}, \tag{1.2.253}$$

so the allowed energy turns out to be

$$E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{m\alpha^2}{2\hbar^2}, \tag{1.2.254}$$

the *only* allowed energy. We then normalise the wavefunction to get

$$B = \sqrt{\kappa} = \frac{\sqrt{m\alpha}}{\hbar}. \tag{1.2.255}$$

So we get the bound state wavefunction,

$$\psi(x) = \frac{\sqrt{m\alpha}}{\hbar}e^{-m\alpha|x|/\hbar^2};\;\; E = \frac{-m\alpha^2}{2\hbar^2}. \tag{1.2.256}$$

1.2.5.4 Delta potential: scattering states

For scattering states we solve, for $x < 0$,

$$\frac{\mathrm{d}\psi}{\mathrm{d}x} = -k^2\psi, \text{ where } k \equiv \frac{\sqrt{2mE}}{\hbar}. \tag{1.2.257}$$

The general solution is

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \tag{1.2.258}$$

similarly for $x > 0$,

$$\psi(x) = Fe^{ikx} + Ge^{-ikx}. \tag{1.2.259}$$

Continuity at $x = 0$ requires

$$F + G = A + B. \tag{1.2.260}$$

We also evalute $\Delta\left(\mathrm{d}\psi/\mathrm{d}x\right)$ at $x = 0$:

$$\Delta\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) = ik(F - G - A + B). \tag{1.2.261}$$

We also have that $\psi(0) = (A + B)$, and according to Equation 1.2.252,

$$ik(F - G - A + B) = -\frac{2m\alpha}{\hbar^2}(A + B) \tag{1.2.262a}$$

$$F - G = A(1 + 2i\beta) - B(1 - 2i\beta), \text{ where } \beta \equiv \frac{m\alpha}{\hbar^2 k}. \tag{1.2.262b}$$

A and F is proportional to the amplitude of wave travelling to the right before and after the potential well (incident and transmitted), B amd G for waves travelling to the left (reflected and right-incident). Now, restricting to a beam of particles coming from the left, we can have

$$G = 0. \tag{1.2.263}$$

Now the system of equations to solve is

$$A + B = F \tag{1.2.264a}$$

$$A(1 + 2i\beta) - B(1 - 2i\beta) = F. \tag{1.2.264b}$$

Solving, we have

$$B = \frac{i\beta}{1 - i\beta}A, \;\; F = \frac{1}{1 - i\beta}A. \tag{1.2.264c}$$

The **reflection coefficient** is the relative probability that an incident particle *in a particle beam* will be reflected back:

$$R \equiv \frac{|\Psi_B|^2}{|\Psi_A|^2} = \frac{|A|^2}{|B|^2} = \frac{\beta^2}{1 + \beta^2}. \tag{1.2.265}$$

And the **transmission coefficient** is

$$T \equiv \frac{|F|^2}{|A|^2} = \frac{1}{1 + \beta^2}. \tag{1.2.266}$$

We note that R and T are functions of β^2, where

$$\beta = \frac{m\alpha}{\hbar^2 k} = \frac{m\alpha^2}{2\hbar^2 E}. \tag{1.2.267}$$

However, as the free particle problem, the 'stationary states' are not normalisable, and must be realised in a wave packet with a range of energies. So the R and T should be treated as approximations near E.

Now notice how R and T are dependent on α^2, so if the 'well' is now inverted to give a *barrier*, the particle beam is equally likely to tunnel through. However the bound state is now impossible due to Theorem 1.2.1.5.

1.3 FORMALISM

1.3.1 Hilbert space

Definition 1.3.1.1 (Hilbert space)**.** A Hilbert space is a vector space consisting all **square-integrable functions** $f(x)$ on a specified interval such that

$$\int_a^b |f(x)|^2 \,\mathrm{d}x < \infty. \tag{1.3.1}$$

In quantum mechanics we usually use the limits $[-\infty, +\infty]$.

Definition 1.3.1.2 (Inner product)**.** The inner product of two functions $f(x)$ and $g(x)$ is defined

$$\langle f|g\rangle \equiv \int_a^b f^* g \,\mathrm{d}x. \tag{1.3.2}$$

Theorem 1.3.1.1 (Schwarz inequality)**.**

$$\left|\int_a^b f^* g \,\mathrm{d}x\right| \le \sqrt{\int_a^b |f|^2 \,\mathrm{d}x \int_a^b |g|^2 \,\mathrm{d}x}. \tag{1.3.3}$$

Proof. Consider the integral

$$I(a) = \int_a^b (af^* + g)(af + g^*) \,\mathrm{d}x, \tag{1.3.4}$$

with a real. Expanding out we have

$$\begin{aligned} I(a) &= \int_a^b a^2|f|^2 + |g|^2 + a(f^*g + fg^*) \,\mathrm{d}x && \text{(1.3.5a)} \\ &= a^2\langle f|f\rangle + \langle g|g\rangle + a(\langle f|g\rangle + \langle g|f\rangle) \,\mathrm{d}x && \text{(1.3.5b)} \\ &= a^2\langle f|f\rangle + \langle g|g\rangle + a(\langle f|g\rangle + \langle f|g\rangle^*) \,\mathrm{d}x && \text{(1.3.5c)} \end{aligned}$$

Because $I(a)$ is necessarily non-negative, we calculate the discriminant wrt a,

$$4|\langle f|g\rangle|^2 - 4\langle f|f\rangle\langle g|g\rangle \ge 0, \tag{1.3.6}$$

which gives the inequality we want.

We have used the fact that

$$\langle g|f\rangle = \langle f|g\rangle^*, \tag{1.3.7}$$

and that

$$\langle f|g\rangle^* \langle f|g\rangle^* = |\langle f|g\rangle|^2. \tag{1.3.8}$$

□

Definition 1.3.1.3 (Orthonormality)**.** A function is said to be normalised if

$$\langle f|f\rangle = 1. \tag{1.3.9}$$

Two functions are orthonormal if

$$\langle f_m|f_n\rangle = \delta_{mn}. \tag{1.3.10}$$

Definition 1.3.1.4 (Completeness)**.** A **set** of functions is complete if any other function in Hilbert space can be expressed as a linear combination of them:

$$f(x) = \sum_{n=1}^{\infty} c_n f_n(x), \tag{1.3.11}$$

if the f_n's are orthonormal, the coefficients are given by

$$c_n = \langle f_n|f\rangle. \tag{1.3.12}$$

1.3.2 Observables

1.3.2.1 Hermitian operators

An observable quantity **must be real**, and so must be the average of many measurements. For a an observable $Q(x,p)$ we can write

$$\langle Q\rangle = \int_{-\infty}^{+\infty} \Psi^* Q \Psi \,\mathrm{d}x = \langle \Psi|Q\Psi\rangle. \tag{1.3.13}$$

The requirement that $\langle Q\rangle$ is real says that

$$\langle Q\rangle = \langle Q\rangle^* \tag{1.3.14a}$$

$$\langle \Psi|Q\Psi\rangle = \langle Q\Psi|\Psi\rangle, \tag{1.3.14b}$$

that is, Q must be a **Hermitian** operator. (Recall Lemma 1.2.3.1), we have proven the theorem

Theorem 1.3.2.1 (Observables correspond to hermitian operators)**.** All physical observables correspond to hermitian operators.

Lemma 1.3.2.1 (Equivalent definition of Hermiticity)**.** A Hermitian operator is equivalently defined by

$$\langle f|Qg\rangle = \langle Qf|g\rangle \tag{1.3.15}$$

for all $f(x)$ and all $g(x)$.

Proof. Let

$$h \equiv f + g, \tag{1.3.16}$$

noting that linear combinations of functions in Hilbert space give functions in Hilber space, we have

$$\langle h|Qh\rangle = \langle Qh|h\rangle \tag{1.3.17a}$$

$$\langle (f+g)|(Qf+Qg)\rangle = \langle (Qf+Qg)|(f+g)\rangle \tag{1.3.17b}$$

$$\langle f|Qf\rangle + \langle f|Qg\rangle + \langle g|Qf\rangle + \langle g|Qg\rangle = \langle Qf|f\rangle + \langle Qf|g\rangle + \langle Qg|f\rangle + \langle Qg|g\rangle \tag{1.3.17c}$$

$$\langle f|Qg\rangle + \langle g|Qf\rangle = \langle Qf|g\rangle + \langle Qg|f\rangle. \tag{1.3.17d}$$

Now setting

$$h \equiv f + ig, \tag{1.3.18}$$

we can similarly write

$$\langle h|Qh\rangle = \langle Qh|h\rangle \tag{1.3.19a}$$

$$\langle (f+ig)|(Qf+iQg)\rangle = \langle (Qf+iQg)|(f+ig)\rangle \tag{1.3.19b}$$

$$\langle f|Qf\rangle + i\langle f|Qg\rangle - i\langle g|Qf\rangle + (-i)i\langle g|Qg\rangle = \langle Qf|f\rangle + i\langle Qf|g\rangle - i\langle Qg|f\rangle + (-i)i\langle Qg|g\rangle \tag{1.3.19c}$$

$$\langle f|Qg\rangle - \langle g|Qf\rangle = \langle Qf|g\rangle - \langle Qg|f\rangle. \tag{1.3.19d}$$

By comparing Equations 1.3.17a and 1.3.19a we immediately have

$$\langle f|Qg\rangle = \langle Qf|g\rangle, \tag{1.3.20}$$

for any $f(x)$ and $g(x)$ in the Hilbert space. □

Theorem 1.3.2.2 (Commutator of two hermitian operators)**.** The commutator of two hermitian operators is anti-hermitian, and same for two anti-hermitian operators.

Proof. Let P and Q be two hermitian operators, we can write

$$[P, Q]^\dagger = Q^\dagger P^\dagger - P^\dagger Q^\dagger = QP - PQ = [Q, P] = -[P, Q]. \tag{1.3.21}$$

For two anti-hermitian operators,

$$[P, Q]^\dagger = Q^\dagger P^\dagger - P^\dagger Q^\dagger = (-Q)(-P) - (-P)(-Q) = [Q, P] = -[P, Q]. \tag{1.3.22}$$

☐

1.3.2.2 Determinate states

Definition 1.3.2.1 (Determinate states)**.** A determinate state returns the same measurement q for the observable Q, in other words, the standard deviation of Q is zero.

Lemma 1.3.2.2 (Determinate states)**.** Determinate states are eignefunctions of Q.

Proof.

$$\sigma^2 = \langle (Q - \langle Q \rangle)^2 \rangle = \langle \Psi | (Q - q)^2 \Psi \rangle = \langle (Q - q)\Psi | (Q - q)\Psi \rangle = 0. \tag{1.3.23}$$

This implies that

$$Q\Psi = q\Psi, \tag{1.3.24}$$

an **eigenvalue equation** for operator Q. ☐

Worked example 1.3.2.1. Consider the operator

$$Q \equiv i\frac{\mathrm{d}}{\mathrm{d}\phi}. \tag{1.3.25}$$

Is Q Hermitian? Find its eigenfunctions and eigenvalues.

Solution:

We are working with $f(\phi)$ on the finite interval $0 \leq \phi \leq 2\pi$, and for physical states we must have that

$$f(\phi + 2\pi) = f(\phi). \tag{1.3.26}$$

Using integration by parts

$$\langle f|Qg\rangle = \int_0^{2\pi} f^* \left(i\frac{\mathrm{d}g}{\mathrm{d}\phi}\right)\mathrm{d}\phi \tag{1.3.27a}$$

$$= if^*g\Big|_0^{2\pi} - \int_0^{2\pi} i\left(\frac{\mathrm{d}f^*}{\mathrm{d}\phi}\right) g\,\mathrm{d}\phi \tag{1.3.27b}$$

$$= \langle Qf|g\rangle, \tag{1.3.27c}$$

where the boundary terms only appeared because we imposed Equation 1.3.26. The eigenvalue equation is given by

$$i\frac{\mathrm{d}}{\mathrm{d}\phi}f(\phi) = qf(\phi). \tag{1.3.28}$$

The general solution is

$$f(\phi) = Ae^{-iq\phi}. \tag{1.3.29}$$

Again, Equation 1.3.26 restricts us to possible values of q:

$$e^{-iq2\pi} = 1 \quad \Rightarrow \quad q = 0, \pm 1, \pm 2, \cdots \tag{1.3.30}$$

It has a discrete spectrum of all integers and it is nondegenerate.

1.3.3 Eigenfunctions of a hermitian operator

1.3.3.1 Discrete spectra

Theorem 1.3.3.1 (Eigenvalues are real)**.** Normalisable eigenfunctions of a hermitian operator have real eigenvalues.

Proof. We have

$$Qf = qf, \tag{1.3.31}$$

and

$$\langle f|Qf\rangle = \langle Qf|f\rangle, \tag{1.3.32}$$

so

$$q\langle f|f\rangle = q^*\langle f|f\rangle. \tag{1.3.33}$$

As

$$\langle f|f\rangle \neq 0 \tag{1.3.34}$$

by definition, we have

$$q = q^*. \tag{1.3.35}$$

☐

Theorem 1.3.3.2 (Orthogonality)**.** Eigenfunctions belonging to distinct eigenvalues are orthogonal.

Proof. We consider two eigenfunctions of Q:

$$Qf = qf \text{ and } Qg = q'g, \tag{1.3.36}$$

with Q hermitian, so

$$\langle f|Qg\rangle = \langle Qf|g\rangle, \tag{1.3.37}$$

and

$$q'\langle f|g\rangle = q^*\langle f|g\rangle. \tag{1.3.38}$$

Because q is real,

$$\langle f|g\rangle = 0. \tag{1.3.39}$$

☐

For degenerate states, we can use the **Gram-Schimidt orthogonalisation procedure** to construct orthogonal eigenfunctions.

A further axiom is given that the eigenfunctions of an observable operator are complete, *i.e.*, any functions in Hilbert space can be expressed as a linear combination of them.

1.3.3.2 Continuous spectra

If the spectrum of a hermitian operator is continuous, the eigenfunctions are not normalisable in the sense we have used so far. We aim to resolve this.

We now inspect the momentum operator for its eigenfunctions, $f_p(x)$, and eigenvalues, p:

$$\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}f_p(x) = pf_p(x). \tag{1.3.40}$$

The general solution is

$$f_p(x) = Ae^{ipx/\hbar}. \tag{1.3.41}$$

For any, even *complex* values of p, these eigenfunctions are not square-integrable, hence the momentum operator has no eigenfunctions in Hilbert space, in the 'traditional' sense.

However, if we were to restrict ourselves to real eigenvalues, we can then write, with the help of Property 1.2.5.5 in the last equality,

$$\int_{-\infty}^{+\infty} f_{p'}^*(x) f_p(x)\,\mathrm{d}x = |A|^2 \int_{-\infty}^{+\infty} e^{i(p'-p)x/\hbar}\,\mathrm{d}x = |A|^2 2\pi\hbar\delta(p-p'). \tag{1.3.42}$$

We should evidently pick $A = 1/\sqrt{2\pi\hbar}$, so that

$$f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}. \tag{1.3.43}$$

We have

Definition 1.3.3.1 (Dirac orthonormality)**.** A function is Dirac-orthonormalised if

$$\langle f_{p'} | f_p \rangle = \delta(p - p'). \tag{1.3.44}$$

Property 1.3.3.1 (Completeness of Dirac orthonormalised functions)**.** These eigenfunctions are complete: for any function $f(x)$

$$f(x) = \int_{-\infty}^{+\infty} c(p) f_p(x)\,\mathrm{d}p = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} c(p) e^{ipx/\hbar}\,\mathrm{d}p, \tag{1.3.45}$$

with the 'coefficient' function $c(p)$ evaualted as follows:

$$\langle f_{p'} | f \rangle = \int_{-\infty}^{+\infty} c(p) \langle f_{p'} | f_p \rangle\,\mathrm{d}p = \int_{-\infty}^{+\infty} c(p)\delta(p-p')\,\mathrm{d}p = c(p'). \tag{1.3.46}$$

Looked at another way these equations just describe Fourier transforms between $f(x)$ and $c(p)$.

Therefore we see that the eigenfunctions of momentum are sinusoidal, with wavelengths

$$\lambda = \frac{2\pi\hbar}{p} = \frac{h}{p}. \tag{1.3.47}$$

This is the de Broglie formula, but with an important point to note: as the eigenfunctions are non-normalisable, a particle cannot have a determinate momentum, hence all we could talk about is a normalisable wave packet with a narrow range of momenta.

We now look at the position operator.

Let $g_y(x)$ be its eigenfunction and y be the eigenvalue:

$$x g_y(x) = y g_y(x), \tag{1.3.48}$$

where y is a fixed number but x is a continuous variable. We can identify immediately that

$$g_y(x) = A\delta(x-y). \tag{1.3.49}$$

The eigenfunctions are Dirac orthonormal:

$$\int_{-\infty}^{+\infty} g_{y'}^*(x) g_y(x)\,\mathrm{d}x = |A|^2 \int_{-\infty}^{+\infty} \delta(x-y')\delta(x-y)\,\mathrm{d}x = |A|^2\delta(y-y'). \tag{1.3.50}$$

Picking $A = 1$,

$$g_y(x) = \delta(x-y). \tag{1.3.51}$$

And

$$\langle g_{y'}|g_y\rangle = \delta(y-y'). \tag{1.3.52}$$

They are also complete:

$$f(x) = \int_{-\infty}^{+\infty} c(y) g_y(x)\,\mathrm{d}y = \int_{-\infty}^{+\infty} c(y)\delta(x-y)\,\mathrm{d}y, \tag{1.3.53}$$

and we can identify

$$c(y) = f(y). \tag{1.3.54}$$

1.3.4 Generalised statistical interpretation

Postulate 1.3.4.1 (Generalised statistical interpretation)**.** If you measure an observable $Q(x,p)$ on a particle in the state $\Psi(x,t)$, you can only get one of the eigenvalues of the hermitian operator $\hat{Q}(x, -i\hbar\mathrm{d}/\mathrm{d}x)$.
If $\hat{Q}$ has a discrete spectrum, the probability of getting eigenvalue q_n of the eigenfunction $f_n(x)$ is

$$|c_n|^2, \quad \text{where } c_n = \langle f_n|\Psi\rangle. \tag{1.3.55}$$

If $\hat{Q}$ has a continuous spectrum, with real eigenvalues $q(z)$ and associated Dirac-orthonormalised eigenfuntions $f_z(x)$, the probability of getting a result in the range $\mathrm{d}z$ is

$$|c(z)|^2\,\mathrm{d}z, \quad \text{where } c(z) = \langle f_z|\Psi\rangle. \tag{1.3.56}$$

Corollary 1.3.4.1 (Position measurement)**.** We try to recover the formula we've been using for position measurements from the generalised statistical interpretation. We have the eigenfunction of position operator

$$g_y(x) = \delta(x-y), \tag{1.3.57}$$

so

$$c(y) = \langle f_y | \Psi \rangle = \int_{-\infty}^{+\infty} \delta(x-y)\Psi(x,t)\,\mathrm{d}x = \Psi(y,t), \tag{1.3.58}$$

so the probability of getting a result in the range of $\mathrm{d}y$ is $|\Psi(y,t)|^2\,\mathrm{d}y$, which recovers the formula nicely.

Corollary 1.3.4.2 (Momentum space wavefunction)**.** The eigenfunctions of momentum operator is

$$f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}, \tag{1.3.59}$$

so the coefficients are

$$c(p) = \langle f_p | \Psi \rangle = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} e^{-ipx/\hbar}\Psi(x,t)\,\mathrm{d}x \tag{1.3.60}$$

$c(p,t)$ here is important enough to get another name and symbol: the **momentum space wavefunction** $\Phi(p,t)$:

$$\Phi(p,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} e^{-ipx/\hbar}\Psi(x,t)\,\mathrm{d}x. \tag{1.3.61}$$

This is in fact just a Fourier transform of $\Psi(x,t)$. The probability that a measurement of momentum would yield a result in the range $\mathrm{d}p$ is (note that we are working in momentum space now):

$$|\Phi(x,t)|^2\,\mathrm{d}p. \tag{1.3.62}$$

Corollary 1.3.4.3 (Momentum space position and momentum operators)**.** The momentum space position operator is

$$\hat{X} \equiv -\frac{\hbar}{i}\frac{\partial}{\partial p}, \tag{1.3.63}$$

and the momentum space position operator is

$$\hat{P} \equiv p. \tag{1.3.64}$$

Proof. For the position operator we first note that

$$-\frac{\hbar}{i}\frac{\partial}{\partial p}\Phi = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty} xe^{-ipx/\hbar}\Psi \,\mathrm{d}x, \tag{1.3.65}$$

so that

$$\begin{aligned}
&\int_{-\infty}^{+\infty} \Phi^* \left(-\frac{\hbar}{i}\frac{\partial}{\partial p}\right)\Phi \,\mathrm{d}p && (1.3.66a)\\
=&\frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty}\left(\int_{-\infty}^{+\infty} e^{ipx'/\hbar}\Psi^*(x')\,\mathrm{d}x'\right)\left(\int_{-\infty}^{+\infty} xe^{-ipx/\hbar}\Psi(x)\,\mathrm{d}x\right)\mathrm{d}p && (1.3.66b)\\
=&\frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty}\left(\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{ip(x'-x)/\hbar}\Psi^*(x')x\Psi(x)\,\mathrm{d}x'\,\mathrm{d}x\right)\mathrm{d}p && (1.3.66c)\\
=&\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \delta(x'-x)\Psi^*(x')x\Psi(x)\,\mathrm{d}x'\,\mathrm{d}x && (1.3.66d)\\
=&\int_{-\infty}^{+\infty} \Psi^*(x)x\Psi(x)\,\mathrm{d}x && (1.3.66e)\\
=&\langle x\rangle. && (1.3.66f)
\end{aligned}$$

The momentum opeerator can be proven similarly. ☐

Theorem 1.3.4.1 (Transform from position to momentum space)**.**
Generally,

$$\langle Q(x,p)\rangle = \begin{cases} \displaystyle\int_{-\infty}^{+\infty} \Psi^*\hat{Q}\left(x, \frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi\,\mathrm{d}x, & \text{in position space;}\\ \displaystyle\int_{-\infty}^{+\infty} \Phi^*\hat{Q}\left(-\frac{\hbar}{i}\frac{\partial}{\partial p}, p\right)\Phi\,\mathrm{d}p, & \text{in momenum space.}\end{cases} \tag{1.3.67}$$

1.3.5 The uncertainty principle

1.3.5.1 Proof of the generalised uncertainty principle

For any oberservable A we have

$$\sigma_A^2 = \langle\Psi|(\hat{A}-\langle A\rangle)^2|\Psi\rangle = \langle(\hat{A}-\langle A\rangle)\rangle\Psi|(\hat{A}-\langle A\rangle)\rangle\Psi\rangle \equiv \langle f|f\rangle, \tag{1.3.68}$$

where we have used the hermiticity of $\hat{A}$ and consequently of $\hat{A}-\langle A\rangle$ in the second equality.

Likewise, for any other observable B for which we define $g \equiv (\hat{B} - \langle B \rangle)\Psi$,

$$\sigma_B^2 = \langle g|g \rangle. \tag{1.3.69}$$

Therefore, invoking the Schwarz inequality we can write

$$\sigma_A^2 \sigma_B^2 = \langle f|f \rangle \langle g|g \rangle \geq |\langle f|g \rangle|^2. \tag{1.3.70}$$

Now for any complex number z,

$$|z|^2 = \mathrm{Re}(z)^2 + \mathrm{Im}(z)^2 \geq \mathrm{Im}(z)^2 = \left[\frac{1}{2i}(z - z^*)\right]^2. \tag{1.3.71}$$

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

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i}[\langle f|g \rangle - \langle g|f \rangle]\right)^2. \tag{1.3.72}$$

Now it's time to evaluate

$$\begin{aligned}
\langle f|g \rangle &= \langle (\hat{A} - \langle A \rangle)\Psi | (\hat{B} - \langle B \rangle)\Psi \rangle && \text{(1.3.73a)} \\
&= \langle \Psi | (\hat{A} - \langle A \rangle)(\hat{B} - \langle B \rangle)\Psi \rangle && \text{(1.3.73b)} \\
&= \langle \Psi | (\hat{A}\hat{B} - \hat{A}\langle B \rangle - \hat{B}\langle A \rangle + \langle A \rangle \langle B \rangle)\Psi \rangle && \text{(1.3.73c)} \\
&= \langle \hat{A}\hat{B} \rangle - \langle B \rangle \langle A \rangle - \langle A \rangle \langle B \rangle + \langle A \rangle \langle B \rangle && \text{(1.3.73d)} \\
&= \langle \hat{A}\hat{B} \rangle - \langle A \rangle \langle B \rangle. && \text{(1.3.73e)}
\end{aligned}$$

Similarly,

$$\langle g|f \rangle = \langle \hat{B}\hat{A} \rangle - \langle A \rangle \langle B \rangle. \tag{1.3.74}$$

So,

$$\langle f|g \rangle - \langle g|f \rangle = \langle \hat{A}\hat{B} \rangle - \langle \hat{B}\hat{A} \rangle = \langle [\hat{A}, \hat{B}] \rangle. \tag{1.3.75}$$

So we reach the conclusion:

Theorem 1.3.5.1 (Generalised uncertainty principle)**.**

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i}\langle [\hat{A}, \hat{B}] \rangle\right)^2. \tag{1.3.76}$$

We now prove a couple commutator identities:

Property 1.3.5.1 (Associativity and distributivity)**.** Commutators are associative:

$$[AB, C] = A[B, C] + [A, C]B, \tag{1.3.77a}$$

$$[A, BC] = B[A, C] + [A, B]C. \tag{1.3.77b}$$

and distributive with respect to addition:

$$[A, B + C] = [A, B] + [A, C]. \tag{1.3.78}$$

Proof. For the first one we can write the LHS as

$$(ABC - CAB), \tag{1.3.79}$$

and the RHS

$$A(BC - CB) + (AC - CA)B = ABC - ACB + ACB - CAB = ABC - CAB = L.H.S. \tag{1.3.80}$$

$[A, BC]$ follows by anticommutativity. For the second one,

$$[A, B + C] = A(B + C) - (B + C)A = [A, B] + [A, C]. \tag{1.3.81}$$

☐

Property 1.3.5.2 (Commutator with momentum)**.**
Generally for any function $f(x)$,

$$[f(x), p] = i\hbar \frac{\mathrm{d}f}{\mathrm{d}x}. \tag{1.3.82}$$

Proof.

$$[f(x), p]g = -fi\hbar \frac{\mathrm{d}g}{\mathrm{d}x} + i\hbar \frac{\mathrm{d}fg}{\mathrm{d}x} \tag{1.3.83a}$$

$$= i\hbar \frac{\mathrm{d}f}{\mathrm{d}x} g. \tag{1.3.83b}$$

☐

Worked example 1.3.5.1. Derive the uncertainty principle of position and energy.
Solution:

We have, from the generalised uncertainty principle that

$$\sigma_x^2\sigma_H^2 = \left(\frac{1}{2i}\langle[\hat{X},\hat{H}]\rangle\right)^2. \tag{1.3.84}$$

Letting the commutator act on a test function $f(x)$, we have

$$\begin{align}[X,H] &= -\frac{\hbar^2}{2m}\left[x\frac{\mathrm{d}^2 f}{\mathrm{d}x^2} + xV(x)f - \frac{\mathrm{d}^2(xf)}{\mathrm{d}x^2} - V(x)xf\right] \tag{1.3.85a}\\ &= -\frac{\hbar^2}{2m}\left(-2\frac{\mathrm{d}f}{\mathrm{d}x}\right) \tag{1.3.85b}\\ &= \frac{\hbar^2}{m}\frac{\mathrm{d}f}{\mathrm{d}x}. \tag{1.3.85c}\end{align}$$

So the uncertainty principle is

$$\sigma_x^2\sigma_H^2 \geq \frac{\hbar^2}{4m^2}\langle p\rangle^2 \;\Rightarrow\; \sigma_x\sigma_H \geq \frac{\hbar}{2m}|\langle p\rangle|. \tag{1.3.86}$$

This relation is not useful for stationary states as $\langle p\rangle = 0$, but can prove useful for linear combinations of stationary states, when the average is non-zero.

Theorem 1.3.5.2 (Eigenfunctions of noncommuting operators)**.** Two noncommuniting operaotrs cannot have a complete set of common eigenfunctions.

Proof. Let P and Q have a complete, *i.e.*, any function can be written as a linear combination of them, set of common eigenfunctions, noting that they can have different eigenvalues, we'll have, for a function g in Hibert space,

$$g = \sum c_n f_n. \tag{1.3.87}$$

But because we know that

$$Pf_n = p_n f_n,\; Qf_n = q_n f_n, \tag{1.3.88}$$

so

$$PQg = QPg = \sum c_n p_n q_n f_n. \tag{1.3.89}$$

So

$$[P,Q] = 0. \tag{1.3.90}$$

□

A relate theorem can be stated as well

Theorem 1.3.5.3 (Eigenfunctions of commuting operators)**.** Two communiting operators share a simultaneous set of eigenstates. todo-supo: check what this means

Proof. Let operators A and B commute, and for A we have

$$A|f_n\rangle = a_n|f_n\rangle, \tag{1.3.91}$$

right-multiplying by B we have

$$BA|f_n\rangle = a_nB|f_n\rangle \equiv a_n|\beta_n\rangle. \tag{1.3.92}$$

Now the commutator tells us that

$$BA|f_n\rangle = AB|f_n\rangle = A|\beta_n\rangle. \tag{1.3.93}$$

Comparing, we have

$$A|\beta_n\rangle = a_n|\beta_n\rangle. \tag{1.3.94}$$

This can mean one of two things:
(a) $|\beta_n\rangle$ is an eigenfunction of A with eigenvalue a_n, which implies

$$|\beta_n\rangle = B|f_n\rangle = b_n|f_n\rangle. \tag{1.3.95}$$

This means the two operators have a common set of eigenfunctions.
(b) todo/todo-supo: check the degenerate case, priority: medium [16], [12] ☐

1.3.5.2 The minimum-uncertainty wave packet

The harmonic oscillator and the Gaussian wave packet for free particle were two previous cases that hit the minimum uncertainty. We now ask when, in general, the equality holds for the uncertainty relation.
The Schwarz inequality, which was used in proving the uncertainty principle, becomes an equality if and only if one function is a multiple of the other, *i.e.*,

$$g(x) = cf(x), \tag{1.3.96}$$

where c is some complex number. Meanwhile, if Equation 1.3.71 were to become an equality, we must also require that

$$\mathrm{Re}(\langle f|g\rangle) = 0. \tag{1.3.97}$$

Combining the two conditions we must have

$$\mathrm{Re}(c\langle f|f\rangle) = 0. \tag{1.3.98}$$

However, $\langle f|f\rangle$ is necessarily real, which means c must be purely imaginary, which is to say

$$c \equiv ia, \tag{1.3.99}$$

where a is real. The condition for minimum uncertainty is then

$$g(x) = iaf(x). \tag{1.3.100}$$

Now recalling the definitions of g and f from Equation 1.3.68, this time for momentum-position uncertainty principle:

$$f = \hat{P} - \langle p\rangle = \frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x} - \langle p\rangle \tag{1.3.101a}$$

$$g = x - \langle x\rangle. \tag{1.3.101b}$$

Therefore we have the resulting differential equation:

$$\left(\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x} - \langle p\rangle\right)\Psi = ia(x - \langle x\rangle)\Psi \tag{1.3.102a}$$

$$\frac{\mathrm{d}\Psi}{\mathrm{d}x} = \frac{i}{\hbar}\left[ia(x - \langle x\rangle) + \langle p\rangle\right]\Psi \tag{1.3.102b}$$

$$\frac{\mathrm{d}\Psi}{\mathrm{d}x} \equiv f(x)\Psi. \tag{1.3.102c}$$

The general solution is then

$$\Psi(x) = Ae^{-a(x-\langle x\rangle)^2/2\hbar}e^{i\langle p\rangle x/\hbar}. \tag{1.3.103}$$

This is an instantaneous waveform as A, a, $\langle x\rangle$, $\langle p\rangle$ can all have time dependence, and the only thing this proves is that at *some* instant in time, the wavefunction can reach minimum uncertainty, and that the waveform at this instant is *Gaussian*.

1.3.5.3 The energy-time uncertainty principle

Theorem 1.3.5.4 (E-t uncertainty principle)**.** The energy-time uncertainty principle states that

$$\Delta t\Delta E \geq \frac{\hbar}{2}. \tag{1.3.104}$$

This may look familiar, and indeed this is an immediate consequence of the x-p uncertainty principle, if we're working in relativistic quantum mechanics. But we're not, and it results from very different principles at work. This requires a proof.

Proof. For some observable $Q(x, p, t)$ (notice the new time dependence), we can compute the time derivative:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle Q\rangle = \frac{\mathrm{d}}{\mathrm{d}t}\langle\Psi|\hat{Q}\Psi\rangle = \left\langle\frac{\partial\Psi}{\partial t}\middle|\hat{Q}\Psi\right\rangle + \left\langle\Psi\middle|\frac{\partial\hat{Q}}{\partial t}\Psi\right\rangle + \left\langle\Psi\middle|\hat{Q}\frac{\partial\Psi}{\partial t}\right\rangle. \tag{1.3.105}$$

Because the Schrödinger equation says

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi, \tag{1.3.106}$$

we can simplify the time derivative

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle Q\rangle = -\frac{1}{i\hbar}\langle\hat{H}\Psi|\hat{Q}\Psi\rangle + \frac{1}{i\hbar}\langle\Psi|\hat{Q}\hat{H}\Psi\rangle + \left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle. \tag{1.3.107}$$

The Hamiltonian is hermitian, so

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle Q\rangle = \frac{i}{\hbar}\langle[\hat{H}, \hat{Q}]\rangle + \left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle. \tag{1.3.108}$$

We will use this in Corollary 1.3.5.1 and Theorem 1.3.5.5 to prove a few very useful theorems. Now, invoking the generalised uncertainty principle, setting $A = H$ and $B = Q$, and *assuming that Q does not depend on t*, we have

$$\sigma_H^2\sigma_Q^2 \geq \left(\frac{1}{2i}\langle[\hat{H}, \hat{Q}]\rangle\right)^2 = \left(\frac{1}{2i}\frac{\hbar}{i}\frac{\mathrm{d}\langle Q\rangle}{\mathrm{d}t}\right)^2, \tag{1.3.109}$$

which is to say

$$\sigma_H\sigma_Q \geq \frac{\hbar}{2}\left|\frac{\mathrm{d}\langle Q\rangle}{\mathrm{d}t}\right|. \tag{1.3.110}$$

We now make the following definitions:

$$\Delta E \equiv \sigma_H \tag{1.3.111a}$$

$$\Delta t \equiv \frac{\sigma_Q}{|\mathrm{d}\langle Q\rangle/\mathrm{d}t|}. \tag{1.3.111b}$$

Δt here does *not* mean the uncertainty in time as it is not a *dynamical variable*, however we can see that

$$\sigma_Q = \left|\frac{\mathrm{d}\langle Q\rangle}{\mathrm{d}t}\right|\Delta t, \tag{1.3.112}$$

therefore Δt represents the time it takes the expecataion value of Q to change by one standard deviation. We arrive at the E-t uncertainty principle:

$$\Delta E \Delta t \geq \frac{\hbar}{2}. \tag{1.3.113}$$

□

Corollary 1.3.5.1 (Time derivative of expectation/Heisenberg equation)**.** From Equation 1.3.108 we have a useful corollary:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle Q\rangle = \frac{i}{\hbar}\langle[\hat{H},\hat{Q}]\rangle + \left\langle \frac{\partial \hat{Q}}{\partial t}\right\rangle. \tag{1.3.114}$$

We apply it to several cases and appreciate its utility.
(a) With $Q = 1$, we know that all operators commute with a constant, and Q has no dependence on time, so

$$\frac{\mathrm{d}\langle Q\rangle}{\mathrm{d}t} = 0. \tag{1.3.115}$$

Looked at another way,

$$\langle Q\rangle = \langle \Psi|\Psi\rangle, \tag{1.3.116}$$

and the fact that time derivative is zero is simply a restatement of preservation of normalisation theorem (Theorem 1.1.1.1).
(b) With $Q = H$, since any operator commutes with itself, *i.e.*, the commutator is 0 we have

$$\frac{\mathrm{d}\langle H\rangle}{\mathrm{d}t} = \left\langle \frac{\partial H}{\partial t}\right\rangle. \tag{1.3.117}$$

If the Hamiltonian has no explicit energy dependence, *i.e.*, the potential is time-independent, then this is a restatment of conservation of energy.
(c) With $Q = x$, we already know the commutator from Equation 1.3.85c:

$$[\hat{H},\hat{X}] = -[\hat{H},\hat{X}] = -\frac{\hbar^2}{m}\frac{\partial}{\partial x} = -\frac{i\hbar}{m}\hat{P}. \tag{1.3.118}$$

As x is independent of time,

$$\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \frac{i}{\hbar}\langle[\hat{H},\hat{X}]\rangle = \frac{\langle p\rangle}{m}. \tag{1.3.119}$$

This is a restatement of the first part of Ehrenfest theorem (Equation 1.1.14a).
(d) With $Q = P$, we need to work out the commutator first:

$$[\hat{H},\hat{P}]g = \hat{H}\left[\frac{\hbar}{i}\frac{\partial g}{\partial x}\right] - \hat{P}\left[-\frac{\hbar^2}{2m}\frac{\partial^2 g}{\partial x^2} + Vg\right] \tag{1.3.120a}$$

$$= -\frac{\hbar^2}{2mi}\frac{\partial^3 g}{\partial x^3} + \frac{\hbar}{i}V\frac{\partial g}{\partial x} + \frac{\hbar^2}{2mi}\frac{\partial^3 g}{\partial x^3} - \frac{\hbar}{i}\left(g\frac{\partial V}{\partial x} + V\frac{\partial g}{\partial x}\right) \tag{1.3.120b}$$

$$= i\hbar\frac{\partial V}{\partial x}g. \tag{1.3.120c}$$

Therefore,

$$\frac{\mathrm{d}\langle p\rangle}{\mathrm{d}t} = -\left\langle\frac{\partial V}{\partial x}\right\rangle. \tag{1.3.121}$$

This is a restatement of Ehrenfest theorem.

Theorem 1.3.5.5 (Virial theorem)**.** The quantum mechanical Virial theorem states that

$$2\langle T\rangle = \left\langle x\frac{\mathrm{d}V}{\mathrm{d}x}\right\rangle, \tag{1.3.122}$$

where T is the kinetic energy.

Proof. We use Corollary 1.3.5.1 to prove this theorem. We can write, for $Q \equiv XP$, the commutator

$$[\hat{H},\hat{X}\hat{P}]f = \left(-\frac{\hbar^2}{2m}\frac{\partial}{\partial x} + V(x)\right)\left(x\frac{\hbar}{i}\frac{\partial}{\partial x}\right)f - \left(x\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\left(-\frac{\hbar^2}{2m}\frac{\partial}{\partial x} + V(x)\right)f \tag{1.3.123a}$$

$$= -\frac{\hbar^3}{im}\frac{\partial^2 f}{\partial x^2} - \frac{\hbar}{i}x\frac{\partial V}{\partial x}f. \tag{1.3.123b}$$

Corollary 1.3.5.1 gives

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle xp\rangle = \frac{i}{\hbar}\langle[H,XP]\rangle + \left\langle\frac{\partial(xp)}{\partial t}\right\rangle. \tag{1.3.124}$$

The last term is zero because the operator $\hat{X}\hat{P}$ has no time dependence (see Footnote 7 of [20]). The LHS can be re-written

$$\langle xp\rangle = \langle\Psi|XP|\Psi\rangle = \langle\Psi|X|\Psi\rangle\langle\Psi|P|\Psi\rangle = \langle x\rangle\langle p\rangle, \tag{1.3.125}$$

therefore, *in stationary states*,

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle xp\rangle = \langle x\rangle'\langle p\rangle + \langle x\rangle\langle p\rangle' = 0. \tag{1.3.126}$$

Therefore

$$0 = \frac{i}{\hbar}\langle [H, XP] \rangle \tag{1.3.127a}$$

$$= \left\langle -\frac{\hbar^2}{m}\frac{\partial^2}{\partial x^2} - x\frac{\partial V}{\partial x} \right\rangle \tag{1.3.127b}$$

$$= 2\langle T \rangle - \left\langle x\frac{\mathrm{d}V}{\mathrm{d}x} \right\rangle . \tag{1.3.127c}$$

Remember that we have assumed that the potential is time-independent. This gives the required theorem. □

Corollary 1.3.5.2 (Virial theorem for harmonic oscillator)**.** For harmonic oscillators we have

$$V(x) = \frac{1}{2}m\omega^2 x^2 \tag{1.3.128}$$

So the Virial theorem gives us

$$2\langle T \rangle = \langle m\omega^2 x^2 \rangle = 2\langle V \rangle \ \Rightarrow \ \langle T \rangle = \langle V \rangle . \tag{1.3.129}$$

1.3.6 Dirac Notation

come back and do the exercises also, priority: medium

Worked example 1.3.6.1. In this problem we deal with **sequential measurements**. Suppose an observable operator A has two normalised eigenstates ψ_1 and ψ_2, and the operator B has ϕ_1 and ϕ_2, and they are related by (remember that both must have a *complete* set of eigenstates, and as such they can *always* be expressed in terms of each other.)

$$\psi_1 = (3\phi_1 + 4\phi_2)/5, \ \psi_2 = (4\phi_1 - 3\phi_2)/5. \tag{1.3.130}$$

(a) Oberservable A is measured and the value a_1 is obtained, what is the state of the system immediately after the measurement?
Solution: The system must now be in state ψ_1 as the wavefunction has collasped.
(b) If B is now measured, what are the possible results and their probabilities?
Solution: As the system is now in the state $\psi_1 = (3\phi_1 + 4\phi_2)/5$, the probability of getting either b_1 or b_2 is $9/25$ or $16/25$.
(c) Right after the measurement of B, A is measured again. What's the probability of getting a_1 again?

Solution: We compute the conditional probabilities

$$P(a_1) = P(a_1|b_1)P(b_1) + P(a_1|b_2)P(b_2). \tag{1.3.131}$$

To get the conditional probabilities we need to invert the relations:

$$\phi_1 = (3\psi_1 + 4\psi_2)/5,\ \phi_2 = (4\psi_1 - 3\psi_2)/5, \tag{1.3.132}$$

so

$$P(a_1) = \frac{9}{25} \cdot \frac{9}{25} + \frac{16}{25} \cdot \frac{16}{25} \approx 0.54. \tag{1.3.133}$$

1.4 QUANTUM MECHANICS IN THREE DIMENSIONS

1.4.1 Schrödinger equation in 3D with non-Coulombic potentials

1.4.1.1 Preparatory work

We introduce the 3D Schrödinger equation as follows:

$$i\hbar\frac{\partial}{\partial t}\boldsymbol{\Psi}(\boldsymbol{r},t) = -\frac{\hbar^2}{2m}\nabla^2\boldsymbol{\Psi}(\boldsymbol{r},t) + V\boldsymbol{\Psi}(\boldsymbol{r},t), \tag{1.4.1}$$

where

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{1.4.2}$$

Property 1.4.1.1 (Canonical commutation relations in 3D)**.** We have

$$[r_i, p_j] = -[p_i, r_j] = i\hbar\delta_{ij},\ [r_i, r_j] = [p_i, p_j] = 0. \tag{1.4.3}$$

The proof is trivial.

Corollary 1.4.1.1 (Heisenberg's uncertainty in 3D)**.** It follows from the canonical commutator relations in 3D that

$$\sigma_{x_i}\sigma_{p_j} \geq \frac{\hbar}{2}\delta_{ij}. \tag{1.4.4}$$

Theorem 1.4.1.1 (Ehrenfest's theorem in 3D)**.**

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\boldsymbol{r}\rangle = \frac{1}{m}\langle\boldsymbol{p}\rangle \tag{1.4.5a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\boldsymbol{p}\rangle = \langle-\nabla V\rangle. \tag{1.4.5b}$$

This is true because in deriving Equation 1.3.108, no calculation depended on the dimensions, so we can do the same calculation in all three cardinal directions separately and get the 3D theorem.

Property 1.4.1.2 (Laplacian in spherical coordinates)**.** The Laplacian ∇^2 in spherical coordinates is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right). \tag{1.4.6}$$

Proof. It can be derived either from a tedious change-of-basis partial differentiation exercise or from generalised curvilinear coordinates, which we will use:
The Laplacian in curvilinear coordinates is

$$\frac{1}{h_1h_2h_3}\left[\frac{\partial}{\partial q_1}\left(\frac{h_2h_3}{h_1}\frac{\partial}{\partial q_1}\right) + \frac{\partial}{\partial q_2}\left(\frac{h_3h_1}{h_2}\frac{\partial}{\partial q_2}\right) + \frac{\partial}{\partial q_1}\left(\frac{h_1h_2}{h_3}\frac{\partial}{\partial q_3}\right)\right], \tag{1.4.7}$$

where q_i's are the cardinal directions and

$$h_i \equiv \left|\frac{\partial \boldsymbol{r}}{\partial q_i}\right|. \tag{1.4.8}$$

So for spherical coordinates we have

$$\boldsymbol{r} = (r\cos\phi\sin\theta, r\sin\phi\sin\theta, r\cos\theta), \tag{1.4.9}$$

so

$$h_r = 1 \tag{1.4.10a}$$
$$h_\phi = r\sin\theta \tag{1.4.10b}$$
$$h_\theta = r. \tag{1.4.10c}$$

Substitution into Equation 1.4.7 yields the desired expression. □

We now write out the time-independent Schrödinger equation in full:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right] + V\psi = E\psi \tag{1.4.11}$$

It is clear that we can use separation of variables to write

$$\psi(r,\phi,\theta) = R(r)Y(\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi). \tag{1.4.12}$$

Using the first equality first, we get after some rearrangement

$$\begin{gathered}\left\{\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right)-\frac{2mr^2}{\hbar^2}(V-E)\right\}\\+\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\}=0.\end{gathered}\tag{1.4.13}$$

The top bracket involves the potential V and only depends on r, and cannot be solved until the potential has been specified, as we will do in Section 1.4.2. The bottome bracket can be solved as it is, and now we introduce the separation constant $l(l+1)$, where l is in general complex as of now (it will be restricted to integers in the course of solving the equation).

1.4.1.2 The angular equation

The angular equation is

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{\partial^2 Y}{\partial\theta^2}=-l(l+1)\sin^2\theta Y.\tag{1.4.14}$$

Separating further according to Equation 1.4.12 we have

$$\left\{\frac{1}{\Theta}\left[\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)\right]+l(l+1)\sin^2\theta\right\}+\frac{1}{\phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}=0.\tag{1.4.15}$$

Now introducing the separation constant m^2, where m is again as of now generally complex, we have

$$\frac{1}{\Theta}\left[\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)\right]+l(l+1)\sin^2\theta=m^2,\tag{1.4.16}$$

the **polar equation** and

$$\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}=-m^2,\tag{1.4.17}$$

the **azimuthal equation**.

The azimuthal equation is readily solved to give

$$\Phi(\phi)=e^{im\phi},\tag{1.4.18}$$

where the arbitrary constant is absorbed into Θ and m runs to negative. For the wavefunction to be physical we impose the condition that

$$\Phi(\phi+2\pi)=\Phi(\phi),\tag{1.4.19}$$

so

$$e^{im(\phi+2\pi)} = e^{im\phi} \;\Rightarrow\; e^{2\pi im} = 1 \;\Rightarrow\; m = 0, \pm 1, \pm 2, \cdots \tag{1.4.20}$$

We have already quantized m to all integers. The normalisation constant is simply $1/\sqrt{2\pi}$. We now solve the polar equation. First of all we introduce the following transformation

$$x \equiv \cos\theta \tag{1.4.21a}$$

$$\Theta(\theta) \equiv P(x), \tag{1.4.21b}$$

with $0 \leq \theta \leq \pi$ and $-1 \leq x \leq 1$, so we have

$$\frac{\mathrm{d}x}{\mathrm{d}\theta} = -\sin\theta \tag{1.4.22a}$$

$$\sin^2\theta = 1 - x^2. \tag{1.4.22b}$$

We are all set to go:

$$\frac{1}{\Theta}\left[\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)\right] + l(l+1)\sin^2\theta = m^2 \tag{1.4.23a}$$

$$\frac{\sin\theta}{P(x)}\frac{\partial x}{\partial\theta}\frac{\partial}{\partial x}\left(\sin\theta\frac{\partial x}{\partial\theta}\frac{\partial}{\partial x}P(x)\right) + l(l+1)\sin^2\theta = m^2 \tag{1.4.23b}$$

$$\frac{-\sin^2\theta}{P(x)}\frac{\partial}{\partial x}\left(-\sin^2\theta\frac{\partial}{\partial x}P(x)\right) + l(l+1)\sin^2\theta = m^2 \tag{1.4.23c}$$

$$-\frac{\partial}{\partial x}\left[(x^2-1)\frac{\partial}{\partial x}P(x)\right] + l(l+1)P(x) - \frac{m^2}{1-x^2}P(x) = 0 \tag{1.4.23d}$$

$$(1-x^2)\frac{\mathrm{d}^2}{\mathrm{d}x^2}P(x) - 2x\frac{\mathrm{d}}{\mathrm{d}x}P(x) + \underbrace{\left[l(l+1) - \frac{m^2}{1-x^2}\right]}_{\equiv K}P(x) = 0. \tag{1.4.23e}$$

This is the **general Legendre's equation**. To solve it we must first solve the **Legendre's equation**, where $m = 0$:

$$(1-x^2)\frac{\mathrm{d}^2}{\mathrm{d}x^2}P(x) - 2x\frac{\mathrm{d}}{\mathrm{d}x}P(x) + \underbrace{l(l+1)}_{\equiv\beta}P(x) = 0. \tag{1.4.24}$$

As x is inherently dimensionless we can skip the non-dimensionalisation, and also a glance at the equation does show any interesting behaviour at $|x| \to \infty$, so we can also skip the asymptotic analysis, and jump straight to Frobenius method:
Let

$$P(x) = \sum_{j=0}^{\infty} a_j, \tag{1.4.25}$$

substitution into Equation 1.4.24 gives

$$(1-x^2)\sum_{j=0}^{\infty} j(j-1)a_j x^{j-2} - 2x\sum_{j=0}^{\infty} j a_j x^{j-1} + \sum_{j=0}^{\infty} a_j \beta x^j = 0 \tag{1.4.26a}$$

$$\sum_{j=0}^{\infty} j(j-1)a_j x^{j-2} - \sum_{j=0}^{\infty} j(j-1)a_j x^{j} - \sum_{j=0}^{\infty} 2j a_j x^{j} + \sum_{j=0}^{\infty} a_j \beta x^j = 0 \tag{1.4.26b}$$

$$\sum_{j=2}^{\infty} j(j-1)a_j x^{j-2} - \sum_{j=0}^{\infty} j(j-1)a_j x^{j} - \sum_{j=0}^{\infty} 2j a_j x^{j} + \sum_{j=0}^{\infty} a_j \beta x^j = 0 \tag{1.4.26c}$$

$$\sum_{j=0}^{\infty} (j+2)(j+1)a_{j+2} x^{j} - \sum_{j=0}^{\infty} j(j-1)a_j x^{j} - \sum_{j=0}^{\infty} 2j a_j x^{j} + \sum_{j=0}^{\infty} a_j \beta x^j = 0 \tag{1.4.26d}$$

$$\sum_{j=0}^{\infty} \left[(j+2)(j+1)a_{j+2} - j(j-1)a_j - 2ja_j + a_j\beta\right] x^j = 0. \tag{1.4.26e}$$

Now let's pause and think what we've done so far: we have set all the powers of x to j, as required by the Frobenius method, and now we have in our hands a $\{a_{j+2}, a\}$ recurrence relation:

$$a_{j+2} = \frac{j(j+1) - l(l+1)}{(j+2)(j+1)} a_j. \tag{1.4.27}$$

We do the same things as we've done with the Hermite polynomials: fix a_0 and a_1 alternately to 0 and terminate series to ensure normalisability. The values are fixed by convention:

$$P_l(1) = 1. \tag{1.4.28}$$

And we observe that we have quantised l to *nonnegative integers, i.e.,*

$$l = 0, 1, 2, \cdots . \tag{1.4.29}$$

$P_l(x)$ is called the **Legendre polynomial** and is defined as follows:

Definition 1.4.1.1 (Legendre polynomials)**.** Legendre polynomials are defined by the generating function $T(x,t)$:

$$T(x,t) = (1-2xt+t^2)^{-1/2} \equiv \sum_{l=0}^{\infty} P_l(x)t^l, \tag{1.4.30}$$

where $P_l(x)$, the Legendre polynomial of order l is the coefficient of the Taylor series in powers of t. This definition is cumbersome however, and we could alternatively use the Rodrigues' formula:

$$P_l(x) = \frac{1}{2^l l!}\frac{\mathrm{d}^l}{\mathrm{d}x^l}(x^2-1)^l. \tag{1.4.31}$$

The recurrence relations are

$$(1-x^2)P_l' = -lxP_l + lP_{l-1} \tag{1.4.32a}$$
$$(l+1)P_{l+1} = (2l+1)xP_l - lP_{l-1}. \tag{1.4.32b}$$

todo: supply proof, priority: low

We list the first few Legendre polynomials:

$$P_0 = 1 \tag{1.4.33a}$$
$$P_1 = x \tag{1.4.33b}$$
$$P_2 = \frac{1}{2}(3x^2-1) \tag{1.4.33c}$$
$$P_3 = \frac{1}{2}(5x^3-3x) \tag{1.4.33d}$$
$$P_4 = \frac{1}{8}(35x^4-30x^2+3) \tag{1.4.33e}$$

And now we solve the general Legendre's equation. We start by differentiating the Legendre's equation

$$\underbrace{(1-x^2)P_l''(x)}_{(1)} - \underbrace{2xP_l'(x)}_{(2)} + \underbrace{l(l+1)P_l(x)}_{(3)} = 0 \tag{1.4.34}$$

m times using the Leibniz formula:

$$\underbrace{(1-x^2)P_l^{(m+2)} - 2mxP_l^{(m+1)} - m(m+1)P_l^{(m)}}_{(1)} - \underbrace{[2xP_l^{(m+1)} + 2mP_l^{(m)}]}_{(2)} + \underbrace{l(l+1)P_l^{(m)}}_{(3)}, \tag{1.4.35}$$

collecting terms we have

$$(1-x^2)P_l^{(m+2)} - 2x(m+1)P_l^{(m+1)} + [l(l+1)-m^2-m]P_l^{(m)} = 0. \tag{1.4.36}$$

Making the substitution [2]

$$P_l^{(m)} \equiv u \equiv v(1-x^2)^{-m/2}, \tag{1.4.37}$$

we obtain

$$\begin{aligned} u' &= v'(1-x^2)^{-m/2} + mvx(1-x^2)^{-m/2-1} \\ &= \left(v' + \frac{mxv}{1-x^2}\right)(1-x^2)^{-m/2}, \end{aligned} \tag{1.4.38}$$

and

$$\begin{aligned} u'' &= \left[v'' + \frac{mv'}{1-x^2} + \frac{2mx^2v}{(1-x^2)^2}\right](1-x^2)^{-m/2} + \left(v' + \frac{mxv}{1-x^2}\right)(1-x^2)^{-m/2-1} \\ &= \left[v'' + \frac{2mxv'}{1-x^2} + \frac{mv}{1-x^2} + \frac{m(m+2)x^2v}{(1-x^2)^2}\right](1-x^2)^{-m/2}. \end{aligned} \tag{1.4.39}$$

Substitution into Equation 1.4.35 gives

$$\begin{aligned} 0 =& (1-x^2)v'' + 2mxv' + mv + \frac{m(m+2)x^2v}{1-x^2} - 2x(m+1)\left(v' + \frac{mxv}{1-x^2}\right) \\ &+ [l(l+1) - m^2 - m]v \end{aligned} \tag{1.4.40a}$$

$$\begin{aligned} =& (1-x^2)v'' + [2mx - 2x(m+1)]v' \\ &+ \left[\frac{2mx^2}{1-x^2} - \frac{2x^2m(m+1)}{1-x^2} + l(l+1) - m^2\right]v \end{aligned} \tag{1.4.40b}$$

$$=(1-x^2)v'' - 2xv' - m^2v + l(l+1)v + \frac{v}{1-x^2}[m(m+2)x^2 - 2mx^2(m+1)] \tag{1.4.40c}$$

$$=(1-x^2)v'' - 2xv' - m^2\frac{1-x^2}{1-x^2}v + l(l+1)v - \frac{m^2x^2v}{1-x^2} \tag{1.4.40d}$$

$$=(1-x^2)v'' - 2xv' + \left[l(l+1) - \frac{m^2}{1-x^2}\right]v, \tag{1.4.40e}$$

which is the general Legendre equation. So we now know, though tortuously, that the **associated Legendre polynomials**, defined as

Definition 1.4.1.2 (Associated Legendre polynomials)**.**

$$v_{ml}(x) \equiv P_l^{|m|}(x) = (1-x^2)^{|m|/2}\frac{\mathrm{d}^{|m|}}{\mathrm{d}x^{|m|}}P_l(x), \tag{1.4.41}$$

are solutions to the general Legendre's equation. Only the magnitude of m is relevant here[3] since inspecting the original equation (Equation 1.4.23e) shows that the equation is invariant under a sign change of m, so we have our condition

---

[2] This substitution is introduced here *ad hoc*, but however it arises from the application of Fuch's theorem to Frobenius method as explained in [18] and worked out in [10].

[3] In some sources such as [19], the polynomials for negative m's have an appended factor in front, but this is unnessarary for us as the solutions are eventually normalised anyway.

$$|m| \leq l, \;\Rightarrow\; m = -l, -l+1, \cdots, 0, \cdots, +l-1, +l. \tag{1.4.42}$$

This condition arises again, and more naturally, when we study angular momentum. Note that although $P_l^m(x)$ is only a polynomial in x when m is odd, $P_l^m(\cos\theta)$ is always a polynomial in $\cos\theta$, multiplied by $\sin\theta$ when m is odd.
At this point we assert that the normalisation constant is

$$N_{lm} = \left[\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} \tag{1.4.43}$$

Therefore the normalised **angular wavefunction** is

$$Y_l^m(\theta,\phi) = \epsilon\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)e^{im\phi}, \tag{1.4.44}$$

where

$$\epsilon = \begin{cases}(-1)^m & \text{for } m > 0;\\ 1 & \text{for } m \leq 0.\end{cases} \tag{1.4.45}$$

This factor is known as the **Condon-Shortley phase**. This sign convention will prove useful when we study the ladder operators for angular momentum: see discussion below Theorem 1.4.3.2. We also notice that the functional makeup of spherical harmonics is invariant under a change of sign.

Definition 1.4.1.3 (Spherical harmonics)**.**
The normalised angular wavefunctions $Y_l^m(\theta,\phi)$ are known as **spherical harmonics**.

Property 1.4.1.3 (Orthogonality of spherical harmonics)**.** Spherical harmonics are orthogonal:

$$\int_0^{2\pi}\int_0^{\pi}[Y_l^m(\theta,\phi)]^*[Y_{l'}^{m'}(\theta,\phi)]\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi = \delta_{ll'}\delta_{mm'}. \tag{1.4.46}$$

Proof. We prove this by explicitly integrating by parts. todo: finish this ☐

1.4.1.3 The radial equation

The radial equation is given as

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right)-\frac{2mr^2}{\hbar^2}(V-E)R=l(l+1)R. \tag{1.4.47}$$

We introduce a change of variables:

$$u(r)\equiv rR(r), \tag{1.4.48}$$

such that

$$R=\frac{u}{r},\ \frac{\mathrm{d}R}{\mathrm{d}r}=\frac{1}{r^2}\left(r\frac{\mathrm{d}u}{\mathrm{d}r}-u\right),\ \frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right)=r\frac{\mathrm{d}^2u}{\mathrm{d}r^2}. \tag{1.4.49}$$

So the equation becomes

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2u}{\mathrm{d}r^2}+\left[V+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u=Eu. \tag{1.4.50}$$

This is identical in form to the one-dimensional Schrödinger equation except for the effective potential:

$$V_{\text{eff}}=V+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}, \tag{1.4.51}$$

which contains a second, **centrifugal term**. We can proceed no further until a specific potential $V(r)$ is given.

Infinite spherical well

Consider the potential

$$V(r)=\begin{cases}0, & \text{if } r\le a;\\ \infty, & \text{if } r>a.\end{cases} \tag{1.4.52}$$

The wavefunction vanishes outside the well of course, and in the well the Schrödinger equation is

$$\frac{\mathrm{d}^2u}{\mathrm{d}r^2}=\left[\frac{l(l+1)}{r^2}-k^2\right]u,\ \text{where } k\equiv\frac{\sqrt{2mE}}{\hbar} \tag{1.4.53}$$

We solve the case of $l=0$ first:

$$\frac{\mathrm{d}^2u}{\mathrm{d}r^2}=-k^2u\ \Rightarrow\ u(r)=A\sin(kr)+B\cos(kr), \tag{1.4.54}$$

or

$$\psi(r) = \frac{A\sin(kr)}{r} + \frac{B\cos(kr)}{r}, \tag{1.4.55}$$

$\cos(x)/x$ is not finite at origin hence non-normalisable (todo: irregular singular point? see Griffiths p.141 footnote 10, priority: low/when going through maths notes), so we must have $B = 0$, the boundary condition

$$\sin(ka) = 0 \;\Rightarrow\; ka = n\pi,\; n = 1, 2, 3, \cdots, \tag{1.4.56}$$

and so

$$E_{n0} = \frac{n^2\pi^2\hbar^2}{2ma^2}, \tag{1.4.57}$$

the exact same energy as allowed by the one-dimensional infinite square well in Equation 1.2.31, but however energy in this case is also indexed by l. The full wavefunction for $l = (m =)0$ is

$$\psi_{n00}(r,\theta,\phi) = AY_0^0(\theta,\phi)\frac{\sin(n\pi r/a)}{r} = \frac{1}{\sqrt{2\pi a}}\frac{\sin(n\pi r/a)}{r}. \tag{1.4.58}$$

The general solution for states with $l \neq 0$ is todo: outline solution

$$u(r) = Arj_l(kr) + Brn_l(kr), \tag{1.4.59}$$

where $j_l(x)$ is the **spherical Bessel function** of order l given by

$$j_l(x) \equiv (-x)^l \left(\frac{1}{x}\frac{\mathrm{d}}{\mathrm{d}x}\right)^l \frac{\sin x}{x}, \tag{1.4.60}$$

and $n_l(x)$ is the **spherical Neumann function** of order l given by

$$n_l(x) \equiv -(-x)^l \left(\frac{1}{x}\frac{\mathrm{d}}{\mathrm{d}x}\right)^l \frac{\cos x}{x}. \tag{1.4.61}$$

As $\sin x/x$ is finite at origin, so are its derivatives, and $\cos x/x$ is'nt. So we must again have $B = 0$ and only keep the spherical Bessel functions, so

$$R(r) = Aj_k(kr). \tag{1.4.62}$$

The boundary condition

$$R(a) = 0 \;\Rightarrow\; j_l(ka) = 0, \tag{1.4.63}$$

means k is given by zeroes of l-th order spherical Bessel functions, which involves numerical calculations because no neat analytical methods exist. In general, we write

$$k = \frac{1}{a}\beta_{nl}, \tag{1.4.64}$$

where β_{nl} is the n-th zero of the l-th order spherical Bessel function. The energy follows:

$$E_{nl} = \frac{\hbar^2}{2ma^2}\beta_{nl}^2, \tag{1.4.65}$$

and the wavefunctions are

$$\psi_{nlm}(r,\theta,\phi) = A_{nl}j_l(\beta_{nl}r/a)Y_l^m(\theta,\phi), \tag{1.4.66}$$

with each energy level being $(2l+1)$-fold degenerate from m.

1.4.2 The hydrogen atom

1.4.2.1 Setting up the radial equation

The potential in a hydrogen atom experienced by the electron is the **Coulombic potential**:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}. \tag{1.4.67}$$

The Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2u}{\mathrm{d}r^2} + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu. \tag{1.4.68}$$

Confining ourselves to *bound states, i.e.,* $E < 0$, we introduce

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}. \tag{1.4.69}$$

Dividing Equation 1.4.68 by E we have

$$\frac{1}{\kappa^2}\frac{\mathrm{d}^2u}{\mathrm{d}r^2} = \left[1 - \frac{me^2}{2\pi\epsilon\hbar^2\kappa}\frac{1}{\kappa r} + \frac{l(l+1)}{(\kappa r)^2}\right]u, \tag{1.4.70}$$

to further simplify, we introduce

$$\rho = \kappa r, \text{ and } \rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}, \tag{1.4.71}$$

so that

$$\frac{\mathrm{d}^2 u}{\mathrm{d}\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right] u. \tag{1.4.72}$$

We have our radial equation.

1.4.2.2 Solving the radial equation

Asymptotic analysis

As $\rho \to \infty$ (remember we are dealing with r here so $\rho \geq 0$), the radial equation becomes

$$\frac{\mathrm{d}^2 u}{\mathrm{d}\rho^2} = u. \tag{1.4.73}$$

Taking the physical $e^{-\rho}$ solution only we have

$$u(\rho) \approx Ae^{-\rho} \;\text{ as } \rho \to \infty. \tag{1.4.74}$$

As $\rho \to 0$, the $1/\rho^2$ term dominates, so

$$\frac{\mathrm{d}^2 u}{\mathrm{d}\rho^2} = \frac{l(l+1)}{\rho^2} u, \tag{1.4.75}$$

we posit that the solution must be a polynomial, we try

$$u(\rho) = \sum_{\infty}^{j=0} a_j \rho^j, \tag{1.4.76}$$

substituting back and rearranging we have

$$\sum_{j=0}^{\infty} [j(j-1) - l(l+1)] a_j \rho^{j-2} = 0, \tag{1.4.77}$$

so we have that $j = l+1$ or $j = -l$, giving

$$u(\rho) = C\rho^{l+1} + D\rho^{-l}. \tag{1.4.78}$$

The ρ^{-l} blows up as $\rho \to 0$, so $D = 0$, so

$$u(\rho) \approx C\rho^{l+1} \;\text{ as } \rho \to 0. \tag{1.4.79}$$

This suggest that we write

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho). \tag{1.4.80}$$

The derivatives are as follows:

$$\frac{\mathrm{d}u}{\mathrm{d}\rho} = \rho^l e^{-\rho}\left[(l+1-\rho)v + \rho\frac{\mathrm{d}v}{\mathrm{d}\rho}\right] \tag{1.4.81a}$$

$$\frac{\mathrm{d}^2u}{\mathrm{d}\rho^2} = \rho^l e^{-\rho}\left\{\left[-2l-2+\rho+\frac{l(l+1)}{\rho}\right]v + 2(l+1-\rho)\frac{\mathrm{d}v}{\mathrm{d}\rho} + \rho\frac{\mathrm{d}^2v}{\mathrm{d}\rho^2}\right\}. \tag{1.4.81b}$$

Now in terms of $v(\rho)$ the radial equation becomes, after a bit of algebra,

$$\rho\frac{\mathrm{d}^2v}{\mathrm{d}\rho^2} + 2(l+1-\rho)\frac{\mathrm{d}v}{\mathrm{d}\rho} + [\rho_0 - 2(l+1)]v = 0. \tag{1.4.82}$$

Frobenius method

We adopt the power series solution for $v(\rho)$:

$$v(\rho) = \sum_{j=0}^{\infty} c_j\rho^j. \tag{1.4.83}$$

The required derivatives are

$$\frac{\mathrm{d}v}{\mathrm{d}\rho} = \sum_{j=0}^{\infty} jc_j\rho^{j-1} = \sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j \tag{1.4.84a}$$

$$\frac{\mathrm{d}^2v}{\mathrm{d}\rho^2} = \sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^{j-1}. \tag{1.4.84b}$$

The equation becomes

$$\begin{aligned}&\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^j + 2(l+1)\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j \\ &-\sum_{j=0}^{\infty} jc_j\rho^j + [\rho_0 - 2(l+1)]\sum_{j=0}^{\infty} c_j\rho^j = 0.\end{aligned} \tag{1.4.85}$$

This implies

$$\begin{aligned}j(j+1)c_{j+1} + 2(l+1)(j+1)c_{j+1} - 2jc_j + [\rho_0 - 2(l+1)]c_j = 0 \\ \Rightarrow c_{j+1} = \frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}c_j.\end{aligned} \tag{1.4.86}$$

Truncation

At large j, hence large ρ, where higher powers dominate, we have

$$c_{j+1} \approx \frac{2j}{j(j+1)}c_j = \frac{2}{j+1}c_j, \tag{1.4.87}$$

so,

$$c_j \approx \frac{2_j}{j!} c_0, \tag{1.4.88}$$

then

$$v(\rho) \approx c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho}. \tag{1.4.89}$$

Therefore

$$u(\rho) = c_0 \rho^{l+1} e^{\rho}, \tag{1.4.90}$$

which is *bad* behaviour. So we must terminate the series, with some maximal integer j_{max} such that

$$c_{(j_{\text{max}}+1)} = 0, \tag{1.4.91}$$

which implies

$$2 \underbrace{(j_{\text{max}} + l + 1)}_{\equiv n} - \rho_0 = 0. \tag{1.4.92}$$

We now must have

$$\rho_{0,n} = 2n. \tag{1.4.93}$$

With this we have quantised our energy (which ρ_0 depends on). We can conclude about the degeneracy of the system:

Property 1.4.2.1 (Degeneracy of hydrogen atom)**.** From Equation 1.4.92, we can see that, given an arbitrary n, with j_{max} as a freely varying integer, we have $(n-1)$ possible values of l:

$$l = 0, 1, 2, \cdots, n-1. \tag{1.4.94}$$

And for each value of l, we refer back to Equation 1.4.42 to see that there are $(2l+1)$ possible values of m. The total degeneracy of E_n is therefore

$$d(n) = \sum_{l=0}^{n-1} (2l+1) = n^2. \tag{1.4.95}$$

Additionally, we make the following definitions:

Definition 1.4.2.1 (Bohr formula and Bohr radius)**.** Remembering that

$$\kappa = \frac{me^2}{2\pi\epsilon_0\hbar^2\rho_0}, \tag{1.4.96}$$

we can write

$$E_n = -\frac{\hbar^2\kappa_n^2}{2m} = -\frac{me^4}{8\pi^2\epsilon_0^2\hbar^2\rho_{0,n}^2} = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} \equiv \frac{E_1}{n^2}, \tag{1.4.97}$$

where n can be positive integers.
Also we have

$$\kappa = \left(\frac{me^2}{4\pi\epsilon_0\hbar^2}\right)\frac{1}{n} \equiv \frac{1}{an}, \tag{1.4.98}$$

where a is the **Bohr radius**, and $E_1 \equiv -1$ Ry $\equiv -1/2$ Ha.

Now we should return to the solution to the radial equation:

$$R_{nl}(r) = \frac{1}{r}u_{nl}(\rho) = \frac{1}{r}\rho^{l+1}e^{-\rho}v(\rho), \tag{1.4.99}$$

where $v_{nl}(\rho)$ is a polynomial determined (up to an overall normalisation factor) by the recursion formula

$$c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)}c_j. \tag{1.4.100}$$

The degree of the polynomial is then $j_{\text{max}} = n-l-1$ in ρ. The polynomial can be *written in terms of* **associated Laguerre polynomials**:

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho). \tag{1.4.101}$$

They are defined as follows

Definition 1.4.2.2 (Laguerre polynomials)**.**

$$L_q(x) \equiv e^x\frac{\mathrm{d}^q}{\mathrm{d}x^q}(e^{-x}x^q) \tag{1.4.102}$$

is the Laguerre polynomial of degree q, and

$$L_{q-p}^p(x) \equiv (-1)^p\frac{\mathrm{d}^p}{\mathrm{d}x^p}[L_q(x)], \tag{1.4.103}$$

is the associated Laguerre polynomial.

Now the complete and normalised radial solution can be written as

$$\begin{aligned} R_{nl}(r) &= A_0 \cdot \frac{1}{na}\left(\frac{r}{na}\right)^l e^{-r/na}\left[L^{2l+1}_{n-l-1}(2r/na)\right] \\ &= \left[\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2} e^{-r/na}\left(\frac{2r}{na}\right)^l \left[L^{2l+1}_{n-l-1}(2r/na)\right]. \end{aligned} \tag{1.4.104}$$

Property 1.4.2.2 (Complete hydrogen wavefunction)**.** The complete solution to this eigenvalue problem

$$H\psi = E\psi \tag{1.4.105}$$

is

$$\begin{aligned} \psi_{nlm} =& R_{nl}(r) Y_l^m(\theta,\phi) \\ =& \epsilon \left[\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} \\ & \times e^{-r/na}\left(\frac{2r}{na}\right)^l L^{2l+1}_{n-l-1}(2r/na) P_l^m(\cos\theta) e^{im\phi}, \end{aligned} \tag{1.4.106}$$

with

$$E = \frac{E_1}{n^2},\ n = 1, 2, 3, \cdots, \text{ or, in atomic units (Hartree), } E = \frac{1}{2n^2}, \tag{1.4.107}$$

where $E_1 \approx -13.6$ eV is the ground state energy of hydrogen.

The three indices specifying the wavefunction is called the **principal, azimuthal and magnetic quantum numbers**, respectively for n, l (henceforce styled as ℓ to avoid confusion) and m.

1.4.2.3 Larger nuclei

In many subsequent treatments of heavier atoms, we can use the form of hydrogen wavefunctions as a first approximation to their true wavefunctions. And this requires us to use the potential of the form

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{Z}{r}. \tag{1.4.108}$$

As the constant e^2 appear nowhere else, we just need to replace e^2 with Ze^2 everywhere. So now, as the full wavefunction involves it, the Bohr radius is replaced with

$$a \leftrightarrow \frac{a}{Z}. \tag{1.4.109}$$

So the full wavefunction is

$$R_{n\ell}(r) = -\left[\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)]^3}\right]^{1/2} Z^{\ell+3/2} e^{-Zr/na} \left(\frac{2r}{na}\right)^l [L^{2\ell+1}_{n-\ell=1}(2Zr/na)], \tag{1.4.110}$$

with the energy

$$E_n = -\frac{Z^2 E_1}{n^2} \tag{1.4.111}$$

1.4.2.4 Discussion of hydrogen atomic orbitals

Constructing real orbitals

By conventions in chemistry the azimuthal quantum numbers ℓ are given names $s, p, d, f, \cdots$ for $\ell = 0, 1, 2, 3, \cdots$. Now if we list the $2p$ wavefunctions:

$$\begin{aligned} \psi_{2p0} &= \left(\frac{1}{32\pi a^5}\right)^{1/2} re^{-r/2a}\cos\theta \\ \psi_{2p\pm1} &= \left(\frac{1}{64\pi a^5}\right)^{1/2} re^{-r/2a}\sin\theta e^{\pm i\phi}. \end{aligned} \tag{1.4.112}$$

Clearly, when $m \neq 0$, the wavefunctions won't be real, and we again invoke the all powerful Theorem 1.2.1.3 - we can always take linear combinations of them to make them real, as long as *they have the same energy*, which our wavefunctions do (m gives the $2\ell + 1$ degenerate states). Now, we tend to visualise better with Cartesian coordinates and that's what we'll re-write our wavefunctions with:

$$\begin{aligned} &\psi_{2p,0} \propto ze^{-r/2a} \\ &\psi_{2p,+1} \propto re^{-r/2a}\sin\theta e^{i\phi} = r\sin\theta(\cos\phi + i\sin\phi)e^{-r/2a} = (x+iy)e^{-r/2a} \\ &\psi_{2p,-1} \propto (x-iy)e^{-r/2a}. \end{aligned} \tag{1.4.113}$$

Following the recipe given in the proof of Theorem 1.2.1.3 (noting that $\psi_{2p,+1}$ and $\psi_{2p,-1}$ are complex conjugates of each other) and by convention (which is just so that the plots actually align with x and y axes), we construct

Definition 1.4.2.3 (Construction of p orbitals)**.**

$$\psi_{2p_x} \equiv \frac{1}{\sqrt{2}}(-\psi_{2p,+1} + \psi_{2p,-1}) \propto x e^{-r/2a} \tag{1.4.114a}$$

$$\psi_{2p_y} \equiv \frac{1}{\sqrt{2}} i(\psi_{2p,+1} + \psi_{2p,-1}) \propto y e^{-r/2a} \tag{1.4.114b}$$

$$\psi_{2p_z} \equiv \psi_{2p,0} \propto z e^{-r/2a}. \tag{1.4.114c}$$

The factors of $1/\sqrt{2}$ are only there to normalise the combined wavefunction and plays no role whatsoever for Theorem 1.2.1.3 to apply.

Now note that Theorem 1.2.1.3 only applies when the eigenvalues are the same, which these are, for H and L^2 but not for L_z (see Theorem 1.4.3.2), so the linearly combined orbitals p_x and p_y todo-supo: should not be acted on by L_z?
Now, for $3d$ orbitals, we have

$$\begin{aligned}
\psi_{3d,0} &= \frac{1}{81\sqrt{6\pi a^7}} r^2 e^{-r/3a}(3\cos^2\theta - 1) \\
\psi_{3d,\pm 1} &= \frac{1}{81\sqrt{\pi a^7}} r^2 e^{-r/3a} \sin\theta\cos\theta e^{\pm i\phi} \\
\psi_{3d,\pm 2} &= \frac{1}{162\sqrt{\pi a^7}} r^2 e^{-r/3a} \sin^2\theta e^{\pm 2i\phi}.
\end{aligned} \tag{1.4.115}$$

Re-writing these in Cartesian we have

$$\psi_{3d,0} \propto (3z^2 - r^2) e^{-r/3a} \tag{1.4.116a}$$

$$\psi_{3d,\pm 1} \propto z(x \pm iy) e^{-r/3a} \tag{1.4.116b}$$

$$\psi_{3d,\pm 2} \propto (x^2 - y^2 \pm ixy) e^{-r/3a}. \tag{1.4.116c}$$

Definition 1.4.2.4 (Construction of d orbitals)**.** Making linear combinations for same $|m|$'s, we have

$$\psi_{3d_{z^2}} = \psi_{3d,0} \propto (3z^2 - r^2) e^{-r/3a} \tag{1.4.117a}$$

$$\psi_{3d_{xz}} = \frac{1}{\sqrt{2}}(\psi_{3d,+1} + \psi_{3d,-1}) \propto xy e^{-r/3a} \tag{1.4.117b}$$

$$\psi_{3d_{yz}} = \frac{1}{\sqrt{2}} i(-\psi_{3d,+1} + \psi_{3d,-1}) \propto yz e^{-r/3a} \tag{1.4.117c}$$

$$\psi_{3d_{x^2-y^2}} = \frac{1}{\sqrt{2}}(\psi_{3d,+2} + \psi_{3d,-2}) \propto (x^2 - y^2) e^{-r/3a} \tag{1.4.117d}$$

$$\psi_{3d_{xy}} = \frac{1}{\sqrt{2}} i(-\psi_{3d,+2} + \psi_{3d,-2}) \propto xy e^{-r/3a}. \tag{1.4.117e}$$

Nodal structure

There are two types of nodes in complete hydrogen wavefunctions: radial and angular.

The **radial nodes** arise entirely from the *associated Laguerre polynomials* as the exponential and the polynomial terms do not introduce nodes. The radial wavefunctions with the same l, *i.e.*, R_{ns}, R_{np} and so on are the solutions to the *same* eigenproblem and so they have to be orthogonal to each other wrt radial integration. This means that each successive radial wavefunction must have one more radial node as n increases by one. Another reason this should be the case is because with more nodes the energy will rise, as is expected for higher n.

The **angular nodes** arise from the *associated Legendre polynomials* , which means that all the nodes are *polar* in nature. The angular equation however is *not* an eigenvalue equation, and as such we do not have *a priori* reason to assert that they are orthogonal. But nonetheless they are indeed orthogonal, and it's proven in Property 1.4.1.3. So we again have the same behaviour as in the radial wavefunction with increasing l giving increasing number of nodes.

In all, the atomic orbitals with principal quantum number n all have $n-1$ nodal surfaces. Of these, l are angular nodes and the rest are radial.

Radial probability density

The radial probability density is defined by

Definition 1.4.2.5 (Radial probability density)**.**

$$\begin{aligned}
P_{nl}(r)\,\mathrm{d}r &= \int_0^{2\pi}\int_0^{\pi} |\psi|^2 r^2\,\mathrm{d}r\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&= \int_0^{2\pi}\int_0^{\pi} (R_{nl}Y_{lm})^* R_{nl}Y_{lm} r^2\,\mathrm{d}r\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&= r^2R_{nl}^2\,\mathrm{d}r\underbrace{\int_0^{2\pi}\int_0^{\pi} Y_{lm}^*Y_{lm}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi}_{1\text{ since normalised}} \\
&= r^2R_{nl}^2\,\mathrm{d}r
\end{aligned} \tag{1.4.118}$$

We can find the *most probable location* to find an electron by finding the maximum value of the probability distribution (the expression without $\mathrm{d}r$). Note that this is emphatically not the same as finding the expectation of r as mode and mean of a distribution are in general different.

1.4.3 Angular momentum

1.4.3.1 Operator properties

The classical angular momentum is

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}, \tag{1.4.119}$$

which means

$$L_x = yp_z - zp_y \tag{1.4.120}$$

and cyclical permutations thereof. We make the canonical substitutions ($p_x \to -i\hbar\partial/\partial x$ and so on) to get the quantum mechanical angular momentum operators:

Definition 1.4.3.1 (Angular momentum operators)**.**

$$\begin{aligned} L_x &= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ L_y &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ L_z &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right). \end{aligned} \tag{1.4.121}$$

The operators have the following commutator relationships:

Property 1.4.3.1 (Fundamental angular momentum commutator relations)**.** The commutators **do not commute with each other**:

$$\begin{aligned} [L_x, L_y] &= [yp_z - zp_y, zp_x - xp_z] \\ &= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z] \\ &= yp_x[p_z, z] - 0 - 0 + xp_y[z, p_z] \\ &= i\hbar(xp_y - yp_x) \\ &= i\hbar L_z. \end{aligned} \tag{1.4.122}$$

In the third and fourth lines we used the 3D canonical commutation relations (Property 1.4.1.1). Cyclic permutations follow:

$$[L_x, L_y] = i\hbar L_z,\ [L_z, L_x] = i\hbar L_y,\ [L_y, L_z] = i\hbar L_x. \tag{1.4.123}$$

Corollary 1.4.3.1 (Uncertainty)**.** The preceeding commutator relation means that the three components of angular momentum are **incompatible observables**, *i.e.*, they cannot be simulaneously measured. We obtain, from the generalised uncertainty principle (Theorem 1.3.5.1):

$$\sigma_{L_x}^2 \sigma_{L_y}^2 \geq \left(\frac{1}{2i} \langle i\hbar L_z \rangle \right)^2 = \frac{\hbar^2}{4} \langle L_z \rangle^2, \tag{1.4.124}$$

which implies

$$\sigma_{L_x} \sigma_{L_y} \geq \frac{\hbar}{2} |\langle L_z \rangle|. \tag{1.4.125}$$

We now introduce the operator for the square of total momentum, L^2:

$$L^2 \equiv L_x^2 + L_y^2 + L_z^2. \tag{1.4.126}$$

Property 1.4.3.2 (Commutator relations with L^2)**.** We can write that

$$\begin{aligned}
[L^2, L_x] &= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x] \\
&= L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z \\
&= -i\hbar([L_y, L_z] - [L_z, L_y]) \\
&= 0,
\end{aligned} \tag{1.4.127}$$

where in the second equality we have used the associativity of commutators (Property 1.3.5.1). We can compactly write

$$[L^2, \boldsymbol{L}] = 0. \tag{1.4.128}$$

This means that we can simultaneously measure the scalar total angular momentum and **one** component of the vectorial angular momentum, which is *conventionally chosen* to be L_z.

1.4.3.2 Angular momentum ladder operators

The above property means that L^2 and L_z (conventionally chosen) can have simultaneous eigenfunctions (Theorem 1.3.5.3), which is to say

$$L^2 f = \lambda f \text{ and } L_z f = \mu f. \tag{1.4.129}$$

And again we define two ladder operators:

Definition 1.4.3.2 (Angular momentum ladder operators)**.** Let

$$L_\pm \equiv L_x \pm iL_y. \tag{1.4.130}$$

The commutators with the ladder operators will be useful later on:

Property 1.4.3.3 (Commutators with $L_\pm$)**.** The commutator with L_z is

$$[L_z, L_\pm] = [L_z, L_x] \pm i[L_z, L_y] = i\hbar L_y \pm i(-i\hbar L_x) = \pm\hbar(L_x \pm iL_y). \tag{1.4.131}$$

And the commutator with L^2 is easy:

$$[L^2, L_\pm] = [L^2, L_x] \pm i[L^2, L_y] = 0. \tag{1.4.132}$$

Property 1.4.3.4 (Further property)**.**

$$\begin{aligned} L_\pm L_\mp &= (L_x \pm iL_y)(L_x \mp iL_y) \\ &= L_x^2 + L_y^2 \mp i(L_xL_y - L_yL_x) \\ &= L^2 - L_z^2 \pm \hbar L_z \end{aligned} \tag{1.4.133}$$

which implies

$$L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z. \tag{1.4.134}$$

From Equation 1.4.132 we can write

$$L^2 L_\pm f = L_\pm L^2 f = L_\pm \lambda f = \lambda L_\pm f. \tag{1.4.135}$$

This means that $L_\pm f$ is an eigenfunction of $L_\pm$ and L_z, with the same eigenvalue λ, meaning that the total scalar angular momentum is unchanged. And from Equation 1.4.131 we can write

$$\begin{aligned} L_z L_\pm f &= (L_z L_\pm - L_\pm L_z)f + L_\pm L_z f \\ &= \pm\hbar L_\pm f + L_\pm \mu f \\ &= (\mu \pm \hbar)(L_\pm f). \end{aligned} \tag{1.4.136}$$

Evidently, L_+ increases the eigenvalue of L_z by $\hbar$ and vice versa for L_-.
So we now know that, given total squared angular momentum λ, we can obtain, by way of our ladder operators, a range of states. But there must be a upper and lower limit of L_z such that it's within 0 to maximum angular momentum.

The 'top rung' wavefunction must have that

$$L_+ f_t = 0. \tag{1.4.137}$$

We now let the eigenvalue of L_z be $\hbar l$, where l is *not necessarily* the azimuthal quantum number ℓ as discussed before, but we'll show in time that it actually is. Anyway, we can write

$$L_z f_t = \hbar l f_t,\ L^2 f_t = \lambda f_t. \tag{1.4.138}$$

It follows, from Property 1.4.3.4, that

$$L^2 f_t = (L_- L_+ + L_z^2 + \hbar L_z) f_t = (0 + \hbar^2 l^2 + \hbar^2 l) f_t = \hbar^2 l(l+1) f_t, \tag{1.4.139}$$

where we have chosen to use $L_- L_+$ because we need to have L_+ directly left-multiplying f_t.

So we conclude that

$$\lambda = \hbar^2 l(l+1). \tag{1.4.140}$$

For the bottom rung, we must have that

$$L_- f_b = 0. \tag{1.4.141}$$

Let the eigenvalue of L_z at bottom rung be $\hbar l'$L

$$L_z f_b = \hbar l' f_b,\ L^2 f_b = \lambda. \tag{1.4.142}$$

Similarly, we write

$$L^2 f_b = (L_+ L_- + L_z^2 - \hbar L_z) f_b = (0 + \hbar^2 l'^2 - \hbar^2 l') f_b = \hbar^2 l'(l'-1) f_b, \tag{1.4.143}$$

so

$$\lambda = \hbar^2 l'(l'-1). \tag{1.4.144}$$

Because we must have that $l > l'$,

$$l' = -l. \tag{1.4.145}$$

So now we have our range of eigenvalues of L_z, and let's say the eigenvalues are $m\hbar$, where m again is not yet necessarily the magnetic quantum number, and that m goes from $-l$ to l in some number of integer steps, say N, so

$$-l + N = l \ \Rightarrow\ l = \frac{N}{2}. \tag{1.4.146}$$

We have now effectively *quantised* l to integers and half-integers [4]. And given a value of l we have $2l+1$ values of m.

Property 1.4.3.5 (Proportionality constant of ladder operators)**.** We have

$$L_{\pm} f_l^m = A_l^m f_l^{m\pm1}, \tag{1.4.147}$$

where

$$A_l^m = \hbar\sqrt{l(l+1) - m^2 \mp m} = \hbar\sqrt{(l \mp m)(l \pm m + 1)}. \tag{1.4.148}$$

Proof. We know that L_x and L_y are hermitian as they are observables (Theorem 1.3.2.1). So we know that $L_{\pm}$ and $L_{\mp}$ are hermitian conjugates:

$$L_{\pm}^{\dagger} = (L_x + iL_y)^{\dagger} = L_x - iL_y = L_{\mp}. \tag{1.4.149}$$

Since we know

$$L_{\pm} f_l^m = A_l^m f_l^{m+1}, \tag{1.4.150}$$

so

$$\begin{aligned} \langle L_{\pm} f_l^m | L_{\pm} f_l^m \rangle &= \langle f_l^m | L_{\mp} L_{\pm} f_l^m \rangle \\ &= \langle f_l^m | (L^2 - L_z^2 \mp \hbar L_z) f_l^m \rangle \\ &= \hbar^2 [l(l+1) - m^2 \mp m] \langle f_l^m | f_l^m \rangle \\ &\equiv (A_l^m)^2 \langle f_l^{m\pm1} | f_l^{m\pm1} \rangle. \end{aligned} \tag{1.4.151}$$

As all the eigenfunctions are assumed to be normalised, we must have that

$$A_l^m = \hbar\sqrt{l(l+1) - m^2 \mp m} = \hbar\sqrt{(l \mp m)(l \pm m + 1)}. \tag{1.4.152}$$

Applying L_+ to $f_t = f_l^l$ or applying L_- to $f_b = f_l^{-l}$ gives zero, as required. ☐

We prove some further commutator relationships.

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[4] Here we have no reason to exclude the half-integers because this is an entirely algebraic treatment. But when we link it to the spherical harmonics in Equations 1.4.169 and 1.4.170, we will have to restrict ourselves to integers. But in the treatment of spin angular momentum, we again have no reason to restrict to integers and it'll turn out that we indeed need to admit half-integers.

Property 1.4.3.6 (Further commutator relations involving L)**.**

$$\begin{gathered}[L_z, x] = i\hbar y,\ [L_z, y] = -i\hbar x,\ [L_z, z] = 0. \\ \text{compactly, } [L_{x_k}, x_i] = i\hbar\epsilon_{ijk}x_j\end{gathered} \tag{1.4.153}$$

And also

$$[L_{x_k}, p_{x_i}] = i\hbar\epsilon_{ijk}p_{x_j}. \tag{1.4.154}$$

Proof is similar to ones we have gone through before.

We can apply this to evaluate $[L_z, L_x]$:

$$\begin{aligned}[L_z, L_x] &= [L_z, (yp_z - zp_y)] \\ &= [L_z, yp_z] - [L_z, zp_y] \\ &= y[L_z, p_z] + [L_z, y]p_z - z[L_z, p_y] - [L_z, z]p_y \\ &= i\hbar(zp_y - xp_z) \\ &= i\hbar L_y.\end{aligned} \tag{1.4.155}$$

Now we evaluate $[L_z, r^2]$:

$$\begin{aligned}[L_z, r^2]f &= [xp_y - yp_x, r^2]f \\ &= [xp_y, r^2]f - [yp_x, r^2]f \\ &= i\hbar(2xyf - xr^2f_y - 2xyf - yr^2f_x - r^2xf_y + r^2yf_x) \\ &= 0.\end{aligned} \tag{1.4.156}$$

And

$$\begin{aligned}[L_z, p^2]f &= [L_z, p_x^2 + p_y^2] \\ &= [xp_y - yp_x, p_x^2]f + [xp_y - yp_x, p_y^2]f \\ &= [xp_y, p_x^2]f - [yp_x, p_y^2]f \\ &= i\hbar^3(xf_{xxy} - xf_{xxy} - 2f_{xy} - yf_{yyx} + yf_{yyx} + 2f_{xy}) \\ &= 0\end{aligned} \tag{1.4.157}$$

And as the Hamiltonian is

$$H \equiv \frac{p^2}{2m} + V(r), \tag{1.4.158}$$

where we have assume that the potential is a function of *only* r. As L_z commutes with p^2 and r^2, and by extension, *any* function of only r (as r^2 can be measured to any degree of accuracy with L_z, any function of the *scalar* r can be evaluated also). We therefore have an important theorem

Theorem 1.4.3.1 (Commutator of angular momentum and Hamiltonian)**.** H, L_z and L^2 are mutually compatible observables.

1.4.3.3 Eigenfunctions

We need to rewrite $\boldsymbol{L}$'s in spherical coordinates. We first note that in classical mechanics,

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} \tag{1.4.159}$$

making the canonical substitutions we have, for our vectorial quantum mechanical operator,

$$\begin{aligned}
\hat{\boldsymbol{L}} &= \frac{\hbar}{i}(\boldsymbol{r} \times \boldsymbol{\nabla}) = \frac{\hbar}{i} r(\hat{\boldsymbol{r}} \times \boldsymbol{\nabla}) && \text{(1.4.160a)}\\
&= \frac{\hbar}{i} r\hat{\boldsymbol{r}} \times \left(\hat{\boldsymbol{r}}\frac{\partial}{\partial r} + \hat{\boldsymbol{\theta}}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\boldsymbol{\phi}}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}\right) && \text{(1.4.160b)}\\
&= \frac{\hbar}{i}\left[r(\hat{\boldsymbol{r}} \times \hat{\boldsymbol{r}})\frac{\partial}{\partial r} + (\hat{\boldsymbol{r}} \times \hat{\boldsymbol{\theta}})\frac{\partial}{\partial \theta} + (\hat{\boldsymbol{r}} \times \hat{\boldsymbol{\phi}})\frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\right] && \text{(1.4.160c)}\\
&= \frac{\hbar}{i}\left(\hat{\boldsymbol{\phi}}\frac{\partial}{\partial \theta} - \hat{\boldsymbol{\theta}}\frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\right) && \text{(1.4.160d)}\\
&= \frac{\hbar}{i}\left[(-\sin\phi\hat{\boldsymbol{\imath}} + \cos\phi\hat{\boldsymbol{\jmath}})\frac{\partial}{\partial \theta} - (\cos\theta\cos\phi\hat{\boldsymbol{\imath}} + \cos\theta\sin\phi\hat{\boldsymbol{\jmath}} - \sin\theta\hat{\boldsymbol{k}})\frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\right], && \text{(1.4.160e)}
\end{aligned}$$

where in Equation 1.4.160d we have used the fact that the unit vectors are oriented $\{\hat{\boldsymbol{r}}, \hat{\boldsymbol{\theta}}, \hat{\boldsymbol{\phi}}\}$ as related by the right-hand rule. Also, the unit vectors are obtained by

$$\hat{\boldsymbol{e}}_{\boldsymbol{i}} = \frac{\partial \boldsymbol{r}/\partial e_i}{|\partial \boldsymbol{r}/\partial e_i|}. \tag{1.4.161}$$

We can identify from Equation 1.4.160e the three components:

Property 1.4.3.7 (Angular momentum operators in spherical coordinates)**.**

$$\begin{aligned}
L_x &= \frac{\hbar}{i}\left(-\sin\phi\frac{\partial}{\partial \theta} - \cos\phi\cot\theta\frac{\partial}{\partial \phi}\right), && \text{(1.4.162a)}\\
L_y &= \frac{\hbar}{i}\left(+\cos\phi\frac{\partial}{\partial \theta} - \sin\phi\cot\theta\frac{\partial}{\partial \phi}\right), && \text{(1.4.162b)}\\
L_z &= \frac{\hbar}{i}\frac{\partial}{\partial \phi}. && \text{(1.4.162c)}
\end{aligned}$$

The same result can be obtained by chain rule (and it's admittedly faster).

Property 1.4.3.8 (Angular momentum ladder operators in spherical coordinates)**.**

$$L_\pm = \pm\hbar e^{\pm i\phi}\left(\frac{\partial}{\partial\theta} \pm i\cot\theta\frac{\partial}{\partial\phi}\right), \tag{1.4.163}$$

$$L_+L_- = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\phi^2} + i\frac{\partial}{\partial\phi}\right), \tag{1.4.164}$$

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \tag{1.4.165}$$

Proof. We can readily write

$$\begin{aligned} L_\pm = L_x \pm iL_y &= \frac{\hbar}{i}\left[(-\sin\phi \pm i\cos\phi)\frac{\partial}{\partial\phi} - (\cos\phi \pm i\sin\phi)\cot\theta\frac{\partial}{\partial\theta}\right] \\ &= \pm\hbar e^{\pm i\phi}\left(\frac{\partial}{\partial\theta} \pm i\cot\theta\frac{\partial}{\partial\phi}\right) \end{aligned} \tag{1.4.166}$$

Now the product of two ladder operators is more arduous:

$$\begin{aligned} L_+L_-f =& \hbar e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)\left[-\hbar e^{-i\phi}\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}\right)\right]f \\ =& -\hbar^2 e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)\left[e^{-i\phi}\left(f_\theta - i\cot\theta f_\phi\right)\right] \\ =& -\hbar^2 e^{i\phi}\left[\frac{\partial}{\partial\theta}\left(e^{i\phi}f_\theta - i\cot\theta e^{-i\phi}f_\phi\right) + i\cot\theta\frac{\partial}{\partial\phi}\left(e^{-i\phi}f_\theta - i\cot\theta e^{-i\phi}f_\phi\right)\right] \\ =& \cdots \\ =& -\hbar^2 e^{i\phi}(e^{-i\phi}f_{\theta\theta} + ie^{-i\phi}\csc^2\theta f_\phi + \cot\theta e^{-i\phi}f_\theta - \cot^2 ie^{-i\phi} + \cot^2\theta e^{-i\phi}f_{\phi\phi}) \\ =& -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\phi^2} + i\frac{\partial}{\partial\phi}\right)f. \end{aligned} \tag{1.4.167}$$

And finally, using Equation 1.4.135, we can write

$$\begin{aligned} L^2 &= L_+L_- + L_z^2 - \hbar L_z \\ &= -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \csc^2\theta\frac{\partial^2}{\partial\phi^2}\right) \\ &= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \end{aligned} \tag{1.4.168}$$

□

We're all set to determine $f_l^m(\theta,\phi)$, which is an eigenfunction of L^2 and L_z, with eigenvalues $\hbar^2 l(l+1)$ and $m\hbar$ respectively, remembering that m and l do not correspond to the spherical harmonics indices *yet*. We can therefore write:

$$L^2 f_l^m = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]f_l^m = \hbar^2 l(l+1)f_l^m, \tag{1.4.169}$$

which is exactly the same as the angular equation (Equation 1.4.15). For L_z we can write

$$L_z f_l^m = \frac{\hbar}{i}\frac{\partial}{\partial\phi}f_l^m = \hbar m f_l^m, \tag{1.4.170}$$

which is the azimuthal equation (Equation 1.4.17). We can therefore identify f_l^m with $Y_\ell^m(\theta,\phi)$ and therefore m with the magnetic quantum number and l with the azimuthal quantum number. We reach the important conclusion

Theorem 1.4.3.2 (Eigenfunctions of L^2, L_z and H)**.** The spherical harmonic, $Y_\ell^m(\theta,\phi)$ are the eigenfunctions of the three *commuting* operators H, L^2 and L_z with the eigenequations:

$$H\psi = E\psi,\ L^2\psi = \hbar^2 l(l+1)\psi,\ L_z\psi = \hbar m\psi. \tag{1.4.171}$$

Incidentally[5], now that we have determined that the spherical harmonics are the function f here, we can see how the introduction of the Condon-Shortley phase in Equation 1.4.45 simplifies notation: the ladder operators alternate the signs of the wavefunctions by means of differentation of $\cos\theta$ and so on, so to be able to write

$$L_\pm Y_l^m = AY_l^{m\pm1}, \tag{1.4.172}$$

where A is always positive as in Property 1.4.3.5, we have to absorb the phase factor into the spherical harmonics expression.

Another aside is, the Schrödinger equation in spherical coordinates can be more compactly written as

$$\frac{1}{2mr^2}\left[-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+L^2\right]\psi + V\psi = E\psi. \tag{1.4.173}$$

---

[5] Adapted from p.778 of [1]

Corollary 1.4.3.2 (Spherical harmonics at the top of the ladder)**.** The angular wavefunction at the top of the ladder is

$$Y_\ell^\ell(\theta, \phi) = Ce^{i\ell\phi} \sin^\ell \theta, \tag{1.4.174}$$

where C is the normalisation constant.

Proof. We construct the proof with the help of the ladder operators:
We know that

$$L_+ Y_\ell^\ell = 0 \ \Rightarrow \ \hbar e^{i\phi} \left[\frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right] \underbrace{Y_\ell^\ell}_{\equiv f} = 0. \tag{1.4.175}$$

We can write

$$f_\theta + i \cot\theta f_\phi = 0 \ \Rightarrow \ \tan\theta f_\theta = -i f_\phi, \tag{1.4.176}$$

where we have noted that $\hbar e^{i\phi}$ is always non-zero, hence the content of the square bracket must be zero. We try separation of variables:

$$f(\theta, \phi) = g(\theta) h(\phi). \tag{1.4.177}$$

Substituting we have

$$\tan\theta \frac{g_\theta}{g} = -i \frac{h_\phi}{h} \equiv \ell, \tag{1.4.178}$$

where we made the separation constant ℓ because we *know* the index can only be ℓ.
Solving both equations give us

$$f = Ce^{i\ell\phi} \sin^\ell \theta. \tag{1.4.179}$$

☐

1.4.4 The rigid rotor

We finally consider the rigid rotor, which is a model of two particles with mass m_1 and m_2, at fixed radius r_1 and r_2 away from the centre of mass. There is no V in the Schrödinger equation in this case, so

$$H = K = \frac{1}{2I} L^2. \tag{1.4.180}$$

Now, to calculate moment of inertia, we know

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 \\ &= \frac{1}{m_1 + m_2} \left(m_1 m_2 r_1^2 + m_1 m_2 r_2^2 + m_1^2 r_1^2 + m_2^2 r_2^2 \right). \end{aligned} \tag{1.4.181}$$

Now that, we recall that our two masses are rotating around the centre of mass, **defined by**

$$m_1 r_1 = m_2 r_2. \tag{1.4.182}$$

So we have

$$\begin{aligned} m_1 r_1 - m_2 r_2 &= 0 \\ m_1^2 r_1^2 + m_2^2 r_2^2 &= 2 m_1 m_2 r_1 r_2. \end{aligned} \tag{1.4.183}$$

So clearly now

$$I = \frac{m_1 m_2}{m_1 + m_2}(r_1 + r_2)^2 \equiv \mu r^2. \tag{1.4.184}$$

L^2 is, from Equation 1.4.168,

$$L^2 = \hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]. \tag{1.4.185}$$

So we have our Hamiltonian:

$$H = -\frac{\hbar^2}{2I} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]. \tag{1.4.186}$$

The eigenproblem is just

$$\frac{1}{2I} L^2 \psi = E\psi. \tag{1.4.187}$$

We have already solved this, the eigenfunction is simply the spherical harmonic Y_J^m[6], and the allowed energies are

$$E_J = \frac{\hbar^2}{2I} J(J+1) \equiv BJ(J+1),\ J = 0, 1, 2, \cdots. \tag{1.4.188}$$

The degeneracy is the same $(2J+1)$ as the angular wavefunction.

todo: Selection rule and transition energies, priority: only when gone through p.177 of [13].

1.4.5 Spin

1.4.5.1 Formalism

Elementary particles carry **intrinsic** spins, *i.e.*, it is unrelated to actual rotation of matter. We also make the assertion that the operator formalism of spin is entirely analogous to that of angular momentumm, which is to say

---

[6] We use J instead of ℓ as the bottom index here to avoid confusion with the azimuthal quantum number of the hydrogen atom, as is standard practice.

Definition 1.4.5.1 (Commutation relations of spin operators)**.**

$$[S_x, S_y] = i\hbar S_z \tag{1.4.189}$$

and cyclic permutations thereof.

And it follows that the eigen*vectors* [7] of S^2 and S_z satisfy

Property 1.4.5.1 (Eigenfunctions of spin operators)**.**

$$S^2|s,m\rangle = \hbar^2 s(s+1)|s,m\rangle,\ S_z|s,m\rangle = \hbar m|s,m\rangle, \tag{1.4.190}$$

and

$$S_\pm|s,m\rangle = \hbar\sqrt{s(s+1) - m(m\pm 1)}|s,(m\pm 1)\rangle, \tag{1.4.191}$$

where

$$S_\pm \equiv S_x \pm iS_y. \tag{1.4.192}$$

We admit these values of s and m:

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, \cdots,\ m = -s, (-s+1), \cdots, (s-1), s. \tag{1.4.193}$$

s turns out to be an intrinsic and immutable value specific to each elementary particle: electrons have spin $1/2$, photons 1, and so on.

1.4.5.2 Spin one half

We focus on the case of spin $1/2$, and the treatment can be easily generalised to other spins. Now there are just two eigenstates: **spin up** (↑, $|1/2,1/2\rangle$), and **spin down**, (↓ , $|1/2,-1/2\rangle$). At this point we assert that the general state of a spin $1/2$ particle can be expressed as a two-element column matrix called a **spinor**, whose elements can be complex: todo-supo: can this even be derived?

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} \equiv a\chi_+ + b\chi_-, \tag{1.4.194}$$

---

[7] We'll soon show that they are indeed vectors and not continuous functions like before

where

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \ \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{1.4.195}$$

representing spin up and down states.

Therefore spin operators *must* be 2×2 matrices, and we will work out their components now. We note that

$$S^2\chi_+ = \frac{3}{4}\hbar^2\chi_+, \ S^2\chi_- = \frac{3}{4}\hbar^2\chi_-. \tag{1.4.196}$$

Therefore we need to solve the matrix equation

$$\underbrace{\begin{pmatrix} c & d \\ e & f \end{pmatrix}}_{S^2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}. \tag{1.4.197}$$

Solving the equation gives

$$S^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{1.4.198}$$

Similar, we use

$$S_z\chi_+ = \frac{\hbar}{2}\chi_+, \ S_z\chi_- = -\frac{\hbar}{2}\chi_- \tag{1.4.199}$$

to work out that

$$S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{1.4.200}$$

Similarly, from

$$= S_+\chi_- = \hbar\chi_+, \ S_-\chi_+ = \hbar\chi_-, \ S_+\chi_+ = S_-\chi_- = 0, \tag{1.4.201}$$

we get

$$S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \ S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{1.4.202}$$

.

And it immediately follwos from definition that

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \ S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \tag{1.4.203}$$

We can compactly write

Property 1.4.5.2 (Components of spin operators)**.**

$$\boldsymbol{S} = \frac{\hbar}{2}\boldsymbol{\sigma}, \tag{1.4.204}$$

where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \; \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \; \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{1.4.205}$$

These σ's are called **Pauli spin matrices**. And

$$S_x^2 = S_y^2 = S_z^2 = \frac{\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \tag{1.4.206}$$

which is to say measurements of $S_{x_i}^2$ are sure to yield only $\hbar^2/4$.

The eigenspinors of S_z are χ_{pm} with eigenvalues $\pm\hbar/2$. So if we measure S_z on a particle in the general state (Equation 1.4.194), we might obtain either of $\pm\hbar/2$ with probabilities $|a|^2$ and $|b|^2$, therefore we must normalise:

$$|a|^2 + |b|^2 = 1, \tag{1.4.207}$$

where a and b can be complex.

If we want to know the outcomes of measuring S_x, we need to know its eigenvalues and eigenspinors. Solving the characteristic equation for S_x we have

$$\chi_+^{(x)} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}, \; \chi_-^{(x)} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}, \tag{1.4.208}$$

with eigenvalues $\pm\hbar/2$. This shuoldn't be surprising as axes are arbitrarily oriented. Similarly, for S_y, the two eigenspinors are

$$\chi_\pm^{(y)} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \pm i \end{pmatrix} \tag{1.4.209}$$

,

with the eigenvalues $\pm\hbar/2$ again of course.

As the eigenvectors of a hermitian matrix, they must span the space, that's why *any* generic spinor χ can be expressed as a linear combination of these eigenspinors.

1.4.5.3 Addition of angular momenta - the intuitive way

Suppose we have two spin half particles, for example an electron and a proton as in the ground state of hydrogen atom [8]. Each can take up spin up or down state so there are four possiblities in all:

$$\uparrow\uparrow,\ \uparrow\downarrow,\ \downarrow\uparrow,\ \downarrow\downarrow, \tag{1.4.210}$$

todo-supo: what's happening here? external product? where the first arrow refers to the electron and second the proton. We want to get the total angular momentum of the atom. Remembering that this is the ground state and $L = 0$, we let

$$\boldsymbol{S} \equiv \boldsymbol{S}^{(1)} + \boldsymbol{S}^{(2)}. \tag{1.4.211}$$

Each of these four composite states is an eigenstate of S_z as the z components simply add together:

$$\begin{aligned} S_z\chi_1\chi_2 &= (S_z^{(1)} + S_z^{(2)})\chi_1\chi_2 \\ &= (S_z^{(1)}\chi_1)\chi_2 + \chi_1(S_z^{(2)}\chi_2) \\ &= \hbar(m_1 + m_2)\chi_1\chi_2. \end{aligned} \tag{1.4.212}$$

The quantum numbers for the composite system, $m = m_1 + m_2$, are

$$\begin{aligned} &\uparrow\uparrow\text{:}\ \ m = 1 \\ &\uparrow\downarrow\text{:}\ \ m = 0 \\ &\downarrow\uparrow\text{:}\ \ m = 0 \\ &\downarrow\downarrow\text{:}\ \ m = -1. \end{aligned} \tag{1.4.213}$$

Does this mean, then, that we have four states, with one transition $\Delta m = 0$? This is unphysical because if we apply the lowering operator to the top state we find:

$$\begin{aligned} S_-(\uparrow\uparrow) &= (S_-^{(1)}\uparrow)\uparrow + \uparrow(S_-^{(2)}\uparrow) \\ &= \hbar(\downarrow\uparrow + \uparrow\downarrow). \end{aligned} \tag{1.4.214}$$

Applying the lowering operator again we find

$$\begin{aligned} S_-(\downarrow\uparrow + \uparrow\downarrow) &\propto (S_-^{(1)} + S_-^{(2)})(\downarrow\uparrow + \uparrow\downarrow) \\ &\propto \downarrow\downarrow . \end{aligned} \tag{1.4.215}$$

---

[8] This is so that the angular momentum is zero.

This means that there are only three states and the middle state is a superposition of two 'mixed' states, and as we see m runs from -1 to $+1$, which means that the total angular momentum $s = 1$

Property 1.4.5.3 (Triplet state)**.** The three (triplet) states with $s = 1$ are

$$\begin{aligned} |1,1\rangle &= \uparrow\uparrow \\ |1,0\rangle &= \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \text{ (symmetric wrt exchange of labels)} \\ |1,-1\rangle &= \downarrow\downarrow . \end{aligned} \tag{1.4.216}$$

However, we notice that for the state

$$|0,0\rangle \equiv \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \text{ (antisymmetric wrt exchange of labels)}, \tag{1.4.217}$$

if we apply the raising or lowering operator we get zero. This means that this state has $s = 0$, therefore the notation.

Therefore we see that the combination of two spin half particles can carry a total spin of either 1 or 0. Therefore according to Equation 1.4.190, an eigenvalue of $2\hbar^2$ or 0 must be obtained if the triplet or singlet state is acted on by S^2. We check if this is the case: first we write S^2:

$$\begin{aligned} S^2 &= (\boldsymbol{S}^{(1)} + \boldsymbol{S}^{(2)}) \cdot (\boldsymbol{S}^{(1)} + \boldsymbol{S}^{(2)}) \\ &= (S^{(1)})^2 + (S^{(2)})^2 + 2\boldsymbol{S}^{(1)} \cdot \boldsymbol{S}^{(2)} \\ &= (S^{(1)})^2 + (S^{(2)})^2 + 2(S_x^{(1)} S_x^{(2)} + S_y^{(1)} S_y^{(2)} + S_z^{(1)} S_z^{(2)}). \end{aligned} \tag{1.4.218}$$

So

$$\begin{aligned} S^2|1,1\rangle &= S^2 \uparrow\uparrow \\ &= \frac{3\hbar^2}{4}[\uparrow\uparrow + \uparrow\uparrow + 2(\downarrow\downarrow - \downarrow\downarrow + \uparrow\uparrow)] \\ &= 2\hbar^2, \end{aligned} \tag{1.4.219}$$

where we have used Equation 1.4.205 to get the effects of the operators on spinors.

Other triplet states and the singlet state can be checked similarly.

1.4.5.4 Addition of angular momenta - the ground-up way

The following section is adapted from Chapter 4 of [2]. We consider a system where there are two sources of angular momentum, j_1 and j_2, which includes orbital and spin momentum. The complete state of the system can be specified as

$$|j_1 m_{j1}; j_2 m_{j_2}\rangle, \tag{1.4.220}$$

because the operators $J_1^2, J_2^2, J_{1z}, J_{2z}$ commute (m_j is the eigenvalue of J_z).

We now see that the total angular momentum, $j = j_1 + j_2$, can also be specified simultaneously. We first see that it is really an angular momentum by evaluating the commutators of its components (we know that the one particle j's are angular momenta and we know their commutators):

$$\begin{aligned}[J_x, J_y] &= [J_{1x} + J_{2x}, J_{1y} + J_{2y}] \\ &= [J_{1x}, J_{1y}] + [J_{2x}, J_{2y}] + 0 + 0 \\ &= i\hbar J_{1z} + i\hbar J_{2z} \\ &= i\hbar J_z.\end{aligned} \tag{1.4.221}$$

This is characteristic of angular momentum. And so we know from the generalised (Theorem 1.4.3.2) properties of angular momentum that its allowed magnitude is[9]

$$\hbar\sqrt{j(j+1)}, \tag{1.4.222}$$

where j can take integer or half-integer values. Its z-component is

$$\hbar m_j,\ m_j = -j, -j+1, \cdots, 0, \cdots, j-1, j. \tag{1.4.223}$$

Because J_1^2 and J_2^2 commutes with all their components and J^2 can be expressed in terms of those components, we can say

$$[J^2, J_i^2] = 0,\ i = 1, 2. \tag{1.4.224}$$

So the total angular momentum can be specified simultaneously with individual angular momenta. Note that although we have found the *allowed* values of total angular momentum, we have yet to find how to calculate the actual value for a system with specified individual momenta.

---

[9] In case you get confused here, remember that j is but a quantum number, *i.e.*, an index, not the actual magnitude of the momentum in question.

We now want to know if we can specify m_{ji} and j together:

$$\begin{aligned}
[J_{1z}, J^2] &= [J_{1z}, J_x^2] + [J_{1z}, J_y^2] + [J_{1z}, J_z^2] \\
&= [J_{1z}, (J_{1x} + J_{2x})^2] + [J_{1z}, (J_{1y} + J_{2y})^2] + [J_{1z}, (J_{1z} + J_{2z})^2] \\
&= [J_{1z}, J_{1x}^2 + 2J_{1x}J_{2x}] + [J_{1z}, J_{1y}^2 + 2J_{1y}J_{2y}] \\
&= [J_{1z}, J_{1x}^2 +, J_{1y}^2] + 2[J_{1z}, J_{1x}]J_{2x} + 2[J_{1z}, J_{1y}]J_{2y} \\
&= [j_{1z}, J_1^2 - J_{1z}^2] + 2i\hbar J_{1y}J_{2x} - 2i\hbar J_{1x}J_{2y} \\
&= 2i\hbar(J_{1y}J_{2x} - J_{1x}J_{2y}).
\end{aligned} \tag{1.4.225}$$

So, no, we cannot specify m_{ji} if we specify j.
Therefore we have to choose between specifying the system as either

$$|j_1 m_{j1}; j_2 m_{j2}\rangle, \tag{1.4.226}$$

the **uncoupled picture**, or

$$|j_1 j_2; j m_j\rangle, \tag{1.4.227}$$

the **coupled picture**. For now the choice is equivalent and arbitrary but in future we will revisit this concept, such as in Section 3.3.2, where the coupled picture makes identification of triplet and singlet states easier.

1.4.5.5 Permitted values of total momentum

We now attempt to identify what the actual values of the total momentum quantum numbers j and m_j can be, amongst the range of allowed values.
Since $j_z = j_{1z} + j_{2z}$, we can immediately obtain

$$m_j = m_{j1} + m_{j2}, \tag{1.4.228}$$

that is, the z-components *simply add*.
The values of j is much thornier: the total number of states, given j_1 and j_2, is

$$(2j_1 + 1)(2j_2 + 1) = 4j_1 j_2 + 2j_1 + 2j_2 + 1. \tag{1.4.229}$$

The maximum value of j is the maximum value of m_j, which is naturally $j_1 + j_2$. So there are

$$2j + 1 = 2j_1 + 2j_2 + 1 \tag{1.4.230}$$

degenerate states corresponding to the maximum total angular momentum. We have $4j_1 j_2$ more states to find. We descend m_j by 1 and note that there are two ways (actually linear combinations due to the indistinguishability) to form this state, $m_{j1} = j_1 - 1$ and $m_{j2} = j_2$ or the other way around. The state with $j = m_{j1} + m_{j_2}$ already account for one of the linear combinations (as the degenerate state with m_j 1 less than the maximum), so there must be another *coupled state* with maximum $j = j_1 + j_2 - 1$, whose maximum m_j, of course, equal to the same value. This coupled state accounts for another $2j + 1 = 2j_1 + 2j_2 - 1$ states, and so on, and we can show that the sum todo-supo: don't know how to proceed

$$(2j_1 + 2j_2)N - 1 - 3 - 5 - \cdots \tag{1.4.231}$$

It turns out by the time we have reached $j = |j_1 - j_2|$ all the states will be accounted for, and this is known as the **Clebsch-Gordan series** for allowed values of j:

$$j = j_1 + j_2, j_1 + j_2 - 1, \cdots, |j_1 - j_2|. \tag{1.4.232}$$

The series can be very intuitively understood in Figure 1.1

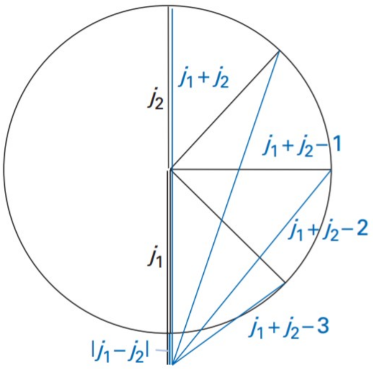

Figure 1.1: The allowed values of j are just the third side of the triangle.

1.4.5.6 Relation between coupling schemes

In Section 1.4.5.4 we have introduced two pictures of coupling, the uncoupled and the coupled picture. Just as a recap, the uncoupled picture specifies the individual quantum numbers j_i and m_{ji}. We usually use the **vector model of coupled angular momenta** to represent the differences between the two schemes, as in Figure 1.2.

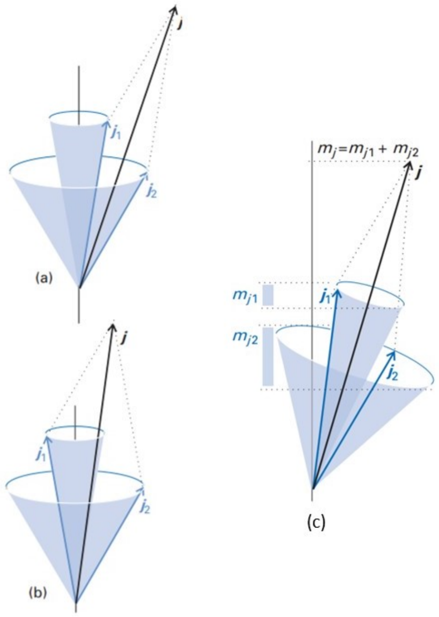

Figure 1.2: (a) and (b) represent the uncoupled picture, in which we can't specify j_i's and j simultaneously but can do so with m_j, as the z-component is specified. (c) represents the coupled picture where the two j_i's are locked together, so j (hence also m_j) is specified, but not the individual components that add up to m_j.

We are more interested in the coupled picture as it gives us more immediate information of the system total parameters, as we shall see in Section 3.3.2. So we should develop a way to quickly transform between the two pictures: the state $|j_1 j_2; j m_j\rangle$ is built from a linear combination of all states with $m_{j1} + m_{j2} = m_j$:

$$|j_1 j_2; j m_j\rangle = \sum_{m_{j1}, m_{j2}} C(m_{j1}, m_{j2}) |j_1 m_{j_1}; j_2 m_{j2}\rangle, \tag{1.4.233}$$

where the coefficients $C(m_{j1}, m_{j2})$ are called **Clebsch-Gordan coefficients**, or vector coupling coefficients. For our case, $m_{j1} = m_{j2} = 1/2$, the coefficients are easily seen to agree with our earlier efforts at establishing the singlet and triplet states. Omitting $j_1 j_2$ in the notation and simply writing $|j, m_j\rangle$ or more specifically, $|S, M_S\rangle$, we have

$$\begin{aligned}
|1, +1\rangle &= \alpha_1 \alpha_2 \\
|1, 0\rangle &= \frac{1}{\sqrt{2}} \alpha_1 \beta_2 + \frac{1}{\sqrt{2}} \beta_1 \alpha_2 \\
|1, -1\rangle &= \beta_1 \beta_2 \\
|0, 0\rangle &= \frac{1}{\sqrt{2}} \alpha_1 \beta_2 - \frac{1}{\sqrt{2}} \beta_1 \alpha_2 .
\end{aligned} \tag{1.4.234}$$

The Clebsch-Gordan coefficients can be calculated as overlap integrals between the coupled and uncoupled states. We do so by right-multiplying Equation 1.4.233 by $\langle j_1 m'_{j1}; j_2 m'_{j2}|$:

$$\langle j_1 m'_{j1}; j_2 m'_{j2} | j_1 j_2; j m_j \rangle = C(m'_{j1}, m'_{j2}), \tag{1.4.235}$$

where other terms in the sum vanishes by the orthogonality of the states. This can be intuitively understood as how much the coupled state resembles the uncoupled state, or 'how much' of the uncoupled state should be in the linear combination. For example, the state $|1, +1\rangle$ must be composed of $\alpha_1\alpha_2$ only as this is the only state with $M_S = +1$.

1.4.5.7 Atomic term symbols

read chap 7 of atkins, and section on spin in B field in griffiths, priority: high. After that, re-write this section Term symbols give better descriptions than electron configurations, as we will see, same electronic configuration will give rise to different energies as a result of electrostatic interactions. The idea is to determine the total orbital angular momentum $\boldsymbol{L}$ and the total spin angular momentum $\boldsymbol{S}$ and then adding them vectorially to get the total angular momentum $\boldsymbol{J}$:

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S} = \sum_i l_i + \sum_j s_j. \tag{1.4.236}$$

This is called the **Russell-Saunders coupling** or **LS coupling**, which is only predominant in lighter $(Z < 30)$ atoms. same as spin-orbit coupling? The result of this sum is summarised as a **term symbol**, like

$$^{2S+1}L_J, \tag{1.4.237}$$

where L, S, J are the total orbital/total spin/total angular momentum quantum numbers, and $2S+1$ is known as the spin multiplicity.

With an argument exactly like the one given in Section 1.4.5.5, we can show that $\boldsymbol{J}$ and $\boldsymbol{S}$ are angular momenta and their values must run through integers and/or half integers. And since individual orbital angular momenta must be integers and individual spins can be both, so do the total. And another argument as in Section 1.4.5.5 will give us that J runs from $L+S$ to $|L-S|$. To summarise, the allowed values for the quantum numbers involved in the term symbol are

Property 1.4.5.4 (Term symbol)**.** The term symbol is

$$^{2S+1}L_J, \tag{1.4.238}$$

where the allowed values are

$$\begin{aligned} S &= 0, 1/2, 1, 3/2, \cdots \\ (2S+1) &= 1, 2, 3, 4, \cdots \\ L &= 0, 1, 2, 3, \cdots \\ J &= L+S, L+S-1, \cdots, |L-S|. \end{aligned} \tag{1.4.239}$$

In analogy to assigning $s, p, d, f, \cdots$ to $\ell = 0, 1, 2, 3, \cdots$, we assign $S, P, D, F, \cdots$ for $L = 0, 1, 2, 3, \cdots$.

Recall that the z-components of angular momenta simply add, *i.e.*,

$$\begin{aligned} L_z &= \sum_i l_{zi} = \sum_i m_{li} = M_L \\ S_z &= \sum_i s_{zi} = \sum_i m_{si} = M_S \end{aligned} \tag{1.4.240}$$

The M_S quantum number gives rise the $2S+1$ multiplicity (their energy will only be further split into levels in presence of external field todo: read up relevant stuff, reference, priority: low). We will now look at a few examples.

Example 1: ns^2

- s orbital means $\ell = 0$, so $m_{li} = 0$, and $M_L = 0$, and this being the only allowed value of M_L means $L = 0$ or the S-state.
- The two spins must be antiparallel, so M_S is also equal 0, and so similarly $S = 0$.
- By the same token, J can also only be 0.
- Therefore, the term symbol for ns^2 is $^1S_0$.

Example 2: np^6

- p orbital means $\ell = 1$, so $m_{li} = -1, 0, 1$ so M_L being the sum of all occupied orbitals (which is all of them) is 0.
- Spins also all pair up to give $M_S = 0$.

- Therefore J can only be 0
- The term symbol for np^6, and actually for **all** fully filled orbitals subshells, is $^1S_0$. It's also called **singlet S zero**.

Example 3: $ns^1n's^1$ (first excited state of Helium)

- M_L can only be zero as $m_{li} = 0$.
- However now the spins are not confined to have antiparallel spins, and can independently take on values of $\pm 1/2$, so M_S can be $-1, 0, 1$. This means the largest value of S is 1 since that's the largest value M_S can take on. So we must have $S = 0, 1$, corresponding to ^3S (triplet) and ^1S (singlet) states.

We list the possible states below:

	M_S		
M_L	1	0	-1
0	$0^+, 0^+$	$0^+, 0^-; 0^-, 0^+$	$0^-, 0^-$

where 0^+ means $m_l = 0$ and $m_s = +1/2$ and vice versa. The middle two states are not indistinguishable because the spatial orbitals are not the same ($1s$ and $2s$)There are 4 **microstates**. The triplet state accounts for one state from each column, and the singlet state must claim the remaining M_S state, and it doesn't matter which one each state takes.

And we are left with J to determine. We add M_L and M_S to get M_J. For the triplet state M_J, $M_J = 1, 0, -1$, so $J = 1$. For the singlet state similarly $J = 0$.

Therefore the two term symbols the configuration $ns^1n's^1$ correspond to are $^3S_1$ and $^1S_0$.

Example 4: Carbon atom

As shown previously, we do not need to worry about fully filled subshells and only need to focus on $2p^2$. Let's derive a general result first:

Lemma 1.4.5.1 (Number of electron assignments)**.** For G number of **equivalent** (same subshell) spin-orbitals and N electrons, which are indistinguishable, the number of ways to assign the electrons, $D(G, N)$ is

$$D(G, N) = \frac{G!}{N!(G-N)!}. \tag{1.4.241}$$

So for carbon, we have 15 ways to assign the electrons. Intuitively, the first electron can take any of the 6 spin-orbitals, the second can take the remaining 5, and a factor of 2! is divided through for they are indistinguishable, giving a total of 15 ways to arrange.

To find all these 15 microstates we again use a table. But before that we need to find out the values of M_L and M_S. It's easily seen that M_L runs from -2 to $+2$ and M_S from -1 to $+1$. So $L = 0, 1, 2$ and $S = 0, 1$. The table is then

	M_S		
M_L	1	0	-1
2	$1^+, 1^+$	$1^+, 1^-$	$1^-, 1^-$
1	$0^+, 1^+$	$1^+, 0^-; 1^-, 0^+$	$0^-, 1^-$
0	$0^+, 0^+; 1^+, -1^+$	$1^+, -1^-; -1^+, 1^-; 0^+, 0^-$	$1^-, -1^-; 0^-, 0^-$
-1	$0^+, -1^+$	$0^+, -1^-; 0^-, -1^+$	$0^-, -1^-$
-2	$-1^+, -1^+$	$-1^+, -1^-$	$-1^-, -1^-$

where we make no distinction like the previous case between $1^+, 0^-$ and $0^-, 1^+$ because the spatial orbitals are equivalent now. The grey terms are forbidden by the Pauli exclusion principle. We now assign term symbols to the microstates.

We start by remarking that although the **allowed** values of L and S is 0 to 2 and 0 to 1 respectively, the actual **permitted** term symbols are not necessarily all possible permutations of these values. For example, the largest value of M_L is 2 and it only occurs with $M_S = 0$, this means that $L = 2$ state only occurs with $S = 0$. For the remaining states, the largest $M_L = 1$, and it occurs with all three M_S values, hence there must be a state with $L = 1$ and $S = 1$. We list the term symbols below:

- $L = 2$, $S = 0$, *i.e.*, ${}^1D$: one state per row in the $M_S = 0$ column. J can only take up one value, which is 2. The complete term symbol is ${}^1D_2$.
- $L = 1$, $S = 1$, *i.e.*, ${}^1P$: nine states per remaining cells. J can take up values from 2 to 0, so complete term symbols are ${}^3P_2$, ${}^3P_1$, and ${}^3P_0$.[10]
- $L = 0$, $S = 0$, term symbol ${}^1S_0$, naturally.

As can be seen, we don't really have to specify J as it can be deduced from S and L. The degeneracies of each state is given by $2J + 1$.

At last, we can introduce Hund's rules, todo: theoretical foundations, priority: medium:

---

[10] Another way to look at this is that the nine states correspond to M_J of $2, 1, 1, 0, 0, -1, 0, -1, -2$, so we can isolate three sets of M_J running from $-J$ to J with $J = 0, 1, 2$ respectively.

Theorem 1.4.5.1 (Hund's rules)**.** The three Hund's rules state that

1. The state with the largest value of S is the most stable (has the lowest energy), and stability decreases with decreasing S.
2. For states with the same value of S, the state with the largest value of L is the most stable.
3. If the states have the same value of L and S, then, for a subshell that is less than half filled, the state with the smallest value of J is the most stable; for a subshell that is more than half filled, the state with the largest value of J is the most stable.

1.4.5.8 Molecular term symbols

The following discussion only strictly applies to homonuclear diatomics, for which only the orbital angular momentum along the internucalear axis is defined.

The molecular term symbol is given in the form of

$$^{2\Sigma+1}\Lambda^{\pm}_{g/u}, \tag{1.4.242}$$

Σ is just the spin angular momentum, effectively the half the number of unpaired electrons in the molecule.

Λ is the orbital angular momentum, given as

$$\Lambda = \sum_i M_{L,i}, \tag{1.4.243}$$

with *unpaired* electrons in σ orbitals having $M_L = 0$ and those in π orbitals having $M_L = 1$ and so on.

The g/u labels denotes the *inversion symmetry*, where the overall inversion symmetry is a direct product of the inversion symmetry of all occupied orbitals, with

$$g \times g = g \;\; u \times u = g \;\; g \times u = u \;\; u \times g = u. \tag{1.4.244}$$

And finally the ± label denotes the *mirror-plane* symmtry, where the mirror plane contains the internuclear axis, where $+$ means unchanged upon reflection and $-$ means the sign changes upon reflection. Mathematically speaking, reflection changes the sign of ϕ. Let's see this in action, say we have the ground state of oxygen, which has an electronic configuration of π^2, which has two orbitals with $M_L = \pm 1$, which leads to two ${}^1\Delta$ states with two electrons in either orbitals, and a ${}^3\Sigma$ and ${}^1\Sigma$ state with two electrons in both states but two orientations. The wavefunctions for the two orbitals are

$$\begin{aligned} \pi_+ &= F(\boldsymbol{r_a}, \boldsymbol{r_b})e^{i\phi} \\ \pi_- &= F(\boldsymbol{r_a}, \boldsymbol{r_b})e^{-i\phi} \end{aligned} \tag{1.4.245}$$

we further define the reflection operator

$$\sigma_{xy}\pi_\pm = \pi_\mp \tag{1.4.246}$$

and the total wavefunction for the two electrons

$$\Psi(\boldsymbol{r_1}, \boldsymbol{r_2}) = \frac{1}{\sqrt{2}}[\pi_+(1)\pi_-(2) \mp \pi_-(1)\pi_+(2)] \times \boldsymbol{\sigma}_\pm \tag{1.4.247}$$

where the top sign denotes triplet, whose spin wavefunction is symmetric to exchange, and the bottom sign denotes singlet. Now the action of the total reflection operator $\sigma_{\text{tot}} = \sigma_{xy}(1)\sigma_{xy}(2)$ is

$$\begin{aligned} \sigma_{\text{tot}}\Psi(\boldsymbol{r_1}, \boldsymbol{r_2}) &= \frac{1}{\sqrt{2}}\sigma_{xy}(1)\sigma_{xy}(2)[\pi_+(1)\pi_-(2) \mp \pi_-(1)\pi_+(2)] \times \boldsymbol{\sigma}_\pm \\ &= \frac{1}{\sqrt{2}}[\pi_-(1)\pi_+(2) \mp \pi_+(1)\pi_-(2)] \times \boldsymbol{\sigma}_\pm \\ &= \mp\Psi(\boldsymbol{r_1}, \boldsymbol{r_2}) \end{aligned} \tag{1.4.248}$$

therefore we see that the final full term symbols are ${}^3\Sigma^-$ and ${}^1\Sigma^+$.

This is only going to matter in $\Lambda = 0$ (Σ) states, this is because all other states have a two-fold degeneracy, so the reflection operation is just going to interchange them, whereas in Σ states there's no degeneracy.

More exmamples

$1\sigma^1\ 2\sigma^1$
As the electrons don't occupy the same orbitals, Pauli exclusion principle doesn't apply anyway, and also, since σ MOs have no ϕ dependence, it has to be unchanged upon reflection, therefore ${}^1\Sigma^+$ and ${}^3\Sigma^+$ are produced.

σ^1
Similar argument produces ${}^2\Sigma^+$.

Closed shell

Close shells must have $S = 0$ which forces the singlet configuration, which means antisymmetric spin wavefunction and hence $^1\Sigma^+$.

π^1
This simply produces $^2\Pi$, specifying the signs is unnecessary as the term is 2-degenerate anyway.

1.5 IDENTICAL PARTICLES

1.5.1 Two particle systems

1.5.1.1 The Schrödinger equation

The state of a two-particle system is a function of both particle's coordinates and time:

$$\Psi(\boldsymbol{r_1}, \boldsymbol{r_2}, t). \tag{1.5.1}$$

Its time evolution is, as always, determined by the Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi, \tag{1.5.2}$$

where the Hamiltonian is

$$H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\boldsymbol{r_1}, \boldsymbol{r_2}, t) \tag{1.5.3}$$

The probability of finding particle 1 in $d^3\boldsymbol{r_1}$ and particle 2 in $d^3\boldsymbol{r_2}$ is

$$|\Psi(\boldsymbol{r_1}, \boldsymbol{r_2}, t)|^2 d^3\boldsymbol{r_1} d^3\boldsymbol{r_2}. \tag{1.5.4}$$

The normalisation requirement is therefore

$$\int |\Psi(\boldsymbol{r_1}, \boldsymbol{r_2}, t)|^2 d^3\boldsymbol{r_1} d^3\boldsymbol{r_2} = 1. \tag{1.5.5}$$

For **time-independent** potentials, we can use the usual separation of variables:

$$\Psi(\boldsymbol{r_1}, \boldsymbol{r_2}, t) = \psi(\boldsymbol{r_1}, \boldsymbol{r_2}) e^{-iEt/\hbar}, \tag{1.5.6}$$

where ψ is such that

$$H\psi = E\psi. \tag{1.5.7}$$

1.5.1.2 Centre-of-mass coordinates

If, in a **two particle system**, where the potential depends only on $\boldsymbol{r} \equiv \boldsymbol{r_1} - \boldsymbol{r_2}$ between the two particles, we can use the centre-of-mass coordinates to simplify and *separate* the

Schrödinger equation as follows: we define the **centre-of-mass coordinate**:

$$\boldsymbol{R} \equiv \frac{m_1\boldsymbol{r_1} + m_2\boldsymbol{r_2}}{m_1 + m_2} \tag{1.5.8}$$

Now, we need to re-write the Schrödinger equation in terms of the new coordinates, and first of all we need to write out the Hamiltonians, which is fiddly to do: we first need to see that

$$\nabla_1 f = \frac{\partial f}{\partial r_{1_x}} + \frac{\partial f}{\partial r_{1_y}} + \frac{\partial f}{\partial r_{1_z}}. \tag{1.5.9}$$

So to re-write it, we note that r_{1_x} is only dependent on r_x and R_x, and so on, so

$$\begin{aligned}\frac{\partial f}{\partial r_{1_x}} &= \frac{\partial f}{\partial r_x}\frac{\partial r_x}{\partial r_{1_x}} + \frac{\partial f}{\partial R_x}\frac{\partial R_x}{\partial r_{1_x}} \\ &= \frac{\partial f}{\partial r_x} + \frac{\partial f}{\partial R_x}\frac{\mu}{m_2},\end{aligned} \tag{1.5.10}$$

and

$$\begin{aligned}\frac{\partial f}{\partial r_{2_x}} &= \frac{\partial f}{\partial r_x}\frac{\partial r_x}{\partial r_{2_x}} + \frac{\partial f}{\partial R_x}\frac{\partial R_x}{\partial r_{2_x}} \\ &= -\frac{\partial f}{\partial r_x} + \frac{\partial f}{\partial R_x}\frac{\mu}{m_1},\end{aligned} \tag{1.5.11}$$

and so on for other components, so

$$\nabla_1 = \nabla_r + \frac{\mu}{m_2}\nabla_R \tag{1.5.12a}$$

$$\nabla_2 = -\nabla_r + \frac{\mu}{m_1}\nabla_R. \tag{1.5.12b}$$

To get the Laplacian, we note that it's not equivalent to left multiplying the transformed nabla operator twice, but instead we have to go back to Equation 1.5.10, and differentiating it again wrt r_{1_x} and so on:

$$\begin{aligned}\frac{\partial^2 f}{\partial (r_{1_x})^2} &= \left(-\frac{\partial}{\partial r_x} + \frac{\mu}{m_2}\frac{\partial}{\partial R_x}\right)\left(-\frac{\partial f}{\partial r_x} + \frac{\partial f}{\partial R_x}\frac{\mu}{m_2}\right) \\ &= \frac{\partial^2 f}{\partial (r_x)^2} - \frac{\partial^2 f}{\partial r_x \partial R_x}\frac{2\mu}{m_2} + \frac{\partial^2 f}{\partial (R_x)^2}\left(\frac{\mu}{m_2}\right)^2,\end{aligned} \tag{1.5.13}$$

and

$$\begin{aligned}\frac{\partial^2 f}{\partial (r_{2_x})^2} &= \left(\frac{\partial}{\partial r_x} + \frac{\mu}{m_1}\frac{\partial}{\partial R_x}\right)\left(\frac{\partial f}{\partial r_x} + \frac{\partial f}{\partial R_x}\frac{\mu}{m_1}\right) \\ &= \frac{\partial^2 f}{\partial (r_x)^2} - \frac{\partial^2 f}{\partial r_x \partial R_x}\frac{2\mu}{m_1} + \frac{\partial^2 f}{\partial (R_x)^2}\left(\frac{\mu}{m_1}\right)^2,\end{aligned} \tag{1.5.14}$$

so we have

$$-\frac{\hbar^2}{2m_1}\nabla_1^2 = -\frac{\hbar^2}{2m_1}\nabla_r^2 - \nabla_R^2\frac{\hbar^2\mu^2}{m_1 m_2^2} - (\text{mixed partial term}) \tag{1.5.15}$$

and

$$-\frac{\hbar^2}{2m_1}\nabla_2^2 = -\frac{\hbar^2}{2m_2}\nabla_r^2 - \nabla_R^2\frac{\hbar^2\mu^2}{m_2 m_1^2} + (\text{same mixed partial term}). \tag{1.5.16}$$

Finally, the Schrödinger equation is

$$\left[-\frac{\hbar^2}{2(m_1+m_2)}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 + V(\boldsymbol{r})\right]\psi = E\psi. \tag{1.5.17}$$

We attempt separation of variables:

$$\psi(\boldsymbol{R},\boldsymbol{r}) = \psi_R(\boldsymbol{R})\psi_r(\boldsymbol{r}), \tag{1.5.18}$$

and we obtain two equations:

$$-\frac{\hbar^2}{2(m_1+m_2)}\nabla_R^2\psi_R = E_R\psi_R \tag{1.5.19a}$$

$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(\boldsymbol{r})\right]\psi_r = E_r\psi_r. \tag{1.5.19b}$$

This is saying that we have successfully decoupled the equation into two independent systems: the total mass $(m_1 + m_2)$, moving as a free particle (0 potential) and the relative motion as a single particle with reduced mass subject to potential V.

1.5.1.3 Bosons and fermions

Suppose we now have a two particle system that is non-interacting, which is to say that the two particles are in their own one-particle states and that they are independent - this is by no means always true, as in the singlet spin configuration where two spins are correlated - we can write

$$\psi(\boldsymbol{r}_1,\boldsymbol{r}_2) = \psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2). \tag{1.5.20}$$

In writing this we have presumed that the two particles are **distinguishable**, otherwise the labels a and b wouldn't make any sense. However, almost all the particles we will be dealing with will *not* be distinguishable. Therefore, the most we can say its that *one* particle is in state a and the other in state b. We note that since they are insdistinguishable, the exchange of labels *must* have no effect on the probability density, *i.e.*,

$$|\psi(1,2)|^2 = |\psi(2,1)|^2, \Rightarrow \psi(1,2) = \pm\psi(2,1). \tag{1.5.21}$$

So this means we can write

$$\psi_{\pm}(\boldsymbol{r}_1, \boldsymbol{r}_2) = A[\psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2) \pm \psi_b(\boldsymbol{r}_1)\psi_a(\boldsymbol{r}_2)]. \tag{1.5.22}$$

This wavefunction is *non-committal* as to which particle is in which state, but when do we use which sign? We introduce the postulate

Postulate 1.5.1.1 (Bosons and fermions)**.**
All particles with *integer* spins are bosons, and
all particles with *half integer* spins are fermions.
We use the *plus sign* for bosons and *minus sign* for fermions.

It then follows that

Theorem 1.5.1.1 (Pauli exclusion principle)**.** Two identical fermions, for example, two electrons, cannot occupy the same state, for if $\psi_a = \psi_b$, then

$$\psi_{-}(\boldsymbol{r}_1, \boldsymbol{r}_2) = A[\psi_a(\boldsymbol{r}_1)\psi_a(\boldsymbol{r}_2) - \psi_a(\boldsymbol{r}_1)\psi_a(\boldsymbol{r}_2)] = 0, \tag{1.5.23}$$

and we are left with no wavefunction at all.

A more general re-formulation of problem requires the introduction of the **exchange operator**:

Definition 1.5.1.1 (Exchange operator)**.** The exchange operators is defined as

$$Pf(\boldsymbol{r}_1, \boldsymbol{r}_2) = f(\boldsymbol{r}_2, \boldsymbol{r}_1). \tag{1.5.24}$$

Definition 1.5.1.2 (Properties of the exchange operator)**.**
(1) It is immediately clear that

$$P^2 = I. \tag{1.5.25}$$

(2) And therefore the eigenvalues of P are ± 1.
(3) If we have two *identical* particles, the Hamiltonian must treat them the same way: $m_1 = m_2$ and $V(\boldsymbol{r}_1, \boldsymbol{r}_2) = V(\boldsymbol{r}_2, \boldsymbol{r}_1)$, therefore P and H are compatible observables:

$$[P, H] = 0. \tag{1.5.26}$$

Theorem 1.5.1.2 (Symmetrisation requirement)**.** Because P and H commute, we can find simultaneous eigenstates of both, *i.e.*, we can find solutions to Schrödinger equation that are either symmetric (eigenvalue $+1$) or antisymmetric (eigenvalue -1) under excahnge of labels:

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \pm\psi(\boldsymbol{r}_2, \boldsymbol{r}_1). \tag{1.5.27}$$

Therefore, if a system begins in a state it must remain in this state. The plus sign is for bosons and negative for fermions.

1.5.1.4 Exchange forces

We examine a 1D example. Let's suppose one particle is in $\psi_a(x)$ and another in $\psi_b(x)$, and these two states are orthogonal and normalised. *If* the two particles are distinguishable, and number 1 is the one in state ψ_a, then the composite wavefunction is

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2). \tag{1.5.28}$$

If they are identical bosons or fermions, the composite will be

$$\psi_\pm(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) \pm \psi_b(x_1)\psi_a(x_2)]. \tag{1.5.29}$$

Let's calculate the expectation value of the square of the separation distance between the two particles, given by

$$\langle(x_1 - x_2)^2\rangle = \langle x_1^2\rangle + \langle x_2^2\rangle - 2\langle x_1 x_2\rangle. \tag{1.5.30}$$

Case 1: Distinguishable particles
We use the wavefunction in Equation 1.5.28:

$$\langle x_1\rangle = \int x_1^2|\psi_a(x_1)|^2\,\mathrm{d}x_1 \int |\psi_b(x_2)|^2\,\mathrm{d}x_2 = \langle x^2\rangle_a, \tag{1.5.31}$$

(the expectation of x^2 in the *one-particle* state ψ_a) so similarly

$$\langle x_2^2\rangle = \langle x_2^2\rangle_b. \tag{1.5.32}$$

And

$$\langle x_1 x_2\rangle = \int x_1|\psi_a(x_1)|^2\,\mathrm{d}x_1 \int x_2|\psi_b(x_2)|^2\,\mathrm{d}x_2 = \langle x\rangle_a\langle x\rangle_b. \tag{1.5.33}$$

Collecting, we have

$$\langle (x_1 - x_2)^2 \rangle = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b. \tag{1.5.34}$$

Case 2: Identical particles

We now have to use the wavefunctions in Equation 1.5.29:

$$\begin{aligned}
\langle x_1^2 \rangle =& \frac{1}{2}\left[\int x_1^2 |\psi_a(x_1)|^2 \, \mathrm{d}x_1 \int |\psi_b(x_2)|^2 \, \mathrm{d}x_2 \right. \\
&+ \int x_1^2 |\psi_b(x_1)|^2 \, \mathrm{d}x_1 \int |\psi_a(x_2)|^2 \, \mathrm{d}x_2 \\
&\pm \int x_1^2 \psi_a(x_1)^* \psi_b(x_1) \, \mathrm{d}x_1 \int \psi_b(x_2)^* \psi_a(x_2) \, \mathrm{d}x_2 \\
&\left. \pm \int x_1^2 \psi_b(x_1)^* \psi_a(x_1) \, \mathrm{d}x_1 \int \psi_a(x_2)^* \psi_b(x_2) \, \mathrm{d}x_2 \right] \\
=& \frac{1}{2}\left[\langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0\right] \\
=& \frac{1}{2}\left(\langle x^2 \rangle_a + \langle x^2 \rangle_b\right).
\end{aligned} \tag{1.5.35}$$

And likewise

$$\langle x_2^2 \rangle = \frac{1}{2}\left(\langle x^2 \rangle_b + \langle x^2 \rangle_a\right). \tag{1.5.36}$$

We observe that

$$\langle x_1^2 \rangle = \langle x_2^2 \rangle \tag{1.5.37}$$

since we can't tell them apart. Now

$$\begin{aligned}
\langle x_1 x_2 \rangle =& \frac{1}{2}\left[\int x_1 |\psi_a(x_1)|^2 \, \mathrm{d}x_1 \int x_2 |\psi_b(x_2)|^2 \, \mathrm{d}x_2 \right. \\
&+ \int x_1 |\psi_b(x_1)|^2 \, \mathrm{d}x_1 \int x_2 |\psi_a(x_2)|^2 \, \mathrm{d}x_2 \\
&\pm \int x_1 \psi_a(x_1)^* \psi_b(x_1) \, \mathrm{d}x_1 \int x_2 \psi_b(x_2)^* \psi_a(x_2) \, \mathrm{d}x_2 \\
&\left. \pm \int x_1 \psi_b(x_1)^* \psi_a(x_1) \, \mathrm{d}x_1 \int x_2 \psi_a(x_2)^* \psi_b(x_2) \, \mathrm{d}x_2 \right] \\
=& \frac{1}{2}\left(\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab}\right) \\
=& \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_a b|^2,
\end{aligned} \tag{1.5.38}$$

where

$$\langle x \rangle_{ab} \equiv \int x \psi_a(x)^* \psi_b(x) \, \mathrm{d}x. \tag{1.5.39}$$

Collecting we have

$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \mp 2|\langle x \rangle_{ab}|^2. \tag{1.5.40}$$

Theorem 1.5.1.3 (Exchange force)**.**
By comparing Equation 1.5.34 and Equation 1.5.40, we see that the difference lies in the final term:

$$\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp 2|\langle x \rangle_{ab}|^2, \tag{1.5.41}$$

where the subscript d stands for 'distinguishable'. Therefore we can see that identical bosons are closer together and identical fermions further apart than distinguishable particles in the same two states. Notice that $\langle x \rangle_{ab}$ **vanishes** unless the two wavefunctions **overlap**. Therefore, it is acceptable to treat electrons with non-overlapping wavefunctions as distinguishable. The increase or decrease in between identical particles are called an **exchange force**.

We now take a look at the hydrogen molecule, H_2. To a good approximation [11], the ground state consists of one electron in the hydrogen atom ground state centred around nucleus 1 and another around nucleus 2. If electrons were bosons, the exchange force would concentrate the electrons towards the middle of the internuclear space, and as a result pull the protons inward, accounting for the covalent bond. However, electrons are fermions, and that would mean the concentration of negative charge should be on the wings, tearing the molecule apart. This is obviously wrong, and we are reminded that we have been ignoring spins all this while - the symmetrisation requirement (Theorem 1.5.1.2) requires that the **complete wavefunctions** of fermions be antisymmetric, not just the spatial wavefunctions. The complete wavefunctions of electrons are

$$\psi_e(\boldsymbol{r}, \boldsymbol{s}) = \psi(\boldsymbol{r})\chi(\boldsymbol{s}). \tag{1.5.42}$$

This is assuming that the spin and the spatial wavefunction are *uncoupled*, therefore separable. Under the same assumption, we can write the two-electron state as

$$\psi_{2e}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{s}_1, \boldsymbol{s}_2) = \psi_{\pm}(\boldsymbol{r}_1, \boldsymbol{r}_2)\chi(\boldsymbol{s}_1, \boldsymbol{s}_2), \tag{1.5.43}$$

where $\chi(\boldsymbol{s}_1, \boldsymbol{s}_2)$ can be one of the four (three triplet one singlet) states in Section 1.4.5.3. Now, we must require bonding, therefore symmetric[12], *spatial* wavefunctions. We remember that the singlet state is antisymmetric[13], therefore the spatial wavefunction of the electron that's multiplied to it can (and must) be symmetric. This can be confusing because we appear to have just derived that all electron wavefunctions must be antisymmetric. But in fact we have not, Theorem 1.5.1.2 only requires that the complete wavefunction be accordingly symmetrised, not spatial or spinor parts separately.

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[11] See next section.

[12] Remember that the exchange force favours bonding as long as the *spatial* wavefunction is symmetric, and it makes no use of the spinor as the 'integration' of orthonormal spinors always return the Kronecker delta.

[13] We can actually derive this from symmetry requirements alone, stating from the four possible combinations and then consider their coefficients as in [11].

Therefore, we have now shown that the bonding orbital will have electrons occupy the singlet configuration, with total spin zero, and the antibonding orbital one of the triplet configurations.

Another more elementary but more intuitive way to look at this is that electrons with the same spin cannot be found at the same spot and the electron density will be low around another electron with the same spin. This is not the case for electrons with opposite spin. Because of the Coulombic repulsion, electrons with like spins are lower in energy than those with opposite spin. This explains in part the Hund's rule. Also, the triplet state is more stable than the singlet state, however the latter is essential for chemical bonding to happen, and bonding happens because the lowering in energy more than compensates for the exchange force.

Part II

Thermodynamics and statistical mechanics

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