Exactly solvable systems

To get back into the habit of thinking about quantum system, to rekindle knowledge of the language and basic methods used, to introduce some new and key ideas that will be picked up on further down the line, and to recognze some deep truths, we start with a couple of systems that yield to analytic analysis.

1 Quantum linear harmonic oscillator

The simple harmonic oscillator is a familiar problem. How does the joke go?

> It is often said that the simple harmonic oscillator is the only problem that physicists understand. This is untrue... but a good approximation.

Here we take another look at the quantum harmonic oscillator, armed with a greater familiarity with quantum mechanics than when we first looked at it. We do so because it allows us to refamiliarise ourselves with important concepts and practice key methods of quantum mechanics, but also because it has many applications, such as vibrations in molecules and solids, nuclear structure[1], the electromagnetic field .... If we think of classical particles moving in a potential, and the potential has a minimum corresponding to stable equilibrium, then for small displacements away from the stable equilibrium we can use a Taylor expansion

$$V(x) \simeq V(x_0) + \frac{1}{2}V''(x_0)(x-x_0)^2$$

which is the potential of an oscillator. Hence the harmonic oscillator provides a description of a variety of systems close to stable equilibrium. The same applies for quantum mechanical systems, such as the nuclear motion in a molecule responsible for the vibrational spectrum of molecular excitations.

Here we consider an ideal oscillator where the potential is quadratic for all separations. Typically corrections become significant for larger distances in actual system – for these one can apply perturbation theory, as previously studied, making use of the results of the following analysis.
Theoretical physicists often refer to the simple harmonic oscillator as the linear harmonic oscillator. The quantum linear harmonic oscillator problem corresponds to the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = \hat{\mathcal{H}}\psi(x,t) \tag{1.1}$$

with the Hamiltonian

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 \tag{1.2}$$

The first term represents the kinetic energy and the second the potential energy $V(x) = \frac{1}{2}kx^2$ written in terms of a frequency ω which is that of a classical oscillator, mass m, restoring force $-kx$: $\omega^2 = k/m$.

We will primarily focus on the stationary states of the quantum linear harmonic oscillator. These are the solutions of (1.1) of the form $\psi(x,t) = \exp(-i\varepsilon t/\hbar)\varphi_\varepsilon(x)$ where

$$\hat{\mathcal{H}}\varphi_\varepsilon(x) = \varepsilon\varphi_\varepsilon(x). \tag{1.3}$$

This is the time-independent Schrödinger equation for the quantum oscillator. We could use $\hat{\mathcal{H}}$ in the form of (1.2) and set about solving the Schrödinger equation as a differential equation. You can find this treatment in various quantum texts[2]. Alternatively, there is an elegant algebraic approach due to Dirac which we will adopt here.

[1] https://arxiv.org/pdf/2005.03134; not an application I know anything about, and the oscillator is relativistic — see later in this course for the necessary background.

[2] e.g. Schiff, p67; Shankar, p190; Griffiths, p48. It is a nice example of the application of methods you should be capable of. It is outside the scope of this course, but do give it a look.

1.1 Ladder operators and the eigenvalue spectrum

Recall the momentum operator which in the position representation is $\hat{p} = -i\hbar\frac{d}{dx}$. The Hamiltonian of the linear harmonic oscillator is equivalently

$$\hat{\mathcal{H}} = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega^2\hat{x}^2. \tag{1.4}$$

Recall also the canonical commutation property of $\hat{p}$ and $\hat{x}$:[3]

$$[\hat{x},\hat{p}] = \hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar \tag{1.5}$$

Looking at (1.4) and motivated by the identity

$$(u-iv)(u+iv) = u^2 - i(vu-uv) + v^2 = u^2 + v^2 \tag{1.6}$$

satisfied by scalar numbers, we look to factorise the Hamiltonian. To this end, we define two new operators:

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\frac{1}{\sqrt{2m\hbar\omega}}\hat{p}, \qquad \hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - i\frac{1}{\sqrt{2m\hbar\omega}}\hat{p} \tag{1.7}$$

Now, $\hat{x}$ and $\hat{p}$ are Hermitian operators (they do, after all, correspond to physical observables) — evidently $\hat{a}$ and $\hat{a}^\dagger$ are not[4]. Instead $(\hat{a})^\dagger = \hat{a}^\dagger$ and $\left(\hat{a}^\dagger\right)^\dagger = \hat{a}$ as the notation implies. Because they are operators and not scalars we cannot assume $\left[\hat{a},\hat{a}^\dagger\right] = \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}$ will be zero needed for (1.6) to hold for $\hat{a}$ and $\hat{a}^\dagger$, and indeed using the commutation properties of $\hat{x}$ and $\hat{p}$ one finds

$$\left[\hat{a},\hat{a}^\dagger\right] = 1 \tag{1.8}$$

as well as

$$\hat{a}^\dagger\hat{a} = \frac{1}{\hbar\omega}\hat{\mathcal{H}} - \frac{1}{2}, \qquad \hat{a}\hat{a}^\dagger = \frac{1}{\hbar\omega}\hat{\mathcal{H}} + \frac{1}{2} \tag{1.9a}$$

or

$$\hat{\mathcal{H}} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right), \qquad \hat{\mathcal{H}} = \hbar\omega\left(\hat{a}\hat{a}^\dagger - \frac{1}{2}\right). \tag{1.9b}$$

These are expressions for the Hamiltonian of the quantum linear oscillator in terms of the new operators $\hat{a}$ and $\hat{a}^\dagger$.

The operators $\hat{a}$ and $\hat{a}^\dagger$ are known as `ladder operators`. To see why, suppose we have a stationary state of the linear oscillator with energy ε. In the position representation it satisfies the time-independent Schrödinger equation

$$\hat{\mathcal{H}}\varphi_\varepsilon(x) = \varepsilon\varphi_\varepsilon(x). \tag{1.10a}$$

Let us denote the corresponding ket $|\varepsilon\rangle$: $\langle x|\varepsilon\rangle = \varphi_\varepsilon(x)$ i.e.

$$\hat{\mathcal{H}}|\varepsilon\rangle = \varepsilon|\varepsilon\rangle. \tag{1.10b}$$

The operators $\hat{a}$ and $\hat{a}^\dagger$ acting upon the ket $|\varepsilon\rangle$ will produce new kets, $\hat{a}|\varepsilon\rangle$ and $\hat{a}^\dagger|\varepsilon\rangle$ respectively. Let us consider the effect of acting on each of these kets using the Hamiltonian. Firstly

$$\begin{aligned}
\hat{\mathcal{H}}\hat{a}^\dagger|\varepsilon\rangle &= \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)\hat{a}^\dagger|\varepsilon\rangle && \text{using (1.9b)} \\
&= \hat{a}^\dagger\left[\hbar\omega\left(\hat{a}\hat{a}^\dagger + \frac{1}{2}\right)\right]|\varepsilon\rangle && \text{pulling } \hat{a}^\dagger \text{ through} \\
&= \hat{a}^\dagger\left(\hat{\mathcal{H}} + \hbar\omega\right)|\varepsilon\rangle && \text{using (1.9b)} \\
&= (\varepsilon + \hbar\omega)\,\hat{a}^\dagger|\varepsilon\rangle && \text{using (1.10b)},
\end{aligned} \tag{1.11a}$$

[3] Remember operators act on kets, so to identify $\hat{x}\hat{p} - \hat{p}\hat{x}$ we can for example use the position representation and let it act upon some wave function $\langle x|\psi\rangle = \psi(x)$:

$$(\hat{x}\hat{p} - \hat{p}\hat{x})\,\psi(x) = x\left(-i\hbar\frac{d}{dx}\psi(x)\right) + i\hbar\frac{d}{dx}(x\psi(x)) = -i\hbar x\frac{d\psi(x)}{dx} + i\hbar\left(\psi(x) + x\frac{d\psi(x)}{dx}\right) = i\hbar\psi(x).$$

[4] But they are real differential operators:

$$\hat{a}\psi(x) = \left(\sqrt{\frac{m\omega}{2\hbar}}x + \sqrt{\frac{\hbar}{2m\omega}}\frac{d}{dx}\right)\psi(x), \qquad \hat{a}^\dagger\psi(x) = \left(\sqrt{\frac{m\omega}{2\hbar}}x - \sqrt{\frac{\hbar}{2m\omega}}\frac{d}{dx}\right)\psi(x).$$

and similarly

$$\begin{aligned}\hat{\mathcal{H}}\hat{a}|\varepsilon\rangle &= \hbar\omega\left(\hat{a}\hat{a}^\dagger - \frac{1}{2}\right)\hat{a}|\varepsilon\rangle \qquad \text{using (1.9b)}\\ &= \hat{a}\left[\hbar\omega\left(\hat{a}^\dagger\hat{a} - \frac{1}{2}\right)\right]|\varepsilon\rangle \qquad \text{pulling } \hat{a} \text{ through}\\ &= \hat{a}\left(\hat{\mathcal{H}} - \hbar\omega\right)|\varepsilon\rangle \qquad \text{using (1.9b)}\\ &= (\varepsilon - \hbar\omega)\,\hat{a}|\varepsilon\rangle \qquad \text{using (1.10b)}.\end{aligned} \tag{1.11b}$$

From (1.11a) we recognise $\hat{a}^\dagger|\varepsilon\rangle$ is a stationary state of the linear oscillator with energy $\varepsilon + \hbar\omega$, and from (1.11b) that $\hat{a}|\varepsilon\rangle$ is a stationary state with energy $\varepsilon - \hbar\omega$. It follows that applying repeatedly

$$\hat{\mathcal{H}}(\hat{a}^\dagger)^m|\varepsilon\rangle = (\varepsilon + m\hbar\omega)\,(\hat{a}^\dagger)^m|\varepsilon\rangle, \qquad \hat{\mathcal{H}}(\hat{a})^m|\varepsilon\rangle = (\varepsilon - m\hbar\omega)\,(\hat{a})^m|\varepsilon\rangle, \tag{1.12}$$

and we see that in this way $\hat{a}^\dagger$ and $\hat{a}$ repeatedly acting upon a state ket generate a heirarchy of stationary states, stepping up or down the energy spectrum in steps $\hbar\omega$. Hence the name ladder operators.

Since we know kinetic energy is never negative, and the potential of our linear oscillator has a minimum value of zero, we expect the spectrum to have a lower bound, which is not evident from (1.12). Let us therefore assume the existence of a state of minimum energy, and let $|\varepsilon_0\rangle$ denote the corresponding ket and ε_0 the value of this minimum energy:the ground state energy. This must satisfy

$$\hat{a}|\varepsilon_0\rangle = 0 \tag{1.13}$$

otherwise (1.11b) shows $\hat{a}|\varepsilon_0\rangle$ is an eigenstate with energy $\varepsilon_0 - \hbar\omega$, lower than the ground state energy ε_0, which is a contradiction. So

$$\begin{aligned}\hat{\mathcal{H}}|\varepsilon_0\rangle &= \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)|\varepsilon_0\rangle \qquad \text{using (1.9b)}\\ &= \frac{1}{2}\hbar\omega|\varepsilon_0\rangle \qquad \text{using (1.13)}.\end{aligned} \tag{1.14}$$

So the ground state ket $|\varepsilon_0\rangle$ is an eigenstate of the Hamiltonian $\hat{\mathcal{H}}$ with ground state energy $\varepsilon_0 = \hbar\omega/2$ (not zero, which is the case for a classical oscillator; this non-zero least amount of energy of the quantum oscillator is known as "zero-point" energy). Therefore, from (1.12) we can write for the energy eigenstates of the harmonic oscillator

$$|n\rangle \propto (\hat{a}^\dagger)^n|0\rangle, \qquad \hat{\mathcal{H}}|n\rangle = \varepsilon_n|n\rangle, \qquad \varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega \tag{1.15}$$

where we now use integer n and not energy $\varepsilon_n = (n + \frac{1}{2})\hbar\omega$ to label the states. Notice we have established this using operators alone. We have not adopted a specific representation.

1.2 Creation and annhiliation

The operators $\hat{a}$ and $\hat{a}^\dagger$ are also known as `annihilation` and `creation` operators respectively. This originates from their effect being to create and annihiliate a quantum of energy $\hbar\omega$. The monikers raising and lowering are also used.

We have seen that, apart from a zero-point energy $\frac{1}{2}\hbar\omega$, a characteristic state of the quantum oscillator has an integer number of such energy quanta.[5] The number operator

$$\hat{\mathcal{N}} = \hat{a}^\dagger\hat{a} \tag{1.16}$$

counts how many: $\hat{\mathcal{N}}|n\rangle = n|n\rangle$. The Hamiltonian expressed in terms of the number operator is $\hat{\mathcal{H}} = \hbar\omega(\hat{\mathcal{N}} + 1/2)$. Instead of thinking of the oscillator moving up and down the ladder of energy states, we can instead picture the oscillator as an object comprising an increasing or decreasing number of quanta. Interaction with the oscillator corresponds to excitation/deexcitation and a transfer in and out of an integer number of the elementary unit of energy. We could attach a physical significance to these energy quanta. The modern theory of particles envisages particles as excitations, quanta, of an underlying quantum field. In the context of the lattice vibrations in solids, they are phonons; spin excitations in a solids are magnons. For the electomagnetic field they are photons. The zero-point energy then represents e.g. the energy in the electromagnetic field when no photons are present.

[5] singular quantum; plural quanta

1.3 Normalised eigenstates

Let us return to the state kets. These must be normalised if they are to be used to calculate expectation values in order to predict the results of measurements performed on the quantum oscillator. A normalised ket $|\psi\rangle$ satisfies $\langle\psi|\psi\rangle = 1$ where $\langle\psi| = (|\psi\rangle)^\dagger$.

That $|n\rangle$ is proportional to $(\hat{a}^\dagger)^n|0\rangle$ (we just showed that! see (1.15)) implies $\hat{a}^\dagger|n\rangle = c_n|n+1\rangle$ where c_n is a constant that ensures that $|n\rangle$ is normalised if $|n+1\rangle$ is. We see then that

$$\begin{aligned}\langle n|\hat{a}\hat{a}^\dagger|n\rangle &= \left(\langle n|\hat{a}\right)\left(\hat{a}^\dagger|n\rangle\right)\\ &= \left(\hat{a}^\dagger|n\rangle\right)^\dagger\left(\hat{a}^\dagger|n\rangle\right)\\ &= \left(c_n|n+1\rangle\right)^\dagger\left(c_n|n+1\rangle\right)\\ &= \left(c_n^*\langle n+1|\right)\left(c_n|n+1\rangle\right) = |c_n|^2\end{aligned} \tag{1.17}$$

since $|n+1\rangle$ is normalised. But

$$\begin{aligned}\hat{a}\hat{a}^\dagger|n\rangle &= \left(\frac{1}{\hbar\omega}\hat{\mathcal{H}} + \frac{1}{2}\right)|n\rangle \qquad \text{using (1.9a)}\\ &= \left(\frac{1}{\hbar\omega}\left(n+\frac{1}{2}\right)\hbar\omega + \frac{1}{2}\right)|n\rangle \qquad \text{using (1.15)}\\ &= (n+1)\,|n\rangle.\end{aligned} \tag{1.18}$$

So $\langle n|\hat{a}\hat{a}^\dagger|n\rangle = n+1 = |c_n|^2$. Choosing c_n real and positive,

$$\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle. \tag{1.19}$$

Rearranging this equation with $n \to n-1$:

$$\begin{aligned}|n\rangle &= \frac{1}{\sqrt{n}}\hat{a}^\dagger|n-1\rangle\\ &= \frac{1}{\sqrt{n(n-1)}}\left(\hat{a}^\dagger\right)^2|n-2\rangle \qquad \text{inserting corresponding expression for } |n-1\rangle\\ &= \frac{1}{\sqrt{n!}}\left(\hat{a}^\dagger\right)^n|0\rangle \qquad \text{repeating a further } n-2 \text{ times.}\end{aligned} \tag{1.20}$$

This is an expression for correctly-normalised ket $|n\rangle$ in terms of the ground state ket $|0\rangle$.

If we want an explicit expression we have to choose the representation we want. Let us choose the position representation. Recall that acting upon the ground state ket with the annihilation operator gives zero: $\hat{a}|0\rangle = 0$. Hence in the position representation

$$a|0\rangle = 0 \qquad \Rightarrow \qquad \left(\sqrt{\frac{m\omega}{2\hbar}}x + \sqrt{\frac{\hbar}{2m\omega}}\frac{d}{dx}\right)\psi_0(x)$$

(see footnote 4). Tidying

$$\begin{aligned}&\frac{d}{dx}\psi_0(x) = -\frac{m\omega x}{\hbar}\psi_0(x)\\ \Rightarrow \qquad &\frac{1}{\psi_0}\frac{d\psi_0}{dx} = \frac{d}{dx}(\ln\psi_0) = -\frac{m\omega x}{\hbar} \qquad \text{assuming } \psi_0 > 0\\ \Rightarrow \qquad &\ln\psi_0 = -\frac{m\omega}{2\hbar}x^2 + A \qquad A \text{ constant}\\ \Rightarrow \qquad &\psi_0(x) = \tilde{A}e^{-\frac{m\omega}{2\hbar}x^2}, \qquad \tilde{A} = e^A, \text{ another constant.}\end{aligned} \tag{1.21}$$

$\tilde{A}$ normalises ψ_0:

$$\begin{aligned}1 = \int_{-\infty}^{\infty}|\psi_0(x)|^2dx &= |\tilde{A}|^2\int_{-\infty}^{\infty}e^{-\frac{m\omega}{\hbar}x^2}dx\\ &= |\tilde{A}|^2\sqrt{\frac{\hbar}{m\omega}}\int_{-\infty}^{\infty}e^{-y^2}dy \qquad y = \sqrt{\frac{m\omega}{\hbar}}x\\ &= |\tilde{A}|^2\sqrt{\frac{\pi\hbar}{m\omega}} \qquad \text{using tables.}\end{aligned} \tag{1.22}$$

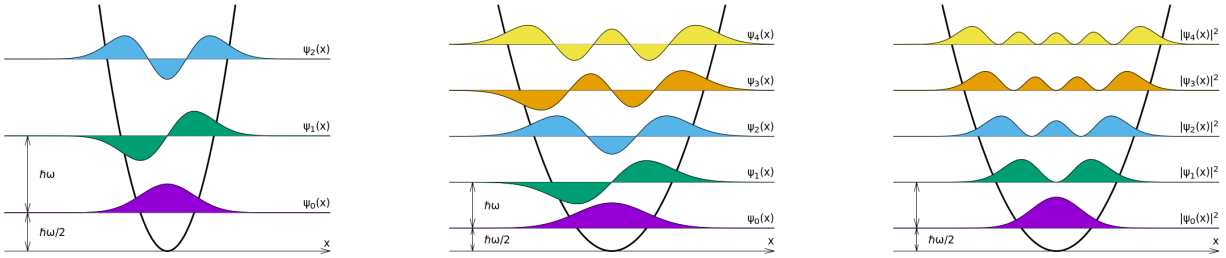

Figure 1: Left and middle: Potential $^1/_2kx^2$ and first few wave functions $\langle x|n\rangle = \psi_n(x)$ of the harmonic oscillator for two different values of k. Right: Probability densities $|\psi_n(x)|^2$ corresponding to the middle case.

Making the natural choice (real, positive)

$$\begin{aligned}\langle x|0\rangle = \psi_0(x) &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2} \\ &= \frac{1}{(\pi\lambda^2)^{1/4}} e^{-x^2/(2\lambda^2)} \end{aligned} \tag{1.23}$$

The ground state wave function is a Gaussian, with characteristic width $\lambda = \sqrt{\hbar/(m\omega)}$. For the other wave functions we use (1.20),

$$\begin{aligned}\langle x|n\rangle = \psi_n(x) &= \frac{1}{\sqrt{n!}}\left(\sqrt{\frac{m\omega}{2\hbar}}x + \sqrt{\frac{\hbar}{2m\omega}}\frac{d}{dx}\right)^n \psi_0(x) \\ &= \frac{1}{(2^{2n}(n!)^2\pi\lambda^2)^{1/4}} e^{-x^2/(2\lambda^2)} H_n(x/\lambda) \qquad \text{after a bit of work!} \end{aligned} \tag{1.24}$$

where $H_n(x)$ is a Hermite polynomial.[6] See Fig. 1. With the exception of the ground state the wave functions oscillate within the classical turning points of the potential, changing sign n times. The wave functions extend slightly into the classically forbidden region, decaying exponentially as they do.

The probability distribution of higher lying states continues to oscillate, unlike the probability of finding a classical oscillator at x. The quantum probability is enhanced near the classical turning point, like that of the classical oscillator where it increases as the mass slows down to rest and then reverses. See Fig. 2.

Class examples

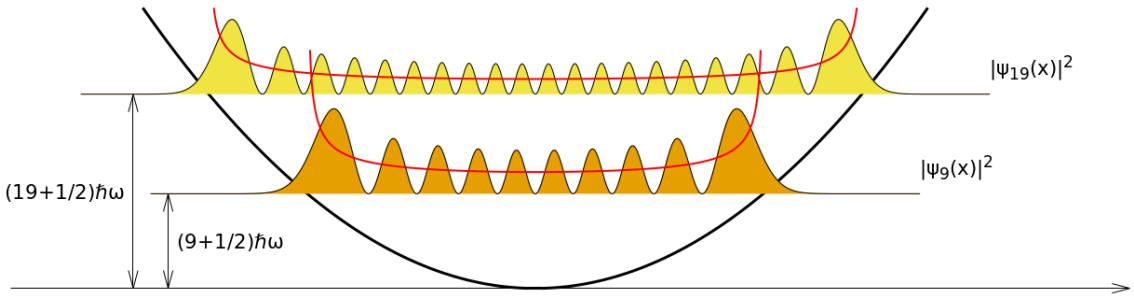

Figure 2: Probability densities of two states of the quantum linear oscillator with higher energy. The classical probability distribution is shown in red.

[6] e.g. https://en.wikipedia.org/wiki/Hermite_polynomials.

2 The Aharonov-Bohm effect

When studying the dynamics of charged particles using classical Newtonian mechanics, forces enter due to electric and magnetic fields $\vec{E}$ and $\vec{B}$ respectively:

$$m\frac{d^2\vec{r}}{dt^2} = q\left(\vec{E} + \vec{v}\times\vec{B}\right) \qquad \vec{v} = \frac{d\vec{r}}{dt}. \tag{2.1}$$

Here, m is the mass and q the charge of the particle. These fields are tangible: we can measure them experimentally[7].

There are no forces or fields in the corresponding Schrödinger equation. Instead[8],

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{\mathcal{H}}\Psi \qquad \text{where} \qquad \hat{\mathcal{H}} = \frac{1}{2m}\left(\vec{\hat{p}} - q\vec{A}\right)^2 + q\phi \tag{2.2}$$

where $\phi = \phi(\vec{r},t)$ and $\vec{A} = \vec{A}(\vec{r},t)$ are the electromagnetic scalar and vector potentials[9]. The fields and potentials are related:

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial\vec{A}}{\partial t}, \qquad \vec{B} = \vec{\nabla}\times\vec{A} \tag{2.4}$$

— it then follows that

$$\begin{aligned}\vec{\nabla}\cdot\vec{B} &= \vec{\nabla}\cdot\left(\vec{\nabla}\times\vec{A}\right) = 0\\ \vec{\nabla}\times\vec{E} &= \vec{\nabla}\times\left(-\vec{\nabla}\phi - \frac{\partial\vec{A}}{\partial t}\right) = -\frac{\partial}{\partial t}\left(\vec{\nabla}\times\vec{A}\right) = -\frac{\partial\vec{B}}{\partial t},\end{aligned}$$

which we recognise as two of the Maxwell equations.

Class discussion

Note that the potentials ϕ and $\vec{A}$ overdescribe the physics. The transformation

$$\vec{A}\to\vec{A}' = \vec{A} + \vec{\nabla}\Lambda, \qquad \phi\to\phi' = \phi - \frac{\partial\Lambda}{\partial t} \tag{2.5}$$

for scalar function $\Lambda(\vec{r},t)$ leaves the measurable electric and magnetic fields unchanged. A transformation that leaves physical observables unchanged is known as a `Gauge transformation`. Gauge transformations are a major concept in modern theoretical physics.

So which is more fundamental? The measurable fields, entering the classical theory, or the potentials that overdescribe the physics but which enter the quantum theory. The Aharanov-Bohm effect tells us. It was one of the "Seven wonders of the Quantum World" in a New Scientist feature[10].

2.1 Electron orbiting a magnetic flux tube

Class example

[7] How?

[8] This is often refered to as **minimal coupling**

[9] Note $\vec{\hat{p}}$ is a differential operator and so does not commute with $\vec{A}$. We have

$$\left(\vec{\hat{p}} - q\vec{A}\right)^2 = \left(\vec{\hat{p}} - q\vec{A}\right)\cdot\left(\vec{\hat{p}} - q\vec{A}\right) = p^2 - q\left(\vec{\hat{p}}\cdot\vec{A} + \vec{A}\cdot\vec{\hat{p}}\right) + q^2A^2 \tag{2.3}$$

which is more obviously Hermitian.

[10] M. Brooks, *Seven wonders of the quantum world*, New Scientist May 5, 2010. Available to subscribers so you will need to access via the University Library link.

Figure 3: Left: Yakir Aharonov (1932-); Right: David Bohm (1917-1992). Government warning: Smoking kills.

2.2 Aharonov-Bohm experiment

The Aharonov-Bohm effect, named after Bristol-based physicists Yakir Aharonov and David Bohm[11] (Fig. 3) is the name given to quantum-mechanical phenomena where a charged particle is influenced by the electromagnetic potentials $\varphi, \vec{A}$ despite moving exclusively through regions of space where the electric and magnetic fields $\vec{E}$ and $\vec{B}$ are zero. The previous thought-experiment illustrates the effect but the original proposal and subsequent experimental verification were based on interference effects.

If $f = f(x)$ and $g = g(x)$, then

$$\frac{d}{dx}\left(fe^{ig}\right) = \left(\frac{df}{dx}\right)e^{ig} + f\left(i\frac{dg}{dx}\right)e^{ig}. \tag{2.6}$$

Similarly, if $\psi = \psi(\vec{r})$ and $\chi = \chi(\vec{r})$,

$$\vec{\nabla}\left(\psi e^{i\chi}\right) = \left(\vec{\nabla}\psi\right)e^{i\chi} + \psi\left(i\vec{\nabla}\chi\right)e^{i\chi}. \tag{2.7}$$

Rearranging,

$$\left(\vec{\nabla} - i\left(\vec{\nabla}\chi\right)\right)\left(\psi e^{i\chi}\right) = \left(\vec{\nabla}\psi\right)e^{i\chi}. \tag{2.8}$$

So

$$\left(\vec{\nabla} - i\left(\vec{\nabla}\chi\right)\right)\cdot\left(\vec{\nabla} - i\left(\vec{\nabla}\chi\right)\right)\left(\psi e^{i\chi}\right) = \left(\vec{\nabla} - i\left(\vec{\nabla}\chi\right)\right)\cdot\left(\left(\vec{\nabla}\psi\right)e^{i\chi}\right) = \left(\vec{\nabla}\left(\vec{\nabla}\psi\right)\right)e^{i\chi}. \tag{2.9}$$

Swapping left and right, multiplying by $(-i\hbar)^2 e^{-i\chi}$ and introducing $\hat{\vec{p}} = -i\hbar\vec{\nabla}$

$$\vec{p}^2\psi = e^{-i\chi}\left(\vec{p} - \hbar\vec{\nabla}\chi\right)^2\left(\psi e^{i\chi}\right). \tag{2.10}$$

It follows that if

$$i\hbar\frac{\partial\psi}{\partial t} = \left(\frac{1}{2m}\vec{p}^2 + q\varphi\right)\psi \tag{2.11}$$

then

$$i\hbar\frac{\partial(\psi e^{i\chi})}{\partial t} = \left(\frac{1}{2m}\left(\vec{p} - \hbar\vec{\nabla}\chi\right)^2 + q\varphi\right)\left(\psi e^{i\chi}\right). \tag{2.12}$$

Choosing

$$\chi(\vec{r}) = \frac{q}{\hbar}\int_{\vec{r}_0}^{\vec{r}}\vec{A}(\vec{r}\,')\cdot d\vec{r}\,' \tag{2.13}$$

where $\vec{r}_0$ is some fixed origin means $\vec{\nabla}\chi = (q/\hbar)\vec{A}$ and we finally see that the solutions of the Schrödinger equation (2.2) with vector potential $\vec{A}$ is $\Psi = \psi_0 e^{i\chi}$ where ψ_0 is solution in the absence of the vector-potential.

In an experiment, Fig. 4, an electron beam is split and passes to either side ($+$ and $-$) of a solenoid before coming together where the two parts (ψ_+ and ψ_-) combine and create an interference pattern. If the $\vec{B}$-field within the solenoid is zero then the vector potential $\vec{A}$ outside is zero and $\psi_+ = \psi_- = \psi_0$. If the $\vec{B}$-field within the solenoid is not zero then the vector potential $\vec{A}$ outside does not vanish outside, and

$$\psi_\pm = \psi_0 e^{i\chi_\pm}, \qquad \chi_\pm = \frac{q}{\hbar}\int_{C_\pm}\vec{A}\cdot d\vec{r}\,'. \tag{2.14}$$

[11] Phys. Rev. **115**, 485 (1959); the effect had actually been predicted by Werner Ehrenberg and Raymond Siday a decade earlier: Proc. Phys. Soc. B**62**, 8 (1949).

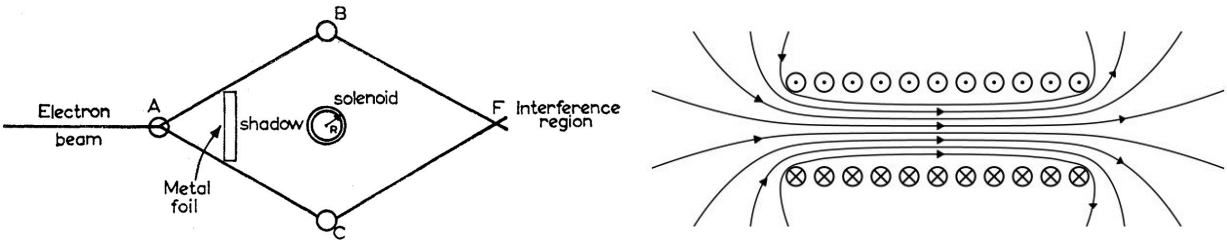

Figure 4: Left: Schematic experiment to demonstrate interference with time-independent vector potential. An electron beam is split and passes around a solenoid taking either path $C_+ \equiv ABF$ or path $C_- \equiv ACF$. [From Aharonov & Bohm, Phys. Rev. **115**, 485 (1959).] Right: Magnetic field lines of an 11-turn solenoid. As the length of the solenoid increases, the strength of the field outside decreases.

At the detector

$$\begin{aligned} |\Psi|^2 &= |\psi_+ + \psi_-|^2 \\ &= |\psi_0|^2 |e^{i\chi_+} + e^{i\chi_-}|^2 \\ &= 4|\psi_0|^2 \cos^2\left(\frac{\chi_+ - \chi_-}{2}\right) \\ &\propto \cos^2\left(\frac{q\Phi}{2\hbar}\right) \end{aligned} \tag{2.15}$$

using

$$\chi_+ - \chi_- = \int_{C_+} \vec{A}(\vec{r}\,') \cdot d\vec{r}\,' - \int_{C_-} \vec{A}(\vec{r}\,') \cdot d\vec{r}\,' = \oint \vec{A}(\vec{r}\,') \cdot d\vec{r}\,' = \Phi. \tag{2.16}$$

Varying the magnetic field inside the solenoid causes variations in the interference pattern, *even though the electrons never move through a region of space where $\vec{B}$ differs from zero*.

Note that once again it is the enclosed flux Φ that the interference pattern depends upon, so that the interference pattern is gauge invarient. $\vec{A}$ itself is not measurable.

Quantum Dynamics

In this topic we will be considering the time-dependence of quantum systems.

If we think of a classical mass m on a spring, displacement from equilibrium x, then the potential energy $V = \frac{1}{2}kx^2$ does not depend explicitly upon time. The resulting equation of motion

$$F\left(=-\frac{dV}{dx}\right) = ma \qquad \Rightarrow \qquad m\frac{d^2x}{dt^2} = -kx \tag{3.1}$$

has solutions $x(t) = A\cos(\omega t + B)$, $\omega^2 = \sqrt{k/m}$. The system evolves in time: it is dynamic.

The same is true of quantum systems with time-independent potentials. The dynamics are governed by the time-*dependent* Schrödinger equation (TDSE)

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{\mathcal{H}}|\psi(t)\rangle \tag{3.2}$$

where $\hat{\mathcal{H}}$ is independent of t. Such a Hamiltonian has energy eigenstates satisfying $\hat{\mathcal{H}}|\varepsilon_n\rangle = \varepsilon_n|\varepsilon_n\rangle$ that form an orthonormal basis set that can be used to expand $|\psi(t)\rangle$ with time-dependent coefficients $\psi_j(t)$:

$$|\psi(t)\rangle = \sum_j \psi_j(t)|\varepsilon_j\rangle. \tag{3.3}$$

Substituting into the TDSE

$$i\hbar\sum_j \frac{\partial\psi_j(t)}{\partial t}|\varepsilon_j\rangle = \sum_j \psi_j(t)\varepsilon_j|\varepsilon_j\rangle, \tag{3.4}$$

and acting from the left with $\langle\varepsilon_n|$

$$i\hbar\frac{\partial\psi_n(t)}{\partial t} = \varepsilon_n\psi_n(t) \tag{3.5}$$

— a first order differential equation, easily solved:

$$\psi_n(t) = \psi_n(0)e^{-i\varepsilon_n t/\hbar}. \tag{3.6}$$

So

$$|\psi(t)\rangle = \sum_n \langle\varepsilon_n|\psi(0)\rangle e^{-i\varepsilon_n t/\hbar}|\varepsilon_n\rangle. \tag{3.7}$$

This equation allows us to obtain solutions to the TDSE, given solutions $\{\varepsilon_n, |\varepsilon_n\rangle\}$ of the time-independent Schrödinger equation and given an initial quantum state $|\psi(0)\rangle$.

If the initial quantum state is an energy eigenstate, $|\psi(0)\rangle = |\varepsilon_m\rangle$, then (3.7) shows

$$|\varepsilon_m, t\rangle = e^{-i\varepsilon_m t/\hbar}|\varepsilon_m, 0\rangle. \tag{3.8}$$

The eigenstates have a simple time-dependence, acquiring a steadily changing phase $\varepsilon_m t/\hbar = \omega_m t$ as time evolves. That means the probability $|\langle x|\varepsilon_m, t\rangle|^2$ of finding a particle in the energy eigenstate at position x is time-independent, as are the probabilities of any other measurement. Hence energy eigenstates are stationary states.

A more general initial state is some superposition of energy eigenstates, i.e. more than one coefficient $c_m = \langle\varepsilon_m|\psi(0)\rangle$ in (3.7) is non-zero. That leads to more varied time-dependence, but still **nothing really happens** in a qualified sense. The expectation value of the energy doesn't change in time, or the probability[1] that the system is found in a particular energy eigenstate ε_n. The probability of finding the particle at position x *will* vary in time, but only due to "beating" of the different frequencies of oscillation of the individual eigenstates — akin to how the detailed motion of a set of masses on springs is a superposition of a set of periodically varying normal modes.

Class example

[1] I feel a problem sheet question coming on, asking you to show these.

3.1 Time evolution and quantum pictures

The evolution in time of a quantum state from initial value $|\psi(0)\rangle$ to $|\psi(t)\rangle$ at time t defines a time evolution operator $\hat{\mathcal{U}}(t)$:

$$|\psi(t)\rangle = \hat{\mathcal{U}}(t)|\psi(0)\rangle. \tag{3.9}$$

If the Hamiltonian is independent of time the formal solution of the TDSE is

$$|\psi(t)\rangle = e^{-i\hat{\mathcal{H}}t/\hbar}|\psi(0)\rangle \tag{3.10}$$

where it is understood that[2] $\exp\hat{A} = \mathbb{1} + \hat{A} + \frac{1}{2!}\hat{A}\hat{A} + \ldots$. Eqn. (3.10) can be verified by taking the derivative with respect to time. We see then that for time-independent Hamiltonians the time-evolution operator is

$$\hat{\mathcal{U}}(t) = e^{-i\hat{\mathcal{H}}t/\hbar}. \tag{3.11}$$

This form does not apply for more general Hamiltonians. Instead, the defining equation of the time-evolution operator is found by substituting the form $|\psi(t)\rangle = \hat{\mathcal{U}}(t)|\psi(0)\rangle$ into the TDSE (3.2) to get

$$i\hbar\frac{\partial}{\partial t}\hat{\mathcal{U}}(t) = \hat{\mathcal{H}}\hat{\mathcal{U}}(t), \qquad \hat{\mathcal{U}}(0) = 1 \tag{3.12}$$

which holds for time-dependent Hamiltonians too. The time-evolution operator satisfies the TDSE!

Hermitian Hamiltonians preserve the state norm, $\langle\psi(t)|\psi(t)\rangle = \langle\psi(0)|\psi(0)\rangle$, from which one recognises

$$\hat{\mathcal{U}}^\dagger(t)\hat{\mathcal{U}}(t) = \mathbb{1}, \qquad \text{or} \qquad \hat{\mathcal{U}}^{-1}(t) = \hat{\mathcal{U}}^\dagger(t). \tag{3.13}$$

The time-evolution operator is unitary.

Heisenberg picture

In the normal Schrödinger picture the state vectors are dynamic, varying in time: $|\psi_S(t)\rangle$.

In practice, we are not so much interested in the states themselves, but in matrix elements and expectation values of operators — which in the Schrödinger picture are normally independent of time:

$$\langle\psi_S(t)|\hat{\mathcal{O}}_S|\chi_S(t)\rangle. \tag{3.14}$$

Using the time-evolution operator all the time-dependence can be transferred to the operator — this is the Heisenberg picture. From (3.9)

$$\langle\psi_S(t)|\hat{\mathcal{O}}_S|\chi_S(t)\rangle = \langle\psi(0)|\hat{\mathcal{U}}^\dagger(t)\hat{\mathcal{O}}_S\hat{\mathcal{U}}(t)|\chi(0)\rangle \tag{3.15}$$

or defining the operator

$$\hat{\mathcal{O}}_H(t) = \hat{\mathcal{U}}^\dagger(t)\hat{\mathcal{O}}_S\hat{\mathcal{U}}(t) \tag{3.16}$$

the matrix element has become

$$\langle\psi(0)|\hat{\mathcal{O}}_H(t)|\chi(0)\rangle. \tag{3.17}$$

In the Heisenberg picture a fixed basis is used for all times, but the operators evolve. How? Differentiating (3.16)

$$\begin{aligned}\frac{d}{dt}\hat{\mathcal{O}}_H &= \left(\frac{\partial\hat{\mathcal{U}}^\dagger}{\partial t}\right)\hat{\mathcal{O}}\hat{\mathcal{U}} + \hat{\mathcal{U}}^\dagger\left(\frac{\partial\hat{\mathcal{O}}}{\partial t}\right)\hat{\mathcal{U}} + \hat{\mathcal{U}}^\dagger\hat{\mathcal{O}}\left(\frac{\partial\hat{\mathcal{U}}}{\partial t}\right)\\ &= \left(\frac{i}{\hbar}\hat{\mathcal{U}}^\dagger\hat{\mathcal{H}}\right)\hat{\mathcal{O}}\hat{\mathcal{U}} + \left(\frac{\partial\hat{\mathcal{O}}}{\partial t}\right)_H + \hat{\mathcal{U}}^\dagger\hat{\mathcal{O}}\left(-\frac{i}{\hbar}\hat{\mathcal{H}}\hat{\mathcal{U}}\right) \text{ using (3.12) and (3.16).}\end{aligned} \tag{3.18}$$

Finally inserting $\hat{\mathcal{U}}^\dagger\hat{\mathcal{U}}$ between the operators $\hat{\mathcal{O}}$ and $\hat{\mathcal{H}}$ in the first and third terms, using (3.16) and recognising the commutator

$$\frac{d}{dt}\hat{\mathcal{O}}_H = -\frac{i}{\hbar}\left[\hat{\mathcal{O}}_H, \hat{\mathcal{H}}_H\right] + \left(\frac{\partial\hat{\mathcal{O}}}{\partial t}\right)_H. \tag{3.19}$$

[2] In general the action of functions of operators is the action of their series expansion.

The last term means differentiate $\hat{\mathcal{O}}$ with respect to explicit time in the Schrödinger picture, (often this is zero), then convert to the Heisenberg picture.

Equation (3.19) is the **Heisenberg equation of motion**. With state kets stationary, the time-evolution and so the equation of motion in the Heisenberg picture is an equation for the evolution of the operators. The initial state is only reintroduced for obtaining specific values.

Class example

Interaction picture

The interaction picture sits between the Schrödinger and Heisenberg pictures. In it, the time dependence due to some "unperturbed" Hamiltonian is stripped off the kets and transferred to the operators, whilst that due to a "perturbation" is left on them. Often the unperturbed Hamiltonian is well-understood and exactly solvable, while the "perturbation", or interaction, is weak in some sense.

Let us split a time-dependent Hamiltonian into a time-independent $\hat{\mathcal{H}}_0$ and time-dependent interaction $\hat{\mathcal{V}}(t)$,

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{V}}(t). \tag{3.20}$$

Defining

$$|\psi_I(t)\rangle = \hat{\mathcal{U}}_0(t)|\psi_S(t)\rangle, \qquad \hat{\mathcal{U}}_0(t) = e^{i\hat{\mathcal{H}}_0 t/\hbar} \tag{3.21}$$

as a state ket in the **interaction picture** then

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}|\psi_I(t)\rangle &= \left(i\hbar\frac{\partial}{\partial t}\hat{\mathcal{U}}_0(t)\right)|\psi_S(t)\rangle + \hat{\mathcal{U}}_0(t)\left(i\hbar\frac{\partial}{\partial t}|\psi_S(t)\rangle\right) \\ &= -\hat{\mathcal{H}}_0\hat{\mathcal{U}}_0(t)|\psi_S(t)\rangle + \hat{\mathcal{U}}_0(t)\left(\hat{\mathcal{H}}_0 + \hat{\mathcal{V}}(t)\right)|\psi_S(t)\rangle \qquad \text{using (3.12) and the TDSE.} \end{aligned} \tag{3.22}$$

$\hat{\mathcal{H}}_0$ and $\hat{\mathcal{U}}_0(t)$ commute[3] so recognising terms that cancel,

$$i\hbar\frac{\partial}{\partial t}|\psi_I(t)\rangle = \hat{\mathcal{V}}_I(t)|\psi_I(t)\rangle, \qquad \hat{\mathcal{V}}_I(t) = \hat{\mathcal{U}}_0(t)\hat{\mathcal{V}}(t)\hat{\mathcal{U}}^\dagger(t) = e^{i\hat{\mathcal{H}}_0 t/\hbar}\hat{\mathcal{V}}(t)e^{-i\hat{\mathcal{H}}_0 t/\hbar} \tag{3.23}$$

is the equation of motion in the interaction picture. The state $|\psi_I(t)\rangle$ is evolved by the interaction $\hat{\mathcal{V}}_I(t)$.

Let us now expand $|\psi_I(t)\rangle$ in the energy eigenstates of $\hat{\mathcal{H}}_0$,

$$|\psi_I(t)\rangle = \sum c_n(t)|n\rangle, \qquad \hat{\mathcal{H}}_0|n\rangle = \varepsilon_n|n\rangle \tag{3.24}$$

If we insert this expansion into the equation of motion (3.23) and then contract with a particular energy eigenstate $\langle m|$,

$$\dot{c}_m = \frac{1}{i\hbar}\sum_n \langle m|\hat{\mathcal{V}}(t)|n\rangle c_n e^{i\omega_{mn}t}, \qquad \omega_{mn} = (\varepsilon_m - \varepsilon_n)/\hbar. \tag{3.25}$$

This is an exact equation for the evolution of the coefficients.

Class example

[3] $\hat{\mathcal{H}}_0\hat{\mathcal{U}}_0(t) = \hat{\mathcal{H}}_0 e^{i\hat{\mathcal{H}}_0 t/\hbar} = \hat{\mathcal{H}}_0\left(1 + i\hat{\mathcal{H}}_0 t/\hbar + (+i\hat{\mathcal{H}}_0 t/\hbar)^2 + \ldots\right) = \left(1 + i\hat{\mathcal{H}}_0 t/\hbar + (+i\hat{\mathcal{H}}_0 t/\hbar)^2 + \ldots\right)\hat{\mathcal{H}}_0 = \hat{\mathcal{U}}_0(t)\hat{\mathcal{H}}_0.$

3.2 Time dependent perturbation theory

Exact solution of systems with time-dependent Hamiltonians is not generally straightforward, but if the disturbance is weak then it can be treated as a perturbation. The sort of problem we have in mind might be atomic electrons in an external electromagnetic field, causing them to jump between energy levels via the absorption or emission of radiation.

The expansion (3.24) means $|c_m(t)|^2$ represents the probability that at time t the system is in state $|m\rangle$: $|\langle m|\psi(t)\rangle|^2 = |\langle m|\psi_I(t)\rangle|^2 = |c_m(t)|^2$. If at $t = 0$ we prepare the system in state i ($c_m(0) = \delta_{m,i}$) and at some later time t we find for some state $f \neq i$ that $|c_f(t)|^2 > 0$ then there is a non-zero probability that the state has made a transition. From how $|c_f(t)|^2$ varies with time we can determine the transition rate, which, for example, will allow us to predict the intensity of spectral lines.

We can exploit that $\hat{\mathcal{V}}(t)$ is weak and expand in orders of its effect. To keep track of these[4], we write $\lambda\hat{\mathcal{V}}$ for $\hat{\mathcal{V}}$ and expand the amplitudes c_n as $c_n^{(0)} + \lambda c_n^{(1)} + \lambda^2 c_n^{(2)} + \ldots$. Then (3.25) reads

$$\frac{d}{dt}\left(c_m^{(0)} + \lambda c_m^{(1)} + \lambda^2 c_m^{(2)} + \ldots\right) = \frac{1}{i\hbar}\sum_n \langle m|\lambda\hat{\mathcal{V}}(t)|n\rangle \left(c_n^{(0)} + \lambda c_n^{(1)} + \lambda^2 c_n^{(2)} + \ldots\right) e^{i\omega_{mn}t}. \tag{3.26}$$

and must be satisfied at each order of λ. Zeroth order (λ^0) gives

$$\frac{d}{dt}c_m^{(0)} = 0 \tag{3.27}$$

so $c_m^{(0)}$ is constant. We know that! The coefficients do not vary in time in the absence of the perturbation. More useful, at first order (λ^1)

$$\frac{d}{dt}c_m^{(1)} = \frac{1}{i\hbar}\sum_n \langle m|\hat{\mathcal{V}}(t)|n\rangle c_n^{(0)} e^{i\omega_{mn}t} \tag{3.28}$$

and integrating up

$$c_m^{(1)}(t) = \frac{1}{i\hbar}\sum_n \int_0^t \langle m|\hat{\mathcal{V}}(t')|n\rangle e^{i\omega_{mn}t'} dt' c_n^{(0)}. \tag{3.29}$$

This assumes the perturbation is switched on at $t = 0$ (the lower limit). $t = -\infty$ may be more appropriate in some problems. At second order (λ^2)

$$\frac{d}{dt}c_m^{(2)} = \frac{1}{i\hbar}\sum_n \langle m|\hat{\mathcal{V}}(t)|n\rangle c_n^{(1)} e^{i\omega_{mn}t} \tag{3.30}$$

so

$$\begin{aligned} c_m^{(2)}(t) &= \frac{1}{i\hbar}\sum_n \int_0^t \langle m|\hat{\mathcal{V}}(t')|n\rangle c_n^{(1)}(t') e^{i\omega_{mn}t'} dt' \\ &= \frac{1}{(i\hbar)^2}\sum_{nk} \int_0^t \langle m|\hat{\mathcal{V}}(t')|n\rangle e^{i\omega_{mn}t'} \int_0^{t'} \langle n|\hat{\mathcal{V}}(t'')|k\rangle e^{i\omega_{nk}t''} dt'' dt' c_k^{(0)} \end{aligned} \tag{3.31}$$

using (3.29) for $c_n^{(1)}(t')$. Note the zeroth order amplitudes are independent of $\hat{\mathcal{V}}$; the first order corrections depend upon $\hat{\mathcal{V}}$ once; the second order corrections involve two factors of $\hat{\mathcal{V}}$.

There is quite a nice diagrammatic representation of these expression. Theoretical physicists often resort to diagrammatic expansions when the maths gets complicated.

The probability of a transition from initial state i to final state f assuming $c_m(0) = \delta_{m,i}$ is

$$P_{i\to f} = |c_f(t)|^2. \tag{3.32}$$

The first order result $P_{i\to f} \simeq |c_f^{(1)}(t)|^2$ is expected to be accurate only if $\ll 1$. A large value would require the examination of second order (and maybe higher) terms.

[4] The same method simplifies the derivation of time-independent perturbation theory.

3.3 Harmonic perturbations

Consider the important case

$$\hat{\mathcal{V}}(t) = \hat{\mathcal{F}} e^{-i\omega t} + \hat{\mathcal{F}}^\dagger e^{i\omega t} \tag{3.33}$$

where $\hat{\mathcal{F}}$ is a time-independent operator and $\omega > 0$. This form ensures $\hat{\mathcal{V}}$ is Hermitian. An example would be a charge q in an electromagnetic field $\vec{E} = E_0 \cos\omega t \hat{\vec{k}}$ (monochromatic light polarised along $\hat{z}$) where $\hat{\mathcal{F}} = -qE_0 z/2$. We now consider the system in initial state $|i\rangle$ ($c_i(0) = 1,\ c_m(0) = 0$ for $m \neq i$) and ask what is the probability the system is in final state $|f\rangle$ after time t, that is, what is $|c_f(t)|^2$. To first order from (3.29)

$$c_f^{(1)}(t) = -\frac{\langle f|\hat{\mathcal{F}}|i\rangle}{\hbar} \frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi} - \omega} - \frac{\langle f|\hat{\mathcal{F}}^\dagger|i\rangle}{\hbar} \frac{e^{i(\omega_{fi}+\omega)t} - 1}{\omega_{fi} + \omega}. \tag{3.34}$$

We see transitions will be most significant for $\omega \simeq \pm\omega_{fi}$ causing one of the denominators to be small and the corresponding term large. The other term can then be neglected. Let us assume $\omega_{fi} + \omega \gg |\omega_{fi} - \omega|$. Then dropping the second term

$$\begin{aligned} c_f^{(1)}(t) &\simeq -\frac{\langle f|\hat{\mathcal{F}}|i\rangle}{\hbar} \frac{e^{i(\omega_{fi}-\omega)t/2}}{\omega_{fi} - \omega} \left[e^{i(\omega_{fi}-\omega)t/2} - e^{-i(\omega_{fi}-\omega)t/2} \right] \\ &= -i\frac{\langle f|\hat{\mathcal{F}}|i\rangle}{\hbar} \frac{\sin[(\omega_{fi}-\omega)t/2]}{(\omega_{fi}-\omega)/2} e^{i(\omega_{fi}-\omega)t/2} \end{aligned} \tag{3.35}$$

and the probability of finding the system in state f at time t is

$$P_{i\to f}(t) \simeq |c_f^{(1)}(t)|^2 = \frac{1}{\hbar^2} |\langle f|\hat{\mathcal{F}}|i\rangle|^2 \left(\frac{\sin[(\omega_{fi}-\omega)t/2]}{(\omega_{fi}-\omega)/2} \right)^2. \tag{3.36}$$

This is illustrated in Fig. 1, both as a function of the frequency of the perturbation, and time. The factor $(\cdots)^2$ is strongly peaked around $\omega = \omega_{fi}$, with a peak value of t^2 and width $4\pi/t$.[5] The transition is most probably for driving frequencies close to the natural frequency – quantum resonance, if you like. If the transition is slow, so t is long, then the width is very narrow and only occurs for frequencies very close to $\omega = \omega_{fi}$. As $\omega > 0$, $\varepsilon_f > \varepsilon_i$ and

$$\hbar\omega \simeq \hbar\omega_{fi} = \varepsilon_f - \varepsilon_i \tag{3.37}$$

— the system absorbs a quantum of energy $\hbar\omega$ and jumps from initial state i to final state f: we have derived Bohr's third postulate.

Similar analysis for when the frequency ω satisfies $|\omega_{fi} - \omega| \gg \omega_{fi} + \omega$ leads to a transition probability strongly peaked for frequencies very close to $\omega = -\omega_{fi}$ i.e.

$$\hbar\omega \simeq -\hbar\omega_{fi} = \varepsilon_i - \varepsilon_f. \tag{3.38}$$

In this case, maybe surprisingly, the system undergoes a downward transition and *emits* a quantum of energy $\hbar\omega$, with exactly the same probability. This is a process known as stimulated emission. Combined with the fact that the

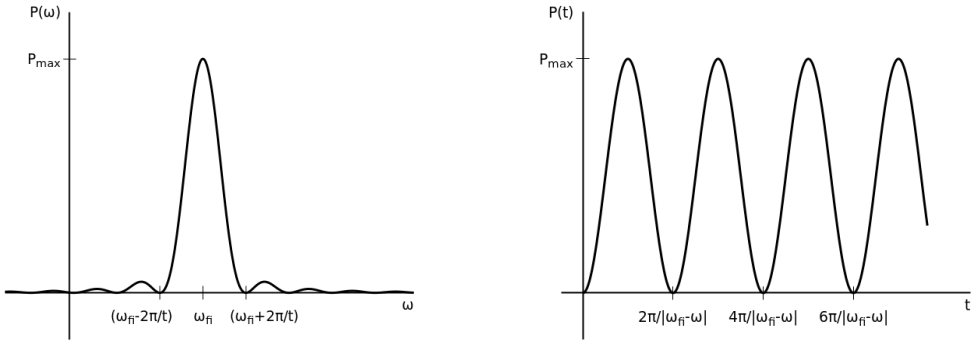

Figure 1: Transition probability as a function of Left: frequency; Right: time.

[5] At it stands our expression for $P_{i\to f}(t)$ increases without bound as t increases, but remember we are working to first order only and so there is an implicit assumption that $|c_f|$ is small. Working to all orders it can never exceed 1.

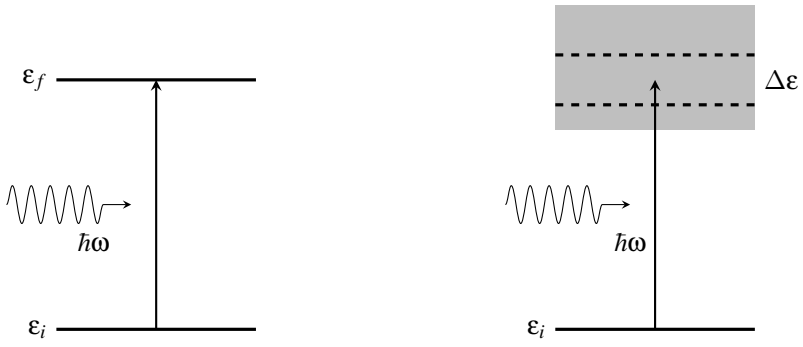

Figure 2: Left: Transition between two discrete levels. Right: Transition between a discrete level and a continuum.

quantum electromagnetic field of the vacuum contains "zero-point" modes, this explains spontaneous emission and why systems containing charges, such as atoms, naturally decay into their ground state.

The transition probability that we have found in (3.36) is oscillatory in time. After reaching a peak at time $t = \pi/|\omega_{fi} - \omega|$ it starts to decrease and is zero at time $2\pi/|\omega_{fi} - \omega|$ before repeating. If you want to induce a transition between two levels in an atom apply an EM wave, but maybe not for too long! What is happening is starting in state i ($c_i(t=0) = 1,\ c_f(0) = 0$), when the frequency ω is in resonance with the transition energy $\varepsilon_f - \varepsilon_i$ there is an increasing probability of the system being excited into the state f absorbing quanta $\hbar\omega$ of energy. This increases $c_f(t)$ at the expense of $c_i(t)$. With $c_f(t)$ non-zero, there becomes the possibility that the system emits quanta $\hbar\omega$ of energy and de-excites, acting to reduce $c_f(t)$. After time $t = \pi/|\omega_{fi} - \omega|$ this process occurs more rapidly then the excitation process, resulting in a net reduction in $c_f(t)$ which eventually becomes zero, after which the cycle repeats.

3.4 Fermi's Golden rule

The finite width of $P(\omega)$ (Fig. 1a) means classical energy conservation $\Delta E = \varepsilon_f - \varepsilon_i = \hbar\omega$ is actually only approximately satisfied. Transitions occur for frequencies both lower and higher[6]. $P(\omega)$ has a width $\delta\omega \sim 1/t$ and the transition takes place some time over the interval 0 to t. Hence

$$\Delta E \Delta t \sim \frac{\hbar}{t} \cdot t \sim \hbar \tag{3.39}$$

which is the energy-time uncertainty relation. There are physical consequences associated with the approximate nature of the energy conservation.

Firstly, if the perturbation corresponds to a range of frequencies (e.g. an electromagnetic field containing a continuum of frequencies) then each will contribute to the transition probability and the contributions must be summed and/or integrated over to get the total probability.

Secondly, the system can make a transition to states in a range ΔE around the classical value, the more so for small t, so there will typically be many final states. For the total probability to *any* final state one must again sum/integrate the individual probabilities. For example, in the photoelectric effect ultraviolet light causes bound electrons to be emitted to a continuum of free-electron states (Fig. 2). Then

$$\begin{aligned} P_{\text{total}}(t) &= \sum_f P_{i\to f}(t) \\ &\to \int P_{i\to f}(t)\rho(\varepsilon_f)d\varepsilon_f \end{aligned} \tag{3.40}$$

where $\rho(\varepsilon)$ is the density of final states. We know $P_{i\to f}(t)$ is sharply peaked. As a function of ε_f its maximum is at $\varepsilon_f = \varepsilon_i + \hbar\omega$ and its width is $\sim 4\pi\hbar/t$. At long times the matrix elements $\langle i|\hat{\mathcal{F}}|f\rangle$ and density of states $\rho(\varepsilon_f)$ will typically vary little over this range and so

$$P_{\text{total}}(t) = \frac{1}{\hbar^2}|\langle f|\hat{\mathcal{F}}|i\rangle|^2\rho(\varepsilon_f)\int_{-\infty}^{\infty}\left(\frac{\sin[(\omega_{fi}-\omega)t/2]}{(\omega_{fi}-\omega)/2}\right)^2 d\varepsilon_f. \tag{3.41}$$

[6] Of course, overall energy is conserved! The difference is supplied or taken up by the perturbation.

Evaluating the integral[7]

$$P_{\text{total}}(t) = \frac{2\pi}{\hbar}|\langle f|\hat{\mathcal{F}}|i\rangle|^2 \rho(\varepsilon_f)t. \tag{3.42}$$

Transitions to the continuum mean the oscillatory transition probability has gone and instead we have a constant transition *rate*:

$$R = \frac{2\pi}{\hbar}|\langle f|\hat{\mathcal{F}}|i\rangle|^2 \rho(\varepsilon_f) \tag{3.43}$$

This is known as Fermi's Golden Rule. It is actually due to Dirac, but Fermi referred to it as "golden rule No. 2" and his name became attached to it.[8]

- For a transition between two discrete states but in the presence of a continuous range of perturbing frequencies similar analysis gives

  $$R_{i\to f} = \frac{2\pi}{\hbar^2}|\langle f|\hat{\mathcal{F}}|i\rangle|^2 \rho(\omega) \tag{3.44}$$

  where $\rho(\omega)d\omega$ is the number of frequencies between ω and $\omega + d\omega$. This can be used to explain the *intensity* of spectral lines — something beyond the Bohr theory.

- We can extend Fermi's Golden Rule to constant perturbations by taking the $\omega \to 0$ limit and continuing to ignore the off-resonance term. Then $\hat{\mathcal{V}}(t) \to \hat{\mathcal{V}}$ and

  $$R = \frac{2\pi}{\hbar}|\langle f|\hat{\mathcal{V}}|i\rangle|^2 \rho(\varepsilon_f). \tag{3.45}$$

  This is the origin of exponential radioactive decay laws, auto-ionisation, and describes the current flowing in a scanning tunneling microscope.

In each case, the transition rate depends upon a matrix element factor which contains the details of the dynamics, and a density of states which factors in how many states or frequencies are available to contribute.

This result has been obtained at first order in perturbation theory. In some circumstances the matrix element can be exactly zero due to symmetry (the origin of selection rules in optical spectra). In this case it is necessary to go to the next order, second order, in the perturbation theory to calculate the rate. Then the transition may still proceed, but as a second order process (e.g. involving the absorption of two photons). The rate will typically be smaller, corresponding to a less efficient process. The second order processes are also present when the first order process is not symmetry-forbidden and would need to be taken into account for a more accurate result.

The derivation required the energy range $\Delta E \sim \hbar/t$ be narrow so that the density of states and matrix elements could be pulled through the integral in Eqn. (3.41) making evaluation possible; and $P_{\text{total}}(t) = Rt$ must be small for first order perturbation theory to be valid. In principle one can check by assuming the Golden Rule, fix t so Rt is small compared to 1, and then check that the density of states and matrix element $\langle f|\hat{\mathcal{F}}|i\rangle$ are roughly constant over range $\hbar/t$.

Class example(s)

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[7] If $x = (\omega_{fi} - \omega)t/2 = (\varepsilon_f - \varepsilon_i - \hbar\omega)t/(2\hbar)$ then $dx = (t/2\hbar)d\varepsilon_f$ and it becomes

$$I = 2\hbar t \int_{-\infty}^{\infty} \frac{\sin^2(x)}{x^2} dx.$$

Then, using Feynman's trick [Google it!] we consider

$$\begin{aligned} J(z) &= \int_{-\infty}^{+\infty} \frac{\sin^2(zx)}{x^2} dx \\ \Rightarrow \quad \frac{dJ(z)}{dz} &= \int_{-\infty}^{+\infty} \frac{\sin(2zx)}{x} dx = \int_{-\infty}^{+\infty} \frac{\sin(y)}{y} dy \quad (y = 2zx) \\ &= \pi \qquad \text{e.g. by contour integration.} \end{aligned}$$

(This last integral is the Dirichlet Integral; it has its own Wikipedia page. It also succombs to a Feynman trick attack as an alternative to contour integration.) So $J(z) = \pi z + c$. But we know $\sin 0 = 0$ so from the integral defining $J(z)$ we identify $J(0) = 0$. Hence c must be zero. Then

$$J(1) = \int_{-\infty}^{+\infty} \frac{\sin^2(x)}{x^2} dx = \pi$$

and finally $I = 2\pi\hbar t$.

[8] Which begs the obvious question, what is Fermi's "golden rule No. 1". I wonder. Google it!

Relativistic quantum mechanics

We know that Newtonian mechanics is an approximation, accurate only for velocities low compared to the speed of light c. It is superceded by Einstein's special theory of relativity. But the Newtonian approximation applies to most of the situations we have had in mind. For example, an electron in the ground state of the hydrogen atom has a binding energy of 13.6 eV. According the the virial theorem that means its kinetic energy is 13.6 eV and hence its speed $\simeq 0.007c$[1] Since the effects of special relativity enter as v^2/c^2 we don't expect much impact on the atomic spectra of hydrogen. In fact, this is not the case. In developing a wave mechanics consistent with the demands of special relativity Dirac found that the description of matter waves needed major revision in ways that impacted even those with low velocities, and reflected intrinsic properties of the electron.

Recall that starting with the fundamental postulates that

- the laws of physics are the same in all inertial reference frames, and
- the constancy of the speed of light,

Einstein developed the special theory of relativity. The position and time (x,y,z,t) that an event occurs in one inertial frame is (x',y',z',t') for an observer in another inertial frame moving at relative speed v in the x direction, the two being related by the Lorentz transformation

$$x' = \frac{x-vt}{\sqrt{1-v^2/c^2}}, \quad y' = y, \quad z' = z, \quad t' = \frac{t-(v/c^2)x}{\sqrt{1-v^2/c^2}}.$$

Momentum $\vec{p}$ and energy behave similarly, $(E/c,\vec{p})$ transforming like $(ct,\vec{r})$, with the energy containing a rest-mass contribution. The energy-momentum relationship for a free particle of mass m is

$$E^2 = p^2c^2 + m^2c^4$$

or, in a electromagnetic field described by vector and scalar potentials $(\varphi/c,\vec{A})$ corresponding to electric and magnetic fields $\vec{E} = -\vec{\nabla}\varphi + \partial\vec{A}/\partial t$ and $\vec{B} = \vec{\nabla}\times\vec{A}$ respectively, it is

$$(E - q\varphi)^2 = (\vec{p} - q\vec{A})^2c^2 + m^2c^4.$$

In one of the greatest achievements of theoretical physics, Dirac developed a quantum theory of the electron that

- Accounts for the effects of relativity, making it appropriate for the description of particles at speeds approaching the speed of light.
- Predicts the intrinsic spin of the electron, and the existence of antimatter.
- Replaces the scalar wavefunction of Schrödinger with a vector of 4 functions.
- Laid the foundations for the development of quantum electrodynamics, the first quantum field theory.

Just like the Schrödinger equation is new physics and cannot be derived from classical mechanics, the Dirac equation is new physics. It was inferred (with great ingenuity) and verified by comparing its predictions with experiment.

Class example

[1] If you prefer, in the Bohr model, equating the Coulomb force $e^2/(4\pi\varepsilon r^2)$ to the centripetal force mv^2/r and quantizing the angular momentum $mvr = n\hbar$ gives $v = e^2/(4\pi\varepsilon\hbar n)$ which is $\simeq 0.007c$ for $n = 1$.

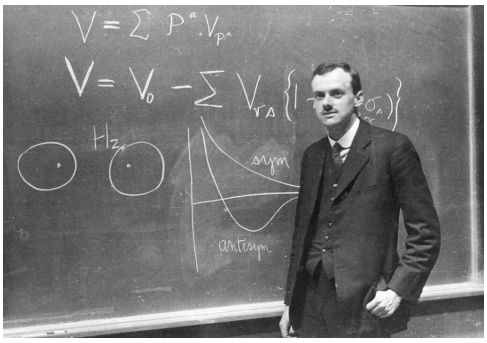

Figure 1: Left: Paul Dirac (1902-1984). Dirac shared the 1933 Nobel prize with Schrödinger, for "the discovery of new productive forms of atomic theory", one year after Heisenberg was awarded the Nobel prize "for the creation of quantum mechanics". Right: Dirac, Heisenberg and Schrödinger, 1933. Here Schrödinger illustrates how to dress when the weather is $(|\text{hot}\rangle + |\text{cold}\rangle)/\sqrt{2}$.

4 The Dirac equation

The non-relativistic energy-momentum relationship $\varepsilon = p^2/(2m)$ along with the substitutions

$$\varepsilon \to i\hbar\partial_t, \qquad \vec{p} \to -i\hbar\vec{\nabla} \tag{4.1}$$

gives

$$i\hbar\partial_t = -\frac{\hbar^2}{2m}\nabla^2 \tag{4.2}$$

which we recognise as the operators in the time-independent Schrödinger equation for a free particle. Then starting from the relativistic energy-momentum relationship

$$E = \pm\sqrt{p^2c^2 + m^2c^4} \tag{4.3}$$

and making the substitution

$$E \to i\hbar\partial_t, \qquad \vec{p} \to -i\hbar\vec{\nabla} \tag{4.4}$$

would suggest the wave equation

$$i\hbar\partial_t\Psi = \pm\sqrt{-c^2\hbar^2\nabla^2 + m^2c^4}\,\Psi. \tag{4.5}$$

Err — what does that even mean, having the differential operator inside of the square root. Are new postulates needed to deal with this?

Instead of that problem, Dirac (Fig. 1) sought a different way of dealing with the radical. He looked to express

$$p_x^2 + p_y^2 + p_z^2 + m^2c^2 \tag{4.6}$$

as a perfect square

$$(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z + \beta mc)^2\,. \tag{4.7}$$

Then the relativistic energy-momentum relationship $E^2 = p^2c^2 + m^2c^4$, or $E = \pm c(p_x^2 + p_y^2 + p_z^2 + m^2c^2)^{1/2}$ could become

$$i\hbar\partial_t\Psi = \pm c\left(\alpha_x\hat{p}_x + \alpha_y\hat{p}_y + \alpha_z\hat{p}_z + \beta mc\right)\Psi \tag{4.8}$$

which makes sense recalling the momentum operator is a partial derivative in the position representation. If we are to have a Lorentz invariant theory, the first order time derivative must be accompanied by first order spatial derivatives.

Expanding out (4.7) preserving the order of the factors, and equating to (4.6), yields[2] the following relations that must be satisfied by the coefficents in (4.7):

$$\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \beta^2 = 1, \tag{4.9a}$$

[2] In this step we use that $p_x p_y = p_x p_y$ etc, so to say that they commute, which is true as is easily seen when they are expressed in terms of the corresponding differential operators.

$$\alpha_x\alpha_y + \alpha_y\alpha_x = \alpha_y\alpha_z + \alpha_z\alpha_y = \alpha_z\alpha_x + \alpha_x\alpha_z = 0, \tag{4.9b}$$

and

$$\alpha_x\beta + \beta\alpha_x = \alpha_y\beta + \beta\alpha_y = \alpha_z\beta + \beta\alpha_z = 0. \tag{4.9c}$$

These make clear that the quantities α_i and β are not ordinary numbers/scalars. Instead, recognising that the $\hat{p}_i$'s are operators that act upon Ψ, we allow for the possibility that so too do the α_i's and β. In particular, the time-dependent equation (4.8) can be solved by a separable solution

$$\Psi = \psi e^{-iEt/\hbar} \tag{4.10}$$

where

$$\hat{\mathcal{H}}\psi = E\psi, \qquad \hat{\mathcal{H}} = c\left(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z\right) + \beta mc^2 \tag{4.11}$$

and Dirac showed that Hermitian α's and β needed to produce the linear Hamiltonian could be represented by 4-by-4 matrices — 2-by-2 and 3-by-3 matrices could not be made to work. The choice of matrices is not unique, but a standard choice is

$$\alpha_x = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \quad \alpha_y = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix}, \quad \alpha_z = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}. \tag{4.12}$$

That the Dirac Hamiltonian contains 4-by-4 matrices implies that the wavefunction ψ must take the form of a four-component vector — the symmetries of four-dimensional space-time have led to a four-component spinor wavefunction

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}. \tag{4.13}$$

Introducing the vector of matrices $\vec{\alpha} = (\alpha_x, \alpha_y, \alpha_z) = \alpha_x\vec{i} + \alpha_y\vec{j} + \alpha_z\vec{k}$ the Dirac Hamiltonian for a free particle becomes

$$\hat{\mathcal{H}} = c\vec{\alpha}\cdot\vec{p} + \beta mc^2 \tag{4.14}$$

and in the position representation where $\vec{p} = -i\hbar(\partial_x, \partial_y, \partial_z) = -i\hbar\vec{\nabla}$ the time-independent Dirac equation is

$$\left(-ic\hbar\vec{\alpha}\cdot\vec{\nabla} + \beta mc^2\right)\psi(\vec{r}) = E\psi(\vec{r}). \tag{4.15}$$

where it is understood that the derivative acts on each of the four components of ψ — now functions of position. Normalisation of the wavefunction (4.13) requires

$$\int \psi^\dagger(\vec{r})\psi(\vec{r})d^3r = \sum_i \int \psi_i^*(\vec{r})\psi_i(\vec{r})d^3r = 1. \tag{4.16}$$

4.1 Plane wave solution

The time-independent Schrödinger equation for a free particle, $\hat{\mathcal{H}}\psi(\vec{r}) = \varepsilon\psi(\vec{r})$ with $\hat{\mathcal{H}} = -(\hbar^2/2m)\nabla^2$ has plane wave solutions[3] $a\exp(i\vec{p}\cdot\vec{r}/\hbar)$ with a a coefficient and energy and momentum related through $E = p^2/(2m)$.

We look to see if the Dirac equation affords similar solutions.

Recall the Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{4.17}$$

Using these the Dirac matrices can be written as

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}, \qquad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{4.18}$$

[3] More commonly written $a\exp i\vec{k}\cdot\vec{r}$ where $\vec{p} = \hbar\vec{k}$, the de Broglie relationship between momentum and wave vector.

where all entries are understood to be 2-by-2 matrices. This suggest we might usefully write ψ in terms of two two-component vectors ψ_+ and ψ_-,

$$\psi = \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}. \tag{4.19}$$

in which case the Dirac equation $(c\vec{\alpha}\cdot\vec{p} + \beta mc^2)\psi = E\psi$ becomes two coupled equations

$$c\left(\vec{\sigma}\cdot\vec{p}\right)\psi_- + mc^2\psi_+ = E\psi_+ \tag{4.20a}$$

$$c\left(\vec{\sigma}\cdot\vec{p}\right)\psi_+ - mc^2\psi_- = E\psi_- \tag{4.20b}$$

each of which is itself two equations. Manipulating the second of these we get

$$\psi_- = \frac{c}{E+mc^2}\left(\vec{\sigma}\cdot\vec{p}\right)\psi_+ \tag{4.21}$$

giving ψ_- in terms of ψ_+, which we can then use to eliminate ψ_- from the first:

$$c^2\left(\vec{\sigma}\cdot\vec{p}\right)^2\psi_+ = \left(E^2 - m^2c^4\right)\psi_+. \tag{4.22}$$

Using basic properties of the Pauli matrices ‘

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1 \tag{4.23a}$$

$$\sigma_x\sigma_y = i\sigma_z, \quad \sigma_y\sigma_z = i\sigma_x, \quad \sigma_z\sigma_x = i\sigma_y, \tag{4.23b}$$

this simplifies to

$$c^2\hat{p}^2\psi_+ = \left(E^2 - m^2c^4\right)\psi_+ \tag{4.24}$$

In the position representation

$$-c^2\hbar^2\nabla^2\psi_+(\vec{r}) = \left(E^2 - m^2c^4\right)\psi_+(\vec{r}) \tag{4.25}$$

which indeed has plane wave solutions, as can be checked by substitution, of the form

$$\psi_+(\vec{r}) = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} e^{i\vec{p}\cdot\vec{r}/\hbar} \tag{4.26}$$

and with arbitrary independent coefficients a_1 and a_2, when the energy and momentum satisfy the relationship

$$E^2 = p^2c^2 + m^2c^4 \tag{4.27}$$

— the relativistic energy-momentum relationship of free particles. The lower two of the four components of $\psi(\vec{r})$ can then be found from (4.21). Note that for a low energy electron $E \simeq mc^2 + \varepsilon$ so that in the $c \to \infty$ non-relativistic limit $\psi_- \to 0$. We are then left with a wavefunction that is a plane wave multiplied by $\begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$ — a form appropriate to the description of a spin-$^1/_2$ particle. This aspect of the wavefunction has not had to be introduced as an extra property, as with the Schrödinger equation, but it has emerged as a natural property of the solutions of the Dirac equation. Furthermore, it has emerged when we have considered plane wave solutions — spin is an essential aspect of translational motion, and not some additional kinematic property.

Class example

4.2 Electron spin

The extension of the Dirac equation to the case of a charged particle in an electromagnetic field is to substitute $E \to E - q\varphi$, $\vec{p} \to \vec{p} - q\vec{A}$ where φ and $\vec{A}$ are the scalar and vector potentials respectively. The time-dependent equation becomes

$$i\hbar\partial_t\Psi = \left(c\vec{\alpha}\cdot(\vec{p} - q\vec{A}) + \beta mc^2 + q\varphi\right)\Psi. \tag{4.28}$$

Expressing Ψ in terms of two two-component vectors (4.19) and repeating the steps leading up to (4.22) yields

$$c^2\left(\vec{\sigma}\cdot(\vec{p} - q\vec{A})\right)^2\psi_+ = \left((E - q\varphi)^2 - m^2c^4\right)\psi_+. \tag{4.29}$$

This requires more care than before, because $\vec{p}$ and $\vec{A}$ do not generally commute. Expanding the operator on the left hand side[4],

$$(\sigma_x(\hat{p}_x - qA_x) + \sigma_y(\hat{p}_y - qA_y) + \sigma_z(\hat{p}_z - qA_z))^2 \tag{4.30}$$

contains terms like

$$\sigma_x(\hat{p}_x - qA_x)\sigma_x(\hat{p}_x - qA_x) = (\hat{p}_x - qA_x)^2 \tag{4.31}$$

and terms that can be paired like

$$\begin{aligned}
&\sigma_x(\hat{p}_x - qA_x)\sigma_y(\hat{p}_y - qA_y) + \sigma_y(\hat{p}_y - qA_y)\sigma_x(\hat{p}_x - qA_x) \\
&\quad = \sigma_x\sigma_y(\hat{p}_x - qA_x)(\hat{p}_y - qA_y) + \sigma_y\sigma_x(\hat{p}_y - qA_y)(\hat{p}_x - qA_x) \\
&\quad = i\sigma_z\left(\hat{p}_x\hat{p}_y - qA_x\hat{p}_y - q\hat{p}_xA_y + q^2A_xA_y\right) - i\sigma_z\left(\hat{p}_y\hat{p}_x - qA_y\hat{p}_x - q\hat{p}_yA_x + q^2A_yA_x\right) \\
&\quad = -iq\sigma_z\left(A_x\hat{p}_y + \hat{p}_xA_y - A_y\hat{p}_x - \hat{p}_yA_x\right) \quad \text{using } \hat{p}_x\hat{p}_y = \hat{p}_y\hat{p}_x
\end{aligned} \tag{4.32}$$

This acts upon ψ_+ in (4.29), and

$$\begin{aligned}
\left(A_x\hat{p}_y + \hat{p}_xA_y - A_y\hat{p}_x - \hat{p}_yA_x\right)\psi_+ &= -i\hbar\left(A_x\partial_y\psi_+ + \partial_x(A_y\psi_+) - A_y\partial_x\psi_+ - \partial_y(A_x\psi_+)\right) \\
&= -i\hbar\left(\partial_xA_y - \partial_yA_x\right)\psi_+.
\end{aligned} \tag{4.33}$$

Remembering $\vec{B} = \vec{\nabla} \times \vec{A}$ so $B_z = \partial_xA_y - \partial_yA_x$ this last result is $-i\hbar B_z\psi_+$. Similar considerations for the other terms enable (4.29) to be written as

$$c^2\left((\vec{\hat{p}} - q\vec{A})^2 - q\hbar\vec{\sigma}\cdot\vec{B}\right)\psi_+ = \left((E - q\varphi)^2 - m^2c^4\right)\psi_+. \tag{4.34}$$

Setting $\varepsilon = E - mc^2$ and taking the $c \to \infty$ non-relativistic limit this becomes

$$\frac{1}{2m}\left((\vec{\hat{p}} - q\vec{A})^2 - q\hbar\vec{\sigma}\cdot\vec{B} + q\varphi\right)\psi_+ = \varepsilon\psi_+ \tag{4.35}$$

and the lower component ψ_- again vanishes. The equation satisfied by ψ_+ is the same as the Pauli (or Schrödinger-Pauli) equation, introduced by Pauli to extend the Schrödinger equation for spin-$1/2$ particles to include their interaction with an electromagnetic field.

For a constant, homogeneous magnetic field $\vec{B}$ we can use for the vector potential $\vec{A} = {}^1\!/_2\vec{B} \times \vec{r}$. If the field is weak[5]

$$(\vec{\hat{p}} - q\vec{A})^2 \simeq \hat{p}^2 - q(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}) = \hat{p}^2 - q(\vec{B}\times\vec{r}\cdot\vec{p}) = \hat{p}^2 - q\vec{L}\cdot\vec{B} \tag{4.36}$$

so (4.35) becomes

$$\frac{1}{2m}\left(\hat{p}^2 - q(\vec{\hat{L}} + 2\vec{\hat{S}})\cdot\vec{B} + q\varphi\right)\psi_+ = \varepsilon\psi_+ \tag{4.37}$$

where $\vec{\hat{L}} = \vec{r} \times \vec{p}$ is the orbital angular momentum and $\vec{\hat{S}} = \hbar\vec{\sigma}/2$ the spin. The spin behaves like angular momentum in the interaction with the magnetic field, with a g-factor of 2. This all emerges naturally from the Dirac theory, rather than having to be introduced to the Schrödinger equation in a phenomenological manner.

4.3 Antiparticles

The classical energy-momentum relation $E^2 = p^2c^2 + m^2c^4$ of a free particle has both positive and negative energy solutions. Positive energy solutions exist with $E > mc^2$ and negative energy solutions with $E < -mc^2$. In classical physics we dismiss the negative energy solutions as unphysical and in any event inaccessible.

We see that negative energy solutions of the Dirac equation are clearly possible, since if we look at (4.22) it only depends upon energy as E^2. Setting $E = -mc^2 - \varepsilon$ in (4.21) shows that in the non-relativistic $c \to \infty$ limit it is the lower two components of the four-component Dirac spinor that persist, with ψ_+ smaller by a factor $1/c$.

In quantum theory we cannot dismiss the negative energy solutions. We have seen that the interaction of a charged particle with an electromagnetic field includes downward transitions. There is nothing to stop a charged particle from making a radiative transition from a state of positive energy to a state of negative energy[6]. Dirac turned this

[4] Recall $(f+g+h)^2 = f^2 + fg + fh + gf + g^2 + gh + hf + hg + h^2$.

[5] The neglected term involving A^2 is responsible for diamagnetic effects.

[6] There are no "selection rule" effects to prevent the transitions — e.g. matrix elements of x between positive and negative energy solutions do not automatically vanish.

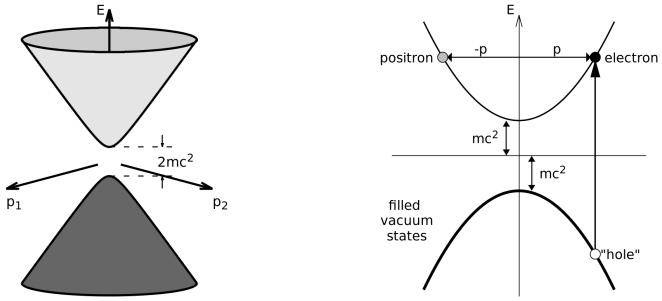

Figure 2: Left: Energy-momentum relationship of free-particle solutions of the Dirac equation. Right: Excitation of an electron from the Dirac sea of filled negative energy states into a positive energy state creates a free electron and leaves a vacancy or "hole". The properties of the Dirac sea plus hole are those of a positron. (Does this figure remind you of anything from Condensed Matter Physics?)

problem into a triumph, with the bold proposal that the negative energy states were already filled. Transitions to them are then forbidden by the Pauli exclusion principle. Within this picture, the vacuum state consists of an infinite sea of negative energy electrons, that exert no electromagnetic or gravitational effects.

What, then, if we excite an electron from a filled state with negative energy $-mc^2 - \varepsilon_i$ to a state with positive energy $mc^2 + \varepsilon_f$, by absorption of a photon of energy $2mc^2 + \varepsilon_f + \varepsilon_i$ — a process illustrated in Fig. 2. For the sake of argument let $\varepsilon_f = \varepsilon_i = \varepsilon$ and we ignore the momentum of the photon. Before the event, the system is the vacuum of filled negative energy states. After the event, we have an electron with energy $mc^2 + \varepsilon$ and momentum $\vec{p}$. Conservation of energy and momentum mean the vacuum must be in an excited state with energy $mc^2 + \varepsilon$ and net momentum $-\vec{p}$. If we imagine applying an electric field, the negatively charged electrons — that's the positive energy electron we have excited but also all the electrons occupying the vacuum states — will be accelerated in the direction opposite to the field. The vacancy will move with them, and so the net momentum $-\vec{p}$ accelerates in the **same** direction as the field. It behaves like a positively charged particle.

Dirac proposed this theory of the vacuum as a quantum many-particle state in which all the negative-energy electron eigenstates are filled, and with unoccupied eigenstates in it acting as positively charged particles, in 1928, two years after Schrödinger first published his equation. Dirac's anti-electron introduced the concept of antimatter. At the time, electrons and protons were believed to be the only fundamental particles and, maybe surprising to us today, Dirac initially identified the hole with the proton. It was Hermann Weyl who demonstrated the hole and electron mass should be the same. In 1932 Carl Anderson discovered the positron in cosmic rays. That, along with the ability of Dirac's theory to account for the fine structure in the spectrum of the hydrogen atom, provided experimental verification of its validity.

Class example(s)

Many-particle systems

Many physical systems of interest involve more than one particle: electrons and nuclei in atoms, molecules and solids; photons in the electromagnetic field; vibrations (phonons) in crystals; neutrons and protons in nuclei, and quarks in mesons and baryons.

Such systems exhibit a wealth of fascinating and often unexpected behaviours. Here we consider aspects of the description of many-particle systems. We do this by initially focusing on the simplest of many-particle systems, systems of two particles, and recognising in them behaviour that generalises. We see why it makes sense to talk of **the** spectrum of hydrogen, when in reality the overwhelming majority of hydrogen atoms are found in interstellar gas clouds and moving at a whole range of different speeds, typically between 1-100 km/s depending upon region and conditions. And we see why quantum mechanics means the indistinguishability of fundamental particles leads to the existence of two possible classes of such particles, with distinctly different behaviours, and providing the foundation of an understanding of the periodic table.

4.1 Two-particle systems

Let us start by considering a system of two particles. For simplicity we consider motion in one-dimension[1].

In this case the state of the system depends upon both the coordinate of particle 1, and the coordinate of particle 2, and also time. Using base kets $|x_1,x_2\rangle$ we have $\langle x_1,x_2|\Psi(t)\rangle = \Psi(x_1,x_2,t)$. The evolution in time is governed by the time-dependent Schrödinger equation $i\hbar\dfrac{\partial\Psi}{\partial t} = \hat{\mathcal{H}}\Psi$ where the Hamiltonian is

$$\hat{\mathcal{H}} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + V(x_1,x_2,t) = -\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} + V(x_1,x_2,t) \tag{4.1}$$

representing the kinetic energies of particle 1 and 2 and the potential energy. The interpretation of Ψ is that $|\langle x_1,x_2|\Psi(t)\rangle|^2 dx_1 dx_2 = |\Psi(x_1,x_2,t)|^2 dx_1 dx_2$ is the probability of measuring at time t the location of particle 1 as being in a small interval dx_1 around x_1 **and** particle 2 in a small interval dx_2 around x_2. It follows that

$$\int |\Psi(x_1,x_2,t)|^2 dx_1 dx_2 = 1 \tag{4.2}$$

— when we perform the measurements, we must find particles 1 and 2 *somewhere*.

When the potential is time-independent, $V = V(x_1,x_2)$, then assuming a solution separable in spatial and temporal variables yields $\Psi(x_1,x_2,t) = \psi(x_1,x_2)e^{-iEt/\hbar}$ where $\psi(x_1,x_2) = \Psi(x_1,x_2,0)$ satisfies the time-independent Schrödinger equation

$$\hat{\mathcal{H}}\psi = E\psi, \qquad \text{or} \qquad -\frac{\hbar^2}{2m_1}\frac{\partial^2\psi}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2\psi}{\partial x_2^2} + V(x_1,x_2)\psi = E\psi. \tag{4.3}$$

This is a partial differential equation. Two important special cases apply:

4.1.1 Central potentials

Let us first consider when the particles interact via a potential that depends upon their separation: $V(x_1,x_2) = V(x_1 - x_2)$. An example (in 3D) would be charged particles interacting via the Coulomb interaction $q_1q_2/(4\pi\varepsilon_0|\vec{r}_1 - \vec{r}_2|)$. In this case for our one-dimensional system we can introduce new variables

$$\begin{aligned} x &= x_1 - x_2 \\ X &= \frac{m_1x_1 + m_2x_2}{m_1 + m_2} \end{aligned} \tag{4.4}$$

[1] You should be able to straightforwardly generalise to 3D systems.

recognisable as the relative (x) and center-of-mass (X) coordinates of the two particles. Using

$$\frac{\partial}{\partial x_i} = \frac{\partial}{\partial x}\frac{\partial x}{\partial x_i} + \frac{\partial}{\partial X}\frac{\partial X}{\partial x_i} \tag{4.5}$$

the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m_1}\frac{\partial^2\psi}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2\psi}{\partial x_2^2} + V(x_1 - x_2)\psi = E\psi \tag{4.6}$$

becomes

$$-\frac{\hbar^2}{2M}\frac{\partial^2\psi}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = E\psi, \tag{4.7}$$

where $M = m_1 + m_2$ is the total mass and

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \tag{4.8}$$

the reduced mass. This equation yields to a separable solution $\psi(x,X) = \Phi(X)\varphi(x)$ where

$$-\frac{\hbar^2}{2M}\frac{\partial^2\Phi}{\partial X^2} = E_{cm}\Phi(X) \tag{4.9a}$$

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2\phi}{\partial x^2} + V(x)\psi = E_{rel}\varphi(x) \tag{4.9b}$$

and total energy $E = E_{cm} + E_{rel}$. Eqn. (4.9a) is a free-particle Schrödinger equation — the center of mass moves like a free particle of mass M — and Eqn. (4.9b) is a single-particle Schrödinger equation for a particle of mass μ moving in potential $V(x)$.

The new coordinates x and X uniquely determine x_1 and x_2 and so base kets $|x,X\rangle$ are just as valid as $|x_1,x_2\rangle$ for describing the state. Indeed we recognise that in this representation the system of two interacting particles has become a system of two non-interacting particles, one of reduced-mass μ and one of total mass M:

$$\langle x,X|\psi\rangle = \varphi(x)\Phi(X) = \langle x|\varphi\rangle\langle X|\Phi\rangle. \tag{4.10}$$

The probability of measuring the system with separation x, center of mass X is

$$|\langle x,X|\psi\rangle|^2 dx dX = |\psi(x,X)|^2 dx dX = |\varphi(x)|^2 dx \times |\Phi(X)|^2 dX \tag{4.11}$$

— which is what one would expect from two independent uncorrelated measurements of separation and center of mass position. This was not the case in the original representation, in which there is correlation between the measurements of the positions of the particles x_1 and x_2: $|\psi(x_1,x_2)| \neq |\psi_1(x_1)|^2|\psi_2(x_2)|^2$. A measurement on one particle affects the other.

An example application of this is to the atomic spectra of hydrogen with potential $V(\vec{r}_1,\vec{r}_2) = -e^2/(4\pi\varepsilon_0|\vec{r}_1 - \vec{r}_2|)$. Assuming a stationary positive charge ($m_1 = m_e$, $m_2 = \infty$) one gets a set of energy levels (as given by Bohr theory)

$$\varepsilon_n = -\frac{m_e e^4}{2(4\pi\varepsilon_0)^2\hbar^2} \times \frac{1}{n^2} = -\frac{1\ \text{Ry}}{n^2} \tag{4.12}$$

where $1\text{Ry} = 13.605\,693\,123$ eV. In reality the positive charge has a finite mass so that a stationary hydrogen atom ($E_{cm} = 0$) has energies $E = E_{rel}$ given by the same formulae but with m_e replaced by μ, or a factor $1/(1 + m_e/m_2)$ smaller. For hydrogen-1 m_e/m_2 is 1/1836 (proton mass), for hydrogen-2 (deuterium) 1/3670 (proton+neutron), for hydrogen-3 (tritium) 1/5498 (proton+2 neutrons) — causing small, but measurable differences. For positronium, an exotic atom consisting of an electron bound to its anti-particle, which has a lifetime of $0.1 - 100 \times 10^{-9}$ sec before decaying to 2 or 3 photons depending upon the spin state, the potential is again $V(\vec{r}_1,\vec{r}_2) = -e^2/(4\pi\varepsilon_0|\vec{r}_1 - \vec{r}_2|)$ but now the positive charge has a mass of m_e and the spectrum is scaled by $1/(1 + m_e/m_2) = 1/(1 + m_e/m_e) = 1/2$. For positronium $\varepsilon_n = -[6.8\text{ eV}]/n^2$.

The separation into center-of-mass and "internal" system also explains why we can typically study the behaviour of center of mass motion of a composite particle without having to worry about its internal structure. A gas of particles can be studied without reference to their atomic levels, or a proton treated as a point particle without reference to its internal composition as a bound set of three quarks. Only if the interaction between the particles are sufficiently

energetic to cause changes in the internal structure (i.e. induce transitions between energy levels) do we need to take account of the particles not being fundamental. And similarly, we can discuss the electronic structure of an atom, without reference to its translational motion. The set of energy levels exist independent of the overall speed of motion of the atom.[2]

4.1.2 Non-interacting particles

It may seem strange to move on from particles interacting via a central potential, to non-interacting particles, but as we shall see there are some profound aspects to be recognised that have wide ramifications.

For a system of two non-interacting particles the Hamiltonian takes the form (in one dimension)

$$\hat{\mathcal{H}} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + V_1(x_1) + V_2(x_2). \tag{4.13}$$

reflecting the kinetic and potential energies of the two particles, with the potentials arising due to some external, not internal, force. This is the sum of two independent Hamiltonians

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_1(x_1) + \hat{\mathcal{H}}_2(x_2), \qquad \hat{\mathcal{H}}_i(x_i) = \frac{\hat{p}_i^2}{2m_i} + V_i(x_i) = -\frac{\hbar^2}{2m_i}\frac{\partial^2}{\partial x_i^2} + V_i(x_i), \;\; i = 1,2. \tag{4.14}$$

Trying as a solution to the Schrödinger equation a product of single-particle functions, $\Psi(x_1,x_2) = \psi_1(x_1)\psi_2(x_2)$, then, because

$$\hat{\mathcal{H}}_1(x_1)\psi_1(x_1)\psi_2(x_2) = \psi_2(x_2)\hat{\mathcal{H}}_1(x_1)\psi_1(x_1), \qquad \hat{\mathcal{H}}_2(x_2)\psi_1(x_1)\psi_2(x_2) = \psi_1(x_1)\hat{\mathcal{H}}_2(x_2)\psi_2(x_2),$$

we find that indeed $\psi_1(x_1)\psi_2(x_2)$ is an eigenstate of $\hat{\mathcal{H}}$ with energy $E = \varepsilon_1 + \varepsilon_2$ where

$$\begin{aligned} -\frac{\hbar^2}{2m_1}\frac{\partial^2\psi_1(x_1)}{\partial x_1^2} + V_1(x_1)\psi_1(x_1) &= \varepsilon_1\psi_1(x_1) \\ -\frac{\hbar^2}{2m_2}\frac{\partial^2\psi_2(x_2)}{\partial x_2^2} + V_2(x_2)\psi_2(x_2) &= \varepsilon_2\psi_2(x_2). \end{aligned} \tag{4.15}$$

ε_1 and ε_2 are seen to be the energies of the individual particles, and the total energy of the two-particle state is just the sum of their separate energies — as one would expect since the two particles do not interact with one another. Furthermore, the probability of measuring particle 1 in a small interval dx_1 around x_1 **and** particle 2 in a small interval dx_2 around x_2 is

$$|\langle x_1,x_2|\Psi\rangle|^2 dx_1 dx_2 = |\Psi(x_1,x_2)|^2 dx_1 dx_2 = |\psi_1(x_1)\psi_2(x_2)|^2 dx_1 dx_2 = |\psi_1(x_1)|^2 dx_1 \times |\psi_2(x_2)|^2 dx_2 \tag{4.16}$$

and is seen to be the probability of measuring particle 1 in a small interval dx_1 **times** the probability of measuring particle 2 in a small interval dx_2 around x_2 — just as one expects from two uncorrelated measurements of the particle positions.

So far, so good. But things are different if the particles are indistinguishable. The above is valid when the particles are distinguishable, but indistinguishable particles behave diferently. Distinguishable particles are those that differ in some *intrinsic* physical property, such as charge, mass, or spin. For examples of indistinguishable (or identical, or indescernible) particles, think of systems of elementary particles such as electrons, composite subatomic particles such as alpha particles and atomic nuclei, or atoms and molecules, which cannot be distinguished through differences in charge, mass or spin. In classical mechanics, individual particles follow well-defined trajectories, meaning one can distinguish otherwise identical particles by the paths that they follow during the course of an experiment. We can assign a precise position and velocity to each of a set of identical particles e.g. the red balls on a snooker table, and follow their deterministic trajectories as they move through space over time following the break-off. But quantum mechanics does not afford such detail. The uncertainty principle prevents us from defining a precise particle location or trajectory. Quantum particles are described by wave functions with a finite spread that can overlap, preventing us from identifying from a particle measurement which of identical particles was recorded, even if they are not interacting. The moment that the wave functions of two identical particles overlap, we can no longer say

[2] A stationary observer will, of course, see the radiation emitted following a transition between the energy levels red-shifted (blue-shifted) if the motion is away from (towards) them, by an amount depending upon the relative speed v: $\frac{\Delta\lambda}{\lambda} = \frac{v}{c}$: the Doppler effect.

whether a measurement of a particle recorded one, or the other. We can no longer follow individual particle trajectories.

If there is no means by which we can perform a measurement on a system of two identical particles and distinguish between them, then any mathematical operator that represents a physical measurement must be unchanged if we swap the labels we have assigned to the particles. The Hamiltonian $\hat{\mathcal{H}}$ is the mathematical operator corresponding to a measurement of the energy of the system and if we denote the Hamiltonian of two indistinguishable particles as $\hat{\mathcal{H}}(1,2)$ then it must be that

$$\hat{\mathcal{H}}(1,2) = \hat{\mathcal{H}}(2,1). \tag{4.17}$$

Let us introduce a mathematical "particle swap" operator $\hat{P}_{12}$ that has the effect of swapping, or exchanging, particle indices 1 and 2. For example,

$$\hat{P}_{12}\hat{\mathcal{H}}(1,2) = \hat{\mathcal{H}}(2,1), \qquad \hat{P}_{12}\Psi(1,2) = \Psi(2,1) \tag{4.18}$$

Explicitly, for examples of non-interacting and interacting indistinguishable particles

$$\hat{P}_{12}\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2} + V(x_1) + V(x_2)\right] = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2} + V(x_2) + V(x_1) \tag{4.19a}$$

and

$$\hat{P}_{12}\left[-\frac{\hbar^2}{2m}\vec{\nabla}_1^2 - \frac{\hbar^2}{2m}\vec{\nabla}_2^2 - \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1 - \vec{r}_2|}\right] = -\frac{\hbar^2}{2m}\vec{\nabla}_2^2 - \frac{\hbar^2}{2m}\vec{\nabla}_1^2 - \frac{e^2}{4\pi\varepsilon_0|\vec{r}_2 - \vec{r}_1|}. \tag{4.19b}$$

Clearly in both cases $\hat{P}_{12}\hat{\mathcal{H}}(1,2) = \hat{\mathcal{H}}(2,1) = \hat{\mathcal{H}}(1,2)$. Then

$$\begin{aligned}\hat{P}_{12}\hat{\mathcal{H}}(1,2)\Psi(1,2) &= \hat{\mathcal{H}}(2,1)\Psi(2,1)\\ &= \hat{\mathcal{H}}(1,2)\Psi(2,1)\\ &= \hat{\mathcal{H}}(1,2)\hat{P}_{12}\Psi(1,2)\end{aligned} \tag{4.20}$$

so

$$\hat{P}_{12}\hat{\mathcal{H}}(1,2) = \hat{\mathcal{H}}(1,2)\hat{P}_{12} \qquad \Rightarrow \qquad \left[\hat{P}_{12}, \hat{\mathcal{H}}(1,2)\right] = 0. \tag{4.21}$$

The particle swap operator commutes with the Hamiltonian — and will likewise commute with any operator corresponding to a physical measurement.

The commutation of the particle swap operator and the Hamiltonan — and any operator corresponding to a physical measurement — means that they share a common set of eigenfunctions.[3] If a two-particle state $\Psi(1,2)$ is an eigenfunction of P_{12} then

$$\hat{P}_{12}\Psi(1,2) = \lambda\Psi(1,2) \tag{4.22}$$

or

$$\Psi(2,1) = \lambda\Psi(1,2), \tag{4.23}$$

recognising the action of particle-swap on the state function. Operating with $\hat{P}_{12}$

$$\begin{aligned}\hat{P}_{12}\Psi(2,1) = \hat{P}_{12}\left(\lambda\Psi(1,2)\right) \quad \Rightarrow \quad \Psi(1,2) &= \lambda\hat{P}_{12}\Psi(1,2)\\ &= \lambda(\lambda\Psi(1,2)) \quad \text{using (4.22)}\end{aligned} \tag{4.24}$$

so $\lambda^2 = 1$ and from (4.23)

$$\Psi(1,2) = \pm\Psi(2,1). \tag{4.25}$$

So eigenstates of the particle-swap operator must be either symmetric ($\lambda = +1$) or anti-symmetric ($\lambda = -1$) under particle interchange. Since the Hamiltonian describing the system of indistinguishable particles commutes with the particle-swap operator, it shares a common set of eigenfunctions. Hence the eigenfunctions of the Hamiltonian — and any operator corresponding to a physical observable — must either be symmetric or anti-symmetric under exchange of identical particles. Other states are physically unacceptable.

[3] If you have not seen this proof before, let operator $\hat{A}$ have (nondegenerate; the proof is more involved if they are degenerate) orthonormal eigenkets $|\psi_n\rangle$ with eigenvalues λ_n:

$$\hat{A}|\psi_n\rangle = \lambda_n|\psi_n\rangle.$$

If operator $\hat{B}$ commutes with $\hat{A}$ then

$$\hat{A}(\hat{B}|\psi_n\rangle) = \hat{A}\hat{B}|\psi_n\rangle = \hat{B}\hat{A}|\psi_n\rangle = \hat{B}(\lambda_n|\psi_n\rangle) = \lambda_n(\hat{B}|\psi_n\rangle)$$

and we see $\hat{B}|\psi_n\rangle$ is also an eigenket of $\hat{A}$ with eigenvalue λ_n. Since the eigenkets are non-degenerate $\hat{B}|\psi_n\rangle$ can differ at most from $|\psi_n\rangle$ by a multiplicative constant. Calling this μ_n then

$$\hat{B}|\psi_n\rangle = \mu_n|\psi_n\rangle$$

which shows $|\psi_n\rangle$, an eigenket of $\hat{A}$, is simultaneously an eigenket of $\hat{B}$.

4.2 Exchange symmetry as a constant of motion: bosons and fermions

This observation applies not just to our two-particle system but to any physical system containing indistinguishable particles with Hamiltonian $\hat{\mathcal{H}}(1,2,\ldots,N)$ and state kets $|\psi(1,2,\ldots,N)\rangle$. We can define a particle-swap operator $\hat{P}_{ij}$ that exchanges identical particles i and j and applying it leaves the Hamiltonian unchanged,

$$\hat{P}_{ij}\hat{\mathcal{H}}(1,\ldots,i,\ldots,j,\ldots,N) = \hat{\mathcal{H}}(1,\ldots,j,\ldots,i,\ldots,N) = \hat{\mathcal{H}}(1,\ldots,i,\ldots,j,\ldots,N) \tag{4.26}$$

while applying it to a state ket

$$\hat{P}_{ij}\Psi(1,\ldots,i,\ldots,j,\ldots,N) = \psi(1,\ldots,j,\ldots,i,\ldots,N) = \lambda\Psi(1,\ldots,i,\ldots,j,\ldots,N) \tag{4.27}$$

multiplies it by $\lambda = +1$ if the state is symmetric or $\lambda = -1$ if the state is anti-symmetric under particle exchange.

We know that the time evolution of a state is governed by the time-dependent Schrödinger equation

$$i\hbar\frac{\partial|\Psi\rangle}{\partial t} = \hat{\mathcal{H}}|\Psi\rangle \tag{4.28}$$

so that for infinitesimal dt

$$|\Psi(t+dt)\rangle = |\Psi(t)\rangle + \frac{\partial|\Psi(t)\rangle}{\partial t}dt = |\Psi(t)\rangle - \frac{i}{\hbar}\hat{\mathcal{H}}|\Psi(t)\rangle dt. \tag{4.29}$$

If, at time t, we have $\hat{P}_{ij}|\Psi(t)\rangle = \lambda|\Psi(t)\rangle$ then

$$\begin{aligned}
\hat{P}_{ij}|\Psi(t+dt)\rangle &= \hat{P}_{ij}\left(|\psi(t)\rangle - \frac{i}{\hbar}\hat{\mathcal{H}}|\Psi(t)\rangle dt\right)\\
&= \hat{P}_{ij}|\Psi(t)\rangle - \frac{i}{\hbar}\hat{P}_{ij}\hat{\mathcal{H}}|\Psi(t)\rangle dt\\
&= \lambda|\Psi(t)\rangle - \frac{i}{\hbar}\hat{\mathcal{H}}\hat{P}_{ij}|\Psi(t)\rangle dt \quad \text{using } [\hat{P}_{ij},\hat{\mathcal{H}}] = 0\\
&= \lambda|\Psi(t)\rangle - \frac{i}{\hbar}\hat{\mathcal{H}}\lambda|\Psi(t)\rangle dt\\
&= \lambda\left(|\Psi(t)\rangle - \frac{i}{\hbar}\hat{\mathcal{H}}|\Psi(t)\rangle dt\right) = \lambda|\Psi(t+dt)\rangle.
\end{aligned} \tag{4.30}$$

We see that $|\Psi(t)\rangle$ and $|\Psi(t+dt)\rangle$ have the same exchange symmetry. A step-by-step integration over time can be used to extend the argument over an arbitrary interval. The symmetry of a state ket under the exchange of indistinguishable particles is a constant of motion.[4]

The Universe is a physical system. It can be described by a Hamiltonian, which must be symmetric under exchange of the indistinguishable particles observed to exist in it. The state ket of the Universe must behave as above under these exchanges. The exchange symmetry never changes, and so all particles in the Universe can be placed into one of two classes for all time: those for which the wave function is unchanged when they are exchanged for another identical particle, and those for which it changes sign. Experiment tells us exchange of the fundamental quarks and leptons (electron, muon, tau, neutrino) and composite particles such as baryons (including the proton and neutron) or triton changes the sign of the state, corresponding to an anti-symmetric state ket. We call such particles **fermions**. Exchange of the fundamental photons, gluons, W, Z and Higgs particles and composite particles such as mesons (e.g. pion, kaon), deuteron and alpha particles leaves the state unchanged, corresponding to a symmetric state ket. We call these particles **bosons**. Theory does not tells us this, that electrons belong to the anti-symmetric class, only that all electrons belong to the same class, and will do so for all time. It is experiment that tells us to which class they belong. Theory can then tell us how they must behave.

Note that there is a connection between exchange-symmetry and particle spin. Fermions always have half-integer spin, and bosons integer spin. Having seen spin emerges naturally as a consequence of relativity you will not be surprised that a proof of the connection between the two lies in relativistic field theory.[5]

[4] An alternative argument follows from the Heisenberg equation of motion $i\hbar\frac{d\hat{\mathcal{O}}}{dt} = \left[\hat{\mathcal{O}},\hat{\mathcal{H}}\right]$ for an operator that is not explicitly time dependent. Since $\hat{P}_{ij}$ commutes with $\hat{\mathcal{H}}$, it is a constant of motion.

[5] The spin-statistics theorem. Proofs have been provided by Pauli and Feynman, amongst others. Want to make a name for yourself? Feynman famously said that the fact that we do not have an elementary explanation means that we do not have a complete understanding of the fundamental principle involved. Maybe you can provide one. The proof applies in 3D. In 2D it is possible to conceive of anyons, that behave as neither bosons or fermions. They have potential applications in topological quantum computers - https://www.nature.com/articles/d41586-020-01988-0.

4.3 Pauli exclusion principle

Let us return to our two-particle system Eqn. (4.13) and consider the case when the two non-interacting particles are indistinguishable. The two masses m_i and potentials V_i must be identical, so that the separate Schrödinger equations (4.15) have identical sets of eigenvalues and orthonormal eigenfunctions. Let us denote these ε_n and ψ_n respectively.

The total energy of states $\psi_n(x_1)\psi_m(x_2)$ and $\psi_m(x_1)\psi_n(x_2)$ are identical: $E = \varepsilon_n + \varepsilon_m$. Any linear combination of these two two-particle states is also an eigenstate with eigenvalue $E = \varepsilon_n + \varepsilon_m$:

$$\Psi_{nm}(x_1,x_2) = \cos(\vartheta)\psi_n(x_1)\psi_m(x_2) + \sin(\vartheta)\psi_m(x_1)\psi_n(x_2). \tag{4.31}$$

The coefficients ensure that the two-particle state is normalised if the single-particle eigenstates are. But if the particles are indistinguishable, then the eigenstate must have the correct symmetry properties under particle exchange, which the general form (4.31) does not. Instead

- If the particles are bosons, then the state must be symmetric:

$$\Psi^{(S)}_{nm}(x_1,x_2) = \frac{1}{\sqrt{2}}\left[\psi_n(x_1)\psi_m(x_2) + \psi_m(x_1)\psi_n(x_2)\right]. \tag{4.32}$$

  We can see explicitly that $\Psi^{(S)}_{nm}(x_2,x_1) = \Psi^{(S)}_{nm}(x_1,x_2)$. If $n = m$ then the properly normalised state is $\Psi^{(S)}_{nn}(x_1,x_2) = \psi_n(x_1)\psi_n(x_2)$.

- If the particles are fermions, then the state must be antisymmetric:

$$\Psi^{(A)}_{nm}(x_1,x_2) = \frac{1}{\sqrt{2}}\left[\psi_n(x_1)\psi_m(x_2) - \psi_m(x_1)\psi_n(x_2)\right]. \tag{4.33}$$

  Clearly $\Psi^{(A)}_{nm}(x_2,x_1) = -\Psi^{(A)}_{nm}(x_1,x_2)$. In this case we recognise that $\Psi^{(A)}_{nm}(x,x) = 0$: the antisymmetric wave function vanishes for equal arguments. Identical fermions cannot occupy the same point in space. Note that this is not a consequence of any repulsive interaction between them — Eqn (4.33) is an eigenstate of a non-interacting system. It is instead a consequence of the fundamental symmetry properties of the wavefunction. This result still applies with interactions present, and for a many-particle state of $N > 2$ electrons: $\Psi^{(A)}(x_1,x_2,\ldots,x_N)$ vanishes whenever $x_i = x_j,\ i \neq j$. This is the **Pauli exclusion principle**. Note also that if $n = m$ in (4.33) then $\Psi^{(A)}_{nn} = 0$; two identical fermions cannot occupy the same quantum state, that is, possess the same quantum numbers. This is another manifestation of the **Pauli exclusion principle**.

There are important consequences for statistical mechanics arising from these symmetry properties of the many-particle states. Let us consider two particles, 1 and 2, that have available to them two states, a and b. Then for distinguishable/classical particles the possible two-particle states are

$$\psi_a(1)\psi_a(2),\ \psi_a(1)\psi_b(2),\ \psi_b(1)\psi_a(2),\ \psi_b(1)\psi_b(2) \qquad \text{[4 states]}. \tag{4.34a}$$

For identical bosons the available states are

$$\psi_a(1)\psi_a(2),\ \psi_b(1)\psi_b(2),\ \left(\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)\right)/\sqrt{2} \qquad \text{[3 states]}, \tag{4.34b}$$

and for identical fermions

$$\left(\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)\right)/\sqrt{2} \qquad \text{[1 state]}. \tag{4.34c}$$

At high temperatures any differences between the energies of the states becomes negligible and all states become equally likely. Then there is zero chance of the two fermions being in the same state (the exclusion principle again), a 50% chance of the distinguishable/classical particles being in the same state (the 1st and 4th) and a 66.7% chance of the bosons being in the same state (the 1st and 2nd). The statistics of classical (Boltzman statistics), fermions (Fermi statistics) and bosons (Bose statistics) differ. Note that bosons are more likely to be found in the same state than classical/distinguishable particles. Their symmetry properties keep them together whilst fermions are kept apart.

That no two identical fermions can occupy the same state has important physical consequences. If the exclusion principle did not apply, there would be no Fermi sphere for electrons in a solid, no filling upwards of energy bands and no distinction between metals, semiconductors and insulators. At low temperatures all electrons would decay

into the lowest energy state at $\vec{k} = 0$.[6] Not that we would notice! The solids we know would not exist, and there would be no sentient life. The periodic table, and all of chemistry, and biology, is a direct consequence of the exclusion principle[7] combined with the atomic structure of atoms[8], where states $|n, \ell, m\rangle$ are sequentially occupied in order of increasing energy with a maximum of two electrons (distinguished by spin-up and spin-down) occupying each. When all states with a given n are filled, a closed shell of charge forms and the atom is chemically inert — an inert gas element. The ability to bond and participate in reactions is directly related to the excess or absence of electrons from a closed shell; closed-shell-plus-one atoms, alkalis metals, bond readily with closed-shell-minus-one atoms, the halogens, forming, for example sodium chloride, table salt.[9] The precise details of atomic structure and atomic interactions require proper consideration of the repulsion between the electrons, but the fundamental principles are what we have seen.

Class examples

[6] Due to downward radiative transitions — see the Quantum Dynamics topic.

[7] Quantum mechanics

[8] Also quantum mechanics!

[9] Essential for the proper functioning of the human body, with sodium needed for nerve function, and chloride ions for controlling blood pH and pressure.

Second Quantisation

Second quantisation is a different approach used in quantum mechanics for dealing with systems with a large number of indistinguishable particles. It uses creation and annihilation operators and a different concept of the state vector to deal with the symmetry/antisymmetry of many-particle wavefunctions.

First quantisation is essentially the quantum mechanics encountered so far, although the operator treatment of the linear harmonic oscillator encountered at the start of this course hints at what is to follow. In first quantisation classical variables such as the position x and momentum p of a particle become operators $\hat{x}$ and $\hat{p}$ satisfying certain commutation relations and that act upon a wavefunction, and we learn to treat particles as waves. In second quantisation it is the wavefunction that acts like an operator, subject to rules of commutation. We learn to treat waves as particles.

5.1 State vectors

We have seen that when dealing with indistinguishable particles we cannot simply treat a two particle state as particle 1 in state 1 and particle 2 in state 2 e.g. $\psi_1(x_1)\psi_2(x_2)$. For indistinguishable particles $\psi_1(x_1)\psi_2(x_2)$ and $\psi_2(x_1)\psi_1(x_2)$ refer to the same two particle state, and we must symmetrise (bosons) or antisymmetrise (fermions) to generate a valid description.

In second quantisation the concept of which particle is in which state is replaced with how many particles are in each state: a many-particle state vector has the form

$$|n_1, n_2, \ldots, n_j, \ldots\rangle \tag{5.1}$$

in what is known as the occupation number representation.

Suppose we have a free particle in a box of length L subject to periodic boundary conditions. Let the particle be a boson. The Hamiltonian $\hat{\mathcal{H}} = \dfrac{\hat{p}^2}{2m}$ commutes with the momentum operator: $[\hat{\mathcal{H}}, \hat{p}] = 0$, meaning that[1] a common set of energy and momentum eigenstates exist. Momentum eigenstates satisfy $\hat{p}|\psi\rangle = p|\psi\rangle$ which in the position representation becomes

$$-i\hbar\frac{\partial\psi}{\partial x} = p\psi \qquad \Rightarrow \qquad \psi_j(x) = \frac{1}{\sqrt{L}}e^{ip_j x/\hbar}, \quad p_j = \hbar\frac{2\pi}{L}j, \ j \text{ integer}. \tag{5.2}$$

The momentum is quantised due to $\psi(x) = \psi(x+L)$ and the eigenfunction normalised: $\int_0^L |\psi_j(x)|^2 dx = 1$. In Dirac notation $\psi_j(x) = \langle x|p_j\rangle$ and $\hat{\mathcal{H}}|p_j\rangle = \dfrac{p_j^2}{2m}|p_j\rangle$ showing the momentum eigenstate $|p_j\rangle$ is — as expected — an energy eigenstate, with energy eigenvalue $\varepsilon_{p_j} = \dfrac{p_j^2}{2m}$.

Now let us have three non-interacting particles, a, b and c, in the box. The Hamiltonian is $\hat{\mathcal{H}} = \hat{\mathcal{H}}_a + \hat{\mathcal{H}}_b + \hat{\mathcal{H}}_c$ and the momentum $\hat{p} = \hat{p}_a + \hat{p}_b + \hat{p}_c$. We can label the particles by their momenta and so the three particle state is $|p_a, p_b, p_c\rangle$ with $\hat{p}|p_a, p_b, p_c\rangle = (p_a + p_b + p_c)|p_a, p_b, p_c\rangle$ and $\hat{\mathcal{H}}|p_a, p_b, p_c\rangle = (\varepsilon_{p_a} + \varepsilon_{p_b} + \varepsilon_{p_c})|p_a, p_b, p_c\rangle$. The particles do not interact and so the energy and momentum are simply the sum of the energies and momenta of the individual particles.

Now consider the state $|p_1, p_3, p_1\rangle$. The energy is $E = 2\varepsilon_{p_1} + \varepsilon_{p_3}$ and the momentum $p = 2p_1 + p_3$. The notation encourages us to think of particles a and c having momentum p_1 and particle b having momentum p_3 but we know that if the particles are indistinguishable and we measure a particle momentum p_1 we will not know which of the particles had that momentum. The question makes no sense as the particles are indistinguishable. Instead there is a 2/3 chance that a particle-momentum measurement will record p_1, and a 1/3 chance that it will record p_3; and that a simultaneous measurement of the momenta of the three particles will find two have momentum p_1 and one has momentum p_3.

[1] See footnote 3 on page 4 of the Many-particle systems notes

So let us instead list the possible values of the particle momentum p_j and how many particles occupy each momentum state, n_j. Then the system is represented by the state $|n_1, n_2, \ldots\rangle$. The particular example is the state $|2,0,1,0,\ldots\rangle$. The total energy of a state is $E = \sum_j n_j \varepsilon_{p_j}$ and the total momentum $p = \sum_j n_j p_j$.

Class example

5.2 Fock space

Let $\{\psi_n(\vec{x})\}$ be a complete set (may be infinite) of orthonormal single-particle functions, where $\vec{x}$ combines position and spin state coordinates. Using this set we can construct symmetric (for bosons) and antisymmetric (for fermions) combinations describing N particles. For electrons (i.e. fermions) these take the form of Slater determinants. For example, we could take the first N functions in the complete set and form the antisymmetric N-particle function as

$$\Psi^{(N)}(\vec{x}_1, \ldots, \vec{x}_N) = \frac{1}{\sqrt{N}} \begin{vmatrix} \psi_1(\vec{x}_1) & \ldots & \psi_1(\vec{x}_N) \\ \vdots & \ddots & \vdots \\ \psi_N(\vec{x}_1) & \ldots & \psi_N(\vec{x}_N) \end{vmatrix}. \tag{5.3}$$

We could form another N-particle function by instead taking the first $N-1$ functions in the set along with the $(N+1)$th and forming the Slater determinant of them; and likewise by taking other sets of N functions drawn from the complete set of single-particle functions. In this way a compete set of determinantal wavefunctions can be formed which can be used to expand an arbitrary N-particle wavefunction.

Each of these determinantal wavefunctions is uniquely specified by the number of particles in each single-particle state. The first is $n_1 = n_2 = \cdots = n_N = 1$, $n_{N+1} = n_{N+2} = \cdots = 0$. The second $n_1 = n_2 = \cdots = n_{N-1} = n_{N+1} = 1$, $n_N = n_{N+2} = n_{N+3} = \cdots = 0$. These are the occupation number states

$$|\underbrace{1,\ldots,1}_{N},0,0,0,\ldots\rangle \qquad \text{and} \qquad |\underbrace{1,\ldots,1}_{N-1},0,1,0,0,\ldots\rangle. \tag{5.4}$$

The occupation number states are states in occupation number space, also known as Fock space, which formally is the direct sum of tensor products of the single-particle Hilbert space. It includes states with zero particles, one particle, two particles, and so on, and so readily allows for the description of problems where the number of particles is not constant. For fermions the states are antisymmetrised, as above, respecting the Pauli exclusion principle. For bosons they are symmetrised.

5.3 Creation and annihilation

In Fock space particles are added or removed from the system using creation and annihilation operators.

We start with the special state

$$|0,0,\ldots,0,\ldots\rangle \equiv |\Omega\rangle. \tag{5.5}$$

This is known as the vacuum state — it contains no particles. This state is normalised:

$$\langle 0,0,\ldots,0,\ldots|0,0,\ldots,0,\ldots\rangle = \langle\Omega|\Omega\rangle = 1. \tag{5.6}$$

The state $|0,\ldots,0,n_j=1,0,\ldots\rangle$ contains a single particle in state j. Hence we can identify it with the single particle states previously encountered. If the single particle states are labelled by their eigenvalue λ then

$$|0,\ldots,0,n_j=1,0,\ldots\rangle \equiv |\lambda_j\rangle \tag{5.7}$$

We now define a set of "field operators" $\hat{a}_j^\dagger$ that act to increase by one the number of particles in the state with eigenvalue λ_j.[2]

$$\hat{a}_j^\dagger |n_1, n_2, \ldots, n_j, \ldots\rangle \propto |n_1, n_2, \ldots, n_j + 1, \ldots\rangle. \tag{5.8}$$

The proportionality is fixed by enforcing normalisation. Requiring that $\hat{a}_j^\dagger$ acts upon the vacuum to create a properly normalised single-particle state means

$$\hat{a}_j^\dagger |\Omega\rangle = |\lambda_j\rangle. \tag{5.9}$$

[2] I retain the circumflex ($\hat{}$) denoting an operator although many authors at this point discard it, favouring de-cluttering and/or efficiency of writing. Their assumption is that if you got this far you are sufficiently aware of what you are doing that you do not need to be reminded as to what is an operator and what is not. I am playing it safe :-)

Since the single particle states are normalised

$$1 = \langle \lambda_j | \lambda_j \rangle = (|\lambda_j\rangle)^\dagger |\lambda_j\rangle = \left(\hat{a}_j^\dagger |\Omega\rangle\right)^\dagger \hat{a}_j^\dagger |\Omega\rangle = \left(\langle\Omega|\hat{a}_j\right)\hat{a}_j^\dagger|\Omega\rangle = \langle\Omega|\left(\hat{a}_j\hat{a}_j^\dagger|\Omega\rangle\right) = \langle\Omega|\hat{a}_j|\lambda_j\rangle. \tag{5.10}$$

Hence

$$\hat{a}_j|\lambda_j\rangle = |\Omega\rangle \tag{5.11a}$$

so that the operator $\hat{a}_j$ acts as a particle annihilator, acting upon the single particle state $|\lambda_j\rangle$ and turning it into the particle-free vacuum state. In summary

$$\hat{a}_j|n_1, n_2, \ldots, n_j, \ldots\rangle \propto |n_1, n_2, \ldots, n_j - 1, \ldots\rangle \tag{5.11b}$$

$$\hat{a}_j|\Omega\rangle = 0 \tag{5.11c}$$

$$\hat{a}_j|\lambda_k\rangle = 0 \quad \text{if} \quad j \neq k \tag{5.11d}$$

are properties required of the field operators $\hat{a}_j$. Equations (5.11a) and (5.11d) are the same as the single statement

$$\hat{a}_j|\lambda_k\rangle = \delta_{jk}|\Omega\rangle. \tag{5.11e}$$

5.4 Symmetrisation

We now look to endow the creation and annhilation operators with properties that enforce the appropriate particle swap or exchange symmetry. To do this we consider putting a first particle in state k and a second in state j, and compare the result with when we exchange them and put the first particle in state j and the second in state k. From our previous considerations we require the resulting states are related by the appropriate symmetry depending upon the indistinguishable particles, namely $\hat{a}_j^\dagger\hat{a}_k^\dagger|\Omega\rangle = \pm\hat{a}_k^\dagger\hat{a}_j^\dagger|\Omega\rangle$ for a two-particle state with the $+$ sign ($-$ sign) for bosons (fermions). Similar considerations exchanging particles in a general many-particle state (5.1) leads to the requirement

$$\hat{a}_j^\dagger\hat{a}_k^\dagger - \hat{a}_k^\dagger\hat{a}_j^\dagger = [\hat{a}_j^\dagger, \hat{a}_k^\dagger]_- = 0 \qquad \text{bosons} \tag{5.12}$$

$$\hat{a}_j^\dagger\hat{a}_k^\dagger + \hat{a}_k^\dagger\hat{a}_j^\dagger = [\hat{a}_j^\dagger, \hat{a}_k^\dagger]_+ = 0 \qquad \text{fermions} \tag{5.13}$$

where we use $[\hat{\mathcal{A}}, \hat{\mathcal{B}}]_- = \hat{\mathcal{A}}\hat{\mathcal{B}} - \hat{\mathcal{B}}\hat{\mathcal{A}}$ for the commutator and $[\hat{\mathcal{A}}, \hat{\mathcal{B}}]_+ = \hat{\mathcal{A}}\hat{\mathcal{B}} + \hat{\mathcal{B}}\hat{\mathcal{A}}$ for the anticommutator, sometimes written $\{\hat{\mathcal{A}}, \hat{\mathcal{B}}\}$. Taking the adjoint / hemitian-transpose

$$[\hat{a}_j, \hat{a}_k]_- = 0 \qquad \text{bosons}$$

$$[\hat{a}_j, \hat{a}_k]_+ = 0 \qquad \text{fermions} \tag{5.14}$$

We see that setting $j = k$ in (5.13) implies $\hat{a}_j^\dagger\hat{a}_j^\dagger = 0$. The fermion creation operator automatically enforces the Pauli exclusion principle, and one cannot put two particles into state j.

Class example

We also need commutator rules for when we combine a creation operator $\hat{a}_j$ with an annihilation operator $\hat{a}_k^\dagger$. In the case of the harmonic oscillator one has $[\hat{a}, \hat{a}^\dagger]_- = 1$ (see Eqn. (1.8)) and leads directly to $\hat{\mathcal{N}} = \hat{a}^\dagger\hat{a}$ (see Eqn. (1.16)) being the number operator which counts the number of quanta in the oscillator. Having the boson creation and annihilation operators satisfy $[\hat{a}_j, \hat{a}_j^\dagger]_- = 1$ allows us to use $\hat{\mathcal{N}}_j = \hat{a}_j^\dagger\hat{a}_j$ to count the number of bosons in single particle state j, and similarly having the fermion creation and annihilation operators satisfy $[\hat{a}_j, \hat{a}_j^\dagger]_+ = 1$ means that $\hat{\mathcal{N}}_j = \hat{a}_j^\dagger\hat{a}_j$ counts the number of fermions in state j. In general

$$\hat{\mathcal{N}} = \sum_j \hat{a}_j^\dagger\hat{a}_j$$

counts the number of identical particles. A summary:

bosons	fermions
$\hat{a}_j^\dagger\hat{a}_k^\dagger - \hat{a}_k^\dagger\hat{a}_j^\dagger = [\hat{a}_j^\dagger, \hat{a}_k^\dagger]_- = 0$	$\hat{a}_j^\dagger\hat{a}_k^\dagger + \hat{a}_k^\dagger\hat{a}_j^\dagger = [\hat{a}_j^\dagger, \hat{a}_k^\dagger]_+ = 0$
$\hat{a}_j\hat{a}_k - \hat{a}_k\hat{a}_j = [\hat{a}_j, \hat{a}_k]_- = 0$	$\hat{a}_j\hat{a}_k + \hat{a}_k\hat{a}_j = [\hat{a}_j, \hat{a}_k]_+ = 0$
$\hat{a}_j\hat{a}_k^\dagger - \hat{a}_k^\dagger\hat{a}_j = [\hat{a}_j, \hat{a}_k^\dagger]_- = \delta_{jk}$	$\hat{a}_j\hat{a}_k^\dagger + \hat{a}_k^\dagger\hat{a}_j = [\hat{a}_j, \hat{a}_k^\dagger]_+ = \delta_{jk}$

(5.15)

The correct normalisation of the states follows by arguments similar to those employed in the treatment of the harmonic oscillator. The result is

$$\begin{array}{ll} \text{boson} & \begin{cases} \hat{a}_j^\dagger|n_1,\ldots,n_j,\ldots\rangle = \sqrt{n_j+1}|n_1,\ldots,n_j+1,\ldots\rangle \\ \hat{a}_j|n_1,\ldots,n_j,\ldots\rangle = \sqrt{n_j}|n_1,\ldots,n_j-1,\ldots\rangle \end{cases} \\ \text{fermions} & \begin{cases} \hat{a}_j^\dagger|n_1,\ldots,n_j,\ldots\rangle = (-1)^{s_j}(1-n_j)|n_1,\ldots,n_j+1,\ldots\rangle \\ \hat{a}_j|n_1,\ldots,n_j,\ldots\rangle = (-1)^{s_j}n_j|n_1,\ldots,n_j-1,\ldots\rangle \end{cases} \end{array} \tag{5.16}$$

In the fermion case $s_j = \sum_{k=1}^{j-1} n_k$ is the number of occupied states up to but excluding state j and this factor is associated with the fermionic operators satisfying anticommutation relations. The Pauli principle is clearly evident in the fermionic case.

There is great similarity between the formalism here and that of the linear harmonic oscillator. That does not mean all particles are oscillators (although we know particles behave like waves!). The connection is that the energy levels of the harmonic oscillator are equally spaced, whilst the energy (or momentum in the example of section 5.1 is proportional to how many particles there are in state j). If we have N independent oscillators the total energy relative to the vacuum zero-point energy is $E = \sum_{j=1}^{N} n_j \hbar\omega_j$ where n_j is how many quanta of energy are in the jth oscillator, and if we have non-interacting particles in N momentum eigenstates the total energy is $E = \sum_{j=1}^{N} n_{p_j}\varepsilon_{p_j}$ where n_{p_j} is the number of particles in momentum state p_j with energy ε_{p_j}. This gets us thinking of particles as quanta of energy associated with excitations of some underlying field.

5.5 Change of basis and representation of operators

If the single particle states $|\lambda_j\rangle$ are eigenstates of single-particle operator $\hat{L}$, so $\hat{L}|\lambda_j\rangle = \lambda_j|\lambda_j\rangle$, then in the many-particle state $|n_1,n_2,\ldots,n_j,\ldots\rangle$ the corresponding many-particle operator $\hat{\mathcal{L}}$ will have eigenvalue $\sum_j n_j\lambda_j$. The energy and momentum of the three-particle system in section 5.1 are examples. We can write this in terms of creation and annihilation operators as

$$\hat{\mathcal{L}} = \sum_j \lambda_j \hat{\mathcal{N}}_j = \sum_j \lambda_j \hat{a}_j^\dagger \hat{a}_j \tag{5.17}$$

Suppose that instead of the basis $\{|\lambda_j\rangle\}$ of single particle states we instead wished to use some other, $\{|\omega_k\rangle\}$. For example instead of using energy eigenstates or momentum eigenstates we may wish to work in the coordinate representation. Using completeness $\sum_k |\omega_k\rangle\langle\omega_k| = \hat{1}$ we can write

$$\begin{aligned} \hat{a}_j^\dagger|\Omega\rangle = |\lambda_j\rangle &= \sum_k |\omega_k\rangle\langle\omega_k|\lambda_j\rangle \\ &= \sum_k \langle\omega_k|\lambda_j\rangle|\omega_k\rangle \\ &= \sum_k \langle\omega_k|\lambda_j\rangle \hat{b}_k^\dagger|\Omega\rangle \end{aligned} \tag{5.18}$$

where $\{\hat{b}_k^\dagger\}$ are operators creating particles in the single particle states $\{|\omega_k\rangle\}$. Thus

$$\hat{a}_j^\dagger = \sum_k \hat{b}_k^\dagger\langle\omega_k|\lambda_j\rangle \qquad \text{and} \qquad \hat{a}_j = \sum_k \langle\lambda_j|\omega_k\rangle\hat{b}_k \tag{5.19}$$

where the second relationship follows by taking the adjoint / hermitian-transpose.

This allows us to express the operator $\hat{\mathcal{L}}$ in terms of the new creation and annihilation operators, for

$$\begin{aligned} \hat{\mathcal{L}} = \sum_j \lambda_j \hat{a}_j^\dagger \hat{a}_j &= \sum_j \lambda_j \left(\sum_k \hat{b}_k^\dagger\langle\omega_k|\lambda_j\rangle\right)\left(\sum_\ell \langle\lambda_j|\omega_\ell\rangle\hat{b}_\ell\right) \\ &= \sum_{k\ell} \hat{b}_k^\dagger\hat{b}_\ell \sum_j \langle\omega_k|\lambda_j\rangle\lambda_j\langle\lambda_j|\omega_\ell\rangle \\ &= \sum_{k\ell} \hat{b}_k^\dagger\hat{b}_\ell\langle\omega_k|\left(\hat{L}\sum_j|\lambda_j\rangle\langle\lambda_j|\right)|\omega_\ell\rangle \\ \text{or} \qquad \hat{\mathcal{L}} &= \sum_{k\ell}\langle\omega_k|\hat{L}|\omega_\ell\rangle\hat{b}_k^\dagger\hat{b}_\ell \end{aligned} \tag{5.20}$$

We can use (5.20) to write in second-quantised form any additive single-particle operator, such as the energy, momentum, or the potential energy due to the interaction with an external field such as occurs in Eqn (4.13). The interpretation of (5.20) is that the single-particle operator scatters a particle from state ℓ to state k with probability amplitude $\langle \omega_k | \hat{L} | \omega_\ell \rangle$.

Using these results, second quantised in the position representation the single-particle Hamiltonian a sum of kinetic and potential energies in one-dimension is

$$\hat{\mathcal{H}} = \hat{\mathcal{T}} + \hat{\mathcal{V}} = \int dx \sum_\sigma \Psi_\sigma^\dagger(x) \left[\frac{\hat{p}^2}{2m} + V(x) \right] \Psi_\sigma(x) \tag{5.21}$$

where $\hat{p} = -i\hbar \frac{\partial}{\partial x}$. The field operators

$$\Psi_\sigma(x) = \sum_j \langle x | \lambda_j \rangle \hat{a}_j, \quad \Psi_\sigma^\dagger(x) = \sum_j \langle \lambda_j | x \rangle \hat{a}_j^\dagger \tag{5.22}$$

satisfy

$$\left[\Psi_\sigma(x), \Psi_{\sigma'}^\dagger(x') \right]_\pm = \delta(x - x') \delta_{\sigma\sigma'}, \qquad \left[\Psi_\sigma(x), \Psi_{\sigma'}(x') \right]_\pm = 0 = \left[\Psi_\sigma^\dagger(x), \Psi_{\sigma'}^\dagger(x') \right]_\pm \tag{5.23}$$

and the total occupation number operator is $\hat{\mathcal{N}} = \int dx \sum_\sigma \Psi_\sigma^\dagger(x) \Psi_\sigma(x)$. The field operators play a similar role to the wavefunction in the Schrödinger theory. In the second quantisation formalism the wavefunctions are replaced by operators satisfying commutation relations.

In many-particle systems we also have interactions between the particles, such as the pairwise Coulomb interaction between the electrons in the helium atom. Assume pairwise interactions that are additive, and V_{jk} the interaction energy between particles in states $|\lambda_j\rangle$ and $|\lambda_k\rangle$. Then in total we have

$$\mathcal{V} = \frac{1}{2} \sum_{j \neq k} V_{jk} n_j n_k + \frac{1}{2} \sum_j V_{jj} n_j (n_j - 1). \tag{5.24}$$

The first term sums all two-particle interactions between particles in different states, with the factor of a half taking account that the interactions are actually pairwise and so corrects for double counting. The second term accounts for the interactions between multiple particles in the same state — there are $n(n-1)/2$ ways of selecting n particles two at a time. This term vanishes for fermions as n_j is either 0 or 1.

We can turn this in to an operator by recalling $\hat{\mathcal{N}}_j = \hat{a}_j^\dagger \hat{a}_j$ counts the number of particles in state j, i.e. n_j. Also noting that the part of the self-energy term containing n_j^2 is just the omitted $j = k$ term in the first sum we get

$$\hat{\mathcal{V}} = \frac{1}{2} \sum_{jk} V_{jk} \left(\hat{\mathcal{N}}_j \hat{\mathcal{N}}_k - \hat{\mathcal{N}}_j \delta_{jk} \right) \tag{5.25}$$

Furthermore

$$\begin{aligned} \hat{\mathcal{N}}_j \hat{\mathcal{N}}_k - \hat{\mathcal{N}}_j \delta_{jk} &= \hat{a}_j^\dagger \hat{a}_j \hat{a}_k^\dagger \hat{a}_k - \hat{a}_j^\dagger \hat{a}_j \delta_{jk} \\ &= \hat{a}_j^\dagger \left(\delta_{jk} \pm \hat{a}_k^\dagger \hat{a}_j \right) \hat{a}_k - \hat{a}_j^\dagger \hat{a}_j \delta_{jk} \quad \text{using (5.15)} \\ &= \pm \hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_j \hat{a}_k \\ &= \hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_k \hat{a}_j \quad \text{using (5.14)} \end{aligned} \tag{5.26}$$

so that we can write

$$\hat{\mathcal{V}} = \frac{1}{2} \sum_{jk} V_{jk} \hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_k \hat{a}_j. \tag{5.27}$$

or

$$\hat{\mathcal{V}} = \frac{1}{2} \sum_{\ell \ell' m m'} \langle \ell \ell' | V | m m' \rangle \hat{b}_\ell^\dagger \hat{b}_{\ell'}^\dagger \hat{b}_m \hat{b}_{m'}, \qquad \langle \ell \ell' | V | m m' \rangle = \sum_{jk} V_{jk} \langle \omega_\ell | \lambda_j \rangle \langle \omega_{\ell'} | \lambda_k \rangle \langle \lambda_k | \omega_m \rangle \langle \lambda_j | \omega_{m'} \rangle \tag{5.28}$$

in a different basis.

Class example