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Topics in Quantum Mechanics

University of Cambridge Part II Mathematical Tripos

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Recommended Books and Resources

There are many good books on quantum mechanics. Here's a selection that I like:

- Griffiths, *Introduction to Quantum Mechanics*

An excellent way to ease yourself into quantum mechanics, with uniformly clear explanations. For this course, it covers both approximation methods and scattering.

- Shankar, *Principles of Quantum Mechanics*
- James Binney and David Skinner, *The Physics of Quantum Mechanics*
- Weinberg, *Lectures on Quantum Mechanics*

These are all good books, giving plenty of detail and covering more advanced topics. Shankar is expansive, Binney and Skinner clear and concise. Weinberg likes his own notation more than you will like his notation, but it's worth persevering.

- John Preskill, Course on Quantum Computation

Preskill's online lecture course has become the default resource for topics on quantum foundations.

A number of lecture notes are available on the web. Links can be found on the course webpage: http://www.damtp.cam.ac.uk/user/tong/topicsinqm.html

Contents

Acknowledgements

The Cambridge mathematics tripos includes a course called "*Applications of Quantum Mechanics*". It is something of a hybrid, containing some topics from these notes (the Variational Principle, and Scattering Theory), together with an introduction to Solid State Physics. I have chosen to split these into two, more traditionally-titled sets of notes, with Lectures on Solid State Physics carved off separately.

If you're a Cambridge student, the relevant chapters making up the lectures on Applications of Quantum Mechanics can be found here.

0. Introduction

> "The true meaning of quantum mechanics can be found in the answers it gives about the world we inhabit."
>
> *Me, in a previous set of lecture notes.*

Our previous courses on quantum mechanics were largely focussed on understanding the mathematical formalism of the subject. The purpose of this course is to put this understanding to use.

The applications of quantum mechanics are many and varied, and vast swathes of modern physics fall under this rubric. Many of these applications naturally fall into different lectures, such as Solid State Physics or Statistical Physics or, if we include relativity into the mix, Particle Physics and Quantum Field Theory. In these lectures we cover a number of topics that didn't have such a natural home. This means that we're left with something of a mishmash of topics.

The first two chapters describe tools that are useful in the study of many different quantum system: they cover the role of discrete symmetries in quantum mechanics, and the use of approximation methods to solve quantum systems. Subsequent chapters are more focussed on specific quantum systems.

We devote a significant amount of time to *atomic physics*. Current research in atomic physics is largely devoted to exquisitely precise manipulation of cold atoms, bending them to our will. Here, our focus is more old-fashioned and we look only at the foundations of the subject, including the detailed spectrum of the hydrogen atom, and a few tentative steps towards understanding the structure of many-electron atoms. We also describe the various responses of atoms to electromagnetic prodding.

We devote one chapter of these notes to revisiting some of the foundational aspects of quantum mechanics, starting with the important role played by entanglement as a way to distinguish between a quantum and classical world. We will provide a more general view of the basic ideas of states and measurements, as well as an introduction to the quantum mechanics of open systems.

The final topic *scattering theory*. In the past century, physicists have developed a foolproof and powerful method to understand everything and anything: you take the object that you're interested in and you throw something at it. This technique was pioneered by Rutherford who used it to understand the structure of the atom. It was used by Franklin, Crick and Watson to understand the structure of DNA. And, more

recently, it was used at the LHC to demonstrate the existence of the Higgs boson. In fact, throwing stuff at other stuff is the single most important experimental method known to science. It underlies much of what we know about condensed matter physics and all of what we know about high-energy physics.

In many ways, these lectures are where theoretical physics starts to fracture into separate sub-disciplines. Yet areas of physics which study systems separated by orders of magnitude — from the big bang, to stars, to materials, to information, to atoms and beyond — all rest on a common language and background. These lectures build this shared base of knowledge.

1. Discrete Symmetries

In this section, we discuss the implementation of discrete symmetries in quantum mechanics. Our symmetries of choice are *parity*, a spatial reflection, and *time reversal*.

1.1 Parity

A cartoon picture of parity is to take a state and turn it into its image as seen in a mirror. This is best viewed as an action on space itself. In three spatial dimensions, we usually take parity to act as

$$P : \mathbf{x} \mapsto -\mathbf{x} \tag{1.1}$$

More generally, in d spatial dimensions the parity operator is a linear map on the d spatial coordinates such that $P \in O(d)$ and $\det P = -1$. This means, in particular, that the definition (1.1) is good whenever d is odd, but not good when d is even where it coincides with a rotation. A definition which works in all dimensions is simply $P : x^1 \mapsto -x^1$ and $P : x^i \mapsto x^i$ for all $i \neq 1$, which differs from (1.1) by a spatial rotation.

Here we will restrict attention to $d = 1$ and $d = 3$, where the definition (1.1) is the standard one. We can use this to tell us how the classical state of a particle changes. Recall that, classically, the state of a particle is defined by a point $(\mathbf{x}, \mathbf{p})$ in phase space. Since $\mathbf{p} = m\dot{\mathbf{x}}$, parity must act as

$$P : (\mathbf{x}, \mathbf{p}) \mapsto (-\mathbf{x}, -\mathbf{p}) \tag{1.2}$$

Here our interest lies in quantum mechanics so we want to introduce a *parity operator* which acts on the Hilbert space. We call this operator π. It is natural to define π by its action on the position basis,

$$\pi|\mathbf{x}\rangle = |-\mathbf{x}\rangle \tag{1.3}$$

This means that, when acting on wavefunctions,

$$\pi : \psi(\mathbf{x}) \mapsto \psi(-\mathbf{x})$$

Note that, in contrast to continuous symmetries, there is no one-parameter family of transformations. You don't get to act by a little bit of parity: you either do it or you don't. Recall that for continuous symmetries, the action on the Hilbert space is implemented by a unitary operator U while its infinitesimal form $U \approx 1 + i\epsilon T$ (with ϵ

small) yields the Hermitian operator T called the "generator". In contrast, the parity operator π is both unitary and Hermitian. This follows from

$$\pi^\dagger\pi = 1 \quad \text{and} \quad \pi^2 = 1 \quad \Rightarrow \quad \pi = \pi^\dagger = \pi^{-1} \tag{1.4}$$

Given the action of parity on the classical state (1.2), we should now derive how it acts on any other states, for example the momentum basis $|\mathbf{p}\rangle$. It's not difficult to check that (1.3) implies

$$\pi|\mathbf{p}\rangle = |-\mathbf{p}\rangle$$

as we might expect from our classical intuition. This essentially follows because $\mathbf{p} = -i\hbar\partial/\partial\mathbf{x}$ in the position representation. Alternatively, you can see it from the form of the plane waves.

The Action of Parity on Operators

We can also define the parity operator by its action on the operators. From our discussion above, we have

$$\pi\mathbf{x}\pi^\dagger = -\mathbf{x} \quad \text{and} \quad \pi\mathbf{p}\pi^\dagger = -\mathbf{p}$$

Using this, together with (1.4), we can deduce the action of parity on the angular momentum operator $\mathbf{L} = \mathbf{x} \times \mathbf{p}$,

$$\pi\mathbf{L}\pi^\dagger = +\mathbf{L} \tag{1.5}$$

We can also ask how parity acts on the spin operator $\mathbf{S}$. Because this is another form of angular momentum, we take

$$\pi\mathbf{S}\pi^\dagger = +\mathbf{S} \tag{1.6}$$

This ensures that the total angular momentum $\mathbf{J} = \mathbf{L}+\mathbf{S}$ also transforms as $\pi\mathbf{J}\pi^\dagger = +\mathbf{J}$.

In general, an object $\mathbf{V}$ which transforms under both rotations and parity in the same way as $\mathbf{x}$, so that $\pi\mathbf{V}\pi^\dagger = -\mathbf{V}$, is called a *vector*. (You may have heard this name before!) In contrast, an object like angular momentum which rotates like $\mathbf{x}$ but transforms under parity as $\pi\mathbf{V}\pi = +\mathbf{V}$ is called a *pseudo-vector*.

Similarly, an object K which is invariant under both rotations and parity, so that $\pi K\pi^\dagger = K$ is called a *scalar*. However, if it is invariant under rotations but odd under parity, so $\pi K\pi^\dagger = -K$, is called a *pseudo-scalar*. An example of a pseudo-scalar in quantum mechanics is $\mathbf{p} \cdot \mathbf{S}$.

Although we've introduced these ideas in the context of quantum mechanics, they really descend from classical mechanics. There too, $\mathbf{x}$ and $\mathbf{p}$ are examples of vectors: they flip sign in a mirror. Meanwhile, $\mathbf{L} = \mathbf{x} \times \mathbf{p}$ is a pseudo-vector: it remains pointing in the same direction in a mirror. In electromagnetism, the electric field $\mathbf{E}$ is a vector, while the magnetic field $\mathbf{B}$ is a pseudo-vector,

$$P : \mathbf{E} \mapsto -\mathbf{E} \quad , \quad P : \mathbf{B} \mapsto +\mathbf{B}$$

1.1.1 Parity as a Quantum Number

The fact that the parity operator is Hermitian means that it is, technically, an observable. More pertinently, we can find eigenstates of the parity operator

$$\pi|\psi\rangle = \eta_\psi|\psi\rangle$$

where η_ψ is called the *parity* of the state $|\psi\rangle$. Using the fact that $\pi^2 = 1$, we have

$$\pi^2|\psi\rangle = \eta_\psi^2|\psi\rangle = |\psi\rangle \quad \Rightarrow \quad \eta_\psi = \pm 1$$

So the parity of a state can only take two values. States with $\eta_\psi = +1$ are called *parity even*; those with $\eta_\psi = -1$ *parity odd*.

The parity eigenstates are particularly useful when parity commutes with the Hamiltonian,

$$\pi H \pi^\dagger = H \quad \Leftrightarrow \quad [\pi, H] = 0$$

In this case, the energy eigenstates can be assigned definite parity. This follows immediately when the energy level is non-degenerate. But even when the energy level is degenerate, general theorems of linear algebra ensure that we can always pick a basis within the eigenspace which have definite parity.

An Example: The Harmonic Oscillator

As a simple example, let's consider the one-dimensional harmonic oscillator. The Hamiltonian is

$$H = \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2 x^2$$

The simplest way to build the Hilbert space is to introduce raising and lowering operators $a \sim (x + ip/m\omega)$ and $a^\dagger \sim (x - ip/m\omega)$ (up to a normalisation constant). The ground state $|0\rangle$ obeys $a|0\rangle = 0$ while higher states are built by $|n\rangle \sim (a^\dagger)^n|0\rangle$ (again, ignoring a normalisation constant).

The Hamiltonian is invariant under parity: $[\pi, H] = 0$, which means that all energy eigenstates must have a definite parity. Since the creation operator $a^\dagger$ is linear in x and p, we have

$$\pi a^\dagger \pi = -a^\dagger$$

This means that the parity of the state $|n+1\rangle$ is

$$\pi|n+1\rangle = \pi a^\dagger|n\rangle = -a^\dagger\pi|n\rangle \quad \Rightarrow \quad \eta_{n+1} = -\eta_n$$

We learn that the excited states alternate in their parity. To see their absolute value, we need only determine the parity of the ground state. This is

$$\psi_0(x) = \langle x|0\rangle \sim \exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$

Since the ground state doesn't change under reflection we have $\eta_0 = +1$ and, in general, $\eta_n = (-1)^n$.

Another Example: Three-Dimensional Potentials

In three dimensions, the Hamiltonian takes the form

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{x}) \tag{1.7}$$

This is invariant under parity whenever we have a central force, with the potential depending only on the distance from the origin: $V(\mathbf{x}) = V(r)$. In this case, the energy eigenstates are labelled by the triplet of quantum numbers n, l, m that are familiar from the hydrogen atom, and the wavefunctions take the form

$$\psi_{n,l,m}(\mathbf{x}) = R_{n,l}(r)Y_{l,m}(\theta,\phi) \tag{1.8}$$

How do these transform under parity? First note that parity only acts on the spherical harmonics $Y_{l,m}(\theta,\phi)$. In spherical polar coordinates, parity acts as

$$P : (r,\theta,\phi) \;\mapsto\; (r,\pi-\theta,\phi+\pi)$$

The action of parity of the wavefunctions therefore depends on how the spherical harmonics transform under this change of coordinates. Up to a normalisation, the spherical harmonics are given by

$$Y_{l,m} \sim e^{im\phi}\, P_l^m(\cos\theta)$$

where $P_l^m(x)$ are the associated Legendre polynomials. As we will now argue, the transformation under parity is

$$P : Y_{l,m}(\theta,\phi) \;\mapsto\; Y_{l,m}(\pi-\theta,\phi+\pi) = (-1)^l\, Y_{l,m}(\theta,\phi) \tag{1.9}$$

This means that the wavefunction transforms as

$$P : \psi_{n,l,m}(\mathbf{x}) \;\mapsto\; \psi_{n,l,m}(-\mathbf{x}) = (-1)^l\, \psi_{n,l,m}(\mathbf{x})$$

Equivalently, written in terms of the state $|n,l,m\rangle$, where $\psi_{n,l,m}(\mathbf{x}) = \langle \mathbf{x}|n,l,m\rangle$, we have

$$\pi|n,l,m\rangle = (-1)^l\,|n,l,m\rangle \tag{1.10}$$

It remains to prove the parity of the spherical harmonic (1.9). There's a trick here. We start by considering the case $l = m$ where the spherical harmonics are particularly simple. Up to a normalisation factor, they take the form

$$Y_{l,l}(\theta,\phi) \sim e^{il\phi}\sin^l\theta$$

So in this particular case, we have

$$P : Y_{l,l}(\theta,\phi) \;\mapsto\; Y_{l,l}(\pi-\theta,\phi+\pi) = e^{il\phi}e^{il\pi}\sin^l(\pi-\theta) = (-1)^l\, Y_{l,l}(\theta,\phi)$$

confirming (1.9). To complete the result, we show that the parity of a state cannot depend on the quantum number m. This follows from the transformation of angular momentum (1.5) which can also be written as $[\pi, \mathbf{L}] = 0$. But recall that we can change the quantum number m by acting with the raising and lowering operators $L_\pm = L_x \pm iL_y$. So, for example,

$$\pi|n,l,l-1\rangle = \pi L_-|n,l,l\rangle = L_-\pi|n,l,l\rangle = (-1)^l L_-|n,l,l\rangle = (-1)^l|n,l,l-1\rangle$$

Repeating this argument shows that (1.10) holds for all m.

Parity and Spin

We can also ask how parity acts on the spin states, $|s,m_s\rangle$ of a particle. We know from (1.6) that the operator $\mathbf{S}$ is a pseudo-vector, and so obeys $[\pi,\mathbf{S}] = 0$. The same argument that we used above for angular momentum $\mathbf{L}$ can be re-run here to tell us that the parity of the state cannot depend on the quantum number m_s. It can, however, depend on the spin s,

$$\pi|s,m_s\rangle = \eta_s|s,m_s\rangle$$

What determines the value of η_s? Well, in the context of quantum mechanics nothing determines η_s! In most situations we are dealing with a bunch of particles all of the same spin (e.g. electrons, all of which have $s = \frac{1}{2}$). Whether we choose $\eta_s = +1$ or $\eta_s = -1$ has no ultimate bearing on the physics. Given that it is arbitrary, we usually pick $\eta_s = +1$.

There is, however, a caveat to this story. Within the framework of quantum field theory it does make sense to assign different parity transformations to different particles. This is equivalent to deciding whether $\eta_s = 1$ or $\eta_s = -1$ for each particle. We will discuss this in Section 1.1.2.

What is Parity Good For?

We've learned that if we have a Hamiltonian that obeys $[\pi, H] = 0$, then we can assign each energy eigenstate a sign, ± 1, corresponding to whether it is even or odd under parity. But, beyond gaining a rough understanding of what wavefunction in one-dimension look like, we haven't yet said why this is a useful thing to do. Here we advertise some later results that will hinge on this:

- There are situations where one starts with a Hamiltonian that is invariant under parity and adds a parity-breaking perturbation. The most common situation is to take an electron with Hamiltonian (1.7) and turn on a constant electric field $\mathbf{E}$, so the new Hamiltonian reads

  $$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r) - e\mathbf{x}\cdot\mathbf{E}$$

  This no longer preserves parity. For small electric fields, we can solve this using perturbation theory. However, this is greatly simplified by the fact that the original eigenstates have a parity quantum number. Indeed, in nearly all situations first-order perturbation theory can be shown to vanish completely. We will describe this in some detail in Section 4.1 where we look at a hydrogen atom in an electric field and the resulting *Stark effect*.

- In atomic physics, electrons sitting in higher states will often drop down to lower states, emitting a photon as they go. This is the subject of *spectroscopy*. It was one of the driving forces behind the original development of quantum mechanics and will be described in some detail in Section 4.3. But it turns out that an electron in one level can't drop down to any of the lower levels: there are *selection rules* which say that only certain transitions are allowed. These selection rules follow from the "conservation of parity". The final state must have the same parity as the initial state.

- It is often useful to organise degenerate energy levels into a basis of parity eigenstates. If nothing else, it tends to make calculations much more straightforward. We will see an example of this in Section 6.1.3 where we discuss scattering in one dimension.

1.1.2 Intrinsic Parity

There is a sense in which every kind particle can be assigned a parity ± 1. This is called *intrinsic parity*. To understand this, we really need to move beyond the framework of non-relativistic quantum mechanics and into the framework of *quantum field theory*

The key idea of quantum field theory is that the particles are ripples of an underlying field, tied into little bundles of energy by quantum mechanics. Whereas in quantum mechanics, the number of particles is fixed, in quantum field theory the Hilbert space (sometimes called a *Fock space*) contains states with different particle numbers. This allows us to describe various phenomena where we smash two particles together and many emerge.

In quantum field theory, every particle is described by some particular state in the Hilbert space. And, just as we assigned a parity eigenvalue to each state above, it makes sense to assign a parity eigenvalue to each kind of particle.

To determine the total parity of a configuration of particles in their centre-of-momentum frame, we multiply the intrinsic parities together with the angular momentum parity. For example, if two particles A and B have intrinsic parity η_A and η_B and relative angular momentum L, then the total parity is

$$\eta = \eta_A \eta_B (-1)^L$$

To give some examples: by convention, the most familiar spin-$\frac{1}{2}$ particles all have even parity:

$$\begin{aligned} \text{electron}: &\quad \eta_e = +1 \\ \text{proton}: &\quad \eta_p = +1 \\ \text{neutron}: &\quad \eta_n = +1 \end{aligned}$$

Each of these has an anti-particle. (The anti-electron is called the positron; the others have the more mundane names anti-proton and anti-neutron). Anti-particles always have opposite quantum numbers to particles and parity is no exception: they all have $\eta = -1$.

All other particles are also assigned an intrinsic parity. As long as the underlying Hamiltonian is invariant under parity, all processes must conserve parity. This is a useful handle to understand what processes are allowed. It is especially useful when discussing the strong interactions where the elementary quarks can bind into a bewildering number of other particles – protons and neutrons, but also pions and kaons and etas and rho mesons and omegas and sigmas and deltas. As you can see, the names are not particularly imaginative. There are hundreds of these particles. Collectively they go by the name *hadrons*.

Often the intrinsic parity of a given hadron can be determined experimentally by observing a decay process. Knowing that parity is conserved uniquely fixes the parity of the particle of interest. Other decay processes must then be consistent with this.

An Example: $\pi^- d \to nn$

The simplest of the hadrons are a set of particles called *pions*. We now know that each contains a quark-anti-quark pair. Apart from the proton and neutron, these are the longest lived of the hadrons.

The pions come in three types: neutral, charge $+1$ and charge -1 (in units where the electron has charge -1). They are labelled π^0, π^+ and π^- respectively. The π^- is observed experimentally to decay when it scatters off a deuteron, d, which is stable bound state of a proton and neutron. (We showed the existence of a such a bound state in Section 2.1.3 as an application of the variational method.). After scattering off a deuteron, the end product is two neutrons. We write this process rather like a chemical reaction

$$\pi^- d \;\to\; n\, n$$

From this, we can determine the intrinsic parity of the pion. First, we need some facts. The pion has spin $s_\pi = 0$ and the deuteron has spin $s_d = 1$; the constituent proton and neutron have no orbital angular momentum so the total angular momentum of the deuteron is also $J = 1$. Finally, the pion scatters off the deuteron in the s-wave, meaning that the combined $\pi^- d$ system that we start with has vanishing orbital angular momentum. From all of this, we know that the total angular momentum of the initial state is $J = 1$.

Since angular momentum is conserved, the final $n\,n$ state must also have $J = 1$. Each individual neutron has spin $s_n = \frac{1}{2}$. But there are two possibilities to get $J = 1$:

- The spins could be anti-aligned, so that $S = 0$. Now the orbital angular momentum must be $L = 1$.

- The spins could be aligned, so that the total spin is $S = 1$. In this case the orbital angular momentum of the neutrons could be $L = 0$ or $L = 1$ or $L = 2$. Recall that the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ ranges from $|L - S|$ to $L + S$ and so for each of $L = 0, 1$ and 2 it contains the possibility of a $J = 1$ state.

How do we distinguish between these? It turns out that only one of these possibilities is consistent with the fermionic nature of the neutrons. Because the end state contains two identical fermions, the overall wavefunction must be anti-symmetric under exchange. Let's first consider the case where the neutron spins are anti-aligned, so that their total spin is $S = 0$. The spin wavefunction is

$$|S = 0\rangle = \frac{|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle}{\sqrt{2}}$$

which is anti-symmetric. This means that the spatial wavefunction must be symmetric. But this requires that the total angular momentum is even: $L = 0, 2, \ldots$. We see that this is inconsistent with the conservation of angular momentum. We can therefore rule out the spin $S = 0$ scenario.

(An aside: the statement that wavefunctions are symmetric under interchange of particles only if L is even follows from the transformation of the spherical harmonics under parity (1.9). Now the polar coordinates (r, θ, ϕ) parameterise the *relative* separation between particles. Interchange of particles is then implemented by $(r, \theta, \phi) \to (r, \pi - \theta, \phi + \pi)$.)

Let's now move onto the second option where the total spin of neutrons is $S = 1$. Here the spin wavefunctions are symmetric, with the three choices depending on the quantum number $m_s = -1, 0, +1$,

$$|S = 1, 1\rangle = |\uparrow\rangle|\uparrow\rangle \quad , \quad |S = 1, 0\rangle = \frac{|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle}{\sqrt{2}} \quad , \quad |S = 1, -1\rangle = |\downarrow\rangle|\downarrow\rangle$$

Once again, the total wavefunction must be anti-symmetric, which means that the spatial part must be anti-symmetric. This, in turn, requires that the orbital angular momentum of the two neutrons is odd: $L = 1, 3, \ldots$. Looking at the options consistent with angular momentum conservation, we see that only the $L = 1$ state is allowed.

Having figured out the angular momentum, we're now in a position to discuss parity. The parity of each neutron is $\eta_n = +1$. The parity of the proton is also $\eta_p = +1$ and since these two particles have no angular momentum in their deuteron bound state, we have $\eta_d = \eta_n \eta_p = +1$. Conservation of parity then tells us

$$\eta_\pi \eta_d = (\eta_n)^2 (-1)^L \quad \Rightarrow \quad \eta_\pi = -1$$

Parity and the Fundamental Forces

Above, I said that parity is conserved if the underlying Hamiltonian is invariant under parity. So one can ask: are the fundamental laws of physics, at least as we currently know them, invariant under parity? The answer is: some of them are. But not all.

In our current understanding of the laws of physics, there are five different ways in which particles can interact: through gravity, electromagnetism, the weak nuclear force, the strong nuclear force and, finally, through the Higgs field. The first four of these are usually referred to as "fundamental forces", while the Higgs field is kept separate. For what it's worth, the Higgs has more in common with three of the forces than gravity does and one could make an argument that it too should be considered a "force".

Of these five interactions, four appear to be invariant under parity. The misfit is the weak interaction. This is not invariant under parity, which means that any process which occur through the weak interaction — such as beta decay — need not conserve parity. Violation of parity in experiments was first observed by Chien-Shiung Wu in 1956.

To the best of our knowledge, the Hamiltonians describing the other four interactions are invariant under parity. In many processes – including the pion decay described above – the strong force is at play and the weak force plays no role. In these cases, parity is conserved.

1.2 Time Reversal Invariance

Time reversal holds a rather special position in quantum mechanics. As we will see, it is not like other symmetries.

The idea of time reversal is simple: take a movie of the system in motion and play it backwards. If the system is invariant under the symmetry of time reversal, then the dynamics you see on the screen as the movie runs backwards should also describe a possible evolution of the system. Mathematically, this means that we should replace $t \mapsto -t$ in our equations and find another solution.

Classical Mechanics

Let's first look at what this means in the context of classical mechanics. As our first example, consider the Newtonian equation of motion for a particle of mass m moving in a potential V,

$$m\ddot{\mathbf{x}} = -\nabla V(\mathbf{x})$$

Such a system is invariant under time reversal: if $\mathbf{x}(t)$ is a solution, then so too is $\mathbf{x}(-t)$.

As a second example, consider the same system but with the addition of a friction term. The equation of motion is now

$$m\ddot{\mathbf{x}} = -\nabla V(\mathbf{x}) - \gamma\dot{\mathbf{x}}$$

This system is no longer time invariant. Physically, this should be clear: if you watch a movie of some guy sliding along in his socks until he comes to rest, it's pretty obvious if it's running forward in time or backwards in time. Mathematically, if $\mathbf{x}(t)$ is a solution, then $\mathbf{x}(-t)$ fails to be a solution because the equation of motion includes a term that is first order in the time derivative.

At a deeper level, the first example above arises from a Hamiltonian while the second example, involving friction, does not. One might wonder if all Hamiltonian systems are time reversal invariant. This is not the case. As our final example, consider a particle of charge q moving in a magnetic field. The equation of motion is

$$m\ddot{\mathbf{x}} = q\dot{\mathbf{x}} \times \mathbf{B} \tag{1.11}$$

Once again, the equation of motion includes a term that is first order in time derivatives, which means that the time reversed motion is not a solution. This time it occurs because particles always move with a fixed handedness in the presence of a magnetic field: they either move clockwise or anti-clockwise in the plane perpendicular to $\mathbf{B}$.

Although the system described by (1.11) is not invariant under time reversal, if you're shown a movie of the solution running backwards in time, then it won't necessarily be obvious that this is unphysical. This is because the trajectory $\mathbf{x}(-t)$ does solve (1.11) if we also replace the magnetic field $\mathbf{B}$ with $-\mathbf{B}$. For this reason, we sometimes say that the background magnetic field flips sign under time reversal. (Alternatively, we could choose to keep $\mathbf{B}$ unchanged, but flip the sign of the charge: $q \mapsto -q$. The standard convention, however, is to keep charges unchanged under time reversal.)

We can gather together how various quantities transform under time reversal, which we'll denote as T. Obviously $T : t \mapsto -t$. Meanwhile, the standard dynamical variables, which include position $\mathbf{x}$ and momentum $\mathbf{p} = m\dot{\mathbf{x}}$, transform as

$$T : \mathbf{x}(t) \mapsto \mathbf{x}(-t) \quad , \quad T : \mathbf{p}(t) \mapsto -\mathbf{p}(-t) \tag{1.12}$$

Finally, as we've seen, it can also useful to think about time reversal as acting on background fields. The electric field $\mathbf{E}$ and magnetic field $\mathbf{B}$ transform as

$$T : \mathbf{E} \mapsto \mathbf{E} \quad , \quad T : \mathbf{B} \mapsto -\mathbf{B}$$

These simple considerations will be useful as we turn to quantum mechanics.

Quantum Mechanics

We'll now try to implement these same ideas in quantum mechanics. As we will see, there is something of a subtlety. This is first apparent if we look at the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \tag{1.13}$$

We'll assume that the Hamiltonian H is invariant under time reversal. (For example, $H = \mathbf{p}^2/2m + V(\mathbf{x})$.) One might naively think that the wavefunction should evolve in a manner compatible with time reversal. However, the Schrödinger equation is first order in time derivatives and this tells us something which seems to go against this intuition: if $\psi(t)$ is a solution then $\psi(-t)$ is not, in general, another solution.

To emphasise this, note that the Schrödinger equation is not very different from the heat equation,

$$\frac{\partial\psi}{\partial t} = \kappa\nabla^2\psi$$

This equation clearly isn't time reversal invariant, a fact which underlies the entire subject of thermodynamics. The Schrödinger equation (1.13) only differs by a factor of i. How does that save us? Well, it ensures that if $\psi(t)$ is a solution, then $\psi^\star(-t)$ is also a solution. This, then, is the action of time reversal on the wavefunction,

$$T : \psi(t) \mapsto \psi^\star(-t) \tag{1.14}$$

The need to include the complex conjugation is what distinguishes time reversal from other symmetries that we have met.

How do we fit this into our general scheme to describe the action of symmetries on operators and states? We're looking for an operator Θ such that the time reversal maps any state $|\psi\rangle$ to

$$T : |\psi\rangle \mapsto \Theta|\psi\rangle$$

Let's think about what properties we want from the action of Θ. Classically, the action of time reversal on the state of a system leaves the positions unchanged, but flips the sign of all the momenta, as we saw in (1.12). Roughly speaking, we want Θ to do the same thing to the quantum state. How can we achieve this?

Let's first recall how we run a state forwards in time. The solution to (1.13) tells us that a state $|\psi(0)\rangle$ evolves into a state $|\psi(t)\rangle$ by the usual unitary evolution

$$|\psi(t)\rangle = e^{-iHt/\hbar}\,|\psi(0)\rangle$$

Suppose now that we instead take the time reversed state $\Theta|\psi(0)\rangle$ and evolve this forward in time. If the Hamiltonian itself is time reversal invariant, the resulting state should be the time reversal of taking $|\psi(0)\rangle$ and evolving it *backwards* in time. (Or, said another way, it should be the time reversal of $|\psi(t)\rangle$, which is the same thing as $\Theta|\psi(-t)\rangle$.) While that's a mouthful in words, it's simple to write in equations: we want Θ to satisfy

$$\Theta\, e^{+iHt/\hbar}\,|\psi(0)\rangle = e^{-iHt/\hbar}\,\Theta\,|\psi(0)\rangle$$

Expanding this out for infinitesimal time t, we get the requirement

$$\Theta i H = -iH\Theta \tag{1.15}$$

Our job is to find a Θ obeying this property.

At this point there's a right way and a wrong way to proceed. I'll first describe the wrong way because it's the most tempting path to take. It's natural to manipulate (1.15) by cancelling the factor of i on both sides to leave us with

$$\Theta H + H\Theta = 0 \quad ? \tag{1.16}$$

Although natural, this is wrong! It's simple to see why. Suppose that we have an eigenstate $|\psi\rangle$ obeying $H|\psi\rangle = E|\psi\rangle$. Then (1.16) tells us that $H\Theta|\psi\rangle = -\Theta H|\psi\rangle = -E|\psi\rangle$. So every state of energy E must be accompanied by a time-reversed state of energy $-E$. But that's clearly nonsense. We know it's not true of the harmonic oscillator.

So what did we do wrong? Well, the incorrect step was seemingly the most innocuous one: we are not allowed to cancel the factors of i on either side of (1.15). To see why, we need to step back and look at a little linear algebra.

1.2.1 Time Reversal is an Anti-Unitary Operator

Usually in quantum mechanics we deal with linear operators acting on the Hilbert space. The linearity means that the action of an operator A on superpositions of states is

$$A(\alpha|\psi_1\rangle + \beta|\psi_2\rangle) = \alpha A|\psi_1\rangle + \beta A|\psi_2\rangle$$

with $\alpha, \beta \in \mathbf{C}$. In contrast, an *anti-linear* operator B obeys the modified condition

$$B(\alpha|\psi_1\rangle + \beta|\psi_2\rangle) = \alpha^\star B|\psi_1\rangle + \beta^\star B|\psi_2\rangle \tag{1.17}$$

This complex conjugation is reminiscent of the transformation of the wavefunction (1.14) under time reversal. Indeed, we will soon see how they are related.

The strange action (1.17) means that an anti-linear operator B doesn't even commute with a constant $\alpha \in \mathbf{C}$ (which, here, we view as a particular simple operator which multiplies each state by α). Instead, when B is anti-linear we have

$$B\alpha = \alpha^\star B$$

But this is exactly what we need to resolve the problem that we found above. If we take Θ to be an anti-linear operator then the factor of i on the left-hand-side of (1.15) is complex conjugated when we pull it through Θ. This extra minus sign means that instead of (1.16), we find

$$[\Theta, H] = 0 \tag{1.18}$$

This looks more familiar. Indeed, we saw earlier that this usually implies we have a conserved quantity in the game. However, that will turn out not to be the case here: conserved quantities only arise when linear operators commute with H. Nonetheless, we will see that there are also some interesting consequences of (1.18) for time-reversal.

We see above that we dodge a bullet if time reversal is enacted by an anti-linear operator Θ. There is another, more direct, way to see that this has to be the case. This arises by considering its action on the operators $\mathbf{x}$, and $\mathbf{p}$. In analogy with the classical action (1.12), we require

$$\Theta \mathbf{x} \Theta^{-1} = \mathbf{x} \quad , \quad \Theta \mathbf{p} \Theta^{-1} = -\mathbf{p} \tag{1.19}$$

However, quantum mechanics comes with a further requirement: the commutation relations between these operators should be preserved under time reversal. In particular, we must have

$$[x_i, p_j] = i\hbar\delta_{ij} \quad \Rightarrow \quad \Theta[x_i, p_j]\Theta^{-1} = \Theta(i\hbar\delta_{ij})\Theta^{-1}$$

We see that the transformations (1.19) are not consistent with the commutation relations if Θ is a linear operator. But the fact that it is an anti-linear operator saves us: the factor of i sandwiched between operators on the right-hand side is conjugated and the equation becomes $\Theta[x_i, p_j]\Theta^{-1} = -i\hbar\delta_{ij}$ which is happily consistent with (1.19).

Linear Algebra with Anti-Linear Operators

Time reversal is described by an anti-linear operator Θ. This means that we're going to have to spend a little time understanding the properties of these unusual operators.

We know that Θ acts on the Hilbert space $\mathcal{H}$ as (1.17). But how does it act on the dual Hilbert space of bras? Recall that, by definition, each element $\langle\phi|$ of the dual Hilbert space should be thought of as a linear map $\langle\phi| : \mathcal{H} \mapsto \mathbf{C}$. For a linear operator A, this is sufficient to tell us how to think of A acting on the dual Hilbert space. The dual state $\langle\phi|A$ is defined by

$$(\langle\phi|A)|\psi\rangle = \langle\phi|(A|\psi\rangle) \tag{1.20}$$

This definition has the consequence that we can just drop the brackets and talk about $\langle\phi|A|\psi\rangle$ since it doesn't matter whether we interpret this as A acting on to the right or left.

In contrast, things are more fiddly if we're dealing with an anti-linear operator B. We would like to define $\langle\phi|B$. The problem is that we want $\langle\phi|B$ to lie in the dual Hilbert space which, by definition, means that it must be a linear operator even if B is an anti-linear operator. But if we just repeat the definition (1.20) then it's simple to check that $\langle\phi|B$ inherits anti-linear behaviour from B and so does not lie in the dual Hilbert space. To remedy this, we modify our definition of $\langle\phi|B$ for anti-linear operators to

$$(\langle\phi|B)|\psi\rangle = [\langle\phi|(B|\psi\rangle)]^\star \tag{1.21}$$

This means, in particular, that for an anti-linear operator we should never write $\langle\phi|B|\psi\rangle$ because we get different answers depending on whether B acts on the ket to the right or on the bra to the left. This is, admittedly, fiddly. Ultimately the Dirac bra-ket notation is not so well suited to anti-linear operators.

Our next task is to define the adjoint operators. Recall that for a linear operator A, the adjoint $A^\dagger$ is defined by the requirement

$$\langle\phi|A^\dagger|\psi\rangle = \langle\psi|A|\phi\rangle^\star$$

What do we do for an anti-linear operator B? The correct definition is now

$$\langle\phi|(B^\dagger|\psi\rangle) = [(\langle\psi|B)|\phi\rangle]^\star = \langle\psi|(B|\phi\rangle) \tag{1.22}$$

This ensures that $B^\dagger$ is also anti-linear. Finally, we say that an anti-linear operator B is *anti-unitary* if it also obeys

$$B^\dagger B = BB^\dagger = 1$$

Anti-Unitary Operators Conserve Probability

We have already seen that time reversal should be anti-linear. It must also be anti-unitary. This will ensure that probabilities are conserved under time reversal. To see this, consider the states $|\phi'\rangle = \Theta|\phi\rangle$ and $|\psi'\rangle = \Theta|\psi\rangle$. Then, using our definitions above, we have

$$\langle\phi'|\psi'\rangle = (\langle\phi|\Theta^\dagger)(\Theta|\psi\rangle) = [\langle\phi|(\Theta^\dagger\Theta|\psi\rangle)]^\star = \langle\phi|\psi\rangle^\star$$

We see that the phase of the amplitude changes under time reversal, but the probability, which is $|\langle\phi|\psi\rangle|^2$, remains unchanged.

1.2.2 An Example: Spinless Particles

So far, we've only described the properties required of the time reversal operator Θ. Now let's look at some specific examples. We start with a single particle, governed by the Hamiltonian

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x})$$

To describe any operator, it's sufficient to define how it acts on a basis of states. The time reversal operator is no different and, for the present example, it's sensible to choose the basis of eigenstates $|\mathbf{x}\rangle$. Because Θ is anti-linear, it's important that we pick some fixed choice of phase for each $|\mathbf{x}\rangle$. (The exact choice doesn't matter; just as long as we make one.) Then we define the time reversal operator to be

$$\Theta|\mathbf{x}\rangle = |\mathbf{x}\rangle \tag{1.23}$$

If Θ were a linear operator, this definition would mean that it must be equal to the identity. But instead Θ is anti-linear and it's action on states which differ by a phase from our choice of basis $|\mathbf{x}\rangle$ is non-trivial

$$\Theta\alpha|\mathbf{x}\rangle = \alpha^\star|\mathbf{x}\rangle$$

In this case, the adjoint operator is simple $\Theta^\dagger = \Theta$. Indeed, it's simple to see that $\Theta^2 = 1$, as is required by unitarity.

Let's see what we can derive from this. First, we can expand a general state $|\psi\rangle$ as

$$|\psi\rangle = \int d^3x\ |\mathbf{x}\rangle\langle\mathbf{x}|\psi\rangle = \int d^3x\ \psi(\mathbf{x})|\mathbf{x}\rangle$$

where $\psi(\mathbf{x}) = \langle \mathbf{x}|\psi\rangle$ is the wavefunction in position variables. Time reversal acts as

$$\Theta|\psi\rangle = \int d^3x\, \Theta\psi(\mathbf{x})|\mathbf{x}\rangle = \int d^3x\ \psi^\star(\mathbf{x})\Theta|\mathbf{x}\rangle = \int d^3x\ \psi^\star(\mathbf{x})|\mathbf{x}\rangle$$

We learn that time reversal acts on the wavefunction as complex conjugation: $T : \psi(\mathbf{x}) \mapsto \psi^\star(\mathbf{x})$. But this is exactly what we first saw in (1.14) from looking at the Schrödinger equation. We can also specialise to momentum eigenstates $|\mathbf{p}\rangle$. These can be written as

$$|\mathbf{p}\rangle = \int d^3x\ e^{i\mathbf{p}\cdot\mathbf{x}}|\mathbf{x}\rangle$$

Acting with time reversal, this becomes

$$\Theta|\mathbf{p}\rangle = \int d^3x\ \Theta e^{i\mathbf{p}\cdot\mathbf{x}}|\mathbf{x}\rangle\langle\mathbf{x}| = \int d^3x\ e^{-i\mathbf{p}\cdot\mathbf{x}}|\mathbf{x}\rangle\langle\mathbf{x}| = |-\mathbf{p}\rangle$$

which confirms our intuition that acting with time reversal on a state should leave positions invariant, but flip the momenta.

Importantly, invariance under time reversal doesn't lead to any degeneracy of the spectrum in this system. Instead, it's not hard to show that one can always pick the phase of an energy eigenstate such that it is also an eigenstate of Θ. Ultimately, this is because of the relation $\Theta^2 = 1$. (This statement will become clearer in the next section where we'll see a system that does exhibit a degeneracy.)

We can tell this same story in terms of operators. These can be expanded in terms of eigenstates, so we have

$$\hat{\mathbf{x}} = \int d^3x\ \mathbf{x}|\mathbf{x}\rangle\langle\mathbf{x}| \quad \Rightarrow \quad \Theta\hat{\mathbf{x}}\Theta = \int d^3x\ \mathbf{x}\Theta|\mathbf{x}\rangle\langle\mathbf{x}|\Theta = \hat{\mathbf{x}}$$

and

$$\hat{\mathbf{p}} = \int d^3p\ \mathbf{p}|\mathbf{p}\rangle\langle\mathbf{p}| \quad \Rightarrow \quad \Theta\hat{\mathbf{p}}\Theta = \int d^3p\ \mathbf{p}\Theta|\mathbf{p}\rangle\langle\mathbf{p}|\Theta = -\hat{\mathbf{p}}$$

where, in each case, we've reverted to putting a hat on the operator to avoid confusion. We see that this reproduces our expectation (1.19).

Before we proceed, it will be useful to discuss one last property that arises when $V(\mathbf{x}) = V(|\mathbf{x}|)$ is a central potential. In this case, the orbital angular momentum $\mathbf{L} = \mathbf{x} \times \mathbf{p}$ is also conserved. From (1.19), we know that $\mathbf{L}$ should be odd under time reversal, meaning

$$\Theta\mathbf{L}\Theta^{-1} = -\mathbf{L} \tag{1.24}$$

We can also see how it acts on states. For a central potential, the energy eigenstates can be written in polar coordinates as

$$\psi_{nlm}(\mathbf{x}) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

The radial wavefunction $R_{nl}(r)$ can always be taken to be real. Meanwhile, the spherical harmonics take the form $Y_{lm}(\theta,\phi) = e^{im\phi}P_l^m(\cos\theta)$ with P_l^m an associated Legendre polynomial. From their definition, we find that these obey

$$\psi^\star_{nlm}(\mathbf{x}) = (-1)^m\psi_{nl,-m}(\mathbf{x}) \tag{1.25}$$

Clearly this is consistent with $\Theta^2 = 1$.

1.2.3 Another Example: Spin

Here we describe a second example that is both more subtle and more interesting: it is a particle carrying spin $\frac{1}{2}$. To highlight the physics, we can forget about the position degrees of freedom and focus solely on the spin.

Spin provides another contribution to angular momentum. This means that the spin operator $\mathbf{S}$ should be odd under time reversal, just like the orbital angular momentum (1.24)

$$\Theta\mathbf{S}\Theta^{-1} = -\mathbf{S} \tag{1.26}$$

For a spin- $\frac{1}{2}$ particle, we have $\mathbf{S} = \frac{\hbar}{2}\boldsymbol{\sigma}$ with $\boldsymbol{\sigma}$ the vector of Pauli matrices. The Hilbert space is just two-dimensional and we take the usual basis of eigenvectors of S_z, chosen with a specific phase

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

so that $S_z|\pm\rangle = \pm\frac{\hbar}{2}|\pm\rangle$. Our goal is to understand how the operator Θ acts on these states. We will simply state the correct form and then check that it does indeed reproduce (1.26). The action of time reversal is

$$\Theta|+\rangle = i|-\rangle \quad , \quad \Theta|-\rangle = -i|+\rangle \tag{1.27}$$

Let's look at some properties of this. First, consider the action of Θ^2,

$$\begin{aligned}\Theta^2|+\rangle &= \Theta(i|-\rangle) = -i\Theta|-\rangle = -|+\rangle \\ \Theta^2|-\rangle &= \Theta(-i|+\rangle) = i\Theta|+\rangle = -|-\rangle\end{aligned}$$

We see that

$$\Theta^2 = -1 \tag{1.28}$$

This is in contrast to the action of time reversal for a particle without spin (1.23). We will see shortly the consequences of $\Theta^2 = -1$.

Since there's a lot of i's floating around, let's go slowly and use this as an opportunity to flesh out other properties of Θ. From (1.21), the action of Θ on the bras is

$$\langle +|\Theta = i\langle -| \quad , \quad \langle -|\Theta = -i\langle +|$$

Meanwhile, from (1.22), the adjoint operator $\Theta^\dagger$ is defined as

$$\Theta^\dagger|+\rangle = -i|-\rangle \quad , \quad \Theta^\dagger|-\rangle = i|+\rangle$$

We see that $\Theta^\dagger = -\Theta$ which, given (1.28), ensures that Θ is anti-unitary.

Now we can look at the action of Θ on the various spin operators. Expanding each in our chosen basis, and using the results above, we find

$$\begin{aligned} S_x &= |+\rangle\langle -| + |-\rangle\langle +| \quad \Rightarrow \quad \Theta S_x \Theta^\dagger = -S_x \\ S_z &= |+\rangle\langle +| - |-\rangle\langle -| \quad \Rightarrow \quad \Theta S_z \Theta^\dagger = -S_z \\ S_y &= -i|+\rangle\langle -| + i|-\rangle\langle +| \quad \Rightarrow \quad \Theta S_y \Theta^\dagger = -S_y \end{aligned}$$

as required.

Time Reversal for General Spin

We can generalise this discussion to a general particle carrying general spin s. (The formulae below also work for any angular momentum). The Hilbert space now has dimension $2s+1$, and is spanned by the eigenstates of S_z

$$S_z|m\rangle = m\hbar|m\rangle \qquad m = -s, \ldots, s$$

We again require that the spin operators transform as (1.26) under time reversal. We can rewrite this requirement as $\Theta\mathbf{S} = -\mathbf{S}\Theta$. When applied to the eigenstates of S_z, this tells us

$$S_z\Theta|m\rangle = -\Theta S_z|m\rangle = -m\hbar\Theta|m\rangle$$

which is the statement that $\Theta|m\rangle$ is an eigenstate of S_z with eigenvalue $-m\hbar$. But the eigenstates of S_z are non-degenerate, so we must have

$$\Theta|m\rangle = \alpha_m|-m\rangle$$

for some choice of phase α_m which, as the notation shows, can depend on m.

There's a clever trick for figuring out how α_m depends on m. Consider the raising and lowering spin operators $S_\pm = S_x \pm iS_y$. The action of time reversal is

$$\Theta S_\pm \Theta^\dagger = \Theta(S_x \pm iS_y)\Theta^\dagger = -S_x \pm iS_y = -S_\mp \tag{1.29}$$

Now consider the action of S_+ on $\Theta|m\rangle$,

$$S_+\Theta|m\rangle = \alpha_m S_+|-m\rangle = \alpha_m \hbar\sqrt{(s+m)(s-m+1)}|-m+1\rangle$$

Alternatively, we can use (1.29) to write

$$\begin{aligned} S_+\Theta|m\rangle = -\Theta S_-|m\rangle &= -\hbar\sqrt{(s+m)(s-m+1)}\Theta|m-1\rangle \\ &= -\alpha_{m-1}\hbar\sqrt{(s+m)(s-m+1)}|-m+1\rangle \end{aligned}$$

We learn that

$$\alpha_m = -\alpha_{m-1}$$

The simplest choice is $\alpha_m = (-1)^m$. Because m can be either integer or half-integer, we will write this as

$$\Theta|m\rangle = i^{2m}|-m\rangle$$

This agrees with our earlier results, (1.25) for orbital angular momentum and (1.27) for spin-$\frac{1}{2}$. For now, the most important lesson to take from this is

$$\begin{aligned} \Theta^2 = 1 \qquad & \text{integer spin} \\ \Theta^2 = -1 \qquad & \text{half-integer spin} \end{aligned}$$

This result is quite deep. Ultimately it associated to the fact that spin-half particles transform in the double cover of the rotation group, so that states pick up a minus sign when rotated by 2π. As we now show, it has consequence.

1.2.4 Kramers Degeneracy

It is not surprising that acting with time reversal twice brings us back to the same state. It is, however, surprising that sometimes we can return with a minus sign. As we have seen, this doesn't happen for spinless particles, nor for particles with integer spin: in both of these situations we have $\Theta^2 = 1$. However, when dealing with particles with half-integer spin, we instead have $\Theta^2 = -1$.

Time reversal with $\Theta^2 = 1$ does not automatically lead to any further degeneracy of the spectrum. (We will, however, see a special case when we discuss the Stark effect in Section 4.1 where a degeneracy does arise.) In contrast, when $\Theta^2 = -1$, there is always a degeneracy.

To see this degeneracy, we argue by contradiction. Suppose that the spectrum is non-degenerate, so that there is a state such that

$$\Theta|\psi\rangle = \alpha|\psi\rangle$$

for some phase α. Then acting twice, we have

$$\Theta^2|\psi\rangle = \alpha^\star\Theta|\psi\rangle = |\alpha|^2|\psi\rangle = |\psi\rangle$$

This means that a non-degenerate spectrum can only arise when $\Theta^2 = +1$.

In contrast, whenever we have a time-reversal system with $\Theta^2 = -1$, all energy eigenstates must come in degenerate pairs. This is known as *Kramers degeneracy*.

For the simple spin $\frac{1}{2}$ system that we described in Section 1.2.3, the degeneracy is trivial: it is simply the statement that $|+\rangle$ and $|-\rangle$ have the same energy whenever the Hamiltonian is invariant under time reversal. If we want to split the energy levels, we need to add a term to the Hamiltonian like $H = \mathbf{B}\cdot\mathbf{S}$ which breaks time reversal. (Indeed, this ties in nicely with our classical discussion where we saw that the magnetic field breaks time reversal, changing as $\mathbf{B} \mapsto -\mathbf{B}$.)

In more complicated systems, Kramer's degeneracy can be a very powerful statement. For example, we know that electrons carry spin $\frac{1}{2}$. The degeneracy ensures that in *any* time reversal invariant system which involves an odd number of electrons, all energy levels are doubly degenerate. This simple statement plays an important role in the subject of *topological insulators* in condensed matter physics.