

MENG SUN

QUANTUM MECHANICS

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1

The wave function

1.1 The schrödinger equation

Particle's wave function $\Psi(x, t)$ follows the Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi \quad (1.1)$$

with

$$\hbar = \frac{h}{2\pi} = 1.054572 \times 10^{-34} Js \quad (1.2)$$

1.2 The statistical interpretation

Born's statistical interpretation of the wave function, which say that $|\Psi(x, t)|^2$ gives the probability of finding the particle at point x at time t . This means

$$\int_a^b |\Psi(x, t)|^2 dx = \text{Probability of finding particle between a and b at time t.} \quad (1.3)$$

The statistical interpretation introduces a kind of indeterminacy into quantum mechanics. All quantum mechanics has to offer is statistical information about the possible result. Suppose I do measure the position of particle, and I find it to be at the point C. Question: Where was the particle just before I made the measurement?

- The **realist** position: The particle was at C. This certainly seemms like a sensible response, and it is the one Einstein advocated. However, this means quantum mechanics is an imcomplete theory, since particle really was at C, and yet quantum mechanics was unable to tell us so. This indeterminacy is not a fact of nature, bt a reflection of our ignorance. Evidently Ψ is not the whole story, some additional information is needed to provide a complete description of the particle.

- The **orthodox** position: The particle wasn't really anywhere. It was the act of measurement that forced the particle to "take a stand". Observations not only disturb what is to be measured, they produce it. This view is associated with Bohr and followers.

Experiments have decisively confirmed the orthodox interpretation. A particle simply does not have a precise position prior to measurement, any more than the ripples on a pond do; it is the measurement process that insists on one particular number, and thereby in a sense creates the specific result, limited only by the statistical weighting imposed by the wave function.

For a second measurement, immediately after the first, the result must be found at C. Since the first measurement radically alters the wave function, so that it is now sharply peaked about C.

1.3 Normalization

Since $|\Psi|^2$ is the probability density, then we have

$$\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 1 \quad (1.4)$$

Physically realizable states correspond to the **square-integrable** solutions to Schrödinger equation.¹

¹ Evidently $\Psi(x, t)$ must go to zero faster than $1/\sqrt{|x|}$ as $|x| \rightarrow \infty$.

The Schrödinger equation preserves the normalization of the wave function for different time. One can prove this,

$$\frac{d}{dt} \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = \int_{-\infty}^{\infty} \frac{\partial}{\partial t} |\Psi(x, t)|^2 dx \quad (1.5)$$

Because of the Schrödinger equation and its complex conjugate say that

$$\frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m} \frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar} V\Psi \quad (1.6)$$

$$\frac{\partial \Psi^*}{\partial t} = -\frac{i\hbar}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar} V\Psi^*. \quad (1.7)$$

We have

$$\frac{\partial}{\partial t} |\Psi|^2 = \frac{\partial}{\partial t} (\Psi^* \Psi) = \frac{\partial}{\partial x} \left[\frac{i\hbar}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \right]. \quad (1.8)$$

Then the integral in Eq. (1.5) can be evaluated explicitly

$$\frac{d}{dt} \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \Big|_{-\infty}^{\infty} \quad (1.9)$$

According to requirement from normalization condition, the wave function must obey $\lim_{|x| \rightarrow \infty} \Psi = 0$, i.e., the particle can not go to the infinity. We know Eq. (1.4) is a constant in time.

Problem Consider the wave function

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

where A , λ , and ω are positive real constant. (1) Normalize the wave function. (2) Determine the expectation values of x and x^2 . (3) Find the standard deviation x . Plot the graph.

1.4 Momentum

For the particle in state Ψ , the expectation value of x is

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\Psi|^2 dx. \quad (1.10)$$

It does not mean that if you measure the position of one particle over and over again. Rather, $\langle x \rangle$ is the average of the ensemble of particles all in the same state Ψ . In short, *the expectation value is the average of repeated measurements on an ensemble of identically prepared system, not the average of repeated measurements on on and the same system.*

Now, as time goes on, $\langle x \rangle$ will change because of the time dependence of Ψ , we are interested in knowing how fast it moves. Referring to Eq. (1.8) and (1.10), we have

$$\frac{d\langle x \rangle}{dt} = \int x \frac{\partial}{\partial t} |\Psi|^2 dx = \frac{i\hbar}{2m} \int x \frac{\partial}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx \quad (1.11)$$

Integration by parts, we have

$$\frac{d\langle x \rangle}{dt} = -\frac{i\hbar}{2m} \int \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx \quad (1.12)$$

Do the integration by parts again

$$\frac{d\langle x \rangle}{dt} = -\frac{i\hbar}{m} \int \Psi^* \frac{\partial \Psi}{\partial x} dx \quad (1.13)$$

Note that we are talking about the “velocity” of the expectation value of x , which is not the same thing as the velocity of particle. Nothing we have seen so far would enable us to calculate the velocity of a particle. It is not even clear what velocity means in quantum mechanics: If particle doesn’t have a determinate position, neither does it have a well-defined velocity. All we could reasonably ask for is the **probability** of getting a particular value as we will discuss in later sections. For now, we postulate that the *expectation value of the velocity is equal to the time derivative of expectation value of position*:

$$\langle v \rangle = \frac{d\langle x \rangle}{dt} \quad (1.14)$$

Similarly, for the **momentum**, we have

$$\langle p \rangle = m \frac{d\langle x \rangle}{dt} = -i\hbar \int \left(\Psi^* \frac{\partial \Psi}{\partial x} \right). \quad (1.15)$$

It is more suggestive to write $\langle x \rangle$ and $\langle p \rangle$ in the **operator** way

$$\langle x \rangle = \int \Psi^*(x) \Psi dx \quad (1.16)$$

$$\langle p \rangle = \int \Psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi dx. \quad (1.17)$$

For all the other classical dynamical variables, they can be expressed in terms of position and momentum, like the angular momentum we have $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, for example. To calculate the expectation value of any such quantity, $Q(x, p)$, we have

$$\langle Q(x, p) \rangle = \int \Psi^* Q \left(x, \frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi dx \quad (1.18)$$

Problem Prove that

$$\frac{d\langle p \rangle}{dt} = \left\langle -\frac{\partial V}{\partial x} \right\rangle$$

This equation and Eq. (1.14) and Eq. (1.15) are instances of **Ehrenfest's theorem**, which tells us that expectation values obey classical laws.

1.5 The uncertainty principle

The wavelength of wave function Ψ is related to the momentum of the particle by the **de Broglie formula**

$$p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda} \quad (1.19)$$

Thus a spread in wavelength corresponds to a spread in momentum, and the general observation now says that the more precisely determined a particle's position is the less precisely is its momentum,

$$\sigma_x \sigma_p \geq \frac{\hbar}{2} \quad (1.20)$$

which is the Heisenberg's **uncertainty principle**. You can construct a state such that repeated position measurement will be very close together, but the price to pay is the momentum measurements on this state will be widely scattered.

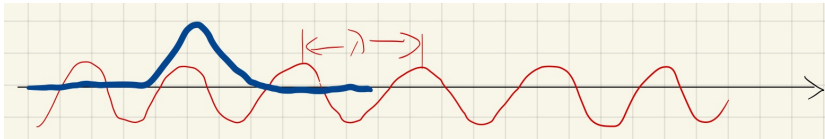


Figure 1.1: The example of wave with will and ill defined wavelength.

2

Time-independent Schrödinger equation

2.1 Stationary states

How do we get $\Psi(x, t)$ in first place. We first consider the potential is independent of t , then

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi. \quad (2.1)$$

In this case, the Schrödinger equation can be solved by the method of **separation of variables**. We look for solutions that are simple products

$$\Psi(x, t) = \psi(x) \phi(t) \quad (2.2)$$

Of course, we cannot hope to get more than a tiny subset of all solutions in this way. But the solution we got turn out to be of great interest. Moreover we will be able at the end to patch together the separable solutions in such a way as to construct the most general solution.

For separable solution we have

$$i\hbar \frac{1}{\phi} \frac{d\phi}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V. \quad (2.3)$$

Now, in Eq. (2.3), the left side is only t dependent and the right side is a function of x alone. The only way this can be true is if both sides are in fact a constant, we denote it E .

$$\frac{d\phi}{dt} = -\frac{iE}{\hbar} \phi \quad (2.4)$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi \quad (2.5)$$

Separation of variables turns the partial differential equation into two ordinary differential equations. For Eq. (2.4), the solution is easy to give

$$\phi(x, t) = e^{-iEt/\hbar}. \quad (2.6)$$

The Eq. (2.5) is called the **time-independent Schrödinger equation**.

There are several advantages to do the separable solution in Eq. (2.2).

1. They are **stationary states**. Although the wave function dependent on t as suggested in Eq. (2.6), the probability density does not. The same thing happens in calculating the expectation value of any dynamical variable. The Eq. (1.18) become

$$\langle Q(x, p) \rangle = \int \psi^* Q \left(x, \frac{\hbar}{i} \frac{d}{dx} \right) \psi dx. \quad (2.7)$$

Thus every expectation value is constant in time.

2. They are states of definite total energy. In classical mechanics, the total energy is called the **Hamiltonian**. The corresponding operator is

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x). \quad (2.8)$$

Then the time-independent Schrödinger equation can be written

$$\hat{H}\psi = E\psi \quad (2.9)$$

One can calculate the variance of H which is $\sigma_H^2 = 0$. This means a separable solution has the property that every measurement of the total energy is certain to return the value E .

3. The general solution is a **linear combination** of separable solution.

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar}. \quad (2.10)$$

Last comment, even the separable solutions themselves are stationary state, their linear combination Eq. (2.10) are usually not.

Problem Prove the following theorems

- For normalizable solutions, the separation constant E must be real.
- The time-independent wave function $\psi(x)$ can always be taken to be real.
- If $V(x)$ is an even function then $\psi(x)$ can always be taken to be either even or odd

Problem Show that E must exceed the minimum value of $V(x)$ for every normalizable solution to the time-independent Schrödinger equation.

2.2 The infinite square well

Suppose the potential is

$$V(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq a, \\ \infty & \text{otherwise.} \end{cases} \quad (2.11)$$

A particle in this potential is complete free, except at the two end point, where an infinite force prevents it from escaping as shown in Fig. 2.1.

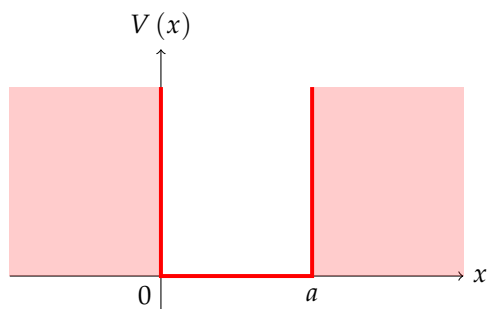


Figure 2.1: The infinite square well potential.

Outside the well, $\psi(x) = 0$, since you can not have a particle with infinite high energy. Inside the well, we have

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \text{ where } k = \frac{\sqrt{2mE}}{\hbar}. \quad (2.12)$$

This is the classical **simple harmonic oscillator** equation; the general solution is

$$\psi(x) = A \sin kx + B \cos kx \quad (2.13)$$

where A and B are arbitrary constants.

3

Formalism

4

Quantum mechanics in three dimensions

4.1 Schrödinger equation in spherical coordinates

The generalization to three dimensions is straightforward.

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \quad (4.1)$$

where the **Laplacian** is

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (4.2)$$

in cartesian coordinates. With the separation of the variables the general solution gives

$$\Psi(\mathbf{r}, t) = \sum c_n \psi_n(\mathbf{r}) e^{-iE_n t/\hbar}. \quad (4.3)$$

4.1.1 Separation of variables

Typically, the potential is a function only of the distance from the origin. In that case it is natural to adopt **spherical coordinates**, as shown in Fig. 4.1, the Laplacian takes the form for our time-independent Schrödinger equation

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right). \quad (4.4)$$

We begin by looking for solutions that are separable into products

$$\psi(r, \theta, \phi) = R(r) Y(\theta, \phi). \quad (4.5)$$

With this ansatz, we have

$$\left\{ \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] \right\} + \frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} = 0 \quad (4.6)$$

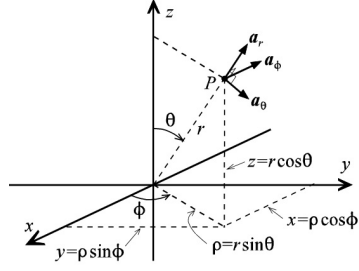


Figure 4.1: Spherical coordinates.

again each curly bracket should equal to a constant $l(l+1)$

$$\left\{ \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] \right\} = l(l+1) \quad (4.7)$$

$$\frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} = -l(l+1). \quad (4.8)$$

4.1.2 The angular equation

We first consider Eq. (4.8), which it equals

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} = -l(l+1) \sin^2 \theta Y. \quad (4.9)$$

Once again we separate the variables $Y(\theta, \phi) = \Theta(\theta) \Phi(\phi)$. Equation (4.9) can be further separate into two by setting a new constant m^2

$$\frac{1}{\Theta} \left[\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \right] + l(l+1) \sin^2 \theta = m^2 \quad (4.10)$$

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2 \quad (4.11)$$

This ϕ equation is easy, we have the general solution

$$\Phi(\phi) = e^{im\phi}. \quad (4.12)$$

Again we could absorb the constant into Θ function. Since when we rotate ϕ by 2π angle, it back to the same point, it is nature to require that $\Phi(\phi + 2\pi) = \Phi(\phi)$. In other words, we have the constrain such that $\exp(2\pi im) = 1$, which means m must be an integer

$$m = 0, \pm 1, \pm 2, \dots \quad (4.13)$$

For the θ equation in Eq. (4.10), the solution is

$$\Theta(\theta) = AP_l^m(\cos \theta) \quad (4.14)$$

where P_l^m is the **associated Legendre function**, defined by

$$P_l^m(x) \equiv (1-x^2)^{|m|/2} \left(\frac{d}{dx} \right)^{|m|} P_l(x), \quad (4.15)$$

and $P_l(x)$ is the l -th **Legendre polynomial**, defined by the **Rodrigues formulae**

$$P_l(x) \equiv \frac{1}{2^l l!} \left(\frac{d}{dx} \right)^l (x^2 - 1)^l. \quad (4.16)$$

Some result of $P_l^m(\cos \theta)$ is listed in Tab. 4.1. Noticee that l must be a

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

Table 4.1: Some associated Legendre functions

nonnegation integer because of senseness of the Rodrigues formula in Eq. (4.16). Moreover, for any $|m| > l$, Eq. (4.14) always says $P_l^m = 0$. Then for any given l , there are $(2l + 1)$ possible value of m ,¹

$$l = 0, 1, 2, \dots; \quad m = -l, -l + 1, \dots, -1, 0, 1, \dots, l - 1, l. \quad (4.17)$$

For normalization condition, we have

$$\int |\psi|^2 r^2 \sin \theta dr d\theta d\phi = \int |R|^2 r^2 dr \int |Y|^2 \sin \theta d\theta d\phi = 1. \quad (4.18)$$

It is convenient to normalize R and Y separately

$$\int_0^\infty |R|^2 r^2 dr = 1 \quad \text{and} \quad \int_0^{2\pi} \int_0^\pi |Y|^2 \sin \theta d\theta d\phi = 1. \quad (4.19)$$

The normalized angular wave functions are called **spherical harmonics**

$$Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}} e^{im\phi} P_l^m(\cos \theta), \quad (4.20)$$

where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$. As expected these spherical harmonics function are orthogonal to each other

$$\int_0^{2\pi} \int_0^\pi [Y_l^m(\theta, \phi)]^* [Y_{l'}^{m'}(\theta, \phi)] \sin \theta d\theta d\phi = \delta_{ll'} \delta_{mm'} \quad (4.21)$$

For historical reason, l is called the **azimuthal quantum number**, and m is the **magnetic quantum number**.

4.1.3 The radial equation

Notice that the angular part of the wavefunction, $Y(\theta, \phi)$, is the same for all spherically symmetric potentials; The actual shape of the potential affects only the radial part of the wave function, $R(r)$, which is

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] R = l(l+1) R. \quad (4.22)$$

One can simplifies this equation if we change the variables

$$u(r) \equiv rR(r), \quad (4.23)$$

¹ Notice Eq. (4.10) is a second-order differential equation: It should have two linearly independent solutions, for any old values of l and m . However the rest of the solution are not physical, because they blow up at $\theta = 0, \pi$.

and hence we have

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu. \quad (4.24)$$

This is called the **radial equation**; it is identical in form to the one-dimensional Schrödinger equation Eq. (2.5), except that the **effective potential**,

$$V_{eff} = V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}. \quad (4.25)$$

Meanwhile the normalization in Eq. (4.19) becomes to the form

$$\int_0^\infty |u|^2 dr = 1. \quad (4.26)$$

This is as far as we can go before the potential is provided.

4.2 The Hydrogen atom

The hydrogen atom consists of a heavy motionless proton of charge e together with a light electron that orbits around it. From the Coulomb's law, the potential energy is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \quad (4.27)$$

and the radial equation Eq. (4.24) reads

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu. \quad (4.28)$$

In principle, the Coulomb potential admits continuum states, (for $E > 0$), describing electron-proton scattering, as well as discrete bound states, representing the hydrogen atom. We will focus on the latter case.

4.2.1 The radial wave function

With the new notation²

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}, \quad (4.29)$$

² For bound states, E is negative, so κ is real.

then Eq. (4.28) reads

$$\frac{1}{\kappa^2} \frac{d^2 u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa} \frac{1}{(kr)} + \frac{l(l+1)}{(\kappa r)^2} \right] u. \quad (4.30)$$

This further suggests that we have

$$\rho \equiv \kappa r, \quad \text{and} \quad \rho_0 \equiv \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa}, \quad (4.31)$$

so that

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right] u. \quad (4.32)$$

Let us examine the asymptotic form of the solutions. As $\rho \rightarrow \infty$, the Eq. (4.32) can be approximated to

$$\frac{d^2u}{d\rho^2} = u. \quad (4.33)$$

The general solution is $u(\rho) = Ae^{-\rho} + Be^{\rho}$. In order to get a finite solution at $\rho \rightarrow \infty$, we have to require $B = 0$. So, for large ρ we have

$$u(\rho) \sim Ae^{-\rho}. \quad (4.34)$$

On the other hand, as $\rho \rightarrow 0$ the centrifugal term dominates³

$$\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u \quad (4.35)$$

The general solution is $u(\rho) = C\rho^{l+1} + D\rho^{-l}$. But we have $D = 0$ since ρ^{-l} blow up as $\rho \rightarrow 0$. Then the solution is

$$u(\rho) \sim C\rho^{l+1} \quad (4.36)$$

for small ρ .

The next step is to peel off the asymptotic behavior, introducing a new function $v(\rho)$

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho), \quad (4.37)$$

in the hope that $v(\rho)$ will turn out to be simpler than $u(\rho)$. By calculating $\frac{du}{d\rho}$ and $\frac{d^2u}{d\rho^2}$, the radial equation, Eq. (4.32), reads

$$\rho \frac{d^2v}{d\rho^2} + 2(l+1-\rho) \frac{dv}{d\rho} + [\rho_0 - 2(l+1)] v = 0 \quad (4.38)$$

Finally, we assume that $v(\rho)$ can be expressed as a power series in ρ

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j. \quad (4.39)$$

Then the problem is boiled down to determine the coefficients. Differentiating term by term, we have

$$\begin{aligned} \frac{dv}{d\rho} &= \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j \\ \frac{d^2v}{d\rho^2} &= \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j-1} \end{aligned}$$

³ This argument does not apply when $l = 0$, although the result we got, Eq. (4.36), is also valid for the case with $l = 0$. Here we provides some motivation for Eq.

Inserting in the Eq. (4.38), we have

$$\begin{aligned} & \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^j + 2(l+1) \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j \\ & - 2 \sum_{j=0}^{\infty} j c_j \rho^j + [\rho_0 - 2(l+1)] \sum_{j=0}^{\infty} c_j \rho^j = 0 \end{aligned}$$

Equating the coefficients of the powers yields

$$c_{j+1} = \left\{ \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right\} c_j. \quad (4.40)$$

Form c_0 which is fixed by normalization condition, we can get c_j .

However, the story is not finished yet!. For large j (this correspond to large ρ , where higher powers dominate), according to Eq. (4.40), we have

$$c_{j+1} \cong \frac{2}{j+1} c_j.$$

⁴ That is the reason we keep the term $j+1$.

Supposes for a moment that this solution was exact. Then we have⁴

$$c_j = \frac{2^j}{j!} c_0, \quad (4.41)$$

and hence $v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho}$, which result to $u(\rho) = c_0 \rho^{l+1} e^{\rho}$. This again blows up at large ρ . To avoid this positive exponential, the series must terminate. There must occur some maximal integer, j_{max} , such that

$$c_{j_{max}+1} = 0. \quad (4.42)$$

This tells us that in Eq. (4.40), we have

$$2(j_{max} + l + 1) - \rho_0 = 0.$$

By defining

$$n \equiv j_{max} + l + 1, \quad (4.43)$$

the so-called **principal quantum number**, we have $\rho_0 = 2n$. From Eq. (4.29) and (4.31), we know ρ_0 is related to the energy E . So the allowed energies are

$$E_n = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \dots \quad (4.44)$$

This is the famous **Bohr formula**.

Considering Eq. (4.31), we have

$$\kappa = \left(\frac{me^2}{4\pi\epsilon_0\hbar^2} \right) \frac{1}{n} = \frac{1}{an} \quad (4.45)$$

⁵ Again from Eq. (4.31), we have $\rho = \frac{r}{a_0 n}$.

where

$$a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10}\text{m} \quad (4.46)$$

is the so-called **Bohr radius**⁵.

Now, we can talk about the spatial wave functions for hydrogen which are labeled by three quantum numbers, n , l , and m

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi), \quad (4.47)$$

where from Eq. (4.37) and Eq. (4.23) we have

$$R_{nl}(r) = \frac{1}{r} \rho^{l+1} e^{-\rho} v(\rho) \quad (4.48)$$

and $v(\rho)$ is a polynomial of degree $j_{\max} = n - l - 1$ in ρ , whose coefficients are determined by the recursion formula from Eq. (4.40) and Eq. (4.43),

$$c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)} c_j. \quad (4.49)$$

The **ground state** is in the case $n = 1$; putting in the accepted values for the physical constants, we have

$$E_1 = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] = -13.6 \text{ eV}. \quad (4.50)$$

So, the **binding energy** of hydrogen (the amount of energy you would have to impart to the electron in the ground state in order to ionize the atom) is 13.6 eV. In ground state, $n = 1$, from Eq. (4.43) and Eq. (4.17) we have

$$\psi_{100}(r, \theta, \phi) = R_{10}(r) Y_0^0(\theta, \phi). \quad (4.51)$$

Since $n = 1$, we have to force $j_{\max} = 0$ to get the sensible quantum number in Eq. (4.51). This, in turn, defines the truncation of the recursion formula in Eq. (4.89). As the result, we have $c_1 = 0$, so the radical part of the wave function is

$$R_{10}(r) = \frac{c_0}{a_0} e^{-\frac{r}{a_0}} \quad (4.52)$$

Normalizing this the radial part of the wavefunction according to Eq. (4.19), we have

$$\int_0^\infty |R_{10}|^2 r^2 dr = 1.$$

So we have $c_0 = \frac{2}{\sqrt{a_0}}$, and we also have $Y_0^0 = \frac{1}{\sqrt{4\pi}}$ from Eq. (4.20). Then the ground state of hydrogen is

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}. \quad (4.53)$$

For the first excited state, $n = 2$, the energy is

$$E_2 = \frac{-13.6}{2^2} \text{ eV} = -3.4 \text{ eV}. \quad (4.54)$$

Since $n = 2$, the possible quantum numbers are $l = 0, m = 0$ and $l = 1, m = 0, \pm 1$, these four different states share this same energy. If $l = 0$, with $n = 2$ we know the $j_{max} = 1$ and the coefficients are $c_1 = -c_0$ and $c_2 = 0$. Therefore, we have the radius part of the wavefunction

$$R_{20}(r) = \frac{c_0}{2a_0} \left(1 - \frac{r}{2a_0}\right) e^{-\frac{r}{2a_0}}. \quad (4.55)$$

If $l = 1$, the recursion formula Eq. (4.89) terminate immediately (since $j_{max} = 0$). Then we have the following result

$$R_{21}(r) = \frac{c_0}{4a_0^2} r e^{-\frac{r}{2a_0}}. \quad (4.56)$$

More general, for arbitrary n , the possible values of l from Eq. (4.43) are

$$l = 0, 1, 2, \dots, n-1, \quad (4.57)$$

and for each l from Eq. (4.17) there are $(2l+1)$ possible values of m . Then the total degeneracy of the energy level E_n is

$$d(n) = \sum_{l=0}^{n-1} (2l+1) = n^2. \quad (4.58)$$

The polynomial $v(\rho)$ defined in Eq. (4.39) and Eq. (4.89) is a well known function

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho) \quad (4.59)$$

where

$$L_{q-p}^p(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x) \quad (4.60)$$

is the **associated Laguerre polynomial**, and

$$L_q(x) \equiv e^x \left(\frac{d}{dx}\right)^q (e^{-x} x^q) \quad (4.61)$$

is the q th **Laguerre polynomial**. The normalized hydrogen wave function are

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\frac{r}{na_0}} \left(\frac{2r}{na_0}\right)^l \left[L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)\right] Y_l^m(\theta, \phi) \quad (4.62)$$

The density plots are shown in Fig. 4.2.

Notice that the wave functions depend on all three quantum numbers, the energy in Eq. (4.44) are determined by n alone. This is a peculiarity of the Coulomb potential⁶. The wave function are mu-

⁶ For the case of infinity spherical well, the energy depend also on l .

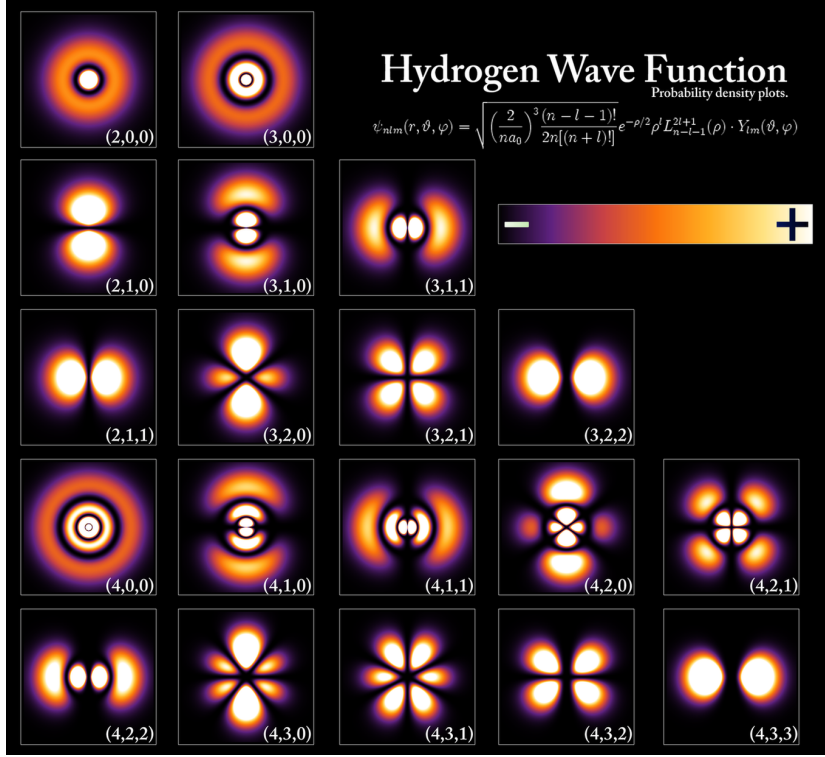


Figure 4.2: Density plot of the wave function $|\psi|^2$ for different quantum number.

tually orthogonal inherit from the spherical harmonic function in Eq. (4.21)

$$\int \psi_{nlm}^* \psi_{n'l'm'} r^2 \sin \theta d\theta d\phi = \delta_{nn'} \delta_{ll'} \delta_{mm'}, \quad (4.63)$$

where $\delta_{nn'}$ is from the fact that they are eigenfunction of different eigenvalues from the Hamiltonian.

4.2.2 The spectrum of Hydrogen

In principle, if you put a hydrogen atom into some station state Ψ_{nlm} , it should stay there forever. However if you tickle it slightly (by collision with other atom, or by shining light on it), the electron may undergo a **transition** to some other station state — either by absorbing energy and moving up to a higher-energy state, or by giving off energy and moving down. In practice such perturbations are always present; transitions are constantly occurring, and the result is that a container of hydrogen gives off photons, whose energy corresponds to the difference in energy between the initial and final states

$$E_\gamma = E_i - E_f = -13.6 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right). \quad (4.64)$$

According to **Planck formula**, the energy of a photon is proportional to its frequency

$$E_\gamma = h\nu \quad (4.65)$$

Meanwhile, the wavelength is given by $\lambda = \frac{c}{\nu}$, so

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (4.66)$$

where

$$R \equiv \frac{m}{4\pi c \hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 = 1.097 \times 10^7 \text{ m}^{-1} \quad (4.67)$$

is known as the **Rydberg constant**. Equation (4.66) is the **Rydberg formula** for the spectrum of hydrogen. This is discovered empirically in the nineteenth century, and it was Bohr's theory to explain the result and calculate R in terms of the fundamental constants of nature.

4.3 Angular momentum

For stationary state, the hydrogen atom are labeled by three quantum numbers: the principal quantum number, n , determines the energy of the state; for l and m are related to the orbital angular momentum. In classical theory of central forces, energy and angular momentum are the fundamental conserved quantities, and it is not surprising that angular momentum plays a significant role in the quantum theory.

Classically, the angular momentum of a particle is given by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}. \quad (4.68)$$

The corresponding quantum operators are obtained by the standard prescription with $p_x \rightarrow -i\hbar \frac{\partial}{\partial x}$ and so on.

4.3.1 Eigenvalues

First the operators are not commute with each other

$$[L_x, L_y] = i\hbar L_z. \quad (4.69)$$

We could cyclicly permute the subindices to get the similar result for other directions. They are the fundamental commutation relations for angular momentum

Notice that L_x , L_y , and L_z are *incompatible* observables, the generalized uncertainty principle indicates that $\sigma_{L_x} \sigma_{L_y} \geq \frac{\hbar}{2} |\langle L_z \rangle|$. It would therefore be futile to look for states that are simultaneously eigenfunctions of L_x and L_y . On the other hand, the *square of the total angular momentum*

$$L^2 \equiv L_x^2 + L_y^2 + L_z^2 \quad (4.70)$$

does commute with $L_{i=x,y,z}$

$$\left[L^2, L_{i=x,y,z} \right] = 0. \quad (4.71)$$

or, in a more compact way⁷

$$\left[L^2, \mathbf{L} \right] = 0. \quad (4.72)$$

So L^2 is compatible with each component of \mathbf{L} , and we can hope to find simultaneous eigenstates of L^2 and L_z for example,

$$L^2 f = \lambda f \quad \text{and} \quad L_z f = \mu f. \quad (4.73)$$

Using the ladder operator technique

$$L_{\pm} \equiv L_x \pm iL_y. \quad (4.74)$$

The commutator with L_z and L^2 are

$$[L_z, L_{\pm}] = \pm \hbar L_{\pm}, \quad (4.75)$$

$$[L^2, L_{\pm}] = 0. \quad (4.76)$$

With Eq. (4.76), we know that if f is an eigenfunction of L^2 and L_z , so also is $L_{\pm} f$. With Eq. (4.75) and Eq. (4.73), we have

$$L_z (L_{\pm} f) = (L_z L_{\pm} - L_{\pm} L_z) f + L_{\pm} L_z f = \pm \hbar L_{\pm} f + L_{\pm} (\mu f) = (\mu \pm \hbar) (L_{\pm} f), \quad (4.77)$$

so $L_{\pm} f$ is an eigenfunction of L_z with the *new* eigenvalue $\mu \pm \hbar$.

For a given value of λ , we obtain a ladder of states, with each rung separated from its neighbors by one unit of \hbar in the eigenvalue of L_z . This ladder is not infinite long, one can not reach a state for which the z -component exceeds the total⁸. There must exist a “top rung”, f_t , such that⁹

$$L_+ f_t = 0. \quad (4.78)$$

Let $\hbar l$ be the eigenvalue of L_z at this top rung,

$$L_z f_t = \hbar l f_t; \quad L^2 f_t = \lambda f_t \quad (4.79)$$

Now, with the identity

$$L^2 = L_{\pm} L_{\mp} + L_z^2 \mp \hbar L_z \quad (4.80)$$

we can calculate the eigenvalue

$$L^2 f_t = (L_- L_+ + L_z^2 + \hbar L_z) f_t = (0 + \hbar^2 l^2 + \hbar^2 l) f_t = \hbar^2 l(l+1) f_t$$

and hence

$$\lambda = \hbar^2 l(l+1). \quad (4.81)$$

⁷ To prove the relation, we use the follow identity $[AB, C] = A[B, C] + [A, C]B$.

⁸ Formally, we have $\langle L^2 \rangle = \langle L_x^2 \rangle + \langle L_y^2 \rangle + \langle L_z^2 \rangle$, but we also have $\langle L_x^2 \rangle = \langle L_x f | L_x f \rangle \geq 0$ for x - and y -direction. Then $\lambda = \langle L_x^2 \rangle + \langle L_y^2 \rangle + \mu^2 \geq \mu^2$.

⁹ Actually all we can conclude is that $L_+ f_t$ is not normalizable. Check the problem.

This tell us the eigenvalue of L^2 in terms of the *maximum eigenvalue* of L_z .

Meanwhile, there is also a “bottom rung”, f_b , such that $L_- f_b = 0$. Let $\hbar \bar{l}$ be the eigenvalue of L_z at this bottom rung $L_z f_b = \hbar \bar{l} f_b$. Using Eq. (4.80), we have

$$\lambda = \hbar^2 \bar{l} (\bar{l} - 1). \quad (4.82)$$

Comparing Eq. (4.81) and Eq. (4.82), we see that $l(l+1) = \bar{l}(\bar{l}-1)$, so either $\bar{l} = l+1$ (which is absurd, the bottom rung is higher than the top rung) or else

$$\bar{l} = -l. \quad (4.83)$$

Apparently, from Eq. (4.83), we known the eigenvalue of L_z are $m\hbar$ where m goes from $-l$ to $+l$ in N integer steps. In particular, it follows that $l = -l + N$, and hence $l = \frac{N}{2}$, so l must be an integer or a half-integer. Then the eigenfunctions are characterized by the number l and m

$$L^2 f_l^m = \hbar^2 l(l+1) f_l^m; \quad L_z f_l^m = \hbar m f_l^m \quad (4.84)$$

where

$$l = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots; \quad m = -l, -l+1, \dots, l-1, l. \quad (4.85)$$

For a given value l , there are $2l+1$ different values of m .

Usually, peopel like to illustrate this result with the diagram Fig. 4.3. The red arrows are supposed to represent possible angular

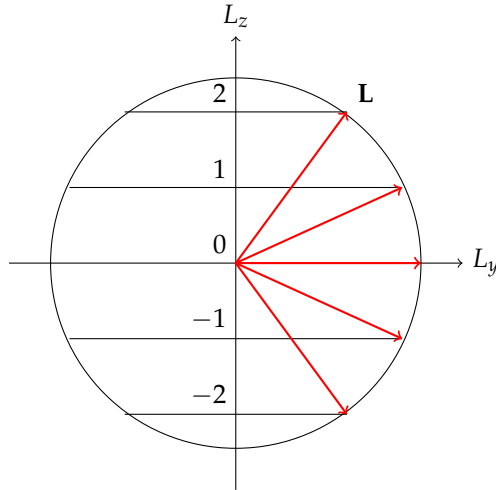


Figure 4.3: Angular momentum starts for $l = 2$.

momenta — in units of \hbar where they all have same length $\sqrt{l(l+1)}$ and their z components are allowed values of $m = -2, -1, 0, 1, 2$. Notice that the magnitude of the vectors is greater than the maximum z component¹⁰. Evidently, you can not get the angular momentum to point perfectly along the z direction. Since to do this, you have to know all thee components simutaneously ($L_x = L_y = 0, L_z =$

¹⁰ In general, $\sqrt{l(l+1)} > l$, except for the “trivial” case $l = 0$.

$\sqrt{l(l+1)})$, and the uncertainty principle tell us that is impossible. It is not merely that you don't know all three components of \mathbf{L} ; there simply aren't three components—a particle just cannot have a determinate angular momentum vector, any more than it can simultaneously have a determinate position and momentum. If L_z has a well-defined value, the L_x and L_y do not.

So, by purely algebraic means, starting with the fundamental commutation relations for angular momentum Eq. (4.69), we have determined the eigenvalues of L^2 and L_z —without ever seeing the eigenfunctions themselves! For the eigenfunctions, $f_l^m = Y_l^m$ —the eigenfunctions of L^2 and L_z are nothing but the old spherical harmonics function in Eq. (4.20). Since they are eigenfunctions of hermitian operators, L^2 and L_z , belonging to distinct eigenvalues.

4.3.2 Eigenfunctions

First, we rewrite the angular momentum in spherical coordinates, since $\mathbf{L} = \frac{\hbar}{i}(\mathbf{r} \times \nabla)$, and the gradient

$$\nabla = \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\phi} \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \quad (4.86)$$

meanwhile, $\mathbf{r} = r\hat{r}$, so

$$\mathbf{L} = \frac{\hbar}{i} \left(\hat{\phi} \frac{\partial}{\partial \theta} - \hat{\theta} \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right). \quad (4.87)$$

The unit vectors $\hat{\theta}$ and $\hat{\phi}$ can be resolved into their cartesian components due to Fig. 4.1

$$\hat{\theta} = (\cos \theta \cos \phi) \hat{x} + (\cos \theta \sin \phi) \hat{y} - (\sin \theta) \hat{z} \quad (4.88)$$

$$\hat{\phi} = -(\sin \phi) \hat{x} + (\cos \phi) \hat{y} \quad (4.89)$$

Thus we have

$$L_x = \frac{\hbar}{i} \left(-\sin \phi \frac{\partial}{\partial \theta} - \cos \phi \cot \theta \frac{\partial}{\partial \phi} \right), \quad (4.90)$$

$$L_y = \frac{\hbar}{i} \left(+\cos \phi \frac{\partial}{\partial \theta} - \sin \phi \cot \theta \frac{\partial}{\partial \phi} \right), \quad (4.91)$$

$$L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}. \quad (4.92)$$

For descending and increasing operators

$$L_{\pm} = \pm \hbar e^{\pm \phi} \left(\frac{\partial}{\partial \theta} \pm i \cot \theta \frac{\partial}{\partial \phi} \right). \quad (4.93)$$

and L^2 ,

$$L^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]. \quad (4.94)$$

We are now in a position to determine $f_l^m(\theta, \phi)$. It's an eigenfunction of L^2 , with eigenvalue $\hbar^2 l(l+1)$. This is precisely the angular equation, Eq. (4.9). And it is also an eigenfunction of L_z , with the eigenvalue $m\hbar$. This is equivalent to the azimuthal equation Eq. (4.11). So the conclusion is the following: Spherical harmonics functions are eigenfunctions of L^2 and L_z . When we solved the Schrödinger equation by separation of variables, we were inadvertently constructing simultaneous eigenfunction of the three commuting operators H , L^2 , and L_z .

At last, there is a curious final twist to this story, for the algebraic theory of angular momentum permits l to take on *half-integer* values in Eq. (4.85), whereas separation of variables yielded eigenfunctions only for *integer* values in Eq. (4.17). In the following section, we will see the profound importance for the half-integer solutions.

4.4 Spin

In classical mechanics, a rigid object admits two kinds of angular momentum: **orbital**, associated with the motion of the center of mass, and **spin**, associated with motion about the center of mass. For quantum mechanics, in addition to orbital angular momentum, associated with the motion of the electron around the nucleus (described by spherical harmonics in hydrogen), the electron also carries another form of angular momentum, which has nothing to do with motion in space. The electron is a structureless point particle, and its spin angular momentum cannot be decomposed into orbital angular momenta of constituent part. Suffice it to say that elementary particles carry **intrinsic** angular momentum in addition to their "extrinsic" angular momentum.

The *algebraic* theory of spin is a carbon copy of the theory of orbital angular momentum, beginning with the fundamental commutation relation

$$[S_i, S_j] = i\hbar S_k. \quad (4.95)$$

It follows that the eigenvectors of S^2 and S_z satisfy

$$S^2 |sm\rangle = \hbar^2 s(s+1) |sm\rangle; \quad S_z |sm\rangle = \hbar m |sm\rangle; \quad (4.96)$$

and

$$S_{\pm} |sm\rangle = \hbar \sqrt{s(s+1) - m(m \pm 1)} |s(m \pm 1)\rangle, \quad (4.97)$$

where $S_{\pm} \equiv S_x \pm iS_y$. But this time the eigenvectors are not spherical harmonics (they are not functions of θ and ϕ at all), and there is no *a priori* reason to exclude the half-integer values of s and m

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots; \quad m = -s, -s+1, \dots, s-1, s. \quad (4.98)$$

It so happens that every elementary particle has a specific and immutable value of s , which we call **the spin** of the particular species: pi mesons have spin 0; electron have spin $\frac{1}{2}$; photons have spin 1; deltas have spin $\frac{3}{2}$; gravitons have spin 2; and so on. By contrast, the orbital angular momentum quantum number l can take on any integer value, and will change from one to another when the system is perturbed. But s is fixed, for any given particle, and this makes the theory of spin comparatively simple.

4.4.1 Spin $\frac{1}{2}$

By far the most important case is $s = \frac{1}{2}$, for this is the spin of the particles that make up ordinary matter (protons, neutrons, and electrons), as well as all quarks and all leptons. There are just two eigenstates which we call it **spin up** $|\frac{1}{2} \equiv \uparrow\rangle$ and **spin down** $|\frac{1}{2} \equiv \downarrow\rangle$.

Using the basis vectors the general state of a spin- $\frac{1}{2}$ particle can be expressed as a two-element column spinor

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_-, \quad (4.99)$$

with

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (4.100)$$

representing spin up and spin down.

Meanwhile, the spin operators become 2×2 matrices. From Eq. (4.96), we know for S^2 ,

$$S^2\chi_{\pm} = \frac{3}{4}\hbar^2\chi_{\pm}, \quad S^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (4.101)$$

Similarly, for S_z we have

$$S_z\chi_{\pm} = \pm\frac{\hbar}{2}\chi_{\pm}, \quad S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (4.102)$$

Consider the properties of ladder operators, we have

$$S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \quad (4.103)$$

Since $S_{\pm} = S_x \pm iS_y$, we have

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \quad (4.104)$$

To make it tidier, we may write $\mathbf{S} = \frac{\hbar}{2}\boldsymbol{\sigma}$, where

$$\sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (4.105)$$

These are the famous **Pauli spin matrices**. Notice that S_x , S_y , S_z , and S^2 are all hermitian. On the other hand, S_{\pm} are not hermitian.

The eigenstates of S_z are

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (4.106)$$

If you measure S_z on a particle in the general state χ in Eq. (4.99), you could get $+\frac{\hbar}{2}$ with probability $|a|^2$ and $-\frac{\hbar}{2}$ with probability $|b|^2$.

If you measure S_x , then, what are the possible result and their probabilities? First, we need to know the eigenvalues and eigenstates of S_x . The characteristic equation is nothing but

$$\begin{vmatrix} -\lambda & \frac{\hbar}{2} \\ \frac{\hbar}{2} & -\lambda \end{vmatrix} = 0 \rightarrow \lambda = \pm \frac{\hbar}{2}.$$

The normalized eigenstates of S_x are

$$\chi_+^x = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}, \quad \chi_-^x = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}. \quad (4.107)$$

The generic spinor Eq. (4.99) can be expressed as a linear combination.

4.4.2 Electron in a magnetic field: Basic

A spinning charged particle constitutes a magnetic dipole. Its **magnetic dipole momentum** $\boldsymbol{\mu}$ is proportional to its spin angular momentum

$$\boldsymbol{\mu} = \gamma \mathbf{S} \quad (4.108)$$

the proportionality constant γ is called the **gyromagnetic ratio**. With a magnetic field \mathbf{B} , it experiences a torque, $\boldsymbol{\mu} \times \mathbf{B}$, which tends to line it up parallel to the field. The energy associated with this torque is

$$H = -\boldsymbol{\mu} \cdot \mathbf{B}, \quad (4.109)$$

so the Hamiltonian of a spinning charged particle, at rest¹¹ in a magnetic field \mathbf{B} is

$$H = -\gamma \mathbf{B} \cdot \mathbf{S}. \quad (4.110)$$

¹¹ If a particle is allowed to move, there will be kinetic energy and Lorentz force, which is not derivable from a potential energy function and hence does not fit the Schrödinger equation as we formulated so far.

4.4.3 Larmor precession

Imagine a particle of spin $\frac{1}{2}$ at rest in a uniform magnetic field, which points in the z -direction

$$\mathbf{B} = B_0 \hat{z}. \quad (4.111)$$

The Hamiltonian in matrix form is

$$H = -\gamma B_0 S_z = -\frac{\gamma B_0 \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (4.112)$$

The eigenstate of this H are the same as those of S_z in Eq. (4.106) with energy $E_{\pm} = \mp \frac{\gamma B_0 \hbar}{2}$.

Since the Hamiltonian is time-independent, the general solution the the time-dependent Schrödinger equation, $i\hbar \frac{\partial \chi}{\partial t} = H\chi$, can be expressed in terms of stationary states

$$\chi(t) = \begin{pmatrix} \cos\left(\frac{\alpha}{2}\right) e^{i\gamma B_0 t/2} \\ \sin\left(\frac{\alpha}{2}\right) e^{-i\gamma B_0 t/2} \end{pmatrix}.$$

The constants $\cos\left(\frac{\alpha}{2}\right)$ and $\sin\left(\frac{\alpha}{2}\right)$ are determined by the initial condition and the physical importance of the phase angle α will discussed later.

One can calculate the expectation value of \mathbf{S} as a function of time

$$\langle S_x \rangle = \chi(t)^\dagger S_x \chi(t) = \frac{\hbar}{2} \sin \alpha \cos(\gamma B_0 t) \quad (4.113)$$

$$\langle S_y \rangle = \chi(t)^\dagger S_y \chi(t) = \frac{\hbar}{2} \sin \alpha \sin(\gamma B_0 t) \quad (4.114)$$

$$\langle S_z \rangle = \chi(t)^\dagger S_z \chi(t) = \frac{\hbar}{2} \cos \alpha \quad (4.115)$$

Evidently $\langle \mathbf{S} \rangle$ is tilted at a constant angle α to the z -axis, and precesses about the field at the **Larmor frequency**

$$\omega = \gamma B_0, \quad (4.116)$$

just as it would classically. This is because the Ehrenfest's theorem guarantees that $\langle \mathbf{S} \rangle$ evolves according to the classical laws.

For example, the **Stern-Gerlach experiment** is an application of this effect as shown in Fig. 4.4. In an *inhomogeneous* magnetic field, there is not only a *torque*, but also a force on a magnetic dipole¹²

$$\mathbf{F} = \nabla (\boldsymbol{\mu} \cdot \mathbf{B}). \quad (4.117)$$

This force can be used to separate out particles with a particular spin orientation. Imagine a beam of relatively heavy neutral atom which pass through a region of inhomogeneous magnetic field

$$\mathbf{B}(x, y, z) = -\alpha x \hat{x} + (B_0 + \alpha z) \hat{z} \quad (4.118)$$

¹² We assume a neutral particle to avoid the Lorentz force and heavy so we can construct localized wave packets and treat the motion in terms of classical particle trajectories. In practice, the Stern-Gerlach experiment does not work, for example, with a beam of free electrons.

¹³ We can not have something only with z component in this case, since it breaks the electromagnetic law $\nabla \cdot \mathbf{B} = 0$.

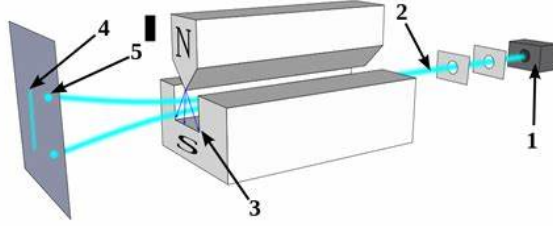


Figure 4.4: The setup of Stern-Gerlach experiment. (1) source; (2) hole; (3) inhomogeneous magnetic field; (4) the classical expectation and (5) the observation.

where B_0 is a strong uniform field and the constant α describes a small deviation from homogeneity¹³.

The corresponding force on the atom is

$$\mathbf{F} = \gamma\alpha (-S_x\hat{x} + S_z\hat{z}).$$

However, as Eq. (4.113) suggested, due to the Larmor precession about B_0 , S_x oscillates rapidly and averages to zero. The *net* force is purely in the z direction

$$F_z = \gamma\alpha S_z \quad (4.119)$$

and the beam is deflected up or down, in proportion to the z component of the spin angular momentum.

In the more *quantum* argument, we examine the process from the perspective of a reference frame that moves along with the beam. In this frame the Hamiltonian starts out zero, turns on for a time T and then turn off again

$$H(t) = \begin{cases} 0, & \text{for } t < 0 \\ -\gamma(B_0 + \alpha a)S_z, & \text{for } 0 \leq t \leq T, \\ 0, & \text{for } t > T \end{cases} \quad (4.120)$$

where we have ignore the x component contribution from \mathbf{B} for the same reason discussed before. Suppose the atom has spin $\frac{1}{2}$ and starts out in the state

$$\chi(t) = a\chi_+ + b\chi_- \quad \text{for } t \leq 0.$$

In the magnetic field region where the non-zero Hamiltonian acts, we have

$$\chi(t) = a\chi_+ e^{-iE_+ t/\hbar} + b\chi_- e^{-iE_- t/\hbar} \quad \text{for } 0 \leq t \leq T,$$

where

$$E_{\pm} = \mp \gamma (B_0 + \alpha z) \frac{\hbar}{2} \quad (4.121)$$

and hence it emerges in the state

$$\chi(t) = \left(a e^{i\gamma T B_0/2} \chi_+ \right) e^{i(\alpha\gamma T/2)z} + \left(b e^{-i\gamma T B_0/2} \chi_- \right) e^{-i(\alpha\gamma T/2)z}. \quad (4.122)$$

The two terms now carry *momentum* in the z direction

$$p_z = \pm \frac{\alpha\gamma T \hbar}{2}. \quad (4.123)$$

Thus χ_+ will move in the plus- z direction and opposite for χ_- state.

4.4.4 Addition of angular momenta

Suppose now that we have two spin- $\frac{1}{2}$ particles—for example, the electron and the proton in the ground state of hydrogen. Each can have spin up or spin down, so there are four possibilities in all¹⁴

¹⁴ We consider the ground state, so there will not any orbital angular momentum to worry about.

$$|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle, \quad (4.124)$$

where the first arrow refer to the electron and the second to the proton. We want to know what is the total angular momentum of the atom $\mathbf{S} \equiv \mathbf{S}_1 + \mathbf{S}_2$. Since each of these four composite states in Eq. (4.124), is an eigenstate of S_z , we have

$$S_z |\chi_1 \chi_2\rangle = (S_1 + S_2) |\chi_1 \chi_2\rangle = \hbar (m_1 + m_2) |\chi_1 \chi_2\rangle$$

So m is just $m_1 + m_2$:

$$\begin{aligned} m = 1 & \quad |\uparrow\uparrow\rangle \\ m = 0 & \quad |\uparrow\downarrow\rangle \\ m = 0 & \quad |\downarrow\uparrow\rangle \\ m = -1 & \quad |\downarrow\downarrow\rangle. \end{aligned}$$

At first glance, this does not look right: m is suppose to advance in integer steps from $-s$ to $+s$ where $s = 1$ in our case. However, there is an “extra” state with $m = 0$. One way to untangle this problem is to apply the lowering operator to the state $|\uparrow\uparrow\rangle$

$$S_- |\uparrow\uparrow\rangle = \hbar (|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle).$$

Evidently, in the notation of $|sm\rangle$, the three states with $s = 1$ are

$$s = 1 \text{ (triplet state)} \rightarrow \begin{cases} |11\rangle & = |\uparrow\uparrow\rangle \\ |10\rangle & = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |1-1\rangle & = |\downarrow\downarrow\rangle \end{cases} \quad (4.125)$$

This is called the **triplet** combination. Meanwhile, the orthogonal state with $m = 0$ carries $s = 0$

$$s = 0 \text{ (singlet state)} \rightarrow |00\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle). \quad (4.126)$$

We found that the combination of two spin- $\frac{1}{2}$ particles can carry a total spin of 1 and 0, depending on whether they occupy the triplet or the single configuration. To verify this, we will prove that the triplet states are eigenvectors of S^2 with eigenvalue $\hbar^2 s(s+1) = 2\hbar^2$ and single is for eigenvalue 0. Now,

$$S^2 = (\mathbf{S}_1 + \mathbf{S}_2) \cdot (\mathbf{S}_1 + \mathbf{S}_2) = S_1^2 + S_2^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2. \quad (4.127)$$

Using Eq. (4.102) and Eq. (4.104), we have

$$\begin{aligned} & \mathbf{S}_1 \cdot \mathbf{S}_2 |\uparrow\downarrow\rangle \\ &= (S_{x1}S_{x2} + S_{y1}S_{y2} + S_{z1}S_{z2}) |\uparrow\downarrow\rangle \\ &= \frac{\hbar^2}{4} (2|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle). \end{aligned}$$

Similarly,

$$\mathbf{S}_1 \cdot \mathbf{S}_2 |\downarrow\uparrow\rangle = \frac{\hbar^2}{4} (2|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle).$$

Then returning to Eq. (4.125), we have

$$S^2 |10\rangle = \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} + 2\frac{\hbar^2}{4} \right) |10\rangle = 2\hbar^2 |10\rangle, \quad (4.128)$$

so $|10\rangle$ is indeed an eigenstate of S^2 with eigenvalue $2\hbar^2$. We can did the similar calculation for $|00\rangle$ and we have $S^2 |00\rangle = 0 |00\rangle$.

This is the simplest example of a larger problem: If you combine spin s_1 with spin s_2 , the total spins s you can get is

$$s = (s_1 + s_2), (s_1 + s_2 - 1), \dots, |s_1 - s_2|, \quad (4.129)$$

where they are in integer steps. For example, if you package together a particle of spin $\frac{3}{2}$ with a particle of spin 2, you could get a total spin of $\frac{7}{2}, \frac{5}{2}, \frac{3}{2}$, or $\frac{1}{2}$, depending on the configuration. Another example, if a hydrogen atom is in the state ψ_{nlm} , the net angular momentum of the electron is $l + \frac{1}{2}$ or $l - \frac{1}{2}$; if you now throw in a *proton*, the atom's total angular momentum quantum number is $l + 1, l$, or $l - 1$.

The combined state $|sm\rangle$ with total spin s and z-component m will be some linear combination of the composite states $|s_1 m_1\rangle |s_2 m_2\rangle$:

$$|sm\rangle = \sum_{m_1+m_2=m} C_{m_1 m_2 m}^{s_1 s_2 s} |s_1 m_1\rangle |s_2 m_2\rangle. \quad (4.130)$$

The constants $C_{m_1 m_2 m}^{s_1 s_2 s}$ are called **Clebsch-Gordan coefficients**. The simplest case are listed in Fig. 4.5. For example, the shaded column

Figure 4.5: Clebsch-Gordan coefficients. A square root sign is understood for every entry; the minus sign, if present, goes outside the radical.

of 2×1 table tell us that

$$|30\rangle = \frac{1}{\sqrt{5}} |21\rangle |1-1\rangle + \sqrt{\frac{3}{5}} |20\rangle |10\rangle + \frac{1}{\sqrt{5}} |2-1\rangle |11\rangle.$$

In particular, if two particles (of spin 2 and spin 1) are at rest in a box, and the total spin is 3, and its z component is 0 (where $|30\rangle$), then a measurement of S_z^1 could return the value \hbar (with probability $\frac{1}{5}$), or 0 (with probability $\frac{3}{5}$), or $-\hbar$ (with probability $\frac{1}{5}$).

These tables also work the other way around

$$|s_1 m_1\rangle |s_2 m_2\rangle = \sum_s C_{m_1 m_2 m}^{s_1 s_2 s} |s m\rangle. \quad (4.131)$$

For example, the shaded row in the $\frac{3}{2} \times 1$ table tells us that

$$\left| \frac{3}{2} 1 \right\rangle |10\rangle = \sqrt{\frac{3}{5}} \left| \frac{5}{2} 1 \right\rangle + \sqrt{\frac{1}{15}} \left| \frac{3}{2} 1 \right\rangle - \sqrt{\frac{1}{3}} \left| \frac{1}{2} 1 \right\rangle$$

If you put particles of spin $\frac{3}{2}$ and spin 1 in the box, and you know that the first has $m_1 = \frac{1}{2}$ and the second has $m_2 = 0$, and you measure the total spin, s , you could get $\frac{5}{2}$ (with probability $\frac{3}{5}$), or $\frac{3}{2}$ (with probability $\frac{1}{15}$), or $\frac{1}{2}$ (with probability $\frac{1}{3}$).

In a mathematical sense this is all applied **group theory**—what we are talking about is the decomposition of the direct product of two irreducible representations of the rotation group into a direct sum of irreducible representations.

5

Identical particles

5.1 Two-particle system

For a single particle, $\Psi(\mathbf{r}, t)$ is a function of the spatial coordinate and time (we will ignore spin). For two-particle system the wave function is $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$. It evolves with the Schrödinger equation with the Hamiltonian

$$H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2, t). \quad (5.1)$$

Typically, the interaction potential depends only the vector $\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2$ between the two particles. We can change the variable to \mathbf{r} and $\mathbf{R} \equiv \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2}$. Relate to the old coordinate, we have $\mathbf{r}_{1,2} = \mathbf{R} \pm \mathbf{r} \frac{\mu}{m_{1,2}}$, and $\nabla_{1,2} = \frac{\mu}{m_{2,1}}\nabla_R \pm \nabla_r$ where

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2} \quad (5.2)$$

is the **reduced mass** of the system. The Schrödinger equation becomes

$$-\frac{\hbar^2}{2(m_1 + m_2)}\nabla_R^2 \psi - \frac{\hbar^2}{2\mu}\nabla_r^2 \psi + V(\mathbf{r})\psi = E\psi. \quad (5.3)$$

We can further separate the variables, $\psi(\mathbf{R}, \mathbf{r}) = \psi_R(\mathbf{R})\psi_r(\mathbf{r})$ to see that they are two single particle problem.

5.1.1 Bosons and Fermions

Suppose there are two particles and they can be represented in the way of simple product¹

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2). \quad (5.4)$$

Of course, this assumes that we can tell the particles apart—otherwise it wouldn't make any sense to claim that number 1 is in state ψ_a and number 2 is in state ψ_b ; all we could say is that one of them is in the

¹ In **entangled states**, you can not decomposed in that way. If particle one is in state a and particle two is in state b , then the two-particle state is a product. The simplest example of entangled state is the singlet spin configuration in Eq. (4.126). You can not tell the state of particle one by itself, because it is "entangled" with the state of particle two. If 2 is measured, and found to be spin up, then 1 is spin down, but if 2 is spin down, then 1 is spin up.

Some discussion from [stackexchange](#):

Entanglement is only a meaningful concept when there is a well-defined notion of subsystems, which generally means spatially separated subsystems. Indeed, the notion of "product state" (or its converse, "entangled state") is only meaningful relative to a given tensor product decomposition of the Hilbert space, which implicitly defines a splitting into subsystems. Hence, it is not obvious that indistinguishable particles with an (anti-)symmetrised wavefunction can be truly regarded as entangled subsystems.

Nevertheless, [Killoran, Cramer and Plenio](#) showed that this is indeed a genuine form of entanglement. That is, the entanglement formally associated with the symmetrised wave function of a system of indistinguishable bosons can be extracted into the equivalent amount of entanglement (asymptotically) between distinguishable modes. I believe a similar result was found also for fermions by [Cavalcanti et al.](#)

state ψ_a and the other is in state ψ_b , but we wouldn't know which is which. This is what happened, since all electrons are utterly identical unlike classical objects.

Quantum mechanics neatly accommodates the existence of particles that are *indistinguishable in principle*: We simply construct a wave function that is *noncommittal* as to which particle is in which state. There are actually two ways to do it

$$\psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) = A [\psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) \pm \psi_b(\mathbf{r}_1) \psi_a(\mathbf{r}_2)]. \quad (5.5)$$

Thus the theory admits two kinds of identical particles: **bosons** (plus sign with integer spin) and **fermions** (minus sign with half integer spin). This connection between **spin and statistics** can be proved in relativistic quantum mechanics; in non-relativistic theory it is taken as an axiom.

It follows, in particular, that *two identical fermions can not occupy the same state*. This is the famous **Pauli exclusion principle**. There is a more general way to formulate the problem. Let us define the **exchange operator**, P , which interchanges the two particles:

$$P f l r(r_1, r_2) = f l r(r_2, r_1). \quad (5.6)$$

Clearly, $P^2 = 1$, and it follows that the eigenvalues of P are ± 1 . Now, if the two particles are identical, the Hamiltonian must treat them the same: $m_1 = m_2$ and $V(r_1, r_2) = V(r_2, r_1)$. This suggest that P and H are compatible observables

$$[P, H] = 0, \quad (5.7)$$

and hence we can find a complete set of functions that are simultaneous eigenstates of both. That is to say, we can find solutions to the Schrödinger equation that are either symmetric or antisymmetric under exchange:

$$\psi(r_1, r_2) = \pm \psi(r_2, r_1). \quad (5.8)$$

Moreover, if a system starts out in such state, it will remain in a such state. For identical particles the wave function is not merely *allowed*, but *required* to satisfy Eq. (5.8), with the plus sign for bosons, and minus sign for fermions.

5.1.2 Exchange force

Suppose one particle is in state $\psi_a(x)$, and the other is in state $\psi_b(x)$, and these two states are orthogonal and normalized. If the two particles are distinguishable, and number 1 is in the state ψ_a , then the combined wave function is

$$\psi(x_1, x_2) = \psi_a(x_1) \psi_b(x_2); \quad (5.9)$$

if they are identical particles, the composite wave function is

$$\psi_{\pm}(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_a(x_1) \psi_b(x_2) \pm \psi_b(x_1) \psi_a(x_2)]. \quad (5.10)$$

We will calculate the expectation value of the square of the separation distance between the two particles,

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2 \langle x_1 x_2 \rangle. \quad (5.11)$$

Case 1: Distinguishable particles. For the wavefunction in Eq. (5.9),

$$\langle x_1^2 \rangle = \int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)| dx_2 = \langle x^2 \rangle_a$$

With similar procedure, we have the result:

$$\langle (x_1 - x_2)^2 \rangle_d = \langle x_1^2 \rangle_a + \langle x_2^2 \rangle_b - 2 \langle x_1 \rangle_a \langle x_2 \rangle_b. \quad (5.12)$$

Case 2: Identical particles. For the wave function in Eq. (5.10),

$$\begin{aligned} \langle x_1^2 \rangle &= \frac{1}{2} \left[\int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)| dx_2 \right. \\ &\quad + \int x_1^2 |\psi_b(x_1)|^2 dx_1 \int |\psi_a(x_2)| dx_2 \\ &\quad \pm \int x_1^2 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int \psi_b(x_2)^* \psi_a(x_2) dx_2 \\ &\quad \left. \pm \int x_1^2 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int \psi_a(x_2)^* \psi_b(x_2) dx_2 \right] \\ &= \frac{1}{2} [\langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0] \end{aligned}$$

Since particle are identical you can not tell them apart, we have same result for $\langle x_2^2 \rangle$. But for the rest part,

$$\begin{aligned} \langle x_1 x_2 \rangle &= \frac{1}{2} \left[\int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)| dx_2 \right. \\ &\quad + \int x_1 |\psi_b(x_1)|^2 dx_1 \int x_2 |\psi_a(x_2)| dx_2 \\ &\quad \pm \int x_1 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int x_2 \psi_b(x_2)^* \psi_a(x_2) dx_2 \\ &\quad \left. \pm \int x_1 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int x_2 \psi_a(x_2)^* \psi_b(x_2) dx_2 \right] \\ &= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2, \end{aligned}$$

where

$$\langle x \rangle_{ab} \equiv \int x \psi_a(x)^* \psi_b(x) dx. \quad (5.13)$$

Evidently, we have the result:

$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x_1^2 \rangle_a + \langle x_2^2 \rangle_b - 2 \langle x_1 \rangle_a \langle x_2 \rangle_b \mp 2 |\langle x \rangle_{ab}|^2. \quad (5.14)$$

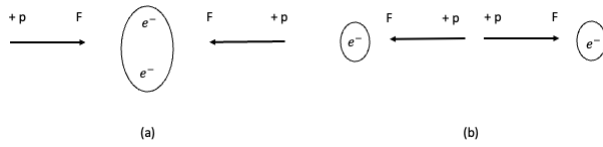


Figure 5.1: Schematic picture of the covalent bond: (a) Symmetric configuration produce attractive force. (b) Antisymmetric configuration produce repulsive force.

Comparing Eq. (5.12) and Eq. (5.14), we see that the difference resides in the final term:

$$\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp 2|\langle x \rangle_{ab}|^2. \quad (5.15)$$

Identical bosons tend to be somewhat closer together, and identical fermions somewhat further apart, than distinguishable particle in the same two states. Notice that $\langle x \rangle_{ab}$ vanishes unless the two wave functions actually overlap. As a *practical* matter, therefore, it is okay to pretend that electrons with non-overlapping wave functions are distinguishable.

The *interesting* case is when there is some overlap of the wave function. The system behaves as through there were a “force of attraction” between identical bosons, pulling them closer together, and a “force of repulsion” between identical fermions, pushing them apart. We call it an **exchange force**, although it is not really a force at all—no physical agency is pushing on the particles; rather, it is a purely *geometrical* consequence of the symmetrization requirement. It is also a strictly quantum mechanical phenomenon, with no classical counterpart.

There has profound consequences. Considering the hydrogen molecule H_2 . Roughly speaking, the ground state consists of one electron in the atomic ground state, Eq. (4.53), centered at nucleus 1, and one electron in the atomic ground state centered at nucleus 2. If electrons were **bosons**, the symmetrization requirement would tend to concentrate the electrons toward the middle, between the two protons, and the resulting accumulation of negative charge would attract the protons inward, accounting for the **covalent bond** as shown in Fig. 5.1. Unfortunately, electron are not bosons, they are fermions, and this means that the concentration of negative charge should actually be shifted to the wings, tearing the molecule apart.

However, this is the conclusion when the spin is ignored. The complete state of the electron includes not only its position wave function, but also a spinor, describing the orientation of the spin. When we put together the two-electron state, it is the **whole works**, not just the spatial part, that has to be antisymmetric with respect to exchange. Now, a glance back at the composite spin states Eq. (4.125) and Eq. (4.126) reveals that the singlet combination is antisymmetric

and hence would have to be joined with a symmetric spatial function, whereas the three triplet states are all symmetric and would require an antisymmetric spatial function. Evidently, then, the singlet state should lead to *binding*, and the triplet to *antibonding*. Sure enough, the chemists tell us that covalent bonding requires the two electrons to occupy the singlet state, with total spin zero.

5.2 Atoms

A neutral atom, of atomic number Z , consists of a heavy nucleus, with electric charge Ze , surrounded by Z electrons. The Hamiltonian for the system²

$$H = \sum_{j=1}^Z \left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_j} \right\} + \frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \right) \sum_{j \neq k}^Z \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|}. \quad (5.16)$$

The term in curly brackets represents the kinetic plus potential energy of the j th electron, in the electric field of the nucleus; the second sum is the potential energy associated with the mutual repulsion of the electrons. The problem is to solve Schrödinger's equation,

$$H\psi = E\psi, \quad (5.17)$$

for the wave function $\psi(\mathbf{r}_1, \dots, \mathbf{r}_Z)$. Because electrons are identical, for the complete state,

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_Z) \chi(\mathbf{s}_1, \dots, \mathbf{s}_Z), \quad (5.18)$$

should be antisymmetric with respect to interchange of any two electrons.

The Schrödinger equation with Hamiltonian in Eq. (5.16) can not be solved exactly. Some qualitative features will be discussed here.

5.2.1 Helium

After the hydrogen, the simplest atom is helium ($Z = 2$). The Hamiltonian,

$$H = \left\{ -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (5.19)$$

consists of two hydrogenic Hamiltonians. If we simply *ignore* the last interaction term, the Schrödinger equation separates, and the solutions can be written as products of *hydrogen* wave function:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{nlm}(\mathbf{r}_1) \psi_{n'l'm'}(\mathbf{r}_2), \quad (5.20)$$

² We are assuming the nucleus is stationary. The nucleus is so much more massive than the electrons that the correction is extremely small even in the case of hydrogen and it is smaller still for the heavier atoms.

only with half the Bohr radius, in Eq. (4.46), and four times the Bohr energies, in Eq. (4.44). The total energy would be

$$E = 4(E_n + E_{n'}), \quad (5.21)$$

where $E_n = -\frac{13.6}{n^2}$ eV. In particular, the ground state would be

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a_0^3} e^{-2(r_1+r_2)/a_0}, \quad (5.22)$$

and its energy would be $E_0 = -109$ eV. Because ψ_0 is a symmetric function, the spin state has to be antisymmetric, so the ground state of helium should be a *singlet* configuration. The actual ground state of helium is indeed a singlet but experimentally determined energy is -78.975 eV. This mismatch is due to the interaction from the last term of Eq. (5.16).

The excited states of helium consist of one electron in the hydrogenic ground state, and the other in an excited state³:

$$\psi_{nlm} \psi_{100}. \quad (5.23)$$

³ If you try to put both electrons in excited states, one immediately drops to the ground state, releasing enough energy to knock the other one into continuum, leaving with a helium ion and a free electron.

6

Bibliography