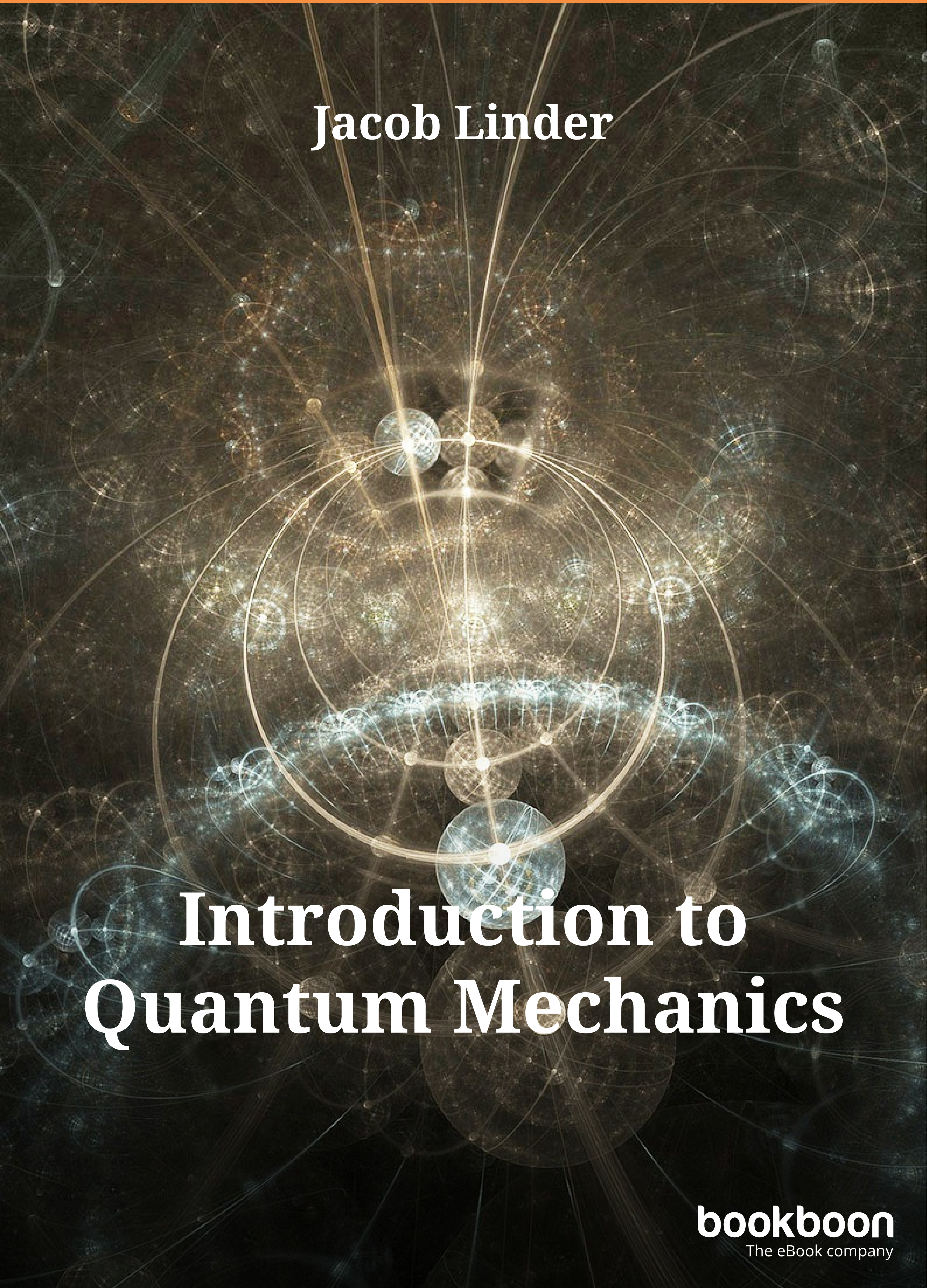

Jacob Linder

Introduction to Quantum Mechanics

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JACOB LINDER

INTRODUCTION TO QUANTUM MECHANICS

Introduction to Quantum Mechanics
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Preface

The aim of this book is to provide the reader with an introduction to quantum mechanics, a physical theory which serves as the foundation for some of the most central areas of physics ranging from condensed matter physics to astrophysics. The basic principles of quantum mechanics are explained along with important belonging theorems. We then proceed to discuss arguably the most central equation in quantum mechanics in detail, namely the Schrödinger equation, and how this may be solved and physically interpreted for various systems. A quantum treatment of particle scattering and the harmonic oscillator model is presented. The book covers how to deal with quantum mechanics in 3D systems and explains how quantum statistics and the Pauli principle give rise to exchange forces. Exchange forces have dramatic consequences experimentally and lie at the heart of phenomena such as ferromagnetism in materials. Finally, we apply quantum mechanics to the treatment of angular momentum operators, such as the electron spin, and also discuss how it may be applied to describe energy bands in solids.

This book is primarily based on my lecture notes from teaching quantum mechanics to undergraduate students, and the notes in turn are based on the book "Kvantemekanikk" by P. C. Hemmer which it follows closely in terms of structure. I have also included additional topics and instructive examples which hopefully will allow the reader to obtain a more thorough physical understanding of the material. This book is suitable as material for a full-semester course in introductory quantum mechanics and serves well as a precursor to the book "Intermediate Quantum Mechanics" which is also freely available to download on Bookboon.

It is my goal that students who study this book afterwards will find themselves well prepared to dig deeper into the remarkable world of theoretical physics at a more advanced level. I welcome feedback on the book (including any typos that you may find) and hope that you will have an exciting time reading it!

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About the author

J.L. holds a position as Professor of Physics at the Norwegian University of Science and Technology. His research is focused on theoretical quantum condensed matter physics and he has received several prizes for his Ph.D work on the interplay between superconductivity and magnetism. He has also received the American Physical Society "Outstanding Referee" award, selected among over 60.000 active referees. In teaching courses such as Quantum Mechanics, Classical Mechanics, and Particle Physics for both undergraduate and graduate students, he has invariably received high scores from the students for his pedagogical qualities and lectures. His webpage is found here. He has also written the books Intermediate Quantum Mechanics, Introduction to Lagrangian & Hamiltonian Mechanics, and Introduction to Particle Physics which are freely available to download on Bookboon.

I. A BRIEF HISTORICAL NOTE ON THE ORIGIN OF QUANTUM MECHANICS

Learning goals. After reading this chapter, the student should:

- Be able to describe shortcomings of classical physics in describing experimentally observable behavior in physical systems.
- Know specifically a few key experiments which paved the way for quantum mechanics becoming an accepted physical theory.

Physics is, ultimately, an experimental science in the sense that what is true about the world around us is determined by observation and measurements. However, that does not mean that theory is obsolete. Far from it, theoretical physics is indispensible in the task of understanding the behavior of nature because it both (i) predicts new phenomena which may subsequently be experimentally verified and (ii) explains new experimental measurements which are not yet understood. A theory can only be regarded as (potentially) correct as long as it is consistent with experimental measurements. It was for this reason that the demise of classical physics (although it certainly still has it uses on the macroscopic scale) started to become apparent at the end of the 19th century. A set of experimental measurements were reported which were inconsistent with the predictions of classical physics. Hence, a need was established for a new theory that would be consistent with the experimental observations. This was the seed that at the beginning of the 20th century eventually would grow into the theory of quantum physics.

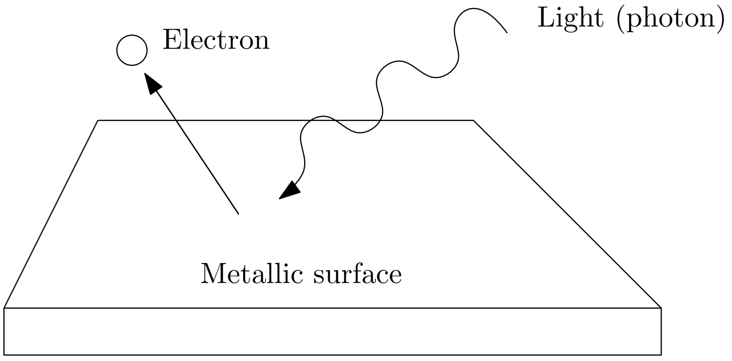
A. The insuffiency of classical physics

We here mention some of the experimental findings which provided the mounting evidence that classical physics was insufficient to describe observable phenomena.

The photoelectric effect
This effect consists of electrons being knocked out of a material, typically a metal, by light hitting the material surface. Classically, light is described as an electromagnetic field with an energy proportional to the intensity of the field. However, what was observed experimentally was that the energy of the electrons excited from the material was independent on the intensity of the light. Instead, the energy depended on the frequency ν of the light as long as the frequency was larger than a threshold ν_0. One found that the energy of the electron was described by:

$$E_{\text{electron}} = h(\nu - \nu_0), \tag{1.1}$$

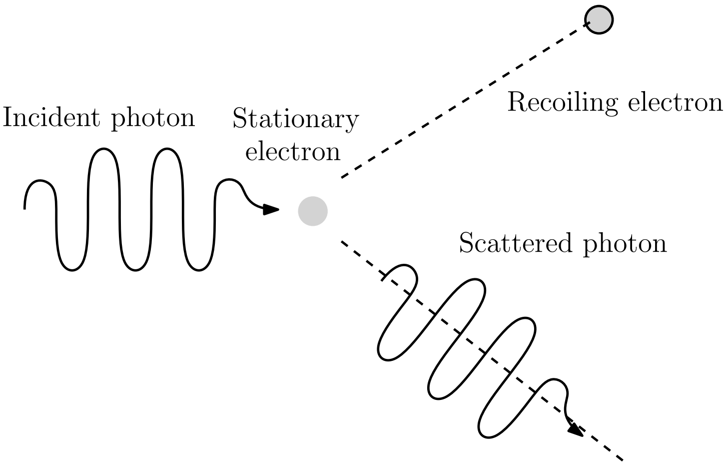
as long as $\nu > \nu_0$. Here, h is Planck's constant. This result could not be explained classically. Einstein, on the other hand, suggested that the photoelectric effect could be explained if one assumed that light instead consisted of discrete quanta of energy, namely *photons*, which each carried an energy $E = h\nu$. An electron on the surface of the metal could then absorb a photon and increase its kinetic energy. If a sufficient amount of energy was absorbed in this way, exceeding the threshold energy required to separate the electron from the metal, the electron would be knocked out of the material, as shown in the figure.



It is important to note that quantization of energy described above was in fact noted by Planck in 1900, prior to Einstein, an achievement he received the Nobel prize in physics for in 1918. Planck had presented the idea of energy quantization in the context of black body radiation, a bold idea which also resolved a discrepancy between classical physics (which predicted a divergent release of energy for a black body) and experimental measurements.

Compton-effect

As if the quantization of the energy of light was not radical enough, an experiment conducted by Compton in 1923 demonstrated yet another surprising property of light: it could behave as a particle rather than a wave. Using X-rays, Compton showed that the incident light would change direction after scattering on a thin sheet of a material in such a manner that the interaction between light and the electrons in the material could be interpreted as a collision between two particles. In other words, the experimental results could be explained by treating light as a particle (photon) with energy $E = h\nu$ and momentum $p = h\nu/c$ and then simply using the conservation laws for energy and momentum, as shown in the figure. One should emphasize that this results does not invalidate the interpretation of light having wave nature, as is clearly demonstrated by *e.g.* diffraction or interference experiments. However, it does show that light exhibits a *particle-wave duality*: depending on the precise experimental setup, it can display the properties of a wave or a particle.

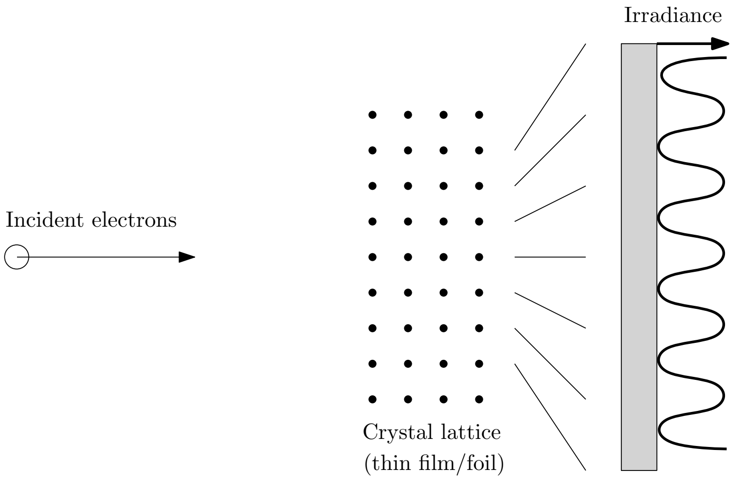


The wavenature of electrons

Light, classically thought of as a wave, can behave as a particle. Is it then possible that an electron, classically thought of as a particle, can behave as a wave? We noted above the momentum associated with the photon was $p = h\nu/c$, meaning that its wavelength $\lambda = c/\nu$ relates to momentum according to $\lambda = h/p$. It was de Broglie who suggested that this relation was not unique for photons, but that it was in fact universally valid even for particles. This necessarily implied that massive particles, such as electrons, would also have an accompanying wavelength λ determined by their momentum p. In his honor, this λ was named the de Broglie wavelength. Although an interesting idea in itself, nothing less than clear experimental proof would be sufficient to confirm this hypothesis. Remarkably, such an experiment was conducted by Davisson and Germer as well as Thomson (all who received the Nobel prize in physics in 1937) which decisively proved the wavenature of electrons. The actual experiment consisted of sending a beam of electrons toward thin films consisting of gold and observing the spatial distribution of electrons emerging on the other side of the film. The scientists observed that the electron distribution pattern was consistent with an interference of waves with a magnitude of the wavelength λ matching the prediction of de Broglie. Mathematically, the interference pattern could be explained by assigning a wavefunction Ψ to the electron:

$$\Psi(\boldsymbol{r}, t) = \Psi_0 \mathrm{e}^{\mathrm{i}(\boldsymbol{p}\cdot\boldsymbol{r} - Et)/\hbar} \tag{1.2}$$

where Ψ_0 is the amplitude of the wave, $\boldsymbol{r}$ is position, t is time, E is the energy of the electron, $\boldsymbol{p}$ is its momentum, and $\hbar = h/2\pi$ is Planck's reduced constant. Moreover, later experiments verified that this effect did not depend on having a large ensemble of electrons incident on a scattering target (such as a film). The electron interference pattern also occurred when single electrons were allowed to scatter, one at a time. In this case, the only possible physical interpretation is that the electron wavefunction actually interferes with itself! We shall later develop the mathematical formalism which shows precisely how this is possible.



Summarizing thus far, the fact that a number of experimental findings were found to be inconsistent with the predictions of classical physics strongly motivated the need to develop a new theory capable of making correct predictions. This is how quantum mechanics was born and consequently developed during the first part of the 20th century by many great physicists such as (in addition to those mentioned above) Bohr, Dirac, Heisenberg, Schrödinger, and many others.

II. FUNDAMENTAL PRINCIPLES AND THEOREMS IN QUANTUM MECHANICS

Learning goals. After reading this chapter, the student should:

- Understand some of the consequences of describing particles as waves and how this is done mathematically in quantum mechanics.
- Know the basic postulates of quantum mechanics and how to set up and approach an eigenvalue problem for a physical quantity F and its belonging operator $\hat{F}$.
- Understand how to compute probability densities and currents from wavefunctions ψ and interpret these physically.
- Know how to compute the time-evolution of expectation values and how to explain Heisenberg's uncertainty principle.

Before establishing the fundamental axioms which quantum mechanics is based on, we will briefly motivate the mathematical form of the Schrödinger equation - probably the most important equation in quantum mechanics. One should also note that quantum mechanics can in fact be formulated in different representations such as the position space representation or the momentum-space representation. To learn quantum mechanics, it is often most convenient to use the position-space representation as it is easier to have an intuitive idea of what happens in the regular position space that we live in rather than a more abstract type of space. However, there exists a more general formulation of quantum mechanics which is both more elegant and powerful to work with, which is covered in detail here.

A. Describing particles as waves

The diffraction experiments done with electron beams described in the previous chapter clearly demonstrated the wavenature of electrons. But how do we describe this mathematically? The simplest type of waves are cosine and sine functions, and it thus seems tempting to use a plane-wave such as Eq. (1.2) to represent a free particle propagating through space. However, a plane-wave is completely delocalized because it extends over the entire space: there is no part of the function which causes it to behave qualitatively different in one part of space compared to another (for instance, being suppressed in one space and finite somewhere else). The very concept of a particle is usually taken to mean an object which is localized in space. This can, however, be achieved by using a *superposition of plane-waves* (a so-called wavepacket) such as those in Eq. (1.2). Namely, we may use

$$\Psi(\boldsymbol{r},t) = (2\pi\hbar)^{-3/2}\int \zeta(\boldsymbol{p})\mathrm{e}^{\mathrm{i}(\boldsymbol{p}\cdot\boldsymbol{r}-Et)/\hbar}d\boldsymbol{p}. \tag{2.1}$$

The prefactor of $(2\pi\hbar)^{-3/2}$ has been chosen for the purpose of convenience, as will become clear later on. The energy for a non-relativistic, free particle is given by $E = p^2/2m$ and the function $\zeta(\boldsymbol{p})$ determines the "weight" of the contribution from momentum $\boldsymbol{p}$ to the total wavefunction Ψ. It is also instructive to distinguish between the phase-velocity v_p and the group-velocity v_g associated with the wavepacket in Eq. (2.1). The phase-velocity is defined by

$$v_p = \frac{\omega}{k} \tag{2.2}$$

where ω is the frequency of the wave while k is its wavenumber. Therefore, $v_p = \omega/k = E/p = p/2m$. The group velocity, on the other hand, is in general different as it is defined via:

$$v_g = \frac{d\omega}{dk} \tag{2.3}$$

which means that $v_g = d\omega/dk = dE/dp = p/m$.

The shape of $\zeta(\boldsymbol{p})$ determines the precise form of the wavefunction $\Psi(\boldsymbol{r}, t)$ that describes the particle under consideration. Depending on the system which the particle is part of, and what type of interactions it is subject to, we should expect $\Psi(\boldsymbol{r}, t)$ to look very different from a simple plane-wave. However, just as the behavior of viscous fluids is determined by the Navier-Stokes equations regardless of the exact details of the system, it seems reasonable that in the same way there should exist an equation governing the behavior of all such wavefunctions Ψ. The precise form of Ψ should certainly depend on the specific system considered, but they should all have in common that they satisfy some type of general quantum mechanical wave equation (just like viscous fluids all have in common that they satisfy the Navier-Stokes equations). Which equation would this be, then? To see which equation our Ψ satisfies, we first note that

$$\begin{aligned}\frac{\partial \Psi}{\partial t} &= \frac{\mathrm{i}}{\hbar}(2\pi\hbar)^{-3/2}\frac{\hbar^2}{2m}\nabla^2 \int \zeta(\boldsymbol{p})\mathrm{e}^{\mathrm{i}(\boldsymbol{p}\cdot\boldsymbol{r}-Et)/\hbar}d\boldsymbol{p} \\ &= \frac{\mathrm{i}}{\hbar}\frac{\hbar^2}{2m}\nabla^2\Psi. \end{aligned} \tag{2.4}$$

Here, we have introduced the Laplace-operator

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{2.5}$$

Therefore, our wavefunction Ψ satisfies the equation:

$$\mathrm{i}\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi. \tag{2.6}$$

This equation is known as the *Schrödinger-equation* (abbreviated SE) for a free particle. An important quality of this equation is that it is linear and first order in time. This means that is is sufficient for us to know Ψ at one single instant $t = t_0$ in order to determine Ψ at any later time t.

Moreover, we note that the ∇^2 part of the equation arose because $E = p^2/2m$ was brought down from the exponent as we differentiated with respect to time. Therefore, if we define the *momentum operator*

$$\hat{\boldsymbol{p}} \equiv \frac{\hbar}{\mathrm{i}}\nabla, \tag{2.7}$$

so that for instance $\hat{p}_x = (\hbar/\mathrm{i})\partial_x$, we can rewrite the SE for a free particle as

$$\mathrm{i}\hbar\frac{\partial \Psi}{\partial t} = \frac{\hat{\boldsymbol{p}}}{2m}\Psi. \tag{2.8}$$

What about a particle that is not free? If the particle is moving in a potential $V(\boldsymbol{r})$, it may for instance be bound to a certain region if the potential is strongly attractive in that region of space. For a free particle, we know that the Hamiltonian contains purely kinetic energy so that $H = p^2/2m$. Now, we just established that for such a free particle is Eq. (2.8), which may be rewritten as:

$$\boxed{\mathrm{i}\hbar\frac{\partial \Psi}{\partial t} = H\Psi.}$$

If a potential energy V is now present, so that $H = p^2/2m + V(\boldsymbol{r})$. If you are not familiar with the concept of a Hamiltonian, which is present also in classical physics, please have a look here for a detailed description. Based on the above, it might be reasonable to suspect that the boxed equation is valid also when V is present so that H can depend on $\boldsymbol{r}$ through $V = V(\boldsymbol{r})$. Although we could not know *a priori* that this is the case, experiments conclusively show that this is in fact true. A non-relativistic particle moving in a potential $V(\boldsymbol{r})$, so that the full Hamiltonian reads $H = p^2/2m + V$, is described by a wavefunction that satisfies the boxed equation above. Solving this equation for a number of scenarios will be our concern in the next chapter.

B. The postulates of quantum mechanics

We now deal with the fundamental postulates which quantum mechanics are based on. Their validity cannot be proven, but must be tested against experimental facts. Quantum mechanics has withstood this test thus far.

Postulate 1. To any observable quantity F, there exists a quantum mechanical operator known as $\hat{F}$. Let q and p be generalized coordinates and momenta in classical mechanics. If the observable quantity depends on these coordinates, $F = F(q_1, q_2, \ldots p_1, p_2 \ldots)$, the operator $\hat{F}$ depends on the operators $\hat{q}$ and $\hat{p}$ defined as:

$$\hat{q}_n = q_n,\ \hat{p}_n = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial q_n}. \tag{2.9}$$

Note that since $\hat{p}$ acts on q_n, the order in which the operators appear is important. The order of the operators must be such that the operator $\hat{F}$ is Hermitian. We shall return to what this means later. In most systems to be considered in this book, q_n may be taken to be a Cartesian coordinate whereas p_n is the belonging momentum $m\dot{q}_n$.

Postulate 2. The physical state of a system is described by a wavefunction Ψ, which depends on the generalized coordinates q_n and time t. The wavefunction satisfies the Schrödinger equation

$$\mathrm{i}\hbar\partial_t\Psi = \hat{H}\Psi \tag{2.10}$$

where $\hat{H}$ is the Hamilton-operator of the system. The Hamilton-operator is constructed from the system's classical Hamiltonian $H = H(q_n, p_n)$ by performing $q_n \to \hat{q}_n$ and $p_n \to \hat{p}_n$. The classical Hamiltonian is generally (although exceptions exist) a function which provides the energy of the system. Equation (2.10) is known as the *time-dependent SE*, which distinguishes it from an equation we shall encounter later, namely the time-independent SE.

Postulate 3. The expectation value for an observable quantity F is computed via the integral:

$$\langle F\rangle = \int \Psi^* \hat{F}\Psi d\boldsymbol{r}. \tag{2.11}$$

Here, Ψ^* is the complex conjugate of Ψ whereas $d\boldsymbol{r} = dq_1 dq_2 \ldots$ is a generalized volume element so that the integral is taken over all allowed values of the generalized coordinates q_n. For instance, if the observable quantity under consideration is the position of a particle moving in one dimension, we have $F = x$. We then find that

$$\langle x\rangle = \int x|\Psi(x)|^2 dx. \tag{2.12}$$

The expectation value of a quantity is a statistical quantity: it may be thought of as the average value obtained if one were to independently measure F many times. The expression for $\langle x\rangle$ above suggests that $|\Psi|^2$ acts as a function which weights how probable a particular value x is. This is precisely the probability interpretation of the wavefunction Ψ put forward by Max Born in 1926, namely that:

The probability of locating a particle in a volume $d\boldsymbol{r}$ centered around position $\boldsymbol{r}$ at a time t is $|\Psi(\boldsymbol{r},t)|^2 d\boldsymbol{r}$.

The probability density ρ is then $\rho = |\Psi(\boldsymbol{r},t)|^2$, which clearly satisfies the requirement that such a probability must be non-negative $(\rho \geq 0)$. Moreover, the total probability of finding the particle at some point in space must be 1, so that $\int |\Psi(\boldsymbol{r},t)| d\boldsymbol{r} = 1$. This can be ensured by *normalizing* the wavefunction properly, which we will discuss in more detail later.

Postulate 4. Measuring an observable quantity F can only provide as a result one of the eigenvalues f_n of the operator $\hat{F}$. If one measures F and obtains the result f_n, the system is immediately after the measurement in the eigenstate ξ_n of $\hat{F}$ which corresponds to the eigenvalue f_n. This means that

$$\hat{F}\xi_n = f_n \xi_n \tag{2.13}$$

where f_n is a scalar.

Hermitian operators

Performing an experimental measurement on a physical quantity can only provide a real (as opposed to imaginary or complex) number. Therefore, the expectation value of a physical quantity F must satisfy

$$\langle F\rangle = \langle F\rangle^*. \tag{2.14}$$

We now show that this is equivalent to the corresponding operator $\hat{F}$ being *Hermitian*. The definition of such an operator is that

$$\int \Psi_1^* \hat{F}\Psi_2 dV = \int \Psi_2 (\hat{F}\Psi_1)^* dV \tag{2.15}$$

for any wavefunctions $\Psi_{1,2}$. We immediately see that this is consistent with the expectation value of F being real for a system described by a wavefunction Ψ since

$$\langle F\rangle = \langle F\rangle^* \to \int \Psi^* \hat{F}\Psi dV = \int \Psi(\hat{F}\Psi)^* dV, \tag{2.16}$$

which is satisfied for $\Psi_1 = \Psi_2$ in Eq. (2.15). In fact, one can show (try it!) that the definitions of a Hermitian operator in Eq. (2.15) and Eq. (2.16), respectively, are in fact equivalent (show this by setting $\Psi = \Psi_1 + \Psi_2 e^{i\phi}$ with $\phi \in \Re$).

A Hermitian operator is also referred to as a self-adjoint operator. In general, the adjoint operator to $\hat{F}$ is denoted $\hat{F}^\dagger$ and is defined by

$$\int \Psi_1^* \hat{F}^\dagger \Psi_2 dV = \int \Psi_2 (\hat{F}\Psi_1)^* dV. \tag{2.17}$$

A self-adjoint operator satisfies $\hat{F} = \hat{F}^\dagger$, which is seen to be the case for a Hermitian operator. Using Eq. (2.17), one can prove that the adjoint of a product of operators exchanges the order of them:

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger. \tag{2.18}$$

Example 1. Physical quantities and their operators. We have previously stated that the momentum operator in one dimension is

$$\hat{p}_x = \frac{\hbar}{\mathrm{i}}\partial_x. \tag{2.19}$$

To check whether or not $\hat{p}_x$ is Hermitian, we note that

$$\int_{-\infty}^{\infty} \Psi_1^* \frac{\hbar}{\mathrm{i}}\partial_x \Psi_2 dx = \frac{\hbar}{\mathrm{i}}[\Psi_1^*\Psi_2]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \Psi_2 \frac{\hbar}{\mathrm{i}}\partial_x \Psi_1^* dx \tag{2.20}$$

where we used a partial integration. Now, the second term on the right hand side of the above equation is zero if the wavefunction vanishes at $x \to \pm\infty$. A physically realizable wavefunction should satisfy this, and we may thus set this so-called surface term to zero. By noting that $-\frac{\hbar}{\mathrm{i}}\partial_x = \hat{p}_x^*$, we see that

$$\int \Psi_1^* \hat{p}_x \Psi_2 dx = \int \Psi_2 (\hat{p}_x \Psi_1)^* dx. \tag{2.21}$$

We have thus proven that $\hat{p}_x$ is Hermitian, as it should be: $\hat{p}_x = \hat{p}_x^\dagger$. Note, however, that $\hat{p}_x^* \neq \hat{p}_x^\dagger$. The adjoint operation † is thus not the same as complex conjugation * for operators, in general.

Any function of position alone, such as a potential energy $V(\boldsymbol{r})$, can trivially be seen to satisfy the requirement of a Hermitian operator. This is because $\hat{V} = V(\boldsymbol{r})$ is a scalar (as opposed to an operator, such as $\hat{p}_x$), and scalars commute with other scalars such as $\Psi_{1,2}$.

As mentioned in **Postulate 1**, the order of quantum mechanical operators is important. We see that $x\hat{p}_x \neq \hat{p}_x x$, as can be verified by noting that

$$x\hat{p}_x F(x) = x\frac{\hbar}{\mathrm{i}}\partial_x F \tag{2.22}$$

while

$$\hat{p}_x x F(x) = \frac{\hbar}{\mathrm{i}}\partial_x(xF) = \frac{\hbar}{\mathrm{i}}(F + x\partial_x F). \tag{2.23}$$

It follows that when $x\hat{p}_x - \hat{p}_x x$ acts on a function F, it has the same effect as multiplying F with $\mathrm{i}\hbar$:

$$x\hat{p}_x - \hat{p}_x x = \mathrm{i}\hbar \tag{2.24}$$

This example demonstrates the importance of the order in which two quantum mechanical operators act on a wavefunction. If the operators are such that the order does not matter, then the operators *commute*. Above, we showed that $\hat{x}$ and $\hat{p}_x$ do not commute. The commutator between two operators $\hat{x}$ and $\hat{p}_x$ is written as

$$\hat{x}\hat{p}_x - \hat{p}_x\hat{x} \equiv [\hat{x}, \hat{p}_x]. \tag{2.25}$$

Whereas we have shown that $[\hat{x}, \hat{p}_x] = \mathrm{i}\hbar$, it can easily be verified that $\hat{x}$ and $\hat{p}_y$ commute. More generally, we have that

$$[\hat{q}_m, \hat{p}_n] = \mathrm{i}\hbar\delta_{mn}. \tag{2.26}$$

Here, δ_{mn} is the Kronecker delta function which is equal to 1 if $m = n$ whereas it is equal to 0 if $m \neq n$. An interesting point is that a particular combination of physical quantities, such as xp_x, is not automatically Hermitian quantum mechanically if one simply represents it as $\hat{x}\hat{p}_x$ (try to verify this). The resolution to this apparent dilemma is that although $xp_x = \frac{1}{2}(xp_x + p_x x)$ classically, since both p_x and x are scalars, the corresponding operators are not equal quantum mechanically: $\hat{x}\hat{p}_x \neq \frac{1}{2}(\hat{x}\hat{p}_x + \hat{p}_x\hat{x})$. In fact, the combination $\frac{1}{2}(\hat{x}\hat{p}_x + \hat{p}_x\hat{x})$ is indeed Hermitian and must therefore be the appropriate quantum mechanical operator corresponding to the classical quantity xp_x.

C. Eigenvalues and eigenfunctions

When an operator $\hat{F}$ acts on a function ξ, the result is not in general proportional to the function ξ itself. If it is, however, we say that ξ is an *eigenfunction* of the operator $\hat{F}$. More specifically, if

$$\hat{F}\xi_n = f_n\xi_n, \tag{2.27}$$

then ξ_n is an eigenfunction of $\hat{F}$ with a belonging *eigenvalue* f_n. The spectrum of eigenvalues $\{f_n\}$ can be either discrete or continuous, or even a mix. For instance, a free particle has a continuous energy eigenvalue spectrum whereas the energy eigenvalues for the hydrogen atoms is a mixture of discrete and continuous. In order to correspond to a physically acceptable eigenfunction, ξ_n has to satisfy certain mathematical requirements. A central concept related to this is if ξ is quadratically integrable, in which case it satisfies

$$\int_{-\infty}^{\infty} |\xi|^2 dx < \infty. \tag{2.28}$$

This is of particular relevance for a discrete eigenvalue spectrum, because for an eigenvalue spectrum that is continuous the eigenfunctions are not in general quadratically integrable. An example of this is the momentum operator $\hat{p}_x$, which has the following eigenvalue equation:

$$\hat{p}_x\xi = \frac{\hbar}{\mathrm{i}}\partial_x\xi = f\xi. \tag{2.29}$$

The solution to this equation is straightforward to obtain:

$$\xi = \xi_0 \mathrm{e}^{\mathrm{i}fx/\hbar}. \tag{2.30}$$

Now, the eigenvalue f has to be real in order to avoid ξ diverging as $x \to \pm\infty$. But in that case, $|\xi|^2$ is not quadratically integrable as can be verified by direct insertion into Eq. (2.28). Unlike the case of a discrete eigenvalue spectrum, where we could have chosen the constant prefactor in a manner that normalizes the wavefunction (meaning it satisfies $\int_{-\infty}^{\infty}|\xi|^2dx = 1$), we have to normalize the eigenfunction in Eq. (2.30) in a different manner. We return to this issue a bit later in this chapter.

If a system is in an eigenstate Ψ_n of an operator $\hat{F}$ with a belonging eigenvalue f_n, then a measurement of the physical quantity F will with certainty yield the result $F = f_n$. First, recall that for a Hermitian operator (which all physical quantities must be represented by), the eigenvalues f_n are always real. Assume now that Ψ_n is normalized, in which case:

$$\int \Psi_n^*\hat{F}\Psi_n d\boldsymbol{r} = f_n \int \Psi_n^*\Psi_n d\boldsymbol{r} = f_n. \tag{2.31}$$

We see that f_n is the expectation value $\langle F\rangle$ according to **Postulate 3**, but to prove that a measurement of F can *only* yield f_n as a result we have to show that there is no statistical variance around this expectation value. This is proven by noting that

$$\langle(F-\langle F\rangle)^2\rangle = \langle(F-f_n)^2\rangle = \int \Psi_n^*(\hat{F}-f_n)^2\Psi_n d\boldsymbol{r} \quad = \int \Psi_n^*(\hat{F}-f_n)(\hat{F}-f_n)\Psi_n d\boldsymbol{r} = 0 \tag{2.32}$$

since $(\hat{F}-f_n)\Psi_n = (f_n - f_n)\Psi_n = 0$.

Another useful result is that eigenfunctions belonging to different eigenvalues are guaranteed to be *orthogonal* for a Hermitian operator: $\int \Psi_m^*\Psi_n = 0$. To see this, assume first that we consider two eigenvalues which are different, $f_m \neq f_n$. It follows that

$$\int \Psi_n^*\hat{F}\Psi_m d\boldsymbol{r} = \int \Psi_m(\hat{F}\Psi_n)^* d\boldsymbol{r} \tag{2.33}$$

since $\hat{F}$ is Hermitian. Moving the right hand side over to the left hand side of the above equation produces

$$(f_m - f_n)\int \Psi_n^*\Psi_m = 0 \tag{2.34}$$

since f_n is real, which completes the proof. Generally, the integral

$$\int \Psi_m^*\Psi_n \equiv \langle\Psi_m, \Psi_n\rangle \tag{2.35}$$

is referred to as the scalar product of the functions Ψ_m and Ψ_n. The notation with the brackets on the right hand side is often used in the literature to denote this particular integral, and direct inspection shows that we have for instance $\langle\Psi_n, \Psi_m\rangle^* = \langle\Psi_m, \Psi_n\rangle$.

In some systems, there are several independent eigenfunctions $\Psi_1, \Psi_2, \ldots \Psi_g$ associated with one particular eigenvalue f. In that case, we have to revise the proof we sketched above regarding orthogonality of the wavefunctions. The eigenvalue f is said to be degenerate with a degree of degeneracy g. Although the eigenfunctions $\{\Psi_i\}$ may not automatically be orthonormal (i.e. both normalized and orthogonal) according to $\int \Psi_m^*\Psi_n \neq \delta_{mn}$, we can still create a set of linear combinations of these eigenfunctions $\{\tilde{\Psi}_i\}$ which are orthonormal. The procedure which accomplishes this is a familiar method from linear algebra known as Gram-Schmidt orthogonalization. The key point here is that even when an eigenvalue is degenerate, a set of orthonormalized eigenfunctions can be obtained.

We previously stated that eigenfunctions associated with a continuous eigenvalue spectrum could not be normalized using the Kronecker delta-function. This was the case for *e.g.* the eigenfunctions of the momentum operator $\hat{p}_x$, which for an eigenvalue f could be written as $\Psi_f = \Psi_0 \mathrm{e}^{\mathrm{i}fx/\hbar}$ (we changed the notation from ξ to Ψ here, but the choice of symbol naturally does not have any consequence physically). However, we can normalize the eigenfunctions in a different manner, namely

$$\int \Psi^*_{f'}\Psi_f d\boldsymbol{r} = \delta(f - f') \tag{2.36}$$

where we have introduced Dirac's delta-function $\delta(x)$. This function can be thought of being infinitely thin, but simultaneously infinitely large, in such a manner that its integral still is well-defined and normalized to 1:

$$\int_{-\infty}^{\infty} \delta(x)dx = 1. \tag{2.37}$$

In effect, $\delta(x) \to \infty$ for $x = 0$ and $\delta(x) = 0$ for $x \neq 0$. It also satisfies:

$$\delta(cx) = \frac{\delta(x)}{|c|},\ \delta(x) = \delta(-x),\ x\delta(x) = 0,\ x\delta'(x) = -\delta(x), \tag{2.38}$$

where c is a scalar. Returning to the eigenfunctions for the momentum operator, we need to choose the integration constant Ψ_0 in a specific manner if we wish for Ψ to satisfy the normalization condition Eq. (2.36), namely $\Psi_0 = 1/\sqrt{2\pi\hbar}$. This follows from the integral representation of the delta-function, which reads

$$\delta(f - f') = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}(f-f')x}dx. \tag{2.39}$$

We mention in passing that there also exist other ways to formally define the delta-function in terms of an integral. We can now apply this procedure to a different operator which also has a continuous eigenvalue spectrum, namely the position operator $\hat{x} = x$. The eigenvalue equation takes the form

$$x\Psi_f(x) = f\Psi_f(x) \tag{2.40}$$

which is solved by $\Psi_f(x) = c\delta(x - f)$ where c is a constant. This can be verified using the property $y\delta(y) = 0$ that we listed in Eq. (2.38) with $y = x - f$. The remaining task is to determine what c has to be in order for Ψ_f to satisfy the Dirac delta-function normalization. Insertion yields:

$$\int \Psi^*_{f'}(x)\Psi_f(x)dx = |c|^2\int \delta(x - f')\delta(x - f)dx = |c|^2\delta(f - f'). \tag{2.41}$$

Thus, any complex number $c = \mathrm{e}^{\mathrm{i}\gamma}$ with $\gamma \in \Re$ will do the job (*e.g.* $c = 1$).

D. Expansion via eigenfunctions

In quantum mechanics, one often expands wavefunctions by using the eigenfunctions Ψ_n of a Hermitian operator, for instance the eigenfunctions of the Hamilton operator $\hat{H}$. We shall see examples of this later on in the book. A prerequisite for this, however, is that one must assume that the eigenfunctions for a Hermitian operator form a *complete set*. In practice, this means that any regular and quadratically integrable function $\xi(\boldsymbol{r})$ can be written as a superposition of the eigenfunctions Ψ_n:

$$\xi(\boldsymbol{r}) = \sum_n c_n\Psi_n(\boldsymbol{r}). \tag{2.42}$$

Assume first that the functions Ψ_n form an orthonormal set and that the eigenvalue spectrum is discrete. To identify what the expansion coefficients c_n are, we make use of the orthonormality $\int \Psi_m^* \Psi_n = \delta_{mn}$ by multiplying $\xi(\boldsymbol{r})$ with $\Psi_m^*(\boldsymbol{r})$ and integrating over all of space:

$$\int \Psi_m^*(\boldsymbol{r})\xi(\boldsymbol{r})d\boldsymbol{r} = \sum_n c_n \int \Psi_m^* \Psi_n = \sum_n c_n \delta_{mn} = c_m \tag{2.43}$$

so that

$$c_n = \int \Psi_n^*(\boldsymbol{r})\xi(\boldsymbol{r})d\boldsymbol{r}. \tag{2.44}$$

If we now insert Eq. (2.44) back into Eq. (2.42), we obtain the equation

$$\xi(\boldsymbol{r}) = \int \xi(\boldsymbol{r}') \sum_n \Psi_n^*(\boldsymbol{r}')\Psi_n(\boldsymbol{r})d\boldsymbol{r}' \tag{2.45}$$

which can only be true if:

$$\sum_n \Psi_n^*(\boldsymbol{r}')\Psi_n(\boldsymbol{r}) = \delta(\boldsymbol{r}' - \boldsymbol{r}). \tag{2.46}$$

This is the completeness relation for the eigenfunctions Ψ_n.

We may proceed in an equivalent manner if the starting point is a continuous spectrum of eigenvalues, with the exception that the arbitrary function $\xi(\boldsymbol{r})$ must now be represented via an integral over the eigenfunctions rather than a sum:

$$\xi(\boldsymbol{r}) = \int c(n)\Psi_n(\boldsymbol{r})dn. \tag{2.47}$$

The completeness relation in this case (try to show this using the same strategy as in the discrete spectrum case above) reads:

$$\int \Psi_n^*(\boldsymbol{r}')\Psi_n(\boldsymbol{r})dn = \delta(\boldsymbol{r}' - \boldsymbol{r}). \tag{2.48}$$

We verify directly that the eigenfunction set for the momentum operator $\hat{p}_x$ indeed satisfies this completeness relation, since

$$\frac{1}{2\pi\hbar}\int \mathrm{e}^{-\mathrm{i}fx'/\hbar}\mathrm{e}^{\mathrm{i}fx/\hbar}df = \delta(x - x'). \tag{2.49}$$

It is reasonable that the expansion coefficients c_n (in the discrete case) and $c(n)$ (in the continuous case) must be chosen mathematically in a specific manner in order for the linear combination of eigenfunctions to reproduce an arbitrary function ξ. But do the coefficients hold any deeper physical meaning? It turns out that they do. Consider a physical quantity F in a system which is described by a quantum mechanical wavefunction Ψ. Assume for concreteness that we are dealing with a discrete eigenvalue spectrum f_n for the belonging operator $\hat{F}$. We may then write the wavefunction Ψ describing the state as an expansion of the eigenfunctions of $\hat{F}$, called Ψ_n, according to our previous treatment:

$$\Psi = \sum_n c_n\Psi_n. \tag{2.50}$$

The expectation value of the quantity F depends on the expansion coefficients c_n, as seen via:

$$\begin{aligned}\langle F\rangle = \int \Psi^*\hat{F}\Psi d\boldsymbol{r} &= \sum_{nm} c_m^* c_n \int \Psi_m^* f_n \Psi_n d\boldsymbol{r} \\ &= \sum_{mn} c_m^* c_n f_n \delta_{mn} = \sum_n |c_n|^2 f_n.\end{aligned} \tag{2.51}$$

Recall now **Postulate 4** where we stated that a measurement of a quantity F can only yield one of the eigenvalues f_n of the operator $\hat{F}$. Since we have just shown that $\langle F\rangle = \sum_n |c_n|^2 f_n$, we can now offer a concrete physical interpretation of the coefficients c_n. The reason for this is that an expectation value is statistically defined as $\langle F\rangle = \sum_n P_n f_n$ where P_n is the probability for obtaining f_n. It follows that $P_n = |c_n|^2$, so that

The probability that a measurement of F yields f_n when the system is in the state Ψ is $|c_n|^2 = \left|\int \Psi_n^*\Psi d\boldsymbol{r}\right|^2$.

As a limiting case, we see that if Ψ is in fact a one particular eigenstate of $\hat{F}$, i.e. $\Psi = \Psi_m$, then $|c_n|^2 = \delta_{mn}$ and the probability for measuring the eigenvalue f_m is equal to unity, as it should. Generally, we must have that $\sum_n |c_n|^2 = 1$, which expresses conservation of probability. The calculation again proceeds in the same way for the scenario of a continuous spectrum, in which case we obtain

$$\langle F\rangle = \int\int df df' c^*(f)c(f')f' \int \Psi_f^*\Psi_{f'}d\boldsymbol{r} = \int df|c(f)|^2 f. \tag{2.52}$$

We may then state that

The probability of measuring F in the interval $(f, f + df)$ is $|c(f)|^2 df = \left|\int \Psi_f^*\Psi d\boldsymbol{r}\right|^2 df$.

An important case is $\hat{F} = \hat{x}$, i.e. the position operator. The eigenfunction was previously shown to be $\delta(x-f)$ in one spatial dimension: $x\delta(x-f) = f\delta(x-f)$. This gives the following expansion coefficients:

$$c(f) = \int \delta(x-f)\Psi(x)dx = \Psi(f). \tag{2.53}$$

According to our above physical interpretation of the expansion coefficients $c(f)$, it follows that $|\Psi(f)|^2 df$ is the probability to measure x in the interval $(f, f+df)$. Therefore, $|\Psi(x)|^2$ is the probability density for position x. In other words, the likelihood of finding a particle described by $\Psi(x)$ at position x is determined by the absolute value squared of the wavefunction $|\Psi(x)|^2$. This is a crucial result as it gives a concrete physical meaning to the magnitude of the wavefunction. We finally note that in the event of a spectrum containing both a discrete and continuous set of eigenvalues, one would have to expand $\xi(\boldsymbol{r})$ according to:

$$\xi(\boldsymbol{r}) = \sum_n c_n \Psi(\boldsymbol{r}) + \int c(f)\Psi_f(\boldsymbol{r})df. \tag{2.54}$$

E. Probability current and density

We showed in the above section that the spatial probability density ρ for a particle described by Ψ (meaning that Ψ is a solution of the Schrödinger equation) is given by

$$\boxed{\rho(\boldsymbol{r},t) = |\Psi(\boldsymbol{r},t)|^2.}$$

and that it is normalized to unity according to

$$\int \rho(\boldsymbol{r},t)d\boldsymbol{r} = 1. \tag{2.55}$$

Since the total probability Eq. (2.55) has to be conserved at all times t (the particle must always be *somewhere*), it follows that any change in probability for finding the particle at one specific location x must be accompanied by an increase in probability at a different location. This is expressed by the continuity equation for probability, which we now derive.

If the probability ρ increases in some volume V, there has to exist an accompanying probability current flowing into that volume through the surface $\mathcal{S}$ enclosing V. Denoting the surface density of this current $\boldsymbol{j}$, it follows that

$$\partial_t \int_V \rho d\boldsymbol{r} = -\int_{\mathcal{S}} (\boldsymbol{j}\cdot\boldsymbol{n})d\mathcal{S} \tag{2.56}$$

where $\boldsymbol{n}$ is a normal vector to the surface $\mathcal{S}$. Using the divergence theorem from calculus:

$$\int_V (\nabla\cdot\boldsymbol{j})d\boldsymbol{r} = \int_{\mathcal{S}} (\boldsymbol{j}\cdot\boldsymbol{n})d\mathcal{S} \tag{2.57}$$

we can rewrite Eq. (2.56) to:

$$\int_V (\partial_t\rho + \nabla\cdot\boldsymbol{j})d\boldsymbol{r} = 0. \tag{2.58}$$

When the integrand vanishes, rather than the entire integral, we are guaranteed that the flow of probability is conserved regardless of which volume V we consider. Therefore, the continuity equation takes the form:

$$\boxed{\partial_t\rho + \nabla\cdot\boldsymbol{j} = 0.}$$

The reader might recognize the form of this equation from classical electrodynamics, where an equivalent equation holds for the conservation of charge. The probability density has above been shown to equal $\rho = |\Psi|^2$ and we know that the wavefunction of the system satisfies the time-dependent SE $\mathrm{i}\hbar\partial_t\Psi = \hat{H}\Psi$. Generally, we know that $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V(\boldsymbol{r},t)\Psi$ so that:

$$\partial_t\rho = \partial_t(\Psi^*\Psi) = \Psi^*\partial_t\Psi + \Psi\partial_t\Psi^* = \frac{\mathrm{i}\hbar}{2m}(\Psi^*\nabla^2\Psi - \Psi\nabla^2\Psi^*). \tag{2.59}$$

We can rewrite this further by using that $ab'' - b''a = (ab' - b'a)'$ where $'$ denotes differentiation. Note also that the terms with $V(\boldsymbol{r},t)$ cancel each other. We obtain

$$\partial_t\rho = \frac{\mathrm{i}\hbar}{2}\nabla\cdot(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*) = -\nabla\cdot\mathrm{Re}\Big(\Psi^*\frac{\hbar}{\mathrm{i}m}\nabla\Psi\Big). \tag{2.60}$$

Comparing this to the boxed expression above, we are now able to identify the quantum mechanical probability current:

$$\boxed{\boldsymbol{j} = \mathrm{Re}\Big(\Psi^*\frac{\hbar}{\mathrm{i}m}\nabla\Psi\Big).}$$

We have then proven that the continuity equation for probability is consistent with the time-dependent SE and the interpretation of $|\Psi|^2$ as the probability density.

We close this chapter by demonstrating how the presence of an external magnetic field $\boldsymbol{B} = \nabla\times\boldsymbol{A}$ can be incorporated in the calculation. The quantity $\boldsymbol{A}$ is the vector potential, just as in classical mechanics. When $\boldsymbol{A}\neq 0$, it is known from classical mechanics that the Hamiltonian of the system becomes modified: the canonical momentum $\boldsymbol{p}$ must be replaced by $\boldsymbol{p} - q\boldsymbol{A}$ where q is the electric charge of the particle. This is necessary to obtain the correct equations of motion for the particle (and also of fundamental importance in order to achieve so-called *gauge invariance*, although we do not discuss this topic further here - a detailed treatment of this topic can be found here).

According to our prescription of how to write down the quantum mechanical Hamilton-operator based on the classical Hamiltonian, the time-dependent SE now takes the form:

$$\mathrm{i}\hbar\partial_t\Psi = \frac{(\hat{\boldsymbol{p}} - q\boldsymbol{A})^2}{2m}\Psi + V(\boldsymbol{r},t)\Psi. \tag{2.61}$$

We note that the presence of an electrostatic potential can also be included in the potentinal energy V. An important consequence of the way that $\boldsymbol{A}$ enters the Hamilton-operator is that it provides a direct coupling to the momentum $\hat{\boldsymbol{p}}$ of the charged particles through the terms $\propto \hat{\boldsymbol{p}}\boldsymbol{A} + \boldsymbol{A}\hat{\boldsymbol{p}}$ (as seen when writing out the square). By proceeding as we did above regarding the derivation of the probability current density (computing $\partial_t\rho$ via the time-dependent SE), we find the same continuity equation $\partial_t\rho + \nabla\cdot\boldsymbol{j} = 0$ where $\boldsymbol{j}$ now reads:

$$\boldsymbol{j} = \frac{1}{m}\mathrm{Re}\Big[\Psi^*\Big(\frac{\hbar}{\mathrm{i}}\nabla - q\boldsymbol{A}\Big)\Psi\Big]. \tag{2.62}$$

As demanded by consistency, Eq. (2.62) reduces to the correct result in the absence of a field, $\boldsymbol{A} \to 0$.

F. Simultaneous eigenfunctions

We have shown earlier that a physical quantity F has a sharply defined value f, i.e. with zero statistical variance, when the system is in an eigenstate ξ of the operator $\hat{F}$:

$$\hat{F}\xi = f\xi. \tag{2.63}$$

Consider now a different physical quantity G. Is it possible for F and G to simultaneously have sharply defined values? If so, the state of the system must be an eigenstate for $\hat{F}$ and $\hat{G}$ simultaneously:

$$\hat{F}\xi = f\xi \text{ and } \hat{G}\xi = g\xi. \tag{2.64}$$

If we act on the two equations with $\hat{F}$ and $\hat{G}$, respectively, and subtract them from each other, the result is:

$$(\hat{G}\hat{F} - \hat{F}\hat{G})\xi = [\hat{G},\hat{F}]\xi = 0 \tag{2.65}$$

since $\hat{G}\hat{F}\xi = fg\xi$ and $\hat{F}\hat{G}\xi = gf\xi$ where g and f are scalars that commute.

This observation becomes considerably more interesting if there exists a complete set of eigenfunctions ξ_n, rather than just one single function ξ, of $\hat{G}$ and $\hat{F}$. The reason for this is that we can, as before, then expand an arbitrary function ξ in the eigenfunctions ξ_n since the latter form a complete set. In this case, $[\hat{F},\hat{G}]\xi = 0$ holds true for *any function* ξ. It follows that the commutator itself must vanish, $[\hat{F},\hat{G}] = 0$. The conclusion is then that

Two physical quantities that always have sharply defined values simultaneously must have commuting operators.

In addition, the inverse statement also holds true: if two operators commute, we may find a common set of eigenfunctions for them. These statements hold both with and without degeneracy.

Consider for instance the case without degeneracy. Let ξ be an eigenfunction of $\hat{F}$ with eigenvalue f. Since $\hat{F}$ and $\hat{G}$ commute, we obtain $\hat{F}\hat{G}\xi = f\hat{G}\xi$. Therefore, the function $\hat{G}\xi$ must be an eigenfunction of $\hat{F}$ with eigenvalue f. Now, if f is not a degenerate eigenvalue, $\hat{G}\xi$ cannot be equal to ξ but must instead be distinct up to a multiplicative factor g. In effect, $G\xi = g\xi$. This means that ξ is indeed an eigenfunction of $\hat{G}$, and the proof is complete.

If the eigenvalue f is degenerate, there may exist several eigenfunctions ξ_j, $j = 1, 2, \ldots p$ associated with this eigenvalue. Therefore, we can no longer claim that $G\xi_j$ must be proportional to ξ_j. Instead, it will generally be a linear combination of all the p eigenfunctions:

$$\hat{G}\xi_j = \sum_{j=1}^{p} g_{ij}\xi_j. \tag{2.66}$$

However, it is still possible to identify a set of eigenfunctions ξ for $\hat{F}$ and $\hat{G}$ which themselves are linear combinations of ξ_j (try this!). The existence of such mutual eigenfunctions turns out to be quite handy in several scenarios. For instance, we will later demonstrate that the operators for energy E, the magnitude of the angular momentum squared $\boldsymbol{L}^2$, and one component of the angular momentum (*e.g.* L_z) all have a shared set of eigenfunctions for spherically symmetric potentials $V(\boldsymbol{r}) = V(r)$.

A practical example of two operators that can share a set of eigenfunctions is the Hamilton operator $\hat{H}$ and the parity operator $\hat{\mathcal{P}}$. The latter inverts the position vector, so that

$$\hat{\mathcal{P}}\psi(\boldsymbol{r}) = \psi(-\boldsymbol{r}). \tag{2.67}$$

To identify the spectrum of eigenvalues that $\hat{\mathcal{P}}$ can have, we consider its eigenvalue equation:

$$\hat{\mathcal{P}}\psi(\boldsymbol{r}) = P\psi(\boldsymbol{r}). \tag{2.68}$$

Acting with $\hat{\mathcal{P}}$ on this equation provides

$$\hat{\mathcal{P}}^2\psi(\boldsymbol{r}) = P^2\psi(\boldsymbol{r}). \tag{2.69}$$

However, acting twice with the parity operator should be tantamount to doing nothing, because the net effect of reversing the sign of $\boldsymbol{r}$ twice is $\boldsymbol{r} \to -\boldsymbol{r} \to \boldsymbol{r}$: we end up with what we started with. Therefore, $\hat{\mathcal{P}}^2\psi = \psi$, which means that $P^2 = 1$ must be satisfied. It is clear that two possibilities exist:

$$P = \begin{cases} +1 & \text{even parity} \\ -1 & \text{odd parity} \end{cases} \tag{2.70}$$

Now, if a Hamiltonian describing a system has inversion symmetry, it should not change upon performing the transformation $\boldsymbol{r} \to (-\boldsymbol{r})$. This means that $\hat{H}(\boldsymbol{r}) = \hat{H}(-\boldsymbol{r})$. If this is the case, we can prove that $\hat{H}$ commutes with $\hat{\mathcal{P}}$:

$$[\hat{\mathcal{P}}, \hat{H}(\boldsymbol{r})]\psi(\boldsymbol{r}) = \hat{\mathcal{P}}\hat{H}(\boldsymbol{r})\psi(\boldsymbol{r}) - \hat{H}(\boldsymbol{r})\hat{\mathcal{P}}\psi(\boldsymbol{r}) = \hat{H}(-\boldsymbol{r})\psi(-\boldsymbol{r}) - \hat{H}(\boldsymbol{r})\psi(-\boldsymbol{r}) = 0. \tag{2.71}$$

Since this holds regardless of ψ, the commutator itself must vanish so that $[\hat{\mathcal{P}}, \hat{H}] = 0$. According to our previous treatment, we then immediately know that it is possible to identify a set of mutual eigenfunctions for $\hat{\mathcal{P}}$ and $\hat{H}$. In the non-degenerate case, these states will automatically have a specific parity. This can be directly verified later when we will treat infinite potential wells by moving the potential to be centered around $x = 0$ so that the potential, and thus Hamilton-operator $\hat{H}$, is inversion symmetric [invariant under the transformation $x \to (-x)$].

G. Time-evolution of expectation values

We have seen how expectation values for physical quantities F are sharply defined and time-independent when we are fortunate enough that the state of the system is an eigenfunction of the operator $\hat{F}$. However, it is far from always that we have that luxury. Generally, quantum mechanical expectation values of physical quantities can be time-dependent and we should thus figure out how the expectation value of such *dynamical variables* evolve as a function of time t. The time-evolution of the expectation value

$$\langle F \rangle = \int \Psi^* \hat{F} \Psi d\boldsymbol{r} \tag{2.72}$$

can be identified using the time-dependent SE

$$\mathrm{i}\hbar\partial_t\Psi = \hat{H}\Psi \tag{2.73}$$

in the following manner [where we also make use of the fact that $\hat{H}$ is Hermitian, so that $\int(\hat{H}\Psi)^*\Phi d\boldsymbol{r} = \int \Psi^*\hat{H}\Phi d\boldsymbol{r}$]:

$$\begin{aligned}\frac{d}{dt}\langle F\rangle &= \int \partial_t\Psi^*\hat{F}\Psi d\boldsymbol{r} + \int \Psi^*\partial_t\hat{F}\Psi d\boldsymbol{r} + \int \Psi^*\hat{F}\partial_t\Psi d\boldsymbol{r} \\ &= \frac{\mathrm{i}}{\hbar}\int \Psi^*\hat{H}\hat{F}\Psi d\boldsymbol{r} + \int \Psi^*\partial_t\hat{F}\Psi d\boldsymbol{r} - \frac{\mathrm{i}}{\hbar}\int \Psi^*\hat{F}\hat{H}\Psi d\boldsymbol{r} \\ &= \frac{\mathrm{i}}{\hbar}\Psi^*[\hat{H},\hat{F}]\Psi d\boldsymbol{r} + \int \Psi^*\partial_t\hat{F}\Psi d\boldsymbol{r}. \end{aligned} \tag{2.74}$$

In other words, we have shown that

$$\boxed{\frac{d}{dt}\langle F\rangle = \frac{\mathrm{i}}{\hbar}\langle[\hat{H},\hat{F}]\rangle + \langle\partial_t\hat{F}\rangle.}$$

A central consequence of this equation is that if the operator $\hat{F}$ does not depend explicitly on time, so that $\partial_t\hat{F} = 0$, then it follows that its expectation value $\langle F\rangle$ will be time-independent so long as $\hat{F}$ commutes with $\hat{H}$. One then refers to F as a constant of motion, since it does not change with time. Consider for instance a free particle which simply has a kinetic energy: $\hat{H} = \hat{\boldsymbol{p}}^2/2m$. Classically, the momentum of this particle would be conserved as no forces (potential gradients) are present. Quantum mechanically, the same is true because the momentum operator $\hat{\boldsymbol{p}}$ commutes with this $\hat{H}$.

H. The Ehrenfest theorem

Although quantum mechanics replaces classical mechanics as the physically valid theory at small length-scales (such as the nanometer scale), we should still expect quantum mechanics to recover classical mechanics as a limiting case when going to larger length-scales (such as the macroscopic world that we experience). To test this, consider a moving particle. We will later comment specifically on how its size matters. The classical equations of motion for this particle is Newton's second law $d\boldsymbol{p}/dt = -\nabla V$ and the definition of momentum $d\boldsymbol{r}/dt = \boldsymbol{p}/m$. Does there now at least exist a set of equivalent quantum mechanical equations for the *expectation values* of the position $\langle\boldsymbol{r}\rangle$ and momentnum $\langle\boldsymbol{p}\rangle$?

As we know well by now, these are defined quantum mechanically as:

$$\langle \boldsymbol{r} \rangle = \int \Psi^* \boldsymbol{r} \Psi d\boldsymbol{r},\ \langle \boldsymbol{p} \rangle = \int \Psi^* \hat{\boldsymbol{p}} \Psi d\boldsymbol{r}. \tag{2.75}$$

Applying our formula in the box above for the time-evolution of a physical quantity, we obtain for the position variable that:

$$\frac{d}{dt}\langle \boldsymbol{r} \rangle = \frac{\mathrm{i}}{\hbar}\langle [\hat{H}, \boldsymbol{r}] \rangle = \frac{\mathrm{i}}{2m\hbar}\langle [\hat{\boldsymbol{p}}^2, \boldsymbol{r}] \rangle. \tag{2.76}$$

We obtained this resulting by using that the Hamilton operator for a particle moving in a potential V is $\hat{H} = \hat{\boldsymbol{p}}^2/2m + V(\boldsymbol{r}, t)$ and that $\boldsymbol{r}$ commutes with V. To evaluate the final commutator in Eq. (2.76), we only need to compute $[\hat{p}_x^2, x]$ since the result will be the same for the y and z components. We find that

$$[\hat{p}_x^2, x] = \hat{p}_x(\hat{p}_x x - x\hat{p}_x) + (\hat{p}_x x - x\hat{p}_x)\hat{p}_x = -2\mathrm{i}\hbar\hat{p}_x. \tag{2.77}$$

Here, we made use of the fundamental commutation relation between momentum and position $[x, \hat{p}_x] = \mathrm{i}\hbar$ that we established earlier in this book. Inserting this in Eq. (2.76), and the corresponding result for the y and z components, we obtain:

$$\frac{d}{dt}\langle \boldsymbol{r} \rangle = \langle \boldsymbol{p} \rangle / m. \tag{2.78}$$

We see that this indeed corresponds well with the classical result $d\boldsymbol{r}/dt = \boldsymbol{p}/m$. What about the equation of motion for $\langle \boldsymbol{p} \rangle$? We obtain:

$$\frac{d}{dt}\langle \boldsymbol{p} \rangle = \frac{\mathrm{i}}{\hbar}\langle [\hat{H}, \hat{\boldsymbol{p}}] \rangle = \frac{\mathrm{i}}{\hbar}\langle [V, \hat{\boldsymbol{p}}] \rangle, \tag{2.79}$$

where the kinetic term in $\hat{H}$ gives no contribution since it commutes with $\hat{\boldsymbol{p}}$ (an operator commutes with itself). It remains to evaluate $[V, \hat{\boldsymbol{p}}]$:

$$[V(\boldsymbol{r}, t), \hat{\boldsymbol{p}}]\Psi = -\mathrm{i}\hbar V \nabla \Psi + \mathrm{i}\hbar \nabla (V\Psi) = \mathrm{i}\hbar (\nabla V)\Psi. \tag{2.80}$$

The final result is then:

$$\frac{d}{dt}\langle \boldsymbol{p} \rangle = \langle -\nabla V \rangle, \tag{2.81}$$

again corresponding well to the classical Newton's second law. Ehrenfest's theorem can now be stated:

> The quantum mechanical equations of motion for the expectation value of position, momentum, and force are the same as the classical equations of motion for these quantities.

What is the difference between the quantum mechanical and classical predictions for these quantities, then? Moreover, we still have not commented on how the size of the particle plays a role in this. To gain further insight, we note that the expectation value $\langle \boldsymbol{F}(\boldsymbol{r}) \rangle$ of the force $\boldsymbol{F} = -\nabla V$ is *not necessarily the same* as the force evaluated at the expectation value of the position, $\boldsymbol{F}(\langle \boldsymbol{r} \rangle)$. Only if this had been the case could we have conluded that the particle would have followed the classical trajectory also in the quantum mechanical treatment. The difference between $\langle \boldsymbol{F}(\boldsymbol{r}) \rangle$ and $\boldsymbol{F}(\langle \boldsymbol{r} \rangle)$ can be evaluated quantitatively by expanding the force around the expectation value of the position (essentially a Taylor expansion). Consider the one-dimensional case for simplicity:

$$F(x) = F(\langle x \rangle) + (x - \langle x \rangle)F'(\langle x \rangle) + \frac{1}{2}(x - \langle x \rangle)^2 F''(\langle x \rangle) \ldots \tag{2.82}$$

Taking the expectation value of Eq. (2.82) yields:

$$\langle F(x) \rangle = F(\langle x \rangle) + \frac{1}{2}\langle (x - \langle x \rangle)^2 \rangle F''(\langle x \rangle) + \ldots \tag{2.83}$$

where the linear term in Eq. (2.82) vanished since $\langle x - \langle x \rangle \rangle = 0$.

Now, we can finally make a connection to the size of the particle/object in question. The point is that for macroscopic "particles" (say, a football), the standard deviation $\Delta x \equiv \langle (x - \langle x \rangle)^2 \rangle^{1/2}$, which according to Eq. (2.83) is precisely what causes the difference between $\langle F(x) \rangle$ and $F(\langle x \rangle)$, is vanishingly small. The reason for this is that Δx can, simply from its definition, be taken as a measure of the spatial extension of the quantum mechanical wave describing the particle, i.e. the de Broglie wavelength λ introduced previously. Macroscopic objects have extremely small wavelengths λ, much smaller than the physical object itself, and in this case classical mechanics works well.

What happens then for microscopically small objects, where quantum physics becomes important? It turns out that classical mechanics can actually be used as a starting approximation in some cases for microscopic objects as well. More specifically, this is allowed if the potential the object moves in varies extremely slowly compared to the de Broglie wavelength λ. If the potential does not vary slowly over a length-scale λ, a full quantum mechanical treatment is required and the particle will not follow its classical trajectory. A special mention of linear (*e.g.* the gravitation field close to the surface of Earth) and quadratic potentials (*e.g.* an idealized oscillating spring without damping) is required, because in those scenarios it follows that F'' and all higher order derivatives are identically equal to zero. In this case, it follows from Eq. (2.83) that $\langle F(x) \rangle = F(\langle x \rangle)$ so that the classical trajectory is obtained even quantum mechanically when computing $\langle \boldsymbol{r} \rangle$.

I. Heisenberg's uncertainty principle

We have seen that two physical quantities with operators that commute have sharply defined values simultaneously. If they do not commute, the standard deviation ΔF from the expectation value $\langle F \rangle$ is a sensible quantitative measure for the "spread" in value one would expect when measuring F many times:

$$\Delta F = \sqrt{\langle (F - \langle F \rangle)^2 \rangle}. \tag{2.84}$$

To be concrete, let us again consider the most fundamental example of two quantities that do not commute, namely position and momentum. It turns out that the degree to which these two quantities can be sharply defined simultaneously is limited via Heisenberg's uncertainty relation:

$$\boxed{\Delta x \Delta p_x \geq \hbar/2.}$$

We will prove this relation below, but let us first comment on how to interpret it. One consequence is that a wavefunction with a quite well-defined momentum (but still finite Δp_x) must have a very large spread Δx in position. This is certainly the case for a plane-wave which has a sharply defined momentum, $\Delta p_x = 0$, which in turn means that $\Delta x \to \infty$ since a plane-wave is completely delocalized and extends over all of space. Conversely, a strongly localized wavefunction with small variance Δx must have a large spread Δp_x in momentum.

Heisenberg's uncertainty principle is in fact just a special case of a more general result, namely:

$$\boxed{\Delta F \Delta G \geq \frac{1}{2} |\langle [\hat{F}, \hat{G}] \rangle|}$$

for two physical quantities F and G. Inserting $F = x$ and $G = p_x$ gives Heisenberg's uncertainty relation, but it remains to prove the general case. To do so, note first that the following integral cannot be negative:

$$\int |\hat{C}\Psi + \mathrm{i}\beta \hat{D}\Psi|^2 d\boldsymbol{r} \geq 0. \tag{2.85}$$

We have here introduced

$$\hat{C} = \hat{F} - \langle F \rangle, \ \hat{D} = \hat{G} - \langle G \rangle \tag{2.86}$$

and the constant $\beta \in \Re$. Note that the operators $\hat{C}$ and $\hat{D}$ are Hermitian if $\hat{F}$ and $\hat{G}$ are Hermitian, since the only difference is that a constant has been subtracted. If we now write the absolute value squared in Eq. (2.85) as the argument of the absolute value times its complex conjugate, we obtain

$$\int [(\hat{C}\Psi)^*\hat{C}\Psi + \alpha^2(\hat{D}\Psi)^*\hat{D}\Psi + \mathrm{i}\beta(\hat{C}\Psi)^*\hat{D}\Psi - \mathrm{i}\alpha(\hat{D}\Psi)^*\hat{C}\Psi]d\boldsymbol{r} \geq 0. \tag{2.87}$$

Using the Hermitian property of these operators, we can rewrite the above equation as:

$$\int \Psi^*[\hat{C}^2 + \beta^2\hat{D}^2 + \mathrm{i}\beta(\hat{C}\hat{D} - \hat{D}\hat{C})]\Psi d\boldsymbol{r} = \langle C^2\rangle + \beta^2\langle D\rangle^2 + \mathrm{i}\beta\langle[\hat{C},\hat{D}]\rangle \geq 0. \tag{2.88}$$

In spite of the presence of the imaginary number i in the last term of Eq. (2.88), we can be sure that that term is real since the original integral Eq. (2.85) must be real. Our treatment so far is completely independent on our particular choice of β. Choosing $\beta = -\frac{\mathrm{i}\langle[\hat{C},\hat{D}]\rangle}{2\langle D^2\rangle}$ gives us:

$$\langle C^2\rangle - \frac{\mathrm{i}\langle[\hat{C},\hat{D}]\rangle^2}{4\langle D\rangle^2} \geq 0. \tag{2.89}$$

If we now reinstate the physical quantities F and G we were interested in to begin with via the definitions of $\hat{C}$ and $\hat{D}$ in Eq. (2.86), we can rewrite Eq. (2.89) to

$$\Delta F \Delta G \geq \frac{1}{2}|\langle[\hat{F},\hat{G}]\rangle| \tag{2.90}$$

where we used that $\langle C^2\rangle = (\Delta F)^2$, $\langle D^2\rangle = (\Delta G)^2$, and $[\hat{C},\hat{D}] = [\hat{F},\hat{G}]$. We have thus proven the general uncertainty relation between the quantities F and G. As a special case, we recover our previous result that two commuting operators can have sharply defined values simultaneously since a vanishing right hand side of Eq. (2.90) allows for $\Delta F \Delta G = 0$.

III. SOLVING THE SCHRÖDINGER EQUATION: BOUND STATES AND SCATTERING

Learning goals. After reading this chapter, the student should:

- Know how to deal with the Schrödinger equation (SE) and stationary states.
- Understand how to obtain suitable boundary conditions for the wavefunction from the SE.
- Understand the concept of a superposition of states and collapse of the wavefunction upon measurement.
- Be able to compute bound energy states in potential wells.

A. Stationary states

Consider a scenario where the Hamiltonian, and thus the Hamilton-operator, does not depend explicitly on time t. In that case, the time-dependent SE we previously have introduced

$$\mathrm{i}\hbar\partial_t\Psi = \hat{H}\Psi \tag{3.1}$$

becomes a separable equation by setting $\Psi(\boldsymbol{r},t) = \psi(\boldsymbol{r})D(t)$. Inserting this into the SE gives:

$$\mathrm{i}\hbar\frac{1}{D(t)}\frac{dD(t)}{dt} = \frac{1}{\psi(\boldsymbol{r})}\hat{H}\psi(\boldsymbol{r}). \tag{3.2}$$

after dividing the entire equation with Ψ. Since the left side only depends on t whereas the right side only depends on $\boldsymbol{r}$, it follows that both sides of the equations must be a constant which we with remarkable foresight shall name E (we shall soon see why this is a suitable name for the constant, as it is in fact the energy). The equation for $D(t)$ then reads

$$\mathrm{i}\hbar\frac{1}{D(t)}\frac{dD(t)}{dt} = E \tag{3.3}$$

which has the solution

$$D(t) = D_0\mathrm{e}^{-\mathrm{i}Et/\hbar}. \tag{3.4}$$

The other equation reads

$$\boxed{\hat{H}\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})}$$

and is known as Schrödingers time-independent equation. The full wavefunction which solves the full time-dependent SE for a stationary system thus takes the form

$$\Psi(\boldsymbol{r},t) = \psi(\boldsymbol{r})\mathrm{e}^{-\mathrm{i}Et/\hbar}. \tag{3.5}$$

We absorbed the constant D_0 into $\psi(\boldsymbol{r})$. The reason this is referred to as a stationary system, is that the corresponding probability density $|\Psi(\boldsymbol{r},t)|^2 = |\psi(\boldsymbol{r})|^2$ is independent on time. Therefore, any expectation values for physical quantities that do not depend explicitly on time should also be time-independent:

$$\langle F\rangle = \int \Psi^*(\boldsymbol{r},t)\hat{F}\Psi(\boldsymbol{r},t) = \int \psi^*(\boldsymbol{r})\hat{F}(\boldsymbol{r},\hat{\boldsymbol{p}})\psi(\boldsymbol{r})d\boldsymbol{r}. \tag{3.6}$$

It is crucial to note that the wavefunction itself is *not* time-independent: it depends on time through the factor $\mathrm{e}^{-\mathrm{i}Et/\hbar}$.

The spatial part of the wavefunction Ψ is determined via the factor $\psi(\boldsymbol{r})$. In turn, this is obtained by solving the time-independent SE $\hat{H}\psi = E\psi$ which really is an eigenvalue equation. Consider for instance a particle moving in a potential $V(\boldsymbol{r})$, in which case it takes the form:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(\boldsymbol{r})\psi = E\psi(\boldsymbol{r}). \tag{3.7}$$

We see now why E was a suitable choice for the constant above: it is the energy eigenvalue of the Hamilton-operator $\hat{H}$. Assume that there exists a set of discrete eigenvalues $\{E_n\}$ of $\hat{H}$. A general solution of the time-dependent SE then reads

$$\Psi(\boldsymbol{r}, t) = \sum_n c_n \psi_n(\boldsymbol{r}) \mathrm{e}^{-\mathrm{i}E_n t/\hbar} \tag{3.8}$$

where $\{c_n\}$ is a set of coefficients which determine the weight of the contribution from eigenstate n. Insertion of Eq. (3.8) into the time-dependent SE shows that it is a solution. When the system is described by a wavefunction $\Psi(\boldsymbol{r}, t)$ which is a sum over several eigenfunctions, the system is said to be in a *superposition of states*. Specifically, when there is a contribution from the eigenstates with different energies E_n, we see that $|\Psi(\boldsymbol{r}, t)|^2$ is no longer time-independent and thus cannot be a stationary state. Put differently, a superposition of stationary states with different energies is in total not a stationary state. Note that Eq. (3.8) is *not* an eigenstate of $\hat{H}$.

B. Time-energy uncertainty: what it ***really*** means

The present section is meant as an interlude and is not essential for understanding how to solve the Schrödinger equation. The reader may thus skip ahead to the next section if desirable - however, the present section does raise an interesting conceptual point which may be worthwhile considering.

Whereas the uncertainty relation $\Delta x \Delta p_x \geq \hbar/2$ discussed in the previous chapter is well-defined mathematically and in terms of physical meaning, one often encounters a similar uncertainty relation involving time and energy in the literature. It has the form

$$\Delta E \Delta t \geq \hbar/2. \tag{3.9}$$

The problem with this relation is that it is not immediately clear how it is obtained or what it even means. For instance, while there is an energy operator in quantum mechanics (the Hamiltonian $\hat{H}$), *there is no time operator* $\hat{t}$ in quantum mechanics. In fact, time is an independent variable in non-relativistic quantum mechanics. Thus, from the very outset it is clear that we cannot derive Eq. (3.9) in the same way as $\Delta x \Delta p_x \geq \hbar/2$, the latter requiring well-defined position and momentum operators.

Moreover, what does Δt even mean? This has caused a lot of discussion regarding the existence and meaning of Eq. (3.9) and, unfortunately, some gross misinterpretations of it. Here, we will show [as was originally done by L. I. Mandelshtam, I. E. Tamm "The uncertainty relation between energy and time in nonrelativistic quantum mechanics", J. Phys. (USSR) 9, 249-254 (1945)] that Eq. (3.9) can be derived in non-relativistic QM as long as one properly defines the meaning of ΔE and Δt. Then, we will discuss its physical interpretation.

Before proceeding, let us briefly remind ourselves of the difference between stationary and non-stationary states. A stationary state Ψ_n solves both the time-dependent SE and is an eigenfunction of a time-independent $\hat{H}$ at the same time. It can be written as $\Psi_n = \psi_n \mathrm{e}^{-\mathrm{i}E_n t/\hbar}$ where ψ is an eigenfunction of $\hat{H}$ while E is the belonging eigenenergy. If the system is in a stationary state, all expectation values of observable quantities are time-independent.

Now, according to the superposition principle we also know that any linear combination of stationary states will also be a solution to the time-dependent SE, so that a general physical state of the system (still for a time-independent Hamiltonian) may be written as

$$\Psi = \sum_n c_n \Psi_n = \sum_n c_n \psi_n \mathrm{e}^{-\mathrm{i}E_n t/\hbar}. \tag{3.10}$$

The key point is that Ψ is no longer an eigenfunction of $\hat{H}$, meaning that Ψ is not a stationary state. Both the probability density $|\Psi|^2$ and the expectation value of physical observables may now depend on time, and energy is not sharply defined anymore ($\Delta E \neq 0$).

Let us now sketch the proof of Eq. (3.9). Let $\hat{H}$ be a time-independent Hamiltonian and let Ψ be the wavefunction of the system, which is not necessarily stationary. In that case, we can show that in the Heisenberg picture (which is explained is explained here), where the time-dependence is placed on the operators whereas the wavefunctions are time-independent, the expectation value of a quantity A that does not depend on time ($\partial A/\partial t = 0$) explicitly satisfies:

$$\frac{d}{dt}\langle A\rangle = \frac{1}{\mathrm{i}\hbar}\langle[\hat{A}, \hat{H}]\rangle \tag{3.11}$$

Let ΔA and ΔE denote the root-mean-square deviations (also known as standard deviations) of A and H, respectively, in which case one can show that $\Delta A \cdot \Delta E \geq \frac{1}{2}|\langle[\hat{A}, \hat{H}]\rangle|$. Inserting our above expression for the commutator between A and H, one obtains:

$$\Delta E \cdot \frac{\Delta A}{|d\langle A\rangle/dt|} \geq \hbar/2. \tag{3.12}$$

which may be written precisely as

$$\Delta E \Delta t \geq \hbar/2, \tag{3.13}$$

if we define

$$\Delta t \equiv \frac{\Delta A}{|d\langle A\rangle/dt|}. \tag{3.14}$$

The crucial point regarding the physical interpretation of this uncertainty relation between ΔE and Δt is to recognize what Δt means. From its definition above, we see that Δt is the time required for the expectation value of A to change by an amount equal to its standard deviation ΔA. Put in more informal terms, it is the time required for the expectation value of A to change appreciably (with "appreciably" quantitatively being defined by the standard deviation).

If the system is in a stationary state, then we know that $d\langle A\rangle/dt = 0$ so that $\Delta t \to \infty$, but that is perfectly fine since $\Delta E \to 0$ then and the inequality is still valid. For a non-stationary state, however, $\Delta E \neq 0$ is the standard deviation of the Hamiltonian $\hat{H}$ and Δt can be thought of as the lifetime of the state Ψ with respect to the observable A, according to our above explanation. More precisely, it is the time interval after which the expectation value of A has changed appreciably (as defined via the standard deviation of A).

How do we interpret this physically? One consequence is that a state that exists only for a short time cannot have a well-defined energy. An excited state in a condensed matter system that has a finite lifetime will then release a slightly different energy each time it decays, and the spread in this energy will be larger (meaning larger ΔE) the shorter its lifetime Δt. For a long-lived excitation $\Delta t \to \infty$, energy becomes well-defined $\Delta E \to 0$. This uncertainty in energy is reflected in the natural linewidth of the distribution of energies released by a particle that has decayed in this manner: fast-decaying states have a broad linewidth. The same principle also applies to fast-decaying particles in particle physics: the faster the particle decays, the shorter its lifetime and the less certain is its mass.

The above reasoning seems to suggest that there should be a strong link between the time-energy uncertainty relation and the concept of *quantum fluctuations*. A well-known example of a quantum fluctuation in particle physics is the bubble polarization diagram where a photon is converted into a temporary electron-positron pair which then collapses back into a photon. The fact that one frequently encounters incorrect statements, such as that this can happen because the $e^- - e^+$ pair "borrows" energy from the environment, underlines the importance of correctly interpreting what the time-energy uncertainty relation means.

In light of the explanation we have given above, we can now understand that the reason that such spontaneous particle pairs can occur as a quantum fluctuation is that the energy of vacuum cannot be sharply defined. In a cartoon picture, one can think of the vacuum fields "jittering" constantly and thus have what is referred to as a zero-point energy, the latter statement really just expressing that $\Delta E \neq 0$. Now, because of this uncertainty in the energy of vacuum, we are allowed to create spontaneous pairs corresponding to the bubble diagram in particle physics that exist a finite time Δt as long as $\Delta E\Delta t \geq \hbar/2$. Please note the important distinction between saying that energy is not sharply defined, which is a statistical statement, and saying that energy can appear out of nothing or being "borrowed" from some ill-defined environment. Vacuum is not a stationary state, because in that case we would have $\Delta E = 0$. Note that a Hamiltonian describing vacuum can still be time-independent even if vaccum is a non-stationary state.

C. Collapse of the wavefunction and superpositions

As we have seen, a quantum mechanical system may be in a superposition of states, $\Psi = \sum_n c_n\psi_n$. Assume that ψ_n are eigenstates of the operator $\hat{Q}$ with eigenvalues q_n. Upon measuring the physical quantity Q which has a quantum mechanical operator $\hat{Q}$, the only values we can obtain for this are q_n with probabilities $|c_n|^2$. Assume that we measure q_m at $t = t_0$. Immediately after the measurement has been performed, the system is in the state $\Psi = \psi_m$ and *no longer in a superposition of states*. Does it revert to a superposition of states? That depends. In fact, the time-dependence of the wavefunction Ψ will be governed by the time-dependent SE and thus by the Hamiltonian of the system, where one uses $\Psi(t = t_0) = \psi_m$ as the initial condition.

Performing a measurement on the system thus collapses the superposition of states into a single state and destroys effects such as the interference pattern in double-slit experiments (if one here detects the electron as it passes through a slit - if one does not detect the electron, the interference pattern is shown in the screen).

D. Wavefunction properties

For simplicity, we from now on restrict our attention to one-dimensional systems in order to keep the notation as compact as possible. The presented results have a natural extension to higher-dimensional systems, which we treat explicitly in a later chapter. To begin with, we concentrate on stationary solutions of the SE so that our main focus will be solutions of the time-independent SE:

$$-\frac{\hbar^2}{2m}\psi'' + V(x)\psi = E\psi. \tag{3.15}$$

A useful first observation is obtained by rewriting this equation to:

$$\frac{\psi''}{\psi} = \frac{2m}{\hbar^2}[V(x) - E], \tag{3.16}$$

which is allowed so long as $\psi(x) \neq 0$. It follows that the wavefunction and its derivative have to be continuous everywhere if $V(x)$ is finite at all x, i.e. does not diverge. If ψ' had been discontinuous at some point, ψ'' would necessarily act singularly in that point and be proportional to the Dirac delta-function δ, which contradicts the finite magnitude of $V(x)$. The reason for why this observation is useful is that it provides us with a set of boundary conditions we can use to solve Eq. (3.15), namely continuity of ψ and ψ'.

Moreover, the curvature of the wavefunction provides us with physical information. Generally, the stronger the curvature of the wavefunction, the higher its kinetic energy. This is true because the kinetic energy operator is $\hat{p}_x^2/2m$ where $\hat{p}_x = \frac{\hbar}{\mathrm{i}}\partial_x$ so that a large value of the derivative translates into a large kinetic energy. The curvature is determined mathematically by ψ'', which in turn is decided by whether or not the energy E is larger than the potential V as seen from the right hand side of Eq. (3.16).

A peculiar feature of one-dimensional systems is that, unlike *e.g.* three-dimensional systems, only one quadratically integrable eigenfunction can accompany each eigenvalue. In effect, there is no degeneracy in one-dimension. This can be proven by considering two functions ψ_1 and ψ_2 which we begin by assuming have the same eigenvalue E. Using the time-independent SE, we see that

$$\frac{\hbar^2}{2m}(\psi_1'\psi_2 - \psi_1\psi_2')' = (V-E)\psi_1\psi_2 - \psi_1(V-E)\psi_2 = 0. \tag{3.17}$$

It follows that $(\psi_1'\psi_2 - \psi_1\psi_2')$ must be a constant. In order to determine the value of the constant, we make use of the fact that a quadratically integrable function must vanish at $x \to \pm\infty$. Therefore, the constant must be zero as follows by evaluating $(\psi_1'\psi_2 - \psi_1\psi_2')$ at $x \to \pm\infty$. This means that $\psi_1'\psi_2 = \psi_1\psi_2'$, which has the solution $\psi_1 = c\psi_2$ where c is an arbitrary, new constant. However, ψ_1 and ψ_2 were supposed to be different, and setting $c = 1$ would make them equal. We must conclude that there is no degeneracy of eigenfunctions with a discrete eigenvalue spectrum in one dimension. Note that this does not hold for a continuous eigenvalue spectrum, because in that case we know that the wavefunctions are not in general quadratically integrable. In turn, this means that ψ does not have to vanish at $x \to \pm\infty$ so that we cannot use the same argument as above.

E. Particle in a potential well

An instructive example which demonstrates how a particle acquires a discrete energy eigenvalue spectrum, corresponding to a *bound state* (confined to a certain region of space), is an infinitely deep potential well:

$$V(x) = \begin{cases} 0 & \text{if } 0 < x < L \\ \infty & \text{otherwise} \end{cases} \tag{3.18}$$

Since the potential is infinitely high outside the well, the particle is confined to being located inside the two hard walls appearing at $x = 0$ and $x = L$. Inside the well ($0 < x < L$), the time-independent SE reads:

$$-\frac{\hbar^2}{2m}\psi'' = E\psi, \tag{3.19}$$

since the potential is zero there. The general solution of this equation reads

$$\psi(x) = a\sin(x\sqrt{2mE/\hbar^2}) + b\cos(x\sqrt{2mE/\hbar^2}) \tag{3.20}$$

with a and b being undetermined coefficients. We determine them by using appropriate boundary conditions, as mentioned previously. Outside of the well, ψ must vanish. This means that $\psi(0) = \psi(L) = 0$. As a consequence, b must be zero in Eq. (3.20), whereas $\psi(L) = 0$ is guaranteed if additionally

$$\sqrt{2mE/\hbar^2}L = n\pi,\ n = 1, 2, 3, \ldots \tag{3.21}$$

Note how $n = 0$ is not included, since that would cause ψ to vanish regardless of the position x. The above equation provides precisely the allowed discrete energy eigenvalue spectrum that the particle inside the potential well can have:

$$\boxed{E_n = \frac{\pi^2\hbar^2}{2mL^2}n^2,\ n = 1, 2, 3, \ldots}$$

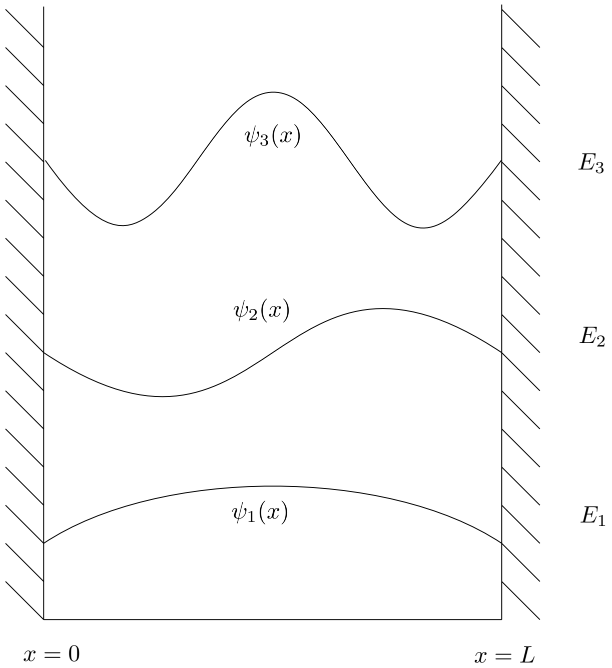
The solution for the wavefunction Eq. (3.20) is then:

$$\psi_n(x) = a\sin(n\pi x/L). \tag{3.22}$$

The remaining coefficient a is determined by demanding that ψ is normalized:

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1 \rightarrow |a|^2 L/2 = 1, \tag{3.23}$$

by performing the integral. This is satisfied by $a = \sqrt{2/L}$. The final result is then that the wavefunction describing a particle with energy E_n is $\psi_n(x) = \sqrt{2}L\sin(n\pi x/L)$. The first few eigenfunctions are shown in the figure.

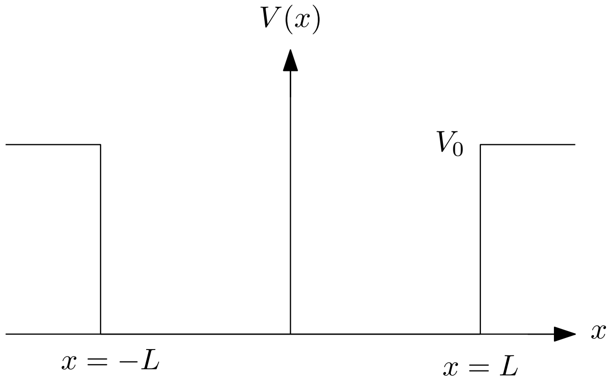


An interesting point is that the minimum energy of the particle is *not zero*, despite the absence of any potential energy. In other words, there exists a finite *zero-point energy* which is a quantum mechanical effect without analogue in classical physics. The minimum energy of the particle is indeed E_1, obtained for $n = 1$, whereas classically the kinetic energy would be allowed to vanish. The fact that a finite zero-point energy must exist follows from Heisenberg's uncertainty principle, which we treat in detail later on in this book.

The fact that the wavefunctions shown in the figure are either symmetric or antisymmetric around the middle of the potential well is not a coincidence. It is a general result that a potential which is symmetric around a specific point in space gives rise to eigenfunctions which also have a specific parity with respect to that point. A more realistic, and thus slightly more complicated, scenario can be considered by relaxing the requirement that the potential must be infinitely high outside of the well. Let us do the same calculation as above, but where the potential energy now is finite $V = V_0$ outside of the well:

$$V(x) = \begin{cases} 0 & \text{if } |x| \leq L \\ V_0 & \text{if } |x| > L \end{cases}. \tag{3.24}$$

The potential well thus extends from $x = -L$ to $x = L$ this time, as shown in the figure.



This situation is interesting not only as an academic example, but also because it has direct relevant in applied physics. Potential wells such as the one considered here are routinely made in experimental labs where the electrical conduction properties of the confined electrons in the well can be controlled via an applied voltage difference.

Our time-independent SE now takes the form:

$$\psi''(x) = \begin{cases} -\frac{2m}{\hbar^2}E\psi & \text{if } |x| \leq L \\ \frac{2m}{\hbar^2}(V_0 - E)\psi & \text{if } |x| > L \end{cases}. \tag{3.25}$$

It is useful to distinguish between the cases where the energy E is larger or smaller than the potential V_0. Considering first the case of $E < V_0$, so that the particle classically would not have enough energy to access the region outside of the well, the solution of the SE for $|x| > L$ is:

$$\psi(x) = A\mathrm{e}^{\kappa x} + B\mathrm{e}^{-\kappa x}. \tag{3.26}$$

We defined here $\kappa = \sqrt{2m(V_0 - E)}/\hbar$ which is a positive, real number since $E < V_0$, while A and B are coefficients to be determined. To make sure that we maintain a quadratically integrable function, we have to remove the exponential term in Eq. (3.26) which diverges when $x \to \infty$ and $x \to -\infty$, respectively. It follows that

$$\psi = \begin{cases} A\mathrm{e}^{\kappa x} & \text{if } x < -L \\ B\mathrm{e}^{-\kappa x} & \text{if } x > L \end{cases}. \tag{3.27}$$

In contrast, inside the well the solution of the SE has the form:

$$\psi = C\sin(kx) + D\cos(kx), \tag{3.28}$$

where the wavenumber now is $k = \sqrt{2mE}/\hbar$. As we discussed at the beginning of this chapter, both ψ and ψ' must be continuous so long as the potential is finite everywhere. This allows us to determine the coefficients by using that ψ and ψ' as given by Eq. (3.27) and Eq. (3.28) must be equal at $x = 0$ and at $x = L$. The boundary conditions at $x = -L$ gives us C and D expressed in terms of A:

$$\begin{aligned} C &= A\mathrm{e}^{-\kappa L}\cos(kL)[\kappa/k - \tan(kL)], \\ D &= A\mathrm{e}^{-\kappa L}\cos(kL)[\kappa/k\tan(kL) + 1]. \end{aligned} \tag{3.29}$$

The boundary condition at $x = L$ gives the equation (after eliminating B):

$$C[\kappa/k\tan(kL) + 1] + D[\kappa/k - \tan(kL)] = 0 \tag{3.30}$$

which upon inserting C and D from Eq. (3.29) gives:

$$2[\kappa/k\tan(kL) + 1][\kappa/k - \tan(kL)] = 0. \tag{3.31}$$

Equation (3.31) is satisfied when either of the square brackets are zero. If the first square bracket is zero, it follows from Eq. (3.29) that $D = 0$. Conversely, if the second bracket is zero, then Eq. (3.29) gives $C = 0$. We may then summarize our findings so far as follows. When the energy E of the particle is such that the equation

$$\tan(kL) = \kappa/k \tag{3.32}$$

is satisfied, we obtain symmetric energy eigenfunctions

$$\psi(-L \leq x \leq L) \propto \cos(kx). \tag{3.33}$$

Instead, when the energy is such that

$$\tan(kL) = -k/\kappa \tag{3.34}$$

is satisfied, we obtain antisymmetric energy eigenfunctions

$$\psi(-L \leq x \leq L) \propto \sin(kx). \tag{3.35}$$

Writing out the expression for k and κ explicitly, we see that

$$\tan(\sqrt{2mL^2E}/\hbar) = \begin{cases} \sqrt{(V_0-E)/E} & \text{for symmetric } \psi \\ -\sqrt{E/(V_0-E)} & \text{for antisymmetric } \psi \end{cases}. \tag{3.36}$$

The remaining task is to attempt to solve Eq. (3.36) for the energy E, in which case we will have succeeded to identify the energy eigenvalues of the problem for the case of a bound state $E < V_0$. Before doing so, we note in passing that we recover the correct result in the limit $V_0 \to \infty$ (the infinite potential well we treated previously). This can be seen by noting that the right hand side of Eq. (3.36) is equal to ∞ (upper line) or 0 (lower line) when $V_0 \to \infty$, which is satisfied when the tan-function on the left hand side has an argument that equals an integer times $\pi/2$. This occurs when $E_n = \hbar^2\pi^2n^2/[2m(2L)^2]$ which is consistent with the result we obtained for the infinite well since the width of the well was L instead of $2L$ there.

Finding a general solution for E from Eq. (3.36) is not possible analytically, as it is a transcendental equation. It is, however, straightforward numerically (try to solve it using *e.g.* MATLAB by plotting the left and right hand side of the equation and identifying the intersections. However, if we instead turn our attention to energies exceeding the potential ($E > V_0$), analytical progress becomes possible. We now have to go back to the time-independent SE which outside of the well ($|x| > L$) reads

$$\psi'' = -K^2\psi \tag{3.37}$$

where we defined $K = \sqrt{2m(E-V_0)}/\hbar$. The solution is:

$$.\psi = a\sin(Kx) + b\cos(Kx) \tag{3.38}$$

where a and b are undetermined coefficients. This solution is fundamentally different from the previously treated one, valid for $E < V_0$, because it is oscillating as a function of position rather than decaying. In effect, the particle now acts as a free particle outside of the well, which is reasonable as its energy exceeds the potential barrier. It is no longer a bound state, which in turn has the consequence that the energy spectrum is continuous rather than discrete: solutions of the type Eq. (3.38) exist for all $E > V_0$.

Some of the key insights we have gained through our treatment of the finite and infinite potential well are thus:

- The energy spectrum is continuous for energies that exceed the potential barrier (i.e. energies where a classical particle would not have been bound).
- The allowed bound states occuring for energies below the potential barrier only exist at specific (discrete) energy values.
- So long as the potential is not infinitely high, there exists a finite probability $|\psi|^2$ of locating the particle outside of the well (i.e. inside the potential barrier region).
- The eigenfunctions for bound states have a definite parity (symmetric or antisymmetric) with respect to the symmetry point of the potential.

F. The δ-function potential

Modelling a potential as a mathematical δ-function might seem like an unrealistic approximation. Nevertheless, such a potential commonly appears in physical models of real systems and works surprisingly well in many cases. We should expect a δ-function to be a reasonable model for an extremely deep and narrow potential. If the potential is attractive (similar to the potential well treated above), we may write:

$$V(x) = -\alpha\delta(x). \tag{3.39}$$

where $\alpha > 0$. If $\alpha < 0$, such a potential instead models a strong barrier upon which *e.g.* electrons may scattering. This is a model which often appears when one calculates electric currents propagating in hybrid structures comprised of two or more materials: the interface region between two such materials, where strong scattering is expected due to the lattice mismatch and other defects, can then be described reasonably well by a δ-function. Away from the point $x = 0$ where $V = 0$, the time-independent SE has exponentially decaying solutions:

$$\psi(x) = \begin{cases} \psi_0 \mathrm{e}^{+\sqrt{-2mE}x/\hbar} & \text{for } x < 0 \\ \psi_0 \mathrm{e}^{-\sqrt{-2mE}x/\hbar} & \text{for } x > 0 \end{cases} \tag{3.40}$$

when $E < 0$. The reason that we are interested in decaying solutions away from $x = 0$ is that we are looking for bound states which thus should be localized near the binding potential at $x = 0$. Moreover, bound states should have an energy $E < 0$ since otherwise they would have enough energy to propagate as free particles away from the potential $(E > 0)$. To find the allowed energies of bound states at the δ-function well, we make use (as before) of boundary conditions. Continuity of the wavefunction does not help us much here, since it is obvious from Eq. (3.40) that the two solutions for $x < 0$ and $x > 0$ are continuously connected at $x = 0$. However, we also know that there exists a boundary condition related to the derivative of the wavefunction. To see how the δ-function modifies the usual continuity of the derivative, we integrate the SE $-\frac{\hbar^2}{2m}\psi'' - \alpha\delta(x)\psi = E\psi$ over a small distance ζ and take the limit $\zeta \to 0$:

$$-\frac{\hbar^2}{2m}[\psi'(+\zeta) - \psi'(-\zeta)] - \alpha\psi(0) = 0 \tag{3.41}$$

since $\lim_{\zeta\to 0} E\int_{-\zeta}^{\zeta}\psi(x)dx = 0$. Using Eq. (3.40) to evaluate the derivates in Eq. (3.41), we obtain

$$\frac{\hbar^2}{2m}2\sqrt{-2mE}/\hbar = \alpha, \tag{3.42}$$

which is rearranged to

$$\boxed{E = -\frac{m\alpha^2}{2\hbar^2}.}$$

We have thus discovered that the δ-function potential well only has one single bound-state which remarkably is *independent* of the sign of α.

IV. QUANTUM HARMONIC OSCILLATOR AND SCATTERING

Learning goals. After reading this chapter, the student should:

- Know how to perform a quantum mechanical treatment of the harmonic oscillator model and understand the procedure for how to obtain the energy eigenvalues of this problem.
- Understand how scattering of particles in quantum mechanics works, in particular with respect to the difference between scattering on potential wells and barriers as well as qualitative differences to particle scattering in classical physics.

One of the primary mannequins of physics is the harmonic oscillator. The treatment of this system is often emphasized not only in quantum mechanics, but already at the classical mechanics level. One reason for its popularity is the fact that it is exactly solvable, which is a privilege one rarely has in physics. More importantly, however, the applications of the harmonic oscillator model goes far beyond the standard system of a spring oscillating back and forth. The reason for this is that the equations governing the behavior of a great deal of physical systems, including the behavior of the electromagnetic field quanta (photons), molecules, and complex electric circuits, can be rewritten in such a way that they are equivalent to a harmonic oscillator model! Therefore, we treat this system quantum mechanically in detail here.

Moreover, we will present a detailed treatment of how particles *scatter* on potentials, rather than how particles are *bound* to potentials as in the previous chapter. Scattering of particles is of crucial importance in physics, as it is one of the most effective ways to gain information about the potential generated by various sources, such as other particles. The particles will scatter in a way which depends on the interaction between them and the scattering center, which allows the experimentalist to understand what type of potential one is dealing with.

A. Harmonic oscillator

From classical mechanics, we know that the Hamiltonian (classical energy function) for a harmonic oscillator reads

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2. \tag{4.1}$$

It describes a particle with mass m which is acted upon by a force $F = -kq$ where $k = m\omega^2$, thus constantly trying to restore it to its equilibrium position $q = 0$. Without damping, this results in a classical oscillation with frequency $\omega = \sqrt{k/m}$. To treat this quantum mechanically, we first write down the Hamilton operator. By now, we know well that the method for doing so is to first let:

$$p \to \hat{p} = \frac{\hbar}{\mathrm{i}}\frac{d}{dq},\ q \to \hat{q} = q \tag{4.2}$$

in the Hamilton-operator. The time-independent SE $\hat{H}\psi = E\psi$ then takes the form:

$$-\frac{\hbar^2}{2m}\psi'' + \frac{1}{2}m\omega q^2\psi = E\psi. \tag{4.3}$$

For brevity of notation, let us introduce some normalized (dimensionless) quantities as follows:

$$\epsilon \equiv \frac{E}{\frac{1}{2}\hbar\omega},\ x = \frac{q}{\sqrt{\hbar/m\omega}}. \tag{4.4}$$

Using these relations in Eq. (4.3) gives:

$$\frac{d^2\psi}{dx^2} + (\epsilon - x^2)\psi(x) = 0. \tag{4.5}$$

Let us examine how a solution to this equation may be identified. It is often useful to consider how an equation behaves in various limiting cases in order to get a "feel" for what the solution should look like. For instance, for large values of x we see that:

$$\frac{1}{x^2}\frac{d^2\psi}{dx^2} = \psi(1-\epsilon/x^2) \simeq \psi. \tag{4.6}$$

The exponential $\mathrm{e}^{\pm x^2/2}$ solves this equation. However, *physically* we additionally demand that ψ should vanish at large distances rather than diverge (in order to at least have a chance of being normalizable). For this reason, we keep only the solution $\mathrm{e}^{-x^2/2}$. Incidentally, it turns that if we start out with $\epsilon = 1$ in Eq. (4.3), then $\mathrm{e}^{-x^2/2}$ is actually the exact solution.

However, we have no valid reason to expect that ψ should behave as $\mathrm{e}^{-x^2/2}$ for small values of x. It is then natural to write down the *ansatz* (a trial function):

$$\psi(x) = \zeta(x)\mathrm{e}^{-x^2/2} \tag{4.7}$$

where $\zeta(x)$ should approach a constant value at large x. Inserting this ansatz into Eq. (4.3) provides the following equation that ζ must satisfy:

$$\zeta'' - 2x\zeta' + (\epsilon-1)\zeta = 0. \tag{4.8}$$

In order to solve Eq. (4.8), and thus identify what the eigenfunctions of the harmonic oscillator are, we first expand ζ as:

$$\zeta(x) = \sum_{k=0}^{\infty} a_k x^k. \tag{4.9}$$

It is then straightforward to obtain ζ' and ζ'':

$$\zeta' = \sum_{k=0}^{\infty} k a_k x^{k-1},\ \zeta'' = \sum_{k=0}^{\infty} k(k-1)a_k x^{k-2}. \tag{4.10}$$

We may note that the $k = 0$ and $k = 1$ terms make no contribution to ζ''. Therefore, we may rewrite it as:

$$\zeta'' = \sum_{k=2}^{\infty} k(k-1)a_k x^{k-2} = \sum_{k=0}^{\infty}(k+2)(k+1)a_{k+2}x^k. \tag{4.11}$$

Inserting these expressions for ζ' and ζ'' into Eq. (4.8) provides

$$\sum_{k=0}^{\infty}[(k+2)(k+1)a_{k+2} - (2k+1-\epsilon)a_k]x^k \tag{4.12}$$

It is then clear why we rewrote ζ'' in the manner we did: it was to be able to collect all terms inside one single summation. The trick is now to choose the coefficients $\{a_k\}$ in such a manner that the terms inside the bracket [...] in the equation above vanishes. Only then will the equation be satisfied regardless of the value of x. We thus obtain the requirement:

$$a_{k+2} = \frac{2k+1-\epsilon}{(k+1)(k+2)}a_k,\ k = 0,1,2,3,\ldots \tag{4.13}$$

This is a recursion formula which enables us to express ζ only via a_0 and a_1 in the following manner:

$$\zeta(x) = a_0\Big[1 + \frac{1-\epsilon}{2!}x^2 + \ldots\Big] + a_1\Big[x + \frac{3-\epsilon}{3!}x^3 + \ldots\Big]. \tag{4.14}$$

We see how all terms $\{a_k\}$ for $k \geq 2$ are determined by a_0 and a_1 via Eq. (4.13).

For large values of $|x|$, $\zeta(x)$ given by Eq. (4.14) diverges, as can be seen in the following manner. Looking at Eq. (4.13), we see that the terms for large k, which are highly relevant in the limit of $|x| \to \infty$ according to how we defined ζ in the first place [Eq. (4.9)], satisfy:

$$\frac{a_{k+2}}{a_k} \simeq \frac{2}{k}. \tag{4.15}$$

Compare this with the coefficients in the expansion of the function e^{x^2}:

$$\mathrm{e}^{x^2} = \sum_{k=0,2,4,\ldots} \frac{1}{(k/2)!} x^k, \tag{4.16}$$

which also satisfy the relation Eq. (4.15) for large k:

$$\frac{(k/2)!}{[(k+2)/2]!} = \frac{1}{1+k/2} \simeq \frac{2}{k}. \tag{4.17}$$

Even if we had multiplied e^{x^2} with a polynomial in x, the same conclusion would hold since the exponential function would dominate. In light of this, it is clear that the brackets proportional to a_0 and a_1 in Eq. (4.14) must both diverge at large x (since we just proved that the relation between the coefficients is the same as for the diverging function e^{x^2}). This is problematic since the total quantum mechanical wavefunction $\psi(x) = \zeta(x)\mathrm{e}^{-x^2/2}$ would then also diverge.

To avoid this, we have to ensure that $\zeta(x)$ is instead a polynomial so that $\mathrm{e}^{-x^2/2}$ dominates at large $|x|$. We can achieve this if the recursion relation Eq. (4.13) starts producing coefficients which are equal to zero when k equals a cutoff index which we name n. Specifically, we see that if we choose $\epsilon = 2n+1$, where now n is a fixed even integer, then $a_{n+2} = 0$ which in turn ensures that $a_{n+4} = a_{n+6} = \ldots = 0$. All coefficients a_k for an even k up to $k = n$ remain non-zero, however.

For the odd-k coefficients, there is no cutoff when n is even, which means that the only way to prevent the divergence is to set $a_1 = 0$. What remains is that $\zeta(x)$ is now a polynomial where the coefficients a_k are only non-zero for even k, are given by Eq. (4.13), and terminate when $k = n$. Conversely, we could make exactly the same argument when n is a fixed odd integer. In that case, ζ becomes a polynomial where the coefficients a_k are only non-zero for odd k, are given by Eq. (4.13), and terminate when $k = n$. In this case, it is a_0 which must be set to zero.

Summarizing so far, we have been able to show that there exists acceptable (normalizable) wavefunctions of the form $\psi(x) = \zeta(x)\mathrm{e}^{-x^2/2}$ where $\zeta(x)$ is a polynomial in x when $\epsilon = 2n + 1,\ n = 0, 1, 2, \ldots$. Looking at our definition of ϵ above, we see that this means that the energy eigenvalues must be:

$$\boxed{E_n = (n + \frac{1}{2})\hbar\omega,\ n = 0, 1, 2, \ldots}$$

This is a discrete set of eigenvalues which constant increments $\hbar\omega$ between each successive eigenvalue. With the eigenvalues in hand, we can now return to the equation determining ζ, namely Eq. (4.8, which takes the form:

$$\zeta_n'' - 2x\zeta_n' + 2n\zeta_n = 0 \tag{4.18}$$

where we added a n subscript to ζ to indicate that it is associated with eigenvalue E_n. According to our above treatment, we now know that this equation has a polynomial solution of degree n. We leave it as an exercise for the reader to show that the solution of ζ_n is such that the normalized eigenfunctions become

$$\boxed{\psi_n(x) = \Big(\frac{m\omega}{\hbar}\Big)^{1/4} \frac{1}{\sqrt{2^n n! \pi^{1/2}}} H_n(x)\mathrm{e}^{-x^2/2},}$$

where H_n are Hermite-polynomials. They satisfy precisely Eq. (4.18):

$$H_n'' - 2xH_n' + 2nH_n = 0 \tag{4.19}$$

and may be defined via

$$H_n(x) = \mathrm{e}^{x^2}\Big(-\frac{d}{dx}\Big)^n \mathrm{e}^{-x^2}. \tag{4.20}$$

Due to their property

$$H_n(-x) = (-1)^n H_n(x) \tag{4.21}$$

it follows that ψ_n all have a specific parity: ψ_n is invariant under $q \to (-q)$ if n is an even number whereas ψ_n changes sign under $q \to (-q)$ for odd n. The specific form of the eigenvalues for the harmonic oscillator that we discovered above turned out to be equidistant from each other, separated by a quantum $\hbar\omega = h\nu$. The reader may recall from the introductory chapter in this book that this is exactly the quantum of energy carried by photons, as postulated by Planck. This is in fact no coincidence, because the electromagnetic field can be expressed as a superposition of harmonic oscillators! This is treated in great detail here.

B. Quantum mechanical scattering

Instead of studying how bound states appear at attractive potentials, as we have done previously in this book, we now want to determine how a potential can *scatter* an incoming particle. This is of crucial importance in physics, because the manner in which the particle is scattered (which can be measured by detecting in which direction the particle is deflected) gives us valuable information about the nature of the source of the scattering potential. For instance, how does the potential depend on the separation distance between the particle and the source of the potential or the angle the particle approaches the potential with?

To illustrate the essence of how this problem can be treated quantum mechanically, we start by focusing here on scattering in one dimension. In that case, there are only two relevant directions: the particle can move forward or backward. In the more general three dimensional case, one can use a more advanced treatment as shown here. The particle will have a probability T for transmitting through the potential and a probability R for being reflected. It stands to reason that $T + R$ must equal one. Both of these coefficients will in general depend on the properties of the particle and the potential itself. In the simplest case where we consider an incident plane-wave toward a potential, the particle is characterized by its energy and mass. Its wavefunction far away from the potential, where $V(x) \to 0$, is

$$\psi(x) = \psi_0 \mathrm{e}^{\pm \mathrm{i}kx} \tag{4.22}$$

where $k = \sqrt{2mE}/\hbar$ and ψ_0 is the amplitude of the wavefunction. The sign in the exponent determines in which direction the particle is moving: toward or away from the barrier. Now, as the particle approaches the potential V, the solution of the time-independent SE is no longer necessarily a plane-wave as in Eq. (4.22). However, if the particle moves through the potential it will again revert to a plane-wave far away on the other side of the potential. In order to determine the probabilities for transmission and reflection of the particle, we have to compute the associated quantum mechanical probability currents. We derived previously that the quantum mechanical probability current is obtained from a wavefunction ψ as:

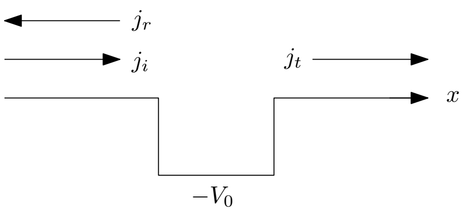
$$j = \mathrm{Re}\{\psi^* \frac{\hbar}{\mathrm{i}m} \psi'\}. \tag{4.23}$$

The probability for transmission is then determined by the ratio of the magnitude of the transmitted, j_t, to the magnitude of the incident current, j_i, and similarly for the reflection probability:

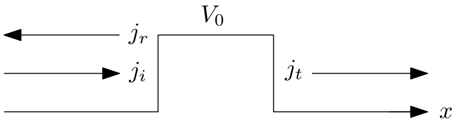
$$R = \frac{|j_r|}{j_i},\ T = \frac{j_t}{j_i}. \tag{4.24}$$

Note how we attached an absolute value sign on the magnitude of the reflected current j_r in order to obtain its magnitude. The reason for this is that the reflected current should have the opposite sign of j_i since the reflected current must move oppositely to the incident current.

Scattering on potential well



Scattering on potential barrier



Let us look at how this works in a practical calculation. We first consider the scenario shown in the left figure, where a particle is incident toward a potential well with depth $|V_0|$. The well is confined to the region $0 < x < L$, which gives us the following solution to the time-independent SE:

$$\psi(x) = \begin{cases} \mathrm{e}^{\mathrm{i}kx} + r\mathrm{e}^{-\mathrm{i}kx} & \text{for } x < 0 \\ a\mathrm{e}^{\mathrm{i}qx} + b\mathrm{e}^{-\mathrm{i}qx} & \text{for } 0 \leq x \leq L\ . \\ t\mathrm{e}^{\mathrm{i}kx} & \text{for } x > L \end{cases} \tag{4.25}$$

Here, the wavevectors inside and outside of the potential well are different due to the presence of the constant $(-V_0)$ in the SE for for $0 \leq x \leq L$. Specifically, we have:

$$k = \sqrt{2mE}/\hbar,\ q = \sqrt{2m(E + V_0)}/\hbar. \tag{4.26}$$

Upon inspection of Eq. (4.25), we see that there is no prefactor in front of the incoming exponential wave. In effect, we have set the amplitude of the wavefunction equal to unity. However, this is standard procedure in the context of scattering because it ultimately does not matter which constant amplitude we choose for the incoming wave. The reason for this is that the reflection and transmission probabilities only depend on the *ratios* of probability currents. Therefore, instead of attaching a constant factor ψ_0 to all the exponentials in Eq. (4.25) and dragging it with us throughout all of the calculations just to see it vanish in the final step, we set it to $\psi_0 = 1$ right away.

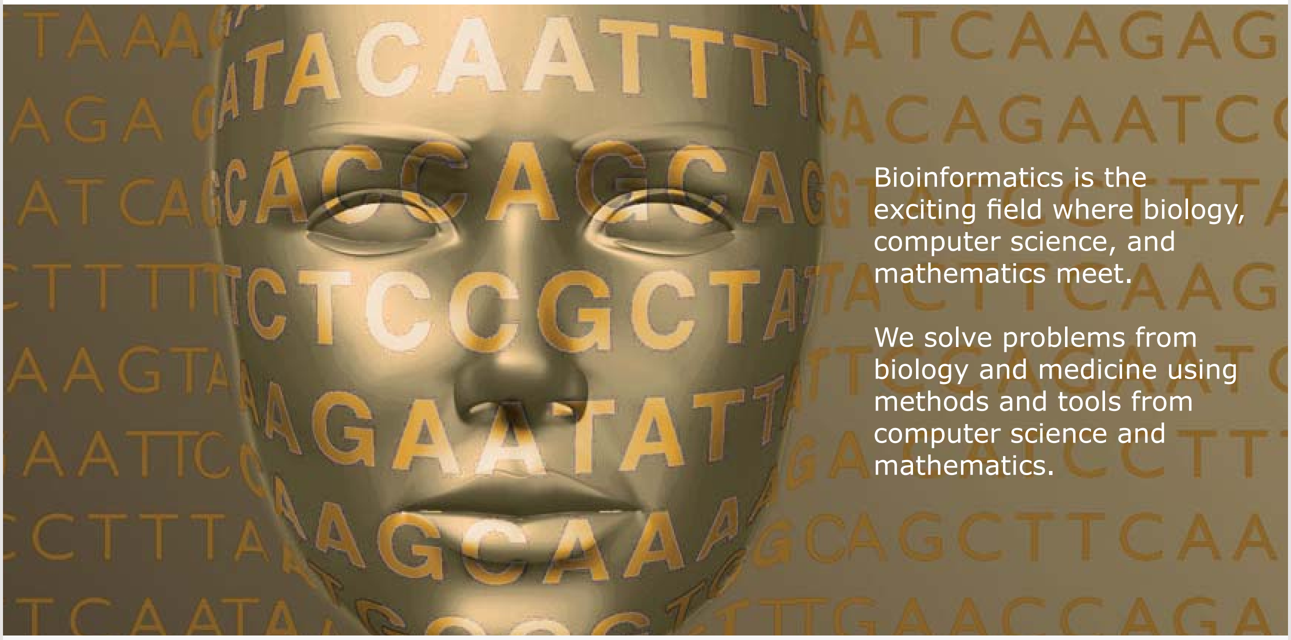
We should also note that on the right side of the barrier, $x > L$, there is no term $\mathrm{e}^{-\mathrm{i}kx}$. A moment of consideration reveals why this is so: such a wave must necessarily describe a particle moving leftward. This exists in the region $x < L$, where such a term corresponds to the reflected wave. But for $x > L$, there may only exist a transmitted wave. In order for us to determine R and T, the first step is to identify the coefficients $\{a, b, r, t\}$ in Eq. (4.25). These may all in general be different, as they correspond to the weight of the waves propagating in different directions in the system. As before, we make use of proper *boundary conditions* to determine them.

To this end, we start by noting that the potential is finite everywhere, and therefore the relevant boundary conditions are (i) continuity of the wavefunction and (ii) continuity of the derivative of the wavefunction. Using these conditions at $x = 0$ and $x = L$ gives us the set of equations:

$$\begin{aligned} 1 + r &= a + b, \\ \mathrm{i}k(1 - r) &= \mathrm{i}q(a - b), \\ a\mathrm{e}^{\mathrm{i}qL} + b\mathrm{e}^{-\mathrm{i}qL} &= t\mathrm{e}^{\mathrm{i}kL}, \\ \mathrm{i}q(a\mathrm{e}^{\mathrm{i}qL} - b\mathrm{e}^{-\mathrm{i}qL}) &= ikt\mathrm{e}^{\mathrm{i}kL}. \end{aligned} \tag{4.27}$$

It is straightforward to solve this set of equations and we are particularly interested in r and t since these are the coefficients associated with the reflected and transmitted waves. We find that:

$$\begin{aligned} t &= \frac{2kq\mathrm{e}^{-\mathrm{i}kL}}{2kq\cos(qL) - \mathrm{i}(q^2 + k^2)\sin(qL)}, \\ r &= \frac{\mathrm{i}(q^2 - k^2)\sin(qL)}{2kq\cos(qL) - \mathrm{i}(q^2 + k^2)\sin(qL)}. \end{aligned} \tag{4.28}$$



With these coefficients in hand, we may now compute the quantum mechanical proability currents by using Eq. (4.23). For the incident wave, $\psi_i = \mathrm{e}^{\mathrm{i}kx}$, which gives

$$j_i = \hbar k/m. \tag{4.29}$$

For the reflected wave, we have $\psi_r = r\mathrm{e}^{-\mathrm{i}kx}$ so that

$$j_r = -\hbar k|r|^2/m. \tag{4.30}$$

Finally, for the transmitted wave, we have $\psi_t = t\mathrm{e}^{\mathrm{i}kx}$ and:

$$j_t = \hbar k|t|^2/m. \tag{4.31}$$

We are now in a position to compute T and R via:

$$\begin{aligned} T &= \frac{j_t}{j_i} = |t|^2 = \frac{4E(E+V_0)}{4E(E+V_0)+V_0^2\sin^2(qL)}, \\ R &= \frac{j_r}{j_i} = |r|^2 = \frac{V_0^2\sin^2(qL)}{4E(E+V_0)+V_0^2\sin^2(qL)}. \end{aligned} \tag{4.32}$$

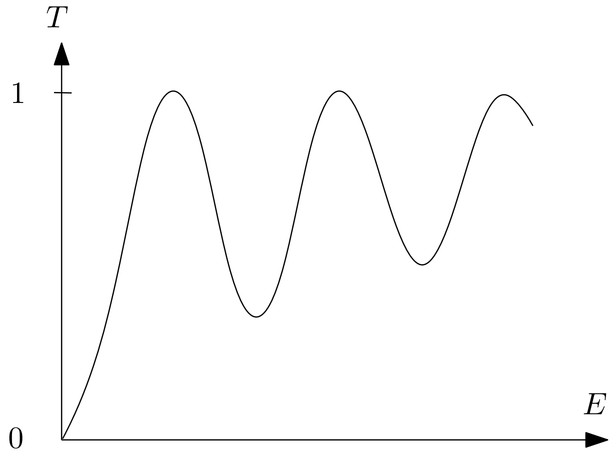
The probabilities for transmission and reflection are seen to oscillate with the length L of the potential well. Interestingly, there is a finite probability for reflection R in spite of the fact that the potential is purely attractive. This has no counterpart in classical mechanics. As a consistency check, we see that $R + T = 1$ is indeed satisfied, as conservation of probability demands.

It is natural to ask the question: what are the ideal circumstances for causing transmission of the particle? In other words, given that we can experimentally design the strength $|V_0|$ and length L of the potential well, what are the optimal choices for causing high transmission? We see from Eq. (4.32) that $T \to 1$ when $\sin(qL) \to 0$. This happens whenever $qL = n\pi$, $n = 1, 2, 3, \ldots$ and since $q = \sqrt{2m(E + V_0)}/\hbar$, this corresponds to

$$\boxed{E = -V_0 + \frac{n^2\hbar^2\pi^2}{2mL^2},\ n = 1, 2, 3, \ldots}$$

For these special energies of the incident particle, there is no reflection. How can we understand this physically? Due to our wavefunction description of the particle, it is natural to expect that there may exist an analogy in optics, and this is indeed the case. To see this, note that the condition $qL = n\pi$ may be rewritten as $2L = 2n\pi/q$. Since the wavelength of the particle is $2\pi/q$, we see that the resonance condition providing $T = 1$ is satisfied when twice the length of the potential well equals an integer number of wavelengths. In other words, $2L$ is the total distance travelled by a wave entering the well and then being reflected at the edge $x = L$ so that it travels back to $x = 0$. When this length equals an integer number of wavelengths, there is a destructive interference between this wave and a wave that is reflected immediately at $x = 0$ (without traversing the potential well first), so that the net reflected wave is extinguished. As a result, no reflection occurs and the wave is fully transmitted. This effect takes place in optics and also here due to the *quantum mechanical wavenature of particles*.

On the other hand, the reflection is *maximal* whenever $qL = (n + 1/2)\pi$. A sketch of the behavior of T vs. the incident particle energy E is shown in the figure.



What happens if we instead consider a particle incident toward a potential *barrier* rather than a *well*? We obviously have to let $-V_0 \to V_0$ in order to make the potential repulsive. This has a crucial consequence when the incident particle energy E is smaller than V_0, because the wavevector now becomes imaginary:

$$q = \sqrt{2m(E - V_0)}/\hbar = \mathrm{i}\kappa \tag{4.33}$$

where $\kappa \in \Re$ for $E < V_0$. Calculating the reflection and transmission probabilities in the same way as above, we arrive at

$$T = \frac{4E(V_0 - E)}{4E(V_0 - E) + V_0^2 \sinh^2(\kappa L)} \tag{4.34}$$

whereas $R = 1 - T$. In contrast to the potential well, there is no way to make $T = 1$ except for removing the barrier all together by setting $L \to 0$. In the case where $\kappa L \gg 1$ (for instance if $V_0 \gg E$ or for wide barriers), we obtain by expanding sinh:

$$T \simeq \mathrm{e}^{-2L\sqrt{2m(V_0 - E)}/\hbar}. \tag{4.35}$$

It is clear that the probability for transmission decays exponentially as L increases, but in contrast to the classical result there is still a finite probability that the particle may appear on the other side of the barrier. This is the essence of *quantum mechanical tunneling*. Interestingly, and also in contrast to classical physics, there is a finite reflection probability even if $E > V_0$ (try to derive an expression for R and T in this scenario). Besides being interesting from a fundamental perspective, quantum mechanical tunneling is used in many practical applications. One example is scanning tunneling microscopy, where tunneling allows one to visualize the atomic landscape of materials. By placing a small metallic tip very close (order nanometer) to the surface of a material and establishing a voltage difference between the tip and the surface, electrons may tunnel between them. The tunneling probability, and thus the net current flowing between tip and surface, depends very sensitively on the tip-surface distance L as we have seen above. Therefore, moving an STM-tip across the surface of a material allows one to very accurately determine the atomic structure (potential) of the material surface. This is merely one example of how quantum mechanics is used in concrete applications.

It is interesting to note depending on the precise form of the kinetic energy term in the Hamilton-operator, the scattering problem can acquire very unusual properties. For instance, whereas conventional free particles are described by $\hat{p}^2/2m$, electrons in the graphene (a single layer of carbon atoms) are described by an effective Hamiltonian that is *linear* in the momentum operator $\hat{p}$. As a consequence, such particles can remarkably propagate through a potential barrier without any decay under special circumstances.

V. QUANTUM MECHANICS BEYOND 1D

Learning goals. After reading this chapter, the student should:

- Understand how to generalize quantum mechanics to 2D and 3D mathematically by using the Schrödinger equation (SE) and suitable eigenfunctions.
- Know how to compute the density of states for free electrons confined to a volume V.
- Understand how to set up the SE and separate the wavefunction ψ in a central potential.

Up to now, we have focused almost exclusively on one-dimensional systems and potentials. We now generalize these results to three spatial dimensions (which, after all, is a more realistic scenario) and see how this influences the results.

A. Particle in a box

Consider first our previous scenario of a particle in a potential well, flanked by infinitely high barriers. This is also commonly referred to as the "particle in a box" scenario. Inside the box with volume $V = L_x L_y L_z$, the particle is free so that:

$$V(\boldsymbol{r}) = \begin{cases} 0 & \text{if } 0 < x < L_x, 0 < y < L_y, 0 < z < L_z \\ \infty & \text{otherwise.} \end{cases} \tag{5.1}$$

The SE $\hat{H}\psi = E\psi$ is separable since the Hamilton-operator inside the box can be written as a sum of three independent terms, $\hat{H} = \sum_j \hat{H}_j$ with:

$$\hat{H}_j = \frac{\hat{p}_j^2}{2m}, \tag{5.2}$$

This means that its solution takes the form $\psi = \psi_x\psi_y\psi_z$ where the solutions for ψ_j are the solutions for a 1D particle in a box (treated earlier in this book) while the eigenvalue is $E = E_x + E_y + E_z$ (verify that this is true by insertion of the wavefunction!). Therefore, we obtain

$$\psi_{n_x n_y n_z}(x, y, z) \propto \sin(n_x\pi x/L_x)\sin(n_y\pi y/L_y)\sin(n_z\pi z/L_z) \tag{5.3}$$

with the belonging energy eigenvalues

$$E_{n_x n_y n_z} = \frac{\pi^2\hbar^2 n_x^2}{2mL_x^2} + \frac{\pi^2\hbar^2 n_y^2}{2mL_y^2} + \frac{\pi^2\hbar^2 n_z^2}{2mL_z^2},\ n_j = 1, 2, 3, \ldots. \tag{5.4}$$

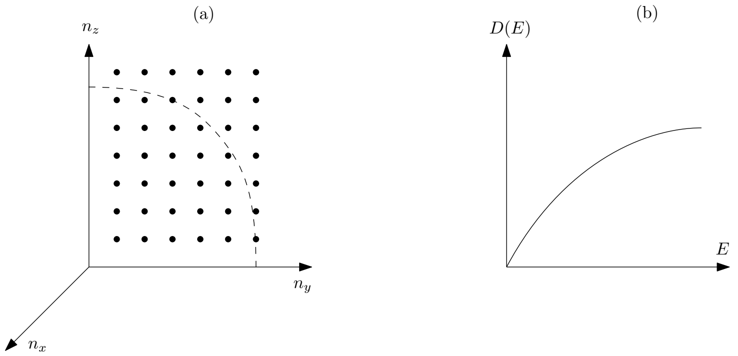
The proportionality constant in Eq. (5.3) may be determined via normalization, as before. The particle in box system goes beyond being an instructive example and in fact has high relevance for experimental systems. For instance, the particle in box wavefunctions and energy eigenvalues establish a foundation for ideal gases. Such gases constitute precisely a confined, many-body system of non-interacting particles.

Density of states

From the form of the eigenvalues in Eq. (5.4) we see that as the volume $V = L_xL_yL_z$ increases, the spacing between the eigenvalues decreases. In other words, when V becomes macroscopically large the quantized eigenvalues will lie very close to each other. A relevant question to ask is then: how many energy levels exist in a small energy interval $(E, E + \Delta E)$? To answer this question, we set out to compute the *density of states* $D(E)$. The total number of energy levels in the small energy interval $(E, E + \Delta E)$ may then be computed as $D(E)\Delta E$.

Consider a three-dimensional space where n_x, n_y, n_z are the coordinate-axes and where only positive values of n_j are allowed. The eigenvalues in Eq. (5.4) then correspond to points in this space (see figure a) so that there is one quantum state per volume element in our (n_x, n_y, n_z)-space. To a very good approximation, the number of states with energy less than some value E will then be equal to the volume of the positive octant of an ellipsiod with axes $a_j, j = x, y, z$ where:

$$a_j = \sqrt{2mEL_j^2/\pi^2\hbar^2}. \tag{5.5}$$



The volume of an ellipsoid with axes a_j is equal to $V = 4\pi a_x a_y a_z/3$, so that according to our above reasoning the number of states $R(E)$ with energy less than E is equal to:

$$R(E) \equiv \frac{1}{8}\frac{4\pi}{3}a_x a_y a_z = \frac{4\pi}{3}\Big(\frac{2m}{h^2}\Big)^{3/2} VE^{3/2}. \tag{5.6}$$

We may then compute the number of states in a small energy interval $(E, E + \Delta E)$ as

$$R(E + \Delta E) - R(E) \simeq \frac{dR}{dE}\Delta E. \tag{5.7}$$

Comparing with our above definition of the density of states $D(E)$, it is clear that $D(E) = dR/dE$. Differentiating Eq. (5.6) with respect to E then provides the final answer:

$$\boxed{D(E) = 2\pi\Big(\frac{2m}{h^2}\Big)^{3/2} V E^{1/2}.}$$

The fact that the density of states goes like $D(E) \propto \sqrt{E}$ (see figure b) is a direct result of the three-dimensionality of the system considered. In general, for a system of dimensionality d with a conventional energy-momentum relation one finds that

$$D(E) \propto E^{\frac{d}{2}-1}. \tag{5.8}$$

As a consequence, the density of available eigenstates in two dimensions ($d = 2$) is then actually independent of energy. A two-dimensional system is far from a theoretical construct - it is in fact routinely studied in physics laboratories. Graphene, a single layer of carbon atoms arranged in a honeycomb lattice, is an example of a two-dimensional material (in this case, the expression for the DOS nevertheless changes since energy is linear rather than quadratic in momentum in graphene). However, even prior to the successful isolation of graphene sheets in 2004, two-dimensional systems were realized experimentally by making the thickness L_z so small that the energy $\pi^2\hbar^2/2mL_z^2$ became much larger than all other available energies. In this case, one is guaranteed that particles will stay in the $n_z = 1$ state and not be excited to higher quantum numbers n_z. Therefore, the physics is governed solely by the behavior in the xy-plane of the system, i.e. the n_x and n_y quantum numbers.

Although we assumed that the volume under consideration was given by $V = L_xL_yL_z$, the calculation of $D(E)$ shown above becomes increasingly more valid even for a different volume geometry when V increases in magnitude. Moreover, our above calculation did not take into account the *spin* degree of freedom (relevant for *e.g.* electrons). We will later in this book return to what spin is, for readers unfamiliar with this concept. For now, we simply mention that if spin is taken into account, one simply multiplies the density of states $D(E)$ with the number of available spin-states for a particle.

The influence of different boundary conditions

One frequently encounters *periodic boundary conditions* in the literature, and we therefore clarify the consequence of using these instead of *hard-wall boundary conditions* (meaning that the wavefunction vanishes at the edge of the system). To illustrate the point, consider for simplicity a one-dimensional particle in a box scenario. Since the potential is taken as infinitely high at $x < 0$ and $x > L$, the wavefunction must satisfy $\psi(x = 0) = \psi(x = L) = 0$. For a free particle inside the box, it is straightforward to show that the vanishing of ψ at the edges leads to the quantization condition

$$k = \frac{\pi n}{L},\ n = 1, 2, 3, \ldots \tag{5.9}$$

for the wavevector k of the wavefunction, which reads $\psi = \sqrt{2/L}\sin(kx)$. Mathematically, negative values of n should also be allowed since if $\sin(kx) = 0$, then clearly $\sin(-kx) = 0$ as well. However, negative values of k only changes ψ with an overall factor (-1) and thus physically corresponds to the same state since $|\psi|^2$ remains unchanged. That is why only positive integers n appear in the above quantization condition. Another way to think of this is that $\sin(kx) = (\mathrm{e}^{\mathrm{i}kx} + \mathrm{e}^{-\mathrm{i}kx})/2\mathrm{i}$ which shows that negative values of n (and thus k) already appear in the wavefunction.

What is used more often than hard-wall boundary conditions, even when considering finite systems, is so-called *periodic boundary conditions*. This means that one demands that the wavefunction satisfies $\psi(x = 0) = \psi(x = L)$. Since the general solution of the wavefunction for a free particle (just as in the particle-in-box case) reads

$$\psi = A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx} \tag{5.10}$$

this imposes the quantization condition

$$k = \frac{2\pi n}{L},\ n = 0, \pm1, \pm2, \ldots \tag{5.11}$$

which is different from Eq. (5.9). Note how we wrote the solution with $\mathrm{e}^{\pm\mathrm{i}kx}$ rather than sin and cos, which is fully allowed since sin and cos are both linear combinations of $\mathrm{e}^{\pm\mathrm{i}kx}$. The main difference between Eq. (5.11) and Eq. (5.9) is that now also *negative values* of n are allowed. Why does this happen? The point is that since

A and B are arbitrary complex coefficients [unlike the particle-in-box case where $\psi(x = 0)$ forces $A = -B$], a new ψ and $|\psi|^2$ is obtained when $k \to (-k)$ *unlike* the particle-in-box scenario with hard walls. There are then twice as many solutions (pluss one since $n = 0$ also gives $\psi \neq 0$) in the periodic boundary condition case compared to the hard wall particle-in-box case. Moreover, the periodic boundary conditions (PBC) allow us to describe propagating waves in both positive and negative directions with different weight A and B, unlike the particle-in-box case which only allows standing waves which is equivalent to counter-propagating waves $\mathrm{e}^{\pm \mathrm{i}kx}$ with equal weight. Choosing $A = -B$ in the PBC case of course reproduces the hard wall case.

Very well - but if we now have an isolated system, should we not still use the hard wall boundary conditions to be accurate? Surely, the wavefunction must vanish at the vacuum edges. Strictly speaking, yes. However, there are at least two good reasons for using periodic boundary conditions:

- Usually, a material does not exist in isolation, but is rather connected to some other type of material. In that case, we want to be able to describe the possibility of propagating electrons in either direction which is accomplished by using PBC. Note that even if we use PBC instead of hard wall boundary conditions, we can still count the number of electron modes k.
- Even if a material does exist in strict isolation, we should not expect the boundary conditions to influence the physics substantially in the bulk of the material (far away from the boundaries) if the material is large enough. In that case, it should not matter which boundary conditions we use, and we may use whichever is more convenient, such as the PBC.

The strongest argument is, in the author's opinion, the first one. If one, for instance, is interested in discussing transport in a finite-sized system, it is clear that we must be able to describe propagating electrons in different directions. The hard wall condition should nevertheless be used if we want to identify edge-modes of a higher-dimensional system which is truly terminated by vacuum.

Summarizing, using periodic boundary conditions for a system in a volume V allows us to characterize the particles in the system with a well-defined momentum. In turn, this means that we can describe particles propagating in various directions in the system, as is relevant for *e.g.* describing electron motion in a metal. It is also important to note that the density of states $D(E)$ obtained using PBC is in fact the same as that obtained using hard wall boundary conditions. I encourage the reader to try to prove this, using the same procedure as we did for the hard wall case! You should find that the number of states in the positive octant with energy less than E is in the PBC case $\frac{1}{8}$ of what we found in the hard wall case. At the same time, negative integers for n_j are allowed in the PBC case, which gives us an additional factor $2^3 = 8$ which cancels the $\frac{1}{8}$, so that the density of states is the same.

B. Harmonic oscillator

A three-dimensional harmonic oscillator, which we allow to be anisotropic (meaning that it may have different spring constants in different spatial directions), has a Hamilton-operator:

$$\hat{H} = \frac{\hat{\boldsymbol{p}}^2}{2m} + \frac{1}{2}m\sum_j \omega_j^2 x_j^2. \tag{5.12}$$

Here, ω_j is the frequency associated with spatial direction x_j ($j = 1, 2, 3$ where $x_1 = x, x_2 = y, x_3 = z$). Since there is no coupling between different spatial coordinates x_j in Eq. (5.12), the motion in each direction should be independent of the motion in the other directions. Since Eq. (5.12) can be written as a sum of three independent terms:

$$\hat{H} = \sum_j \hat{H}_j,\ \hat{H}_j = \frac{\hat{p}_j^2}{2m} + \frac{1}{2}\omega_j^2 x_j^2, \tag{5.13}$$

the time-independent SE $\hat{H}\psi = E\psi$ is *separable*. Just as for the particle in a box, this means that the wavefunction

$$\psi = \prod_j \psi_j \tag{5.14}$$

solves the equation, where ψ_j satisfies

$$\hat{H}_j\psi_j = E_j\psi_j,\ E = \sum_j E_j. \tag{5.15}$$

At this point, we can simply reuse the already derived result for the one-dimensional harmonic oscillator where we know that

$$E_j = \hbar\omega_j(n_j + \frac{1}{2}),\ n_j = 0, 1, 2, \ldots \tag{5.16}$$

so that the total energy eigenvalue becomes

$$E = \hbar\omega_x(n_x + \frac{1}{2}) + \hbar\omega_y(n_y + \frac{1}{2}) + \hbar\omega_z(n_z + \frac{1}{2}). \tag{5.17}$$

In the previous chapter in this book where we treated the harmonic oscillator model in detail, we mentioned that the harmonic oscillator is the relevant model for a large amount of seemingly disparate physical systems. The present generalization of the harmonic oscillator to 3D is for instance relevant both for an electromagnetic field and the quantized lattice vibrations in crystals that comprise materials. In the special case where all eigenfrequencies are equal, $\omega_j = \omega$, we say that the system is *isotropic* (behaving the same in all spatial directions). The eigenvalue of the system then becomes $E = (N + 3/2)\hbar\omega$ where $N = n_x + n_y + n_z$. Whereas the ground state E_0 is not degenerate, excited states are since a given finite value of N can be obtained in several different ways by combining $\{n_x, n_y, n_z\}$ in a suitable manner. A crucial point to note here is that the degeneracy following from the isotropic behavior is accompanied by the fact that the Hamilton operator $\hat{H}$ acquires a symmetry, namely rotational symmetry. This can be seen since the potential takes the form $V(\boldsymbol{r}) = \frac{1}{2}m\omega\boldsymbol{r}^2$, which is invariant under rotations as it only depends on the absolute value of $|\boldsymbol{r}|$ ($\boldsymbol{r}^2 = |\boldsymbol{r}|^2$). The observation that symmetries and degeneracies are closely related is not accidental, and we shall return to this issue later.

C. 2D potentials with polar coordinates

So far, we have used Cartesian coordinates in our treatment of all systems. We now turn our attention to a polar coordinate treatment using coordinates (r, ϕ) instead of (x, y), not simply for the sake of pedagogical value, but also as a precursor to our treatment of the important case of 3D rotationally symmetric systems.

Our starting point is a potential $V(\boldsymbol{r})$ which is rotationally symmetric, meaning that it only depends on the magnitude $r = |\boldsymbol{r}|$. Therefore, $V(\boldsymbol{r}) = V(r)$ and the SE is:

$$-\frac{\hbar^2}{2M}(\partial_r^2 + r^{-1}\partial_r + r^{-2}\partial_\phi^2)\psi(r,\phi) + V(r)\psi(r,\phi) = E\psi(r,\phi). \tag{5.18}$$

Here, we used M for the particle mass rather than m, since the latter symbol will be used for a quantum number associated with angular momentum. Moreover, we used the short-hand notation $\partial_j \equiv \partial/\partial j$ and $\partial_j^2 = \partial^2/\partial j^2$ with $j = r, \phi$. Finally, we made use of the fact that the Laplace-operator ∇^2 in 2D and using polar coordinates is:

$$\nabla^2 = \partial_r^2 + r^{-1}\partial_r + r^{-2}\partial_\phi^2. \tag{5.19}$$

Eq. (5.18) is a separable equation. It is left as an exercise for the reader to show that when setting

$$\psi(r,\phi) = R(r)\Phi(\phi) \tag{5.20}$$

in Eq. (5.18), the equation can be rearranged to read:

$$\frac{r^2}{R(r)}\Big(\partial_r^2 R + r^{-1}\partial_r R + \frac{2M}{\hbar^2}[E - V(r)]R\Big) = -\frac{1}{\Phi(\phi)}\partial_\phi^2\Phi. \tag{5.21}$$

Although R and Φ depend only on one variable each, we stick with the short-hand notation ∂_j for brevity. Since the left hand side of the above equation only depends on r whereas the right hand side only depends on ϕ, both sides must equal a constant. We name this constant m^2. The equation for the angular part Φ of the wavefunction ψ then has the form

$$-\frac{1}{\Phi(\phi)}\partial_\phi^2\Phi = m^2 \tag{5.22}$$

which has the solution

$$\psi \propto \mathrm{e}^{\mathrm{i}m\phi}. \tag{5.23}$$

This solution gives us information about which values m is allowed to take. Consider the fact that ϕ and $\phi + 2\pi$ must correspond to the same physical angle, since a 2π advancement of the angle brings the position vector back to its original location. Therefore, m must be an integer to ensure that $\Phi(\phi) = \Phi(\phi + 2\pi)$. We have then established that the total wavefunction has the form

$$\psi(r,\phi) = R(r)\mathrm{e}^{\mathrm{i}m\phi},\ m = 0, \pm 1, \pm 2, \ldots \tag{5.24}$$

where $R(r)$ must obey the following equation

$$-\frac{\hbar^2}{2M}(\partial_r^2 + r^{-1}\partial_r - m^2 r^{-2})R(r) + V(r)R(r) = ER(r). \tag{5.25}$$

Its specific solution depends on the shape of $V(r)$. We shall return to this type of equation later on.

VI. QUANTIZATION OF SPIN AND OTHER ANGULAR MOMENTA

Learning goals. After reading this chapter, the student should:

- Know how to deal with the quantization of orbital angular momentum operators and the belonging commutation relations.
- Understand how to arrive at the quantized energy eigenvalues of the Coulomb potential.
- Be able to account for the properties of generalized angular momentum operators in quantum mechanics, in particular the spin operator.

From classical mechanics, we know that angular momentum is an important quantity which is conserved whenever a particle moves in a central potential $V(\boldsymbol{r}) = V(r)$. We will now see how this result holds also quantum mechanically, meaning that the eigenvalues associated with the operator for angular momentum will be crucial in order to describe the quantum states.

A. Orbital angular momentum

Classically, we know that the angular momentum of a particle at position $\boldsymbol{r}$ with momentum $\boldsymbol{p}$ with respect to the center of the coordinate system is defined as

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}. \tag{6.1}$$

Therefore, the quantum mechanical operators for each of the components L_j are obtained via our usual prescription $p_j \to \hat{p}_j$ and $x_j \to \hat{x}_j$ for $j = x, y, z$:

$$\hat{L}_x = y\hat{p}_z - z\hat{p}_y,\ \hat{L}_y = z\hat{p}_x - x\hat{p}_z,\ \hat{L}_z = x\hat{p}_y - y\hat{p}_x. \tag{6.2}$$

It is straightforward to verify that these operators are all Hermitian (try it), as they should be since they correspond to physically observable quantities: $\hat{L}_j = \hat{L}_j^\dagger$. Now, when treating the position and momentum operators in the early chapters of this book we saw that they did not commute: $[\hat{x}, \hat{p}_x] \neq 0$. As a consequence, they could not have sharply defined eigenvalues simultaneously according to Heisenberg's uncertainty principle $\Delta x \Delta p_x \geq \hbar/2$. What about the angular momentum components? Can they have sharply defined values simultaneously? By making repeated use of $[\hat{x}, \hat{p}_x] = \mathrm{i}\hbar$ (and similarly for y and z), it follows from the definitions in Eq. (6.2) that:

$$[\hat{L}_x, \hat{L}_y] = [\hat{L}_x, z\hat{p}_x - x\hat{p}_z] = -\mathrm{i}\hbar y\hat{p}_x + \mathrm{i}\hbar x\hat{p}_y = \mathrm{i}\hbar\hat{L}_z. \tag{6.3}$$

In the same way, one finds for the other commutators that $[\hat{L}_y, \hat{L}_z] = \mathrm{i}\hbar\hat{L}_x$ and $[\hat{L}_z, \hat{L}_x] = \mathrm{i}\hbar\hat{L}_y$. Note how we could obtain the different commutators from each other by a cyclic permutation of the variables. We can also show that the operator for the magnitude squared of the total angular momentum, $\hat{\boldsymbol{L}}^2$, and one of the angular momentum components $\hat{L}_j$ commute (try to show this):

$$[\hat{\boldsymbol{L}}^2, \hat{L}_z] = 0 \tag{6.4}$$

by using the relations in Eq. (6.3)!] The same goes for $[\hat{\boldsymbol{L}}^2, \hat{L}_x] = [\hat{\boldsymbol{L}}^2, \hat{L}_y] = 0$. Therefore, we conclude that

- Two Cartesian components of the angular momentum cannot have sharply defined values simultaneously.
- One component of the angular momentum and the magnitude squared of the angular momentum can have sharply defined values simultaneously.

With this in mind, we should be able to identify simultaneous eigenfunctions for $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$. We choose $\hat{L}_z$ rather than $\hat{L}_x$ or $\hat{L}_y$ simply by convention: the z-component is not special compared to the others for any reason. Before obtaining the common set of eigenfunctions (which must exist since $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$ commute), we express the angular momentum operators in spherical coordinates instead. This is more convenient since rotations are more easily dealt with using angles than Cartesian coordinates. We found above that

$$\hat{L}_x = y\frac{\hbar}{\mathrm{i}}\partial_z - z\frac{\hbar}{\mathrm{i}}\partial_y,\ \hat{L}_y = z\frac{\hbar}{\mathrm{i}}\partial_x - x\frac{\hbar}{\mathrm{i}}\partial_z,\ \hat{L}_z = x\frac{\hbar}{\mathrm{i}}\partial_y - y\frac{\hbar}{\mathrm{i}}\partial_x. \tag{6.5}$$

Since $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$, and $z = r\cos\theta$, we find that

$$\partial_z = (\partial r/\partial z)\partial_r + (\partial\theta/\partial z)\partial_\theta + (\partial\phi/\partial z)\partial_\phi = \cos\theta\partial_r - (\sin\theta/r)\partial_\theta, \tag{6.6}$$

since ϕ does not depend on z ($\tan\phi = y/x$). We may express ∂_x and ∂_y in terms of spherical coordinates and corresponding derivatives following the same route, and inserting the results into Eq. (6.5) provides:

$$\begin{aligned}\hat{L}_x &= \frac{\hbar}{\mathrm{i}}(-\sin\phi\partial_\theta - \cot\theta\cos\phi\partial_\phi),\\ \hat{L}_y &= \frac{\hbar}{\mathrm{i}}(\cos\phi\partial_\theta - \cot\theta\sin\phi\partial_\phi),\\ \hat{L}_z &= \frac{\hbar}{\mathrm{i}}\partial_\phi. \end{aligned}\tag{6.7}$$

Using that $\hat{\boldsymbol{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$, we also identify:

$$\hat{\boldsymbol{L}}^2 = \hbar^2(\partial_\theta^2 + \cot\theta\partial_\theta + (1/\sin^2\theta)\partial_\phi^2). \tag{6.8}$$

Having established what the orbital angular momentum operators are (we specify "orbital" to distinguish them from *internal* angular momentum operator we shall introduce soon, namely spin), we can now discuss their eigenfunctions.

For $\hat{L}_z$, it follows that the eigenvalue equation

$$\hat{L}_z\Phi(\phi) = \frac{\hbar}{\mathrm{i}}\partial_\phi\Phi = m\hbar\Phi(\phi) \tag{6.9}$$

is satisfied by $\Phi(\phi) = \mathrm{e}^{\mathrm{i}m\phi}$. Since an advancement of ϕ by 2π should land us at exactly the same physical point, m must be an integer to ensure that $\Phi(\phi) = \Phi(\phi + 2\pi)$. Note that this is *exactly* the same property and eigenfunction that we discussed for a rotationally symmetric potential in 2D in the previous chapter [see Eq. (5.23)]! This is no coincidence: a rotationally symmetric potential in 2D (say, the xy-plane) results in the angular momentum along the z-direction being conserved. Therefore, the eigenfunction of such a system should be an eigenstate of $\hat{L}_z$ with a well-defined eigenvalue. Since $\hat{L}_z$ only acts on ϕ, and not θ, it follows that a common set of eigenfunctions for $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$ must have the general form:

$$Y(\theta, \phi) = \Theta(\theta)\mathrm{e}^{\mathrm{i}m\phi}. \tag{6.10}$$

Let us then write the eigenvalue problem for $\hat{\boldsymbol{L}}^2$ as:

$$\hat{\boldsymbol{L}}^2 Y = \lambda\hbar^2 Y. \tag{6.11}$$

The reason for why we have written the eigenvalue as $\lambda\hbar^2$, rather than simply some constant c, is that $\boldsymbol{L}^2$ has dimension $\hbar^2$. In this way, λ is guaranteed to be a dimensionless quantum number. Inserting Eq. (6.10) into Eq. (6.11) gives an equation that determines $\Theta(\theta)$:

$$\Big(\frac{1}{\sin\theta}\partial_\theta \sin\theta\partial_\theta + \lambda - \frac{m^2}{\sin^2\theta}\Big)\Theta(\theta) = 0. \tag{6.12}$$

We introduce the auxiliary quantity $X \equiv \cos\theta$ and rewrite the equation as

$$\Big((1 - X^2)\partial_X^2 - 2X\partial_X + \lambda - \frac{m^2}{1 - X^2}\Big)\Theta = 0. \tag{6.13}$$

To solve this equation, we draw upon the *Legendre-polynomials*. The differential equation

$$\Big((1 - X^2)\partial_X^2 - 2X\partial_X + \lambda\Big)\Theta = 0, \tag{6.14}$$

which is obtained by setting $m = 0$ in Eq. (6.13) is known as Legendre's differential equation. Although it can be solved mathematically for arbitrary values of λ, it only has a physically acceptable solution for specific, discrete values of λ. To examine it further, we expand Θ in powers of X (the same strategy we used in the harmonic oscillator problem):

$$\Theta = \sum_{n=0}^{\infty} a_n X^n. \tag{6.15}$$

Plugging this into Eq. (6.14) gives us a recursion formula for the coefficients (again, similarly to the harmonic oscillator case):

$$\frac{a_{n+2}}{a_n} = \frac{n(n+1) - \lambda}{(n+1)(n+2)},\ n = 0, 1, 2, \dots \tag{6.16}$$

To obtain a physically acceptable wavefunction, we must ensure that Θ does not diverge. A potential problem arises when $X = 1$ (corresponding to $\theta = 0$) in which case we have $\Theta = \sum_{n=0}^{\infty} a_n$. For large n, however, it follows from Eq. (6.16) that $a_{n+2}/a_n \to 1$ which in turn means that $\sum_{n=0}^{\infty} a_n$ is not guaranteed to converge (the same happens *e.g.* for the divergent harmonic seriers $\sum_n a_n$ where $a_n = 1/n$). We are forced to choose λ in Eq. (6.16) so that the series is truncated (stopped) at some point. This happens when

$$\lambda = l(l + 1),\ l = 0, 1, 2, 3, \dots \tag{6.17}$$

When l is an odd number, the series with odd powers of X will cease with X^l as the final term. Additionally, we demand that $a_0 = 0$ since the even powers of X are not truncated. Similarly, when l is an even number, we demand that $a_1 = 0$.

This procedure ensures that we obtain physically acceptable solutions of Eq. (6.13) which converge for any X, and that these solutions are polynomials of degree l. When the solutions are normalized so that the value of the solution in $X = 1$ is 1, the solution is referred to as the Legendre polynomial $P_l(X)$ of degree l:

$$P_l(X = 1) = P_l(\theta = 0) = 1. \tag{6.18}$$

From now on, we shall stick with the notation P_l for the solution rather than using Θ. A useful property is that $P_l(-X) = (-1)^l P_l(X)$.

So far, however, we have only considered the special case $m = 0$. In order to solve the original eigenvalue equation Eq. (6.13) for $m \neq 0$, we differentiate Eq. (6.14) m times (using the notation P_l for the solution rather than Θ, as mentioned before) and obtain:

$$\left[(1 - X^2)\partial_x^2 - 2x\partial_x + l(l+1) - \frac{m^2}{1 - X^2}\right]\left[(1 - X^2)^{m/2}\partial_X^m P_l(X)\right] = 0. \tag{6.19}$$

Comparing this to Eq. (6.13) shows that we have now identified the solution. Namely, the function

$$P_l^m(X) = (1 - X^2)^{m/2}\partial_x^m P_l(X) \tag{6.20}$$

is the solution to Eq. (6.13) for arbitrary m (including $m = 0$).

When treating the $m = 0$ case, an important issue was that we wanted to obtain solutions that were physically acceptable (non-diverging). The same goes here: we are not just interested in any mathematical solution, but only those solutions that can be normalized since the solution determines the quantum mechanical wavefunction. Since the range of values that $|X|$ can take lies within $[0, 1]$, it is clear that Eq. (6.20) is a physically acceptable solution for any X since $P_l^m(X)$ is finite for $|X| \leq 1$. Moreover, since $P_l(X)$ is a polynomial of the l-th degree, $P_l^m(X)$ can only be finite when $m \leq l$ due to the differentiation $\partial_x^m P_l(X)$.

The functions $P_l(X)$ are the Legendre polynomials, whereas the functions $P_l^m(X)$ are known as the *associated Legendre polynomials.* It is clear from Eq. (6.19) that since only m^2 appears, the relation $P_l^m(X) = P_l^{-m}(X)$ is satisfied. The first few associated Legendre polynomials read:

$$P_{l=1}^{m=1}(X) = \sqrt{1 - X^2},\ P_{l=2}^{m=1}(X) = 3X\sqrt{1 - X^2},\ P_{l=2}^{m=2}(X) = 3(1 - X^2). \tag{6.21}$$

They are normalized according to

$$\int_{-1}^{1} [P_l^m(X)]^2 dX = \frac{2}{2l + 1} \frac{(l + |m|)!}{(l - |m|)!} \tag{6.22}$$

and their parity [behavior under the transformation $X \to (-X)$] is:

$$P_l^m(-X) = (-1)^{l-m} P_l^m(X). \tag{6.23}$$

The reader is encouraged to try to show this from the parity property of $P^l(X)$, which we discussed earlier, and from how we obtained the equation for $P_l^m(X)$ in the first place.

Let us summarize our treatment of the common set of eigenfunctions for $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$ so far. We have found that the functions $Y_{lm}(\theta, \phi)$, which are products of $\mathrm{e}^{\mathrm{i}m\phi}$ and $P_l^m(\cos\theta)$, are eigenfunctions of *both* $\hat{L}_z$ and $\hat{\boldsymbol{L}}^2$ with belonging eigenvalues:

$$\boxed{\hat{\boldsymbol{L}}^2 Y_{lm} = l(l + 1)\hbar^2 Y_{lm} \text{ where } l = 0, 1, 2, \dots \text{ and } \hat{L}_z Y_{lm} = m\hbar Y_{lm} \text{ where } m = -l, -l + 1, \dots l - 1, l.}$$

When Y_{lm} are normalized to unity upon integration over all solid angles:

$$\int |Y_{lm}|^2 d\Omega = \int_0^{2\pi} \int_0^{\pi} |Y_{lm}|^2 \sin\theta d\theta d\phi = 1 \tag{6.24}$$

they are referred to as *harmonics*. The full form of Y_{lm} is then:

$$\boxed{Y_{lm}(\theta, \phi) = t_m \sqrt{\frac{2l + 1}{4\pi} \frac{(l - |m|)!}{(l + |m|)!}} P_l^{|m|}(\cos\theta) \mathrm{e}^{\mathrm{i}m\phi}.}$$

where t_m can be freely chosen as $+1$ or -1. Usually, one sets $t_m = 1$ for $m \leq 0$ and $t_m = (-1)^m$ for $m \geq 0$.

We also mention the parity properties of Y_{lm}, since these are often useful when performing integrals. Inversion has the effect that $\boldsymbol{r} \to -\boldsymbol{r}$, which in spherical coordinates is equivalent to $r \to r$, $\theta \to \pi - \theta$, and $\phi \to \phi + \pi$. Consequently, $\mathrm{e}^{\mathrm{i}m\phi} \to (-1)^m \mathrm{e}^{\mathrm{i}m\phi}$ and $X = \cos\theta \to -X$ which means that

$$Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta, \phi). \tag{6.25}$$

The parity of the spherical harmonics is thus exclusively determined by the quantum number l. The parity is odd for odd l whereas it is even for even l. It should be noted that often times in the literature, one uses letters to classify the spherical harmonics rather than their quantum number l. Specifically, one uses

- s for $l = 0$
- p for $l = 1$

- d for $l = 2$
- f for $l = 3$

and so forth. The origin of this nomenclature is the characterization of certain groups of spectral lines analyzed toward the end of the 19th century, where for instance s stands for "sharp" and p for principal. Some specific expressions for the spherical harmonics are as follows:

$$Y_{00} = \frac{1}{\sqrt{4\pi}},\ Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta,\ Y_{1,\pm 1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta \mathrm{e}^{\pm \mathrm{i}\phi}. \tag{6.26}$$

Note how the s-component Y_{00} is rotationally invariant, as it is independent of both θ and ϕ. The spherical harmonics form a complete orthonormal set, which means that an arbitrary function $g(\theta, \phi)$ existing on the surface of a sphere can be expanded in these (a property often made use of in physics):

$$g(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} c_{ml} Y_{lm}(\theta, \phi) \tag{6.27}$$

where c_{ml} are the expansion coefficients. The orthonormality property is expressed in the standard way:

$$\int Y^*_{lm}(\theta, \phi) Y_{l'm'}(\theta, \phi) d\Omega = \delta_{ll'}\delta_{mm'}. \tag{6.28}$$

B. Central potentials and application to the Coulomb potential

We previously saw how the eigenfunctions for a 2D rotationally symmetric potential were proportional to $\mathrm{e}^{\mathrm{i}m\phi}$, which we by now know is the eigenfunction for $\hat{L}_z$. This makes sense since L_z is a conserved quantity for system that is rotationally symmetric around the z-axis. We now extend these considerations to 3D and also have a look at the Coulomb-potential as a specific example.

A mass m moving in a spherically symmetric potential $V(\boldsymbol{r}) = V(r)$ has the Hamilton-operator:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r). \tag{6.29}$$

Introducing spherical coordinates, and making using of the definition of $\hat{\boldsymbol{L}}^2$ in Eq. (6.8), this can be rewritten as:

$$\hat{H} = -\frac{\hbar^2}{2m}\Big(\partial_r^2 + (2/r)\partial_r\Big) + \frac{\hat{\boldsymbol{L}}^2}{2mr^2} + V(r). \tag{6.30}$$

The terms associated with the kinetic energy of the particle thus describe both motion in the radial direction and rotation, the latter described precisely by the term $\propto \hat{\boldsymbol{L}}^2$. When faced with a Hamilton-operator, one of the first things which are useful to note is which other operators corresponding to physical quantities that commute with it. In this case, it is clear that $\hat{\boldsymbol{L}}^2$ commutes with $\hat{H}$, since $\hat{H}$ depends on $\hat{\boldsymbol{L}}^2$ and $\hat{\boldsymbol{L}}^2$ commutes with itself. Moreover, we showed in the previous section that the components of angular momentum all commute in general with $\hat{\boldsymbol{L}}^2$. Because of this, we can state that $\boldsymbol{L}^2$ and L_j $(j = x, y, z)$ are all conserved quantities and that there exists a set of common eigenfunctions for the (i) energy, (ii) square of the total angular momentum, and (iii) one of the angular momentum components (conventionally chosen to be L_z). We proved in the previous section that $Y_{lm}(\theta, \phi)$ are the eigenfunctions for $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$, which means that the common set of eigenfunctions for these operators and $\hat{H}$ must have the form:

$$\psi(r, \theta, \phi) = R(r) Y_{lm}(\theta, \phi). \tag{6.31}$$

Using that $\hat{\boldsymbol{L}}^2 Y = l(l+1)\hbar^2 Y$, insertion of Eq. (6.31) into $\hat{H}\psi = E\psi$ gives

$$\partial_r^2 R + (2/r)\partial_r R + \Big(\frac{2m}{\hbar^2}[E - V(r)] - \frac{l(l+1)}{r^2}\Big)R = 0. \tag{6.32}$$

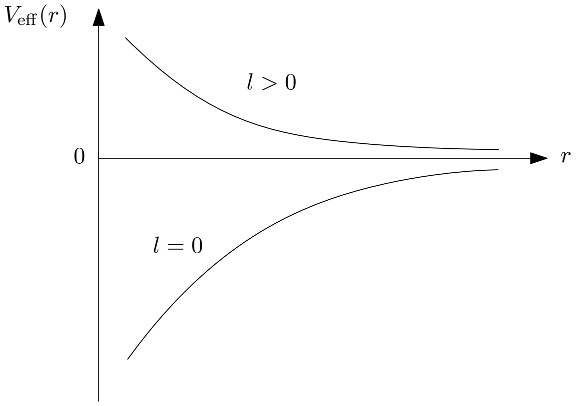
Remarkably, we can rewrite this equation as the usual one-dimensional SE for a particle moving in an *effective* potential V_{eff}. This is done by introducing $u(R) = rR(r)$ and

$$V_{\text{eff}} = V + \frac{l(l+1)\hbar^2}{2mr^2}, \tag{6.33}$$

in which case Eq. (6.32) takes the form:

$$\boxed{-\frac{\hbar^2}{2m}\partial_r^2 u(r) + \Big(V(r) + \frac{l(l+1)\hbar^2}{2mr^2}\Big)u(r) = Eu(r).}$$

We see that the effective potential V_{eff} consists of the original potential and a so-called *centrifugal term* $l(l+1)\hbar^2/2mr^2$. The sketch of V_{eff} below [where $V(r)$ is an attractive potential] shows that the effect of the centrifugal term is, in general, to make small values of r less accessible to the particle whenever $l \neq 0$. In many cases, V_{eff} acquires a minimum at a finite value $r = r_0$ (not shown in the figure).



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To determine the full wavefunction $\psi(r,\theta,\phi)$ for a spherically symmetric potential, the only remaining task is to solve the equation above for $u(r)$ for $r \geq 0$, since that provides us with the $R(r)$ that goes into Eq. (6.31) (we have already determined Y_{lm}). Before attempting to solve the equation generally, let us make some considerations regarding how $u(r)$ should behave in various limits. First of all, it is clear that $u(r=0)$ must vanish, the reason being that otherwise $R(r) = u(r)/r$ will diverge as $r \to 0$. Secondly, consider the asymptotic limit $r \to \infty$. Assuming that the potential satisfies $V(r \to \infty) \to 0$ (as virtually all real potentials do), the equation for u reduces to

$$u'' = -2mE\hbar^{-2}u \tag{6.34}$$

where $'$ denotes differentiation with respect to r. Any bound state with $E < 0$ will then exponentially decay to zero as follows

$$u(r) \propto \mathrm{e}^{-\kappa r} \text{ for } r \to \infty, \tag{6.35}$$

where $\kappa = \sqrt{2m|E|/\hbar^2}$. Another important case occurs when the potential $V(r)$ diverges slower than $1/r^2$, in which case the centrifugal term will dominate when $r \to 0$. The equation for u then takes the form:

$$u'' \simeq \frac{l(l+1)}{r^2}u \tag{6.36}$$

which has the physically acceptable solution $u(r) \simeq r^{l+1}$. Therefore, assuming that the centrifugal potential dominates as $r \to 0$, we have $R(r) \propto r^l$ for $r \to 0$.

Starting out with a spherically symmetric potential in 3D, we have managed to reduce the problem to solving a one-dimensional problem (with r as coordinate) with an effective potential $V_{\text{eff}}(r)$. We now consider specifically the Coulomb-potential, as the most important application of this problem. The electrostatic interaction between a particle with charge Ze, position in the origin of our coordinate system, and a moving electron with charge $-e$, is:

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r}. \tag{6.37}$$

We will begin by focusing on *bound states*, which thus have negative energy $E < 0$. It is important to note that the term "bound state" generally refers to a state which has less energy than the asymptotic value of the potential energy. In our case, this asymptotic value is zero and thus a bound state has $E < 0$. There is nothing weird about the fact that the energy is negative, because we can always choose the reference level of energy as we like. It should be noted that besides the presumably discrete bound state spectrum we will find, there also exists a conntinuous energy spectrum $E \geq 0$ corresponding to particles with too high energy to be bound by the potential. The continuous part of the spectrum will be of importance when discussing scattering of charged particles on each other.

The radial equation that needs to be solved in the specific case of a Coulomb equation reads:

$$\frac{\hbar^2}{2m}\partial_r^2 u + \Big[\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r} - \frac{l(l+1)\hbar^2}{2mr^2} + E\Big]u(r) = 0. \tag{6.38}$$

We can bring this equation to a more convenient form by introducing the auxiliary quantity $\rho = r\sqrt{-8mE/\hbar^2}$ and dividing the equation on $-4E$:

$$\partial_\rho^2 u + \Big[\frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2} - \frac{1}{4}\Big]u(\rho) = 0. \tag{6.39}$$

Here, we introduced the quantity:

$$\lambda = \frac{Ze^2}{4\pi\epsilon_0\hbar}\sqrt{\frac{m}{-2E}}. \tag{6.40}$$

It turns out that the method we used to identify the energy eigenvalues in the harmonic oscillator case is very useful, because we can apply precisely the same strategy here as well. We start by considering how $u(\rho)$ behaves for large distances ρ, in which case Eq. (6.39) reduces to

$$\partial_\rho^2 u \simeq u/4. \tag{6.41}$$

There are two solutions: $u = \mathrm{e}^{\pm\rho/2}$. However, only the solution $\mathrm{e}^{-\rho/2}$ is physically acceptable, as the other one diverges as $\rho \to \infty$. Therefore, we can now set

$$u(\rho) = v(\rho)\mathrm{e}^{-\rho/2} \tag{6.42}$$

where $v(\rho)$ should be a polynomial that is completely dominated by $\mathrm{e}^{-\rho/2}$ for large ρ. Inserting Eq. (6.42) into Eq. (6.39) gives us the equation for $v(\rho)$:

$$\partial_\rho^2 v - \partial_\rho v + \lambda v/\rho - l(l+1)v/\rho^2 = 0. \tag{6.43}$$

Since v must be a converging polynomial, we expand it in ρ:

$$v(\rho) = c_0\rho^{l+1} + c_1\rho^{l+2} + \ldots = \sum_{k=0}^{\infty} c_k\rho^{l+1+k}. \tag{6.44}$$

Note how the lowest order of ρ is $l+1$ rather than zero, the reason being that we have already identified above that $u(r) \simeq r^{l+1}$ as $r \to 0$. Inserting our expansion into Eq. (6.43) provides

$$\sum_k \Big(c_k[k(2l+1+k)]\rho^{l+k-1} - c_k[l+1+k-\lambda]\rho^{l+k}\Big) = 0. \tag{6.45}$$

As in the harmonic oscillator case, this is equivalent to a recursion equation for the coefficients $\{c_k\}$ since the coefficient in front of each order of ρ have to vanish in order to satisfy the equation. From Eq. (6.45), we obtain:

$$\frac{c_k}{c_{k-1}} = \frac{l+k-\lambda}{k(2l+1+k)}, \tag{6.46}$$

so that the full solution of $v(\rho)$ can be written as:

$$v(\rho) = c_0\Big[\rho^{l+1} + \frac{l+1-\lambda}{2l+2}\rho^{l+2} + \frac{(l+1-\lambda)(l+2-\lambda)}{(2l+2)(4l+6)}\rho^{l+3} + \ldots\Big]. \tag{6.47}$$

The necessity to truncate this series can be seen by noting that for large k, it follows from Eq. (6.46) that $c_k/c_{k-1} \simeq 1/k$. This is the same ratio between two successive coefficients as in the series expansion of e^ρ for large k. The asymptotic behavior for large ρ, where the large values of k are most relevant, would then be $v(\rho) = \mathrm{e}^\rho \mathrm{e}^{-\rho/2} = \mathrm{e}^{\rho/2}$ which diverges and is thus not acceptable. Therefore, we must choose λ as an integer we name n which is larger than or equal to $l+1$ in order to truncate the series in Eq. (6.47), as seen from the coefficients. For instance, if we choose

$$\lambda = l + 1 + j, \tag{6.48}$$

where $j = 0, 1, 2, \ldots$, it follows from Eq. (6.45) that $c_{j+1} = 0$. The smallest value accessible for n is 1, so that

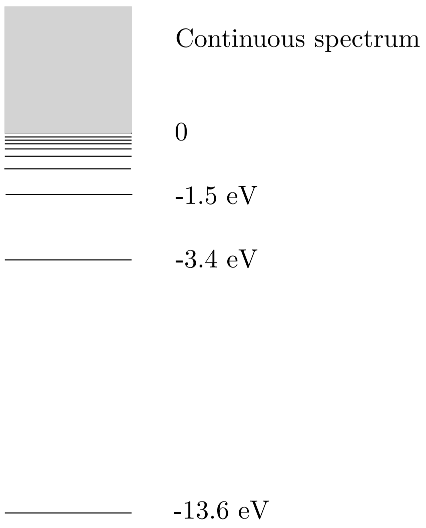
$$l \leq n - 1. \tag{6.49}$$

Going back to the definition of λ in Eq. (6.40), we see that the criterium that $\lambda = n$ gives us a quantization condition for the energy E:

$$\boxed{E_n = -\frac{m}{2\hbar^2}\Big(\frac{Ze^2}{4\pi\epsilon_0}\Big)^2\frac{1}{n^2},\ n = 1, 2, \ldots}$$

Since n, which is known as the *principal quantum number*, can take on any value among the natural numbers, there are infinitely many bound states. Note how the energy levels *only* depend on n, and not *e.g.* on quantum numbers l and m associated with the angular momentum. The number of discrete, available energy states pile up as one approaches $E = 0$ (see figure).

Coulomb spectrum for hydrogen



Another common way to write the quantized bound state energies of a charged particle in a Coulomb potential is

$$E_n = -\frac{1}{2}m_e c^2\alpha^2\frac{Z^2}{n^2}. \tag{6.50}$$

Here, m_e is the electron mass while

$$a_0 \equiv \frac{4\pi\epsilon_0}{e^2}\frac{\hbar^2}{m_e} \simeq 0.529\times10^{-10}\text{ m}. \tag{6.51}$$

is the Bohr radius, which is a convenient length scale to work with (*e.g.* to normalize lengths against) in atomic physics. Also, we introduced the *fine-structure constant* in Eq. (6.50):

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \simeq \frac{1}{137}. \tag{6.52}$$

We noted previously that the energy levels in Eq. (6.50) depend only on the principal quantum number n, which means that there is a large degeneracy associated with each eigenenergy. For a specific value of n, we know that l takes the values $l = 0, 1, 2, \ldots n-1$. Moreover, for each l-value there are $(2l+1)$ possible values for the quantum number m associated with the z-component of the angular momentum. The total degeneracy for a given eigenvalue E_n is then g_n where:

$$\sum_{l=0}^{n-1}(2l+1) = n^2. \tag{6.53}$$

Having identified the eigenvalues of the Coulomb-potential, we can now turn our attention to the eigenfunctions. In our above treatment, we concluded that the radial eigenfunctions had to have the form:

$$R_{nl} = \rho^l \mathrm{e}^{-\rho/2}M(\rho), \tag{6.54}$$

where $\rho = r\sqrt{-8mE/\hbar^2}$ (where the m is the *mass* of the particle) and $M(\rho)$ is a polynomial of degree $n-l-1$. The latter is defined via

$$M(\rho) = \sum_{k=0}^{\infty} c_k\rho^k \tag{6.55}$$

where the expansion coefficients are determined by

$$\frac{c_k}{c_{k-1}} = \frac{l+k-n}{k(2l+1+k)}, \tag{6.56}$$

in effect Eq. (6.46) where we have set $\lambda = n$ to truncate the series and ensure convergence. Only one coefficient, namely the first one (c_0), remains undetermined via the recursion formula above. However, c_0 can be determined from the normalization:

$$\int_0^\infty |R_{nl}(r)|^2 r^2 dr = 1. \tag{6.57}$$

Using the above equations, we find that:

$$\begin{aligned} R_{n=1,l=0} &= 2a^{-3/2}\mathrm{e}^{-\rho/2}, \\ R_{n=2,l=0} &= 2^{-1/2}a^{-3/2}(1-\rho/2)\mathrm{e}^{-\rho/2}, \\ R_{n=2,l=1} &= 24^{-1/2}a^{-5/2}\rho\mathrm{e}^{-\rho/2}. \end{aligned} \tag{6.58}$$

and so forth. Since we may rewrite ρ as $\rho = 2r/na$ with $a = a_0 m_e/Zm$, we confirm the above comment that a_0 is a natural length scale characterizing the spatial extent of the wavefunctions. We also emphasize that ρ depends on n, meaning that ρ is different for each R_{nl} in Eq. (6.58).

Application to two-particle systems

It might seem like our present treatment of a particle moving in a Coulomb potential can be directly applied to the hydrogen atom, describing the electron-proton interaction. However, strictly speaking, the atomic core is not necessarily at rest while the electron is moving: it depends on the relative mass of the two constituents. Nevertheless, we know from classical mechanics that we may reduce a two-particle problem with central interactions (depending only on $|\boldsymbol{r}| = r$) to an effective one-body problem. Interestingly, even when the interaction is *not central*, the two-body problem can be reduced to two decoupled one-body problems. This is done as follows. Consider the classical Hamiltonian for two particles with mass m_1 and m_2 that interact via a potential $V(\boldsymbol{r})$ (that is not necessarily rotationally symmetric):

$$H(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{p}_1, \boldsymbol{p}_2) = \frac{\boldsymbol{p}_1^2}{2m_1} + \frac{\boldsymbol{p}_2^2}{2m_2} + V(\boldsymbol{r}_1 - \boldsymbol{r}_2). \tag{6.59}$$

Let us introduce the center-of-mass coordinate $\boldsymbol{R}$ and the relative coordinate $\boldsymbol{r}$:

$$\boldsymbol{R} = \frac{m_1\boldsymbol{r}_1 + m_2\boldsymbol{r}_2}{m_1 + m_2},\ \boldsymbol{r} = \boldsymbol{r}_2 - \boldsymbol{r}_1. \tag{6.60}$$

To find the quantum mechanical Hamilton operator in terms of these coordinates, we follow the usual prescription of identifying the classical Hamiltonian and then letting $\boldsymbol{r} \to \hat{\boldsymbol{r}}$ and $\boldsymbol{p} \to \hat{\boldsymbol{p}}$. Using that

$$\boldsymbol{r}_1 = \boldsymbol{R} - \frac{m_2}{m_1 + m_2}\boldsymbol{r},\ \boldsymbol{r}_2 = \boldsymbol{R} + \frac{m_1}{m_1 + m_2}\boldsymbol{r}, \tag{6.61}$$

we can rewrite Eq. (6.59) to

$$H(\boldsymbol{R}, \boldsymbol{r}, \boldsymbol{P}, \boldsymbol{p}) = \frac{\boldsymbol{P}^2}{2M} + \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r}). \tag{6.62}$$

Here, we introduced the CM mass $M = m_1 + m_2$, the reduced mass $m = m_1 m_2/(m_1 + m_2)$, and the center-of-mass momentum $\boldsymbol{P}$ and relative momentum $\boldsymbol{p}$ according to:

$$\boldsymbol{P} = M\dot{\boldsymbol{R}},\ \boldsymbol{p} = m\dot{\boldsymbol{r}}. \tag{6.63}$$

The corresponding SE for stationary states is obtained by introducing the operators as mentioned above, so that:

$$\Big[-\frac{\hbar^2}{2M}\nabla_{\boldsymbol{R}}^2 - \frac{\hbar^2}{2m}\nabla_{\boldsymbol{r}}^2 + V(\boldsymbol{r})\Big]\psi(\boldsymbol{R}, \boldsymbol{r}) = E\psi(\boldsymbol{R}, \boldsymbol{r}). \tag{6.64}$$

The point is now that Eq. (6.64) is a *separable* equation, which occurs precisely when we have two decoupled subsystems. This can be seen by writing

$$\psi(\boldsymbol{R}, \boldsymbol{r}) = \psi_{\text{CM}}(\boldsymbol{R})\psi_{\text{rel}}(\boldsymbol{r}), \tag{6.65}$$

where the equation for the center-of-mass (CM) wavefunction ψ_{CM} is:

$$-\frac{\hbar^2}{2M}\nabla_{\boldsymbol{R}}^2\psi_{\text{CM}} = E_{\text{CM}}\psi_{\text{CM}}(\boldsymbol{r}). \tag{6.66}$$

Similarly, the equation for the wavefunction ψ_{rel} is:

$$-\frac{\hbar^2}{2m}\nabla_{\boldsymbol{r}}^2\psi_{\text{rel}} + V(\boldsymbol{r})\psi_{\text{rel}} = E_{\text{rel}}\psi. \tag{6.67}$$

and the total energy of the system is the sum of the energies associated with the center-of-mass motion (E_{CM}) and the relative motion (E_{rel}) of the particles: $E = E_{\text{CM}} + E_{\text{rel}}$.

The results we have obtained in this way can then be interpreted physically as follows. The two-particle problem with an interaction $V(\boldsymbol{r}_1 - \boldsymbol{r}_2)$ is formally equivalent to two independent one-body problems: one for the center-of-mass motion and one for the relative motion of the particles. The CM motion is that of a free particle with mass M whereas the relative motion is that of a particle with mass m moving in a potential $V(\boldsymbol{r})$.

C. Generalized angular momentum operators

Our treatment of the magnitude squared of the angular momentum, $\boldsymbol{L}^2$, showed that the possible eigenvalues for its quantum mechanical operator $\hat{\boldsymbol{L}}^2$ where $l(l+1)\hbar^2$ where $l = 0, 1, 2, \ldots$. Similarly, the allowed eigenvalues for $\hat{L}_z$ where $m\hbar$, where $m = -l, -l+1, \ldots l-1, l$. Since not all angular momentum operators can be expressed as $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$, it is necessary to generalize the treatment given previously. This will allow us to describe *internal* angular momentum such as *spin*, which we treat in the next section.

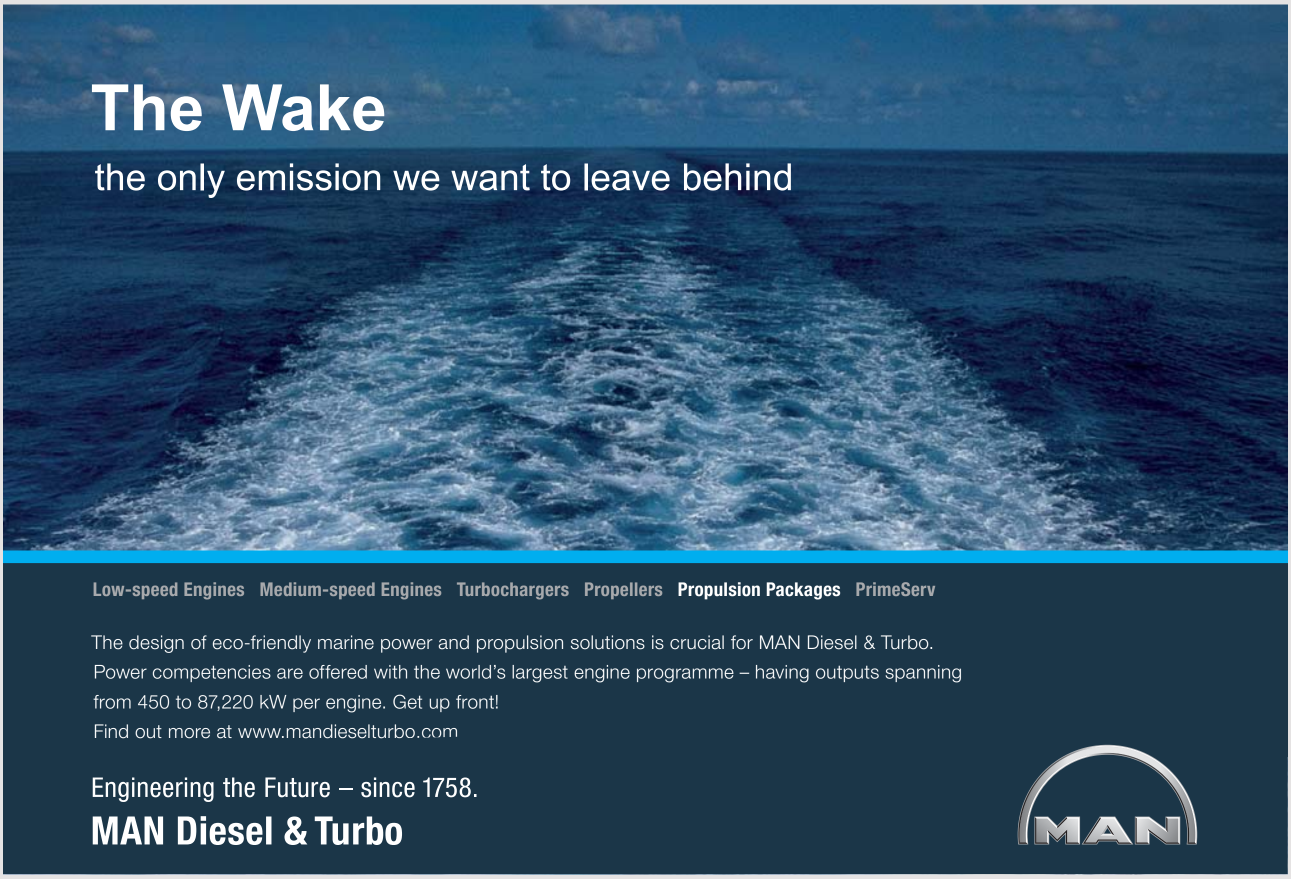
A general angular momentum operator $\hat{\mathbf{J}}$ in quantum mechanics (of which $\hat{\boldsymbol{L}}$ is a special case) is defined by the commutation rules satisfied by its components:

$$\boxed{[\hat{J}_x, \hat{J}_y] = \mathrm{i}\hbar\hat{J}_z,}$$

whereas the two other commutation rules follow from a cyclic change of coordinates: $x \to y, y \to z, z \to x$. These are precisely the commutation relations that we proved are valid for $\hat{\boldsymbol{L}}$. For brevity of notation, we skip the $.\hat{.}.$ notation for operators in what follows. It is crucial to note that the commutation relation $[\boldsymbol{J}^2, J_i] = 0$ for $i = x, y, z$ follows exclusively from the above set of commutation rules for the components. Therefore, we know from our previous treatment of $\boldsymbol{L}$ that there exists a common set of eigenstates for $\boldsymbol{J}^2$ and for one of the components, conventionally taken to be J_z. In this section, we introduce a new notation for the eigenstates which enables the eigenvalue equations to be written as follows:

$$\begin{aligned} \boldsymbol{J}^2|j,m\rangle &= \hbar^2 j(j+1)|j,m\rangle \\ J_z|j,m\rangle &= \hbar m|j,m\rangle. \end{aligned} \tag{6.68}$$

The notation $|j,m\rangle$ for the "wavefunction" (more precisely, state) of the system is due to Dirac and known as bra-ket notation. It is used in the general formulation of quantum mechanics and treated in full detail here.



Using wavefunctions to describe the system is in fact only relevant for a position representation of quantum mechanics, and this representation is *a special case* of a more general theory (described in the book linked above). For our present purposes, where the main focus is the properties and quantization of angular momentum operators, we shall be content with simply using the object $|\ldots\rangle$ to describe the state of the system in terms of the quantum numbers j and m.

Which values can j and m take in general? A dimensional check of Eq. (6.68) reveals that j and m must be dimensionless numbers. Since the square of a Hermitian operator, $\boldsymbol{J}^2$, must be a real and non-negative number, we know that $j(j+1) \geq 0$. Moreover, we can set $j \geq 0$ without loss of generality since any non-negative number can be written as $j(j+1)$ when $j \geq 0$. For now, that is all we know about these numbers, but we shall now investigate how we can find out more. To determine the precise values that j and m can take, we define the operators:

$$J_\pm = J_x \pm \mathrm{i}J_y. \tag{6.69}$$

Since J_x and J_y commute with $\boldsymbol{J}^2$, $J_\pm$ also commutes with $\boldsymbol{J}^2$ since it is a linear combination of the former. Let us also compute the commutator between J_z and $J_\pm$, which will come in handy soon:

$$[J_z, J_\pm] = \mathrm{i}\hbar J_y \pm \mathrm{i}(-\mathrm{i}\hbar J_x) = \pm\hbar(J_x \pm \mathrm{i}J_y) = \pm\hbar J_\pm. \tag{6.70}$$

Let us also examine the effect that $J_\pm$ has when acting on the state $|j,m\rangle$:

$$\boldsymbol{J}^2 J_\pm|j,m\rangle = J_\pm\boldsymbol{J}^2|j,m\rangle = j(j+1)\hbar^2 J_\pm|j,m\rangle. \tag{6.71}$$

In effect, $J_\pm|j,m\rangle$ is an eigenvector for $\boldsymbol{J}^2$ with the same eigenvalue as $|j,m\rangle$ has. Similarly, we find that

$$J_z J_\pm|j,m\rangle = (J_\pm J_z \pm \hbar J_\pm)|j,m\rangle = \hbar(m\pm 1)J_\pm|j,m\rangle. \tag{6.72}$$

From Eq. (6.71) and (6.72), we may conclude that $J_\pm|j,m\rangle$ is a set of common eigenvectors for both $\boldsymbol{J}^2$ and J_z, but with a different set of eigenvalues for the J_z operator. In particular, m has been advanced by one unit compared to the eigenstates $|j,m\rangle$. Specifically, we have shown in Eq. (6.72) that:

$$J_\pm|j,m\rangle = c_\pm|j,m\pm 1\rangle, \tag{6.73}$$

where $c_\pm$ is a constant. The operators J_+ and J_- thus earn their name of *raising* and *lowering* operators, respectively, as their effect is to raise or lower the m-value of the eigenstate. Their collective name is *ladder operators*.

It is physically reasonable that the maximum value that m can take should be limited by j, just as we found in the orbital angular momentum case when $\boldsymbol{J} = \boldsymbol{L}$. This can be understood by noting that when the magnitude is determined by j, one of the components (*e.g.* J_z) cannot be arbitrarily large, but rather limited by precisely the magnitude of the total vector. Indeed, one can show formally (try it!) that for a given value of the quantum number j, the allowed values for m are:

$$\boxed{m = -j, j+1, \ldots j-1, j.}$$

while the allowed values for j are:

$$\boxed{j = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots}$$

These results are consistent with our treatment of the special case where $\boldsymbol{J}$ is the orbital angular momentum $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$. In this case, the quantum number l (corresponding to j above) was found to take integer values. However, other types of angular momentum allows j to take half-integer values. One peculiar consequence of this is that in some cases, one needs to do a 4π rotation rather than 2π in order to get back to the original starting point! Such angular momenta must have a fundamentally different origin than the orbital angular momentum $\boldsymbol{L}$, and we shall now have a look at precisely such an example.

D. Quantum spin

Our treatment thus far has focused on either a particle moving in some external potential or particles interacting with each other. As we saw in our treatment of the Coulomb potential in the previous section, the orbital angular momentum of the system is a pivotal part of the physical description of the problem. However, it turns out that a single particle, even when at rest, also has an *internal angular momentum known as spin.* When an elementary particle is charged, there is also a magnetic moment $\boldsymbol{\mu}$ associated with the spin $\boldsymbol{S}$. For instance, electrons have spin and an internal magnetic moment, whereas neutrinos have spin but no magnetic moment. Composite particles (such as neutrons consisting of three quarks) can have a magnetic moment in spite of having zero net charge. Particles such as electrons, positrons, protons, neutrons, and neutrinos all are characterized by the quantum number $s = 1/2$. The number s plays the same role as the quantum number l did for the angular momentum: it characterizes the magnitude of the spin. A photon has spin $s = 1$. Moreover, the quantum number m_s is the equivalent of the number m we introduced for angular momentum: it characterizes the magnitude of the spin angular momentum component along a specific axis.

How do we know that particles have spin? There is abundant experimental proof of this, such as the Zeeman-effect and the Stern-Gerlach experiment. Strictly speaking, the latter experiments probe the magnetic moment $\boldsymbol{\mu}$ that exists due to the spin $\boldsymbol{S}$, but the spin is actually manifested in atomic spectra even without the presence of a magnetic field (we shall have more to say about this later). To think about spin in a simplified manner, one may envision an electron spinning around its own axis and creating an angular momentum. However, this is just a "cartoon" picture which cannot be taken literally for several reasons, one being that our previous treatment of the orbital angular momentum $\boldsymbol{L}$ showed that the associated quantum number l only took *integer* values. The spin of electrons, on the other hand, takes a half-integer value. Therefore, it should not be literally be considered a rotational motion in space.

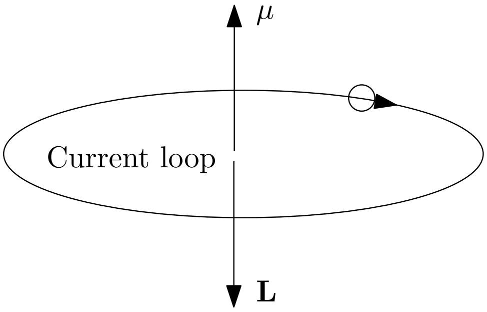
From our treatment of generalized angular momentum operators $\boldsymbol{J}$ in the preceeding section, we know that if $s = 1/2$ the allowed values for the quantum number m_s associated with the operator S_z are $m_s = \pm 1/2$. We may then write the two common eigenstates $|s, m_s\rangle$ for $\boldsymbol{S}^2$ and S_z as:

$$\Big|\frac{1}{2},\frac{1}{2}\Big\rangle \text{ and } \Big|\frac{1}{2},-\frac{1}{2}\Big\rangle. \tag{6.74}$$

How does spin enter in the Hamilton-operator? For a charged particle, we stated above that the spin $\boldsymbol{S}$ is accompanied by a magnetic moment $\boldsymbol{\mu}$. The same thing happens for the orbital angular momentum associated with a circulating charge current, which produces a magnetic moment according to:

$$\boldsymbol{\mu}_L = \frac{q}{2m}\boldsymbol{L} \tag{6.75}$$

where $\boldsymbol{L}$ is the orbital angular momentum associated with the circular motion of the particle. A charge moving in a circular orbit with velocity v has $L = mvR$ where R is the radius of the orbit, and the current is $I = \frac{q}{2\pi R/v}$. Therefore, the magnetic moment (the product between current and area) is $\mu_L = IA = qvR/2 = qL/2m$.



Now, if angular momentum operators $\boldsymbol{J}$ *in general* have a magnetic moment $\boldsymbol{\mu}_J$ associated with them, then we may conclude that generally we should be able to write

$$\boldsymbol{\mu}_J = g_J\frac{q}{2m}\boldsymbol{J} \tag{6.76}$$

where g_J, known as the g-value, for the sake of consistent dimensionality must be a dimensionless number. For orbital angular momentum, we thus have $g_J = g_L = 1$. For the magnetic moment arising in this manner from the spin of an electron with charge $q = -e$, we thus have

$$\boldsymbol{\mu}_S = g_S \frac{(-e)}{2m_e} \boldsymbol{S} \tag{6.77}$$

where g_S is predicted to be $g_S = 2$ whereas one experimentally finds that it is very close to this value: $g_S \simeq 2.002$.

If we accept that the electron spin produces a magnetic moment, one consequence is that it will enter the Hamilton-operator via a term $-\boldsymbol{\mu} \cdot \boldsymbol{B}$ in the presence of an external magnetic field $\boldsymbol{B}$. This is because of the well-known coupling between magnetic fields and magnetic moments present in electromagnetic theory. The difference in the quantum mechanical treatment is, as we have seen consistently throughout the book, that we replace the classical quantities with their corresponding operators. In effect, $\boldsymbol{\mu}$ is proportional to the quantum mechanical angular momentum operator $\boldsymbol{S}$. A further treatment of spin is more conveniently handled using the generalized formulation of quantum mechanics introduced in the beginning of the freely available book Intermediate Quantum Mechanics.

VII. QUANTUM STATISTICS AND EXCHANGE FORCES

Learning goals. After reading this chapter, the student should:

- Understand where the symmetry requirements for the wavefunction of bosons and fermions come from and some of its physical consequences.
- Be able to account for the Pauli principle and why it is of physical relevance in real systems.
- Understand how exchange forces arise due to the symmetry requirements of the wavefunction and how these are of physical relevance.

We have seen multiple examples of the SE for various single-particle systems throughout this book so far. In principle, the SE is established for a many-body system by generalizing the single-particle Hamilton-operator and including interactions between the particles. However, there is a fundamental principle in the theory of quantum mechanics that we have not mentioned yet, which becomes of crucial importance when treating many-body systems with *identical particles*. The concept of identical particles is something pertaining uniquely to quantum theory, because from a classical physics perspective there is no such thing: the motion of particles can (in principle) always be computed sharply without any uncertainty. In quantum mechanics, on the other hand, one cannot distinguish between identical particles such as electrons. This is more than semantics, as it has real experimental consequences. For instance, the energy spectra of atoms would in general be completely different if identical particles were not indistinguishable, as we shall see. Therefore, something as fundamental as the periodical system in fact relies on quantum mechanical considerations of identical particles in the form of the so-called *Pauli exclusion principle* (we shall have much more to say about this in this chapter).

A. Symmetry of the wavefunction

Consider a quantum mechanical wavefunction $\Psi = \Psi(1,2)$ describing a system consisting of two identical particles labelled 1 and 2. The label "1" thus refers to both the position $\boldsymbol{r}_1$ of the particle and its spin quantum number $m_{s,1}$. Since all electrons have $s = \frac{1}{2}$, it suffices to explicitly consider $m_s = \{\frac{1}{2}, -\frac{1}{2}\}$. Now, if the particles are truly identical, the physical properties of the system must be completely invariant if we exchange the two: $1 \leftrightarrow 2$. Since we know that the absolute value squared of Ψ corresponds to the probability density, we must thus demand that

$$|\Psi(1,2)|^2 = |\Psi(2,1)|^2. \tag{7.1}$$

Mathematically, only a phase-factor of the type $\mathrm{e}^{\mathrm{i}\alpha}$ with $\alpha \in \Re$ can separate the two wavefunctions so that

$$\Psi(1,2) = \mathrm{e}^{\mathrm{i}\alpha}\Psi(2,1). \tag{7.2}$$

We see that this can be achieved in at least two ways. If $\alpha = 0$, the wavefunction is *symmetric* under an exchange of particle coordinates. If $\alpha = \pi$, the wavefunction is antisymmetric (acquires a minus sign) under an exchange of particle coordinates. Particles which have a symmetric wavefunction under exchange of the coordinates are known as *bosons*, whereas the antisymmetric case occurs for *fermions*:

$$\Psi(1,2) = \begin{cases} +\Psi(2,1) \text{ for bosons} \\ -\Psi(2,1) \text{ for fermions.} \end{cases} \tag{7.3}$$

In systems where the spatial and spin coordinates are independent on each other, we can write the total wavefunction as a $\Psi(1,2) = \psi(\boldsymbol{r}_1, \boldsymbol{r}_2)\chi(m_{s,1}, m_{s,2})$ where ψ describes the spatial behavior of the particles whereas χ describes the spin behavior. It follows from Eq. (7.3) that if a system consisting of two fermions has a spatial part ψ that is symmetric under exchange of 1 and 2, then the spin part *must* be antisymmetric.

For instance, let $\uparrow$ and $\downarrow$ be short-hand notation for the states $|s=\frac{1}{2}, m_s=\frac{1}{2}\rangle$ and $|s=\frac{1}{2}, m_s=-\frac{1}{2}\rangle$, respectively. The notation stems from thinking of $m_s=+\frac{1}{2}$ as a spin pointing upwards since $L_z>0$, whereas $m_s=-\frac{1}{2}$ corresponds to a spin pointing downward since $L_z<0$. A *singlet* state

$$\chi \propto (\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2) \tag{7.4}$$

is clearly antisymmetric under an exchange $1 \leftrightarrow 2$. On the other hand, either of the *triplet* states

$$\chi \propto \begin{cases} \uparrow_1\downarrow_2 + \downarrow_1\uparrow_2 \\ \uparrow_1\uparrow_2 \\ \downarrow_1\downarrow_2 \end{cases} \tag{7.5}$$

is symmetric under the same exchange.

Whether a particle is regarded as a boson or fermion is in fact determined by the spin quantum number s:

> Integer spin particles ($s=0,1,\ldots$) are bosons, while half-integer spin ($s=\dfrac{1}{2},\dfrac{3}{2},\ldots$) particles are fermions.

Experimentally, this relation between the spin of the particle and the symmetry property of a wavefunction describing multiple such particles is well documented. It is common terminology to state that bosons adhere to Bose-Einstein statistics whereas fermions adhere to Fermi-Dirac statistics, with the word "statistics" pointing to the behavior of the distribution of such particles in a system.

It is also possible to take the viewpoint that a system comprised of N number of identical particles should collectively act as either a boson or a fermion. For such composite systems, it is the fermion number F of the composite system which decides how permutation of the coordinates of two such composite systems will affect the sign of the total wavefunction Ψ describing the composite systems. In particular, such a permutation gives a factor $(-1)^F$ when both composite systems have fermion number F. Therefore, a system comprised of two fermions $(F=2)$ act as an effective boson in terms of its statistical properties whereas any odd number F of fermions will have act as an effective fermion. This difference manifests very clearly experimentally, for instance in the behavior of ^{4}He-atoms (which act as bosons since F is even for that system) versus ^{3}He-atoms (where F is odd).

B. The Pauli exclusion principle and its range

One of the most fundamental consequences of the symmetry properties of bosons and fermions under an exchange of particle coordinates in the system is the Pauli exclusion principle (or simply the Pauli principle):

> Two fermions cannot occupy exactly the same single-particle quantum state.

To see this, consider for concreteness a system consisting of two fermions in the states ψ_i and ψ_j, where i and j refer to *e.g.* specific values of the principal quantum number n for particles moving in a Coulomb-potential. We consider only the spatial part ψ of the wavefunction to keep the notation simple. The antisymmetric combination:

$$\psi(1,2) = \frac{1}{\sqrt{2}}[\psi_i(1)\psi_j(2) - \psi_j(1)\psi_i(2)] \tag{7.6}$$

satisfies $\psi(1,2)=-\psi(2,1)$, as required for fermions. Note that this wavefunction indeed is a solution to the SE for the system which may be written as

$$\hat{H} = \hat{H}(1) + \hat{H}(2) \tag{7.7}$$

for two non-interacting particles, since (as we have seen previously in this book) product states of the type $\psi_i(1)\psi_j(2)$ are eigenstates of this $\hat{H}$ with belonging energy eigenvalue $E=E_i+E_j$.

Importantly, it follows from Eq. (7.6) that $\psi=0$ when the two particles are in the same state $i=j$ *even if the particles occupy different positions in space* ($1\neq 2$). The same holds true also in the presence of interactions between the particles. We also note that even if the particles are in different quantum states $(i \neq j)$ for the system described by Eq. (7.6), they cannot occupy exactly the same spatial position since $\psi(1,1) = 0$. The factor $1/\sqrt{2}$ ensures that the total wavefunction is normalized to unity when ψ_i and ψ_j are individually normalized to unity. Thus, the Pauli principle follows directly from the required symmetry property of fermionic wavefunctions: the total wave function for two identical fermions is antisymmetric with respect to an exchange of the particles.

Now, there exists a general strategy for writing down wavefunctions that are ensured to have the correct fermion symmetry, namely via determinants. For instance, we can write Eq. (7.6) as:

$$\psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_i(1) & \psi_i(2) \\ \psi_j(1) & \psi_j(2) \end{vmatrix}. \tag{7.8}$$

Such a wavefunction is known as a *Slater-determinant*. It can be generalized to a wavefunction describing N fermions residing in the single-particle states $\psi_1, \psi_2, \ldots \psi_N$:

$$\psi(1,2,\ldots N) = \frac{1}{\sqrt{Z!}} \begin{vmatrix} \psi_1(1) & \psi_1(2) & \ldots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & \ldots & \psi_2(N) \\ \ldots & \ldots & \ldots & \ldots \\ \psi_Z(1) & \psi_Z(2) & \ldots & \psi_Z(Z) \end{vmatrix} \tag{7.9}$$

which then by constructing is antisymmetric. An exchange of two particle coordinates, such as 3 and 7, will give a determinant which only differs from the original one by the exchange of two columns. Such an operation mathematically provides precisely the desired changed in overall sign. Moreover, if two of the states the particles are residing in are equal, such as $\psi_4 = \psi_5$, two rows in the determinant become identical which again mathematically renders the determinant (and thus the wavefunction) equal to zero. If the fermions interact with each other, Eq. (7.9) is no longer the exact solution of the SE, but it is still useful as a starting point for an approximative calculation of *e.g.* the energy eigenvalues.

Does the Pauli principle apply to any two electrons in the universe? Yes, the Pauli principle has an *infinite range*. However, it *only has a practical consequence when the two electrons are close enough* so that there is an overlap between their wavefunctions. We know now that a wavefunction describing two electrons must be antisymmetric in their coordinates, such as their positions. Neglect spin in what follows for brevity of notation. If we have two electrons 1 and 2 belonging to an atom where the eigenfunctions are labelled ψ_j where j is a quantum number describing the state, we can then antisymmetrize the total wavefunction in the following way to describe the total state:

$$\Psi(1,2) = \psi_n(\boldsymbol{r}_1)\psi_m(\boldsymbol{r}_2) - \psi_m(\boldsymbol{r}_1)\psi_n(\boldsymbol{r}_2). \tag{7.10}$$

where (n, m) are a set of quantum numbers describing the state and (1,2) describes the electron coordinates. Clearly, the above satisfies $\Psi(1,2) = -\Psi(1,2)$. The generalization of this to N fermions is called a Slater determinant, as we have seen above. We see from this expression that the two electrons should not be able to reside in exactly the same type of state ψ_n, even if they have different positions, because the wavefunction then vanishes:

$$\psi_n(\boldsymbol{r}_1)\psi_n(\boldsymbol{r}_2) - \psi_n(\boldsymbol{r}_2)\psi_n(\boldsymbol{r}_1) = 0. \tag{7.11}$$

Now, it is important to distinguish such a scenario from a case where two electrons belong to different atoms separated in space. In that case, these electrons can be in the same quantum state because their wavefunctions are separated in space and thus centered around different points (the core of each atom). Let the separation distance between the atoms be $\boldsymbol{R}$. Then, their wavefunction is

$$\Psi(1,2) = \psi_n(\boldsymbol{r}_1)\psi_m(\boldsymbol{r}_2 - \boldsymbol{R}) - \psi_m(\boldsymbol{r}_1 - \boldsymbol{R})\psi_n(\boldsymbol{r}_2) \tag{7.12}$$

Now, we see that even if $m = n$, the wavefunction does not vanish. It only vanishes if $n = m$ and $\boldsymbol{r}_1 = \boldsymbol{r}_2$: the electrons cannot be at exactly the same position and in the same quantum state. This is actually the basic principle behind ferromagnetism: since electrons cannot be at the same position when they are in the same quantum state (both spins pointing in the same direction, *e.g.* $m_s = +\frac{1}{2}$), they avoid the Coulomb interaction and lower the energy of the system.

C. Exchange forces due to the Pauli principle

The example of ferromagnetism arising fundamentally from the symmetry requirement of fermionic many-body wavefunctions demonstrates the importance of this result. The ferromagnetic case is an example of an *exchange interaction* at work. Put differently, we can think of the electrons effectively interacting with each other because of the symmetry property of the wavefunction that must be obeyed upon exchange of the particles. Let us take a look at an additional example. Consider two non-interacting particles residing in a harmonic oscillator potential $V(q) = mq^2/2$ where q is the spatial coordinate and we define $x \equiv q\sqrt{m\omega/\hbar}$ as a dimensionless length. The spin-part of the total wavefunction for the two particles is taken to be symmetric, for instance one of the triplet states in Eq. (7.5). We stress that the Pauli principle holds even when interactions are taken into account: the reason we are neglecting interparticle interactions is simply because they severly complicate the problem and do not permit an exact analytical treatment. We are here interested in computing the quantity

$$\langle (q_1 - q_2)^2 \rangle = \frac{\hbar}{m\omega}\langle (x_1 - x_2)^2 \rangle \tag{7.13}$$

which physically tells us something about the average distance between the particles. The two lowest-lying energy eigenstates ψ_0 and ψ_1 for a particle in this potential read

$$\begin{aligned} \psi_0(x) &= \left(\frac{1}{pi}\right)^{1/4} \mathrm{e}^{-x^2/2}, \\ \psi_1(x) &= \left(\frac{4}{\pi}\right)^{1/4} x\mathrm{e}^{-x^2/2} = \sqrt{2}x\psi_0(x). \end{aligned} \tag{7.14}$$

The expectation value for x^2 in these two eigenstates, respectively, is straightforward to compute:

$$\begin{aligned}\langle x^2\rangle_{\psi_0} &= \int_{-\infty}^{\infty}\psi_0^* x^2\psi_0 dx = \frac{1}{2},\\ \langle x^2\rangle_{\psi_1} &= \int_{-\infty}^{\infty}\psi_1^* x^2\psi_1 dx = \frac{3}{2}.\end{aligned} \tag{7.15}$$

We now want to compute $\langle (x_1-x_2)^2\rangle = \langle x_1^2 + x_2^2 - 2x_1x_2\rangle$ and compare how the results differ for the scenario where (i) the particles are *different* and (ii) where the particles are *identical*. In both cases, we shall let one particle be in the ground-state ψ_0 whereas the other is in the state ψ_1.

Consider scenario (i) first. Let particle 1 be in the ground-state. Then, the wavefunction

$$\Psi(x_1,x_2) = \psi_0(x_1)\psi_1(x_2), \tag{7.16}$$

solves the stationary SE. Note how the above wavefunction does not have any particular symmetry properties, which there is no need for when the particles are not identical. It is clear that $\langle x_i\rangle = 0$, so that the result is

$$\langle (x_1-x_2)^2\rangle = \langle x_1^2\rangle_{\psi_0} + \langle x_2^2\rangle_{\psi_1} = 2. \tag{7.17}$$

Let us compare this with scenario (ii). We may treat bosons and fermions simultaneously by writing the wavefunction as

$$\Psi(x_1,x_2) = \frac{1}{\sqrt{2}}[\psi_0(x_1)\psi_1(x_2) \pm \psi_0(x_2)\psi_1(x_1)] \tag{7.18}$$

where the upper sign refers to the bosonic case and the lower sign refers to the fermionic case. Computing the expectation value in the standard way now produces

$$\langle (x_1-x_2)^2\rangle = 2\mp 1 = \begin{cases}1 \text{ for bosons}\\ 3 \text{ for fermions}\end{cases}. \tag{7.19}$$

We are now in a position where we can compare the results. The average distance between the fermions is larger than both the bosons and the case where the particles were distinguishable. On the other hand, the average distance between the bosons is smaller than both the fermions and the case where the particles were different. Put in other words, the fermions seem to *repel* while the bosons *attract* each other due to the symmetry requirement of the wavefunction. It is precisely in this way that we can think of an effective *exchange interaction* between identical particles which is traced back to the behavior of the wavefunction under an exchange of the particles.

There are many remarkable consequences of this exchange interaction. Besides the above mentioned example of ferromagnetism occurring via electrons, the exchange attraction between bosons can under suitable circumstances trigger a so-called Bose-Einstein condensation where a macroscopic number of bosons all reside in the same quantum state. Such a Bose-Einstein condensate can display fascinating properties, such as superfluidity (although this additionally requires bosons which have an interaction in the first place). Yet another example, which is of high practical relevance to describe fundamental properties of materials, is that of a large number of non-interacting fermions confined to a volume V. From the previous chapter in this book where we computed the density of states for such a system, we know that the number of states $R(E)$ with energy smaller than E is equal to:

$$R(E) = n_s\frac{4\pi}{3}\Big(\frac{2m}{(2\pi\hbar)^2}\Big)^{3/2} V E^{3/2}, \tag{7.20}$$

where n_s denotes the number of spin-states per particle. For electrons, $n_s = 2$. Now, a metal should be decently approximated by a large number of non-interacting (due to Coulomb screening) electrons in a volume V. If there exists in total N_0 electrons in this volume, then we can imagine that the electrons gradually fill up the energy levels available in the system until they reach a maximum energy E_F. This is the so-called *Fermi energy*. The reason for why electrons have to reside in increasingly higher-lying energy levels is precisely due to the Pauli principle: no two electrons can reside in exactly the same quantum state, and hence the electrons have no choice but to occupy higher and higher energy levels. The Fermi energy must then be defined by

$$R(E_F) = N_0 \tag{7.21}$$

since all electrons have an energy lower than or equal to the Fermi energy. We can rearrange this equation to

$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N_0}{V}\right)^{2/3}. \tag{7.22}$$

Since the Fermi energy depends on the density of electrons N_0/V, one can estimate its magnitude in a typical metal to be between 1 and 10 eV. Comparing this with the thermal energy available at room-temperature $T = 300$ K, which is $k_B T \simeq 0.025$ eV, we see that the Fermi energy is much larger. Therefore, even at room-temperature, the total system comprised of electrons is close to being in its ground state.

VIII. PERIODIC POTENTIALS AND APPLICATION TO SOLIDS

Learning goals. After reading this chapter, the student should:

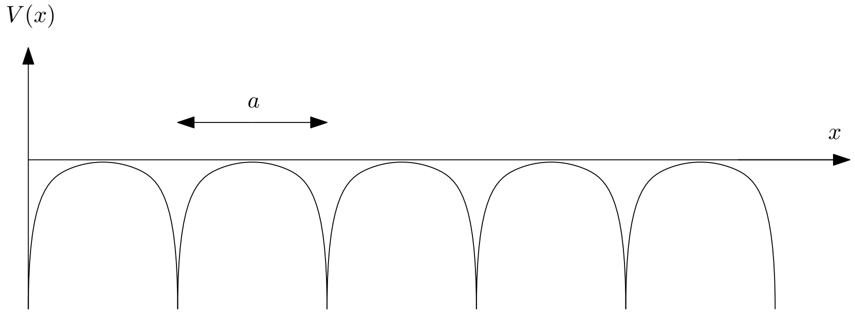
- Know how the quantum mechanical wavefunction ψ behaves in a periodic potential and understand the strategy for obtaining ψ in the Kronig-Penney model.
- Understand how periodic potentials in quantum mechanics gives rise to energy bands and band gaps, and how these can be used to describe real physical materials.

Quantum mechanics is a fundamental theory which pervades physics, not only shaping our understanding of how nature works, but with real consequences for applied physics. For instance, quantum mechanics is the foundation for the band theory of solid state materials. Why are some materials conductors, semiconductors, or insulators? Whereas we previously stated that our free-electron model in a constant potential could be suitable to approximate the behavior of metals, such a framework is no longer suitable when it comes to decsribing the properties of insulating or even semiconducting materials. However, as it turns out, quantum mechanics encompasses a description of such materials as well by introducing a more realistic potential profile that the electrons in a solid move through - namely, periodic potentials.

Including electron-electron interactions in quantum mechanical calculations of many-body systems is an important, yet very difficult task which does not permit any exact analytical solution. The band-theory of quantum mechanics is based on a picture where electrons do not interact with each other. Although some types of solids cannot be described without properly accounting for interactions, such as Mott insulators, it turns out that such an effective *single-particle* theory works well in many circumstances and gives predictions which have been experimentally verified. Note that by effective single-particle theory, we mean a Hamiltonian comprised of a sum of independent particles as opposed to a Hamiltonian where interactions between the particles are included. The electrons moving through the crystal of a solid feel a periodic potential $V(\boldsymbol{r})$ due to the periodic nature of the crystal lattice. Proceeding in one dimension for brevity of notation (the results can be generalized to 3D in a straightforward manner), the potential must then satisfy:

$$V(x) = V(x+a) \tag{8.1}$$

for any x. We have introduced the lattice constant a as the length of periodicity. The complete lattice of the material is built up from *unit cells* which repeat throughout the entire material, and each unit cell thus has a length a.



A. Bloch functions

We start out by examining the energy eigenfunctions for an electron moving in a periodic potential. The SE is as usual $\hat{H}\psi = E\psi$ where

$$\hat{H} = -\frac{\hbar^2}{2m}\partial_x^2 + V(x). \tag{8.2}$$

Due to the periodic nature of the potential, the physics must be invariant upon moving from one unit cell to another (i.e. spatial *translation* with a distance a). Therefore, we should demand that

$$|\psi(x)|^2 = |\psi(x+a)|^2. \tag{8.3}$$

This means that $\psi(x)$ and $\psi(x+a)$ should be distinguished by a multiplicative factor with absolute value equal to unity. Let us write this specifically as:

$$\psi(x+a) = \mathrm{e}^{\mathrm{i}ka}\psi(x) \tag{8.4}$$

where k is a real quantity. We should thus be able to write generally that:

$$\psi(x) = \mathrm{e}^{\mathrm{i}kx}u_k(x) \tag{8.5}$$

is an acceptable solution where $u_k(x) = u_k(x+a)$ is a periodic function. In effect, we see that the wavefunction for a periodic potential is a plane-wave $\mathrm{e}^{\mathrm{i}kx}$ modulated by a function u_k which must have the same periodicity as the potential (lattice in this case) itself. An eigenfunction of the type shown in Eq. (8.5) is known as a *Bloch-function*.

It is often instructive to derive results in different ways to gain more insight, and we therefore show how Eq. (8.5) can be derived in a different way. Now, we want to make explicit use of the translational operator $\hat{T}_a$ which has the following effect on the wavefunction:

$$\hat{T}_a\psi(x) = \psi(x+a). \tag{8.6}$$

$\hat{T}_a$ thus advances the position with a length a. This operator commutes with $\hat{H}$:

$$[\hat{T}_a, \hat{H}]\psi(x) = (\hat{H} - \hat{H})\psi(x+a) = 0. \tag{8.7}$$

Therefore, a common set of eigenfunctions should exist for these two operators. The eigenvalue problem for $\hat{T}_a$ has the form:

$$\hat{T}_a\psi(x) = t\psi(x), \tag{8.8}$$

which implies that $\psi(x+a) = t\psi(x)$ with t being a constant. If we repeat this procedure n times, we find

$$\psi(x+na) = t^n\psi(x). \tag{8.9}$$

To prevent the wavefunction ψ from diverging, we have to set $|t| = 1$ to prevent t^n from growing indefinitely. This means that we can parametrize t as $\mathrm{e}^{\mathrm{i}ka}$ precisely as before. Thus, $\psi(x) = \mathrm{e}^{\mathrm{i}kx}u_k(x)$ with $u_k(x+a) = u_k(x)$ is indeed satisfied by the common set of eigenfunctions for $\hat{T}_a$ and $\hat{H}$.

Some comments are in order regarding the result that we have obtained. There is a striking similarity between Eq. (8.5) and a regular plane-wave describing a free particle moving in zero potential: the main difference is that the *amplitude* $u_k(x)$ is periodically modulated in the presence of a periodic potential. This is a fundamentally important result: electrons moving in an ideal periodic structure will not scatter! They will behave qualitatively similar to free electrons and move around without difficulty. It is a common misconception that the electrical resistance of materials is caused by electrons scattering on the ion lattice of a solid state material (which sets up the periodic potential). This is not the case: a perfect crystal at zero temperature has zero electrical resistance. Instead, it is thermal vibrations of the lattice (which in quantum mechanical language is known as *phonons*) or lattice imperfections/defects (such as impurity atoms) which cause scattering of electrons and thus cause electrical resistance of currents.

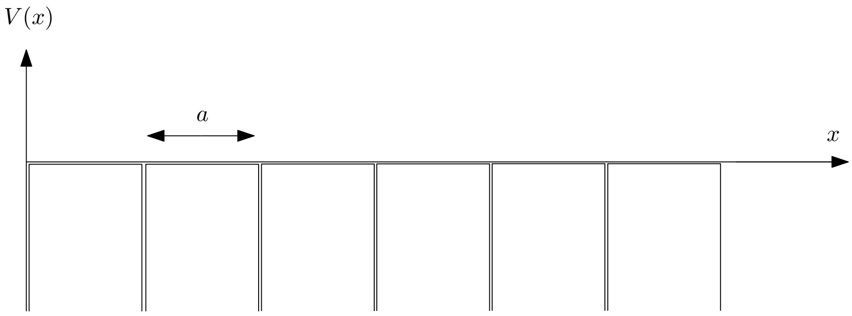
B. Band structure and the Kronig-Penney model

Above, we treated the wavefunctions of a periodic potential. What about the energy eigenvalues? We will here discover that the energy spectrum behaves quite differently compared to the other systems we have considered so far in this book. Specifically, we will find that the eigenvalues form continuous *energy bands* which are interrupted by *band gaps* where no allowed energy eigenvalues exist. To show this explicitly, we consider the Kronig-Penney model which has an analytical solution.

The potential is illustrated in the figure: it consists of periodically appearing δ-function wells, which can alternatively be thought of as a piecewise constant potential repeating itself. In terms of relevance for a lattice model, one could then think of this model as a first approximation (quite crude, but it gets the point across) of a constant potential between atomic sites and an attractive potential right at each site. We may write the potential energy as

$$V(x) = -\frac{\hbar^2\alpha}{ma}\sum_{-\infty}^{\infty}\delta(x-na). \tag{8.10}$$

In this way, the coefficient α characterizing the strength of the potential becomes dimensionless, which is handy. We see that the δ-function wells are placed at a distance a from each other. Earlier in this book, we treated the case of a single δ-function well, so let us reuse some of the results from that treatment. Our strategy will to solve for ψ in certain regions and then connect the regions via suitable boundary conditions.



In the interval $-a < x < a$, the SE only includes one potential well:

$$-\frac{\hbar^2}{2m}\psi'' - \frac{\hbar^2\alpha}{ma}\delta(x)\psi = E\psi. \tag{8.11}$$

A suitable boundary condition for ψ at $x = 0$ is obtained by integrating Eq. (8.11) from $x = -\epsilon$ to $x = \epsilon$ and taking $\lim_{\epsilon\to 0}$. This gives us:

$$a[\psi'(0^-) - \psi'(0^+)] = 2\alpha\psi(0), \tag{8.12}$$

where 0^- means $x = 0$ approached from negative x and similarly for 0^+. In between the potential wells, we have $V = 0$ so that the SE describes a free particle. Therefore, in the interval $-a < x < 0$, the solution for $-\frac{\hbar^2}{2m}\psi'' = E\psi$ is

$$\psi = A\cos(qx/a) + B\sin(qx/a), \tag{8.13}$$

where the relation between E and the dimensionless number q is:

$$E = \frac{\hbar^2 q^2}{2ma^2}. \tag{8.14}$$

We also need the wavefunction in the interval $0 < x < a$. However, this can easily be obtained from Eq. (8.13) via Bloch's theorem Eq. (8.4) for wavefunctions in a periodic potential: $\psi(x + a) = \mathrm{e}^{\mathrm{i}ka}\psi(x)$. We obtain

$$\psi(0^-) = A,\ \psi'(0^-) = Bq/a \tag{8.15}$$

while on the right side of the potential well centered at $x = 0$ we get

$$\psi(0^+) = \mathrm{e}^{\mathrm{i}ka}(A\cos q - B\sin q),\ \psi'(0^+) = \mathrm{e}^{\mathrm{i}ka}(q/a)(A\sin q + B\cos q). \tag{8.16}$$

In addition to the boundary condition Eq. (8.12), we require continuity of the wavefunction at $x = 0$

$$\psi(0^-) = \psi(0^+), \tag{8.17}$$

which provides

$$A = \mathrm{e}^{\mathrm{i}ka}(A\cos q - B\sin q). \tag{8.18}$$

This will be our first equation needed to identify A and B. The second one is obtained by inserting our wavefunction into Eq. (8.12), yielding:

$$\mathrm{e}^{\mathrm{i}ka}q(A\sin q + B\cos q) = Bq - 2\alpha A. \tag{8.19}$$

These equations then provide two homogeneous equations for A and B, allowing us to identify two separate expressions (one from each equation) for the ratio A/B:

$$\frac{A}{B} = \frac{\sin q}{\cos q - \mathrm{e}^{-\mathrm{i}ka}} = \frac{1 - \mathrm{e}^{\mathrm{i}ka}\cos q}{\mathrm{e}^{ika}\sin q + 2\alpha/q}. \tag{8.20}$$

After some algebraic manipulations, we rewrite Eq. (8.20) as:

$$\cos(ka) = \cos q - (\alpha/q)\sin q. \tag{8.21}$$

The left hand side of this equation is bounded in magnitude: it must lie between -1 and 1. Therefore, the only way that this equation can be satisfied is if the right hand side satisfies:

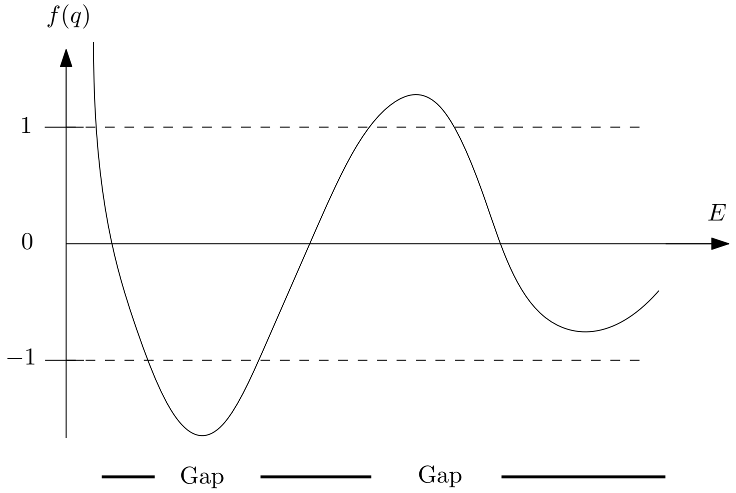
$$|\cos q - (\alpha/q)\sin q| \leq 1. \tag{8.22}$$

We have then obtained the following central result:

$$\boxed{\text{The allowed energies are } E = \frac{\hbar^2 q^2}{2ma^2} \text{ where } q \text{ must satisfy } |\cos q - (\alpha/q)\sin q| \leq 1.}$$

Note that the energy is positive when q is real, but there is no part of our calculation which requires that q must be real. Therefore, the above result is also valid for negative energies (corresponding to an imaginary q).

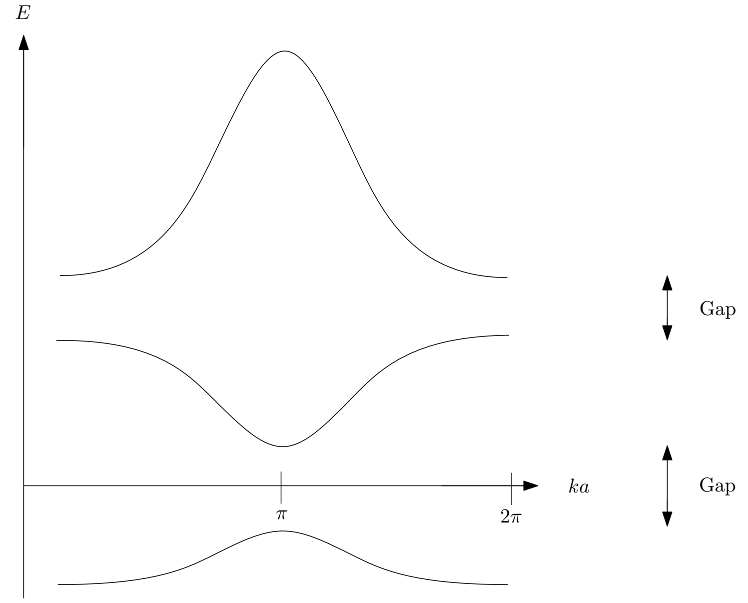
The presence of an inequality governing the permitted eigenvalues is a new feature we have not encountered previously. It results in the presence of allowed energies only in specific intervals. The qualitative behavior of the function $f(q) = \cos q - (\alpha/q)\sin q$ is sketched in the figure as a function of the energy E [since $q = q(E)$]. It is clear that the energy spectrum has a band structure where allowed energy bands are interrupted by band gaps where no energy eigenvalues exist.



To understand the dependence of the band structure on the potential strength α, we first note that for $\alpha \to 0$ the inequality governing the appearance of energy bands reduces to $|\cos q| \leq 1$ which is satisfied for any positive energy. This is reasonable since we then have a completely free particle with an uninterrupted continuous spectrum for $E > 0$. On the other hand, the band gaps shown in the figure grow larger with increasing α. In turn, the energy bands then become very narrow. It is also instructive to establish the relation between the energy E and the wavevector k associated with the free-particle behavior in the Bloch wavefunction. This relation is inferred via Eq. (8.21) which explicitly reads

$$\cos(ka) = \cos\left(\sqrt{2ma^2E/\hbar^2}\right) - \alpha\frac{\sin\left(\sqrt{2ma^2E/\hbar^2}\right)}{\sqrt{2ma^2E/\hbar^2}}. \tag{8.23}$$

Due to the periodic dependence on k, it is sufficient to consider an interval $0 < k < 2\pi/a$ (or any other interval where k advances with $2\pi/a$, for that matter). The behavior of E vs. k is shown in the figure below. As k advances from 0 to π/a, $\cos(ka)$ varies between $+1$ and -1. In this interval, there exists several energy bands with different energies. All the bands are separated by gaps, in accordance with our previous observation. Note how each energy eigenvalue is twofold degenerate since k and $(2\pi/a) - k$ provide the same energy in Eq. (8.23).



The relation $E = E_n(k)$ where n corresponds to the band number in the above figure is known as the *dispersion relation*. Its importance in condensed matter physics cannot be overstated, as it provides crucial information to determine how electrons behave under the influence of *e.g.* an external electric field. The dispersion relation thus dictates for instance whether a material behaves as a metal, semiconductor, or insulator. The difference between these types of materials is shown in the figure below. The rectangles represent energy bands which are either filled (dark gray) or empty (light gray). In metals (figure a), the Fermi energy (energy of the highest occupied electron state at $T = 0$) is located inside a band of allowed energy values. As a consequence, there are available electronic states even for an infinitesimal energy increase of an electron with $E = E_F$. This enables electrons to move in response to an electric field and thus conduct electricity. In semiconductors (figure b), the Fermi energy falls inside the gap separating two energy bands. The lower band is known as the *valence band* while the upper is the *conduction band*. Although the valence band is full in the figure, an infinitesimal energy increase is not sufficient to promote an electron from the valence to the conduction band. Instead, it would require an energy comparable to the energy gap E_g to excite an electron into the conduction band. At low temperatures, where the thermal energy $k_BT \ll E_g$, no electrons reside in the conduction band. An insulating material (figure c) qualitatively is similar to a semiconductor, but is distinguished by having a much larger band gap between the allowed enery bands. For instance, diamond is considered to be an electric insulator with $E_g \simeq 5.5$ eV whereas silicon is a semiconductor due to its lower band gap $E_g \simeq 1.1$ eV.