

## Chapter 2

# Quantum Mechanics in a Nutshell

### 2.1 Introduction

### 2.2 Photons

Time: end of the 19th century. Maxwell's equations have established Faraday's hunch that light is an electromagnetic wave. However, by early 20th century, experimental evidence mounted pointing towards the fact that light is carried by 'particles' that pack a definite momentum and energy. Here is the crux of the problem: consider the double-slit experiment. Monochromatic light of wavelength  $\lambda$  passing through two slits separated by a distance  $d \sim \lambda$  forms a diffraction pattern on a photographic plate. If one tunes down the intensity of light in a double-slit experiment, one does not get a 'dimmer' interference pattern, but discrete strikes on the photographic plate and illumination at specific points. That means light is composed of 'particles' whose energy and momentum are concentrated in one point which leads to discrete hits. But their wavelength extends over space, which leads to diffraction patterns.

Planck postulated that light is composed of discrete lumps of momentum  $\mathbf{p} = \hbar\mathbf{k}$  and energy  $E = \hbar\omega$ . Here  $\mathbf{k} = (2\pi/\lambda)\hat{\mathbf{n}}$ ,  $\hat{\mathbf{n}}$  the direction of propagation,  $\hbar$  is Planck's constant, and  $\omega = c|\mathbf{k}|$  with  $c$  the speed of light. Planck's hypothesis explained spectral features of the blackbody radiation. It was used by Einstein to explain the photoelectric effect. Einstein was developing the theory of relativity around the same time. In this theory, the momentum of a particle of mass  $m$  and velocity  $v$  is  $p = mv/\sqrt{1 - (v/c)^2}$ , where  $c$  is the speed of light. Thus if a particle has  $m = 0$ , the only way it can pack a momentum is if its velocity is  $v = c$ . Nature takes advantage of this possibility and gives us such particles. They are now called photons. Thus photons have no mass, but have

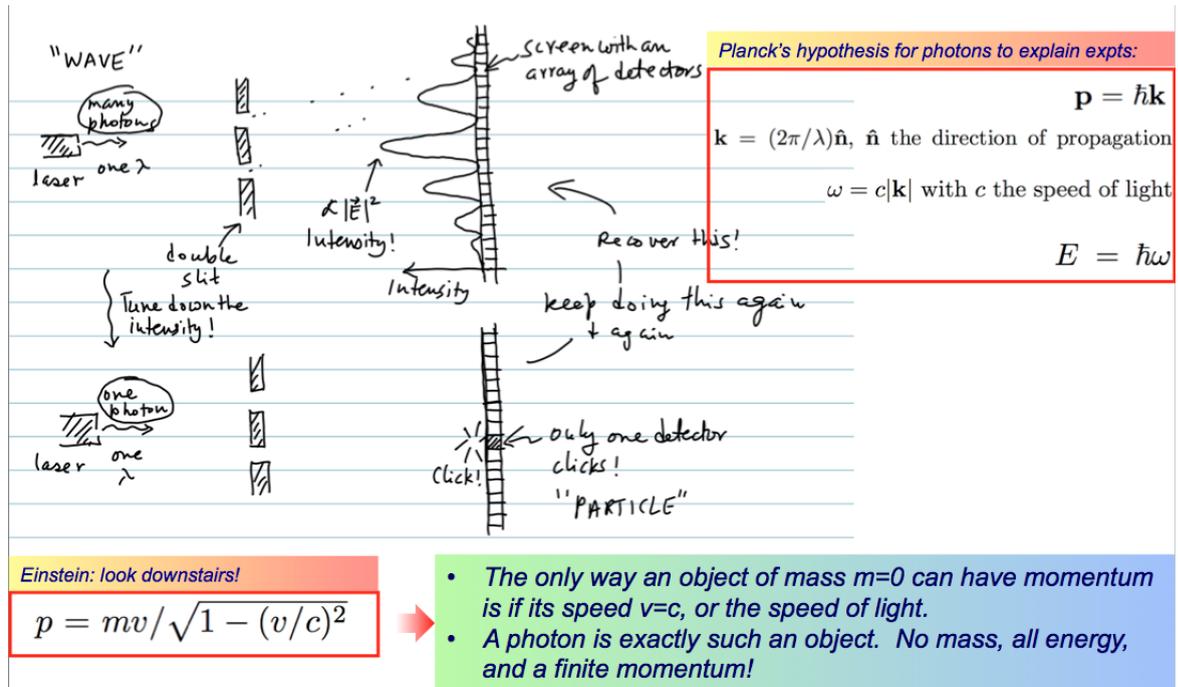


FIGURE 2.1: Photons behaving as particles.

momentum. Thus light, which was thought a wave acquired a certain degree of particle attributes. So what about particles with mass - do they have wave nature too? Nature is too beautiful to ignore this symmetry!

## 2.3 Wave-Particle Duality

de Broglie hypothesized in his PhD dissertation that classical 'particles' with mass also have wavelengths associated with their motion. The wavelength is  $\lambda = 2\pi\hbar/|\mathbf{p}|$ , which is identical to  $\mathbf{p} = \hbar\mathbf{k}$ . How could it be proven? The wavelength of light was such that diffraction gratings (or slits) were available at that time. But electron wavelengths were much shorter, since they had substantial momentum due to their mass. Elsassaer proposed using a crystal where the periodic arrangement of atoms will offer a diffraction grating for electrons. Davisson and Germer at Bell labs shot electrons in a vacuum chamber on the surface of crystalline Nickel. They observed diffraction patterns of electrons. The experiment proved de Broglie's hypothesis was true. All particles had now acquired a wavelength.

The experiment challenged the understanding of the motion or 'mechanics' of particles, which was based on Newton's classical mechanics. In classical mechanics, the question is the following: a particle of mass  $m$  has location  $x$  and momentum  $p$  now. If a force  $F$  acts on it, what are  $(x', p')$  later? Newton's law  $F = md^2x/dt^2$  gives the answer.

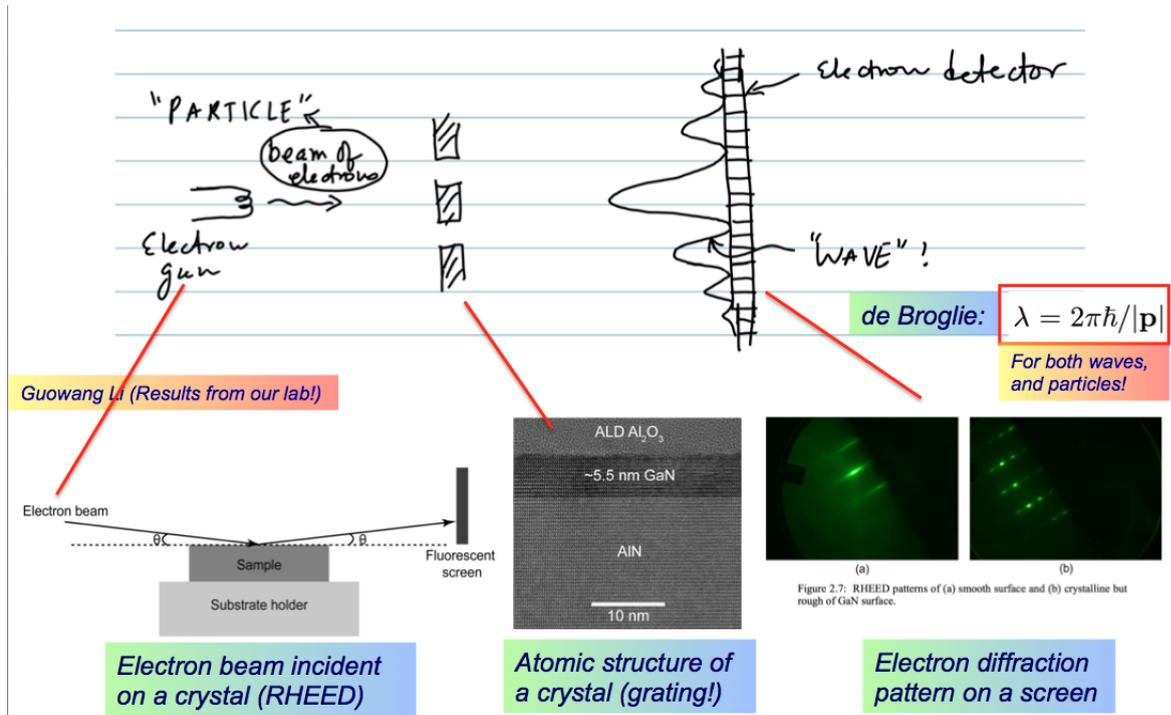


FIGURE 2.2: Electrons behaving as waves.

The answer is deterministic, the particle's future fate is completely determined from its present. This is no longer correct if the particle has wave-like nature. The wave-particle duality is *the central fabric* of quantum mechanics. It leads to the idea of a wavefunction.

## 2.4 The wavefunction

If a particle has a wavelength, what is its location  $x$ ? A wave is an extended quantity. If a measurement of the particle's location is performed, it may materialize at location  $x_0$ . But repeated measurements of the same state will yield  $\langle x \rangle = x_0 + \Delta x$ . Separate measurements of the momentum of the particle prepared in the same state will yield  $\langle p \rangle = p_0 + \Delta p$ . The 'uncertainty' relation  $\Delta x \Delta p \geq \hbar/2$  is a strictly mathematical consequence (\*more description needed\*) of representing a particle by a wave.

Because the 'numbers'  $(x, p)$  of a particle cannot be determined with infinite accuracy simultaneously, one has to let go of this picture. How must one then capture the mechanics of a particle? Any mathematical structure used to represent the particle's state must contain information about its location  $x$  and its momentum  $p$ , since they are forever intertwined by the wave-particle duality. One is then forced to use a *function*, not a number. The function is denoted by  $\psi$ , and is called the wavefunction.

Quantum states (electrons, photons) behave as waves AND particles. How do we describe them quantitatively?

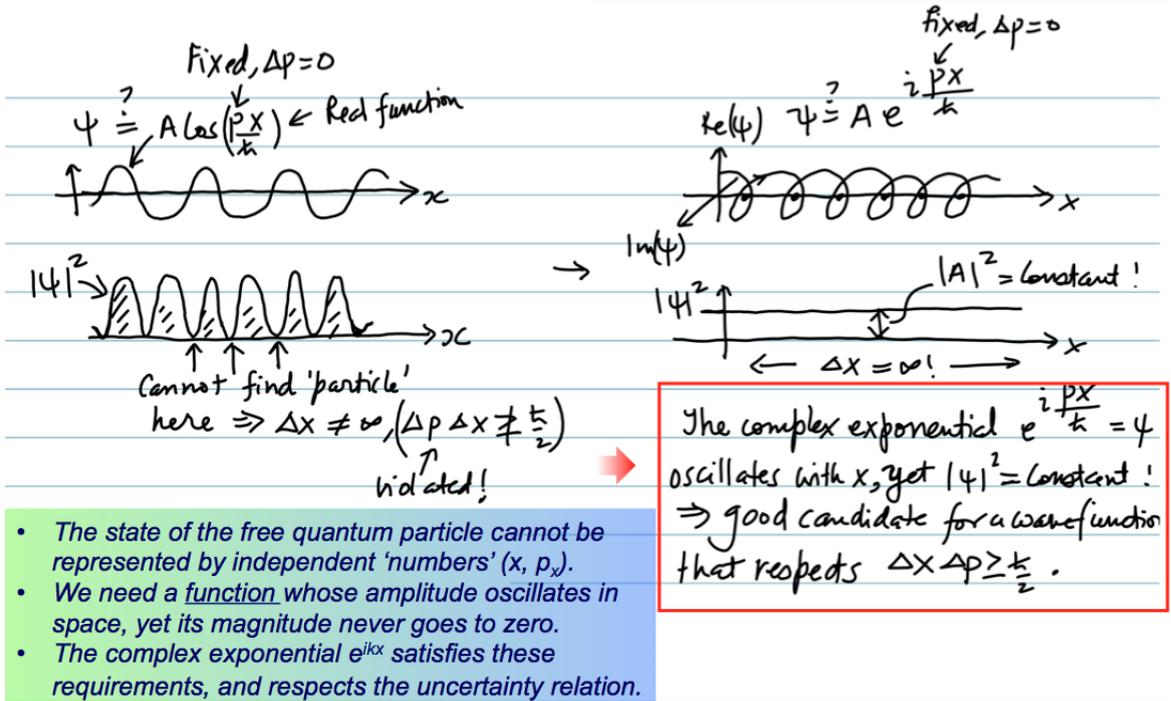
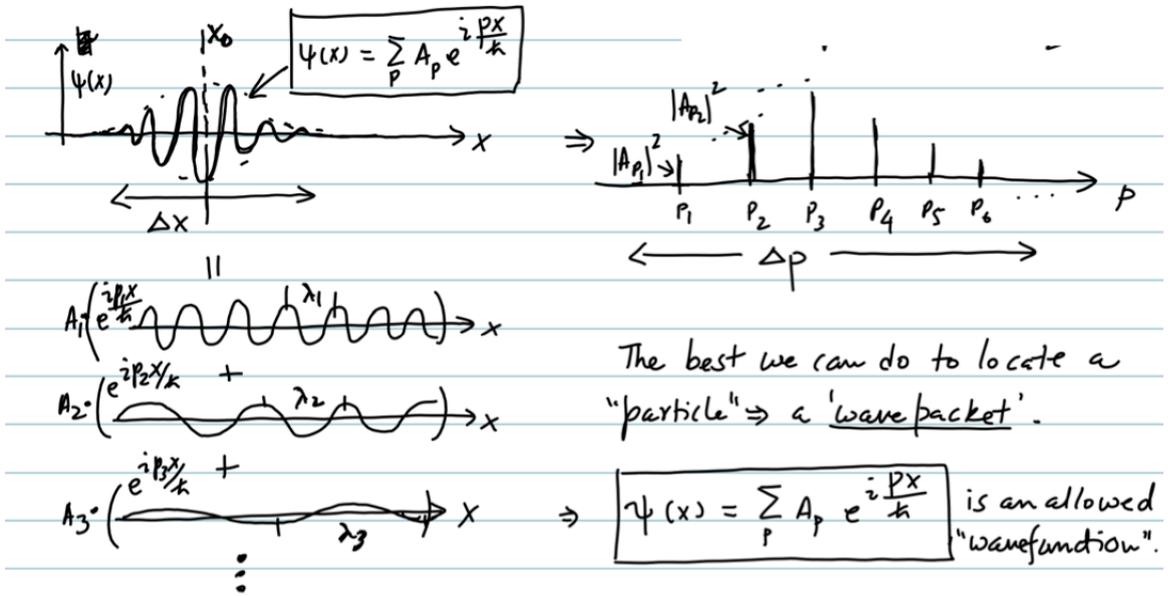


FIGURE 2.3: Birth of the wavefunction to account for the wave-particle duality.

A first attempt at constructing such a function is  $\psi(x) = A \cos(px/\hbar)$ . This guess is borrowed from the classical representation of waves in electromagnetism, and in fluid dynamics. The wavefunction can represent a particle of a definite momentum  $p$ . Max Born provided the statistical interpretation of the wavefunction by demanding that  $|\psi|^2$  be the probability density, and  $\int |\psi|^2 dx = 1$ . In this interpretation,  $|\psi(x)|^2 dx$  is the probability that a measurement of the particle's location will find the particle in the location  $(x, x + dx)$ . It is clear that  $|\psi(x)|^2 = |A|^2 \cos^2(px/\hbar)$  assigns specific probabilities of the location of the particle, going to zero at certain points. Since the momentum  $p$  is definite, the location of the particle must be equally probable at all points in space. Thus we reject the attempted wavefunction as inconsistent with the uncertainty principle.

The simplest wavefunction that is consistent with the wave-particle duality picture is  $\psi_p(x) = A e^{ipx/\hbar}$ . The complex exponential respects the wave-nature of the particle by providing a periodic variation in  $x$ , yet it never goes to zero. The probability (density) is  $|\psi_p(x)|^2 = |A|^2$ , equal at all  $x$ . Thus, complex numbers are *inevitable* in the construction of the wavefunction representing a particle.

By linear superposition of complex exponentials, we can create 'particle' like or 'wave' like states as desired for the problem.



• Drawing on Fourier series, we realize that we can create any wavefunction shape to capture the correct physics of the problem. Note the corresponding reciprocal space weight distribution.

FIGURE 2.4: The superposition principle allows us to create wavefunctions that can represent as 'wave-like' or as 'particle-like' states we want. Wave-like states have large  $\Delta x$  and small  $\Delta p$ , and particle-like states have small  $\Delta x$  and large  $\Delta p$ . All the while, they satisfy the uncertainty principle  $\Delta x \Delta p \geq \hbar/2$ .

## 2.5 Operators

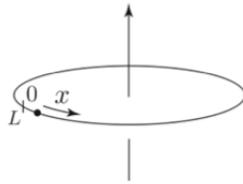
Every physical observable in quantum mechanics is represented by an operator. When the operator 'acts' on the wavefunction of the particle, it extracts the value of the observable. For example, the momentum operator is  $\hat{p} = -i\hbar\partial/\partial x$ , and for states of definite momentum  $\hat{p}\psi_p(x) = (\hbar k)\psi_p(x)$ . We note that  $(x\hat{p} - \hat{p}x)f(x) = i\hbar f(x)$  for any function  $f(x)$ . The presence of the function in this equation is superfluous, and thus one gets the identity

$$x\hat{p} - \hat{p}x = [x, \hat{p}] = i\hbar. \tag{2.1}$$

The square brackets define a commutation relation. The space and momentum operators do not commute. In classical mechanics,  $[x, p] = 0$ . Quantum mechanics elevates the 'status' of  $x$  and  $p$  to those of mathematical operators, preventing them from commuting. This is referred to as the 'first quantization' from classical to quantum mechanics. In this scheme, the dynamical variables  $(x, p)$  that were scalars in classical mechanics are promoted to operators, and the wavefunction  $\psi$  is a scalar. If the number of particles

is not conserved, then one needs to go one step further, and elevate the status of the wavefunction  $\psi \rightarrow \hat{\psi}$  too, which is called second quantization.

## 2.6 States of definite momentum and location



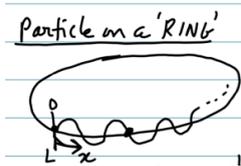
$$\psi(x + L) = \psi(x) \rightarrow e^{ik(x+L)} = e^{ikx} \rightarrow e^{ikL} = 1 \rightarrow kL = 2n\pi$$

Momentum is quantized

$$k_n = \frac{2\pi}{L}n, n = 0, \pm 1, \pm 2, \dots$$

$$\psi(n, x) = Ae^{ik_n x}.$$

Particle on a ring



$$\int_0^L dx |\psi(n, x)|^2 = 1 \rightarrow |A|^2 \times L = 1 \rightarrow A = \frac{1}{\sqrt{L}} \rightarrow \psi(n, x) = \frac{1}{\sqrt{L}} e^{ik_n x}$$

Note that  $n = 0$  is allowed as a result of the periodic boundary condition.

Energy spectrum is discrete, Zero energy is allowed

$$E_n = \frac{\hbar^2 k_n^2}{2m_e} = n^2 \frac{(2\pi\hbar)^2}{2m_e L^2} = n^2 \frac{\hbar^2}{2m_e L^2}$$

Angular momentum is quantized

$$L = p \times r = \hbar k_n \times \frac{L}{2\pi} = \frac{2\pi\hbar}{L} n \times \frac{L}{2\pi} = n\hbar$$

FIGURE 2.5: Quantum mechanics of the particle on a ring.

The wavefunction  $\psi_p(x) = Ae^{ipx/\hbar}$  is a state of definite momentum since it is an eigenstate of the momentum operator  $\hat{p}\psi_p(x) = p\psi_p(x)$ . One may demand the location of the particle to be limited to a finite length  $L$ . This may be achieved by putting an electron on a ring of circumference  $L$ , which yields upon normalization  $A = 1/\sqrt{L}$ . In that case, the wavefunction must satisfy the relation  $\psi_p(x + L) = \psi_p(x)$  to be single-valued. This leads to  $e^{ikL} = 1 = e^{i2\pi n}$ , and  $k_n = n \times (2\pi/L)$ . Here  $n = 0, \pm 1, \pm 2, \dots$ . The linear momentum of the electron is then *quantized*, allowing only discrete values. Since  $L = 2\pi R$  where  $R$  is the radius of the ring,  $k_n L = 2\pi n \rightarrow pR = n\hbar$ , showing angular momentum is quantized to  $0, \pm\hbar, \pm 2\hbar, \dots$ . This indeed is the *quantum* of quantum mechanics! One may then index the wavefunctions of definite linear momentum by writing  $\psi_n(x)$ . Expressing states of definite momentum in terms of states of definite location similarly yields

$$\psi_n(x) = \frac{1}{\sqrt{L}} e^{ik_n x} \tag{2.2}$$

The set of wave functions  $[\dots\psi_{-2}(x), \psi_{-1}(x), \psi_0(x), \psi_1(x), \psi_2(x), \dots] = [\psi_n(x)]$  are special. We note that  $\int_0^L dx \psi_m^*(x)\psi_n(x) = \delta_{nm}$ , i.e., the functions are orthogonal. Any

general wavefunction representing the particle  $\psi(x)$  can be expressed as a linear combination of this set. This is the principle of superposition, and a basic mathematical result from Fourier theory. Thus the quantum mechanical state of a particle may be represented as  $\psi(x) = \sum_n A_n \psi_n(x)$ . Clearly,  $A_n = \int dx \psi_n^*(x) \psi(x)$ . Every wavefunction constructed in this fashion represents a permitted state of the particle, as long as  $\sum_n |A_n|^2 = 1$ .

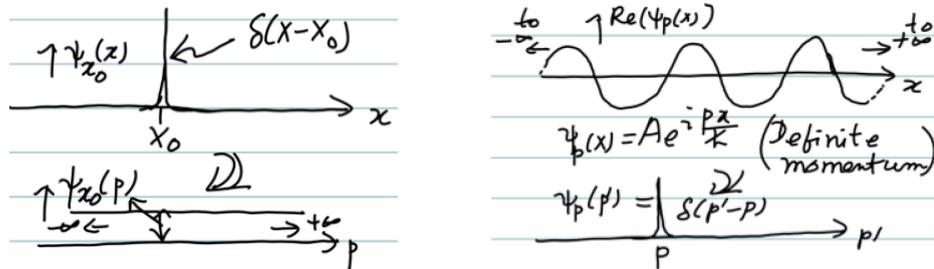


FIGURE 2.6: States of definite location and states of definite momentum.

It is useful here to draw an analogy to the decomposition of a vector into specific coordinates. The ‘hybrid’ state function  $\psi(x)$  is pictured as a vector  $|\psi\rangle$  in an abstract space. The definite momentum wavefunctions  $\psi_n(x)$  are pictured as the ‘coordinate’ vectors  $|n\rangle$  in that space of vectors. This set of vectors is called the basis. Since there are an infinite set of integers  $n = 0, \pm 1, \pm 2, \dots$ , the vector space is infinite dimensional. It is called the Hilbert space. One may then consider the coefficients  $A_n$  as the length of the projections of the state on the basis states. The abstract picture allows great economy of expression by writing  $|\psi\rangle = \sum_n A_n |n\rangle$ . The orthogonality of the basis states is  $\langle m|n\rangle = \delta_{mn}$ , and thus  $A_n = \langle n|\psi\rangle$ . Then it is evident that  $|\psi\rangle = \sum_n \langle n|\psi\rangle |n\rangle = \sum_n |n\rangle \langle n|\psi\rangle$ , and  $\sum_n |n\rangle \langle n| = 1$ .

A vector may be decomposed in various basis coordinates. For example, a vector in 3-d real space may be decomposed into cartesian, spherical, or cylindrical coordinate systems. Similarly, the choice of basis states of definite momentum is not unique. The wavefunctions for states of definite location are those functions that satisfy  $x\psi_{x_0}(x) = x_0\psi_{x_0}(x)$ , which lets us identify  $\psi_{x_0}(x) = \delta(x - x_0)$ . Here  $\delta(\dots)$  is the Dirac-delta function, sharply peaked at  $x = x_0$ . It is instructive to expand the states of definite location in the basis of the states of definite momentum. From the uncertainty relation, we expect a state of definite location to contain many momenta. The expansion yields  $A_n = \int_{-\infty}^{+\infty} dk / (2\pi/L) \times (e^{ik_n x} / \sqrt{L}) \delta(x - x_0) = e^{ik_n x_0} / \sqrt{L}$  (\*\*check this!!\*\*), whereby  $|A_n|^2 = 1/L$ . Thus, the state of definite location  $x_0$  is constructed of an infinite number of states of definite momentum  $n = 0, \pm 1, \pm 2, \dots$ , each with equal probability  $1/L$ .

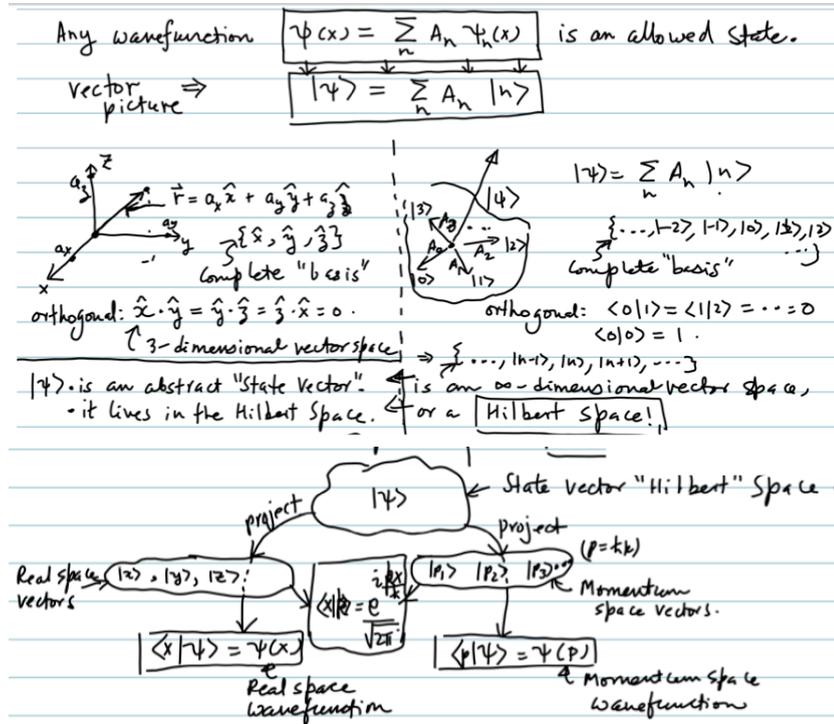


FIGURE 2.7: Vector spaces for quantum states: we can use results of linear algebra for quantum mechanics problems.

## 2.7 States of definite energy: Schrodinger equation

States of definite energy  $\psi_E(x)$  are special. Unlike the states of definite momentum or definite location, we cannot write down their general wavefunction without more information. That is because the energy of a particle depends on its potential and kinetic components. In classical mechanics, the total energy is  $p^2/2m + V(x)$ , i.e., split between kinetic and potential energy components. Once  $x$  &  $p$  are known for a classical particle, the energy is completely defined, meaning one does not need to ask another question. However, since  $x$  and  $p$  cannot be simultaneously defined for a quantum-mechanical particle with arbitrary accuracy, the energy must be obtained through operations performed on the wavefunction.

Schrodinger provided the recipe, and the equation is thus identified with his name. The Schrodinger equation is

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)\right]\psi_E(x) = E\psi_E(x). \tag{2.3}$$

The solution of this eigenvalue equation for a  $V(x)$  identifies the special wavefunctions  $\psi_E(x)$ . These wavefunctions represent states of definite energy. How did we ascertain the accuracy of the Schrodinger equation? The answer is through experiments. A

major unresolved problem at the time was explaining the discrete spectral lines emitted from excited hydrogen atoms. Neils Bohr had a heuristic model to explain the spectral lines that lacked mathematical rigor. The triumph of Schrodinger equation was in explaining the precise spectral lines. An electron orbiting a proton in a hydrogen atom sees a potential  $V(r) = -q^2/4\pi\epsilon_0 r$ . Schrodinger solved this equation (with help from a mathematician), and obtained energy eigenvalues  $E_n = -13.6/n^2$  eV. Thus Bohr's semi-qualitative model was given a rigid mathematical basis by Schrodinger's equation. The equation also laid down the recipe for solving similar problems in most other situations we encounter. Just as the case for states of definite energy or definite location, one may expand *any* state of a quantum particle in terms of the states of definite energy  $\psi(x) = \sum_E A_E \psi_E(x)$ , or equivalently  $|\psi\rangle = \sum_E A_E |E\rangle$

So why do states of definite energy occupy a special position in applied quantum mechanics? That becomes clear if we consider the time-dependent Schrodinger equation.

## 2.8 Time-dependent Schrodinger equation

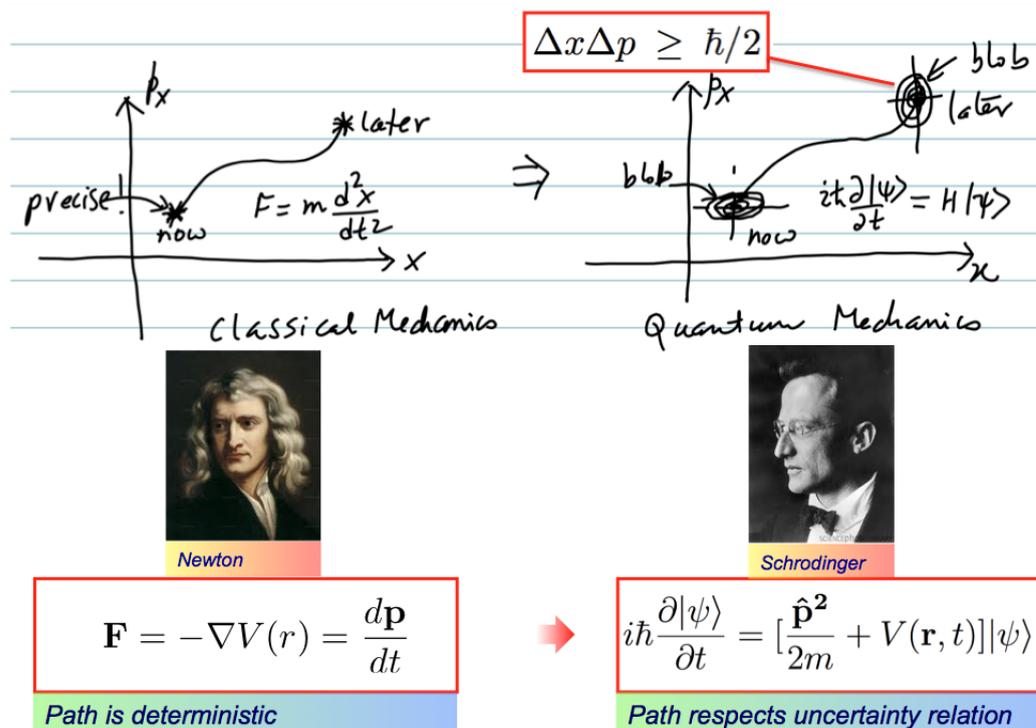


FIGURE 2.8: The dynamics of quantum states is governed by the time-dependent Schrodinger equation. Note that it looks like a hybrid of the classical energy and a wave equation, which is how it must be to account for the wave-particle duality.

Newton's law  $F = dp/dt$  provides the prescription for determining the future  $(x', p')$  of a particle given its present  $(x, p)$ . Schrodinger provided the quantum-mechanical equivalent, through the time-dependent equation

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = \underbrace{\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right]}_{\hat{H}} \Psi(x, t). \quad (2.4)$$

To track the time-evolution of quantum states, one must solve this equation and obtain the composite space-time wavefunction  $\Psi(x, t)$ . Then physical observables can be obtained by operating upon the wavefunction by the suitable operators. Let's look at a particular set of solution wavefunctions which allow the separation of the time and space variables, of the form  $\Psi(x, t) = \chi(t)\psi(x)$ . Inserting it back into the time-dependent Schrodinger equation and rearranging, we obtain

$$i\hbar \frac{\dot{\chi}(t)}{\chi(t)} = \frac{\hat{H}\psi(x)}{\psi(x)} = E. \quad (2.5)$$

Note that since the left side does not depend on space, and the right side does not depend on time, both the fractions must be a constant. The constant is called  $E$ , and clearly has dimensions of energy in Joules. The right half of the equation lets us identify that  $\hat{H}\psi_E(x) = E\psi_E(x)$  are states of definite energy. Then the left side dictates that the time dependence of these states is described by  $\chi(t) = \chi(0)e^{-iEt/\hbar}$ . Thus the particular set of solutions

$$\Psi_E(x, t) = \psi_E(x)e^{-i\frac{E}{\hbar}t} \quad (2.6)$$

now define the time evolution of the states. Here  $\psi_E(x)$  are states of definite energy, as obtained by solving the time-independent Schrodinger equation.

## 2.9 Stationary states and time evolution

We note that  $|\Psi_E(x, t)|^2 = |\psi_E(x)|^2$ , that is, the state  $\Psi_E(x, t)$  does *not* change with time. That means that a particle prepared in a state of definite energy will stay in that energy if there are no perturbations. Its wavefunction does evolve as  $\exp(-iEt/\hbar)$ , but this evolution is 'unitary' since its absolute value is unity. Notice the analogy with Newton's first law, which states that a particle at rest or moving with constant velocity will continue to do so unless acted upon by a force. The states of definite energy are therefore special since they do not evolve with time unless perturbed, and are called 'stationary states'. Thus the expansion may be written as

$$\Psi(x, t) = \sum_E A_E \Psi_E(x, t) = \sum_E A_E \psi_E(x) e^{-i\frac{E}{\hbar}t}. \quad (2.7)$$

The states of definite energy form a convenient and often-used basis for expansion of general states of a particle. That is because they are stationary states - it is simpler if the basis states are fixed.

Consider a simple case where a hybrid state  $\Psi(x, t)$  is prepared with components in two states  $|E_1\rangle$  and  $|E_2\rangle$ . Then, the expansion is  $\Psi(x, t) = A_{E_1} \psi_{E_1}(x) e^{-iE_1 t/\hbar} + A_{E_2} \psi_{E_2}(x) e^{-iE_2 t/\hbar}$ . The probability density of this state then is, for real  $A$ 's

$$|\Psi(x, t)|^2 = |A_{E_1}|^2 |\psi_{E_1}(x)|^2 + |A_{E_2}|^2 |\psi_{E_2}(x)|^2 + A_{E_1} A_{E_2} \psi_{E_1}(x) \psi_{E_2}(x) \cos\left(\frac{E_1 - E_2}{\hbar}t\right), \quad (2.8)$$

which *does* oscillate with time with frequency  $\omega_{12} = (E_1 - E_2)/\hbar$ . Such two-level systems are being currently explored for making quantum-bits or qubits for a form of analog computation called quantum-computation.

All transport and optical phenomena involve time evolution. So most of the time in semiconductor physics we are working with the solutions of the time-dependent Schrodinger equation. The states of definite energy as a function of momentum  $E(k)$  that form the *energy bandstructure* of the solid thus provide a most convenient basis for the analysis of electronic and optical phenomena of semiconductors.

The time evolution of the expectation value of an operator is given by Ehrenfest's theorem

$$\frac{d\langle \hat{A} \rangle}{dt} = -\frac{i}{\hbar} \langle [\hat{A}, \hat{H}] \rangle, \quad (2.9)$$

where the operator itself is time-independent. By using  $\hat{A} = \hat{p}$  and  $\hat{H} = \hat{p}^2/2m + V(x)$ , Ehrenfest's theorem directly leads to Newton's 2nd law. It forms the starting point for the density-matrix formulation of the time-evolution of quantum states.

## 2.10 Fermions and Bosons

Consider two quantum states  $|a\rangle$  and  $|b\rangle$  with real-space wavefunctions  $\psi_a(x)$  and  $\psi_b(x)$ . What is the many-particle wavefunction when *two* particles are put in the two states?

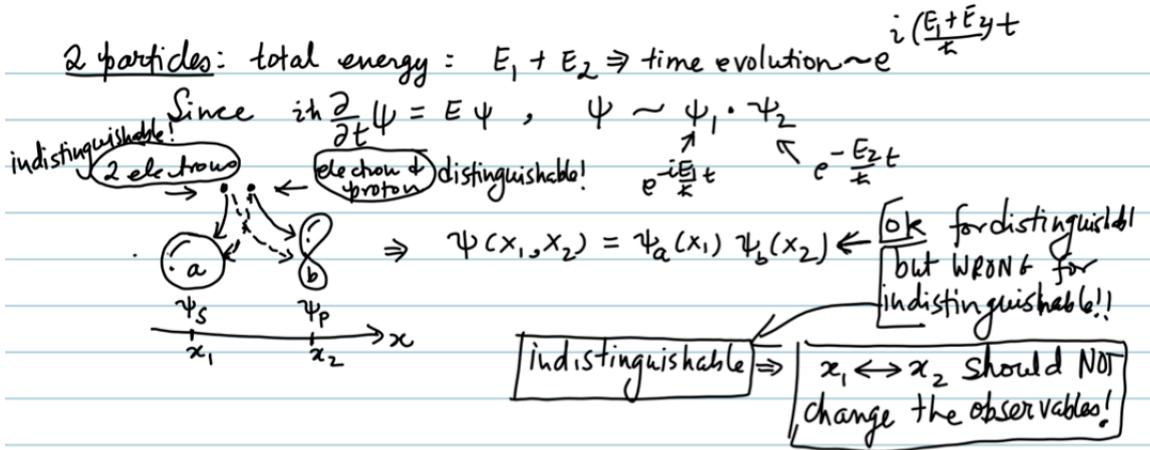


FIGURE 2.9: Indistinguishable particles suffer an identity crisis when we try constructing a wavefunction for more than one particle!

Lets label the locations of the two particles as  $x_1$  and  $x_2$ . If the two particles are *distinguishable*, such as an electron and a proton, then the composite wavefunction may be written as the product of the single-particle wavefunctions

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2). \tag{2.10}$$

But if the two particles are *indistinguishable*, such as two electrons, the wavefunction must satisfy further requirements. Specifically, if we swap the locations of the two electrons  $x_1 \leftrightarrow x_2$ , the physical observables of the composite state must remain the same. This requirement dictates that the probability density must satisfy

$$P(x_2, x_1) = P(x_1, x_2) \rightarrow |\psi(x_2, x_1)|^2 = |\psi(x_1, x_2)|^2. \tag{2.11}$$

The original product wavefunction does not satisfy this requirement. It cannot represent indistinguishable particles. A symmetrized form, however does the job:

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2) + \psi_a(x_2)\psi_b(x_1) \tag{2.12}$$

because

$$\psi(x_2, x_1) = +\psi(x_1, x_2) \tag{2.13}$$

and the probability density does not change upon swapping. We also note that *both* particles may be in the same  $x$  since

$$\psi(x_1, x_1) = +\psi(x_1, x_1) \quad (2.14)$$

is OK. Particles in nature that choose the ‘+’ sign are bosons. Multiple bosons can occupy the same quantum state.

The anti-symmetrized form

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2) - \psi_a(x_2)\psi_b(x_1) \quad (2.15)$$

leads to

$$\psi(x_2, x_1) = -\psi(x_1, x_2), \quad (2.16)$$

which is also permitted, since the probability density remains unaltered by the negative sign upon swapping the particles. Particles that choose the ‘-’ sign are fermions. However, an attempt to put both fermions in the same location leads to

$$\psi(x_1, x_1) = -\psi(x_1, x_1) \rightarrow \psi(x_1, x_1) = 0. \quad (2.17)$$

This is the Pauli exclusion principle. It states the simple result that two identical fermions (e.g. electrons) cannot be in the same quantum state. It is responsible for all chemical behavior of matter and the existence of the periodic table of elements.

In the presence of large number of electrons, the Pauli-exclusion principle leads to an occupation probability of quantum states. The result was first derived by Dirac, and is called the Fermi-Dirac relation

$$f_{FD}(E) = \frac{1}{1 + e^{\frac{E-E_F}{kT}}}, \quad (2.18)$$

where  $E_F$  is the Fermi-energy,  $k$  the Boltzmann constant, and  $T$  the absolute temperature. Note that the value cannot exceed 1.

The equivalent statistical result for bosons is

$$f_{BE}(E) = \frac{1}{e^{\frac{E-\mu}{kT}} - 1}, \quad (2.19)$$

where  $\mu$  is the chemical potential. The Bose-Einstein distribution allows values larger than 1. Dramatic effects such as the Bose-Einstein condensation (BEC), lasers, and the existence of superconductivity occurs when many bosons can co-exist in the same state. The bosons can be composite particles, for example Cooper-pairs in superconductors that are electron-phonon-electron quasiparticles where electrons are ‘glued’ together by phonons.

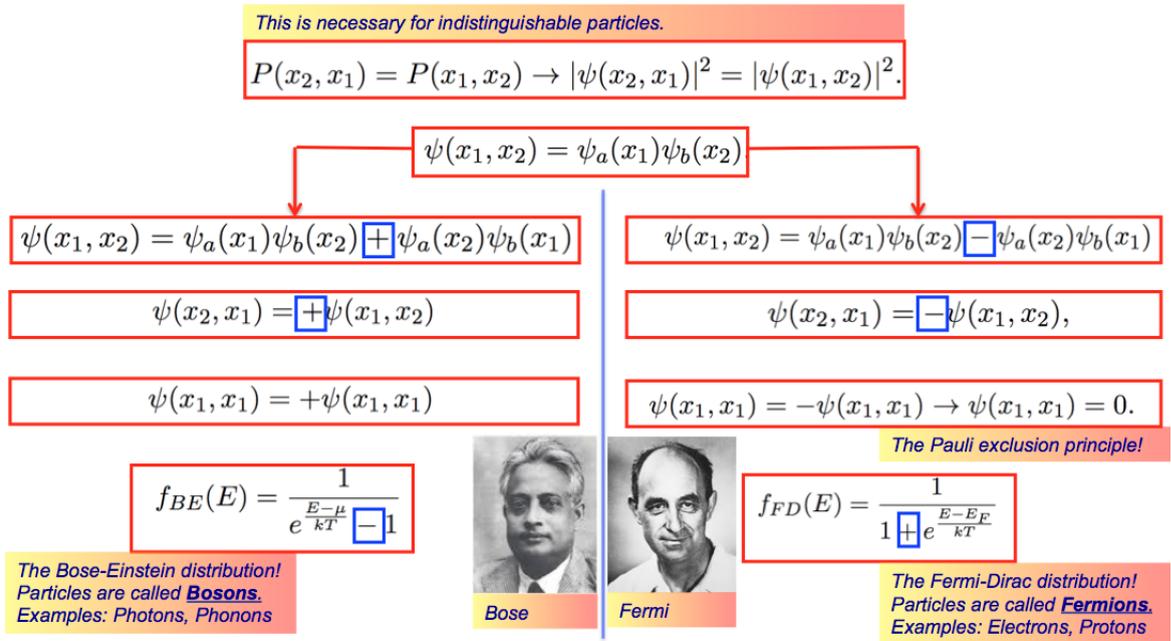


FIGURE 2.10: Indistinguishable particles can be of two types: Bosons, or Fermions. They have very different properties!

## 2.11 Spin, and the Spin-Statistics Theorem

In addition to linear momentum  $\mathbf{p} = \hbar\mathbf{k}$  and angular momentum  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ , electrons also possess an extra bit of spin angular momentum. In semiconductors, electron spin plays an important role in the electronic band structure. The net angular momentum of electron states is obtained by adding the various components of the angular momenta.

The exclusion principle is central to the spin-statistics theorem from relativistic quantum field-theory. It states that bosonic particles have integer spins, and fermionic particles have half-integer spins. That means bosons have spins  $S = 0, \pm\hbar, \pm 2\hbar, \dots$ , and fermions have spins  $S = \pm\hbar/2, \pm 3\hbar/2, \dots$ . Electrons have spin  $\pm\hbar/2$ .

The fundamental dichotomy of particles in nature has received increasing attention the last three decades. Quasi-particle states have been observed (for example in the fractional quantum Hall effect) that behave neither like fermions nor bosons. Swapping the single-particle states for such quasi-particles leads to the accumulation of a phase factor:

$$\psi(x_2, x_1) = e^{i\phi} \psi(x_1, x_2). \quad (2.20)$$

These particles evidently satisfy the indistinguishability criteria, but accumulate a(ny) phase, leading to their name *anyons*. Anyon states can exhibit a richer range of statistics than fermions and bosons. For anyons, commuting (or Abelian) statistics has similarity to fermions and bosons, but non-commuting (or non-Abelian) statistics does not have such an analog. Non-Abelian anyons are of current interest due to their proposed usage in topological quantum computation.

## 2.12 The Dirac equation and the birth of particles

Dirac was not comfortable with Schrodinger's equation since it was not consistent with relativity, and did not predict spin of electrons. He was able to reformulate the quantum-mechanics of electrons from Schrodinger's equation

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = \left[ \frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{r}, t) \right] |\psi\rangle \quad (2.21)$$

to the Dirac equation

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = [c\hat{\alpha} \cdot \hat{\mathbf{p}} + \beta mc^2 + V(\mathbf{r}, t)] |\psi\rangle \quad (2.22)$$

where  $c$  is the speed of light, and  $\hat{\alpha}, \beta$  are matrices. Before Dirac, the concept of a 'particle' was not very clear. Dirac's assertion was to the effect: 'a particle is the solution of my equation'. Dirac's equation described the electron energy spectrum with more accuracy than Schrodinger's equation, and accounted for spin naturally. It also predicted the existence of negative energy states, or anti-electrons. This was the first prediction of antimatter. A few years after the prediction, such particles were discovered in cloud chambers by Carl Anderson; these particles are called positrons. Electrons and positrons annihilate each other, emitting light of energy  $\hbar\omega = 2m_0c^2$ .

The philosophy of Dirac that 'particles are solutions to equations' gave rise to the prediction of a number of new particles that have since been observed such as quarks, gluons,

Higgs boson, etc... Majorana fermions fall under the category of predicted exotic particles, and there is intense interest in realizing such exotic states in matter for topological quantum computation. What was exotic yesterday will become commonplace tomorrow, so keep track of those ‘particles’!

## 2.13 The Postulates of Quantum Mechanics

The five basic postulates of quantum mechanics are:

- (1) The state of any physical system at a given time  $t$  is completely represented by a state vector  $|\Psi\rangle = |\Psi(\mathbf{r}, t)\rangle$ .
- (2) For an observable quantity  $A$  there is an operator  $\hat{\mathbf{A}}$ . The eigenvalues of  $\hat{\mathbf{A}}$  are the possible results of the measurements of  $A$ , that is, denoting the eigenvalues of  $\hat{\mathbf{A}}$  by  $a$ ,

$$\hat{\mathbf{A}}|a\rangle = a|a\rangle, \quad (2.23)$$

and the probability of a measurement of  $A$  yielding the value  $a$  at time  $t$  is  $|\langle a|\Psi(t)\rangle|^2$ . The  $a$ 's, which are the results of possible measurements, must be real. This implies that  $\hat{\mathbf{A}}$  must be a linear hermitian operator.

- (3) A measurement of  $|\Psi\rangle$  that leads to an eigenvalue  $a_i$  leads the quantum mechanical system to *collapse* into the eigenstate  $|\Psi_i\rangle$ , which is the eigenstate corresponding to the eigenvalue  $a_i$ . So a measurement affects the state of the quantum system.
- (4) There exists a hermitian operator  $\hat{\mathbf{H}}$  such that

$$i\hbar \frac{\partial |\Psi(\mathbf{r}, t)\rangle}{\partial t} = \hat{\mathbf{H}}|\Psi(\mathbf{r}, t)\rangle. \quad (2.24)$$

- (5) Two classical dynamical variables  $a, b$ , which are conjugate in the Hamiltonian sense, are represented by Schrodinger operators  $\hat{\mathbf{A}}, \hat{\mathbf{B}}$ , which obey

$$\hat{\mathbf{A}}_i \hat{\mathbf{B}}_j - \hat{\mathbf{B}}_j \hat{\mathbf{A}}_i = i\hbar \delta_{ij}. \quad (2.25)$$

## Chapter 3

# Exact Results from Quantum Mechanics

### 3.1 Introduction

In this chapter we summarize a few *exactly* solved problems of quantum mechanics<sup>1</sup>. The set of exactly solved problems is important, because they form the basis on which most analysis of deviations is based.

### 3.2 States of definite energy

As discussed in Chapter 2, *all possible information* about the quantum states of the electron are buried in the wavefunction  $|\psi\rangle$ . In this chapter, we want to identify this wavefunction projected to the real space, i.e.,  $\psi(x) = \langle x|\psi\rangle$  for certain cases. We then want to extract the information that interests us from  $\psi(x)$  by applying corresponding operators on them. To do that, we have to first solve the time-independent Schrodinger equation for an electron in various potentials  $V(x)$ :

$$-\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} \psi(x) + V(x)\psi(x) = E\psi(x). \quad (3.1)$$

The set of solutions  $\langle x|n\rangle = \psi(n, x)$  will then be the eigenfunctions corresponding to states of *definite energy* with corresponding eigenvalues  $E_n$ . As discussed in Chapter 2, the states of definite energy are also *stationary* states. They form the most convenient basis for describing the situations when the potential deviates from the ideal, i.e., if

---

<sup>1</sup>Exactly solvable within the assumptions made, that is!

$V(x) \rightarrow V(x) + W(x, t)$ . Thus, the states of definite energy form the basis to uncover what happens when we perturb the quantum system. We begin with the simplest of potentials: when  $V(x) = 0$ .

### 3.3 The free electron

For  $V(x) = 0$ , the Schrodinger equation reads

$$-\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} \psi(x) = E\psi(x). \quad (3.2)$$

The equation has the most general solution of the form

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad (3.3)$$

where

$$k = \sqrt{\frac{2m_e E}{\hbar^2}} = \frac{2\pi}{\lambda}. \quad (3.4)$$

The energy can be expressed as

$$E = \frac{\hbar^2 k^2}{2m_e} \quad (3.5)$$

We note that the general solution in Eq. 3.3 represents a superposition of two waves: one going to the right ( $\psi_{\rightarrow}(x) = Ae^{ikx}$ ) and the other to the left ( $\psi_{\leftarrow}(x) = Be^{-ikx}$ ). Since it is a ‘mixed’ state, clearly it is *not* a state of a definite momentum. We verify this by operating upon the wavefunction by the momentum operator:

$$\hat{p}_x \psi(x) = -i\hbar \frac{d}{dx} \psi(x) = -i\hbar(ikAe^{ikx} - ikBe^{-ikx}) = \hbar k(Ae^{ikx} - Be^{-ikx}) \neq p\psi(x) \quad (3.6)$$

but... for just the right going state we get

$$\hat{p}_x \psi_{\rightarrow}(x) = -i\hbar \frac{d}{dx} \psi_{\rightarrow}(x) = -i\hbar(ikAe^{ikx}) = \hbar k \psi_{\rightarrow}(x) = p\psi_{\rightarrow}(x) \quad (3.7)$$

and it *is* a state of definite momentum. The free electron wavefunction *cannot* be normalized, because it extends over all space from  $-\infty \leq x \leq +\infty$ . To normalize it, we wrap the infinitely long line and join the infinities to form a circle.

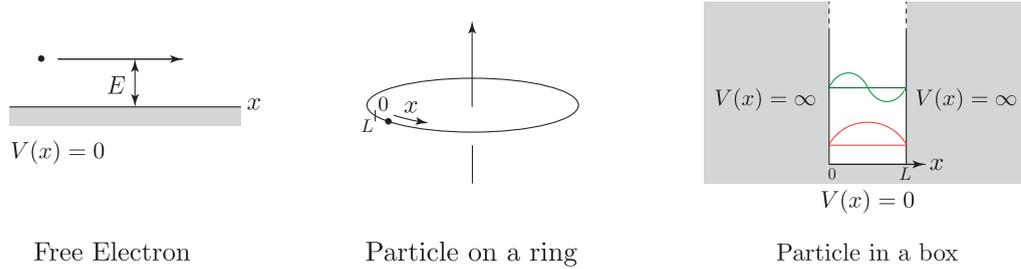


FIGURE 3.1: XX.

### 3.4 Not so free: particle in a ring

$$\psi(x + L) = \psi(x) \rightarrow e^{ik(x+L)} = e^{ikx} \rightarrow e^{ikL} = 1 \rightarrow kL = 2n\pi \quad (3.8)$$

$$\boxed{k_n = \frac{2\pi}{L}n}, n = 0, \pm 1, \pm 2, \dots \quad (3.9)$$

$$\psi(n, x) = Ae^{ik_n x}.$$

$$\int_0^L dx |\psi(n, x)|^2 = 1 \rightarrow |A|^2 \times L = 1 \rightarrow A = \frac{1}{\sqrt{L}} \rightarrow \boxed{\psi(n, x) = \frac{1}{\sqrt{L}} e^{ik_n x}} \quad (3.10)$$

Note that  $n = 0$  is *allowed* as a result of the periodic boundary condition.

$$E_n = \frac{\hbar^2 k_n^2}{2m_e} = n^2 \frac{(2\pi\hbar)^2}{2m_e L^2} = n^2 \frac{h^2}{2m_e L^2} \quad (3.11)$$

$$L = p \times r = \hbar k_n \times \frac{L}{2\pi} = \frac{2\pi\hbar}{L} n \times \frac{L}{2\pi} = n\hbar \quad (3.12)$$

### 3.5 The particle in a box

$$V(x) = 0, \quad 0 \leq x \leq L \quad (3.13)$$

$$V(x) = \infty, \quad x < 0, x > L \quad (3.14)$$

The major change is that  $\psi(x) = 0$  in regions where  $V(x) = \infty$ .

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \rightarrow \psi(0) = 0 = A + B, \psi(L) = Ae^{ikL} + Be^{-ikL} = 0 \quad (3.15)$$

$$\frac{A}{B} = -e^{-i2kL} = -1 \rightarrow 2kL = 2n\pi \rightarrow \boxed{k_n = n\frac{\pi}{L}}, n = \pm 1, \pm 2, \pm 3, \dots \quad (3.16)$$

Note that  $n = 0$  is *not allowed*, because then  $\psi(x) = 0$  and there is no particle. The wavefunction after normalization over the length  $L$  is

$$\psi(n, x) = \sqrt{\frac{2}{L}} \sin(n\frac{\pi}{L}x) = \sqrt{\frac{2}{L}} \sin(k_n x) \quad (3.17)$$

$$E_n = n^2 \frac{(\pi\hbar)^2}{2m_e L^2} = n^2 \frac{h^2}{8m_e L^2} \quad (3.18)$$

### 3.6 The harmonic oscillator

$$V(x) = \frac{1}{2} m_e \omega^2 x^2 \quad (3.19)$$

$$E_n = (n + \frac{1}{2})\hbar\omega \quad (3.20)$$

$$a = \sqrt{\frac{m\omega}{2\hbar}} (\hat{x} + \frac{i}{m\omega} \hat{p}) \quad (3.21)$$

$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}} (\hat{x} - \frac{i}{m\omega} \hat{p}) \quad (3.22)$$

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(a^\dagger + a) \quad (3.23)$$

$$\hat{p} = i\sqrt{\frac{m\omega\hbar}{2}}(a^\dagger - a) \quad (3.24)$$

$$[a, a^\dagger] = 1 \quad (3.25)$$

$$a|n\rangle = \sqrt{n}|n-1\rangle \quad (3.26)$$

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \quad (3.27)$$

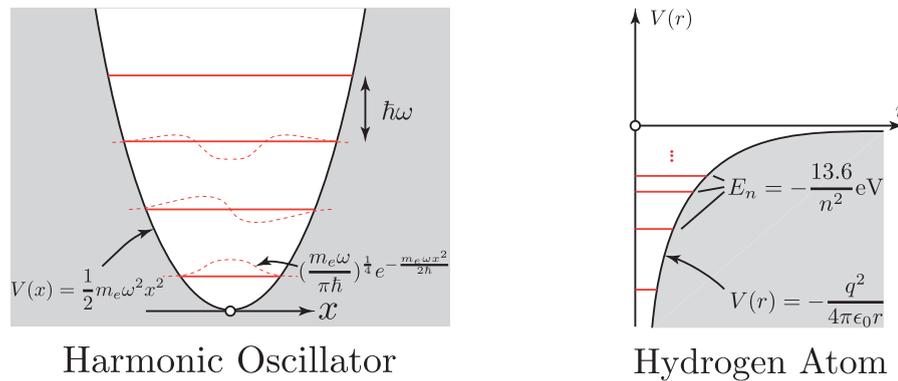


FIGURE 3.2: XX.

### 3.7 The Hydrogen atom

$$V(r) = -\frac{q^2}{4\pi\epsilon_0 r} \quad (3.28)$$

### 3.8 Electrons in a periodic potential: Bloch Theorem

We finally consider an electron in a periodic potential,

$$-\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} \psi(x) + V(x)\psi(x) = E\psi(x), \quad (3.29)$$

where  $V(x+a) = V(x)$ . In the absence of the potential  $V(x)$ , the wavefunctions were of the form  $\psi_0(x) = Ae^{ikx}$ , where  $k$  was allowed to take all values. If we considered a ring of length  $L$ , then  $k_n = \frac{2\pi}{L}n$ , and  $\psi(n, x) = \frac{1}{\sqrt{L}}e^{ik_n x}$ . Imagine the ring has a periodic lattice, such that  $L = Na$ . Then,  $k_n = \frac{2\pi}{a} \frac{n}{N}$ , where  $n = 0, 1, \dots, N - 1$ .

### 3.9 The WKB Method

The WKB method is a recipe for solving the time-independent Schrodinger equation for arbitrary potentials. There is typically a misconception that this method is a crude approximation. Far from it. Consider the time-independent Schrodinger equation in 1D:

$$-\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} \psi(x) + V(x)\psi(x) = E\psi(x) \quad (3.30)$$

rewritten in the form

$$\psi''(x) = Q(x)\psi(x), \quad (3.31)$$

with

$$Q(x) = \frac{2m_e}{\hbar^2} (V(x) - E). \quad (3.32)$$

This is in general analytically unsolvable, except for the few cases considered in this chapter such as the harmonic oscillator, or the hydrogen atom. George Green (the same person who is credited with Green's functions) had a brilliant insight to crack into an asymptotic approach to a solution. He suggested that we try a solution of the form

$$\psi(x) = e^{S(x)} \quad (3.33)$$

Substituting, we obtain  $(S'' + (S')^2)e^S = Qe^S$  which leads to

$$S'' + (S')^2 = Q \quad (3.34)$$

Note that this is *exact*. But unfortunately we have just converted the already unsolvable Schrodinger equation into another insolvable equation: the Riccati equation. It is also a non-linear equation!

Green made the crucial observation that if  $S(x) = ax^b$  where  $b < 0$ , then  $S'' \ll (S')^2$  for small  $x$ . This makes the asymptotic form of Eq. [3.34](#)

$$(S')^2 \sim Q, \quad (3.35)$$

which leads to

$$S' \sim \pm\sqrt{Q}, \quad (3.36)$$

and

$$S(x) \sim \pm \int_a^x du \sqrt{Q(u)}. \quad (3.37)$$

Here  $a$  is any chosen constant. Now lets write

$$S(x) = \underbrace{\pm \int_a^x du \sqrt{Q(u)}}_{S_0(x)} + \underbrace{C(x)}_{S_1(x)+S_2(x)+S_3(x)+\dots} \quad (3.38)$$

Now we have gone back from an asymptotic form to an exact form here. Note that the leading functional form is defined  $S_0(x) = \pm \int_a^x du \sqrt{Q(u)}$ . Consequently, we have the relations

$$S'_0(x) = \pm\sqrt{Q(x)} \quad (3.39)$$

$$S''_0(x) = \pm \frac{Q'(x)}{2\sqrt{Q(x)}} \quad (3.40)$$

Now we substitute  $S = S_0 + C$  into 3.34 to get

$$S''_0 + C'' + (S'_0 + C')^2 = Q. \quad (3.41)$$

Note that this is back to being *exact*. Writing it out, we get

$$S''_0 + C'' + (S'_0)^2 + (C')^2 + 2S'_0C' = Q, \quad (3.42)$$

and substituting all terms related to  $S_0(x)$  and its derivatives, we get

$$\pm \frac{Q'(x)}{2\sqrt{Q(x)}} + C'' + Q + (C')^2 \pm 2\sqrt{Q(x)}C' = Q. \quad (3.43)$$

This is still *exact*. Note the crucial cancellation of  $Q$ . The result is a differential equation, but *now for the correction function*  $C(x)$ :

$$\pm \frac{Q'(x)}{2\sqrt{Q(x)}} + C'' + (C')^2 \pm 2\sqrt{Q(x)}C' = 0 \quad (3.44)$$

But this equation is not very different from the Riccati equation either! Now we step back to asymptotics again: since  $S_0(x)$  is the leading order or dominant function, we have the relations  $C(x) \ll \pm \int_a^x dt \sqrt{Q(t)}$ , and consequently

$$C'(x) \ll \pm \sqrt{Q(x)}, \quad (3.45)$$

$$C''(x) \ll \pm \frac{Q'(x)}{2\sqrt{Q(x)}}, \quad (3.46)$$

As a result, we may throw away the  $C''$  and  $(C')^2$  terms to obtain:

$$C'(x) \sim -\frac{Q'(x)}{4Q(x)}, \quad (3.47)$$

which yields

$$C(x) \sim -\frac{1}{4} \ln Q(x) = \underbrace{-\frac{1}{4} \ln Q(x)}_{S_1(x)} + S_2(x) + S_3(x) + \dots, \quad (3.48)$$

Thus, the solution to the Schrodinger equation is

$$\psi(x) = e^{S(x)} = e^{S_0(x)+S_1(x)+S_2(x)+\dots} = e^{S_0(x)} e^{S_1(x)} e^{S_2(x)+\dots} \quad (3.49)$$

Substituting the values of  $S_0$  and  $S_1$ , we obtain

$$\psi(x) = e^{S(x)} = e^{\pm \int_a^x du \sqrt{Q(u)}} e^{-\frac{1}{4} \ln Q(x)} e^{S_2(x)+\dots} \quad (3.50)$$

which is rewritten in the form

$$\psi(x) = e^{S(x)} = \frac{1}{(Q)^{\frac{1}{4}}} e^{\pm \int_a^x du \sqrt{Q(u)}} e^{S_2(x)+\dots} \quad (3.51)$$

This process may be repeated again and again. Each step will generate new functional forms  $S_2(x), S_3(x), \dots$ . Green's method extracts out the "non-Frobenius" and "non-Fuchs" terms, and thereafter the series becomes rational powers of  $x$ :  $D(x) = S_2(x) + S_3(x) + \dots = \sum_n a_n (\sqrt{x})^n$ . But this is rarely necessary in our work. For most cases, it turns out that  $D(x) \ll 1$ , and the 'WKB' approximation to use looks like

$$\psi(x) \approx \frac{K}{Q(x)^{\frac{1}{4}}} e^{\pm \int_a^x du \sqrt{Q(u)}}. \quad (3.52)$$

where  $K$  is a constant.

One can *mechanize* the extraction of the successive functions  $S_n(x)$  by the following *perturbative* approach. We recast the Schrodinger equation as a function of a parameter  $\epsilon$  of the form  $\epsilon^2 \psi'' = Q\psi$ , and assume a solution

$$\psi(x) = e^S = e^{\frac{1}{\epsilon} \sum_{n=0}^{\infty} S_n \epsilon^n} = e^{\frac{1}{\epsilon} S_0 + S_1 + S_2 \epsilon + S_3 \epsilon^2 + \dots} \quad (3.53)$$

Substituting this form into the Schrodinger equation  $\epsilon^2 \psi'' = Q\psi$  leads to the set of equations defined by

$$(S'_0 + S'_1 \epsilon + S'_2 \epsilon^2 + S'_3 \epsilon^3)^2 + (S''_0 \epsilon + S''_1 \epsilon^2 + S''_2 \epsilon^3 + \dots) = Q, \quad (3.54)$$

from where we equate like powers of  $\epsilon$  on both sides of the equation to obtain

$$(S'_0)^2 = Q \quad \text{for } \epsilon^0 \quad (3.55)$$

$$2S'_0 S'_1 + S''_0 = 0 \quad \text{for } \epsilon^1 \quad (3.56)$$

$$2S'_0 S'_2 + S''_1 + (S'_1)^2 = 0 \quad \text{for } \epsilon^2 \quad (3.57)$$

$$2S'_0 S'_n + S''_{n-1} + \sum_{j=1}^{n-1} S'_j S'_{n-j} = 0 \quad \text{for } \epsilon^n \quad (3.58)$$

So what is this  $\epsilon$ ? One way to look at it is to 'relate' it to  $\hbar$ , which is a small number. But  $\epsilon$  is a variable in the above formulation, which renders the Schrodinger equation into a polynomial series, enabling the WKB evaluation.