

## Prologue

# Review of Wave Mechanics and Examples

Usually, a first course on quantum theory focuses quite a bit on the study of the Schrödinger equation (primarily time-independent, but occasionally time-dependent) for single-particle wave functions in one, two, or three spatial dimensions. These topics generally fall within the realm of what is often called *wave mechanics*. We include in this preparatory section a brief reprisal of that formalism along with a review of some standard examples that should be familiar from your previous studies. In the remainder of this course we will freely refer back to these standard results. This is not meant to be a comprehensive review of the material from **All Quantum Theory**; you should be prepared to refer back to material from that course when necessary.

**WARNING: THE MATERIAL IN THIS SECTION WILL NOT BE THE SUBJECT OF ANY LECTURES.**

### 0.1 Review of wave mechanics

The primary object of wave mechanics is Schrödinger's *wave function* for a particle moving in, say, one spatial dimension. This is a  $\mathbb{C}$ -valued function, often denoted  $\Psi$ ,

$$\Psi : \mathbb{R}_x \times \mathbb{R}_t \rightarrow \mathbb{C}, \quad (0.1)$$

of a position variable  $x$  on the real line and time  $t$ . The wave function is conventionally normalised to obey (at any time  $t$ )

$$\int_{-\infty}^{\infty} dx |\Psi(x, t)|^2 = 1. \quad (0.2)$$

When so normalised, the wave function encodes, in particular, the probability density  $\rho$  for detecting the presence of the particle in question at a given point and at a given time according to

$$\rho(x, t) = |\Psi(x, t)|^2. \quad (0.3)$$

The normalisation condition ensures that the total probability for finding the particle *somewhere* at any given time is one. Alternatively, one can work with wave functions that don't necessarily obey (0.2), in which case we have

$$\rho(x, t) = \frac{|\Psi(x, t)|^2}{\int_{-\infty}^{\infty} ds |\Psi(s, t)|^2}. \quad (0.4)$$

If a particle moves subject to an external potential energy function  $V(x)$ , then the *time-dependent Schrödinger equation*—a partial differential equation that encodes time evolution of the wave function—takes the form

$$i\hbar \frac{\partial \Psi}{\partial t}(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2}(x, t) + V(x)\Psi(x, t). \quad (0.5)$$

Here  $\hbar$  is the reduced Planck constant, which is a fundamental unit of angular momentum (*i.e.*, it has units of  $[mass] \times [length]^2 \times [time]^{-1}$ ).<sup>1</sup> It is a simple exercise to confirm that if  $\Psi(x, t)$  evolves in time according to (0.5) then the normalisation condition (0.2) will hold for all time  $t$  if it holds at any given time  $t_0$ .

The differential operator (with respect to  $x$ ) that acts on the wave function on the right hand side of this equation is the *Hamiltonian operator* for the theory. If we introduce operators  $P$  and  $X$  that act on wave functions according to

$$(P\Psi)(x, t) = -i\hbar \frac{\partial \Psi}{\partial x}(x, t), \quad (X\Psi)(x, t) = x\Psi(x, t), \quad (0.6)$$

<sup>1</sup>In SI units, the reduced Planck constant is  $\hbar \approx 1.0546 \times 10^{-34} \text{ kg} \cdot \text{m}^2/\text{s}^2$ . In a quantum mechanical world, it is often a better idea to make a choice of units for which  $\hbar = 1$  (so-called natural units). At some point in this course, it will make sense to think of  $\hbar$  more like a formally small parameter.

then the Hamiltonian operator appears analogous to the total classical energy (alternatively, the Hamiltonian of the corresponding classical system if you have taken **B7.1 Classical Mechanics**) with momentum and position replaced by their operator counterparts,

$$H = \frac{P^2}{2m} + V(X) . \quad (0.7)$$

The time-dependent Schrödinger equation then takes the abstract form

$$i\hbar \frac{\partial \Psi}{\partial t}(x, t) = (H\Psi)(x, t) . \quad (0.8)$$

In sufficiently well-behaved cases,<sup>2</sup> we can look for separable solutions to this equation of the form

$$\Psi(x, t) = \psi_n(x) \exp\left(-\frac{iE_n t}{\hbar}\right) , \quad (0.9)$$

in which case the (real) numbers  $E_n$  are identified with the *energies* of these solutions, and the functions  $\psi_n(x)$  are *stationary state wave functions* (depending only on position) that obey the *time-independent Schrödinger equation*,

$$(H\psi_n)(x) = -\frac{\hbar^2}{2m} \psi_n''(x) + V(x)\psi_n(x) = E_n \psi_n(x) . \quad (0.10)$$

The time-dependence for a stationary state is determined by its energy through the time-dependent phase in (0.9). If the stationary state wave functions  $\{\psi_n\}$  form a basis for the space of possible wave functions at a fixed time, we can (in principle) understand time-evolution in complete generality,

$$\Psi(x, 0) = \sum_n a_n \psi_n(x) \implies \Psi(x, t) = \sum_n a_n \exp\left(-\frac{iE_n t}{\hbar}\right) \psi_n(x) . \quad (0.11)$$

This follows from the linearity of the time-dependent Schrödinger equation and is one of the fundamental and unusual features of the quantum picture of reality.

## 0.2 Standard examples

A significant portion of any introductory course on quantum mechanics involves learning the details of assorted standard examples where the stationary-state wave functions  $\psi_n(x)$  can be understood completely. In this subsection, we review the most important of these for ease of reference in the future and to fix certain notational conventions.

**Example 0.2.1** (Particle in a box). When a particle is restricted to move in a fixed interval, say  $x \in [0, a]$  for some positive real number  $a$ , the system is referred to as the particle in a (one-dimensional) box. As part of the definition of the system, one specifies that the wave function vanishes at the endpoints of the interval. This is sometimes phrased as a particle moving on the real line with a potential that is zero in the given interval and (positive) infinite outside of it.

The stationary state wave functions for the particle in the box satisfy the simple ordinary differential equation,

$$-\frac{\hbar^2}{2m} \psi_n''(x) = E_n \psi_n(x) , \quad \psi_n(0) = \psi_n(a) = 0 . \quad (0.12)$$

This can be solved by inspection. The wave functions must be sin functions, and the boundary condition at  $a$  further constrains the possible energies  $E_n$ , giving the following set of solutions,

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) , \quad E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} , \quad n = 1, 2, 3, \dots . \quad (0.13)$$

The numerical prefactor is chosen so the wave functions will satisfy the standard normalisation condition, and more

<sup>2</sup>At this point we won't dwell on the conditions under which this is a sound strategy.

generally we have the relation

$$\int_0^a dx \overline{\psi_n(x)} \psi_m(x) = \delta_{n,m}. \quad (0.14)$$

These functions form an orthonormal basis for the space of wave function on the interval in the sense of Fourier series. Time-evolution of any given wave function (taken as the wave function at time  $t = 0$ ) can then be determined by decomposing it into its Fourier representation and introducing time-dependent phases depending on the energies in (0.13).

**Example 0.2.2 (Harmonic Oscillator).** Our next example is the *simple harmonic oscillator*, for which a particle is allowed to range over the entire real line but with quadratic potential function  $V(x) = \frac{1}{2}m\omega^2x^2$  (here by convention we take  $\omega \in \mathbb{R}_+$ ). This potential is parameterised so the *classical* angular frequency of oscillation for the system would be  $\omega$ .

Analysis of this system is simplified by introducing the first-order differential “ladder” operators,<sup>3</sup>

$$\alpha_{\pm} = \frac{1}{\sqrt{2m\hbar\omega}}(P \pm im\omega X), \quad (0.15)$$

which obey a number of important relations,

$$[\alpha_-, \alpha_+] = 1, \quad (0.16)$$

$$[H, \alpha_{\pm}] = \hbar\omega\alpha_{\pm}, \quad (0.17)$$

$$H = \hbar\omega(\alpha_{\pm}\alpha_{\mp} \pm \frac{1}{2}). \quad (0.18)$$

Here we’ve adopted standard notation for the *commutator* of two differential operators  $A$  and  $B$ :  $[A, B] := AB - BA$ . Equation (0.17) implies that if  $H\psi = E\psi$ , then  $H\alpha_{\pm}\psi = (E \pm \hbar\omega)\alpha_{\pm}\psi$ , so the  $\alpha_{\pm}$  operators move amongst stationary states in the space of wave functions, shifting energy by a definite amount.

Consequently, the ground state wave function (the stationary state wave function of least energy) must obey  $\alpha_-\psi_0 = 0$ , and this can be immediately solved to give the expression

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \exp\left(-\frac{m\omega x^2}{2\hbar}\right), \quad (0.19)$$

which has energy  $E_0 = \hbar\omega/2$  by virtue of (0.18) or direct calculation. The higher energy states are obtained by the iterated action of  $\alpha_+$ ,

$$\psi_n = \frac{(-i\alpha_+)^n}{\sqrt{n!}}\psi_0, \quad (0.20)$$

where the prefactor is such that the results are normalised and real. With a little bit of work, one finds that these stationary state wave functions can be expressed explicitly as follows,

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \exp\left(-\frac{m\omega x^2}{2\hbar}\right) H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right), \quad (0.21)$$

where  $H_n(x)$  is the  $n$ ’th *Hermite polynomial*.<sup>4</sup> These form a basis for the space of normalisable wave functions on the real line, so the possible energies (the energy *spectrum*) of the quantum harmonic oscillator is as follows,

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right). \quad (0.23)$$

**Example 0.2.3 (Hydrogenic atom).** A famous example, which is also of key historical and physical importance, is

<sup>3</sup>Beware, the conventions for the ladder operators here differ from some appearing in standard text books by factors of  $\pm i$ .

<sup>4</sup>The Hermite polynomials are defined as

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} (e^{-x^2}). \quad (0.22)$$

the *Hydrogen atom* (or the Hydrogen-like, or Hydrogenic, atom if you allow general nuclear charge  $Z > 0$ ) in three dimensions. This is the problem of a single electrically charged particle (the electron) moving in three dimensions subject to a *Coulomb potential*,<sup>5</sup>

$$V(\mathbf{r}) = -\frac{Zq_e}{|\mathbf{r}|}. \quad (0.24)$$

A detailed analysis of the time-independent Schrödinger equation for this problem appeared in **All Quantum Theory**, and we give a lightning review of the solution here. We will return to it several times throughout this course.

The normalisable stationary states for this system are labelled by three *quantum numbers*,  $(n, \ell, m)$ , known as the principal, orbital, and magnetic quantum numbers, respectively. These are restricted according to  $n = 1, 2, 3, \dots$ ,  $\ell = 0, 1, \dots, n-1$ , and  $m = -\ell, -\ell+1, \dots, \ell-1, \ell$ . The stationary state wave functions take the form,<sup>6</sup>

$$\psi_{n\ell m}(r, \theta, \varphi) = R_{n,\ell}(r)Y_{\ell}^m(\theta, \varphi) = \sqrt{\frac{2\ell+1}{4\pi} \frac{(\ell-m)!}{(\ell+m)!}} R_{n,\ell}(r)P_{\ell}^m(\cos\theta)e^{im\varphi}. \quad (0.26)$$

The  $Y_{\ell}^m(\theta, \varphi)$  are spherical harmonic functions, which obey

$$L^2 Y_{\ell}^m(\theta, \varphi) = \hbar^2 \ell(\ell+1) Y_{\ell}^m(\theta, \varphi), \quad L_3 Y_{\ell}^m(\theta, \varphi) = \hbar m Y_{\ell}^m(\theta, \varphi), \quad (0.27)$$

with respect to the *orbital angular momentum operators*,

$$\mathbf{L} = -i\hbar(\mathbf{x} \wedge \nabla), \quad L_3 = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = -i\hbar\partial_{\varphi}. \quad (0.28)$$

The  $P_{\ell}^m(\cos\theta)$  are the *associated Legendre polynomials*.<sup>7</sup> The radial wave function takes the form

$$R_{n,\ell}(r) = \exp\left(-\frac{Zr}{na_0}\right) f_{n,\ell}(r), \quad (0.31)$$

where  $f_{n,\ell}(r)$  is a polynomial of degree  $n-1$  and  $a_0 = \hbar^2/(mq_e^2)$  is the *Bohr radius*. The energy,  $E_n$ , depends only on the principal quantum number and is given by

$$E_n = -\frac{mq_e^4 Z^2}{2\hbar^2 n^2} = -\frac{q_e^2 Z^2}{2a_0 n^2} = -\frac{\alpha^2 mc^2 Z^2}{2n^2}, \quad (0.32)$$

where in the last expression,  $\alpha = q_e^2/\hbar c \approx 1/137$  is the *fine structure constant*. Note that these stationary state energies are always negative, so the exponential in (0.31) is decaying with  $r$  and the wave functions are indeed normalisable.

In contrast to the previous two examples, the stationary state wave functions for the Hydrogen atom *do not* form a basis for all possible normalisable wave functions for the electron in a Coulomb potential. Rather, they form a basis only for the *bound state wave functions*.<sup>8</sup> The possibility of additional wave functions for the Hydrogen atom that are not bound states is relevant in the context of scattering theory.

<sup>5</sup>We adopt Gaussian units to avoid factors of  $4\pi\epsilon_0$ . Here  $q_e$  is the charge of the electron, often written as  $e$ .

<sup>6</sup>The normalisation in the last term in (0.26) is so that

$$\int_{\mathbb{S}^2} Y_{\ell}^m(\theta, \varphi) Y_{\ell'}^{m'}(\theta, \varphi) d\theta d\varphi = \delta_{\ell,\ell'} \delta_{m,m'}. \quad (0.25)$$

<sup>7</sup>We recall that the (misnamed) associated Legendre polynomials, which in general are not polynomials, are given for non-negative  $m$  by

$$P_{\ell}^m(x) = \frac{(-1)^m}{2^{\ell}\ell!} (1-x^2)^{\frac{m}{2}} \frac{d^{\ell+m}}{dx^{\ell+m}} (x^2-1)^{\ell}, \quad (0.29)$$

while for negative  $m$  they are determined by the relation

$$P_{\ell}^{-m}(x) = (-1)^m \frac{(\ell-m)!}{(\ell+m)!} P_{\ell}^m(x). \quad (0.30)$$

Evaluating these for  $x = \cos\theta$ , we get that the  $P_{\ell}^m(\cos\theta)$  are indeed polynomials (of degree  $\ell$ ) in  $\cos\theta$  and  $\sin\theta$ .

<sup>8</sup>We do not give a technical definition of bound state here, but physically it corresponds to states where the electron stays localised in the neighborhood of the nucleus instead of running off to infinity, analogous to the classical distinction between bound (elliptical) orbits versus parabolic or hyperbolic orbits in the Kepler problem.