1.2: Wave Mechanics Postulates

Let us consider a spinless, [22] non-relativistic point-like particle, whose classical dynamics may be described by a certain Hamiltonian function $H(\mathbf{r}, \mathbf{p}, t)$, [23] where $\mathbf{r}$ is the particle's radius-vector and $\mathbf{p}$ is its momentum. (This condition is important because it excludes from our current discussion the systems whose interaction with their environment results in irreversible effects, in particular the friction leading to particle energy's decay. Such "open" systems need a more general description, which will be discussed in Chapter 7.) Wave mechanics of such Hamiltonian particles may be based on the following set of postulates that are comfortingly elegant - though their final justification is given only by the agreement of all their corollaries with experiment. [24]

(i) Wavefunction and probability. Such variables as $\mathbf{r}$ or $\mathbf{p}$ cannot be always measured exactly, even at "perfect conditions" when all external uncertainties, including measurement instrument imperfection, varieties of the initial state preparation, and unintended particle interactions with its environment, have been removed. [25] Moreover, $\mathbf{r}$ and $\mathbf{p}$ of the same particle can never be measured exactly simultaneously. Instead, the most detailed description of the particle's state allowed by Nature, is given by a certain complex function $\Psi(\mathbf{r}, t)$, called the wavefunction (or "wave function"), which generally enables only probabilistic predictions of the measured values of $\mathbf{r}, \mathbf{p}$, and other directly measurable variables - in quantum mechanics, usually called observables.

Specifically, the probability dW of finding a particle inside an elementary volume $dV \equiv d^3r$ is proportional to this volume, and hence may be characterized by a volume-independent probability density $w \equiv dW/d^3r$, which in turn is related to the wavefunction as

$$w = |\Psi(\mathbf{r}, t)|^2 \equiv \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t), \tag{1.2.1}$$

Where the sign * denotes the usulal complex conjugation. As a result, the total probability of finding the ribability where the sign * denotes the usual complex conjugation. As a result, the total probability of finding the via
particle somewhere inside a volume V may be calculated as
wavefunction

$$W = \int_V w d^3r = \int_V \Psi^*\Psi d^3r. \tag{1.2.2}$$

In particular, if volume V contains the particle definitely (i.e. with the 100% probability, $W = 1$), Eq. (22 b) is reduced to the so-called wavefunction normalization condition

$$\int_V \Psi^*\Psi d^3r = 1 \tag{1.2.3}$$

(ii) Observables and operators. With each observable A, quantum mechanics associates a certain linear operator $\hat{A}$, such that (in the perfect conditions mentioned above) the average measured value of A (usually called the expectation value) is expressed as [26]

$$\langle A\rangle = \int_V \Psi^*\hat{A}\Psi d^3r, \tag{1.2.4}$$

where $\langle\ldots\rangle$ means the statistical average, i.e. the result of averaging the measurement results over a large ensemble (set) of macroscopically similar experiments, and Ψ is the normalized wavefunction that obeys Eq. (22c). Note immediately that for Eqs. (22) and (23) to be compatible, the identity (or "unit") operator defined by the relation

$$\hat{I}\Psi = \Psi, \tag{1.2.5}$$

has to be associated with a particular type of measurement, namely with the particle's detection.

(iii) The Hamiltonian operator and the Schrödinger equation. Another particular operator, Hamiltonian $\hat{H}$, whose observable is the particle's energy E, also plays in wave mechanics a very special role, because it participates in the Schrödinger equation,

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi, \tag{1.2.6}$$

that determines the wavefunction's dynamics, i.e. its time evolution.

(iv) The radius-vector and momentum operators. In wave mechanics (in the "coordinate representation"), the vector operator of particle's radius-vector $\mathbf{r}$ just multiples the wavefunction by this vector, while the operator of the particle's momentum is proportional to the spatial derivative:

$$\hat{\mathbf{r}}=\mathbf{r}, \quad \hat{\mathbf{p}}=-i \hbar \nabla, \tag{1.2.7}$$

$$\hat{\mathbf{r}}=\mathbf{r}=\{x, y, z\}, \quad \hat{\mathbf{p}}=-i \hbar\left\{\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right\} \tag{1.2.8}$$

(v) The correspondence principle. In the limit when quantum effects are insignificant, e.g., when the characteristic scale of action [28] (i.e. the product of the relevant energy and time scales of the problem) is much larger than Planck's constant $\hbar$, all wave mechanics results have to tend to those given by classical mechanics. Mathematically, this correspondence is achieved by duplicating the classical relations between various observables by similar relations between the corresponding operators. For example, for a free particle, the Hamiltonian (which in this particular case corresponds to the kinetic energy $T=p^2/2m$ alone) has the form

$$\hat{H}=\hat{T}=\frac{\hat{p}^2}{2 m}=-\frac{\hbar^2}{2 m} \nabla^2 \tag{1.2.9}$$

Now, even before a deeper discussion of the postulates' physics (offered in the next section), we may immediately see that they indeed provide a formal way toward resolution of the apparent contradiction between the wave and corpuscular properties of particles. Indeed, for a free particle, the Schrödinger equation (25), with the substitution of Eq. (27), takes the formwhose particular, but the most important solution is a plane, single-frequency ("monochromatic") traveling wave, [29]

$$\Psi(\mathbf{r}, t)=a e^{i(\mathbf{k} \cdot \mathbf{r}-\omega t)} \tag{1.2.10}$$

where a, $\mathbf{k}$ and ω are constants. Indeed, plugging Eq. (29) into Eq. (28), we immediately see that such plane wave, with an arbitrary complex amplitude a, is indeed a solution of this Schrödinger equation, provided a specific dispersion relation between the wave number $k \equiv|\mathbf{k}|$ and the frequency ω :

$$\hbar \omega=\frac{(\hbar k)^2}{2 m}. \tag{1.2.11}$$

The constant a may be calculated, for example, assuming that the wave (29) is extended over a certain volume V, while beyond it, $\Psi=0$. Then from the normalization condition $(22\mathrm{c})$ and Eq. (29), we get [30]

$$|a|^2 V=1. \tag{1.2.12}$$

Let us use Eqs. (23), (26), and (27) to calculate the expectation values of the particle's momentum $\mathbf{p}$ and energy $E=H$ in the state (29). The result is

$$\langle\mathbf{p}\rangle=\hbar \mathbf{k}, \quad\langle E\rangle=\langle H\rangle=\frac{(\hbar k)^2}{2 m} \tag{1.2.13}$$

according to Eq. (30), the last equality may be rewritten as $\langle E\rangle=\hbar \omega$.

Next, Eq. (23) enables calculation of not only the average (in the math speak, the first moment) of an observable but also its higher moments, notably the second moment - in physics, usually called variance:

$$\left\langle\widetilde{A}^2\right\rangle \equiv\left\langle(A-\langle A\rangle)^2\right\rangle=\left\langle A^2\right\rangle-\langle A\rangle^2, \tag{1.2.14}$$

and hence its uncertainty, alternatively called the "root-mean-square (r.m.s.) fluctuation",

$$\delta A \equiv\left\langle\widetilde{A}^2\right\rangle^{1/2}. \tag{1.2.15}$$

The uncertainty is a scale of deviations $\widetilde{A} \equiv A-\langle A\rangle$ of measurement results from their average. In the particular case when the uncertainty δA equals zero, every measurement of the observable A will give the same value $\langle A\rangle$; such a state is said to have a definite value of the variable. For example, in application to the state with wavefunction (29), these relations yield $\delta E=0, \delta \mathbf{p}=0$. This means that in this plane-wave, monochromatic state, the energy and momentum of the particle have definite values, so that the statistical average signs in Eqs. (32) might be removed. Thus, these relations are reduced to the experimentally-inferred Eqs. (5) and (15).

Hence the wave mechanics postulates indeed may describe the observed wave properties of nonrelativistic particles. (For photons, we would need its relativistic generalization - see Chapter 9 below.) On the other hand, due to the linearity of the Schrödinger equation (25), any sum of its solutions is also a solution - the so-called linear superposition principle. For a free particle, this means that any set of plane waves (29) is also a solution to this equation. Such sets, with close values of $\mathbf{k}$ and hence $\mathbf{p}=\hbar\mathbf{k}$ (and, according to Eq. (30), of ω as well), may be used to describe spatially localized "pulses", called wave packets - see Fig. 6. In Sec. 2.1, I will prove (or rather reproduce H. Weyl's proof :-) that the wave packet's extension δx in any direction (say, x) is related to the width δk_x of the distribution of the corresponding component of its wave vector as $\delta x \delta k_x \geq 1/2$, and hence, according to Eq. (15), to the width δp_x of the momentum component distribution as

$$\text{Heisenberg's uncertainty relation} \qquad \delta x \cdot \delta p_x \geq \frac{\hbar}{2}. \tag{1.2.16}$$

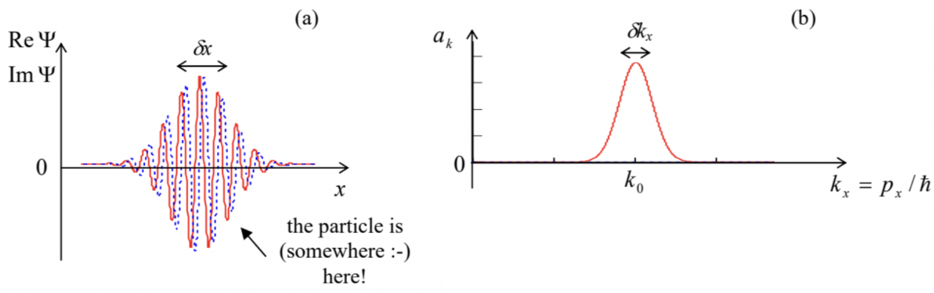

Fig. 1.6. (a) A snapshot of a typical wave packet propagating along axis x, and (b) the corresponding distribution of the wave numbers k_x, i.e. the momenta p_x.

This is the famous Heisenberg's uncertainty principle, which quantifies the first postulate's point that the coordinate and the momentum cannot be defined exactly simultaneously. However, since the Planck's constant, $\hbar \sim 10^{-34}\ \mathrm{J\cdot s}$, is extremely small on the human scale of things, it still allows for particle localization in a very small volume even if the momentum spread in a wave packet is also small on that scale. For example, according to Eq. (35), a 0.1% spread of momentum of a $1\mathrm{keV}$ electron $(p \sim 1.7\times 10^{-24}\ \mathrm{kg\cdot m/s}$) allows its wave packet to be as small as $\sim 3\times 10^{-10}\ \mathrm{m}$. (For a heavier particle such as a proton, the packet would be even tighter.) As a result, wave packets may be used to describe the particles that are quite point-like from the macroscopic point of view.

In a nutshell, this is the main idea of wave mechanics, and the first part of this course (Chapters 1-3) will be essentially a discussion of various effects described by this approach. During this discussion, however, we will not only witness wave mechanics' many triumphs within its applicability domain but also gradually accumulate evidence for its handicaps, which will force an eventual transfer to a more general formalism - to be discussed in Chapter 4 and beyond.

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[20] See, e.g., EM Sec. 8.4

[21] The orbital motion is the historic (and rather misleading) term used for any motion of the particle as a whole.

[22] Actually, in wave mechanics, the spin of the described particle has not to be equal to zero. Rather, it is assumed that the particle spin's effects on its orbital motion are negligible.

[23] As a reminder, for many systems (including those whose kinetic energy is a quadratic-homogeneous function of generalized velocities, like $mv^2/2$) , H coincides with the total energy $E-$ see, e.g., CM Sec. 2.3. In what follows, I will assume that $H=E$.

[24] Quantum mechanics, like any theory, may be built on different sets of postulates/axioms leading to the same final conclusions. In this text, I will not try to beat down the number of postulates to the absolute possible minimum, not only because that would require longer argumentation, but chiefly because such attempts typically result in making certain implicit assumptions hidden from the reader - the practice as common as regrettable. [25] I will imply such perfect conditions in the further narrative, until the discussion of the system's interaction with its environment in Chapter 7.

[26] This key measurement postulate is sometimes called the Born rule, though sometimes this term is used for the (less general) Eqs. (22).

[27] If you need, see, e.g., Secs. 8-10 of the Selected Mathematical Formulas appendix - below, referred to as MA. Note that according to those formulas, the del operator follows all the rules of the usual (geometric) vectors. This is, by definition, true for other quantum-mechanical vector operators to be discussed below.

[28] See, e.g., CM Sec. 10.3.

[29] See, e.g., CM Sec. 6.4 and/or EM Sec. 7.1.

[30] For infinite space $(V \to \infty)$, Eq. (31) yields $a \to 0$, i.e. wavefunction (29) vanishes. This formal problem may be readily resolved considering sufficiently long wave packets - see Sec. 2.2 below.