

## I.3. Quantum Mechanics

### I.3.1. Bragg Reflections and Interference

Consider a free particle in a  $D$ -D Euclidean space. In terms of Cartesian coordinates, its position & momentum are

$$\mathbf{x} = (x^1, \dots, x^D) \quad (1.74)$$

$$\mathbf{p} = (p^1, \dots, p^D) \quad (1.73)$$

The diffraction of electrons by a crystal can be explained by setting the wave function of a free electron to be a plane wave

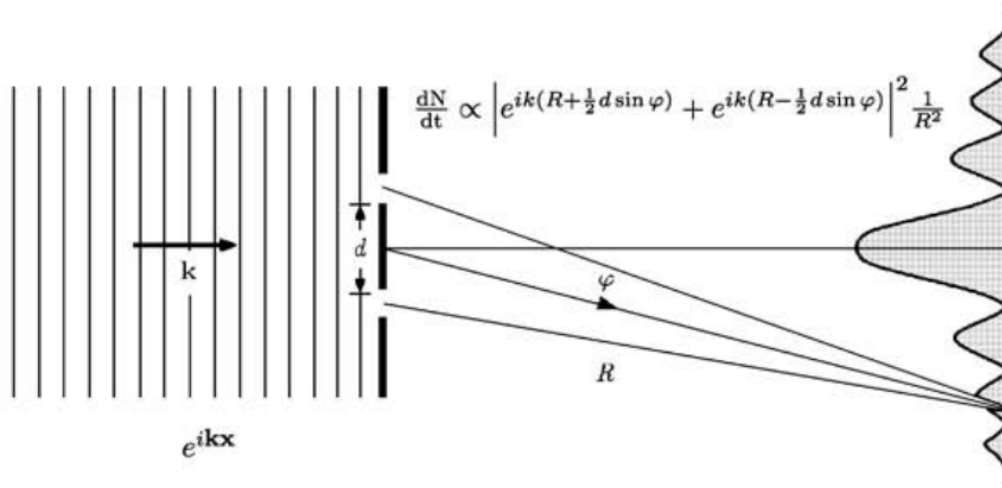
$$\Psi_{\mathbf{p}}(\mathbf{x}, t) = e^{i\mathbf{k}\cdot\mathbf{x} - i\omega t} \quad (1.75)$$

where  $\mathbf{k}$  is the **wave vector** parallel to  $\mathbf{p}$  and  $\omega$  is the angular **frequency**.

Each scattering center at  $\mathbf{x}'$  in the path of the plane wave becomes a source of a spherical wave with spatial part  $\frac{e^{ikR}}{R}$ , where  $R = |\mathbf{x} - \mathbf{x}'|$  and  $k = |\mathbf{k}| = \frac{2\pi}{\lambda}$ , with  $\lambda$  being the wave length. The field strength  $\Psi(\mathbf{x}, t)$  at the detector is the sum of all these scattered waves. The number of electrons arriving at the detector is proportional to  $|\Psi(\mathbf{x}, t)|^2$ .

For the idealized two-slit experiment shown in the figure below, the number  $N$  of particles arriving at the detector per unit time is therefore

$$\frac{dN}{dt} \propto \frac{1}{R^2} \left| e^{ik(R + \frac{1}{2}d \sin \varphi)} + e^{ik(R - \frac{1}{2}d \sin \varphi)} \right|^2 \quad (1.76)$$



Note that if  $\Psi$  is normalized so that

$$\int d^3x |\Psi|^2 = 1$$

then  $|\Psi|^2$  is the probability density and  $d^3x |\Psi|^2$  is the probability of finding the particle in volume  $d^3x$ .

### I.3.2. Matter Waves

From the diffraction experiments, one deduced that a free particle behaved like a plane wave (called **matter wave**) with,

$$\mathbf{p} = \hbar \mathbf{k} \tag{1.77}$$

where  $\hbar$  is the **reduced Planck constant** with value

$$\hbar = \frac{h}{2\pi} = 1.0545919(80) \times 10^{-27} \text{ erg} \cdot \text{s} \tag{1.78}$$

From the photoelectric effect measurements, one deduced that electromagnetic waves behaved like particles (called **photons**) with the energy  $E$  related to the frequency by

$$\begin{aligned} E &= \hbar \omega \\ &= \hbar |\mathbf{k}| c \end{aligned} \tag{1.79}$$

where  $c = 299\,792.458 \text{ km/s}$  is the speed of light in vacuum.

For a relativistic particle travelling at the speed of light,  $E = |\mathbf{p}| c$  so that (1.79) agrees with (1.77) and the wave-particle duality is universal. Thus, all free particles of momentum  $\mathbf{p}$  are described by

a plane wave of wavelength  $\lambda = \frac{2\pi}{|\mathbf{k}|} = \frac{2\pi\hbar}{|\mathbf{p}|}$ , with the explicit form

$$\Psi_{\mathbf{p}}(\mathbf{x}, t) = \mathcal{N} e^{i(\mathbf{p} \cdot \mathbf{x} - E_{\mathbf{p}} t) / \hbar} \tag{1.80}$$

where  $\mathcal{N}$  is a **normalization constant**. In a finite volume, the wave function is normalized to unity. In an infinite volume, the same normalization makes the wave function vanish. To avoid this, we switch the normalization condition on the **current density** of the particle probability

$$\mathbf{j}(\mathbf{x}, t) = \frac{\hbar}{2mi} \psi^* \overleftrightarrow{\nabla} \psi \tag{1.81}$$

where the operator  $\overleftrightarrow{\nabla}$  is defined as

$$\begin{aligned} a \overleftrightarrow{\nabla} b &\equiv a \vec{\nabla} b - a \overleftarrow{\nabla} b \\ &= a \nabla b - (\nabla a) b \end{aligned} \tag{1.82}$$

For particles that are not free, the corresponding matter waves (usually called **wave functions**) can be written as

$$\Psi(\mathbf{x}, t) = \int \frac{d^3 p}{(2\pi\hbar)^3} f(\mathbf{p}) e^{i(\mathbf{p} \cdot \mathbf{x} - E_{\mathbf{p}} t) / \hbar} \tag{1.83}$$

By the Fourier inversion theorem,

$$f(\mathbf{p}) = \int d^3 x e^{-i\mathbf{p} \cdot \mathbf{x} / \hbar} \Psi(\mathbf{x}, 0) \tag{1.84}$$

which leads to the relation

$$\Delta x \Delta p \sim \hbar \tag{1.85}$$

where  $\Delta x$  is the linear extend of  $\Psi(\mathbf{x}, 0)$  and  $\Delta p$  is that of  $f(\mathbf{p})$ . (1.85) is an example of the **Heisenberg's principle of uncertainty**.

A localized wave with a well-defined average-peak at momentum  $\bar{\mathbf{p}}$  is called a **wave packet**. It is easily shown that the peak moves with the **group velocity**

$$\bar{\mathbf{v}} = \left. \frac{\partial E_{\mathbf{p}}}{\partial \mathbf{p}} \right|_{\bar{\mathbf{p}}} \tag{1.86}$$

which coincides with the classical velocity.

### 1.3.3. Schrodinger Equation

The next task is to construct a differential equation for the wave function  $\Psi(\mathbf{x}, t)$ . Beginning with the case of a free particle, we already know the solution to the equation is  $\Psi_{\mathbf{p}}(\mathbf{x}, t)$  given by (1.80).

For a nonrelativistic free particle of mass  $M$  and energy  $E_p$ , the classical Hamiltonian is given by

$$H(\mathbf{p}) = E_p = \frac{\mathbf{p}^2}{2M} \quad (1.87)$$

Turning this into a differential equation on  $\Psi_p$ , we have

$$[\hat{H}(\mathbf{p}) - \hat{E}] \Psi_p(\mathbf{x}, t) = 0 \quad (1.88a)$$

where  $\hat{H}(\mathbf{p})$  and  $\hat{E}$  are now differential operators such that, when operating on  $\Psi_p$ , can be replaced by the numerical values given by (1.87). This is easily done by setting

$$\hat{H}(\mathbf{p}) = H(\hat{\mathbf{p}}) = \frac{\hat{\mathbf{p}}^2}{2M} \quad \hat{\mathbf{p}} = \frac{\hbar}{i} \nabla \hat{E} = i\hbar \frac{\partial}{\partial t} \quad (1.89)$$

Operating  $\hat{H}(\mathbf{p}) - \hat{E}$  on both sides of (1.83) gives

$$\begin{aligned} [\hat{H}(\mathbf{p}) - \hat{E}] \Psi(\mathbf{x}, t) &= \int \frac{d^3 p}{(2\pi\hbar)^3} f(\mathbf{p}) [\hat{H}(\mathbf{p}) - \hat{E}] e^{i(\mathbf{p}\cdot\mathbf{x} - E_p t)/\hbar} \\ &= \int \frac{d^3 p}{(2\pi\hbar)^3} f(\mathbf{p}) [H(\mathbf{p}) - E_p] e^{i(\mathbf{p}\cdot\mathbf{x} - E_p t)/\hbar} \\ &= 0 \end{aligned} \quad (1.88b)$$

which is a generalization of (1.88a) to arbitrary wave functions of a free particle.

Assuming (1.88b) is valid for any Hamiltonian, we obtain the **Schrodinger eq.**

$$\left( \hat{H} - i\hbar \frac{\partial}{\partial t} \right) \Psi(\mathbf{x}, t) = 0 \quad (1.91)$$

where

$$\hat{H} = H(\mathbf{x}, \hat{\mathbf{p}}, t) = H\left(\mathbf{x}, \frac{\hbar}{i} \nabla, t\right) \quad (1.92)$$

is the classical Hamiltonian with the momentum  $\mathbf{p}$  replaced by the operator  $\frac{\hbar}{i} \nabla$ . This substitution

rule is an example of the **corresponding principle**.

By direct calculations using (1.89), one can easily verify that

$$[x_i, \hat{p}_j] = i\hbar \delta_{ij} \quad [t, \hat{E}] = -i\hbar \quad (1.93)$$

where the subscripts  $i$  &  $j$  refer to Cartesian components.

Generalization of (1.89, 1.92 & 1.93) to general coordinates is non-trivial.

For a time-independent Hamiltonian  $H(\mathbf{x}, \mathbf{p})$ , (1.91) is separable so that for a given energy  $E_n$ , its solution takes the form

$$\Psi_{E_n}(\mathbf{x}, t) = e^{-iE_n t/\hbar} \Psi_{E_n}(\mathbf{x}) \quad (1.93a)$$

where the **stationary state**  $\Psi_{E_n}(\mathbf{x})$  satisfies the **time-independent Schrodinger eq.**

$$[H(\mathbf{x}, \hat{\mathbf{p}}) - E_n] \Psi_{E_n}(\mathbf{x}) = 0 \quad (1.94)$$

For an hydrogen atom, the Hamiltonian of the reduced particle is

$$H(\mathbf{x}, \mathbf{p}) = \frac{\mathbf{p}^2}{2M} - \frac{e^2}{r} \quad (1.95)$$

Let

$$\int d^3 x \left| \Psi(\mathbf{x}, t) \right|^2 = C \quad (1.96)$$

If  $C = 1$ , then  $|\Psi(\mathbf{x}, t)|^2$  is the probability density of the particle at time  $t$ . For a stable particle, the normalization (1.96) should be independent of time.

Taking the time derivative of (1.96), we have

$$\begin{aligned}\frac{dC}{dt} &= \int d^3x \left( \frac{\partial \Psi^*}{\partial t} \Psi + \Psi^* \frac{\partial \Psi}{\partial t} \right) \\ &= \frac{1}{i\hbar} \int d^3x \left[ -(\hat{H}\Psi)^* \Psi + \Psi^* \hat{H}\Psi \right]\end{aligned}\quad (1.100)$$

The condition for a particle to be stable is therefore

$$\int d^3x (\hat{H}\Psi)^* \Psi = \int d^3x \Psi^* \hat{H}\Psi \quad (1.97a)$$

The **adjoint** (or **Hermitian conjugate**)  $A^\dagger$  of the operator  $A$  is defined as

$$\int d^3x \Psi_2^* A^\dagger \Psi_1 = \int d^3x (A \Psi_2)^* \Psi_1 \quad (1.98)$$

(1.97a) is therefore satisfied if  $\hat{H}$  is **self-adjoint** (or **hermitian**):

$$\hat{H}^\dagger = \hat{H} \quad (1.99)$$

Since  $\hat{p}$  &  $x$  are hermitian, the non-relativistic hamiltonian

$$H(\mathbf{x}, \mathbf{p}, t) = H(\mathbf{p}) + V(\mathbf{x}, t) \quad (1.101)$$

is hermitian if  $V$  is real.

If the classical hamiltonian contains mixed terms such as  $x_i p_i = p_i x_i$ , the quantum version cannot be written down off-hand since  $x_i \hat{p}_i \neq \hat{p}_i x_i$ . This is called the **problem of operator ordering**. Fortunately, if the ordering problem originates from geometry, there is a surprisingly simple solution [see Chap 10].

Until then, we shall assume  $H$  contains no mixed terms.

### 1.3.4. Particle Current Conservation

Consider the probability density

$$\rho(\mathbf{x}, t) = \psi^*(\mathbf{x}, t) \psi(\mathbf{x}, t) \quad (1.103)$$

For a hermitian  $H$ , the Schrodinger eq. (1.91) gives [ c.f. (1.100) ],

$$\begin{aligned}\frac{\partial \rho}{\partial t} &= \frac{\partial \psi^*}{\partial t} \psi + \psi^* \frac{\partial \psi}{\partial t} \\ &= \frac{\hbar}{2mi} \left[ (\nabla^2 \psi^*) \psi - \psi^* \nabla^2 \psi \right] \\ &= \frac{\hbar}{2mi} \nabla \cdot \left[ (\nabla \psi^*) \psi - \psi^* \nabla \psi \right]\end{aligned}\quad (1.104a)$$

Defining the **probability current density** as [ see (1.81) ]

$$\mathbf{j} = \frac{\hbar}{2mi} \left[ \psi^* \nabla \psi - (\nabla \psi^*) \psi \right] \quad (1.102)$$

we can write (1.104a) as

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0 \quad (1.104)$$

which takes the form of the continuity eq. for fluids with no sink or source, i.e.,

$$\frac{d}{dt} \int_V d^3x \rho = 0 \quad (1.104a)$$

where  $V$  is any volume. We have thus proved that a hermitian  $H$  preserves the normalization of its wave functions.

Integrating (1.104) over a volume  $V$  and then applying the Green's theorem gives

$$\begin{aligned} \int_V d^3x \frac{\partial \rho}{\partial t} &= - \int_V d^3x \nabla \cdot \mathbf{j} \\ &= - \int_S d\mathbf{S} \cdot \mathbf{j} \end{aligned} \quad (1.05)$$

where  $\mathbf{S}$  is the surface enclosing  $V$ . Thus, any change of probability inside  $V$  must be caused entirely by a probability flux crossing  $\mathbf{S}$ .

For a system of  $N$  non-interacting particles,

$$H(\mathbf{x}, p, t) = \sum_{v=1}^N \left[ \frac{\mathbf{p}_v^2}{2M_v} + V(\mathbf{x}_v, t) \right] \quad (1.106)$$

and

$$i\hbar \frac{\partial \Psi(\mathbf{x}, t)}{\partial t} = \left\{ \sum_{v=1}^N \left[ -\frac{\hbar^2}{2M_v} \nabla_v^2 + V(\mathbf{x}_v, t) \right] \right\} \Psi(\mathbf{x}, t) \quad (1.107)$$

where  $\mathbf{x} = (\mathbf{x}_1, \dots, \mathbf{x}_N)$ .