A3. Concepts of Quantum Mechanics

In this Annex the Reader is reminded of some concepts from quantum mechanics that will be used in this book.

1) A particle can be fully described by a function, called wave function. The wave function is noted $\Psi(x,y,z,t)$ and it contains all measurable information about the particle.

2) To each dynamic variable corresponds a quantum-mechanic operator:

   ◊ To the position x corresponds the operator $\hat{x} \equiv x$ (A3.1)

   ◊ To momentum p_x corresponds the operator $p_x \equiv \frac{\hbar}{j}\frac{\partial}{\partial x}$ (A3.2)

   ◊ To the total energy E corresponds the operator $\hat{E} \equiv -\frac{\hbar}{j}\frac{\partial}{\partial t}$ (A3.3)

   ◊ To the potential energy $V(x,y,z)$ corresponds the operator

   $$\hat{V} \equiv V(x,y,z) \quad \text{(A3.4)}$$

   where $j = \sqrt{-1}$ and where $\hbar = h/2\pi$, h being Planck's constant.

3) The wave function also gives the probability of finding the particle in a given region of space. If the wave function is real (*i.e.,* not complex) the probability of finding the particle between positions a and b in one dimension (x) is given by:

   $$probability = \int_a^b \Psi^* \Psi \, dx \quad \left(= \int_a^b \Psi^2 \, dx \text{ if } \Psi \text{ is a real function}\right)$$

   For all space in one dimension the particle must be *somewhere* between $x = -\infty$ and $x = +\infty$ and therefore, we obtain the normalization condition:

   $$\int_{-\infty}^{+\infty} \Psi^* \Psi \, dx = 1 \quad \left(\int_{-\infty}^{+\infty} \Psi^2 \, dx = 1 \text{ if } \Psi \text{ is a real function}\right) \quad \text{(A3.5)}$$

Consider the total energy of a particle in a classical Newtonian physics approach. If the particle has a momentum p and a potential energy V, its total energy is given by:

$$E = \frac{p^2}{2m} + V \quad \text{(A3.6)}$$

Note that $p=p(x,y,z)$, $p^2 = p_x^2 + p_y^2 + p_z^2$ and $V=V(x,y,z)$

Applying these concepts to an electron having a mass m for the one-dimensional case one obtains Table A. 1:

Table A.1: Physical variables and operators.

Quantity	Classical mechanics	Quantum mechanics
Momentum	$p = mv$	$\frac{\hbar}{j}\frac{d}{dx}$
Kinetic energy	$\frac{p^2}{2m}$	$\frac{1}{2m}\frac{\hbar}{j}\frac{d}{dx}(\frac{\hbar}{j}\frac{d}{dx}) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$
Potential energy	V	$\hat{V}$
Total energy	$E = \frac{p^2}{2m} + V$	$-\frac{\hbar}{j}\frac{\partial}{\partial t}$
Mass	$m = \frac{1}{d^2E/dp^2}$	$m = \frac{\hbar^2}{d^2E/dk^2}$
Velocity, group velocity	$v = \frac{dE}{dp}$	$v_k = \frac{1}{\hbar}\frac{dE}{dk}$

In this Table, k is a wave vector or a wave number that corresponds to the momentum of the particle.

The Schrödinger equation is basically the quantum mechanical equivalent of classical mechanics $E = \frac{p^2}{2m} + V$. For the one-dimensional case the quantum mechanical equivalent of total energy is:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x,t)\Psi = -\frac{\hbar}{j}\frac{\partial\Psi}{\partial t} \qquad \text{(A3.7)}$$

and, in three dimensions:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V(x,y,z,t)\Psi = -\frac{\hbar}{j}\frac{\partial\Psi}{\partial t} \qquad \text{(A3.8)}$$

where ∇^2 is the Laplacian operator defined by:

$$\nabla^2\Psi(x,y,z,t) \equiv \frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}$$

If the potential energy function is time independent ($\partial V/\partial t = 0$) one is able to construct a solution to the Schrödinger equation through the technique of separation of variables where the wave function is written as the product of a time-independent term, $\psi(x,y,z)$ and a space-independent term, $T(t)$, such that $\Psi(x,y,z,t) = \psi(x,y,z)\ T(t)$. The introduction of these terms into (A3.8) yields:

$$T(t)\left(-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z)\right) + V(x,y,z)\ \psi(x,y,z)\ T(t) = \psi(x,y,z)\left(-\frac{\hbar}{j}\frac{\partial T(t)}{\partial t}\right)$$

or

$$\frac{1}{\psi(x,y,z)}\left(-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) + V(x,y,z)\ \psi(x,y,z)\right) = \frac{1}{T(t)}\left(-\frac{\hbar}{j}\frac{\partial T(t)}{\partial t}\right) \qquad \text{(A3.9)}$$

The left-hand term of this equation depends only on space, while the right-hand term depends only on time, which indicates that the separation of Ψ into the product of ψ and T was successful. We can now solve the Schrödinger equation for the variables ψ and T separately, and with this solution find $\Psi = \psi T$. Equation A3.9 makes sense only if both terms are equal to a constant which we shall call E, therefore, we can write:

$$E\ T(t) = -\frac{\hbar}{j}\frac{\partial T(t)}{\partial t} \Rightarrow T(t) = \exp\left(\frac{-jEt}{\hbar}\right) \qquad \text{(A3.10)}$$

and therefore:

$$\Psi(x,y,z,t) = \psi(x,y,z)\ \exp\left(\frac{-jEt}{\hbar}\right) \qquad \text{(A3.11)}$$

Introducing Expression A3.11 into A3.8 one obtains the time-independent Schrödinger equation:

Time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) + [V(x,y,z) - E]\ \psi(x,y,z) = 0 \qquad \text{(A3.12)}$$

where E is the (constant) energy of the particle, where the energy of the particle is given by:

$$-\frac{h}{j}\frac{\partial\Psi(x,y,z,t)}{\partial t} = \psi(x,y,z)\left(-\frac{\hbar}{j}\frac{\partial T(t)}{\partial t}\right) = \psi(x,y,z)\ E\ T(t) = E\ \Psi(x,y,z,t)$$