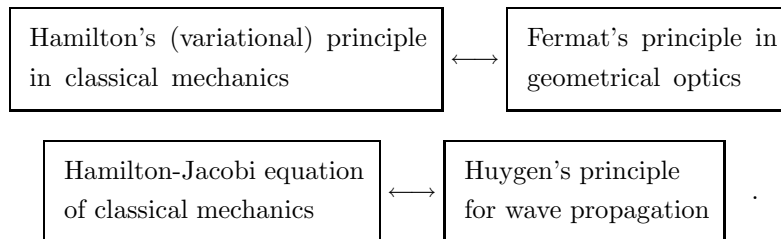


Chapter 1

How Did Schrödinger Get His Equation?

The short answer to the question posed in the title of this chapter is: from Hamilton's formulation of classical mechanics.

In one of his seminal papers, "*Quantization as a Problem of Proper Values (Part II)*" (Schrödinger 1926, an English translation of which can be found in Schrödinger 1982), Schrödinger recognized and stressed the importance of the following pair of correspondences:



In this paper Schrödinger exploited fully the analogy between the Hamiltonian formulation of classical mechanics and optics. This is one of the most fascinating episodes of theory building in the history of physics. In this chapter we will give a brief and heuristic account of the main ideas behind it.

Consider the classical motion of a point particle from point A to point B in three-dimensional Euclidean space under the influence of a given potential energy function $V(x, y, z)$. The total energy $E = T + V$, where T is the kinetic energy of the particle, is conserved. Out of the totality of classical paths beginning at point A at time t_1 and ending at point B at time t_2 , **Hamilton's variational principle** picks out the correct one. This principle states that

$$\delta \int_{t_1}^{t_2} L(q, \dot{q}) dt = 0 \quad , \quad (1.1)$$

where $L = T - V$, called the **Lagrangian** of the system, is a function of the (collective) spatial coordinates q and their time derivatives \dot{q} . For $E = \text{constant}$,

$$L = T - V = T - (E - T) = 2T - E . \quad (1.2)$$

Then Hamilton's principle translates to

$$\delta \int_{t_1}^{t_2} 2T dt = 0 , \quad (1.3)$$

which is the form of Hamilton's principle given by Maupertuis. Now, since $T = p^2/2m$,

$$2T = m \left(\frac{ds}{dt} \right)^2 = p \frac{ds}{dt} = \sqrt{2mT} \left(\frac{ds}{dt} \right) = \sqrt{2m(E - V)} \frac{ds}{dt} . \quad (1.4)$$

Hence (1.3) implies

$$\delta \int_A^B \sqrt{2m(E - V)} ds = 0 . \quad (1.5)$$

Hamilton noticed that (1.5) is formally the same as **Fermat's principle of least time** in the geometrical optics of non-homogeneous media:

$$\delta \int_A^B \frac{ds}{u} = 0 , \quad (1.6)$$

if one sets, in (1.6),

$$u = \frac{C(E)}{\sqrt{2m(E - V)}} , \quad (1.7)$$

where $C(E)$ is a function only of the total energy E and is independent of the spatial coordinates (x, y, z) . In (1.6), $u(x, y, z)$ denotes the variable speed of light in a non-homogeneous medium.

The formal equivalence of (1.5) and (1.6), under the condition (1.7), establishes the correspondence between Hamilton's principle for the classical mechanical motion of a particle on the one hand, and Fermat's principle for the motion of light rays in geometrical optics, on the other.

It is important to distinguish between the two velocities $u(E; x, y, z)$ [given by (1.7)] and

$$v = \frac{1}{m} \sqrt{2m(E - V)} . \quad (1.8)$$

While u is the velocity of a light ray, v is the velocity of a mass point. The fact that u is a function of E suggests that we are also dealing with a **dispersive medium**, namely, one in which the velocity of light depends on the frequency of the light ray, in addition to a non-homogeneous one. This is implied by Einstein's formula for the energy of photons:

$$E = hf , \quad (1.9)$$

where h is Planck's constant.

The two velocities $u(E; x, y, z)$ [(1.7)] and $v(E; x, y, z)$ [(1.8)] cannot be the same for arbitrary potential energy function $V(x, y, z)$ since $C(E)$ is not a function of (x, y, z) . To establish a connection between u and v , we first note that u , as the velocity of a light ray in geometrical optics, is also the **phase velocity** of a light wave in a non-homogeneous and dispersive medium. Consider a **localized wave packet** constructed from a superposition of plane waves with different frequencies. Corresponding to a wave packet one has the **group velocity** v_g given by

$$v_g = \frac{d\omega}{dk} = \frac{df}{d\left(\frac{1}{\lambda}\right)} = \frac{df}{d\left(\frac{f}{u}\right)} . \quad (1.10)$$

Thus

$$\frac{1}{v_g} = \frac{d}{df} \left(\frac{f}{u} \right) = \frac{d}{dE} \left(\frac{E}{u} \right) , \quad (1.11)$$

where in the second equality of the above equation we have used Einstein's formula (1.9).

At this point we impose the condition

$$v = v_g . \quad (1.12)$$

Then, using (1.7) and (1.8) in (1.11), we have

$$\frac{d}{dE} \left(\frac{E\sqrt{2m(E-V)}}{C(E)} \right) = \frac{m}{\sqrt{2m(E-V)}} = \frac{d}{dE} \sqrt{2m(E-V)} , \quad (1.13)$$

which implies

$$\frac{E\sqrt{2m(E-V)}}{C(E)} = \sqrt{2m(E-V)} + \text{a quantity independent of } E , \quad (1.14)$$

or

$$\left(\frac{E}{C(E)} - 1 \right) \sqrt{2m(E-V)} = \text{a quantity independent of } E . \quad (1.15)$$

In order for the last equation to hold, it must be true that

$$C(E) = E . \quad (1.16)$$

It then follows from (1.7) that

$$u(E; x, y, z) = \frac{E}{\sqrt{2m(E-V)}} . \quad (1.17)$$

Problem 1.1 Consider a wave packet

$$\psi(\mathbf{x}) = \int d^3k a(\mathbf{k}) e^{i(\mathbf{k} \cdot \mathbf{x} - \omega t)} ,$$

where $\omega(\mathbf{k})$ is a function of \mathbf{k} (given by a dispersion relation). Assume that $a(\mathbf{k})$ is significantly different from zero only in some small region around \mathbf{k}_0 . The position of the center of the packet is then given by

$$\langle \mathbf{x}(t) \rangle = \frac{\int d^3x \mathbf{x} |\psi|^2}{\int d^3x |\psi|^2} .$$

Show that

$$\langle \mathbf{x}(t) \rangle = \mathbf{x}_0 + \mathbf{v}_g t ,$$

where

$$\mathbf{x}_0 \equiv \frac{i \int d^3k a^*(\mathbf{k}) \nabla_{\mathbf{k}} a(\mathbf{k})}{\int d^3k a^* a} ,$$

and the group velocity of the packet is given by

$$\mathbf{v}_g = \langle \nabla_{\mathbf{k}} \omega \rangle \equiv \frac{\int d^3k |a(\mathbf{k})|^2 \nabla_{\mathbf{k}} \omega(\mathbf{k})}{\int d^3k |a(\mathbf{k})|^2} .$$

Now let us take a more formal look at how Hamilton's formulation of classical mechanics gives rise to Schrödinger's wave mechanics, this time via the so-called **Hamilton-Jacobi equation** :

$$\boxed{\frac{\partial W}{\partial t} + T\left(q^i, \frac{\partial W}{\partial q^i}\right) + V(q^i) = 0} , \quad (1.18)$$

where $W = W(q^i, P_i, t)$ is the **generating function** of the **canonical transformation**

$$(q^i, p_i) \longrightarrow (Q^i, P_i) , \quad H \longrightarrow H + \frac{\partial W}{\partial t} , \quad (1.19)$$

with

$$p_i = \frac{\partial W}{\partial q^i} , \quad Q^i = \frac{\partial W}{\partial P_i} . \quad (1.20)$$

The new variables P_i are usually taken to be the constants of motion if the Hamiltonian is **integrable**. One of these is the total energy E . Let

$$W = -Et + S(q^i) \quad (1.21)$$

and $T = p^2/(2m)$. Then the Hamilton-Jacobi equation yields

$$-E + \frac{(\nabla S)^2}{2m} + V = 0 , \quad (1.22)$$

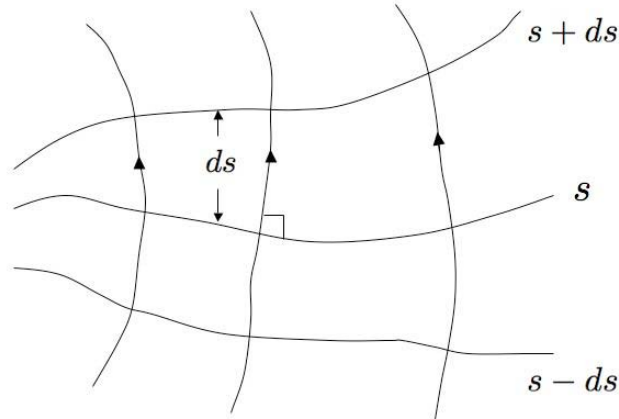


Fig. 1.1

or

$$ds = \frac{dS}{\sqrt{2m(E-V)}} \quad , \quad (1.23)$$

where ds denotes the direction normal to the surfaces of constant “phase” S . (See Fig. 1.1.) The picture presented by the Hamilton-Jacobi equation is thus the propagation of surfaces of constant phase (constant value of W) in time. Thus, from (1.21), the constant phase condition $dW = 0$ implies $dS = E dt$, which, together with (1.23), gives

$$u = \frac{ds}{dt} = \frac{E}{\sqrt{2m(E-V)}} \quad . \quad (1.24)$$

This, of course, is none other than (1.17)!

Problem 1.2 Solve the simple harmonic oscillator problem the hard way: using the Hamilton-Jacobi equation. Let

$$H = \frac{p^2}{2m} + \frac{kq^2}{2} \quad .$$

Set

$$W(q, E, t) = S(q) - Et \quad , \quad (P = E) \quad .$$

Then the Hamilton-Jacobi equation becomes

$$\frac{1}{2m} \left(\frac{\partial W}{\partial q} \right)^2 + \frac{kq^2}{2} + \frac{\partial W}{\partial t} = 0 \quad ,$$

or

$$\frac{1}{2m} \left(\frac{\partial S}{\partial q} \right)^2 + \frac{kq^2}{2} = E \quad .$$

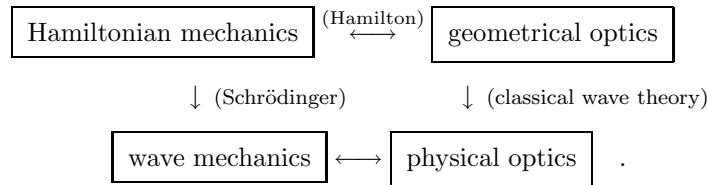
Integrate this equation to find S and W . Then use

$$Q = \frac{\partial W}{\partial P} = \frac{\partial W}{\partial E} = \text{constant}$$

to obtain the solution

$$q(t) = \sqrt{\frac{2E}{k}} \cos\{\omega(t + Q)\}, \quad \omega \equiv \sqrt{\frac{k}{m}} \quad .$$

The above development establishes the remarkable fact that, inherent in the Hamiltonian formulation of classical mechanics, there is a picture of wave propagation. Now, whereas Hamilton explicitly recognized the analogy between classical mechanics and geometrical optics, an insight that Schrödinger called “powerful and momentous”, Schrödinger himself went one step further and established a relationship between the wave mechanics of particles and physical (wave) optics. The following diagram illustrates the amazing interplay between the relevant theories.



Let us now see how Schrödinger provided the crucial steps linking Hamiltonian mechanics to wave mechanics.

The classical **wave equation** in physical optics for a wave function $\Psi(x, y, z; t)$ is given by

$$\nabla^2 \Psi = \frac{1}{u^2} \frac{\partial^2 \Psi}{\partial t^2} \quad . \quad (1.25)$$

The solution of this equation for a monochromatic wave of frequency f must be of the form

$$\Psi(x, y, z; t) = \psi(x, y, z) e^{-2\pi i f t} \quad . \quad (1.26)$$

Plugging this into (1.25), we obtain the time-independent equation

$$\nabla^2 \psi + \frac{4\pi^2 f^2}{u^2} \psi = 0 \quad , \quad (1.27)$$

where u is the phase velocity of the wave. Now use (1.17) for u in (1.27) to get

$$\nabla^2 \psi + \frac{4\pi^2 f^2 \cdot 2m(E - V)}{E^2} \psi = 0 \quad . \quad (1.28)$$

Finally, with the help of Einstein's equation $E = hf$, one arrives at the so-called **time-independent Schrödinger equation** :

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad . \quad (1.29)$$

To restore the time dependence, we multiply (1.29) by $\exp(-2\pi iEt/h)$:

$$\nabla^2 (\psi e^{-2\pi iEt/h}) + \frac{8\pi^2 m}{h^2} E \psi e^{-2\pi iEt/h} - \frac{8\pi^2 mV}{h^2} e^{-2\pi iEt/h} = 0 \quad . \quad (1.30)$$

Recognizing that the second term on the LHS is equal to $\frac{4\pi im}{h} \frac{\partial}{\partial t} (\psi e^{-2\pi iEt/h})$ we can clean up the above equation by rewriting $\psi e^{-2\pi iEt/h}$ as ψ and obtain

$$\nabla^2 \psi - \frac{8\pi^2 m}{h^2} V \psi = -4\pi i \frac{m}{h} \frac{\partial \psi}{\partial t} \quad . \quad (1.31)$$

The standard form of the so-called **time-dependent Schrödinger equation** is finally obtained by multiplying both sides of (1.31) by $-\hbar^2/(2m)$, where $\hbar \equiv h/(2\pi)$:

$$\boxed{-\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = i\hbar \frac{\partial \psi}{\partial t}} \quad . \quad (1.32)$$

This time-dependent equation is a trivial generalization of the time-independent equation (1.29) *if* the potential function V is time-independent. But Schrödinger took the bold step of postulating that (1.32) is a completely general equation, even though V may be a function of time [in which case the time-dependence of ψ will no longer be of the simple form $\exp(-2\pi iEt/h)$]. He offered no logical justification and only claimed that “success will justify our procedure”. The breath-taking development of quantum mechanics would soon vindicate his leap of faith, at least as far as non-relativistic quantum mechanics was concerned.

It is interesting to note that if we make the formal correspondence

$$\boxed{p_i \longleftrightarrow \frac{\hbar}{i} \frac{\partial}{\partial q^i}} \quad , \quad (1.33)$$

where p_i is the **canonical momentum** conjugate to the **canonical coordinate** q^i , we obtain the “operator” equation

$$H \equiv \frac{p^2}{2m} + V = -\frac{\hbar^2}{2m} \nabla^2 + V \quad . \quad (1.34)$$

H is called the **Hamiltonian operator** (operating on the function ψ). The time-independent Schrödinger equation then appears as

$$\boxed{H\psi \equiv \left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) \psi = E\psi} \quad . \quad (1.35)$$

The function $\psi(x, y, z; t)$ is called the **wave function** of a non-relativistic quantum mechanical system, whose dynamics is governed by the time-dependent Schrödinger equation (1.32), in which the potential function V may depend explicitly on time.

The big question is: What does ψ mean, physically?

We cannot answer this question definitively at this time, except to say that knowledge of ψ allows one to know everything possible about the system, in the sense that one can use ψ to maximally predict all observational results obtained by performing experiments on the system. The question, in fact, has never been answered definitively, and has been the subject of heated debates since the inception of quantum mechanics. This is a big topic, and goes under the name of “**the interpretation of quantum mechanics**”. Suffice it to mention at this time that, under the most commonly accepted interpretation (the so-called **Copenhagen interpretation**), the quantity $\psi^*\psi$ is interpreted as the spatial probability density of a quantum mechanical object described by the wave function at the time t . We will consider this question in more detail in Chapters 10 and 11.

Problem 1.3 Consider a free particle (not subjected to any force) of mass m moving in 3-dimensional Euclidean space, and its classical trajectories starting at time t_0 at positions \mathbf{x}_0 and ending at time t at (one) position \mathbf{x} . The **Green’s function (propagator)** relating two space-time points is defined to be the function $G(\mathbf{x} - \mathbf{x}_0; t - t_0)$ satisfying the following relationship between the Schrödinger wave functions at different space-time points:

$$\psi(\mathbf{x}, t) = \int d^3x_0 G(\mathbf{x} - \mathbf{x}_0; t - t_0) \psi(\mathbf{x}_0, t_0) \quad ,$$

where the integral is over all space. Show that the free-particle Green’s function is given by

$$G(\mathbf{x} - \mathbf{x}_0; t - t_0) = \left(\frac{m}{2\pi i \hbar (t - t_0)} \right)^{3/2} \exp \left\{ \frac{im|\mathbf{x} - \mathbf{x}_0|^2}{2\hbar(t - t_0)} \right\} \quad ,$$

by plugging this expression for G into the above defining equation for the Green’s function and showing that the resulting expression for the wave function $\psi(\mathbf{x}, t)$ satisfies the time-dependent Schrödinger equation.

Problem 1.4 Consider a free particle of mass m which, at $t = 0$, is prepared in the state

$$\begin{aligned}\psi(\mathbf{x}, 0) &= 1/\sqrt{V}, & (x \leq R) \quad , \\ &= 0, & (x > R) \quad ,\end{aligned}$$

where $V = 4\pi R^3/3$. Show that for $x \gg R$, and for all t ,

$$\psi(\mathbf{x}, t) = \left(\frac{2}{\pi V}\right)^{1/2} \left(\frac{aR}{ix^2}\right)^{3/2} \left[\sin\left(\frac{x}{a}\right) - \frac{x}{a} \cos\left(\frac{x}{a}\right)\right] \exp\{ix^2 m/(2\hbar t)\},$$

where $a \equiv \hbar t/(mR)$. What is the significance of the length a ? Determine the behavior of the probability distribution in the limits $x \gg a$ and $x \ll a$. [*Hint*: Use the free particle Green's function to compute $\psi(\mathbf{x}, t)$ from $\psi(\mathbf{x}_0, 0)$.]

Problem 1.5 Consider the one-particle Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{x}, t) = -\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{x}, t) + [V_1(\mathbf{x}) + iV_2(\mathbf{x})] \psi(\mathbf{x}, t) \quad ,$$

where V_1 and V_2 are real functions. If we interpret $\rho = \psi^* \psi$ as the spatial probability density at the time t , show that the probability is not conserved, and give an expression for the rate at which probability is “lost” or “gained” in a spatial volume Ω . [*Hint*: Compute

$$\frac{\partial}{\partial t} \int d^3x \psi^*(\mathbf{x}, t) \psi(\mathbf{x}, t) \quad ,$$

and show that the **equation of continuity**

$$\nabla \cdot \mathbf{j} + \frac{\partial \rho}{\partial t} = 0$$

is *not* satisfied, where

$$\mathbf{j} \equiv -\frac{i\hbar}{2m} (\psi^* \nabla \psi - \psi \nabla \psi^*)$$

can be interpreted as the quantum mechanical **current density**.

We close this chapter with some technical matters of the utmost importance. Define the **commutator** of two operators A and B , denoted by $[A, B]$, by

$$[A, B] \equiv AB - BA \quad . \quad (1.36)$$

Then (1.33) implies the following commutation relations for q^i and p_i , regarded as operators:

$$[q^i, p_j] = i\hbar \delta_j^i, \quad [q^i, q^j] = [p_i, p_j] = 0 \quad . \quad (1.37)$$

These are also called the **quantum conditions** for the canonical coordinate and canonical momentum operators. As will be seen later (in Chapter 11), they constitute the mathematical basis of **Heisenberg's Uncertainty Principle**.

In the so-called Schrödinger picture, q^i and $p_j = \frac{\hbar}{i} \frac{\partial}{\partial q^j}$ are all operators on **square-integrable functions** $\psi(q^i)$. These are defined to be functions satisfying the condition

$$\int dq^1 \dots dq^{3N} \psi^* \psi < \infty \quad , \quad (1.38)$$

where N is the total number of particles in the system. Were this condition to be violated, the Copenhagen interpretation of the wave function mentioned above would not make sense.

Finally, we mention that if ψ is a solution of the time-dependent Schrödinger equation (1.32), then, for systems of spinless particles, ψ^* (the complex conjugate of ψ) is a solution of the so-called **time-reversed** Schrödinger equation, which is obtained by replacing t in (1.32) by $-t$. This can be shown easily by taking the complex conjugate of (1.32):

$$-\frac{\hbar^2}{2m} \nabla^2 \psi^* + V \psi^* = -i\hbar \frac{\partial \psi^*}{\partial t} = i\hbar \frac{\partial \psi^*}{\partial(-t)} \quad , \quad (1.39)$$

where we have assumed that V is real.

Problem 1.6 Verify the quantum conditions (1.37) by using the correspondence (1.33).

Problem 1.7 In special relativity the relationship between the energy E and the momentum \mathbf{p} of a free particle of rest mass m is given by

$$E^2 = p^2 c^2 + m^2 c^4 \quad ,$$

where c is the speed of light. Use the quantum translation keys

$$\mathbf{p} \longrightarrow -i\hbar \nabla \quad \text{and} \quad E \longrightarrow i\hbar \frac{\partial}{\partial t}$$

to construct a relativistic wave equation for the particle. (The energy correspondence will be discussed in more detail in Chapter 17.) The resulting equation

$$\left(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \psi = \frac{m^2 c^2}{\hbar^2} \psi$$

is called the **Klein-Gordon equation** for a spin-zero particle. For a massless particle ($m = 0$, as for the photon), the **wave equation** results. Note that if we had used the non-relativistic relationship $E = p^2/(2m)$ we would have ended up with the non-relativistic Schrödinger equation instead.