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Basics

In 1900, Planck found that he could explain the spectrum of blackbody radiation by introducing a new physical constant with the dimensions of angular momentum. The Planck constant is the basis of quantum mechanics, determining when classical concepts no longer apply, specifying the inevitable uncertainties introduced by measurement, and fixing the size of atoms. The gradual development of wave mechanics led by Niels Bohr over the next twenty years was superseded by the extraordinarily rapid progress that followed de Broglie's proposal that particles were also waves. By 1927, the canon was largely in place and was codified by Dirac's magisterial text in 1930. Suddenly there was a comprehensive theory of atoms and molecules and their electromagnetic interactions: our material world.

We review some of the essential aspects of quantum mechanics, the wave function and Born's interpretation of its absolute square as a probability density. The Schrödinger equation prescribes the non-relativistic behavior of the wave function in space and time in terms of a Hamiltonian, which combines the kinetic and potential energies. A free particle already evidences the effects of quantum mechanics by gradually spreading from any initially confined configuration. The behavior of a particle in the field of a constant conservative force is closely related to what would be expected classically, with motion that is bounded or unbounded depending on the potential and the particle's energy. The Schrödinger equation brought with it the power of the well-developed mathematics of differential equations. A recurrent concept is that of an eigenvalue, a value of a parameter that allows the solution of a differential equation subject to boundary conditions. The Rayleigh-Ritz method provides a means of determining a good approximation to the smallest eigenvalue, generally the lowest energy, by varying parameters in a trial function.

1.1 Wave Mechanics of de Broglie and Schrödinger

Louis duc de Broglie, in his 1924 Ph.D. thesis, proposed that material particles of mass m , momentum $\mathbf{p}$ and energy $E = \sqrt{p^2 c^2 + m^2 c^4}$ have associated with them a wave vector and angular frequency through the Planck constant $\hbar = h/2\pi$

$$\mathbf{k} = \mathbf{p}/\hbar; \quad \omega = E/\hbar. \quad (1.1)$$

This leads us to associate with a particle of momentum $\mathbf{p}$ and energy E a *wave amplitude*

$$\psi_{\mathbf{p}}(\mathbf{x}, t) = e^{i\mathbf{k} \cdot \mathbf{x} - i\omega t} = e^{i\frac{\mathbf{p} \cdot \mathbf{x}}{\hbar} - i\frac{E}{\hbar} t}. \quad (1.2)$$

de Broglie's insight led to the rapid development of quantum mechanics by Werner Heisenberg, Erwin Schrödinger, Paul Dirac, Max Born, and others. We review here the elements of quantum mechanics from the wave perspective. Quantum mechanics, like any physical theory, cannot be derived as if it were a mathematical theorem. Its validity can be judged only by its ability to predict correctly what is observed. Later, we will show how a quantum mechanical prescription can be derived from some reasonable assumptions. But such derivations are not proofs, but rather logical arguments in favor of a theory that must face the test of experiment.

The idea of localized particles (“at $\mathbf{x}$, with momentum $\mathbf{p}$ ”) plus experience with superposition of waves, lead to consideration of a *general wave amplitude*

$$\psi(\mathbf{x}, t) = \int d^3p A(\mathbf{p}) e^{i\frac{\mathbf{p}\cdot\mathbf{x}}{\hbar} - i\frac{E(\mathbf{p})}{\hbar}t} \quad (1.3)$$

in association with a free particle of mass m . For a one-dimensional case, as we show more completely below, if $A(p)$ is narrowly confined about $p = 0$ with a spread Δp , $\psi(x)$ will describe a particle with a spread $\Delta x \approx \hbar/\Delta p$. We shall return to the uncertainty principle later.

With classical ideas (sound intensity, Poynting vector, etc.) to guide us, we are led fairly directly to Born's probability interpretation of $|\psi|^2$, i.e. the probability of finding a particle “at $\mathbf{x}$ ” at time t in a volume d^3x is proportional to $|\psi(\mathbf{x}, t)|^2 d^3x$. Thus we speak of $|\psi(\mathbf{x}, t)|^2$ as the *probability density at $(\mathbf{x}, t)$* .

1.2 Klein-Gordon Equation

With Einstein's relation $E = \sqrt{p^2c^2 + m^2c^4}$ we see that

$$\frac{\partial^2 \psi}{\partial t^2} = \int d^3p A(\mathbf{p}) \left[-\frac{E^2}{\hbar^2} \right] e^{i\frac{\mathbf{p}\cdot\mathbf{x}}{\hbar} - i\frac{E(\mathbf{p})}{\hbar}t} = \int d^3p A(\mathbf{p}) \left[-\frac{p^2c^2}{\hbar^2} - \frac{m^2c^4}{\hbar^2} \right] e^{i\frac{\mathbf{p}\cdot\mathbf{x}}{\hbar} - i\frac{E(\mathbf{p})}{\hbar}t}. \quad (1.4)$$

But we can write

$$\nabla^2 \psi = \int d^3p A(\mathbf{p}) \left[-\frac{p^2}{\hbar^2} \right] e^{i\frac{\mathbf{p}\cdot\mathbf{x}}{\hbar} - i\frac{E(\mathbf{p})}{\hbar}t}. \quad (1.5)$$

Thus, independent of $A(\mathbf{p})$

$$\frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2} = \nabla^2 \psi - \left(\frac{mc}{\hbar} \right)^2 \psi. \quad (1.6)$$

This is the Klein-Gordon equation, a relativistic wave equation for free spinless particles, e.g. π mesons. We note that this equation allows solutions with $-E$ in place of E .

1.3 Non-Relativistic Approximation

If $\psi(\mathbf{x}, t)$ describes a state of motion of a particle, so also does $e^{i\alpha}\psi(\mathbf{x}, t)$, where α is independent of the motion of the particle. For example, we could take $\alpha = (10 \text{ eV}/\hbar)t$ or $\alpha = \pi/4$. This is permissible because only $|\psi|^2$ is relevant as a probability density.

Consider the non-relativistic limit

$$E(p) = \sqrt{p^2 c^2 + m^2 c^4} \approx mc^2 + \frac{p^2}{2m} \equiv mc^2 + E_{\text{NR}} \quad (1.7)$$

so that

$$\psi_{\mathbf{p}}(\mathbf{x}, t) = e^{i\frac{\mathbf{p}\cdot\mathbf{x}}{\hbar} - i\frac{E}{\hbar}t} \approx e^{-i\frac{mc^2}{\hbar}t} \cdot e^{i\frac{\mathbf{p}\cdot\mathbf{x}}{\hbar} - i\frac{E_{\text{NR}}}{\hbar}t}. \quad (1.8)$$

Thus, by superposition, in the non-relativistic limit

$$\psi(\mathbf{x}, t) = e^{-i\frac{mc^2}{\hbar}t} \int d^3p A(\mathbf{p}) e^{i\frac{\mathbf{p}\cdot\mathbf{x}}{\hbar} - i\frac{E_{\text{NR}}}{\hbar}t}. \quad (1.9)$$

Because the choice of phase is at our disposal, we define the non-relativistic wave amplitude

$$\psi_{\text{NR}}(\mathbf{x}, t) = e^{imc^2t/\hbar} \psi(\mathbf{x}, t). \quad (1.10)$$

Now dropping the subscript NR, we have

$$\psi(\mathbf{x}, t) = \int d^3p A(\mathbf{p}) e^{i\frac{\mathbf{p}\cdot\mathbf{x}}{\hbar} - i\frac{E_{\text{NR}}}{\hbar}t} \quad (1.11)$$

so that

$$\frac{\partial \psi}{\partial t} = \int d^3p A(\mathbf{p}) \left[-\frac{ip^2}{2m\hbar} \right] e^{i\frac{\mathbf{p}\cdot\mathbf{x}}{\hbar} - i\frac{E_{\text{NR}}}{\hbar}t} \quad (1.12)$$

and as before

$$\nabla^2 \psi = \int d^3p A(\mathbf{p}) \left[-\frac{p^2}{\hbar^2} \right] e^{i\frac{\mathbf{p}\cdot\mathbf{x}}{\hbar} - i\frac{E_{\text{NR}}}{\hbar}t}. \quad (1.13)$$

Thus we obtain the general equation describing non-relativistic motion of free particles, the Schrödinger equation,

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi. \quad (1.14)$$

1.4 Free-Particle Probability Current

If $|\psi|^2$ is a density, there should be a probability current and a continuity equation to connect them because probability is conserved.

$$\int |\psi(\mathbf{x}, t)|^2 d^3x = \text{constant in time.} \quad (1.15)$$

Consider

$$\frac{\partial}{\partial t} |\psi|^2 = \psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} \quad (1.16)$$

and use the Schrödinger equation to get

$$\begin{aligned} \frac{\partial}{\partial t} |\psi|^2 &= -\frac{\hbar}{2mi} [\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*] \\ &= -\frac{\hbar}{2mi} \nabla \cdot [\psi^* \nabla \psi - \psi \nabla \psi^*]. \end{aligned} \quad (1.17)$$

So if we write

$$\mathbf{J} = \frac{\hbar}{2mi} (\psi^* \nabla \psi - \psi \nabla \psi^*). \quad (1.18)$$

we have a continuity equation,

$$\frac{\partial |\psi|^2}{\partial t} + \nabla \cdot \mathbf{J} = 0. \quad (1.19)$$

Note that $\mathbf{J}$ is arbitrary to the extent of adding a curl of some vector function, since the divergence of a curl is always zero. This is analogous to the arbitrariness of the Poynting vector in electromagnetism.

To find $\mathbf{J}$ for our general free-particle $\psi(\mathbf{x}, t)$, consider

$$\nabla \psi = \int d^3 p A(\mathbf{p}) \left(\frac{i\mathbf{p}}{\hbar} \right) e^{i\frac{\mathbf{p}\cdot\mathbf{x}}{\hbar} - i\frac{E(p)}{\hbar}t}. \quad (1.20)$$

Combining this with its complex conjugate, we find

$$\mathbf{J}(\mathbf{x}, t) = \frac{1}{2m} \int d^3 p \int d^3 p' A^*(\mathbf{p}') A(\mathbf{p}) [\mathbf{p} + \mathbf{p}'] e^{i\frac{(\mathbf{p}-\mathbf{p}')\cdot\mathbf{x}}{\hbar}} e^{-i(E-E')t/\hbar}. \quad (1.21)$$

The presence of the factor $(\mathbf{p} + \mathbf{p}')/(2m)$ shows that each component wave of definite momentum contributes a factor of $\mathbf{v} = \mathbf{p}/m$ to the flux, as expected. Note that there is a correspondence

$$\nabla \psi \leftrightarrow i\frac{\mathbf{p}}{\hbar} A(\mathbf{p}). \quad (1.22)$$

The identification by de Broglie of the momentum $\mathbf{p}$ with $\hbar\mathbf{k}$, where $\mathbf{k}$ occurs in a plane wave as $e^{i\mathbf{k}\cdot\mathbf{x}}$, leads through the Fourier transform with the identification of $\mathbf{p}$ with $\frac{\hbar}{i}\nabla$.

1.5 Expectation Values

If $|\psi|^2$ is the probability density in space, then it is natural to define averages of coordinates and functions of coordinates for the particular state of motion as integrals over all space, weighted with $|\psi|^2$. Suppose $F(\mathbf{x}, t)$ is a reasonable real function of $\mathbf{x}$ and t and assume $F|\psi|^2$ has a finite integral over all space. Then the average of (or *expectation value* of) F is

$$\langle F \rangle = \int d^3 x F(\mathbf{x}, t) |\psi(\mathbf{x}, t)|^2. \quad (1.23)$$

In general, $\langle F \rangle$ is a function of time through both the explicit time dependence of F and the time dependence of $|\psi|^2$. For example,

$$\langle \mathbf{x} \rangle = \int d^3 x \mathbf{x} |\psi(\mathbf{x}, t)|^2. \quad (1.24)$$

This all seems plausible, even obvious and necessary. If $|\psi(\mathbf{x}, t)|^2$ is big somewhere, the $\langle \mathbf{x} \rangle$ will reflect that. If the place where $|\psi|^2$ is big moves in time, then $\langle \mathbf{x} \rangle$ will move in time. This leads to the question: what is the expression for $\langle \mathbf{p} \rangle$?

We look at this in two ways: what is $m\langle\dot{\mathbf{x}}\rangle$ and what is $\langle\mathbf{p}\rangle$ in terms of $|A(\mathbf{p})|^2$? First, using the continuity equation, Eq. (1.19)

$$\begin{aligned} m \frac{d}{dt} \langle \mathbf{x} \rangle &= m \int d^3x \mathbf{x} \frac{\partial}{\partial t} |\psi|^2 \\ &= -m \int d^3x \mathbf{x} (\nabla \cdot \mathbf{J}) = m \int d^3x \mathbf{J}(\mathbf{x}, t). \end{aligned} \quad (1.25)$$

The last step follows from integration by parts if the current $\mathbf{J}$ is confined to some finite portion of space:

$$\int d^3x x_i \nabla_k J_k = - \int d^3x J_k \nabla_k x_i = \int d^3x J_k \delta_{ik} = \int d^3x J_i. \quad (1.26)$$

The use of integration by parts is ubiquitous. This is inevitable because, when confronted with a formal integral expression, there is no way to proceed other than integration by parts.

Returning to the calculation at hand,

$$\begin{aligned} m \frac{d}{dt} \langle \mathbf{x} \rangle &= m \int d^3x \mathbf{J} \\ &= \frac{\hbar}{2i} \int d^3x [\psi^* \nabla \psi - \psi \nabla \psi^*]. \end{aligned} \quad (1.27)$$

Once again invoking integration by parts,

$$\int d^3x \psi \nabla \psi^* = - \int d^3x \psi^* \nabla \psi. \quad (1.28)$$

We conclude that

$$m \frac{d}{dt} \langle \mathbf{x} \rangle = \int d^3x \left(\psi^* \frac{\hbar}{i} \nabla \psi \right). \quad (1.29)$$

On the other hand, if we think of $|A(\mathbf{p})|^2$ as the probability density in momentum space, then we would define

$$\langle \mathbf{p} \rangle = \int d^3p \mathbf{p} |A(\mathbf{p})|^2 (2\pi)^3, \quad (1.30)$$

where our normalization has been

$$\int d^3p |A(\mathbf{p})|^2 (2\pi)^3 = 1. \quad (1.31)$$

To check whether this is all consistent, we evaluate

$$\begin{aligned} m \int d^3x \mathbf{J} &= \frac{1}{2} \int d^3p \int d^3p' A^*(\mathbf{p}') A(\mathbf{p}) (\mathbf{p} + \mathbf{p}') (2\pi)^3 \delta(\mathbf{p} - \mathbf{p}') \\ &= \int d^3p (2\pi)^3 |A(\mathbf{p})|^2 \mathbf{p}. \end{aligned} \quad (1.32)$$

This confirms our picture that

$$\langle \mathbf{p} \rangle = \int d^3x \psi^* \frac{\hbar}{i} \nabla \psi \quad (1.33)$$

and allows us to identify

$$\mathbf{p} = \frac{\hbar}{i} \nabla. \quad (1.34)$$

Using this identification, we can find the expectation value of a function of $\mathbf{p}$ as

$$\langle G \rangle = \int d^3x \psi^* G\left(\frac{\hbar}{i} \nabla\right) \psi. \quad (1.35)$$

To give this unambiguous meaning, $G(\mathbf{p})$ must be well-behaved, e.g. developable in a power series in $\mathbf{p}$.

1.6 Particle in a Static, Conservative Force Field

So far we have just considered the de Broglie relation and Born's probability interpretation of $|\psi|^2$ for free particles. Suppose a particle is moving in a potential $V(\mathbf{x})$. What equation governs the motion? Motivated by classical treatments of the index of refraction, Fermat's principle, etc. we modify our equations for a free particle:

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi = \frac{p^2}{2m} \psi, \quad (1.36)$$

where we used our identification $\mathbf{p}_{\text{operator}} = (\hbar/i)\nabla$, with the substitution

$$\frac{p^2}{2m} \rightarrow \frac{p^2}{2m} + V(\mathbf{x}). \quad (1.37)$$

In this way, we arrive at the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \left[\frac{p^2}{2m} + V(\mathbf{x}) \right] \psi. \quad (1.38)$$

This familiar equation will occupy us for some time. We note that the picture developed for the free particle requires no significant modification. The probability interpretation of Born is unaffected. The argument for the conservation of probability and the construction of the current survive as long as the potential V is real. The expression of expectation values and the representation of momentum as an operator are unchanged.

1.7 Ehrenfest Theorem

Consider the motion of a particle of mass m described by $\psi(\mathbf{x}, t)$, with ψ satisfying

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

We want to see to what extent we can make a connection between the Schrödinger equation and Newton's Laws, so let's calculate

$$\begin{aligned}
 \frac{d}{dt} \langle \mathbf{p} \rangle &= \frac{d}{dt} \int d^3x \left(\psi^* \frac{\hbar}{i} \nabla \psi \right) \\
 &= \int d^3x \left[\frac{\partial \psi^*}{\partial t} \left(\frac{\hbar}{i} \nabla \psi \right) + \psi^* \left(\frac{\hbar}{i} \nabla \frac{\partial \psi}{\partial t} \right) \right] \\
 &= \int d^3x \left[\left(\frac{\hbar}{i} \nabla \psi \right) \left(-\frac{i\hbar}{2m} \nabla^2 \psi^* + \frac{i}{\hbar} V \psi^* \right) - \psi^* \nabla \left(-\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi \right) \right] \\
 &= \int d^3x \left\{ \frac{\hbar^2}{2m} [\psi^* \nabla^2 \nabla \psi - (\nabla^2 \psi^*) \nabla \psi] + (\nabla \psi) V \psi^* - \psi^* \nabla (V \psi) \right\}. \quad (1.40)
 \end{aligned}$$

Integration by parts, assuming the wave function vanishes fast enough at infinity, enables us to resolve this. Terms with any combination of ψ^* and ψ like

$$\int d^3x \nabla f(\psi^*, \psi) \quad (1.41)$$

are zero as long as ψ vanishes fast enough at infinity. This is just the divergence theorem as is apparent if we introduce a constant vector $\mathbf{A}$

$$\int d^3x \nabla \cdot (\mathbf{A} f(\psi^*, \psi)) = \int d\mathbf{S} \cdot \mathbf{A} f(\psi^*, \psi) = 0, \quad (1.42)$$

where the surface elements $d\mathbf{S}$ are at infinity. Thus

$$\int d^3x \psi^* \nabla^2 \nabla \psi = - \int d^3x [\nabla \psi^*][\nabla^2 \psi] = \int d^3x [\nabla^2 \psi^*][\nabla \psi]. \quad (1.43)$$

Thus, the term in square brackets in Eq. (1.40) vanishes with integration by parts. The last two pieces combine with an integration by parts to leave us with

$$\frac{d}{dt} \langle \mathbf{p} \rangle = - \int d^3x \psi^* (\nabla V) \psi = - \langle \nabla V \rangle, \quad (1.44)$$

which looks a bit like Newton's equation of motion. A more direct connection would have $-\nabla V(\langle \mathbf{x} \rangle)$ in place of $-\langle \nabla V(\mathbf{x}) \rangle$. If $V(\mathbf{x})$ changes slowly enough in $\mathbf{x}$ and $\psi(\mathbf{x}, t)$ is reasonably localized, then we can show the correspondence with $m\dot{\mathbf{x}}_{\text{classical}} = \mathbf{F}_{\text{classical}}$.

Consider the force at $\mathbf{x}$ evaluated by expanding about $\langle \mathbf{x} \rangle$.

$$\begin{aligned}
 \mathbf{F}(\mathbf{x}) &= \mathbf{F}(\langle \mathbf{x} \rangle) + (\mathbf{x} - \langle \mathbf{x} \rangle) \cdot \nabla \mathbf{F}(\langle \mathbf{x} \rangle) \\
 &\quad + \frac{1}{2} \sum_{i,j} (x_i - \langle x_i \rangle)(x_j - \langle x_j \rangle) \frac{\partial^2 \mathbf{F}}{\partial x_i \partial x_j} + \dots \quad (1.45)
 \end{aligned}$$

Then

$$\langle \mathbf{F}(\mathbf{x}) \rangle = \mathbf{F}(\langle \mathbf{x} \rangle) + \frac{1}{2} \sum_{i,j} \langle \Delta x_i \Delta x_j \rangle \frac{\partial^2 \mathbf{F}}{\partial x_i \partial x_j} + \dots \quad (1.46)$$

So if $\mathbf{F}$ doesn't vary too much over the spread of the wave amplitude, our correspondence holds.

1.8 Schrödinger Equation in Momentum Space

We can define a momentum-space wave amplitude by

$$\phi(\mathbf{p}, t) = \frac{1}{(2\pi\hbar)^{3/2}} \int d^3x \psi(\mathbf{x}, t) e^{-i\mathbf{p}\cdot\mathbf{x}/\hbar}. \quad (1.47)$$

What equation does ϕ satisfy? We compute

$$\begin{aligned} i\hbar \frac{\partial \phi}{\partial t} &= \frac{1}{(2\pi\hbar)^{3/2}} \int d^3x i\hbar \frac{\partial \psi}{\partial t} e^{-i\mathbf{p}\cdot\mathbf{x}/\hbar} \\ &= \frac{1}{(2\pi\hbar)^{3/2}} \int d^3x \left[-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi \right] e^{-i\mathbf{p}\cdot\mathbf{x}/\hbar} \\ &= \frac{p^2}{2m} \phi + \frac{1}{(2\pi\hbar)^{3/2}} \int d^3x V\psi e^{-i\mathbf{p}\cdot\mathbf{x}/\hbar}, \end{aligned} \quad (1.48)$$

where we integrated by parts to get the first term. Now suppose that V could be written in a series expansion

$$V = V_i x_i + V_{ij} x_i x_j + \dots, \quad (1.49)$$

where summation over repeated indices is assumed. Then

$$V e^{-i\mathbf{p}\cdot\mathbf{x}/\hbar} = \left[V_i \left(i\hbar \frac{\partial}{\partial p_i} \right) + V_{ij} \left(i\hbar \frac{\partial}{\partial p_i} \right) \left(i\hbar \frac{\partial}{\partial p_j} \right) + \dots \right] e^{-i\mathbf{p}\cdot\mathbf{x}/\hbar}. \quad (1.50)$$

We see, then, that in momentum space the operators are $\mathbf{p}_{\text{op}} = \mathbf{p}$, $\mathbf{x}_{\text{op}} = i\hbar \nabla_{\mathbf{p}}$. So we can write the momentum-space Schrödinger equation as

$$i\hbar \frac{\partial \phi}{\partial t} = \frac{p^2}{2m} \phi + V(\mathbf{x}_{\text{op}}) \phi. \quad (1.51)$$

1.9 Spread in Time of a Free-Particle Wave Packet

If we represent a particle by a wave packet, quantum mechanics, as represented by the Schrödinger equation, results in the spreading of that wave packet. If, in particular, we start with a normalized Gaussian wave packet,

$$\psi(x, t=0) = \frac{e^{-x^2/4\Delta_x^2}}{(2\pi\Delta_x^2)^{1/4}} \quad (1.52)$$

so that

$$\langle x^2 \rangle_{t=0} = \Delta_x^2; \quad \langle p^2 \rangle_{t=0} = \left\langle -\hbar^2 \frac{d^2}{dx^2} \right\rangle_{t=0} = \left(\frac{\hbar}{2\Delta_x} \right)^2, \quad (1.53)$$

we find (see Problem 1.6) that at time t

$$\int_{-\infty}^{\infty} dx \psi(x, t)^* x^2 \psi(x, t) = \Delta_x^2 + \frac{\hbar^2 t^2}{4m^2 \Delta_x^2} = \Delta_x^2 + t^2 \frac{\langle p^2 \rangle_{t=0}}{m^2}. \quad (1.54)$$

More generally, without assuming a Gaussian wave packet, for a given $(\Delta x)_0$, there is an uncertainty in the corresponding momentum $(\Delta p)_0 \sim \hbar/(\Delta x)_0$. This means that $(\Delta v)_0 \approx$

$\frac{\hbar}{m(\Delta x)_0} = \frac{(\Delta p)_0}{m}$. There will be built up in time t a smearing in x of an amount $t(\Delta v)_0$. Thus, the new spreading in the packet is $(\Delta x)_{\text{new}} = [t(\Delta p)_0]/m \sim \hbar t/[m(\Delta x)_0]$. If the original and new Δx 's are combined quadratically (appropriate for uncorrelated effects), we get essentially the above result.

1.10 The Nature of Solutions to the Schrödinger Equation

A free particle can have any momentum and its corresponding energy. If the particle is otherwise free, but confined to a rectangular box by infinitely high potential walls, we constrain the function to vanish at the walls. The result is that only certain momenta are allowed. There are states of arbitrarily high energy, but the states can be counted one-by-one, from the lowest energy on up. The spectrum of states is discrete, whereas, for the completely free particle, any positive energy is possible and the spectrum of states is continuous. A simple inference can be drawn by considering classical analogs. If the motion is bounded, as for the particle in the box, the spectrum of states is discrete. If the motion is unbounded, the spectrum is continuous.

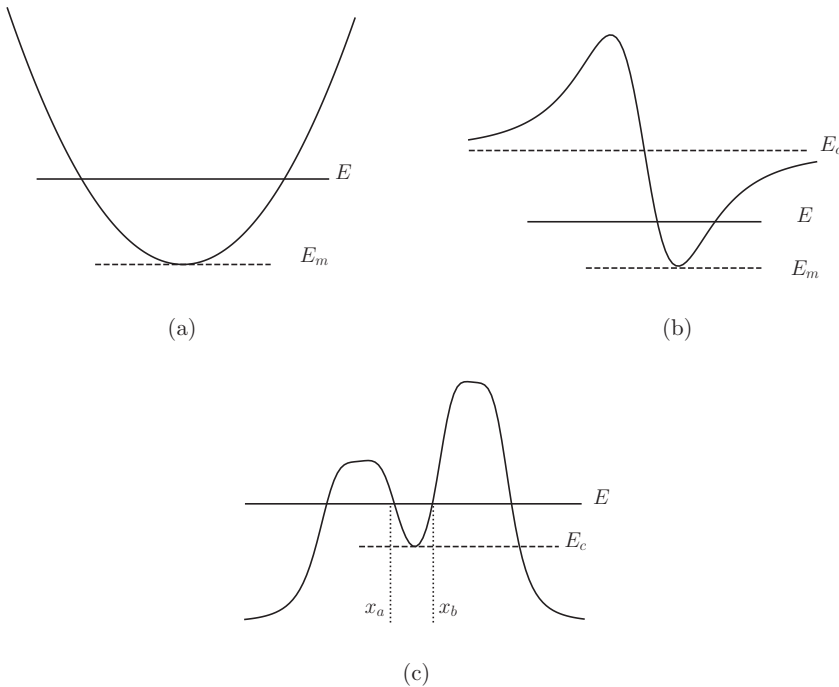


Figure 1.1 Connection between the classical motion of a particle in different potentials and its corresponding eigenvalue spectra. (a) Classical motion bounded in space, denumerable discrete energy eigenvalues with $E_0 > E_m$. (b) For $E_m < E < E_c$, classical motion bounded in space, so denumerable discrete eigenenergies. For $E > E_c$, unbounded classical motion, continuum E_j for $E_j \geq E_c$. (c) Classical motion is bounded between x_a and x_b , but same E has “orbits” that are unbounded. The energy spectrum is continuous. Figures adapted from Gottfried, *Quantum Mechanics: Fundamentals*, p. 50.

These simple observations can be extended to consider more complex potentials. This is illustrated in Figure 1.1.

1.11 A Bound-State Problem: Linear Potential

We consider a quite general Schrödinger equation defined by a Hamiltonian operator

$$H = \frac{p^2}{2m} + V(\mathbf{x}) = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{x}) \quad (1.55)$$

and its associated differential equation

$$H\psi_E(\mathbf{x}) = E\psi_E(\mathbf{x}). \quad (1.56)$$

A solution ψ_E that is physically reasonable in the sense described below determines an *eigenvalue*, E . For any eigenstate ψ_E , the expectation value of any operator not containing time dependence explicitly is independent of time. We therefore speak of a *stationary state*. There is no dispersion in energy since $\langle H^n \rangle = E^n$.

How should the problem of solving the time-independent Schrödinger equation be posed? We want ψ_E to be “reasonable.” One criterion might be $\int |\psi_E|^2 d^3x < \infty$ because ψ_E is a probability density. This is often true, but it is too restrictive. For example, $e^{i\mathbf{p}\cdot\mathbf{x}/\hbar}$ is allowed in some circumstances. However, $\psi_E \propto e^{\alpha x}$ ($\alpha > 0, x \rightarrow \infty$) is not allowed because it says the particle is mostly at infinity.

Some experience can be found in determining numerically solutions to the Schrödinger equation for a linear potential: $V = V_0|x|/a$ for $x > 0$. This is a potential we shall encounter again.

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V_0 \frac{x}{a} \psi = E\psi. \quad (1.57)$$

With the substitutions

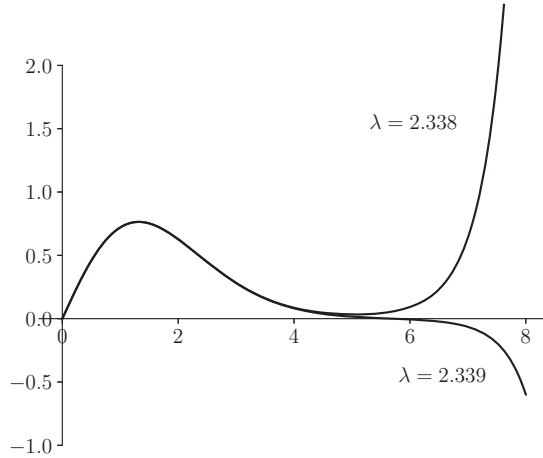
$$y = \left(\frac{2ma^2V_0}{\hbar^2} \right)^{1/3} \frac{x}{a}; \quad \lambda = \left(\frac{2ma^2V_0}{\hbar^2} \right)^{1/3} \frac{E}{V_0}, \quad (1.58)$$

we have the dimensionless form

$$\frac{d^2\psi}{dy^2} - y\psi = -\lambda\psi. \quad (1.59)$$

There are two classes of solutions: ones that are even under $x \rightarrow -x$ ($y \rightarrow -y$) and ones that are odd under this symmetry. The ones that are odd must have $\psi(0) = 0$. To solve the differential equation numerically, one must in this case take some value for $\psi'(0)$ and then integrate in steps of Δx . If the solution is even, then $\psi'(0) = 0$. In either case, there is just one parameter to set at the origin and this is equivalent to setting the scale for ψ . Thus, the only open issue is the value of λ : For what values of λ do we get physically acceptable solutions? In particular, the solution must vanish in the limit $x \rightarrow \infty$.

Figure 1.2 Numerical integration of the linear potential, Eq. (1.59), shows that the first eigenvalue lies between 2.338 and 2.339 if the function is odd in x . The equation can also be solved analytically in terms of the Airy function $Ai(x)$, which will be encountered in a later chapter.



It is convenient to think of the second-order equation as a pair of first-order equations. Without loss of generality, one can take $a = 1$, which is to say that x is measured in units of a .

$$v = \frac{d\psi}{dx}$$

$$\frac{dv}{dx} = (x - \lambda)\psi. \quad (1.60)$$

Whatever the assumed value of λ , upon starting the integration at $x = 0$, at some point the integration reaches the value $x = \lambda$, where the motion is forbidden classically. In general, beyond this point the solution will be the sum of two pieces, one of which dies exponentially in x and the other of which grows exponentially in x . This latter is unacceptable physically. Only for certain values of λ will the solution be purely exponentially dying. These values are the eigenvalues. By varying λ and seeing whether the solution diverges to $+\infty$ or to $-\infty$, one can narrow down the range for λ until a good approximation for the eigenvalue is obtained. See Figure 1.2.

1.12 Sturm-Liouville Eigenvalue Problem

The time-independent Schrödinger equation is ubiquitous. It is therefore worthwhile to consider more generally the properties of the class of differential equations that arise from it.

Sturm-Liouville theory considers the ordinary differential equation in one dimension for $y(x)$:

$$\frac{d}{dx} \left(f(x) \frac{dy}{dx} \right) + g(x)y + \lambda h(x)y = 0 \quad (1.61)$$

for $a < x < b$ with f real and positive on this interval and λ a parameter. We impose boundary conditions $dy/dx = \alpha y$ at $y = a$ and $dy/dx = \beta y$ at $y = b$, with α, β independent of λ . These

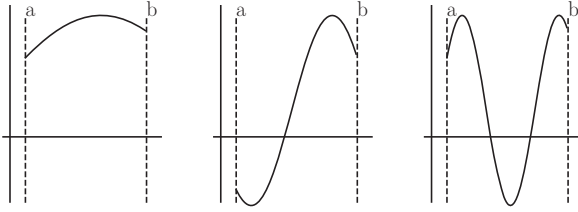


Figure 1.3 Examples showing the homogeneous boundary conditions at a and b : at a , $dy/dx = \alpha y(a)$ and at b , $dy/dx = \beta y(b)$. The chosen values have $\alpha > 0$, $\beta < 0$ and $\alpha = 2|\beta|$. With each increasing eigenvalue, the number of nodes of the eigenfunction increases by one.

are homogeneous boundary conditions in that if $y(x)$ is a solution, so is any constant times $y(x)$ (See Figure 1.3.). The Schrödinger equations we will encounter will often have $f(x) = 1$ and $\alpha = \beta = 0$ as special examples of the more general theory.

One can prove the following (see, e.g. Margenau and Murphy, *The Mathematics of Physics and Chemistry*, Vol.1, 2nd edition, pp. 270 ff., Morse and Feshbach, *Methods of Theoretical Physics*, pp. 736–739 or pp. 720–24, Courant and Hilbert, *Methods of Mathematical Physics*, Chap. V):

If $f(x)$ and $h(x)$ are positive on the interval, solutions $y_j(x)$ exist only for a countably infinite discrete set of eigenvalues λ_j with a smallest non-negative member λ_0 . The eigenvalues have no upper bound as $j \rightarrow \infty$. The solutions are called eigenfunctions with eigenvalues λ_j . Eigenfunctions with increasing energy have an increasing number of nodes. We shall see this is a recurring feature of relevant solutions to the Schrödinger equation.

Moreover, if we order the solutions by $\lambda_{j+1} > \lambda_j$, then the number of nodes (zeros) of f_j in the interval (a, b) is j . Writing the equation twice and multiplying by y_i^* and y_j we find

$$\begin{aligned} \int_a^b dx \left\{ y_i^* \frac{d}{dx} \left(f(x) \frac{dy_j}{dx} \right) + [g(x) + \lambda_j h(x)] y_i^* y_j \right\} &= 0 \\ \int_a^b dx \left\{ y_j \frac{d}{dx} \left(f(x) \frac{dy_i^*}{dx} \right) + [g(x) + \lambda_i^* h(x)] y_i^* y_j \right\} &= 0. \end{aligned} \quad (1.62)$$

Now subtracting

$$\int_a^b dx \left\{ y_i^* \frac{d}{dx} \left(f(x) \frac{dy_j}{dx} \right) - y_j \frac{d}{dx} \left(f(x) \frac{dy_i^*}{dx} \right) + (\lambda_j - \lambda_i^*) h(x) y_i^* y_j \right\} = 0. \quad (1.63)$$

Integration by parts gives

$$\begin{aligned} &\int_a^b dx \left\{ y_i^* \frac{d}{dx} \left(f(x) \frac{dy_j}{dx} \right) - y_j \frac{d}{dx} \left(f(x) \frac{dy_i^*}{dx} \right) \right\} \\ &= f(x) \left[y_j \frac{dy_i^*}{dx} - y_i^* \frac{dy_j}{dx} \right] \Big|_a^b = 0 \\ &= -(\lambda_j - \lambda_i^*) \int_a^b dx h(x) y_i^* y_j. \end{aligned} \quad (1.64)$$

The vanishing of the term at the end points is a consequence of the boundary conditions $dy/dx = \alpha y$ at $y = a$ and $dy/dx = \beta y$ at $y = b$. It follows that the eigenfunctions for different eigenvalues are orthogonal on the interval (a, b) with the weight $h(x)$. If instead $i = j$, we see that $\Im \lambda_i = 0$, that is, the eigenvalues are real. It can be proved that the eigenfunctions in fact are complete: any “reasonable” function satisfying the same boundary conditions can be expanded as a linear combination of the eigenfunctions. For a proof, see, for example, Morse and Feshbach, *Methods of Theoretical Physics*, pp. 738–9.

1.13 Linear Operators on Functions

The Sturm-Liouville problem is an example of a more general eigenvalue problem with linear operators, i.e. an operator K on functions $f, g, \dots$ such that for constants α and β

$$K(\alpha f(x) + \beta g(x)) = \alpha K(f(x)) + \beta K(g(x)). \quad (1.65)$$

Examples:

$$K(f(x)) = 5f(x); \quad K(f(x)) = \frac{d^3 f}{dx^3} + 7f(x). \quad (1.66)$$

Another particular example is the integral operator

$$K(f(x)) = \int_a^b dx' k(x, x') f(x'). \quad (1.67)$$

Suppose we define a scalar product of two functions by

$$(f, g) = \int_a^b dx g^*(x) f(x) = (g, f)^*. \quad (1.68)$$

Given a linear operator K , we define its adjoint by

$$(K^\dagger g, f) = (g, Kf). \quad (1.69)$$

In the case of our integral operator we see that we need to take

$$k^\dagger(x, x') = k(x', x)^*. \quad (1.70)$$

This is analogous to the usual meaning of adjoint for matrices: $A_{ij}^\dagger = A_{ji}^*$. An operator is self-adjoint or Hermitian if $K^\dagger = K$. In this case

$$(f, Kf) = (K^\dagger f, f) = (Kf, f) = (f, Kf)^*, \quad (1.71)$$

that is, the expectation value $\langle K \rangle$ of a Hermitian operator K is real. Conversely, if we want an operator to represent a physical quantity, it must be Hermitian. For an anti-Hermitian operator we have $K^\dagger = -K$. If K is Hermitian, then iK is anti-Hermitian.

1.14 Eigenvalue Problem for a Hermitian Operator

We suppose K is a Hermitian operator on functions on an interval (a, b) with some boundary conditions. If we indicate a function by ξ , then the eigenvalue problem is

$$K\xi_j = \lambda_j \xi_j. \quad (1.72)$$

We know the λ_j are real because

$$\lambda_j = \frac{(\xi_j, K\xi_j)}{(\xi_j, \xi_j)} \quad (1.73)$$

and both the numerator and denominator are real. If K is Hermitian then

$$(\xi_j, K\xi_i) = \lambda_i(\xi_j, \xi_i) = (K^\dagger \xi_j, \xi_i) = (K\xi_j, \xi_i) = \lambda_j^*(\xi_j, \xi_i). \quad (1.74)$$

Since the eigenvalues are real

$$(\lambda_i - \lambda_j)(\xi_j, \xi_i) = 0. \quad (1.75)$$

Thus if the eigenvalues are different, then the eigenfunctions are orthogonal. In general, it is possible that there are linearly independent eigenfunctions with the same eigenvalue, in which case orthogonality doesn't follow. This won't happen in the specific instance at hand, a one-dimensional differential equation with boundary conditions.

We now show how this formalism can incorporate the Sturm-Liouville problem. We take

$$K = \frac{d}{dx} \left(f(x) \frac{d}{dx} \right) + g(x) + \lambda \quad (1.76)$$

and ask under what conditions K is Hermitian.

$$\begin{aligned} (\eta, K\xi) &= \int_a^b \eta^* \left[\frac{d}{dx} \left(f(x) \frac{d\xi}{dx} \right) + g(x)\xi + \lambda\xi \right] dx \\ &= f \left(\eta^* \frac{d\xi}{dx} - \xi \frac{d\eta^*}{dx} \right) \Big|_a^b + \int_a^b \left[\frac{d}{dx} \left(f^* \frac{d\eta}{dx} \right) + g^* \eta + \lambda^* \eta \right]^* \xi dx. \end{aligned} \quad (1.77)$$

We want the first term to vanish and the second term to be equal to $(K\eta, \xi)$. The latter is achieved if f, g, λ are all real. For the former, it suffices for $f = 0$ at a and b , or alternatively, for

$$\left(\frac{1}{\eta^*} \frac{d\eta^*}{dx} \right)_{a,b} = \left(\frac{1}{\xi} \frac{d\xi}{dx} \right)_{a,b}. \quad (1.78)$$

These are precisely the conditions we postulated in the treatment above of the Sturm-Liouville problem.

1.15 Variational Methods for Energy Eigenvalues

A powerful method of generating approximate energies of quantum mechanical systems is the so-called variational technique – Rayleigh-Ritz method is another term. Rayleigh used it in acoustics. We phrase it terms of the Schrödinger equation and energy eigenvalues, but it has very general applicability.

Consider a well-posed energy eigenvalue problem:

$$H\psi_n = E_n\psi_n \quad (1.79)$$

with a spectrum of eigenvalues $E_n = E_0, E_1 > E_0, E_2 > E_1, \dots$, with corresponding eigenfunctions $\psi_0, \psi_1, \psi_2, \dots$, but suppose we do not know the eigenvalues or eigenfunctions. Suppose that we are somehow given a function ψ that is not too far from the correct wave function ψ_0 . We can form the quantity

$$[E] = \frac{\int dx \psi^* H \psi}{\int dx \psi^* \psi}, \quad (1.80)$$

where x might be one-dimensional or three-dimensional and ψ is some trial function, obeying the boundary conditions. What can we say about $[E]$ as an estimate of E_0 ? Two things:

- (i) $[E] \geq E_0$
- (ii) If ψ differs from the true solution by a small amount, characterized by ϵ , so $\psi = \psi_0 + \epsilon\phi$ then $[E] - E_0 = \mathcal{O}(\epsilon^2)$.

This means that $[E]$ is stationary with respect to small variations away from the true eigenfunction, ψ_0 .

To prove this, expand ψ in the basis of true eigenfunctions

$$\psi = \sum_n a_n \psi_n, \quad (1.81)$$

where we assume orthonormality of the eigenfunctions

$$\int dx \psi_m^* \psi_n = \delta_{mn} \quad (1.82)$$

and that ψ is normalized:

$$\sum_n |a_n|^2 = 1. \quad (1.83)$$

Then immediately

$$[E] = \sum_n |a_n|^2 E_n = \sum_n |a_n|^2 E_0 + \sum_n |a_n|^2 (E_n - E_0) \quad (1.84)$$

$$= E_0 + \sum_n |a_n|^2 (E_n - E_0) \geq E_0. \quad (1.85)$$

Now consider a trial wave function that is near the true one

$$\psi = \psi_0 + \epsilon\phi \quad (1.86)$$

where ψ_0 and ϕ are normalized: $\int dx |\psi_0|^2 = 1$; $\int dx |\phi|^2 = 1$. It suffices to consider only a ϕ that is orthogonal to ψ_0 since any part of ϕ that is not can be absorbed into ψ , after which we can renormalize so that the coefficient of ψ_0 is unity. Now expand the expression for $[E]$, but impose the normalization by dividing by $\int dx |\psi|^2$.

$$\begin{aligned}
[E] &= E_0 + \delta E = \frac{\int dx \psi_0^* H \psi_0 + \epsilon^* \int dx \phi^* H \psi_0 + \epsilon \int dx \psi_0^* H \phi + |\epsilon|^2 \int dx \phi^* H \phi}{\int dx \psi_0^* \psi_0 + \epsilon^* \int dx \phi^* \psi_0 + \epsilon \int dx \psi_0^* \phi + |\epsilon|^2 \int dx \phi^* \phi} \\
&= \frac{E_0 \int dx \psi_0^* \psi_0 + E_0 \epsilon^* \int dx \phi^* \psi_0 + E_0 \epsilon \int dx \psi_0^* \phi + |\epsilon|^2 \int dx \phi^* H \phi}{\int dx \psi_0^* \psi_0 + \epsilon^* \int dx \phi^* \psi_0 + \epsilon \int dx \psi_0^* \phi + |\epsilon|^2 \int dx \phi^* \phi}.
\end{aligned} \tag{1.87}$$

Then to order ϵ^2 we have

$$E_0 + \delta E \approx \left(E_0 + |\epsilon|^2 \int dx \phi^* H \phi \right) (1 - |\epsilon|^2), \tag{1.88}$$

so that

$$\delta E = |\epsilon|^2 \left(\int dx \phi^* H \phi - E_0 \int dx \phi^* \phi \right) \geq 0, \tag{1.89}$$

where the inequality follows from the observation that if it were not true then ϕ would have lower energy than the ground state. If we can make a good guess at ψ_0 with ψ , then we will get a good estimate of E_0 . This approach is systematized in the Rayleigh-Ritz method.

1.16 Rayleigh-Ritz Method

We construct a “trial” eigenfunction $\psi(\alpha_i, x)$, with α_i a set of n variational parameters. Then we form the functional

$$[E(\alpha_i)] = \frac{\int dx \psi^*(\alpha_i, x) H \psi(\alpha_i, x)}{\int dx \psi^*(\alpha_i, x) \psi(\alpha_i, x)} \tag{1.90}$$

of the parameters α_i . We know that $[E(\alpha_i)] \geq E_0$, with equality only for $\psi(\alpha_i, x) = \psi_0(x)$. We therefore vary the parameters to find a minimum, where we must have

$$\frac{\partial [E(\alpha_i)]}{\partial \alpha_j} = 0, \quad j = 1, 2, \dots, n. \tag{1.91}$$

The solution to these simultaneous equations yields the optimal value for E_0 possible within the limitations of the form of our trial function.

As a very simple example, let us seek the energy of the ground state in a one-dimensional box, $0 \leq x \leq 1$ and take $\psi(x) = [x(1-x)]^\alpha$. Then

$$[E] = \frac{\int dx \psi^* \frac{p^2}{2m} \psi}{\int dx \psi^* \psi} = \frac{\hbar^2}{2m} \frac{\int_0^1 dx |\psi'|^2}{\int_0^1 dx |\psi|^2}. \tag{1.92}$$

Since

$$\psi' = \alpha x^{\alpha-1} (1-x)^{\alpha-1} (1-2x) \tag{1.93}$$

we find

$$\frac{2m}{\hbar^2} [E] = \frac{\alpha^2 \int_0^1 dx x^{2\alpha-2} (1-x)^{2\alpha-2} (1-4x+4x^2)}{\int_0^1 dx x^{2\alpha} (1-x)^{2\alpha}}. \tag{1.94}$$

With the standard integral

$$\int_0^1 dx x^{m-1} (1-x)^{n-1} \equiv \beta(m, n) = \frac{\Gamma(m)\Gamma(n)}{\Gamma(m+n)}, \quad (1.95)$$

where the gamma function

$$\Gamma(z) = \int_0^\infty dt t^{z-1} e^{-t} \quad (1.96)$$

has the properties

$$z\Gamma(z) = \Gamma(z+1); \quad \Gamma(n) = (n-1)! \text{ for } n \text{ a positive integer} \quad (1.97)$$

we find

$$\frac{2m}{\hbar^2} [E] = \frac{(2\alpha)(4\alpha+1)}{2\alpha-1}. \quad (1.98)$$

The requirement $\partial E / \partial \alpha = 0$ gives

$$\alpha^2 - \alpha - \frac{1}{8} = 0; \quad a = \frac{1}{2} \left(1 + \sqrt{\frac{3}{2}} \right) = 1.11237 \quad (1.99)$$

and

$$\frac{2m[E]_{\min}}{\hbar^2} = 9.89898 \dots, \quad (1.100)$$

while the exact result is $\pi^2 = 9.86960 \dots$, a 0.3% error. The moral is that even simple choices for the trial wave function can give remarkably good results for the ground state energy.

References and Suggested Reading

There are numerous accounts of the history of quantum mechanics. Some particularly notable ones written by physicists are:

Gamow, G. *Thirty Years that Shook Physics*. New York: Doubleday.

Pais, A. *Inward Bound: Of Matter and Forces in the Physical World*. Oxford University Press.

Segrè, G. *Faust in Copenhagen: A Struggle for the Soul of Physics*, Viking. New York.

Every student of quantum mechanics should thrill to the remarkable story told in these books.

For classic presentations of mathematical physics:

Courant and Hilbert, *Methods of Mathematical Physics*.

Margenau and Murphy, *The Mathematics of Physics and Chemistry*, Vol.1, 2nd edition.

Morse and Feshbach, *Methods of Theoretical Physics*.

Problems

1.1 A one-dimensional wave amplitude $\psi(x, t)$ is given by

$$\psi(x, 0) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dp \phi(p) e^{ipx/\hbar} \quad (1.101)$$

with

$$\phi(p) = \sqrt{\frac{2}{\pi\hbar}} \frac{\alpha^{3/2}}{(p - p_0)^2 + \alpha^2}. \quad (1.102)$$

- (a) Find $\psi(x, 0)$ and sketch $\phi(p)$ and $\Re \psi(x, 0)$. What is the significance of α and $1/\alpha$?
- (b) Find $\langle p \rangle$, $\langle p^2 \rangle$, $\langle x \rangle$, and $\langle x^2 \rangle$.
- (c) Show from the results of (b) that the r.m.s. deviations Δx and Δp satisfy $\Delta x \Delta p > \hbar/2$, independent of α .

1.2 A particle is in the ground state of a one-dimensional box of length L . with wave amplitude given by

$$\psi(x, t) = \sqrt{2/L} \sin(\pi x/L) e^{-i\pi^2 \hbar t/(2mL^2)}. \quad (1.103)$$

At $t = 0$ the walls are suddenly dissolved and the particle subsequently moves freely. What is the probability that, after $t = 0$, the particle's momentum is between p and $p + dp$? Sketch fairly accurately $|\phi(p)|^2$ versus p .

1.3 An anti-proton can be bound to a proton by electromagnetic interaction to form a hydrogenic atomic system. At short distances ($r \leq 10^{-13}$ cm) the interaction is augmented by strong forces, including annihilation.

- (a) Neglecting annihilation and other strong-interaction effects, scale the $\bar{p}p$ system appropriately from the e^-p atom and compute the Bohr radius, and the spacing between the $1s$ and $2p$ levels, in keV.
- (b) From the known $2p \rightarrow 1s$ transition probability in hydrogen ($\Gamma(2p \rightarrow 1s) = 6.2 \times 10^8 \text{ sec}^{-1}$) and the scaling properties of the Larmor (electric dipole) radiation formula, find the corresponding transition probability for the $\bar{p}p$ atom.

1.4 A particle with mass m and charge e interacts with a real potential $V(\mathbf{x})$ and also an external electromagnetic field described by the real potentials $\mathbf{A}$ and Φ . The Schrödinger equation is

$$i\hbar \frac{\partial \psi}{\partial t} = \frac{1}{2m} (\mathbf{p}_{\text{op}} - \frac{e}{c} \mathbf{A})^2 \psi + V\psi + e\Phi\psi \quad (1.104)$$

Show that the normal expression for the probability current $\mathbf{J}$ is augmented by the term

$$\Delta \mathbf{J} = -\frac{e}{mc} \psi^* \mathbf{A} \psi. \quad (1.105)$$

Interpret.

1.5* (a) Show that a free-particle wave amplitude $\psi(\mathbf{x}, t)$ evolves in time from the amplitude $\psi(\mathbf{x}', t')$ according to

$$\psi(\mathbf{x}, t) = \int d^3x' \psi(\mathbf{x}', t') K(\mathbf{x} - \mathbf{x}', t - t'), \quad (1.106)$$

where the kernel (propagation function) is given by the Fourier integral

$$K(\mathbf{r}, \tau) = \frac{1}{(2\pi\hbar)^3} \int d^3p \exp\left(i\frac{\mathbf{p} \cdot \mathbf{r}}{\hbar} - i\frac{p^2\tau}{2m\hbar}\right). \quad (1.107)$$

(b) As a preliminary to evaluating this integral, prove that

$$\lim_{\epsilon \rightarrow 0} \int_{-\infty}^{\infty} d\xi e^{-i\xi^2} e^{-\epsilon\xi^2} = \sqrt{\pi} e^{-i\pi/4} = \sqrt{\pi/i}. \quad (1.108)$$

(c) Show that

$$K(\mathbf{r}, \tau) = \left(\frac{m}{2\pi i\hbar\tau}\right)^{3/2} \exp\left(-\frac{m\mathbf{r}^2}{2i\hbar\tau}\right). \quad (1.109)$$

1.6 Suppose that at $t = 0$, a one-dimensional wave amplitude is

$$\psi(x, 0) = A e^{-x^2/4(\Delta x)_0^2}. \quad (1.110)$$

Using the one-dimensional analog of the solution to Problem 1.5, show that the amplitude at a later time t has the form

$$\psi(x, t) \propto \exp\left[-\frac{x^2}{4(\Delta x)_t^2} \left(1 - \frac{i\hbar t}{2m(\Delta x)_0^2}\right)\right]. \quad (1.111)$$

where

$$(\Delta x)_t^2 = (\Delta x)_0^2 + \frac{\hbar^2 t^2}{4m^2(\Delta x)_0^2} \quad (1.112)$$

is the r.m.s. spread in $|\psi(x, t)|^2$.

1.7 (a) By explicit construction with the Schrödinger equation, show that for any wave amplitude $\psi(\mathbf{x}, t)$

$$\frac{d}{dt} \langle x^2 \rangle = \frac{1}{m} \langle x p_x + p_x x \rangle, \quad (1.113)$$

where $p_x = (\hbar/i)\partial/\partial x$.

(b) Similarly, show that

$$\frac{d}{dt} \langle \mathbf{r} \cdot \mathbf{p} \rangle = 2 \left\langle \frac{p^2}{2m} \right\rangle - \langle \mathbf{r} \cdot \nabla V \rangle. \quad (1.114)$$

This is the basis for the quantum mechanical virial theorem (for energy eigenstates only).

1.8 The power of the variational method can be illustrated by estimating the ground state energies of the hydrogen atom and the isotropic harmonic oscillator, using trial wave functions that are appropriate to the corresponding potential. For the ground state, the

angular momentum is zero and the wave function depends only on r . We can write the Schrödinger equation as

$$\left(-\frac{\hbar^2}{2m} \frac{1}{r} \frac{d^2}{dr^2} r + V(r) \right) \psi = E\psi. \quad (1.115)$$

It is conventional to introduce a radial wave function $u = r\psi$ so that the equation is

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + V(r)u = Eu \quad (1.116)$$

and $u(r)$ must vanish at $r = 0$.

Use a variational principle for the radial wave-function $u(r)$ in an s-wave state.

(a) For the hydrogen atom, take a trial wave function of the form

$$u(r) = re^{-r^2/4b^2}, \quad (1.117)$$

where b is the parameter to be varied. Find the best value of b/a_0 and the corresponding binding energy. How accurate is the estimate?

(b) For the three-dimensional isotropic oscillator, take a trial wave function

$$u(r) = re^{-r/2d}, \quad (1.118)$$

where d is the variational parameter. Find the optimal value of d and the corresponding energy. How accurate is the estimate?

1.9 A hydrogen atom is confined in a spherical box of radius Ra_0 , with the proton at the center. In atomic units, the radial equation for s-states is

$$-\frac{1}{2} \frac{d^2 u}{dx^2} - \frac{u}{x} = Eu, \quad (1.119)$$

where $x = r/a_0$ and $u(0) = u(R) = 0$. Make a variational estimate of the ground state energy as a function of R using the trial wave function

$$u(x) = x(1 - x/R)^b, \quad (1.120)$$

where b is a variational parameter. Find the value of R when the atom has zero binding energy. Find the values of E for $R \gg 1$ and $R \ll 1$, and compare with known results. For positive binding energies, plot the energy as a function of R .

Hint: the variational energy takes the form, $E = R^{-2}f(b) - R^{-1}g(b)$. The stationary point is specified by a relation of the form $R = h(b)$. Rather than solving for b , choose a series of values of b , determine each corresponding R and $E(R(b), b)$.