

Chapter 3

Foundations of Complex Mechanics

Chapter Outline

3.1 Quantum Hamilton Mechanics	56
3.2 Dynamical Representation of Quantum State	58
3.3 Complex Variables and Quantum Operators	61
3.4 Orbital and Spin Angular Momentum	66
3.5 Complex Hamiltonian and Complex Energy	74
3.6 Chapter Summary	78
3.7 Problems	78

Quantum mechanics had been established from the following two postulates:

- (1) Postulate of correspondence: to any self-consistent and well-defined observables A , there corresponds an operator \hat{A} .
- (2) Postulate of quantization: The operator \hat{A} corresponds to the observable $A(\mathbf{q}, \mathbf{p})$ can be constructed by replacing the coordinate \mathbf{q} and momentum \mathbf{p} in the expression for A by the assigned operators $\mathbf{q} \rightarrow \hat{\mathbf{q}} = \mathbf{q}$ and $\mathbf{p} \rightarrow \hat{\mathbf{p}} = -i\hbar\nabla$.

The validity of the two postulates was justified indirectly via the voluminous precise predictions of quantum mechanics. Although the two postulates work very successfully, until now, we still do not know why they should work and a formal proof of their origin still lacks. We also do not know very clearly about the underlying reason that to obtain the correct operators in coordinate system other than Cartesian coordinates, it is always necessary to transform $A(\mathbf{q}, \mathbf{p})$ into Cartesian coordinates before putting in the operators. This chapter aims to prove the two postulates by the first principle of Hamilton mechanics, to expound the reason why the postulate of quantization is only true in the Cartesian coordinates, to demonstrate how to obtain directly quantum operators in spherical coordinates without transforming back to Cartesian coordinates..

3.1 Quantum Hamilton Mechanics

The main idea of the complex mechanics is based on the equivalence between a complex observable $A(\mathbf{q}, \mathbf{p})$ in Hamilton mechanics and its associated operator \hat{A} in quantum mechanics, where (\mathbf{q}, \mathbf{p}) are canonical variables defined in complex domain. Based on this equivalence and the requirement that the behavior of $A(\mathbf{q}, \mathbf{p})$ must obey Hamilton equations, we can determine the expression and the various quantization properties of \hat{A} directly from Hamilton equations of motion, regardless of the coordinate system being used. The Hamilton equations considered here are derived from a quantum Hamiltonian H , which is different from the classical one. To find out the correct quantum Hamiltonian, we first recall a classical result that for a given classical Hamiltonian $H_c(t, \mathbf{q}, \mathbf{p})$, the classical Hamilton-Jacobi (H-J) equation reads

$$\frac{\partial S_c}{\partial t} + H_c(t, \mathbf{q}, \mathbf{p})|_{\mathbf{p}=\nabla S_c} = 0, \quad (3.1.1)$$

where S_c is the classical action function. We may regard the classical H-J equation as the short wavelength limit of Schrödinger equation (Goldstein, 1980):

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi, \quad (3.1.2)$$

as can be seen via the following transformation

$$\psi = \exp(iS / \hbar), \quad (3.1.3)$$

from which Schrödinger equation becomes

$$\frac{\partial S}{\partial t} + \left[\frac{1}{2m} (\nabla S)^2 + V \right] = \frac{i\hbar}{2m} \nabla^2 S. \quad (3.1.4)$$

We recognize the quantity in brackets as the classical Hamiltonian for a single particle described in Cartesian coordinates. Eq.(3.1.4) is known as the quantum H-J equation, which reduces to the classical H-J equation (3.1.1) if the right-hand side of Eq.(3.1.4) is negligible, which means that the wavelength of the matter wave is so short that the momentum changes by a negligible fraction over a distance of wavelength (Goldstein, 1980). The transformation (3.1.3) was first introduced by Schrödinger in transforming the phase function $\phi = S/h$ governed by Fresnel's wave equation to the wavefunction ψ governed by Schrödinger's wave equation.

If we treat Eq.(3.1.4) as the quantum-mechanical counterpart of the classical H-J equation (3.1.1), it is natural to ask what will be the corresponding quantum-mechanical counterpart of the classical Hamiltonian H_c . Rewriting Eq.(3.1.4) in a form analogous to Eq.(3.1.1):

$$\frac{\partial S}{\partial t} + H(t, \mathbf{q}, \mathbf{p}) \Big|_{\mathbf{p}=\nabla S} = 0, \quad (3.1.5)$$

we obtain the desired quantum Hamiltonian H , compatible with Schrödinger equation, as

$$H(\psi) = \frac{1}{2m} \mathbf{p}^2 + V(\mathbf{q}) + Q(\psi(\mathbf{q})), \quad (3.1.6)$$

where Q is known as quantum potential defined by

$$Q(\psi(\mathbf{q})) = \frac{\hbar}{2mi} \nabla \cdot \mathbf{p} = \frac{\hbar}{2mi} \nabla^2 S = -\frac{\hbar^2}{2m} \nabla^2 \ln \psi(\mathbf{q}). \quad (3.1.7)$$

The usage of the notation $H(\psi)$ is to emphasize the state-dependent nature of the quantum Hamiltonian H . The classical Hamiltonian H_c depends only on the externally applied potential $V(\mathbf{q})$, whereas the quantum Hamiltonian $H(\psi)$ depends on $V(\mathbf{q})$ as well as on the internal state ψ where the particle lies. For a given state described by $\psi(\mathbf{q})$, the quantum Hamiltonian $H(\psi)$ defined in Eq.(3.1.6) is an explicit function of the canonical variables \mathbf{q} and \mathbf{p} that are regarded as independent variables. There are two roles played by the wavefunction ψ in the quantum Hamiltonian H . Firstly, as indicated in Eq.(3.1.5), it determines the canonical momentum p_j according to

$$p_j = \frac{\partial S}{\partial q_j} = -i\hbar \frac{\partial \ln \psi}{\partial q_j}. \quad (3.1.8)$$

Secondly, it generates the quantum potential Q according to Eq.(3.1.7). The equations of motion for a particle moving in the quantum state ψ are derived by applying the quantum Hamiltonian H to the Hamilton equations

$$\frac{d\mathbf{q}}{dt} = \frac{\partial H(\psi)}{\partial \mathbf{p}} = \frac{1}{m} \mathbf{p}, \quad (3.1.9a)$$

$$\frac{d\mathbf{p}}{dt} = -\frac{\partial H(\psi)}{\partial \mathbf{q}} = -\frac{\partial}{\partial \mathbf{q}} \left[V(\mathbf{q}) - \frac{\hbar^2}{2m} \nabla^2 \ln \psi(\mathbf{q}) \right]. \quad (3.1.9b)$$

Note that as in classical Hamilton mechanics, we have obtained $\partial H / \partial \mathbf{p}$ and $\partial H / \partial \mathbf{q}$ by treating \mathbf{q} and \mathbf{p} as independent variables in the Hamiltonian H in Eq.(3.1.6). The Hamilton equations (3.1.9) are distinct from the classical ones in two aspects: the complex nature and the state-dependent nature. The complex nature is a consequence of the fact that the canonical variables (\mathbf{q}, \mathbf{p}) solved from Eq.(3.1.8) and Eqs.(3.1.9) are, in general, complex variables. The state-dependent nature means that the Hamilton equations of motion (3.1.9) govern the quantum motion exclusively in the specific quantum state described by ψ . We will show in the subsequent sections and chapters that all the quantum operators and the various quantum effects can be derived from the complex canonical

momentum in Eq.(3.1.8) and from the complex-extended Hamilton equations of motion in Eqs.(3.1.9).

In the next section, we first discuss the meanings of a wavefunction in Hamilton mechanics by pointing out that each wavefunction ψ represents a dynamic system described by Eqs.(3.1.9). Hence, information contained in ψ can be extracted from the dynamic system (3.1.9) using methods developed in analytical mechanics. Section 2.3 establishes the relationship between a complex observable $A(\mathbf{q}, \mathbf{p})$ in Hamilton mechanics and its associated operator \hat{A} in quantum mechanics. This relationship allows us to derive any operator \hat{A} from its counterpart complex function $A(\mathbf{q}, \mathbf{p})$ in Hamilton mechanics and to express the commutator $[\hat{A}, \hat{B}]$ in terms of the Poisson bracket $\{A, B\}$ in Hamilton mechanics. Hamilton equations of motion (3.1.9) are valid only for Cartesian coordinates. In Section 2.4, we derive quantum operators and Hamilton equations of motion in spherical coordinates, based on which we will allow us to solve quantum central-force problems, such as the electron motion in hydrogen atom, in Chapter 9. Quantum operators expressed in general curvilinear coordinates and in the presence of electromagnetic field are derived from the Hamilton equations of motion in chapter 12.

3.2 Dynamical Representation of Quantum State

In the framework of quantum Hamilton mechanics, a wavefunction ψ is not merely an abstract function in an infinite-dimensional vector space; it also represents a concrete dynamic system.

Definition 3.2.1

The quantum state assigned by a wavefunction ψ is a dynamic system whose phase-space trajectory $(\mathbf{q}(t), \mathbf{p}(t))$ obeys the Hamilton equations (3.1.9) with the Hamiltonian H given by Eq.(3.1.6). \square

According to this definition, when we say that a quantum observable $A(\mathbf{q}, \mathbf{p})$ is evaluated in the state ψ_0 , it actually means that $A(\mathbf{q}, \mathbf{p})$ is evaluated along a phase-space trajectory $(\mathbf{q}(t), \mathbf{p}(t))$ determined from Eqs.(3.1.9) with H specified by ψ_0 . On solving $(\mathbf{q}(t), \mathbf{p}(t))$ from Eqs.(3.1.9), it can be shown as in the following theorem that the solution for \mathbf{p} is already given by Eq.(3.1.8); that is to say, the solution of Schrödinger equation, ψ , provides the first integration of the Hamilton equations (3.1.9).

Theorem 3.2.1.

For a given solution ψ of Schrödinger equation, the quantum momentum \mathbf{p} determined from Eq.(3.1.8) and the quantum potential $Q(\psi(\mathbf{q}))$ determined from Eq.(3.1.7), satisfy automatically the quantum Newton equation (3.1.9b), i.e.,

$$\dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{q}} = -\frac{\partial}{\partial \mathbf{q}}(V + Q). \quad (3.2.1)$$

Proof: We shall start with Eq.(3.1.5) and show that it leads directly to Eq.(3.1.9b). The total differentiation of Eq.(3.1.5) with respect to the Cartesian coordinates $\mathbf{q} = (q_1, q_2, \dots, q_N)$ reads

$$\frac{d}{dq_i} \left(\frac{\partial S}{\partial t} + H \right) = 0, \quad i = 1, 2, \dots, N, \quad (3.2.2)$$

where with $S = S(t, \mathbf{q})$, we have $d(\partial S / \partial t) / dq_i = \partial^2 S / \partial q_i \partial t$, while with $H = H(t, \mathbf{q}, \mathbf{p}(\mathbf{q}))$, we have

$$\frac{dH}{dq_i} = \frac{\partial H}{\partial q_i} + \sum_{k=1}^N \frac{\partial H}{\partial p_k} \frac{\partial p_k}{\partial q_i}, \quad (3.2.3)$$

with p_k given by Eq.(3.1.8) as $p_k = \partial S / \partial q_k$. Assuming that S is twice continuously differentiable with respect to q_k , we may rewrite $\partial p_k / \partial q_i$ as

$$\frac{\partial p_k}{\partial q_i} = \frac{\partial}{\partial q_i} \frac{\partial S}{\partial q_k} = \frac{\partial}{\partial q_k} \frac{\partial S}{\partial q_i} = \frac{\partial p_i}{\partial q_k}. \quad (3.2.4)$$

Inserting the above identity and Eq.(3.1.9a) into Eq.(3.2.3) yields

$$\frac{dH}{dq_i} = \frac{\partial H}{\partial q_i} + \sum_{k=1}^N \frac{\partial p_i}{\partial q_k} \dot{q}_k$$

from which Eq.(3.2.2) becomes

$$\frac{\partial p_i}{\partial t} + \sum_{k=1}^N \frac{\partial p_i}{\partial q_k} \dot{q}_k = -\frac{\partial H}{\partial q_i}.$$

This is just Eq.(3.1.9b) by noting that the left-hand side is equal to dp_i/dt , the total differentiation of p_i with respect to time t . \square

The inverse of Theorem 3.2.1 is also true, i.e. starting with Hamilton equations (3.1.9) and assuming the solution of p in the form of Eq.(3.1.8), we can show that the to-be-determined functions S and ψ satisfy the quantum H-J equation (3.1.5) and the Schrödinger equation (3.1.2), respectively.

Example 3.2.1

As an illustrating example of Theorem 3.2.1, we consider the dynamic systems corresponding to the quantum states of harmonic oscillator. The Hamiltonian (3.1.6) with $V = Kx^2/2$ has the form

$$H(\psi_n) = \frac{1}{2m} p^2 + \frac{1}{2} Kx^2 - \frac{\hbar^2}{2m} \frac{d^2}{dx^2} \ln \psi_n(x). \quad (3.2.5)$$

The eigenfunction $\psi_n(x)$ for harmonic oscillator is found to be

$$\psi_n(x) = C_n H_n(\alpha x) e^{-\alpha x^2/2}, \quad n = 0, 1, 2, \dots, \quad (3.2.4)$$

where $\alpha = \sqrt{mk}/\hbar$ and H_n is the n th-order Hermite polynomial. The dynamic system associated with $\psi_n(x)$ is represented by the following Hamilton equations:

$$\frac{dx}{dt} = \frac{\partial H(\psi_n)}{\partial p} = \frac{p}{m}, \quad (3.2.7a)$$

$$\frac{dp}{dt} = -\frac{\partial H(\psi_n)}{\partial x} = -\frac{d}{dx} \left(\frac{1}{2} Kx^2 - \frac{\hbar^2}{2m} \frac{d^2}{dx^2} \ln \psi_n(x) \right) = -\frac{d}{dx} (V + Q). \quad (3.2.7b)$$

Substituting Eq.(3.2.7a) into Eq.(3.2.7b) yields,

$$m \frac{dx^2}{dt^2} = -\frac{dV}{dx} - \frac{dQ}{dx}. \quad (3.2.8)$$

This equation has the form of Newton's second law, in which the particle is subjected to a quantum force $-dQ/dx$ in addition to the classical force $-dV/dx$. Treating p as a function of x , we can recast dp/dt into the form

$$\frac{dp}{dt} = \frac{dp}{dx} \frac{dx}{dt} = \frac{p}{m} \frac{dp}{dx} = \frac{1}{2m} \frac{d}{dx} p^2. \quad (3.2.9)$$

Combination of Eq.(3.2.7b) and Eq.(3.2.9) yields

$$H(x, p) = \frac{1}{2m} p^2 + V(x) + Q = E = \text{constant}, \quad (3.2.10)$$

where Q is the quantum potential present in the state ψ_n

$$Q = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \ln \psi_n(x). \quad (3.2.11)$$

Accordingly, we can regard Eq.(3.2.10) as the energy conservation law for one-dimensional quantum Hamilton system. By substituting the relation

$$p = -i\hbar \frac{d}{dx} \ln \psi_n(x) = -\frac{i\hbar}{\psi_n} \frac{d\psi_n(x)}{dx} \quad (3.2.12)$$

from Eq.(3.2.1.8) into Eq.(3.2.10), it turns out that Eq.(3.2.10) is just the time-independent Schrödinger equation for harmonic oscillator

$$\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} + (E - V(x))\psi_n = 0. \quad (3.2.13)$$

The equivalence among the Hamilton equations (3.2.7), the energy conservation law (3.2.10) and the Schrödinger equation (3.2.13) indicates that the wavefunction ψ_n actually represents a dynamic system whose behavior obeys the Hamilton equations (3.2.7), as stated in Definition 2.1. \square

The constant C_n in Eq.(3.2.4) has an important role in normalizing the wavefunction ψ_n , but as can be seen from Eq.(3.2.12), the dynamic representation of ψ_n is independent of C_n . An alternative expression of Eq.(3.2.10) may be obtained by replacing ψ_n with p via the relation (3.2.12),

$$H(x, p) = \frac{1}{2m} p^2 + V(x) + \frac{1}{2m} \frac{\hbar}{i} \frac{dp}{dx} = E, \quad (3.2.14)$$

which was known as Riccati equation in the mathematical literature. Quantum Hamilton-Jacobi theory (Leacock and Padgett, 1983; Bhalla, Kapoor, and Panigrahi, 1997), which was developed from Eq.(3.2.14), permits the exact determination of the bound-state energy levels and the related eigenfunctions without the necessity of solving the corresponding Schrödinger equation.

The quantum potential Q has a close relation to the probability interpretation of standard quantum mechanics; it explains the underlying reason why some locations are hard to access, while some are accessible with large probability.

Theorem 3.2.2

The total potential $V_{\text{Total}} = Q + V$ is inversely proportional to the probability density function $\psi^*\psi$ in the manner that the locations with zero probability are where the total potential approaches infinity and the locations with maximum probability are where the total potential arrives at its minimum. Moreover, the locations with maximum probability are just the equilibrium points of the dynamic system (3.1.9) representing the quantum state ψ .

Proof: From the energy conservation law of Eq.(3.2.10), we can express the total potential as

$$V_{\text{Total}} = Q + V = E - \frac{1}{2m} p^2 = E + \frac{\hbar^2}{2m} \left(\frac{d \ln \psi}{dx} \right)^2. \quad (3.2.15)$$

A succinct expression of quantum Newton equation (3.2.8) then turns out to be

$$m\ddot{x} = -\frac{dV_{\text{Total}}}{dx} = -\frac{\hbar^2}{2m} \frac{d}{dx} \left(\frac{d \ln \psi}{dx} \right)^2. \quad (3.2.16)$$

Since this equation of motion is independent of the constant E , we can choose $E = 0$ as the reference energy level for V_{Total} . The magnitude of the total potential barrier now becomes

$$|V_{\text{Total}}| = \left| \frac{\hbar^2}{2m} \left(\frac{d \ln \psi}{dx} \right)^2 \right| = \frac{\hbar^2}{2m} \frac{|d\psi/dx|^2}{\psi^*\psi}, \quad (3.2.17)$$

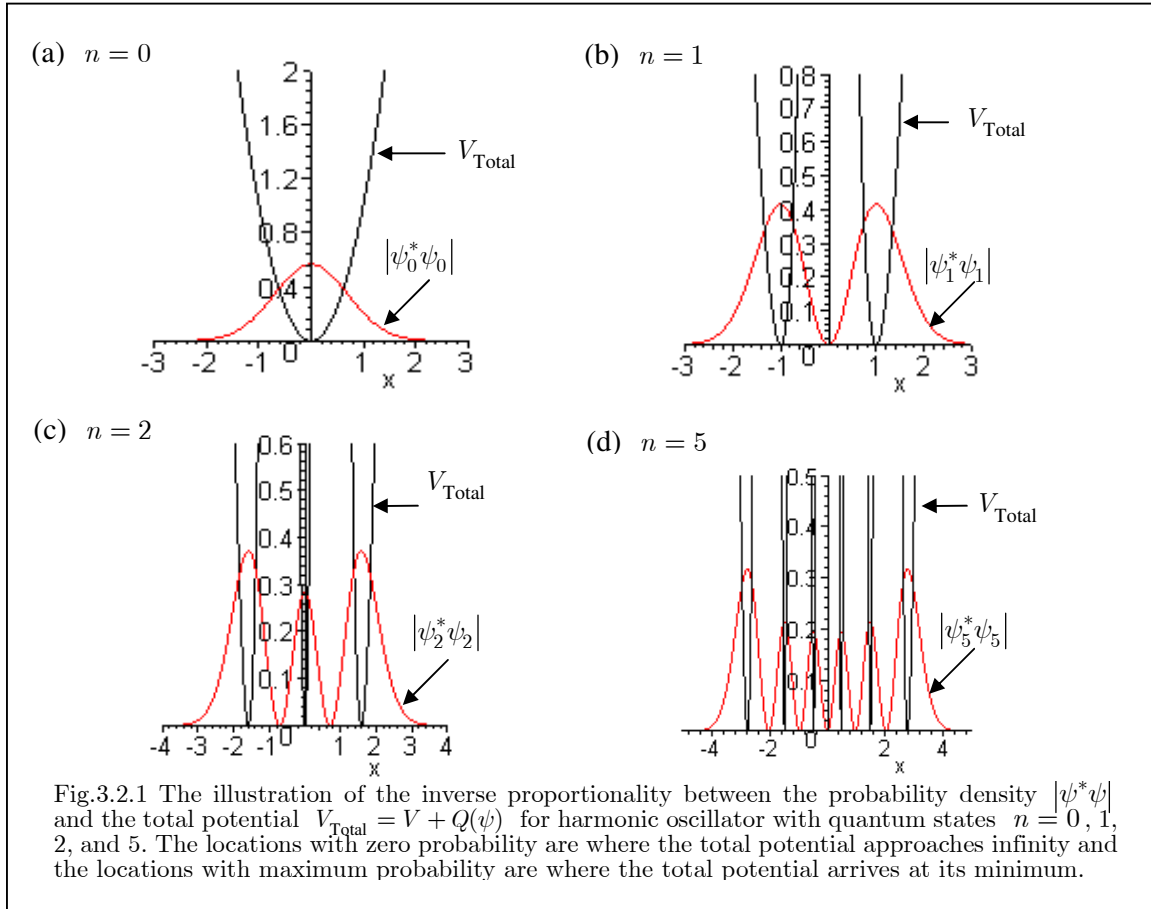
which states that the height of the total potential barrier is inversely proportional to $\psi^*\psi$. A spatial point with large value of $\psi^*\psi$ corresponds to the location of low potential barrier and hence large accessibility to this point. This fact legitimates the use of $\psi^*\psi$ as the probability measure for a particle to appear at a specified spatial point. Besides the probability information provided by $\psi^*\psi$, the detailed trajectory under the action of V_{Total} can be found by integrating Eq.(3.2.16) whose first integration, as has been shown in Theorem 3.2.1, is given by Eq.(3.1.8) and Eq.(3.1.9a):

$$\frac{dx}{dt} = \frac{p}{m} = -\frac{i\hbar}{m} \frac{d\psi/dx}{\psi}. \quad (3.2.18)$$

The equilibrium point of the above nonlinear system is the position having the property of $\dot{x} = 0$, i.e., $d\psi/dx = 0$, which in turn is the necessary condition that the probability density $\psi^*\psi$ achieves its maximum. \square

Fig.3.2.1 is an illustration of Theorem 3.2.2 by taking harmonic oscillator as an example. The total potential V_{Total} and the probability density $\psi^*\psi$ are plotted together for quantum states $n = 0, 1, 2$, and 5. The inverse proportionality between V_{Total} and $\psi^*\psi$ is clearly displayed, from which the positions with zero probability are justified by the presence of infinity potential and the

positions with the maximum probability are justified by the lowermost points of the potential.



3.3 Complex Variable and Quantum Operator

Besides the state-dependent property, quantum Hamiltonian mechanics is distinct from classical Hamiltonian mechanics in the unique feature that the observables appeared in quantum Hamiltonian mechanics, such as \mathbf{q} , \mathbf{p} , and H , are in general complex-valued. For instance, if we determine the momentum \mathbf{p} from Eq.(3.1.8) for a given wavefunction ψ , we should find that \mathbf{p} has real component as well as imaginary component. This complex-valued nature inherits from Schrödinger equation, which produces the complex-valued wavefunction that, in turn, leads to the complex-valued quantum Hamiltonian H and quantum potential Q . It is this complex-valued nature that allows us to derive the correct quantum operator accompanying each quantum observable. In the following, we first introduce the definition of quantum operator in Hamilton mechanics, and then demonstrate how the commonly used quantum operators in Cartesian coordinates can be derived from this definition. Operators in curvilinear coordinates will be considered in the later sections.

Definition 3.3.1

For a quantum observable A evaluated in the quantum state ψ , its associated quantum operator \hat{A} is defined via the relation

$$A = \frac{1}{\psi} \hat{A} \psi. \quad (3.3.1)$$

Using this definition, we can give a formal proof of the quantization axiom $\mathbf{p} \rightarrow -i\hbar\nabla$ that governs the critical transition from classical systems to quantum-mechanical systems. \square

Theorem 3.3.1 (Yang, 2007A)

The canonical operators $(\hat{\mathbf{q}}, \hat{\mathbf{p}})$ corresponding to the canonical variables (\mathbf{q}, \mathbf{p}) are given by $\hat{\mathbf{q}} = \mathbf{q}$ and $\hat{\mathbf{p}} = -i\hbar\nabla$, whereas the Hamiltonian operator \hat{H} corresponding to the quantum Hamiltonian defined in Eq.(3.1.6) is given by $\hat{H} = -\hat{\mathbf{p}}^2/2m + V$.

Proof: Rewriting Eq.(3.1.8) in the form of Eq.(3.3.1), we obtain

$$\mathbf{p} = \nabla S = -i\hbar\nabla \ln \psi = (1/\psi)(-i\hbar\nabla)\psi. \quad (3.3.2)$$

The comparison of the above equation with the definition $\mathbf{p} = (1/\psi)\hat{\mathbf{p}}\psi$ gives $\hat{\mathbf{p}} = -i\hbar\nabla$. As for $\hat{\mathbf{q}}$, we may express \mathbf{q} as $\mathbf{q} = (1/\psi)\mathbf{q}\psi$ and contrast this with the definition $\mathbf{q} = (1/\psi)\hat{\mathbf{q}}\psi$ to obtain $\hat{\mathbf{q}} = \mathbf{q}$. To derive the Hamiltonian operator \hat{H} from the definition $H = (1/\psi)\hat{H}\psi$, we need to express the quantum Hamiltonian H in terms of the wavefunction ψ . The insertion of $\mathbf{p} = -i\hbar\nabla \ln \psi$ in Eq.(3.1.6) yields

$$H = \frac{1}{2m}(-i\hbar\nabla \ln \psi)^2 - \frac{\hbar^2}{2m}\nabla^2 \ln \psi + V = \frac{1}{\psi}\left(\frac{-\hbar^2}{2m}\nabla^2 + V\right)\psi. \quad (3.3.3)$$

In comparison with Eq.(3.3.1), Eq.(3.3.3) produces the Hamiltonian operator $\hat{H} = -\hat{\mathbf{p}}^2/2m + V$. \square

The canonical momentum operator $\hat{\mathbf{p}}$ derived in Theorem 3.3.1 must not be confused with the mechanical momentum operator $\hat{\mathbf{P}}$. In Cartesian coordinates, the mechanical momentum \mathbf{P} is given by $\mathbf{P} = m\dot{\mathbf{q}}$ and from Eq.(3.1.9a) we find $\mathbf{p} = m\dot{\mathbf{q}} = \mathbf{P}$, which indicates $\hat{\mathbf{P}} = \hat{\mathbf{p}} = -i\hbar\nabla$ in Cartesian coordinates. However, in curvilinear coordinates, \mathbf{p} and \mathbf{P} are, in general, different and the quantization axiom $\hat{\mathbf{P}} = -i\hbar\nabla$ is no longer valid as will be expounded further in later chapters.

Eq.(3.3.2) indicates that defining quantum momentum $\mathbf{p} = \nabla S$ in complex domain is necessary to result in the correct momentum operator $\hat{\mathbf{p}}$. A similar but different quantum momentum was proposed by Bohm (1952) in the form of $\mathbf{p}_B = \nabla S_B$, where S_B is the phase of the wavefunction defined by $\psi = R_B e^{iS_B/\hbar}$ with R_B and S_B being real functions. If we follow the same procedures leading to Eq.(3.3.2) but employ the real quantum momentum $\mathbf{p}_B = \nabla S_B$ instead of the complex momentum $\mathbf{p} = \nabla S$, we shall find that it is not possible to arrive at the correct momentum operator $\hat{\mathbf{p}} = -i\hbar\nabla$.

A natural outcome of defining canonical variables (\mathbf{q}, \mathbf{p}) in complex domain is the quantization of action variable, a postulate proposed by Sommerfeld (1915) and Wilson (1915),

$$J_i = \oint_{c_i} p_i dq_i = nh, \quad n = 0, 1, 2, \dots, \quad i = 1, 2, \dots, N, \quad (3.3.4)$$

where c_i is a closed trajectory in the complex q_i plane obtained from the integration of the Hamilton equations (3.1.9) and the complex momentum p_i is given by Eq.(3.1.8) as $p_i = -i\hbar\partial \ln \psi / \partial q_i$. To prove the quantization rule (3.3.4), we define the following conformal mappings from the q_i complex plane to the ψ complex plane:

$$\psi_i = \psi(q_i): \quad q_i \rightarrow \psi, \quad i = 1, 2, \dots, N \quad (3.3.5)$$

where $\psi(q_i)$ is a function of the single complex variable q_i obtained by fixing other coordinates in the wavefunction $\psi(q_1, \dots, q_i, \dots, q_N)$. The function ψ_i maps a closed path c_i in the q_i plane into a closed path c'_i in the ψ plane. Counting the number of encirclement of the origin in the ψ plane by the closed path c'_i provides us with the quantum number n in Eq.(3.3.4).

Theorem 3.3.2: (Yang, 2006D)

Let c_i be any closed complex trajectory traced out by the coordinate q_i . Then the contour integral defined in Eq.(3.3.4) over the contour c_i is quantized and the related quantum number n is equal to the number of encirclement of the origin in the ψ plane by the closed path c'_i obtained from c_i via the mapping ψ_i .

Proof: With the substitution $p_i = -i\hbar\partial \ln \psi / \partial q_i$, the action variable J_i becomes

$$J_i = \oint_{c_i} p_i dq_i = \frac{\hbar}{i} \oint_{c_i} \frac{\partial \ln \psi}{\partial q_i} dq_i = \frac{\hbar}{i} \oint_{c_i} \frac{d \ln \psi_i}{dq_i} dq_i = \frac{\hbar}{i} \oint_{c'_i} d \ln \psi_i, \quad (3.3.6)$$

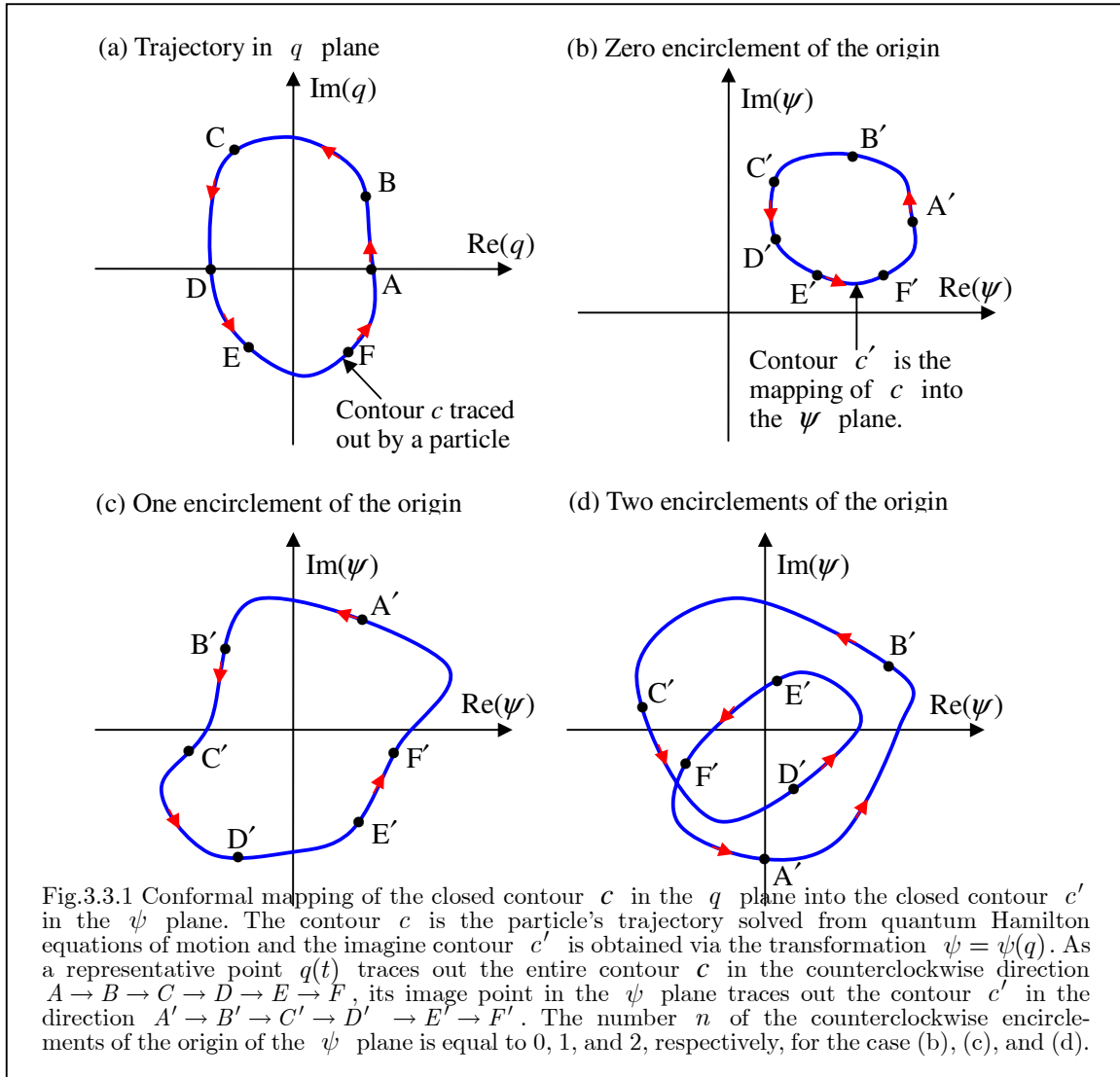
where in the last equality we have expressed J_i in terms of the net change of $\ln \psi_i$ along the closed path c'_i . By expressing ψ_i in a polar form $\psi_i = |\psi_i| e^{i\theta}$, we can further simplify J_i as

$$J_i = \frac{\hbar}{i} \oint_{c'_i} d \ln |\psi_i| + \hbar \oint_{c'_i} d\theta. \quad (3.3.7)$$

The first term in the right-hand side is zero because the net change of $\ln|\psi_i|$ is zero along any closed path. The second term is relevant to the net phase change of ψ_i along the closed path c'_i , which must be an integral multiple of 2π . Therefore, Eq.(3.3.7) is reduced to the expected result

$$J_i = \hbar \oint_{c'_i} d\theta = \hbar(2n\pi) = nh,$$

where n is the number of encirclement of the origin in the ψ_i plane by the closed path c'_i and $2n\pi$ represents the corresponding net phase change. Fig.3.3.1 illustrates the mapping between the contour c_i in the complex plane q_i and the contour c'_i in the complex ψ_i plane. Observing the number of encirclement of the origin by the closed path c'_i allows us to identify the quantum number n graphically. \square



The quantization rule (3.3.4) is independently valid for any coordinate $q_i(t)$ that has periodic motion and thus has closed trajectory in the complex q_i plane, regardless of whether the whole quantum system is periodic or not. We shall revisit Theorem 3.3.2 in Chapter 4 for the quantization of harmonic oscillator and in Chapter 9 for the quantization of hydrogen atom. In Theorem 3.3.1 and Theorem 3.3.2, we have witnessed the necessity of extending quantum observables such as q and p to complex domain. It is worth noting that the relation between the complex quantum observable A and the quantum operator \hat{A} in Eq.(3.3.1) is in the form of strict equality, but not merely an

abstract correspondence. In the standard approach, we obtained \hat{H} by applying the abstract corresponding principle of replacing the momentum \mathbf{p} in the classical Hamiltonian $H_c = \mathbf{p}^2/2m + V$ with the momentum operator $\hat{\mathbf{p}}$, but in doing so we could not establish any equality between \hat{H} and H_c . However, under the framework of quantum Hamiltonian mechanics, we have a quantum Hamiltonian H in Eq.(3.1.6), which is directly related to \hat{H} via the equality $H = (1/\psi)\hat{H}\psi$.

For any given observable A defined in quantum Hamilton mechanics, we can identify its accompanying operator \hat{A} by using Eq.(3.3.1); conversely, for a given operator \hat{B} , an explicit expression for its accompanying quantum observable B is found to be $B = (1/\psi)\hat{B}\psi$. To familiarize us with this equivalence, let us consider a textbook example regarding the operator of the angular momentum $\mathbf{L} = \mathbf{q} \times \mathbf{p}$.

Example 3.3.1

In quantum Hamilton mechanics, the expression for \mathbf{L} is the same but with $\mathbf{q} = [x \ y \ z]$ and $\mathbf{p} = [p_x \ p_y \ p_z]$ satisfying the quantum Hamilton equations (3.1.9), instead of the classical Hamilton equations. Evaluating the x components of \mathbf{L} with \mathbf{p} given by Eq.(3.1.8), we obtain

$$L_x = yp_z - zp_y = y \left(\frac{\hbar}{i} \frac{\partial \ln \psi}{\partial z} \right) - z \left(\frac{\hbar}{i} \frac{\partial \ln \psi}{\partial y} \right) = \frac{-i\hbar}{\psi} \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \psi. \quad (3.3.8)$$

Comparing the above equation to the definition $L_x = (1/\psi)\hat{L}_x\psi$ gives \hat{L}_x as:

$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) = y\hat{p}_z - z\hat{p}_y, \quad (3.3.9)$$

where the expressions for \hat{p}_y and \hat{p}_z has been derived in Theorem 3.3.1. We recognize that an explicit expression of L_x in terms of the wavefunction ψ naturally leads to the expression for \hat{L}_x . The other two components $\hat{L}_y = z\hat{p}_x - x\hat{p}_z$ and $\hat{L}_z = x\hat{p}_y - y\hat{p}_x$ can be derived in a similar way. \square

There exists a special wavefunction ψ_n such that Eq.(3.3.1) yields $A(\mathbf{p}, \mathbf{q}) = A_n = (1/\psi_n)\hat{A}\psi_n = \text{constant}$. In such a case, the observable $A(\mathbf{p}, \mathbf{q})$ becomes a constant in the state ψ_n . In conjunction with ψ_n , a remarkable link can be established between the conservation law in quantum Hamilton mechanics and the concept of stationary observable in quantum mechanics.

Lemma 3.3.1

A quantum observable $A(\mathbf{p}, \mathbf{q})$ is stationary in the quantum state ψ_n , if and only if $A(\mathbf{p}, \mathbf{q})$ is conservative along any phase-space trajectory $(\mathbf{q}(t), \mathbf{p}(t))$ determined from Eqs.(3.1.9) with the Hamiltonian H induced by ψ_n ; furthermore, this conserved value of $A(\mathbf{p}, \mathbf{q})$ is just equal to the eigenvalue of \hat{A} with respect to the eigenfunction ψ_n .

Proof: In quantum mechanics, an observable A is said to be stationary in the state ψ_n , if its related operator \hat{A} satisfies $\hat{A}\psi_n = A_n\psi_n$, where A_n is the eigenvalue of \hat{A} corresponding to the eigenfunction ψ_n . Now we can apply Eq.(3.3.1) to evaluate A in the state ψ_n as $A(\mathbf{q}, \mathbf{p}) = (1/\psi_n)\hat{A}\psi_n = (1/\psi_n)A_n\psi_n = A_n$, which states that the value of $A(\mathbf{p}, \mathbf{q})$ evaluated in the state ψ_n is a constant equal to the eigenvalue A_n . According to Definition 3.1, the constancy of $A(\mathbf{q}, \mathbf{p})$ in the state ψ_n amounts to the conservation of $A(\mathbf{p}, \mathbf{q})$ along any phase-space trajectory $(\mathbf{q}(t), \mathbf{p}(t))$ determined from Eqs.(3.1.9) with the Hamiltonian H induced by ψ_n . Conversely, if we are given that A is a constant A_n in the state ψ_n , then Eq.(3.3.1) implies $A = A_n = (1/\psi_n)\hat{A}\psi_n$, i.e., $\hat{A}\psi_n = A_n\psi_n$, which ensures that A is stationary in ψ_n . \square

As a demonstration of Lemma 2.3.1, we consider $\hat{A} = \hat{H}$ and assume that H is stationary in ψ_n , i.e., $\hat{H}\psi_n = E_n\psi_n$. If we apply this stationary condition to Eq.(3.3.1), we obtain $H(\mathbf{q}, \mathbf{p}) = (1/\psi_n)\hat{H}\psi_n = (1/\psi_n)E_n\psi_n = E_n$, showing that the Hamiltonian $H(\mathbf{q}(t), \mathbf{p}(t))$ in Eq.(3.1.6) is conservative along any phase-space trajectory $(\mathbf{q}(t), \mathbf{p}(t))$ in the state ψ_n . We may confirm the conservation of H by showing $dH/dt = 0$ in the state ψ_n . Because $\mathbf{q}(t)$ and $\mathbf{p}(t)$ in the state ψ_n satisfy the Hamilton equations (3.1.9), we obtain the expected result

$$\frac{dH}{dt} = \frac{\partial H}{\partial \mathbf{q}} \frac{d\mathbf{q}}{dt} + \frac{\partial H}{\partial \mathbf{p}} \frac{d\mathbf{p}}{dt} = \frac{\partial H}{\partial \mathbf{q}} \frac{\partial H}{\partial \mathbf{p}} - \frac{\partial H}{\partial \mathbf{p}} \frac{\partial H}{\partial \mathbf{q}} = 0. \quad (3.3.10)$$

Example 3.3.2 (Yang, 2006A)

Continue the discussion of harmonic oscillator in Example 3.2.1 and consider the energy conservation in the ground state, for which the wavefunction is given by $\psi_0 = C_0 H_0 e^{-\alpha x^2}$. Inserting ψ_0 into Eq.(3.2.11) and Eq.(3.2.12) yields, respectively, the quantum potential $Q = \hbar\omega/2 = (\hbar/2)\sqrt{K/m}$ and the quantum momentum $p = i\hbar\alpha x$. The total energy in the ground state is then found to be a constant equal to

$$H = \frac{p^2}{2m} + \frac{1}{2}Kx^2 + Q = -\frac{1}{2m}\hbar^2\alpha^2x^2 + \frac{1}{2}Kx^2 + \frac{\hbar\omega}{2} = \frac{\hbar\omega}{2} = E_0, \quad (3.3.11)$$

where $E_0 = \hbar\omega/2$ is just the eigenvalue corresponding to ψ_0 . By a similar way, we can show in the n^{th} eigenstate ψ_n , the total energy H is a constant equal to the eigenvalue corresponding to ψ_n , i.e., $H = (n+1/2)\hbar\omega = E_n$. \square

On the other hand, when ψ is not an eigenfunction of \hat{A} , we have $A(\mathbf{q}, \mathbf{p}) = (1/\psi)\hat{A}\psi \neq \text{constant}$ with its value being varying with $(\mathbf{q}(t), \mathbf{p}(t))$. In such a case, quantum mechanics says that A is uncertain in the state ψ and suggests adopting $\psi^*\psi$ as the probability density function to extract the statistical properties of A . Quantum Hamilton mechanics provides us with an alternative way to evaluate a nonstationary observable; we may employ the expression $A(\mathbf{q}, \mathbf{p}) = (1/\psi)\hat{A}\psi$ to explicitly trace the variation of $A(\mathbf{q}(t), \mathbf{p}(t))$ along any phase-space trajectory $(\mathbf{q}(t), \mathbf{p}(t))$ in the dynamic system (3.1.9) prescribed by ψ .

The equivalence established in Lemma 3.3.1 can be elucidated more concisely in terms of the equality (not merely a correspondence) between the commutator defined in quantum mechanics and the Poisson bracket defined in Hamilton mechanics. Given two operators \hat{A} and \hat{B} , their commutator is defined as $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$. The accompanying observables A and B evaluated in the state ψ are given, respectively, as $A(\mathbf{q}, \mathbf{p}) = (1/\psi)\hat{A}\psi$ and $B(\mathbf{q}, \mathbf{p}) = (1/\psi)\hat{B}\psi$ according to Definition 3.3.1. Having obtained $A(\mathbf{q}, \mathbf{p})$ and $B(\mathbf{q}, \mathbf{p})$, we can evaluate the Poisson bracket of A and B in a usual way:

$$\{A, B\} = \sum_i \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i}. \quad (3.3.12)$$

Lemma 3.3.2

If an observable $A(\mathbf{q}, \mathbf{p})$ is stationary in the eigenfunction ψ of \hat{H} , then

$$\{A, H\} = \frac{1}{\psi}[\hat{A}, \hat{H}]\psi = 0. \quad (3.3.13)$$

Proof: For the given condition, we have $\hat{H}\psi = E_n\psi$ and $\hat{A}\psi = A_n\psi$, which yields $\hat{A}\hat{H}\psi = \hat{H}\hat{A}\psi = A_n E_n\psi$ and hence $[\hat{A}, \hat{H}]\psi = (\hat{A}\hat{H} - \hat{H}\hat{A})\psi = 0$. On the other hand, evaluating A in the state ψ results in $A(\mathbf{q}, \mathbf{p}) = (1/\psi)\hat{A}\psi = (1/\psi)A_n\psi = A_n$. This means that $A(\mathbf{q}(t), \mathbf{p}(t))$ is conservative along any phase-space trajectory $(\mathbf{q}(t), \mathbf{p}(t))$ in the state ψ . From the viewpoint of Hamilton mechanics, the conservation of $A(\mathbf{q}(t), \mathbf{p}(t))$ requires

$$\frac{d}{dt}A(\mathbf{q}(t), \mathbf{p}(t)) = 0 = \sum_i \frac{\partial A}{\partial q_i} \dot{q}_i + \frac{\partial A}{\partial p_i} \dot{p}_i = \sum_i \frac{\partial A}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial H}{\partial q_i},$$

where $\mathbf{q}(t)$ and $\mathbf{p}(t)$ satisfy the Hamilton equations (3.2.1.9) specified by ψ . The above equation amounts to $\{A, H\} = 0$ which, together with $[\hat{A}, \hat{H}]\psi = 0$, gives Eq.(3.3.13). \square

We say that \hat{A} and \hat{H} satisfying Eq.(3.3.13) are compatible with each other. For two operators \hat{A} and \hat{B} that are incompatible, their commutator and Poisson bracket are both nonzero, but useful relation between $\{A, B\}$ and $[\hat{A}, \hat{B}]$ still exists. One typical example comes from the case of \hat{x} and \hat{p}_x , which have commutator $[\hat{x}, \hat{p}_x] = i\hbar$ and Poisson bracket $\{x, p_x\} = 1$. Expressing them in a form analogous to Eq.(3.3.13), we have

$$i\hbar\{x, p_x\} = \frac{1}{\psi}[\hat{x}, \hat{p}_x]\psi = i\hbar. \quad (3.3.14)$$

This suggests an identity that the operator corresponding to the observable $i\hbar\{A, B\}$ is $[\hat{A}, \hat{B}]$, i.e.,

$$i\hbar\{A, B\} = \frac{1}{\psi} [\hat{A}, \hat{B}]\psi. \quad (3.3.15)$$

This relation does hold for most commonly used quantum operators. The following examples cite two of them.

Example 3.3.3

Given the two observables $A = L_x = yp_z - zp_x$ and $B = L_y = zp_x - xp_z$, we have their Poisson bracket as $\{L_x, L_y\} = xp_y - yp_x = L_z$; on the other hand, the commutator of the associated operators \hat{L}_x and \hat{L}_y is known to be $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$. Accordingly, we have

$$\frac{1}{\psi} [\hat{L}_x, \hat{L}_y]\psi = \frac{1}{\psi} (i\hbar\hat{L}_z)\psi = i\hbar\left(\frac{1}{\psi}\hat{L}_z\psi\right) = i\hbar L_z = i\hbar\{L_x, L_y\}, \quad (3.3.16)$$

which satisfies the identity (3.3.15). \square

Example 3.3.4

Consider $A = H$ and $B = x$, and their commutator $[\hat{H}, \hat{x}] = (-i\hbar/m)\hat{p}_x$. The observable related to $[\hat{H}, \hat{x}]$ is found from the relation

$$\frac{1}{\psi} [\hat{H}, \hat{x}]\psi = -\frac{i\hbar}{m}\left(\frac{1}{\psi}\hat{p}_x\psi\right) = -\frac{i\hbar}{m}p_x. \quad (3.3.17)$$

This observable is to be linked to the Poisson bracket $\{H, x\}$ with H given by Eq.(3.1.6),

$$\{H, x\} = -\frac{\partial H}{\partial p_x} \frac{\partial x}{\partial x} = -\frac{1}{m}p_x \quad (3.3.18)$$

The combination of Eq.(3.3.17) and Eq.(3.3.18) yields

$$i\hbar\{H, x\} = \frac{1}{\psi} [\hat{H}, \hat{x}]\psi, \quad (3.3.19)$$

which again is a special case of Eq.(3.3.15). \square

3.4 Orbital and Spin Angular Momentum

The above discussions on quantum Hamilton mechanics and the related quantum problems are all limited to Cartesian coordinates. In this section, we shall continue to demonstrate how quantum operators can be derived directly in spherical coordinates under the framework of Hamilton mechanics. According to the definition of the Quantum Hamiltonian H in Eq.(3.1.6), we first have to express $\mathbf{p} \cdot \mathbf{p}$ and $\nabla \cdot \mathbf{p}$ in spherical coordinates (r, θ, ϕ) as

$$\mathbf{p} \cdot \mathbf{p} = p_r^2 + \frac{p_\theta^2}{r^2} + \frac{p_\phi^2}{r^2 \sin^2 \theta}, \quad (3.4.1a)$$

$$\begin{aligned} \nabla \cdot \mathbf{p} &= \frac{1}{r^2 \sin \theta} \left[\frac{\partial}{\partial r} (r^2 p_r \sin \theta) + \frac{\partial}{\partial \theta} (p_\theta \sin \theta) + \frac{\partial}{\partial \phi} \left(\frac{p_\phi}{\sin \theta} \right) \right] \\ &= \frac{1}{r^2 \sin \theta} \left[2rp_r \sin \theta + p_\theta \cos \theta + r^2 \sin \theta \frac{\partial p_r}{\partial r} + \sin \theta \frac{\partial p_\theta}{\partial \theta} + \frac{1}{\sin \theta} \frac{\partial p_\phi}{\partial \phi} \right]. \end{aligned} \quad (3.4.1b)$$

Before evaluating $\partial p_r / \partial r$, $\partial p_\theta / \partial \theta$, and $\partial p_\phi / \partial \phi$, we need to express p_r , p_θ , and p_ϕ as explicit functions of r , θ , and ϕ . These explicit expressions are afforded by Eq.(3.1.8) as

$$p_r = \frac{\partial S}{\partial r} = -i\hbar \frac{\partial \ln \psi}{\partial r}, \quad p_\theta = \frac{\partial S}{\partial \theta} = -i\hbar \frac{\partial \ln \psi}{\partial \theta}, \quad p_\phi = \frac{\partial S}{\partial \phi} = -i\hbar \frac{\partial \ln \psi}{\partial \phi}, \quad (3.4.2)$$

where $\psi(r, \theta, \phi)$ is the given wavefunction. By applying Eq.(3.4.2) to the differentiations involved in Eq.(3.4.1b), the quantum Hamiltonian H defined in Eq.(3.1.6) becomes

$$H = \frac{1}{2m} \left[p_r^2 + \frac{\hbar}{i} \left(\frac{2}{r} p_r + \frac{\hbar}{i} \frac{\partial^2 \ln \psi}{\partial r^2} \right) \right] + \frac{1}{2mr^2} \left[p_\theta^2 + \frac{\hbar}{i} \left(p_\theta \cot \theta + \frac{\hbar}{i} \frac{\partial^2 \ln \psi}{\partial \theta^2} \right) \right]$$

$$+ \frac{1}{\sin^2 \theta} \left(p_\phi^2 - \hbar^2 \frac{\partial^2 \ln \psi}{\partial \phi^2} \right) + V(r, \theta, \phi) = \frac{1}{2m} P_r^2 + \frac{L^2}{2mr^2} + V. \quad (3.4.3)$$

It can be seen that the Hamiltonian H is uniquely determined by the given wavefunction $\psi(r, \theta, \phi)$. The following theorem gives the dynamic representation of ψ in spherical coordinates.

Theorem 3.4.1 (Yang, 2006D)

A quantum state $\psi(r, \theta, \phi)$, expressed in spherical coordinates, is a dynamic system whose behavior obeys the following Hamilton equations:

$$\dot{r} = \frac{\hbar}{im} \frac{\partial \ln \psi}{\partial r} + \frac{\hbar}{i} \frac{1}{mr}, \quad \dot{\theta} = \frac{\hbar}{imr^2} \frac{\partial \ln \psi}{\partial \theta} + \frac{\hbar}{i} \frac{\cot \theta}{2mr^2}, \quad \dot{\phi} = \frac{\hbar}{imr^2 \sin^2 \theta} \frac{\partial \ln \psi}{\partial \phi} \quad (3.4.4)$$

Proof: The dynamic representation of the state ψ in spherical coordinates can be derived from Eq.(3.1.9a) with H given by Eq.(3.4.3):

$$\dot{r} = \frac{\partial H}{\partial p_r} = \frac{p_r}{m} + \frac{\hbar}{i} \frac{1}{mr}, \quad \dot{\theta} = \frac{\partial H}{\partial p_\theta} = \frac{p_\theta}{mr^2} + \frac{\hbar}{i} \frac{\cot \theta}{2mr^2}, \quad \dot{\phi} = \frac{\partial H}{\partial p_\phi} = \frac{p_\phi}{mr^2 \sin^2 \theta}. \quad (3.4.5)$$

On deriving the above Hamilton equations, the canonical variables $\mathbf{q} = (r, \theta, \phi)$ and $\mathbf{p} = (p_r, p_\theta, p_\phi)$ must be regarded as independent variables in the quantum Hamiltonian H , as in classical Hamilton mechanics. The adjoint Hamilton equations $\dot{\mathbf{p}} = -\partial H / \partial \mathbf{q}$ from Eq.(3.1.9b) are redundant, since, according to Theorem 3.2.1, the solution for \mathbf{p} is already given by Eq.(3.4.2), as long as ψ is a solution of the Schrödinger equation. By substituting Eq.(3.4.2) into Eqs.(3.4.5), we obtain the dynamic representation of ψ as in Eqs.(3.4.4). \square

In comparison with their classical counterparts, the mechanical momenta P_r^2 and L^2 in quantum Hamiltonian (3.4.3) contain additional quantum correction terms:

$$P_r^2 = p_r^2 + \frac{\hbar}{i} \left(\frac{2}{r} p_r + \frac{\hbar}{i} \frac{\partial^2 \ln \psi}{\partial r^2} \right), \quad (3.4.6a)$$

$$L^2 = p_\theta^2 + \frac{\hbar}{i} \left(p_\theta \cot \theta + \frac{\hbar}{i} \frac{\partial^2 \ln \psi}{\partial \theta^2} \right) + \frac{L_z^2}{\sin^2 \theta}, \quad L_z^2 = p_\phi^2 - \hbar^2 \frac{\partial^2 \ln \psi}{\partial \phi^2}, \quad (3.4.6b)$$

where the terms involving Planck constant stem from quantum correction. The corresponding operators for P_r^2 , L^2 , and L_z^2 can be identified by expressing Eqs.(3.4.6) in the form of Eq.(3.3.1).

Theorem 3.4.2 (Yang, 2006D)

The momentum operators \hat{P}_r , \hat{L}^2 , and \hat{L}_z corresponding to the observables P_r , L^2 , and L_z defined in Eqs.(3.4.6) are given by

$$\hat{P}_r = \frac{\hbar}{i} \left(\frac{\partial}{\partial r} + \frac{1}{r} \right), \quad \hat{L}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right), \quad \hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}, \quad (3.4.7)$$

in terms of which the spherical Hamiltonian operator can be expressed as

$$\hat{H} = \frac{1}{2m} \hat{P}_r^2 + \frac{1}{2mr^2} \hat{L}^2 + V. \quad (3.4.8)$$

Proof: Substituting $p_r = \partial S / \partial r = -i\hbar \partial(\ln \psi) / \partial r$ from Eq.(3.4.2) into Eq.(3.4.6a) yields

$$P_r^2 = -\frac{\hbar^2}{\psi} \left(\frac{2}{r} \frac{\partial \psi}{\partial r} + \frac{\partial^2 \psi}{\partial r^2} \right) = \frac{1}{\psi} \left[\frac{\hbar}{i} \left(\frac{\partial}{\partial r} + \frac{1}{r} \right) \right] \left[\frac{\hbar}{i} \left(\frac{\partial}{\partial r} + \frac{1}{r} \right) \right] \psi.$$

Comparing the above equation to the definition $P_r^2 = (1/\psi) \hat{P}_r^2 \psi$ gives the desired expression for \hat{P}_r , the associated operator for the linear momentum in the r direction. Similarly, The expression of Eq.(3.4.6b) in terms of the wavefunction ψ by using $p_\theta = -i\hbar \partial(\ln \psi) / \partial \theta$ and $p_\phi = -i\hbar \partial(\ln \psi) / \partial \phi$ gives rise to

$$L^2 = \frac{-\hbar^2}{\psi} \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \psi, \quad L_z^2 = \frac{1}{\psi} \left(\frac{\hbar}{i} \frac{\partial}{\partial \phi} \right) \left(\frac{\hbar}{i} \frac{\partial}{\partial \phi} \right) \psi, \quad (3.4.9)$$

from which the definitions of $L^2 = (1/\psi) \hat{L}^2 \psi$ and $L_z^2 = (1/\psi) \hat{L}_z^2 \psi$ yield the expressions for \hat{L}^2 , and

\hat{L}_z . We thus have obtained the operators \hat{P}_r , \hat{L}^2 , and \hat{L}_z directly from their associated observables defined in quantum Hamiltonian mechanics without using quantization axiom. In the same way, we can obtain the Hamiltonian operator \hat{H} by writing Eq.(3.2.4.3) in the form of $H = (1/\psi)\hat{H}\psi$ as

$$\begin{aligned} H &= -\frac{\hbar^2}{2m} \frac{1}{\psi} \left[\frac{2}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} + \frac{1}{r^2} \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \right] \psi + V \\ &= \frac{1}{\psi} \left(\frac{1}{2m} \hat{P}_r^2 + \frac{1}{2mr^2} \hat{L}^2 + V \right) \psi \end{aligned} \quad (3.4.10)$$

from which \hat{H} reads as in Eq.(3.4.8). \square

It seems that \hat{H} may be obtained by simply applying the quantization axiom to the classical Hamiltonian $H = p_r^2/2m + L^2/(2mr) + V$, but it is noted that p_r should be replaced by the mechanical momentum operator \hat{P}_r in Eq.(3.4.7) instead of the canonical momentum operator $\hat{p}_r = -i\hbar\partial/\partial r$. This situation is what we had encountered in standard quantum mechanics that the quantization axiom $\mathbf{p} \rightarrow -i\hbar\nabla$ cannot be applied directly to Spherical coordinates.

In case of central-force field $V = V(r)$, we have $[\hat{L}^2, \hat{H}] = [\hat{L}_z, \hat{H}] = 0$, which implies that the observables L^2 and L_z^2 are stationary in an eigenstate ψ of \hat{H} . From Lemma 2.3.1, it means that L^2 and L_z^2 are conservative along any phase-space trajectory $(\mathbf{q}(t), \mathbf{p}(t))$ determined from Eqs.(3.4.4). Since we have already derived the expressions for L^2 and L_z^2 , we can verify their conservation by simply showing $dL^2/dt = dL_z^2/dt = 0$. With the property that the wavefunction ψ has a separable solution $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$ for central-force problem and with the expressions for H , L^2 and L_z^2 in Eq.(3.4.3) and Eq.(3.4.6b), we obtain readily the expected results

$$\frac{dL_z^2}{dt} = \{L_z^2, H\} = \frac{\partial L_z^2}{\partial \phi} \frac{\partial H}{\partial p_\phi} - \frac{\partial L_z^2}{\partial p_\phi} \frac{\partial H}{\partial \phi} = 0, \quad \frac{dL^2}{dt} = \{L^2, H\} = \frac{\partial L^2}{\partial \theta} \frac{\partial H}{\partial p_\theta} - \frac{\partial L^2}{\partial p_\theta} \frac{\partial H}{\partial \theta} = 0$$

As Lemma 3.3.1 indicates, the conserved values for H , L^2 and L_z^2 in the state ψ are just the eigenvalues of \hat{H} , \hat{L}^2 , and \hat{L}_z^2 , respectively. This property is reflected in the relations of $\hat{H}\psi = H\psi$, $\hat{L}^2\psi = L^2\psi$, and $\hat{L}_z^2\psi = L_z^2\psi$, as expressed in Eq.(3.4.10) and Eq.(3.4.9).

Given a quantum state $\psi(r, \theta, \phi)$, we determine its dynamical representation from Eqs.(3.4.4); on the other hand, $\psi^*\psi$ also gives us the probability of the particle's spatial distribution. Consequently, there exists close relation between these two different descriptions of ψ .

Theorem 3.4.3

The stable equilibrium radial position predicated from the dynamic representation of ψ in Eqs.(3.4.4) is identical to the position with the maximum radial probability $P(r) = 4\pi r^2 R^*(r)R(r)$ determined from $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$; or stated mathematically,

$$\frac{dr}{dt} = 0 \quad \Leftrightarrow \quad \frac{d}{dr} P(r) = 0. \quad (3.4.11)$$

Proof:

Using $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$, we may rewrite Eq.(3.4.4a) as

$$\dot{r} = \frac{\hbar}{im} \frac{d}{dr} \ln(rR(r)). \quad (3.4.12)$$

Hence, the equilibrium position for r is found from the condition $\dot{r} = d(\ln(rR))/dr = 0$, i.e., $d(rR)/dr = 0$. On the other hand, the radial probability function has the expression $P(r) = 4\pi r^2 R^*(r)R(r) = 4\pi (rR(r))^2$ by noting that $R(r)$ is a real function of r for central-force problems. Accordingly, the maximum radial probability occurs at the location of $dP/dr = d(rR)/dr = 0$, which is just the condition of $\dot{r} = 0$. \square

Example 3.4.1 (Yang, 2005A)

For hydrogen atom at ground state, we have $R(r) = e^{-r/a_0}$ with $a_0 = 4\pi\epsilon_0\hbar^2/(me^2)$ being the Bohr radius and $\Theta(\theta) = \Phi(\phi) = 1$. Substituting this wavefunction into Eqs.(3.4.4) yields the equations of motion for the ground-state electron as:

$$\frac{d\rho}{d\tau} = \frac{2}{i} \frac{1-\rho}{\rho}, \quad \frac{dz_\theta}{d\tau} = i \frac{z_\theta}{\rho^2}, \quad \frac{d\phi}{d\tau} = 0, \quad z_\theta = \cos \theta \quad (3.4.13)$$

where $\rho = r/a_0$ is the dimensionless radial distance and $\tau = t\hbar/(2ma_0^2)$ is the dimensionless time. Eq.(3.4.13) shows that the ground-state hydrogen atom has an equilibrium radial position r_{eq} at the Bohr radius a_0 , i.e., $\rho = 1$. Meanwhile, the radial probability function is given by $P(r) = 4\pi r^2 R(r)^2 = 4\pi r^2 e^{-2r/a_0}$ that yields a maximum value at $r_{\text{max}} = a_0$ by letting $dP(r)/dr = 0$. Therefore, we have $r_{\text{eq}} = r_{\text{max}} = a_0$. \square

It is not surprising that the probability of finding a particle at the stable equilibrium position has a maximum value, since there is always a restoring force acting on the particle toward the stable equilibrium position, and once the particle reaches the stable equilibrium position, it will remain there as long as no disturbance is applied. However, Eq.(3.4.11) alone cannot tell us directly the stability of the equilibrium points. The information of the force action around the equilibrium points is required to judge their stability. The force information is provided by the total potential $V_{\text{Total}} = Q(\psi(\mathbf{q})) + V$ with $Q(\psi(\mathbf{q}))$ being the quantum potential determined from Eq.(3.1.7). With the help of Eq.(3.4.4), the Hamiltonian in Eq.(3.4.3) can be recast into the following form

$$H = \frac{m}{2} [\dot{r}^2 + (r\dot{\theta})^2 + (r\dot{\phi} \sin \theta)^2] + V_{\text{Total}}(r, \theta, \phi) = E, \quad (3.4.14)$$

where the total potential is expressed in terms of the wavefunction ψ as

$$V_{\text{Total}} = \frac{\hbar^2}{8mr^2} (4 + \cot^2 \theta) - \frac{\hbar^2}{2m} \left(\frac{\partial^2 \ln \psi}{\partial r^2} + \frac{1}{r^2} \frac{\partial^2 \ln \psi}{\partial \theta^2} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \ln \psi}{\partial \phi^2} \right) + V(r). \quad (3.4.15)$$

When applied to atomic models, the total potential V_{Total} exhibits the observed atomic shell structure.

Example 3.4.2 (Yang, 2005A, 2006C)

Considering hydrogen atom, we have wave function $\psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r)\Theta_{lm_l}(\theta)\Phi_{m_l}(\phi)$, where $R_{nl}(r)$ is expressed in terms of the Laguerre polynomial $L_\alpha^\beta(\rho)$ as $R_{nl}(\rho) = (2\rho/n)^l e^{-\rho/n} L_{n-l-1}^{2l+1}(2\rho/n)$, $\rho = r/a_0$, $n \in \mathbb{N}$; $\Theta_{lm_l}(\theta)$ is expressed in terms of the associated Legendre polynomial $P_\alpha^\beta(z)$ as $\Theta_{lm_l}(\theta) = P_l^{m_l}(\cos \theta)$, $l = 0, 1, 2, \dots, n-1$, and $\Phi_{m_l}(\phi) = e^{im_l\phi}$, $m_l = 0, \pm 1, \pm 2, \dots, \pm l$. The total potential V_{Total} is state-dependent, and the V_{Total} relating to ψ_{nlm_l} is denoted by V_{nlm_l} as

$$\bar{V}_{nlm_l} = V_{\text{Total}} / \left(\frac{\hbar^2}{2ma_0^2} \right) = -\frac{2}{\rho} + \left[\frac{1}{4\rho^2} (4 + \cot^2 \theta) - \frac{d^2 \ln R_{nl}(\rho)}{d\rho^2} - \frac{1}{\rho^2} \frac{d^2 \ln \Theta_{lm_l}(\theta)}{d\theta^2} \right], \quad (3.4.16)$$

where the first term $\bar{V} = -2/\rho$ is the dimensionless Coulomb potential and the remaining terms in \bar{V}_{nlm_l} constitute the quantum potential \bar{Q} . The shell structure observed in hydrogen atom is actually caused by \bar{V}_{nlm_l} , and the quantum force derived from \bar{V}_{nlm_l} provides the necessary driving force to maintain the electron within the shell. Two typical examples \bar{V}_{300} and \bar{V}_{310} are considered here, which are given by

$$\bar{V}_{300}(\rho, \theta) = -\frac{2}{\rho} + \frac{4 + \cot^2 \theta}{4\rho^2} - \frac{4}{2\rho^2 - 18\rho + 27} + \frac{(4\rho - 18)^2}{(2\rho^2 - 18\rho + 27)^2}, \quad (3.4.17)$$

$$\bar{V}_{310}(\rho, \theta) = -\frac{2}{\rho} + \frac{12 + 4 \tan^2 \theta + \cot^2 \theta}{4\rho^2} + \frac{1}{(\rho - 6)^2}. \quad (3.4.18)$$

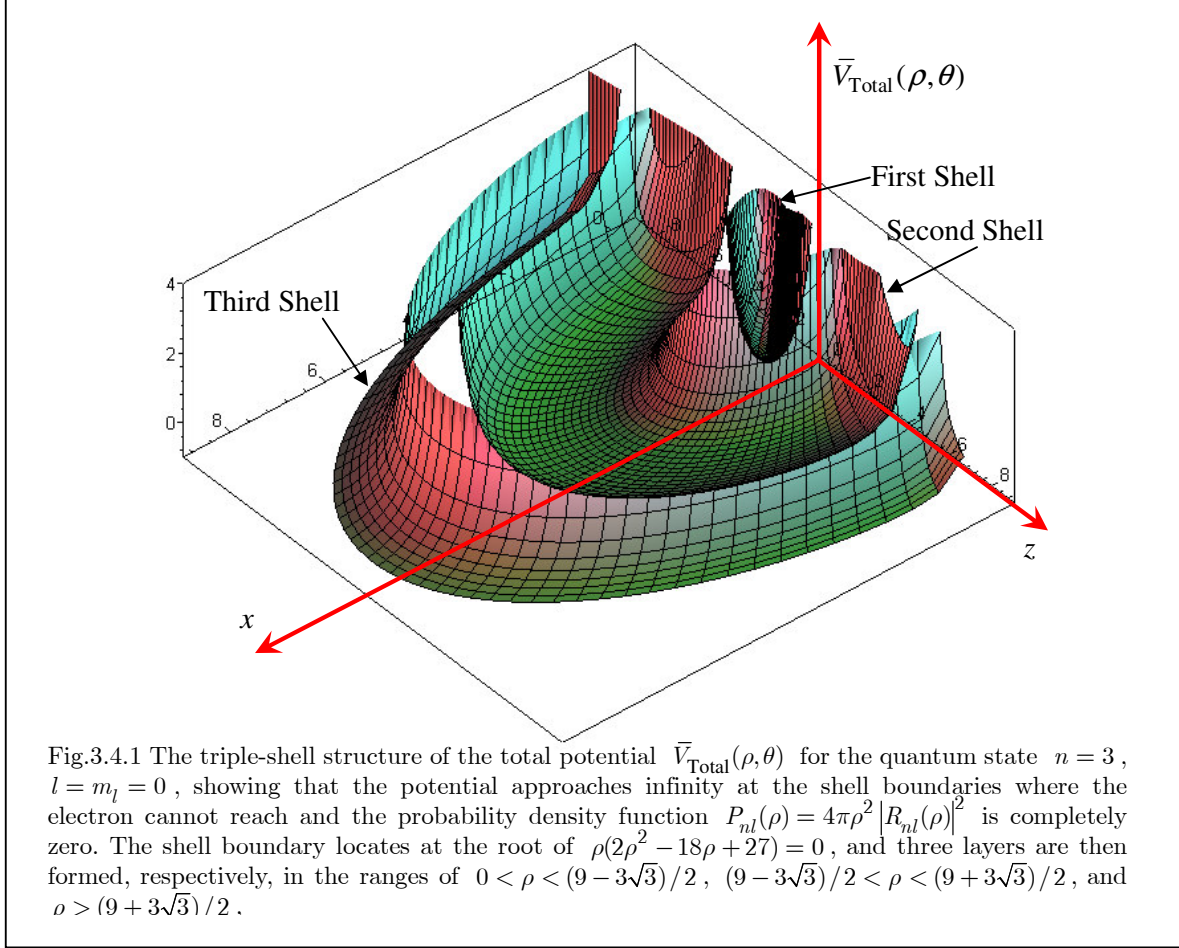
\bar{V}_{300} has three layers distributed in the radial direction and \bar{V}_{310} has four layers with two of them in the radial direction and the other two in the azimuth direction, as shown in Fig.3.4.1 and Fig.3.4.2 According to the definition of \bar{V}_{nlm_l} in Eq.(3.4.16), the radial layers are separated by the infinite potential barriers located at the points:

$$\rho = 0, \quad \text{and} \quad R_{nl}(\rho) = (2\rho/n)^l e^{-\rho/n} L_{n-l-1}^{2l+1}(2\rho/n) = 0. \quad (3.4.19)$$

For a given value of n , there are $n-l$ different values of ρ satisfying Eq.(3.4.19), and hence at most n shells can be divided by these values of ρ , when $l = 0$,

Eq.(3.4.19) gives $\rho(2\rho^2 - 18\rho + 27) = 0$, which can also be obtained directly from the denominator of \bar{V}_{300} in Eq.(3.4.17). The three layers of \bar{V}_{300} are then located, respectively, in the ranges of $0 < \rho < (9 - 3\sqrt{3})/2$, $(9 - 3\sqrt{3})/2 < \rho < (9 + 3\sqrt{3})/2$, and $\rho > (9 + 3\sqrt{3})/2$, as is shown in Fig.3.4.1 for a 3D surface plot. From probability consideration, the probability that the electron appears at the boundary of the layer is zero, since the radial probability density $P_{nl}(\rho) = 4\pi\rho^2 |R_{nl}(\rho)|^2$ is identical to zero at the layer boundary determined from Eq.(3.4.19).

The shell structure of \bar{V}_{310} is distributed in the both radial and azimuth directions. The number and the separation of the azimuth shells are determined by the roots of $\Theta_{lm_l}(z_\theta)$. From Eq.(3.4.16), the potential approaches infinity at the following azimuth angle:

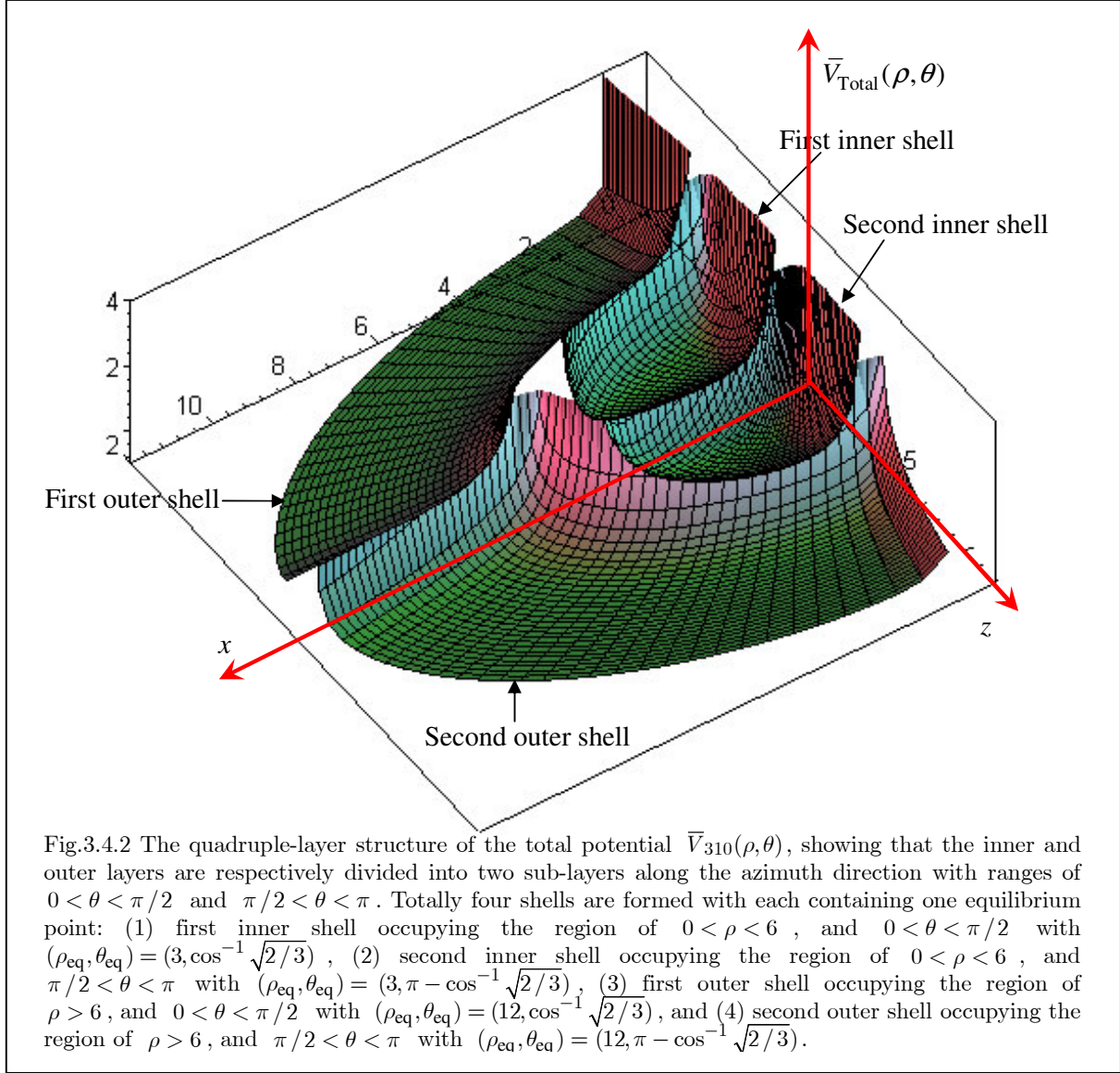


$$z_\theta = 1, \quad \Theta_{lm_l}(z_\theta) = (1 - z_\theta^2)^{|m_l|/2} \frac{d^{|m_l|}}{dz_\theta^{|m_l|}} P_l(z_\theta) = 0, \quad (3.4.20)$$

where $z_\theta = \cos \theta$. For a given quantum number l , the number of azimuth shells is $l - |m_l| + 1$, and the maximum number is $l + 1$ in the case of $m_l = 0$. Accordingly, \bar{V}_{310} has two azimuth shells with boundaries at $z_\theta = 1$ and $\Theta_{310}(z_\theta) = z_\theta = 0$, i.e., at $\theta = 0$ and $\theta = \pi/2$. On the other hand, the number of radial shells of \bar{V}_{310} is equal to $n - l = 2$ with inner shell in the range of $0 < \rho < 6$ and outer shell in the range of $\rho > 6$, as shown in Fig.3.4.2. Combining together the radial and azimuth shells, we have totally four shells with each containing one equilibrium point: (1) first inner shell occupying the region of $0 < \rho < 6$, and $0 < \theta < \pi/2$ with $(\rho_{\text{eq}}, \theta_{\text{eq}}) = (3, \cos^{-1} \sqrt{2/3})$, (2) second inner shell occupying the region of $0 < \rho < 6$, and $\pi/2 < \theta < \pi$ with $(\rho_{\text{eq}}, \theta_{\text{eq}}) = (3, \pi - \cos^{-1} \sqrt{2/3})$, (3) first outer shell occupying the region of $\rho > 6$, and $0 < \theta < \pi/2$ with $(\rho_{\text{eq}}, \theta_{\text{eq}}) = (12, \cos^{-1} \sqrt{2/3})$, and (4) second outer shell occupying the region of $\rho > 6$, and $\pi/2 < \theta < \pi$ with $(\rho_{\text{eq}}, \theta_{\text{eq}}) = (12, \pi - \cos^{-1} \sqrt{2/3})$. A three-dimensional illustration of the four shells of \bar{V}_{310} is shown in Fig.3.4.2. By evaluating the radial probability density function $P_{nl}(\rho) = 4\pi\rho^2 |R_{nl}(\rho)|^2$, it can be checked that the maximum value of $P_{nl}(\rho)$ just occurs at the

equilibrium points $(\rho_{\text{eq}}, \theta_{\text{eq}})$, i.e., the lowermost point in each subshell, as proved in Theorem 3.4.3. \square

With given V_{Total} , the quantum forces in the three directions can be determined, respectively, as $f_r = -\partial V_{\text{Total}} / \partial r$, $f_\theta = -\partial V_{\text{Total}} / \partial \theta$ and $f_\phi = -\partial V_{\text{Total}} / \partial \phi$. These quantum forces together with the Coulomb force establish the stable configurations for atomic structure, as will be discussed in Chapter 5.



It is well known that the angular momentum L^2 defined in Eq.(3.4.9) involves only orbit motion. By contrast, the angular momentum $P_\theta = mr^2\dot{\theta}$ derived in Eq.(3.4.5b) contains both spin and orbit motions. The corresponding local angular momentum P_θ can be found from the relation (3.4.5b) or Eq.(3.4.4b) as

$$P_\theta = mr^2\dot{\theta} = \frac{\hbar}{i} \frac{1}{\psi} \frac{\partial \psi}{\partial \theta} + \frac{\hbar}{i} \frac{\cot \theta}{2} = L_\theta + S, \quad (3.4.21)$$

where L_θ is the θ -component orbital angular momentum, and S is the local spin angular momentum. It can be seen that the local spin $S = \hbar/(2i) \cot \theta$ is independent of the wavefunction ψ and thus also independent of the applied potential V . Like the proof of the quantization of action variable mentioned in Theorem 3.3.2, the quantization of the mean value of L_θ can be determined from the contour integral over a closed path c_θ in the θ complex plane as

$$\begin{aligned}\langle L_\theta \rangle &= \frac{1}{2\pi} \oint_{c_\theta} L_\theta d\theta = \frac{\hbar}{2\pi i} \oint_{c_\theta} \frac{1}{\psi} \frac{\partial \psi}{\partial \theta} d\theta = \frac{\hbar}{2\pi i} \oint_{c_\psi} \frac{1}{\psi} \frac{d\psi_\theta}{d\theta} d\theta = \frac{\hbar}{2\pi i} \oint_{c_\psi} d(\ln \psi_\theta) \\ &= \hbar n_\theta, \quad n_\theta = 0, 1, 2, 3, \dots\end{aligned}\quad (3.4.22)$$

where $\psi_\theta(\theta)$ is a function of the single variable θ obtained from $\psi(r, \theta, \phi)$ by treating r and ϕ as constants. The function ψ_θ maps the closed path c_θ in the complex θ plane into a closed path c_ψ in the complex ψ_θ plane, and the quantum number n_θ is the number of encirclement of the origin in the ψ_θ plane by the closed path c_ψ . Analogously, we have the quantization of the ϕ -component orbital angular momentum as

$$\langle L_\phi \rangle = \frac{\hbar}{2\pi i} \oint_{c_\phi} \frac{1}{\psi} \frac{\partial \psi}{\partial \phi} d\phi = \hbar n_\phi, \quad n_\phi = 0, 1, 2, 3, \dots \quad (3.4.23)$$

We now turn the attention to the spin quantization. Using Eq.(3.4.21), the mean local spin is given by

$$\langle S \rangle = \frac{1}{2\pi} \oint_{c_\theta} S d\theta = \frac{\hbar}{4\pi i} \oint_{c_\theta} \cot \theta d\theta. \quad (3.4.24)$$

Noting the residue of $\cot \theta$ at its poles $\theta = n\pi$, $n \in \mathbb{Z}$, is equal to 1, we have from the residue theory

$$\langle S \rangle = \frac{\hbar}{4\pi i} (2\pi i n_\theta) = \frac{\hbar}{2} n_s, \quad n_s = 0, 1, 2, 3, \dots, \quad (3.4.25)$$

where n_s is the number of zero of $\sin \theta$, i.e., $n\pi$, $n \in \mathbb{Z}$, enclosed by the contour c_θ , and also note that since $\sin \theta$ is an analytical function, the number of pole of $\sin \theta$ enclosed by c_θ is always zero. It is worth noting that upon arriving at the result (3.4.25), we do not specify the type of particles, neither the type of the applied potential. The spin quantization rule (3.4.25) says that the value of the mean spin is only allowed to be integer multiple of $\hbar/2$; furthermore, it provides us with a geometrical method to identify the spin of a given particle by

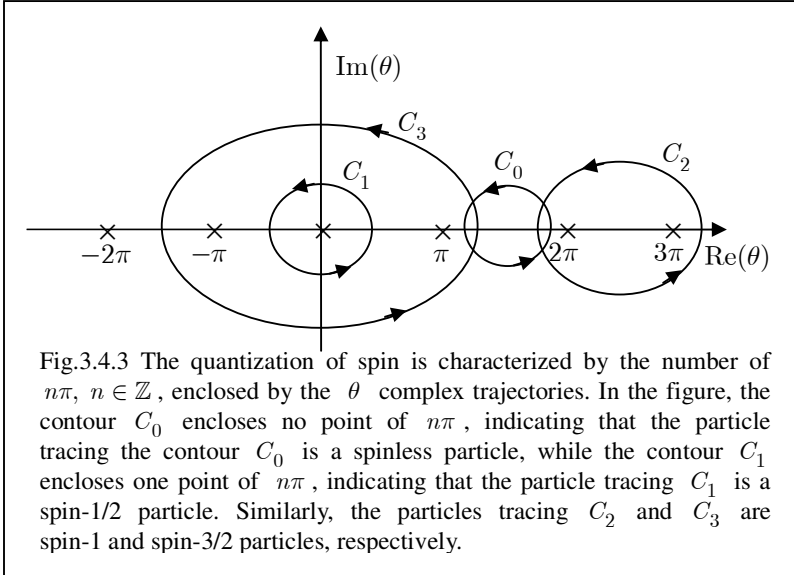


Fig.3.4.3 The quantization of spin is characterized by the number of $n\pi$, $n \in \mathbb{Z}$, enclosed by the θ complex trajectories. In the figure, the contour C_0 encloses no point of $n\pi$, indicating that the particle tracing the contour C_0 is a spinless particle, while the contour C_1 encloses one point of $n\pi$, indicating that the particle tracing C_1 is a spin-1/2 particle. Similarly, the particles tracing C_2 and C_3 are spin-1 and spin-3/2 particles, respectively.

inspecting any of its θ trajectory c_θ and counting the number of the point $n\pi$, $n \in \mathbb{Z}$ within it. The θ trajectory can be found by integrating Eqs.(3.4.4).

Referring to the demonstration in Fig.3.4.3, the contour C_0 encloses no point of $n\pi$, indicating that the particle tracing the contour C_0 is spinless, while the contour C_1 encloses one point of $n\pi$, indicating that the particle tracing C_1 is a spin-1/2 particle. Similarly, the particles tracing C_2 and C_3 are spin-1 and spin-3/2 particles, respectively. The practical computation of the electron trajectory in the hydrogen atom using the Hamilton equations of motion (3.4.4) shows that the related trajectory belongs to the type of C_1 and thus confirms an electron as being a spin-1/2 particle.

Corresponding to the canonical momenta p_r , p_θ , and p_ϕ , we can find their associated canonical operators \hat{p}_r , \hat{p}_θ , and \hat{p}_ϕ from Eq.(3.4.2) :

$$p_r = \frac{\hbar}{i} \frac{1}{\psi} \frac{\partial \psi}{\partial r}, \quad p_\theta = \frac{\hbar}{i} \frac{1}{\psi} \frac{\partial \psi}{\partial \theta}, \quad p_\phi = \frac{\hbar}{i} \frac{1}{\psi} \frac{\partial \psi}{\partial \phi}, \quad (3.4.26)$$

and from the definition (3.3.1)

$$p_r = \frac{1}{\psi} \hat{p}_r \psi, \quad p_\theta = \frac{1}{\psi} \hat{p}_\theta \psi, \quad p_\phi = \frac{1}{\psi} \hat{p}_\phi \psi. \quad (3.4.27)$$

The comparison of Eq.(3.4.26) with Eq.(3.4.27) gives

$$\hat{p}_r = \frac{\hbar}{i} \frac{\partial}{\partial r}, \quad \hat{p}_\theta = \frac{\hbar}{i} \frac{\partial}{\partial \theta}, \quad \hat{p}_\phi = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \quad (3.4.28)$$

The canonical momenta p_r , p_θ , and p_ϕ must not be confused with the mechanical momenta $P_r = \dot{r}$, $P_\theta = mr^2 \dot{\theta}$, and $P_\phi = mr^2 \dot{\phi} \sin^2 \theta$, which can be found from Eqs.(3.4.4) as

$$P_r = m\dot{r} = \frac{1}{\psi} \left(\frac{\hbar}{i} \frac{\partial}{\partial r} + \frac{1}{r} \right) \psi = \frac{1}{\psi} \hat{P}_r \psi \quad (3.4.29a)$$

$$P_\theta = mr^2 \dot{\theta} = \frac{1}{\psi} \left(\frac{\hbar}{i} \frac{\partial}{\partial \theta} + \frac{\cot \theta}{2} \right) \psi = \frac{1}{\psi} \hat{P}_\theta \psi \quad (3.4.29b)$$

$$P_\phi = mr^2 \dot{\phi} \sin^2 \theta = \frac{1}{\psi} \left(\frac{\hbar}{i} \frac{\partial}{\partial \phi} \right) \psi = \frac{1}{\psi} \hat{P}_\phi \psi \quad (3.4.29c)$$

from the which the mechanical momentum operators can be identified as

$$\hat{P}_r = \frac{\hbar}{i} \left(\frac{\partial}{\partial r} + \frac{1}{r} \right), \quad \hat{P}_\theta = \frac{\hbar}{i} \left(\frac{\partial}{\partial \theta} + \frac{\cot \theta}{2} \right), \quad \hat{P}_\phi = \frac{\hbar}{i} \frac{\partial}{\partial \phi}. \quad (3.4.30)$$

It can be seen that unlike Cartesian coordinates, in spherical coordinates the canonical momentum operators \hat{p}_r , \hat{p}_θ , and \hat{p}_ϕ are distinct from the mechanical momentum operators \hat{P}_r , \hat{P}_θ , and \hat{P}_ϕ in the additional terms $-\hbar/r$ and $(-\hbar/2) \cot \theta$. It can be seen that \hat{P}_r and $\hat{P}_\phi = \hat{L}_z$ are identical to those derived in Eq.(3.4.7), where they have been obtained alternatively from the expressions for P_r and p_ϕ . Here we obtain the same \hat{P}_r and \hat{P}_ϕ directly from the Hamilton equations of motion (3.4.4).

The combination of \hat{P}_θ and \hat{P}_ϕ in Eq.(3.4.30) affords us the information of total angular momentum.

Theorem 3.4.4

In spherical coordinates, the total angular momentum operator is given by

$$\hat{\mathbf{J}}^2 = \hat{P}_\theta^2 + \frac{\hat{P}_\phi^2}{\sin^2 \theta} = \hat{\mathbf{L}}^2 + (\hbar/2)^2 + \frac{(\hbar/2)^2}{\sin^2 \theta}, \quad (3.4.31)$$

where $\hat{\mathbf{L}}^2$ is the usual orbit angular momentum operator defined in Eq.(6.7).

Proof: The combination of the θ -component and the ϕ -component angular momenta gives the total angular momentum vector as

$$\mathbf{J} = P_\theta \mathbf{e}_\theta + \frac{P_\phi}{\sin \theta} \mathbf{e}_\phi = P_\theta \mathbf{e}_\theta + \frac{L_z}{\sin \theta} \mathbf{e}_\phi, \quad (3.4.32)$$

which has the operator representation:

$$\hat{\mathbf{J}} = \hat{P}_\theta \mathbf{e}_\theta + \frac{\hat{L}_z}{\sin \theta} \mathbf{e}_\phi, \quad (3.4.33)$$

where \mathbf{e}_θ and \mathbf{e}_ϕ are, respectively, the unit vectors in the θ and ϕ directions. Using the definitions of \hat{P}_θ and $\hat{P}_\phi = \hat{L}_z$ from Eq.(3.4.30), the operation represented by $\hat{\mathbf{J}}^2$ becomes

$$\hat{\mathbf{J}}^2 \psi = (\hat{\mathbf{J}} \cdot \hat{\mathbf{J}}) \psi = \hat{P}_\theta^2 \psi + \frac{1}{\sin^2 \theta} \hat{P}_\phi^2 \psi, \quad (3.4.34)$$

where $\hat{P}_\theta^2 \psi$ and $\hat{P}_\phi^2 \psi$ are evaluated, respectively, as

$$\begin{aligned} \hat{P}_\theta^2 \psi &= \hat{P}_\theta (\hat{P}_\theta \psi) = \left(\frac{\hbar}{i} \right)^2 \left(\frac{\partial}{\partial \theta} + \frac{\cot \theta}{2} \right) \left(\frac{\partial \psi}{\partial \theta} + \frac{\cot \theta}{2} \psi \right) \\ &= -\hbar^2 \left(\frac{\partial^2 \psi}{\partial \theta^2} + \cot \theta \frac{\partial \psi}{\partial \theta} \right) + \left[(\hbar/2)^2 + \frac{(\hbar/2)^2}{\sin^2 \theta} \right] \psi \end{aligned} \quad (3.4.35a)$$

$$\hat{P}_\phi^2 \psi = \left(\frac{\hbar}{i} \frac{\partial}{\partial \phi} \right) \left(\frac{\hbar}{i} \frac{\partial \psi}{\partial \phi} \right) = -\hbar^2 \frac{\partial^2 \psi}{\partial \phi^2}. \quad (3.4.35b)$$

The substitution of \hat{P}_θ^2 and \hat{P}_ϕ^2 into Eq.(3.4.34) gives rise to the representation of \hat{J}^2 as

$$\hat{J}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) + \left[(\hbar/2)^2 + \frac{(\hbar/2)^2}{\sin^2 \theta} \right], \quad (3.4.36)$$

where the first three terms in \hat{J}^2 is the orbital angular momentum operator \hat{L}^2 already derived in Eq.(3.4.7) and the remaining two terms are due to spin motion \square

3.5 Complex Hamiltonian and Complex Energy

Since in complex mechanics, position and momentum are defined in a complex domain, it is natural to expect that energy in complex mechanics is also defined in a complex sense. Let us begin this discussion with the harmonic oscillator in Example 3.2.1. Classical Hamiltonian for a harmonic oscillator in dimensionless form is given by

$$H_1^{(c)} = \frac{1}{2}(p_1^2 + x_1^2), \quad (3.5.1)$$

and its related Hamiltonian operator reads

$$\hat{H}_1 = \frac{1}{2} \hat{p}_1^2 + \frac{1}{2} \hat{x}_1^2 = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial x_1^2} + \frac{1}{2} x_1^2. \quad (3.5.2)$$

Solving the eigenvalue problem of $\hat{H}_1 \psi = E \psi$, we can find the eigenvalue and eigenfunction as

$$\psi_{1,n} = C_n H_n(x_1) e^{-x_1^2/2}, \quad E_{1,n} = n + 1/2, \quad n = 0, 1, 2, \dots \quad (3.5.3)$$

It can be seen that the eigen energies $E_{1,n}$ of a harmonic oscillator are real. Real energy has a deeper implication in complex mechanics, if we call that the position and momentum are both complex and consider why energy composed from them is real. According to Eq.(3.2.18), the equation of motion in the eigen state $\psi_{1,n}$ is given by

$$\frac{dx_1}{dt} = p_1 = \frac{\hbar}{i} \frac{1}{\psi_n(x_1)} \frac{d\psi_n(x_1)}{dx_1}. \quad (3.5.4a)$$

Especially for $n = 0$ and $n = 1$, we have

$$n = 0: \quad \frac{dx_1}{dt} = i x_1, \quad (3.5.4b)$$

$$n = 1: \quad \frac{dx_1}{dt} = i \frac{x_1^2 - 1}{x_1}. \quad (3.5.4c)$$

We can see that the momentum p_1 given by Eq.(3.5.4a) is complex and the position $x_1(t)$ solved from Eq.(3.5.4a) is also complex. However, the total energy formed from p_1 and $x_1(t)$ are real, as shown in Eq.(3.2.14):

$$H_1(x_1, p_1) = \frac{1}{2} p_1^2 + \frac{1}{2} x_1^2 - \frac{1}{2} \frac{d^2 \ln \psi_n(x_1)}{dx_1^2} = E_{1,n} = n + 1/2, \quad (3.5.5)$$

where $p_1 \in \mathbb{C}$ and $x_1 \in \mathbb{C}$, but E_n is real. Such a situation that complex position and momentum result in real energy is not an accident. Not every Hamiltonian operator \hat{H} has real eigenvalues.

In conventional quantum mechanics, one imposes the Hermitian condition $H^{(c)*} = H^{(c)}$, where $*$ represents complex conjugate transpose, to ensure that the Hamiltonian operator \hat{H} has a real eigenvalue (real energy). It was pointed out by Bender [1998] that the reality of the eigenvalue of \hat{H} is actually due to a weaker condition called PT symmetry. PT represents combined parity reflection P and time reversal T . The effect of parity reflection P is to make spatial reflections, $p \rightarrow -p$ and $x \rightarrow -x$, while the effect of time reversal T is to make the replacements $p \rightarrow -p$, $x \rightarrow x$, and $i \rightarrow -i$. Consider the following classical Hamiltonian

$$H_2^{(c)} = \frac{1}{2}(p_2^2 + x_2^2 + ix_2), \quad (3.5.6)$$

which is neither P symmetric nor T symmetric, but is nevertheless PT symmetric. Hence, \hat{H}_2 has real eigenvalues though it has an imaginary component ix_2 . From the viewpoint of quantum mechanics, the complexity of the Hamiltonian in Eq.(3.5.6) is only due to the multiplication by the imaginary number i , since p_2 and x_2 are treated as real variables therein; while in complex mechanics, p_2 and x_2 are complex variables, and the Hamiltonian is complex, regardless of the appearance of the i factor. Consider another classical Hamiltonian

$$H_3^{(c)} = \frac{1}{2}(p_3^2 + x_3^2 - x_3 + ix_3), \quad (3.5.7)$$

which is not PT symmetric, and the eigenvalue of \hat{H}_3 is complex.

Defining canonical variables (x, p) in a complex plane has a remarkable significance that Hermitian systems such as $H_1^{(c)}$, PT-symmetry systems such as $H_2^{(c)}$, and non-PT-symmetry systems such as $H_3^{(c)}$, can be unified into a more general class of Hamiltonians whose elements are all shift-invariant over the complex plane. The eigenfunctions for \hat{H}_2 and \hat{H}_3 can be found as

$$\psi_{2,n}(x_2) = C_n H_n(x_2 + i/2) e^{-(x_2 + i/2)^2/2}, \quad (3.5.8a)$$

$$\psi_{3,n}(x_3) = C_n H_n(x_3 + i/2 - 1/2) e^{-(x_3 + i/2 - 1/2)^2/2}. \quad (3.5.8b)$$

In terms of the Hermitian eigenfunction $\psi_{1,n}$ in Eq.(3.5.3), we can express $\psi_{2,n}$ and $\psi_{3,n}$ as

$$\psi_{2,n}(x_2) = \psi_{1,n}(x_1) \Big|_{x_1=x_2+i/2}, \quad \psi_{3,n}(x_3) = \psi_{1,n}(x_1) \Big|_{x_1=x_3+i/2-1/2}. \quad (3.5.9)$$

which means that the three eigenfunctions $\psi_{1,n}$, $\psi_{2,n}$, and $\psi_{3,n}$ can be made identical by linear coordinate translation over the complex plane. This relation also reflects in their respective intrinsic complex Hamiltonian:

$$H_2(x_2) = \frac{1}{2} \left[p_2^2 + (x_2 + i/2)^2 - \frac{d^2}{dx_2^2} \ln \psi_{2,n}(x_2) \right] + \frac{1}{8}, \quad (3.5.10a)$$

$$H_3(x_3) = \frac{1}{2} \left[p_3^2 + (x_3 + i/2 - 1/2)^2 - \frac{d^2}{dx_3^2} \ln \psi_{3,n}(x_3) \right] + \frac{i}{4}. \quad (3.5.10b)$$

Using the relations (3.5.9) and the definition of H_1 , we can rewrite Eqs.(3.5.10) as

$$H_2(x_2) = H_1(x_1) \Big|_{x_1=x_2+i/2} + 1/8, \quad H_3(x_3) = H_1(x_1) \Big|_{x_1=x_3+i/2-1/2} + i/4, \quad (3.5.11)$$

which shows that there is a constant real energy shift, $1/8$, between $H_2(x_2)$ and $H_1(x_1)$, and a constant imaginary energy shift, $i/4$, between $H_3(x_3)$ and $H_1(x_1)$. According to the energy conservation law (3.5.5), the energy levels for H_2 and H_3 in Eqs.(3.5.11) can be expressed in terms of $E_{1,n}$ as

$$E_{2,n} = E_{1,n} + 1/8 = n + 5/8, \quad E_{3,n} = E_{1,n} + i/4 = n + 1/2 + i/4, \quad n = 0, 1, 2, \dots \quad (3.5.12)$$

The same results can also be obtained by calculating the eigenvalues of \hat{H}_2 and \hat{H}_3 directly. The results of Eq.(3.5.12) confirm the prediction that the PT-symmetric system \hat{H}_2 has real eigenvalues, while the non-Pt-symmetric system \hat{H}_3 has complex eigenvalues.

In the usual interpretation, x_1 , x_2 , and x_3 are regarded as real variables, and consequently, the eigenfunction $\psi_{1,n}(x_1)$ in Eq.(3.5.3) is regarded as real because x_1 is real, but the eigenfunctions $\psi_{2,n}(x_2)$ and $\psi_{3,n}(x_3)$ in Eqs.(3.5.8) are complex due to the appearance of the imaginary number i . This is the very reason why the distinctions between Hermitian systems, PT-symmetry systems, and non-PT-symmetry systems can be brought out. The system \hat{H}_1 is said to be Hermitian, because both its eigenfunction $\psi_{1,n}(x_1)$ and eigenvalue $E_{1,n}$ are real. The eigenfunction $\psi_{2,n}(x_2)$ of \hat{H}_2 is complex, but its eigenvalue $E_{2,n}$ is real as ensured by the PT-symmetric property. The system \hat{H}_3

is non-PT-symmetric and both its eigenfunction and eigenvalue are complex. However, if we treat x_1 , x_2 , and x_3 as complex variables, the above distinctions between \widehat{H}_1 , \widehat{H}_2 , and \widehat{H}_3 no longer exist, because now their eigenfunctions are all complex and can be made identical by complex coordinate translation as indicated in Eq.(3.5.9), and meanwhile their eigenvalues can be made coincident by constant shift of complex energy as shown in Eq.(3.5.11) and Eq.(3.15.2).

It can be further shown that the eigen-trajectories for \widehat{H}_1 , \widehat{H}_2 , and \widehat{H}_3 are also shift-invariant. Like Eq.(3.5.4a), the eigen-trajectories for \widehat{H}_2 , and \widehat{H}_3 are governed by the following equations of motion:

$$\frac{dx_2}{dt} = -i \frac{d \ln \psi_{2,n}(x_2)}{dx_2}, \quad \frac{dx_3}{dt} = -i \frac{d \ln \psi_{3,n}(x_3)}{dx_3}, \quad (3.5.13)$$

where $\psi_{2,n}(x_2)$ and $\psi_{3,n}(x_3)$ are given by Eqs.(3.5.8). Especially, for $n = 0$ and $n = 1$ we have

$$n = 0: \quad \frac{dx_2}{dt} = i(x_2 + i/2), \quad \frac{dx_3}{dt} = i(x_3 + i/2 - 1/2), \quad (3.5.14a)$$

$$n = 1: \quad \frac{dx_2}{dt} = i \frac{(x_2 + i/2)^2 - 1}{x_2 + i/2}, \quad \frac{dx_3}{dt} = i \frac{(x_3 + i/2 - 1/2)^2 - 1}{x_3 + i/2 - 1/2}. \quad (3.5.14b)$$

In comparison with Eqs.(3.5.4), it can be seen that the eigen-trajectories $x_1(t)$, $x_2(t)$, and $x_3(t)$ also obey the shift-invariant properties appearing in Eq.(3.5.9) and Eq.(3.5.11), i.e.,

$$\bar{x}_H(\tau) = \bar{x}_S(\tau) + i/2, \quad \bar{x}_H(\tau) = \bar{x}_U(\tau) + i/2 - 1/2. \quad (3.5.15)$$

A numerical illustration of this shift-invariant property for ground-state trajectories is shown in Fig.3.5.1, where we can see that the eigen-trajectory $x_2(t)$ is obtained from $x_1(t)$ by a parallel translation $-i/2$, while $x_3(t)$ is obtained from $x_1(t)$ by a parallel translation $-i/2 + 1/2$ as predicted by Eq.(3.5.15). Similar translational relation between $x_1(t)$ and $x_2(t)$ can be observed for the first excited state, as depicted in the left figure of Fig.3.5.1.

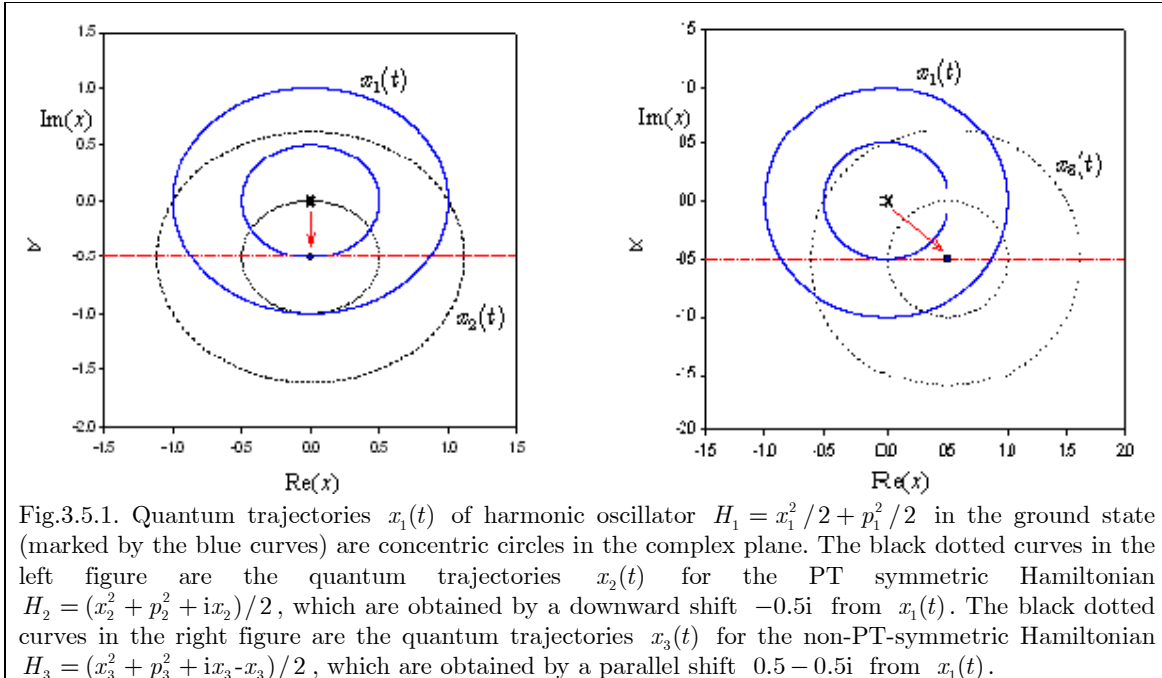


Fig.3.5.1. Quantum trajectories $x_1(t)$ of harmonic oscillator $H_1 = x_1^2/2 + p_1^2/2$ in the ground state (marked by the blue curves) are concentric circles in the complex plane. The black dotted curves in the left figure are the quantum trajectories $x_2(t)$ for the PT symmetric Hamiltonian $H_2 = (x_2^2 + p_2^2 + ix_2)/2$, which are obtained by a downward shift $-0.5i$ from $x_1(t)$. The black dotted curves in the right figure are the quantum trajectories $x_3(t)$ for the non-PT-symmetric Hamiltonian $H_3 = (x_3^2 + p_3^2 + ix_3 - x_3)/2$, which are obtained by a parallel shift $0.5 - 0.5i$ from $x_1(t)$.

Eq.(3.2.14) shows that a system's total energy $H(x, p)$ becomes complex when it has complex eigenvalue E . A system transiting between two real eigenstates may also possess complex energy during the transition process. To reveal this property, we analyze a harmonic oscillator transiting from the ground state $\psi_0(x) = e^{-x^2/2}$ with energy level $E_0 = 1/2$ to the first excited state $\psi_1(x) = 2xe^{-x^2/2}$ with energy level $E_1 = 3/2$. The whole transition behavior is described by the following wavefunction

$$\Psi(x, t) = \begin{cases} e^{-x^2/2} e^{-iE_0 t} & t \leq 0 \\ (1-t)e^{-x^2/2} + 2txe^{-x^2/2}, & 0 < t < 1. \\ 2xe^{-x^2/2} e^{-iE_1 t} & t \geq 1 \end{cases} \quad (3.5.16)$$

Inserting Eq.(3.5.16) into Eq.(3.2.18) yields the governing equations for this state transition process

$$p = \frac{dx}{dt} = \begin{cases} ix & t \leq 0 \\ ix - i \frac{2t}{2tx - t + 1}, & 0 < t < 1. \\ i(x^2 - 1)/x & t \geq 1 \end{cases} \quad (3.5.17)$$

Complex trajectories in the time range $t \leq 0$ and $t \geq 1$ are just the eigen-trajectories for $n = 0$ and $n = 1$, as shown in Fig.3.5.1 and Fig.3.5.2, respectively. The governing equation in the time interval $0 < t < 1$ is a non-autonomous nonlinear differential equation whose solution can only be found numerically. Connecting the complex trajectories $x(t) = x_R(t) + ix_I(t)$ for the above three time ranges offers a continuous manifestation of the entire state transition process from $n = 0$ state to $n = 1$ state. The total energy E_{Total} is observed to evolve continuously from $E_{\text{Total}} = E_0 = 1/2$ to $E_{\text{Total}} = E_1 = 3/2$ via a complex trajectory. The overall time history of $E_{\text{Total}}(t)$ can be described by

$$E_{\text{Total}}(t) = \frac{p^2}{2} + \frac{x^2}{2} + Q(x, t) = \begin{cases} 1/2 & t \leq 0 \\ \frac{1}{2} \frac{6tx(t) - t + 1}{2tx(t) - t + 1}, & 0 < t < 1, \\ 3/2 & t \geq 1 \end{cases} \quad (3.5.18)$$

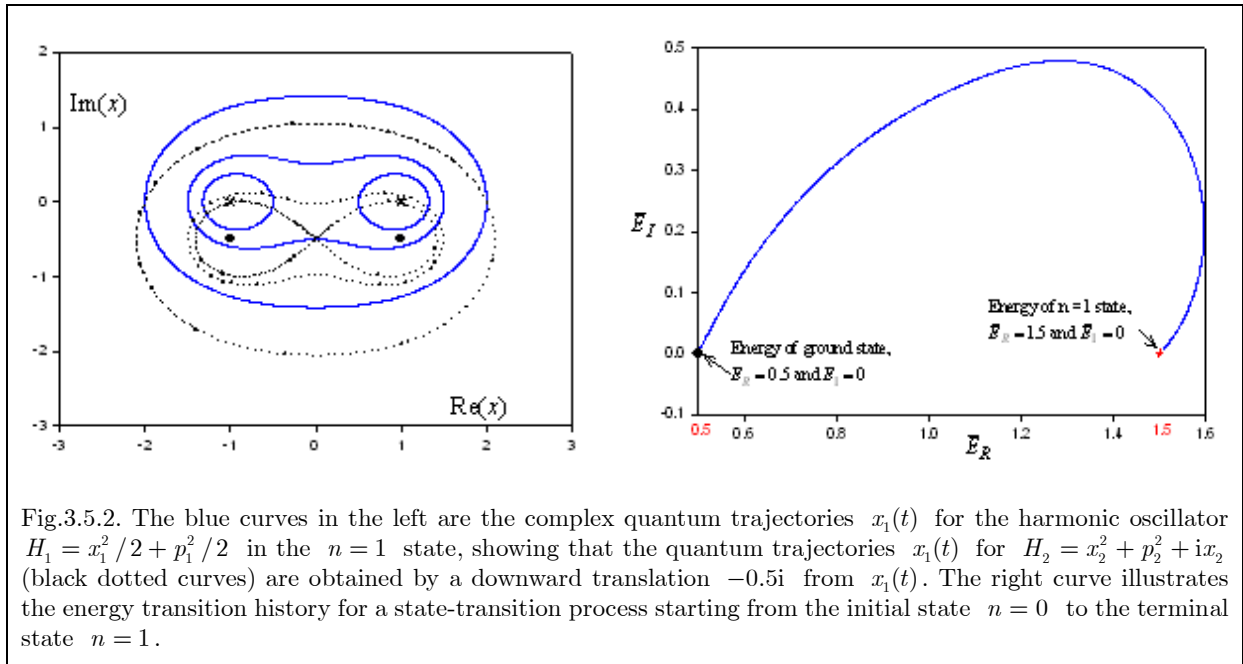


Fig.3.5.2. The blue curves in the left are the complex quantum trajectories $x_1(t)$ for the harmonic oscillator $H_1 = x_1^2/2 + p_1^2/2$ in the $n = 1$ state, showing that the quantum trajectories $x_0(t)$ for $H_0 = x_0^2/2 + p_0^2/2$ (black dotted curves) are obtained by a downward translation $-0.5i$ from $x_1(t)$. The right curve illustrates the energy transition history for a state-transition process starting from the initial state $n = 0$ to the terminal state $n = 1$.

where the momentum p and the quantum potential Q are determined, respectively, by Eq.(3.2.11) and Eq.(3.5.16), and the quantum complex trajectory $x(t)$ are solved from Eq.(3.5.17). It can be seen from Eq.(3.5.18) that the total energy $E_{\text{Total}}(t)$ is complex-valued due to the complex nature of $x(t)$. The evolution of $E_{\text{Total}}(t)$ in the complex plane is demonstrated in the right figure of Fig.3.5.2, showing that except at $\tau = 0$ and $\tau = 1$, the harmonic oscillator during the transition process does

have complex total energy.

3.6 Chapter Summary

In summary, under the framework of complex mechanics a quantum operator \hat{A} is not merely an abstract mathematic operation; it indeed represents a physical entity $A(\mathbf{q}, \mathbf{p})$ in complex-extended Hamilton mechanics. Knowing the expression for $A(\mathbf{q}, \mathbf{p})$ with \mathbf{q} and \mathbf{p} satisfying Hamilton equations of motion allows us to deduce \hat{A} readily. The Hamilton-mechanical approach to deriving quantum operator has released two limitations encountered in the quantization axiom $\mathbf{p} \rightarrow \hat{\mathbf{p}} = i\hbar\nabla$, i.e., the limitation to Cartesian coordinates and the limitation to observables having classical counterpart. Under complex spacetime, we have shown that quantum operators can be derived directly in any coordinate system without transforming back to Cartesian coordinates, and that angular momentum operator containing spin effect can be derived naturally without assuming any spin motion in advance.

3.7 Problems

3.1 This problem is designed to guide you step by step to derive the orbital angular momentum operator \hat{L}^2 in Eq.(3.4.7) from the Cartesian coordinates. In Theorem 3.4.2, we have derived \hat{L}^2 directly in spherical coordinates. By contrast, standard quantum mechanics have to derive \hat{L}^2 firstly in Cartesian coordinates, as done in Example 3.3.1

$$\hat{L}_x = \frac{\hbar}{i} \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \quad \hat{L}_y = \frac{\hbar}{i} \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right), \quad \hat{L}_z = \frac{\hbar}{i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad (3.7.1)$$

and then to obtain the spherical \hat{L}^2 by the following coordinate transformation:

$$x = r \sin(\theta) \cos(\phi), \quad y = r \sin(\theta) \sin(\phi), \quad z = r \cos(\theta). \quad (3.7.2a)$$

or inversely,

$$r = \sqrt{x^2 + y^2 + z^2}, \quad \theta = \cos^{-1} \left(z / \sqrt{x^2 + y^2 + z^2} \right), \quad \phi = \tan^{-1}(y/x) \quad (3.7.2b)$$

(a) Express the partial differentiations $\partial/\partial x$, $\partial/\partial y$, and $\partial/\partial z$ involved in Eq.(3.7.1) in terms of r , θ , ϕ , $\partial/\partial r$, $\partial/\partial\theta$, and $\partial/\partial\phi$. Hint: Use the relations (3.7.2) and apply the following chain rules:

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x} \frac{\partial}{\partial \phi}, \quad (3.7.3a)$$

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial y} \frac{\partial}{\partial \phi}, \quad (3.7.3b)$$

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial z} \frac{\partial}{\partial \phi}. \quad (3.7.3c)$$

(b) Employ the above result in Eq.(3.7.1) and show

$$\hat{L}_x = i\hbar \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \quad (3.7.4b)$$

$$\hat{L}_y = i\hbar \left(-\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right), \quad \hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} \quad (3.7.4a)$$

(c) Square Eq.(3.7.4) to verify the final expression

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]. \quad (3.7.5)$$

Notice that to square an operator means to repeat the operation twice. For instance,

$$\widehat{L}_x^2 \psi = \widehat{L}_x (\widehat{L}_x \psi) = -\hbar^2 \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \psi.$$

3.2 This problem aims to familiarize you with the quantum Hamilton equations of motion under polar coordinates.

- (a) Express $\mathbf{p} \cdot \mathbf{p}$ and $\nabla \cdot \mathbf{p}$ in polar coordinates (r, ϕ) and show that the quantum Hamiltonian (3.1.6) turns out to be

$$\begin{aligned} H &= \frac{1}{2m} \left[p_r^2 + \frac{\hbar}{i} \left(\frac{1}{r} p_r + \frac{\partial^2 S}{\partial r^2} \right) \right] + \frac{1}{2mr^2} \left(p_\phi^2 + \frac{\hbar}{i} \frac{\partial^2 S}{\partial \phi^2} \right) + V(r, \phi) \\ &= \frac{1}{2m} P_r^2 + \frac{1}{2mr^2} L^2 + V(r, \phi) \end{aligned} \quad (3.7.6)$$

In comparison with their classical counterparts, the mechanical momenta P_r and L contain additional quantum correction terms:

$$P_r^2 = p_r^2 + \frac{\hbar}{i} \left(\frac{1}{r} p_r + \frac{\partial^2 S}{\partial r^2} \right), \quad L^2 = p_\phi^2 + \frac{\hbar}{i} \frac{\partial^2 S}{\partial \phi^2}, \quad (3.7.7)$$

where the terms involving Planck constant stem from quantum correction.

- (b) Show that the Hamilton equations $\dot{r} = \partial H / \partial p_r$ and $\dot{\phi} = \partial H / \partial p_\phi$ become

$$\dot{r} = \frac{p_r}{m} + \frac{\hbar}{2mri}, \quad \dot{\phi} = \frac{p_\phi}{mr^2} \quad (3.7.8)$$

where the canonical momenta p_r and p_ϕ are related to the action function S and the wave function ψ via

$$p_r = \frac{\partial S}{\partial r} = \frac{\hbar}{i} \frac{\partial \ln \psi}{\partial r}, \quad p_\phi = \frac{\partial S}{\partial \phi} = \frac{\hbar}{i} \frac{\partial \ln \psi}{\partial \phi}. \quad (3.7.9)$$

- (c) Starting with Eq.(3.7.7) or Eq.(3.7.8) and referring to the Definition 3.3.1, show that the mechanical momenta $P_r = m\dot{r}$ and $P_\phi = L = mr^2\dot{\phi}$ have the following operator representation:

$$\widehat{P}_r = \frac{\hbar}{i} \left(\frac{\partial}{\partial r} + \frac{1}{2r} \right), \quad \widehat{P}_\phi = \widehat{L} = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \quad (3.7.10)$$

- (d) Show that the other set of the Hamilton equations $\dot{p}_r = -\partial H / \partial r$ and $\dot{p}_\phi = -\partial H / \partial \phi$ is reduced to the Lagrange equations of motion:

$$m\ddot{r} - mr\dot{\phi}^2 = -\frac{\partial V}{\partial r} - \frac{\partial Q}{\partial r}, \quad 2mri\dot{\phi} + mr^2\ddot{\phi} = -\frac{\partial V}{\partial \phi} - \frac{\partial Q}{\partial \phi} \quad (3.7.11)$$

where $Q(r, \phi)$ is the quantum potential defined as

$$Q(r, \phi) = -\frac{\hbar^2}{2m} \left(\frac{1}{r} \frac{\partial \ln \psi}{\partial r} + \frac{\partial^2 \ln \psi}{\partial r^2} + \frac{1}{r^2} \frac{\partial^2 \ln \psi}{\partial \phi^2} \right). \quad (3.7.12)$$

$\partial Q / \partial r$ and $\partial Q / \partial \phi$ are the quantum forces in the r and ϕ directions, respectively.

- (e) The wave function ψ in Eq.(3.7.8) is a solution of the Schrödinger equation, which can be derived from the energy conservation law $H = E = \text{constant}$ with H given by Eq.(3.7.6). By substituting Eq.(3.7.8) into Eq.(3.7.6), show that the Schrödinger equation in polar coordinates has the following form:

$$\frac{\partial^2 \psi}{\partial r^2} + \frac{1}{r} \frac{\partial \psi}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad (3.7.13)$$

- (f) In case of a central-force field $V(r, \phi) = V(r)$, Eq.(3.7.13) has a separable solution. Apply the separation of variable $\psi(r, \phi) = R(r)\Phi(\phi)$ to Eq.(3.7.13) and show that $R(r)$ and $\Phi(\phi)$ satisfy the following ODEs

$$\frac{d^2 R}{dr^2} + \frac{1}{r} \frac{dR}{dr} + \left[\frac{2m}{\hbar^2} (E - V) - \frac{m_l^2}{r^2} \right] R = 0, \quad \frac{d^2 \Phi}{d\phi^2} + m_l^2 \Phi = 0 \quad (3.7.14)$$

- (g) The radial function $R(r)$ depends on the applied potential V , while the azimuth function $\Phi(\phi)$ always possesses the eigen solutions:

$$\Phi_{m_l}(\phi) = e^{im_l\phi}, \quad m_l \in \mathbb{Z}. \quad (3.7.15)$$

In the above eigen state Φ_{m_l} , show that the orbital angular momentum L^2 in Eq.(3.7.7) is a constant, i.e.,

$$L^2 = p_\phi^2 + \frac{\hbar}{i} \frac{\partial^2 S}{\partial \phi^2} = m_l^2 \hbar^2 = \text{constant}. \quad (3.7.16)$$

3.3 There are very few potentials V for which Eq.(3.7.14a) has an analytical solution $R(r)$. But without an analytical expression for $\psi(r, \phi) = R(r)\Phi(\phi)$, the quantum equations of motion in Eq.(3.7.8) and Eq.(3.7.11) cannot be integrated. This problem is to introduce you a method to find quantum trajectories without the information of the wavefunction ψ . This method will be revisited in Section 10.3 regarding the 3-dimensional quantum scattering in Coulomb potential.

- (a) For a separable solution $\psi(r, \phi) = R(r)\Phi(\phi)$, we have

$$S = -i\hbar \ln \psi = -i\hbar \ln R(r) + -i\hbar \ln \Phi(\phi) = S_r(r) + S_\phi(\phi)$$

and hence

$$p_r = \frac{\partial S}{\partial r} = \frac{dS_r}{dr} = p_r(r), \quad p_\phi = \frac{\partial S}{\partial \phi} = \frac{dS_\phi}{d\phi} = p_\phi(\phi) \quad (3.7.17)$$

Using the above relations together with the energy conservation $H = E$ in Eq.(3.7.6) and the angular momentum conservation law (3.7.16), show

$$\frac{dp_r}{dr} = \frac{i}{\hbar} \left[2m(E - V(r)) - p_r^2 - \frac{m_l^2 \hbar^2}{r^2} - \frac{\hbar}{i} \frac{p_r}{r} \right], \quad \frac{dp_\phi}{d\phi} = \frac{i}{\hbar} (m_l^2 \hbar^2 - p_\phi^2) \quad (3.7.18)$$

- (b) With the help of Eq.(3.7.18), a set of differential equations now can be developed for the four canonical variables r , ϕ , p_r , and p_ϕ without the wavefunction ψ

$$\dot{r} = \frac{p_r}{m} + \frac{\hbar}{2mri}, \quad \dot{\phi} = \frac{p_\phi}{mr^2}, \quad \dot{p}_r = \frac{i}{\hbar} \frac{p_\phi}{mr^2} (m_l^2 \hbar^2 - p_\phi^2) \quad (3.7.19a)$$

$$\dot{p}_r = \frac{i}{\hbar} \left(\frac{p_r}{m} + \frac{\hbar}{2mri} \right) \left[2m(E - V(r)) - p_r^2 - \frac{m_l^2 \hbar^2}{r^2} - \frac{\hbar}{i} \frac{p_r}{r} \right] \quad (3.7.19b)$$

Given the four initial conditions $r(0)$, $\phi(0)$, $p_r(0)$, and $p_\phi(0)$, and the two constants E and m_l , Eqs.(3.7.19) can be integrate to find the quantum trajectories $r(t)$, $\phi(t)$, $p_r(t)$, and $p_\phi(t)$. However, it is noted that the canonical variables in Eqs.(3.7.19) are complex-valued and only the real parts of the four initial conditions can be fixed. Due to the uncertainties existing in the imaginary parts of the initial conditions, we will encounter multi-path solutions in Eqs.(3.7.19).

3.4 As mentioned in Section 3.4, in central-force field $V(r, \theta, \phi) = V(r)$ we have three motion constants, the conserved total energy E in Eq.(3.4.3), the conserved orbit angular momentum L^2 in Eq.(3.4.6b), and the conserved z-component orbit angular momentum L_z^2 in Eq.(3.4.6b). In this problem, you will learn that these three conservation laws just provide three differential equations to solve the three separable functions in the wavefunction $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$.

3.5 Let the two motion constants in Eq.(3.4.6b) be denoted as $L^2 = l(l+1)\hbar^2$ and $L_z^2 = m_l^2 \hbar^2$.

Show that Eq.(3.4.6b) yields the following two differential equations to determine $\Theta(\theta)$ and $\Phi(\phi)$:

$$\frac{d^2 \Phi}{d\phi^2} = -m_l^2 \Phi, \quad -\frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{m_l^2}{\sin^2 \theta} = l(l+1) \Theta \quad (3.7.20)$$

whose solution can be found readily as

$$\Phi_{m_l}(\phi) = e^{im_l\phi}, \quad \Theta_{m_l}(\theta) = P_l^{m_l}(\cos \theta), \quad (3.7.21)$$

where $P_l^{m_l}$ is the associate Legendre function. To ensure a bound solution, $P_l^{m_l}$ must be of polynomial form, which in turn requires the two parameters l and m_l to be the following integers:

$$m_l = 0, 1, 2, \dots, l, \quad l = 0, 1, 2, \dots \quad (3.7.22)$$

The multiplication $Y_l^m(\theta, \phi) = \Theta_{lm}(\theta)\Phi_{ml}(\phi)$ is called spherical harmonics. List all the spherical harmonics for $l = 0, 1, 2, 3$.

- (b) By letting the Hamiltonian H in Eq.(3.4.3) be a constant E and incorporating with Eq.(3.4.6b), show that Eq.(3.4.3) can be recast into a differential equation involving only $R(r)$:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} (E - V(r)) R = l(l+1) \frac{R}{r^2} \quad (3.7.23)$$

Conventionally, we obtained Eq.(3.7.20) and (3.7.23) by solving Schrödinger's partial differential equation with a separable solution $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$. We have seen in this problem that the separability of Schrödinger equation indeed implies three conservation laws.

3.5 Following this problem, you will learn to solve Eq.(3.7.23) for the one-electron Coulomb potential

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{KZe^2}{r}, \quad K = \frac{1}{4\pi\epsilon_0} \quad (3.7.24)$$

where Ze is the nucleus charge ($Z = 1$ for neutral hydrogen, $Z = 2$ for singly ionized helium).

- (a) By writing $E = -|E|$ and defining a new variable,

$$\rho = r\sqrt{8m|E|}/\hbar \quad (3.7.25)$$

show that Eq.(3.7.23) can be reduced to the following dimensionless form

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} + \left(\frac{\sigma}{\rho} - \frac{l(l+1)}{\rho^2} - \frac{1}{4} \right) R = 0 \quad (3.7.26)$$

where the parameter σ is given by

$$\sigma = \frac{KZe^2}{\hbar^2} \sqrt{\frac{\mu}{2|E|}} = Z\alpha \sqrt{\frac{\mu c^2}{2|E|}}, \quad \alpha = \frac{Ke^2}{\hbar c} \quad (3.7.27)$$

and the parameter α is called fine structure constant.

- (b) Search a solution $R(\rho)$ for Eq.(3.7.26) in the form of

$$R(\rho) = G(\rho)\rho^l e^{-\rho/2}, \quad (3.7.28)$$

and show that $G(\rho)$ is a solution of

$$\frac{d^2 G(\rho)}{d\rho^2} + \left(\frac{2l+2}{\rho} - 1 \right) \frac{dG(\rho)}{d\rho} + \left(\frac{\sigma-l-1}{\rho} \right) G(\rho) = 0. \quad (3.7.29)$$

- (c) As a wavefunction, $R(\rho)$ must be bound, which requires that $G(\rho)$ be a polynomial. Show that to this end, the parameter σ has to meet the condition

$$\sigma - l - 1 = n_r = 0, 1, 2, \dots \quad (3.7.30)$$

Condition (3.7.30) restricts the constant σ to the discrete values of

$$\sigma \equiv n = n_r + l + 1 = 1, 2, 3, \dots \quad (3.7.31)$$

where n is called the principle quantum number, which must be a positive integer. For a given principle quantum number n , the quantum number l has the values

$$l = 0, 1, \dots, n-1 \quad (3.7.32)$$

- (d) Recall that σ is related to the energy E via equation (3.7.27), and then show that the requirement of (3.7.31) leads to the quantization of E as

$$E_n = -\left(\frac{\mu K^2 Z^2 e^4}{2\hbar^2} \right) \frac{1}{n^2} = -\frac{\mu(Z\alpha c)^2}{2} \frac{1}{n^2}, \quad n = 1, 2, 3, \dots \quad (3.7.33)$$

With this energy quantization, the dimensionless variable ρ in Eq.(3.7.25) becomes

$$\rho = \frac{\sqrt{8m|E|}}{\hbar} r = \frac{2Z}{na_0} r \quad (3.7.34)$$

- (e) Substituting the condition $\sigma = n$ in Eq.(3.7.29), show that the solution $G(\rho)$ can be expressed by the associate Laguerre polynomial $L_p^q(\rho)$ as

$$G(\rho) = L_{n-l-1}^{2l+1}(\rho), \quad l = 0, 1, \dots, n-1, \quad n = 1, 2, \dots \quad (3.7.35)$$

Inserting Eq.(3.7.35) to Eq.(3.7.28) yields the solution for $R(\rho)$ as

$$R(\rho) \triangleq R_{nl}(\rho) = \rho^l e^{-\rho/2} L_{n-l-1}^{2l+1}(\rho), \quad l = 0, 1, \dots, n-1, \quad n = 1, 2, \dots \quad (3.7.36)$$

Tabularize the $R_{nl}(\rho)$ functions for $n = 1, 2, 3$.

- (f) Combine the above three functions $R_{nl}(r)$, $\Theta_{lm_l}(\theta)$, and $\Phi_{m_l}(\phi)$, and show that the wavefunction for an one-electron atom can be expressed by

$$\psi_{nlm_l}(r, \theta, \phi) = A_{nlm_l} R_{nl}(r) \Theta_{lm_l}(\theta) \Phi_{m_l}(\phi) \quad (3.7.37)$$

$$= \left(\frac{2Z}{na_0} \right)^{3/2} \frac{(n-l-1)!}{\sqrt{2n[(n+1)!]^3}} \left(\frac{2Z}{na_0} r \right)^l e^{-(Z/na_0)r} L_{n-l-1}^{2l+1} \left(\frac{2Z}{na_0} r \right) Y_l^m(\theta, \phi) \quad (3.7.38)$$

where A_{nlm_l} is a normalization factor making the integration of $\psi^* \psi$ equal to one. Tabularize $\psi_{nlm_l}(r, \theta, \phi)$ for the first several quantum numbers and confirm your answer with the following table.

n	l	m_l	Wavefunctions ψ_{nlm_l}
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\psi_{200} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$
2	1	0	$\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos \theta$
2	1	± 1	$\psi_{21\pm 1} = \frac{1}{8\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin \theta e^{\pm i\phi}$
3	0	0	$\psi_{300} = \frac{1}{81\sqrt{3\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \left(27 - 18 \frac{Zr}{a_0} + 2 \frac{Z^2 r^2}{a_0^2} \right) e^{-Zr/3a_0}$
3	1	0	$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \left(6 - \frac{Zr}{a_0} \right) \frac{Zr}{a_0} e^{-Zr/3a_0} \cos \theta$
3	1	± 1	$\psi_{31\pm 1} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \left(6 - \frac{Zr}{a_0} \right) \frac{Zr}{a_0} e^{-Zr/3a_0} \sin \theta e^{\pm i\phi}$
3	2	0	$\psi_{320} = \frac{1}{81\sqrt{6\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \frac{Z^2 r^2}{a_0^2} e^{-Zr/3a_0} (3 \cos^2 \theta - 1)$
3	2	± 1	$\psi_{32\pm 1} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \frac{Z^2 r^2}{a_0^2} e^{-Zr/3a_0} \sin \theta \cos \theta e^{\pm i\phi}$
3	2	± 2	$\psi_{32\pm 2} = \frac{1}{162\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \frac{Z^2 r^2}{a_0^2} e^{-Zr/3a_0} \sin^2 \theta e^{\pm 2i\phi}$

3.6 In quantum mechanics, each physical observable is accompanied by an operator. The two basic

quantum-mechanical operators are those corresponding to position (x, y, z) and momentum (p_x, p_y, p_z) . One prescription for making the transition from classical to quantum mechanics is to perform the following replacement:

$$(x, y, z) \rightarrow (\hat{x}, \hat{y}, \hat{z}), \quad (p_x, p_y, p_z) \rightarrow (\hat{p}_x, \hat{p}_y, \hat{p}_z) = \left(\frac{\hbar}{i} \frac{\partial}{\partial x}, \frac{\hbar}{i} \frac{\partial}{\partial y}, \frac{\hbar}{i} \frac{\partial}{\partial z} \right) \quad (3.7.39)$$

where \hat{x} is a multiplicative operator defined by $\hat{x}f = xf$, and similarly, $\hat{y}f = yf$ and $\hat{z}f = zf$; \hbar is the Planck constant and i is the imaginary number $\sqrt{-1}$.

(a) By making the above substitution rules, find the corresponding quantum-mechanical operators \hat{L}_x , \hat{L}_y , and \hat{L}_z for the following components of classical angular momentum:

$$L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x. \quad (3.7.40)$$

(b) The commutator $[\hat{A}, \hat{B}]$ of two operator \hat{A} and \hat{B} is defined by

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \quad (3.7.41)$$

By using the results of (a), show

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z, \quad [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x, \quad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y \quad (3.7.42)$$

3.7 Continuing Problem 3.6, two operator \hat{A} and \hat{B} are said to commute if their commutator is zero, i.e., $[\hat{A}, \hat{B}] = 0$. Consider the following eigenvalue problems:

$$\hat{A}\psi_A = \lambda_A\psi_A, \quad \hat{B}\psi_B = \lambda_B\psi_B \quad (3.7.43)$$

where ψ_A and λ_A are the eigenfunction and eigenvalue of \hat{A} ; while ψ_B and λ_B are the eigenfunction and eigenvalue of \hat{B} . Show that if \hat{A} and \hat{B} are commuting, then they share the same eigenfunction, i.e., $\psi_A = \psi_B$. Hint: $[\hat{A}, \hat{B}] = 0$ means $\hat{A}\hat{B} = \hat{B}\hat{A}$.