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Advanced Quantum Mechanics

高等量子力学

苏汝铿　王　斌 编著

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Abstract

This book is intended for use as a textbook for a graduate course in Advanced Quantum Mechanics, and as a reference book for workers in the field.

Before the subject is presented, a brief but self-contained review on the foundation of Quantum Mechanics is given. A large part of this book is devoted to select applications of quantum mechanics, such as scattering theory, second quantization, superconductive theory, superfluidity, phase of wave function, path integral and relativistic quantum mechanics. The selection is guided by the interest of topic to physicists, its value as an illustration of calculating techniques, and our personal taste.

To read the book, the reader need basic knowledge of quantum mechanics, some intuitive feeling for electrodynamics and special relativity, and a good mathematical knowledge.

PREFACE

As an advanced study of quantum mechanics, this textbook deals with topics likely to be encountered in a graduate-level course. The authors believe there is no material difference between quantum mechanics and advanced quantum mechanics except that the latter targets an in-depth study. However, we can see basic differences between advanced quantum mechanics and quantum statistics and/or quantum field theory in that the former does not cope with effects of temperature and quantization of fields.

This book is written for advanced-level students or graduate students studying physics or the related disciplines. There are all together six chapters in this book, centering on such topics as relativistic quantum mechanics, path intergral, scattering theory, second quantization, superconductive theory, superfluidity as well as the phase of wave function. Though the textbook adopts a rigorous style, it is easy to read since no other background knowledge than the basics of quantum mechanics is required. In addition, the first chapter serves to equip the reader with the necessary basic knowledge. Throughout the book, the authors take painstaking efforts to demonstrate the mathematical steps and intermediate calculations in a thorough way, which will enable the reader to understand with ease.

We owe our thanks to Prof. Xun Wang for his encouragement, Prof. L. K. Wang for editing this book and Dr. Wei-Liang Qian for preparing the LATEX format for the current edition. We would like to dedicade this book to the 100th annivensary of Fudan University.

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Ru-Keng Su
Bin Wang
Apr. 2004.
Fudan University

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前　　言

高等量子力学是一些高年级本科生及研究生学习的量子力学课程。作者认为，量子力学和高等量子力学并没有本质的不同，只不过后者涉及的面更深和更广。但是，高等量子力学与量子统计和量子场论有本质的不同，前者无需考虑温度效应和场的量子化。

本书是为高年级本科生或研究生学习物理学或相关课程所准备的。全书共分六章，包括相对论量子力学、路径积分、散射理论、二次量子化、超导理论、超流动性以及波函数的位相等。本书叙述严谨，但易于阅读和学习。它只要求读者具有在本书第一章中给出的量子力学的基础知识，而不要求其他。本书的数学推导力求详尽，以便读者更易于掌握。

感谢王迅教授的支持和鼓励，感谢汪礼康教授校订本书及钱卫良博士为本书准备的 LaTeX 文件。我们希望将本书献给母校——复旦大学一百周年校庆。

苏汝铿　王斌
2004 年 4 月于复旦大学

CONTENTS

Foundation of Quantum Mechanics

1.1 State Vector, Wave Function and Superposition of States

Advanced quantum mechanics is a continuing course of *quantum mechanics* at undergraduate level. There is no material difference between the two courses except that the latter presents a detailed and insightful introduction to the fundamental concepts and their simple applications, but the former targets an in-depth study. This book introduces relativistic quantum mechanics, path integral, scattering theory, second quantization, superconductive theory, superfluidity as well as the further study of the phase of wave function. This chapter evolves from an attempt of a brief review over the basic ideas and formulae in undergraduate-level quantum mechanics. The details of this chapter can be found in the usual references of quantum mechanics[1].

In classical mechanics, the state of a particle is described in terms of its coordinate and momentum at some instant of time. The evolution of the state complys with the Newton equations or the Hamiltonian canonical equations. With the initial data of coordinate and momentum at a given instant, the Newton equation of motion can predict the behavior of the particle at all subsequent instants. In quantum mechanics the prediction is in principle impossible because the exact coordinate and the corresponding momentum cannot be given according to the uncertainty

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[1] For example, Ru-Keng Su, *Quantum Mechanics*, Second Edition. High Education Press, 2002

principle.

In quantum mechanics, because of the wave-particle duality, the state of a quantum system is described in terms of a wave vector in a Hilbert space. The wave vector can be expressed as a wave function in a specific representation, i. e. a complete set of basics of the Hilbert space. For example, the eigenfunctions of coordinate operator x are δ-functions

$$x\,\delta(x - x') = x'\,\delta(x - x') . \qquad (1.1.1)$$

If we choose the δ-functions to be the basics of the Hilbert space, the wave function at instant t is expressed as $\psi(x,t)$. According to the Born statistic explanation of wave function, the square of the modulus of this function determines the probability distribution of the values of the coordinates: $|\psi|^2\,dx$ is the probability that a measurement made on the system will find the values of coordinates in the element dx of the configuration space. Since the sum of the probabilities of all possible values of the system coordinates must be unity, the wave function $\psi(x,t)$ satisfies the normalization condition

$$\int |\psi(x,t)|^2\,dx = 1 . \qquad (1.1.2)$$

If the integral of $|\psi|^2$ diverges and ψ cannot be normalized by using Eq. (1.1.2), $|\psi|^2$ will not determine the absolute values of the probability of the coordinates, but the ratio of the values of $|\psi|^2$ at two different points will still determine the relative probability of the corresponding values of coordinates.

Quantum states follow a general principle of superposition. Suppose a state with wave function $\psi_m(q)$, where measuring on it leads to a definite result m, and a state with $\psi_n(q)$ leads to result n. It is assumed that every linear combination of ψ_m and ψ_n,

$$\psi = c_m\psi_m + c_n\psi_n \qquad (1.1.3)$$

gives a state in which the measurement leads to either result m or n. The probability of belting result m or n is $\dfrac{|c_m|^2}{|c_m|^2 + |c_n|^2}$ or $\dfrac{|c_n|^2}{|c_m|^2 + |c_n|^2}$. If ψ_i is an eigenfunction of Hermitian operator $\hat{F}$ and f_i is the corresponding eigenvalue, then all eigenfunctions of $\hat{F}$ form a complete set $\{\psi_i\}$ in Hilbert space. A wave function ψ can be expanded into

$$\psi = \sum_i c_i \psi_i. \qquad (1.1.4)$$

If we make a measurement of dynamical quantity F in a state with wave function ψ, we reach the result that the square modulus $|c_i|^2$ of each coefficient in Eq. (1.1.4) determines the probability of the corresponding value f_n of the quantity F in a state with ψ provided that the wave functions satisfy

$$\int \psi^* \psi \, dr = 1, \qquad (1.1.5)$$

$$\int \psi_m^* \psi_n \, dr = \delta_{mn}, \qquad (1.1.6)$$

and

$$\sum_i |c_i|^2 = 1. \qquad (1.1.7)$$

It is worth noting that the superposition of quantum states in quantum mechanics is with essentially different nature from that in the classical theory. The quantum coherence cannot be found in classical mechanics.

1.2 Schrödinger Equation and Its Solutions

In quantum mechanics, as in classical mechanics, a system is governed by the equation of motion which tells us that the state at one time determines the state at a later time. In classical mechanics, the equation of motion is Newton equation. In quantum mechanics, Schrödinger assumed that the equation of motion for wave function reads

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi = \left[-\frac{\hbar^2}{2m} \nabla^2 + U(r,t) \right] \psi, \qquad (1.2.1)$$

where

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + U(r,t) \qquad (1.2.2)$$

is the Hamilton operator and $U(r,t)$ is the potential energy. If the potential energy depends on r alone, we can prove that the wave function becomes

$$\psi(r,t) = \psi(r) e^{-iEt/\hbar}. \qquad (1.2.3)$$

Eq. (1.2.3) is called stationary state. In this state, the density of probability does not depend on time

$$|\psi(r,t)|^2 = |\psi(r)|^2,\qquad(1.2.4)$$

and the energy has a definite value. Schrödinger equation for stationary state reads

$$H\psi = E\psi,\qquad(1.2.5)$$

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(r).\qquad(1.2.6)$$

In principle, the solutions of Schrödinger equation can be obtained for definite boundary conditions. However, due to mathematical problems, only a few exact solutions have been found. Examples are given as follows:

1.2.1 One-dimensional infinite potential well

Considering one-dimension Schrödinger equation with potential

$$U(x) = \begin{cases} 0 & (\,|x| < a\,) \\ \infty & (\,|x| \geqslant a\,) \end{cases},\qquad(1.2.7)$$

we find that the energy levels and the normalized wave function are

$$E_n = \frac{n^2\pi^2\hbar^2}{8ma^2}\qquad(n = 1,2,3,\cdots),\qquad(1.2.8)$$

$$\psi_n = \begin{cases} \dfrac{1}{\sqrt{a}}\sin\dfrac{n\pi}{2a}(x + a) & (\,|x| < a\,) \\ 0 & (\,|x| \geqslant a\,) \end{cases},\qquad(1.2.9)$$

respectively.

1.2.2 One-dimensional harmonic oscillator

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2 x^2,\qquad(1.2.10)$$

where ω is the frequency of the oscillation. The corresponding

Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \right)\psi(x) = E\psi(x) . \qquad (1.2.11)$$

One can prove that the energy levels and the normalized wave function are

$$E_n = \left(n + \frac{1}{2} \right)\hbar\omega \quad (n = 0,1,2,\cdots) , \qquad (1.2.12)$$

$$\psi_n(x) = \left(\frac{\alpha}{\pi^{1/2}2^n n!} \right)^{1/2} e^{-\frac{1}{2}\alpha^2 x^2} H_n(\alpha x) , \qquad (1.2.13)$$

where $\alpha = \sqrt{m\omega/\hbar}$ and $H_n(\alpha x)$ is the Hermit polynomials

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n}(e^{-\xi^n})$$

$$= (2\xi)^n - n(n-1)(2\xi)^{n-2}$$

$$+ \frac{n(n-1)(n-2)(n-3)}{2!}(2\xi)^{n-4}$$

$$+ \cdots + (-1)^{\left[\frac{n}{2}\right]} \frac{n!}{\left[\frac{n}{2}\right]!}(2\xi)^{n-2\left[\frac{n}{2}\right]}, \qquad (1.2.14)$$

$$\left[\frac{n}{2}\right] = \begin{cases} n/2 & (n \quad even) \\ (n-1)/2 & (n \quad odd) \end{cases} . \qquad (1.2.15)$$

Here is a list of the first few Hermit polynomials

$$H_0(\xi) = 1, \qquad H_1(\xi) = 2\xi,$$
$$H_2(\xi) = 4\xi^2 - 2, \quad H_3(\xi) = 8\xi^3 - 12\xi. \qquad (1.2.16)$$

The energy spectra of linear oscillator can be obtained easily in the occupation representation. Introducing the creation operator $\hat{a}^+$ and the annihilation operator $\hat{a}$

$$\hat{a}^+ = \left(\frac{m\omega}{2\hbar} \right)^{1/2}\left(\hat{x} - \frac{i}{m\omega}\hat{p} \right)$$

$$\hat{a} = \left(\frac{m\omega}{2\hbar} \right)^{1/2}\left(\hat{x} + \frac{i}{m\omega}\hat{p} \right) \qquad (1.2.17)$$

we can rewrite Eq. (1. 2. 10) into

$$\hat{H} = \hbar\omega\left(\hat{a}^+ \, \hat{a} \, + \frac{1}{2}\right), \qquad (1.2.18)$$

and prove that the operators $\hat{a}$ and $\hat{a}^+$ satisfy

$$\left[\, \hat{a} \, , \hat{a}^+ \, \right] \, = 1 \, . \qquad (1.2.19)$$

Defining the operator of particle number $\hat{N}$ as

$$\hat{N} \, = \, \hat{a}^+ \, \hat{a} \, , \qquad (1.2.20)$$

the eigenvectors $| \, n \, \rangle$ of operator $\hat{N}$ are

$$\hat{N} \, | \, n \, \rangle \, = \, n \, | \, n \, \rangle \, , \qquad (1.2.21)$$

where $n = 0, 1, 2, \cdots$ are the occupied numbers of the corresponding states $| \, 0 \, \rangle$, $| \, 1 \, \rangle$, $| \, 2 \, \rangle$, $\cdots$ respectively. In occupation representation $\{ \, | \, n \, \rangle \, \}$, we have

$$\hat{a}^+ \, | \, n \, \rangle \, = \, \sqrt{n + 1} \, | \, n + 1 \, \rangle$$

$$\hat{a} \, | \, n \, \rangle \, = \sqrt{n} \, | \, n - 1 \, \rangle \, . \qquad (1.2.22)$$

Combining Eqs. (1. 2. 18) and (1. 2. 21) , we get

$$E_n \, = \, \left(n \, + \frac{1}{2}\right) \hbar\omega \, . \qquad (1.2.23)$$

1.2.3　Central potential

　　The central potential U only depends on the distance r of the particle from the center. Spherical coordinates are best adapted to the problem. The Schrödinger equation is

$$\left(- \frac{\hbar^2}{2m} \, \nabla^2 + U(r) \right) \psi(r) \, = \, E\psi(r) \, . \qquad (1.2.24)$$

We express Eq. (1. 2. 24) in terms of spherical coordinates

$$- \frac{\hbar^2}{2m}\left[\frac{\partial}{\partial r}\left(r^2 \, \frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta}\left(\sin\theta \, \frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2}\right] \psi$$

$$+ U(r)\psi = E\psi . \qquad (1.2.25)$$

The solution is

$$\psi(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi) , \qquad (1.2.26)$$

where $Y_{lm}(\theta,\varphi)$ is the spherical harmonic functions

$$Y_{lm}(\theta,\varphi) = N_{lm}P_l^{|m|}(\cos\theta)e^{im\varphi} , \qquad (1.2.27)$$

and

$$N_{lm} = \sqrt{\frac{(l - |m|)!(2l + 1)}{(l + |m|)!4\pi}} , \qquad (1.2.28)$$

is the normalized constant, and $P_l^{|m|}(\cos\theta)$ is the associated Lagendre polynomials. The first few spherical harmonics are listed below:

$$Y_{00} = \frac{1}{\sqrt{4\pi}},$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta, \qquad\qquad Y_{1\pm1} = \sqrt{\frac{3}{8\pi}}\sin\theta\,e^{\pm i\varphi},$$

$$Y_{20} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1), \quad Y_{2\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\,e^{\pm i2\varphi}.$$

$$(1.2.29)$$

The orthonormalized condition for Y_{lm} is

$$\int_0^{2\pi}\int_0^{\pi} Y_{lm}^*(\theta,\varphi)Y_{l'm'}(\theta,\varphi)\sin\theta\,d\theta\,d\varphi = \delta_{ll'}\delta_{mm'}. \quad (1.2.30)$$

If $U(r)$ is attractive Coulomb potential

$$U(r) = -\frac{Ze^2}{r}, \qquad (1.2.31)$$

the radial part R_{nl} of solution Eq. (1.2.26) is

$$R_{nl}(r) = N_{nl}e^{-\xi/2}\xi^l F(-n + l + 1, 2l + 2, \xi) , \qquad (1.2.32)$$

where

$$N_{nl} = \frac{2}{a_0^{3/2} n^2 (2l+1)!} \sqrt{\frac{(n+l)!}{(n-l-1)!}},$$

$$\xi = \frac{2r}{na_0}$$

(1.2.33)

$a_0 = \dfrac{\hbar^2}{m_e e^2} = 0.529 \times 10^{-10}$ m is the first Bohr radius and $F(\alpha, \gamma, \xi)$ is the confluent hypergeometric polynomial. The first few radial solutions of $R_{nl}(r)$ are listed below

$$n = 1, \quad R_{10}(r) = \left(\frac{Z}{a_0}\right)^{3/2} 2\, e^{-Zr/a_0}$$

$$n = 2, \quad R_{20}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/a_0}. \quad (1.2.34)$$

$$R_{21}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{a_0 \sqrt{3}} e^{-Zr/a_0}$$

The values of principal quantum number n, radial quantum number l and the magnetic quantum number m are

$$n = 1, 2, 3, \cdots$$

$$l = 0, 1, 2, \cdots, n - 1. \quad (1.2.35)$$

$$m = 0, \pm 1, \cdots, \pm l$$

The energy levels of hydrogen read

$$E_n = -\frac{e^2}{2a_0 n^2} = \frac{-m_e e^4}{2\hbar^2 n^2} \quad (n = 1, 2, 3, \cdots). \quad (1.2.36)$$

Other cases with exact solutions can be found in ref[1].

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[1] S. Flugge, *Practical Quantum Mechanics*, Spinger-Verlag, 1974

1.3 Operators

The expectation values of dynamic quantity A for a given probability distribution is defined as the weighted sum

$$\langle A \rangle = \sum_k A_k p_k, \qquad (1.3.1)$$

where p_k is the corresponding probability.

In quantum mechanics, according to the Born statistical interpretation, $|\psi(r,t)|^2$ is proportional to the probability density that upon a measurement on its position the particle will be found at position r. Therefore, the expectation value of the position vector can be expressed by

$$\langle r \rangle = \int r |\psi(r)|^2 \, dr. \qquad (1.3.2)$$

An arbitrary function of r has the expectation value

$$\langle f(r) \rangle = \int f(r) |\psi|^2 \, dr = \int \psi^* f(r) \psi \, dr, \qquad (1.3.3)$$

where ψ satisfies the normal condition

$$\int \psi^* \psi \, dr = 1. \qquad (1.3.4)$$

To calculate the expectation value of momentum p, we must find the probability density that upon a measurement on its momentum that particle will be found at momentum p in the momentum space. Performing a Fourier transformation

$$c(p,t) = \frac{1}{(2\pi\hbar)^{3/2}} \int \psi(r,t) e^{\frac{i}{\hbar}(Et - p \cdot r)} \, dr. \qquad (1.3.5)$$

the probability density in the momentum space reads $|c(p,t)|^2$ and the expectation value of momentum is

$$\langle p \rangle = \int c^*(p,t) p c(p,t) \, dp. \qquad (1.3.6)$$

Its component of x direction is