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Applications of Quantum Dynamics in Chemistry

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Applications of Quantum Dynamics in Chemistry

 Springer

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Foreword

Quantum physics is certainly one of the most astonishing intellectual constructions ever achieved. Its Rosetta stone consisted in some unexplained regularities in the fluorescence light of simple elements, such as hydrogen or helium atoms. The next building block was the radiation emitted by an oven in thermal equilibrium, the famous blackbody problem. From these mere facts and some strokes of genius, quantum theory was built. Quite rapidly the intuition of the founding fathers became a well-established theory, still full of surprises and paradoxical conclusions, but entirely consistent and with an unprecedented range of validity. Quantum theory applies to microscopic objects like nuclei, atoms, molecules, as well as to macroscopic systems such as superconductors and superfluids, and even astrophysical objects. Quantum physics is simultaneously a framework where uncertainty is included at the core of the theory, and a method of calculation that agrees with experimental facts with an outstanding precision, at the level of 10^{-12} for some observables, like the gyromagnetic ratio of the electron.

The present book explains how to use the quantum formalism in order to address the dynamics of molecular systems, and it provides a nice illustration of the diversity of the quantum world. I had the chance to have one of its four authors, Fabien Gatti, in my quantum mechanics class about twenty years ago, and it is a real pleasure to see how some simple ideas that we had been discussing at that time have flourished in such a fruitful manner. The book is organized in a remarkably progressive way, starting with simple systems like the hydrogen molecule, and then moving towards notably more complex molecular edifices. This smooth progression is quite valuable for readers with a physics background like me, who were taught by A. Schawlow, 1981 physics Nobel Prize winner, that “a diatomic molecule is a molecule with one atom too many”! This statement illustrates the fear that potential readers could have had in front of the subject if they were not properly guided. To tell the whole truth, Schawlow himself knew a lot about “non-monoatomic molecules” and he performed outstanding experiments in molecular spectroscopy.

When reading through “Application of Quantum Dynamics in Chemistry”, one realizes the wealth of phenomena that can occur in the dynamics of two- or several-atom molecules. With well-conceived lab sessions, the authors guide the reader through key molecular processes such as photo-dissociation, simple chemical reactions and coherent control. The key notion is the concept of molecular wave-packets, created and probed using ultra-short pulses of light. This is at the basis of the rapidly developing field of femto-chemistry initiated by the late Ahmed Zewail, 1999 chemistry Nobel Prize winner, whose major discoveries were acknowledged in both the chemistry and the physics communities. With femto-chemistry it is now possible to manipulate chemical reactions, using proper light pulses that influence the breaking of particular molecular bonds.

An appealing aspect of this book is that it will ring many bells in the mind of physicists, in addition of course to the chemistry community towards which it is targeted at first. Fundamental notions like quantum coherence revealed by interferences between various quantum paths, atomic or molecular states dressed with laser light, are very dear to a physicist’s heart. These physicists will thus find in many instances a renewed playground for such notions, which illustrates once more the universality of quantum concepts. For instance, the authors discuss the Berry phase accumulated when travelling along a path around in a conical intersection; the essence of this phenomenon is very similar to what is found for the properties of graphene in condensed matter physics, or in quantum gas physics, when atoms move in an optical lattice with Dirac points in the Brillouin zone. In a different, but related perspective, the Multi-Configuration Time-Dependent Hartree (MCTDH) package that is intensively exploited here to address the dynamics of molecular edifices can be used to approach other problems emerging in quantum many-body physics. This is notably the case for the non-linear Schrödinger equation that governs the evolution of light beams in non-linear materials, or of interacting Bose–Einstein condensates, two research domains that have been also very active worldwide over the last two decades.

Overall I am convinced that F. Gatti, B. Lasorne, H.-D. Meyer and A. Nauts have produced a very useful text, with a clear orientation towards solving practical problems. All the necessary background is presented in a pedagogical manner, with numerous illustrations. Molecular spectra now replace the hydrogen fluorescence lines deciphered by the founding fathers, but the desire to understand complex phenomena from simple microscopic modeling is still present. I am convinced that the material developed in the book will constitute a perfect guide for the reader who wishes to start a fruitful journey in the rapidly developing field of Quantum Molecular Dynamics.

Paris, France
November 2016

Jean Dalibard

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Second affiliation for book author has been
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The material of this book is largely based on our research but also on lectures and seminars we have given to a variety of audiences during the past 10 to 15 years so that it has been largely tested through teaching.

For instance, in 2016 in Rolla, at the Missouri University of Science and Technology (USA) in the group of Richard Dawes, in Beijing at the Peking University (China) in the group of Jian Liu and in Dalian (China) in the groups of Zhigang Sun and Dong-Hui Zhang in the context of the French-Chinese network of theoretical chemistry (GDRI RFCCT).

Fabien Gatti also tested the content of the book through teaching in the context of the French Network of Theoretical Chemistry (RFCT) and, together with Benjamin Lasorne and André Nauts, in the context of the CNRS thematic summer schools (Aussois 2009 and Gif-sur-Yvette 2013). Benjamin Lasorne also gave lectures on related topics during an intensive course of the European Master in Theoretical Chemistry and Computational Modeling organized in Porto in 2010.

We are particularly grateful to the Ecole de Physique of the Université catholique de Louvain (Louvain-la-Neuve) for repeatedly inviting Fabien Gatti over the last 15 years. It initiated an intensive master-level teaching collaboration with André Nauts, combining an introduction to the fundamentals of molecular dynamics with hands-on lab-sessions in MCTDH example simulations. The idea of the present book largely arose out of this longstanding collaboration.

Many people contributed to improving this book and some of its chapters. We would like to thank them here for their help and for their critical reading of parts of the manuscript.

David Lauvergnat read preliminary versions of Chaps. 3 (*Molecular Hamiltonian Operators*) and 6 (*The Kinetic Energy Operator in Curvilinear Coordinates*). We thank him for his insightful comments and remarks.

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Chapter 1

Introduction

The main goal of this book is to illustrate how the concept of a *wavepacket* becomes central in quantum mechanics when turning to concrete applications, for instance in molecular physics and chemistry. In other words, *the Schrödinger equation in its time-dependent form provides the central framework* here. This book is not a textbook: the foundations of quantum mechanics have been detailed in many seminal references (see for instance [1, 2]). More recently, D. Tannor has given a comprehensive description of the time-dependent perspective in quantum mechanics [3].

Here, our approach is different and complementary. Indeed, the most original aspect of the present book is to propose lab-sessions using the Heidelberg Multi-Configuration Time-Dependent Hartree (MCTDH) package. The latter is freely available and can be easily installed. MCTDH can be seen as an algorithm to solve the time-dependent Schrödinger equation (i.e. to propagate wavepackets) for multidimensional dynamical systems consisting of distinguishable particles [4–9]. The present book and the lab-sessions have two levels: one more dedicated to Master's students, typically for advanced courses on quantum mechanics for physicists or on theoretical chemistry for chemists. The teachers and the students can then use MCTDH as a black box to visualize the time evolution of quantum systems and observe pure quantum effects, on which special emphasis will be placed. At a higher level, the book may come in useful for thematic schools for Ph.D. students and postdocs in different fields of quantum physics or computational chemistry. Here, we offer the possibility to have a look at the input files, the users can even change themselves the characteristics of the wavepackets they propagate. The lab-sessions should also be helpful for any scientist who wishes to learn how to use the MCTDH package.

The processes presented as illustrations correspond to realistic situations involving several degrees of freedom. Most of the examples have been chosen so that the students can compare their results with data that have been measured experimentally (photoabsorption spectra, cross sections, etc.). The systems studied in this book are all *molecular systems*, i.e. *we apply quantum physics (more precisely quantum*

dynamics) to chemistry. However, *the concepts developed in the present book can be easily transferred to applications in physics and even in biology.* Generally speaking, quantum dynamics is a very diverse field ranging from entangled photons to biologically relevant response to laser light, cold atoms and molecules, etc. In this context it is worth noting that MCTDH has been extended to treat the dynamics of fermions (MCTDHF) or bosons (MCTDHB) and is commonly used to study Bose-Einstein condensates [10–13] and the dynamics of electrons in solid-state physics, atomic physics or in the context of attophysics [14–20].

The authors of the present book are all researchers in the field of “molecular quantum dynamics”, an emerging field at the border between quantum physics and chemistry. We do not intend to give a general introduction to this field here and we refer the readers to a previous book edited in 2014 in the series “physical chemistry in action” by Springer [21]. We just remind that, from the point of view of a physicist, a molecule can be viewed as a quantum-mechanical aggregate composed of electrons and nuclei. However, chemistry is rarely taught within a full quantum-mechanical perspective. In particular, an elementary chemical process is generally not described as the evolution of a quantum system. However, very early within the advent of quantum mechanics, it became clear that the wave aspects of electrons could not be neglected as well as the quantization of the electronic states. This led to the field known as *quantum chemistry* with the concepts of molecular orbitals and potential energy surfaces. On the other hand, the motion of the nuclei, which is crucial in chemistry since there is no chemical process if the nuclei in molecules do not change their relative arrangement (the *reaction coordinate* describes a collective motion of the nuclei), is often conceived classically.

However, there is growing evidence that a significant number of chemical reactions are impacted by strong quantum-mechanical effects involving both the electrons *and the nuclei*. Let us simply consider two examples. Chemical reaction rates, when light particles such as protons, hydrogen atoms, and hydride ions are exchanged, can be greatly enhanced by quantum tunnelling, namely by the fact that particles can tunnel through a barrier that they classically cannot surmount [22–25]. Another quantum effect is the involvement of *quantum resonances* in reactivity. Resonant states are metastable states, the nuclei being temporarily trapped during a reactive collision. The presence of resonances can change a chemical reaction decisively, in particular at low temperatures [26–28].

Perhaps even more important is the fact that such quantum effects can be used to create a radically new chemistry at a higher level of efficiency and selectivity. For instance, lasers are sources of coherent light. After absorption of the latter by a molecular system, a coherent superposition of quantum eigenstates can be produced, i.e., a *molecular wavepacket*. Indeed, we know that, in quantum mechanics, a system can be in a *coherent superposition* of different quantum states. The different components of the quantum superposition can interfere, yielding new properties that can be measured and that have no classical counterpart. The exact definitions of a wavepacket and quantum coherence will be given in Chap. 2. We just mention here that experimentalists can now produce vibrational wavepackets in a systematic way. In addition, time-resolved pump-probe laser techniques allow them to study chemi-

cal processes on the femtosecond time scale (10^{-15} s), i.e., on the scale of a typical period of molecular vibrations [29–31]. This was at the origin of the development of femtochemistry that earned Ahmed Zewail the 1999 Nobel Prize in Chemistry. This technique allows one to follow the motion of the nuclei in real time: when chemical bonds break, form, or change geometrically. Moreover, the quantum coherence itself can be exploited to change and guide the reactivity [32, 33]. The quantum coherence can be preserved during a time that is sufficient to drastically modify the reactivity of complex systems even when they are embedded in an environment (in general, since a system is never isolated, it interacts with its environment that dissipates quantum coherence). In particular, recent experiments provided observation of long-lived electronic quantum coherence, after excitation by laser pulses, for energy transfer processes in light-harvesting complexes of biological systems such as photosynthetic systems at ambient temperature and in the condensed phase [34].

Since the advent of femtochemistry, remarkable and decisive progress has been achieved on the experimental front with the possibility to align molecules with lasers [35, 36] and study electron motion using tools from the new field of attophysics [37–40]. In other words, it is now feasible to create rotational, vibrational, and electronic wavepackets and to control all the different aspects of a chemical elementary act. In particular, we are close to what some already call the field of *attochemistry* where, at each step of a molecular process, the *coupled motion of electrons and nuclei* could be controlled on its natural time scale [41]. This will clearly lead, on the long term, to a major breakthrough: a new chemistry working at an elementary microscopic level and based on the systematic use of quantum phenomena. It is thus not surprising that molecular quantum dynamics and the description of molecular systems in terms of wavepackets has become an enormously active field of research.

As we will show in the present book, for a theoretician, a wavepacket has a broader significance than a quantum state created in a molecule after absorption of the light produced by a laser. Most of the wavepackets that we will encounter in the different chapters can be considered as “artificial” wavepackets, in the sense that their utility is often independent of whether these wavepackets can be created or not experimentally. From their mathematical properties, wavepackets can be exploited to obtain indirectly observable data including all the quantum effects involved in the process. We will see, for instance in the applications and in the corresponding lab-sessions, that the propagation of wavepackets can provide access to photoabsorption spectra of molecules or to cross sections of collisions.

The book is divided into two parts: Part I, Concepts and Methods; Part II, Applications. Some parts of the book are labelled as advanced topics, indicated by an asterisk in the table of contents. They can be skipped for teaching at the Master’s level. In Part I, Chap. 2 is a very brief reminder of the main concepts of quantum mechanics that are essential to the understanding of the book: eigenstate, wavepacket, coherent superposition, quantum decoherence, etc. Chapter 3 presents the molecular Hamiltonian operator along with the Born-Oppenheimer separation, i.e. the separation of the electronic and nuclear motions. The cases where the Born-Oppenheimer approximation fails are described in detail by the introduction of the diabatic representation and of conical intersections. Chapter 6 is dedicated to the derivation of the nuclear kinetic

energy operator in any set of coordinates and we provide examples of operators for several molecular systems. In Chap. 5, we address the major issue of the choice of the set of nuclear coordinates used to describe molecular processes. Again several examples are given. The last chapter of Part I (Chap. 8) contains a rather thorough description of the numerical methods used to solve the Schrödinger equation for the nuclei. Special emphasis is placed on the MCTDH algorithm.

Part II focuses on illustrations of the theoretical background described in the first Part. At the end of each chapter, we propose a lab-session using the MCTDH package that allows one to visualize the evolution of wavepackets for realistic systems. The input files and a version of the code are provided as supporting material. As they are conceived, the lab-sessions are rather adapted to Ph.D. students and postdocs. However, teachers can easily simplify the lab-sessions (by removing some parts of the text) so that Master's students can use MCTDH as a "black box". It is worth noting that Sect. 9.6 explains how to install the code.

For each chapter of application, there is a preliminary part explaining the physical context with several figures. We have tried to present a wide variety of processes from infrared spectroscopy (Chap. 9) to photodissociation processes (Chap. 10); from non-adiabatic (or non-Born-Oppenheimer) couplings (Chap. 12) to reactive collisions (Chap. 11). To recall that wavepackets are not only "artificial" tools for theoreticians, and that they can also be produced and measured in experiments, we conclude the book with applications in the field of coherent control by laser pulses (Chap. 13).

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Part I
Concepts and Methods

Chapter 2

Quantum Mechanical Background

Quantum mechanics is certainly one of the most successful theories in science. It has deeply influenced many areas of pure and applied physics and pervades many branches of science, from physics, matter sciences, computer science to chemistry and even to molecular biology. However, quantum mechanics has to face several conceptual difficulties of which most relate to the process of quantum measurement and its randomness so that, almost one century after its birth, a complete consensus has still not been reached concerning the interpretation of the theory and its foundations.

Quantum mechanics is also known to be *counter-intuitive* and to lead to representations of physical phenomena very different from our daily experience, such as *superposition*, *entanglement* and *non-locality*. To pinpoint this microscopic “quantum strangeness”, the fathers of the quantum theory, especially Einstein and Bohr, resorted to “*thought experiments*” involving the manipulations of isolated particles. These experiments, which were believed to remain virtual, have now been performed (see “Exploring the Quantum” by Haroche and Raimond [1]) and may help shed light on the conceptual difficulties mentioned above. In their turn, they may also raise other intriguing issues such as, for instance, the connection between quantum and classical physics. Indeed, macroscopic systems, i.e. systems directly accessible to our senses, never display non-locality and other strange features of quantum mechanics such as *state superposition* (Schrödinger’s cat) or *quantum interference*.

A nice, lively and non-technical overview of the major interpretations and strangeness of quantum mechanics can be found in “Beyond measure” by Baggot [2]. More in-depth and technical discussions are given in “Do we really understand Quantum Mechanics?” by Laloë [3].

It is perhaps also worth mentioning that, by casting doubts on fundamental concepts such as space, material objects, and causality quantum mechanics demands serious *reconsideration* of most of traditional philosophy and has become a central issue in the realm of the *philosophy of science*. A huge amount of literature exists on the subject and we will only mention here two examples: “On Physics and Philosophy” by d’Espagnat [4] and “Making Sense of Quantum Mechanics” by Bricmont [5].

Nevertheless, *in spite of all these conceptual difficulties, the extraordinary feature of quantum mechanics is that, although we do not understand it nor know how to interpret it, we can apply it* and, by means of the rules of calculation it inspires, compute *properties of matter with unparalleled accuracy*. However, in the present book, we will adopt what can be viewed as a *pragmatic approach* in which quantum mechanics is regarded as an operational theory designed to predict the outcomes of measurements on physical systems under well-defined conditions.

The purpose of the present chapter is not to provide a general and detailed introduction to quantum mechanics, which is available in most textbooks, e.g. Refs. [6–15]. Our purpose here is merely to provide a *quantum mechanical background* with emphasis on the concepts and rules needed for the various topics covered in the book. (for a lively and pedagogical further reading see “Lectures on Quantum Mechanics” by Basdevant [16].)

2.1 General Principles

2.1.1 Wavefunctions

In quantum mechanics, the *state of a system*, at a given time t , parametrized by a set of coordinates \mathbf{R} , is completely determined by a complex *wavefunction*, $\Psi(\mathbf{R}, t)$ [10]. In our case, the system will often be a *molecular system* in the wider sense of the term, and the coordinates \mathbf{R} , a set of *generalized or curvilinear coordinates well-adapted* to the description and the evolution in time of the molecular and chemical processes under consideration. According to the standard interpretation of quantum mechanics, the square of the modulus of $\Psi(\mathbf{R}, t)$,

$$|\Psi(\mathbf{R}, t)|^2 = \Psi^*(\mathbf{R}, t)\Psi(\mathbf{R}, t), \quad (2.1)$$

has the meaning of a *probability density*. The *probability* of finding the system in the volume $d\mathbf{R}$ around the point \mathbf{R} at time t , is given by

$$d\mathcal{P}(\mathbf{R}, t) = |\Psi(\mathbf{R}, t)|^2 d\mathbf{R}. \quad (2.2)$$

The wavefunction $\Psi(\mathbf{R}, t)$ is also called the *probability amplitude* of finding the system at point \mathbf{R} . It is square integrable and, in view of the probabilistic interpretation, must be normalized to unity¹:

$$\int |\Psi(\mathbf{R}, t)|^2 d\mathbf{R} = 1. \quad (2.3)$$

¹In the following, \int denotes the integral over the complete domain of definition.

2.1.2 Superposition Principle

Another property of wavefunctions, regarded as a fundamental principle of quantum mechanics, is the *superposition principle*: it means that, if $\Psi_1(\mathbf{R}, t)$ and $\Psi_2(\mathbf{R}, t)$ describe possible states for the system, any linear combination

$$\Psi(\mathbf{R}, t) = c_1\Psi_1(\mathbf{R}, t) + c_2\Psi_2(\mathbf{R}, t), \quad (2.4)$$

where c_1 and c_2 are arbitrary complex coefficients, also represents a possible state. The additivity of probability *amplitudes* is at the origin of *interference phenomena* in quantum mechanics (see Eq. (2.38) below). Moreover, from a more theoretical perspective, this additivity property hints to the fact that the set of all the possible wavefunctions of a given system has the properties of a *linear vector space* \mathcal{E} (see below).

The non-classical aspect of the superposition principle is illustrated by Schrödinger's famous cat, which can be alive and dead simultaneously. In other words, *Schrödinger's cat* can be in a *coherent superposition* of both a dead state and an alive state. These two states can interfere to create new behaviors that cannot be observed for a cat that is either alive or dead. For instance, let us consider an assembly of, let us say, one thousand Schrödinger's cats. This assembly is not constituted of cats that are either dead or alive but of one thousand cats where the dead and alive aspects interact to create a completely different behavior. Schrödinger's cat can be seen as a *paradox* only because the cat is a large-scale system and creating a coherent superposition for a cat is not realistic.

2.1.3 Measurements of Physical Quantities

One of the most intriguing features of quantum mechanics is, as indicated by its name, the hypothesis of *quantization*. This notion implies that, under particular conditions, physical observables measured experimentally can only take certain discrete values. More precisely, in quantum mechanics, physical quantities measured experimentally can only take a *restricted set of values* that can be discrete or continuous or a mixture of both.

This is the reason why, whereas in classical mechanics the physical observables are represented by functions of time such as position, in quantum mechanics, to each physical quantity \mathcal{A} , we associate an observable \hat{A} , which is a *linear Hermitian operator* acting in the space \mathcal{E} of *wavefunctions* called a *Hilbert space*.

More explicitly, let us define in the space \mathcal{E} a *Hermitian scalar product*² of two wavefunctions $\Psi(\mathbf{R})$ and $\Phi(\mathbf{R})$ as follows

²Equation (2.5) is also known as the *overlap between the wavefunctions* $\Psi(\mathbf{R})$ and $\Phi(\mathbf{R})$.

$$\int \Phi^*(\mathbf{R})\Psi(\mathbf{R})d\mathbf{R} = \langle \Phi|\Psi \rangle, \quad (2.5)$$

where the so-called Dirac *bracket notation* is introduced. This bracket notation is very elegant and allows, among other things, to avoid to explicitly specify the coordinates, \mathbf{R} , their conjugate momenta \mathbf{P} , or any other set of coordinates, used to describe the system. Combined with the superposition principle, this leads naturally to considering $|\Psi\rangle$, called a “ket”, as a *vector* of space \mathcal{E} , and $\langle\Phi|$ called a “bra” as a linear form³ that acts on the ket $|\Psi\rangle$ to yield the “bracket” $\langle\Phi|\Psi\rangle$, which, being a scalar product, is generally a complex number.

$|\Psi\rangle$ and $\langle\Phi|$ are quantum *state vectors* corresponding to the “ \mathbf{R} representation” wavefunctions $\Psi(\mathbf{R})$ and $\Phi(\mathbf{R})$. The *normalization condition* of Eq. (2.3) now reads

$$\langle\Psi|\Psi\rangle = 1, \quad (2.6)$$

and the *orthogonality condition*

$$\langle\Phi|\Psi\rangle = \int \Phi^*(\mathbf{R})\Psi(\mathbf{R})d\mathbf{R} = 0 \quad (2.7)$$

may be regarded as an extension of the geometrical notion of orthogonality to state vectors and wavefunctions.

An *operator* \hat{A} transforms any given vector $|\Psi\rangle$ into another vector $|\Psi'\rangle = |\hat{A}\Psi\rangle = \hat{A}|\Psi\rangle$. When acting on a vector $\alpha|\Psi\rangle + \beta|\Phi\rangle$, where α and β are complex numbers, such as

$$\hat{A}(\alpha|\Psi\rangle + \beta|\Phi\rangle) = \alpha\hat{A}|\Psi\rangle + \beta\hat{A}|\Phi\rangle. \quad (2.8)$$

the operator is called a *linear operator*. We will work only with linear operators. *Matrix elements* of an operator \hat{A} are written as

$$\langle\Psi|\hat{A}|\Phi\rangle = \langle\Psi|\hat{A}\Phi\rangle = \int \Psi^*(\mathbf{R})\hat{A}\Phi(\mathbf{R})d\mathbf{R}. \quad (2.9)$$

³In a finite Hermitian space \mathbb{C}^n , the “kets” are the column matrices $|u\rangle = \begin{bmatrix} u_1 \\ u_2 \\ \vdots \\ u_n \end{bmatrix}$ and the “bra” are the row matrices $\langle v| = [v_1^* v_2^* \dots v_n^*]$ so that $\langle v|u\rangle = \sum_{i=1}^n v_i^* u_i$ is a matrix product.

The *product* of two operators \hat{A} and \hat{B} is defined as $(\hat{A}\hat{B})|\Psi\rangle = \hat{A}(\hat{B}|\Psi\rangle)$. It is interesting to note that multiplying a ket by a bra, $|\Psi\rangle\langle\Phi|$ is an operator.⁴ Indeed, applied to a vector $|\varphi\rangle$, it yields another vector: $|\Psi\rangle\langle\Phi|\varphi\rangle = \langle\Phi|\varphi\rangle|\Psi\rangle$, where $\langle\Phi|\varphi\rangle$ is a complex number. In particular, $\hat{\Pi}_\Psi = |\Psi\rangle\langle\Psi|$ is the *projection* operator onto $|\Psi\rangle$, since

$$\hat{\Pi}_\Psi^2 = |\Psi\rangle\langle\Psi|\Psi\rangle\langle\Psi| = |\Psi\rangle\langle\Psi| = \hat{\Pi}_\Psi \quad (2.10)$$

holds, which shows that $\hat{\Pi}_\Psi$ is a projector, and since

$$\hat{\Pi}_\Psi|\Psi\rangle = |\Psi\rangle\langle\Psi|\Psi\rangle = |\Psi\rangle \quad (2.11)$$

holds, which shows that the projector projects onto $|\Psi\rangle$. Note that a normalized $|\Psi\rangle$ is assumed.

The *commutator* of two operators \hat{A} and \hat{B} is defined as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \quad (2.12)$$

When $[\hat{A}, \hat{B}] = 0$, which implies $\hat{A}\hat{B} = \hat{B}\hat{A}$, the two operators are said to *commute*.

For each linear operator \hat{A} , there exists an *adjoint operator*, \hat{A}^\dagger , defined as follows:

$$\langle\Psi|\hat{A}^\dagger|\Phi\rangle = \langle\hat{A}\Psi|\Phi\rangle = \langle\Phi|\hat{A}|\Psi\rangle^* \quad (2.13)$$

or, in integral form, with wavefunctions

$$\begin{aligned} \langle\Psi|\hat{A}^\dagger|\Phi\rangle &= \int \Psi^*(\mathbf{R})\hat{A}^\dagger\Phi(\mathbf{R})d\mathbf{R} = \int (\hat{A}\Psi(\mathbf{R}))^*\Phi(\mathbf{R})d\mathbf{R} \\ &= \left(\int \Phi^*(\mathbf{R})\hat{A}\Psi(\mathbf{R})d\mathbf{R}\right)^* = \langle\Phi|\hat{A}|\Psi\rangle^*. \end{aligned} \quad (2.14)$$

An operator \hat{A} is *Hermitian* if

$$\hat{A}^\dagger = \hat{A}. \quad (2.15)$$

If \hat{A} is Hermitian, its *expectation value*, i.e. $\langle\Psi|\hat{A}|\Psi\rangle$ for a given state vector $|\Psi\rangle$, is real. Indeed, in view of Eq. (2.14) and since $\hat{A}^\dagger = \hat{A}$

$$\langle\Psi|\hat{A}|\Psi\rangle^* = \langle\Psi|\hat{A}^\dagger|\Psi\rangle = \langle\Psi|\hat{A}|\Psi\rangle. \quad (2.16)$$

⁴In a finite Hermitian space \mathbb{C}^n , $|u\rangle\langle v| = \begin{bmatrix} u_1 \\ u_2 \\ \vdots \\ u_n \end{bmatrix} [v_1^* v_2^* \dots v_n^*] = \begin{bmatrix} u_1 v_1^* & u_1 v_2^* & \dots & u_1 v_n^* \\ u_2 v_1^* & u_2 v_2^* & \dots & u_2 v_n^* \\ \vdots & \vdots & \ddots & \vdots \\ u_n v_1^* & u_n v_2^* & \dots & u_n v_n^* \end{bmatrix}$, which is a $(n \times n)$ matrix, i.e. an operator in \mathbb{C}^n .

A *nonzero* vector $|\varphi_k\rangle$ is said to be an *eigenvector* of an operator \hat{A} if

$$\hat{A}|\varphi_k\rangle = a_k|\varphi_k\rangle, \quad (2.17)$$

and a_k is the *eigenvalue* associated with this eigenvector. The set $\{a_k\}$ is called the *spectrum* of \hat{A} . For simplicity, we assume the spectrum to be discrete and non-degenerate (i.e. there are no two or more equal eigenvalues).

If \hat{A} is Hermitian, the eigenvalues a_k are real and the eigenvectors corresponding to different eigenvalues are orthogonal. Thus, taking eigenvectors normalized to unity, we have

$$\langle\varphi_k|\varphi_l\rangle = \delta_{kl}, \quad (2.18)$$

where δ_{kl} is the *Kronecker delta*. In addition, the set $\{\varphi_k\}$ of normalized eigenvectors forms a complete set of orthonormal basis vectors (*spectral theorem*), i.e. any state vector $|\Psi\rangle$ can be expanded as follows

$$|\Psi\rangle = \sum_k c_k|\varphi_k\rangle, \quad (2.19)$$

or, in terms of wavefunctions,

$$\Psi(\mathbf{R}) = \sum_k c_k\varphi_k(\mathbf{R}), \quad (2.20)$$

where the c_k are complex coefficients. In fact,

$$c_k = \langle\varphi_k|\Psi\rangle = \int \varphi_k^*(\mathbf{R})\Psi(\mathbf{R})d\mathbf{R}, \quad (2.21)$$

and, since $\Psi(\mathbf{R})$ is normalized to unity, i.e. $\langle\Psi|\Psi\rangle = 1$,

$$\sum_k |c_k|^2 = 1. \quad (2.22)$$

If two observables *commute*, there exists a basis of *eigenvectors common* to the two operators.

To summarize: to each *physical quantity* \mathcal{A} corresponds an *observable* \hat{A} that is a Hermitian linear operator acting in the space of wavefunctions \mathcal{E} , and characterized by its spectrum, i.e. the set $\{a_k\}$ of its eigenvalues and the set $\{\varphi_k(\mathbf{R})\}$ of the corresponding normalized eigenfunctions, which constitute an orthonormal basis set of \mathcal{E} (spectral theorem).

We are now ready to state⁵ the *measurement principles* of quantum mechanics:

(a) In the measurement of a physical quantity \mathcal{A} , the only possible results of the measurement are the eigenvalues a_k of the corresponding observable \hat{A} (it is also known as the *quantization principle*).

(b) Owing to the *spectral theorem*, the wavefunction *before* the measurement can be expressed in terms of the normalized eigenfunctions of \hat{A} :

$$\Psi(\mathbf{R}) = \sum_k c_k \varphi_k(\mathbf{R}). \quad (2.23)$$

When the measurement occurs, the *probability* of finding the value a_k as *result* is

$$\mathcal{P}(a_k) = |c_k|^2 = |\langle \varphi_k | \Psi \rangle|^2. \quad (2.24)$$

The above equation is also known as *Born's probability rule*.

(c) Immediately after the measurement of the physical quantity \mathcal{A} has been performed and *has given the result* a_k , the new state wavefunction of the system is the (normalized) eigenfunction $\varphi_k(\mathbf{R})$. This “instantaneous” change from $\Psi(\mathbf{R})$ to $\varphi_k(\mathbf{R})$ is known as the *reduction of the wavepacket* or *wavefunction collapse*. According to the standard interpretation of quantum mechanics, this wavefunction collapse is due to the interaction between the system and the measuring apparatus.⁶

As already briefly mentioned, for a given wavefunction $\Psi(\mathbf{R})$, the *expectation value* of any physical quantity \mathcal{A} is given by

$$\int \Psi^*(\mathbf{R}) \hat{A} \Psi(\mathbf{R}) d\mathbf{R} = \langle \Psi | \hat{A} | \Psi \rangle. \quad (2.25)$$

Introducing Eq. (2.23) into Eq. (2.25) yields

$$\begin{aligned} \int \Psi^*(\mathbf{R}) \hat{A} \Psi(\mathbf{R}) d\mathbf{R} &= \sum_k \sum_l c_k^* c_l \int \varphi_k^*(\mathbf{R}) \hat{A} \varphi_l(\mathbf{R}) d\mathbf{R} \\ &= \sum_k \sum_l c_k^* c_l \int \varphi_k^*(\mathbf{R}) a_l \varphi_l(\mathbf{R}) d\mathbf{R} \\ &= \sum_k \sum_l c_k^* c_l a_l \int \varphi_k^*(\mathbf{R}) \varphi_l(\mathbf{R}) d\mathbf{R} \\ &= \sum_k \sum_l c_k^* c_l a_l \delta_{kl}, \end{aligned} \quad (2.26)$$

⁵We do it mainly in terms of wavefunctions since the “ \mathbf{R} representation” will be predominantly used in the present book.

⁶The mechanism and meaning of the wavepacket collapse is a difficult and much debated topic in quantum mechanics. For an introduction see, for instance Chap. 8 of Ref. [3].