Quantum Physical Chemistry

Basic Quantum Mechanics for Process Description

O. Tapia

Department of Physical and Analytical Chemistry
Uppsala University

Box 259- Ångström

S-751 05 Uppsala, Sweden

orlando.tapia@fki.uu.se

PREFACE

Quantum state is a central concept that this book try to construct and develop. Quantum states play central roles in the study of phenomena in physics, chemistry, biochemistry, material chemistry, biology, etc. Developments in quantum technology are associated to the ability to construct material systems sustaining quantum states expressing properties of interest at the laboratory space that finally find out the way to the market.

Quantum physical chemistry embodies conceptual developments in quantum mechanics required to understand quantum state behavior sustained by single-material-systems. Quantum states belong to abstract Hilbert space. While a single-system has fixed elementary composition in terms of fundamental matter elements: electrons and nuclei is the most common case yet not unique.

A 1-system is located with the help of an inertial frame whose origin belongs to laboratory space. An abstract quantum state belonging to Hilbert space is projected with the help of a set of configuration basis vectors; the labels associated to these base vectors correspond to the configuration space coordinates; this new space is also a pure mathematical one.

A projected quantum state is nothing but the wave function *sustained* by the material 1-system. Laboratory evolution of the I-frame is hence separated from the quantum evolution of the wave function. There is no need of statistical descriptions that are usual for standard Quantum Mechanics (QM).

Single-molecule measurement methods have pervaded chemistry, material sciences, biochemistry and many other research fields thereby pointing to a need for such one-system description of quantum phenomena. The method sketched above is perfectly adapted to describing single systems' quantum states. They are not fit to describe the material components as such. In view of the schooling we sufered during student times where the paradigm is precisely the opposite this new approach may look paradoxical.

There are plenty of books on quantum mechanics, most of them outstanding. The question is: do we need another book, or extensive chapters, on this matter?

To partially answer this question let us see what do these books have in common from a fundamental standpoint. There are two themes underlying them all, namely, a particle model and a probabilistic (statistical) interpretation of the wave function implying object-like descriptions.

One problem is that with a 1-system, a statistical understanding is not fully appropriate. For the approach developed here, no molecular or atomic objects enter the theoretical description but quantum states required for representing 1-systems that sustain such quantum states; location in laboratory space is determined by the

introduction of I-frames, therefore internal quantum states must be distinguished from the states associated to the I-frame taken in a global sense.

The bottom line can be summarized as follows: quantum measurement is about responses of quantum states. It is not a response from an object towards a quantum interaction that is sensed with a measuring device. This is a fundamental tenet.

This makes a difference with respect to the dominating view in this field. The concept of objects is replaced by quantum states sustained by elementary matter. The quantum states and their way to change with other (external) quantum states via interactions is what identify the material system via a set of responses.

The book starts from basic concepts of quantum states in Hilbert space advancing in a construction that avoids introducing traditional particle themes at too an early stage. A sharp difference between base states and quantum states permits developing a quantum mechanics of states rather than particles the number of which is an invariant; a quantum chemical (QC) state is hence introduced. The QC-state concept is a natural extension of the quantum state concept to handle chemically reacting systems; this type of states incorporate all chemistry that can be related to a given set of basic material constituents via molecular eigenstates (Mol-ESs) models; the Mol-ESs are sustained by electrons and nuclei introducing mass and charge parameters into the quantum framework.

In a laboratory setting a chemical system can be associated to multiple I-frame subsystems so that special care must be exercised to include base states coming from the many I-frame case with those coming from the one I-frame global representation. This is an issue that has not been carefully attended in the literature.

To be more specific: a set of 16 electrons and a positive charge background making a total of 16 positive charge will show quantum states related to a number of chemical systems: ethylene; di-oxygen (O_2); two carbene radical fragments (CH_2 twice); the diatomic carbon molecule plus two hydrogen molecules (C_2+H+H); a sulfur atom (S); and many more chemical systems. It is the nuclear charge that permits identifying atomic species. For those systems where the nuclear background is invariant, chemistry will show up as differences in electronic quantum states. More exotic systems, such as quantum dots, share the same type of quantum mechanical behavior.

The core of this book is a presentation of quantum mechanics from a perspective adapted as much as possible to present-day molecular sciences; the concept of QC-state for 1-systems is at center stage. The standard statistical themes enter the scene latter on where a step towards classical physics appears naturally in the trek to understand quantum knowledge in a laboratory context.

A common brand of theory takes the wave function of systems as a representation of particles in real space via a probability density concept. Moreover, charge conjugation symmetry in relativistic theory permits relating quantum base states of particle-antiparticle material systems. Relativistic quantum mechanics can be used to calculate base states but fail to yield a particle picture. In

the 1-system model charge conjugated quantum systems can be handled in a unified manner. The lesson is summarized: There are quantum states not particles as basic elements of the theory allowing for characterization of material systems. For abstract quantum mechanics it is the quantum state that is the central concept as initially emphasized in Quantum Mechanics book by Dirac.

With hindsight, most of, but not all, the fray with quantum mechanics lays in the paradoxes derived from the wave-particle duality. To overcome this troublesome situation the founding fathers introduced quantum entities that could behave like particles or waves, depending on how they were "observed". In actuality such language blurs the situation even further. These classical concepts are not adapted to quantum physical descriptions; yet they pervade the talking about, and talking lead to thinking in this blur manner.

However, Dirac seminal book starts from the idea that quantum states and the principle of linear superposition are central concepts to Quantum Mechanics. He observe that "[one of] the objects of physical science is not the provision of pictures, but is the formulation of laws governing phenomena and the application of these laws to the discovery of new phenomena". Pictures should hinge at well-defined and relevant places as didactic tools, no more & no less.

Quantum mechanics implies a measurement theory linking the theoretic (mathematical) world to a laboratory one. A measurement relates a change of the quantum state sustained by a given material system to changes of specific quantum states of measuring apparatuses; these latter correspond to material systems that, eventually, may be classed as macroscopic, but this is not an issue.

A measurement presents two complementary aspects. First, for the measuring device, a change of its quantum state must be translatable (mapped) into recording obtained from *interactions* with the system under measure to end up with readings (translations to a language) of such recordings. These interactions may include preparations carried out to set up the system of interest in particular quantum states as well as the measuring apparatus. The readings boil down to event observation; recordings correspond to preparations of potentially readable material systems.

Reading and recording do qualify as real space events; accordingly, they are not commensurate to quantum evolution. Quantum states evolve in Hilbert space. Recordings and readings are located in real (laboratory) space where *conservation* laws are enforced, in particular, the *energy* to be traded among subsystems. Phenomenologically speaking, the former appears as events localized in space-time. These issues are discussed in Chapter 10, while key ideas are introduced as we go along the chapters in this e-book.

In classical physics, mechanics for instance, theoretical elements are abstracted from real space objects. Such is not the case for quantum physics; an abstract quantum state in Hilbert must be projected with the help of configuration spaces. An abstract quantum state projected on a given configuration space defines a wave function; the quantum state is sustained by the material system. Thus, a borderline,

a Fence as it were, between Hilbert space and real space is introduced to help descriptions.

There are no events in Hilbert space; events belong to real space. This is a key issue.

Events are well adapted to handling with counting (eventually probabilistic) schemes. Such "discontinuity" was early discovered but never well assimilated. The standard complementarity principle refers to the "ability" of quantum mechanical entities to behave as particles or waves under different experimental conditions. However, as already emphasized, time evolution occurs in Hilbert space only, while events revealing energy exchanges between (sub) systems occur at a different level; they result from quantum interactions defining a Fence domain.

At the Fence an arrow of time can be defined: A state must be prepared first before a measuring event can be detected (registered). Time evolution at the Fence would differ from Hilbert space evolution. One has to get used to the way one has to look at quantum phenomena.

Because different levels must be related, the interpretation of the formalism differs in a radical way from the orthodox one as will be sensed in this book. From the fence "outwards", i.e. real space, semi-classical and probabilistic views are welcome most of the time, although not always in tandem; there will be no big quarrel with any of present day interpretations once the appropriate definition of wave functions is introduced. From the Fence "inwards" the state of affairs differs, as this book will illustrate some aspects of; mappings allow knitting spectroscopic responses in real space to internal dynamic (eventless) evolution in Hilbert space. The role of this latter is to provide specific (mathematical) language.

If we keep in mind the chain leading from objects to particles and thereto particle-states and vice versa then we would be able to separate the levels mentioned above:

$$\Rightarrow \left]\begin{matrix}\mathrm{Re}\,al-space\\ objects\end{matrix}\right[\Rightarrow \left]\begin{matrix}Chemical\\ Particles\end{matrix}\right[\Rightarrow \left[\begin{matrix}Particle-states\\ (QM)\end{matrix}\right] \Rightarrow \left[\begin{matrix}Quantum\\ States\end{matrix}\right] \Rightarrow$$

Events in Real space |**Fence**| *Hilbert space representations*

There are two aspects involved in this separation. First, it is the formalism of quantum mechanics. This is fully concerned with Hilbert space; it is pure mathematics. Second, there are interactions at the Fence leading to real space sensing. Here, a theory of measurement occupies central stage and by necessity it is phenomenological.

The book is designed as an introduction to quantum physics for chemist, physical chemist, biologist and persons interested in global aspects of the natural sciences. Physicists are welcome to browse it too albeit it is an elementary approach to quantum mechanics in a broad sense with probably some didactic surprises.

The first part of the book concerns the language of quantum mechanics, i.e. the domain of quantum states and base-states included in Hilbert space. A somewhat clumsy replacement of the term “basis” extensively used in Quantum Chemistry by an equivalent term “base” is introduced to avoid misunderstandings. Base stand for the states that represent the single-system states that enter linear superpositions representing quantum states: e.g. molecular eigenstates. Basis stands more with practical functions used to calculate properties of the system as if it were an object (molecule). Bases are used in abstract Hilbert space, basis do the job at the computing level at and beyond the Fence. Bases and basis are eigen functions of specific operators; in this sense, both are employed to represent quantum states at the appropriate level.

The book is organized as follows. First chapter presents attempts to construct a bridge between simple languages describing chemical change and the counterpart in the quantum world. A correct appraisal of the theoretical stance is necessary to follow the trek through the rest of the text. In Chapter 2 basic elements of quantum formalism are exposed. Most of the material has to be taken as acquaintance with common language in quantum mechanics. References to deepen some aspects are given. The global treatment is however given in abstract space meaning with this that no specific material systems are examined. This may be new for most readers. The aim is to familiarize them with the general form of quantum physics as the field is not deductible from experiments and in particular the concept of quantum state. Because of this unique situation, there is no need for philosophical interpretations of wave functions. We have to take the mathematics at face value first and see what we do get from.

A first step to move theory towards real world while keeping its basic abstract form is accomplished by introducing inertial frames (I-frames); precisely as those used in Special Relativity, one gains a loto f mathematical properties that Hill be elicited stepwise. Configuration spaces covering the degrees of freedom associated to the material system are introduced. A rigged Hilbert space is defined with the help of bases vectors label with configuration space coordinates. Onece you get appropriate projection operators the abstract quantum state is simple projected into this configuration space to get a wave function representing such abstract state. In other words, the abstract formalism is translated into I-frame language. The quantum states in abstract space (Hilbert space) cannot depend upon specifics associated to I-frames, in particular origin and frame orientation with respect to second I-frame must lead the wave function invariant. In Chapter 3 some of these invariances (origin translation and I-frame rotations) are implemented following Wigner procedures. Many sections here are difficult. Readers not bound to develop specialized skills in theoretical chemistry should glance the content to get a first exposure to linguistic issues; the introduction to each chapter will give basic elements to proceed without a thorough study of the remaining sections.

There is a crucial result concerning time evolution of a quantum state. The so-called generator of time displacement corresponds to a Hamiltonian operator having the dimension of energy. For systems where the time dependence and configuration space dependence can be separated, the fundamental form of quantum mechanics follows, namely, Schrödinger equation.

We move deeper into the direction of laboratory world in Chapter 4. Readers may sense the gradual change happening when one moves from formalisms via theories down to models. The abstract formalism applies to any system whose quantum states are described with abstract Hilbert spaces. In our case, all the approach is non-relativistic in the sense that time is treated separately. The material system includes electrostatic charges implying that electromagnetic interactions cannot be avoided. Chapter 4 discusses the formalism required at a Fence.

Chapter 5 presents a complement in quantum electromagnetism. Starting from Maxwell equations we take readers non-initialted in quantum electrodynamics into a trek to make them conversant with some basic aspects of contemporary quantum aspects of electromagnetic radiation, in particlular Light.

Chapter 6 gives a short description of relativistic quantum mechanics. Here we find the opportunity to construct actual Hamiltonian operators. We find partial differential equations leading to the construction of base sets for simple material systems. A relativistic approach to hydrogen-like atoms is derived from Dirac equation. We also study the non-relativistic limit to Dirac equation. A detailed exam of Pauli 2-spinor equation is given.

Chapter 7 is dedicated to statistical aspects based on the quantum mechanical approach introduced here. Due to the 1-system approach, a new perspective to statistics obtains by using Jaynes-Shannon model. Bosonic systems are examined. Bose-Einstein condensates for two material systems are included. In particular the hydrogen atom system is discussed.

In Chapter 8 we come back to quantum states. This time we learn how to modulate (change) quantum states with particular physical devices. Diffraction and interferente phenomena are considered; in particlular single and double slit(s) set ups. Events counting and recording are briefly discussed. Mirrors and Beam splitter devices are taken to acto n specific quantum states. Mach-Zender interferometer quantum states are calculated. Keeping in the laboratory World we introduce quantum states to represent periodic potentials. Crystal solids quantum states are griten down.

Chapter 9 closes this Webb version. Here, preparing and recording quantum states are discussed. A full section is dedicated to measurement theory in quantum mechanics; it includes a discussion between the concepts of possibilities and probabilities.

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CHAPER 5. Elements of quantum electromagnetism

CHAPTER 6. Basic Relativistic Quantum Mechanics

CHAPTER 7. Statistics and quantum molecular issues

CHAPTER 8. Modulating quantum states: Fence

Quantum chemistry is a branch of chemistry whose primary focus is the application of quantum mechanics in physical models and experiments of chemical systems. It is also called molecular quantum mechanics. Experimental quantum chemists rely heavily on spectroscopy, through which information regarding the quantization of energy on a molecular scale can be obtained. Common methods are infra-red (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and scanning probe microscopy. Advances in Quantum Chemistry presents surveys of current topics in this rapidly developing field that has emerged at the cross section of the historically established areas of mathematics, physics, chemistry and biology. It features detailed reviews written by leading international researchers. This series provides a one-stop resource for following progress in this interdisciplinary area.Â - proceedings of the physical society. Most recent volume. Volume 80. Rufus Ritchie, A Gentleman and a Scholar.