2. Basic Quantum Formalism

Quantum physics has a well-defined mathematical structure. This chapter deals with some mathematical elements required to get a little bit on its foundations. This corresponds to a level 1 where no direct correspondence to laboratory situations is sought. Yet one must prepare the reader to connect abstract theory to the one to be projected in configuration spaces at the Fence; this situation produces a lack of logical consistency. The price must be pay because Physics is not just mathematics and mathematics is even less physics.

There is a foundational concept: a quantum state is sustained by a material system. The material system belongs to laboratory (real) space; a quantum state belongs to (abstract) *Hilbert space*. One cannot define such foundational relationship in terms of other concepts. This point is crucial to the development of a language adapted to such state of affairs. Such relationship defines the physical state associated to a material system. We define a physical state via a quantum state sustained by the corresponding material system.

E&E.2-1 Reminder

Fron Chapter 1 let us remind some ideas. Quantum states form linear manifolds, where a unitary scalar product is defined; to each vector |g> there corresponds one and only one conjugated transpose, <g|; the symbol <g|h>, is a complex number, standing for the scalar product between two vectors |f> and |g>; <g|g> is a real number.

Remember the concept of quantum state as being different from *base states* that are used to representing quantum states. Base states are particular eigenfunctions to an operator $\hat{O}$ such that $\hat{O}|y_k> \propto |y_k>$, the proportionality constant is the eigenvalue associated to the operator, $\hat{O}|y_k>=O_k|y_k>$. Those operators having real eigenvalues interest us; they are known asHermitian operators. Among them, the energy operator (the Hamiltonian) plays a fundamental role as we saw already.

Let us axiomatically introduce the pertinent mathematical grounds.

2.1. Axioms of quantum mechanics

It is common practice, to help organizing the theory in a better logical manner, to introduce a set of axioms. In the preceding chapter, we have followed a different path, as the prime objective was to find connections between chemical and quantum physical languages. The ways we relate laboratory tools and experiments to abstract linear superposition states differ from standard presentations of quantum mechanics in several respect that are discussed all along.

2.1.1. Hilbert space axioms

Now we write down axioms compatible with the present approach.

Axiom 1: *At a given time t_o, the quantum physical state of a given system is defined entirely as a state vector $|\Psi(t_o)>$ belonging to a linear vector space over complex numbers field $\mathbb{C}$, namely, a Hilbert space $\mathcal{H}$. The vectors are normalized to one (or to a Dirac distribution, case of rigged Hilbert space for configuration space projected states).*

Note that *it is not* the material system as an object that is represented by a vector in Hilbert space but a quantum state that we have to correlate to response to probes controlled at the laboratory level; this statement might sound almost irrelevant but is of paramount import.

Axiom 2: *Quantities $\mathcal{A}$ to which correspond linear self-adjoint (Hermitian) operatosr $\hat{A}$ defined in $\mathcal{H}$ provides elements to be included in probing operations.*

A self-adjoint operator implies existence of a complete set of *ordered* eigenvalues and eigenvectors:

$$\hat{A}|a_i> = a_i \mid a_i> \text{ for } i=0,1,\ldots. \qquad (2.1.1)$$

The eigenvectors form a complete orthonormal set, the complex number $<a_j|a_i>$ is zero if $j\neq i$ otherwise it is equal to one. If $\hat{A}$ is Hermitean then the eigenvalues are real numbers; these numbers can be used to label a basis (eigen) vector.

The ladder of eigenvalues provides stuff to construct invariant functions useful in establishing maps to measurable quantities in the laboratory space. In particular, for time independent Hamiltonian, differences of energy related to eigenvalues are accessible to measurements; the eigenvalues themselves are not.

Example, for the hydrogen atom, in a non-relativistic model, energy eigenvalues are given as: $E_n = -R/n^2$ where R is Rydberg constant. The series $E_n - E_2$ with $n > 2$ correspond to a family of spectral lines known as Balmer series.

The business of workers in quantum mechanics is to construct the operators and solve for these types of eigenvalue problems. Here, we assume that this is true and done.

The complete and denumerable set $\{|a_i>\}$ serves as a base for representing a quantum state $|\Psi(t)>$ as a linear superposition:

$$|\Psi(t)> = \Sigma_i <a_i|\Psi(t))> |a_i> = \Sigma_i C_i(\Psi(t)) \mid a_i> \quad (2.1.2)$$

The average value of the measurable quantity $\mathcal{A}$ over the quantum state represented by eq.(2.1.2) is given by the mapping:

$$<\mathcal{A}> = <\Psi(t) \mid \hat{A} \mid \Psi(t)> =$$
$$\Sigma_i \Sigma_j C_i^*(\Psi(t)) C_j(\Psi(t)) < a_i| \hat{A} \mid a_j> \quad (2.1.3)$$

From eq.(2.1.1) and orthonormality of basis vectors (e.g. $< a_i| a_j> = \delta_{ij}$) the average value (2.1.3) can be cast in terms of the eigenvalues of the magnitude $\mathcal{A}$:

$$<\mathcal{A}(t)> = \Sigma_i \Sigma_j C_i^*(\Psi(t)) C_j(\Psi(t)) a_i \delta_{ij} =$$
$$\Sigma_i C_i^*(\Psi(t)) C_i(\Psi(t)) a_i \quad (2.1.4)$$

$<\mathcal{A}(t)>$ is a weighted mean over the eigenvalues of the corresponding operator; the weight factor being directly related to the amplitude function,

$$C_i^*(\Psi(t)) C_i(\Psi(t)) = | C_i(\Psi(t))|^2$$

for each eigenvalue a_i. All zero amplitudes cancel out the contribution for the corresponding eigenvalues.

To the extent that the amplitudes are time-dependent, it is apparent that the average value calculated above is time dependent also.

At initial time t_o the amplitudes are assumed known, so that $<\mathcal{A}(t_o)>$ is a datum given by the sum that includes all non-zero terms from eq. (2.1.4). The initial average would differ from $<\mathcal{A}(t)>$ if after time interval $t-t_o$ some or all amplitudes had changed while keeping the global state normalized. Thus the change is located at the level of amplitudes; the base vectors form a constant denumerable set.

It is important to insist on the difference between quantum states (vectors in Hilbert space) and base states. Formally, arrange the amplitudes as a row vector: $(C_1(\Psi(t)) \ldots C_k(\Psi(t)) \ldots)$ and the base set as a column vector: $[| a_1> \ldots | a_k> \ldots]$ the linear superposition is given by the scalar product:

$$(C_1(\Psi(t)) \ldots C_k(\Psi(t)) \ldots) \bullet [| a_1> \ldots | a_k> \ldots] =$$
$$\Sigma_i C_i(\Psi(t)) \mid a_i> = |\Psi(t)> \quad (2.1.5)$$

This is eq.(2.1.2) written in an alternative manner that help define a pure state. To a pure state corresponds a vector where all amplitudes but one are zero:

$$(0_1 \ldots 1_k \ldots) \rightarrow 1_k \mid a_k> \quad (2.1.6)$$

This is a presentation of the k-th pure state. Thus, a pure state is associated to a base vector expressing as the row of zeros except at the position of the associated eigenvector; the remaining base vectors do not "evaporate". We can put such pure state as $1_k|\ a_k\rangle$ and $0_j|\ a_j\rangle$ (zero) for the remaining components of the sum, but this latter way does not help much.

It is apparent that for a pure state the average energy is just the corresponding energy eigenvalue. But a pure state looks like a classical physics state with well-defined physical magnitudes. The measurement models accepted so far in quantum mechanics are based on this type of state; thus there would be collapse of quantum state to a pure state as result of quantum measurement. This model is not adequate to the present way to understand a quantum state as we show below.

A measurable quantity via selfadjoint operators provides labels to introduce base states and eigenvalues that can be used to organize spectral responses of the 1-system towards appropriate probes that are controlled in laboratory. It is not necessary to resort to a collapse model to understand measurement.

2.1.2. Probing quantum states

There is another way to sense changes in quantum states via quantum probes. A quantum probe is a quantum system that can exchange energy quanta with a system to be investigated; this process involves two base states from the probed system, one serves as a root (target) state the other is an end (arrival) state. For the Balmer series example given above, E_2 is the root state and the arrival one are above, E_n and $n>2$. The operators involved here are the Hamiltonian of the measured and measuring systems and an interaction operator coupling both systems during a interaction process (probing, testing).

*Axiom 3: *Quantum states are detected via a response to external probes. The response can be expressed as a function over the set of eigenvalues of the associated operator $\hat{A}$, once entanglement states have faded away, namely, the spectral response of the system expressed with physical quantity $\mathcal{A}$.*

For the energy operator, the spectral probing relates eigenvalue differences. The energy being given: $\Delta_{ij} = \varepsilon_i - \varepsilon_j = \hbar\omega = h\nu$. An energy difference puts in correspondence a frequency of an electromagnetic field ($\nu=2\pi\ \omega$) at the Fence; it is described as photon energy $\hbar\omega = h\nu$ matched to Hilbert space function $\varepsilon_i - \varepsilon_j$. Thus, what an EM field would probe is a gap (interval) between two energies eigenvalues

and it is in this dual aspect that many misunderstandings lay; see Chapter 6 for detailed analyses. The case of continuum spectrum must be examined with care.

E&E.2.1-1 A simple model involving possible energy exchange

The response involves two eigenstates of the probed quantum system. Let us define the operator $\hat{\Delta}_{ji}$ in terms of the energy eigenstates as: $\hat{\Delta}_{ji} = |\varepsilon_j><\varepsilon_i|$. Calculate the commutator of Δ_{ji} with the Hamiltonian:

$$[\hat{H}, \hat{\Delta}_{ji}] = \hat{H}\,\hat{\Delta}_{ji} - \hat{\Delta}_{ji}\,\hat{H}$$

It is easy to see that this commutator equals:

$$[\hat{H}, \Delta_{ji}] = \hat{H}|\varepsilon_j><\varepsilon_i| - |\varepsilon_j><\varepsilon_i|\hat{H} = (\varepsilon_j - \varepsilon_i)\,|\varepsilon_j><\varepsilon_i|$$

Let us take the i-th level as root level and calculate $[\hat{H}, \Delta_{ij}]\,|\Psi(t)>$:

$$[\hat{H}, \Delta_{ji}]\,|\Psi(t)> = (\varepsilon_j - \varepsilon_i)\,|\varepsilon_j><\varepsilon_i|(\Sigma_k\, C_k(\Psi(t))\,|\,\varepsilon_k>) =$$
$$(\varepsilon_j - \varepsilon_i)\,|\varepsilon_j>\,(\Sigma_k\, C_k(\Psi(t))\,<\varepsilon_i|\,\varepsilon_k>) =$$
$$(\varepsilon_j - \varepsilon_i)\,|\varepsilon_j>\,(\Sigma_k\, C_k(\Psi(t))\,\delta_{ik}) = (\varepsilon_j - \varepsilon_i)\,|\varepsilon_j>\; C_i(\Psi(t))$$

Thus multiplying from the left with end state $<\varepsilon_j|$ one gets the amplitude:

$$<\varepsilon_j|[\hat{H}, \Delta_{ji}]\,|\Psi(t)> = <\varepsilon_j|\,(\varepsilon_j - \varepsilon_i)\,|\varepsilon_j>\,(\Sigma_k\, C_k(\Psi(t))\,\delta_{ik}) =$$
$$(\varepsilon_j - \varepsilon_i)\,<\varepsilon_j|\,\varepsilon_j>\; C_i(\Psi(t)) = (\varepsilon_j - \varepsilon_i)\, C_i(\Psi(t))$$

The matrix element $<\varepsilon_j|\,[\hat{H}, \Delta_{ji}]\,|\Psi(t)>$ relates excitation energy and the amplitude at the root state. Thus, if the amplitude there was zero, this operator yields zero value. If the amplitude is different from zero this operator can be matched to an external EM frequency such that: $(\varepsilon_j - \varepsilon_i) = \hbar\omega$.

Note that the operator $\hat{\Delta}_{ji} = |\varepsilon_j><\varepsilon_i|$ is a property of the system while $|\Psi(t)>$ depends upon the way we can prepare the system: $<\varepsilon_j|\,[\hat{H}, \Delta_{ji}]\,|\Psi(t)> = (\varepsilon_j - \varepsilon_i)\, C_i(\Psi(t))$. Note that one should take the absolute value of this complex number. Finally, sources/sinks are required to pay the energy bill; but this is a Fence phenomenon. See Chapter 12 for detailed discussions.

E&E.2.1-2 Objects and quantum states

An aggregate of *finite* basic constituents, say n-electrons and m-nuclei, what one calls a material 1-system, can sustain an *infinite number* of quantum states that can be identified (at a Fence) in many chemical guises depending upon external laboratory manipulations. See the example of a chemical reaction where the matter content is invariant but diverse quantum states relate to different chemical compounds; also keto/enol equilibrium qualifies as a simple example.

Objects have a place in real space at a given time so that an inertial frame can be assigned allowing for localization and orientation of the I-frame with respect to another one. Quantum states belong to Hilbert space; in our case they are represented by collections of complex numbers where time dependence would reside associated to well-defined base states. These, real and Hilbert, spaces are fundamentally different.

In this model, the detector device (real world object) as a whole would get the full picture of the quantum state under measurement if energy conservation were

ensured. Here, it is the excitation spectrum rooted at base state with eigenvalue a_i that is physically responsible for the recordings leading to given readings after interaction with the probe. Given a quantum state, the amplitude $<a_i|\ \Psi>$ is either zero or has a finite value. This statement holds at any time measured after time t_o. If the amplitude were zero the system would remain silent to a probe targeted to activate the spectra rooted at that i-th base state response. Otherwise the root state will put a response even if the relative intensity is extremely small.

It is common practice to construct statistical ensembles where each element is pure state (see chapt.8). The ensemble permits increasing the signal intensity for very small $\{|<a_i|\Psi>|^2\}$; at the laboratory level this is equivalent to increase concentrations of the species sustaining the quantum state.

E&E.2.1-3 Standard statements of measurement in the literature

It is commonly stated that *every physical experiment reduces to a measurement of the numerical value of an observable for the system under conditions determined by the experimental setup*. Reproducibility of conditions under which experiments are carried out is taken for granted, while the value of the observable obtained for different measures can be different. This type of statement assumes that events related to the measurement are collected one-by-one on a given real space detector. It is then apparent that this type of description mixes at least two elements: 1) The theoretical QM states to be measured; 2) A real space event detection that was not included in the axioms. Results may be logically inconsistent.

At the Fence one assumes an external (probing) system interacts with the system to be measured. The numerical value of a measurable physical quantity $\mathcal{A}$ expresses the spectrum of $\hat{A}$ via response or correlation functions.

*Axiom 4a: *The measurement in intensity regime of the spectral response associated to the component $C_i\ |a_i>$ for the quantum state $|\Psi>$ will show a relative intensity $\mathcal{I}_1$ in the detector devices that is given by*:

$$\mathcal{I}_i = |<a_i|\ \Psi>|^2 \qquad (2.1.7a)$$

Linear superpositions represent coherent states. Measurements in amplitude of the whole state are required to sense interference terms. This requires a quantum state projected over a configuration space leading to a wave function concept: $<\mathbf{x}|\Psi>$ (cf. Chapt.3).

*Axiom 4b: *The measurement in amplitude regime includes all interference effects: it is the modulus square of the sum evaluated at a ball (*$\mathrm{d}\mathbf{x}$**)** around a point* **x** *in configuration space that matters here:*

$$| \Sigma_i C_i(\Psi(t)) <\mathbf{x}| a_i> |^2 d\mathbf{x} =$$
$$\Sigma_{i,k} C_k^*(\Psi(t)) C_i(\Psi(t)) <a_k|\mathbf{x}> <\mathbf{x}| a_i> d\mathbf{x} \qquad (2.1.7b)$$

A probing (measurement) in amplitude targeting a complete linear superposition ought to have frequency spectra including excitations for all root states. A response to a (colored) probe will reflect the set of initial amplitudes; for probes having all spectral possibilities, only transitions amplitudes rooted at base state having non-zero amplitudes at event-time can be sensed. Axiom 3 states just this property.

Note that $<\mathbf{x}|a_i>$ corresponds to a base function of a projected Hilbert space, that is: $<\mathbf{x}| a_i>= \phi_{ai}(\mathbf{x})$. And, $<\mathbf{x}|\Psi> = \Psi(\mathbf{x})$, is the wave function standing for the quantum state sustained by the material system (Cf.Chapt.3).

The case represented in Axiom 4a corresponds to a measurement in intensity regime independent with disruption of coherence. It does not imply a collapse of the wave function. It tells us that if we measure the spectra associated to all those root states with non-zero amplitude and separate them, their relative intensities are controlled by eq.(2.1.3). In other words, each term with non-zero amplitude can contribute to the global spectra with weight $\mathcal{I}_i$. This can be seen if we look at the average energy:

$$<\mathcal{E}(t)> =<\Psi| \hat{H} |\Psi> = \Sigma_i \Sigma_j C_i^*(\Psi(t)) C_j(\Psi(t)) \varepsilon_i \delta_{ij} =$$
$$\Sigma_i C_i^*(\Psi(t)) C_i(\Psi(t)) \varepsilon_i = \Sigma_i \mathcal{I}_i(t) \varepsilon_i \qquad (2.1.8)$$

The energy is extracted, as it were, from the quantum state where amplitudes in square modulus weights energy eigenvalues. It is apparent that this energy reflects all non-zero amplitudes in the infinite dimension state vector.

Axioms with a star prefix differ from the standard frequentist (probabilistic) model. For a complete set of commuting Hermitian operators, the joint eigen states provide a base set to represent quantum states as linear superpositions.

The spectra elicit characteristic responses to external interaction; they are invariant properties of a given material system. A quantum state is given by the set of complex amplitudes appearing in the linear superposition; when put in interaction with a probing (measuring) system, amplitude changes in time would elicit physical and chemical processes undergone by the material system.

The measurement does not concern the base states as such. Because they remain unchanged, it is not possible to induce changes susceptible to be measured upon these base states. In quantum chemistry for example, the base functions 1s, 2s, 2p,…, are not that what is determined in a quantum probing. Understanding the quantum state the way herein used gives precision to the statement saying that it is a wave function that is measured; and this means precisely series of spectroscopic determinations as well as registering any function of the amplitudes.

E-E.2.1-3 Why does probability language is not used here yet?
The reader might have noticed that for 1-system with infinities of quantum states the concept of probability is not adequate. There is need for an ensemble of 1-systems and a decoherence hypothesis to be able to apply probabilistic concepts. These latter are better suited when, at a Fence, interactions with external systems (probing devices) can physically produce such decoherence effect. Measurement in intensity is an example; here there is need for a large number of 1-systems to imprint the recorders. Planck law, i.e. energy is exchanged in finite quanta between quantum systems, leads to events that *can be seen* as local responses.

In defining probabilities one finds statements of the following kind: "If one performs on the system a simultaneous measurement of a complete set of compatible dynamical variables, the probability of finding the system *in the state* $|\kappa>$ (i.e. of finding the particular values of these variables defining the dynamical state represented by $|\kappa>$) is equal to the square modulus of the scalar product of the vector $|\psi>$ (normalized to unity) representing the dynamical state of the system at the instant of measurement is carried out, by $|\kappa>$, namely $|<\kappa|\psi>|^2$ ". (Cf. Messiah, p.313,vol.I, North-Holland Pub.Co.,1970). This is a representative statement found with small variation in almost all textbooks on quantum mechanics.

The symbols referred to above corresponds to

$$\mathcal{I}_i = |<a_i|\ \Psi>|^2 \rightarrow |<\kappa|\psi>|^2\ ;\ |a_i> \rightarrow |\kappa>;\ |\Psi> \rightarrow |\psi>.$$

Some of the assumptions underlying the above type of statements are: 1) the material system is to be found in one and only one of the (base) states, say $|\kappa>$; 2) quantum mechanics is statistical in nature; 3) one measures the energy associated to base states; 4) the actual measuring device is not relevant to the measurement process; 5) the formalism of quantum mechanics is complete.

This interpretation predates the emergence of experimental devices that can control the extent of coherence. The fundamental concept introduced by quantum mechanics is the linear superposition principle. Thus, if we plan a probing (measurement) of the state of a quantum system we have to be prepared to detect the quantum state, i.e. the linear superposition as one and unique state not its components in isolation. We usually do not have probes able to detect coherent states. Instead, the apparatuses designed to measure intensity response have a clear local nature. It is the measuring device, which imposes a certain way to extract the information about the state of a given system. Quantum mechanics is not complete in the sense that the local nature of some measuring devices must be specially defined; in particular one must go for quantum field theory if local aspect are required as a matter of principle. But, then, you are back into a particle representation again. More on these problems will be discussed in chapter 12.

E-E.2.1-4 Standard foundational axioms

Caves and Schack (Ann.Phys.315, 123-146 (2005)) paraphrased standard graduate-level textbook introduction to foundational postulates. With the nomenclature developed so far you can get the message. i) The state of a physical system is a normalized vector $|\phi\rangle$ in a Hilbert space $\mathcal{H}$; ii) every measurable quantity is described by a Hermitean operator (observable) A acting in $\mathcal{H}$; iii) *the only possible result of measuring a physical quantity is one of the eigenvalues of the corresponding observable A*; iv) the probability of obtaining eigenvalue λ in a measurement of A having eigenvalue λ is $Pr(\lambda)= \langle\phi| \hat{P}_{\lambda}|\phi\rangle$, where $\hat{P}_{\lambda}$ is the projector operator onto the subspace of A having eigenvalue λ; and v) the post-measurement state in such measurement is $\hat{P}_{\lambda}|\phi\rangle/\sqrt{Pr(\lambda)}$.

As we saw in the preceding E&E the probability postulate iv) is instead derived from the frequency properties of repeated measurements of an observable on a finite or infinite number of copies of a system. Caves and Schack paper actually disprove claims in the literature asserting that quantum probability postulate can be derived from frequency models.

E-E.2.1-5 Historic measurement axioms

It is beyond doubt that von Neumann's measurement axiom fit the mathematical structure he proposed for quantum mechanics in the fundamental book: Mathematical foundations of quantum mechanics. Actual measurements are obviously done in laboratory space and no wonder axioms defined for Hilbert space instances would have a faint relationship to the actual measurement process. But, to construct an interpretation of QM from assumed outcomes from measurement in laboratory space is not an appropriate procedure either. The origin of the probabilistic model in a frequency context arises from scattering processes of material objects such as electrons or protons. The imprints on a screen are then assigned to a sort of un-concealment of the quantum state very much in the spirit of classical physics science. Thence comes out the idea that a wave function represents a particle as an object.

Well, one may think that it was obvious to subsume particle idea with a wave function. At this point lies one of the difficulties to understand quantum mechanics. For an object has definite properties while quantum states stand for the possibilities the material system may show. And those are infinite in number. Basic logic indicates that both statements are not commensurate.

Thus, an imprint on a screen is much more than the trace of an object that after the impact one can say that it was right there. But this is the least relevant aspect of such event. In so far the quantum state is concerned one can conclude that the amplitude of the linear superposition was likely to be non-zero. Such a statement assumes that the detector is perfect so that the impact events actually tell us something about the pattern of the quantum state elicited by interaction. If you are patient and collect more data one will start seeing elements of the whole pattern. Moreover, the recording device may show blind zones, namely, irrespectively of the value of a wave function over that zone the detector would never sense an event. Blindness may be caused by systematic errors during preparation.

Using the wave function to calculate the probability to find a particle in a small volume (ball) around a given configuration point tells us nothing on actual events. The calculated

probability may well be large and for sets of experimental runs never detect events at that specific ball due to any sort of blindness.

A positivistic approach that was popular by the time such model was proposed would go for a translation of impact frequencies as revealing the probability of finding the "particle" just at the given domain around one point. As a result the meaning of the wave function would be irretrievably lost unless one let information to accumulate during infinite time.

A wave function represents a quantum state of a given material system in Hilbert space. The wave function does not describe the material elements as such (as particles, for instance) in real 3-dimensional space. Thus axiom iii) from Standard foundational axioms namely, iii) *the only possible result of measuring a physical quantity is one of the eigenvalues of the corresponding observable A* cannot be given much value. All this book suggests that this is not a good choice for an axiom.

Let resume presentation of some characteristics of the mathematics related to Hilbert spaces. They are given in summary just to complete language aspects.

2.2. Operators in Hilbert space

Before proceeding with more materials concerning quantum physics, let us pause to give some elementary definitions about linear operators. Readers are assumed to be chemist, physical chemist, molecular biologist, biochemist, etc. so that they are not necessarily trained in specials mathematical topics. Yet, they need concepts of this science without entering a full operational knowledge. In what follows, some key terms are defined.

Given a linear vector space with elements $|\psi>$ and $|\phi>$, operators represents different types of mappings of the space onto itself. Some of their properties are summarized as theorems others are given as definitions. These subsections can be skipped if readers are interested in general ideas and applications; you may go to sect.2.5 directly.

i) Linear operators

A linear operator $\hat{L}$ on a vector space assigns to each vector $|\psi>$ a vector $\hat{L}|\psi>$ that also belongs to the same space and such that

$$\hat{L}(|\psi>+|\phi>) = \hat{L}|\psi> + \hat{L}|\phi>$$
$$\hat{L}\ (C\ |\psi>\ ) = C\,\hat{L}\ |\psi>$$

for any vectors $|\psi\rangle$ and $|\phi\rangle$ and scalar C (i.e. a real or complex number). Linear operators form a linear space with the sum $\hat{L}_1 + \hat{L}_2$ of two operators $\hat{L}_1$ and $\hat{L}_2$ and a scalar multiple C $\hat{L}$ of an operator $\hat{L}$ and scalar C defined by

$$(\hat{L}_1 + \hat{L}_2)\,|\psi\rangle = \hat{L}_1|\psi\rangle + \hat{L}_2|\psi\rangle$$
$$(C\,\hat{L})\,|\psi\rangle = C\,(\hat{L}|\psi\rangle)$$

for every vector $|\psi\rangle$.

E-E.2.2-1 Show that the operator $\hat{L}_{12}$ defined as the sum $(C_1\hat{L}_1 + C_2\hat{L}_2)$ is an operator in Hilbert space

The hypothesis is that $\hat{L}_1$ and $\hat{L}_2$ are linear operators in Hilbert space. This means that $\hat{L}_1|\phi\rangle$ maps onto another vector of this space as $\hat{L}_2|\phi\rangle$ does.

Let us apply $\hat{L}_{12}$ to $|\phi\rangle$ that is an arbitrary element of Hilbert space: $\hat{L}_{12}|\phi\rangle=(C_1\hat{L}_1+C_2\hat{L}_2)|\phi\rangle$. Using the properties indicated above one gets:

$$(C_1\hat{L}_1+C_2\hat{L}_2)|\phi\rangle = C_1\,(\hat{L}_1|\phi\rangle)+C_2(\hat{L}_2|\phi\rangle)$$

By hypothesis $(\hat{L}_1|\phi\rangle)$ is an element of this space as well as $(\hat{L}_2|\phi\rangle)$. Call them $|\phi_1\rangle$ and $|\phi_2\rangle$, respectively. So that we get:

$$\hat{L}_{12}|\phi\rangle = C_1\,(\hat{L}_1|\phi\rangle)+C_2(\hat{L}_2|\phi\rangle) = C_1\ |\phi_1\rangle + C_2\,|\phi_2\rangle$$

The sum of two elements of a Hilbert space, i.e. $C_1\ |\phi_1\rangle + C_2\,|\phi_2\rangle$ is a new element of that same space. Therefore, $\hat{L}_{12}|\phi\rangle$ is a vector in this space too and $\hat{L}_{12}$ is a linear operator in Hilbert space.

Now, introduce the dual conjugate space, with element written as "bra", $\langle\psi|$, so that the mapping corresponding to the scalar product of vectors $|\psi\rangle$ and $|\phi\rangle$ is just the "bracket" $\langle\psi|\phi\rangle$ that equals the transpose complex conjugate: $\langle\phi|\psi\rangle^*$. The bracket $\langle\psi|\phi\rangle$ is a complex number related to the vectors $|\psi\rangle$ and $|\phi\rangle$ in abstract Hilbert space. By abstract we mean that no specific mathematical representation has been chosen yet. Thus, for any pair of vectors there is a complex number $\langle\psi|\phi\rangle$ such that:

$\langle\psi|\phi\rangle = \langle\phi|\psi\rangle^*$
For $|\phi\rangle = C_1\,|\phi_1\rangle + C_2\,|\phi_2\rangle$ then,
$\langle\psi|\phi\rangle = C_1\langle\psi|\,\phi_1\,\rangle + C_2\,\langle\psi|\phi_2\rangle$
For $|\psi\rangle = C_1\,|\psi_1\rangle + C_2\,|\psi_2\rangle$
the mapping $\rightarrow \langle\psi| = C_1{}^*\langle\psi_1| + C_2{}^*\langle\psi_2|$;
The scalar product reads: $\langle\psi|\,\phi\rangle = C_1{}^*\,\langle\psi_1|\,\phi\,\rangle + C_2{}^*\,\langle\psi_2|\phi\rangle$

The *norm* $\langle\phi|\phi\rangle$ satisfies a positive-value condition $\langle\phi|\phi\rangle \geq 0$; it vanishes if and only if $|\phi\rangle$ is a zero vector.

ii) Anti linear operators

Let $\hat{K}$ be an operator acting on a complex number replacing it by its complex conjugate: $\hat{K}$ <b|ψ> = <b|ψ>*. The vector <b| is arbitrary. The equality: $\hat{K}$<b|ψ> = <b|ψ>* = <ψ|b> holds. For a linear superposition one gets an anti-linear operator:

$$\hat{K}\langle b|\ (\Sigma_i\ C_i\ |a_i\rangle) = \Sigma_i\ C_i^*\ \langle a_i|b\rangle = \Sigma_i\ C_i^*\ \langle b\ |\ a_i\rangle^*$$

or

$$\hat{K}\ (\Sigma_i\ C_i\ \langle b|a_i\rangle) = \Sigma_i\ C_i^*\ \langle b\ |\ a_i\rangle^*$$

iii) Adjoint operators

For any linear operator $\hat{A}$ the adjoint $\hat{A}^\dagger$ is defined by:

$$\langle\psi|(\hat{A}^\dagger|\phi\rangle) = (\langle\psi|\hat{A})|\phi\rangle = (\langle\phi|\hat{A}|\psi\rangle)^*$$

iv) *Self-adjoint operators*

Hermitian operators are self-adjoint, $\hat{A} = \hat{A}^\dagger$. Taking the diagonal element from the line above,

One gets: $\langle\psi|(\hat{A}^\dagger|\psi\rangle) = (\langle\psi|\hat{A}|\psi\rangle)^*$ and now take the definition: $(\langle\psi|\hat{A}|\psi\rangle)^* = (\langle\psi|\hat{A}|\psi\rangle)$, the spectrum is formed by real eigen value numbers.

Theorem 2.2.1: If $\hat{A}$ is a self-adjoint, Hermitian, operator then it has a denumerable complete set of eigenvectors $|a_i\rangle$ with real eigenvalues a_i.

The point to be retained here is that the eigenvalues of a self-adjoint operator can be used to label base states as we did in the preceding chapter.

Let $\hat{A}$ and $\hat{B}$ be two self-adjoint (Hermitian) operators; eigenvalues of $\hat{B}$ are represented by the set $\{b_i\}$. There are two cases we consider:

1) Operators commute, $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = \hat{0}$; or do not commute

2) $[\hat{A}, \hat{B}] \neq \hat{0}$.

In case 1) we say that these operators commute, for case 2) these operators are incompatible, as they do not commute.

Define now with respect to the average value:

$$\Delta\hat{A} = \hat{A} - \langle\hat{A}\rangle \quad \text{and}$$

$$\Delta\hat{B} = \hat{B} - \langle\hat{B}\rangle \qquad (2.2.1)$$

The <>-bracket implies an average value over an arbitrary quantum state. It is clear that

$$\langle\Delta\hat{A}\rangle = 0 \text{ and } \langle\Delta\hat{B}\rangle = 0 \qquad (2.2.2)$$

The square fluctuations $(\Delta\hat{A})^2$ and $(\Delta\hat{B})^2$ are different from zero as you can easily check. These fluctuations reflect the preparation of the quantum state implied by the average. For each quantum state there will be a possibly different square

fluctuation. What about the product of such fluctuations? The answer, in mathematical terms is:

$$(\Delta \hat{A})^2 (\Delta \hat{B})^2 \geq (1/4) |[\hat{A}, \hat{B}]|^2 \qquad (2.2.3)$$

If the operators commute, the product of the square fluctuations is zero. This reflects the independence of operators. On the contrary, if the operators commute, the fluctuation product has a lower bound. This uncertainty relationship applies to preparation stage. It is not the result of interactions at some other instance.

E&E.2.2-2 Show inequality (2.2.3).
Even if you do not succeed in doing it, note that this inequality is a mathematical fact. Accept the result as true.

E&E.2.2-3 Hilbert and pre-Hilbert spaces
A pre-Hilbert space is what we have been using as definition of Hilbert space, namely, a normed linear vector space. Now, if this pre-Hilbert space is complete then the space is called Hilbert space. A space is complete when any Cauchy sequence converges in this space. This is a key property. This is a reason why finite dimensional spaces are pre-Hilbert so that results obtained therefrom are not apodictic.

Theorem 2.2.2: The set of diagonal exterior products $\{|a_i><a_i|\}$ form a resolution of the identity operator $\hat{I}$:

$$\hat{I} = \Sigma_i |a_i><a_i| \qquad (2.2.4)$$

Theorem 2.2.3: Any arbitrary quantum state in Hilbert space $|\Psi>$ is representable by the set of complex numbers $\{<a_i|\Psi> = C_i(\Psi)\}$ corresponding to the linear superposition (2.2.5):

$$|\Psi> = \hat{I}|\Psi> = \Sigma_i |a_i><a_i|\Psi> = \Sigma_i |a_i> C_i(\Psi) \qquad (2.2.5)$$

If you want to determine a quantum state referred to a given base set you must determine (measure) these complex numbers.

Theorem 2.2.4: If, given initial state vector $|\Psi>$ prepared in a reproducible manner, the results of measurement of $\mathcal{A}$ give always a response rooted at the eigen value a_i (or a function thereof) then the measured quantum state is given by the row vector with one element differing from zero at the i-th position: $(0\ldots1_{(i)}\ldots)$.

Corollary to Theorem 2.2.4: If we try to measure the spectral response of $\hat{A}$ with the quantum state $(0\ldots1_{(i)}\ldots)$ then the measurement will show the spectra originated at eigen state $|a_i>$ with unit relative intensity, $\mathcal{I}_i = 1$. The intensity of different lines rooted in one and the same base state depend upon intrinsic properties of the system.

Theorem 2.2.5: Given the quantum state vector $|\Psi> = \Sigma_i |a_i> <a_i| \Psi>$ and using a filter device to project out the spectral response of all but one eigen state, say $|a_k>$, then conditions are fulfilled that make theorem 2.2.4 to hold except for relative intensity, i.e. $\mathcal{I}_k < 1$.

Theorem 2.2.6: Given an operator $\hat{B}$ acting in the space where the unit operator $I= \Sigma_i |a_i> <a_i|$ in terms of the eigenvectors of a diagonal operator $\hat{A}$ show that the matrix elements are given as $<a_k| \hat{B} |a_{k'}>$.

The matrix $\underline{\underline{B}} = (<a_k| \hat{B} |a_{k'}>)$ is obtained from the identity:

$$\hat{B} = \hat{I}\,\hat{B}\,\hat{I} = \Sigma_k |a_k> <a_k|\ \hat{B}\ (\Sigma_{k'} |a_{k'}> <a_{k'}|) =$$
$$\Sigma_k \Sigma_{k'} |a_k> <a_k| \hat{B} |a_{k'}> <a_{k'}| =$$
$$\Sigma_k \Sigma_{k'} <a_k| \hat{B} |a_{k'}> |a_k> <a_{k'}| \qquad (2.2.6)$$

There are two points of interest. First, the operator $\hat{B}$ can be represented in a complete operator base with elements $|a_k> <a_{k'}|$. Second, the effect of the operator $\hat{B}$ on a base state is given by:

$$\hat{I} = \hat{B}\ (\Sigma_{k'} |a_{k'}> <a_{k'}|) =$$
$$\Sigma_{k'} \hat{B} |a_{k'}> <a_{k'}| = \Sigma_k \Sigma_{k'} <a_k| \hat{B} |a_{k'}> |a_k> <a_{k'}| \quad (2.2.7)$$

The results are identical. From these two latter equations we can check that

$$\hat{B} |a_{k'}> = \Sigma_k\ <a_k| \hat{B} |a_{k'}> |a_k> \qquad (2.2.8)$$

The numbers $<a_k| \hat{B} |a_{k'}>$ are identified (labeled) by two indexes forming either a finite nxn array or an infinite square array depending on the dimension of the space used for the given problem. The integers k=1,2,… k'=1,2,… identify a number of the array (matrix) in a one-to-one manner. This is named as the matrix $\underline{\underline{B}}_A$ in the base given by the operator $\hat{A}$; the dimensions are specified according to the particular problem under study. It is a common practice to signal the base used to calculate the matrix elements of the operator $\hat{B}$. The matrix representations of the operators having special interest to us are calculated with the complete base set provided by the Hamiltonian operator.

2.3. Base change: Similarity transformations

Consider the case of *non-commuting* self adjoint operators $\hat{A}$ and $\hat{B}$ each one having the base sets $\{|a_k>\}$ and $\{|b_k>\}$, respectively. Their quantum labels cannot be simultaneously used to characterize base states in Hilbert space. It is said that

such operators ($\hat{A}$ and $\hat{B}$) are incompatible. Still, one must have a way to compare the same quantum state expanded in these incompatible bases. This is the problem examined below.

The unitary operator $\hat{U}$(b,a) required to do the job must relate base vectors from $\hat{A}$ to those of $\hat{B}$. One way to do this is by using mapping such as: $\hat{U}$(b,a)| a_k> has as image |b_k>, i.e. $\hat{U}$(b,a)| a_k> = |b_k> $\forall$k; for all values of k. By definition, the operator takes on the form:

$$\hat{U}(a,b) = \Sigma_k \mid a_k><b_k| \;;$$
$$\hat{U}(b,a) = \Sigma_k \mid b_k><a_k| \qquad (2.3.1a)$$

Taking the transpose and complex conjugate of the above operators we get:

$$\hat{U}^{\dagger}(a,b) = \Sigma_k \mid b_k><a_k| = \hat{U}(b,a);$$
$$\hat{U}^{\dagger}(b,a) = \Sigma_k \mid a_k><b_k| = \hat{U}(a,b) \qquad (2.3.1b)$$

This operator is unitary as $\hat{U}(a,b)\ \hat{U}^{\dagger}(a,b) = \hat{U}^{\dagger}(b,a)\ \hat{U}(b,a) = \hat{1}$.

Consider an arbitrary quantum state |Ψ>. Either expand it on the A-basis or in the B-basis. The state is the same. With this information get the transformation law between both base sets. For, write first an identity such as: $\hat{1}_B|\Psi> = \hat{1}_A|\Psi>$. It is easy to show that:

$$\Sigma_k < a_{k'}|\ \hat{U}(b,a)|\ a_k> <b_k|\Psi> = < a_{k'}|\Psi> \qquad (2.3.2a)$$
$$\Sigma_k < b_{k'}|\ \hat{U}^{\dagger}(b,a)|\ b_k> <a_k|\Psi> = < b_{k'}|\Psi> \qquad (2.3.2b)$$

The matrix elements $< a_{k'}|\hat{U}(b,a)|\ a_k>$ are equal to $< a_{k'}|\ b_k>^{\dagger}$; these correspond to the direction cosines of the transformation. Equation (2.3.2b) can be cast in terms of the old base by replacing the $< a_{k'}|\hat{U}(b,a)|\ a_k>$ matrix elements one gets:

$$< b_{k'}|\Psi> = \Sigma_k < a_{k'}|\ b_k>^{\dagger} <a_k|\Psi> =$$
$$\Sigma_k <b_k|\ a_{k'}> <a_k|\Psi> \qquad (2.3.3)$$

Thus, one has to know the set of transformation functions from {<b_k|$a_{k'}$>} in order to compute the image of the vector given by the set of amplitudes {<a_k|Ψ>} into the new basis set {<$b_{k'}$|Ψ>}. The change introduced here is one of perspective.

Finally, given an arbitrary operator $\hat{O}$ we want to get the matrix representation in both base sets and their connection: $< a_{k'}|\hat{O}|a_k>$ and $< b_{k'}|\hat{O}|b_k>$. Let transform these latter:

$$< b_{k'}|\ \hat{O}|\ b_k> = \Sigma_k\Sigma_{k'} < b_k|\ a_k> < a_{k'}|\ \hat{O}\ |\ a_{k''}>< a_{k''}|\ b_k> =$$
$$\Sigma_k\Sigma_{k'} < a_{k'}|\ \hat{U}^{\dagger}(b,a)|\ a_k> < a_{k'}|\ \hat{O}\ |\ a_{k''}>< a_{k'}|\hat{U}(b,a)|\ a_k> \qquad (2.3.4)$$

In pure operator terms one has a typical similarity transformation if we call the operator acting on the b-space as $\hat{O}^{(b)}$ and in a-space just $\hat{O}^{(a)}$, then:

$$\hat{O}^{(b)} = \hat{U}^{\dagger}\hat{O}^{(a)}\hat{U} \qquad (2.3.5)$$

This is then a way to "rotate" an operator from one base set to another.

Finally, the trace (tr) of an operator $\hat{X}$ is a mapping defined as the sum of diagonal elements:

$$\text{Trace}\,(\hat{X}) = \text{tr}(\hat{X}) = \Sigma_{k'} < a_{k'}| \hat{X} | a_{k'}> \qquad (2.3.6)$$

This closes the overview of general linear transformations.

2.4. Density matrix operators

The operator $|\Psi><\Psi| = \hat{\rho}$ is known as the *density matrix operator* associated to the quantum state $|\Psi>$. With the help of eq.(2.2.2) and the transpose complex conjugate the density operator is given by:

$$\hat{\rho} = |\Psi><\Psi| = \Sigma_i \Sigma_k (<a_k| \Psi>)^{t*} <a_i| \Psi> |a_i><a_k| = \Sigma_i \Sigma_k C_k(\Psi))^* C_i(\Psi) |a_i><a_k| \qquad (2.4.1)$$

The infinite dimension matrix $[|a_i><a_k|]$ represents the explicit matrix form $[\hat{\rho}_{ik}]$.

The diagonal matrix element $\hat{\rho}_{ii}$ calculated from eq.(2.2.4) is $C_i(\Psi)^* C_i(\Psi) = |C_i(\Psi)|^2$. According Axiom 4 this is $\mathcal{I}_i$ that is equal to the intensity (relative to the remaining channels) of the response associated to the root state characterized by the eigen value a_i. This is one of the advantages offered by this operator; it will bridge (at the fence) Hilbert space elements to real space detectable effects. So far, there is nothing statistical with this operator. It is just an adequate bridging operator (see below).

Furthermore, the off-diagonal products $C_k(\Psi))^* C_i(\Psi)$ are related to joint relative intensity detection via $| C_k(\Psi,t)^* C_i(\Psi,t) |^2$. Today, such type of experiments can be carried out in real laboratory.

In due time, one introduces statistical elements if the theoretical construction is made from real world detections (outside the fence). It is at this level that population concepts and particle models are most useful.

Time dependent density matrix can be derived from $\hat{\rho}(t) = |\Psi(t)><\Psi(t)|$ and use of eq.(1.3.1.5) to get the differential equation:

$$\partial \hat{\rho}(t)/\partial t = (-i/\hbar) [\hat{H}, \hat{\rho}(t)] = (i/\hbar)[\hat{\rho}(t), \hat{H}] \qquad (2.4.2)$$

The average value <A> of the operator defined in eq.(2.1.1) is the weighted sum of the eigen values a_i with the weight given by $\mathcal{I}_i$:

$$< \hat{A} > = \Sigma_i \, a_i \, \mathcal{I}_i \qquad (2.4.3)$$

Determining this average value implies the knowledge of $\hat{A}$ spectra and the non-zero complex numbers defining the quantum state in the base set of $\hat{A}$. Let us calculate the diagonal matrix element of the product $\hat{\rho}\,\hat{A}$ using eqs.(2.4.1) and (2.1.1). It is easy to show that:

$$\begin{aligned}
&\Sigma_i < a_i \mid \hat{\rho}\,\hat{A} \mid a_i > = \\
&\Sigma_i < a_i \mid \Sigma_j \Sigma_k \, C_k(\Psi))^* \, C_j(\Psi) \mid a_i >< a_k \mid \hat{A} \mid a_i > = \\
&\Sigma_i < a_i \mid \Sigma_j \Sigma_k \, C_k(\Psi))^* \, C_j(\Psi) \mid a_i >< a_k \mid a_i \mid a_i > = \\
&\Sigma_i < a_i \mid C_i \, (\Psi))^* \, C_i(\Psi) \, a_i \mid a_i > = \\
&\Sigma_i \, C_i \, (\Psi))^* \, C_i(\Psi) \, a_i = \Sigma_i \, \mathcal{I}_i \, a_i = \\
&< \hat{A} > = \mathrm{Trace}(\hat{\rho}\,\hat{A}) \qquad (2.4.4)
\end{aligned}$$

The first and last terms in this equation define the trace operation. Finally, calculate $\partial < \hat{A} > / \partial t$ to get:

$$\partial < \hat{A} > / \partial t = (i/\hbar) \, \mathrm{Trace}([\hat{H}, \hat{A}]\,\hat{\rho}) \qquad (2.4.5)$$

The density matrix offers a way out Hilbert space into real space. For the standard view, a measurement often consists of a recording of many numbers, each purportedly a quantitative realization of the same thing. An average of the results is performed to obtain statistically significant estimates of the quantity to be measured, i.e. an average value.

However, there are some subtleties to be considered. Take then $C_k(\Psi,t_o)$ approximately equal to one, zero over the remaining space. If k-state is the ground state there is no problem at least apparently. But the interesting case corresponds to a "metastable" state. For in this case it is not sufficient to say $C_k(\Psi,t_o+\Delta)=1$ with large time intervals, we must supply the root state wherefrom such state was reached. Not only this, one should also get the transition amplitudes relevant to the path leading to such situation.

To prepare such k-state an electromagnetic field provides an energy source. The photon field used to prepare the system in this unique state must also be known. To postulate, as the old model takes that the system may be in one and only one energy eigenstate is physically unacceptable if the energy conservation principle is to be respected. The presence of a vacuum photon field would prompt for spontaneous emission, while a field with energy inside may produce induced emission.

The formalism involving an isolated system of interest is not sufficient to incorporate physical situations of interest.

2.5. Time evolution & scattering operators

These operators allow for connections between quantum states prepared at a given time with a causally related quantum state that can be probed at a alter time. For time independent scattering, the operators relate two sets of quantum states that are expressed in the same base seta t two different configuration space points.

In what follows, only the most relevant (to chemistry) properties are examined.

2.5.1. Time separability: base sets and Amplitudes

For time independent $\hat{H}$ Eq.(1.3.1.1) can be separated into two coupled equations:

$$\hat{H}|\Psi> = E\,|\Psi> \qquad (2.5.1.1)$$

Because $\hat{H}$ is anHermitian operators the eigen value E is a real number. The time dependent part reads:

$$(i\hbar)\,\partial|\,f(t)>/\partial t = E\,|f(t)> \qquad (2.5.1.2)$$

Be careful, albeit E has energy dimension, it is not directly attached to the energy of the material system; in abstract Hilbert space it is a constant separating the terms of (1.3.1.1). The solutions have the form: $|\,f(t)> \rightarrow \exp(i\mathrm{t}E/\hbar)$.

Expression (2.5.1.1) is an eigen value equation. For self-adjoint Hamiltonians, this eigen value equation shows a complete denumerable set of eigen states, say $\{|E_k>\}$, with energy-eigen-values set $\{E_k\}$. The symbol E_k is a label for a given base state; one can keep the energy dimension but in general these symbols play the role of labels. In this case, eq.(2.5.1.1) because the set of energy eigen values (energy levels) is an ordered set one gets:

$$\hat{H}|\,E_k> = E_k\,|\,E_k> \qquad (2.5.1.3)$$

The following inequalities hold: $E_o < E_1 < \ldots < E_k < \ldots$.

The time dependent factor from eq. (2.5.1.2) takes on the form: $\exp(i\,t\,E_k/\hbar)$.

Retain the mapping $E_k \rightarrow |E_k>$ that is a key result associated to self-adjointness. Now, it is convenient to introduce an energy scale and range the energy eigen values. An energy eigen value is degenerate if it has associated a subset of eigen vectors differing among themselves by their labels: $\{|E_{ki}> : i=1,\ldots,m\}$, for a fixed k, label m is an integer, all energy eigen values are equal so that the i-label must depend upon a property differing from energy.

A representation of the unit operator obtains with a complete base set:

$$\hat{1} = \Sigma_k \mid E_k >< E_k \mid \qquad (2.5.1.4)$$

This expression is useful to open up an abstract quantum state in the particular energy base:

$$|\Upsilon> = \hat{1}\,|\Upsilon> = \Sigma_k \mid E_k >< E_k \mid \Upsilon> = \Sigma_k \mid E_k > C_k(\Upsilon) \qquad (2.5.1.5)$$

It is this energy representation that plays a central role for describing physical processes.

For the separable case, the quantum state is given as a direct product of $|\Psi>$ with time base states $|t>$; the symbol t is just a name indicating a connection with a real number set. For a particular energy eigen value, the time dependent factor reads: $|t> = \exp(itE_k)/\hbar)$, that is a solution to eq.(2.5.1.2) for $E=E_k$. Furthermore, changing the energy scale origin by an arbitrary amount, say δE, all energy eigen values are equally shifted by δE: $\{E'_k \rightarrow E_k + \delta E\}$. The time dependent factors takes on the form $\exp(it(E_k+\delta E)/\hbar)$ showing that only a common phase factor would multiply all time dependent terms: $\exp(it\delta E/\hbar)\exp(itE_k)/\hbar)$.

Assuming that we have at hand the spectrum of the time-independent Hamiltonian, there is interest to determine the time evolution of a given quantum state prepared at time t_o, from $|\Upsilon>|t_o> = |\Upsilon,t_o>$ to $|\Upsilon>|t> = |\Upsilon,t>$, both base time states referred to the same origin. As shown above, this is accomplished by the unitary evolution operator, $\hat{U}(t,t_o)$, calculated with the time independent Hamiltonian and its spectrum.

The symbol $|\Upsilon,t_o>$ contains the information about those amplitudes that are different from zero in the general linear superposition, eq. (2.5.1.5). To signify this fact, the summation symbol is written down as Σ'. The result coming from time evolution and using the ground state as root state is:

$$\begin{aligned} |\Upsilon,t> &= \Sigma'_{j=0,1,\ldots} C_j(\Upsilon,t_o)\ \hat{U}(t,t_o)|\varepsilon_j> = \\ &\Sigma'_{j=0,1,\ldots} C_j(\Upsilon)\exp(i(t-t_o)\varepsilon_j/\hbar)\,|\varepsilon_j> = \\ &\exp(-i(t-t_o)\,\varepsilon_o/\hbar)\,\Sigma'_{j=0,1,\ldots} C_j(\Upsilon)\,\exp(i(t-t_o)\,(\varepsilon_j-\varepsilon_o)/\hbar)\,|\varepsilon_j> = \\ &\exp(-i(t-t_o)\,\varepsilon_o/\hbar)\,\Sigma'_{j=0,1,\ldots} C_j(\Upsilon)\,\exp(i(t-t_o)\,\omega_{jo})/\hbar)\,|\varepsilon_j> \qquad (2.5.1.6) \end{aligned}$$

Result: the subspace indicated by Σ' is invariant, there is no amplitude outside the subset defining the initial state, only the phases, $\exp(i(t-t_o)\,\omega_{jo})/\hbar)$, periodically change in time, the set of labels for these amplitudes $C_j(\Upsilon)$ remains unchanged.

Isolated systems are described by time independent Hamiltonians. By construction, energy is a conserved magnitude. One may safely conclude that any quantum state prepared somehow will never evolve in time except for the phases.

For non-zero amplitudes to emerge at base states other than those in the initial set, there is need for an interaction with an external system. With the word external it is meant the inclusion of spectral states that do not belong to the material system under study.

2.5.2. External driving forces

Quantum states evolve due to interactions with systems other than the one we have been looking at. Energy and momentum conservation rules must be respected. However, one still can develop the formalism by focus on the selected system and representing the external system by an external coupling potential $\hat{V}$.

Assume a partitioning of the kind $\hat{H}' = \hat{H} + \hat{V}$, where the interaction between the 1-system and the interaction with an external system is represented by an operator, $\hat{V}$. The eigen functions of $\hat{H}$ are used to expand quantum states and the transformation from time independent $\hat{V}$ to a time dependent one $\hat{V}(t)$ is given by: $\hat{V}(t) = \exp(i\hat{H}t/\hbar)\hat{V}\exp(-i\hat{H}t/\hbar)$. Here, we quote the more general result concerning arbitrary amplitudes:

$$C_k(\Upsilon,t) = \Sigma'_{j=0,1,\ldots}\{C_j(\Upsilon,t_o)\,\delta_{jk} - (i/\hbar)\,C_j(\Upsilon,t_o)\int_{to}^{t} dt' \langle\varepsilon_j|\hat{V}(t')|\varepsilon_k\rangle + (i/\hbar)^2 C_j(\Upsilon,t_o)\int_{to}^{t} dt' \int_{to}^{t'} dt'' \langle\varepsilon_j|\hat{V}(t')\hat{V}(t'')\hat{U}(t'', t_o))|\varepsilon_k\rangle\} \quad (2.5.2.1)$$

There are two elements we should paid attention in this formula. 1) see the key role played by $\{C_j(\Upsilon,t_o)\}$; if all the number were null then no time evolution is to take place. 2) We can see that for an k-th base state having zero amplitude at t_o, there might be a non-zero amplitude if there is a non-zero matrix element

$$\langle\varepsilon_j|\hat{V}(t')|\varepsilon_k\rangle = \exp(it'(\varepsilon_j - \varepsilon_k)/\hbar)\langle\varepsilon_j|\hat{V}|\varepsilon_k\rangle.$$

Thus, one can be sure that amplitudes over base states outside the initial subset would emerge with values different from zero if there are matrix elements $\langle\varepsilon_j|\hat{V}|\varepsilon_k\rangle$ that differ from zero.

Three general results can be discussed at this point.

A: For the null initial vector state, ($C_0(0,t_o)=0$ $C_1(0,t_o)=0$ … $C_n(0,t_o)=0$ …) there is no time evolution because all the amplitudes continue to be zero according to (2.5.2.7);

B: The response to an external interaction only functions if the amplitude for the initial state is different from zero. The response of the j-th root state depends upon $C_j(\Upsilon,t_o)\langle\varepsilon_j|\hat{H}(t')|\varepsilon_k\rangle$ which proves the statement;

C: Even if the initial amplitude for a given root state is zero, there is a possibility to sense a response after a time if there is a non-zero matrix element $<\varepsilon_j|\hat{V}|\varepsilon_k>$ that couples the initial non-zero amplitude, say $C_j(\Upsilon,t_o)$ to the k-th component: $C_k(\Upsilon,t)$.

D: If this matrix element $<\varepsilon_j|\hat{V}|\varepsilon_k>$ is zero for all j, then one has to search second order terms involving integrals including terms such as:

$$\Sigma_i <\varepsilon_j|\hat{V}(t')|\varepsilon_i><\varepsilon_i|\hat{V}(t'')|\varepsilon_k>$$

In this case, the levels of interest must have transition amplitudes to a common level.

E: For higher order terms, one should look to terms such as,

$$\Sigma_i \Sigma_{i'} <\varepsilon_j|\hat{V}(t')|\varepsilon_i><\varepsilon_i|\hat{V}(t'')|\varepsilon_{i'}><\varepsilon_{i'}|\hat{V}(t''')|\varepsilon_k>,$$

define more complex pathways; summations here are over the whole spectrum; may of them might be zero due to selection rules.

The above results underscore the importance of the excited states levels beyond those found at initial time. This opens new perspectives to understand quantum catalytic effects.

Back to Chapter 1 one can see that these matrix elements offer mechanisms that would open reactive channels.

2.5.3. Scattering and asymptotic states

Scattering experiment is one of the most important experimental techniques in quantum physics and chemistry. Experiments are set up in laboratory (real) space. As far as we know, quantum physics is constructed in abstract spaces (Hilbert space). We are hence forced to state explicitly the theory at a Fence. This will be done after Chapter 3. Here, only abstract elements are considered just to complete the discussion in Chapter 1.

Dirac noticed the difference between a simple unitary transformation and a fundamental one. The former corresponds to a "rotation" of axis where the quantum state is "seen" from a different perspective. But it is the same initial state prepared in a laboratory.

A fundamental transformation allows for transition amplitudes different from zero connecting base states. To check this contention, let us formally integrate the operator equation (1.3.1.5), and bearing in mind $\hat{U}(t_o,t_o) = \hat{1}$, leads to:

$$\hat{U}(t, t_o) = \hat{1} - (i/\hbar)\int_{to}^{t} dt'\ \hat{V}(t')\hat{U}(t', t_o) \qquad (2.5.3.1)$$

In terms of quantum states, $|\Psi,t>$, it can be seen that the quantum state at time t would require intervention of the state propagated at intermediate times t'. But experimental knowledge cannot be available as a matter of principle. For, as soon as we probe the system, the phases passed on until time t' will be altered; initiating a time evolution from a system with different relative phases is equivalent to start from an "initial" state that is different from the one arrived at time t'. External probes break Schrödinger time evolution.

Formally, a scattering operator $\hat{S}$ is defined with the help of eq.(2.5.3.1) by taking time limits t_o=-∞ and t=+∞ as:

$$\hat{S} = \hat{U}(+\infty, -\infty) - \hat{1} \qquad (2.5.3.2)$$

The selection t=+∞ ensures that anything that might be taking time during the evolution actually took place; and, by taking the limit t=-∞ the formalism is turn into one showing reversibility. The selection implies that no interruption of quantum evolution is allowed in Hilbert space. The final result concerns special models we will discuss in Chapter 10.

What is needed to generate a true time evolution?

Theorem 2.5.3.1.1

Operators showing transition amplitudes non-diagonal in the base set selected to represent quantum states do generate true quantum evolution.

Consider an operator $\hat{V}$ such that $\hat{V}|E_{k''}> = |\pi>$ that in the complete base set reads as:

$$|\pi> = \Sigma_j \, | E_{aj}> \, (<E_{aj} \, | \, \pi>) \, = \Sigma_j \, (<E_{aj}| \hat{V} |E_{k''}>) \, | \, E_{aj}> = \hat{V} |E_{k''}> \qquad (2.5.3.3)$$

Thus, only non-diagonal operators can prompt for non-zero transition amplitudes, i.e. for j≠k the matrix element $(<E_{aj}| \hat{V} |E_k>)$ is different from zero. Consider $\hat{H}' = \hat{H} + \hat{V}$ to be a Hamiltonian where $\hat{H}$ generates a complete base set $\{|E_{k''}>\}$; $\hat{V}$ is non-diagonal in that base. This is a sufficient condition to generate true time evolution.

When the operator $\hat{V}$ is time independent, a corresponding time dependent operator $\hat{V}(t)$ is given as:

$$\hat{V}(t) = \exp(i \hat{H} t/\hbar) \; \hat{V} \; \exp(-i \hat{H} t/\hbar) \qquad (2.5.3.4)$$

This transformation permits recast the evolution operator as a series involving $\hat{V}(t)$ from eq.(2.5.3.4) as follows:

$$\hat{U}(t,t_o) = \hat{1} + (-i/\hbar) \int_{to}^{t} \hat{V}(t_1) dt_1 +$$

$$(-i/\hbar)^2 \int_{to}^{t} \hat{V}(t_1)dt_1 \int_{to}^{t1} \hat{V}(t_2)dt_2 + \ldots$$

$$+(-i/\hbar)^n \int_{to}^{t} \hat{V}(t_1)dt_1 \int_{to}^{t1} \hat{V}(t_2)dt_2 \ldots \int_{to}^{tn-1} \hat{V}(t_n)dt_n + \ldots \quad (2.5.3.5)$$

The time sequence is ordered: $t_1 < t_2 < t_3 < \ldots t_{n-1}$.

Equation (2.5.3.5) appears to be forbiddingly complex. Right now we are not in the business of calculating it, just to know the way it relates to the interaction operator. Whatever it might be, the evolution operador depends on time dependent coupling operators; this is the path used to convey presence of external sources. With this form one can have a look at amplitudes evolution.

2.5.4. Amplitude evolution

In general, the amplitudes as a function of time are simply given by:

$$C_k(t) = \Sigma_j \, U_{jk}(t,t_o) \, C_j(t_o) \quad (2.5.4.1)$$

We calculate the amplitudes as a function of time starting from $|\Psi,t_o>$. First, the general form:

$$|\Psi,t> = \hat{U}(t, t_o) \, |\Psi,t_o> = \Sigma'_{j=0,1,\ldots} C_j(\Psi,t_o) \; \hat{U}(t, t_o) \, |\varepsilon_j> =$$
$$\Sigma_{k=0,1,\ldots} \Sigma'_{j=0,1,\ldots} U_{jk}(t,t_o) \, |\varepsilon_k> C_j(\Psi,t_o) \quad (2.5.4.2)$$

The sum symbol Σ' emphasizes the eventual set of non-zero amplitudes an experimenter prepared for the occasion. It follows that $C_k(\Upsilon,t)$ is given by:

$$C_k(\Psi,t) = \Sigma'_{j=0,1,\ldots} C_j(\Psi,t_o) \, \delta_{jk} - (i/\hbar)$$
$$\int_{to}^{t} dt' \; \Sigma'_{j=0,1,\ldots} C_j(\Psi,t_o) <\varepsilon_j| \hat{V}(t') \hat{U}(t', t_o))|\varepsilon_k> \quad (2.5.4.3)$$

If one is interested on one of the amplitudes different from zero in the initial quantum state, say $C_{k'}(\Psi,t_o)$, then one gets:

$$C_{k'}(\Psi,t) = C_{k'}(\Psi,t_o) \; -$$
$$(i/\hbar) \int_{to}^{t} dt' \; \Sigma'_{j=0,1,\ldots \neq k'} C_j(\Psi,t_o) <\varepsilon_j| \hat{V}(t') \, |\varepsilon_{k'}> +$$
$$(i/\hbar)^2 \int_{to}^{t} dt' \; \Sigma'_{j=0,1,\ldots \neq k'} C_j(\Psi,t_o)$$
$$\int_{to}^{t'} dt'' <\varepsilon_j| \hat{V}(t') \; \hat{V}(t'') \hat{U}(t'', t_o))|\varepsilon_{k'}> \quad (2.5.4.4)$$

The variation in the amplitudes depend upon the presence of non-zero matrix elements $<\varepsilon_j| \hat{V}(t')|\varepsilon_{k'}>$ provided only first order terms are retained. The next term obtains by replacing the evolution operator in (2.5.4.4) by the unit operator:

$$C_{k'}(\Psi,t) = C_{k'}(\Psi,t_o) - (i/\hbar)\int_{to}^{t} dt' \ \Sigma'_{j=0,1,\ldots\neq k'} C_j(\Psi,t_o) \langle\varepsilon_j|\hat{V}(t')|\varepsilon_{k'}\rangle + (i/\hbar)^2 \int_{to}^{t} dt' \ \Sigma'_{j=0,1,\ldots\neq k'} C_j(\Psi,t_o) \int_{to}^{t'} dt'' \langle\varepsilon_j|\hat{V}(t')\ \hat{V}(t'')|\varepsilon_{k'}\rangle + \ldots \quad (2.5.4.5)$$

Let us follow the amplitude for a base state having zero value at $t=t_o$, say, ε_n. Look at eq. (2.5. 3.5) with k' replaced by n, and adapt the indexes, $C_n(\Psi,t_o) = 0$. The first order term contains matrix elements $\langle\varepsilon_j|\hat{V}(t')|\varepsilon_n\rangle$, we have $j \neq n$. If this transition is not allowed (for some reason), the following term is written as:

$$C_n(\Psi,t) \approx (i/\hbar)^2 \Sigma_{m=0,1,\ldots}\Sigma'_{j=0,1,\ldots\neq n} \int_{to}^{t} dt' \int_{to}^{t'} dt'' \ C_j(\Psi,t_o) \langle\varepsilon_j|\hat{V}(t')|\varepsilon_m\rangle\langle\varepsilon_m|\hat{V}(t'')|\varepsilon_n\rangle \quad (2.5.4.6)$$

The sub-index m runs over the full spectrum. For sure, there exists a level such that $\langle\varepsilon_j|\hat{V}(t')|\varepsilon_m\rangle$ and $\langle\varepsilon_m|\hat{V}(t'')|\varepsilon_n\rangle$ are both different from zero for a subset of m-levels.

The conclusion just attained was used to construct the model for a chemical reaction representation as a time evolution of a 1-system quantum state.

The point is that time evolution of the amplitude $C_k(t)$ can be experimentally measured. Thus, even if we cannot calculate from first principle all contributing $\{U_{jk}(t,t_o)\}$, models can be constructed that may help figuring out the most important contributors. Here lies one of the keys to the quantum control of molecular processes seen as quantum state evolution. But such matters involving a Fence will be treated later on.

Finally, let us take a time derivative of eq.(2.5.1.7)

$$i\hbar\ dC_{k'}(\Psi,t)/dt = \Sigma'_{j=0,1,\ldots\neq k'} C_j(\Psi,t_0) \langle\varepsilon_j|\hat{V}(t)|\varepsilon_{k'}\rangle + (i/\hbar)\Sigma'_{j=0,1,\ldots\neq k'} \int_{to}^{t} dt'' \langle\varepsilon_j|\hat{V}(t'')\ \hat{V}(t'')|\varepsilon_{k'}\rangle C_j(\Psi,t_o) + \ldots \quad (2.5.4.7)$$

Eq.(2) of the introduction can be considered a model for this particular form. The point is that even if the amplitude $C_{k'}(\Psi,t_0)$ was equal to zero it will evolve thanks to couplings until showing a non-zero value that would evolve in time, $C_{k'}(\Psi,t)$. Now, the energy eigenvalue $\varepsilon_{k'}$ can serve as a root state wherefrom a characteristic spectrum could be detected (calculated). This situation can be experimentally probed.

If one can experimentally control relevant chains of interactions leading to specific amplitudes over base state representing new “compounds”, then chemistry will be much easier to perform under novel and controlled circumstances.

2.6.What is in motion actually?

Time dependence eliciting motion locates at the amplitudes if we stick to the formalism shown so far. But there is no obvious answer to this kind of question if one focus attention on the material system. Motion is a concept used in laboratory and real life space. This chapter has focused on time evolution of quantum states. But we have not yet mapped them to a space compatible with our expectations of motions. In abstract Hilbert space as eq.(2.5.2.1) informs us the amplitudes reflect time change so that motion expresses in this unusual (to us) manner.

Because a quantum state is supported by a given material system the time evolution would also express in a way we have to examine in the chapters to come.

The operator $\hat{V}(t)$ includes the probe one is using to measure the system. As the quantum state evolves in time one would see the material system changing the response towards probes that elicit such changes; for instance, if the probes are multi-frequency EM radiations time evolution may permit us to "see" the changes usually expressed in terms of concentration.

One has to bear in mind that a base state affected with zero amplitude at a given time conceals the possible response rooted at that base state; the spectra itself will be determined by the root state. If as a function of time the amplitude starts to grow up then a response becomes unconcealed with a relative intensity signaled in Axiom 4a then we could see spectral pieces in our detectors. So far, the mathematical representation of motion is taking place in Hilbert space; namely, amplitudes changing as a function of the time parameter. We still have to construct theories at the Fence to sense in the material system what is changing as the response to the external fields. In one word, there is need to develop quantum theory with the help of inertial frames.

It should be clear to the reader that mathematics by itself is not physics. One uses mathematics because all the quantities are well defined and logical pitfalls can be eradicated. Once mathematical results obtain, they have to be mapped in terms of magnitudes accessible to recording and reading magnitudes (experiments).

In this book, the linear superposition standing as representation of the physical state provides the principal map. In the abstract domain it is an element of a Hilbert space devoid of special meaning; and as such does not require interpretation. Now, when both aspects are taken together the system has been translated to a Fence as it were. Here, we would certainly need some sort of interpretation.

2.7. Key points to retain

For all non-physicist readers there are some key issues to retain. They are:

1) The quantum state characterizing a given fixed-component material system is the one that changes in time.
2) The general form of parametric time evolution is given by Schrödinger-type of equation.
3) Parametric time plays a central role in the abstract quantum formalism; this implies existence of an Hermitean (energy) operator mediating time displacement.
4) Any material system, be it "macroscopic", "nanoscopic" or "microscopic" presents quantum states; whether we can calculate them or not is another story.
5) Because there is no yet introduction of space reference coordinates quantum states are elements of abstract Hilbert spaces.
6) The quantum state concept is *foundational*; it cannot be defined in terms of assumed properties of the material system. This is one reason to recur to axiomatic approaches as done here.
7) Inertial frames permit localizing material systems at laboratory space.
8) The preceding statement permits hinting at the possibility that some classes of quantum states may show properties independent of local coordinate variables: this means existence of non-local quantum dynamics as a possibility beyond classical dynamics.

The present abstract formalism will be projected in space coordinates in order to approach material systems that can be space-localized. Because a quantum state must be invariant to the manner reference frames are introduced a number of properties can be associated to projected quantum states.