

# 1. Quantum Language in Chemistry

The concepts of material system and quantum state occupy a foundational place in quantum physical chemistry. The material system sustains quantum states. This statement implies a requirement for the material system to be present in the domain where quantum changes would take place. Thus, its presence is essential but its localizability is not an issue. It is on this foundations that one can construct quantum mechanical descriptions of processes sustained by physical, chemical, biochemical and other types materials.

A material system is defined by the nature and quantity of its basic elements, e.g. number of electrons and nuclei in the case of electromagnetic materials (atoms, molecules, solids, aggregates,...); from a different perspectiva, sets of material systems relate to objects and things in laboratory (real) world.

The concept of quantum state is central to quantum mechanics. It plays a foundational role in the sense that is a pure mathematical concept belonging to an abstract mathematical space, viz. Hilbert space. Vectors in Hilbert space represent quantum states. Changes of state are represented with operators mapping one state to another.

To handle quantum states supported by material systems there is need for a procedure able to label them in definite ways. The symbol  $|label\rangle$  stands for a quantum state whose name is “label”. A Hilbert space includes a countable infinite set of base states we designate for instance as  $\{|j\rangle \mid j=1,2,\dots\}$ . The quantum state “label” is then given as a linear superposition over the base set:

$$|label\rangle = \sum_j |j\rangle \langle j|label\rangle.$$

The symbol  $\langle j|label\rangle$  is a complex number characterizing the label-state in the basis set we have chosen somehow. The base set is fixed which means that any change of quantum state is to appear as a change in the set of complex numbers that we will call from now on as: amplitudes.

Chemistry introduces structure as fundamental concept. Reagents and products are substances that are manipulated in laboratory space. To make contact between abstract space and laboratory space introduce inertial frame characteristic of the special relativity for reasons to be analyzed later on. The origin and orientation of such frame belongs to laboratory and we use this frame to introduce configuration

space coordinate; the dimension of such space is determined by the degrees of freedom introduced by the material system.

At this level of theory, a material system is characterized by quantum states projected in configuration space, they are named as wave functions; this would include the way a material system can respond towards appropriate (quantum) external probes by showing specific changes in a quantum state. At one stage or another, models of probes used to modulate the state of a material system must be included in the theory. Photon-field quantum states are among commonest probes to material systems and for chemist this is essential because, for example, a thermal bath that is a special distribution of frequencies control kinetic and mechanistic issues for chemical reactions. All kinds of spectroscopy based on electromagnetic interactions enter the field interesting to quantum phys-chem.

The material system being, by definition, an invariant to the extent its basic constitutive elements cannot change; it is a modification of quantum state that would allow for a theoretical understanding of change perceived at laboratory level. In particular, chemical evolution may lead to justify a concept of object, substance, and their production in laboratory world once mappings are built relating abstract evolution to material systems.

The focus is on change. That is change of quantum state. Static aspects temporarily cede the place to process description. In a nutshell, specific processes elicit changes of quantum states affecting appearances of material systems when sensed in laboratory (real) world.

However, if everything changes, there is no way to describe with respect to what such changes are being sensed. Thus, in Hilbert space there is to be found invariant elements as well. These elements form a base set in abstract space. The static (invariant) aspects provide the skeleton required to get at process descriptions.

The language of quantum physics is designed to describe changes of states in general; in particular, of material systems. Physics, Chemistry, Biophysics, Biochemistry, or any other region of scientific inquire that conserve the elements defining its characteristic materiality, are concerned with process description at this fundamental level. An exposure, albeit brief, to quantum mechanics (QM) is required to the extent that this is the theoretical framework where processes can be properly presented. QM plays a role of grammar for the language.

Getting into the QM field requires a mathematical training that is commonly not accessible to students in chemistry, biochemistry and molecular biology; even some practitioners may have limited knowledge of contemporary QM as an abstract mathematical framework. Note that the practical level is plagued with misunderstandings that can be relieved if we injects a sober dose of abstract QM. Thus, even if one cannot use grammar at a professional level, one can learn to speak and honorably write texts without detailed mastering language meanders.

Let us go straight ahead and give a couple of basic elements that would enable us to give a presentation of the quantum linear superposition principle. Technically, quantum states belong to (or form part of) a linear vector space over the field of complex numbers; for more details wait for Chapt.2; just rudiments are given in what follows.

Use the symbols  $|\Psi, t\rangle$  to stand out as a member of such a set with label (name)  $\Psi$  that is expected to change in time ( $t$ ). For this Hilbert space, as stated above, one has a complete *countable* set of states serving the purpose of base states:  $\{|j\rangle\}$  an  $j$ -label identifies each base state it ranges from  $j=0,1,\dots,n,\dots$ ; so that an arbitrary quantum state appears as a linear superposition in this base; a sum of terms that is also an element of the space.

One can select an energy-based representation:  $\{|j\rangle\} \rightarrow \{|\epsilon_j\rangle\}$ ; where a denumerable (countable) energy label is associated to each order index,  $\epsilon_j$ ; the energy origin may be arbitrary, only differences between states stands out as a quantity that can enter interaction processes; energy conservation laws can be implemented when the material system interact with external systems (fields).

Energies as labels are positions on energy ladders with finite (variable) steps distances; again, the origin of the energy scale can be fixed arbitrarily. In an energy representation, the set of eigenvectors  $\{|\epsilon_j\rangle\}$  provides a base to expand arbitrary quantum states, e.g.:

$$|Y,t\rangle \rightarrow C_0(Y,t) |\epsilon_0\rangle + C_1(Y,t) |\epsilon_1\rangle + \dots C_j(Y,t) |\epsilon_j\rangle + \dots = \sum_{k=0,1,\dots} C_k(Y,t) |\epsilon_k\rangle \quad (1)$$

The base set being fixed; the amplitudes represent the quantum state in the chosen base and the symbol  $C_j(Y,t)$  is a complex number that just emphasize that the set of amplitudes define the quantum state  $|Y,t\rangle$ .

The abstract part of the scenario must be mapped to a laboratory side. Because the energy labels are just that, labels, they can be positive or negative; what really matter are differences between two of them. Taking a specific energy label, say  $k$ , that we name as root state, an absorption spectrum obtains from differences with respect to energy-labels ordered higher up in a ladder; the differences  $\Delta E_{jk} = \epsilon_j - \epsilon_k$  are positive and mapped to energy that can be exchanged with surroundings; conversely, an emission spectrum follows for energy-labels found below the chosen root state. Thus, at the end of the day, to speak of energy, there must be a source or sink to satisfy energy conservation. If we have it, this level of presentation corresponds to a borderline case (Fence). In the laboratory side inertial frames provide a mean to relate the abstract to the real sides of this scenario. This is a characteristic of quantum phys-chemical (phys-chem) situations.

For a given quantum state, the spectral response to external appropriate probes show non-zero intensity only from those base states that have non-zero amplitude.

In other words, one can activate a response via spectra rooted at a given energy if and only if its amplitude is (becomes) different from zero; the response sensed at

the laboratory may appear after a delay time from the initial state due to time evolution.

To accomplish the mapping in a general way, the quantum state must be normalized to one. This operation can be performed at the probing stage. In this way one can work all along with vectors instead of rays that are normalized vectors.

The representation of a chemical process such as a keto/enol reaction will be embedded in  $\{C_j(Y,t)\}$ -sets of time dependent amplitudes. Quantum dynamics is just the study of the way amplitudes change in time. As we will show later on, a typical set of differential equations to get time evolution is given by:

$$i\hbar \frac{dC_k(Y,t)}{dt} = \sum_j V_{kj}(t) \exp(i\omega_{kj}t) C_j(Y,t) \quad (2)$$

The symbols mean:  $\omega_{kj} = \Delta E_{kj} / \hbar = (\epsilon_k - \epsilon_j) / \hbar$  is a frequency,  $V_{kj}$  is a coupling between base states  $|\epsilon_j\rangle$  and  $|\epsilon_k\rangle$  produced by an external probe (field);  $\sum_j$  is the symbol implying a sum over all base states  $|\epsilon_j\rangle$ ;  $\hbar$  is Planck's constant with dimension of energy by time for the present case. The term  $dC_k(Y)/dt$  is the rate of change in time of the k-th amplitude. Solving the set of equations for  $k=0,1,2,\dots$  one would get the amplitudes as a function of time.

### E&E-0 Energy representation

In the energy representation the basis states are label by the energy eigenvalues:  $|\epsilon_j\rangle$ . These are fixed elements. Anyone among them can be the root of a spectral series, namely, transitions towards higher or lower energy states; for the hydrogen atom we are well aware of Balmer, Pashen, Pfund spectral series. Because  $(\epsilon_k - \epsilon_j) / \hbar$  is a frequency, an external EM source can be coupled (as indicated in eq.(2)) with a frequency  $\omega$  such that

$$V_{kj}(t) = V_{kj} \exp(i\omega t) \quad (3)$$

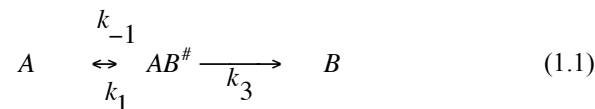
so that energy in the field is characterized by  $\hbar\omega$ ; this is real energy you might use to tan yourself if the frequency is appropriate. The factor  $V_{kj}$  is time independent, it represents the (complex) number  $\langle \epsilon_j | V | \epsilon_k \rangle$  to be defined later on.

Observe that we refer to energy label and not energy level when indicating the origin for the base state one is probing. In this work, the system is assumed to be in a particular quantum state but no occupying a particular energy level. The amplitudes will tell us whether a given base state may be the origin for an interaction; if it is zero, then no response via that channel. It is the linear superposition that always makes sense and is probed with external fields or systems.

Thus, the first step is the construction of a theoretical framework to determine amplitudes' time dependencies. The quantum mechanics needed for our purposes shares the same mathematical basis as found in any good QM textbook. However, the emphasis is changed, so it takes some extra effort to incorporate some necessary mathematical language. This is presented in a way that can go into helping theoretical thinking for chemist, biochemist and (molecular) biologists.

## 1. Chemical change and Q-Language

The graph of a chemical reaction purports a number of informative data to chemists, e.g.



Scheme (1.1) stands for a uni-molecular change from species A into B via transition structure  $AB^{\#}$ . The product B may be a dissociation asymptotic state or an isomer state (keto-enol case) or any species one can detect via experimental procedures.

At time  $t_0$ , concentrations  $[A]_0$ ,  $[B]_0$ ,  $[AB^{\#}]_0$  are input data in a laboratory setup; in a simple case when  $[B]_0 = [AB^{\#}]_0$  equals to zero, only reactant  $[A]_0 \neq 0$  is present.  $k_1$ ,  $k_{-1}$  and  $k_3$  are rate constants that control concentrations change for the system in time,  $[A]_t$ ,  $[B]_t$ ,  $[AB^{\#}]_t$ ; these quantities are time dependent laboratory measurable.

There is a common, invariant element underlying eq.(1.1), namely, the analytic composition in terms of basic elements: number of electrons and nuclei; this is the matter content offering a common ground to introduce an alternative quantum description. Quantum states are sustained by the invariant material system.

Chemical (molecular) base states for the material system are identified with names or symbols e.g.  $|A\rangle$ ,  $|B\rangle$  and  $|AB^{\#}\rangle$ ; this is a schematic presentation. A linear superposition over them stands for a quantum state and the time variations of amplitudes are traced back to magnitudes determined with analytical chemistry techniques; spectroscopic responses are of especial import. Note that pure A and B are identifiable by their spectra, namely, the way they respond to electromagnetic radiation for varied frequency ranges or by mass spectroscopic techniques or by any combination thereof. They have different spectral response albeit the same "constituent" elements; and the question is: How does the same set of electrons and nuclei put such different responses so that at the laboratory level they are identifiable as different objects? The question itself suggests that it is not the material elements as such that may sustain the differentiation into laboratory objects but there must be something else, namely, quantum states.

From the operational standpoint it is required that, at least, a clear difference of the quantum states should manifest so that characteristic spectral responses show up. The question becomes: Is there a relationship between chemical and quantum change epitomized as physical process echoed in Hilbert space? The answer is yes; a path leading to this response is presented in this book.

Note that by considering quantum states associated with specific responses (to external probes), the concept of object is no longer a primary element to the

theoretical description; here lies one of the difficulties to understand QM, so that one has to get used to it.

Quantum states are linear superpositions on specific base states (Cf.eq.(1)), the base set is invariant; to represent a physical change only the amplitudes of the linear superposition change. The base states form a complete set so that sets of amplitudes span all possible quantum states a material system can show; all possible chemistry is hence imprint in the space of quantum states. Observe that a quantum state is a foundational element of the theory thereby implying no definitions in terms of other concepts.

We move on examining via simple examples some fundamental concepts of quantum language (quantum mechanics). There will be no mathematical demonstrations, just basic concepts.

### 1.1. Chemical versus quantum state concept: a model

To an arbitrary chemical state in real space assign a quantum state in Hilbert space ( $\mathcal{H}$ ) represented by the ket symbol:  $|\Psi, \underline{t}\rangle$ . The symbol  $|\Psi, \underline{t}\rangle$  names the quantum state at time  $\underline{t}$ ; it stands for the arbitrary chemical state, the symbol  $\Psi$ , reminds us of its origin i.e. the way it was reproducibly generated in the laboratory; we are talking about the same material system. Here, label  $\underline{t}$  is an element in the real number axis with all associated topologic properties; it plays the role of time. The inclusion of time in the symbol of quantum state underlies the fact of a possible ordered change of state as a process goes on; in this space, time inversion may lead to an allowed symmetry. To relate this parameter to a laboratory clock there is need for special mappings because in real space time inversion is not a feasible operation; further more one address here time lapses as measured by a clock, differences between two marks on the axis of time.

As note above, Hilbert space has the structure of a linear vector space over the field  $\mathbf{C}$  of complex numbers. If  $|\Psi_1\rangle$  and  $|\Psi_2\rangle$  are two vectors of  $\mathcal{H}$ , and  $C_1, C_2$  two arbitrary complex numbers, then the sum  $C_1|\Psi_1\rangle + C_2|\Psi_2\rangle$  corresponds to another element of  $\mathcal{H}$ , say  $|Y\rangle$ ; thus, here is a map between ket  $|Y\rangle$  and the ordered pair  $C_1, C_2$  in the given *fixed* base; for this reason one writes the amplitudes with an argument,  $C_1(Y), C_2(Y)$  to emphasize such connection. The set of all these linear superpositions form a linear vector space also. This latter set is a dual space (or has the structure of); it is sometimes called simple dual space to differentiate it from a conjugate dual space to be introduced later on. Note that, in our context, to serve the purpose of base states,  $|\Psi_1\rangle$  and  $|\Psi_2\rangle$  must be time independent thereby endowing the amplitudes with the time dependency:  $C_1(t), C_2(t)$  or  $C_1(Y,t), C_2(Y,t)$ .

In eq.(1.1) the symbols A, AB# and B label reactant, transition state and products; take them as names with the property to cover the same 1-system in

terms of basic elements. Consider the base states with symbols:  $|A\rangle$ ,  $|B\rangle$  and  $|AB^\# \rangle$ , where chemical labels identify three generic base vectors; implicit is the fact covered by these symbols, namely, to stand for a specific energy ladder but we will stick to a simplified notation. By now you know that an arbitrary *quantum state* is given by a linear superposition over base vectors:

$$|\Psi, t\rangle = C_A(\Psi, t)|A\rangle + C_B(\Psi, t)|B\rangle + C_{AB^\#}(\Psi, t)|AB^\# \rangle \quad (1.1.1)$$

Determining these numbers, i.e. the *amplitudes*, define the quantum state.

### E&E.1.1-1 Alternative notations

Equation (1.1.1) can be written with alternative symbols to emphasize the difference between amplitudes and base states.

Define a row vector with the base set elements:  $(|A\rangle |B\rangle |AB^\# \rangle)$  the object has dimension  $1 \times 3$ , i.e. one line and three columns. The column vector  $(C_A(\Psi, t) \ C_B(\Psi, t) \ C_{AB^\#}(\Psi, t))^t = [C_A(t) \ C_B(t) \ C_{AB^\#}(t)]$  with dimension  $3 \times 1$ , three lines and one column, is used to define the scalar product (1.1.1):

$$\begin{aligned} (|A\rangle |B\rangle |AB^\# \rangle) \cdot (C_A(t) \ C_B(t) \ C_{AB^\#}(t))^t &= \\ (|A\rangle |B\rangle |AB^\# \rangle) \cdot [C_A(t) \ C_B(t) \ C_{AB^\#}(t)] &= \\ |\Psi, t\rangle & \quad (1.1.1') \end{aligned}$$

In this manner, the difference between the mathematical object formed with the amplitudes and base set elements is underlined. In terms of dimensions:  $1 \times 3$  times  $3 \times 1$  results in a Hilbert space element that stands for the abstract quantum state  $|\Psi, t\rangle$ ; Cf. Eq.(1.1.1'). The base states are fixed, chosen in one way or another that is convenient to handle a particular system, while the amplitudes would sense changes of quantum states related to specific material systems. We select the base set based on the particular measuring devices at hand. A quantum state is defined the row vector where all amplitudes including those that might be zero at a given time must be included. So we need to bear in mind that column vector  $(C_A(\Psi, t) \ C_B(\Psi, t) \ C_{AB^\#}(\Psi, t))^t$  as a whole is the key mathematical construct not each amplitude separately.

The complex number  $C_X(t)$  is mapped on to a real number by taking the square modulus  $|C_X(t)|^2$ . A quantum state is hence normalized at all times ( $\forall t$ ) if equation (1.1.2) holds:

$$|C_A(t)|^2 + |C_B(t)|^2 + |C_{AB^\#}(t)|^2 = 1, \quad \forall t \quad (1.1.2)$$

Using the analogy of vectors in real 3-space, the surface of a ball of unit radius will be the locus of all possible vectors with length one. The quantum states are located on a hyper-sphere of unit radius in Hilbert space.

The normalization condition concerns a QM understanding of processes. If one amplitude changes for some reason, fulfilment of eq.(1.1.2) enforces the change of at least one remaining amplitude to compensate for the variation keeping normalization equal to one. Note, however, that albeit norm is conserved, projections of the quantum state along the base vectors can be changing in time

thereby eliciting a (chemical) change. Again, the base vectors must remain unchanged; they provide a reference frame in Hilbert space.

For a concise presentation of Hilbert space consult the web address: [http://en.wikipedia.org/wiki/Hilbert\\_space](http://en.wikipedia.org/wiki/Hilbert_space).

### E&E.1.1-2 Material system concept

To discuss the concept of material system let us select one showing 1 carbon, 1 oxygen and two hydrogen nuclei; define the atomic number vector:  $\mathbf{Z} = (Z_C \ Z_O \ Z_H \ Z_H) = (6 \ 8 \ 1 \ 1)$  making for +16 positive charge and select 16 electrons; the global system is electrically neutral. Also, nuclear spins can be introduced:  $\mathbf{I} = (I_C \ I_O \ I_H \ I_H)$ .  $\mathbf{A} = (A_C \ A_O \ A_H \ A_H)$ . The material system sustains infinities of quantum states among which there are chemical quantum states. Take species A to be formaldehyde  $H_2CO$  with a corresponding base state label  $|H_2CO \rangle$ ; species B can be  $H_2 + CO$ , base state label  $|H_2 \rangle |CO \rangle$ , namely a direct product of *asymptotic* states; species  $AB^\#$  maps, for instance, to a lowest energy  $n \rightarrow \pi^*$  excited state of formaldehyde, so one takes base state label  $|H_2CO, n \rightarrow \pi^* \rangle$ .

For this  $\mathbf{Z}$ -vector system, there are many more possible base states. For instance: water plus carbon atom,  $|H_2O \rangle |C \rangle$ ; hydrogen atom plus H-C-O; hydrogen atom plus C-O-H; and much more. In a 1-system representation, a complete base will show them all, including ionized states with electron states in a given continuum.

Here, for the sake of simplicity, we retain three root states, the remaining base states belong to its orthogonal complement; they can implicitly be taken into account. The quantum states belong to the 1-system represented by 16 electrons and the nuclear species already indicated. These states encompass all possible chemistry in Hilbert space. Equations (1.1.1) and (1.1.2) albeit truncated are valid for single systems called a 1-system here; the number of electrons and nuclei is conserved only the quantum state can change.

In chemistry, reagent (analyte, substance) concentrations as a function of a laboratory time enter kinetic descriptions. Kinetic equations relate to a large number of 1-systems, usually of the order of Avogadro number  $N_0$ . Let  $N$  be the number of *non-interacting* 1-systems in a volume  $V$  (number density =  $N/V$ , and put  $V=1$ ), the quantity  $N|C_A(t_0)|^2$  would be associated to the relative intensity response from the A-root-state. And that's it. The spectral response in intensity of the material system are modulated by  $N|C_A(t_0)|^2$  which is a mixed quantity:  $N$  is the number of copies of 1-systems and  $|C_A(t_0)|^2$  a function of amplitudes coming from Hilbert space.

The temptation might be great to take for instance  $N|C_A(t_0)|^2$  as the concentration in the laboratory (real world) of A-species. But you have to introduce two extra hypotheses to do this conversion. First, it is necessary to introduce a particle model and, second, a statistical approach. The particle model requires that each element of the  $N$ -copies be in one and only one base state, namely,  $C_A(t)=1$  for one copy,  $C_B(t)=1$  for another copy and  $C_{AB^\#}(t)=1$  for still another one. Thus, counting the number of copies having  $C_A(t)=1$ , say  $N_A(t)$ , etc., one imposes the equality  $|C_A(t)|^2 = N_A(t)/N$ ,  $|C_B(t)|^2 = N_B(t)/N$ , and  $|C_{AB^\#}(t)|^2 = N_{AB^\#}(t)/N$ . This is



what is called a population model. In this framework,  $N|C_A(t_0)|^2 \Leftrightarrow [A]_0$  and prepare for a case where  $N|C_B(t_0)|^2 \Leftrightarrow [B]_0 = 0$  and  $N|C_{AB^\#}(t_0)|^2 \Leftrightarrow [AB^\#]_0 = 0$ . This is a way chemists may think to start running system (1.1).

In Hilbert space there are no objects, at time  $t_0$ , the row vector  $(1 \ 0 \ 0)$  stands for the *quantum state* of the material system, not for the molecular species A. For quantum states no pictures are required, base states can be mapped through the Fence to chemical eigen states that for chemists may convey some new valuable information. This aspect is not under study yet.

Possibilities to sense amplitudes are always present. From zero amplitude at a given time it may develop a non-zero value at later times that will be characteristic of specific processes. For a given material system, quantum states associated to all possible chemical species are always there in Hilbert space. All possible chemistry finds its representation in the quantum states for that 1-system. In Figure 1, a simple model is sketched.

The model system crucially depend upon the quantum coupling between base states  $|A\rangle$  and  $|B\rangle$  accomplished via the transition (excited) state spectra,  $|AB^\#\rangle$ . At a given value of the reaction coordinate, the quantum state is formally given by  $(C_A(x) \ C_B(x) \ C_{AB^\#}(x))$ . Thus, if there were zero coupling, and the system was prepared as reactant  $(1 \ 0 \ 0)$ , the pattern of amplitudes would be a straight line intercepting at 1 and for state  $(0 \ 1 \ 0)$  a straight line with interception at  $C_B=0$ .

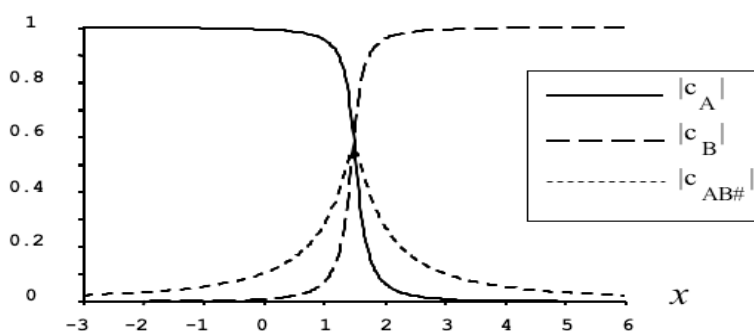


Figure 1.

Quantum model for a chemical reaction related to eq.(1.1.1); amplitudes in absolute value are plotted as a function of a reaction coordinate  $x$ . At each value of  $x$ , the quantum state is normalized to unity. For  $x$  negative, the system is dominated by the spectrum of  $|A\rangle$ . At  $x=0$  the interaction leading to a coupling of these generic quantum states start changing the amplitudes of reactant and product. In this model, the amplitude of the transition state increases continuously until getting at a maximum; at this place reactant and product amplitudes cross just above the amplitude of  $|AB^\#\rangle$ . Thereafter, the amplitude of the product  $|B\rangle$  increases while both the reactant and transition state go down. (Figure adapted from our work with Prof.G.A.Arteca).

Now, introducing a specific coupling such as the one elicited by Fig.1, the amplitudes appear to change in a narrow region usually called bottleneck. See Sect.1.4 for further details.

Another aspect of this model: the reaction coordinate specifies (somehow) the coupling with external field to the reactant system. It can be an electromagnetic field (laser) tantamount to a photochemical reaction; or it can be, a bath of microwaves or a thermal bath at a specified absolute temperature. Yields can in principle be modulated if the reaction coordinate is forced to attain specified values inside the bottleneck region.

Absent from the presentation of the model are aspects related to the spectrum that will be examined later on. But, as suggested above, the scheme encompasses all type of chemical processes you may think of for electromagnetic materials.

How do we identify the states  $|A\rangle$ ,  $|B\rangle$  and  $|AB\rangle$ ? Chemists know how to do this with the help of characteristic spectra related to each one of them. This is an invariant property of the material system under study. The quantum level serving to generate series of excitations (spectrum) is called root state or parent state (e.g. Balmer and Lyman series for the hydrogen atom have their root states); whenever necessary, part of the spectral states are incorporated in the Hilbert subspace, otherwise they stay in the orthogonal complement.

Why do we need amplitudes?

The answer is simple:

*If the root state shows zero amplitude in the quantum state vector at all times, there will be no response in intensity rooted at that base state.*

Measurements relying on the square modulus of amplitudes are said to be in the *intensity regime*, i.e. related to concentration or event-counting (clicks). Measurements done in *amplitude regime* address the whole quantum state. The novelty of chemical quantum dynamics resides in the coherent state represented by linear superpositions.

Consider a simple thought experiment: at time  $t_0$  the chemist switch the spectrometer tuned to the spectral response of base state  $|B\rangle$ , what one would expect as a result? An answer elaborated with the help of Fig.1 would be as follows: start from state  $|A\rangle$ , there will be no detection (response) as long as the relevant amplitude at root state  $|B\rangle$  remains zero or below sensitivity of the recording apparatus. In the reaction coordinate ( $x$ ) range below zero  $|C_A|$  is almost equal to one; note that for this model  $|C_C|$  starts increasing before than  $|C_B|$  which indicates that an early coupling with channel A is active; there after  $|C_C|$  reaches a maximum an begins decreasing as  $|C_B|$  rapidly increases until getting at a plateau  $|C_B|=1$ .

*Chemical change for 1-system expresses as a change of quantum state:*

*All chemistry develops in a 1-system.*

This is a fundamental difference with standard approaches. Objects (substances) are replaced by quantum states. For the opposite process, from quantum states to objects, one speaks about *decoherence* of the ensemble of 1-systems. The phenomenon of *coherence/decoherence* lies at the heart of chemical change seen not only in the particle model.

Implicit in the preceding statements is the fact that asymptotic base states are in one way or another included. This would grant descriptions of association/dissociation reactions, entanglement/disentanglement processes, etc; find more on these issues in following chapters.

The fundamental outcome, when focus is onto the concept of quantum state, is that it permits working with only one copy of the material system. The infinite dimensional space that sustains the infinity of possibilities (base states) of a one material system suffices to handle any process. Connection with laboratory work obtains for cases involving any number of non-interacting copies of 1-material-system for which normalization is now equal to the number of copies. The analog of a Gibbs ensemble obtains by multiplying with the number  $N$ ; the normalization constant equals now  $N$ , the number of copies that might be representing a system with response function that may be detectable in laboratory space; the product  $N|C_B(t)|^2$  is usually taken as the number of copies of the system in state  $|B\rangle$ , the interference effects are averaged out to zero (decoherence). This forms a particle model to the quantum system we have been examining. For the thermodynamic limit, namely,  $N/V$  finite density when the number of copies  $N \rightarrow \infty$  and the volume  $V \rightarrow \infty$ ; the 1-copy approach permits constructing quantum thermodynamics.

Thus, when the number of 1-systems is of the order of Avogadro number, then it is practical to work with kinetic descriptions involving rate constants. However, keep in mind that the actual mechanism is quantum mechanical.

## 1.2 From chemical to quantum time evolution

The key result for a 1-system quantum state is: chemical change can be followed up via time evolution of the amplitudes that at the Fence will be mapped via measurements procedures. Times in Hilbert space and at the Fence (laboratory) are not the same. Pure mathematical construct in the former, at the Fence it is the subject of measurement endowing time with properties that are not shared by abstract time.

Let us obtain a mathematical expression for time evolution in Hilbert space; a mapping between two elements of Hilbert space is designated as an operator.

Thus, introduce a time evolution operator  $\hat{U}(t, t_0)$  that when acting on the quantum state at a given marked time, e.g.  $|\Psi, t_0\rangle$  shift the origin so that one has the definition:

$$|\Psi, t\rangle = \hat{U}(t, t_0) |\Psi, t_0\rangle \quad (1.2.1)$$

The operator  $\hat{U}(t, t_0)$  executes a time translation from a quantum state at initial time  $t_0$  up to one at time  $t$  in an inertial frame; so long *no* measurement or probing is carried out, all possibilities offered are expressed by the amplitude  $|\Psi, t\rangle$ . Again, the operator is a rule (map) connecting elements of a given vector space,  $|\Psi, t\rangle \leftarrow |\Psi, t_0\rangle$ , this is the meaning of eq.(1.2.1). We still have a long way to go to construct a representation of, but what is of interest right now is the construction of a formal differential equation for this mathematical object. Although it is not required that you master all aspects, it is useful to follow the path from a simple definition to the construction of the equation directing the change.

In Hilbert space, time is a (continuous) parameter used to label base states; note that in this particular case the  $t$ -label is not a time measured in a laboratory even if one might feign a “clock” to be attached to an inertial frame used to project and obtain  $|t\rangle$  base vectors. Clocks belong to the Fence that is the place where energy and momenta are conserved while the quantum 1-system interacts with an external field. Keep in mind this qualitative difference to avoid surprises. While one can explore the symmetries related to time inversion in Hilbert space, there will be serious operational problems to make sense in real space.

The operator  $\hat{U}(t, t_0)$  must leave the *norm* of the state vector unchanged. This defines a *unitary operator*. To calculate the norm, the dual conjugate space is introduced now.

### E&E.1.2-1 Dual conjugated space

The elements of the dual conjugate (dc) space are designated by “bras” symbols:  $\langle A|$ ,  $\langle B|$ ,  $\langle AB^\#|$ ,  $\langle \Psi, t|$ . There is a one-to-one map between bras and kets; if  $\langle Z|$  is an arbitrary bra there always exists a dual conjugate ket written as  $|Z\rangle$  such that the number standing for the scalar product  $\langle Z|Z\rangle$  is a real number: This scalar product is the *norm* of the vector  $|Z\rangle$ . The symbol  $|Z\rangle\langle Z|$  is an operator that permits finding the component of a quantum state  $|\Phi\rangle$  along the vector  $|Z\rangle$ : i.e.  $(|Z\rangle\langle Z|) |\Phi\rangle$  yields  $\langle Z|\Phi\rangle |Z\rangle$  where the factor in front of vector  $|Z\rangle$  is a complex number featuring the projection of the quantum state  $|\Phi\rangle$  along this axis.

If we have two states  $|Z\rangle$  and  $|Z'\rangle$ , then the mapping  $\langle Z|Z'\rangle$  is a complex number and  $\langle Z'|Z\rangle = (\langle Z|Z'\rangle)^*$ , where the star (\*) means complex conjugation. The *scalar product* between vectors  $|Z'\rangle$  and  $|Z\rangle$  is given as  $\langle Z'|Z\rangle$ . Two different vectors that have scalar product equal zero are said to be orthogonal:  $\langle Z'|Z\rangle = 0 + i0$ .

**E&E.1.2-2 More definitions**

The dual conjugate space is a linear vector space. This means that the equivalent to eq.(1.1.1) reads as:

$$\langle \Psi, t | = C_A(\Psi, t)^* \langle A | + C_B(\Psi, t)^* \langle B | + C_{AB\#}(\Psi, t)^* \langle AB\# | =$$

$$\left( \langle A | \quad \langle B | \quad \langle AB\# | \right) \cdot \begin{pmatrix} C_A^* \\ C_B^* \\ C_{AB\#}^* \end{pmatrix} \quad (1.1.1')$$

The dual-conjugation operator transpose and complex conjugate the given mathematical object. Now the mapping from one space, say bra-space, on to the complex numbers is formed by a scalar product of the kind:

$$\langle \Psi, t | X \rangle = C_X(t)^* \quad (1.2.2)$$

Here,  $C_X(t)^*$  is the complex conjugate of the number  $C_X(t)$  as indicated in eq.(1.1.1') and we see that functionally depends upon the quantum state it is assumed to represent:  $C_X(\Psi, t)$ .

The norm of a base vector  $|X\rangle$  is just the scalar product with itself:  $\langle X|X\rangle = N_X$ ; base vectors are usually taken normalized to unity ( $N_X=1$ ); sometimes to a different measure (see below).

The real number  $|C_X(\Psi, t)|^2 = \langle \Psi, t | X \rangle \langle X | \Psi, t \rangle$  tells how large is the amplitude at base state  $|X\rangle$  in the quantum state  $|\Psi, t\rangle$ ; it signals the possibility the system has to put a response when shining frequencies serving the purpose of identification of the corresponding root state; in this case  $|X\rangle$ . In other words, it is related to the cross section shown by the system with respect to the channel  $|X\rangle$ ; this is a common name for the real number  $|C_X(t)|^2$ .

Operators acting on the dual space are symbolized with a dagger super index acting as:  $\langle \Psi, t_0 | \hat{U}^\dagger(t, t_0)$  which tells us the result is  $\langle \Psi, t |$ . We form the scalar product of this vector by putting side by side  $\langle \Psi, t_0 | \hat{U}^\dagger(t, t_0)$  to  $\hat{U}(t, t_0) |\Psi, t_0\rangle$  so that:

$$\langle \Psi, t | \Psi, t \rangle = \langle \Psi, t_0 | \hat{U}^\dagger(t, t_0) \hat{U}(t, t_0) |\Psi, t_0\rangle \quad (1.2.3)$$

Because we want the norm to be conserved, i.e.  $\langle \Psi, t | \Psi, t \rangle = \langle \Psi, t_0 | \Psi, t_0 \rangle$  it must be true that:

$$\hat{U}^\dagger(t, t_0) \hat{U}(t, t_0) = \hat{1} \quad (1.2.4)$$

The unit operator  $\hat{1}$  is given as:  $\hat{1}|X\rangle = |X\rangle$ . Operators sharing property (1.2.4) are known as *unitary* operators. They are norm-conserving operators.

Some continuity properties can be mentioned. Thus, for

$$\lim_{t \rightarrow t'} \hat{U}(t, t_0) = \hat{U}(t', t_0) \quad (1.2.5)$$

In particular, if  $t$  has as a limit  $t_0$ , then  $\lim_{t \rightarrow t_0} \hat{U}(t, t_0) = \hat{U}(t_0, t_0) = \hat{1}$ .

Note again that the symbols  $|\Psi, t_0\rangle$  and  $|\Psi, t\rangle$  do not stand for things constructed with the elements of the material object but relate to the concept of (quantum) state the material system may be sensed by appropriate mappings

(measurements). While both states  $|\Psi, t_0\rangle$  and  $|\Psi, t\rangle$  are not the same, they originate from the same abstract state  $|\Psi\rangle$ , indicated by capital Greek letter, Psi label. One has to have an initial state to start propagating it.

## 1.3. Quantum dynamics

We need to move from the formal definition, eq.(1.2.1), to a differential equation allowing us to calculate the evolution operator. This is done below. The time dimension is assigned to the t-parameter, consequently, the conjugate variable has energy dimension.

### 1.3.1. Time dependent Schrödinger equation

We show below that time evolution of quantum states is determined by the Schrödinger equation:

$$(i\hbar) \partial|\Psi, t\rangle/\partial t = \hat{H} |\Psi, t\rangle \quad (1.3.1.1)$$

The operator  $\hat{H}$  stands for the system Hamiltonian. The Dirac relativistic equation and Klein-Gordon equation in their “Hamiltonian” form maintain the same structure (Cf.Chapt.8). So much for symbols, one can now skip E&E.1.3 below and continue until the end of this section.

#### E&E.1.3. Derive the form of the time dependent equation 1.3.1.1

The form of Schrödinger equation follows from mathematical properties assigned to the time evolution operators after four steps:

1)  $\hat{U}(t_0, t_0) = \hat{1}$ . This property is logically consistent with the definition eq.(1.2.1).

2) Then expand  $\hat{U}(t_0 + \delta t, t_0)$  to linear terms in  $\delta t$ : i.e.  $\hat{U}(t_0 + \delta t, t_0) = \hat{1} - i \hat{A} \delta t$ , for any arbitrary  $t_0$ . The infinitesimal time displacement  $\delta t$  permits a Taylor-like expansion of  $\hat{U}(t_0 + \delta t, t_0)$ ; note the implied continuity property:  $\lim_{\delta t \rightarrow 0} \hat{U}(t_0 + \delta t, t_0) = \hat{U}(t_0, t_0)$  for all  $t_0$ . Now look at properties following from unitarity:

3) Construct the product  $\hat{U}^\dagger \hat{U}$ . To this end use the result of point 2):

$$\begin{aligned} \hat{U}^\dagger(t_0 + \delta t, t_0) \hat{U}(t_0 + \delta t, t_0) &= (\hat{1} + i \hat{A}^\dagger \delta t) (\hat{1} - i \hat{A} \delta t) = \\ &= \hat{1} + i (\hat{A}^\dagger - \hat{A}) \delta t + O(\delta t^2) \end{aligned} \quad (1.3.1.2)$$

According to eq.(1.2.3) the result of eq.(1.3.1.2) must be equal to  $\hat{1}$ , the unit operator. One concludes that the operator  $\hat{A}$  must fulfill the identity:  $(\hat{A}^\dagger - \hat{A}) = \hat{0}$ . An operator that is equal to its transpose-complex-conjugate is a *Hermitian* operator.

So we have that 2) is true if operator  $\hat{A}$  is Hermitian. The dimension of  $\hat{A}$  must be canonically conjugate to time, this simply correspond to energy; such operators are known as *Hamiltonians* and use the symbol  $\hat{H}$  for that. The evolution operator  $\hat{U}$  has no dimensions, and this is the moment to introduce the universal Planck constant  $h$  divided by  $2\pi$ :  $\hbar$  that has dimension of energy by time. We get the fundamental equation:

$$\hat{U}(t+\delta t, t) = \hat{1} - (i/\hbar) \hat{H} \delta t \quad (1.3.1.3)$$

The Hamiltonian operator is a *generator* for time displacement.

The operator of interest now is  $\hat{U}(t+\delta t, t_0)$  that would do the job to bring the quantum state from initial time  $t_0$  up to time  $t$ . Let us seek now for actual translations along the time axis by using:

4) The (group) property of time evolution operators:

$$\hat{U}(t+\delta t, t_0) = \hat{U}(t+\delta t, t) \hat{U}(t, t_0) \quad (1.3.1.4)$$

Introducing eq.(1.3.1.3) in this identity one gets:

$$\hat{U}(t+\delta t, t_0) = (\hat{1} - (i/\hbar) \hat{H} \delta t) \hat{U}(t, t_0).$$

Taking the limit  $\delta t \rightarrow 0$  and ordering the terms,  $(\hat{U}(t+\delta t, t_0) - \hat{U}(t, t_0))/\delta t = -(i/\hbar) \hat{H} \hat{U}(t, t_0)$ , one gets a fundamental equation concerning the time evolution operator:

$$(i\hbar) \partial \hat{U}(t, t_0) / \partial t = \hat{H} \hat{U}(t, t_0) \quad (1.3.1.5)$$

This is the time dependent Schrödinger equation for the operator  $\hat{U}(t, t_0)$ .

If we make this operator equation to act on the initial quantum state  $|\Psi, t_0\rangle$  formally, Schrödinger equation obtains:  $(i\hbar) \partial \hat{U}(t, t_0) |\Psi, t_0\rangle / \partial t = \hat{H} \hat{U}(t, t_0) |\Psi, t_0\rangle$ . To see this more clearly remember that  $\hat{U}(t, t_0) |\Psi, t_0\rangle = |\Psi, t\rangle$ .

The key to time evolution of a quantum state resides in the construction of  $\hat{U}(t, t_0)$  by solving eq.(1.3.1.5). This implies knowledge of the Hamiltonian operator.

Time independent Hamiltonians are considered first. Thereafter, time dependent ones are discussed.

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

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \quad (1.3.1.6)$$

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

$$(i\hbar) \partial |\chi, t\rangle / \partial t = E |\chi, t\rangle \quad (1.3.1.7)$$

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:  $|\chi, t\rangle \rightarrow \exp(itE/\hbar)$ .

It is worth notice that construction of a formal Schrödinger equation involves the time parameter only. The space coordinates are not entering the formal process.

## 1.4. Basic chemical quantum dynamics

At the Fence, it is not the absolute value of the energy levels that matters but their difference. The difference between two eigenvalues is an amount of energy that the material system can give or receive from the exterior. This is the way atomic and molecular spectra have been rationalized. Further more, in agreement with Planck's discovery, the difference  $E_k - E_{k'}$  corresponds to an amount of energy the material system can exchange with the surroundings. This energy can be made equal to  $\hbar\omega_{kk'}$  where  $\omega_{kk'}$  is the frequency of an electromagnetic radiation;  $E_k - E_{k'} = \hbar\omega_{kk'}$ , this corresponds to Bohr's postulate. The formalism is made more definite by including the source of energy required to change the quantum state, otherwise, each base state is multiplied by a time dependent phase function  $\exp(i E_k t / \hbar)$  and no change is detected; there is no effective change of amplitudes in square modulus. The total Hamiltonian should include the mechanism allowing for transition among the chosen eigen states. Moreover, the material systems we talking about are defined by their charge, mass and spin. The linear momentum of a charge is partitioned between the mechanical term and the electromagnetic field; as a matter of fact, the charge system is not separable from transverse electromagnetic potentials,  $\mathbf{A}$ . For this reason, the interaction operator in a semi-classical picture will contain the term  $(e/c)(\hat{\mathbf{p}} \cdot \mathbf{A} + \mathbf{A} \cdot \hat{\mathbf{p}})$ ; to simplify the discussion let us take the form,  $\mathbf{A} = \mathbf{n}|\mathbf{A}|\cos(\omega t)$ , for a field with frequency  $\omega$ , direction  $\mathbf{n}$  and intensity  $|\mathbf{A}|$ . The field contains at least the equivalent one photon energy  $\hbar\omega$  to interact with the material system.

We can now move back to consider the initial problem related to eq.(1.1). Take a model where the Hamiltonian operator is separated into a molecular term  $\hat{H}_M$  and a coupling term  $\hat{V} = \hat{H} - \hat{H}_M$ . The choice is made so that the base states are eigen states of  $\hat{H}_M$  with energy eigen values  $E_A$ ,  $E_B$  and  $E_{AB\#}$ ,

$$\begin{aligned}\hat{H}_M|A\rangle &= E_A|A\rangle; \\ \hat{H}_M|B\rangle &= E_B|B\rangle; \\ \hat{H}_M|AB\#\rangle &= E_{AB\#}|AB\#\rangle\end{aligned}\quad (1.4.1)$$

Vibration levels are implicit and a few of them are signaled in Scheme I as  $E_{A_0}$ ,  $E_{A_n}$  and  $E_{B_m}$ .

For the sake of simplicity  $\langle A|\hat{V}|A\rangle = \langle B|\hat{V}|B\rangle = \langle AB\#|\hat{V}|AB\#\rangle = 0$ . Moreover,  $\langle A|\hat{V}|B\rangle = Z_{A,B} = 0$  which means that no direct transitions between states of A and B are allowed.

Non-zero matrix elements are for  $\langle A|\hat{V}|AB\#\rangle = Z_{A,AB\#}$  and  $\langle AB\#|\hat{V}|B\rangle = Z_{AB\#,B} \neq 0$ . This choice opens the possibilities for the change of chemical state that become under control by the quantum transition state,  $|AB\#\rangle$ ; this means that in



eq.(1.3.3.5) first order terms are nil, the evolution operator is controlled by second order terms and higher. These provisos define the elements of a reactant model. The model  $E_A \ll E_B < E_{AB\#}$  corresponds to an endothermic-like reaction.

In Scheme I, the amplitudes as a function of an external energy parameter  $E$  can be obtained as solutions to the secular equation indicated in the upper inset. Changes of  $E$  are measured from the lowest energy level:  $E = E_{A_0} + \Delta_A$ ; this quantity represents energy drawn from external sources or deposited into external systems as the case may be. For the present model it plays the role of a “reaction coordinate”.

For non-resonant situations the amplitudes are given by equations:

$$\begin{aligned} \text{a) } |C_A(\Delta_A)| &= Z_{A,AB\#} C_{AB\#}(\Delta_A) / |(\Delta_A - E_{AB\#})|; \\ \text{b) } |C_B(\Delta_A)| &= Z_{AB\#,B} C_{AB\#}(\Delta_A) / |(E_B - \Delta_A)|; \\ \text{c) } |C_{AB\#}(\Delta_A)| &= \{ |Z_{A,AB\#}|^2 / (\Delta_A - E_{AB\#})^2 + |Z_{AB\#,B}|^2 / (\Delta_A - E_B)^2 \}^{1/2}. \end{aligned}$$

The structure of equations (1.4.2) show that the amplitude  $|C_{AB\#}(\Delta_A)|$  controls the possible values of the amplitudes at root states  $|A\rangle$  or  $|B\rangle$ . *To put some amplitude at product root state it is necessary that the amplitude at the transition state becomes different from zero.*

The model emphasizes the role of the transition state in a way differing from simple energy discussions. As expected from the evolution operator, amplitude in modulus,  $|C_{AB\#}(\Delta_A)|$ , depends on the couplings squared.

Consider the case where the coupling  $|Z_{AB\#,B}|^2$  corresponds to a “forbidden” transition, its numerical value will be smaller than  $|Z_{A,AB\#}|^2$  in the case that this latter were an “allowed” one and take the reaction in the opposite direction, i.e. prepare the initial quantum state as  $(0 \ 1 \ 0)$ . The reaction  $B \rightarrow A$  is exothermic and one would expect a rapid conversion, i.e. increase of amplitude at  $|A\rangle$  due to favorable energy gap. Nevertheless, and contrary to energy expectations, with the quantum conditions defined already the chemical reaction is expected to run slowly for at least two reasons:

i) The energy gap  $E_{AB\#} - E_{A_0}$  is too large so that a direct transfer with  $|C_{A_0}(\Delta_A = E_{AB\#})| \neq 0$  is unlikely;

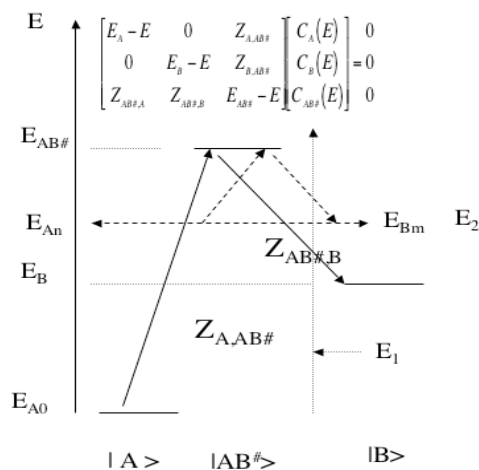
ii) The amplitude  $C_{AB\#}(\Delta_A = E_{AB\#} - E_{B_0})$  is bound to be very small as indicated by case c) in eq.(1.13). The analysis is of course very simple but it serves a pedagogic purpose.

Experimentally, there are a number of cases showing such behavior and an explanation may be found following the present line of thought.

Consider now the endothermic direction:  $A \rightarrow B$  in more detail. In the scheme we have singled out a few vibration (rotation) energy levels. To avoid complicated formalisms we study couplings starting from specific vibration states, equations (1.13) can easily be adapted for each case.

There is one way to experimentally change the energy gaps that is well known to chemists and physicists alike. Transform external energy into internal energy. The parameter  $\Delta_A$  can be used for this purpose.

Let us control some responses from this model. For  $\Delta_A \ll E_B \ll E_{AB\#}$ , the amplitude  $|C_{AB\#}(\Delta_A)|$  would be negligible due to the large denominators in eq.(1.4.2). Thus, if the system was prepared as  $(1\ 0\ 0)$ , i.e.  $C_A(t_0) = 1$ , the coupling to the quantum system is not going to change the initial amplitudes. The system stay put.



Scheme I

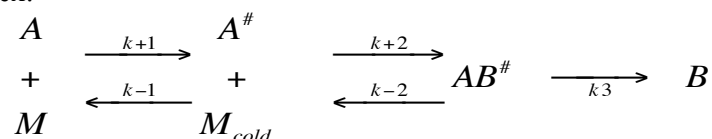
Apparently, the system A must be energy activated. Take  $\Delta_A$  below the energy gap  $E_B$  the amplitude  $|C_{AB\#}(\Delta_A)|$  may take on values different from zero; the size of  $Z^2$  controls the actual value. But now remember the reaction actually taking place at the Fence requires energy conservation; this situation in real space prevents a non-zero amplitude at root state  $|B\rangle$  that could be translated into actual population; a decoherence process. We complete the model with this experience. A simple rule: Non-zero transition amplitude requires a non-zero density of states at the outgoing state ( $|B\rangle$ -channel here). For our model, any energy level above the ground state of channel A but below energy of channel B will never “face” a quantum base state of  $|B\rangle$ ; the density of states at the outgoing channel is hence zero and no time dependent conversion of amplitude in the relevant A-state will be zero. In the language of laboratory, you have to pay the energy difference between reactants and products in real (chemical) space. Therefore, at point  $E_1$  signal by an arrow in Scheme 1, there is no mixing of states leading to product state  $(0\ 1\ 0)$ .

Activation must put the energy pointer  $\Delta_A$  above  $E_B$  to expect a coupling that eventually would lead to products, i.e.  $(0\ 1\ 0)$  in Hilbert space. Consider the value  $E_{An}$  corresponding to a vibration-rotation level chosen in such a way that there is a corresponding level  $E_{Bm}$  the amplitude  $|C_B(\Delta_A = E_{Am})|$  will be different from zero if and only if the coupling with the transition state above leads to a non-zero amplitude there. There might be a linear superposition with finite amplitude at the excited vibration state in the product channel. If a mechanism of relaxation towards  $(0\ 1\ 0)$  is operating, thence a response of the reaction products can be obtained.

Observe that were  $|Z_{AB\#,B}|=0$ , i.e. a forbidden transition, then the system will remain in the initial state at all times (if forced to follow this mechanism!).

To make contact with real chemistry, we have to move from abstract space to the Fence. Consider the case where the energy is being transferred at constant volume  $V$ . This can be used to climb the vibration energy ladder until a threshold value obtains where a non-zero  $|C_{AB\#}(\Delta_A)|$  shows up. Seeing from the external world, the energy density is increasing. In real world this is equivalent to an increase of pressure,  $p = E/V$ . Remind that relative kinetic energy between pairs of reactant systems increases with pressure so that we can relate this situation with Lindemann-Hinshelwood (LH) mechanism.

In LH-mechanism the activation energy comes from collisions between molecules:  $A+A$  turn into  $A^*+A$ . The rate of de-activation competes with the rate at which product starts being detectable. The simple kinetic scheme of eq.(1.1) must be supplemented to take into account the need for activation and deactivation processes; we use  $M$  as the activating species, the energy withdrawn from  $M$  is indicated as sub index:



The quantum mechanical analysis shows that the intervention of the transition state is subtler than the standard chemical view would suggest. The activation energy may well be below the lowest energy state of  $AB^\#$ . Interestingly, *in Hilbert space there is no need for molecular structures because it is the spectra that determine possible chemical paths.*

To sum up, coupling between ingoing and outgoing channel effectuates best at resonance. In the Scheme I we illustrate this point with energy levels  $E_{An}$  and  $E_{Bm}$ . Pumping with high intensity laser via a multi photon process that put the ground state and a vibration state in a coherent superposition, put a time dependent amplitude at level  $E_{An}$ ; this may prompt for an interaction with another level (transition state for example) which in turn interacts with the level  $E_{Bm}$ ; so that the initial amplitude may be taken away from that coherent state to another one ending at the product level  $E_{Bm}$ ; and amplitude transfer seen as a sort of decaying if relaxation towards ground state of product happen.

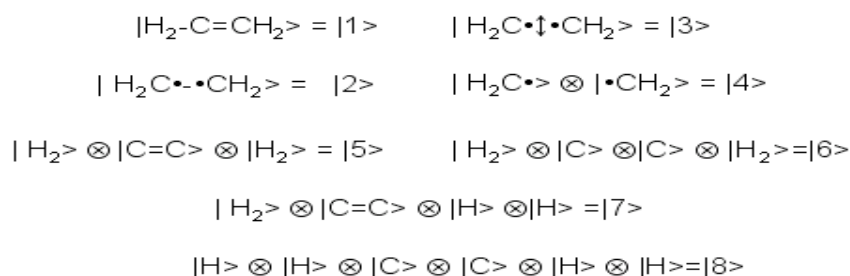
Time evolution in a 1-system appears as “diffusion” in the quantum state space.

The model discussed so far appears simple. There are, however, many aspects that concern complex 1-systems. To keep things at a very general level observe that energy labels, base states of otherwise undefined 1-system are the elements of the model. At the Fence, such states can be associated to spatially distributed systems: for instance, enzyme catalyzed reactions. The energy resonance between the lowest energy levels in the reactant and product channels may be associated, at the Fence, with large “structural” differences. This would imply the possibility of “clocking” the structural change. Time would no longer be a parameter but it can be quantified in terms of lifetimes: time as duration. Characteristic times would emerge from pure time evolution in Hilbert space measurable from the response in intensity of specific  $|C_k(t)|^2$ .

## 1.5. Formal chemical base sets

A chemical graph would serve now the purpose of a label identifying something related to a chemical system. In Scheme II a set of chemical graphs for a 1-system with  $n=16$  electrons and four nuclei  $Z=(Z_C, Z_C, Z_H, Z_H, Z_H, Z_H)$  are depicted.

Bases states labels



SCHEME II

The number of I-frames required to represent base states for the present system serves to classify them: base states  $|1\rangle$ ,  $|2\rangle$  and  $|3\rangle$  with one-I-frame each; base states  $|4\rangle$  with two-I-frames; base state  $|5\rangle$  with three I-frames; base states  $|6\rangle$  and  $|7\rangle$  with four I-frames; base state  $|8\rangle$  with six I-frames. The direct product symbol is used to indicate asymptotic base states. Base states  $|3\rangle$  and  $|4\rangle$  are related to a description from an asymptotic state  $|4\rangle$  towards a one-I-frame state  $|3\rangle$ . There are many more base labels associated to electronic states for this well known organic

chemistry system. Ionized base states, charge transfer base states are understood when one speaks about a complete base set. All possible base states would then cover any aspect of chemical changes related to the 1-system initially named ethylene.

Many I-frame systems describe situations that are characteristic of laboratory experiments related for instance to scattering and chemical processes. The I-frame is a classical physics device with location and orientation with respect to another I-frame or to a fixed laboratory frame. By assigning the total mass to the respective origin (as a first model) the frame may show definite linear momentum and angular momentum. Thus, for a two-beam experiment introduce a reference frame so that the beam sources are located and the beam directions fixed. The chemical process is described with the help of only one internal I-frame. The shared I-frame is used to project the 1-system internal states and the states of the two-I-frame system must be included.

The chemical reaction starting from two space separated methylene radicals would involve the first four label states: ( $|1\rangle$   $|2\rangle$   $|3\rangle$   $|4\rangle$ ). The quantum states are given by a column vector with the corresponding amplitudes (complex numbers) that at a given time  $t$  they are written as  $[C_1(t) C_2(t) C_3(t) C_4(t)]$ . The initial state is given by  $[C_1(t_0) C_2(t_0) C_3(t_0) C_4(t_0)] = [0 0 0 1]$ . The objective being to construct a quantum state such that  $[C_1(t) C_2(t) C_3(t) C_4(t)] = [1 0 0 0]$  at a sufficiently long reaction time.

The first thing you have to do is focusing the beams so that their cross section lies within a reactive domain. Also, the relative kinetic energy can enter into a process of activation. These are classical aspects and if we stay at this level of description there would be no way to find out the factors that would determine the amplitude shift we are hoping for.

A commensurate description requires a one-I-frame description for the asymptotic states. This is achieved by taking the system as if it were an aggregate that can be related to the one-I-frame system. The base quantum state for this case must be given by an “anti-bonding” state so that it can dissociate. The vertical double arrow in base state  $|3\rangle$  just indicate this property. In terms of space internal functions constructed with the fragments there must be a node along the inter-group distance; the distance we pick up from the two I-frames but now the space base function is referred to the common one I-frame. Let us pick up a relative kinetic energy for which a quasi-resonance condition obtains with one or more internal states associated to the generic base state  $|2\rangle$ . Thus, according to this analysis, only generic base states  $|1\rangle$ ,  $|2\rangle$  and  $|3\rangle$  enter the reactive space. In common chemical language there are four unpaired electron states associated to base state  $|3\rangle$  that define two spin triplet states.

Which is a relevant difference between base states  $|3\rangle$  and  $|2\rangle$ ? The symbol “-” indicates a spin entangled state with  $S=0$ , namely a singlet spin state; this entails a symmetric space state for this spin subspace. Let us leave the other electron-states

as spectators to the extent they correspond to a triplet spin state. Thus, the changes of base states  $|2\rangle$  and  $|3\rangle$  involve the space part and the spin part. One can excite vibration state of the single C-C bond associated to base state  $|2\rangle$  as much as you like but a change of spin state you cannot expect to get at with such mechanism. You need something else. Such is the role of transition states as we saw in the preceding model. An appropriate external field must mediate the coupling between these base states so that an amplitude different from zero would appear at  $C_2(t)$ .

The base states  $|2\rangle$  and  $|1\rangle$  differ by the number of unpaired electron states. The former belongs to a triplet spin state; the latter is a spin singlet. Thus,  $|2\rangle$  is anti-bonding and  $|1\rangle$  features a full bonding state.

Let us write the linear superpositions required for a quantum mechanical setup able to give an understanding about chemical reactions:

$$|\Psi, t\rangle = [C_1(t) |1\rangle + C_2(t) |2\rangle + C_3(t) |3\rangle + C_4(t) |4\rangle] \quad (1.5.1)$$

Within Hilbert space  $C_4(t)$  at all times is equal to zero. It is only at the Fence that one may include this state thereby leading to a semi-classic quantum mechanics.

The concept of a material system and the quantum states sustained by such a system are totally different. Laboratory chemistry involves the material system. Quantum physical chemistry addresses to quantum states. Is there any difference with quantum chemistry, as we know it? Quantum chemistry requires wave functions endowed with a particle model representation. This makes a difference to be examined at the last chapter of this book.

In order to make some progress along the quantum chemical physics direction, let us first introduce quantum mechanical principles in a more rigorous way. This will be the content of the following sections. Emphasis is put on a “linguistic” approach to the mathematics. The key for readers not having a specialized training is to realize that one should go through these sections with the aim to get a better comprehension of the concepts of quantum states and available base sets. The examples and exercises are given to help those with less mathematical knowledge: they are very simple.