4. Quantum states for simple systems

Quantum states belong to Hilbert spaces that, at a Fence, are projected in configuration spaces sustained by I-frames. Conditions are then fulfilled to help introduce material systems that present themselves in real (laboratory) space.

A sharp distinction must be made between quantum formalisms in abstract Hilbert space and quantum theories at Fence domains. The abstract formalism is projected in configuration space thereby relying on the concept of I-frames coming from special relativity theory; the mathematical space so introduced keeps an abstract nature, only frame's origin and orientation remain in real space. In this manner, sets of base states, namely, $\{|\mathbf{q}>\}$ and $\{|\mathbf{k}>\}$ enter the picture. Quantum formalism of Chapters 2 and 3 would concern rigged Hilbert spaces with all its general properties as a mathematical corpus. Introduction of models permit quantum theories to move at an interface with real productive worlds.

In the structure of a quantum theory, the concepts of quantum states in Hilbert space are transferred to quantum states projected in configuration spaces. The quantum state is sustained by a material system; this latter does not populate the basis energy levels. The connexion will be made explicit as we go along. Being a new foundational principle, it cannot be defined in more simple terms. We have to get used to it.

It is the inertial frame that opens the first contact between abstract space and real space. The results are independent of the uniform state of motion of the I-frames. The possibility opens to introduce concepts of place and location that are not akin to quantum physics. To the extent one follows motion of material systems somehow anchored to an I-frame classical physics concepts can cautiously be used. The invariance of quantum states projected in configuration space sustained by this frame lead to base sets already discussed so far in previous chapters, e.g. angular momentum base sets, reciprocal (**k**-) space, etc.

Quantum states are sustained by material systems, this statement will be slowly substantiated; to the extent the materiality is present in the laboratory space where the experiments are carried out there is no need to fix its exact location, the parameters defining materiality are data entering differential

equations that are used to determine appropriate basis sets. So that questions concerning which way a matter system has gone in an experimental setup might not be relevant issues in describing quantum processes. All along this book we will encounter particular situations that will be carefully discussed.

Here the projected formalism is developed. Model systems introduced to get sets of basis states. The formalism of the density matrix is outlined. Two Fence models are described: harmonic oscillator and hydrogen-like atoms.

4.1. At a Fence: time-projected quantum formalism

In abstract space, Schrödinger time dependent equation follows from a unitary time evolution operator, $\hat{U}$ (t,t$_o$), namely,

$$(i\,\hbar)\, \partial|\,\Psi,t>/\partial t = \hat{H}\,|\Psi,t> \qquad (4.1.1)$$

The space representation helps constructing mappings bridging Hilbert to real spaces. In this sense the introduction of the I-frame is essential as shown in preceding chapters. Now a coordinate projected formalism is sketched.

4.1.1. Global scheme

The general structure of quantum mechanics does not require of a particle or a wave model; there is no interpretation required, incommensurabily between quantum states and materiality does not claim for an interpretation. Quantum physics produces its own "reality" as quantum technology shows today and will likely be showing in the future.

This results in an abstract m odern quantum theory separating "kinematic" from "dynamic" aspects. Projecting the abstract framework in configuration space, that is a pure mathematic space, the time-dependent Schrödinger equation (4.1.1), can be cast in the form:

$$\{(i\,\hbar)\, \partial<\mathbf{q}'|\,\Psi,t>/\partial t - <\mathbf{q}'|\,\hat{H}\,|\mathbf{q}'><\mathbf{q}'|\Psi,t>\} = 0$$
$$(4.1.1.1)$$

This equation is commensurate to abstract Schrödinger equation (1.3.1.1), this time expressed in configuration space. To close the loop one takes the assignment in the integrand of eq.(1.1.3):

$$<\mathbf{q}|\,\hat{H}\,|\mathbf{q}> <\mathbf{q}|\Psi,t> \rightarrow \hat{H}\,(\hat{q}\,,t) <\mathbf{q}|\Psi,t>.$$

This ansatz once introduced in eq.(4.1.1.1) leads to the time dependent equation having the form Schrödinger's used in his seminal paper (1926):

$$\{i\hbar\ \partial/\partial t - \hat{H}(\hat{q},t)\}\ \Psi(\mathbf{q},t) = 0 \qquad\qquad (4.1.1.2)$$

The introduction of operator $\hat{H}(\hat{q},t)$ is not a logical step. It is a hypothesis that permits giving to Schrödinger equation, in configuration space, the same form as in abstract space, eq.(4.1.1). Furthermore, the explicit time dependence of this operator permits incorporating couplings to external sources to ensure appropriate time evolution at a Fence.

We assume that the mapping $\hat{H} \to \hat{H}(\hat{q},t)$ holds true or at least the latter permits grabbing essential aspects of the physics for the given system. Now, from $<\mathbf{q}|\Psi,t>$ we can see that it is the time dependence of the abstract quantum state that which matters, the ways and means used to accomplish the task $\hat{H}(\hat{q},t)$ is what matters. This operator will also convey the materiality of the system.

The family of time-independent Hamiltonians $\{\hat{H}(\hat{q})\}$ qualifying to represent the spectrum of a given physical system must be invariant under Lorentz transformations. They are called Hamiltonian operators of Schrödinger type. If they are to serve as generators of time translation, the self-adjoint property must hold.

Whence fence model operators should satisfy specific symmetry properties. Classical models, when they exist, are used to construct operator Hamiltonians. In the preceding chapter we found the general mapping $\hat{p} \to (\hbar/i)\nabla$ and $E \to (i\hbar)\partial/\partial t$ permits classical expressions to be translated into model quantum operators; they are dubbed quantum because $\hbar$ appears in the symbols definig them. In doing this, qualitatively, focus moves from classical trajectories into a search for quantum states sustained by material systems.

For time independent Hamiltonians, the wave function separates into a space and a time component: $\Psi(\mathbf{q},t) = \Phi(\mathbf{q})\ X(t)$. The separation constant E is an energy related to the physical situation, this defines an E-mapping. One gets a time independent Schrödinger equation where this time the origin of the I-frame is taken to be at a Fence:

$$\hat{H}(\hat{q})\ \Phi(\mathbf{q}) = E\ \Phi(\mathbf{q}) \qquad\qquad (4.1.1.3)$$

The number E depends upon the quantum state: $E = <\Phi(\mathbf{q})|\hat{H}(\hat{q})|\Phi(\mathbf{q})>$ for wave functions normalized to one: $<\Phi(\mathbf{q})|\Phi(\mathbf{q})>=1$. This property implies particular boundary conditions.

The eigen value problem is completely solvable for self-adjoint operators which means that there exists a complete set of denumerable (countable) eigenfunctions, $\{\phi_k(\mathbf{q})\}$. To calculate such functions is essential to set up a base set serving to construct the quantum states of the system. Let us design the set of energy eigenvalues $\{E_k\}$, the eigenvalue equation in configuration space reads:

$$\hat{H}(\hat{q})\phi_k(\mathbf{q}) = E_k \, \phi_k(\mathbf{q}) \qquad (4.1.1.4)$$

The quantum state of a given system is expressed as a column vector with complex amplitudes in the base set arranged as a row vector:

$$|\Psi> \rightarrow \Psi(\mathbf{q}) = \Sigma_k \, \phi_k(\mathbf{q}) \, C_k(\Psi) =$$
$$(\phi_{k=0}(\mathbf{q}), \, \phi_{k=1}(\mathbf{q}),\ldots, \phi_k(\mathbf{q}),\ldots)\cdot$$
$$[C_{k=0}(\Psi), C_{k=1}(\Psi),\ldots, C_k(\Psi),\ldots] \qquad (4.1.1.5)$$

The basis functions are fixed so the quantum state is represented by the column vector: $[C_{k=0}(\Psi), C_{k=1}(\Psi),\ldots, C_k(\Psi),\ldots]$.

These amplitudes only depend upon a given quantum state; they are fundamental invariants to the extent that they must be the same as those to be found in abstract Hilbert space. This is true for an exact scheme.

What can be measured or recorded is expressed as a response from a given quantum state (linear superposition) towards external probes; response that is sustained by the material system at the Fence and as one gets a response detected at an instrument you put somewhere, the localization of the material system after probing is not an issue. Chapter 10 is dedicated to further analyses.

In abstract, any base state can act as the origin of a spectral series describable as energy differences between an origin (the root) state and any other base state. In fact, only those base states having amplitudes different from zero can respond to external probes. This is a fundamental condition.

For sensing in intensity regime, the square modulus of the amplitude yields a relative intensity: for this to be exact, the quantum state must be normalized to unity. In this sense, one can speak of E-observables associated to a Hamiltonian and complete base set $\{\phi_k(\mathbf{q})\}$ related to the energy spectrum (not to individual eigen values).

The set of all linear superpositions on the base of energy eigen states form a vector space over the field of complex numbers. This means that column vectors with amplitudes defining a quantum state form also a linear vector space. Those are the physical states of the material system underlying the construction of the Hamiltonian. In this space a pure state is defined by a set of zero amplitudes everywhere except at the position assigned to the eigenvector:

$$\text{k-th pure state} \rightarrow [0_1, 0_2,\ldots, 0_{k-1}, 1_k, 0_{k+1},\ldots] \qquad (4.1.1.6)$$

The set of pure states is naturally ordered:

$[1_1, 0_2, \ldots, 0_{k-1}, 0_k, 0_{k+1}, \ldots], [0_1, 1_2, \ldots, 0_{k-1}, 1_k, 0_{k+1}, \ldots] \ldots [0_1, 0_2, \ldots, 0_{k-1}, 1_k, 0_{k+1}, \ldots] \ldots$

(4.1.1.7)

We have to produce results using a Hilbert space where the base set is explicitly made with the eigenfunctions: $(\phi_{k=0}(\mathbf{q}), \phi_{k=1}(\mathbf{q}), \ldots, \phi_k(\mathbf{q}), \ldots) \Leftrightarrow (\ldots \phi_k(\mathbf{q}) \ldots)$.
The amplitudes define the quantum state:

$$[C_{k=0}(\Psi), C_{k=1}(\Psi), \ldots, C_k(\Psi), \ldots] \Leftrightarrow [\ldots C_k(\Psi) \ldots].$$

The quantum state (representation) is subsidiary to the base set and the scalar product $(\ldots \phi_k(\mathbf{q}) \ldots) \cdot [\ldots C_k(\Psi) \ldots]$ when given as an explicit sum makes disappear all zero terms giving an incomplete (truncated) picture. For the set of base states is not a property of the objects defining the material system but it relies on the fundamental constituents. QM and quantum chemistry textbooks do not address this issue as they have hands plenty with actual model calculations of base functions.

There are two aspects, seldom identified also, concerning simple "invariance" of equations (4.1.1.4). The eigenvalues are ordered in a unique manner; the ordering does not depend on the hyper-ball around any configuration space point $\mathbf{q}$. And, while the absolute value of these numbers can be made arbitrary, only the set of energy differences is a fundamental invariant. These latter are included in the definition of the spectra of the given system. Thus, if the I-frame has a uniform speed with respect to a frame where one is measuring the spectra, this latter will be shifted as a whole in an energy scale.

It is a current misunderstanding to believe that microscopic objects are usually found in specific energy eigenstates. The argument in favor of this statement runs as follows: At a Fence, such state has equal energy that the one constructed with a direct product of 1-photon base state and the corresponding ground state. Moreover, an entangled state between the EM field and the material system sets up. This type of quantum state is examined in Chapter 6; see below Sect.4.2.3. In a quantum physical chemistry set up such a type of states cannot be ignored.

Now we touch another formal point. The mapping between base function $\phi_k(\mathbf{q})$ and abstract base state $|E_k>$ together with the assumption $\hat{H}(\hat{q}) \rightarrow \hat{H}$ can be used to write eq.(4.1.1.4) as follows:

$$\hat{H}|E_k> = E_k|E_k> \qquad (4.1.1.8)$$

The Hamiltonian $\hat{H}$ is hence given as:

$$\hat{H} = \Sigma_k |E_k> E_k <E_k| \qquad\qquad (4.1.1.9)$$

The different forms given to the Hamiltonian operator are equivalent; each one applies to a different representation of Hilbert space.

E&E-4.1.1. Calculate (4.1.1.9) from (4.1.1.8)

Take the eigenvalue equation and multiply both side from the right by the bra $<E_k|$:

$$\hat{H} | E_k><E_k| = E_k | E_k><E_k|$$

The operator is independent from the sub indexes so that we can sum over k to get:

$$\Sigma_k \hat{H} | E_k><E_k| = \Sigma_k E_k | E_k><E_k|$$

But

$$\Sigma_k \hat{H} | E_k><E_k| = \hat{H} \Sigma_k | E_k><E_k|$$

This commutation property permits writing:

$$\hat{H} \Sigma_k | E_k><E_k| = \Sigma_k E_k | E_k><E_k|$$

And, by completeness $\Sigma_k | E_k><E_k| = \hat{1}$, you get eq.(4.1.1.9).

E&E-4.1.1-2 Calculate the effect of $| E_j><E_k|$ on a basis vector

Form the object:

$$| E_j><E_k| (|E_0> | E_1>…| E_k>…)$$

The row vector resultant is

$$(|E_j>\delta_{k0} |E_j>\delta_{k1} …|E_j>\delta_{kk}…) = |E_j> (0_1\ 0_2\quad 1_k\ 0_{k+1}…)$$
$$(0_1\ 0_2\quad |E_j>1_k\ 0_{k+1}…)$$

Take the scalar product with $[C_{k=0}(\Psi), C_{k=1}(\Psi),…, C_k(\Psi),…]$ the result is:

$$| E_j><E_k| (|E_0> | E_1>…| E_k>…)$$
$$\times[C_{k=0}(\Psi), C_{k=1}(\Psi),…, C_k(\Psi),…] = |E_j> C_k(\Psi)$$

Now we form

$$[<E_0|\ <E_1|…<E_k|…]| E_j><E_k| (|E_0> | E_1>…| E_k>…)$$

This infinite matrix has zero everywhere except at the j,k position. Multiplying from the left with $(C_{k=0}(\Psi), C_{k=1}(\Psi),…, C_k(\Psi),…)^*$ the result of $< \Psi| E_j><E_k| \Psi>$ is just:

$$< \Psi| E_j><E_k| \Psi> = C_j^*(\Psi) C_k(\Psi)$$

The quantum state is projected into transition amplitude. If the amplitude over these base states is always zero the transition amplitude would be always zero.

We can now scrutinize the transition amplitude at two times:

$$< \Psi,t_0| E_j><E_k| \Psi,t> = C_j^*(\Psi, t_0) C_k(\Psi,t)$$

This is a correlation function sensing the effect on the amplitudes associated to the base states j,k. All the information lies in the amplitudes. One uses the same symbol Ψ because the base state is an invariant.

Go back to the configuration space representation. It is not difficult to see that $<\mathbf{q}|E_k>$ should correspond to $\phi_k(\mathbf{q})$. The form gotten to $\hat{H}$ in eq.(4.1.1.8) is general. If the spectra $\{E_k\}$ of this Hamiltonian were to coincide with the spectra of the system in abstract Hilbert space, we would have obtained a faithful representation via eq.(4.1.1.4). At any rate, results obtained with this theory must be checked against experimental results. More often than not, we determine energy differences between eigenvalues and intensities (emission-absorption), the numbers entering the characterization of a quantum state must then be related to such measurable properties. We seldom "observe" an energy eigen value, only responses are recorded and thereafter interpreted as observations or transformed via a measurement into data.

The Hamiltonian operator $\hat{H}(\hat{q})$ commutes with the total spin operator $\hat{S}$. The degrees of freedom of the configuration space, $\mathbf{q}_1,\ldots,\mathbf{q}_n$, are now supplemented with a new spin space where the total spin operator is a sum of 1-spin operators:

$$\hat{S} = \Sigma_{j=1,n} \; \hat{S}_j \tag{4.1.1.10}$$

For spin operators, the following eigenvalue equations hold:

$$\hat{S}_j{}^2 \; |S_j,M_{Sj}> = S_j \; (S_j+1) \; |S_j,M_{Sj}> \tag{4.1.1.11}$$

and

$$\hat{S}_{3j} \; |S_j,M_{Sj}> = M_{Sj} \; |S_j,M_{Sj}> \tag{4.1.1.12}$$

For the global system, spin base states are direct products:

In the business of constructing base functions we will use spin independent Hamiltonians and, consequently, the spin functions are constructed as direct product of the type:

$$\Pi_j \; |S_j,M_{Sj}> = |S_1,M_{S1}> \otimes \ldots \otimes |S_n M_{Sn}> \tag{4.1.1.13}$$

More specific forms are given for particular cases in following Chapters.

Remember that the I-frame might be in uniform motion seen from laboratory perspective. Because focus is on quantum states and the base sets relevant to their representation all what one calculate with the help of the configuration space is considered to be "internal" quantum states related to that frame; just a name, albeit it is unavoidable that an experimenter (or a recording device) hooked to

another I-frame must detect not only the "internal" response but also the relative frame motion. This is a key result. For what is detected between I-frames is electromagnetic radiation that is affected by the state of motion between sources and sinks.

4.1.2. Schrödinger and Heisenberg Representations

There are two formal ways to characterize time dependence named Schrödinger and Heisenberg representations, respectively.

In Schrödinger representation, time dependence is carried out by the quantum state: $\Psi(\mathbf{q},t)$. We have already discussed this point, now we look at time dependence of other quantities.

The average value of operator $\hat{B}$ given by $<\Psi(\mathbf{q},t)|\hat{B}|\Psi(\mathbf{q},t)>$, is written in a way where the operator is transformed into a time dependent one:

$$<\Psi(\mathbf{q},t)|\hat{B}|\Psi(\mathbf{q},t)> =$$
$$<\Psi(\mathbf{q},t=t_o)|\hat{U}^\dagger(t,t_o)\,\hat{B}\,\hat{U}(t,t_o)|\Psi(\mathbf{q},t=t_o)> =$$
$$<\Psi(\mathbf{q},t=t_o)|\hat{B}(t)|\Psi(\mathbf{q},t=t_o)> \qquad (4.1.2.1)$$

To better distinguish the time independent operator in Schrödinger picture a supra index is usually added: $\hat{B}=\hat{B}^{(S)}$. In Heisenberg picture, time dependent operators are defined as:

$$\hat{B}^{(H)}(t) = \hat{B}(t) = \hat{U}^\dagger(t,t_o)\,\hat{B}^{(S)}\,\hat{U}(t,t_o) \qquad (4.1.2.2)$$

Heisenberg equation of motion can directly be obtained from the above equation:

$$d\hat{B}^{(H)}(t)/dt = \partial(\hat{U}^\dagger(t,t_o)\,\hat{B}^{(S)}\,\hat{U}(t,t_o))/\partial t =$$
$$(1/i\hbar)[\hat{B}^{(H)}(t),\hat{U}^\dagger(t,t_o)\hat{H}\,\hat{U}(t,t_o)] \qquad (4.1.2.3)$$

This equation transforms into the well-known Heisenberg equation of motion:

$$d\hat{B}^{(H)}(t)/dt = (1/i\hbar)[\hat{B}^{(H)}(t),\hat{H}] \qquad (4.1.2.4)$$

We have to learn how to calculate commutators of a Heisenberg operator with the Hamiltonian to get the differential equation allowing calculation of time dependence. One thing is, however, clear: once $\hat{H}$ is chosen, it is the initial quantum state $|\Psi(\mathbf{q},t=t_o)>$ that determines specific aspect of evolution, the final

result, that is the new set of amplitudes different from zero at the end of $t-t_o$ stems from this origin. Note that comparing eqs. (4.1.2.3) and (4.1.2.4) we have $\hat{H} = \hat{U}^\dagger(t,t_o)\,\hat{H}\,\hat{U}(t,t_o) = \hat{H}^{(H)} = \hat{H}^{(S)}$; this means that $\hat{H}$, the Hamiltonian of the system in this case commutes with the time evolution operator. Of course, this is only natural because $\hat{U}(t,t_o) = \exp(i\,(t-t_o)\,\hat{H}/\hbar)$; the Schrödinger time evolution is another way to put the problem.

E&E-4.1.2. Calculate the time derivative of the Hamiltonian operator

Replace $\hat{B}^{(H)}(t)$ by $\hat{H}$ in equation ((4.1.2.4). You get d$\hat{H}$/dt $= (1/\,i\hbar)\,[\,\hat{H},\hat{H}\,]$. By definition of the commutation operation $[\,\hat{H},\hat{H}\,] = \hat{0}$. Thus, for any quantum state the result is: d$\hat{H}$/dt $= \hat{0}$. The system is closed and energy is conserved.

Equation (4.1.2.4) can formally be integrated with the initial condition: $\hat{B}^{(H)}(t_o)$ equals Schrödinger operator representation at $t_o = 0$:

$$\hat{B}^{(H)}(t) = \hat{B}^{(H)}(t=t_o) + \int_o^t (dt'/\,i\hbar)\,[\,\hat{B}^{(H)}(t'),\hat{H}\,]$$

$$(4.1.2.5)$$

This equation clearly indicates that any change of a quantum state induced by a Heisenberg operator depend upon the commutator $[\,\hat{B}^{(H)}(t'),\hat{H}\,]$. Therefore, if such an operator commutes with the Hamiltonian at all times there will be no change of the initial quantum state: $\hat{B}^{(H)}(t)|\,\Psi(\mathbf{q},t_o)> = \hat{B}^{(H)}(t_o=0)|\,\Psi(\mathbf{q},t_o)>$.

The operator form of time evolution yields a theorem equivalent to theorem 1.3.2.1. For now replacing $\hat{B}^{(H)}(t)$ by the evolution operator $\hat{U}^{(H)}(t)$ that is equivalent to $\hat{U}(t,t_o=0)$ one gets $[\,\hat{U}^{(H)}(t'),\hat{H}\,] = [\,\hat{U}(t',t_o=0),\hat{H}\,]$, the commutator equals to a zero operator. In this case we conclude that $\hat{U}(t',t_o=0) = \hat{1}$ at all times. Thus, there is no effective time evolution meaning with this statement that the absolute values of amplitudes do not change.

For the reason signaled above, the set of operators commuting with the system Hamiltonian are known as constant of motion. Eigenvalues afforded by such operators may serve to label quantum base states.

A general comment can be made at this point. Time evolution for a Hamiltonian that either provides a complete base set in the Schrödinger picture or commute with the operator one is seeking to follow a time evolution of in Heisenberg picture reduces to changes of phase. No effective physical change could be represented. External interactions are required to set evolution in action.

4.1.3. Interaction representation

Factors prompting for a time evolution can be isolated and make them act on a quantum state. This method is known as the interaction picture. For this picture, the Hamiltonian is expressed as a sum of a self-adjoint Hamiltonian $\hat{H}_o$ and an interaction operator $\hat{V}$. The base set usually comes from $\hat{H}_o$; it is an invariant part of the scheme, for some cases it is selected taking into account the simplifications it might introduce to calculate time evolution. For example, in Section 1.3.2 we used the notation $\hat{H}_o = \hat{H}'$. By now we know that the commutator $[\hat{H}_o, \hat{V}]$ must be different from zero operator; in other words, $\hat{V}$ is non-diagonal when it is represented in the complete base provided by $\hat{H}_o$. Then, theorem 1.3.2.1 should hold thereby leading to an effective time evolution. The time dependent $\hat{V}$-operator in the interaction picture is defined as in eq.(1.3.2.4), namely,

$$\hat{V}^{(I)}(t) = \exp(i\hat{H}_o t/\hbar)\,\hat{V}\,\exp(-i\hat{H}_o t/\hbar) \qquad (4.1.3.1)$$

We have not explicitly indicated time dependence for the $\hat{V}$-operator to alleviate notation. When t_o is different from zero, the base set for the interaction picture (representation) is given by: $|\Psi,t_o;t\rangle^{(I)} = \exp(+i\hat{H}_o(t-t_o)/\hbar)|\Psi,t_o;t\rangle$. This transformation permits extracting all relative time dependent phases:

$$|\Psi,t_o;t\rangle^{(I)} = \Sigma_k\, C_k^{(I)}(t)\, \exp(+i\, E_{ok}(t-t_o)/\hbar)\, |\phi_k^{(S)}\rangle.$$

The time evolution equation characterizing the state ket in the interaction picture is obtained after the time derivative of eq. (4.1.3.2):

$$i\hbar\, \partial|\Psi,t_o=0;t\rangle^{(I)}/\partial t = \hat{V}^{(I)}(t)\,|\Psi, t_o=0; t\rangle^{(I)} \quad (4.1.3.2)$$

Observe that this equation relates the quantum state $|\Psi,t_o=0;t\rangle^{(I)}$ in a self-consistent fashion. The quantum state is two-time mathematical object. It tells us that having prepared the quantum state at initial time the evolution is related to this origin at all times. Assuming the quantum state at time t is there then the new quantum state produced by the interaction starts from $\hat{V}^{(I)}(t)\,|\Psi, t_o=0; t\rangle^{(I)}$. Thus, the interaction operator controls the effective change of the quantum state. This differential equation can formally be integrated from the time you set up the experiment $t=t_o$ until time t:

$$|\Psi, t_o;t\rangle^{(I)} = |\Psi,t_o;t_o\rangle^{(I)} + (1/i\hbar)\int_{t_o}^{t} dt'\, \hat{V}^{(I)}(t')|\Psi,t_o;t'\rangle^{(I)}$$
$$(4.1.3.3)$$

The integration being made between t_o and t; note that $|\Psi,t_o;t_o>^{(I)}$ equals to $|\Psi,t_o>$ in the Schrödinger picture. It is then the interaction operator, which pushes the system to evolve in time. This result is the most important for our following the changes in the quantum state amplitudes.

The interaction operator $\hat{B}^{(I)}(t)$ corresponding to Schrödinger picture operator $\hat{B}$, fulfils the differential equation:

$$d \hat{B}^{(I)}(t) /dt = (1/ i\hbar) [\hat{B}^{(I)}(t), \hat{H}_o] \qquad (4.1.3.4)$$

In this picture, time dependent operators are driven by $\hat{H}_o$ while the *amplitudes* are being changed by $\hat{V}^{(I)}(t')$. The reference state, $|\Psi,t_o;t_o>^{(I)}$, is the initial Schrödinger quantum state. This latter is the one that can be prepared in the laboratory or at the Fence. The base states serving to represent the linear superposition are those coming from Schrödinger picture:

$$|\Psi,t_o;t>^{(I)} = \exp(+i \hat{H}_o t /\hbar)|\Psi,t_o;t>.$$

The exponential will pick out the time dependent phases for each base state that are solutions of:

$$\hat{H}_o(\hat{q}) \phi_k^{(S)}(\mathbf{q}) = E_{ok} \phi_k^{(S)}(\mathbf{q}) \qquad (4.1.3.5)$$

The base function $\phi_k^{(S)}(\mathbf{q})$ is the projection in configuration space of the abstract base ket $|k>$, solution to the formal equation: $\hat{H}_o|k> = E_{ok}|k>$.

The complete base set $\{|k>\}$ is, by hypothesis, robust and it is used to represent a ket state in the interaction picture:

$$|\Psi,t_o;t>^{(I)} = \Sigma_k C_k(\Psi,t) |k> \qquad (4.1.3.6)$$

The amplitudes are defined as usual by the mapping: $C_k(\Psi,t) = <k| \Psi,t_o;t>^{(I)}$. Introducing this linear superposition in eq. (4.1.3.3), after simple calculations one gets the differential equations for the amplitudes:

$$i\hbar \, \partial C_k(\Psi,t)/\partial t = \Sigma_m <k| \hat{V}^{(I)}(t)|m> C_m(\Psi,t) \qquad (4.1.3.7)$$

The matrix element $<k| \hat{V}^{(I)}(t)|m>$ are transition amplitudes that can be made explicit because we are using the base set of eigenfunctions of $\hat{H}_o$.

From the definition given in eq.(4.1.3.1), we assume that the operator $\hat{V}$ can have its own time dependence, to get: $<k| \exp(i \hat{H}_o t/\hbar) \hat{V}(t)\exp(-i \hat{H}_o t/\hbar)|m>$ that

equals $<k|\hat{V}(t)|m>\exp(i(E_{ok}-E_{om})t/\hbar)$. The differential equation with $<k|\hat{V}(t)|m>$ $=V_{km}(t)$ looks like:

$$i\hbar\ \partial\ C_k(\Psi,t)/\partial t =$$
$$\Sigma_m\ V_{km}(t)\ \exp(i(E_{ok}-E_{om})t/\hbar)\ C_m(\Psi,t) \quad (4.1.3.8)$$

The sub index k takes on the values 1,2,…, which makes this set to take the form of coupled differential equations. If we keep in abstract space albeit projected Eq. (4.1.3.8) must be represented by a (infinite) matrix equation:

$$i\hbar\ \partial_t\ [C_{k=0}(\Psi,t),\ C_{k=1}(\Psi,t),\dots\ C_k(\Psi,t),\dots] = \Sigma_m[V_{km}(t)\ ]$$
$$\times\ [C_{m=0}(\Psi,t),\ C_{m=1}(\Psi,t),\dots\ C_m(\Psi,t),\dots] \quad (4.1.3.9)$$

The symbol $[V_{km}(t)\ ]$ stands for a matrix of infinite dimensions including factors with the exponentials; this latter equation is another way to write eq. (4.1.3.8).

Now, coming to the Fence, in a laboratory experiment only a few amplitudes defining the specific quantum state are different from zero; this is a state you can prepare as initial state.

The quantum state vector then is usually reduced to a sum of non-zero initial terms. This finiteness may have some catastrophic consequences if you do not reckon with those base states that might develop non-zero amplitude during time evolution at the Fence. Why the Fence and not Hilbert space? A physical time evolution requires energy exchanges between the source of the perturbing potential (operator $\hat{V}(t)$) and the material system associated to $\hat{H}_o$ even if at the end of interaction time there is no finite energy exchange. In a mathematical space you do not exchange energy as no energy conservation principle makes sense there. At the Fence you have to pay the bills even if barter is the call.

4.1.4. Lippmann-Schwinger scheme

We are interested to calculate the quantum state starting from space projected states. The wave functions are given by:

$$\Psi(\mathbf{q},t)= \Psi(\mathbf{q},t_o) - (i/\hbar)\int_{to}^{t} dt'\ \int d\mathbf{q}'x$$
$$<\mathbf{q}|\hat{H}|\mathbf{q}'>\exp(i\hat{H}(\mathbf{q}')(t'-t_o)/\hbar)\ \Psi(\mathbf{q}',t_o) \quad (4.1.4.1)$$

In the interaction representation one gets:

$$\Psi^{(I)}(\mathbf{q},t) = \Psi^{(I)}(\mathbf{q},t_o) - (i/\hbar)\int d\mathbf{q}'\int_{to}^{t} dt'$$
$$\times\hat{V}^{(I)}(\mathbf{q},\mathbf{q}';t,t')\ \exp(i\hat{V}^{(I)}(\mathbf{q},\mathbf{q}',t,t'))\ \Psi^{(I)}(\mathbf{q}',t_o) \quad (4.1.4.2)$$

This is a generalized Lippmann-Schwinger equation relating the initial wave function to the wave function obtained after unitary time evolution in configuration space. This can be seen if one defined the operator $\hat{G}(\mathbf{q},\mathbf{q}';t,t_o)$ by:

$$\hat{G}(\mathbf{q},\mathbf{q}';t,t_o) = \hat{V}^{(I)}(\mathbf{q},\mathbf{q}') \exp(i\,\hat{V}^{(I)}((\mathbf{q},\mathbf{q}')(t-t_o)/\hbar)$$

$$(4.1.4.3)$$

The propagated wave function is cast in the form familiar to the quantum scattering theory:

$$\Psi^{(I)}(\mathbf{q},t) = \Psi^{(I)}(\mathbf{q},t_o)-$$
$$(i/\hbar)\int d\mathbf{q}' \int_{t_o}^{t} dt' \ \hat{G}(\mathbf{q},\mathbf{q}';t,t_o) \ \Psi^{(I)}(\mathbf{q}',t_o) \qquad (4.1.4.4)$$

The operator $\hat{G}(\mathbf{q},\mathbf{q}';t,t_o)$ generates new amplitudes via the interaction operator $\hat{V}^{(I)}(\mathbf{q},\mathbf{q}')$ in eq. (4.1.4.3).

Once the operator kernel $\hat{G}(\mathbf{q},\mathbf{q}';t,t_o)$ has been calculated or somehow modeled the integral equation opens a way to obtain the resultant wave function value in a neighborhood of the configuration space point $\mathbf{q}$.

If everything were, as it should, the procedure outlined above permits constructing the portrait of the quantum state for the system of interest at time t.

Remember that the wave function hides the linear superposition in the fixed base set related to $\hat{H}_o$ that may be more relevant to the process discussion.

4.1.5. Born and higher approximations

Let us underline the importance of amplitudes and their time evolution equations. The set $\{C_m(\Psi,t_o)\}$ is fixed after a specific preparation that in general produces a bunch of zeroes and a few non-zero amplitudes. In order to take advantage of the differential equation (4.1.3.8) we must integrate it as follows:

$$C_k(\Psi,t) = C_k(\Psi,t_o) - (i/\hbar) \int_{t_o}^{t} dt'$$
$$\Sigma_m \, V_{km}(t') \exp(i(E_{ok}- E_{om})t'/\hbar) \, C_m(\Psi,t') \qquad (4.1.5.1)$$

Iterating this equation once we get Born's approximation by stopping the series at terms linear in V:

$$C_k(\Psi,t) = C_k(\Psi,t_o) - (i/\hbar)\int_{t_o}^{t} dt'$$
$$\Sigma_m \, V_{km}(t') \exp(i(E_{ok}- E_{om})t'/\hbar) \, C_m(\Psi,t_o) \qquad (4.1.5.2)$$

One more step in the iteration of eq. (4.1.5.1) and simplifying the energy sub index leads to:

$$C_k(\Psi,t) = C_k(\Psi,t_o) - (i/\hbar)\int_{t_o}^{t} dt' \text{ x}$$
$$\Sigma_m \, V_{km}(t') \exp(i(E_k- E_m)t'/\hbar) \, C_m(\Psi,t_o) +$$

$$(i/\hbar)^2 \int_{to}^{t} dt' \int_{to}^{t'} dt'' \Sigma_m \Sigma_{m'} V_{km'}(t') V_{m'm}(t'')$$
$$\times \exp(i(E_k-E_{m'})t'/\hbar) \exp(i(E_{m'}-E_m)t''/\hbar) C_m(\Psi,t_o)+\dots$$
$$O(V^3) \quad (4.1.5.3)$$

Time evolution for these latter two cases always start from the initial state given by the set $\{C_m(\Psi,t_o)\}$. The operator $\hat{V}$ via its matrix elements V_{km} opens channels that might initially show zero amplitude.

In amplitude space we can see that only those base states having non-zero initial amplitude generate time evolution leading to non-zero amplitudes; we have arranged the dummy indexes so that the initial amplitudes are designated by $C_m(\Psi,t_o)$. Let us state it again, in Born approximation for base states that had zero amplitude at the beginning of the experiment it may be possible to find non-zero amplitude at a later time provided the transition amplitude, say, $V_{km}(t')$ relating initial state $C_m(\Psi,t_o)\neq0$ to a final state $C_k(\Psi,t)\neq0$ in spite of $C_k(\Psi,t_o)=0$.

It is worth emphasizing that the set of transition amplitudes $\{V_{km}(t')\}$ is a fixed property of the systems. The only thing that can change is the quantum state, namely, the amplitudes.

Factors contributing to time evolution for given amplitude relate to three different sources. First to the intrinsic coupling between the system of interest and the probe used. This is represented by $V_{km}(t)$. The second is the spectra of the system being probed. This is reflected in the exponentials $\exp(i(E_{ok}-E_{om})t/\hbar)$. The third signals the manner used to prepare the system via the selection of the initial quantum state: the set $\{C_m(\Psi,t=t_o)\}$. At a Fence, the system can be controlled via $V_{km}(t)$ that may contain the excitation frequency used to set the system in evolution.

From the physical point of view in order to produce a change of quantum state you have to ensure interaction of the initial state with $\hat{V}$; this is the key lesson to retain when laboratory setups are to be examined. As soon as the interaction becomes effective the new quantum state becomes a new linear superposition. How many new channels, or amplitudes that initially were zero, show non-zero amplitudes after interactions depend upon the matrix elements (V_{km}) involved. If this one is zero, second order effects may open the channel: $V_{kn} \times V_{nm}$ as one sum up over the complete spectrum will certainly pick up "intensity" as spectroscopists use to say. Remember the discussion of chemical processes in the first chapter.

4.2. Model systems of broader interest

Many I-frame systems show relative kinetic energy and diverse internal quantum states. Improved control of these degrees of freedom of ultracold neutral and ions

is an active field of research. Three cases are discussed here: 1) Systems of single or several trapped neutral atoms (molecules); 2) Systems of single and/or few trapped ions; 3) A trapped single ion in a Bose-Einstein condensate (Zipkes et al. Nature, 464 (2010) 388-391). Of special interest to us is a group corresponding to chemically reactants elements in gas phase that are related to a supermolecule (1-system).

Ashkin's book on Optical Trapping and Manipulations of Neutral Particles Using Lasers presents exhaustive analyses and relevants reprints. The reader has there an invaluable source. Duplicate this work is beyond the possibilities of the present writer. We focus on basic materials that might help those non-specialists to be able reading specialized work.

Multipartite systems whose total matter content corresponds to a 1-system are of broad interest; bi- and ter-molecuar chemical reactions are conspicuous examples. Each element of the multipartite (cluster) is independently referred to an I-frame because one can prepare them independently at a laboratory facility. The relative velocity, position and orientation are well-defined concepts in Special Relativity context. A one I-frame system is not commensurate to the many I-frame systems included the multipartite case; this is a problem requiring careful attention.

First we revisit the states of a material system in a box followed by a specific analysis of a two-state quantum system.

4.2.1. Particle-states and I-frames system in a box

Box particle-states are quantum mechanical concepts. Particles in a box for us correspond to collections of I-frame systems in confined 3-space.

In the laboratory, both concepts are required to describe the phenomenology. An I-frame system can be prepared locally. Assign to it a particular velocity $\mathbf{v}$ so that the classical state of motion is $M\mathbf{v}=\mathbf{P}$. To simplify the analysis, let us take the direction of $\mathbf{v}$ along the x-axis and ask for a quantum correlate. To fulfill this end let us study a 1-dimensional quantum system.

The base states are arranged in the row vector $(\exp(ik_x x) \quad \exp(-ik_x x))$ and an arbitrary quantum state is the linear superposition:

$$(\exp(ik_x x) \quad \exp(-ik_x x))\cdot[\ A\ \ B\ ].$$

This represents the quantum state:

$$\Psi_{A,B}(x) = A \exp(ik_x x) + B \exp(-ik_x x);$$
$$|A|^2 + |B|^2 =1 \qquad\qquad (4.2.11)$$

It is the set of complex numbers (A,B) that define the quantum state if the base vectors are kept fix.

The base state $\exp(ik_x x)$ stands for a plane wave displacing from left to right (from negative towards positive x-values). The base state $\exp(-ik_x x)$ is said to stand for a plane wave along the x-axis moving from positive towards negative values of the coordinate x.

What characterizes the base function is k_x. This number is invariant so that one will determine the same plane wave state whatever the value of the coordinate x. Displace the origin of the I-frame along axis y or z, the quantum state is always the same for this particular case. One can fix a (y,z)-plane and according to the preceding analysis the quantum state $A\exp(ik_x x)$ *is the same* over the whole surface perpendicual to the displacement direction of the plane wave.

Equation (4.6.3) is the generic solution to the quantum problem. In fact, it contains the solution to all possible problems you can imagine in this context. For each one of them, we have to fix the values of A and B that must fulfill the normalization condition.

Now, we have to ask for the problem we want to be solved. This belongs to laboratory level (Fence). We have no problems with quantum physics in real space.

At the Fence you master the I-frame system. It can be found or put anywhere. Is up to you. No quantum mechanics involved yet. Consider some examples to train our language skill.

-A: Prepare an I-frame system at point $x=-x_o$, velocity $\mathbf{v}_x$, momentum M $\mathbf{v}_x$ at time t_o.
 i) What is the quantum state before time t_o? Answer: [A B] = [0 0]. You have no quantum state before preparation. Of course the base set is still there!
 ii) What is the quantum state after time t_o? Answer: [A B] = [1 0]. You just prepared it.

-B: Prepare the I-frame system at point $x=+x_o$ with velocity $-\mathbf{v}_x$ and momentum $-M\mathbf{v}_x$ at time t_o.
 i) What is the quantum state before time t_o? Answer: [A B] = [0 0]. You have no quantum state before preparation. Albeit you still have the base set. Actually, we can call the quantum state [0 0] as the vacuum for this special system.
 ii) What is the quantum state right before time t' required for the I-frame to rebound at a wall located at $x=-x_o$? Answer: [A B] = [0 1].

 iii) What is the state after rebound? Answer: [A B] = [1 0].

-C: Take the system prepared as in 1) but now put a wall perpendicular to the x-axis at the origin (x=0). Thus, if we launch the I-frame system from the left it cannot be detected beyond the wall (to the right of it). Moreover, consider the plan perpendiculat to the x-axis and give a thought to the following statement: any neighborhood on the 2-D surface can be a possible place where the I-frame system may go through. When we say that the wave function is identical on any neighborhood of equal size on the 2-D surface the statement closes the quantum state description. This is a plane wave state.

The wall introduces a way to distinguish left from right. The base states are the same. But now we have to distinguish a quantum state to the left from another to the right. The amplitudes at the right are designated as (F, G):

$$\Psi_{(F,G)}(x) = F \exp(ik_x x) + G \exp(-ik_x x);$$
$$|F|^2 + |G|^2 = 1 \text{ for } x>0 \qquad (4.2.12)$$

Equation (4.2.11) is valid for x≤0 only.

The anisotropy induced by the wall does not affect the base set but only the quantum state. Observe that we are taking the system as a whole and the external constraints as generating possible different quantum states.

-i) What is the quantum state before the I-frame system comes to the origin? What do we have here is a classical system moving as the case 1)-i) and the quantum state should look as (1 0).

-ii) What is the quantum state when the I-frame system comes to the origin? The classical I-frame system rebounds at the wall leading to a momentum inversion. While the quantum system ought to suffer a transition from (1 0) to state (0 1). Here we have not specified location on a 2-D surface because this cannot be done.

The classical rebounding at the wall translates in Hilbert space as a transition changing the quantum state. The wall must be non-transparent.

In everyday world a rebound can be taken as an event, a change of the classic state of motion. In Hilbert space the event will be represented by a change of quantum state. It is no more complicated than this.

-D: Let us construct a box by putting walls at $+x_o$ and $-x_o$. Do the same along other directions. Here we analyze the 1-D case. The base functions are the same as above. Now we have boundary conditions at walls positions:

$$\Psi_{(A,B)}(x=+x_o) = A \exp(ik_x x_o) + B \exp(-ik_x x_o) =$$
$$0 - 0i \qquad (4.2.13a)$$
$$\Psi_{(A,B)}(x=-x_o) = A \exp(-ik_x x_o) + B \exp(ik_x x_o) \quad =$$
$$0 + 0i \qquad (4.2.13b)$$

The base function $\exp(ik_xx_o) = \cos(k_xx_o) + i\sin(k_xx_o)$ cannot be simultaneously zero, together with the fact that both $\Psi_{(A,B)}(x=-x_o)$ and $\Psi_{(A,B)}(x=+x_o)$ must be zero, the sum $A(\exp(ik_xx_o) + \exp(-ik_xx_o))$ must also be zero; the same happens to $B((\exp(ik_xx_o) + \exp(-ik_xx_o))$. Two solutions for this constraints are obtained by taking $k_xx_o = n_x\pi/2$ with the integer n_x odd one gets $\cos(n_x\pi/2)$ equals to zero and $B\neq0$, or n_x even and $A\neq0$. The solutions look like:

$$\Psi_{n(odd)}(x) = A\ \{\exp(i\ n_x\pi x/2x_o) + \exp(-in_x\pi x/2x_o)\} \rightarrow$$
$$A'\ \cos(n_x\pi x/2x_o) \qquad (4.2.1.4a)$$

$$\Psi_{n(even)}(x) = B\ \{\exp(i\ n_x\pi x/2x_o) - \exp(-in_x\pi x/2x_o)\} \rightarrow$$
$$B'\ \sin(n_x\pi x/2x_o) \qquad (4.2.1.4b)$$

The energy levels associated to these states are given by $p_x=\hbar k_x$ with kinetic energy:

$$E= (1/2M)\ p_x^2=(1/2M)(\hbar k_x)^2=(1/2M)\ (\hbar n_x\pi/2x_o)^2 =$$
$$(\pi^2\hbar^2 n_x^2/8Mx_o^2) = E_{nx} \qquad (4.2.1.5)$$

The functions found in equations (4.2.4) correspond to eigen functions for this system. Thus, to each eigen function corresponds a quantized energy level E_n.

The boundary conditions allowing for a cubic box, namely $L=2x_o=2y_o=2z_o$, lead to a quantization of the space therein included. For a set of quantum numbers (n_x, n_y, n_z) the energy level is given by:

$$E(n_x, n_y, n_z) = (\pi^2\hbar^2/2ML^2)\ (n_x^2+ n_y^2+ n_z^2) \qquad (4.2.1.6)$$

For a rectangular box you can see that the energy level is given by:
$$(\pi^2\hbar^2/2M)^{-1}\ E(n_x, n_y, n_z) =$$
$$((n_x/L_x)^2+(n_y/L_y)^2+ (n_z/L_z)^2) \qquad (4.2.1.7)$$

The base state associated to energy eq.(4.2.7) $\Psi(n_x, n_y, n_z) = \zeta_{nx}(x)\ \zeta_{ny}(y)\ \zeta_{nz}(z)$. And the base functions read: $\zeta_{nx}(x) = (1/\sqrt{L_x})\ \exp(in_x\pi x/L_x)$, etc.

Let us consider a cubic box, namely, $L_x = L_y = L_z = L$. Eq.(4.2.1.7) can be cast in terms of box (L) and material (M) parameters:

$$E(n_x, n_y, n_z)/ (\pi^2\hbar^2/2ML^2) =$$
$$((n_x)^2+ (n_y)^2+ (n_z)^2) = R^2 \qquad (4.2.1.8)$$

For large R we can *treat* this parameter and the energy E as continuous variables and restricting to positive integers, the number of states in one octant would

correspond to 1/8 of the volume $4\pi R^3/3$. This is taken to be the number of states N(E), namely,

$$N(E) = (1/8) \, 4\pi R^3/3 = (1/8)(4\pi/3) \, (2ML^2 \, E/\pi^2 \, \hbar^2)^{3/2} =$$
$$(\pi/6)(8ML^2E/h^2)^{3/2} \qquad\qquad (4.2.1.9)$$

The *density of states* $\rho(E,\delta E) = N(E+\delta E) - N(E)$ gives the equation:

$$\rho(E,\delta E) = (\pi/4)(8ML^2/\hbar^2)^{3/2} \, E^{1/2} \, \delta E \quad =$$
$$(\pi/4) \, (8M/\hbar^2)^{3/2} \, V \, E^{1/2} \, \delta E \qquad\qquad (4.2.1.10)$$

The density of states depends upon the volume $V=L^3$ and a function of the mass $M^{3/2}$ and note that Planck's constant h appears in the denominator. One would then expect a pretty large number of states for example for an electron in the box. Observe that we are talking about base states sustained by the system. The energy corresponds to kinetic energy accessible to the global I-frame system.

The materiality of the system expresses itself via the parameter M leading to particular densities of states. The only physical condition is that of presence within the volume V. It is irrelevant to localize the material system at any place in this volume. If there is no material system in V the formulae above are irrelevant.

The I-frame system in a cubic (rectangular) box shows a quantization of the **k**-vector induced by the confinement. The quality of Hilbert space would then depend upon external parameters for confined systems. This is an important result for Fence systems. This opens the possibility for control of such systems.

More detailed analyses will be taken up in the following to relate these situations with the general (Fourier) continuum basis set employed in Sect.(3.2).

The analyses presented above implicitly assume a kind of particle model. The reason explaining the model is due to the total oversight of an attempt at constructing a representation of quantum states. The standard method used is adapted to statistical aspects of I-frame collections. Now, let us turn to study quantum states for one I-frame system trapped in a cubic box of length L.

One I-frame system containing a mass M associates to the energy levels: $E_{nx} = (\pi^2 \, \hbar^2 n_x^2/8ML^2)$. The set $\{\Psi(n_x, n_y, n_z)\}$ or more simple $\{\zeta_{n1}(x_1) \, \zeta_{n2}(x_2) \, \zeta_{n3}(x_3)\}$ are base states. A generic quantum state along direction x_1 looks like:

$$\Psi_{A,B}(x_1) = A \, \exp(ik_1x_1) + B \, \exp(-ik_1x_1) \qquad (4.2.1.11)$$

Information carried out by an I-frame in so far mass and angular momentum are concerned has a bearing on a classical world description. However, focus on quantum aspects shift the description towards quantum states and associated basis states. The eigen values of the material system in a box incorporate input on box-length (L) and mass (M). The magnitude $(\hbar/2M)k^2$ corresponds to kinetic energy

and $\hbar\mathbf{k}$ stands for linear momentum. This information is included in $\exp(ik_1x_1)$ that is a basis function.

The quantum number k_1 is at disposal to simulate situations at the Fence. The statement: *a quantum state is sustained by a material system*, means that we loose detailed contact with the materiality in the sense used in classical dynamics. Of course, if no material system is left or trapped in the box then there is way to introduce the quantized magnitudes. In the quantum world what counts are the ways one can prepare and modify quantum states.

At the Fence, besides box states there are internal quantum states. Yes, even a proton displays a quantum mechanical structure. But this issue is left out as it is now.

4.2.2. Several I-frame systems

Consider now the material system constituted for example by 2 independent hydrogen atoms and consequently from the perspective of a classical world there are two I-frames.

In the preparation phase it is useful to use classical mechanics quantities but once we come to examine quantum mechanical behavior obviously leave outside classical physics descriptive elements. Once the material systems are trapped at cold and ultracold conditions the quantum physics description is the only one adequate.

Hydrogen atoms are composite bosons. The total spin angular momentum, $J=I+S$, can be zero or one. There then 4 internal spin base states for each H-atom. Base functions in projected quantum states are label with energy eigenvalues.

An arbitrary base function would look like $\Phi_{(n1,n'1)}(x_{11}, x_{12})$; label permutation leads to $\Phi_{(n'1,n1)}(x_{11},x_{12})$ that is identical to the non-permuted one. The case where both labels are identical reads: $\Phi_{(n'1,n'1)}(x_{11}, x_{12})$.

A base function of lowest energy is given by: $\Phi_{(01,01)}(x_{11}, x_{12})$. Thus, for n-bosons the base state of lowest energy reads: $\Phi_{(01,\ldots,01)}(x_{11},\ldots,x_{1n})$. This is a pure quantum state.

The process leading from an n-aggregate to (n+1)-aggregate is called a Bose-Einstein condensation (BEC):

$$\Phi_{(01,\ldots,01)}(x_{11},\ldots,x_{1n})\Phi_{(01)}(x_{1(n+1)}) \rightarrow$$
$$\Phi_{(01,\ldots,01,01)}(x_{11},\ldots,x_{1n},x_{1(n+1)}) \qquad (4.2.1)$$

It is a sepwise passage from simple product base function to a non-separable base function. The stepwise change can be described with a quantum state:

$$\Psi(x_{11},\ldots,x_{1n},x_{1(n+1)}) =$$

$$C_n \; \Phi_{(01,\ldots,01)}(x_{11},\ldots,x_{1n})\Phi_{(01)}(x_{1(n+1)}) \; +$$
$$C_{n+1} \; \Phi_{(01,\ldots,01,01)}(\; x_{11},\ldots,x_{1n},x_{1(n+1)}) \qquad\qquad (4.2.2)$$

Because the base functions given in (4.2.1) belong to Hilbert space one can construct a meaningful linear superposition eq.(4.2.2). We can move backwards to find out the direct product $\Phi_{(01)}(x_{11}) \; \Phi_{(01)}(x_{12})\ldots \; \Phi_{(01)}(x_{1n}) \; \Phi_{(01)}(x_{1(n+1)})$. This base state stands for the unentangled set sustained by n+1 material systems. We write the linear superposition as follows:

$$\Psi(\; x_{11},\ldots,x_{1n},x_{1(n+1)}) =$$
$$C_1 \; \Phi_{(01)}(x_{11}) \; \Phi_{(01)}(x_{12})\ldots \; \Phi_{(01)}(x_{1n}) \; \Phi_{(01)}(x_{1(n+1)}) \; +$$
$$C_2 \; \Phi_{(01,01)}(x_{11}, \; x_{12})\ldots \; \Phi_{(01)}(x_{1n}) \; \Phi_{(01)}(x_{1(n+1)}) \; +\ldots+$$
$$C_n \; \Phi_{(01,\ldots,01)}(x_{11},\ldots,x_{1n})\Phi_{(01)}(x_{1(n+1)}) \; +$$
$$C_{n+1} \; \Phi_{(01,\ldots,01,01)}(\; x_{11},\ldots,x_{1n},x_{1(n+1)}) \qquad\qquad (4.2.3)$$

The column vector $(C_1, C_2,\ldots, C_n, C_{n+1})^t$ characterizes a quantum state in the progressive basis set starting with no-entanglement ending at full one.

The quantum state $(1,0,\ldots,0,0)^t$ stands for an aggregate of bosons totally uncorrelated. The quantum state $(0,0,\ldots,0,1)^t$ stands for a fully entangled material system made of n+1 bosons. This state represents a BEC.

As you might have already noticed, the configuration space is referred to one I-frame only. The material system must certainly be there inside the trapp volume but besides this datum the quantum physical description is not concerned with the "particles". This point is worth emphasizing. We leave now this aspect and move on to examine specific model systems.

4.2.3. Two-state model

Consider a system with two base states, |a> and |b>, fulfilling the eigenvalue equations related to (4.1.1.9) for which $|E_1>=|a>$ and $|E_2>= |b>$ so that the Hamiltonian is:

$$\hat{H} = |E_1> E_1 <E_1| + |E_2> E_2 <E_2| \qquad\qquad (4.2.3.1)$$

The total energy $E = E_1+E_2$ is a conserved quantity as well as the energy difference $\hbar\Delta= E_1-E_2$. In terms of these new parameters one can write:

$$E^+ = (E_1+ E_2)/2 \text{ and } E^- = (E_1-E_2)/2 = \hbar\Delta/2.$$

Take Δ in frequency units and Planck constant as energy by time.

To reduce the two-state problem to a generic case, namely, one defined in terms of E^+ playing the role of energy origin and Δ, the old in terms of new labels and $\hbar=1$ read:

$$E_1 = E^+ + \Delta/2 \text{ and } E_2 = E^+ - \Delta/2.$$

Take now as energy origin E^+ and the new base state labels read: $|-\Delta/2>$ and $|+\Delta/2>$. Thus, there are to base states $|+>$ and $|->$ whenever we use the relative energy variables. A generic quantum state $|\Psi>$ is given by the linear superposition:

$$
\begin{aligned}
|\Psi> &= \hat{1}|\Psi> = (|-\Delta/2> <-\Delta/2| + |+\Delta/2> <+\Delta/2|) |\Psi> = \\
&(|-\Delta/2> <-\Delta/2|\Psi> + |+\Delta/2> <+\Delta/2|\Psi>) = \\
&|-\Delta/2> C_- + |+\Delta/2> C_+ \rightarrow \\
&(|-> \quad |+>) [C_- \ C_+]
\end{aligned}
\qquad (4.2.3.2)
$$

A row vector represents the base set, the quantum state (amplitudes) by a column vector. The amplitudes are normalized as usual: $|C_-|^2 + |C_+|^2 = 1$.

Take a state prepared as follows: $[C_-=1 \quad C_+=0]$. With the Hamiltonian (4.2.3.1) you can easily show that this state stay put; no time evolution.

The model permits studying interactions with external sources that can drive changes of quantum states. As we already know, the external coupling operator $\hat{V}^{(I)}(t)$ must have non-zero transition matrix element: $<-|\hat{V}^{(I)}(t)|+>$. The Hamiltonian corresponds to an open system; the interaction source is assumed to provide or withdraw energy during the dynamics. Thus the model is semi-classical to the extent an external source provides with an external potential but it is not included at the same level of theory.

The Hamiltonian reads now:

$$
\begin{aligned}
\hat{H}_{opn} &= \hat{H} + \hat{V} = \\
&\{|-> (-\Delta/2)<-| \} + \{|+> (\Delta/2) <+| \} + \{V_\mp(t)|-><+| + \\
&\qquad V_\pm(t)|+><-| \} = \\
&\Delta/2 \{ |+><+| - |-><-| \} + \{V_\mp(t) |-><+| + \\
&\qquad V_\pm(t) |+><-| \}
\end{aligned}
\qquad (4.2.3.3)
$$

The operator $|-><+|$ and its transpose complex conjugate are transition operators relating the two energy levels. In the context of Born scheme, eq.(4.1.5.2) simplifies because we take the case $C_+(\Psi,t_o)=0$ and $C_-(\Psi,t_o)=1$ to get:

$$C_+(\Psi,t) = -(i)\int_{to}^{t} dt' V_\pm(t')\exp(i\Delta t')C_-(\Psi,t_o) \qquad (4.2.3.4)$$

There are two interesting cases sharing the form: $V_\pm(t) = V_\pm \cos(\nu t)$.

Case 1: $\nu = 0$, time independent;   (4.2.3.5a)
Case 2: $2 \cos(\nu t) = \exp(i \nu t) + \exp(-i \nu t)$.   (4.2.3.5b)

Integration for Case 1 is simple:

$C_+(\Psi, t) = - (i) V_\pm \int_{to}^{t} dt' \exp(i\Delta t') =$
$-(i) V_\pm (\exp(i\Delta t) - 1)/(i\Delta) =$
- $-(i)V_\pm (\exp(i\Delta t/2) \sin(\Delta t)/2)/(\Delta /2)$ (4.2.3.6)

- The coupling with the external source generates a time-dependent linear superposition.
- The response in relative intensity from base state $|+>$ originated by interaction with base state $|->$ is then $I_{\rightarrow+}(t-t_o) = |C_+(\Psi,t)|^2$. Thus results in the standard formula obtains by re-introducing Planck constant explicitly in the amplitude only to get contact with standard notations:

-

$$| C_+(\Psi, t)|^2 = (|V_\pm|^2/\hbar^2) \sin^2(t \Delta)/2)/(\Delta/2)^2$$ (4.2.3.7)

In order to analyze $| C_+(\Psi,(t)|^2$ we introduce some auxiliary functions. First, the time elapsed $t-t_o$ is made equal to T and replace Δ by a variable energy E. Define the function $g_T(E)$:

$$g_T(E) = T^2 \sin^2 (T E/2\hbar)/(T E/2\hbar)^2$$ (4.2.3.8)

Note that when the dimension of $V_\pm$ is energy, $| C_+(\Psi,(t)|^2$ has dimension of inverse of time (T^{-2}). For the specific case above we have $E = \hbar\Delta$ that can be taken now as a variable in (4.2.3.8). The principal characteristics of $g_T(E)$ are: i) at E=0 the function has a maximum; ii) the half-width is of the order $2\pi\hbar/T$; iii) its surface (integral) is proportional to T:

$$\int_{-\infty}^{\infty} dE \ g_T(E) = 2\pi\hbar T$$ (4.2.3.9)

The function $g_T(E)$ with energy and T fixed has nodes symmetrically distributed to the right and left of its maximum value at E=0 corresponding to two degenerate energy levels case. The amplitudes in between nodes are negligible. Now, for parametric values of E, $g_T(E)$ as a function of T presents three regimes. For low energy, the function increases with T; at intermediate energies, $g_T(E)$ increases, get at a maximum and thereafter decreases; finally, at higher energies, the function shows recurrences, namely, go to a maximum, decreases to attain a zero value and again increases, etc.

The function $g_T(E)$ can be normalized with the integral (4.2.3.9) as follows:

$$\delta_T(E) = g_T(E) /(2\pi \hbar T) =$$
$$\sin^2 (T E/\hbar 2)/(\pi T E^2) \qquad\qquad (4.2.3.10)$$

Taking the limit $T\to\infty$ on $\delta_T(E)$ one gets $\delta(E)$, Dirac's function.

In this framework, the response intensity $I_{\to+}(T)$ is given by:

$$I_{\to+}(T) = T (2\pi/\hbar)|V_\pm|^2 \, \delta_T(E_+ - E_-) \qquad\qquad (4.2.3.11)$$

The term $\pi\hbar/T$ has the dimension of energy; it is a *bound to the energy brought by the external source*. The energy range $E_- \pm \pi\hbar/T$ must include E_+ in order to get non-zero amplitude $C_+(T)$ thereby leading to the inequality:

$$E_- - \pi\hbar/T < E_+ < E_- + \pi\hbar/T \qquad\qquad (4.2.3.12)$$

The energy pulse from the external source must pay for energy conservation. The connected (initial and final) energy levels must be equal to within $2\pi\hbar/T$.

Note that $\partial I_{\to+}(T)/\partial T$ becomes time independent and equals to $(2\pi/\hbar)|V_\pm|^2$ multiplied by the energy conserving factor $\delta_T(E_+ - E_-)$. This derivative basically stands for the cross section for the scattering process.

If we had chosen the case where there is a dense set of energy levels about E_+ in a neighborhood of E_-, the inequality above holds. The half-width of the distribution involved in the interaction δE would approximately equal to $\hbar/2T$ thereby leading to the relationship:

$$\delta E \, T \sim \hbar/2 \qquad\qquad (4.2.3.13)$$

This is a typical relationship at a Fence that we have qualitatively gleaned. It involves an internal property (I-frame one) with an external world factor.

Analysis of Case 2: $\cos(\nu t) = (1/2)(\exp(i\,\nu t) + \exp(-i\,\nu t))$, leads to the result:

$$C_+(\Psi,t) = -(i/\hbar) V_\pm \int_{to}^{t} dt' \, (\exp(i\,\nu t') + \exp(-i\,\nu t'))$$
$$\times \exp(i\Delta t') = -(i/2\hbar) V_\pm \{\exp(i(\nu+\Delta)t)/i(\nu+\Delta)$$
$$+ \exp(i(-\nu+\Delta)t)/i(\Delta-\nu)\} \qquad\qquad (4.2.3.14)$$

The frequency ν is controlled in the laboratory; it can take those values we deem of interest. The 2-state system has an energy gap determined by the material used to construct it; but once chosen it remains a datum of the problem. The denominators $(\nu+\Delta)$ and $(\nu-\Delta)$ (in frequency units) can be modulated with the external field so that $(\nu-\Delta)$ can be made very small while $(\nu+\Delta)$ would be by necessity much larger than the difference. It is a common model, named the

rotating-wave approximation, that retains the term near resonance thereby neglecting the $(\nu+\Delta)$-term.

The relative intensity at $|+>$ in the rotating-wave approximation reads now:

$$|C_+(\Psi,t)|^2 = (|V_\pm|^2/4\hbar^2)\sin^2(\Delta-\nu)\,t)/2)\,/$$
$$\times\{(\Delta-\nu)^2/4\} \qquad (4.2.3.15)$$

If quasi resonance conditions are fulfilled, then $\sin^2(\Delta-\nu)\,t)/2)/\{(\Delta-\nu)^2/4\}$ is a generalized function corresponding to Dirac function in the limit $(\Delta-\nu)$ going to zero.

In other words, when the external field provides enough energy, the amplitude at $|+>$ becomes finite albeit time dependent.

It remains to dig up the structure of $V_\pm$. In the dipole model, $V_\pm = -\mu_\pm\,|E_o|\cos(\nu t)$. Here, $\mu_\pm$ is the transition dipole moment between the base states; $|E_o|$ is the amplitude of the electric field in the direction of the transition dipole.

Thus, $(|V_\pm|^2/4\hbar^2)$ in eq.(4.1.6.15) becomes $(|\mu_\pm E_o|^2/2\hbar)^2$. And,

$$|C_+(\Psi,t)|^2 = |\mu_\pm\,E_o/2\hbar|^2$$
$$\sin^2(\Delta-\nu)t)/2)/\{(\Delta-\nu)^2/4\} \qquad (4.2.3.16)$$

This equation is valid at times not far from the initial one.

$$C_+(\Psi,t) = -(i/2\hbar)\,V_\pm\{\exp(i(\nu+\Delta)t)/i(\nu+\Delta)+$$
$$\exp(i(-\nu+\Delta)t)/i(\Delta-\nu)\} \qquad (4.2.3.17)$$

All elements presented here will be used later on when handling specific physical cases. The two-state model is pervasive.

However, this type of semi-classic approach misses the representation of the source. For some important cases the source cannot be neglected. In the following chapter a simple model is examined. Here we continue presenting some important model systems.

4.3. Density matrix at a Fence

The formalism presented in section 2.3 was just quantum mechanics in another guise. This is true for a 1-system. We take advantage of eq. (4.2.3.2) to give the form of this operator for the two-state case:

$$|\Psi> <\Psi| = [C_- \; C_+]^t\,\{(|-> \; |+>)\otimes(<-| \; <+|)\}\,[C_- \; C_+]$$

The term in curly brackets do direct products of base vectors form a 2x2 matrix.

$$\{(|-> \quad |+>) \otimes (<-| \quad <+|)\} = \begin{bmatrix} |-\rangle\langle-| & |-\rangle\langle+| \\ |+\rangle\langle-| & |+\rangle\langle+| \end{bmatrix}$$

The density matrix is given by:

$$|\Psi> <\Psi| = [C^*_- \quad C^*_+]^t \begin{bmatrix} |-\rangle\langle-| & |-\rangle\langle+| \\ |+\rangle\langle-| & |+\rangle\langle+| \end{bmatrix} [C_- \quad C_+]$$

The transition amplitude $<+|\Psi> <\Psi|->$ is just given by the product $C_+^* C_-$.

Extension to an ensemble of N non-interacting copies each one in the same quantum state does not put a problem so long the "ideal gas" keeps it ideal. Because this is a model, no problems arise to speak of concentrations as we did for the chemical reaction model.

There is another way widely used in the literature. This consists of a particle (object) model. In this case, each member of the ensemble is assumed to be a 1-system with only one non-zero amplitude: each 1-system appears to be in a base state. Let N_k be the number of elements in the ensemble that have the special quantum state reduced to one non-zero amplitude. In the limit $N\rightarrow\infty$ it is claimed that $|C_k|^2 = N_k/N$. The constraint being:

$$\Sigma_k N_k/N = 1 \tag{4.3.1}$$

Thus, one can speak of the probability to find one member of the ensemble in k-th state to be $|C_k|^2 \rightarrow N_k/N$. This mapping is important.

The passage from the coherent superposition (row vector with more that one amplitude different from zero) to the vector with only one component different from zero in a representation where one forgets the dimension of the base so that a simple component remains. This way of reporting a process has received the name of *collapse of the wave function*. It is certainly not a quantum process.

At the Fence, this density matrix is useful when counting events that are translated to a frequency representation of probability. In this case, the definition is operationally modified.

It is interesting to see that a chemist isolating the products in pure form would be actually executing a sort of collapse of the wave function. It is obvious that such process cannot be described in the framework of the present theory. Yet, some elements permitting a more subtle understanding are given by quantum mechanics at the Fence where space-time I-frames are required.

4.4. External potentials: Fence models

A number of material systems when subjected to specific interactions with surrounding media may show specific quantum states. One way to construct base states is via external potentials that depend upon configuration space relevant to the given system. Once again, one should then get either algebraic or differential equations leading to the desired result. Here, some cases are examined. First will be the harmonic oscillator.

4.4.1. Harmonic oscillator

The Hamiltonian of an I-frame system having mass M at the origin in free real space is the kinetic energy operator: $\hat{H}_{free} = \hat{K} = (1/2M)\hat{P}^2$. In coordinate space:

$$\hat{P} = -i\hbar\nabla = -i\hbar\ (\partial/\partial x, \partial/\partial y, \partial/\partial z) \text{ and}$$
$$\hat{K} = -(\hbar^2/2M)\nabla^2. \qquad (4.4.1.1)$$

The reference system is independent from the I-frame internal configuration space frame.

   The spin state of the I-frame system can also be specified. Let it be named by the eigen values of the operators $\hat{S}^2$ and $\hat{S}_z$, namely, $|S,M_S>$. Spin degrees of freedom are at this point taken as constants including the quantum state of the "internal" I-frame at least in so far the search of base sets is concerned.

   Introduce now the potential energy function $V(\mathbf{r}) = (M\omega^2/2)\mathbf{r}^2$. The total Hamiltonian is given by the sum of these two terms:

$$\hat{H}_{ho} = \hat{K} + V(\hat{r}) = -(\hbar^2/2M)\nabla^2 + V(\hat{r}) =$$
$$(1/2M)\hat{P}^2 + (M\omega^2/2)\ \hat{r}^2 \qquad (4.4.1.2a)$$

This is a model for a spherical symmetric harmonic oscillator. Observe that there is no particle model involved. The system is characterized besides the mass M by an angular frequency ω. Our task is to construct the base functions and energy eigen values in the configuration space where **r** is the vector signaling a point in real space. In the coordinate representation we have: $\hat{r}|\mathbf{r}> = \mathbf{r}|\mathbf{r}>$.

      From the general invariance properties we know that a base state cannot be label with position and momentum eigen values in a simultaneous fashion. The canonical operators do not commute: $[\hat{r}, \hat{P}] = i\hbar$.

Condition the Hamiltonian by diving the expression by $\hbar\omega$. This is the energy unit related to the oscillator frequency: $\hat{H}_{ho}/\hbar\omega$.

$$\hat{H}_{ho}/\hbar\omega = (1/2M\hbar\omega)\,\hat{P}^2 + (M\omega/2\hbar)\,\hat{r}^2 \qquad (4.4.1.2b)$$

The Hamiltonian is measured in units of the energy quantum $\hbar\omega$. Base states for such operator can hence be label in terms of the number of quanta, say n: |n>. We need a transformation of variables to get at the Hamiltonian acting on this space named Fock space.

E&E-4.4.1-1 Construct a dimensionless Hamiltonian

Observe that the coefficients defining the Hamiltonian contains all information there is concerning the harmonic oscillator; mass and frequency. The number of quanta is the degree of freedom at disposal. This is a number, no dimensions. So, search a dimensionless set of operators:

$$\hat{p} = (1/2M\hbar\omega)^{1/2}\,\hat{P}$$
$$\hat{Q} = (M\omega/2\hbar)^{1/2}\,\hat{r} \qquad (4.4.1.3)$$

The dimension of $(1/M\hbar\omega)$ is a square of inverse momentum and $(M\omega/\hbar)$ has dimension inverse square distance. Therefore, $\hat{p}$ and $\hat{Q}$ are dimensionless. The commutation relationship reads now:

$$[\hat{Q},\hat{p}] = 1 \qquad (4.4.1.4)$$

The dimensionless Hamiltonian reads:

$$\hat{H}_{ho}/\hbar\omega = (1/2)\,(\hat{p}^2 + \hat{Q}^2). \qquad (4.4.1.5)$$

E&E-4.4.1-2 Construct a Fock Hamiltonian

The operator must act on the space generated by base vectors {|n>} where n is the number of energy quanta. Following a pattern similar to angular momentum ladder operators define:

$$\hat{a} = (\hat{Q}+i\hat{p})/\surd 2 \; ; \; \hat{a}^\dagger = (\hat{Q}-i\hat{p})/\surd 2 \qquad (4.4.1.6)$$

Use the Hamiltonian eq. (4.4.1.5) to get with the help of eq.(4.4.1.6) the operator:

$$\hat{H}_{ho}/\hbar\omega = (1/2)\,(\hat{a}\,\hat{a}^\dagger + \hat{a}^\dagger\,\hat{a})$$

Using now the commutation relations derived from eq.(4.6.1.4) and (4.6.1.6), namely,

$$[\hat{a},\hat{a}^\dagger] = 1 \qquad (4.4.1.7)$$

The Hamiltonian is cast in terms of creation ($\hat{a}^\dagger$) and annihilation ($\hat{a}$) operators:

$$\hat{H}_{ho}/\hbar\omega = \hat{a}\,\hat{a}^\dagger - 1/2 \qquad (4.4.1.8)$$

By using commutation relationship one gets:

$$\hat{H}_{ho}/\hbar\omega = \hat{a}^\dagger\,\hat{a} + 1/2 \qquad (4.4.1.9)$$

These operators are defined in Fock space by:

$$\hat{a}^\dagger \ |n> \ \propto \ |n+1> \ \text{and} \ \hat{a} \ |n> \ \propto \ |n-1>$$

The base vectors $\{|n>\}$ with $n=1,2,\ldots$ span Fock space. The argument indicates the number of excitations involved in energy exchange between the electromagnetic field and matter. The base vector, for a given frequency is the column $[|0>, |1>,\ldots|n>,\ldots]$ where we have added the base state for zero available excitation $|0>$. A process for which the quantum state goes from $(0,\ldots,0_{n-1},1_n,0_{n+1},\ldots)$ to $(0,\ldots,1_{n-1},0_n,0_{n+1},\ldots)$ signals the loss of one excitation from the EM-field; while $(0,\ldots,0_{n-1},1_n,0_{n+1},\ldots)$ to $(0,\ldots,0_{n-1},0_n,1_{n+1},\ldots)$ signals the emission of a photon into the EM field. See preceding chapter and Chpt.6.

The absence of negative energy eigen values implies the lowest energy state, $|0>$, to fulfill the relation:

$$\hat{a} \ |0> \ = 0 \qquad\qquad\qquad (4.4.1.10)$$

This condition has a fundamental meaning as the absence of negative norm base states:

$$<n| \ \hat{a}^\dagger \ \hat{a} \ |n> \ = \ | \ \hat{a} \ |n>|^2 \geq 0 \qquad\qquad\qquad (4.4.1.11)$$

The operator $\hat{a}^\dagger \ \hat{a}$ in eq.(4.4.1.9) is named as number operator $\hat{N}$. The commutation rules are:

$$[\hat{N},\hat{a}^\dagger] = \hat{a}^\dagger \ ; \ [\hat{N},\hat{a}] = - \ \hat{a} \qquad\qquad\qquad (4.4.1.12)$$

E&E-4.4. Derive the above relationships

Let us construct the commutation relationships between $\hat{N}$, $\hat{a}$ and $\hat{a}^\dagger$. To obtain these relationships we need the operator identity, $[\ \hat{X} \ \hat{Y},\hat{Z}] = \hat{X}[\ \hat{Y},\hat{Z}] + [\ \hat{X},\hat{Z}]\hat{Y}$.

Use them to work the commutation relations by replacing $\hat{N} = \hat{X} \ \hat{Y} = \hat{a}^\dagger \ \hat{a}$, $\hat{a} = \hat{Y}$, $\hat{a}^\dagger = \hat{X}$ and $\hat{Z}$ can be taken to be either $\hat{a}^\dagger$ or $\hat{a}$:

$$[\hat{N},\hat{a}^\dagger] = \hat{a}^\dagger[\hat{a},\hat{a}^\dagger] + [\hat{a}^\dagger,\hat{a}^\dagger] \ \hat{a} = \hat{a}^\dagger .$$

Take $\hat{Z}$ equal to $\hat{a}$:

$$[\hat{N},\hat{a}] = \hat{a}^\dagger[\hat{a},\hat{a}] + [\hat{a}^\dagger,\hat{a}] \ \hat{a} = - \ \hat{a}$$

These are the equations appearing in (4.4.1.12).

The spectrum of the harmonic oscillator can be obtained from the above commutation relations. Assume that $\hat{N}|n> = n \ |n>$ and $<n|n> \neq 0$. With this definition examine the effect of $\hat{a}$ on a base vector $|n>$. Because $\hat{N}$ picks up the

number of excitations on a particular base vector we calculate $\hat{N}\,\hat{a}|n>$ with the help of the commutator $[\,\hat{N},\hat{a}\,] =-\,\hat{a}$:

$$\hat{N}\,\hat{a}|n> =(\hat{N}\,\hat{a})\,|n> = (\hat{a}\,\hat{N} - \hat{a})\,|n> =$$

$$\hat{a}\,\hat{N}|n> - \hat{a}\,|n> = \hat{a}n|n> - \hat{a}\,|n> =$$

$$(n-1)\,\hat{a}|n> \qquad\qquad (4.4.1.13)$$

Comparing the first and last terms then $\hat{a}|n> = \sqrt{n}\,|n-1>$. Following a similar pattern one gets

$$\hat{a}^{\dagger}\,|n> = \sqrt{(n+1)}\,|n+1> \qquad\qquad (4.4.1.14)$$

The product $\hat{a}^{\dagger}\,\hat{a}|n> = \sqrt{n}\,\hat{a}^{\dagger}\,|n-1> = \sqrt{n}\sqrt{(n+1-1)}\,|n+1-1> = n\,|n> = \hat{N}|n>$ closing the relation between the number operator. It is not difficult to see that

$$|n> = (1/\sqrt{n!})\,(\hat{a}^{\dagger})^{n}\,|0> \; ; <n|n> = 1 \qquad (4.4.1.15)$$

The interesting point is that the base functions can be generated with the help of adequate operators. Such procedures will be used several times in future applications. Now we go back to the real space representation.

The algebraic procedure permits solving an important part of the problem, namely, the construction of a base set, $\{|n>\}$. Projected in configuration space one gets $<r|n> = \phi_n(\mathbf{r})$. The time development of the Schrödinger quantum state $|\psi(t)>$: $|\psi(t)> = \exp(-i\hat{H}_{ho}t/\hbar)|\psi(0)>$. This can be written as:

$$<\mathbf{r}|\psi(t)> =$$

$$\int d\mathbf{r}' <\mathbf{r}|\exp(-i\hat{H}_{ho}t/\hbar)|\mathbf{r}'><\mathbf{r}'|\psi(0)> \qquad (4.4.1.16)$$

The kernel of time evolution operator $<\mathbf{r}|\exp(-i\hat{H}_{ho}t/\hbar)|\mathbf{r}'>$ is fundamental. Compared to (4.6.3) the Green function kernel happens to be isomorphic to $<\mathbf{r}|\exp(-i\hat{H}_{ho}t/\hbar)|\mathbf{r}'>$. This kernel is similar to the one found in eq.(4.1.1.1).

One has to be very careful when coming to interpret (4.4.1.16). In the standard model the equation is seen as a propagation in real space of a particle represented by the wave function $<\mathbf{r}|\psi(t)>$; starting at point r', the propagator

$$<\mathbf{r}|\exp(-i\hat{H}_{ho}t/\hbar)|\mathbf{r}'>$$

would allow following the wave function as a function of time. The problem is that the quantum theory handle the quantum states in Hilbert space; the projected state <**r**|ψ(t)>, even if we use real space coordinates, is the range for a mathematical function standing for the quantum state. The only thing one is doing is to calculate the same wave function at different domains in configuration space. A change of quantum state will be achieved whenever an interaction operator is included in the propagator.

4.4.2. Hydrogen-like atoms

The material system associated to an I-frame separates in two parts. One is a source at frame origin of Coulomb field with charge Ze, the other a mass M with total charge Qe, the charge of one electron being –e.

The Coulomb operator reads: $V(|\hat{r}|)= ZQe^2 |(\hat{r})|^{-1}$. It is spherically symmetric. Note the case Z=1 and Q=-1 corresponds to an hydrogen-like system; if M is equal to the electron mass we get a model (non-relativistic) for the hydrogen atom.

The kinetic energy operator $\hat{K}$ is given as $(-\hbar^2/2M)\hat{p}\cdot\hat{p}$. This operator is spherically symmetric as well. From (3.2.2.3) we get $\hat{p}= -i\hbar(\partial/\partial\mathbf{r})= -i\hbar\,\boldsymbol{\nabla}$ and the Hamiltonian operator looks like:

$$\hat{H} = \hat{K}+V(|\hat{r}|) = (-\hbar^2/2M)\,\boldsymbol{\nabla}^2 + ZQe^2 |(\hat{r})|^{-1} \quad (4.4.2.1)$$

From the theory of angular momentum reviewed in section 3.5 we can suspect that $\hat{H}$ will commute with the total orbital angular momentum $\hat{L}$ and one of its component that we select to be $\hat{L}_3$. We know thus

$$\hat{L}^2 |L,M_L> = \hbar^2 L(L+1) |L,M_L> \text{ and } \hat{L}_3 |L,M_L> = \hbar M_L |L,M_L> \quad (4.4.2.2)$$

For each L-value the system will show a 2L+1 degeneracy in such a way that M_L ranges from –L up to +L.

By taking a unit sphere with radius $\mathbf{r}/|\mathbf{r}| =\mathbf{n}_r$ the projected base states are
$$< \mathbf{n}_r |L,M_L> = Y_L^{ML}(\mathbf{n}_r) = Y_L^{ML}(\theta, \phi) \quad (4.4.2.3)$$

The spherical harmonics are represented by symbols $Y_L^{ML}(\theta, \phi)$. Check section 3.5 for further details.

The base functions reflect the symmetries via quantum numbers. For the present case, the angular part is covered by the spherical harmonics. As we saw in (3.5.1) for fully spherical systems, these functions can be put as products of base functions depending only upon one of the variables θ and ϕ. The point of interest is that the quantum number are partially coupled so that one gets:

$$Y_L^{ML}(\theta, \phi) = \Theta_L^{ML}(\theta) \, \Phi^{ML}(\theta, \phi) \qquad (4.4.2.4)$$

The radial part enters in the base states via the dynamics of the system. One may suspect that they would have the structure like: $R_{nLML}(r)$ with $r=|\mathbf{r}|$. The quantum number n relates to the energy levels of the system. The are generic solutions to the differential equation:

$$(-\hbar^2/2M) \, \{(1/r)d(rd/dr)/dr+(1/r)d/dr) -$$
$$L(L+1)/r^2\} \, R_{nLML}(r) + ZQe^2 \, |(\hat{r})|^{-1} \, R_{nLML}(r) =$$
$$E_{nLML} \, R_{nLML}(r) \qquad (4.4.2.5)$$

For the hydrogenic atoms Q=-1 and Z is the positive charge at the origin of the I-frame.

E&E-4.4.2-2 Transform eq.(4.4.2.5) to find out its solutions
The first thing you do is to separate the differential terms with unit coefficient. Since we do not yet know the base functions call them by R(r) and put E instead of E_{nLML}. For this multiply the eq. by $(-\hbar^2/2M)$-1 and reorganize terms such as $d(rd/dr)/dr = d^2/dr^2 + (2/r)d/dr$ to get:

$$\{d^2/dr^2 + (2/r)d/dr \} R(r) + (2M/\hbar^2)\{E+ Ze^2/r -$$
$$\hbar^2 \, L(L+1)/2Mr^2 \} R(r) = 0 \qquad (4.4.2.6)$$

Note the difference between the two last equations. The eq.(4.4.2.5) is an eigen value equation that due to symmetry constraint the system must fulfill; we have to check this later on. Eq.(4.4.2.6) is a differential equation where the values of the energy are at our disposal. For negative energy, E<0 we call the possible solutions as bound states; these must be solutions to the eigen value equation. To solve this equation it is useful to have a dimension less r-variable.

E&E-4.4.2-3 Transform eq.(4.4.2.5) to dimensionless radial variable.

To do this observe that the factor $(2M|E|/\hbar^2)$ has the dimension of inverse square length. Thus, define the dimensionless variable ρ by the simple equation:

$$\rho = (8M|E|/\hbar^2)^{1/2}\, r \qquad\qquad (4.4.2.7)$$

Doing the algebra show that the following equation obtains:

$$\{ d^2/d\rho^2 + (2/\rho)d/d\rho \}\, R(\rho) - L(L+1)/\rho^2\, R(\rho) +$$
$$\{(Ze^2/\hbar)(M/2|E|)^{1/2}/\rho - 1/4\}\, R(\rho) = 0$$

The factor $\{(Ze^2/\hbar)(M/2|E|)^{1/2}$ contains the Coulomb interaction that can be recast in terms of a more general constant characterizing the interactions between charges and the electromagnetic field: $\alpha = e^2/\hbar c$, where c is the speed of light. This is known as hyperfine structure and it is a dimensionless number. Thus, $\{(Ze^2/\hbar)(M/2|E|)^{1/2} = Z\alpha\,(Mc^2/2|E|)^{1/2}$ and we call it with the letter λ to get the final differential equation (4.4.2.8) below.

After performing the above replacements one gets:

$$d^2R(\rho)/d\rho^2 + (2/\rho)dR(\rho)/d\rho - L(L+1)R(\rho)/\rho^2 +$$
$$\{ \lambda/\rho - 1/4 \}\, R(\rho) = 0 \qquad\qquad (4.4.2.8)$$

One of the approaches used to construct solutions to this equation is to look at asymptotic behavior, namely, for $\rho \to \infty$. In this case, terms showing ρ in the denominator are discarded and one gets:

$$d^2R(\rho)/d\rho^2 - 1/4\, R(\rho) = 0$$

The asymptotic solution looks like $\exp(-\rho^2/2)$. The global solution can hence be factored. Take then, $R(\rho) = \exp(-\rho^2/2)\, X(\rho)$. Putting this into eq.(4.4.2.8) and after some algebra we get the equation in the form required to get appropriate solution:

$$d^2X(\rho)/d\rho^2 + (1-2/\rho)dX(\rho)/d\rho\, \{+ \{(\lambda-1)/\rho -$$
$$L(L+1)/\rho^2 \}\, X(\rho) = 0 \qquad\qquad (4.4.2.9)$$

E&E-4.5.2-4 Find solutions to eq.(4.4.2.9)
A common technique to construct solutions to $X(\rho)$ is by series expansion:

$$X(\rho) = \rho^L \sum_{n=0}^{\infty} b_n\, \rho^n = \rho^L\, Z(\rho) \qquad\qquad (4.4.2.10)$$

By now you suspect that $\rho^L Z(\rho)$ will be plug in (4.4.2.9) to get a differential equation for the function $Z(\rho)$. There from, recursion relations between the coefficients b_n can be worked out and relationships between n, λ and L can be obtained. Remember that the

parameter λ contains the energy. To make the story short, for a given L the series must end at a specific n' and from the relation you will derive one can write down:

$$\lambda = n' + L + 1 \qquad (4.4.2.11)$$

Here, the principal quantum number n is introduced as:

$$n = n' + L + 1$$

Thus, if n'$\geq$0 then

i) $n \geq L+1$
ii) n is an integer

The relation $\lambda = n$ leads to:

$$E = E_n = - \{(1/2) Mc^2 (Z\alpha)^2\} / n^2 \qquad (4.4.2.12)$$

This is the result obtained by N.Bohr in his famous model for the hydrogen atom. The key to the discussion is the emergence of quantized energy eigen values. The base states depend only on quantum numbers n and L. Equation (4.4.2.5) must be written as;

$$(-\hbar^2/2M)\{(1/r)d(rd/dr)/dr + (1/r) \, d \, /dr) - L(L+1)/r^2\} \, R_{nL}(r) + ZQe^2 \, |(\hat{r})|^{-1} \, R_{nL}(r) = E_n \, R_{nL}(r)$$
$$(4.4.2.5b)$$

The energy is associated to the *radial part* while the eigen functions collect two labels. The third one $M_L = m$ is not present.

The mathematical gymnastics is essential to illustrate practical ways to construct base sets. This is however not the full story. While base states are the invariants of the problem, they do not describe physical processes involving the material system. Let us here elaborate this point a little further.

What do we measure is a change of quantum state that correlates with the one we use to detect the change. Use the hydrogen base states (at the non-relativistic level) to illustrate some points.

First. Each base state can be the root identifying a given spectral sequence. Balmer series corresponds to transition from or to level n=2. Two levels are involved (not one). The photon field relates two states differing in angular momentum by one unit. With the standard names, L=0→s, L=1→p, L=2→d, L=3→f and so on, allowed transitions related L states differing in one unit of angular momentum: s→p, p→s or d, etc. The change of state in the photon field correlates with the one corresponding to the material system. Astronomical spectroscopy gives us plenty of examples. Actually, visible universe is plenty of hydrogen atoms in diverse quantum states. In the following section a more

detailed discussion on these matters is presented. Here we remind that the system can set a spectroscopic response only if the amplitude at the root state being probed is different from zero.

The quantum numbers are sufficient to identify a base state. Here, for the spin free case |nlm> is the base state associated to the radial quantum number n, orbital angular momentum l and projection along 3-direction m. The energy only depends upon n: $E_n = - R/n^2$ with $R=\{(1/2)Mc^2(Za)^2\}$. The base states for given l and m values correspond to sequences that have limit zero as n increases without bounds (n→∞). Reminds that $0 \le l \le n-1$. Thus 1s,2s,…, 2p,3p,…, 3d,4d,…have limit at same energy value, the energy difference between the lowest (1s) and the ns→∞ limit is the ionization energy of the system. For Z=1 the energy value can be obtained from $(1/2)mc^2(\alpha)^2$ where m is the electron mass at rest.

The principal quantum number is related to the number of radial nodes shown by the base states. More exactly, this number is n-1. The ground state 1s is node less. The 2s has one node; 2p still has one radial node plus the nodes related to the L=1 state. The base functions are thence characterized by the number of nodes and some other properties we will discuss in due time.

Finally, buried in all these mathematics there is a fundamental result, namely,

$$L \le n - 1 \qquad\qquad\qquad (4.4.2.13)$$

This means that maximum value of the orbital angular momentum is limited by the radial quantum number. Thus, one has a maximum magnetic level M_{Lmax}=+ (n − 1) and a minimum value M_{Lmin}= - (n − 1). This innocent result is most important for the study of Rydberg states. Keep this result in mind for the next chapter.

4.5. Symmetry breaking interactions

The strict separation introduced by an I-frame between laboratory world and the configuration space used to project abstract Hilbert space elements permits constructing base sets in a simple manner. However, once laboratory situations are to be handled the strict separation must be relaxed in one way or another.

Consider the effect on an external electric field $\mathbf{F}(r_1,r_2,r_3)$ acting on an hydrogen-like system. To extract the symmetry breaking element assume that the field is quasi-static, meaning by this that it is independent of local coordinates, i.e. it is a constant vector $\mathbf{F}$. For instance, take $\mathbf{F} = |\mathbf{F}| (\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3) = |\mathbf{F}| \mathbf{n}$; the unit vector $\mathbf{n}$ indicates a direction in laboratory space. The interaction operator $\hat{V}$ is given as the scalar product: -e$\hat{r}$·$\mathbf{F}$. The Hamiltonian is $\hat{H}(\mathbf{F}) = \hat{H} + \hat{V}$.
Eq.(4.4.2.1) defines the zero order term.

To illustrate the quantum procedure, let us take the 2s,2p manifold (all base states with same energy label). The base states are:

$$|200> = |1>, |210> = |2>, |21+1> = |3> \text{ and } |21-1> = |4>;$$

with obvious notation. A general quantum state is given by the linear superposition:

$$<\mathbf{r}|\Psi> = C_1<\mathbf{r}|1> + C_2<\mathbf{r}|2> + C_3<\mathbf{r}|3> + C_4<\mathbf{r}|4> \qquad (4.5.1)$$

In the fully spherical symmetric base state without perturbation there are four special linear superpositions:

$$[1\ 0\ 0\ 0], [0\ 1\ 0\ 0], [0\ 0\ 1\ 0] \text{ and } [0\ 0\ 0\ 1] \qquad (4.5.2)$$

These are eigen vectors for the non-interacting system written in a fancy way. We want now to calculate four linear superpositions corresponding to $\hat{H}(\mathbf{F})$ fully diagonal. We will take advantage to learn a new technique to solving this and many other problems.

The average value of the energy operator calculated with the wave function (4.5.1) is given by:

$$<\Psi|\hat{H}(\mathbf{F})|\Psi> = \Sigma_{i=1,4}\Sigma_{j=1,4} <i|\hat{H}(\mathbf{F})|j> C_1^* C_j \qquad (4.5.3)$$

Including the normalization condition on the wave function form the functional:

$$J = <\Psi|\hat{H}(\mathbf{F})|\Psi> - \lambda <\Psi|\Psi> \qquad (4.5.4)$$

By calculating $\partial J/\partial C_i^*$ for i=1,2,3 and 4 and imposing stationary solutions, namely $\partial J/\partial C_j^* = 0$ one obtains the set of equations:

$$\Sigma_{j=1,4} (<i|\hat{H}(\mathbf{F})|j> - \lambda<i|j>) C_j = 0 \quad \text{ for } i=1,..,4. \qquad (4.5.5)$$

There are four equations to determine the amplitudes and λ. The system has non-trivial solutions if and only if the determinant of the matrix $(<i|\hat{H}(\mathbf{F})|j> - \lambda<i|j>)$ is zero.

To calculate the matrix elements go back to the original definitions. The diagonal terms for the interaction operator are zero because the dipole moment operator has parity -1. Then $E_{2s} = E_{2p}$ and we take it to be zero leading to $-\lambda$ term along the diagonal. The term $<1|\hat{V}|2> = <200|\hat{V}|210>$ has the right symmetry, namely a change of angular momentum with m=0; the dipole operator, we call it

Z. The terms $<1|\hat{V}|3> = <200|\hat{V}|211>$ and $<1|\hat{V}|4> = <200|\hat{V}|21\text{-}1>$ are equal to zero as the operator do not depend upon φ. The matrix looks like

$$\det \begin{bmatrix} -\lambda & Z & 0 & 0 \\ Z & -\lambda & 0 & 0 \\ 0 & 0 & -\lambda & 0 \\ 0 & 0 & 0 & -\lambda \end{bmatrix} = 0 \qquad (4.5.6)$$

We have two solutions with $\lambda = 0$ and two solutions coming from $\lambda^2 - Z^2 = 0$, namely, $\lambda = \pm Z$. The corresponding eigen vectors are:

$$1/\sqrt{2}\,|1> -1/\sqrt{2}\,|2> ,\ \lambda = -Z\ ;$$
$$1/\sqrt{2}|1>+1/\sqrt{2}|2>,\ \lambda =+Z;$$
$$|3> ,\ \lambda = 0;\ |4>,\ \lambda =0 \qquad (4.5.7)$$

We can rewrite this result in a matrix form as follows:

$$\left(|1\rangle\ \ |2\rangle\ \ |3\rangle\ \ |4\rangle\right) \begin{bmatrix} \sqrt{1/2} & \sqrt{1/2} & 0 & 0 \\ -\sqrt{1/2} & \sqrt{1/2} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} =$$

$$\begin{bmatrix} \sqrt{1/2}\,|1> -\sqrt{1/2}\,|2> \\ \sqrt{1/2}\,|1> +\sqrt{1/2}\,|2> \\ |3> \\ |4> \end{bmatrix} = \left(|1'\rangle\ \ |2'\rangle\ \ |3'\rangle\ \ |4'\rangle\right)\ (4.5.8)$$

The system presents a new base set once the total Hamiltonian is rendered to a diagonal form.

Now we can go back to the study of quantum states (row vectors). A comparison makes sense if we keep fixed the base set and use the 4x4 matrix to transform the row vectors standing for the initial conditions. Thus is we prepare the state as [1 0 0 0]:

$$\left(|1\rangle\ \ |2\rangle\ \ |3\rangle\ \ |4\rangle\right) \begin{bmatrix} \sqrt{1/2} & \sqrt{1/2} & 0 & 0 \\ -\sqrt{1/2} & \sqrt{1/2} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} =$$

$$1/\sqrt{2}\,|1> -1/\sqrt{2}\,|2> =$$

$$\left(\langle 1| \quad \langle 2| \quad \langle 3| \quad \langle 4| \right) \begin{bmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \\ 0 \\ 0 \end{bmatrix} \qquad (4.5.9)$$

After interaction the system is found on a linear superposition. What will happen if we switch off the interaction if the quantum state is $1/\sqrt{2}$ |1> $+1/\sqrt{2}$ |2>? The answer should be simple: it will stay in that linear superposition because there is no coupling available.

Thus, interaction introduced via $\hat{V}$-operator yields a subspace of dimension 2 and eigenvalues $\lambda = -Z$ and $\lambda = +Z$. The initially degenerate levels in absence of interaction are coupled producing a pair of orthonormal states such that if one prepares the quantum state with only one component belonging to this subspace after interaction we will get coherent linear superpositions. If we prepare an initial state with amplitude outside the virtual subspace, say [0 0 1 0] nothing will happen in first order.

There are two points that we would like to stress before opening the Fence to the electro-magnetic (EM) radiation in the following sections. The first concern a physical description of the coupling operator -e$\hat{r}$·**F**. The source generating the force is "external" to the I-frame system. If we were to use a Newtonian simile, the force put on acceleration as it were onto the I-frame system that is always fully spherically symmetric. We can start timing the process by initiating the force at a given moment and keep it in action. The quantum state of the system would have changed as indicated above. By switching off the force, we set up to measure the time evolution of the system until getting at a stationary state.

The second aspect concerns our example of chemical reaction introduced in Chapter 1. Now the force will be useful to introduce activation effects. Energy exchange would require a time dependent force. Once you switch off the external field we will measure the system by monitoring the intensity response for the product channel. That response is just the amplitude at the product channel taken as the square modulus.

One of the sources providing effective forces on to an electronic system is the radiation field.

4.6. Revisiting projected equations

The general structure of quantum mechanics does not require of a particle or a wave model. This results in an abstract modern quantum theory separating "kinematic" from "dynamic" aspects. Projecting the abstract framework in configuration space, that is a pure mathematic space, the time-dependent Schrödinger equation (1.3.1.6), namely, $(i\hbar)\, \partial| \Psi,t>/\partial t = \hat{H} |\Psi,t>$ becomes with

the help of unit projector operator $\hat{1}$, namely, $\int d\mathbf{q}'| \mathbf{q}'> <\mathbf{q}'|$, (Cf. eq.(3.1.4) a linear superposition with amplitudes indicated in curly brackets:

$$\int d\mathbf{q}'| \mathbf{q}'> \{(i\hbar) \partial<\mathbf{q}'| \Psi,t>/\partial t -$$

$$\int d\mathbf{q}''<\mathbf{q}'| \hat{H} |\mathbf{q}''> <\mathbf{q}''|\Psi,t> \} = 0 \qquad (4.6.1)$$

This equation is formally equivalent to eq.(1.3.1.6). Introducing a time evolution operator we can relate an initial quantum state projected in configuration space to the quantum state at another space-time. To do this, take the curly bracket expression and insert the operator $\hat{U}(t,t_o)$ as follows:

$$\{(i\hbar) \partial<\mathbf{q}'| \Psi,t>/\partial t -$$

$$\int d\mathbf{q}''<\mathbf{q}'| \hat{H} |\mathbf{q}''> <\mathbf{q}''|\hat{U}(t,t_o)|\Psi,t_o> \}=0.$$

Integrating in time we get:

$$<\mathbf{q}'| \Psi,t> = <\mathbf{q}'| \Psi, t_o> +$$

$$(i\hbar)^{-1}\int_{t_o}^{t} dt' \int d\mathbf{q}''<\mathbf{q}'| \hat{H} |\mathbf{q}''><\mathbf{q}''| \hat{U}(t',t_o)|\Psi, t_o>.$$

That in terms of wave functions reads:

$$\Psi(\mathbf{q}',t)= \Psi(\mathbf{q}',t_o) -$$

$$(i/\hbar) \int_{t_o}^{t} dt' \int d\mathbf{q}'' \int d\mathbf{q}'''$$

$$<\mathbf{q}'| \hat{H} |\mathbf{q}''> <\mathbf{q}''| \hat{U}(t',t_o) |\mathbf{q}'''> \Psi(\mathbf{q}''',t_o) \quad (4.6.2)$$

The equation tells us that the wave function of the system can be constructed starting from knowledge of the quantum state $\Psi(\mathbf{q}''',t_o)$ prepared in the laboratory and the knowledge of the projected evolution operator, $<\mathbf{q}''|\hat{U}(t',t_o)|\mathbf{q}'''>$; integration over the configuration space $\int d\mathbf{q}''$ ensures that all relevant information gathered at t_o will be included.

Equation (4.6.2) contains all what is necessary to calculate time evolution of the initial quantum state once the complete configuration space $\mathbf{q}'$ is covered. From this point onwards there are many ways to transform the equation into a more simple form by using appropriate models. We will do it below. The results then at one stage or another must be contrasted to data collected in laboratory experiments.

First a diagonal model:

$$<\mathbf{q}'| \hat{H} |\mathbf{q}''> = \delta(\mathbf{q}'-\mathbf{q}'') <\mathbf{q}'| \hat{H} |\mathbf{q}'>.$$

Introducing this equation into (4.6.1) after performing the integration over the $d\mathbf{q}''$ measure the result is an integral equation that is valid for all neighborhoods of the base state $| \mathbf{q}'>$:

$$\{(i\hbar) \partial<\mathbf{q}'| \Psi,t>/\partial t - <\mathbf{q}'| \hat{H} |\mathbf{q}'> <\mathbf{q}'|\Psi,t > \} = 0$$

$$(4.6.3)$$

For this linear superposition to hold it is necessary and sufficient that for any neighborhood of a configuration point $\mathbf{q}'$ and the entire integration domain (configuration space), the term in curly brackets be equal zero.

The eq.(4.6.3) is commensurate to abstract Schrödinger equation (1.3.1.1) this time expressed in configuration space. To close the loop one takes the assignment in the integrand of eq.(1.1.3):

$$<\mathbf{q}|\hat{H}|\mathbf{q}> <\mathbf{q}|\Psi,t> \rightarrow \hat{H}(\hat{q}) <\mathbf{q}|\Psi,t> \qquad (4.6.4)$$

This rearrangement, once introduced in eq.(1.1.3) leads to the time dependent equation having the form Schrödinger's used in his seminal paper (1926). Combining eq.(4.6.3-4) one gets:

$$\{ i\hbar \, \partial/\partial t - \hat{H}(\hat{q}) \} \, \Psi(\mathbf{q},t) = 0 \qquad (4.6.5)$$

The introduction of $\hat{H}(\hat{q})$ is not a logical step. It is a hypothesis that permits giving to Schrödinger equation, in configuration space, the same form as in abstract space. We assume that the mapping $\hat{H} \rightarrow \hat{H}(\hat{q})$ holds true or at least the latter permits grabbing essential aspects of the physics for the given system. The Hamiltonians $\{\hat{H}(\hat{q})\}$ qualifying to represent a given physical system must be fully invariant under Lorentz transformations. They are called Hamiltonian operators of Schrödinger type. If they are to serve as generators of time translation, the self-adjoint property must hold.

A second possibility transform Eq.(4.6.2) by taking:

$$<\mathbf{q''}|\hat{U}(t',t_o)|\mathbf{q'''}>=\delta(\mathbf{q''}-\mathbf{q'''})$$

$$<\mathbf{q''}|\exp(i\hat{H}(t'-t_o)/\hbar)|\mathbf{q'''}> =$$

$$\delta(\mathbf{q''}-\mathbf{q'''}) \exp(i\hat{H}(\mathbf{q''},\mathbf{q''')}) (t'-t_o)/\hbar),$$

to get after integration over $d\mathbf{q'''}$:

$$\Psi(\mathbf{q'},t)= \Psi(\mathbf{q'},t_o) - (i/\hbar) \int_{t_o}^{t} dt' \int d\mathbf{q''}$$

$$<\mathbf{q'}|\hat{H}|\mathbf{q''}> \exp(i\hat{H}(\mathbf{q''}) (t'-t_o)/\hbar) \Psi(\mathbf{q''},t_o).$$

This equation is commensurate to eq. (4.6.2). The kernel of this equation $G(\mathbf{q'},\mathbf{q''};t')$ is known as the propagator kernel:

$$\hat{G}(\mathbf{q'},\mathbf{q''};t') = <\mathbf{q'}|\hat{H}|\mathbf{q''}> \exp(i\hat{H}(\mathbf{q''}) (t'-t_o)/\hbar)$$
$$(4.6.6)$$

Therefore, the wave function can be simply written as:

$$\Psi(\mathbf{q},t)= \Psi(\mathbf{q},t_o) - (i/\hbar) \int_{t_o}^{t} dt' \int d\mathbf{q''} \hat{G}(\mathbf{q},\mathbf{q'};t') \Psi(\mathbf{q'},t_o)$$
$$(4.6.7)$$

This equation is another form of representing the quantum state obtained by time evolution in a space-time scheme. We will be back to this form once the interaction picture is introduced below.

A word of caution is in place here. The coordinate space is an abstract mathematical space. No particle position is implied. It is important to get this point right. Because, the particle system referred to as material system, sustains the quantum state. The theory works with abstract quantum states not with the particles. The only requirement we can make is to ensure the material system is somewhere in the space covered by the I-frame.

As consequence, there are conceptual difficulties to incorporate basis states from the asymptotic fragments referred to separate I-frames into the global system basis set set.

Some of these issues have been discussed above and we will continue to address them as we pursue this work. As a matter of fact, this is not a mathematical problem but a physical difficulty to marry abstract Hilbert space with fragments that can be independently obtained in real space.

4.7. Overview

The issues discussed here have been varied but with a principal motto. A quantum state is what will mediate interactions between material systems.

There is a conservation requirement: the matter content of interacting system must be invariant.

The quantum state belongs to Hilbert space but it is sustained by the material system. There are infinities of quantum states but only one material system reckoned in terms of fundamental elements. Electrons and nuclei belong to such fundamental components.

The idea that a material system *is* in a given quantum base state as a hand is in a glove is recussed by logical inconsistency. The linear superposition is not telling a material system to be in many base states simultaneously. Acert such proposition collides with standard positive logics.

A material system belons to laboratory (real) space while a quantum state belongs to Hilbert space. These two space are not commensurate.

It is a totally different proposition saying that quantum states are sustained by material systems. The example we gave in this chapter when the quantum states of particle in a box was analyzed permits appraizing a little better the difference.

Most of the weirdness associated by many to quantum physics is due to use of terms totally inappropriate to describe the state of affair.

The world as we know it is fully quantum physical. Classical physics categories are useful but not compulsory. Out of pragmatism we use them. Thus, wave-particle duality is non-sense when applied to describe quantum phenomena. This will be more and more clear as we move on examining a host of quantum situation without language that is not appropriate because one is mixing non-commensurate levels.

This last section has as objective to remind the readers on suc drawbacks.