A

2.4 Pauli program and the quantum $\mathcal{H}$-theorem

In 1928, Pauli followed Boltzmann's procedure to get irreversibility starting from reversible dynamics [4]. At the time of Boltzmann, this fact was pointed as a paradox, and several arguments were raised against his work. Boltzmann then advanced a probabilistic explanation that did not contradict microscopic reversibility. In addition, Boltzmann equation was very successful at explaining transport properties. Using this equation and the *Stosszahlansatz* assumption (*molecular chaos*), he was able to formulate his celebrated *$\mathcal{H}$-theorem* to furnish a statistical mechanical interpretation of the Second Law of thermodynamics. The *molecular chaos* assumption is now recognized as the essential ingredient to obtain irreversibility. In extending Boltzmann's approach to Quantum Mechanics, Pauli initiated the study of master equations in quantum physics. The general idea was to obtain a macroscopic time evolution in term of a balance equation for the microscopic probabilities. Due to perturbations, a physical system undergoes transitions among the different microstates, thus changing the corresponding occupation probabilities. Such random perturbations may have different origins: molecular collisions in a macroscopic gas, or random fields acting on an almost isolated system. In Boltzmann hypothesis of *molecular chaos*, velocities of colliding molecules are uncorrelated and independent of position.

If the system has a macroscopic number of degrees of freedom, and the perturbations are of random character, one hopes to obtain an irreversible evolution at the macroscopic level. Such an equation should be obtained from the Liouville-von Neumann equation for the density operator, making some 'appropriate assumptions', which at the end constitute the quantum analog of the Boltzmann's *Stosszahlansatz*, and render the process irreversible. As shown in Section **1.2**, if one initially prepares the density matrix in diagonal form, time evolution will immediately generate off-diagonal elements if we are out of the equilibrium situation. Those off-diagonal elements keep in part information concerning quantum coherence, and will drive the system to recur, at least partially, from time to time. Pauli suggested that, in the presence of random interactions, one can neglect off-diagonal elements of the density matrix, due to cancellations of random accumulated phases. Now, we proceed to show Pauli's original deduction. If one represents $\boldsymbol{\rho}$ in terms of the linear coefficients, as done in Sub-Section **1.1.5**, one writes:

$$< n|\boldsymbol{\rho}(t)|m>=\sum_i w_i \; a_n^{(i)}(t)a_m^{(i)*}(t) \equiv \overline{a_n(t)a_m^*(t)} \ ,$$

where members of the ensemble are written in the form $|\psi^{(i)}(t)>=\sum_n a_n^{(i)}(t)|n>$ in relation to a fixed basis $\{|n>\}$. Using the polar representation for the coefficients

$$a_n^{(i)} = r_n^{(i)} \exp i\phi_n^{(i)} \ ,$$

with both $r_n^{(i)}$ and $\phi_n^{(i)}$ real and time dependent, one gets

$$< n|\boldsymbol{\rho}(t)|m>=\sum_i w_i \, r_n^{(i)}(t)r_m^{(i)}(t) \exp i\left[\phi_n^{(i)}(t)-\phi_m^{(i)}(t)\right] \equiv \overline{r_n(t)r_m(t)\exp i\left[\phi_n(t)-\phi_m(t)\right]} \, . \tag{2.17}$$

If after a time scale τ_0 the phases $\left\{\phi_n^{(i)}(t)\right\}$ in (2.17) are random, then averaging over the ensemble yields a vanishing matrix element

$$< n|\boldsymbol{\rho}|m> \to 0$$

for $n \neq m$, and it follows that the density matrix only keeps diagonal terms

$$< n|\boldsymbol{\rho}(t)|n> = P_n(t) \ = \overline{r_n^2(t)} \ .$$

We now look for the evolution of $P_n(t)$ during times Δt which are longer than τ_0 but much shorter than the macroscopic relaxation time τ_R

$$\tau_0 \lessapprox \Delta t \ll \tau_R \ .$$

This problem is better analyzed using the interaction picture [7]. We assume that the system Hamiltonian is written as a stationary part plus a time dependent perturbation:

$$\mathbf{H}{=}\mathbf{H}_0 + \mathbf{V}(t) \ .$$

We refer the perturbation theory to the eigenstates of $\mathbf{H}_0$

$$\mathbf{H}_0|n >= E_n|n > \ ,$$

and assume that the perturbation $\mathbf{V}(t)$ has no diagonal elements and can be separated into a rapidly fluctuating part $\mathbf{V}^{'}$ and a slowly varying one $\bar{\mathbf{V}}$. They have different roles for the perturbed system. $\mathbf{V}^{'}$ includes rapid fluctuations for the time scale τ_0, and is responsible for the random phases and the cancellation of off-diagonal elements of the density matrix. $\bar{\mathbf{V}}$ varies in time scales that are much longer, and induces transitions between microstates which at the end, are responsible for the final relaxation to equilibrium. Using $t_0 = 0$ as the initial time, transforming from the Shrödinger to the interaction picture yields

$$|\psi>_I = \exp\left(\frac{i}{\hbar}\mathbf{H}_0 t\right)|\psi> \ ,$$

$$\mathbf{A}_I = \exp\left(\frac{i}{\hbar}\mathbf{H}_0 t\right)\mathbf{A}\exp\left(-\frac{i}{\hbar}\mathbf{H}_0 t\right) \ ,$$

for ket states and operators. It follows that time evolution of kets is dictated by the perturbation Hamiltonian $\mathbf{V}(t)$:

$$i\hbar\frac{\partial|\psi(t)>_I}{\partial t} = \mathbf{V}_I(t)|\psi(t)>_I, \tag{2.18}$$

where $\mathbf{V}_I = \exp\left(\frac{i}{\hbar}\mathbf{H}_0 t\right)\mathbf{V}\exp\left(-\frac{i}{\hbar}\mathbf{H}_0 t\right)$ is the perturbation in the interaction picture. Equation (2.18) can be formally integrated to obtain the time evolution operator in the interaction picture, in the form

$$\mathbf{U}(t, t_1) = \exp\left\{-\frac{i}{\hbar}\int_{t_1}^{t} d\tau \ \mathbf{V}_I(\tau)\right\} \ , \tag{2.19}$$

if $[\mathbf{V}_I(t), \mathbf{V}_I(t')] = 0$. In the general case, one has to use the Dyson series, with the time ordering operator [7] . For first order perturbation theory, one can safely employ expression (2.19) to calculate transition amplitudes and probabilities. As usual, we employ the basis $\{|n>\}$ of the eigenstates of $\mathbf{H}_0$. Note that diagonal matrix elements of $\boldsymbol{\rho}$ do not depend on the picture

$$< n|\boldsymbol{\rho}_I|n > = < n|\boldsymbol{\rho}|n > = \ P_n \ .$$

In the following, we will work in the interaction picture but will drop the I subindex in ρ to simplify the notation. Suppose that at time t we prepare the system in the microstate $|n >$. We analyze the evolution a time Δt after, that is

$$\boldsymbol{\rho}(t+\Delta t) = \mathbf{U}(\Delta t)\boldsymbol{\rho}(t)\mathbf{U}^{\dagger}(\Delta t) \ , \tag{2.20}$$

where

$$\mathbf{U}(\Delta t) = \exp\left\{-\frac{i}{\hbar}\int_t^{t+\Delta t} d\tau \ \mathbf{V}_I(\tau)\right\} \ . \tag{2.21}$$

For the diagonal matrix element we get from (2.20):

$$< n|\boldsymbol{\rho}(t+\Delta t)|n >= \boldsymbol{\rho}_{nn}(t+\Delta t) = \sum_{k,m} \mathbf{U}_{nk}(\Delta t)\boldsymbol{\rho}_{km}(t)\mathbf{U}^*_{nm}(\Delta t) \ ,$$

and making the finite difference:

$$\boldsymbol{\rho}_{nn}(t+\Delta t) - \boldsymbol{\rho}_{nn}(t) = \sum_{k,m} \mathbf{U}_{nk}(\Delta t)\boldsymbol{\rho}_{km}(t)\mathbf{U}^*_{nm}(\Delta t) \ - \boldsymbol{\rho}_{nn}(t) \ . \tag{2.22}$$

Now, we explicitly separate in the first term of the r.h.s. diagonal from off-diagonal elements:

$$\begin{aligned} \boldsymbol{\rho}_{nn}(t+\Delta t) - \boldsymbol{\rho}_{nn}(t) \ &= \ \left\{\sum_m \left|\mathbf{U}_{nm}(\Delta t)\right|^2 \boldsymbol{\rho}_{mm}(t) - \boldsymbol{\rho}_{nn}(t)\right\} + \\ &\quad + \sum_{k\neq m} \mathbf{U}_{nk}(\Delta t)\boldsymbol{\rho}_{km}(t)\mathbf{U}^*_{nm}(\Delta t) \ . \end{aligned} \tag{2.23}$$

At this point, a discussion of the time scales involved is in order. As noted above, we assume that time variation Δt is such that $\tau_0 \lessapprox \Delta t \ll \tau_R$, that is during this time we get cancellation of off-diagonal matrix elements, due to Pauli's random phases assumption. But in comparison with τ_R, the time Δt is small, and we can think in taking the limit $\Delta t \to 0$ in (2.23). Thus, discarding off-diagonal elements of $\boldsymbol{\rho}$, and noting that unitarity of $\mathbf{U}$ implies

$$\sum_m |\mathbf{U}_{mn}(\Delta t)|^2 = 1 \ ,$$

one gets from (2.23)

$$\boldsymbol{\rho}_{nn}(t+\Delta t) - \boldsymbol{\rho}_{nn}(t) = \sum_m \left[|\mathbf{U}_{nm}(\Delta t)|^2 \boldsymbol{\rho}_{mm}(t) - |\mathbf{U}_{mn}(\Delta t)|^2 \boldsymbol{\rho}_{nn}(t) \right] \ , \tag{2.24}$$

and dividing by the finite Δt one gets:

$$\frac{\boldsymbol{\rho}_{nn}(t+\Delta t) - \boldsymbol{\rho}_{nn}(t)}{\boldsymbol{\Delta} t} = \sum_m \left[\frac{|\mathbf{U}_{nm}(\Delta t)|^2}{\Delta t} \boldsymbol{\rho}_{mm}(t) - \frac{|\mathbf{U}_{mn}(\Delta t)|^2}{\Delta t} \boldsymbol{\rho}_{nn}(t) \right] \ . \tag{2.25}$$

One then defines the transition rates by:

Definition 12 *Transition rates*

$$W(m \to n) \equiv \lim_{\Delta t \to 0} \frac{|\mathbf{U}_{nm}(\Delta t)|^2}{\Delta t} \ . \tag{2.26}$$

That is, $W(m \to n)$ is defined as the transition probability from $|m>$ to $|n>$ per unit time. Intuitively, one expects transition probabilities to increase linearly with time for small times, so that the limit defined in (2.26) exists. Since diagonal elements are interpreted as occupation probabilities, we use the notation $< n|\boldsymbol{\rho}|n > = P_n$, and take the limit $\boldsymbol{\Delta} t \to 0$ in the finite difference (2.25). We obtain the balance equation:

$$\frac{dP_n}{dt}(t) = \sum_m \left[W(m \to n)P_m(t) - W(n \to m)P_n(t)\right] \ , \tag{2.27}$$

where $\boldsymbol{\Delta} t \to 0$ has to be interpreted as a 'coarse-grained' limiting process, with $\boldsymbol{\Delta} t \ll \tau_R$, where τ_R is a typical macroscopic relaxation time, but $\boldsymbol{\Delta} t \gtrsim \tau_0$, with τ_0 being the time required to randomize the phases of off-diagonal matrix elements of the statistical operator. Relation (2.27) is a 'gain-loss' equation called Pauli Master Equation (PME). Some properties are immediately noted:

1. A condition leading to the stationary case is given by:

   $$W(n \to m)P_n(t) = W(m \to n)P_m(t) \ , \tag{2.28}$$

   for all pairs (n, m). This condition is known as *Detailed Balance* for equilibrium. Quantum mechanical transition rates satisfy

   $$W(n \to m) = W(m \to n) \ = W_{mn}$$

   i.e. the transition rate from one state to other is equal to the inverse transition, resulting from (2.28) that equilibrium is characterized by

   $$P_m = P_n = P \ ,$$

   for all pairs of state (n, m). That is all populations are equal in equilibrium (*equiprobable condition*). In the previous section, we have demonstrated that this situation leads to maximum entropy, with the value

$$\sigma_{\max} = \ln \mathcal{N}_0 \ ,$$

where $\mathcal{N}_0$ is the total number of states $\{|n>\}$.

2. Transition rates are calculated using time-dependent perturbation theory. One gets expression (2.21) for the time evolution operator within the 'infinitesimal' time interval $[t, t+\Delta t]$. We will discuss the meaning of 'infinitesimal $\boldsymbol{\Delta} t$' as a 'coarse-graining' concept. Within first order perturbation theory, one writes:

$$\mathbf{U}(\Delta t) = \exp\left\{-\frac{i}{\hbar}\int_t^{t+\Delta t} d\tau\ \mathbf{V}_I(\tau)\right\} \approx 1 - \frac{i}{\hbar}\int_t^{t+\Delta t} d\tau\ \mathbf{V}_I(\tau) \ ,$$

and the corresponding amplitude for the transition $|m> \longrightarrow |n>$ is given by:

$$\begin{aligned} < \ n|\mathbf{U}(\Delta t)|m > &\approx -\frac{i}{\hbar}\int_t^{t+\Delta t} d\tau\ \ < n|\mathbf{V}_I(\tau)|m >= \\ = \ & -\frac{i}{\hbar}\int_t^{t+\Delta t} d\tau\ \ < n|\mathbf{V}(\tau)|m > \exp i\omega_{nm}\tau \ , \end{aligned}$$

with the frequency ω_{nm} defined as:

$$\omega_{nm} = \frac{E_n - E_m}{\hbar} \ ,$$

since the $\{|n>\}$ are eigenstates of $\mathbf{H}_0$. As discussed above, the perturbation is separated into the form $\mathbf{V}(\tau)$=$\mathbf{V}^{'}(\tau)$+ $\bar{\mathbf{V}}(\boldsymbol{\tau})$. The term $\mathbf{V}^{'}(\tau)$ fluctuates very rapidly within times $\tau_0 \lesssim \boldsymbol{\Delta} t$ and is responsible for the Pauli assumption of phase randomization. The 'secular' part $\bar{\mathbf{V}}(\boldsymbol{\tau})$ is of slow variation compared to $\boldsymbol{\Delta} t$ and leads to the final relaxation at long times τ_R, with $\mathbf{\Delta}t \ll \tau_R$. With the above assumptions, one has:

$$-\frac{i}{\hbar}\int_t^{t+\Delta t} d\tau \ \exp i\omega_{nm}\tau < n|\mathbf{V}^{'}(\tau)|m > \rightarrow \ 0 \ ,$$

yielding to:

$$< \ n|\mathbf{U}(\Delta t)|m > \approx -\frac{i}{\hbar}\int_t^{t+\Delta t} d\tau \ < n|\bar{\mathbf{V}}(\boldsymbol{\tau})|m > \exp i\omega_{nm}\tau \approx$$

$$\approx \ -\frac{i}{\hbar} \ < n|\bar{\mathbf{V}}|m > \int_t^{t+\Delta t} d\tau \exp i\omega_{nm}\tau \ ,$$

where $\bar{\mathbf{V}}(\boldsymbol{\tau})$ is considered as a constant for time intervals of the order of $\mathbf{\Delta}t$. Now, integration can readily be done, leading to the transition probability:

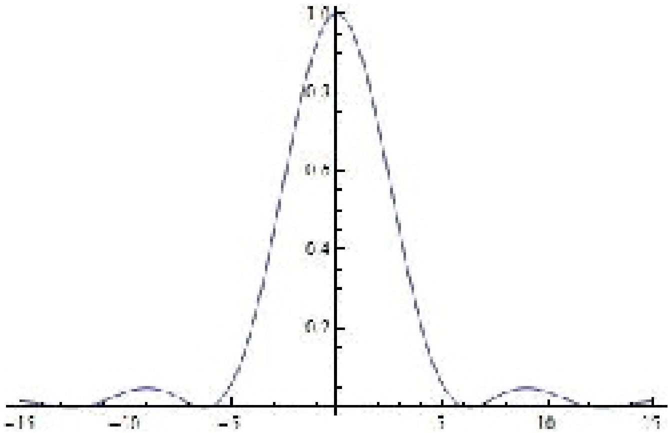
$$| < n|\mathbf{U}(\Delta t)|m > |^2 = \frac{\mathbf{\Delta}t}{\hbar^2}\left|< n|\bar{\mathbf{V}}|m >\right|^2 \mathbf{D}(\omega_{nm}, \mathbf{\Delta}t) \ ,$$

with the definition

$$\mathbf{D}(\omega_{nm}, \mathbf{\Delta}t) \equiv \frac{4\sin^2{(\omega_{nm}\mathbf{\Delta}t/2)}}{\omega_{nm}^2\mathbf{\Delta}t} \ .$$

sually, the final states lie in a quasi-continuum and $E_n \approx E$ and $\omega_{nm} \approx \omega = \frac{E-E_m}{\hbar}$ can be considered as continuous variables, with a density of states $\mathbf{D}(\omega, \mathbf{\Delta}t)$.

Conservation of energy for the transition is only obtained at the condition $\omega = 0$, where the distribution $\mathbf{D}(\omega, \mathbf{\Delta}t)$ has a peak of height $\mathbf{\Delta}t$, as a function of ω. The so called 'Fermi golden rule'[1] is obtained in the limit of very long observation



times, with:

$$\lim_{\Delta t \to \infty} \mathbf{D}(\omega, \mathbf{\Delta}t) = 2\pi\ \delta\left(\frac{E_n - E_m}{\hbar}\right) \ ,$$

and the corresponding transition probability

$$| < n|\mathbf{U}(\Delta t)|m > |^2 = \frac{2\pi\mathbf{\Delta}t}{\hbar}\left|< n|\bar{\mathbf{V}}|m >\right|^2 \delta\left(E_n - E_m\right) \ ,$$

which is proportional to the observation time $\mathbf{\Delta}t$ (actually, one notes that $\mathbf{\Delta}t$ cannot be arbitrarily large, since the probability is bounded by unity). The transition rate W_{mn}, defined in (2.26), gives the Fermi's famous equation:

$$W_{mn} = \frac{2\pi}{\hbar}\left|< n|\bar{\mathbf{V}}|m >\right|^2 \delta\left(E_n - E_m\right) \ , \tag{2.29}$$

which limits the transitions to states of the same energy. But formula (2.29) is obtained when the observation time is infinite. For finite times, the delta distribution acquires a finite width, described by the density function $\mathbf{D}(\omega, \mathbf{\Delta}t)$, which allows transitions between states of approximately the same energy, within a range ΔE:

$$W_{mn} = \frac{2\pi}{\hbar} \left|< n|\bar{\mathbf{V}}|m >\right|^2 [\mathbf{D}(\omega_{nm}, \mathbf{\Delta}t)/h] \tag{2.30}$$

PME plus golden rule (2.30) lead to an equilibrium situation which is described by the *microcanonical ensemble*, where all the allowed states of approximately the same energy, are equiprobable (see discussion of point 1 above).

3. Master equations are real and intrinsically irreversible. To show the latter property, we follow the discussion given in [8]. We discard off-diagonal elements of the Density Matrix (Pauli hypothesis), and look at variation of diagonal ones during an infinitesimal time interval $\mathbf{\Delta}t$ [see relation (2.24)]. We have:

$$P_n(t + \Delta t) = \sum_m |\mathbf{U}_{nm}(\Delta t)|^2 \;\; P_m(t) \equiv \sum_m \mathbf{T}_{nm} \; P_m(t) \;,$$

where we have changed notation, writing $\mathbf{T}_{nm}$ for the transition probabilities, *i.e.* $\mathbf{T}_{nm} = |\mathbf{U}_{nm}(\Delta t)|^2$. Now we assume that the above relation is more general in nature, with $\mathbf{T}_{nm}$ representing transition probabilities for any dynamical process, even a classical one (for example, we may think of states in the classical Ising model). The relation

$$P_n(t + \Delta t) = \sum_m \mathbf{T}_{nm}(\Delta t) \; P_m(t) \;, \tag{2.31}$$

yields the change of probability P_n for small Δt in terms of the transition probabilities $\{\mathbf{T}_{nm}(\Delta t)\}$, and is at the heart of the origin of master equations. Since

$\mathbf{T}_{nm}$ and P_m are probabilities, they satisfy the relations:

$$\sum_n P_n = 1 \ ,$$

$$\tag{2.32}$$

$$\sum_m \mathbf{T}_{nm} = \sum_m \mathbf{T}_{mn} \ = 1 \ .$$

Using (2.32), one sees that normalization of $\{P_n\}$ does not depend on time, namely:

$$\sum_n P_n(t+\Delta t) = \sum_m \ P_m(t) = 1 \ ,$$

as it should be for a probability distribution. From (2.31) one readily obtains:

$$P_n(t+\Delta t) - P_n(t) = \sum_m \mathbf{T}_{nm} \ P_m(t) \ - \left(\sum_m \mathbf{T}_{mn}\right) \ P_n(t) \ ,$$

where the sum in brackets is equal to unity [see relation (2.32)]. Transition rates are defined as the limit

$$W_{nm} = \lim_{\Delta t \to 0} \left(\frac{\mathbf{T}_{nm}}{\Delta t}\right) \ ,$$

assuming that this limit exists (that was the case of Fermi golden rule). The time rate of change of P_n is then given in the form of a master equation:

$$\frac{d}{dt} P_n(t) = \sum_m \left[W_{nm} \ P_m(t) \ - W_{mn} \ P_n(t)\right] \ ,$$

which is an immediate consequence of relation (2.31). Now we show that master equations are intrinsically irreversible. Let's assume that relation (2.31) can be inverted:

$$P_m(t) = \sum_m \left(\mathbf{T}^{-1}\right)_{mn} \ P_n(t+\Delta t) \ ,$$

where $\left(\mathbf{T}^{-1}\right)_{mn}$ is the inverse matrix of $\mathbf{T}_{nm}$. Our hypothesis assumes that the latter represents transition probabilities, that is $0 \leq \mathbf{T}_{nm} \leq 1$. For the inverse matrix one should have

$$\sum_{m} \mathbf{T}_{nm} \left(\mathbf{T}^{-1}\right)_{mk} = \delta_{nk} \ ,$$

which implies that not all the $\left(\mathbf{T}^{-1}\right)_{mk}$ are positive and less than unity. Even if the matrix $\mathbf{T}^{-1}$ exists, its matrix elements cannot be interpreted as transition probabilities, and master equations are irreversible.

The derivation presented here has a heuristic character, and one notes that some assumptions may be objectionable. Subsequent works after Pauli, specially those accomplished by Van Hove [9] and Prigogine [10], have better justified the central hypotheses. Note that a quantum system, in general, does not obey a master equation, since the density matrix can not be considered diagonal at all times. We know that this is not possible out of the equilibrium condition, since the microscopic time evolution is reversible. Irreversibility is introduced through several important ingredients [11]: *i*) the *thermodynamic limit*, that is, an infinite number of degrees of freedom. Stationary unperturbed states then depend on several quantum numbers in addition of the energy, and one can introduce continuous densities of states for the description of the physical system. One can also assume that phases of off-diagonal elements of the density matrix are randomly distributed. Eventual degeneracies of the spectrum are removed by the perturbations, which are also of random character. In the case of the Boltzmann gas, a macroscopic number of molecules (thermodynamic limit) is essential to attain the *molecular chaos* condition; *ii*) short memory approximation, meaning that accumulated random phases lead to cancellation of off-diagonal terms in a short time scale τ_0. For the Boltzmann gas, τ_0 is of the order of the time spanning a small number of molecular collisions, which destroy any correlation of molecular velocities; *iii*) *coarse grained* description of time evolution. The PME is established for times Δt, such that $\tau_0 \lessapprox \Delta t \ll \tau_R$, that is, PME yields the time development with a resolution limited to τ_0. The whole time evolution, for arbitrary large times, can be envisaged as a type of *Markov chain*, where randomization of the phases is accomplished again and again in the course of time.

As discussed in point 1 above, solutions of master equations at long times agree with the postulate of equal a priori probability at equilibrium. We perceive that the method of master equations appears as physically superior, if compared to the ergodic theorem approach to describe the road to equilibrium. Characteristic time scales associated to ergodicity are of the order of the so called *Poincaré cycles*, which are physically meaningless for real macroscopic systems, as Boltzmann himself pointed out. Thus, there is no dynamics involved, and no possibility of obtaining realistic relaxation times. We are led to conclude that master equations are much more satisfactory for deriving Statistical Mechanics.

B

2.4.1 $\mathcal{H}$-theorem of Boltzmann-Pauli

The irreversibility displayed by master equations leads to an association with the second law of thermodynamics. Great similarities with Boltzmann transport equation can be noted, with the assumption of *molecular chaos* being the counterpart of the quantum *random phase* assumption of Pauli. Exploring this similarity, one can prove a quantum $\mathcal{H}$-theorem. We consider a density matrix which is 'coarse grained' in time, *i.e.*, random perturbations have cancelled out its off-diagonal terms. Diagonal elements P_n satisfy in turn, a master equation of the type given by (2.27).

Definition 13 *$\mathcal{H}$ function of Boltzmann-Pauli.*

It is defined as

$$\mathcal{H} \equiv \sum_{n} P_n \ln P_n \ . \tag{2.33}$$

Note the formal resemblance with $-\sigma$, with σ defined in (2.15) as the von Neumann entropy. However, in $\mathcal{H}$ we use a truncated density matrix, since off-diagonal elements are being discarded due to Pauli hypothesis. With the $\mathcal{H}$-theorem, to be proved below, one finds that $\mathcal{H}$ decreases monotonically with time. In contrast, $-\sigma$ displays fluctuations at very short time. After a time Δt, off-diagonal terms cancelled out due to accumulated random phases, and $-\sigma$ approaches the behavior of $\mathcal{H}$. But we know that off-diagonal terms reappear later on in the time evolution, if the system is not at equilibrium. As a result, $-\sigma$ fluctuates around the behavior of $\mathcal{H}$, the development of the $\mathcal{H}$ function representing a coarse grained behavior of $-\sigma$, not including short-time entropy fluctuations.

Theorem 14 *The $\mathcal{H}$-theorem is stated as*

$$\boxed{\frac{d}{dt}\mathcal{H} \leq 0 \ ,}$$

that is, $\mathcal{H}$ is a monotonically decreasing function up to the time when $\frac{d}{dt}\mathcal{H} = 0$, which characterizes the equilibrium state.

Demonstration is straightforward if one assumes that probabilities $\{P_n\}$ satisfy a master equation. It follows from:

$$\begin{aligned} \frac{d}{dt}\mathcal{H} &= \sum_n \left(1 + \ln P_n\right) \frac{d}{dt} P_n = \\ &= \sum_n \ln P_n \sum_m \left(W_{nm} P_m - W_{mn} P_n\right) \ , \end{aligned} \tag{2.34}$$

due to the fact that $\sum_n \left(\frac{d}{dt} P_n\right) = 0$, since probabilities are normalized. Changing dummy indexes in the second term in the r.h.s. of (2.34), one obtains

$$\frac{d}{dt}\mathcal{H} = \sum_{n,m} \ln\left(P_n/P_m\right) \ W_{nm} P_m = -\sum_{n,m} \ln\left(P_n/P_m\right) \ W_{mn} P_n \ ,$$

where the last term was obtained changing dummy indexes again. Noting that quantum mechanical transition rates satisfy $W_{nm} = W_{mn}$, one finally writes:

$$\frac{d}{dt}\mathcal{H} = \frac{1}{2} \sum_{n,m} \ln\left(P_n/P_m\right) W_{nm} \left(P_m - P_n\right) \ . \tag{2.35}$$

At this stage, we use the following lemma:

Lemma 15 *Let's consider two quantities* (X, Y)*, which are real and positive and represent probabilities,* i.e.*,* $0 \leq X, Y \leq 1$*. Then, the following inequality holds:*

$$(X - Y) \ln (Y/X) \leq 0 \ , \tag{2.36}$$

where the value 0 *is obtained when* $X = Y$*.*

Validity of (2.36) is self-evident, and since $W_{nm} \geq 0$, we can use the inequality in all the terms of (2.35), to get the result:

$$\frac{d}{dt}\mathcal{H} \leq 0 \ .$$

At equilibrium, all the probabilities $\{P_n\}$ and the $\mathcal{H}$ function are stationary. This condition is attained when all occupation probabilities are equal, that is $P_n = P$, for all n, and the $\mathcal{H}$ function is constant at its minimum value. Probabilities $\{P_n\}$ that satisfy a master equation yield an always decreasing $\mathcal{H}$ function, thus providing a smooth approach to the equilibrium state. In contrast, $-\sigma$ fluctuates around the values of $\mathcal{H}$, within the so called *noise range* most of the time. Very large fluctuations are very rare to occur spontaneously, and for all practical purposes we may say that $\mathcal{H}$ and $-\sigma$ are essentially identical at equilibrium, where σ is a maximum. We identify σ with the macroscopic entropy at equilibrium. For an isolated system, the Fermi Golden Rule limits quantum transitions to states of about the same energy, and at equilibrium, all the occupancy probabilities of those states are equal. We have already shown in section 2.3 that this condition maximizes σ. As remarked by Boltzmann, the $\mathcal{H}$-theorem gives a statistical interpretation of the Second Law. In the next chapter, we will present the theory for equilibrium ensembles and will develop in full the connections with the macroscopic properties described by classical Thermodynamics.

CT

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