## Quantum Thermodynamics, Non-Equilibrium Fluctuations

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http://physics.bgu.ac.il/~dcohen/ARCHIVE/sqn.pdf

#### **References:**

- [arXiv 1107.0568] DC, Lecture Notes in Statistical Mechanics and Mesoscopics
- [PRE 2012] DC, Joe Imry
- [arXiv 2403.06296] Cheolhee Han, DC, Eran Sela
- [PRL 2012] Experiment, Pekola
- [NPHYS 2013] Experiment, Pekola
- [PRB 2016] Experiment, Hofmann et al
- $\left[ \text{PSS } 2017 \right]$  Experiment, Hofmann et al
- [arXiv 2024] Experiment, microwave resonator

#### **Outline:**

- Thermodynamical perspective + Take home message.
- Rate equation version of the NFT / Heat-NFT.
- Mechanical version of the NFT / Work-NFT.
- Proposed quantum dot experiment.
- Quantum master equations / Lindblad framework.

## [1] Thermodynamical perspective

## = [1.1] The universe

The universe consists of a system, heat baths, and work agents.

The system exchange Heat (Q) and Work (W) with the baths and the agents.

What is the proper definition of Q and W...?



DC and Joe Imry [PRE 2012]

Quantum perspective of Work-NFT, the "Work Agent" paradigm



Cheolhee Han, DC, Eran Sela [arXiv 2024]

Experimental perspective of Work-NFT, realization and testing of the "Work Agent" paradigm

## [1.2] Thermodynamics

$$H = H_{\text{sys}}(r; X_a, X_b) + \sum H_{\text{agent}}(X_a, P_a) + \sum H_{\text{bath}}(X_b, P_b)$$
(1.1)

We have a system, heat baths, and work agents.

In stochastic picture work agent is like a bath that has infinite temperature.





$$E(\text{final}) - E(\text{initial}) = \sum_{a} W_a + \sum_{b} Q_b$$
(1.2)

**Remark.**– the following is not definition of work:

$$W = E(\text{final}) - E(\text{initial}) \tag{1.3}$$

Remark.– Thermodynamics is not the same as spectroscopy

$$\omega \equiv E(\text{final}) - E(\text{initial}) \tag{1.4}$$

Issues.-

- Measurement of the initial energy creates a clash between Thermodynamics and Quantum Mechanics.

- Energy is not an observable!

- Continuous monitoring of a quantum system destroys coherence and affects the dynamics.

## = [1.4] The second law

Microscopic version of the second law:

$$S^{universe}[B] - S^{universe}[A] > 0 aga{1.5}$$

Decomposing the universe:

$$\left[S^{sys}[B] - S^{sys}[A]\right] - \int_{A}^{B} \frac{dQ}{T_{baths}} > 0$$
(1.6)

Quasi-Static version, with  $dS^{\text{sys}} = (d\mathcal{Q} + d\mathcal{W}_{\text{irvrs}})/T_{\text{sys}}$ 

$$\int_{A}^{B} \frac{d\mathcal{W}_{\text{irvrs}}}{T_{sys}} + \int_{A}^{B} \left(\frac{1}{T_{sys}} - \frac{1}{T_{baths}}\right) dQ > 0$$

$$(1.7)$$

Single bath version, with Q = (E(B) - E(A)) - W, and  $F = E - T_0 S$ 

$$W > [F(B) - F(A)] =$$
minimal work required to carry out the process (1.8)

## ===== [1.5] The NFTs

Thermodynamic version of the second law for a cycle [Clausius]:

$$S \equiv \text{Entropy production} \equiv -\oint \sum_{b} \frac{dQ_{b}}{T_{b}}$$
 (1.9)

Mechanical version of the second law for driven system. Assume that  $T_0$  is the initial temperature. Assume cyclic driving with  $X(t_f) = X(t_i)$ .

$$S \equiv \text{Entropy production} \equiv \frac{W}{T_0}$$
 (1.10)

The Thermodynamic inequality

 $\langle \mathcal{S} \rangle > 0 \tag{1.11}$ 

The NFT implies

$$\left\langle e^{-\mathcal{S}} \right\rangle = 1 \tag{1.12}$$

General versions of the NFT concern  $P(\mathcal{S})$  for non-cyclic protocols. In particular the Jarzynski equality

$$\left\langle \exp\left[-\frac{W}{T_0}\right] \right\rangle = \exp\left[-\frac{F(B) - F(A)}{T_0}\right]$$
(1.13)

## [1.6] Experimental demonstration

Trivial example: piston

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Quantum do example...



## [1.7] Experimental demonstration - Results



The ratio between  $\left\langle \exp\left[-\frac{W}{T_0}\right] \right\rangle$  and  $\exp\left[-\frac{F(B)-F(A)}{T_0}\right]$ 



## The Math of the NFTs

[1.8]

It is customary to say that at equilibrium the expectation value of an observable reflects the typical value of this observable, while the fluctuations are relatively small. If the central limit theorem applies the RMS/mean should scale as  $1/\sqrt{N}$ . However, it turns out that the *full* statistics might reveal interesting information about the underlying dynamics. In the following we shall discuss processes where the distribution function of work or entropy production does not satisfy the symmetry relation P(-s) = P(s). Rather it satisfies a detailed-balance look-alike relation:

$$P(-s) = e^{-\beta s} P(s),$$
 [beta-symmetric distribution] (1.14)

It follows that P(s) can be written as a product of a symmetric function and an exponential factor  $e^{\beta s/2}$ . Another consequence of the  $\beta$ -symmetry is

$$\langle e^{-\beta s} \rangle = 1, \qquad [convex average]$$
 (1.15)

The latter equality can be re-phrased as follows: In analogy with the definition of *harmonic* average and *geometric* average that are defined as the inverse of  $\langle (1/s) \rangle$  and as the exp of  $\langle \log(s) \rangle$  respectively, here we can define a *convex* average that is defined as the log of the above expression. The convex average is zero for a  $\beta$ -symmetric distribution, while the standard algebraic average is positive

$$\langle s \rangle > 0,$$
 [convex inequality] (1.16)

While for a symmetric distribution the average value  $\langle s \rangle$  has to be zero, this is no longer true for a  $\beta$ -symmetric distribution. Rather the average should be related to the variance. To be specific let us assume that s has Gaussian distribution. It can be easily verified that such distribution has  $\beta$ -symmetry with  $\beta = 2\mu/\sigma^2$ , where  $\mu = \langle s \rangle$  is the average value and  $\sigma^2 = \text{Var}(s)$  is the variance. This relation between the first and second moment can be regarded as a fluctuation dissipation relation:

$$\langle s \rangle = \frac{1}{2} \beta \operatorname{Var}(s), \qquad ["fluctuation dissipation" relation]$$
 (1.17)

We can formalize this relation for non-Gaussian distribution in terms of comulant generating function  $g(\lambda)$  which is defined through

$$\langle e^{-\lambda s} \rangle \equiv e^{g(\lambda)}$$
 (1.18)

Note that due to normalization g(0) = 0, while  $g'(0) = -\mu$  and  $g''(0) = \sigma^2$ . In particular for a Gaussian  $g(\lambda) = -\mu\lambda + (1/2)\sigma^2\lambda^2$ . For a symmetric distribution  $g(-\lambda) = g(\lambda)$ . But for  $\beta$ -symmetry we must have

$$g(\beta - \lambda) = g(\lambda),$$
 [characterization of beta-symmetric distribution] (1.19)

Again we see that for a Gaussian  $\beta$ -symmetry implies a relation between the mean and the variance.

In the following we shall consider two versions of the non-equilibrium fluctuation theorem. In one version we consider the statistics P(W) of the work W that is done by an agent during a cycle that involves a thermally isolates system. In the second version we consider the statistics P(S) of the entropy production S during a cycle that involves exchange of energy with several heat baths.

## [2] Rate equation version of the NFT

#### = [2.1] Rate equations

A rate equation is merely a discrete version of the diffusion or Fokker-Planck equation. It can be regarded as describing a generalized "random walk" problem, where the transition rates  $w_{nm}$  are not necessarily equal in the  $n \mapsto m$  and  $m \mapsto n$  directions. The state of the system is described by a column vector  $\boldsymbol{p}$  whose entries are the occupation probabilities  $p_n$ , such that  $\sum_n p_n = 1$ . The dynamics is determined by the rate equation

$$\frac{d\boldsymbol{p}}{dt} = \boldsymbol{W}\boldsymbol{p}, \qquad \qquad \boldsymbol{W} = \text{diagonal}\{-\gamma_n\} + \text{offdiagonal}\{w_{nm}\}$$
(2.1)

The off-diagonal elements are the rates of transitions, namely,  $w_{nm}$  is the rate of transition from m to n. The diagonal elements  $-\gamma_i$  of the W matrix are determined such that each column sums to zero. Accordingly  $\sum_n p_n = 1$  is conserved.

**Detailed balance.** In the context of the "system-bath" paradigm it is common to model the system as a set of levels  $\{E_n\}$  with transition rates that reflect detailed balance considerations, such that  $p_n^{SS} \propto \exp[-E_n/T_B]$ . Namely,

$$\frac{w_{mn}}{w_{nm}} \equiv \exp\left[\mathcal{E}_{n \to m}\right] = \exp\left[\frac{E_n - E_m}{T_B}\right]$$
(2.2)

where  $\mathcal{E}_{n \sim m}$  is called *stochastic field*. From a mathematical point of view detailed-balance means that any circulation of the stochastic filed is zero, i.e.  $\mathcal{E}$  is a conservative field that can be derived from a potential  $U_n$ . To get equilibrium the stochastic potential has to be  $U_n = E_n/T$ .

A driving noise source or a work agent (see below) can be regarded as a bath that has infinite temperature. More generally one can regard the average value  $(w_{nm} + w_{mn})/2$  as the *noise* which is introduced into the system by the bath, while the difference  $(w_{nm} - w_{mn})$  is the *friction*. However this point of view is strictly correct only for constant density of states. If the level density grows with energy there will be a heating effect even if  $T_B = \infty$ .

### [2.2] Three level/site system

The three-level system is the simplest setup for illustration of non-equilibrium thermodynamics. For example, it can be regarded as a model for a 3-level laser heat engine (see figure) or a mathematically equivalent rolling marble machine (see figure). The transitions are induced by a hot bath  $(T_H)$  and by a cold bath  $(T_C)$ . In the first example photons can be either emitted or absorbed by a work agent  $(T_A = \infty)$ . The second example is further discussed below. Either way the dynamics is generated by the matrix

$$\boldsymbol{W} = \begin{pmatrix} -\gamma_1 & w_C^- & w_A \\ w_C^+ & -\gamma_2 & w_H^- \\ w_A & w_H^+ & -\gamma_3 \end{pmatrix}$$
(2.3)

where  $\gamma_1 = w_C^+ + w_A$ , and  $\gamma_2 = w_C^- + w_H^+$ , and  $\gamma_3 = w_H^- + w_A$ . The affinity of the cycle is defined as

$$\Phi = \mathcal{E}_{1 \sim 2} + \mathcal{E}_{2 \sim 3} + \mathcal{E}_{3 \sim 1} = \ln \left[ \frac{w_{13} w_{32} w_{21}}{w_{12} w_{23} w_{31}} \right] = \frac{\omega_C}{T_C} - \frac{\omega_H}{T_H}$$
(2.4)

In order to have a working engine cycle we require  $\Phi > 0$ , which implies  $(\omega_C/\omega_H) > (T_C/T_H)$ . The efficiency of the engine is

$$\eta \equiv \frac{\omega_H - \omega_C}{\omega_H} < 1 - \frac{T_C}{T_H}$$
(2.5)

The limiting efficiency is the so-called Carnot efficiency. We can solve  $\boldsymbol{W}\boldsymbol{p} = 0$  to find the probabilities  $(p_1, p_2, p_3)$  at steady state. Then we can find the probability current  $I(\Phi) = (p_3 - p_1)w_A$  at steady state, and the power output of the engine  $(\omega_H - \omega_C)I(\Phi)$ .

Work agent.— The mechanical rolling marble machine possibly clarifies better the concept of *work agent*. Here the task of the engine is to pulls up a weight. The hot bath induce with some probability a transition of the marble form position "2" to position "3". From there, with some probability, it gets into a car of the roller coaster wheel. Then is rolls (trapped in the car) to position "1". The wheel pulls up the weight. In order to maximize efficiency it is designed such that the potential energy of the whole system (including the weight) is the same at "3" and at "1". Consequently there is an equal probability to make the ride from "1" to "3". However, considering the full cycle, the condition  $\Phi > 0$  ensures that the net work is positive.



#### [2.3] The non-equilibrium fluctuation theorem

The non-equilibrium fluctuation theorem (Bochkov, Kuzovlev, Evans, Cohen, Morris, Searles, Gallavotti) regards the probability distribution of the *entropy production* during a general non-equilibrium process. The clearest formulation of this idea assumes that the dynamics is described by a rate equation. The transition rates between state n and state m satisfies

$$\frac{w(m|n)}{w(n|m)} = \exp\left[-\frac{E_m - E_n}{T_{nm}}\right]$$
(2.6)

Where  $T_{nm}$  is the temperature that controls the nm transition. We can regard the rate equation as describing a random walk process. Consider a trajectory r(t). If the particle makes a transition from m to n the entropy production is  $(E_m - E_n)/T_{nm}$ . Hence we get for example

$$\frac{w(1|2)w(2|3)w(3|4)}{w(4|3)w(3|2)w(2|1)} = \exp\left[-\frac{E_1 - E_2}{T_{1,2}} - \frac{E_2 - E_3}{T_{2,3}} - \frac{E_3 - E_4}{T_{3,4}}\right] \equiv e^{-\mathcal{S}[1 \rightsquigarrow 2 \rightsquigarrow 3 \rightsquigarrow 4]}$$
(2.7)

In general we write

$$\frac{P[r(-t)]}{P[r(t)]} = \exp\left[-\mathcal{S}[r]\right]$$
(2.8)

From this "microscopic" relation we deuce that the probability distribution of the energy production satisfies  $P(-S)/P(S) = e^{-S}$ , hence  $\langle e^{-S} \rangle = 1$  and  $\langle S \rangle > 0$ .

#### ===== [2.4] Fluctuations of current in a ring

A simple example for the practicality of this relation concerns the fluctuations of the current I that emerge due to the motion of a particle in a ring. Given a trajectory  $q \equiv It$  is the winding number and  $S \equiv q\Phi$  is the entropy production. The non-equilibrium fluctuation theorem implies that  $P(-q)/P(q) = \exp(-q\Phi)$ . Note that in the case of an electric current  $\Phi = eV/T$ , where V is the electro-motive force.

#### [2.5] Thermodynamic Uncertainty Relations

The prototype thermodynamic uncertainty relations concerns a stochastic cyclic process (e.g. the motion of a molecular motor) that is described by a rate equation. The rate of a forward step is  $w^+$ , and the the rate of a backward step is  $w^-$ . The ratio is  $w^-/w^+ = \exp(Q_0/T)$ , where  $Q_0$  is the energy of the chemical reaction. Thus the count q of cycles (the net number of "steps" of the molecular rotor) executes a biased random walk process, with  $\langle q \rangle = (w^+ - w^-)t$  and  $\operatorname{Var}(q) = (w^+ + w^-)t$ . The associated entropy production is  $S = \langle q \rangle \times (Q_0/T)$ . It follows that the signal to noise ratio (SNR) is

$$SNR = \frac{\langle q \rangle}{\sqrt{Var(q)}} = \sqrt{S\frac{T}{Q_0} \tanh\left(\frac{Q_0}{2T}\right)} < \sqrt{\frac{S}{2}}$$
(2.9)

This relation expresses the observation that the the SNR of a stochastic process is bounded by the entropy production.

## [2.6] Analysis of heat conduction

A prototype application of the non-equilibrium fluctuation theorem concerns the analysis of heat flow form hot bath  $T_H$  to cold bath  $T_C$ . The temperature difference is  $\epsilon = T_H - T_C$ . We assume that the conductor that connects the two baths can be modeled using a master equation. The transition between states of the conductor are induced by the bath and are like a random walk. With any trajectory we can associate quantities  $Q_H$  and  $Q_C$  that represent that heat flow from the baths into the conductor. From the fluctuation theorem it follows that

$$\frac{P(-Q_H, -Q_C)}{P(Q_H, Q_C)} = \exp\left[\frac{Q_C}{T_C} + \frac{Q_H}{T_H}\right]$$
(2.10)

Next we define the absorbed energy  $\bar{Q} = Q_H + Q_C$  and the heat flow  $Q = (Q_H - Q_C)/2$ . We realize that in the long time limit  $Q \sim t$  while the fluctuations of  $\bar{Q}$  are bounded. Accordingly we get

$$\frac{P(-Q)}{P(Q)} = \exp\left[-\left(\frac{1}{T_C} - \frac{1}{T_H}\right)Q\right]$$
(2.11)

If we use a Gaussian approximation, we get a "fluctuation-dissipation" relation

$$\langle Q \rangle = \frac{1}{2} \left( \frac{1}{T_C} - \frac{1}{T_H} \right) \operatorname{Var}(Q)$$

$$(2.12)$$

The relation can be linearized with respect to  $\epsilon = T_H - T_C$ . The thermal conductance is defined through  $\langle Q \rangle = K\epsilon \times t$ , and the intensity of fluctuations through  $\operatorname{Var}(Q) = \nu \times t$ . Thus we deduce that

$$\langle \dot{Q} \rangle = K \times (T_H - T_C), \qquad \text{with } K = \frac{1}{2T^2} \nu$$

$$(2.13)$$

## [3] Mechanical version of the NFT

#### = [3.1] The distribution function of the work

The Crooks relation and Jarzynski equality concern the probability distribution of the *work* that is done during a non-equilibrium process. For presentation purpose let us consider a gas in cylinder with a movable piston. Initially the piston is in position A, and the gas in equilibrium with temperature  $T_0$ . The canonical probabilities are

$$p_r^{(A)} = \frac{1}{Z(A)} e^{-(1/T_0)E_r^{(A)}}, \qquad \text{where } Z(A) = \exp\left[-\frac{F(A)}{T_0}\right]$$
(3.1)

Now we displace the piston to position B doing work W. After that we can optionally allow the system to relax to the bath temperature  $T_0$ , but this no longer affects W. The distribution of work is defines as

$$P_{A \sim B}(\mathcal{W}) = \sum_{r} p_{r}^{(A)} \, \delta \Big( \mathcal{W} - (E_{r}^{(B)} - E_{r}^{(A)}) \Big)$$
(3.2)

It is implicit here that we assume a conservative deterministic classical system with a well-defined invariant measure that allows division of phase space into "cells". The phase-space states  $|r^{(B)}\rangle$  are associated with  $|r^{(A)}\rangle$  through the dynamics in a one-to-one manner. In other words, the index r in the above definition labels a trajectory that starts at r. If the dynamics is non-adiabatic the order of the cells in energy space is likely to be scrambled: if the  $E_r^{(A)}$  are indexed in order of of increasing energy; it is likely that  $E_r^{(B)}$  will become disordered.

If the dynamics is not deterministic the above definition can be modified in an obvious way. To be specific let us consider the quantum case, where the probability to make a transition form an eigenstate  $|n^{(A)}\rangle$  of the initial Hamiltonian, to an eigenstate  $|m^{(A)}\rangle$  of the final Hamiltonian, is given by

$$P_{A \sim B}(m|n) = \left| \langle m^{(B)} | U_{A \sim B} | n^{(A)} \rangle \right|^2$$
(3.3)

Then we define the spectral kernel:

$$P_{A \sim B}(\omega) = \sum_{n,m} p_n^{(A)} \operatorname{P}_{A \sim B}(m|n) \,\delta\left(\omega - (E_m^{(B)} - E_n^{(A)})\right)$$
(3.4)

Accordingly,

$$\frac{P_{B \sim A}(-\omega)}{P_{A \sim B}(\omega)} = \frac{Z_A}{Z_B} e^{-\beta\omega}$$
(3.5)

Since we consider here a closed system, we can identify the work as the energy difference  $W = \omega$ . For further discussion of how work can be defined in the quantum context see arXiv:1202.4529

#### [3.2] The Crooks relation

We have defined the probability distribution  $P_{A \sim B}(W)$  for a process that starts at equilibrium with the piston at position A. The probability distribution  $P_{B \sim A}(W)$  is defined in the same way for a reversed process: initially the piston is in position B, and the gas in equilibrium with temperature  $T_0$ , then the piston is displaced to position A. The Crooks relation states that

$$\frac{P_{B \sim A}(-\mathcal{W})}{P_{A \sim B}(\mathcal{W})} = \exp\left[-\frac{\mathcal{W} - (F(B) - F(A))}{T_0}\right]$$
(3.6)

The derivation of this relation using the "quantum" language is trivial and follows exactly the same steps as in the derivation of the detailed balance relation for any spectral function  $\tilde{S}(\omega)$ . The only difference is that here we have an extra factor  $\exp[F(B) - F(A)]$ , on top of the Boltzmann factor, that arises because the  $p_n^{(A)}$  in the forward process involves a normalization factor 1/Z(A), while the  $p_m^{(B)}$  is the reversed process involves a normalization factor 1/Z(B).

### = [3.3] The Jarzynski equality

Multiplying both sides of the Crooks relation by  $P_{B \sim A}(W)$ , integrating over W, and taking into account the normalization of P(-W), one obtains the Jarzynski equality

$$\left\langle \exp\left[-\frac{\mathcal{W}}{T_0}\right] \right\rangle = \exp\left[-\frac{F(B) - F(A)}{T_0}\right]$$
(3.7)

It follows from the Jarzynski equality that  $\langle W \rangle > [F(B) - F(A)]$ , which is equivalent to the maximum work principle. It reduces to  $\mathcal{W} = (F(B) - F(A))$  in the the case of a quasi-static adiabatic process.

An optional one line derivation of the Jarzynski equality in the context of deterministic classical dynamics is as follows:

$$\left\langle \exp\left[-\frac{\mathcal{W}}{T_0}\right] \right\rangle = \frac{1}{Z(A)} \sum_r e^{-(1/T_0)E_r(A)} \exp\left[-\frac{E_r(B) - E_r(A)}{T_0}\right] = \exp\left[-\frac{F(B) - F(A)}{T_0}\right]$$
(3.8)

The Crooks relation could have been derived in a similar way, but we had preferred to get it using the "quantum" language, and to regard the Jarzynski equality as its implication.

## = [3.4] The fluctuation dissipation relation

Let us see what is the implication on the Crooks relation with regard to a simple closed cycle for which F(B) = F(A). In such case P(W) is a  $\beta$ -symmetric distribution. It follows that there is a "fluctuation dissipation relation"

$$\langle \mathcal{W} \rangle = \frac{1}{2T} \operatorname{Var}(\mathcal{W})$$
 (3.9)

Considering a multi-cycle process  $\operatorname{Var}(\mathcal{W}) = 2D_E t$  and  $\langle \mathcal{W} \rangle = \mathcal{W} t$ , leading to the dissipation-diffusion relation that we have derived in past lecture  $\mathcal{W} = (1/T)D_E$ , from which follows the dissipation-fluctuation relation  $\eta = \nu/(2T)$ .

# [4] Quantum dot experiment

## =----- [4.1] Hamiltonian

Toy model:

$$H_{\mathcal{S}}(X) = \epsilon \sigma_x + X \frac{1}{2} (\sigma_z - 1)$$

$$H_{\mathcal{A}} = \frac{\omega}{2} \left[ \left( \ell \hat{P} \right)^2 + \left( \frac{\hat{X}}{\ell} \right)^2 \right]$$
(4.1)
(4.2)

Dot model:

$$H_{\mathcal{S}}(Q) = \sum_{k} \epsilon_k \hat{n}_k + \frac{Q}{C_G} e \hat{n}_{\text{QD}}$$

$$H_{\mathcal{A}} = \left[ \frac{1}{2C_0} \hat{Q}^2 + \frac{c^2}{2L_0} \hat{\Phi}^2 \right]$$

$$(4.3)$$

$$\hat{X} = e\hat{Q}/C_G = \text{gate volatage}$$
  
 $C_G = (C_g + C_r)C_0/C_g$   
 $\omega = 1/\sqrt{L_0C_0}$   
 $\ell^2 = \omega e^2 C_0/C_G^2$ 



## [4.2] NFT accuracy measure

The Work distribution for classical driving:

$$P(W) = \sum_{a,b} p_a |\langle b|U|a \rangle|^2 \delta(W - (E_b^{(f)} - E_a^{(i)}))$$
(4.5)

$$= \sum_{j=0,1,2} q_j \delta(W+jX_0)$$
(4.6)



The NFT:

$$\langle e^{-W/T} \rangle_{\text{ideal}} = \int dW P(W) e^{-W/T} = \frac{Z_f}{Z_i} \equiv e^{-\Delta F/T}$$

$$(4.7)$$

The Work distribution, driving by agent:

$$P_{\mathcal{A}}(W) = \sum_{n} P_n^{(f)} \delta(W + (E_{\mathcal{A},n} - E_{\mathcal{A}}^{(i)}))$$

$$(4.8)$$

Broadening and Shifting:

$$\delta(W + X_0) \quad \mapsto \quad \frac{1}{\sqrt{\pi}\Delta} e^{-\frac{(W + X_0 - \delta)^2}{\Delta^2}} \tag{4.9}$$



NFT accuracy measure:

$$\left\langle e^{-\frac{W-\Delta F}{T}} \right\rangle = e^{-\frac{\delta(\ell)}{T}} e^{-\frac{\Delta(\ell)^2}{4T^2}}$$
(4.10)



Conditions for high accuracy:

$$\{\Delta(\ell), \ \delta(\ell)\} \ll T \tag{4.11}$$

$$\Delta(\ell) \approx \omega \frac{X_0}{\ell} \tag{4.12}$$

$$\delta(\ell) \sim \frac{\ell^2}{\omega} \tag{4.13}$$

For  $T \sim X_0$ 

$$1 \ll \ell/\omega \ll \sqrt{X_0/(2\omega)} \tag{4.14}$$

Optional view of the uncertainty condition: Energy uncertainty:  $\Delta(\ell) = \omega X_0/\ell$ Condition:  $\Delta(\ell) \ll X_0$ .

Application to the quantum dot model:

 $\omega \ll (C_0/C_G)^2 [e^2/C_0]$ 

## [4.3] Born Oppenheimer picture



Born Oppenheimer surfaces:

$$V_{\text{empty}}(X) = V_k(X) = \frac{\omega}{2} \left(\frac{\hat{X}}{\ell}\right)^2 + \left[\varepsilon_k\right]$$
(4.15)

$$V_{\text{occupied}}(X) = V_0(X) = \frac{\omega}{2} \left(\frac{\hat{X}}{\ell}\right)^2 + \left[\varepsilon_0 + X\right]$$
(4.16)

Turning point X found from:

$$V_k(X) = V_0(-X_0) (4.17)$$

For the estimate we take typical value for emission, say  $\varepsilon_k \sim 0$ . Back-reaction condition:

$$\delta(\ell) \equiv |X - X_0| \approx \frac{\ell^2}{\omega} \ll X_0 \tag{4.18}$$

**Remark:** This is a classical condition...

## [5] Quantum master equations

#### ==== [5.1] General perspective

The description of the reduced dynamics of a system that is coupled to a bath using a Master equation is commonly based on the following working hypothesis: (i) The bath is fully characterized by a single spectral function. (ii) There is a way to justify the neglect of memory effects. The latter is known as the Markovian approximation. In particular it follows that the initial preparation, whether it is factorized or not, is not an issue. If the master equation is regarded as *exact* description of the reduced dynamics it should be of the Lindblad form. Otherwise is should be regarded merely as an approximation.

There are two common approximation schemes: (A) In the *Microscopic regime* of atomic physics (e.g. two level atom) it is assumed that the bath induced rates are much smaller than the level spacing, and a "secular approximation" is employed. (B) In the *Mesoscopic regime* of condense matter physics (e.g. Brownian motion) it is assumed that the bath is Ohmic, and accordingly its effect can be treated as a generalization of "white noise".

#### === [5.2] The general Lindblad form

A master equation for the time evolution of the system probability matrix is of Lindblad form if it can be written as

$$\frac{d\rho}{dt} = -i[\boldsymbol{H},\rho] + \sum_{r} \nu_{r} \boldsymbol{L}_{r} \rho \boldsymbol{L}_{r}^{\dagger} - \frac{1}{2} [\boldsymbol{\Gamma}\rho + \rho \boldsymbol{\Gamma}], \qquad \boldsymbol{\Gamma} = \sum_{r} \nu_{r} \boldsymbol{L}_{r}^{\dagger} \boldsymbol{L}_{r}$$
(5.1)

where  $L_r$  are called Lindblad generators, and  $\nu_r$  are positive coefficients. An optional style of writing the above master equation is

$$\frac{d\rho}{dt} = -i[\boldsymbol{H},\rho] + \sum_{r} \nu_{r} \left[ \boldsymbol{L}_{r}\rho\boldsymbol{L}_{r}^{\dagger} - \frac{1}{2} \{\boldsymbol{L}_{r}^{\dagger}\boldsymbol{L}_{r},\rho\} \right], \qquad (5.2)$$

Lindblad equation is the most general form of a Markovian master equation for the probability matrix.

#### ===== [5.3] The Ohmic Master Equation

We shall discuss later the general procedure to derived this master equation from an Hamiltonian, where the interaction with the bath is via the system operator W = x. The same procedure can be uses for any W, leading to

$$\frac{d\rho}{dt} = -i[\mathcal{H},\rho] - \frac{\nu}{2}[W,[W,\rho]] - i\frac{\eta}{2}[W,\{V,\rho\}] - \frac{\nu_{\eta}}{2}[V,[V,\rho]]$$
(5.3)

where v has been replaced by  $V = i[\mathcal{H}, W]$ , and where  $\nu_{\eta} = 0$ . This Ohmic master equation does not have the Lindblad form (see below), and hence in general complete positivity is not guaranteed. For example: if we consider the relaxation of a wavepacket in damped harmonic oscillator, then at low temperatures we end up with a sub-minimal wavepacket that violates the uncertainty relation.

In order for this equation to be Lindblad, the minimal modification would be to set a non-zero  $\nu_{\eta} = \eta^2/(4\nu)$ . With this substitution, after diagonalization, one ends up with a single Lindblad term with the generator

$$\boldsymbol{L} = \boldsymbol{W} + i\frac{\eta}{2\nu}\boldsymbol{V} \tag{5.4}$$

Note that the pre-factors of the three terms in the modified Ohmic version are  $\nu/2$  and  $\nu/(2T)$  and  $\nu/(32T^2)$  respectively. These terms can be regarded as arsing from an expansion in powers of  $(\Omega/T)$ , where  $\Omega$  is the frequency of the motion. Accordingly in the high temperature regime the deviation of the standard Fokker-Planck equation from the Lindblad form is negligible.

#### The secular approximation [5.4]

We come back one step, and consider again general bath, not necessarily Ohmic. Instead of assuming small correlation time, we shall assume weak interaction. Specifically, in atomic physics applications the induced rate of transitions wbecomes much smaller compared with the Rabi-Bloch frequency  $\Omega$  of the coherent oscillations. Accordingly it is appropriate to write that master equation in the interaction picture:

$$\frac{d\tilde{\rho}}{dt} = \tilde{W}(t)\tilde{\rho}W(t) + W(t)\tilde{\rho}\tilde{W}(t)^{\dagger} - W(t)\tilde{W}(t)\tilde{\rho} - \tilde{\rho}\tilde{W}(t)^{\dagger}W(t)$$
(5.5)

Substitution of the  $\mathcal{H}$ -induced spectral decomposition of the W-s one observes terms that oscillate with frequencies  $\Omega + \Omega'$ . We keep only the terms that oscillate with ~ 0 frequency, and hence do not average to zero. For example, in  $W\rho W$  we keep only the  $G(\Omega)W_{\Omega}\rho W_{-\Omega}$  terms. Consequently we obtain the so called secular approximation

$$\frac{d\rho}{dt} = -i[\mathcal{H},\rho] + \sum_{\Omega} \left[ \tilde{C}(\Omega) \ W_{\Omega}\rho W_{\Omega}^{\dagger} - G(\Omega) \ W_{\Omega}^{\dagger}W_{\Omega}\rho - G(\Omega)^{*} \ \rho W_{\Omega}^{\dagger}W_{\Omega} \right]$$
(5.6)

The imaginary part of  $G(\Omega)$ , aka Lamb shift, can be absorbed into the Hamiltonian  $\mathcal{H}$ , so we end up with a simple sum over Lindblad terms that are weighted by the spectral intensities  $\tilde{C}(\Omega)$ , namely,

$$\frac{d\rho}{dt} = -i[\mathcal{H}_{\text{eff}},\rho] + \sum_{\Omega} \tilde{C}(\Omega) \left[ W_{\Omega}\rho W_{\Omega}^{\dagger} - \frac{1}{2} \{ W_{\Omega}^{\dagger} W_{\Omega},\rho \} \right]$$
(5.7)

In particular one should distinguish the  $\Omega \neq 0$  terms that induce inter-level transitions from the  $\Omega = 0$  term that commutes with the Hamiltonian.

#### ==== [5.5] The Pauli master equation

For a system that has no degeneracies (for example a few-level atom) it is natural to write the secular equation in the  $\mathcal{H}$  basis. One realizes that the dynamics of the diagonal elements decouples from that of the off-diagonal elements. Namely, the first term in the secular approximation induces FGR transitions with rates

$$w_{nm} = \tilde{C}(-(E_n - E_m)) |W_{nm}|^2$$
(5.8)

The corresponding decay constants are  $\Gamma_n = \sum_{m=1}^{\prime} w_{nm}$ . The ratio  $w_{nm}/w_{mn}$  is not unity unless we consider white noise source (infinite temperature). For finite temperatures the FGR rates favor downwards transitions. Consequently we get the so-called Pauli rate equation for the probabilities  $p_n$ 

$$\frac{d\boldsymbol{p}}{dt} = \mathcal{W} \boldsymbol{p}, \qquad \qquad \mathcal{W} = \begin{pmatrix} -\Gamma_1 & w_{12} & \dots \\ w_{21} & -\Gamma_2 & \dots \\ \dots & \dots & \dots \end{pmatrix}$$
(5.9)

For the off-diagonal terms we get

$$\frac{d\rho_{nm}}{dt} = \left[-i(E_n - E_m) - \gamma_{nm}\right]\rho_{nm}, \qquad \text{[for } n \neq m\text{]}$$
(5.10)

with dephasing rates

$$\gamma_{nm} = \frac{\nu}{2} |W_{nn} - W_{mm}|^2 + \frac{1}{2} (\Gamma_n + \Gamma_m) \equiv \gamma_{\varphi} + \Gamma_{\rm rlx}$$
(5.11)

where the first term originates from the  $\Omega = 0$  generator, while the second term originates from the  $\Omega \neq 0$  transitions.