Statistische Mechanik I - Computergestützte Methoden

TU Berlin, SS 2007

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July 4, 2007

CONTENTS

1. MASTER EQUATION METHODS

1.1 Introduction

1.1.1 Motivation

The goal of *dissipative quantum mechanics* or ‘quantum dissipation theory’ is to formulate microscopic theories of irreversible behaviour of quantum systems. Simply speaking, one would like to understand processes like, e.g., *friction* or ‘damping’ on a microscopic level. This requires at least two things: ‘friction’ means that physical objects interact with each other, i.e., we need to talk about interactions. Furthermore, this occurs as a function of time for systems which are usually out of equilibrium, i.e., we need to talk about dynamics.

A further, more ambitious goal is to better understand the relation between microscopic and macroscopic theories, e.g., the relation between mechanics (classical or quantum) and statistical mechanics (again classical or quantum).

Already in classical (Newtonian) mechanics, the description of irreversible behaviour is a non-trivial problem. One can often introduce dissipation into microscopic equations by adding phenomenological terms, such as the velocity-dependent damping term $\gamma\dot{x}(t)$ ($\gamma > 0$) in the damped (forced) harmonic oscillator,

$$\ddot{x}(t) + \gamma\dot{x}(t) + \omega^2 x(t) = f(t). \tag{1.1.1}$$

In this example, one of the goals would be to derive this equation and to actually calculate γ from an underlying microscopic theory.

Other examples (some of these are very tough, some not so tough problems):

- What is the spontaneous photon emission rate of an atom in vacuum?
- What is the electrical resistance of a (small or large) piece of metal at very low temperatures?
- How does a Laser work?
- What is the typical time after which a given realisation of a qubit (a quantum two-level system as realised in, e.g., a linear ion trap, the charge or

magnetic flux in superconducting junctions, the electron charge or spin in semiconductor quantum dots, the nuclear spin etc.) fails to operate in the desired manner?

1.1.2 Origin of Dissipation, System-Bath Theories

The most successful approach to quantum dissipation has been the use of *System-Bath Theories*, which will be the main topic of this chapter. The main idea is the following:

STEP 1: we divide the 'world' into two parts: a) the part we are really interested in (for example, all the conduction band electrons in a piece of metal), and b) the part we are not so much interested in (for example, all the rest of the metal). This splitting obviously is a choice that depends on what we want to describe/calculate

STEP 2: Call these two parts 'system' and 'reservoir', identify the interaction between system and reservoir, and then derive an effective theory for the system only.

1.1.2.1 Example

Single oscillator ('system') with angular frequency ω_0, mass M, position x, coupled to $N \gg 1$ oscillators ('reservoir') $i = 1, ..., N$ with angular frequencies ω_i, masses m_i, position x_i, coupling of the form $c_i x_i x$ via position coordinates.
Exercise: derive and solve the equations of motion a) for the *total system* (system plus reservoir) and b) for the system only.

The coupling leads to an effective dynamics of the system oscillator governed by the sum of many eigenmodes with eigenfrequencies. This sum is determined by the coupling constants c_i. For finite N, this is just a problem of coupled oscillators, and the motion of the system oscillator must therefore be periodic with a (large) period T. The time T after which the entire system returns back to its initial starting point is called *Poincaré* time.

The key point now is: 1. For times $t \ll T$, the effective dynamics of the system (x and p of the system oscillator) very much resembles the dynamics we would expect from a *damped* system: a sum of many oscillatory terms with 'nearly random' coefficients decays as a function of time $t \ll T$. 2. In most known cases, T is very, very large ('larger than the age of the universe'). This means that one can savely neglect the periodic 'Poincaré return' of the system.

1.1.2.2 Formal Splitting

The basic idea in microscopic theories of dissipation is a decomposition of a total system into a system S and a reservoir part R or B, 'bath'. The (Hamiltonian) dynamics of the total system is reversible, but the dynamics of the system S is effectively not reversible for times $t \ll T$.

In this lecture, we formulate these ideas for quantum systems. The Hilbert space of the total system is defined by the tensor product

$$\mathcal{H}_{\text{total}} = \mathcal{H}_S \otimes \mathcal{H}_B. \tag{1.1.2}$$

The Hamiltonian of the total system is defined as

$$H_{\text{total}} \equiv H \equiv H_S + H_{SB} + H_B \tag{1.1.3}$$

Here and in the following, we will mostly discuss *time-independent* Hamiltonians. Time-dependent Hamiltonians $H = H(t)$ can be treated as well but require additional techniques (e.g., Floquet theory for period time-dependence; adiabatic theorems for slow time-dependence).

1.1.3 Overview

1. 'Simple' Systems with *few* degrees of freedom: typically quantum optics systems, atoms, few-level systems, cavity modes.

- Weak coupling approximation: Master Equation (Born and Markov Approximation)
- Damped harmonic oscillator.
- Solution methods: phase-space methods (P-representation etc.).
- Solution methods: quantum trajectories.
- Correlation Functions, Quantum Regression Theorem.
- Beyond weak coupling approximation: Feynman-Vernon influence functional (path integral) theories; R. P. Feynman, F. L. Vernon, Ann. Phys. (N.Y.) **24**, 118 (1963). Non-exponential decay laws at low temperatures.
- Exact solution of damped harmonic oscillator.
- Spin-Boson Problem, Two-Level System.
- Non-Markovian versus Markovian, Lindblad versus non-Lindblad.
- 'Non-standard' methods.

2. Systems with *many* degrees of freedom: typically condensed matter systems, electrons + phonons (particle statistics).

- Quasiclassical kinetic theories, Boltzmann equation.
- Quantum Many-Body Non-Equilibrium Methods. (Keldysh) Greens Function Methods, quantum Boltzmann equation.

In this chapter, we will concentrate on 1. ('Simple' Systems with *few* degrees of freedom). Also, not discussed in detail in this lecture are

- Nakajima-Zwanzig theories, Mori projection operator theories. These give a more formal approach towards system-bath theories.
- 'Early approaches' such as Wigner-Weisskopf theory of spontaneous emission.
- ...

Generally speaking, quantum dissipation can be regarded as a subfield of non-equilibrium quantum statistics/ non-equilibrium many-body theory.

1.1.4 Literature

Quite a few text books are available:

H. Carmichael, 'An Open System Approach to Quantum Optics', Springer Lecture Notes in Physics m 18, (Berlin, Heidelberg, 1993): good introduction into Master equations, quantum trajectories, quantum optics.

D. F. Walls and G. J. Milburn, 'Quantum Optics', Springer (Berlin) 1994: quantum optics book; good reference book but very condensed.

U. Weiss, 'Quantum Dissipative Systems', World Scientific (Singapore) (1993): advanced methods (path integral) beyond Master equation approach.

H. Haug and A.-P. Jauho, 'Quantum Kinetics in Transport and Optics of Semiconductors', Springer 1996: non-equilibrium (Keldysh) Green's function approach.

F. Haake, 'Quantum Signatures of Chaos', Springer (Berlin, Heidelberg) 2001: good chapter on dissipation.

A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, and W. Zwerger, Rev. Mod. Phys. **59**, 1 (1987): famous review of dissipative two-level system.

1.2 Master Equation I: Derivation

1.2.1 Interaction Picture

We define an interaction picture by writing

$$H \equiv H_0 + V, \quad H_0 \equiv H_S + H_B, \quad V \equiv H_{SB} \qquad (1.2.1)$$

with the Hamiltonian H_0 describing the time evolution of the uncoupled system and bath, and the perturbation V describing the interaction H_{SB}.

We define $\chi(t)$ as the total density matrix (system + bath) which obeys the Liouville-von-Neumann equation ,

$$\frac{d}{dt}\chi(t) = -i[H, \chi(t)] \rightsquigarrow \chi(t) = e^{-iHt}\chi(t=0)e^{iHt}, \tag{1.2.2}$$

where we start with the initial condition $\chi(t = 0)$ at time $t = 0$. In the interaction picture,

$$\begin{aligned} \tilde{\chi}(t) &\equiv e^{iH_0t}\chi(t)e^{-iH_0t} &(1.2.3)\\ \tilde{A}(t) &\equiv e^{iH_0t}Ae^{-iH_0t}. &(1.2.4)\end{aligned}$$

The equation of motion for the density operator in the interaction picture becomes

$$\begin{aligned} \frac{d}{dt}\tilde{\chi}(t) &= i[H_0, \tilde{\chi}(t)] + e^{iH_0t}\frac{d}{dt}\chi(t)e^{-iH_0t} \\ &= i[H_0, \tilde{\chi}(t)] - ie^{iH_0t}[H, \chi(t)]e^{-iH_0t} \\ &= i[H_0, \tilde{\chi}(t)] - ie^{iH_0t}[H_0 + V, \chi(t)]e^{-iH_0t} \\ &= i[H_0, \tilde{\chi}(t)] - i[H_0 + \tilde{V}(t), \tilde{\chi}(t)] \\ &= -i[\tilde{V}(t), \tilde{\chi}(t)]. \end{aligned} \tag{1.2.5}$$

In integral form, this can be written as

$$\tilde{\chi}(t) = \chi(t=0) - i\int_0^t dt'[\tilde{V}(t'), \tilde{\chi}(t')] \tag{1.2.6}$$

which we insert into Eq. (1.2.5) to obtain

$$\boxed{\frac{d}{dt}\tilde{\chi}(t) = -i[\tilde{V}(t), \chi(t=0)] - \textstyle\int_0^t dt'[\tilde{V}(t), [\tilde{V}(t'), \tilde{\chi}(t')]].} \tag{1.2.7}$$

Up to here, everything is still exact.

1.2.2 Perturbation Theory in the System-Bath Coupling

1.2.2.1 Effective Density Matrix of the System

We wish to obtain an equation of motion for the *effective density matrix of the system* at time $t > 0$,

$$\rho(t) \equiv \mathrm{Tr}_B[\chi(t)]. \tag{1.2.8}$$

This object is sufficient to calculate expectation values of *system* operators A_S:

$$\begin{aligned} \langle A_S \rangle_t &\equiv \mathrm{Tr}_{\mathrm{total}}[\chi(t) A_S] \\ &= \mathrm{Tr}_S\left[\mathrm{Tr}_B \chi(t)\right] A_S = \mathrm{Tr}_S\left[\rho(t) A_S\right]. \end{aligned} \tag{1.2.9}$$

Now use

$$\begin{aligned} \mathrm{Tr}_B[\tilde{\chi}(t)] &= \mathrm{Tr}_B e^{iH_0 t}\chi(t)e^{-iH_0 t} \\ &= e^{iH_S t}\left(\mathrm{Tr}_B e^{iH_B t}\chi(t)e^{-iH_B t}\right)e^{-iH_S t} = e^{iH_S t}\rho(t)e^{-iH_S t} \\ &\equiv \tilde{\rho}(t). \end{aligned} \tag{1.2.10}$$

Note that the interaction picture $\rho(t) \leftrightarrow \tilde{\rho}(t)$ involves only the free *System* Hamiltonian H_S and not H_0,

$$\tilde{\rho}(t) \equiv e^{iH_S t}\rho(t)e^{-iH_S t}. \tag{1.2.11}$$

Using

$$\tilde{A}_S(t) \equiv e^{iH_0 t}A_S e^{-iH_0 t} = e^{iH_S t}A_S e^{-iH_S t} \tag{1.2.12}$$

for system operators, one has

$$\langle A_S \rangle_t = \mathrm{Tr}_S\left[\tilde{\rho}(t)\tilde{A}_S(t)\right] = \mathrm{Tr}_S\left[\rho(t)A_S(t)\right]. \tag{1.2.13}$$

1.2.2.2 Equation of Motion for $\tilde{\rho}(t)$

This follows from Eq.(1.2.8) and (1.2.7) by taking the trace over the bath,

$$\boxed{\frac{d}{dt}\tilde{\rho}(t) = -i\mathrm{Tr}_B[\tilde{V}(t), \chi(t=0)] \quad - \quad \int_0^t dt' \mathrm{Tr}_B[\tilde{V}(t), [\tilde{V}(t'), \tilde{\chi}(t')]].} \tag{1.2.14}$$

1.2.2.3 Assumption (factorising initial condition):

$$\begin{aligned} \chi(t=0) &= R_0 \otimes \rho(t=0) \\ R_0 &\equiv \mathrm{Tr}_S[\chi(t=0)], \quad \rho(t=0) \equiv \mathrm{Tr}_B[\chi(t=0)]. \end{aligned} \tag{1.2.15}$$

This *factorisation assumption* is key to most of the results that follow. Its validity has been discussed and criticised in the past (see Weiss book for further references). Some of the issues are:

- Does the factorisation assumption only affect transient or also the long-time behaviour of the density matrix?

- Are there exactly solvable models where these issues can be clarified?

A theoretical formulation of time-evolution for arbitrary initial condition is sometimes possible: ‘preparation function’ (exact solution of dissipative quantum oscillator; Grabert, Ingold et al); generalisation of many-body Keldysh GF (three-by-three matrix instead of two-by-two matrix, M. Wagner).

1.2.2.4 Born Approximation

In the interaction picture,

$$\tilde{\chi}(t') \quad = \quad R_0 \otimes \tilde{\rho}(t=0) \quad \text{to zeroth order in } V. \tag{1.2.16}$$

The Born approximation in the equation of motion Eq.(1.2.14) consists in

$$\tilde{\chi}(t') \quad \approx \quad R_0 \otimes \tilde{\rho}(t') \quad \text{Born approximation.} \tag{1.2.17}$$

This means one assumes that for all times $t' > 0$, the total density matrix remains a product of the initial bath density matrix R_0 and the system density matrix $\tilde{\rho}(t')$. Intuitively, one argues that this is justified when the bath is ‘very large’ and the coupling H_{SB} ‘weak’, so that the back-action of the system onto the bath can be neglected. In practice, one usually assumes a thermal equilibrium for the bath,

$$R_0 = \frac{e^{-\beta H_B}}{\mathrm{Tr} e^{-\beta H_B}}, \quad \text{thermal equilibrium bath,} \tag{1.2.18}$$

where $\beta = 1/k_B T$ with T the bath equilibrium temperature.

Remark: A more detailed analysis of the Born approximation and alternative approximations can be done within the framework of the *Projection Operator formalism.*

Within the Born approximation, with Eq. (1.2.17), (1.2.15), and (1.2.14), one obtains a *closed integro-differential equation* for the reduced density operator $\tilde{\rho}(t)$ of the system in the interaction picture,

$$\boxed{\begin{array}{rcl} \dfrac{d}{dt}\tilde{\rho}(t) & = & -i\mathrm{Tr}_B[\tilde{V}(t), R_0 \otimes \tilde{\rho}(t=0)] \\ & - & \int_0^t dt' \mathrm{Tr}_B[\tilde{V}(t), [\tilde{V}(t'), R_0 \otimes \tilde{\rho}(t')]]. \end{array}} \tag{1.2.19}$$

Remark: Eq.(1.2.19) is exact up to second order in the perturbation V: set $\tilde{\rho}(t') = \rho(0)$ on the r.h.s. of Eq.(1.2.19). Since $\tilde{\rho}(t')$ in the double commutator on the r.h.s. of Eq.(1.2.19) depends on V, Eq.(1.2.19) is to infinite order in V though not exact. Diagrammatically this corresponds to a summation of an infinite series of diagrams. It is non-trivial to make this statement more precise, but roughly speaking these diagrams contain certain vertex corrections as can be seen from the fact that $\rho(t)$ is a density matrix and not a wave function.

1.2.3 Explicit Form of Master Equation

The equation of motion Eq.(1.2.17) is pretty useless unless one specifies at least some more details for the interaction Hamiltonian $V \equiv H_{SB}$. Denoting system operators by S'_j and bath operators by B_k, the most general form of V is

$$V = \sum_{jk} c_{jk} S'_j \otimes B_k \equiv \sum_k S_k \otimes B_k, \tag{1.2.20}$$

where we have re-defined the sum over j as a new system operator (→ similarity to Schmid-decomposition).

Remark: Note that S_k and B_k need not necessarily be hermitian. Inserting Eq.(1.2.20) into Eq.(1.2.19), we have

$$\begin{aligned} \frac{d}{dt}\tilde{\rho}(t) &= -i \sum_k \mathrm{Tr}_B[\tilde{S}_k(t)\tilde{B}_k(t), R_0\rho(t=0)] \\ &- \int_0^t dt' \sum_{kl} \mathrm{Tr}_B[\tilde{S}_k(t)\tilde{B}_k(t), [\tilde{S}_l(t')\tilde{B}_l(t'), R_0\tilde{\rho}(t')]]. \end{aligned}$$

To simplify things, we will assume

$$\mathrm{Tr}_B \tilde{B}_k(t) R_0 = 0 \tag{1.2.21}$$

from now on. This is no serious restriction. We furthermore introduce the *bath correlation functions*

$$C_{kl}(t,t') \equiv \mathrm{Tr}_B\left[\tilde{B}_k(t)\tilde{B}_l(t')R_0\right]. \tag{1.2.22}$$

Assumption 1:

$$[R_0, H_B] = 0 \quad \text{bath in equilibrium.} \tag{1.2.23}$$

This means

$$C_{kl}(t,t') \equiv C_{kl}(t-t'). \tag{1.2.24}$$

We then have

$$\begin{aligned} \frac{d}{dt}\tilde{\rho}(t) &= -\int_0^t dt' \sum_{kl} \Big[C_{kl}(t-t')\left\{\tilde{S}_k(t)\tilde{S}_l(t')\tilde{\rho}(t') - \tilde{S}_l(t')\tilde{\rho}(t')\tilde{S}_k(t)\right\} \\ &+ C_{lk}(t'-t)\left\{\tilde{\rho}(t')\tilde{S}_l(t')\tilde{S}_k(t) - \tilde{S}_k(t)\tilde{\rho}(t')\tilde{S}_l(t')\right\}\Big]. \end{aligned} \tag{1.2.25}$$

Assumption 2a (Markov approximation): the bath correlation function $C_{kl}(\tau)$ is strongly peaked around $\tau \equiv t - t' = 0$ with a peak width $\delta\tau \ll \gamma^{-1}$, where γ is a 'typical rate of change of $\tilde{\rho}(t')$.' Note that the condition $\delta\tau \ll \gamma^{-1}$ can only be checked *after* the equation of motion for $\tilde{\rho}(t)$ has been solved. In the interaction picture, one then replaces $\tilde{\rho}(t') \to \tilde{\rho}(t)$ under the integral to obtain

$$\begin{aligned}\frac{d}{dt}\tilde{\rho}(t) &= -\int_0^t dt' \sum_{kl} \Big[C_{kl}(t-t') \Big\{ \tilde{S}_k(t)\tilde{S}_l(t')\tilde{\rho}(t) - \tilde{S}_l(t')\tilde{\rho}(t)\tilde{S}_k(t) \Big\} \\ &+ C_{lk}(t'-t) \Big\{ \tilde{\rho}(t)\tilde{S}_l(t')\tilde{S}_k(t) - \tilde{S}_k(t)\tilde{\rho}(t)\tilde{S}_l(t') \Big\} \Big]. \qquad (1.2.26)\end{aligned}$$

The important fact is that this approximation is carried out in the interaction (and not in the original Schrödinger) picture: in the interaction picture, the only relevant time-scale the change of the density matrix is γ^{-1} and not (the usually much faster) timescales from the free evolution with H_S. In fact, one now transforms back into the Schrödinger picture, using Eq.(1.2.11),

$$\begin{aligned}\frac{d}{dt}\tilde{\rho}(t) &= i[H_S, \tilde{\rho}(t)] + e^{iH_St}\frac{d}{dt}\rho(t)e^{-iH_St} \\ \rightsquigarrow \frac{d}{dt}\rho(t) &= -i[H_S, \rho(t)] + e^{-iH_St}\frac{d}{dt}\tilde{\rho}(t)e^{iH_St} \qquad (1.2.27)\end{aligned}$$

which leads to

$$\begin{aligned}\rightsquigarrow \frac{d}{dt}\rho(t) &= -i[H_S, \rho(t)] \\ &- \int_0^t dt' \sum_{kl} \Big[C_{kl}(t-t') \Big\{ e^{-iH_St}\tilde{S}_k(t)\tilde{S}_l(t')\tilde{\rho}(t) - \tilde{S}_l(t')\tilde{\rho}(t)\tilde{S}_k(t) \Big\} e^{iH_St} \\ &+ C_{lk}(t'-t) \Big\{ e^{-iH_St}\tilde{\rho}(t)\tilde{S}_l(t')\tilde{S}_k(t) - \tilde{S}_k(t)\tilde{\rho}(t)\tilde{S}_l(t') \Big\} e^{iH_St} \Big] \\ &= -i[H_S, \rho(t)] \\ &- \int_0^t dt' \sum_{kl} \Big[C_{kl}(t-t') \Big\{ S_k\tilde{S}_l(t'-t)\rho(t) - \tilde{S}_l(t'-t)\rho(t)S_k \Big\} \\ &+ C_{lk}(t'-t) \Big\{ \rho(t)\tilde{S}_l(t'-t)S_k - S_k\rho(t)\tilde{S}_l(t'-t) \Big\} \Big]. \qquad (1.2.28)\end{aligned}$$

Assumption 2b (Markov approximation): the integral over t' can be carried out to $t = \infty$. This in fact is completely consistent with assumption 2a (see above). Defining

$$D_k \equiv \lim_{t\to\infty} \int_0^t d\tau \sum_l C_{kl}(\tau)\tilde{S}_l(-\tau), \quad E_k \equiv \lim_{t\to\infty} \int_0^t d\tau \sum_l C_{lk}(-\tau)\tilde{S}_l(-\tau), (1.2.29)$$

we can write

$$\boxed{\begin{aligned} \frac{d}{dt}\rho(t) &= -i[H_S,\rho(t)] \\ &- \sum_k \Big[S_k D_k \rho(t) - D_k \rho(t) S_k + \rho(t) E_k S_k - S_k \rho(t) E_k\Big]. \end{aligned}} \tag{1.2.30}$$

1.3 Master Equation II: the Damped Harmonic Oscillator

1.3.1 Introduction

In the following, we will discuss two models for damped harmonic oscillators and derive the explicit forms for the corresponding Master equations.

1.3.1.1 Non-RWA Model

$$\begin{aligned} H_{\text{total}} &\equiv H_S + H_{SB} + H_B \\ &= \Omega a^\dagger a + \sum_Q \gamma_Q (a_Q + a_Q^\dagger)(a + a^\dagger) + \sum_Q \omega_Q a_Q^\dagger a_Q. \end{aligned} \tag{1.3.1}$$

Here, $V \equiv H_{SB} = S \otimes B$ with $S = a + a^\dagger$ and $B = \sum_Q \gamma_Q (a_Q + a_Q^\dagger)$. The indices k and l play no role here.

1.3.1.2 RWA-Model

$$\begin{aligned} H_{\text{total}} &\equiv H_S + H_{SB} + H_B \\ &= \Omega a^\dagger a + \sum_Q \gamma_Q (a_Q a^\dagger + a_Q^\dagger a) + \sum_Q \omega_Q a_Q^\dagger a_Q. \end{aligned} \tag{1.3.2}$$

Here, $V \equiv H_{SB} = \sum_{i=1,2} S_i \otimes B_i$ with $S_1 = a^\dagger$, $S_2 = a$, an $B_1 = \sum_Q \gamma_Q a_Q$, $B_2 = \sum_Q \gamma_Q a_Q^\dagger)$. The indices k and l now do play a role.

1.3.2 Master Equation (RWA)

We first derive the master equation for the RWA model.

1.3.2.1 Thermal Bath Correlation Functions (RWA)

The bath correlation functions simply are

$$\begin{aligned}
C_{12}(t) &\equiv \mathrm{Tr}_B\left[\tilde{B}_1(t)B_2R_0\right] = \mathrm{Tr}_B\left[\sum_{QQ'}\gamma_Q\gamma_{Q'}a_Qe^{-i\omega_Qt}a^\dagger_{Q'}R_0\right]\\
&= \sum_Q \gamma_Q^2 e^{-i\omega_Qt}(1+n_B(\omega_Q)) = \int_0^\infty d\omega\rho(\omega)e^{-i\omega t}(1+n_B(\omega))\\
C_{21}(t) &\equiv \mathrm{Tr}_B\left[\tilde{B}_2(t)B_1R_0\right] = \mathrm{Tr}_B\left[\sum_{QQ'}\gamma_Q\gamma_{Q'}a^\dagger_Qe^{i\omega_Qt}a_{Q'}R_0\right]\\
&= \sum_Q \gamma_Q^2 e^{i\omega_Qt}n_B(\omega_Q) = \int_0^\infty d\omega\rho(\omega)e^{i\omega t}n_B(\omega)\\
C_{11}(t) &= C_{22}(t) = 0, \qquad (1.3.3)
\end{aligned}$$

where all the information on the microscopic coupling to the bath in now comprised within one single function, the bath *spectral density* $\rho(\omega)$

$$\boxed{\rho(\omega) \equiv \sum_Q \gamma_Q^2\delta(\omega_Q-\omega).} \qquad (1.3.4)$$

Using $\tilde{S}_1(t)=a^\dagger e^{i\Omega t}$, $\tilde{S}_2(t)=ae^{-i\Omega t}$, we have

$$\begin{aligned}
D_1 &\equiv \int_0^\infty d\tau C_{12}(\tau)\tilde{S}_2(-\tau) = \int_0^\infty d\tau C_{12}(\tau)ae^{i\Omega t} = \hat{C}_{12}(-i\Omega)a \qquad (1.3.5)\\
D_2 &\equiv \int_0^\infty d\tau C_{21}(\tau)\tilde{S}_1(-\tau) = \int_0^\infty d\tau C_{21}(\tau)a^\dagger e^{-i\Omega t} = \hat{C}_{21}(i\Omega)a^\dagger\\
E_1 &\equiv \int_0^\infty d\tau C^*_{21}(\tau)\tilde{S}_2(-\tau) = \int_0^\infty d\tau C^*_{21}(\tau)ae^{i\Omega t} = [\hat{C}_{21}(i\Omega)]^*a = D_2^\dagger\\
E_2 &\equiv \int_0^\infty d\tau C^*_{12}(\tau)\tilde{S}_1(-\tau) = \int_0^\infty d\tau C^*_{12}(\tau)a^\dagger e^{-i\Omega t} = [\hat{C}_{12}(-i\Omega)]^*a^\dagger = D_1^\dagger
\end{aligned}$$

Here, we defined the Laplace transformation of a function $f(t)$,

$$\hat{f}(z) = \int_0^\infty dte^{-zt}f(t). \qquad (1.3.6)$$

The Master equation therefore is

$$\begin{aligned}
\frac{d}{dt}\rho(t) &= -i[\Omega a^\dagger a, \rho(t)] \\
&- \sum \Big\{ S_k D_k \rho(t) - D_k \rho(t) S_k + \rho(t) E_k S_k - S_k \rho(t) E_k \Big\} \qquad (1.3.7) \\
&= -i[\Omega a^\dagger a, \rho(t)] \\
&- \Big\{ \Big[\hat{C}_{12}(-i\Omega) a^\dagger a + \hat{C}_{21}(i\Omega) a a^\dagger \Big] \rho(t) + \rho(t) \Big[[\hat{C}_{21}(i\Omega)]^* a a^\dagger + [\hat{C}_{12}(-i\Omega)]^* a^\dagger a \Big] \\
&- \hat{C}_{12}(-i\Omega) a \rho(t) a^\dagger - \hat{C}_{21}(i\Omega) a^\dagger \rho(t) a - [\hat{C}_{21}(i\Omega)]^* a^\dagger \rho(t) a - [\hat{C}_{12}(-i\Omega)]^* a \rho(t) a^\dagger \Big\}.
\end{aligned}$$

1.3.3 Rates and Energy Shift (RWA)

Let us have a closer look at the expressions

$$\hat{C}_{12}(z) = \int_0^\infty d\omega \rho(\omega)[1 + n_B(\omega)] \int_0^\infty dt e^{-(z+i\omega)t}. \qquad (1.3.8)$$

The Laplace transform exists for $\mathrm{Im}(z) > 0$ to ensure convergence of the integral, but in the expressions above we need $\hat{C}_{12}(z = -i\Omega)$ etc., i.e. purely imaginary arguments! The limit $t \to \infty$, if explicitely written, reads

$$\hat{C}_{12}(z = -i\Omega) = \lim_{t\to\infty} \int_0^\infty d\omega \rho(\omega)[1 + n_B(\omega)] \int_0^t dt' e^{i(\Omega-\omega)t'}. \qquad (1.3.9)$$

Now,

$$\lim_{t\to\infty} \int_0^t dt' e^{ixt'} = \lim_{t\to\infty} \left[\frac{\sin xt}{x} + i\frac{1 - \cos xt}{x} \right] = \pi\delta(x) + iP\left(\frac{1}{x}\right), \qquad (1.3.10)$$

where P denotes the principal value.

For the first term, we used a very useful

Theorem:
For any integrable, normalised function $f(x)$ with $\int_{-\infty}^\infty dx f(x) = 1$,

$$\lim_{\varepsilon\to 0} \frac{1}{\varepsilon} f\left(\frac{x}{\varepsilon}\right) = \delta(x). \qquad (1.3.11)$$

Since $\int_{-\infty}^\infty dx \sin(x)/x = \pi$, this yields the Delta function above.

We split the two bath correlation functions into real and imaginary parts,

$$\begin{aligned}
\hat{C}_{12}(-i\Omega) &\equiv \frac{1}{2}\gamma_+ + i\Delta_+, \quad \hat{C}_{21}(i\Omega) \equiv \frac{1}{2}\gamma + i\Delta \\
\gamma_+ &\equiv \gamma_+(\Omega) \equiv 2\pi\rho(\Omega)[1 + n_B(\Omega)], \quad \gamma \equiv \gamma(\Omega) \equiv 2\pi\rho(\Omega) n_B(\Omega) \\
\Delta_+ &\equiv P\int_0^\infty \frac{d\omega}{2\pi} \frac{\gamma_+(\omega)}{\Omega - \omega}, \quad \Delta \equiv -P\int_0^\infty \frac{d\omega}{2\pi} \frac{\gamma(\omega)}{\Omega - \omega}. \qquad (1.3.12)
\end{aligned}$$

Remarks:

- Real and imaginary parts of the correlation functions are related to each other: Kramers-Kronig relations.
- Note the minus-sign in the definition of Δ.

1.3.4 Final Form of Master Equation

Using these definitions, we can now write

$$\begin{aligned}\frac{d}{dt}\rho(t) &= -i[\Omega a^\dagger a,\rho(t)] - \frac{1}{2}\Big\{ \left[(\gamma_+ + 2i\Delta_+)a^\dagger a + (\gamma + 2i\Delta)aa^\dagger\right]\rho(t) \qquad (1.3.13)\\ &+ \rho(t)\left[(\gamma - 2i\Delta)aa^\dagger + (\gamma_+ - 2i\Delta_+)a^\dagger a\right] - 2\gamma_+ a\rho(t)a^\dagger - 2\gamma a^\dagger\rho(t)a\Big\}.\end{aligned}$$

We write $2i\Delta aa^\dagger = 2i\Delta(a^\dagger a + 1)$ and obtain

$$\begin{aligned}\frac{d}{dt}\rho(t) &= -i[(\Omega + \Delta_+ + \Delta)a^\dagger a,\rho(t)] \qquad (1.3.14)\\ &- \frac{1}{2}\gamma_+\Big\{a^\dagger a\rho(t) + \rho(t)a^\dagger a - 2a\rho(t)a^\dagger\Big\} - \frac{1}{2}\gamma\Big\{aa^\dagger\rho(t) + \rho(t)aa^\dagger - 2a^\dagger\rho(t)a\Big\}.\end{aligned}$$

This can be further re-arranged into

$$\boxed{\begin{aligned}\frac{d}{dt}\rho(t) &= -i\bar{\Omega}[a^\dagger a,\rho] - \kappa\Big\{a^\dagger a\rho + \rho a^\dagger a - 2a\rho a^\dagger\Big\}\\ &- 2\kappa n_B(\Omega)\Big\{a^\dagger a\rho + \rho aa^\dagger - a\rho a^\dagger - a^\dagger\rho a\Big\},\end{aligned}} \qquad (1.3.15)$$

where

$$\bar{\Omega} \equiv \Omega + P\int_0^\infty d\omega\frac{\rho(\omega)}{\Omega-\omega}, \quad \kappa \equiv \pi\rho(\Omega). \qquad (1.3.16)$$

Remarks

- This is the 'standard' Master equation for the damped harmonic oscillator, as discussed in many text books and used for many applications.
- Modifications appear if one uses the non-RWA model Hamiltonian instead of the RWA Hamiltonian.
- Eq.(1.3.15) is, of course, not exact because we have used 2nd order perturbation theory (in the system-bath coupling γ_Q), and the Markov approximation.

- The oscillator energy $\hbar\Omega$ is renormalised due to the coupling to the environment. The renormalised frequency $\bar{\Omega}$ is *temperature independent*.
- The integral for the renormalised frequency $\bar{\Omega}$ may diverge, depending on the form of the spectral density $\rho(\omega)$, Eq.(1.3.4), in which case this theory breaks down. We will make this statement more precise below.
- One can show that the Master equation Eq.(1.3.15) (and its non-RWA analogon, model 1) is indeed 'wrong' in the sense that there is an *exact* solution for the density operator $\rho(t)$ within the same model, which is different from the solution of Eq.(1.3.15). This again will be discussed below.
- Comparing the exact $\rho(t)$ with that obtained from Eq.(1.3.15), one could now discuss the 'validity of the entire Master equation approach'. However, the damped harmonic oscillator is (with very few exceptions) the only quantum dissipative system where an exact solution exists.

1.3.5 Expectation Values (RWA Model)

We would like to use our Master equation Eq.(1.3.15)

$$\begin{aligned}\frac{d}{dt}\rho(t) &= -i\bar{\Omega}[a^\dagger a,\rho] - \kappa\Big\{a^\dagger a\rho + \rho a^\dagger a - 2a\rho a^\dagger\Big\}\\ &- 2\kappa n_B(\Omega)\Big\{a^\dagger a\rho + \rho a a^\dagger - a\rho a^\dagger - a^\dagger\rho a\Big\}\end{aligned}$$

and calculate some 'useful' quantities as, for examples, expectation values of System (= oscillator) observables $\hat{\theta}$. Let us do this for the number operator, $\hat{\theta} = \hat{n} = a^\dagger a$. Multiplying with n and taking the trace, we obtain

$$\begin{aligned}\frac{d}{dt}\langle n\rangle(t) &= -i\bar{\Omega}\mathrm{Tr}\left(n[a^\dagger a,\rho]\right) - \kappa\mathrm{Tr}\Big\{a^\dagger a a^\dagger a\rho + \rho a^\dagger a a^\dagger a - 2a\rho a^\dagger a^\dagger a\Big\}\\ &- 2\kappa n_B(\Omega)\mathrm{Tr}\Big\{a^\dagger a a^\dagger a\rho + \rho a a^\dagger a^\dagger a - a^\dagger a a\rho a^\dagger - a^\dagger a a^\dagger\rho a\Big\}\\ &= -i\bar{\Omega}\mathrm{Tr}\left(a^\dagger a a^\dagger a\rho - a^\dagger a\rho a^\dagger a\right) - \kappa\mathrm{Tr}\Big\{2a^\dagger a a^\dagger a\rho - 2\rho a^\dagger(a a^\dagger - 1)a\Big\}\\ &- 2\kappa n_B(\Omega)\mathrm{Tr}\Big\{a^\dagger a a^\dagger a\rho + \rho(a^\dagger a + 1)a^\dagger a - a^\dagger(a a^\dagger - 1)a\rho - a a^\dagger a a^\dagger\rho\Big\}\\ &= -2\kappa\mathrm{Tr}\Big\{\rho a^\dagger a\Big\}\\ &- 2\kappa n_B(\Omega)\mathrm{Tr}\Big\{a^\dagger a a^\dagger a\rho + \rho(a^\dagger a + 1)a^\dagger a - a^\dagger(a a^\dagger - 1)a\rho - (a^\dagger a + 1)(a^\dagger a + 1)\rho\Big\}\\ &= -2\kappa\mathrm{Tr}\Big\{\rho a^\dagger a\Big\} + 2\kappa n_B(\Omega)\\ &= -2\kappa\left(\langle n\rangle(t) - n_B(\Omega)\right). \qquad (1.3.17)\end{aligned}$$

This now is a simple first order differential equation which has the solution

$$\langle n\rangle(t) = \langle n\rangle(t=0)e^{-2\kappa t} + \kappa n_B(\Omega)\left(1-e^{-2\kappa t}\right). \tag{1.3.18}$$

In particular, one has

$$\langle n\rangle(t\to\infty) = n_B(\Omega). \tag{1.3.19}$$

For large times, the occupation number is thus given by the thermal equilibrium Bose distribution, regardless of the initial condition $\langle n\rangle(t=0)$.

1.3.6 Master Equation (Non-RWA Model)

Let us re-call that now

$$\begin{aligned} H_{\text{total}} &\equiv H_S + H_{SB} + H_B \\ &= \Omega a^\dagger a + \sum_Q \gamma_Q (a_Q + a_Q^\dagger)(a+a^\dagger) + \sum_Q \omega_Q a_Q^\dagger a_Q. \end{aligned}$$

1.3.7 Thermal Bath Correlation Function (non-RWA)

In the following, we will have a closer look at the properties of bath correlation functions.

1.3.7.1 Definition

We first re-call the definition of the bath correlation function,

$$\begin{aligned} C(t) &\equiv \mathrm{Tr}_B\left[\tilde{B}(t)BR_0\right] = \mathrm{Tr}_B\left[\sum_{QQ'}\gamma_Q\gamma_{Q'}(a_Q e^{-i\omega_Q t} + a_Q^\dagger e^{i\omega_Q t})(a_{Q'}+a_{Q'}^\dagger)R_0\right] \\ &= \sum_Q \gamma_Q^2\left[e^{-i\omega_Q t}(1+n_B(\omega_Q)) + e^{i\omega_Q t} n_B(\omega_Q)\right] \\ &= \int_0^\infty d\omega \rho(\omega)\left[e^{-i\omega t}(1+n_B(\omega)) + e^{i\omega t} n_B(\omega)\right] = C^*(-t). \end{aligned} \tag{1.3.20}$$

Furthermore, $n_B(\omega) \equiv 1/[e^{\beta\omega}-1]$ is the Bose function.

1.3.7.2 Bosonic Spectral Density $\rho(\omega)$

All the dependence on the coupling constants γ_Q is encapsulated within the spectral density $\rho(\omega)$. The latter is often parametrised as

$$\boxed{\rho(\omega) = 2\alpha\omega_c^{1-s}\omega^s e^{-\omega/\omega_c},} \tag{1.3.21}$$

where α is the dimensionless *coupling parameter* and ω_c is the *cutoff frequency.* Note that $\rho(\omega)$ has the dimension $[\omega]$ which is the reason for the pre-factor ω_c^{1-s}. The parameter s determines the low-frequency behaviour of $\rho(\omega)$, and one calls couplings with

$$\begin{aligned} s<1 &: \quad \text{sub-ohmic} \\ s=1 &: \quad \text{ohmic} \\ s>1 &: \quad \text{super-ohmic.} \end{aligned} \tag{1.3.22}$$

This classification has its origin in the analysis of the dissipative two-level (spin-boson) system which we will discuss below.

The case $s=1, \omega_c \to \infty$

$$\rho(\omega) = 2\alpha\omega \tag{1.3.23}$$

is called *scaling limit* of the ohmic bath and has the special property of homogeneity $\rho(k\omega) = k\rho(\omega)$.

1.3.7.3 Properties of $C(t)$

One can write

$$C(t) = \int_0^\infty d\omega \rho(\omega) \left[\coth\left(\beta\omega/2\right)\cos(\omega t) - i\sin(\omega t)\right], \tag{1.3.24}$$

where we used the useful identity

$$\coth\left(\beta\omega/2\right) = 1 + 2n_B(\omega). \tag{1.3.25}$$

Calculation of the integral with $\rho(\omega)$ given by Eq.(1.3.21) yields

$$\begin{aligned} C(t) &= 2\alpha\omega_c^{1-s}\beta^{-(s+1)} \times \qquad (1.3.26) \\ &\quad \Gamma(s+1)\left[\zeta\left(s+1, \frac{1+\beta\omega_c - i\omega_c t}{\beta\omega_c}\right) + \zeta\left(s+1, \frac{1+i\omega_c t}{\beta\omega_c}\right)\right], \end{aligned}$$

where Γ is the Gamma function and

$$\zeta(z,u) \equiv \sum_{n=0}^{\infty} \frac{1}{(n+u)^z}, \quad u \neq 0, -1, -2, ... \tag{1.3.27}$$

is the generalised Zeta function (cf. W. Magnus, F. Oberhettinger, and R. P. Soni, *Formulas and Theorem for the Special Functions of Mathematical Physics*, Springer, Berlin 1966). The zero temperature limit is obtained either from the $\beta \to \infty$ limit of Eq.(1.3.26) or directly by calculating the integral,

$$C(t) = 2\alpha\omega_c^{s+1}\Gamma(s+1)\left(1+i\omega_c t\right)^{-(s+1)}. \tag{1.3.28}$$

1.3.7.4 Validity of Markov Assumption

With explicit expressions like Eq. (1.3.26) and Eq. (1.3.28), one can now directly assess the validity of the Markov assumption (Assumption 2a above): ‘ *the bath correlation function* $C_{kl}(\tau)$ *is strongly peaked around* $\tau = 0$ *with a peak width* $\delta\tau \ll \gamma^{-1}$, *where* γ *is a typical rate of change of* $\tilde{\rho}(t')$.’ For example, for $T = 0$, $\gamma = 2\pi\rho(\Omega)$, and within the model $\rho(\omega) = 2\alpha\omega_c^{1-s}\omega^s e^{-\omega/\omega_c}$, Eq.(1.3.21), one has $\delta\tau \sim \omega_c^{-1}$, cf. Eq.(1.3.28). This would mean

$$\begin{aligned} \omega_c^{-1} 4\pi\alpha\omega_c^{1-s}\Omega^s e^{-\Omega/\omega_c} &\ll 1 \\ 4\pi\alpha \left(\Omega/\omega_c\right)^s e^{-\Omega/\omega_c} &\ll 1, \end{aligned} \tag{1.3.29}$$

which is fulfilled for large ω_c ($\Omega/\omega_c \lesssim 1$), $s > 0$, and small α. The condition of small α is consistent with the Born approximation (perturbation theory in the coupling to the bath).

1.3.8 Derivation of Master equation (non-RWA), secular approximation

We now move on to derive the Master equation for the non-RWA model. Using $\tilde{S}(t) = ae^{-i\Omega t} + a^\dagger e^{i\Omega t}$, we have

$$\begin{aligned} D &\equiv \int_0^\infty d\tau C(\tau)\tilde{S}(-\tau) = \int_0^\infty d\tau C(\tau)\left[ae^{i\Omega\tau} + a^\dagger e^{-i\Omega\tau}\right] \\ &= \hat{C}(-i\Omega)a + \hat{C}(i\Omega)a^\dagger \equiv c_- a + c_+ a^\dagger \\ E &\equiv \int_0^\infty d\tau C^*(\tau)\tilde{S}(-\tau) = \int_0^\infty d\tau C^*(\tau)\tilde{S}^\dagger(-\tau) = D^\dagger \\ &= c_+^* a + c_-^* a^\dagger, \end{aligned} \tag{1.3.30}$$

where we used the Laplace transform of $C(\tau)$,

$$\hat{C}(z) \equiv \int_0^\infty d\tau e^{-z\tau} C(\tau). \tag{1.3.31}$$

1.3.8.1 ‘Secular approximation’

We note that $\hat{C}(z) = \hat{C}_{12}(z) + \hat{C}_{21}(z)$. In the secular approximation, one sets

$$\begin{aligned} \hat{C}_{12}(i\Omega) &\equiv \int_0^\infty d\omega \rho(\omega) e^{-i\omega t} e^{-i\Omega t}(1 + n_B(\omega)) \to 0 \\ \hat{C}_{21}(-i\Omega) &\equiv \int_0^\infty d\omega \rho(\omega) e^{i\omega t} e^{i\Omega t} n_B(\omega) \to 0. \end{aligned} \tag{1.3.32}$$

The real parts of $\hat{C}_{12}(i\Omega)$ and $\hat{C}_{21}(-i\Omega)$ are zero because $\delta(\omega+\Omega)$ yields no contribution from the integral (remember that $\Omega>0$). This approximation therefore neglects the imaginary parts of $\hat{C}_{12}(i\Omega)$ and $\hat{C}_{21}(-i\Omega)$ which, however, do not lead to damping but only to a renormalisation of the system Hamiltonian H_S. For consistency, we therefore neglect the imaginary parts of $\hat{C}_{12}(-i\Omega)$ and $\hat{C}_{21}(i\Omega)$ as well. Therefore,

$$\begin{aligned} c_- + c_+ &\approx \frac{1}{2}(\gamma_+ + \gamma) = \pi\rho(\Omega)[1+2n_B(\omega)] \\ c_- - c_+ &\approx \frac{1}{2}(\gamma_+ - \gamma) = \pi\rho(\Omega). \end{aligned} \tag{1.3.33}$$

1.3.8.2 x-p Representation

We now can write

$$D = \frac{1}{\sqrt{2}}\left((c_- + c_+)\,x + i\,(c_- - c_+)\,p\right) \approx \frac{\pi\rho(\Omega)}{\sqrt{2}}\left(x\coth\left(\frac{\beta\Omega}{2}\right) + ip\right), \tag{1.3.34}$$

where we again used $\coth(\beta\Omega/2) = 1 + 2n_B(\Omega)$. Using $E = D^\dagger$, one obtains the *Master equation from the Non-RWA Model in secular approximation*,

$$\boxed{\begin{aligned} \frac{d}{dt}\rho &= -i[H_S,\rho] - \tfrac{\pi\rho(\Omega)}{2}\coth\left(\tfrac{\beta\Omega}{2}\right)\left(x^2\rho + \rho x^2 - 2x\rho x\right) \\ &- i\tfrac{\pi\rho(\Omega)}{2}\left(xp\rho - \rho p x - p\rho x + x\rho p\right). \end{aligned}} \tag{1.3.35}$$

1.4 Electronic Quantum Transport: Few-Level Systems

1.4.1 Model Hamiltonian

Quantum system as a few-level system,

$$H_S = \sum_i \varepsilon_i |i\rangle\langle i| \tag{1.4.1}$$

with electronic many-body states $|i\rangle$. Example: quantum dot with strong Coulomb blockade, only one additional 'transport' (valence) electron in one of the levels $|i\rangle$, $i\neq 0$, with the state $|0\rangle$ describing the state without additional electron.

Electron transport through the system is introduced by connecting to left and right electron reservoirs in thermal equilibrium at chemical potential μ_L (μ_R) with positive source-drain voltage $V_{SD}\equiv\mu_L-\mu_R>0$, inducing tunneling of electrons from the left to the right. The coupling to the electron reservoirs $\mathcal{H}_{\rm res}$ is described by the usual tunnel Hamiltonian $\mathcal{H}_V$,

$$H_B \equiv \mathcal{H}_{\rm res} = \sum_{k,\alpha=L/R} \varepsilon_{k,\alpha} c^\dagger_{k\alpha} c_{k\alpha}, \quad H_{SB} \equiv \mathcal{H}_V = \sum_{k\alpha i} (V_{k\alpha i} c^\dagger_{k\alpha} \hat{s}_i + H.c.), \quad (1.4.2)$$

where the $V_{k\alpha i}$ couple to a continuum of channels k in reservoir $\alpha = L/R$ and

$$\hat{s}_i \equiv |0\rangle\langle i|. \quad (1.4.3)$$

We note that the splitting of the whole electron system into reservoir and dot regions bears some fundamental problems that are inherent in all descriptions that use the tunnel Hamiltonian formalism. This relatively old problem of how to describe tunnel junctions in a quantum mechanical model has been pointed out first by Prange [**?**, **?**, **?**]. We do not discuss this point here but only note that the tunnel Hamiltonian formalism has turned out to be a successful tool for a variety of problems in electronic transport in mesoscopic systems [**?**, **?**, **?**]. Including the 'empty' state $|0\rangle$, the completeness relation for the system Hilbert space is

$$\hat{1} = \sum_i \hat{n}_i, \quad \hat{n}_i \equiv |i\rangle\langle i|. \quad (1.4.4)$$

In the above description, the lead electron spin index is included in the quantum number k.

1.4.2 Master Equation: single level ($i = 0, 1$)

In this case,

$$\mathcal{H}_V = \sum_{k\alpha} (V_{k\alpha} c^\dagger_{k\alpha} \hat{s} + H.c.), \quad \hat{s} \equiv |0\rangle\langle 1|. \quad (1.4.5)$$

Performing the commutators and using the free time evolution of the electron reservoir operators, one finds

$$\begin{aligned}
\frac{d}{dt}\tilde{\rho}(t) &= -\sum_{k\alpha=L/R} \int_0^t dt' g_{k\alpha}(t-t') \left\{ \tilde{s}(t)\tilde{s}^\dagger(t')\tilde{\rho}(t') - \tilde{s}(t')^\dagger \tilde{\rho}(t')\tilde{s}(t) \right\} \\
&- \sum_{k\alpha} \int_0^t dt' \bar{g}_{k\alpha}(t'-t) \left\{ \tilde{s}^\dagger(t)\tilde{s}(t')\tilde{\rho}(t') - \tilde{s}(t')\tilde{\rho}(t')\tilde{s}^\dagger(t) \right\} \\
&- \sum_{k\alpha} \int_0^t dt' g_{k_\alpha}(t'-t) \left\{ \tilde{\rho}(t')\tilde{s}(t')\tilde{s}^\dagger(t) - \tilde{s}^\dagger(t)\tilde{\rho}(t')\tilde{s}(t') \right\} \\
&- \sum_{k\alpha} \int_0^t dt' \bar{g}_{k\alpha}(t-t') \left\{ \tilde{\rho}(t')\tilde{s}^\dagger(t')\tilde{s}(t) - \tilde{s}(t)\tilde{\rho}(t')\tilde{s}^\dagger(t') \right\} \\
g_{k\alpha}(\tau) &\equiv |V_{k\alpha}|^2 f^\alpha(\varepsilon_k) e^{i\varepsilon_k \tau}, \quad \bar{g}_{k\alpha}(\tau) \equiv |V_{k\alpha}|^2 [1 - f^\alpha(\varepsilon_k)] e^{i\varepsilon_k \tau}, \quad (1.4.6)
\end{aligned}$$

with the Fermi distributions $f^{\alpha}(\varepsilon_{k_i}) \equiv \mathrm{Tr}_{\mathrm{res}}(R_0 c^{\dagger}_{k\alpha} c_{k\alpha})$. The sums over k can be written as integrals, introducing the tunneling density of states $\nu_{\alpha}(\varepsilon)$ in lead α,

$$\sum_k |V_{k\alpha}|^2 f^{\alpha}(\varepsilon_k) e^{i\varepsilon_k(t-t')} = \int_{-\infty}^{\infty} d\varepsilon \nu_{\alpha}(\varepsilon) f^{\alpha}(\varepsilon) e^{i\varepsilon(t-t')}, \quad \nu_{\alpha}(\varepsilon) \equiv \sum_k |V_{k\alpha}|^2 \delta(\varepsilon - \varepsilon_k). \tag{1.4.7}$$

1.4.3 Infinite Bias Limit

In the infinite source-drain voltage limit $\mu_L \to \infty$ and $\mu_R \to -\infty$ introduced by Gurvitz and Prager [**?**, **?**], and Stoof and Nazarov [**?**], the left Fermi function is one and the right Fermi function is zero. In this case, an additional simplification is obtained for *constant tunneling densities of states*,

$$\nu_{\alpha}(\varepsilon) = \nu_{\alpha} = \Gamma_{\alpha}/2\pi, \tag{1.4.8}$$

with constant tunnel rates

$$\Gamma_{\alpha} \equiv 2\pi \sum_k |V_{k\alpha}|^2 \delta(\varepsilon - \varepsilon_k), \tag{1.4.9}$$

cf. Eq. (**??**). This leads to delta functions like

$$\sum_k |V_{kL}|^2 f^{L}(\varepsilon_k) e^{i\varepsilon_k(t-t')} \;=\; \Gamma_L \delta(t-t'), \tag{1.4.10}$$

and correspondingly for the other terms. As a result, one directly obtains the *Markov limit* without any further assumptions in this limit, and the Master equation Eq.(1.4.6) in the interaction picture becomes

$$\begin{aligned} \frac{d}{dt}\tilde{\rho}(t) = &- \frac{\Gamma_L}{2}\left\{\tilde{s}(t)\tilde{s}^{\dagger}(t)\tilde{\rho}(t) - 2\tilde{s}(t)^{\dagger}\tilde{\rho}(t)\tilde{s}(t) + \tilde{\rho}(t)\tilde{s}(t)\tilde{s}^{\dagger}(t)\right\} \\ &- \frac{\Gamma_R}{2}\left\{\tilde{s}^{\dagger}(t)\tilde{s}(t)\tilde{\rho}(t) - 2\tilde{s}(t)\tilde{\rho}(t)\tilde{s}^{\dagger}(t) + \tilde{\rho}(t)\tilde{s}^{\dagger}(t)\tilde{s}(t)\right\}, \end{aligned} \tag{1.4.11}$$

where

$$\int_0^t dt' \delta(t-t') f(t') = \frac{1}{2} f(t) \tag{1.4.12}$$

was used. Now back-transformation into Schrödinger picture,

$$\begin{aligned} \frac{d}{dt}\rho(t) = &- i[H_S, \rho(t)] \\ &- \frac{\Gamma_L}{2}\left\{ss^{\dagger}\rho(t) - 2s^{\dagger}\rho(t)s + \rho(t)ss^{\dagger}\right\} \\ &- \frac{\Gamma_R}{2}\left\{s^{\dagger}s\rho(t) - 2s\rho s^{\dagger} + \rho(t)s^{\dagger}s\right\}. \end{aligned} \tag{1.4.13}$$

EXERCISE: Determine the occupation probabilities for the single level system in this Infinite Bias Limit,

$$\langle 0|\rho(t)|0\rangle, \quad \langle 1|\rho(t)|1\rangle. \tag{1.4.14}$$

1.5 NEMS (Nano Electro-Mechanical Systems)

1.5.1 Introduction

To follow.

1.5.2 Model Hamiltonian

Similar to few-level quantum systems: electron number i and vibrational degrees of freedom n. Assume system eigenstates of the form

$$|i,n\rangle \equiv |i\rangle \otimes |n\rangle, \tag{1.5.1}$$

the simplest case is $i = 0, 1$ and $n = 0, 1, 2, 3, ...n_{\max}$. The system Hamiltonian

$$H_S = \sum_{i,n} \varepsilon_{i,n} |in\rangle\langle in| \tag{1.5.2}$$

is the result of the diagonalisation of the isolated NEMS (no contact to external leads and no vibrational damping).

1.5.3 Master Equation: single electronic level ($i = 0, 1$)

As before, electrons jump off and onto the system according to

$$\mathcal{H}_V = \sum_{k\alpha} (V_{k\alpha=L/R} c_{k\alpha}^{\dagger} \hat{s} + H.c.), \quad \hat{s} \equiv |0\rangle\langle 1|. \tag{1.5.3}$$

There is no dependence on the vibrational degree of freedom at this stage! This comes in at the point where we formulate the Master equation. As before, we use our general expression Eq. (1.4.6):

1. Take matrix elements of Eq. (1.4.6) by ‘sandwiching’ as

   $$\langle 0,n|...|0,n'\rangle, \quad \langle 1,n|...|1,n'\rangle. \tag{1.5.4}$$

   EXERCISE: Check that there are no terms $\langle 0,n|...|1,n'\rangle$, $\langle 1,n|...|0,n'\rangle$. This means that there are no coherences between occupied and un-occupied states.

2. Explicitely insert the time-dependence of the $\tilde{s}(t')$ etc.
3. Transform back into the Schrödinger picture via

$$\langle 0,n|\rho(t)|0,n'\rangle = e^{i(\varepsilon_{0n'}-\varepsilon_{0n}t)}\langle 0,n|\tilde{\rho}(t)|0,n'\rangle \tag{1.5.5}$$

etc.

4. Check that in all exponents the time-dependence is always via $t-t'$

This derivation yields

$$\begin{aligned}\left[\frac{d}{dt}-i(\varepsilon_{0n'}-\varepsilon_{0n})\right]\langle 0,n|\rho(t)|0,n'\rangle = -\sum_{mm'\alpha}\int_{-\infty}^{\infty}d\varepsilon\nu_\alpha(\varepsilon)\int_0^t dt' \times \\ f_\alpha(\varepsilon)\langle 0,m'|\rho(t)|0,n'\rangle\langle 0,n|1,m\rangle\langle 1,m|0,m'\rangle e^{i(\varepsilon-\varepsilon_{1m}+\varepsilon_{0m'})(t-t')} \\ + \quad f_\alpha(\varepsilon)\langle 0,n|\rho(t)|0,m\rangle\langle 0,m|1,m'\rangle\langle 1,m'|0,n'\rangle e^{-i(\varepsilon-\varepsilon_{1m'}+\varepsilon_{0m})(t-t')} \\ - \quad \bar{f}_\alpha(\varepsilon)\langle 1,m|\rho(t)|1,m'\rangle\langle 0,n|1,m\rangle\langle 1,m'|0,n'\rangle e^{-i(\varepsilon-\varepsilon_{1m}+\varepsilon_{0n})(t-t')} \\ - \quad \bar{f}_\alpha(\varepsilon)\langle 1,m|\rho(t)|1,m'\rangle\langle 0,n|1,m\rangle\langle 1,m'|0,n'\rangle e^{i(\varepsilon-\varepsilon_{1m'}+\varepsilon_{0n'})(t-t')}\end{aligned} \tag{1.5.6}$$

and a corresponding equation for the $\langle 1,n|\rho(t)|1,n'\rangle$. The **Franck-Condon Factors**

$$\langle 0,n|1,m\rangle \tag{1.5.7}$$

are determined by the overlap of the vibrational wave functions before and after tunneling of one electron.

1.5.4 Franck-Condon Factors

to follow. Example linear oscillator coupling and explicit calculation of Franck-Condon Factors there.

1.5.5 Markov Approximation

The Master equation is a system of linear integro-differential equations of the type

$$\frac{d}{dt}y_i(t) \quad = \quad \sum_{ki}\int_{-\infty}^{\infty}d\varepsilon g_{ik}(\varepsilon)\int_0^t dt' e^{i(\varepsilon-\varepsilon_{ik})(t-t')}y_k(t'). \tag{1.5.8}$$

This system could in principle be solved as an **initial value problem** by **Laplace transformation**, leading to

$$z\hat{y}_i(z)-y_i(t=0) \quad = \quad \sum_{ki}\int_{-\infty}^{\infty}d\varepsilon\frac{g_{ik}(\varepsilon)}{z-i(\varepsilon-\varepsilon_{ik})}\hat{y}_k(z). \tag{1.5.9}$$

The Markov approximation amount to replacing the kernel of this equation by its $z = 0$ (long time) value as follows

$$\begin{aligned}\int_{-\infty}^{\infty} d\varepsilon \frac{g_{ik}(\varepsilon)}{z - i(\varepsilon - \varepsilon_{ki})} &\to \lim_{\delta\to 0} \int_{-\infty}^{\infty} d\varepsilon \frac{g_{ik}(\varepsilon)}{\delta - i(\varepsilon - \varepsilon_{ik})} \\ &= i \lim_{\delta\to 0} \int_{-\infty}^{\infty} d\varepsilon \frac{g_{ik}(\varepsilon)}{i\delta + (\varepsilon - \varepsilon_{ik})} \\ &= \pi g_{ik}(\varepsilon_{ki}) + P \int_{-\infty}^{\infty} d\varepsilon \frac{g_{ik}(\varepsilon)}{\varepsilon - \varepsilon_{ik}} \qquad (1.5.10)\end{aligned}$$

Often, the principle value part is neglected (depending on the problme at hand) as it leads to un-interesting energy-shifts. Transforming back into the time domain, the Master equation becomes

$$\frac{d}{dt} y_i(t) = \pi \sum_{ki} g_{ik}(\varepsilon_{ik}) y_k(t). \qquad (1.5.11)$$

Alternative ‘derivation’: to follow.

1.6 Master Equation III: Phase Space Solution Methods

We discuss these methods here only for the Master equation of the damped harmonic oscillator in RWA,

$$\begin{aligned}\frac{d}{dt}\rho(t) &= -i\bar{\Omega}[a^\dagger a, \rho] - \kappa\Big\{a^\dagger a\rho + \rho a^\dagger a - 2a\rho a^\dagger\Big\} \\ &- 2\kappa n_B(\Omega)\Big\{a^\dagger a\rho + \rho a a^\dagger - a\rho a^\dagger - a^\dagger \rho a\Big\}. \qquad (1.6.1)\end{aligned}$$

1.6.1 P-representation

The idea here is to convert the operator equation into a partial differential equation (PDE) for the P-representation of the reduced density operator ρ.

1.6.1.1 Revision: P-representation

We recall that the P-representation of an operator $\hat{\theta}$ was defined as (cf. 4.137)

$$\hat{\theta} = \int \frac{d^2z}{\pi} P(\hat{\theta}; z)|z\rangle\langle z|. \qquad (1.6.2)$$

Remarks:

1. Other authors use a definition without the $1/\pi$.

2. Some books write $P(z)$ (instead of $P(\hat{\theta}=\rho;z)$) for the P-representation of the density operator, and use the form

$$P(z) \equiv P(z,z^*) = \mathrm{Tr}\left[\rho\delta(z^*-a^\dagger)\delta(z-a)\right]. \tag{1.6.3}$$

(again multiply this by π to get our P).

3. For coherent states $\rho = |z_0\rangle\langle z_0|$, one has $P(z) = \pi\delta(z-z_0)$.

4. We have the Metha-formula (4.149),

$$P(\hat{\theta};z) = e^{|z|^2}\int\frac{d^2z'}{\pi}\langle -z'|\hat{\theta}|z'\rangle e^{|z'|^2}e^{zz'^*-z^*z'}. \tag{1.6.4}$$

5. The P-distribution can be highly singular. Example: number state.

1.6.1.2 Derivation of the PDE

In order to transform the master equation, we require the P-representation of terms like $a\rho a^\dagger$ etc. Let us start with $a^\dagger\rho$.
Method 1: We follow Walls/Milburn and introduce *Bargmann states*

$$||z\rangle \equiv e^{|z|^2/2}|z\rangle \equiv \sum_n \frac{z^n}{(n!)^{1/2}}|n\rangle, \tag{1.6.5}$$

('coherent states without the normalisation factor in front'). Therefore,

$$a^\dagger||z\rangle = \frac{\partial}{\partial z}||z\rangle, \quad \langle z||a = \frac{\partial}{\partial z^*}\langle z||. \tag{1.6.6}$$

We use this to write

$$\begin{aligned}
\rho &= \int\frac{d^2z}{\pi}||z\rangle\langle z||e^{-|z|^2}\underline{P(z)} \rightsquigarrow \qquad (1.6.7)\\
a^\dagger\rho &= \int\frac{d^2z}{\pi}a^\dagger||z\rangle\langle z||e^{-|z|^2}P(z) = \int\frac{d^2z}{\pi}\left[\frac{\partial}{\partial z}||z\rangle\right]\langle z||e^{-|z|^2}P(z)\\
&= -\int\frac{d^2z}{\pi}||z\rangle\langle z||\frac{\partial}{\partial z}e^{-zz^*}P(z) = \int\frac{d^2z}{\pi}||z\rangle\langle z||e^{-|z|^2}\underline{\left(z^*-\frac{\partial}{\partial z}\right)P(z)},
\end{aligned}$$

using integration by parts, $\frac{\partial}{\partial z}\langle z|| = 0$, and assuming the vanishing of $P(z)$ at infinity. Comparison yields

$$a^\dagger\rho \leftrightarrow \left(z^*-\frac{\partial}{\partial z}\right)P(z). \tag{1.6.8}$$

Method 2: Use the Metha formula for $\hat{\theta} = a^\dagger\rho$,

$$\begin{aligned}
P(a^\dagger\rho;z) &= e^{|z|^2}\int\frac{d^2z'}{\pi}\langle -z'|a^\dagger\rho|z'\rangle e^{|z'|^2}e^{zz'^*-z^*z'}\\
&= e^{zz^*}\int\frac{d^2z'}{\pi}(-z'^*)\langle -z'|\rho|z'\rangle e^{|z'|^2}e^{zz'^*-z^*z'} =\\
&= \left[-\frac{\partial}{\partial z}+z^*\right](e^{zz^*})\int\frac{d^2z'}{\pi}\langle -z'|\rho|z'\rangle e^{|z'|^2}e^{zz'^*-z^*z'}. \qquad (1.6.9)
\end{aligned}$$

Here, we generate $-z'^*$ in the integral by differentiation with respect to the parameter z and subsequent compensation of the term aring from e^{zz^*}, thus arriving even faster at Eq.(1.6.8). Similarly,

$$\begin{aligned}
P(\rho a;z) &= e^{zz^*}\int\frac{d^2z'}{\pi}\langle -z'|\rho|z'\rangle z' e^{|z'|^2}e^{zz'^*-z^*z'} =\\
&= \left[-\frac{\partial}{\partial z^*}+z\right](e^{zz^*})\int\frac{d^2z'}{\pi}\langle -z'|\rho|z'\rangle e^{|z'|^2}e^{zz'^*-z^*z'}. \qquad (1.6.10)
\end{aligned}$$

For the terms $a^\dagger a\rho$, the first method is easier:

$$\begin{aligned}
a^\dagger a\rho &= \int\frac{d^2z}{\pi}a^\dagger a||z\rangle\langle z||e^{-|z|^2}P(z) = \int\frac{d^2z}{\pi}\left[\frac{\partial}{\partial z}||z\rangle\right]\langle z||e^{-|z|^2}zP(z)\\
&= -\int\frac{d^2z}{\pi}||z\rangle\langle z||\frac{\partial}{\partial z}e^{-zz^*}zP(z) = \int\frac{d^2z}{\pi}||z\rangle\langle z||e^{-|z|^2}\underline{\left(z^*-\frac{\partial}{\partial z}\right)zP(z)}\\
\rho a^\dagger a &= \int\frac{d^2z}{\pi}||z\rangle\langle z||a^\dagger a e^{-|z|^2}P(z) = \int\frac{d^2z}{\pi}||z\rangle\left[\frac{\partial}{\partial z^*}\langle z||\right]e^{-|z|^2}z^*P(z)\\
&= -\int\frac{d^2z}{\pi}||z\rangle\langle z||\frac{\partial}{\partial z^*}e^{-zz^*}z^*P(z) = \int\frac{d^2z}{\pi}||z\rangle\langle z||e^{-|z|^2}\underline{\left(z-\frac{\partial}{\partial z^*}\right)z^*P(z)}\\
a\rho a^\dagger &= \int\frac{d^2z}{\pi}a||z\rangle\langle z||a^\dagger e^{-|z|^2}P(z) = \int\frac{d^2z}{\pi}||z\rangle\langle z||e^{-|z|^2}\underline{zz^*P(z)}\\
a^\dagger\rho a &= \int\frac{d^2z}{\pi}\left[\frac{\partial}{\partial z}||z\rangle\right]\left[\frac{\partial}{\partial z^*}\langle z||\right]e^{-|z|^2}P(z) = \int\frac{d^2z}{\pi}||z\rangle\langle z||\frac{\partial}{\partial z^*}\frac{\partial}{\partial z}e^{-|z|^2}P(z)\\
&= \int\frac{d^2z}{\pi}||z\rangle\langle z||e^{-|z|^2}\underline{\left(z-\frac{\partial}{\partial z^*}\right)\left(z^*-\frac{\partial}{\partial z}\right)P(z)}.
\end{aligned}$$

In particular, for the master equation we need

$$\begin{aligned}
\left\{a^\dagger a\rho + \rho a^\dagger a - 2a\rho a^\dagger\right\} &\leftrightarrow \left\{\left(z^* - \frac{\partial}{\partial z}\right) z + \left(z - \frac{\partial}{\partial z^*}\right) z^* - 2zz^*\right\} P(z) \\
= -\left\{\frac{\partial}{\partial z} z + \frac{\partial}{\partial z^*} z^*\right\} P(z) &= -\left\{z\frac{\partial}{\partial z} + z^*\frac{\partial}{\partial z^*} + 2\right\} P(z) \\
\left\{a^\dagger a\rho + \rho(a^\dagger a + 1) - a\rho a^\dagger - a^\dagger \rho a\right\} &\leftrightarrow \left\{\left(z^* - \frac{\partial}{\partial z}\right) z + \left(z - \frac{\partial}{\partial z^*}\right) z^* + 1\right. \\
&- \left. zz^* - \left(z - \frac{\partial}{\partial z^*}\right)\left(z^* - \frac{\partial}{\partial z}\right)\right\} P(z) \\
= \left\{-\frac{\partial}{\partial z} z + z\frac{\partial}{\partial z} + 1 + \frac{\partial}{\partial z^*}\frac{\partial}{\partial z}\right\} P(z) &= \frac{\partial}{\partial z^*}\frac{\partial}{\partial z} P(z) \\
\left[a^\dagger a, \rho\right] &\leftrightarrow \left[-\frac{\partial}{\partial z} z + \frac{\partial}{\partial z^*} z^*\right] P(z) = \left[-z\frac{\partial}{\partial z} + z^*\frac{\partial}{\partial z^*}\right] P(z).
\end{aligned}$$

The whole master equation is therefore transformed into

$$\boxed{\frac{\partial}{\partial t} P(z,t) = \left\{2\kappa + i\left[\bar\Omega - i\kappa\right] z\frac{\partial}{\partial z} - i\left[\bar\Omega + i\kappa\right] z^*\frac{\partial}{\partial z^*} + 2\kappa n_B \frac{\partial^2}{\partial z^* \partial z}\right\} P(z,t)} \tag{1.6.11}$$

Here, we have explicitely indicated that the P-function depends both on z *and* on the time t.

Remarks:

- The first order derivate terms are called drift terms, the second order derivate terms diffusion term.
- This is not directly solvable by Fourier transformation: z,z^*-dependence of coefficients.
- Written in real coordinates, this has the form of a *Fokker-Planck equation*

$$\frac{\partial}{\partial t} P(\mathbf{x}) = \left(-\sum_j \frac{\partial}{\partial x_j} A_j(\mathbf{x}) + \frac{1}{2}\sum_{ij} \frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j} D_{ij}(\mathbf{x})\right) P(\mathbf{x}) \tag{1.6.12}$$

1.6.1.3 Solution of the PDE I: zero temperature $T = 0 \rightsquigarrow n_B = 0$

In this case, we only have first order derivatives. There is a (more or less) complete theory of first order PDEs: they are solved by the method of characteristics (cf. Courant/Hilbert).

We write the PDE as

$$\left\{\frac{\partial}{\partial t} - i\left[\bar\Omega - i\kappa\right] z\frac{\partial}{\partial z} + i\left[\bar\Omega + i\kappa\right] z^*\frac{\partial}{\partial z^*}\right\} P(z, z^* t) = 2\kappa P(z, z^* t) \tag{1.6.13}$$

and consider the function $P(z,z^*,t)$ on *trajectories* $z=z(t)$ and $z^*=z^*(t)$ where $P(z,z^*,t)=P(z(t),z^*(t),t)$. We regard the l.h.s. of Eq.(1.6.13) as a total differential. Along the trajectories, the temporal change of P is

$$\begin{aligned} \frac{d}{dt}P(z(t),z^*(t),t) &= \{\dot{z}(t)\partial_z+\dot{z}^*(t)\partial_{z^*}+\partial_t\}\,P(z(t),z^*(t),t)\\ &= 2\kappa P(z(t),z^*(t),t) \end{aligned} \tag{1.6.14}$$

Comparison yields

$$\begin{aligned} \dot{z}(t) &= -i\left[\bar{\Omega}-i\kappa\right]z(t) \rightsquigarrow z(t)=z_0e^{-i\left[\bar{\Omega}-i\kappa\right]t}\\ \dot{z}^*(t) &= i\left[\bar{\Omega}+i\kappa\right]z^*(t) \rightsquigarrow z^*(t)=z_0^*e^{i\left[\bar{\Omega}+i\kappa\right]t}. \end{aligned} \tag{1.6.15}$$

On the other hand, $\frac{d}{dt}P=2\kappa P$ yields

$$P(z(t),z^*(t),t) = e^{2\kappa t}P_0(z_0,z_0^*). \tag{1.6.16}$$

Here, P_0 is the initial condition for P, with $z_0=z(t=0)$ and $z_0^*=z^*(t=0)$. This looks very innocent but has a deep physical (and geometrical) meaning: we can trace back our trajectories $z(t)$,$z^*(t)$ to their origin z_0, z_0^*, writing

$$z_0 = z(t)e^{+i\left[\bar{\Omega}-i\kappa\right]t},\quad z_0^*=z^*(t)e^{-i\left[\bar{\Omega}+i\kappa\right]t}. \tag{1.6.17}$$

We thus have expressed the inital values z_0, z_0^* in terms of the 'final' values $z(t)$,$z^*(t)$. Insertion into Eq.(1.6.16) yields

$$P(z(t),z^*(t),t) = e^{2\kappa t}P_0\left(z(t)e^{+i\left[\bar{\Omega}-i\kappa\right]t},z^*(t)e^{-i\left[\bar{\Omega}+i\kappa\right]t}\right). \tag{1.6.18}$$

We now write again z and z^* instead of $z(t)$, $z^*(t)$, and therefore have

$$P(z,z^*,t) = e^{2\kappa t}P_0\left(ze^{+i\left[\bar{\Omega}-i\kappa\right]t},z^*e^{-i\left[\bar{\Omega}+i\kappa\right]t}\right). \tag{1.6.19}$$

1.6.1.4 Solution of the PDE II: finite temperature $T\ge 0 \rightsquigarrow n_B\ge 0$

Since we know the solution for $n_B=0$, we perform a transformation of variables and seek the solution for $n_B>0$ in the form

$$P(z,z^*t)=F(u,u^*,s),\quad u=ze^{+i\left[\bar{\Omega}-i\kappa\right]t},u^*=z^*e^{-i\left[\bar{\Omega}+i\kappa\right]t},s=t, \tag{1.6.20}$$

which leads to

$$\begin{aligned} \partial_tP &= \left(i\left[\bar{\Omega}-i\kappa\right]ze^{+i\left[\bar{\Omega}-i\kappa\right]t}\partial_u+-i\left[\bar{\Omega}+i\kappa\right]z^*e^{-i\left[\bar{\Omega}+i\kappa\right]t}\partial_{u^*}+\partial_s\right)F(u,u^*,s)\\ &= \left(i\left[\bar{\Omega}-i\kappa\right]z\partial_z-i\left[\bar{\Omega}+i\kappa\right]z^*\partial_{z^*}\right)P(z,z^*t)+\partial_sF(u,u^*,s)\\ &\stackrel{\vee}{=} \left(i\left[\bar{\Omega}-i\kappa\right]z\partial_z-i\left[\bar{\Omega}+i\kappa\right]z^*\partial_{z^*}+2\kappa+2\kappa n_B\partial_z\partial_{z^*}\right)P(z,z^*t), \end{aligned} \tag{1.6.21}$$

where in the last line we compared with the original PDE. Therefore, one has

$$\begin{aligned}\partial_s F(u,u^*,s) &= 2\kappa F(u,u^*,s) + 2\kappa n_B \partial_z \partial_{z^*} P(z,z^*t)\\ &= 2\kappa F(u,u^*,s) + 2\kappa n_B e^{2\kappa s}\partial_u \partial_{u^*} F(u,u^*,s), \qquad (1.6.22)\end{aligned}$$

where we used $\partial_z\partial_{z^*} = e^{2\kappa s}\partial_u\partial_{u^*}$, cf. Eq.(1.6.20). The big advantage now is that we had got rid of the first order derivatives with the z,z^*-dependent coefficients. Eq.(1.6.22) is now a standard diffusion equation with time ($s = t$)-dependent coefficients, which can be solved by Fourier transformation:

Reminder: Complex Fourier Transformation, cf (4.141)

$$\begin{aligned}\text{Fourier Trafo } \tilde{f}(w) &\equiv \int d^2 z e^{i\mathbf{zw}} f(z), \quad f(z) = \int \frac{d^2 w}{(2\pi)^2} e^{-i\mathbf{zw}} \tilde{f}(w)\\ \text{scalar product } \mathbf{zw} &\equiv \frac{1}{2}(zw^* + z^* w) = (z_1, z_2)\begin{pmatrix} w_1 \\ w_2 \end{pmatrix} \qquad (1.6.23)\end{aligned}$$

Reminder: Gauß Integrals

$$\begin{aligned}\int_{-\infty}^{\infty} dx e^{-ax^2+bx} &= \sqrt{\frac{\pi}{a}} e^{\frac{b^2}{4a}}, \quad \Re a > 0 \qquad (1.6.24)\\ \int \frac{d^2 w}{(2\pi)^2} e^{-i\mathbf{zw}} e^{-\frac{a}{4}\mathbf{ww}} &= \frac{1}{\pi a} e^{-\frac{|z|^2}{a}}. \qquad (1.6.25)\end{aligned}$$

We now Fourier-transform Eq.(1.6.22), $\partial_s F = (2\kappa + 2\kappa n_B e^{2\kappa s}\partial_u\partial_{u^*})F$, to obtain

$$\begin{aligned}\partial_s \tilde{F}(w,w^*,s) &= \left(2\kappa + 2\kappa n_B e^{2\kappa s}\left(-\frac{1}{4}\mathbf{ww}\right)\right)\tilde{F}(w,w^*,s) \qquad (1.6.26)\\ \rightsquigarrow \tilde{F}(w,w^*,s) &= \exp\left\{2\kappa s - \frac{1}{4} n_B \left(e^{2\kappa s} - 1\right)\mathbf{ww}\right\}\tilde{F}(w,w^*,s=0)\\ \rightsquigarrow F(u,u^*,s) &= \int \frac{d^2 w}{(2\pi)^2} e^{-i\mathbf{uw}} \exp\left\{2\kappa s - \frac{1}{4} n_B \left(e^{2\kappa s} - 1\right)\mathbf{ww}\right\}\tilde{F}(w,w^*,s=0)\\ &= \int d^2 u' \int \frac{d^2 w}{(2\pi)^2} e^{-i(\mathbf{u}-\mathbf{u}')\mathbf{w}} e^{\left\{2\kappa s - \frac{1}{4} n_B \left(e^{2\kappa s}-1\right)\mathbf{ww}\right\}} F(u', u'^*, s=0)\\ &= \frac{e^{2\kappa s}}{\pi n_B \left(e^{2\kappa s} - 1\right)} \int d^2 u' \exp\left\{-\frac{|u-u'|^2}{n_B\left(e^{2\kappa s}-1\right)}\right\} F(u', u'^*, s=0)\end{aligned}$$

Now we remember $u = ze^{+i\left[\bar{\Omega} - i\kappa\right]t}$, $s = t$, and write $u' = z'$ in $F(u', u'^*, s = 0) =$

$P(z', z'^*, t=0)$, to find

$$\begin{aligned} P(z,z^*,t) &= \int d^2z' \frac{1}{\pi n_B\left(1-e^{2\kappa t}\right)} \exp\left\{-\frac{|ze^{+i\left[\bar{\Omega}-i\kappa\right]t}-z'|^2}{n_B\left(e^{2\kappa t}-1\right)}\right\} P(z',z'^*,t=0) \\ &= \int d^2z' \frac{1}{\pi n_B\left(1-e^{-2\kappa t}\right)} \exp\left\{-\frac{|z-z'e^{-i\left[\bar{\Omega}-i\kappa\right]t}|^2}{n_B\left(1-e^{-2\kappa t}\right)}\right\} P(z',z'^*,t=0) \\ &\equiv \int d^2z' G(z,z';t) P(z',z'^*,t=0), \\ G(z,z';t) &\equiv \frac{1}{\pi n_B\left(1-e^{-2\kappa t}\right)} \exp\left\{-\frac{|z-z'e^{-i\left[\bar{\Omega}-i\kappa\right]t}|^2}{n_B\left(1-e^{-2\kappa t}\right)}\right\}. \qquad (1.6.27) \end{aligned}$$

This is the solution of the *initial value problem* of the PDE: we have explicitely constructed the *propagator* $G(z,z';t)$ and expressed the solution of the PDE at times $t>0$ in terms of the *initial* P-distribution $P(z',z'^*,t=0)$.

1.6.2 W-representation

An alternative phase-space method is to convert the operator master equation into a PDE for the Wigner function $W(A;z)$ of an operator A. We recall Formula (4.177b) for the Wigner function of an *operator product* AB,

$$W(AB;z) = W(A;z) \exp\left[\frac{1}{2}\left(\overleftarrow{\partial}_z \overrightarrow{\partial}_{z^*} - \overleftarrow{\partial}_{z^*} \overrightarrow{\partial}_z\right)\right] W(B;z) \qquad (1.6.28)$$

We obtain

$$\begin{aligned} W(a) &= z, \quad W(a^\dagger) = z^* \\ W(a^\dagger a) &= z^* \left(1 + \frac{1}{2}\left(\partial_z\partial_{z^*} - \partial_{z^*}\partial_z\right)\right) z = z^*z - \frac{1}{2} \\ W(a^\dagger a\rho) &= \left(z^*z - \frac{1}{2}\right)\left(1 + \frac{1}{2}\left(\partial_z\partial_{z^*} - \partial_{z^*}\partial_z\right) + \frac{1}{8}\left(\partial_z\partial_{z^*} - \partial_{z^*}\partial_z\right)\left(\partial_z\partial_{z^*} - \partial_{z^*}\partial_z\right)\right) W(\rho) \\ &= \left(z^*z - \frac{1}{2}\right) W(\rho) + \frac{1}{2} z^* \partial_{z^*} W(\rho) - \frac{1}{2} z \partial_z W(\rho) - \frac{2}{8} \partial_z \partial_{z^*} W(\rho) \\ W(\rho a^\dagger a) &= W(\rho)\left(1 + \frac{1}{2}\left(\partial_z\partial_{z^*} - \partial_{z^*}\partial_z\right) + \frac{1}{8}\left(\partial_z\partial_{z^*} - \partial_{z^*}\partial_z\right)\left(\partial_z\partial_{z^*} - \partial_{z^*}\partial_z\right)\right)\left(z^*z - \frac{1}{2}\right) \\ &= \left(z^*z - \frac{1}{2}\right) W(\rho) - \frac{1}{2} z^* \partial_{z^*} W(\rho) + \frac{1}{2} z \partial_z W(\rho) - \frac{2}{8} \partial_z \partial_{z^*} W(\rho) \qquad (1.6.29) \end{aligned}$$

Similarly,

$$
\begin{aligned}
W(a\rho) &= z\left(1+\frac{1}{2}\left(\partial_z\partial_{z^*}-\partial_{z^*}\partial_z\right)\right)W(\rho) = zW(\rho)+\frac{1}{2}\partial_{z^*}W(\rho)\\
W(a\rho a^\dagger) &= \left(zW(\rho)+\frac{1}{2}\partial_{z^*}W(\rho)\right)\left(1+\frac{1}{2}\left(\partial_z\partial_{z^*}-\partial_{z^*}\partial_z\right)\right)z^*\\
&= \left(zz^*W(\rho)+\frac{1}{2}z^*\partial_{z^*}W(\rho)\right)+\frac{1}{2}\partial_z(zW(\rho))+\frac{1}{4}\partial_z\partial_{z^*}W(\rho)\\
W(a^\dagger\rho) &= z^*\left(1+\frac{1}{2}\left(\partial_z\partial_{z^*}-\partial_{z^*}\partial_z\right)\right)W(\rho) = z^*W(\rho)-\frac{1}{2}\partial_zW(\rho)\\
W(a^\dagger\rho a) &= \left(z^*W(\rho)-\frac{1}{2}\partial_zW(\rho)\right)\left(1+\frac{1}{2}\left(\partial_z\partial_{z^*}-\partial_{z^*}\partial_z\right)\right)z\\
&= \left(zz^*W(\rho)-\frac{1}{2}z\partial_zW(\rho)\right)-\frac{1}{2}\partial_{z^*}(z^*W(\rho))+\frac{1}{4}\partial_z\partial_{z^*}W(\rho)
\end{aligned}
\tag{1.6.30}
$$

Thus,

$$
\begin{aligned}
\left\{a^\dagger a\rho+\rho a^\dagger a-2a\rho a^\dagger\right\} &\leftrightarrow -\left\{2+z\partial_z+z^*\partial_{z^*}+\partial_z\partial_{z^*}\right\}W(\rho)\\
\left\{a^\dagger a\rho+\rho(a^\dagger a+1)-a\rho a^\dagger-a^\dagger\rho a\right\} &\leftrightarrow -\partial_z\partial_{z^*}W(\rho)\\
\left[a^\dagger a,\rho\right] &\leftrightarrow \left(z^*\partial_{z^*}-z\partial_z\right)W(\rho).
\end{aligned}
\tag{1.6.31}
$$

Therefore, the master equation Eq.(1.6.1) is converted into

$$
\begin{aligned}
\frac{\partial}{\partial t}W(z,t) &= -i\bar{\Omega}\left(z^*\partial_{z^*}-z\partial_z\right)W(z,t)+\kappa\left\{2+z\partial_z+z^*\partial_{z^*}+\partial_z\partial_{z^*}\right\}W(z,t)\\
&+ 2\kappa n_B(\Omega)\partial_z\partial_{z^*}W(z,t)\\
=\{2\kappa &+ i\left[\bar{\Omega}-i\kappa\right]z\frac{\partial}{\partial z}-i\left[\bar{\Omega}+i\kappa\right]z^*\frac{\partial}{\partial z^*}+\kappa[1+2n_B]\frac{\partial^2}{\partial z^*\partial z}\Bigg\}W(z,t).
\end{aligned}
\tag{1.6.32}
$$

We compare this with the PDE for the P-function, Eq.(1.6.11):

$$
\frac{\partial}{\partial t}P(z,t)=\left\{2\kappa+i\left[\bar{\Omega}-i\kappa\right]z\frac{\partial}{\partial z}-i\left[\bar{\Omega}+i\kappa\right]z^*\frac{\partial}{\partial z^*}+2\kappa n_B\frac{\partial^2}{\partial z^*\partial z}\right\}P(z,t)
$$

The difference is just in the diffusion term, i.e., 1+$2n_B$ in the Wigner representation instead of $2n_B$ in the P representation. In the Wigner representation, even at zero temperature $T=0$ ($n_B=0$) one has a diffusion term in the PDE. Technically, the solution proceeds as before: one first solves the first order part via characteristics and then the diffusive part via Fourier transformation.

- A similar derivation can be done for the Q-representation, cf. Walls/Milburn. The Q-representation is more convenient for systems where the initial oscillator state is squeezed, or the decay is into a bath not in thermal equilibrium but in a squeezed state.

1.6.3 Remarks

Phase space methods are powerful tools for solving Master equations. The resulting PDEs, however, are often non-trivial and cannot be solved exactly. This is particularly true if more than one degree of freedom is involved and one has to solve *systems of PDEs*.

Systems of partial differential equations are really complicated beasts: in contrast to systems of ordinary differential equations, they are not equivalent to a single PDE of higher order, cf. the discussion in Courant/Hilbert 'Methoden der Mathematischen Physik'.

Related problems occur in the theory of the Laser, where one has to deal with PDEs containing derivatives up to infinite order. This is discussed in the book by Scully/Lamb. Another, very recent challenge are systems of Master equations with non-linear couplings between bosonic and electronic degrees of freedom in *nano-electromechanical systems*.

1.7 The Two-Level System I

1.7.1 Generic Model: Two-Level System Interacting with Bosonic Modes

1.7.1.1 System

Assume a system with Hilbert space $\mathcal{H} = C^2$ with basis vectors $(1,0)^\dagger$ and $(0,1)^\dagger$. In general, a 'System'-Hamiltonian will have the form of the Hamiltonian of a *Pseudo Spin* $\frac{1}{2}$ in a (time-dependent) *classical pseudo magnetic field* $\mathbf{B}(t)$ (c-number),

$$H_S(t) \equiv \mathbf{B}(t)\vec{\sigma}, \quad \vec{\sigma} = \begin{pmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \end{pmatrix}. \tag{1.7.1}$$

- Note that for a time-dependent $\mathbf{B}(t)$, the free Schrödinger equation with $H_S(t)$ only is in general not analytically solvable. For an isolated two-level system ($H_S(t)$ only), this is not a problem because one can easily solve a two-by two differential equation on a computer. However, problems start when it comes to system-bath Hamiltonians. Many of the 'simpler' system bath theories implicitely assume that the time-evolution under H_s is trivial (which it is for constant $\mathbf{B}(t) = \mathbf{B}$).

- Some special cases are analytically solvable: Landau-Zener-Rosen tunneling (Landau 1932).
- For a periodic time-dependence of $\mathbf{B}(t)$: Floquet theory (Shirley 1965).
- The wave function can aquire a geometrical phase (Berry phase, Berry 1984).

1.7.1.2 System-Bath Interaction

Assume a 'bath' of bosonic modes Q (the index Q contains all quantum numbers of that mode) with creation operator $a_Q^\dagger$. The simplest interaction between the two-level system and the bath is *linear* in $a_Q^\dagger$ and a_Q and can be written with coupling constant vectors $\mathbf{g}_Q(t)$,

$$H_{SB}(t) \equiv \hat{\mathbf{A}}(t)\vec{\sigma} \equiv \sum_Q \left(\mathbf{g}_Q(t)a_Q^\dagger + \mathbf{g}_Q^\dagger(t)a_Q\right)\vec{\sigma}. \tag{1.7.2}$$

Note that $\hat{\mathbf{A}}(t)$ can be regarded as a *fluctuating (quantum operator) pseudo magnetic field.*

1.7.1.3 Bath

The simplest Hamiltonian for a bosonic bath is

$$H_B = \sum_Q \omega_Q a_Q^\dagger a_Q. \tag{1.7.3}$$

- Example: free photons, $\omega_Q = c|Q|$.
- Example: phonons in crystals. However, more realistic Hamiltonians would contain phonon-phonon interaction. In particular, in order to explain the thermal expansion of materials one needs boson-boson interaction ($\rightsquigarrow$ 'Grüneisen parameter'), cf. N. W. Ashcroft and N. D. Mermin, *'Solid State Physics'*, Saunders College (Philadelphia, 1976).
- Photonic or phononic crystals or cavities have more complicated bandstructures and nontrivial dispersion relations $\omega = \omega_Q$. Example: Phonon cavities in 2-dimensional thin elastic plate, Rayleigh-Lamb waves; cf. L. D. Landau and E. M. Lifshitz, *'Theory of Elasticity'*, Vol. 7 of Landau and Lifshitz, Course of Theoretical Physics (Pergamon Press, 1970); B. Auld, '*Acousic Fields and Waves*', (Wiley, New York, 1973).

1.7.1.4 Further Remarks

1. Coupling to non-bosonic baths: this is a relatively unexplored field. The most prominent examples are *spin-baths*, where the system is coupled to a collection of spins or other two-level systems. Connection to theory of glasses.
2. Dissipative dynamics of qubit with geometrical phase: this is the topic of some current activities, cf. (Y. Makhlin *et al.* etc.)

1.7.2 Atom + Electrical Field

1.7.2.1 Model Atom

Assume a single electron within an atom, described as a two-level system with states $|g\rangle$ (ground state), $|e\rangle$ (excited state), and energy difference $\hbar\omega_0$ between ground and excited state. Then,

$$H_{\rm atom} = \frac{\hbar\omega_0}{2}\sigma_z, \quad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \equiv |e\rangle\langle e| - |g\rangle\langle g|. \tag{1.7.4}$$

Remember

$$\begin{aligned} \sigma_x &\equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\ \sigma_- &\equiv \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \quad \sigma_+ \equiv \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \\ \sigma_\pm &= \frac{1}{2}(\sigma_x \pm i\sigma_y), \quad \sigma_x = \sigma_+ + \sigma_-, \quad \sigma_y = -i(\sigma_+ - \sigma_-) \\ [\sigma_+, \sigma_-] &= \sigma_z, \quad [\sigma_z, \sigma_\pm] = \pm 2\sigma_\pm. \end{aligned} \tag{1.7.5}$$

1.7.2.2 Dipole Approximation

Consider an electrical field in the form of a linearly polarised, monochromatic plain wave with wave vector $\mathbf{k}$,

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}\cos(\mathbf{kr} - \omega t). \tag{1.7.6}$$

Describe the interaction of the atom with the electrical field in *dipole approximation*: the energy of a dipole $\mathbf{d}$ in a field $\mathbf{E}(\mathbf{r}, t)$ is given by $-\mathbf{dE}(\mathbf{r}, t)$. Treating the field classically, we obtain the time-dependent dipole Hamiltonian

$$\begin{aligned} H_L(t) &= -\langle g|\mathbf{dE}(\mathbf{r}, t)|e\rangle|g\rangle\langle e| - \langle e|\mathbf{dE}(\mathbf{r}, t)|g\rangle|e\rangle\langle g| \\ &\approx -(\hbar\Omega\sigma_- + \hbar\Omega^*\sigma_+)\cos(\omega t), \end{aligned} \tag{1.7.7}$$

where we used $\mathbf{kr} \ll 1$ in the overlap integral (wave length $\gg$ dimension of atom, '*dipole approximation*'), and introduced

$$\sigma_- \equiv |g\rangle\langle e|, \quad \sigma_+ \equiv |e\rangle\langle g|. \tag{1.7.8}$$

and the *Rabi frequency*

$$\Omega \equiv \frac{1}{\hbar}\langle g|\mathbf{dE}|e\rangle, \tag{1.7.9}$$

which in general is a complex number. The total system Hamiltonian therefore is

$$H_S(t) = H_{\text{atom}} + H_L(t) = \frac{\hbar\omega_0}{2}\sigma_z - (\hbar\Omega\sigma_- + \hbar\Omega^*\sigma_+)\cos(\omega t). \tag{1.7.10}$$

One usually assumes real $\Omega = \Omega^*$, in this case we can formally write $H_S(t) = \mathbf{B}(t)\vec{\sigma}$ with

$$\mathbf{B}(t) = \begin{pmatrix} -\hbar\Omega\cos(\omega t) \\ 0 \\ \frac{1}{2}\hbar\omega_0 \end{pmatrix}. \tag{1.7.11}$$

1.7.2.3 Rotating Wave Approximation (RWA)

We introduce the System Hamiltonian $H_S^{\text{RWA}}(t)$ in rotating wave approximation (RWA) by writing $\cos(\omega t) = \frac{1}{2}(e^{i\omega t} + e^{-i\omega t})$ and neglecting the counter-rotating terms $\sigma_- e^{-i\omega t}$ and $\sigma_+ e^{i\omega t}$

$$H_S^{\text{RWA}}(t) \equiv \frac{\hbar\omega_0}{2}\sigma_z - \left(\frac{\hbar\Omega}{2}\sigma_- e^{i\omega t} + \frac{\hbar\Omega}{2}\sigma_+ e^{-i\omega t}\right). \tag{1.7.12}$$

In this case, $H_S^{\text{RWA}}(t) = \mathbf{B}^{\text{RWA}}(t)\vec{\sigma}$ with

$$\mathbf{B}^{\text{RWA}}(t) = \begin{pmatrix} -\frac{1}{2}\hbar\Omega\cos(\omega t) \\ -\frac{1}{2}\hbar\Omega\sin(\omega t) \\ \frac{1}{2}\hbar\omega_0 \end{pmatrix} \tag{1.7.13}$$

1.7.3 Spontaneous Emission (Atom without Driving Field)

1.7.3.1 Model for H_{SB}: Two-Level System Coupled to Photon Bath in RWA

The microscopic interaction between a two-level *atom* and a photon bath is via a coupling

$$(a_Q + a_Q^\dagger)(\sigma_+ + \sigma_-) = (a_Q + a_Q^\dagger)\sigma_x, \tag{1.7.14}$$

cf. Walls/Milburn, Carmichael, Baym or other quantum optics (quantum mechanics) books. Comparing with our generic form Eq.(1.7.2),

$$H_{SB}(t) \equiv \hat{\mathbf{A}}(t)\vec{\sigma} \equiv \sum_Q \left(\mathbf{g}_Q(t) a_Q^\dagger + \mathbf{g}_Q^\dagger(t) a_Q \right) \vec{\sigma},$$

this case would correspond to a (time-independent) coupling vector $\mathbf{g}_Q(t) = \mathbf{g}_Q^\dagger(t) = (g_Q, 0, 0)$. Within the RWA, this interaction is further simplified by neglecting the 'counter-rotating' terms and by writing

$$\mathbf{g}_Q = \frac{1}{2}\gamma_Q \begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix}, \gamma_Q \text{real}. \tag{1.7.15}$$

Assuming a *free photon* bath, the total Hamiltonian then is

$$\begin{aligned} H_{\text{total}} &\equiv H_S + H_{SB} + H_B \\ &= H_S + \sum_Q \gamma_Q (a_Q \sigma_+ + a_Q^\dagger \sigma_-) + \sum_Q \omega_Q a_Q^\dagger a_Q. \end{aligned} \tag{1.7.16}$$

1.7.3.2 Mapping onto harmonic oscillator master equation

We now use the fact that H_{SB} has the same form as for the the damped single bosonic mode if we identify $\sigma_+ \to a^\dagger$, $\sigma_- \to a$. We can therefore 'copy' the derivation of the master equation of the damped harmonic oscillator, as long as no commutation relations are used! This is the case up to Eq.(1.3.13),

$$\begin{aligned} \frac{d}{dt}\rho(t) &= -i[\Omega a^\dagger a, \rho(t)] \\ &- \frac{1}{2}\Big\{ \left[(\gamma_+ + 2i\Delta_+) a^\dagger a + (\gamma + 2i\Delta) a a^\dagger\right] \rho(t) \\ &+ \rho(t) \left[(\gamma - 2i\Delta) a a^\dagger + (\gamma_+ - 2i\Delta_+) a^\dagger a\right] \\ &- 2\gamma_+ a \rho(t) a^\dagger - 2\gamma a^\dagger \rho(t) a \Big\}, \quad \text{harmonic oscillator.} \end{aligned}$$

The interaction picture for the two-level atom is with respect to the Hamiltonian

$$H_0 \equiv \frac{\omega_0}{2}\sigma_z + H_B \rightsquigarrow \tilde{\sigma}_\pm(t) = \sigma_\pm e^{\pm i\omega_0 t}, \quad \tilde{\sigma}_z(t) = \sigma_z. \tag{1.7.17}$$

In the interaction picture, the Master equation for the two-level atom therefore reads

$$\begin{aligned} \frac{d}{dt}\tilde{\rho}(t) &= -\frac{1}{2}\Big\{ \left[(\gamma_+ + 2i\Delta_+)\sigma_+\sigma_- + (\gamma + 2i\Delta)\sigma_-\sigma_+\right] \tilde{\rho}(t) \\ &+ \tilde{\rho}(t) \left[(\gamma - 2i\Delta)\sigma_-\sigma_+ + (\gamma_+ - 2i\Delta_+)\sigma_+\sigma_-\right] \\ &- 2\gamma_+ \sigma_- \tilde{\rho}(t) \sigma_+ - 2\gamma \sigma_+ \tilde{\rho}(t) \sigma_- \Big\}. \end{aligned} \tag{1.7.18}$$

We now use

$$\sigma_+\sigma_- = \frac{1}{2}\left(1+\sigma_z\right), \quad \sigma_-\sigma_+ = \frac{1}{2}\left(1-\sigma_z\right), \tag{1.7.19}$$

re-arrange and transform back into the Schrödinger picture,

$$\boxed{\begin{aligned} \frac{d}{dt}\rho(t) &= -i\tfrac{1}{2}\left(\omega_0+\Delta_+-\Delta\right)[\sigma_z,\rho] - \tfrac{1}{2}\gamma_+\Big\{\sigma_+\sigma_-\rho+\rho\sigma_+\sigma_- - 2\sigma_-\rho\sigma_+\Big\} \\ &- \tfrac{1}{2}\gamma\Big\{\sigma_-\sigma_+\rho+\rho\sigma_-\sigma_+ - 2\sigma_+\rho\sigma_-\Big\}. \end{aligned}} \tag{1.7.20}$$

We recall (note that the harmonic oscillator frequency Ω has to be replaced by ω_0)

$$\begin{aligned} \gamma_+ &\equiv 2\pi\rho(\omega_0)[1+n_B(\omega_0)], \quad \gamma\equiv 2\pi\rho(\omega_0)n_B(\omega_0) \\ \Delta_+-\Delta &\equiv \delta\omega_0 \equiv P\int_0^\infty d\omega\frac{\rho(\omega)[1+2n_B(\omega)]}{\omega_0-\omega}. \end{aligned} \tag{1.7.21}$$

Remarks:

- In contrast to the harmonic oscillator, the energy shift $\hbar\delta\omega_0$ is now *temperature dependent.*
- The $T=0$ contribution is the *Lamb-shift* within RWA.

1.7.4 Expectation Values, Einstein Equations, Bloch Equations

We can write the Master equation with the help of

$$\begin{aligned} \sigma_- &\equiv |g\rangle\langle e|, \quad \sigma_+\equiv|e\rangle\langle g|, \quad \sigma_-\sigma_+ = |g\rangle\langle g|, \quad \sigma_+\sigma_- = |e\rangle\langle e| \\ \rightsquigarrow \frac{d}{dt}\rho(t) &= -i\frac{1}{2}\bar{\omega}_0[|e\rangle\langle e|-|g\rangle\langle g|,\rho] \\ &- \frac{1}{2}\gamma_+\Big\{|e\rangle\langle e|\rho+\rho|e\rangle\langle e|-2|g\rangle\langle e|\rho|e\rangle\langle g|\Big\} \\ &- \frac{1}{2}\gamma\Big\{|g\rangle\langle g|\rho+\rho|g\rangle\langle g|-2|e\rangle\langle g|\rho|g\rangle\langle e|\Big\}. \end{aligned} \tag{1.7.22}$$

Taking matrix elements, we obtain

$$\frac{d}{dt}\langle e|\rho|e\rangle = -\gamma_+\langle e|\rho|e\rangle + \gamma\langle g|\rho|g\rangle \tag{1.7.23}$$

$$\frac{d}{dt}\langle g|\rho|g\rangle = +\gamma_+\langle e|\rho|e\rangle - \gamma\langle g|\rho|g\rangle \tag{1.7.24}$$

$$\frac{d}{dt}\langle e|\rho|g\rangle = \left(-i\bar{\omega}_0 - \frac{\gamma_++\gamma}{2}\right)\langle e|\rho|g\rangle \tag{1.7.25}$$

$$\frac{d}{dt}\langle g|\rho|e\rangle = \left(+i\bar{\omega}_0 - \frac{\gamma_++\gamma}{2}\right)\langle g|\rho|e\rangle. \tag{1.7.26}$$

The first two equations for the *diagonal elements* (which are linearly dependent because $\langle e|\rho|e\rangle + \langle g|\rho|g\rangle = 1$) are called *Einstein equations*. We can re-write the four equations, subtracting the second from the first, as three equations,

$$\boxed{\begin{array}{rcl} \frac{d}{dt}\langle\sigma_z\rangle & = & -(\gamma_+ + \gamma)\langle\sigma_z\rangle + (\gamma - \gamma_+) \\ \frac{d}{dt}\langle\sigma_+\rangle & = & \left(+i\bar{\omega}_0 - \frac{\gamma_+ + \gamma}{2}\right)\langle\sigma_+\rangle \\ \frac{d}{dt}\langle\sigma_-\rangle & = & \left(-i\bar{\omega}_0 - \frac{\gamma_+ + \gamma}{2}\right)\langle\sigma_-\rangle . \end{array}} \tag{1.7.27}$$

These equations are called *Bloch equations*. Introducing the *relaxation time* T_1 and the *decoherence time* T_2,

$$T_1 = \frac{1}{2}T_2 \equiv (\gamma_+ + \gamma)^{-1}, \tag{1.7.28}$$

we can write

$$\begin{aligned} \frac{d}{dt}\langle\sigma_z\rangle &= -\frac{1}{T_1}\left(\langle\sigma_z\rangle - \langle\sigma_z\rangle_\infty\right), \quad \langle\sigma_z\rangle_\infty \equiv \frac{\gamma - \gamma_+}{\gamma + \gamma_+} \\ \frac{d}{dt}\langle\sigma_+\rangle &= \left(+i\bar{\omega}_0 - \frac{1}{T_2}\right)\langle\sigma_+\rangle \\ \frac{d}{dt}\langle\sigma_-\rangle &= \left(-i\bar{\omega}_0 - \frac{1}{T_2}\right)\langle\sigma_-\rangle . \end{aligned} \tag{1.7.29}$$

2. NUMERICAL IMPLEMENTATION OF MASTER EQUATIONS

2.1 Master Equations as Matrix Equations

Master equations for the system density operator ρ in Born-Markov approximation have the form

$$\dot{\rho} = \mathcal{L}\rho, \tag{2.1.1}$$

where $\mathcal{L}$ sometimes is called a *superoperator*. For practical calculations, one has to choose a complete basis $\{|n\rangle\}$, $n = 1, ..., N$ of system states. Here and in the following, we always assume finite dimensional Hilbert spaces. For infinite dimensional Hilbert spaces, a suitable truncation to a finite number of basis states has to be carried out.

The matrix elements of ρ are then written as a column vector $\mathbf{r}$ with components $\langle 1|\rho|1\rangle$, $\langle 1|\rho|2\rangle$, ..., $\langle 2|\rho|2\rangle$,..., $\langle N|\rho|N\rangle$. The Master equation then becomes a linear matrix equation,

$$\dot{\mathbf{r}} = M\mathbf{r}. \tag{2.1.2}$$

The main task in practical calculations in the construction of M, i.e. finding and implementing the correct matrix elements $M_{nn'}$ from a Master equation (the Master equations is usually given in analytical form, involving system projection operators and density matrix elements).

More formally, one can write

$$\langle n|\dot{\rho}|n'\rangle \equiv \mathcal{L}_{nn';mm'}\langle m|\rho|m'\rangle, \tag{2.1.3}$$

which is called Bloch-Redfield equation with the Bloch-Redfield tensor $\mathcal{L}_{nn';mm'}$. Therefore, the above standard matrix form is nothing but a mapping from a higher-rang tensor to a lower-rang tensor.

2.2 Stationary versus Time-Dependent

The simplest solution is the stationary solution for $t \to \infty$ when

$$0 = \mathcal{L}\rho \rightsquigarrow 0 = M\mathbf{r}. \tag{2.2.1}$$

Formally, the stationary solution ρ_∞ thus is the eigenvector of M with eigenvalue zero.

Often it is easier to calculate ρ_∞ by inversion. To this end and since M must be singular, one invokes the one additional *normalisation condition*

$$\sum_{n=1}^{N} \langle n|\rho|n\rangle = 1. \tag{2.2.2}$$

In matrix language, this yields one additional equation to $0 = M\mathbf{r}$. For example,

$$\mathbf{e}_N = M'\mathbf{r}, \tag{2.2.3}$$

where $\mathbf{e}_N = (0,0,...,1)^T$ and M' is M where the last (the Nth) row, which must be linearly dependent on the first $N-1$ rows, has been replaced by the correct sequence of 'ones' such as $(1,0,0,0,....1,...,1)$, corresponding to the diagonal elements of ρ.

Using M', standard *matrix inversion* can then be used provided the dimension of the matrix is not too large.

Example: system with 4 electronic and 15 vibrational states, thus $N = 4\times 15 = 60$. The dimension of the matrix M scales as $N^2 \sim 3600$. If this goes up to say 10000 or more, one already has to start thinking about computer memory, better algorithms etc.

2.3 Some Linear Algebra Programming

2.3.1 Fortran

The 'emacs' editor to write Fortran source code. Starting the GNU project Fortran 77 compiler on the Fortran source code 'diagonalisation.for', linking the 'lapack' package, creating binary 'diag.out':

```
g77 -o diag.out  diagonalisation.for -llapack
```

Fortran auf unseren Linux-Rechnern:

```
gfortran -o diag.out  diagonalisation.for -llapack
```

Dann diag.out aufrufen mit

```
./diag.out
```

2.3.1.1 Compilers

The g77 compiler from GNU GCC project http://gcc.gnu.org/ comes free with Linux but is no longer actively supported. ‘Today, truly free Fortran 90 or Fortran 95 compilers do not exist. We are trying to make one available to the Fortran community’ (Nov. 2005).

2.3.1.2 Precision

Single and double precision.

2.4 Packages, Books

2.4.1 GENERAL

How to get freely available software for scientific computing? One way is Netlib:

```
 2.1) What is Netlib?
The Netlib repository contains freely available software, documents,
 and databases  of interest to the numerical, scientific computing,
and other communities. The repository is maintained by
AT&T Bell Laboratories, the University of Tennessee
and Oak Ridge National Laboratory, and by colleagues world-wide.
The collection is replicated at several sites around the world,
automatically synchronized, to provide reliable and network efficient
service to the global community.

2.2) How do I retrieve software or documents from Netlib?
Mechanisms include the World Wide Web (WWW), email, ftp, gopher, xnetlib:

    * World Wide Web (WWW)
      http://www.netlib.org/
```

2.4.2 LAPACK

From the manual entry (‘man lapack’):

```
LAPACK(l)               LAPACK FORTRAN LIBRARY ROUTINES              LAPACK(l)

WHAT IS LAPACK?
```

> LAPACK is a transportable library of Fortran 77 subroutines for solving the most common problems in numerical linear algebra: systems of linear equations, linear least squares problems, eigenvalue problems, and singular value problems. It has been designed to be efficient on a wide range of modern high-performance computers.

LAPACK is intended to be the successor to LINPACK and EISPACK. It extends the functionality of these packages by including equilibration, iterative refinement, error bounds, and driver routines for linear sys-

Further info from http://www.netlib.org/lapack/index.html and
http://www.netlib.org/lapack/lug/

2.4.2.1 LAPACK routines: Example SUBROUTINE DSYEV

They all have detailed explanations at the beginning of the code which always have a similar structure. This is a routine

```
file dsyev.f  dsyev.f plus dependencies
prec double
for  Computes all eigenvalues, and optionally, eigenvectors of a real
,    symmetric matrix.
gams d4a1
```

for the diagonalisation of a real symmetric matrix.

```
     SUBROUTINE DSYEV( JOBZ, UPLO, N, A, LDA, W, WORK, LWORK, INFO )
*
*  -- LAPACK driver routine (version 3.0) --
*     Univ. of Tennessee, Univ. of California Berkeley, NAG Ltd.,
*     Courant Institute, Argonne National Lab, and Rice University
*     June 30, 1999
*
*     .. Scalar Arguments ..
      CHARACTER          JOBZ, UPLO
      INTEGER            INFO, LDA, LWORK, N
*     ..
*     .. Array Arguments ..
      DOUBLE PRECISION   A( LDA, * ), W( * ), WORK( * )
*     ..
*
*  Purpose
```

```
*  =======
*
*  DSYEV computes all eigenvalues and, optionally, eigenvectors of a
*  real symmetric matrix A.
*
*  Arguments
*  =========
*
*  JOBZ    (input) CHARACTER*1
*          = 'N':  Compute eigenvalues only;
*          = 'V':  Compute eigenvalues and eigenvectors.
*
*  UPLO    (input) CHARACTER*1
*          = 'U':  Upper triangle of A is stored;
*          = 'L':  Lower triangle of A is stored.
*
*  N       (input) INTEGER
*          The order of the matrix A.  N >= 0.
*
*  A       (input/output) DOUBLE PRECISION array, dimension (LDA, N)
*          On entry, the symmetric matrix A.  If UPLO = 'U', the
*          leading N-by-N upper triangular part of A contains the
*          upper triangular part of the matrix A.  If UPLO = 'L',
*          the leading N-by-N lower triangular part of A contains
*          the lower triangular part of the matrix A.
*          On exit, if JOBZ = 'V', then if INFO = 0, A contains the
*          orthonormal eigenvectors of the matrix A.
*          If JOBZ = 'N', then on exit the lower triangle (if UPLO='L')
*          or the upper triangle (if UPLO='U') of A, including the
*          diagonal, is destroyed.
*
*  LDA     (input) INTEGER
*          The leading dimension of the array A.  LDA >= max(1,N).
*
*  W       (output) DOUBLE PRECISION array, dimension (N)
*          If INFO = 0, the eigenvalues in ascending order.
*
*  WORK    (workspace/output) DOUBLE PRECISION array, dimension (LWORK)
*          On exit, if INFO = 0, WORK(1) returns the optimal LWORK.
*
```

```
*  LWORK   (input) INTEGER
*          The length of the array WORK.  LWORK >= max(1,3*N-1).
*          For optimal efficiency, LWORK >= (NB+2)*N,
*          where NB is the blocksize for DSYTRD returned by ILAENV.
*
*          If LWORK = -1, then a workspace query is assumed; the routine
*          only calculates the optimal size of the WORK array, returns
*          this value as the first entry of the WORK array, and no error
*          message related to LWORK is issued by XERBLA.
*
*  INFO    (output) INTEGER
*          = 0:  successful exit
*          < 0:  if INFO = -i, the i-th argument had an illegal value
*          > 0:  if INFO = i, the algorithm failed to converge; i
*                off-diagonal elements of an intermediate tridiagonal
*                form did not converge to zero.
*
*  =====================================================================
```

3. EXCURSION: REAL MOLECULES AND FRANCK-CONDON FACTORS

3.1 Introduction

(This is from my lectures notes ‘Quantum Mechanics of Atoms and Molecules’).

Molecules are system consisting of electrons and nuclei. This definition covers the full range from rather simple molecules like H_2 up to extremely complex situations with billions of nuclei, or in principle even solids or fluids although one usually thinks of something like a microscopic object. The question, of course, is what microscopic really means. In principle, one could have molecules with macroscopic large numbers (like 10^{23}) of electrons and nuclei. Would these behave as quantum or as classical objects?

Even for small molecules, there are in fact some fundamental, conceptual issues in the field of molecular structure, cf. for example the article by B. T. Sutcliffe in ch. 35 of Vol. 1 of the ‘Handbook of Molecular Physics and Quantum Chemistry’, Wiley (2003). These are related to the question of whether or not molecular structure and properties of molecules can be strictly derived from a microscopic Schrödinger equation of an isolated molecule, including all the Coulomb interaction among the constituents. For example, the total Hamiltonian commutes with the parity operator which means that itsd eigenstates are parity eigenstates and therefore cannot must have zero expectation value of the static dipole moment. This would mean that there exist no molecules with static dipole moments, which apparently is in contradiction to what we learn from chemistry. Another such ‘paradoxon’ seems to be isomers of polyatomic molecules, and the concept of the chemical bond (‘deconstructing the bond’) is not an easy one, either. These seem to be open questions.

3.1.1 Model Hamiltonian

We start from a Hamiltonian describing a system composed of two sub-systems, electrons (e) and nuclei (n)

$$\mathcal{H} = \mathcal{H}_{\rm e} + \mathcal{H}_{\rm n} + \mathcal{H}_{\rm en}, \tag{3.1.1}$$

where $\mathcal{H}_{\rm en}$ is the interaction between the two systems. Note that the splitting of the Hamiltonian $\mathcal{H}$ is not unique: for example, $\mathcal{H}_{\rm n}$ could just be the kinetic energy of the nuclei with their mutual interaction potential included into $\mathcal{H}_{\rm en}$ (as in the BO approximation).

The set-up $\mathcal{H} = \mathcal{H}_{\rm e}+\mathcal{H}_{\rm n}+\mathcal{H}_{\rm en}$ is quite general and typical for so-called 'system-bath' theories where one would say the electrons are the 'system' and the nuclei are the 'bath' (or vice versa!). In the theory of molecules, however, things are a little bit more complicated as there is a back-action of from the electrons on the nuclei. This back-action is due to the electronic charge density acting as a potential for the nuclei.

There is no *a priori* reason why the nuclei and the electronic system should not be treated on equal footing. However, the theory has a small parameter

$$\kappa = \left(\frac{m}{M}\right)^{\frac{1}{4}} \tag{3.1.2}$$

given by the ratio of electron mass m and a typical nuclear mass $M \gg m$, and the exponent $1/4$ is introduced for convenience in the perturbation theory used by Born and Oppenheimer in their original paper. The smallness of this parameter makes it possible to use an approximation which is called the **Born-Oppenheimer approximation**.

We assume there is a position representation, where $q \equiv \{\mathbf{x_1}, ..., \mathbf{x_N}\}$ represents the positons of all electrons, $X \equiv \{\mathbf{X_1}, ..., \mathbf{X_N}\}$ the positions of all nuclei, and correspondingly for the momenta p and P,

$$\mathcal{H} = \mathcal{H}(q,p;X,P) = \mathcal{H}_{\rm e}(q,p) + \mathcal{H}_{\rm n}(X,P) + \mathcal{H}_{\rm en}(q,X). \tag{3.1.3}$$

Spin is not considered here. Also note that the interaction only depends on (q, X) and not on the momenta.

3.2 The Born-Oppenheimer Approximation

This is the central aproximation used in many calculations.

3.2.1 Derivation

We now try to attack the Schrödinger equation $\mathcal{H}\Psi = \mathcal{E}\Psi$ for the total system (electron plus nuclei).

3.2.1.1 Unsuccessful Attempt

A first guess to solve the stationary Schrödinger equation $\mathcal{H}\Psi = \mathcal{E}\Psi$ for the total system would be a separation *ansatz*

$$\begin{aligned} \mathcal{H}(q,p;X,P)\Psi(q,X) &= \mathcal{E}\Psi(q,X) \\ \Psi(q,X) &= \psi_e(q)\phi_n(X) \quad \text{unsuccessful}, \end{aligned} \tag{3.2.1}$$

which does not work because the interaction $\mathcal{H}_{\text{en}}(q,X)$ depends on both q *and* X.

3.2.1.2 More Successful Attempt

As $\mathcal{H}_{\text{en}}(q,X)$ depends on the positions of the nuclei X, let us try an *ansatz*

$$\Psi(q,X) = \psi_e(q,X)\phi_n(X) \quad \text{successful} \tag{3.2.2}$$

where now the electronic part depends on the nuclear coordinates X as well. This looks unsymmetric: why shouldn't one have $\Psi(q,X) = \psi_e(q,X)\phi_n(q,X)$? First, there *is* an asymmetry in the problem in the form of $M \gg m$, and $\Psi(q,X) = \psi_e(q,X)\phi_n(q,X)$ is no more better than $\Psi(q,X)$ in the first place.

The idea with writing $\Psi(q,X) = \psi_e(q,X)\phi_n(X)$ is that the electronic part $\psi_e(q,X)$ already solves part of the problem, i.e.

$$\left[\mathcal{H}_{\text{e}}(q,p) + \mathcal{H}_{\text{en}}(q,X)\right]\psi_e(q,X) = E(X)\psi_e(q,X), \tag{3.2.3}$$

an equation in which X, of course, appears as an *external classical parameter* that commutes with all other variables. Consequently, the eigenvalue $E(X)$ has to depend on X. We thus obtain

$$\begin{aligned} \mathcal{H}\psi_e\phi_n &\equiv \left[\mathcal{H}_{\text{e}} + \mathcal{H}_{\text{n}} + \mathcal{H}_{\text{en}}\right]\psi_e\phi_n \\ &= \left[\mathcal{H}_{\text{n}} + E(X)\right]\psi_e\phi_n \quad (?) = \mathcal{E}\psi_e\phi_n \end{aligned} \tag{3.2.4}$$

where the last questionmark indicated what we would like to have! Since $\mathcal{H}_{\text{n}}$ and $E(X)$ depend on the nuclear coordinates only, one would like to use an equation like

$$\left[\mathcal{H}_{\text{n}} + E(X)\right]\phi_n(X) = \mathcal{E}\phi_n(X), \tag{3.2.5}$$

because then we would have achieved our goal. However, the operator $\mathcal{H}_{\text{n}}$ contains the nuclear momenta P which operate on the X in $\psi_e(q,X)$, i.e.

$$\begin{aligned} \mathcal{H}\psi_e\phi_n &= \psi_e\left[\mathcal{H}_{\text{n}} + E(X)\right]\phi_n + \underline{\left[\mathcal{H}_{\text{n}}\psi_e\phi_n - \psi_e\mathcal{H}_{\text{n}}\phi_n\right]} \\ &= \mathcal{E}\psi_e\phi_n + \underline{\left[\mathcal{H}_{\text{n}}\psi_e\phi_n - \psi_e\mathcal{H}_{\text{n}}\phi_n\right]}. \end{aligned} \tag{3.2.6}$$

This shows that we are almost there if it wasn't for the underlined term. One now tries to find arguments why this term can be neglected. If it can be neglected, then we have achieved the full solution of the Schrödinger equation by the two separate equations

$$\begin{aligned} \left[\mathcal{H}_{\rm e}(q,p)+\mathcal{H}_{\rm en}(q,X)\right]\psi_e(q,X) &= E(X)\psi_e(q,X) \quad \text{electronic part}\\ \left[\mathcal{H}_{\rm n}+E(X)\right]\phi_n(X) &= \mathcal{E}\phi_n(X) \quad \text{nuclear part.} \end{aligned} \tag{3.2.7}$$

These two equations Eq. (3.2.7) are the central equations of the **Born-Oppenheimer approximation**. Even without solving them, some quite interesting observations can already be made:

- The electronic part is calculated as if the nuclei were at fixed positions X ('clamped nuclei').
- The eigenvalue of the energy of the electronic part serves as a *potential* energy for the nuclei in the nuclear part of the equations.

3.2.2 Discussion of the Born-Oppenheimer Approximation

We now have to justify the neglect of the underlined term in

$$\mathcal{H}\psi_e\phi_n = \mathcal{E}\psi_e\phi_n + \underline{[\mathcal{H}_{\rm n}\psi_e\phi_n - \psi_e\mathcal{H}_{\rm n}\phi_n]}. \tag{3.2.8}$$

Up to here, everything was still fairly general. Now we make out choice for $\mathcal{H}_{\rm n}$ as just the kinetic energy of the nuclei,

$$\mathcal{H}_{\rm n} = \sum_{i=1}^{N}\frac{P_i^2}{2M_i}. \tag{3.2.9}$$

We simplify the following discussion by writing

$$\mathcal{H}_{\rm n} = \frac{P^2}{2M} = -\frac{\hbar^2}{2M}\nabla_X^2, \tag{3.2.10}$$

which refers to a) a single relative motion of two nuclei of effective mass M, or alternatively b) represents an 'abstract notation' for $\mathcal{H}_{\rm n} = \sum_{i=1}^{N}\frac{P_i^2}{2M_i}$ (to which the following transformations can easily be generalised).

We write

$$\begin{aligned} \mathcal{H}_{\rm n}\psi_e\phi_n - \psi_e\mathcal{H}_{\rm n}\phi_n &= -\frac{\hbar^2}{2M}\left[\nabla_X^2\psi_e(q,X)\phi_n(X) - \psi_e(q,X)\nabla_X^2\phi_n(X)\right]\\ &= -\frac{\hbar^2}{2M}\Big[\nabla_X\left\{\phi_n\nabla_X\psi_e + \phi_e\nabla_X\psi_n\right\} - \psi_e\nabla_X^2\phi_n\Big]\\ &= -\frac{\hbar^2}{2M}\Big[2\nabla_X\phi_n\nabla_X\psi_e + \phi_n\nabla_X^2\psi_e\Big]. \end{aligned} \tag{3.2.11}$$

This term is therefore determined by the derivative of the electronic part with respect to the nuclear positions X, and it has the factor $1/M$ in front. The 'handwaving' argument now is to say that the derivatives $\nabla_X \psi_e$ and $\nabla_X^2 \psi_e$ are small.

3.2.3 Adiabaticity and Geometric Phases

The electronic part equation

$$[\mathcal{H}_{\rm e}(q,p) + \mathcal{H}_{\rm en}(q,X)]\,\psi_e(q,X) \;=\; E(X)\psi_e(q,X) \tag{3.2.12}$$

usually should give not only one but a whole set of eigenstates,

$$[\mathcal{H}_{\rm e} + \mathcal{H}_{\rm en}]\,|\alpha(X)\rangle \;=\; E_\alpha(X)|\alpha(X)\rangle. \tag{3.2.13}$$

Assume that for a fixed X we have orthogonal basis of the electronic Hilbert space with states $|\alpha(X)\rangle$, no degeneracies and a discrete spectrum $E_\alpha(X)$,

$$\langle\alpha(X)|\beta(X)\rangle = \delta_{\alpha\beta}. \tag{3.2.14}$$

Adiabaticity means that when X is changed slowly from $X \to X'$, the corresponding state slowly changes from $|\alpha(X)\rangle \to |\alpha(X')\rangle$ and does not jump to another $\alpha' \neq \alpha$ like $|\alpha(X)\rangle \to |\alpha'(X')\rangle$. In that case, we can use the $|\alpha(X)\rangle$ as a basis for all X and write

$$\Psi(q,X) = \sum_\alpha \phi_\alpha(X)\psi_\alpha(q,X). \tag{3.2.15}$$

Now

$$\mathcal{H}\sum_\alpha |\phi_\alpha\rangle_n \otimes |\psi_\alpha\rangle_e \;=\; \sum_\alpha [\mathcal{H}_{\rm n} + E_\alpha(X)]\,|\phi_\alpha\rangle_n \otimes |\psi_\alpha\rangle_e, \tag{3.2.16}$$

and taking the scalar product with a $\langle\psi_\alpha|$ of the Schrödinger equation $\mathcal{H}\Psi = \mathcal{E}\Psi$ therefore gives

$$[\langle\psi_\alpha|\mathcal{H}_{\rm n}|\psi_\alpha\rangle_e + E_\alpha(X)]\,|\phi_\alpha\rangle_n = \mathcal{E}|\phi_\alpha\rangle_n \tag{3.2.17}$$

This is the Schrödinger equation for the nuclei within the adiabatic approximation. Now using again

$$\begin{aligned}
\mathcal{H}_{\rm n} \;&=\; -\frac{\hbar^2}{2M}\nabla_X^2 \rightsquigarrow \mathcal{H}_{\rm n}\psi_\alpha(q,X)\phi_\alpha(X)\\
&=\; -\frac{\hbar^2}{2M}\Big[\psi_\alpha(q,X)\nabla_X^2\phi_\alpha(X) + \phi_\alpha(X)\nabla_X^2\psi_\alpha(q,X)\\
&+\; 2\nabla_X\phi_\alpha(X)\nabla_X\psi_\alpha(q,X)\Big]
\end{aligned} \tag{3.2.18}$$

and therefore the nuclear Schrödinger equation becomes

$$
\begin{aligned}
& [\langle\psi_\alpha|\mathcal{H}_{\rm n}|\psi_\alpha\rangle_e + E_\alpha(X)]\,|\phi_\alpha\rangle_n = \mathcal{E}|\phi_\alpha\rangle_n \rightsquigarrow \\
& \left[-\frac{\hbar^2}{2M}\nabla_X^2 + E_\alpha(X) - \langle\psi_\alpha|\frac{\hbar^2\nabla_X^2}{2M}|\psi_\alpha\rangle - \langle\psi_\alpha|\frac{\hbar^2\nabla_X}{M}|\psi_\alpha\rangle\nabla_X\right]|\phi_\alpha\rangle_n \\
= \ & \mathcal{E}|\phi_\alpha\rangle_n \qquad (3.2.19)
\end{aligned}
$$

which can be re-written as

$$
\begin{aligned}
\left[-\frac{\hbar^2}{2M}\nabla_X^2 + E_\alpha(X) - \frac{\hbar^2}{2M}G(X) - \frac{\hbar^2}{M}F(X)\nabla_X\right]|\phi_\alpha\rangle_n \ &= \ \mathcal{E}|\phi_\alpha\rangle_n \\
G(X) \equiv \langle\psi_\alpha|\nabla_X^2\psi_\alpha\rangle, \quad F(X) \equiv \langle\psi_\alpha|\nabla_X\psi_\alpha\rangle \qquad , \qquad (3.2.20)
\end{aligned}
$$

where we followed the notation by Mead and Truhlar in their paper J. Chem. Phys. **70**, 2284 (1979). Eq. (3.2.20) is an important result as it shows that the adiabatic assumption leads to extra terms $F(X)$ and $G(X)$ in the nuclear Schrödinger equation in BO approximation on top of just the potential created by the electrons. In particular, the term $F(X)$ is important as it leads to a non-trivial **geometrical phase** in cases where the curl of $F(X)$ is non-zero. This has consequences for molecular spectra, too. geometric phases such as the abelian **Berry phase** and the non-abelian **Wilczek-Zee holonomies** play an important role in other areas of modern physics, too, one example being 'geometrical quantum computing'. For more info on the geometric phase in molecular systems, cf. the Review by C. A. Mead, Prev. Mod. Phys. **64**, 51 (1992).

3.2.4 Breakdown of the Born-Oppenheimer Approximation

This is a non-trivial, much discussed issue and in actual fact still the topic of present research. From our discussion in the previus section we understand that adiabaticity is lost if transitions between electronic states $|\alpha(X)\rangle \rightarrow |\alpha'(X')\rangle$ occur while change X. One example for is the so-called Landau-Zener tunneling between nearby energy levels $E_\alpha(X)$ and $E_{\alpha'}(X)$. Also discussed in this context are the Renner-Teller and the Jahn-Teller effects, cf. the short summary by B. T. Sutcliffe in ch. 36 of Vol. 1 of the 'Handbook of Molecular Physics and Quantum Chemistry', Wiley (2003).

3.3 Vibrations and Rotations in Diatomic Molecules

Here, we follow Weissbluth [**?**] ch. 27, and Landau-Lifshitz III [**?**].

3.3.1 Hamiltonian

Before deriving the Hamiltonian, a short excursion to classical mechanics of two particles:

3.3.1.1 Angular Momentum of Two Particles

If two particles have positions $\mathbf{r}_1$ and $\mathbf{r}_2$ and momenta $\mathbf{p}_1$ and $\mathbf{p}_2$, the angular momentum of the total system of the two particles is

$$\mathbf{L} = \mathbf{r}_1 \times \mathbf{p}_1 + \mathbf{r}_2 \times \mathbf{p}_2. \tag{3.3.1}$$

We introduce center-of-mass and relative coordinates according to

$$\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2}, \quad \mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1, \tag{3.3.2}$$

and furthermore momenta

$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2 \tag{3.3.3}$$

$$\mathbf{p} = \frac{m_1\mathbf{p}_2 - m_2\mathbf{p}_1}{m_1 + m_2}. \tag{3.3.4}$$

Note that the *relative momentum* $\mathbf{p}$ is not just the difference of the individual momenta. It is rather defined such that in terms of

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2} \quad \text{reduced mass}, \tag{3.3.5}$$

one has

$$\mu\dot{\mathbf{r}} = \mu(\dot{\mathbf{r}}_2 - \dot{\mathbf{r}}_1) = \mu\left(\frac{\mathbf{p}_2}{m_2} - \frac{\mathbf{p}_1}{m_1}\right) = \mathbf{p}. \tag{3.3.6}$$

Using these definitions, one checks

$$\mathbf{L} = \mathbf{r}_1 \times \mathbf{p}_1 + \mathbf{r}_2 \times \mathbf{p}_2 \tag{3.3.7}$$

$$= \mathbf{R} \times \mathbf{P} + \mathbf{r} \times \mathbf{p}. \tag{3.3.8}$$

This is the sum of a center-of-mass angular momentum, $\mathbf{R} \times \mathbf{P}$, and a relative angular momentum, $\mathbf{r} \times \mathbf{p}$.

3.3.1.2 Born-Oppenheimer Approximation

We recall the Born-Oppenheimer Approximation for the total wave function $\Psi(q,X)$ of a molecule, cf. Eq. (3.2.15),

$$\Psi(q,X)=\sum_{\alpha}\phi_{\alpha}(X)\psi_{\alpha}(q,X), \tag{3.3.9}$$

where q stands for the electronic, X for the nuclear coordinates, and the sum is over a complete set of adiabatic electronic eigenstates with electronic quantum numbers α. This form leads to the Schrödinger equation in the adiabatic approximation Eq. (3.2.17),

$$\left[\langle\psi_{\alpha}|\mathcal{H}_{\rm n}|\psi_{\alpha}\rangle_e+E_{\alpha}(X)\right]|\phi_{\alpha}\rangle_n=\mathcal{E}|\phi_{\alpha}\rangle_n. \tag{3.3.10}$$

Here, $E_{\alpha}(X)$ is the potential acting on the nuclei. We now specify the kinetic energy of the nuclear part for a diatomic molecule,

$$\mathcal{H}_{\rm n}=\frac{\mathbf{P}^2}{2M}+\frac{\mathbf{p}^2}{2\mu}. \tag{3.3.11}$$

Exercise Check that $\mathcal{H}_{\rm n}=\frac{\mathbf{p}_1^2}{2m_1}+\frac{\mathbf{p}_2^2}{2m_2}$.

The effective nuclear Hamiltonian corresponding to an electronic eigenstate α thus is

$$\mathcal{H}_{{\rm n},\alpha}=\langle\psi_{\alpha}|\frac{\mathbf{P}^2}{2M}|\psi_{\alpha}\rangle+\langle\psi_{\alpha}|\frac{\mathbf{p}^2}{2\mu}|\psi_{\alpha}\rangle+E_{\alpha}(r), \tag{3.3.12}$$

which is a sum of a center-of-mass Hamiltonian and a Hamiltonian for the relative motion of the two nuclei. Only the latter is interesting because it contains the potential $E_{\alpha}(r)$. Note that both center-of-mass and relative Hamiltonian still contain the geometrical phase terms, cf. Eq. (3.2.20), which however we will neglect in the following.

3.3.2 Angular Momentum

Neglecting the geometric phase terms, Eq. (3.2.20), we have in three spatial dimensions

$$\begin{aligned}\mathcal{H}_{{\rm n},\alpha}^{\rm rel} &= \frac{\mathbf{p}^2}{2\mu}+E_{\alpha}(r)=-\frac{\hbar^2}{2\mu}\Delta_{\mathbf{r}}+E_{\alpha}(r)\\ &= -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{\mathbf{J}^2}{2\mu r^2}+E_{\alpha}(r),\end{aligned} \tag{3.3.13}$$

where $\mathbf{J}$ is the *relative* angular momentum operator of the nuclei. We have a three-dimensional problem which however due to the radial symmetry of $E_\alpha(r)$ is reduced to a one-dimensional radial eqaution, very much as for the case of the hydrogen atom! We could write the eigenfunctions of $\mathcal{H}^{\rm rel}_{\rm n,\alpha}$ as

$$\Psi(\mathbf{r}) = R(r)Y_{JM}(\theta,\phi) \tag{3.3.14}$$

with the corresponding angular quantum numbers J and M of the nuclear relative motion separated off in the spherical harmonics.

Instead of dealing with the angular momentum operator of the nuclei, one would rather descrive rotations of the whole molecule by the *total* angular momentum $\mathbf{K}$ of the molecule

$$\mathbf{K} = \mathbf{J} + \mathbf{L} + \mathbf{S}, \tag{3.3.15}$$

where $\mathbf{L}$ is the total angular momentum of all electrons and $\mathbf{S}$ is the total spin.

3.3.2.1 Spin $\mathbf{S} = 0$

This is the simplest case. The total angular momentum of the nuclei is then

$$\mathbf{J} = \mathbf{K} - \mathbf{L}. \tag{3.3.16}$$

Since we have neglected geometric phase terms, we can replace $\Delta_{\mathbf{r}}$ by its expectation value in the electronic state α under consideration,

$$\begin{aligned} \Delta_{\mathbf{r}} &= \langle\psi_\alpha|\Delta_{\mathbf{r}}|\psi_\alpha\rangle & (3.3.17)\\ \rightsquigarrow \mathbf{J}^2 &= \langle\psi_\alpha|\mathbf{J}^2|\psi_\alpha\rangle = \langle\psi_\alpha|(\mathbf{K}-\mathbf{L})^2|\psi_\alpha\rangle. & (3.3.18)\end{aligned}$$

This allows one to express everything in terms of total angular quantum numbers K as follows: We first write

$$\begin{aligned} \mathbf{J}^2 &= \langle\psi_\alpha|(\mathbf{K}-\mathbf{L})^2|\psi_\alpha\rangle & (3.3.19)\\ &= \langle\psi_\alpha|\mathbf{K}^2|\psi_\alpha\rangle - 2\langle\psi_\alpha|\mathbf{K}\mathbf{L}|\psi_\alpha\rangle + \langle\psi_\alpha|\mathbf{L}^2|\psi_\alpha\rangle. \end{aligned}$$

First, $\mathbf{K}^2$ is conserved and can be replaced by its eigenvalue $K(K+1)$ whence

$$\langle\psi_\alpha|\mathbf{K}^2|\psi_\alpha\rangle = K(K+1). \tag{3.3.20}$$

Second, $\langle\psi_\alpha|\mathbf{L}^2|\psi_\alpha\rangle$ only depends on the electronic degrees of freedom and can therefore be simply added to the potential $E_\alpha(r)$.

Finally, we assume that the electronic state α is an eigenstate of the z component L_z with eigenvalue Λ of the electronic angular momentum. Then,

$$\langle\psi_\alpha|\mathbf{K}\mathbf{L}|\psi_\alpha\rangle = \mathbf{K}\langle\psi_\alpha|\mathbf{L}|\psi_\alpha\rangle = \mathbf{K}\mathbf{e}_z\Lambda. \tag{3.3.21}$$

On the other hand, we have $\mathbf{J}\mathbf{e}_z = 0$ since the angular momentum of the two nuclei is perpendicular to the molecule axis $\mathbf{e}_z \propto \mathbf{r}$, thus

$$(K_z - L_z) = 0 \leadsto K_z = L_z \tag{3.3.22}$$

and

$$\begin{aligned}\langle\psi_\alpha|\mathbf{K}\mathbf{L}|\psi_\alpha\rangle &= \mathbf{K}\mathbf{e}_z\Lambda = L_z\Lambda \\ &= \langle\psi_\alpha|L_z|\psi_\alpha\rangle\Lambda = \Lambda^2.\end{aligned} \tag{3.3.23}$$

Summarizing, we now have for the radial part

$$\begin{aligned}&-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{K(K+1)}{2\mu r^2}\underline{-\frac{2\Lambda^2}{2\mu r^2}+\frac{\langle\psi_\alpha|\mathbf{L}^2|\psi_\alpha\rangle}{2\mu r^2}+E_\alpha(r)}\\ \equiv\ &-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{K(K+1)}{2\mu r^2}+U_\alpha(r).\end{aligned}$$

Thus we have finally arrived at the form for the effective potential energy,

$$\frac{K(K+1)}{2\mu r^2}+U_\alpha(r). \tag{3.3.24}$$

The first term $\frac{K(K+1)}{2\mu r^2}$ is the centrifugal energy as in the hydrogen problem. Since $K_z = L_z$ with fixed eigenvalue Λ for the given state α, the eigenvalues of the total angular momentum must fulfill

$$K \geq \Lambda. \tag{3.3.25}$$

3.3.3 Radial SE

Our SE for the radial motion of the two nuclei has the form

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{K(K+1)}{2\mu r^2}+U_\alpha(r)\right]R_{\alpha;Kv}(r)=\varepsilon_{\alpha;Kv}R_{\alpha;Kv}(r). \tag{3.3.26}$$

We therefore have two sets of quantum numbers K and v that describe the rotational and vibrational and state of the molecule for a given electronic state α. Setting

$$R_{\alpha;Kv}(r)=\frac{1}{r}P_{\alpha;Kv}(r) \tag{3.3.27}$$

leads to a standard one-dimensional SE with a 'proper' $\frac{d^2}{dr^2}$ kinetic energy term,

$$\left[-\frac{1}{2\mu}\frac{d^2}{dr^2}+U_\alpha(r)+\frac{K(K+1)}{2\mu r^2}\right]P_{\alpha;Kv}(r)=\varepsilon_{\alpha;Kv}P_{\alpha;Kv}(r),\quad r\geq 0. \tag{3.3.28}$$

3.3.3.1 Harmonic Approximation

The rotation term $\frac{K(K+1)}{2\mu r^2}$ is assumed as small, and the potential $U_\alpha(r)$ is expanded around a minimum r_α,

$$U_\alpha(r) = U_\alpha(r_\alpha) + \frac{1}{2}\frac{d^2}{dr^2}U_\alpha(r = r_\alpha)(r - r_\alpha)^2 + ... \tag{3.3.29}$$

Here, r_α can be considered as the equilibrium distance of the two nuclei which clearly still depends on the electronic quantum number α. If the higher order terms in the Taylor expansion are neglected, and $\frac{K(K+1)}{2\mu r^2}$ replaced by $\frac{K(K+1)}{2\mu r_\alpha^2}$, the approximate SE becomes

$$\begin{aligned} &\left[-\frac{1}{2\mu}\frac{d^2}{dr^2} + \frac{K(K+1)}{2\mu r_\alpha^2} + U_\alpha(r_\alpha) + \frac{1}{2}\mu\omega_\alpha^2(r - r_\alpha)^2\right] P^{\rm harm}_{\alpha;Kv}(r) \\ =\ & \varepsilon_{\alpha;Kv}P^{\rm harm}_{\alpha;Kv}(r), \quad \omega_\alpha^2 = \frac{1}{\mu}\frac{d^2}{dr^2}U_\alpha(r = r_\alpha). \end{aligned} \tag{3.3.30}$$

This is the equation of a linear harmonic oscillator apart from the fact that $r \geq 0$. However, $|r - r_\alpha|$ has been assumed to be small anyway and within this approximation, the energy levels are therefore those of a linear harmonic oscillator shifted by $\frac{K(K+1)}{2\mu r_\alpha^2} + U_\alpha(r_\alpha)$,

$$\varepsilon^{\rm harm}_{\alpha;Kv} = \frac{K(K+1)}{2\mu r_\alpha^2} + U_\alpha(r_\alpha) + \omega_\alpha\left(v + \frac{1}{2}\right). \tag{3.3.31}$$

3.3.3.2 The Energy Spectrum

The structure of the energy spectrum is determined by the magnitude of the three terms $\frac{K(K+1)}{2\mu r_\alpha^2}$, $U_\alpha(r_\alpha)$, and $\omega_\alpha\left(v + \frac{1}{2}\right)$. These differ strongly due to their dependence on the relative nuclei mass μ. In terms of the small dimensionless parameter m/μ (where m is the electron mass), we have

$$U_\alpha = O(1), \quad \text{electronic part} \tag{3.3.32}$$

$$\omega_\alpha\left(v + \frac{1}{2}\right) = O(m/\mu)^{1/2}, \quad \text{vibrational part} \tag{3.3.33}$$

$$\frac{K(K+1)}{2\mu r_\alpha^2} = O(m/\mu), \quad \text{rotational part.} \tag{3.3.34}$$

In spectroscopic experiments, one determined energy differences δE which therefore are broadly determined by

$$\delta E_{\rm el} \gg \delta E_{\rm vib} \gg \delta E_{\rm rot}. \tag{3.3.35}$$

3.3.4 Spin $\mathbf{S} > 0$

Things get a little bit more complicated for $\mathbf{S} > 0$ which leads to the so-called *Hund's cases a, b, c and d*. For more details cf. Landau-Lifshitz III [**?**], or Atkins-Friedman.

3.3.5 Beyond the Harmonic Approximation

The harmonic approximation has to break down somewhere. A diatomic molecule with its two nuclei harmonically bound would never be able to dissociate into two individual atoms or ions.

One way is to introduce phenomenological potentials with fitting parameters, e.g. the **Morse potential**

$$U_\alpha(r) \to U_\alpha^{\rm Morse}(r) \equiv D_\alpha \left[1 - e^{-\beta_\alpha(r-r_\alpha)}\right]^2, \tag{3.3.36}$$

where D_α is the depth of the minimum below the asymptote and represents the dissociation energy of the molecule.

3.4 Selection Rules

3.4.1 Dipole Approximation

Assume system of charges q_n localised around a spatial position $\mathbf{r}_0 = 0$. The coupling to an electric field $\mathbf{E}(\mathbf{r}, t)$ within dipole approximation is then given by

$$H_{\rm dip}(t) = -\mathbf{d}\mathbf{E}(t), \quad \mathbf{d} \equiv \sum_n q_\alpha \mathbf{r}_\alpha, \tag{3.4.1}$$

where $\mathbf{E}(t) \equiv \mathbf{E}(\mathbf{r}_0, t)$ is the electric field at $\mathbf{r}_0 = 0$. The dipole approximation is valid if the spatial variation of $\mathbf{E}(\mathbf{r}, t)$ around $\mathbf{r}_0$ is important only on length scales l with $l \gg a$, where a is the size of the volume in which the charges are localised. For a plane wave electric field with wave length λ one would have $l \sim \lambda$.

3.4.2 Pure Rotation

Pure rotational transitions are between states where only rotational quantum numbers are changed,

$$|Km_K, v, \alpha\rangle \to |K'm'_K, v, \alpha\rangle \tag{3.4.2}$$

leaving the vibrational quantum number(s) v and the electronic quantum number(s) α unchanged. Such transitions then depend on matrix elements of the dipole operator,

$$\langle Km_K|\mathbf{d}|K'm'_K\rangle. \tag{3.4.3}$$

The calculation of this matrix element, using spherical harmonics, yields the purely rotational selection rules

$$\Delta K = \pm 1, \quad \Delta m_K = 0, \pm 1. \tag{3.4.4}$$

Writing the rotational part of the energy as

$$\begin{aligned} & \varepsilon_{\text{rot}}(K) = BK(K+1) && (3.4.5) \\ \rightsquigarrow \quad & \Delta\varepsilon_{\text{rot}}(K) \equiv B(K+1)(K+2) - BK(K+1) = 2B(K+1). \end{aligned}$$

The distance between the corresponding spectral lines is constant, $\Delta\varepsilon_{\text{vib}}(K+1) - \Delta\varepsilon_{\text{vib}}(K) = 2B$.

3.4.3 Pure Vibration

In this case, we have to deal with the harmonic oscillator.

3.4.3.1 Recap of the Harmonic Oscillator

The Hamiltonian of the harmonic oscillator

$$\hat{H}_{\text{osc}} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2 \tag{3.4.6}$$

can be re-written using the ladder operators

$$\begin{aligned} a &\equiv \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i}{\sqrt{2m\hbar\omega}}\hat{p}, \quad a^\dagger \equiv \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - \frac{i}{\sqrt{2m\hbar\omega}}\hat{p} && (3.4.7) \\ \hat{x} &= \sqrt{\frac{\hbar}{2m\omega}}\left(a + a^\dagger\right), \quad \hat{p} = -i\sqrt{\frac{m\hbar\omega}{2}}\left(a - a^\dagger\right), && (3.4.8) \end{aligned}$$

as

$$\hat{H}_{\text{osc}} = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right). \tag{3.4.9}$$

The commutation relation is

$$[\hat{x}, \hat{p}] = i\hbar, \quad [a, a^\dagger] = 1. \tag{3.4.10}$$

The eigenfunctions of the harmonic oscillator are n-phonon states,

$$\begin{aligned} \hat{H}_{\text{osc}}|n\rangle &= \varepsilon_n |n\rangle, \quad \varepsilon_n = \hbar\omega\left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, ... \\ |n\rangle \leftrightarrow \psi_n(x) &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{n! 2^n}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) e^{-\frac{m\omega}{2\hbar}x^2}, && (3.4.11) \end{aligned}$$

where H_n are the Hermite polynomials.

The ladder operators are also called creation ($a^\dagger$) and annihiliation (a) operators. They act on the states $|n\rangle$ as

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle, \quad a|n\rangle = \sqrt{n}|n-1\rangle, \quad a|n\rangle = 0. \tag{3.4.12}$$

The state $|0\rangle$ is called ground state.

3.4.3.2 Pure Vibrational Dipole Transitions

Pure vibrational transitions are between states where only vibrational quantum numbers are changed,

$$|Km_K, v, \alpha\rangle \rightarrow |Km_K, v', \alpha\rangle. \tag{3.4.13}$$

Such transitions then depend on matrix elements of the dipole operator,

$$\langle v|\mathbf{d}_\alpha|v'\rangle, \tag{3.4.14}$$

where $|v\rangle$ is an harmonic oscillator eigenstate (we write v instead of n now), and

$$\mathbf{d}_\alpha = \langle\alpha|\mathbf{d}|\alpha\rangle \tag{3.4.15}$$

is the diagonal matrix element of the dipole operator between the adiabatic electronic eigenstates $|\alpha\rangle$.

Remember that the harmonic potential came from the Taylor expansion of the Born-Oppenheimer energy,

$$\begin{aligned}
U_\alpha(r) &\approx U_\alpha(r_\alpha) + \frac{1}{2}\frac{d^2}{dr^2}U_\alpha(r=r_\alpha)(r-r_\alpha)^2 \\
\rightsquigarrow \hat{H}_{\text{osc}} &= \frac{\hat{p}^2}{2\mu} + \frac{1}{2}m\omega_\alpha^2\hat{x}^2 = \hbar\omega_\alpha\left(a^\dagger a + \frac{1}{2}\right) && (3.4.16) \\
\omega_\alpha^2 &= \frac{1}{\mu}\frac{d^2}{dr^2}U_\alpha(r=r_\alpha) && (3.4.17)
\end{aligned}$$

where the harmonic oscillator coordinate $x = r - r_\alpha$.

The dipole moment operator $\mathbf{d}_\alpha$ depends on the electronic wave functions α and thus parametrically on the coordinate x that describes the internuclear separation. We Taylor-expand

$$\mathbf{d}_\alpha(x) = \mathbf{d}_\alpha(0) + \mathbf{d}'_\alpha(0)x + O(x^2). \tag{3.4.18}$$

For transitions between v and $v' \neq v$, one therefore has to linear approximation

$$\begin{aligned}\langle v|\mathbf{d}_\alpha|v'\rangle &= \mathbf{d}'_\alpha(0)\langle v|x|v'\rangle = \mathbf{d}'_\alpha(0)\sqrt{\frac{\hbar}{2\mu\omega}}\langle v|a+a^\dagger|v'\rangle \\ &= \mathbf{d}'_\alpha(0)\sqrt{\frac{\hbar}{2\mu\omega}}\left(\delta_{v+1,v'}\sqrt{v+1}+\delta_{v-1,v'}\sqrt{v}\right). \qquad (3.4.19)\end{aligned}$$

The vibrational selection rule thus is

$$\Delta v = \pm 1. \qquad (3.4.20)$$

The corresponding energy differences determine the transition frequency,

$$\Delta\varepsilon_{\rm vib}(v) = \hbar\omega_\alpha, \qquad (3.4.21)$$

which means that a purely vibrational, harmonic spectrum just consists of a single spectral line!

3.4.4 Vibration-Rotation Spectra

Vibrational and Rotational transitions are coupled, and one now has to discuss the various transition possibilities. This leads to a description in terms of **P-, Q-, and R-branch** for the allowed transitions in diatomic molecules. For further reading, cf. Atkins/Friedman [**?**] ch. 10.11 or Weissbluth [**?**] ch. 27.2

3.5 Electronic Transitions

Transitions between two molecular states in general involve all quantum numbers: electronic, vibrational, and rotational, i.e.

$$|Km_K, v, \alpha\rangle \to |K'm'_K, v', \alpha'\rangle. \qquad (3.5.1)$$

3.5.1 The Franck-Condon Principle

Here, a good description is in Atkins/Friedman ch. 11.4.

For simplicity, we leave out the rotations here and just discuss electronic and vibrational transitions. In a classical picture (with respect to the large mass nuclear motion), one considers the two potential curves $U_\alpha(r)$ and $U_{\alpha'}(r)$ and argues that the electronic transition occurs so fast that the nuclear system has no time to react: before and after the transition, the nuclear coordinate X is the same. This, however, means that the distance $|x'| \equiv |X - r_{\alpha'}|$ from the equilibrium position $r_{\alpha'}$

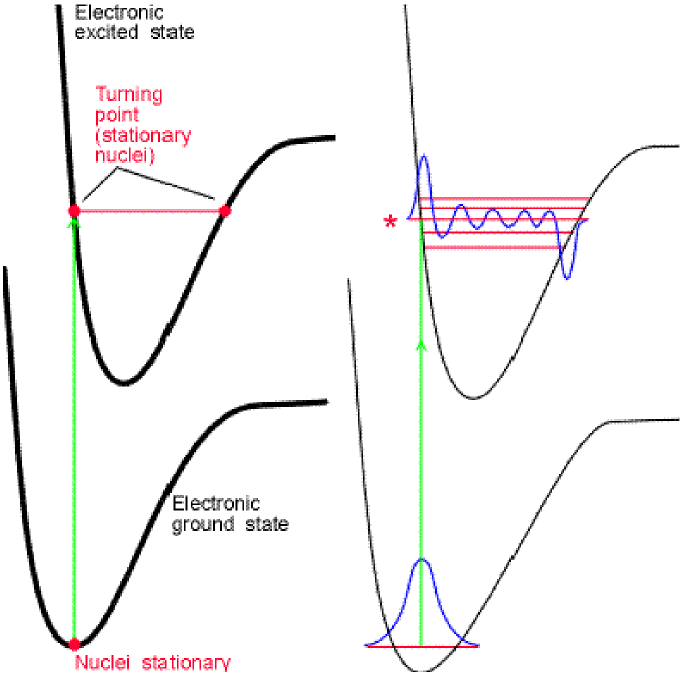


Figure 3.1: Franck-Condon-Principle. **Left:** Classical picture, **right:** quantum-mechanical picture. From Prof. Ed Castner's lecture http://rutchem.rutgers.edu/.

after the transition and the distance $|x| \equiv |X - r_\alpha|$ from the equilibrium position r_α before the transition are not the same: when the nuclei are in equilibrium before the transition ($X = r_\alpha, x = 0$), their new coordinate x' *relative to the new equilibrium* $r_{\alpha'}$ is $x' \equiv X - r_{\alpha'} = r_\alpha - r_{\alpha'} \neq 0$ after the transition.

The total dipole moment operator is a sum of electronic and nuclear dipole moment,

$$\mathbf{d} = -e \sum_i \mathbf{q}_i + e \sum_s Z_s \mathbf{X}_s = \mathbf{d}_e + \mathbf{d}_\mathrm{n}. \tag{3.5.2}$$

The transition matrix element in Born-Oppenheimer approximation is ($\alpha \neq \alpha'$)

$$\begin{aligned}
\langle \alpha' v' | \mathbf{d}_e + \mathbf{d}_{\rm n} | \alpha v \rangle &= \int dq dX \psi^*_{\alpha'}(qX) \phi^*_{\alpha',v'}(X) (\mathbf{d}_e + \mathbf{d}_{\rm n}) \phi_{\alpha,v}(X) \psi_\alpha(qX) \\
&= \int dX \phi^*_{\alpha',v'}(X) \left[\int dq \psi^*_{\alpha'}(qX) \mathbf{d}_e \psi_\alpha(qX) \right] \phi_{\alpha,v}(X) \\
&+ \int dX \phi^*_{\alpha',v'}(X) \phi_{\alpha,v}(X) \mathbf{d}_{\rm n} \int dq \psi^*_{\alpha'}(qX) \psi_\alpha(qX) \\
&= \int dX \phi^*_{\alpha',v'}(X) \left[\int dq \psi^*_{\alpha'}(qX) \mathbf{d}_e \psi_\alpha(qX) \right] \phi_{\alpha,v}(X) + 0 \\
&\approx \langle \alpha' | \mathbf{d}_e | \alpha \rangle S(v, v'), \quad S(v, v') \equiv \langle v' | v \rangle. \qquad (3.5.3)
\end{aligned}$$

Here it was assumed that the integral

$$\int dq \psi^*_{\alpha'}(qX) \mathbf{d}_e \psi_\alpha(qX) \approx \langle \alpha' | \mathbf{d}_e | \alpha \rangle \qquad (3.5.4)$$

does not depend on the nuclear coordinates X.

The transition between two electronic levels α and α' is therefore determined by the dipole matrix element $\langle \alpha' | \mathbf{d}_e | \alpha \rangle$ and the **Franck-Condon factors** $S(v, v')$, which are the overlap integrals of the corresponding vibronic states. As these states belong to different electronic states α and α', the overlaps are not zero, and there is also no selection rule for Δv.

4. QUANTUM NOISE AND COUNTING STATISTICS

4.1 Correlation Functions and the Quantum Regression Theorem

4.1.1 Correlation Functions

Correlation functions are important since they can tell us a lot about the dynamics of dissipative systems. Moreover, they are often directly related to experimentally accessible quantities, such as photon or electron *noise*. In quantum optics, *fluctuations* of the photon field are expressed by correlations functions such as $g^{(1)}(\tau)$ and $g^{(2)}(\tau)$.

We would like to calculate the correlation function of two *system* operators A and B,

$$\boxed{C_{BA}(t,\tau) \quad\equiv\quad \langle B(t)A(t+\tau)\rangle \equiv \mathrm{Tr}_{\mathrm{total}}\left(\chi(0)B(t)A(t+\tau)\right), \quad \tau > 0.} \tag{4.1.1}$$

We insert the time evolution of the operators,

$$\chi(t) = e^{-iHt}\chi(0)e^{iHt}, \quad B(t) = e^{iHt}Be^{-iHt}, \quad A(t+\tau) = e^{iH(t+\tau)}Ae^{-iH(t+\tau)} \tag{4.1.2}$$

to find

$$\begin{aligned}
C_{BA}(t,\tau) &= \mathrm{Tr}_{\mathrm{total}}\left(\chi(0)B(t)A(t+\tau)\right)\\
&= \mathrm{Tr}_{\mathrm{total}}\left(e^{iHt}\chi(t)Be^{-iHt}e^{iH(t+\tau)}Ae^{-iH(t+\tau)}\right)\\
&= \mathrm{Tr}_{\mathrm{total}}\left(e^{-iH\tau}\underline{\chi(t)}Be^{iH\tau}A\right)\\
&= \mathrm{Tr}_{\mathrm{total}}\left(e^{-iH\tau}\underline{\rho(t)R_0}Be^{iH\tau}A\right) \quad \text{Born Approximation}\\
&\equiv \mathrm{Tr}_{\mathrm{S}}\left(A\mathrm{Tr}_{\mathrm{Bath}}\left\{e^{-iH\tau}\underline{\underline{\rho(t)B}}R_0e^{iH\tau}\right\}\right)\\
&\equiv \mathrm{Tr}_{\mathrm{S}}\left(A\mathrm{Tr}_{\mathrm{Bath}}\left\{e^{-iH\tau}\underline{\underline{\rho_{B;t}}}R_0e^{iH\tau}\right\}\right)\\
&\equiv \mathrm{Tr}_{\mathrm{S}}\left(A\rho_{B;t}(\tau)\right).
\end{aligned} \tag{4.1.3}$$

The correlation function can therefore be written as an expectation value of A with a 'modified system density matrix' $\rho_{B;t}(\tau)$ which starts at $\tau = 0$ as $\rho_{B;t}(\tau = 0) = \rho(t)B$ and evolves as a function of time $\tau > 0$.

For the time-evolution of a *system* operator $\hat{O}$ according to

$$\hat{O}(\tau) \equiv \mathrm{Tr}_{\mathrm{Bath}} \left\{ e^{-iH\tau} \hat{O} R_0 e^{iH\tau} \right\}, \tag{4.1.4}$$

we can write a formal operator equation

$$\frac{d}{d\tau} \hat{O}(\tau) \equiv \mathcal{L}_\tau \hat{O}(\tau), \tag{4.1.5}$$

where we introduced the *super-operator* $\mathcal{L}_\tau$.

Example: Master equation for $\hat{O} = \rho(0)$ in Born and Markov approximation, cf. Eq.(1.2.30)

$$\begin{aligned} \frac{d}{dt}\rho(t) &= -i[H_S, \rho(t)] \\ &- \sum_k \Big[S_k D_k \rho(t) - D_k \rho(t) S_k + \rho(t) E_k S_k - S_k \rho(t) E_k \Big]. \end{aligned}$$

It is important to realise that $\mathcal{L}_\tau$ is a linear operator. We now assume that the system has a basis of kets $\{|\alpha\rangle\}$ and express the linearity of $\mathcal{L}_\tau$ by writing the matrix elements of $\mathcal{L}_\tau \hat{O}(\tau)$,

$$\langle \alpha | \mathcal{L}_\tau \hat{O}(\tau) | \beta \rangle = \sum_{\gamma\delta} \int_0^\tau d\tau' M^{\alpha\beta}_{\gamma\delta}(\tau, \tau') \langle \gamma | \hat{O}(\tau') | \delta \rangle. \tag{4.1.6}$$

with a time-dependent *memory kernel* as a fourth-order tensor $M(\tau, \tau')$ that relates the matrix elements of the system operator $\hat{O}$ at earlier times to its matrix elements of the (time-evolved) system operator at later times.

Using now $A = |\beta\rangle\langle\alpha|$ in C_{BA}, we have

$$\begin{aligned} C_{B,|\beta\rangle\langle\alpha|}(t,\tau) &= \langle \alpha | \rho_{B;t}(\tau) | \beta \rangle, \\ \frac{d}{d\tau} C_{B,|\beta\rangle\langle\alpha|}(t,\tau) &= \frac{d}{d\tau} \langle \alpha | \rho_{B;t}(\tau) | \beta \rangle = \langle \alpha | \mathcal{L}_\tau \rho_{B;t}(\tau) | \beta \rangle \\ &= \sum_{\gamma\delta} \int_0^\tau d\tau' M^{\alpha\beta}_{\gamma\delta}(\tau,\tau') \langle \gamma | \rho_{B;t}(\tau') | \delta \rangle \\ &= \sum_{\gamma\delta} \int_0^\tau d\tau' M^{\alpha\beta}_{\gamma\delta}(\tau,\tau') C_{B,|\delta\rangle\langle\gamma|}(t,\tau') \end{aligned} \tag{4.1.7}$$

Introducing

$$\begin{aligned} k &\equiv (\alpha\beta), \quad l \equiv (\gamma\delta) \\ A_k &\equiv |\beta\rangle\langle\alpha|, \quad M^{\alpha\beta}_{\gamma\delta}(\tau,\tau') \equiv M_{kl}(\tau,\tau'), \end{aligned} \tag{4.1.8}$$

we convert the tensor equation into a vector equation,

$$\frac{d}{d\tau}C_{B,A_k}(t,\tau) = \sum_l \int_0^\tau d\tau' M_{kl}(\tau,\tau')C_{B,A_l}(t,\tau') \tag{4.1.9}$$

which can be written in compact form using the *vector of operators*,

$$\mathbf{A} \equiv \begin{pmatrix} A_1 \\ A_2 \\ .. \\ A_k \\ .. \end{pmatrix}. \tag{4.1.10}$$

In vector and matrix notation, we thus obtain the *quantum regression theorem* ,

$$\boxed{\frac{d}{d\tau}\langle B(t)\mathbf{A}(t+\tau)\rangle = \int_0^\tau d\tau' \underline{\underline{M}}(\tau,\tau')\langle B(t)\mathbf{A}(t+\tau')\rangle, \quad \tau > 0.} \tag{4.1.11}$$

Remarks:

- We have not made use of the *Markov* approximation here.
- Within the Markov approximation (assumptions 2a and 2b), one has a simple differential (tensor) equation instead of an integro-differential (tensor) equation:

  $$\begin{aligned} \langle\alpha|\mathcal{L}_\tau\hat{O}(\tau)|\beta\rangle &= \sum_{\gamma\delta} M^{\alpha\beta}_{\gamma\delta}\langle\gamma|\hat{O}(\tau)|\delta\rangle \\ \rightsquigarrow \frac{d}{d\tau}\langle B(t)\mathbf{A}(t+\tau)\rangle &= \underline{\underline{M}}\langle B(t)\mathbf{A}(t+\tau')\rangle, \quad \tau > 0. \end{aligned} \tag{4.1.12}$$

  This is the usual form of the quantum regression theorem as discussed in many textbooks.
- For $\tau < 0$, the derivation of the quantum regression theorem is analogous to the case $\tau > 0$ (exercise!)
- The first derivation of the quantum regression theorem has been given by Melvin Lax, Phys. Rev. **129**, 2342 (1963). He emphasises that the only approximation one needs is the factorisation (in our notation $\chi(t) = \rho(t)R_0$, Born approximation). In the 'Note added in proof' in his paper he states that the derivation therefore is correct even for non-Markoffian systems.
- However, it has been shown that the quantum regression theorem only really holds for the Markovian case!

4.2 Photon-Counting in Quantum Optics: Introduction

When it comes to counting photons, one has to answer the eternal question: 'What is a photon', and 'What is light ?'. Einstein said in 1951: '...these days every fool pretends to know what a *photon* is. I have been thinking about this for the whole of my life, and I haven't found the answer'.

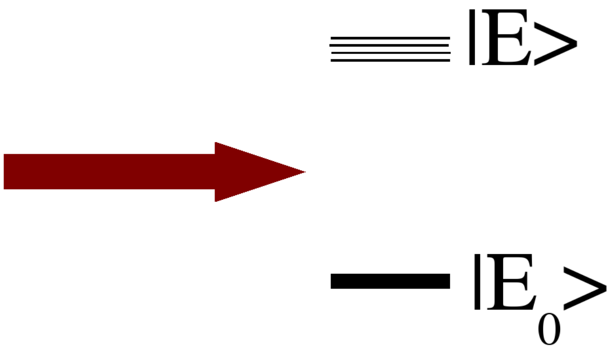
A 'practical' answer for us is to consider cavity modes with $H = \omega a^\dagger a$ and n-photon eigenstates $|n\rangle$. A more profound answer is to regard the photon as the gauge-boson of QED (modern view). The irony in the history of quantum mechanics, which was discovered in its own classical limit, is that one does not need photons in order to explain the photoelectric effect!

The main idea of counting photons is to count photo-electrons in photo-detectors instead of photons. The counting statistics then is a theory for

$$p_n(t, t+T) \quad \text{probability for } n \text{ photo-electrons in } [t, t+T). \tag{4.2.1}$$

Some challenges: one has to deal with detector back-action and a system-bath problem 'with two baths', which is not entirely trivial.

4.3 Photoelectric Counting: Classical Fields



4.3.1 The Mandel Formula

The simplest photodetector model is the ionization of a single atom. We consider a classical electromagnetic field with vector potential $\mathbf{A}(\mathbf{r})e^{-i\omega t} + \mathbf{A}^*(\mathbf{r})e^{i\omega t}$. The probability $p_1(t,t+\Delta t)$ of one count is then given by Fermi's Golden Rule as

$$\begin{aligned} p_1(t,t+\Delta t) &= \int_0^\infty dE\nu(E)\left|\langle E|\frac{e}{m}\mathbf{p}\mathbf{A}(\mathbf{r})|E_0\rangle\right|^2 D_{\Delta t}(E-E_0-\omega) \\ &= \eta I(\mathbf{r})\Delta t, \quad I(\mathbf{r}) = |A(\mathbf{r})|^2(\text{intensity}). \end{aligned} \tag{4.3.1}$$

Here, $D_{\Delta t}(\varepsilon) \equiv \left([\sin\frac{1}{2}\varepsilon\Delta t]/[\frac{1}{2}\varepsilon]\right)^2$ mit $\Delta t \to 0$ und $\mathbf{A}(\mathbf{r}) = \vec{\varepsilon}A(\mathbf{r})$. Note that the concept of a PHOTON is not used here - one rather uses the discreteness of atomic energy levels.

How to obtain the probability of n transitions $p_n(t,t+T)$ now? One has the short-time probability $p_1(t,t+\Delta t) = \eta I(\mathbf{r})\Delta t$ for *single* electron transitions, with $\eta I(\mathbf{r})$ as the transition rate. The long-time probability of n transitions $p_n(t,t+T)$ then corresponds to transitions of n electrons. Individual transitions are statistically independent which leads to a Poisson distribution, characterized by an average $\bar{n}$,

$$p_n(t,t+T) = \frac{\bar{n}^n}{n!}e^{-\bar{n}}, \quad \bar{n} = \eta I(\mathbf{r})T. \tag{4.3.2}$$

In more detail, one performs the transit from short to long times via a Markovian Master equation for the probabilities $p_n(t) \equiv p_n(0,t)$,

$$p_n(t+dt) = p_n(t) \times [1-\eta I(\mathbf{r})dt] + p_{n-1}(t) \times \eta I(\mathbf{r})dt \tag{4.3.3}$$

$$\frac{d}{dt}p_n(t) = \eta I(\mathbf{r})[p_{n-1}(t) - p_n(t)]. \tag{4.3.4}$$

This is solved by introducing a generating function

$$G(s,t) \equiv \sum_{n=0}^{\infty} s^n p_n(t), \quad \partial_t G(s,t) = \eta I(\mathbf{r})(s-1)G(s,t) \tag{4.3.5}$$

and solving with $p_0(0)=1$, $p_n(0)=0$, $n>0$, $G(s,0)=1$, thus obtaining

$$G(s,t) = \exp[\eta I(\mathbf{r})t(s-1)] = \sum_{n=0}^{\infty} s^n \frac{\bar{n}^n}{n!}e^{-\bar{n}}, \tag{4.3.6}$$

where $\bar{n} = \eta I(\mathbf{r})t$. We thus have the classical photo-electron counting formula (Mandel formula),

$$p_n(t,t+T) = \frac{\bar{n}^n}{n!}e^{-\bar{n}}, \quad \bar{n} = \eta I(\mathbf{r})T. \tag{4.3.7}$$

4.4 The Photo-Count Formula in Quantum Optics

4.4.1 The Scully-Lamb Photodetector

Reference: M. Scully, W. Lamb Jr., Phys. Rev. **179**, 368 (1969). Key ideas:

- ‘Photon statistics’ means (reduced) density operator $\rho(t)$ of a light field (more generally: boson field).
- ‘Photon statistics’ is inferred by photoelectric counting techniques.

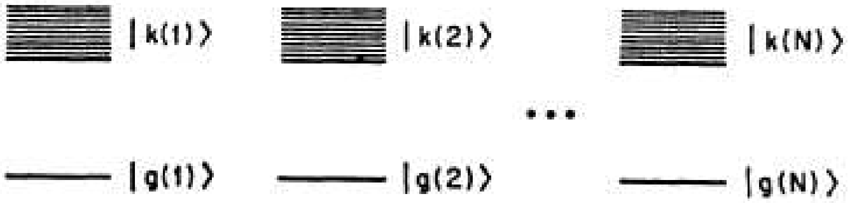
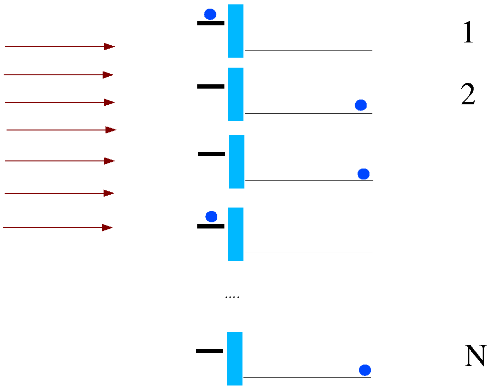


FIG. 1. Pictorial representation of photodetector consisting of N-independent atoms. Each atom in detector has a ground state $|g\rangle$ and continuum of excited states $|k\rangle$. Atoms are labeled by indexing atomic state with particle number, e.g., $|k(m)\rangle$.

The detector model is formulated as a system-bath theory with the system as a single photon mode a and N detector single level ‘quantum dots’ j with one ($|1\rangle_j$) or zero ($|0\rangle_j$) electrons. Photon absorption then empties the dots into the *bath*, which is a collection of leads j, $c^\dagger_{\alpha j}|vac\rangle$. We thus write

$$\mathcal{H}_{\rm SB} = \sum_{\alpha j} \left(V^j_\alpha c^\dagger_{\alpha j} |0\rangle_j \langle 1| a + \bar{V}^j_\alpha c_{\alpha j} |1\rangle_j \langle 0| a^\dagger \right) \equiv \sum_k S_k \otimes B_k. \tag{4.4.1}$$



We now use the Master equation technique in order to trace out the leads, We assume 'broadband detection' at all energies, $\sum_\alpha |V_\alpha^j|^2\delta(\varepsilon - \varepsilon_{\alpha j}) = \nu$ and obtain

$$\frac{d}{dt}\tilde{\rho}_t = -\pi\nu \sum_j \left\{ |1\rangle_j\langle 1|a^\dagger a\tilde{\rho}_t + \tilde{\rho}_t a^\dagger a|1\rangle_j\langle 1| - 2|0\rangle_j\langle 1|a\tilde{\rho}_t a^\dagger|1\rangle_j\langle 0| \right\} \quad (4.4.2)$$

Now let us consider detector states

$$|m;\lambda\rangle \equiv \hat{\Pi}_\lambda |0\rangle_1 ... |0\rangle_m |1\rangle_{m+1} ... |1\rangle_N \quad (4.4.3)$$

with m excitations. Here, $\hat{\Pi}_\lambda$ is a certain permutation of the ions. The m-resolved field 'pseudo' density matrix is

$$\tilde{\rho}_t^{(m)} \equiv \sum_\lambda \langle m;\lambda|\tilde{\rho}_t|m;\lambda\rangle. \quad (4.4.4)$$

Our Master equation becomes

$$\frac{d}{dt}\tilde{\rho}_t = -\pi\nu\sum_j\left\{|1\rangle_j\langle 1|a^\dagger a\tilde{\rho}_t + \tilde{\rho}_t a^\dagger a|1\rangle_j\langle 1| - 2|0\rangle_j\langle 1|a\tilde{\rho}_t a^\dagger|1\rangle_j\langle 0|\right\} \tag{4.4.5}$$

$$\sum_j\langle m;\lambda|\tilde{\rho}_t|1\rangle_j\langle 1|m;\lambda\rangle = (N-m)\langle m;\lambda|\tilde{\rho}_t|m;\lambda\rangle \tag{4.4.6}$$

$$\sum_j\langle m;\lambda|0\rangle_j\langle 1|\tilde{\rho}_t|1\rangle_j\langle 0|m;\lambda\rangle = \sum_{\lambda'}^{m\text{terms}}\langle m-1;\lambda'|\tilde{\rho}_t|m-1;\lambda'\rangle \tag{4.4.7}$$

$$\frac{d}{dt}\tilde{\rho}_t^{(m)} = -\pi\nu\left\{(N-m)\left[a^\dagger a\tilde{\rho}_t^{(m)} + \tilde{\rho}_t^{(m)}a^\dagger a\right] - 2(N-m+1)a\tilde{\rho}_t^{(m-1)}a^\dagger\right\} \tag{4.4.8}$$

This can be simplified in the limit $N \gg m$, $\gamma \equiv 2\pi N\nu \rightsquigarrow$

$$\frac{d}{dt}\rho_t^{(m)} = -i[\mathcal{H}_{\mathrm{F}},\rho_t^{(m)}] - \frac{\gamma}{2}\left(a^\dagger a\rho_t^{(m)} + \rho_t^{(m)}a^\dagger a - 2a\rho_t^{(m-1)}a^\dagger\right). \tag{4.4.9}$$

The *counting statistics* is now defined as

$$p_m(t) \equiv \mathrm{Tr}\rho_t^{(m)}. \tag{4.4.10}$$

Analysing the above Master equation, we recognize that there are two types of super-operators: The **jump super-operator** J, $J\rho \equiv \gamma a\rho a^\dagger$, and the time evolution generator $\mathcal{L}_0$. Defining $\mathcal{L}_0\rho \equiv Y\rho + \rho Y^\dagger$ with $Y \equiv -i\mathcal{H}_{\mathrm{F}} - \frac{\gamma}{2}a^\dagger a$ gives

$$\boxed{\dot{\rho}_t^{(m)} = \mathcal{L}_0\rho_t^{(m)} + J\rho_t^{(m-1)}.} \tag{4.4.11}$$

Introducing the generating operator $\hat{G}(s,t)$ as

$$\hat{G}(s,t) \equiv \sum_{m=0}^{\infty} s^m\rho_t^{(m)} \tag{4.4.12}$$

with the *counting variable* $s = e^{i\chi}$, the infinite set of master equations now becomes a single equation,

$$\boxed{\tfrac{\partial}{\partial t}\hat{G}(s,t) = (\mathcal{L}_0 + sJ)\hat{G}(s,t).} \tag{4.4.13}$$

4.5 Photo-Counting and the P-representation

The above operator equation,

$$\frac{d}{dt}\hat{G} = -i[\mathcal{H}_{\mathrm{F}},\hat{G}] - \frac{\gamma}{2}\left(a^\dagger a\hat{G} + \hat{G}a^\dagger a - 2sa\hat{G}a^\dagger\right), \tag{4.5.1}$$

can be solved using the *P-representation* in the harmonic oscillator Hilbert space. Glauber introduced coherent states

$$|z\rangle, \quad a|z\rangle = z|z\rangle, \tag{4.5.2}$$

which are used in the Glauber-Sudarshan representation of operators such as $\hat{G}$ as

$$\hat{G} = \int d^2z P(\hat{G}; z, z^*)|z\rangle\langle z|. \tag{4.5.3}$$

Here, z and z^* are independent variables. In the following, we use the short form $P(z)$ instead $P(\hat{G}; z, z^*)$. The rules for translating the Master equation into the P-representation are (cf. QOptics books), $a\hat{G}a^\dagger \leftrightarrow zz^*P(z)$, $a^\dagger a\hat{G} \leftrightarrow (z^* - \partial_z)P(z)$, $\hat{G}a^\dagger a \leftrightarrow (z - \partial_{z^*})P(z)$.

4.5.1 PDE for P-function of generating operator

Using the field Hamiltonian $\mathcal{H}_\mathrm{F} = \Omega a^\dagger a$, we obtain

$$\begin{aligned} \frac{\partial}{\partial t}P_s(z,t) &= \left[-yz\partial_z - y^*z^*\partial_{z^*} + \gamma(1 + |z|^2(s-1))\right] P_s(z,t) & (4.5.4)\\ y &\equiv -i\Omega - \frac{\gamma}{2}. & (4.5.5)\end{aligned}$$

In the case $s = 1$, this simply is the damped harmonic oscillator, where the 1st order PDE is solved by the method of characteristics

$$P_1(z,t) = e^{\gamma t}P^{(0)}\left(ze^{i(\Omega - i\gamma/2)t}\right). \tag{4.5.6}$$

For example, for $G(s, t = 0) \equiv \rho^{(0)}(t = 0) = |z_0\rangle\langle z_0|$ one obtains

$$\begin{aligned} P_1(z,t=0) &= \delta^{(2)}(z - z_0) \rightsquigarrow & (4.5.7)\\ P_1(z,t>0) &= e^{\gamma t}\delta^{(2)}\left(ze^{i(\Omega-i\gamma/2)t} - z_0\right) = \delta^{(2)}\left(z - z_0e^{-i(\Omega-i\gamma/2)t}\right), & (4.5.8)\end{aligned}$$

(two-dimensional Delta-function!) and thus a state that spirals into the origin.

For arbitrary s, one has

$$P_s(z,t) = e^{\gamma t}P^{(0)}\left(ze^{i(\Omega-i\gamma/2)t}\right)\exp\{-|z|^2(s-1)(1-e^{\gamma t})\} \tag{4.5.9}$$

Now from

$$\mathrm{Tr}\hat{G}(s,t) \equiv \sum_{m=0}^{\infty} s^m \mathrm{Tr}\rho_t^{(m)}, \tag{4.5.10}$$

we read off the *photoelectron counting distribution*

$$p_m(t) \equiv \mathrm{Tr}\rho_t^{(m)} \tag{4.5.11}$$

as

$$\begin{aligned}\mathrm{Tr}\hat{G}(s,t) &= \int d^2z P_s(z,t) = \int d^2z P^{(0)}(z) e^{-|z|^2(s-1)(e^{-\gamma t}-1)} \\ &= \sum_{m=0}^{\infty} s^m \int d^2z P^{(0)}(z) \frac{\left(|z|^2\eta_t\right)^m}{m!} e^{-|z|^2\eta_t}, \quad \eta_t \equiv 1-e^{-\gamma t}. \end{aligned} \tag{4.5.12}$$

Using the normal ordering property of the P-representation, we thus obtain the single-mode counting distribution

$$\boxed{p_m(t) = \mathrm{Tr}\rho(0) : \frac{\left(a^\dagger a \eta_t\right)^m}{m!} e^{-a^\dagger a \eta_t} :, \quad \eta_t \equiv 1-e^{-\gamma t}.} \tag{4.5.13}$$

4.5.2 Single-mode counting formula: discussion

For a coherent state $\rho(0) = |z_0\rangle\langle z_0|$, the distribution is

$$p_m(t) = \frac{\left(\langle n\rangle \eta_t\right)^m}{m!} e^{-\langle n\rangle \eta_t}, \tag{4.5.14}$$

i.e. a Poisson-distribution with average $\langle n\rangle \equiv \langle a^\dagger a\rangle = |z_0|^2$. This coincides with the semiclassical Mandel formula for $\gamma t \ll 1$.

For a Fock-state $\rho(0) = |n\rangle\langle n|$, the distribution is

$$p_m(t) = \left(\begin{array}{c} n \\ m \end{array}\right) \eta_t^m (1-\eta_t)^{n-m}, \quad n \geq m, \tag{4.5.15}$$

which is a Bernoulli-distribution that counts m successful events (photo-counts) and $n-m$ failures (no counts) regardless of the order.

4.6 Photo-Counting in Spontaneous Emission and Resonance Fluorescence

Now we move from one single mode $a^\dagger$ to many modes $a_Q^\dagger$: we do quantum optics by quantization of Maxwell's equations, using the vector potential in Coulomb gauge, and Fourier expansion into field modes $\mathbf{u}_Q(\mathbf{r})$ with mode index Q,

$$(\nabla^2 + \omega_Q^2)\mathbf{u}_Q(\mathbf{r}) = 0. \tag{4.6.1}$$

The electric field operator is written as

$$\mathbf{E}(\mathbf{r}) \;=\; i\sum_Q \left(\frac{\hbar\omega_Q}{2\varepsilon_0}\right)^{1/2} \mathbf{u}_Q(\mathbf{r}) a_Q + H.c. = \mathbf{E}^{(+)}(\mathbf{r}) + \mathbf{E}^{(-)}(\mathbf{r}).$$

4.6.1 Quantum sources of light

The most basic source is a single two-level atom. We first discuss spontaneous emission from a two-level atom with states $|1\rangle$, $|0\rangle$,

$$H = \frac{\omega_0}{2}\sigma_z + \sum_Q \gamma_Q \left(\sigma_+ a_Q + \sigma_- a_Q^\dagger\right) + \sum_Q \omega_Q a_Q^\dagger a_Q. \qquad (4.6.2)$$

with the usual Pauli matrices and photon creation operators $a_Q^\dagger$.

This problem was first discussed by Wigner and Weisskopf. We write the Schrödinger equation for the total wave function

$$|\Psi(t)\rangle = c(t)|1\rangle|\mathrm{vac}\rangle + \sum_Q b_Q(t)|0\rangle a_Q^\dagger|\mathrm{vac}\rangle, \quad c(0) = 1 \qquad (4.6.3)$$

One finds approximately the exponential decay

$$c(t) = e^{-\Gamma t/2 - i\omega_0 t} \qquad (4.6.4)$$

and no re-absorption of any emitted photon. Note that this differes from the single mode model where one has only one mode Q (Jaynes-Cummings Hamiltonian) and where 'revivals' occur. Here, we do not discuss these but move on towards an expression for the electric field $\mathbf{E}^{(+)}(\mathbf{r},t) = \mathbf{E}_f^{(+)}(\mathbf{r},t) + \mathbf{E}_s^{(+)}(\mathbf{r},t)$ and the source field in terms of *source* operators: The Heisenberg EOM $\dot{a}_Q(t) = -i\omega_Q a_Q(t) - i\gamma_k \sigma_-(t)$ in particular lead to

$$a_Q(t) = a_Q e^{-i\omega_Q t} - i\gamma_Q \int_0^t dt' \sigma_-(t') e^{-i\omega_Q(t-t')}. \qquad (4.6.5)$$

Expressing the field at the detector in terms of the atom dipole operator, one finds

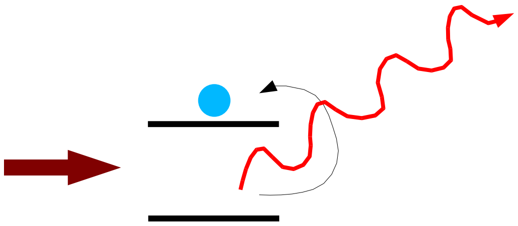
$$\underline{\mathbf{E}_s^{(+)}(\mathbf{r},t)} = \int_0^t dt' \left[\sum_Q \mathbf{f}_Q(\mathbf{r}) e^{-i\omega_Q(t-t')}\right] \sigma_-(t') \qquad (4.6.6)$$

$$\approx \int_0^t dt' \left[\mathcal{E}(\hat{\mathbf{r}})\delta(t-t'-r/c)\right]\sigma_-(t') = \underline{\mathcal{E}(\hat{\mathbf{r}})\sigma_-(t-r/c)}. \qquad (4.6.7)$$

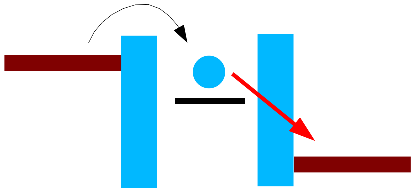
Note the dipole form of $\mathcal{E}(\hat{\mathbf{r}})$ (cf. Carmichael).

In this example, however, we haven't learnded too much - we just have a transient process with an exponentially decaying probability, as could be expected. What turns out to be much more interesting is the stationary process of 'driven spontaneous emission' (resonance fluorescence). In particular, this quantum optics example has many interesting commonalities with electron transport, i.e.

tunneling of a single electron through a single level quantum dot (cf. figure).



Resonance fluorescence



CB dot, tunneling

4.6.2 Resonance Fluorescence Model

We assume spontaneous emission from a two-level system plus driving with a classical field $E\cos(\omega_L t)$ at *Rabi-frequency* $\Omega \equiv dE/\hbar$ and with dipole moment d. In RWA the model reads

$$\mathcal{H}_t \equiv \mathcal{H}_{\rm SE} + \frac{\Omega}{2}\left(e^{-i\omega_L t}\sigma_+ + e^{i\omega t}\sigma_-\right), \quad \text{(RWA)}. \tag{4.6.8}$$

A time-dependent unitary trafo leaves Liouville-v.Neumann equation invariant,

$$\bar{\mathcal{H}}_t \equiv -iU_t^\dagger \frac{\partial U_t}{\partial t} + U_t^\dagger \mathcal{H}_t U_t, \quad \bar{\rho}_t \equiv U_t^\dagger \rho_t U_t. \tag{4.6.9}$$

The form

$$U_t = \exp(-i\hat{N}_{\rm F}\omega_L t)\mathrm{diag}(e^{-i\omega_L t}, 1) \tag{4.6.10}$$

leads to ($\omega_0 = \omega_L$)

$$\boxed{\bar{\mathcal{H}}_t \equiv \tfrac{\Omega}{2}\left(\sigma_+ + \sigma_-\right) + \textstyle\sum_Q \gamma_Q \left(\sigma_+ a_Q + \sigma_- a_Q^\dagger\right) + \textstyle\sum_Q (\omega_Q - \omega_L) a_Q^\dagger a_Q} \tag{4.6.11}$$

The corresponding master equation for TLS-'source' density operator ρ_t can now be derived as

$$\dot{\rho}_t = i\frac{\Omega}{2}[\sigma_+ + \sigma_-, \rho_t] - \beta\left(\sigma_+\sigma_-\rho_t + \rho_t\sigma_+\sigma_- - 2\sigma_-\rho_t\sigma_+\right). \tag{4.6.12}$$

Here, in the spontaneous emission rate $\beta = \pi\sum_Q \gamma_Q^2\delta(\omega_L - \omega_Q)$, the effect of the external driving field has been neglected (otherwise one obtains what is called the 'intra-collisional field effect' - this plays a role however only at very high field strengths). We now compare this with our previous photo-detector equation,

$$\dot{\rho}_t^{(m)} = -i[\mathcal{H}_{\mathrm{F}}, \rho_t^{(m)}] - \frac{\gamma}{2}\left(a^\dagger a\rho_t^{(m)} + \rho_t^{(m)}a^\dagger a - 2a\rho_t^{(m-1)}a^\dagger\right). \tag{4.6.13}$$

We also remember that in spontaneous emission, the field at the detector is expressed in terms of atom dipole operator,

$$\mathbf{E}_s^{(+)}(\mathbf{r}, t) \approx \mathcal{E}(\hat{\mathbf{r}})\sigma_-(t - r/c). \tag{4.6.14}$$

This suggests the correspondence

$$a \sim \mathbf{E}_s^{(+)} \sim \sigma_-. \tag{4.6.15}$$

The absorption of a photon in the detector thus corresponds to an electron jumping from up to down, as described by the operator σ_-.

4.6.3 Cook's 'counting at the source'

We are now closing into the final approach towards 'jump'-resolved Master equations which are at the core of counting statistics within the Master equation framework: In 1981, R. J. Cook published a paper on n-resolved master equations for resonance fluorescence (R. J. Cook PRA **23**, 1243 (1981)). His key idea was to expand the resonance fluourescence Master equation by introducing a further label (index) n,

$$\dot{\rho}_t^{(n)} = i\frac{\Omega}{2}[\sigma_+ + \sigma_-, \rho_t^{(n)}] - \beta\left(\sigma_+\sigma_-\rho_t^{(n)} + \rho_t^{(n)}\sigma_+\sigma_- - 2\sigma_-\rho_t^{(n-1)}\sigma_+\right) \tag{4.6.16}$$

by splitting up the total density operator as

$$\rho_t = \sum_{n=0}^{\infty}\rho_t^{(n)} \tag{4.6.17}$$

according to the number n of photon emissions that have taken place after time t. Cook's original idea was actually to count the number of momentum transfers between atom and driving field: every time a spontaneous emission event takes place, the atom is ready to absorb another photon from the laser which leads to a 'recoil', i.e. a momentum transfer in discrete units $n\hbar k$. In fact, we can introduce the jump super-operator J with

$$J\rho = 2\beta\sigma_-\rho\sigma_+ = 2\beta|-\rangle\langle+|\rho|+\rangle\langle-|. \tag{4.6.18}$$

This operator takes the atom from the excited to the ground state. We then proceed as in photo-detector theory: introducing the generating operator as usual, $G(s,t) \equiv \sum_{n=0}^{\infty} s^n \rho_t^{(n)}$ with *counting variable* s, we *define* the counting statistics as

$$p_n(0,t) = \mathrm{Tr}\rho_t^{(n)}. \tag{4.6.19}$$

The photons are, of course, already integrated out, and we just end up with a 4 by 4 equation

$$\partial_t G = i\frac{\Omega}{2}[\sigma_+ + \sigma_-, G] - \beta\left(\sigma_+\sigma_- G + G\sigma_+\sigma_- - 2s\sigma_- G\sigma_+\right) \tag{4.6.20}$$

that is formally solved as

$$G = \exp\{(\mathcal{L}_0 + sJ)t\}\rho(0), \tag{4.6.21}$$

for example by diagonalization.

In Laplace space, we write $\hat{G}(s,z) = [z - \mathcal{L}_0 - sJ]^{-1}\rho(0)$ which then can be inverted. Writing $\hat{G}$ as a vector, the corresponding resolvent matrix is

$$[z - \mathcal{L}_0 - sJ]^{-1} = \begin{pmatrix} z+2\beta & 0 & 0 & -\Omega \\ -2\beta s & z & 0 & \Omega \\ 0 & 0 & z+\beta & 0 \\ \frac{\Omega}{2} & -\frac{\Omega}{2} & 0 & z+\beta \end{pmatrix}. \tag{4.6.22}$$

The result in Laplace space

$$\mathrm{Tr}\hat{G}(s,z) = \frac{(z+\beta)(z+2\beta) + \Omega^2 + (s-1)2\beta\left[(z+\beta)\rho_0^{++} + \Omega\mathrm{Im}\rho_0^{+-}\right]}{z(z+\beta)(z+2\beta) + \Omega^2[z+\beta(1-s)]} \tag{4.6.23}$$

can now be used for further discussions. Let us assume initial conditions $\rho_0^{++} = \rho_0^{+-} = 0$, $\rho_0^{--} = 1$ for simplicity in the following.

4.6.4 Resonance fluorescence: sub-Poissonian counting statistics

In order to extract information from

$$\mathrm{Tr}\hat{G}(s,z) = \frac{f(z)}{zf(z) + \beta\Omega^2(1-s)}, \quad f(z) \equiv (z+\beta)(z+2\beta) + \Omega^2,$$

we need to transform back into time-domain,

$$
\begin{aligned}
p_n(0,t) &= \frac{\partial^n}{\partial s^n}\,\mathrm{Tr}G(s,t)\big|_{s=0}\,. && (4.6.24)\\
\langle n\rangle_t &= \frac{\partial}{\partial s}\,\mathrm{Tr}G(s,t)\big|_{s=1} \quad \text{1st moment.} && (4.6.25)\\
\langle n(n-1)_t\rangle &= \frac{\partial^2}{\partial s^2}\,\mathrm{Tr}G(s,t)\big|_{s=1} \quad \text{2nd factorial moment.} && (4.6.26)
\end{aligned}
$$

An expansion for large times t corresponds to an expansion in Laplace space around the pole z_0 closest to $z = 0$. If we expand $z_0 = \sum_{m=1}^{\infty} c_m (s-1)^m$, we find

$$
\begin{aligned}
\rightsquigarrow \langle n\rangle_{t\to\infty} &= \frac{\beta\Omega^2}{2\beta^2+\Omega^2}t && (4.6.27)\\
\rightsquigarrow \sigma_t^2 \equiv \langle \Delta n^2\rangle_{t\to\infty} &= \langle n\rangle_{t\to\infty}\left[1-\frac{6\beta^2\Omega^2}{(2\beta^2+\Omega^2)^2}\right]. && (4.6.28)
\end{aligned}
$$

This results into a negative *Mandel Q-parameter* $Q \equiv F - 1$ and a *Fano factor* $F \equiv \langle \Delta n^2\rangle / \langle n\rangle < 1$ (sub-Poissonian statistics).

Note that both $\langle n\rangle$ and σ are proportional to t for large times t. We will see below that this is a general feature of *cumulants*, which is just an expression of the central limit theorem. For large $t \gg \beta^{-1}$, the counting statistics $p_n(t)$ in fact becomes a Gaussian,

$$
\lim_{t\to\infty} p_n(t) = \frac{1}{\sqrt{2\pi\sigma_t^2}} e^{-(n-\bar{n}_t)^2/2\sigma_t^2}. \qquad (4.6.29)
$$

(D. Lenstra, PRA **26**, 3369 (1982)).

4.7 The Quantum Jump (Quantum Trajectory) Approach

References: M. B. Plenio and P. L. Knight, Rev. Mod. Phys. **70**, 101 (1998); H. Carmichael 'An Open System Approach to Quantum Optics', Springer Lecture Notes in Physics $m18$, Springer (Berlin, Heidelberg, 1993).

4.7.1 Introduction

- Method for numerically solving Master equations in a Monte-Carlo-like simulation: wave functions instead of density matrix ⇝ computational advantages.
- Restricted to Markovian Master equations of Lindblad form.
- Some regard it as more physical than usual density operator theory.

4.7.1.1 Motivation: telegraphic fluorescence (driven spontaneous emission) of single atoms

Example single V-systems: two upper levels 1 (fast spontaneous emission) and 2 (slow spontaneous emission), one lower level 0 driven by two lasers. Transition $0 \rightarrow 2$ traps the system in 2 for a long time. Resonance fluorescence intensity $I(t)$ therefore exhibits jumps: 'telegraphic fluorescence' with random switching between bright and dark periods. Aim: calculate distribution of dark periods.

Length T_D of dark period can be simply calculated from the density matrix element ρ_{22}

$$T_D^{-1} \;=\; \dot{\rho}_{22}(t=0), \quad \rho_{22}=0, \tag{4.7.1}$$

where the derivative is calculated from the underlying equation of motion (Master equation). However, the calculation of other, more complicated quantities related to the description of telegraphic fluorescence turns out to be technically complicated within the Master equation formalism. Example: 'exclusive probability' $P_0(t)$ that, after an emission at time $t=0$, no other photon has been emitted in the time interval $[0,t]$.

- Some people raise 'objections' against the traditional Master equation approach: the density operator ρ describes *ensembles* of quantum systems and is therefore inappropriate to describe *single* quantum systems such as a single ion in an ion trap. However, these objections are unjustified; as long as one sticks with the probabilistic interpretation of Quantum Mechanics, the density operator description is perfectly valid for a *single* quantum system.
- 'Single quantum systems' can not only be realised in ion traps, but also in 'artificial atoms' and 'artificial molecules' (solid state based quantum dots, superconducting charge or flux qubits). These will be discussed in a later chapter.

4.7.2 Unravelling and Decomposition into Histories

4.7.2.1 Super-Operators

We have another look at the (Markoffian) Master equation of the damped harmonic oscillator at zero temperature $T=0$ (spontaneous emission only);

$$\frac{d}{dt}\rho(t) \;=\; -i\bar{\Omega}[a^\dagger a,\rho]-\kappa\Big\{a^\dagger a\rho+\rho a^\dagger a-2a\rho a^\dagger\Big\}. \tag{4.7.2}$$

Suppose we started from a pure state $\rho(0) = |\Psi\rangle\langle\Psi|$ at time $t = 0$: after a short time Δt, this would evolve according to

$$\begin{aligned} |\Psi\rangle\langle\Psi| &\to |\Psi\rangle\langle\Psi| + \Delta t\Big\{ \left(-i\bar{\Omega}a^\dagger a - \kappa a^\dagger a\rho\right) |\Psi\rangle\langle\Psi| \left(i\bar{\Omega}a^\dagger a - \kappa a^\dagger a\rho\right) \Big\} \\ &+2\kappa a|\Psi\rangle\langle\Psi|a^\dagger \\ &\equiv |\Psi\rangle\langle\Psi| + \Delta t\Big\{\mathcal{L}_0|\Psi\rangle\langle\Psi| + \mathcal{L}_1|\Psi\rangle\langle\Psi|\Big\}, \end{aligned} \tag{4.7.3}$$

where we defined the *super-operators* via

$$\begin{aligned} \mathcal{L}_0\rho &\equiv -iH_{\text{eff}}\rho + \rho iH_{\text{eff}}^\dagger, \quad H_{\text{eff}} \equiv H - i\kappa a^\dagger a = \bar{\Omega}a^\dagger a - i\kappa a^\dagger a \\ \mathcal{L}_1\rho &\equiv 2\kappa a\rho a^\dagger. \end{aligned} \tag{4.7.4}$$

For pure states $|\Psi\rangle\langle\Psi|$: $\mathcal{L}_0$ generates time-evolution with non-hermitian Hamiltonian H_{eff}, but $\mathcal{L}_1$ generates a *quantum jump*;

$$\begin{aligned} \mathcal{L}_0 &: |\Psi\rangle \to -iH_{\text{eff}}|\Psi\rangle \\ \mathcal{L}_1 &: |\Psi\rangle \to \sqrt{2\kappa}a|\Psi\rangle. \end{aligned} \tag{4.7.5}$$

The state $a|\Psi\rangle$ corresponds to a state with one photon less.

4.7.2.2 Decomposition into Histories

We may write the Master equation Eq.(4.7.2) as

$$\frac{d}{dt}\rho(t) = \left(\mathcal{L}_0 + \mathcal{L}_1\right)\rho(t). \tag{4.7.6}$$

This can be formally solved as follows: we define

$$\bar{\rho}(t) \equiv e^{-\mathcal{L}_0 t}\rho(t), \quad \bar{\mathcal{L}}_1(t) \equiv e^{-\mathcal{L}_0 t}\mathcal{L}_1 e^{\mathcal{L}_0 t} \tag{4.7.7}$$

$$\begin{aligned} \rightsquigarrow \frac{d}{dt}\bar{\rho}(t) &= -\mathcal{L}_0\bar{\rho}(t) + e^{-\mathcal{L}_0 t}\left(\mathcal{L}_0 + \mathcal{L}_1\right)e^{\mathcal{L}_0 t}\bar{\rho}(t) = \bar{\mathcal{L}}_1(t)\bar{\rho}(t) \\ \rightsquigarrow \bar{\rho}(t) &= \rho(0) + \int_0^t dt_1 \bar{\mathcal{L}}_1(t_1)\bar{\rho}(t_1) \\ &= \rho(0) + \int_0^t dt_1 \bar{\mathcal{L}}_1(t_1)\rho(0) + \int_0^t dt_1 \int_0^{t_1} dt_2 \bar{\mathcal{L}}_1(t_1)\bar{\mathcal{L}}_1(t_2)\bar{\rho}(t_2) \\ &\ldots \\ &= \rho(0) + \sum_{n=1}^{\infty} \int_0^t dt_1 \ldots \int_0^{t_n} dt_n \bar{\mathcal{L}}_1(t_1)\ldots\bar{\mathcal{L}}_1(t_n)\rho(0). \end{aligned} \tag{4.7.8}$$

Transforming back to $\rho(t)$, we can explicitely write this as

$$\begin{aligned}
\rho(t) &= e^{\mathcal{L}_0 t}\rho(0) \\
&+ \sum_{n=1}^{\infty}\int_0^t dt_1 ... \int_0^{t_n} dt_n e^{\mathcal{L}_0 t} e^{-\mathcal{L}_0 t_1}\mathcal{L}_1 e^{\mathcal{L}_0 t_1} e^{-\mathcal{L}_0 t_2}\mathcal{L}_1 e^{\mathcal{L}_0 t_2} ... e^{-\mathcal{L}_0 t_n}\mathcal{L}_1 e^{\mathcal{L}_0 t_n}\rho(0) \\
&= e^{\mathcal{L}_0 t}\rho(0) \\
&+ \sum_{n=1}^{\infty}\int_0^t dt_1 ... \int_0^{t_n} dt_n \underline{e^{\mathcal{L}_0 (t-t_1)}\mathcal{L}_1 e^{\mathcal{L}_0 (t_1-t_2)}\mathcal{L}_1 e^{\mathcal{L}_0 (t_2-t_3)} ... e^{\mathcal{L}_0 (t_{n-1}-t_n)}\mathcal{L}_1 e^{\mathcal{L}_0 t_n}\rho(0)} \\
&\equiv e^{\mathcal{L}_0 t}\rho(0) + \sum_{n=1}^{\infty}\int_0^t dt_1 ... \int_0^{t_n} dt_n \underline{\rho_c(t; t_1, ..., t_n)}, \qquad (4.7.9)
\end{aligned}$$

where we defined the un-normalised, *conditioned* 'density matrix' $\rho_c(t; t_1, ..., t_n)$ at time t with n quantum jumps occuring at times $t_1, ..., t_n$. This object (the underlined term in Eq.(4.7.9)) indeed corresponds to the original density matrix $\rho(0)$, 'freely' time-evolved with the effective Hamiltonian $H_{\rm eff}$ during the time intervals $(0, t_n]$, $(t_n, t_{n-1}]$,... interrupted by n 'jumps' at times t_n, t_{n-1}, ..., t_1. The total density matrix $\rho(t)$ at time t then is the sum over all possible 'trajectories' with $n = 0, ..., \infty$ jumps occuring in between a 'free', effective time evolution.

4.7.2.3 'Monte Carlo' Procedure

The decomposition of histories can now be simulated on a computer in order to actually solve the Master equation. Here, we only describe the simplest version (spontaneous emission, no driving field), starting from a pure state $|\Psi\rangle$ of the total system. For more details, see Carmichael or Plenio/Knight.

Step 1: Fix a time step Δt. Calculate the probability ΔP of photon emission;

$$\Delta P \equiv \gamma \Delta t \langle\Psi|a^\dagger a|\Psi\rangle. \qquad (4.7.10)$$

Step 2: Compare ΔP with a random number $0 \le r \le 1$

- For $\Delta P > r$: 'emission', replace

$$|\Psi\rangle \to \frac{a|\Psi\rangle}{\|a|\Psi\rangle\|} \qquad (4.7.11)$$

- For $\Delta P \le r$: no emission but time-evolution under effective Hamiltonian $H_{\rm eff}$,

$$|\Psi\rangle \to \frac{(1 - i\Delta t H_{\rm eff})|\Psi\rangle}{(1-\Delta P)^{1/2}} \qquad (4.7.12)$$

Step 3: Go back to Step 1.

This procedure (performed with small time-steps Δt up to a final time $t_{\rm final}$) yields a 'curve' of simulated states $|\Psi(t)\rangle$, $t\in[0,t_{\rm final}]$ in the system Hilbert space $\mathcal{H}_S$. The procedure is then repeated many times in order to obtain time-dependent averages $\langle\Psi|\hat\theta|\Psi\rangle$ of observables $\hat\theta$.

The entire procedure yields a density operator $\rho(t)=|\Psi\rangle\langle\Psi|$ that solves the original Master equation, Eq.(4.7.2): in one time step Δt, we have

$$\begin{aligned}\rho(t+\Delta t) &= \Delta P\frac{a|\Psi(t)\rangle\langle\Psi(t)|a^\dagger}{\|a|\Psi(t)\rangle\|^2}+(1-\Delta P)\frac{(1-i\Delta t H_{\rm eff})|\Psi(t)\rangle\langle\Psi(t)|(1+i\Delta t H_{\rm eff}^\dagger)}{(1-\Delta P)^{1/2}(1-\Delta P)^{1/2}}\\ &= \gamma\Delta t a\rho(t)a^\dagger+\rho(t)-i\Delta t[H,\rho(t)]+\kappa\Delta t\left(a^\dagger a\rho(t)+\rho(t)a^\dagger a\right)+O(\Delta t)^2\\ \rightsquigarrow \frac{d}{dt}\rho(t) &= -i[H,\rho(t)]-\kappa\Big\{a^\dagger a\rho+\rho a^\dagger a-2a\rho a^\dagger\Big\}. \qquad (4.7.13)\end{aligned}$$

Remarks:

- The splitting of $\mathcal{L}$ as $\mathcal{L}=\mathcal{L}_0+\mathcal{L}_1$ is not unique, there are ususally several ways of how to 'unravel' the Master equation.
- For more complicated Master equations, one has to extend and modify the above procedure.

4.8 Full Counting Statistics in Master Equations

Let us once more look at a generic form of an n-resolved Master equation in Born-Markov approximation,

$$\dot\rho_t^{(n)}=\mathcal{L}_0\rho_t^{(n)}+J\rho_t^{(n-1)}. \qquad (4.8.1)$$

Here, the Jump operator J is related to the quantum jump approach as we saw in the previous section. Splitting up $\rho_t=\sum_{n=0}^\infty\rho_t^{(n)}$ as

$$\rho_t=\sum_{n=0}^\infty\int_0^t dt_n...\int_0^{t_2}dt_1 S_{t-t_n}JS_{t_n-t_{n-1}}J...JS_{t_1}\rho(0) \qquad (4.8.2)$$

with $S_t\equiv e^{\mathcal{L}_0 t}$, we define the probabilities $p_n(0,t)={\rm Tr}\rho_t^{(n)}$ for n jumps after time t.

Emary and co-workers have re-formulated the counting problem in an elegant way: we define the Fourier transform

$$\rho(\chi,t)=\sum_{n=0}^\infty\rho_t^{(n)}e^{i\chi n} \qquad (4.8.3)$$

with χ called *counting variable.* At large times t, this quantity decays as

$$\rho(\chi, t \to \infty) \sim e^{-\lambda_0(\chi)t}, \tag{4.8.4}$$

where λ_0 is the eigenvalue with $\lambda_0(\chi = 0) = 0$ which is unique if the stationary solution for ρ is unique. The full solution is formally obtained as

$$\rho(\chi, t) = \Omega(\chi, t - t_0)\rho(\chi, t_0), \quad \Omega(\chi, t) \equiv e^{(\mathcal{L}_0 + e^{i\chi}\mathcal{J})t}\theta(t), \tag{4.8.5}$$

which is a useful starting point for frequency-dependent noise spectra. Here, we only discuss the time-independent *Full Counting Statistics* (FCS).

4.8.1 Full Counting Statistics

One first defines a cumulant generating function $\mathcal{F}$ via

$$e^{-\mathcal{F}(\chi,t)} = \mathrm{Tr}\rho(\chi, t) = \sum_{n=0}^{\infty} p_n(0, t)e^{i\chi n} \to e^{-\lambda_0(\chi)t}, \quad t \to \infty \tag{4.8.6}$$

which means

$$\mathcal{F}(\chi, t \to \infty) = \lambda_0(\chi)t. \tag{4.8.7}$$

The cumulants of the probability distributions $p_n(0, t)$ at any fixed time $t \geq 0$ are now obtained via differentiation of $\mathcal{F}(\chi)$ with respect to χ. For example,

$$C_1 \equiv \langle n\rangle_t = -(-i)\frac{\partial}{\partial\chi}\, \mathcal{F}(\chi, t)\big|_{\chi=0} \tag{4.8.8}$$

$$C_2 \equiv \sigma_t^2 = \langle n^2\rangle_t - \langle n\rangle_t^2 = -(-i)^2\frac{\partial^2}{\partial\chi^2}\, \mathcal{F}(\chi, t)\big|_{\chi=0}. \tag{4.8.9}$$

4.8.2 Central Limit Theorem for Cumulants

The cumulants are all proportional to t at large times t owing to $\rho(\chi, t \to \infty) \sim e^{-\lambda_0(\chi)t}$. We therefore introduce the reduced variable

$$x_n \equiv \frac{n - \langle n\rangle_t}{\sigma_t} \tag{4.8.10}$$

and a corresponding new cumulant generating function $K(\chi, t)$,

$$e^{-K(\chi,t)} \equiv \sum_n p_n(0, t)e^{i\chi x_n} \tag{4.8.11}$$

$$\propto e^{\lambda_0\left(\frac{\chi}{\sigma_t}\right)t - i\chi\langle n\rangle_t/\sigma_t}, \quad t \to \infty. \tag{4.8.12}$$

which means

$$K(\chi, t \to \infty) \;=\; i\chi\langle n\rangle_t/\sigma_t - \lambda_0\left(\frac{\chi}{\sigma_t}\right)t \qquad (4.8.13)$$

A Taylor expansion leads to

$$\begin{aligned} K(\chi, t \to \infty) &= -t\left[\lambda_0(0) + \frac{\chi}{\sigma_t}\lambda_0'(0) + \frac{1}{2}\left(\frac{\chi}{\sigma_t}\right)^2\lambda_0''(0) + \frac{1}{6}\left(\frac{\chi}{\sigma_t}\right)^3\lambda_0'''(0) + ...\right] + i\chi\langle n\rangle_t/\sigma_t \\ &= -t\left[0 + i\frac{\chi\langle n\rangle_t}{t\sigma_t} - \frac{1}{2}\left(\frac{\chi}{\sigma_t}\right)^2\frac{\sigma_t^2}{t} + \frac{1}{6}\left(\frac{\chi}{\sigma_t}\right)^3\lambda_0'''(0) + ...\right] + i\chi\langle n\rangle_t/\sigma_t \\ &= \frac{1}{2}\chi^2 + O\left(\frac{1}{t^{1/2}}\right). \qquad (4.8.14) \end{aligned}$$

This means that the distribution of the reduced variable x_n approaches a Gaussian with mean zero and variance one for $t \to \infty$, which is just the central limit theorem for the case of counting: as discussed by Lenstra (D. Lenstra, Phys. Rev. A **26**, 3369 (1982)), we can divide the counting interval into N identical intervals within which the electron numbers are then almost identically distributed.

4.8.3 Simple Application: Single Resonant Level

For transport through a single level dot in the infinite bias limit, one has

$$\mathcal{L}_0 + e^{i\chi}J = \begin{pmatrix} -\Gamma_L & e^{i\chi}\Gamma_R \\ \Gamma_L & -\Gamma_R \end{pmatrix}. \qquad (4.8.15)$$

From the first moment, one obtains the stationary current

$$\langle I\rangle \equiv \lim_{t\to\infty}\frac{1}{t}\langle n\rangle_t = \frac{C_1}{t} = \frac{\Gamma_L\Gamma_R}{\Gamma_L + \Gamma_R}. \qquad (4.8.16)$$

We define the *Fano factor*

$$F \equiv \frac{C_2}{C_1} = 1 - \frac{2\Gamma_L\Gamma_R}{\Gamma^2}, \quad \Gamma \equiv \Gamma_L + \Gamma_R. \qquad (4.8.17)$$

This means that the electronic quantum noise (shot noise) through a single resonant level is sub-Poissonian.

5. BEYOND THE MASTER EQUATION

5.1 Feynman-Vernon Influence Functional Theories

5.1.1 Introduction, Motivation

This is a technique to solve the Liouville-von-Neumann Equation,

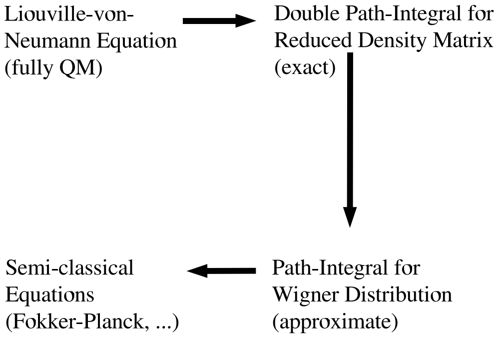
$$\frac{d}{dt}\chi(t) = -i[H,\chi(t)], \rightsquigarrow \chi(t) = e^{-iHt}\chi(t=0)e^{iHt}, \tag{5.1.1}$$

for the time-dependent density matrix $\rho(t)$ of system-bath Hamiltonians

$$H \equiv H_S + H_B + H_{SB}, \tag{5.1.2}$$

cf. Eq. (1.2.1). It is mainly useful for cases where the system Hamiltonian H_S referees to a single (or a few) degrees of freedom, coupled via H_{SB} to a bath H_B of many degrees of freedom. The technique is based on **double path integrals**. The original reference is R. P. Feynman, F. L. Vernon, Ann. Phys. (N. Y.) **24**, 118 (1963).

One of the applications of influence functional theories is the systematic derivation of a semiclassical dynamics (Fokker-Planck equations, ...) from an exact quantum-mechanical theory:



5.1.2 Single Path Integrals

We assume a time-independent Hamiltonian for a particle of mass M in a one-dimensional potential $V(x)$ (the generalisation to larger than one dimension is easy),

$$H \equiv T + V, \quad T \equiv \frac{p^2}{2M}. \tag{5.1.3}$$

The solution of the Schrödinger equation can be written as

$$|\Psi(t)\rangle = e^{-iHt}|\Psi(0)\rangle, \quad \langle x|\Psi(t)\rangle = \int dx' G(x,t;x',t'=0)\langle x'|\Psi(0)\rangle, \quad t > 0 \tag{5.1.4}$$

with the help of the **propagator**

$$G(x,t;x') \equiv G(x,t;x',t'=0) \equiv \langle x|e^{-iHt}|x'\rangle. \tag{5.1.5}$$

We now use the Trotter product formula

$$e^{-\lambda(T+V)} = \left(e^{-\frac{\lambda}{N}(T+V)}\right)^N = \lim_{N\to\infty}\left(e^{-\frac{\lambda}{N}T}e^{-\frac{\lambda}{N}V}\right)^N \tag{5.1.6}$$

with $\lambda = it$ ($\hbar = 1$) and write (inserting the identity $N-1$ times)

$$\begin{aligned} G(x,t;x') &= \lim_{N\to\infty}\int dx_1...dx_{N-1}\prod_{j=0}^{N-1}\langle x_{j+1}|e^{-\frac{\lambda}{N}T}e^{-\frac{\lambda}{N}V}|x_j\rangle, \quad x_N \equiv x, x_0 \equiv x' \\ &= \lim_{N\to\infty}\int dx_1...dx_{N-1}\prod_{j=0}^{N-1}\langle x_{j+1}|e^{-\frac{\lambda}{N}T}|x_j\rangle e^{-\frac{\lambda}{N}V(x_j)}. \end{aligned} \tag{5.1.7}$$

Now use (cf. p 1.15, 1.17),

$$\begin{aligned} \int\frac{dp}{(2\pi)}|p\rangle\langle p| &= 1, \quad \langle x|p\rangle = e^{ipx} \rightsquigarrow \\ \langle x|e^{-\frac{\lambda}{N}T}|y\rangle &= \langle x|e^{-\frac{\lambda}{2MN}p^2}|y\rangle \\ \int\frac{dp}{2\pi}\langle x|p\rangle e^{-\frac{\lambda}{2MN}p^2}\langle p|y\rangle &= \int\frac{db}{2\pi}e^{-\frac{\lambda}{2MN}p^2+LP(x-y)} = \sqrt{\frac{MN}{2\pi\lambda}}e^{-MN(x-y)^2/2\lambda}, \end{aligned} \tag{5.1.8}$$

where we analytically continued the formula for Gaussian integrals

$$\boxed{\int_{-\infty}^{\infty} dx e^{-ax^2+bx} = \sqrt{\frac{\pi}{a}}e^{b^2/4a}, \quad \text{Re } a > 0,} \tag{5.1.9}$$

$a \to ia+\eta, \eta > 0$, cf. Fresnel integrals and the book by H. Kleinert, '*Path Integrals*' 2nd edition, World Scientific (Singapore, 1995).

We now introduce $\varepsilon = t/N = \lambda/iN$ and have

$$\begin{aligned} G(x,t;x') &= \lim_{N\to\infty} \int dx_1...dx_{N-1} \left(\frac{MN}{2\pi\lambda}\right)^{\frac{N}{2}} \prod_{j=0}^{N-1} \exp\left[-\frac{MN(x_j - x_{j+1})^2}{2\lambda} - \frac{\lambda V(x_j)}{N}\right] \\ &= \lim_{N\to\infty} \int dx_1...dx_{N-1} \left(\frac{M}{2\pi i\varepsilon}\right)^{\frac{N}{2}} \exp\left[i\varepsilon \sum_{j=0}^{N-1} \left[\frac{M}{2}\frac{(x_j - x_{j+1})^2}{\varepsilon^2} - V(x_j)\right]\right] \\ &\equiv \int_{x'}^{x} \mathcal{D}x e^{i\int_0^t dt' \mathcal{L}(x,\dot{x})}, \quad \mathcal{L}(x,\dot{x}) = \frac{1}{2}M\dot{x}^2 - V(x). \end{aligned} \tag{5.1.10}$$

Here, we have defined the **Lagrange Function** $\mathcal{L}$ for the **path** $x(t'), 0 \le t' \le t, x(0) \equiv x', x(t) \equiv x$ with start point x and end point x' in configuration space. The **Feynman path integral measure** $\mathcal{D}x$ is a symbolic way of writing the limit $N \to \infty$,

$$\mathcal{D}x = \lim_{N\to\infty} \int dx_1...dx_{N-1} \left(\frac{M}{2\pi i\varepsilon}\right)^{\frac{N}{2}}. \tag{5.1.11}$$

- When calculating the path integral explicitely, one always has to go back to the finite N version and then take $N \to \infty$.
- The path integral represents an integration over *all* paths of the particle starting at x' and ending at x', not only the ones allowed by the Euler-Lagrange equations of classical mechanics. Each path is weighted with the factor $\exp(iS_{\text{cl}})$, where

  $$S_{\text{cl}} \equiv \int_0^t dt' \frac{1}{2}M\dot{x}(t')^2 - V(x(t')) \tag{5.1.12}$$

  is the classical action integral of the individual path $x(t')$. We therefore can write

  $$\boxed{G(x,t;x') = \int_{x'}^{x} \mathcal{D}x \exp(iS_{\text{cl}}).} \tag{5.1.13}$$

  Note, however, that this is only a shorthand notation for the discretised version in the $N \to \infty$ limit.

5.1.3 Double Path Integrals

Now let us come back to our density operator for our system-bath Hamiltonian,

$$H \equiv H_S + H_B + H_{SB}, \chi(t) = e^{-iHt}\chi(t=0)e^{iHt}. \tag{5.1.14}$$

For the moment, let us assume that the system has one degree of freedom q and the bath the degree of freedom x (the generalisation to many bath degrees of freedom x_i is straightforward). We then use a representation of $\chi(t)$ in spatial coordinates,

$$\begin{aligned} \langle x, q|\chi(t)|q', x'\rangle &= \int dq_0 dq_0' dx_0 dx_0' \langle x, q|e^{-iHt}|q_0, x_0\rangle\langle x_0 q_0|\chi(t=0)|q_0', x_0'\rangle \\ &\times \langle x_0' q_0'|e^{iHt}|q', x'\rangle. \end{aligned} \tag{5.1.15}$$

We trace out the bath degree of freedoms to obtain an effective density matrix

$$\rho(t) \equiv \mathrm{Tr}_{\mathrm{B}}\chi(t) \tag{5.1.16}$$

of the system,

$$\begin{aligned} \langle q|\rho(t)|q'\rangle &= \int dq_0 dq_0' dx_0 dx_0' dx \langle x, q|e^{-iHt}|q_0, x_0\rangle\langle x_0 q_0|\chi(t=0)|q_0', x_0'\rangle \\ &\times \langle x_0' q_0'|e^{iHt}|q', x\rangle. \end{aligned} \tag{5.1.17}$$

Now we realise that the Hamiltonian $H \equiv H_S + H_B + H_{SB}$ induces a classical action $S_{\text{total}} \equiv S_S[q] + S_B[x] + S_{SB}[xq]$, where in the following for notational simplicity we omit indices at the three S. We use the path integral representation for the propagator matrix elements,

$$\begin{aligned}
\langle q|\rho(t)|q'\rangle &= \int dq_0 dq_0' dx_0 dx_0' dx \int_{q_0}^{q} \mathcal{D}q \int_{x_0}^{x} \mathcal{D}x \int_{q_0'}^{q'} \mathcal{D}^* q' \int_{x_0'}^{x'=x} \mathcal{D}^* x' \\
&\times \exp\left[i\left(S[q]+S[x]+S[xq]\right) - i\left(S[q']+S[x']+S[x'q']\right)\right] \\
&\times \langle x_0 q_0|\chi(t=0)|q_0', x_0'\rangle \\
&= \int dq_0 dq_0' \int_{q_0}^{q} \mathcal{D}q \int_{q_0'}^{q'} \mathcal{D}^* q' \exp\left[i\left(S[q]-S[q']\right)\right] \\
&\times \int dx_0 dx_0' dx \int_{x_0}^{x} \mathcal{D}x \int_{x_0'}^{x} \mathcal{D}^* x' \exp\left[i\left(S[x]+S[xq]\right) - i\left(S[x']+S[x'q']\right)\right] \\
&\times \langle x_0 q_0|\chi(t=0)|q_0', x_0'\rangle \\
&= [\text{assume } \chi(t=0) = \rho(0)\otimes\rho_B] \\
&= \int dq_0 dq_0' \langle q_0|\rho(0)|q_0'\rangle \int_{q_0}^{q} \mathcal{D}q \int_{q_0'}^{q'} \mathcal{D}^* q' \exp\left[i\left(S[q]-S[q']\right)\right] \underline{\mathcal{F}[q(t'),q'(t')]} \\
\mathcal{F}[q(t'),q'(t')] &\equiv \int dx_0 dx_0' dx \langle x_0|\rho_B|x_0'\rangle \\
&\times \int_{x_0}^{x} \mathcal{D}x \int_{x_0'}^{x} \mathcal{D}^* x' \exp\left[i\left(S[x]+S[xq]\right) - i\left(S[x']+S[x'q']\right)\right]
\end{aligned}$$

- In the original Feynman-Vernon method, one assumes *a factorising initial condition* $\chi(t=0) = \rho(0)\otimes\rho_B$, although that can be generalised to non-factorising initial density matrices $\chi(t=0)$, cf. for example H. Grabert, P. Schramm, G. L. Ingold, Phys. Rep. **168**, 115 (1988), or the book by Weiss.
- The functional $\mathcal{F}[q(t'),q'(t')]$ is called **influence functional** . It describes the effect of the bath on the time-evolution of the system density matrix.
- For zero system-bath coupling $H_{SB}=0$, $\mathcal{F}[q(t'),q'(t')]=1$

5.1.4 The Influence Functional

Let us assume that we can write

$$H_{SB} = H_{SB}[q] = f(\hat{q})\hat{X} \tag{5.1.18}$$

with some given bath operator $\hat{X}$ and some given function $f(\hat{q})$ of the system coordinate $\hat{q}$. The influence functional can then be written as

$$\begin{aligned}
\mathcal{F}[q(t'), q'(t')] &\equiv \int dx_0 dx_0' dx \langle x_0|\rho_B|x_0'\rangle \\
&\times \int_{x_0}^{x} \mathcal{D}x \exp\left[i\left(S[x] + S[xq]\right)\right] \int_{x_0'}^{x} \mathcal{D}^* x' \exp\left[-i\left(S[x'] + S[x'q']\right)\right] \\
&= \int dx_0 dx_0' dx \langle x_0|\rho_B|x_0'\rangle \langle x|U_B[q]x_0\rangle \left[\langle x|U_B[q']x_0'\rangle\right]^* \\
&= \mathrm{Tr_B}\left(\rho_B U_B^\dagger[q'] U_B[q]\right), \qquad (5.1.19)
\end{aligned}$$

where $U_B[q]$ is the unitary time-evolution operator for the time-dependent Hamiltonian $H_B + H_{SB}[q]$ with a given $q(t'), 0 \le t' \le t$. Note that $q(t')$ and $q'(t')$ are independent paths, they enter as 'external' parameters into the influence functional which then in the final expression for $\langle q|\rho(t)|q'\rangle$ is integrated over all paths $q(t')$ and $q'(t')$. This form is useful to recognise general properties of $\mathcal{F}[q(t'), q'(t')]$,

- $q(t') = q'(t') \rightsquigarrow \mathcal{F}[q(t'), q'(t')] = 1$.
- $|\mathcal{F}[q(t'), q'(t')]| \le 1$.

The

$$\boxed{\begin{array}{c}\text{Operator Form of Influence Functional} \\ \mathcal{F}[q(t'), q'(t')] \equiv \mathrm{Tr_B}\left(\rho_B U_B^\dagger[q'] U_B[q]\right),\end{array}} \qquad (5.1.20)$$

is particularly useful for discussing the coupling to other baths (spin-baths, Fermi baths etc.)

5.1.5 Influence Functional for Coupling to Harmonic Oscillators

We start with the coupling of the system to a single harmonic oscillator,

$$H_B + H_{SB}[q] \equiv H_B(t) \equiv \frac{p^2}{2M} + \frac{1}{2} M\Omega^2 x^2 + g(t)x, \qquad (5.1.21)$$

where without loss of generality we set $f[q(t)] = g(t)$.

5.1.5.1 Time-evolution operator $U_B[q] \equiv U_B(t)$

This is given by the solution of the Schrödinger equation,

$$i\frac{\partial}{\partial t} U_B(t) = H_B(t) U_B(t), \quad U_B(0) = 1, \qquad (5.1.22)$$

the formal solution of which is

$$U_B(t) = \mathrm{T}e^{-i\int_0^t dt' H_B(t')} \tag{5.1.23}$$

with the time-ordering operator T. Now, $U_B(t)$ can't be directly calculated from Eq. (5.1.23) because the $H_B(t')$ do not commute with each other at different times [1]. One solution is to calculate $U_B(t)$ by direct evaluation of the path integral which is tedious but can be done. Here, we show an alternative solution: introduce the interaction picture and write

$$\begin{aligned} H_B(t) &= H_0 + g(t)x \equiv H_0 + V(t) \\ U_B(t) &= e^{-iH_0t}\tilde{U}(t), \quad i\partial_t\tilde{U}(t) = \tilde{V}(t)\tilde{U}(t) \\ \tilde{V}(t) &= e^{iH_0t}V(t)e^{-iH_0t} = g(t)\left(\hat{x}\cos\Omega t + \frac{\hat{p}}{M\Omega}\sin\Omega t\right). \end{aligned} \tag{5.1.24}$$

We solve for $\tilde{U}(t)$ by making the general *ansatz*

$$\tilde{U}(t) = e^{-iA(t)}e^{-iB(t)\hat{x}}e^{-iC(t)\hat{p}} \tag{5.1.25}$$

with functions $A(t)$ etc to be determined by taking the time-derivative of $\tilde{U}(t)$. This yields

$$\begin{aligned} i\frac{\partial}{\partial t}\tilde{U}(t) &= \dot{A}(t)\tilde{U}(t) + \hat{x}\dot{B}(t)\tilde{U}(t) + \dot{C}(t)e^{-iA(t)}\underline{e^{-iB(t)\hat{x}}\hat{p}}e^{-iC(t)\hat{p}} \\ &= \dot{A}(t)\tilde{U}(t) + \hat{x}\dot{B}(t)\tilde{U}(t) + \dot{C}(t)e^{-iA(t)}\underline{\left(\hat{p}e^{-iB(t)\hat{x}} + \left[e^{-iB(t)\hat{x}},\hat{p}\right]\right)}e^{-iC(t)\hat{p}} \\ &= \text{use } [e^{-i\alpha x},p] = i\partial_x e^{-i\alpha x} = \alpha e^{-i\alpha x} \\ &= \left(\dot{A}(t) + \hat{x}\dot{B}(t) + \hat{p}\dot{C}(t) + B(t)\dot{C}(t)\right)\tilde{U}(t) \equiv \tilde{V}(t)\tilde{U}(t). \end{aligned} \tag{5.1.26}$$

Therefore, comparing with the expression for $\tilde{V}(t)$ yields

$$\begin{aligned} B(t) &= \int_0^t dt' g(t')\cos\Omega t', \quad C(t) = \frac{1}{M\Omega}\int_0^t dt' g(t')\sin\Omega t' \\ A(t) &= -\frac{1}{M\Omega}\int_0^t dt' \int_0^{t'} ds g(t')g(s)\cos\Omega s\sin\Omega t' \end{aligned} \tag{5.1.27}$$

and therefore,

$$\begin{aligned} \langle x|U_B(t)|x'\rangle &= \langle x|e^{-iH_0t}e^{-iA(t)}e^{-iB(t)\hat{x}}e^{-iC(t)\hat{p}}|x'\rangle \\ &= e^{-iA(t)}\langle x|e^{-iH_0t}e^{-iB(t)\hat{x}}|x'+C(t)\rangle \\ &= e^{-iA(t)}\langle x|e^{-iH_0t}|x'+C(t)\rangle e^{-iB(t)[x'+C(t)]} \end{aligned} \tag{5.1.28}$$

---

[1] This is a dangerous source of mistakes, cf. J. H. Reina, L. Quiroga, and N. F. Johnson, '*Decoherence of quantum registers*', Phys. Rev. A **65**, 032326 (2002)

In order to get explicit results here, we now need the propagator matrix elements for the harmonic oscillator,

$$\boxed{\langle x|e^{-iH_0t}|x'\rangle = \sqrt{\frac{M\Omega}{2\pi i\sin\Omega t}}\exp\left\{\frac{iM\Omega}{2\sin\Omega t}\left[\left(x^2+x'^2\right)\cos\Omega t-2xx'\right]\right\}.} \quad (5.1.29)$$

These again can either be obtained by direct evaluation of the single path integral for the harmonic oscillator or (somewhat simpler) by using the stationary eigenstates. The matrix element for the driven harmonic oscillator, $\langle x|U_B(t)|x'\rangle$, can then after some transformations (straightforward algebra with trig functions) be written as

$$\begin{aligned}
\langle x|U_B(t)|x'\rangle &= \sqrt{\frac{M\Omega}{2\pi i\sin\Omega t}}\exp\left\{iS(x,t;x')\right\}\\
S(x,t;x') &\equiv \frac{iM\Omega}{2\sin\Omega t}\Big[\left(x^2+x'^2\right)\cos\Omega t-2xx'\\
&- \frac{2x}{M\Omega}\int_0^t dt' g(t')\sin\Omega t' - \frac{2x'}{M\Omega}\int_0^t dt' g(t')\sin\Omega(t-t')\\
&- \frac{2}{M^2\Omega^2}\int_0^t\int_0^{t'} dt' ds g(t')g(s)\sin\Omega(t-t')\sin\Omega s\Big]. \quad (5.1.30)
\end{aligned}$$

This coincides with the result given in L. S. Schulman, *Techniques and Applications of Path Integration*, Wiley (1981).

5.1.5.2 Influence Phase

The influence phase can be obtained directly from its definition, Eq. (5.1.19),

$$\begin{aligned}
\mathcal{F}[q(t'),q'(t')] &\equiv \mathrm{Tr_B}\left(\rho_B U_B^\dagger[q']U_B[q]\right) = \mathrm{Tr_B}\left(\rho_B\tilde{U}^\dagger[q']e^{iH_0t}e^{-iH_0t}\tilde{U}[q]\right)\\
&= \mathrm{Tr_B}\left(\rho_B e^{iC'\hat{p}}e^{iB'\hat{x}}e^{iA'}e^{-iA}e^{-iB\hat{x}}e^{-iC\hat{p}}\right)\\
&= e^{i(A'-A)}\int dx\langle x|\rho_B|e^{iC'\hat{p}}e^{i(B'-B)\hat{x}}e^{-iC\hat{p}}|x\rangle\\
&= e^{i(A'-A)}\int dx\langle x|\rho_B|x+C-C'\rangle e^{i(B'-B)(x+C)},
\end{aligned}$$

where for a moment we abbreviated A, A' etc. for the integrals Eq. (5.1.27) with $g(t')\equiv f(q(t'))$ in the undashed and $g'(t')\equiv f(q'(t'))$ in the dashed (not the derivative) quantities. We now assume a *thermal equilibrium* for the density operator ρ_B,

$$\begin{aligned}
\rho_B &= \frac{e^{-\beta H_0}}{Z}, \quad Z = \mathrm{Tr} e^{-\beta H_0} = \frac{1}{2\sinh \beta\Omega/2} \qquad (5.1.31)\\
\langle x|\rho_B|x'\rangle &= \frac{1}{Z}\sqrt{\frac{M\Omega}{2\pi \sinh \Omega\beta}} \exp\left\{\frac{-M\Omega}{2\sinh\beta\Omega}\left[\left(x^2+x'^2\right)\cosh\beta\Omega - 2xx'\right]\right\},
\end{aligned}$$

where we used the matrix elements of the propagator $\langle x|e^{-iH_0 t}|x'\rangle$ for $it=\beta$ (Wick rotation of the time t). Doing the Gaussian integral yields

$$\begin{aligned}
&\mathcal{F}[q(t'), q'(t')] = e^{i(A'-A)} \int dx \langle x|\rho_B|x+C-C'\rangle e^{i(B'-B)(x+C)}\\
=& \; e^{i(A'-A)}\frac{1}{Z}\sqrt{\frac{M\Omega}{2\pi\sinh\Omega\beta}}\int dx e^{i(B'-B)(x+C)}\\
\times& \; \exp\left\{-\frac{M\Omega}{2\sinh\beta\Omega}\left[\left(x^2+(x+C-C')^2\right)\cosh\beta\Omega - 2x(x+C-C')\right]\right\}\\
=& \; \left[\text{use } \tanh\frac{x}{2} = \frac{\cosh x - 1}{\sinh x}, \quad \coth x - \frac{1}{2}\tanh\frac{x}{2} = \frac{1}{2}\coth\frac{x}{2}\right]\\
=& \; \exp\left\{i(A'-A) + \frac{i}{2}(B'-B)(C+C')\right\}\\
\times& \; \exp\left\{-\frac{1}{4M\Omega}\coth\frac{\beta\omega}{2}\left[(B'-B)^2 + M^2\Omega^2(C-C')^2\right]\right\}. \qquad (5.1.32)
\end{aligned}$$

the last step now is to re-insert the definitions of A, B, C, A', B', C'. The resulting long expression

$$\begin{aligned}
&\mathcal{F}[q(t'), q'(t')] \qquad (5.1.33)\\
=& \; \exp\left\{-\frac{1}{4M\Omega}\coth\frac{\beta\omega}{2}\int_0^t dt'\int_0^t ds(g'_{t'}-g_{t'})(g'_s-g_s)\cos\Omega(t'-s)\right\}\\
\times& \; \exp\left\{-\frac{i}{M\Omega}\int_0^t dt'\int_0^{t'} ds(g'_{t'}g'_s - g_{t'}g_s)\cos\Omega s\sin\Omega t'\right\}\\
\times& \; \exp\left\{\frac{i}{2M\Omega}\int_0^t dt'\int_0^t ds(g'_{t'}g'_s - g_{t'}g_s)\cos\Omega t'\sin\Omega s\right\}\\
\times& \; \exp\left\{\frac{i}{2M\Omega}\int_0^t dt'\int_0^t ds(g'_{t'}g_s - g_{t'}g'_s)\cos\Omega t'\sin\Omega s\right\} \qquad (5.1.34)
\end{aligned}$$

can be further simplified with $\sin\alpha\cos\beta = \frac{1}{2}[\sin(\alpha-\beta)+\sin(\alpha+\beta)]$ and carefully considering the limits of the integrals and the symmetry of the integrands. Re-installing furthermore $g_{t'} \equiv g(t') \equiv f[q_{t'}]$ (we write the time-arguments as an index to avoid bulky expressions with too many brackets), the result can be written in a compact form, the Feynman-Vernon Influence Functional for the coupling of a single particle to a single harmonic oscillator in thermal equilibrium,

$$\begin{aligned}
H &= H_S[q] + H_B[x] + H_{SB}[xq] = H_S[q] + \frac{p^2}{2M} + \frac{1}{2}M\Omega^2 x^2 + f[q]x \\
\langle q|\rho(t)|q'\rangle &= \int dq_0 dq_0' \langle q_0|\rho(0)|q_0'\rangle \int_{q_0}^{q} \mathcal{D}q \int_{q_0'}^{q'} \mathcal{D}^* q' \exp\left[i\left(S[q] - S[q']\right)\right] \underline{\mathcal{F}[q_{t'}, q_{t'}']} \\
\mathcal{F}[q_{t'}, q_{t'}'] &= \exp\left\{-\Phi[q_{t'}, q_{t'}']\right\} \quad \text{Influence Functional} \\
\Phi[q_{t'}, q_{t'}'] &= \int_0^t dt' \int_0^{t'} ds \left\{f[q_{t'}] - f[q_{t'}']\right\}\left\{L(t'-s)f[q_s] - L^*(t'-s)f[q_s']\right\} \\
L(\tau) &= \frac{1}{2M\Omega}\left(\coth\frac{\beta\Omega}{2}\cos\Omega\tau - i\sin\Omega\tau\right). \qquad (5.1.35)
\end{aligned}$$

5.1.5.3 Linear Response, Fluctuation-Dissipation Theorem for $L(t)$

We first check that

$$L(t) = \langle x(t)x\rangle_0, \qquad (5.1.36)$$

the (van-Hove) position correlation function of the harmonic oscillator with coordinate x in thermal equilibrium: write

$$\begin{aligned}
x &= \sqrt{\frac{1}{2M\Omega}}\left(a + a^\dagger\right), \quad x(t) = \sqrt{\frac{1}{2M\Omega}}\left(ae^{-i\Omega t} + a^\dagger e^{i\Omega t}\right) \\
L(t) &= \langle x(t)x\rangle_0 = \frac{1}{2M\Omega}\langle aa^\dagger e^{-i\Omega t} + a^\dagger a e^{i\Omega t}\rangle = \frac{1}{2M\Omega}\left\{(1+n_B)e^{-i\Omega t} + n_B e^{i\Omega t}\right\} \\
&= \frac{1}{2M\Omega}\left\{(1+2n_B)\cos\Omega t - i\sin\Omega t\right\} = \frac{1}{2M\Omega}\left\{\coth\frac{\beta\Omega}{2}\cos\Omega t - i\sin\Omega t\right\} \qquad (5.1.37)
\end{aligned}$$

where we again have used the relation

$$1 + 2n_B = 1 + \frac{2}{e^{\beta\Omega} - 1} = \frac{e^{\beta\Omega} + 1}{e^{\beta\Omega} - 1} = \coth\frac{\beta\Omega}{2}. \qquad (5.1.38)$$

Now let us have another look at this function. Consider the Hamiltonian

$$H_B[x] + H_{SB}[xq] \equiv H(t) = \frac{p^2}{2M} + \frac{1}{2}M\Omega^2 x^2 + f(t)x, \qquad (5.1.39)$$

where we consider the function $f[q_t] = f(t)$ for a fixed path q_t as an external classical force acting on the oscillator. The density matrix $\rho_B(t)$ of the oscillator in the interaction picture fulfills, cf Eq.(1.2.6),

$$\begin{aligned}\tilde{\rho}_B(t) &= \rho_0 - i\int_0^t dt' f(t')[\tilde{x}(t'),\tilde{\rho}_B(t')] \qquad (5.1.40)\\ &\approx \rho_0 - i\int_0^t dt' f(t')[\tilde{x}(t'),\rho_0] \quad \text{1st order,}\end{aligned}$$

where $\rho_0 = \rho_B(t=0)$ is assumed to be the thermal equilibrium density matrix. The expectation value of the position is then

$$\begin{aligned}\langle x\rangle_t &\equiv \mathrm{Tr}\rho_B(t)x = \mathrm{Tr}\tilde{\rho}_B(t)\tilde{x}(t)\\ &= \langle x\rangle_0 - i\int_0^t dt' f(t')\mathrm{Tr}[\tilde{x}(t'),\rho_0]\tilde{x}(t) = \langle x\rangle_0 - i\int_0^t dt' f(t')\mathrm{Tr}\rho_0[\tilde{x}(t),\tilde{x}(t')]\\ &= \langle x\rangle_0 - i\int_0^t dt' f(t')\langle[\tilde{x}(t),\tilde{x}(t')]\rangle_0, \quad \text{1st order.}\end{aligned}$$

We check that

$$\langle[\tilde{x}(t),\tilde{x}(t')]\rangle_0 = \langle[\tilde{x}(t-t'),\tilde{x}(0)]\rangle_0 \qquad (5.1.41)$$

(definition of ρ_0 !) and define the **linear susceptibility**

$$\chi_{xx}(t-t') \equiv i\theta(t-t')\langle[\tilde{x}(t-t'),\tilde{x}(0)]\rangle_0, \qquad (5.1.42)$$

so that we can write

$$\langle x\rangle_t = \langle x\rangle_0 - i\int_0^t dt' \chi_{xx}(t-t')f(t'). \qquad (5.1.43)$$

The theta function in $\chi_{xx}(t-t')$ guarantees causality: the *response* of x at time t is determined by the system at *earlier* times $t' \le t$ only.

Define additional functions and their symmetric and antisymmetric (in time) linear combinations,

$$\begin{aligned}C^+(t) &\equiv \langle\tilde{x}(t)x\rangle_0, \quad C^-(t) \equiv \langle\tilde{x}(-t)x\rangle_0 = \langle x\tilde{x}(t)\rangle_0\\ C^\pm(t) &\equiv S(t) \pm iA(t) \qquad (5.1.44)\\ S(t) &= S(-t) = \frac{1}{2}\langle\tilde{x}(t)x + x\tilde{x}(t)\rangle_0, \quad A(t) = -A(-t) = \frac{1}{2i}\langle\tilde{x}(t)x - x\tilde{x}(t)\rangle_0.\end{aligned}$$

We thus have

$$\chi_{xx}(t) = -2\theta(t)A(t) \qquad (5.1.45)$$

We define the Fourier transforms,

$$\hat{C}^{\pm}(\omega) \equiv \int_{-\infty}^{\infty} dt C^{\pm}(t) e^{i\omega t}, \quad \hat{S}(\omega) \equiv \int_{-\infty}^{\infty} dt S(t) e^{i\omega t}, \quad \hat{A}(\omega) \equiv \int_{-\infty}^{\infty} dt A(t) e^{i\omega t}$$
$$\hat{\chi}(\omega) \equiv \int_{0}^{\infty} dt \chi(t) e^{i\omega t} \tag{5.1.46}$$

and use

$$\begin{aligned} \mathrm{Tr}(e^{-\beta H_B} x \tilde{x}(t)) &= \mathrm{Tr}(e^{-\beta H_B} x e^{\beta H_B} e^{-\beta H_B} \tilde{x}(t)) = \mathrm{Tr}(\tilde{x}(i\beta) e^{-\beta H_B} \tilde{x}(t)) \\ &= \mathrm{Tr}(e^{-\beta H_B} \tilde{x}(t) \tilde{x}(i\beta)) = \mathrm{Tr}(e^{-\beta H_B} \tilde{x}(t - i\beta) x) \\ &\leadsto C^{-}(t) = C^{+}(t - i\beta), \end{aligned} \tag{5.1.47}$$

and therefore in the Fourier transform

$$C^{-}(\omega) = C^{+}(\omega) e^{-\beta\omega} \quad \text{(detailed balance relation).} \tag{5.1.48}$$

We now define real and imaginary part of the Fourier transform of the susceptibility,

$$\hat{\chi}_{xx}(\omega) \equiv \hat{\chi}'_{xx}(\omega) + i \hat{\chi}''_{xx}(\omega). \tag{5.1.49}$$

Then,

$$\begin{aligned} \hat{\chi}''(\omega) &= \mathrm{Im} \int_0^{\infty} dt \chi(t) e^{i\omega t} = -2\mathrm{Im} \int_0^{\infty} dt A(t) e^{i\omega t} = -2 \frac{1}{2i} \int_0^{\infty} dt \left(A(t) e^{i\omega t} - A(t) e^{-i\omega t} \right) \\ &= i \int_0^{\infty} dt \left(A(t) e^{i\omega t} - \int_{-\infty}^{0} dt A(-t) e^{i\omega t} \right) = [A(t) = -A(-t)] = i \int_{-\infty}^{\infty} dt A(t) e^{i\omega t} \\ &= i \hat{A}(\omega) = i \frac{1}{2i} \left(\hat{C}^{+}(\omega) - \hat{C}^{-}(\omega) \right) = \frac{1}{2} \left(1 - e^{-\beta\omega} \right) \hat{C}^{+}(\omega) \end{aligned} \tag{5.1.50}$$

The relation

$$\hat{\chi}''(\omega) = \frac{1}{2} \left(1 - e^{-\beta\omega} \right) \hat{C}^{+}(\omega) \tag{5.1.51}$$

is called **Fluctuation-Dissipation Theorem (FDT)** (Callen, Welton 1951) and can be re-written, using

$$\hat{S}(\omega) = \frac{1}{2} (\hat{C}^{+}(\omega) + \hat{C}^{-}(\omega)) = \frac{1}{2} \left(1 + e^{-\beta\omega} \right) \hat{C}^{+}(\omega), \tag{5.1.52}$$

leading to

$$\boxed{\hat{S}(\omega) = \hat{\chi}''(\omega) \coth \frac{\beta\omega}{2}.} \tag{5.1.53}$$

Example- harmonic oscillator: we have

$$\begin{aligned}
\chi(t) &= i\theta(t)\langle[x(t),x]\rangle_0 = \frac{i\theta(t)}{2M\Omega}\left(e^{-i\Omega t}-e^{i\Omega t}\right)\\
\rightsquigarrow \hat{\chi}_{xx}(\omega) &= \mathrm{Im}\frac{i}{2M\Omega}\int_0^\infty dt\left(e^{-i\Omega t}-e^{i\Omega t}\right)e^{i\omega t}\\
&= \frac{1}{2M\Omega}\int_0^\infty dt\left\{\cos(\omega-\Omega)t-\cos(\omega+\Omega)t\right\}\\
&= \frac{1}{2M\Omega}\frac{1}{2}\int_{-\infty}^\infty dt\left\{\cos(\omega-\Omega)t-\cos(\omega+\Omega)t\right\},
\end{aligned}\tag{5.1.54}$$

therefore

$$\hat{\chi}_{xx}(\omega)=\frac{1}{2M\Omega}\frac{2\pi}{2}\left\{\delta(\omega-\Omega)-\delta(\omega+\Omega)\right\}.\tag{5.1.55}$$

On the other hand,

$$\begin{aligned}
C(t) &\equiv L(t)=\langle\tilde{x}(t)x\rangle_0=\frac{1}{2M\Omega}\left\{\coth\frac{\beta\Omega}{2}\cos\Omega t-i\sin\Omega t\right\}\\
\rightsquigarrow S(t) &= \frac{1}{2M\Omega}\coth\frac{\beta\Omega}{2}\cos\Omega t\\
\rightsquigarrow S(\omega) &= \frac{1}{2M\Omega}\pi\left\{\delta(\omega+\Omega)+\delta(\omega-\Omega)\right\}\coth\frac{\beta\Omega}{2}\\
&= \frac{1}{2M\Omega}\pi\left\{-\delta(\omega+\Omega)+\delta(\omega-\Omega)\right\}\coth\frac{\beta\omega}{2}=\hat{\chi}_{xx}(\omega)\coth\frac{\beta\omega}{2}
\end{aligned}\tag{5.1.56}$$

which is consistent with the FDT.

5.1.6 Applications: Linear Coupling, Damped Harmonic Oscillator

Our result for the influence phase can immediately be generalised to a single particle, coupled to a system of $N>1$ harmonic oscillators in thermal equilibrium,

$$\begin{aligned}
H &= H_S[q]+H_B[x]+H_{SB}[xq]=H_S[q]+\sum_{\alpha=1}^N\frac{p_\alpha^2}{2M_\alpha}+\frac{1}{2}M_\alpha\Omega_\alpha x^2+f_\alpha[q]x_\alpha\\
\mathcal{F}[q_{t'},q'_{t'}] &= \exp\left\{-\Phi[q_{t'},q'_{t'}]\right\}\quad\text{Influence Functional}\\
\Phi[q_{t'},q'_{t'}] &= \sum_{\alpha=1}^N\int_0^t dt'\int_0^{t'}ds\left\{f_\alpha[q_{t'}]-f_\alpha[q'_{t'}]\right\}\left\{S_\alpha(t'-s)f_\alpha[q_s]-S_\alpha^*(t'-s)f_\alpha[q'_s]\right\}\\
S_\alpha(\tau) &= \frac{1}{2M_\alpha\Omega_\alpha}\left(\coth\frac{\beta\Omega_\alpha}{2}\cos\Omega_\alpha\tau-i\sin\Omega_\alpha\tau\right).
\end{aligned}\tag{5.1.57}$$

5.1.6.1 Linear Coupling

In many applications, one assumes (often for simplicity) a *linear coupling* to the bath,

$$\begin{aligned}
H_B[x] + H_{SB}[xq] &= \sum_{\alpha=1}^{N} \left[\frac{p_\alpha^2}{2M_\alpha} + \frac{1}{2} M_\alpha \Omega_\alpha^2 \left(x_\alpha - \frac{c_\alpha}{M_\alpha \Omega_\alpha^2} q \right)^2 \right] \\
&= \sum_{\alpha=1}^{N} \left[\frac{p_\alpha^2}{2M_\alpha} + \frac{1}{2} M_\alpha \Omega_\alpha^2 x_\alpha^2 - c_\alpha q x_\alpha + \frac{1}{2} \frac{c_\alpha^2}{M_\alpha \Omega_\alpha^2} q^2 \right] \\
\mathcal{F}[q_{t'}, q'_{t'}] &= \exp\left\{ -\Phi[q_{t'}, q'_{t'}] \right\} \quad \text{Influence Functional} \\
\Phi[q_{t'}, q'_{t'}] &= \int_0^t dt' \int_0^{t'} ds \left\{ q_{t'} - q'_{t'} \right\} \left\{ L(t'-s) q_s - L^*(t'-s) q'_s \right\} \\
&+ i \frac{\mu}{2} \int_0^t dt' \left\{ q_{t'}^2 - (q'_{t'})^2 \right\} \qquad (5.1.58)
\end{aligned}$$

Here, the kernel $L(t)$ and the spectral density $J(\omega)$ are

$$\boxed{L(\tau) \equiv \frac{1}{\pi} \int_0^\infty d\omega J(\omega) \left(\coth \frac{\beta\omega}{2} \cos \omega\tau - i \sin \omega\tau \right)}$$

$$\boxed{J(\omega) \equiv \frac{\pi}{2} \sum_{\alpha=1}^{N} \frac{c_\alpha^2}{M_\alpha \Omega_\alpha} \delta(\omega - \Omega_\alpha).} \qquad (5.1.59)$$

Note that in this form, an additional term appears in H_{SB} as a potential

$$V_{\text{counter}}(q) \equiv \frac{1}{2} \mu q^2, \quad \mu \equiv \frac{1}{2} \sum_\alpha \frac{c_\alpha^2}{M_\alpha \Omega_\alpha^2} = \frac{2}{\pi} \int_0^\infty \frac{J(\omega)}{\omega}. \qquad (5.1.60)$$

Since the action S appears as $\exp(iS[q])$ in the path integral for q and $\exp(-iS[q])$ in the path integral for q', we could absorb the counter term into the influence phase as

$$\exp(i \frac{\mu}{2} \int_0^t dt' \left\{ q_{t'}^2 - (q'_{t'})^2 \right\}).$$

Note that the entire information on the coupling to the bath is now contained in the spectral density $J(\omega)$, which we have defined following the notation of Weiss, ‘Quantum Dissipative Systems’.

5.1.6.2 Propagator for Damped Harmonic Oscillator

One now has to face the tedious task to (exactly) evaluate the double path integral, which can be done because it is Gaussian. Reference: H. Grabert, P. Schramm, and G.-L. Ingold, Phys. Rep. **168**, 115 (1988).

Comparison to Master Equation Approach: R. Karrlein, H. Grabert, Phys. Rev. E **55**, 153 (1997).

5.1.7 Another Look at Influence Functionals for General Baths

(This sub-section is partly due to private communications from W. Zwerger). Feynman and Vernon realised that the coupling of a system S to *any* bath B can be mapped onto the coupling to an equivalent oscillator bath, if the coupling is weak and second order perturbation theory can be applied: let us have another look at the operator form of the influence functional, Eq. (5.1.20),

$$\begin{aligned}\mathcal{F}[q(t'),q'(t')] &\equiv \mathrm{Tr_B}\left(\rho_B U_B^\dagger[q']U_B[q]\right)\\ H_B(t) &= H_0+V(t),\quad H'_B(t)=H_0+V'(t),\end{aligned}\qquad(5.1.61)$$

where $U_B[q]$ is the time-evolution operator for $H_B(t)$ and $U_B^\dagger[q']$ the (backwards in time) evolution operator for $H'_B(t)$. Here, $H_B(t)$ and $H'_B(t)$ refer to different paths q and q'.

Example: For a Fermi bath, we could have

$$H_0=\sum_k \varepsilon_k c_k^\dagger c_k,\quad V(t)\equiv V[q_t]=\sum_{kk'} M_{kk'}\exp(i(k-k')q_t)c_{k'}^\dagger c_k.\qquad(5.1.62)$$

where $c_k^\dagger$ creates a Fermion with quantum number k.

We again introduce the interaction picture and write

$$\begin{aligned}U_B[q] &= e^{-iH_0t}\left\{1+i\int_0^t dt'\tilde{V}(t')-\int_0^t\int_0^{t'}dt'ds\tilde{V}(t')\tilde{V}(s)+...\right\}\\ U_B^\dagger[q'] &= \left\{1-i\int_0^t dt'\tilde{V'}(t')-\int_0^t\int_0^{t'}dt'ds\tilde{V'}(s)\tilde{V'}(t')+...\right\}e^{iH_0t}\end{aligned}\qquad(5.1.63)$$

The product of the two time-evolution operators therefore becomes

$$\begin{aligned}
U_B^\dagger[q']U_B[q] &= 1 - i\int_0^t dt' \left\{\tilde{V}'(t') - \tilde{V}(t')\right\} + \int_0^t dt'\tilde{V}'(t')\int_0^t ds\tilde{V}(s) \\
&- \int_0^t\int_0^{t'} dt'ds\left\{\tilde{V}'(s)\tilde{V}'(t') + \tilde{V}(t')\tilde{V}(s)\right\} + ... \\
&= 1 - i\int_0^t dt' \left\{\tilde{V}'(t') - \tilde{V}(t')\right\} + \frac{1}{2}\int_0^t\int_0^t dt'ds\left\{\tilde{V}'(t')\tilde{V}(s) + \tilde{V}'(s)\tilde{V}(t')\right\} \\
&- \int_0^t\int_0^{t'} dt'ds\left\{\tilde{V}'(s)\tilde{V}'(t') + \tilde{V}(t')\tilde{V}(s)\right\} + ... \\
&= 1 - i\int_0^t dt' \left\{\tilde{V}'(t') - \tilde{V}(t')\right\} + \int_0^t\int_0^{t'} dt'ds\left\{\tilde{V}'(t')\tilde{V}(s) + \tilde{V}'(s)\tilde{V}(t')\right\} \\
&- \int_0^t\int_0^{t'} dt'ds\left\{\tilde{V}'(s)\tilde{V}'(t') + \tilde{V}(t')\tilde{V}(s)\right\} + ... \\
&= 1 - i\int_0^t dt' \left\{\tilde{V}'(t') - \tilde{V}(t')\right\} + \int_0^t\int_0^{t'} dt'ds\left\{\left[\tilde{V}'(t') - \tilde{V}(t')\right]\tilde{V}(s)\right\} \\
&- \int_0^t\int_0^{t'} dt'ds\left\{\tilde{V}'(s)\left[\tilde{V}'(t') - \tilde{V}(t')\right]\right\} + ... \qquad (5.1.64)
\end{aligned}$$

In order to be a little bit more definite, a useful parametrisation of the interaction operators might be

$$\hat{V}(t) \equiv \sum_{\alpha\beta} g_{\alpha\beta}(t)\hat{X}_{\alpha\beta}, \quad \hat{V}'(t) \equiv \sum_{\alpha\beta} g'_{\alpha\beta}(t)\hat{X}_{\alpha\beta}, \qquad (5.1.65)$$

with bath operators $\hat{X}_{\alpha\beta}$. Note that this comprises the cases considered so far (harmonic oscillator, Fermi bath). Taking the trace over ρ_B, we obtain

$$\begin{aligned}
\mathcal{F}[q(t'), q'(t')] &\equiv \mathrm{Tr_B}\left(\rho_B U_B^\dagger[q']U_B[q]\right) \equiv \langle U_B^\dagger[q']U_B[q]\rangle_0 \\
&= 1 - i\sum_{\alpha\beta}\int_0^t dt'\left\{g'_{\alpha\beta}(t') - g_{\alpha\beta}(t')\right\}\langle\tilde{X}_{\alpha\beta}(t')\rangle_0 \\
&+ \sum_{\alpha\beta\gamma\delta}\int_0^t\int_0^{t'} dt'ds\left\{g'_{\alpha\beta}(t') - g_{\alpha\beta}(t')\right\}\left[g_{\gamma\delta}(s)\langle\tilde{X}_{\alpha\beta}(t')\tilde{X}_{\gamma\delta}(s)\rangle_0\right. \\
&- \left. g'_{\gamma\delta}(s)\langle\tilde{X}_{\gamma\delta}(s)\tilde{X}_{\alpha\beta}(t')\rangle_0\right] + ... \qquad (5.1.66)
\end{aligned}$$

Introducing the correlation tensor

$$L_{\alpha\beta\gamma\delta}(t', s) \equiv \langle\tilde{X}_{\alpha\beta}(t')\tilde{X}_{\gamma\delta}(s)\rangle_0, \qquad (5.1.67)$$

this can be written as

$$
\begin{aligned}
&\mathcal{F}[q(t'),q'(t')] = 1 - i\sum_{\alpha\beta}\int_0^t dt'\left\{g'_{\alpha\beta}(t') - g_{\alpha\beta}(t')\right\}\langle\tilde{X}_{\alpha\beta}(t')\rangle_0 \\
+ &\sum_{\alpha\beta\gamma\delta}\int_0^t\int_0^{t'} dt'ds\left\{g'_{\alpha\beta}(t') - g_{\alpha\beta}(t')\right\}\left[g_{\gamma\delta}(s)L_{\alpha\beta\gamma\delta}(t',s) - g'_{\gamma\delta}(s)L_{\gamma\delta\alpha\beta}(s,t')\right] \\
+ &\ \ldots
\end{aligned}
\qquad (5.1.68)
$$

5.1.7.1 ‘Re-Exponentiation’

So far this expression for the influence functional is very general, but it is only to second order in the system-bath interaction! In principle, one should write down the entire Dyson series for $U_B^\dagger[q']$ and $U_B[q]$ and sum up all the terms of the resulting expression in order to obtain the final result for the influence functional. Clearly, this is in general not possible, and it is even not guaranteed that such an expression would be convergent and mathematically meaningful.

For simplicity, let us assume that the linear term vanishes,

$$\langle\tilde{X}_{\alpha\beta}(t')\rangle_0 \equiv 0. \qquad (5.1.69)$$

For example, this is fullfilled for coupling to a linear harmonic oscillator, $\hat{X}_{\alpha\beta} \equiv \delta_{\alpha\beta}\hat{x}$ with $\hat{x}$ the oscillator coordinate.

At least some contributions to the infinite series for $\mathcal{F}[q(t'),q'(t')]$ can be summed up in closed form: this is done by ‘re-exponentiation’. In fact, up to second order in the system-bath interaction, we can write (summarising all our definitions so far)

$$
\begin{aligned}
\hat{V}[q_t] &\equiv \sum_{\alpha\beta} g_{\alpha\beta}[q_t]\hat{X}_{\alpha\beta}, \quad L_{\alpha\beta\gamma\delta}(t',s) \equiv \langle\tilde{X}_{\alpha\beta}(t')\tilde{X}_{\gamma\delta}(s)\rangle_0 \\
\mathcal{F}^{\rm pert}[q(t'),q'(t')] &= \exp\{-\Phi^{\rm pert}[q(t'),q'(t')]\}, \\
\Phi^{\rm pert}[q(t'),q'(t')] &= \sum_{\alpha\beta\gamma\delta}\int_0^t\int_0^{t'} dt'ds\left\{g_{\alpha\beta}[q_{t'}] - g_{\alpha\beta}[q'_{t'}]\right\} \\
&\times \left[g_{\gamma\delta}[q_s]L_{\alpha\beta\gamma\delta}(t',s) - g_{\gamma\delta}[q'_s]L_{\gamma\delta\alpha\beta}(s,t')\right]
\end{aligned}
\qquad (5.1.70)
$$

by simply expanding the exponential. The ‘re-exponentiation’ automatically sums up an infinite number of terms. Such ‘exponentiation’ schemes are known, e.g., from cluster expansions of the statistical operator $e^{-\beta\hat{H}}$. The important observation here is that for the harmonic oscillator case, this re-exponentiation becomes exact: with $\hat{V} = f[q]\hat{x}$ and $\hat{V}' = f[q']\hat{x}$, we recognise

$$\begin{aligned} \Phi[q(t'), q'(t')] &= \int_0^t \int_0^{t'} dt' ds \left\{ f[q_{t'}] - f[q'_{t'}] \right\} \left\{ L(t', s) f[q_s] - L(s, t') f[q'_s] \right\} \qquad (5.1.71) \\ L(t', s) &= \langle x(t')x(s)\rangle_0 = \langle x(t'-s)x\rangle_0 = L(t'-s) \\ L(s, t') &= \langle x(s)x(t')\rangle_0 = \langle x(t')x(s)\rangle_0^* = L^*(t'-s), \qquad (5.1.72) \end{aligned}$$

and therefore by comparison with Eq. (5.1.35) we find that both expressions co-incide.

5.1.8 'Semiclassical' Limit for Damped Single Particle Motion

References: A. Schmid, J. Low Temp. Phys. **49**, 609 (1982); W. Zwerger, Phys. Rev. B **35**, 4737 (1987); N. Janssen and W. Zwerger, Phys. Rev. B **52**, 9406 (1995); U. Weiss, 'Quantum Dissipative Systems' (2nd ed.), World Scientific (Singapore) (1999), ch. 5.5.

Let us assume a single particle in a potential $V(q)$,

$$H_S = \frac{p^2}{2m} + V(q). \tag{5.1.73}$$

We consider the reduced density matrix $\rho(t)$ of the system S,

$$\rho(x, y, t) \equiv \langle x + y/2|\rho(t)|x - y/2\rangle, \tag{5.1.74}$$

where we set

$$q = x + y/2, \quad q' = x - y/2; \quad x = \frac{1}{2}\left(q + q'\right), \quad y = q - q', \tag{5.1.75}$$

thus introducing the 'center-of-mass' coordinate x and the relative coordinate y. Note that the **Wigner distribution function** $f(x, p, t)$ is obtained from the density matrix as a Fourier transform with respect to the relativ co-ordinate y,

$$f(x, p, t) = \int_{-\infty}^{\infty} \frac{dy}{2\pi} \rho(x, y, t) e^{-ipy}. \tag{5.1.76}$$

Correspondingly, in the double path integral we integrate over center-of-mass-coordinate and relative-coordinate paths,

$$x_t = \frac{1}{2}\left(q_t + q'_t\right), \quad y_t = q_t - q'_t \tag{5.1.77}$$

The Jacobian of the corresponding discretised variable transformation is one whence one can write

$$\begin{aligned}
\rho(x,y,t) &= \int dx_0 dy_0 \rho_0(x_0,y_0) J(x,y,t;x_0,y_0) \\
J(x,y,t;x_0,y_0) &= \int_{x_0}^{x} \mathcal{D}x \int_{y_0}^{y} \mathcal{D}y \exp\left[i \int_0^t dt' \left(M\dot{x}_{t'}\dot{y}_{t'} - V(x+y/2) + V(x-y/2) \right) \right] \\
&\times \exp\left\{ -\Phi[x_{t'},y_{t'}] \right\}
\end{aligned} \tag{5.1.78}$$

5.1.8.1 Expansion of the Influence Phase

In order to derive a semiclassical limit from the double path integral, the central idea is to expand the influence phase in powers of the paths $y_{t'}$. The $y_{t'}$-paths describe 'off-diagonal excursions' from the diagonal paths $x_{t'}$ in the time-evolution of $\rho(t)$. We write

$$\begin{aligned}
\mathcal{F}[x_{t'},y_{t'}] &= \exp\left\{ -\Phi[x_{t'},y_{t'}] \right\} \quad \text{Influence Functional} \\
-\Phi[x_{t'},y_{t'}] &= -\sum_{\alpha=1}^{N} \int_0^t dt' \int_0^{t'} ds \left\{ f_\alpha[x_{t'}+y_{t'}/2] - f_\alpha[x_{t'}-y_{t'}/2] \right\} \\
&\times \left\{ S_\alpha(t'-s) f_\alpha[x_s+y_s/2] - S_\alpha^*(t'-s) f_\alpha[x_s-y_s/2] \right\} \\
&= -\sum_{\alpha=1}^{N} \int_0^t dt' \int_0^{t'} ds f'_\alpha[x_{t'}] y_{t'} \\
&\times \left\{ \text{Re } S_\alpha(t'-s) f'_\alpha[x_s] y_s + 2i \text{Im } S_\alpha(t'-s) f_\alpha[x_s] \right\} + O\left[y_s^3\right]
\end{aligned} \tag{5.1.79}$$

In the semiclassical approximation, we thus can write the influence functional as

$$\mathcal{F}_{\text{sc}}[x_{t'},y_{t'}] \equiv \exp\left\{ -\Phi[x_{t'},y_{t'}] \right\} = \exp\left\{ i\phi_1 - \phi_2 \right\} \tag{5.1.80}$$

$$\begin{aligned}
i\phi_1 &\equiv -i \int_0^t dt' \int_0^{t'} ds \varphi_1[x_s] \underline{\underline{y_{t'}}}, \quad \varphi_1[x_s] \equiv \sum_{\alpha=1}^{N} 2\text{Im } S_\alpha(t'-s) f'_\alpha[x_{t'}] f_\alpha[x_s] \\
\phi_2 &\equiv \int_0^t dt' \int_0^{t'} ds \varphi_2[x_s] \underline{\underline{y_{t'} y_s}}, \quad \varphi_2[x_s] \equiv \sum_{\alpha=1}^{N} \text{Re } S_\alpha(t'-s) f'_\alpha[x_{t'}] f'_\alpha[x_s].
\end{aligned}$$

Exercise: Check that for the linear model (coupling linear in q), Eq.(5.1.58), the influence phase becomes

$$\begin{aligned}
\Phi[x_{t'},y_{t'}] &= \int_0^t dt' \int_0^{t'} ds y_{t'} \left\{ \text{Re } L(t'-s) y_s + 2i \text{Im } L(t'-s) x_s \right\} \\
&+ i\mu \int_0^t dt' x_{t'} y_{t'}.
\end{aligned} \tag{5.1.81}$$

For the linear model, the semiclassical expansion of the influence phase is therefore exact.

In a similar way, we expand the potential $V(x \pm y/2)$ in the action in powers of the off-diagonal path y, thus arriving at

$$\begin{aligned} \rho_{\mathrm{sc}}(x,y,t) &= \int dx_0 dy_0 \rho_0(x_0,y_0) J_{\mathrm{sc}}(x,y,t;x_0,y_0) \qquad (5.1.82)\\ J_{\mathrm{sc}}(x,y,t;x_0,y_0) &= \int_{x_0}^{x} \mathcal{D}x \int_{y_0}^{y} \mathcal{D}y \exp\left[i \int_0^t dt' \left(M\dot{x}_{t'}\dot{y}_{t'} - V'(x_{t'})y_{t'} \right) \right] \\ &\times \exp\left\{ -i \int_0^t dt' \int_0^{t'} ds \varphi_1[x_s] y_{t'} - \int_0^t dt' \int_0^{t'} ds \varphi_2[x_s] y_{t'} y_s \right\}. \end{aligned}$$

The first step now is to perform an integration by parts to transform the term $M\dot{x}_{t'}\dot{y}_{t'}$, and to re-arrange

$$J_{\mathrm{sc}}(x,y,t;x_0,y_0) = \int_{x_0}^{x} \mathcal{D}x \int_{y_0}^{y} \mathcal{D}y \exp\left[iM(\dot{x}_t y - \dot{x}_0 y_0) \right]$$

$$\begin{aligned} &\times \exp\left[-i \int_0^t dt' y_{t'} \left\{ M\ddot{x}_{t'} + V'(x_{t'}) + F_B[x_s,t'] \right\} - \int_0^t dt' \int_0^{t'} ds \varphi_2[x_s] y_{t'} y_s \right] \\ F_B[x_s,t'] &\equiv \int_0^{t'} ds \varphi_1[x_s] = \int_0^{t'} ds \sum_{\alpha=1}^{N} 2\mathrm{Im}\, S_\alpha(t'-s) f'_\alpha[x_{t'}] f_\alpha[x_s] \\ &= -\sum_{\alpha=1}^{N} \int_0^{t'} ds \frac{\sin \Omega_\alpha(t'-s)}{M_\alpha \Omega_\alpha} f'_\alpha[x_{t'}] f_\alpha[x_s]. \qquad (5.1.83) \end{aligned}$$

This is an interesting expression: the term in the brackets {} looks likely to lead to a classical equation of motion,

$$M\ddot{x}_{t'} + V'(x_{t'}) + F_B[x_s,t'] = 0, \qquad (5.1.84)$$

where $-V'(x_{t'})$ is the force due to the potential $V(x)$, and $F_B[x_s,t']$ is a retarded, position-dependent deterministic friction force due to the bath. In addition, however, there is the term quadratic in y containing the function

$$\begin{aligned} \varphi_2[x_s] &\equiv \sum_{\alpha=1}^{N} \mathrm{Re}\, S_\alpha(t'-s) f'_\alpha[x_{t'}] f'_\alpha[x_s] \\ &= \sum_{\alpha=1}^{N} \frac{1}{2M_\alpha \Omega_\alpha} \coth \frac{\beta \Omega_\alpha}{2} \cos \Omega_\alpha(t'-s) f'_\alpha[x_{t'}] f'_\alpha[x_s], \qquad (5.1.85) \end{aligned}$$

which is the only place where the bath temperature $T = 1/\beta$ enters.

5.1.8.2 Completing the Square

This is a useful trick when dealing with functional integrals. We start from the identity for a real symmetric, positive definite $n \times n$ matrix A,

$$\boxed{e^{-\frac{1}{2}\mathbf{y}A\mathbf{y}} = [2\pi \det A]^{-n/2} \int_{-\infty}^{\infty} dx_1 ... dx_n e^{-\frac{1}{2}\mathbf{x}A^{-1}\mathbf{x}+i\mathbf{y}\mathbf{x}}} \quad (5.1.86)$$

Exercise: Prove this identity. Hint: use the standard formula for Gaussian integrals and a linear transformation that diagonalises A.

We now obtain

$$\begin{aligned}
\exp\left[-\frac{1}{2}\int_0^t\int_0^t dt'dsA(t',s)y_{t'}y_s\right] &= \lim_{N\to\infty}\exp\left[-\frac{\varepsilon^2}{2}\sum_{j,k=0}^{N-1}A_{jk}y_jy_k\right]\\
= \lim_{N\to\infty}[2\pi\det A]^{-N/2}\int d\xi_0...d\xi_{N-1}\exp\left[-\frac{\varepsilon^2}{2}\sum_{j,k=0}^{N-1}\xi_j\frac{A^{-1}_{jk}}{\varepsilon^2}\xi_k + i\varepsilon\sum_{j=0}^{N-1}y_j\xi_j\right]&\\
= \int\mathcal{D}\xi\exp\left[-\int_0^t\int_0^t dt'ds\xi_{t'}A^{-1}(t',s)\xi_s + i\int_0^t dt'y_{t'}\xi_{t'}\right] & \quad (5.1.87)\\
\mathcal{D}\xi \equiv \lim_{N\to\infty}[2\pi\det A]^{-N/2}d\xi_0...d\xi_{N-1}&\\
A(t',s) = \varphi_2[x](t',s), \quad \text{cf. Eq. (5.1.85).}&
\end{aligned}$$

Here, we have used the fact that the discrete inverse of an operator needs to be divided by ε^2,

$$A^{-1}(t',s) \leftrightarrow \frac{1}{\varepsilon^2}A^{-1}_{jk}. \quad (5.1.88)$$

This can be derived by considering the discrete equivalent of the delta function and leads to the following translation table between continuous and discrete:

$$\begin{aligned}
f(x) &= \int dx'\delta(x-x')f(x'), \quad f_m = \sum_m \delta_{mn}f_n = \varepsilon\sum_m\frac{\delta_{mn}}{\varepsilon}f_n\\
&\leadsto \delta(x-x') \leftrightarrow \frac{\delta_{mn}}{\varepsilon}\\
\int dx'A^{-1}(x,x')A(x',x'') &= \delta(x-x'), \quad \varepsilon\sum_{m'}\frac{A^{-1}_{mm'}}{\varepsilon^2}A_{m'm''} = \frac{\delta_{mm''}}{\varepsilon}\\
&\leadsto A^{-1}(x,x') \leftrightarrow \frac{1}{\varepsilon^2}A^{-1}_{mm'}. \quad (5.1.89)
\end{aligned}$$

Now using the fact that φ_2 is symmetric in t' and s, we have

$$\int_0^t dt' \int_0^{t'} ds\varphi_2[x_s]y_{t'}y_s = \frac{1}{2}\int_0^t dt \int_0^t ds\varphi_2[x_s]y_{t'}y_s \tag{5.1.90}$$

and therefore

$$\begin{aligned}
J_{\rm sc}(x,y,t;x_0,y_0) &= \int_{x_0}^x \mathcal{D}x \int_{y_0}^y \mathcal{D}y e^{iM(\dot{x}_t y - \dot{x}_0 y_0)} \\
\times \quad & \exp\left[-i\int_0^t dt' y_{t'}\left\{M\ddot{x}_{t'} + V'(x_{t'}) + F_B[x_s,t']\right\} - \frac{1}{2}\int_0^t\int_0^t dt'ds\varphi_2[x_s]y_{t'}y_s\right] \\
= \quad & \int_{x_0}^x \mathcal{D}x \int_{y_0}^y \mathcal{D}y e^{iM(\dot{x}_t y - \dot{x}_0 y_0)} \int \mathcal{D}\xi[x] \exp\left[-\frac{1}{2}\int_0^t\int_0^t dt'ds\xi_{t'}\varphi_2[x_s]^{-1}\xi_s\right] \\
\times \quad & \exp\left[-i\int_0^t dt' y_{t'}\left\{M\ddot{x}_{t'} + V'(x_{t'}) + F_B[x_s,t'] - \xi_{t'}\right\}\right].
\end{aligned} \tag{5.1.91}$$

Here we have explicitly indicated the dependence of the measure $\mathcal{D}\xi[x]$ on the paths x_s, which enters through the determinant of the operator $\varphi_2[x_s]$. The pathintegral over $\mathcal{D}y$ is now very easy: we find ($\varepsilon = t/N$)

$$\begin{aligned}
\int_{y_0}^y \mathcal{D}y \exp\left[-i\int_0^t dt' y_{t'} b_{t'}\right] &= \lim_{N\to\infty}\int dy_1 ... dy_{N-1}\left(\frac{M}{2\pi i\varepsilon}\right)^{\frac{N}{2}} \exp\left[-i\varepsilon\sum_{j=0}^{N-1} y_j b_j\right] \\
= \quad \lim_{N\to\infty}\left(\frac{M}{2\pi i\varepsilon}\right)^{\frac{N}{2}} & \frac{2\pi\delta(b_0)}{\varepsilon}\cdot ... \cdot\frac{2\pi\delta(b_{N-1})}{\varepsilon} e^{-i\varepsilon y_0 b_0} \equiv \Delta(y_{t'} - b_{t'}),
\end{aligned} \tag{5.1.92}$$

Here, Δ indicates the product of delta functions that fixes the $y_{t'}$ path to the $b_{t'}$ path, and for $\varepsilon \to 0$ the $e^{-i\varepsilon y_0 b_0}$ becomes irrelevant. Inserting yields

$$\begin{aligned}
J_{\rm sc}(x,y,t;x_0,y_0) &= e^{iM(\dot{x}_t y - \dot{x}_0 y_0)} \int_{x_0}^x \mathcal{D}x \int \mathcal{D}\xi[x] \exp\left[-\frac{1}{2}\int_0^t\int_0^t dt'ds\xi_{t'}\varphi_2[x_s]^{-1}\xi_s\right] \\
\times \quad & \Delta(M\ddot{x}_{t'} + V'(x_{t'}) + F_B[x_s,t'] - \xi_{t'}).
\end{aligned} \tag{5.1.93}$$

5.1.8.3 Wigner Distribution in 'Semi-classical' Limit

Considering now the definition of the Wigner distribution function,

$$\begin{aligned} f_{\mathrm{sc}}(x,p,t) &= \int_{-\infty}^{\infty}\frac{dy}{2\pi}\rho(x,y,t)e^{-ipy} = \int_{-\infty}^{\infty}\frac{dy}{2\pi}e^{-ipy}\int dx_0dy_0\rho_0(x_0,y_0)J_{\mathrm{sc}}(x,y,t;x_0,y_0)\\ = &\int\frac{dy}{2\pi}dx_0dy_0\rho_0(x_0,y_0)e^{-ipy}e^{iM(\dot{x}_ty-\dot{x}_0y_0)}\int_{x_0}^{x}\mathcal{D}x\int\mathcal{D}\xi[x]e^{-\frac{1}{2}\int_0^t\int_0^t dt'ds\xi_{t'}\varphi_2[x_s]^{-1}\xi_s}\\ \times\ &\Delta(M\ddot{x}_{t'}+V'(x_{t'})+F_B[x_s,t']-\xi_{t'})\\ = &\int dx_0f_0(x_0,p_0=M\dot{x_0})\delta(p-M\dot{x})\int_{x_0}^{x}\mathcal{D}x\int\mathcal{D}\xi[x]e^{-\frac{1}{2}\int_0^t\int_0^t dt'ds\xi_{t'}\varphi_2[x_s]^{-1}\xi_s}\\ \times\ &\Delta(M\ddot{x}_{t'}+V'(x_{t'})+F_B[x_s,t']-\xi_{t'}). \end{aligned} \tag{5.1.94}$$

Here, the y-integral generated $\delta(p-M\dot{x})$, and the y_0-integral transformed the initial condition $\rho_0(x_0,y_0)$ into its Wigner transform $f_0(x_0,p_0=M\dot{x_0})$. We summarise,

$$\boxed{\begin{aligned} &f_{\mathrm{sc}}(x,p,t)=\int dx_0f_0(x_0,M\dot{x_0})\delta(p-M\dot{x})\\ \times\ &\int_{x_0}^{x}\mathcal{D}x\int\mathcal{D}\xi[x]\exp\left[-\frac{1}{2}\int_0^t\int_0^t dt'ds\xi_{t'}\varphi_2[x_s]^{-1}\xi_s\right]\\ \times\ &\Delta(M\ddot{x}_{t'}+V'(x_{t'})+F_B[x_s,t']-\xi_{t'}). \end{aligned}} \tag{5.1.95}$$

5.1.8.4 Discussion

In the semi-classical approximation, the time-evolution of the Wigner-distribution function is determined by Eq. (5.1.95). This equation describes a *stochastic process* for the center-of-mass co-ordinate $x_{t'}$ of the particle, moving within a potential $V(x)$ under the action of a deterministic friction force $F_B[x_s,t']$,

$$F_B[x_s,t'] = -\sum_{\alpha=1}^{N}\int_0^{t'}ds\frac{\sin\Omega_\alpha(t'-s)}{M_\alpha\Omega_\alpha}f'_\alpha[x_{t'}]f_\alpha[x_s], \tag{5.1.96}$$

and a stochastic force $\xi_{t'}$. The motion of the particle is governed by the *stochastic integro-differential equation*

$$M\ddot{x}_{t'}+V'(x_{t'})+F_B[x_s,t'] = \xi_{t'}, \tag{5.1.97}$$

where the stochastic force $\xi_{t'}$ is a random force which itself depends on the coordinate of the particle: this can be seen by the fact that its variance,

$$\langle\xi_{t'}\xi_s\rangle = \varphi_2[x] = \sum_{\alpha=1}^{N}\frac{1}{2M_\alpha\Omega_\alpha}\coth\frac{\beta\Omega_\alpha}{2}\cos\Omega_\alpha(t'-s)f'_\alpha[x_{t'}]f'_\alpha[x_s], \tag{5.1.98}$$

depends on the particle path x_s. The Wigner distribution is obtained by integrating over all possible realisations of the stochastic force, such that Eq. (5.1.98) is fulfilled. Since the ξ path-integral is Gaussian, one speaks of a *Gaussian* stochastic process. This of course is due to the fact that we truncated the $y_{t'}$ expansion in the influence phase after the term quadratic in $y_{t'}$.

Our results shows that the influence of the bath is two-fold: it leads to a deterministic, retarded 'friction' force, and to a stochastic force. The latter contains the temperature and, by means of the $\coth(\beta\hbar\Omega/2)$ terms in $\varphi_2[x]$, a fully quantum mechanical description of the bath.

For certain types of system-bath couplings, one can explicitely show that the operator φ_2 is positive definite and therefore, the term quadratic in $y_{t'}$ in the original double path integral exponentially suppresses strong deviations from the diagonal paths with $y_{t'} = 0$. In this case, the expansion of the one-particle potential V,

$$-V(x+y/2)+V(x-y/2) \approx -V'(x)y \tag{5.1.99}$$

becomes more plausible. One should, however, expect that quantum mechanical effects (like particle tunneling) are destroyed by the approximation Eq. (5.1.99).

5.1.8.5 Linear Dissipation ('Ohmic Bath')

The influence phase for the linear model, Eq.(5.1.58), the influence phase is (cf. Eq. (5.1.81,5.1.60,5.1.59))

$$\begin{aligned}
\Phi[x_{t'},y_{t'}] &= \int_0^t dt' \int_0^{t'} ds y_{t'} \left\{ \mathrm{Re}\ L(t'-s)y_s + 2i \mathrm{Im}\ L(t'-s)x_s \right\} \\
&+ i\mu \int_0^t dt' x_{t'} y_{t'}, \quad \mu \equiv \frac{1}{2}\sum_\alpha \frac{c_\alpha^2}{M_\alpha \Omega_\alpha^2} = \frac{2}{\pi}\int_0^\infty \frac{J(\omega)}{\omega} \\
L(\tau) &\equiv \frac{1}{\pi}\int_0^\infty d\omega J(\omega) \left(\coth\frac{\beta\omega}{2}\cos\omega\tau - i\sin\omega\tau \right),
\end{aligned} \tag{5.1.100}$$

whence the deterministic friction force $F_B[x_s,t']$ becomes

$$\begin{aligned}
F_B[x_s,t'] &= \mu x_{t'} + \int_0^{t'} ds 2\mathrm{Im}\ L(t'-s)x_s \\
&= \frac{2}{\pi}\int_0^\infty d\omega \frac{J(\omega)}{\omega}x_{t'} - \frac{2}{\pi}\int_0^\infty d\omega J(\omega)\int_0^{t'} ds \sin\omega(t'-s)x_s \\
&= \frac{2}{\pi}\int_0^\infty d\omega \frac{J(\omega)}{\omega}x_{t'} - \frac{2}{\pi}\int_0^\infty d\omega J(\omega)\left[\frac{x_{t'}}{\omega} - \frac{\cos\omega t'}{\omega}x_0 - \int_0^{t'} ds \frac{\cos\omega(t'-s)}{\omega}\dot{x}_s\right] \\
&= \frac{2}{\pi}\int_0^\infty d\omega J(\omega)\left[\frac{\cos\omega t'}{\omega}x_0 + \int_0^{t'} ds \frac{\cos\omega(t'-s)}{\omega}\dot{x}_s\right]. \qquad (5.1.101)
\end{aligned}$$

The term $x_{t'}$ from the integration by parts has cancelled exactly with the counterterm $\mu x_{t'}$. If one now assumes a *linear* spectral function $J(\omega)$,

$$J_{\text{ohmic}}(\omega) \equiv \eta\omega, \qquad (5.1.102)$$

we recover the original Caldeira-Leggett description of quantum friction (plus the additional term $2\eta x_0\delta(t')$ that was missing there, cf. A. O. Caldeira, A. J. Leggett, Physica **121 A**, 587 (1983); *ibid.* **130 A**, 374(E), (1985); Weiss book chapter 5.1),

$$\begin{aligned}
F_{\text{ohmic}}[x_s,t'] &= \frac{2\eta}{\pi}\int_0^\infty d\omega \left[x_0\cos\omega t' + \int_0^{t'} ds \cos\omega(t'-s)\dot{x}_s\right] \\
&= 2\eta x_0\delta(t') + 2\eta\int_0^{t'} ds\delta(t'-s)\dot{x}_s = 2\eta x_0\delta(t') + \eta\dot{x}_{t'} \qquad (5.1.103)
\end{aligned}$$

The resulting stochastic equation of motion Eq. (5.1.97) is

$$M\ddot{x}_{t'} + \eta\dot{x}_{t'} + V'(x_{t'}) = \xi_{t'} - 2\eta x_0\delta(t'). \qquad (5.1.104)$$

Note that the 'awkward' term $2\eta x_0\delta(t')$ brings in a dependence on the 'initial condition' x_0.

5.1.8.6 Application: Polaron-Transport

Feynman *et al.* (R. P. Feynman, R. W. Hellwarth, C. K. Iddings, and P. M. Platzman, Phys. Rev. **127** 1004 (1962), K. K. Thornber, R. P. Feynman, Phys. Rev. B **1**, 4099 (1970)), and Janssen and Zwerger (N. Janssen and W. Zwerger, Phys. Rev. B **52**, 9406 (1995)) have used the influence functional theory for the *non-equilibrium polaron problem*, i.e. the motion of a single electron coupled to optical phonons in a crystal. The periodic crystal potential is considered in the form of an effective band-mass m^*, and the potential V is due to an accelerating, homogeneous force in which case the expansion Eq. (5.1.99) becomes exact.

6. NUMERICAL RENORMALISATION GROUP

Literature: K. G. Wilson, Rev. Mod. Phys. **47**, 773 (1975); H. R. Krishna-murthy, J. W. Wilkins, and K. W. Wilson, Phys. Rev. B **21**, 1003 (1980). These are the main original articles.

For a contemporary 'hands-on' approach I recommend material from recent PhD theses, e.g. the one by Michael Sindel (LMU Munich, 2004) which I partly used here.

6.1 Kondo Model

6.1.1 Historical Background

The $s-d$-Hamiltonian to be discussed in this lecture was introduced very early in order to study ferromagnetism in metals (Zener), cf. the book 'Theory of Magnetism' by K. Yoshida (Springer, 1996). One question is whether the magnetic moment of an impurity embedded into a metal is screened at low temperatures, or whether it persists.

Kondo introduced his model later (in 1964) in order to explain the resistivity minimum (as a function of temperature) of non-magnetic metals containing magnetic impurities, for example magnetic Co impurities in Au metal. These impurities lead to *spin-flip scattering*: a scattering process where the spin of an impurity and a metal electron are flipped simultaneously. This scattering is temperature dependent and becomes particularly strong below a temperature T_K called the *Kondo temperature*. Together with the other scattering mechanisms in metals (electron-phonon, electron-electron, electron-impurity), this leads to the resistivity minimum that was already observed in the 1930s.

6.1.2 Model Hamiltonian

The Kondo Hamiltonian describes a localized magnetic impurity with spin S which is coupled to a gas of free, non-interacting electrons, for example electrons in a conduction band.

The impurity is described by second-quantized creation operators $d^\dagger_\sigma$ with $\sigma = \uparrow,\downarrow$ for impurity spin 1/2. The impurity spin operators are

$$\begin{aligned} S^z &\equiv \frac{1}{2}\left(d^\dagger_\uparrow d_\uparrow - d^\dagger_\downarrow d_\downarrow\right), \quad S^+ \equiv d^\dagger_\uparrow d_\downarrow, \quad S^- \equiv d^\dagger_\downarrow d_\uparrow && (6.1.1)\\ S^x &\equiv \frac{1}{2}\left(S^+ + S^-\right), \quad S^y \equiv \frac{1}{2i}\left(S^+ - S^-\right). && (6.1.2)\end{aligned}$$

The band electrons are described by the Hamiltonian of a free electron gas,

$$\mathcal{H}_B \equiv \sum_{\mathbf{k}\sigma=\uparrow,\downarrow} (\varepsilon_{\mathbf{k}} - \mu) a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}, \qquad (6.1.3)$$

where μ is the chemical potential. The spin of the band electrons at the origin $\mathbf{x} = 0$ (site of the impurity) is correspondingly described by electron field operators in d dimensions. For example, an operator that flips the band electron spin at $\mathbf{x} = 0$ is given by

$$s_0^+ \equiv \Psi^\dagger_\uparrow(0)\Psi_\downarrow(0) = \frac{1}{\Omega}\sum_{\mathbf{k}\mathbf{k}'} a^\dagger_{\mathbf{k}\uparrow} a_{\mathbf{k}'\downarrow}, \qquad (6.1.4)$$

where we used an expansion into plane waves and where Ω is the total volume of the system. In a spin-flip, the total spin of the system (band electrons + impurity) must be conserved.

The total Kondo Hamiltonian $\mathcal{H}_K$ is given by a sum of two terms,

$$\mathcal{H}_K = \mathcal{H}_B - 2J\mathbf{S}\mathbf{s}_0, \qquad (6.1.5)$$

where $\mathbf{S} = (S^x, S^y, S^z)$ ($\mathbf{s}$ correspondingly) and J is a (simplified) coupling parameter between the magnetic impurity spin and the free electron spins. Its microscopic origin is the *exchange interaction* between band electrons and the magnetic impurity electrons. $J < 0$ is called ferromagnetic exchange interaction, whereas $J > 0$ is called anti-ferromagnetic exchange interaction. For a detailed discussion of the exchange interaction, cf. quantum mechanics text books or similar, e.g. 'Statistical Mechanics' by R. Feynman.

Explicitly, the scalar product $\mathbf{S}\mathbf{s}_0$ is given by (EXERCISE)

$$\mathbf{S}\mathbf{s}_0 = S^z s_0^z + \frac{1}{2}\left(S^+ s_0^- + S^- s_0^+\right), \qquad (6.1.6)$$

and we can thus write the Kondo Hamiltonian

$$\begin{aligned} \mathcal{H}_K &= \sum_{\mathbf{k}\sigma} (\varepsilon_{\mathbf{k}} - \mu) a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma} + \mathcal{H}_{sd}\\ \mathcal{H}_{sd} &\equiv -\frac{J}{\Omega}\sum_{\mathbf{k}\mathbf{k}'}\left[S^z\left(a^\dagger_{\mathbf{k}\uparrow}a_{\mathbf{k}'\uparrow} - a^\dagger_{\mathbf{k}\downarrow}a_{\mathbf{k}'\downarrow}\right) + S^+ a^\dagger_{\mathbf{k}\downarrow}a_{\mathbf{k}'\uparrow} + S^- a^\dagger_{\mathbf{k}\uparrow}a_{\mathbf{k}'\downarrow}\right], (6.1.7)\end{aligned}$$

where the part $\mathcal{H}_{sd} \equiv -2J\mathbf{S}\mathbf{s}_0$ is called $s-d$-Hamiltonian.

In the discussion of the Kondo-Hamiltonian one often has $J < 0$, i.e. antiferromagnetic exchange coupling. In the following, we write $\mathcal{H}_{sd} = 2|J|\mathbf{S}\mathbf{s}_0$ or $\mathcal{H}_{sd} = 2J\mathbf{S}\mathbf{s}_0$ with $J > 0$ instead.

6.1.3 Key Questions, Relation to Other Models

The Kondo model can be derived from the Single Impurity Anderson Model (SIAM) via a *Schrieffer-Wolff transformation*, cf. Bruus/Flensberg or other textbooks.

6.2 The Kondo Hamiltonian and Many-Body Physics

6.2.1 Why is it difficult?

The Kondo Hamiltonian almost looks like a simple one-body problem - but it is not! It is in fact one of the best studied non-trivial many-body problems in Condensed Matter Physics.

'The importance of the impurity is simple: it forces one to study the conduction band as a many-electron *system'* (Wilson). Example: consider two spin-up electrons and the impurity with spin down. The first electron can scatter off the impurity and spin flip both their spin ('spin-flip scatter'). The impurity is then left with its spin up. But then the second electron can *not* spin-flip scatter because it has spin up and this would violate spin conservation. The two electrons thus are *correlated* through the spin-flip scattering at the impurity spin.

6.2.2 Key idea

As we have to solve an interacting problem, there is no other way but to diagonalise the full many-body problem, i.e. all the band electrons combined with the impurity spin. This is, of course, impossible to by exact numerical diagonalisation: the Hilbert space simply is too large - already for a very moderate number of electrons distributed among a small number of single-particle levels, this is an impossible task. One therefore has to find an alternative strategy.

6.2.3 New basis

The first step is to find a very good basis of single particle states in which to diagonalise the problem. One part of the strategy will then be to consider only a fraction of all single particle states, i.e. to work with a truncated basis with a truncation that is good enough to produce very accurate results, at least for a

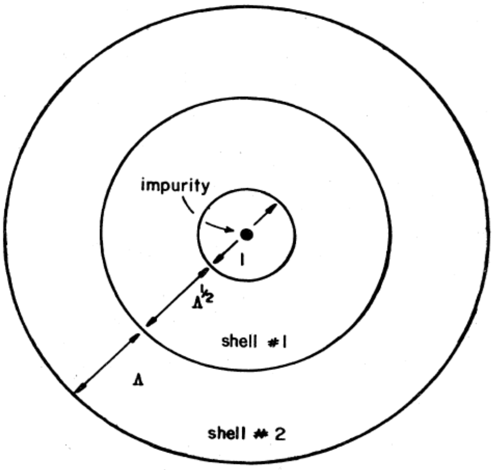


FIG. 13. Onion-like spherical shells giving the location of successive wave functions in the Kondo basis. The size of the smallest (inner) shell is a few Ångström units.

Figure 6.1: Onion-like states around the impurity, from Wilson (1975).

certain part of the total energy spectrum. It will turn out that the *low-enery* part of the spectrum can be obtained in this way to a very good accuracy.

The usual plane-wave basis for the conduction band is not very suitable to treat the Kondo-Hamiltonian: it is better to use basis states that emphasise the interaction between the impurity at the origin and the conduction band electrons. Such basis states roughly resemble spherical **Wannier functions** (localized electrons) around the impurity at the origin.

The first single particle state has a very strong overlap with the impurity. The second is already further away from the impurity. One thus has 'onion-like spherical shells' (Kondo basis), i.e. an infinite set of electron levels with ever increasing width of order $\Lambda^{n/2}$, where $\Lambda > 1$ is a parameter and n labels the shells around the impurity, cf. the figure. The shells increase in width and therefore the momentum spread becomes smaller and smaller: as n increases, the states are concentrated closer and closer around the Fermi surface in momentum space. The energy scale for shells decreases as $\Lambda^{-n/2}$.

6.2.4 Strategy and numerical procedure

First solve the impurity coupled to first Kondo state: this yields a few eigenvalues. Then add the second layer and solve combined system, etc.: this yields more eigenvalues of the total spectrum. The eigenvalues are already on a finer scale, as we have moved towards single particle states, i.e. shells, with larger width in real space. Continuing this procedure corresponds to solving for more and more eigenvalues at smaller and smaller energy scales $\sim \Lambda^{-n/2}$ (note that $\Lambda > 1$.

The numerical solution of Kondo Hamiltonian in 'Kondo-basis' thus starts with step $n = 0$: impurity coupled to first Kondo state, then proceeds to step $n = 1$ (couple to second onion layer), etc. In doing so, the total number of *many-body* states increases as

$$2^{2n+3} \tag{6.2.1}$$

in each step: step zero corresponds to 2 impurity times 4 'onion shell' states ($|0\rangle$, $|\uparrow\rangle$, $|\downarrow\rangle$, $|\uparrow\downarrow\rangle$. In each step four additional states are added, and thus the dimension of the problem is multiplied by four in each step. Already at moderate n, a complete diagonalization is therefore totally out of the question.

One therefore develops an approximation where only a certain number of the lowest eigenstates are kept in each of the subsequent steps, i.e. the matrices are truncated. It turns out that the eigenstates and eigenvalues after the n-th truncation step then very accurately describe thermodynamic properties for temperatures T of the order $\sim \Lambda^{-n/2}$. This argument relies on a consideration of Boltzmann factors $e^{-E_m/k_B T}$ (which enter the partition sum). For large n one therefore can describe properties at very low temperatures.

As a further remark: if we are interested in low-temperature properties, only electrons close to the Fermi surface are excited. These correspond to states far away from the impurity. Therefore, we neglect states far away from the impurity *and* far way from Fermi surface.

6.2.5 Where does this procedure lead to?

Of course, the key question is now whether the truncation procedure outlined above will lead to any meaningful results. A less stringent requirement is that such a procedure shoudl at least converge in some sense, i.e., it should lead to some sort of stable numerical result once the iteration index n is large enough.

It now turns out that for the problem at hand (the Kondo Hamiltonian), this is exactly the case. Moreover, the convergence of the procedure can best be described in the language of the **renormalisation group** (RG): in adding another shell, we move from Hamiltonian H_N to H_{N+1}, which is called a **renormalisation group step**,

$$H_{N+1} = \mathcal{R}[H_N], \tag{6.2.2}$$

where $\mathcal{R}$ is a **renormalisation group transformation** - this is a non-linear transformation that maps the energies and the matrix elements of the previous Hamiltonian H_N into a new Hamiltonian, H_{N+1}.

6.3 The NRG Hamiltonian and the Wilson Chain

We now try to understand how this all works out in detail.

6.3.1 Using the spherical symmetry

We first expand the operators $\Psi^\dagger_\uparrow(0)\Psi_\downarrow(0)$ etc. into spherical waves, using spherical harmonics Y_{lm}s in three dimensions. We recognize that the impurity only couples to s-waves $l = 0, m = 0$. As a consequence, one only needs to consider the s-wave part of the Kondo Hamiltonian. The energies $\varepsilon_{\mathbf{k}}$ then only depend on $|\mathbf{k}|$.

Furthermore, we count energies from the Fermi energy ε_F. A linearisation is also carried out,

$$\varepsilon_{\mathbf{k}} = \varepsilon_F + (k - k_F)\frac{\partial \varepsilon_k}{\partial k} + ... \tag{6.3.1}$$

Energies are counted from ε_F, one introduces units such that within this linearized approximation

$$\varepsilon_{\mathbf{k}} = k = \varepsilon. \tag{6.3.2}$$

Note that we are not interested in details of the bandstructure $\varepsilon_{\mathbf{k}}$ other than the fact that there is a cutoff at some (high) energy, which is modelled by introducing cutoffs $-D$ and D,

$$\mathcal{H}_K = \sum_\sigma \int_{-D}^{D} d\varepsilon \varepsilon a^\dagger_{\varepsilon\sigma} a_{\varepsilon\sigma} + 2J\mathbf{S}\mathbf{s}_0 \tag{6.3.3}$$

For the transformation of the term $2J\mathbf{S}\mathbf{s}_0$ see below.

6.3.2 Logarithmic discretisation of conduction band

This is the main idea of the procedure. First of all, the coupling term $2J\mathbf{S}\mathbf{s}_0$ in the Kondo Hamiltonian couples the impurity to all k, i.e. to electrons across the whole conduction band thus involving all *continuous* energies of the conduction band. Wilson therefore divides the energy band $[-D, D]$ into *discrete* intervals $[-\Lambda^{-n}, -\Lambda^{-(n+1)}]$ on the negative side and $[\Lambda^{-(n+1)}, \Lambda^{-n}]$ on the positive side where $n = 0, 1, 2, ...$ (Figure). Here, $2D$ is the bandwidth of the conduction band which is det to $D = 1$.

In order to transfrom from operators $a^\dagger_{\varepsilon\sigma}$ with continous labels ε to an equivalent set of operators with discrete labels. This is done by defining a Fourier series inside each energy interval (analogous to wave functions on a ring)

$$\Psi^\pm_{np}(\varepsilon) = \begin{cases} \frac{1}{\sqrt{d_n}} e^{\pm i\omega_n p\varepsilon}, & \Lambda^{-(n+1)} < \pm\varepsilon < \Lambda^{-n} \\ 0 & \text{else} \end{cases} \tag{6.3.4}$$

$$p = 0, \pm1, \pm2, ..., \quad d_n \equiv \Lambda^{-n}(1 - \Lambda^{-1}), \quad \omega_n = 2\pi/d_n. \tag{6.3.5}$$

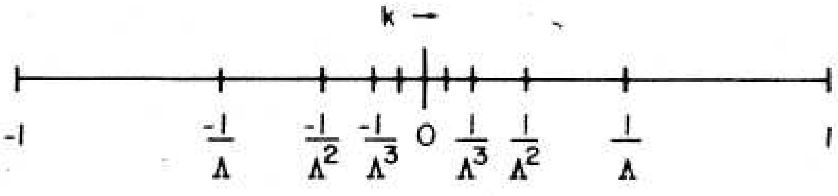


Figure 6.2: Logarithmic discretisation of conduction band, from Wilson (1975).

Correspondingly, expand the operators

$$a_{\varepsilon\sigma} = \sum_{np} \left[a_{np\sigma} \Psi^{+}_{np}(\varepsilon) + b_{np\sigma} \Psi^{-}_{np}(\varepsilon) \right] \tag{6.3.6}$$

into new operators $a_{np\sigma}$ and $b_{np\sigma}$ with Fermionic commutation relations and with discrete quantum numbers n, p instead of the continuous energy ε. The peculiarity here is that the transformation is directly done on the second quantised Fermionic operators and not on the wave functions in real space!

6.3.3 Main approximation: neglect all terms with $p \neq 0$

This means one only keeps the $p = 0$ component in each interval n. We denote the $p = 0$ components as $a_{np=0\sigma} \equiv a_{n\sigma}$ and $b_{np=0\sigma} \equiv b_{n\sigma}$ for simplicity. The conduction band part of the Hamiltonian, $\mathcal{H}_B$, then becomes (EXERCISE)

$$\mathcal{H}_B = \frac{1}{2}(1 + \Lambda^{-1}) \sum_{n\sigma} \Lambda^{-n} \left(a^{\dagger}_{n\sigma} a_{n\sigma} - b^{\dagger}_{n\sigma} b_{n\sigma} \right) \tag{6.3.7}$$

The validity or otherwise of this approximation is, of course, the crucial point, and Wilson discussed it in quite some detail in his work.

6.3.4 Coupling Term

In the coupling term

$$2J\mathbf{S}\mathbf{s}_0 \;=\; J\Big[S^z\Big(\Psi^\dagger_\uparrow(0)\Psi_\uparrow(0)-\Psi^\dagger_\downarrow(0)\Psi_\downarrow(0)\Big)+S^+\Psi^\dagger_\downarrow(0)\Psi_\uparrow(0)+S^-\Psi^\dagger_\uparrow(0)\Psi_\downarrow(0)\Big] \tag{6.3.8}$$

we write the field operator

$$\Psi_\sigma(0) \;=\; \frac{1}{\sqrt{\Omega}}\sum_{\mathbf{k}} a_{\mathbf{k}\sigma} \to \int_{-D}^{D} d\varepsilon a_{\varepsilon\sigma} = \int_{-D}^{D} d\varepsilon \sum_n \left[a_{n\sigma}\Psi^+_n(\varepsilon)+b_{n\sigma}\Psi^-_n(\varepsilon)\right]. \tag{6.3.9}$$

Now we use

$$\int_{-D}^{D} d\varepsilon \Psi^\pm_n(\varepsilon) = \frac{1}{\sqrt{d_n}}\left(\Lambda^{-n}-\Lambda^{-n-1}\right) \tag{6.3.10}$$

such that

$$\int_{-D}^{D} d\varepsilon a_{\varepsilon\sigma} \;=\; (1-\Lambda^{-1})^{1/2}\sum_n \Lambda^{-n/2}\left[a_{n\sigma}+b_{n\sigma}\right]. \tag{6.3.11}$$

As only this operator couples to the impurity spin, we define

$$f_{0\sigma} \equiv \sqrt{\frac{1-\Lambda^{-1}}{2}}\sum_n \Lambda^{-n/2}\left[a_{n\sigma}+b_{n\sigma}\right] = \frac{1}{\sqrt{2}}\Psi_\sigma(0) \tag{6.3.12}$$

where the $1/\sqrt{2}$ has been inserted such that one gets the correct anti-commutation relations (EXERCISE),

$$\{f_{0\sigma}, f^\dagger_{0\sigma'}\} = \delta_{\sigma\sigma'}. \tag{6.3.13}$$

Finally, the total model now has the following form,

$$\begin{aligned}\mathcal{H}_K \;&=\; \frac{1}{2}(1+\Lambda^{-1})\sum_{n\sigma}\Lambda^{-n}\left(a^\dagger_{n\sigma}a_{n\sigma}-b^\dagger_{n\sigma}b_{n\sigma}\right)\\ &+\; 2J\Big[S^z\Big(f^\dagger_{0\uparrow}f_{0\uparrow}-f^\dagger_{0\downarrow}f_{0\downarrow}\Big)+S^+f^\dagger_{0\downarrow}f_{0\uparrow}+S^-f^\dagger_{0\uparrow}f_{0\downarrow}\Big]\end{aligned} \tag{6.3.14}$$

The Kondo-term can be written as

$$2J\Big[S^z\Big(f^\dagger_{0\uparrow}f_{0\uparrow}-f^\dagger_{0\downarrow}f_{0\downarrow}\Big)+S^+f^\dagger_{0\downarrow}f_{0\uparrow}+S^-f^\dagger_{0\uparrow}f_{0\downarrow}\Big] = 2J\mathbf{S}\sum_{\mu\nu} f^\dagger_{0\mu}\vec{\sigma}_{\mu\nu}f_{0\nu}, \tag{6.3.15}$$

where $\vec{\sigma}$ is the vector of the Pauli matrices.

6.3.5 The Wilson chain

In the next step, one now tries to diagonalize the whole Hamiltonian $\mathcal{H}_K$ directly. Note that only the band part $\mathcal{H}_B$ is diagonal in the a_n, b_n basis. By transforming the operators a_n and b_n to new operators f_n, one ideally would like to diagonalize the band part $\mathcal{H}_B$. This is, however, not possible because the band electrons couple to the impurity via f_0. The best one can hope for is therefore a *tridiagonal* form.

Therefore, the following calculation is in fact a (unusual) analytical version of the Lanczos method. We want to tridiagonalize a Hamiltonian

$$\mathcal{H}_B \equiv \sum_\sigma H_\sigma = \sum_\sigma \sum_n \alpha_n \left(a^\dagger_{n\sigma} a_{n\sigma} - b^\dagger_{n\sigma} b_{n\sigma} \right). \tag{6.3.16}$$

We start from a single reference state, i.e. one electron with spin σ at the impurity,

$$|0\sigma\rangle \equiv f^\dagger_{0\sigma} |vac\rangle, \tag{6.3.17}$$

where $|vac\rangle$ is the vacuum with zero electrons. In fact, this part is a one-electron calculation! Also, the spin σ is not changed by $\mathcal{H}_B$ and is therefore fixed, the label σ is omitted.

Now, the Lanczos procedure is to write

$$|1\rangle = \frac{1}{\lambda_0} \left(H|0\rangle - |0\rangle\langle 0|H|0\rangle \right) \tag{6.3.18}$$

$$|n+1\rangle = \frac{1}{\lambda_n} \left(\left[1 - |n\rangle\langle n| - |n-1\rangle\langle n-1| \right] H|n\rangle \right) \tag{6.3.19}$$

with coefficients λ_n to be determined. As a result, the states $|n\rangle$ form a normalised basis of orthogonal vectors in which H becomes tridiagonal. The whole calculational difficulty here is to find an analytical expression for the λ_n. Simple calculation yields (EXERCISE)

$$\begin{aligned} \langle 0|H|0\rangle &= 0 \\ \lambda_0^2 &\equiv \langle 0|H^2|0\rangle = \frac{1}{4} \frac{(1+\Lambda^{-1})^2 (1-\Lambda^{-1})}{1-\Lambda^{-3}} \end{aligned} \tag{6.3.20}$$

First of all, one can see quite easily that

$$\langle n|H|n\rangle = 0, \quad n = 0, 1, 2, ... \tag{6.3.21}$$

Going through a considerable amount of algebra, Wilson furthermore found an analytical form for *all* λ_n (note: typo in (VII.35) there)

$$\lambda_n = \Lambda^{-n/2} \left[1 - \Lambda^{-(n+1)} \right] \left[1 - \Lambda^{-2n-1} \right]^{-1/2} \left[1 - \Lambda^{-(2n+3)} \right]^{-1/2} \left[1 + \Lambda^{-1} \right] / 2 \tag{6.3.22}$$

This means that one has fermion operators $f^\dagger_{n\sigma}$ with

$$f^\dagger_{n\sigma}|vac\rangle \quad = \quad |n\sigma\rangle \tag{6.3.23}$$

which creates an electron in the n-th state of the **Wilson chain**. The Kondo Hamiltonian becomes a chain,

$$\mathcal{H}_K = 2J\mathbf{S}\sum_{\mu\nu} f^\dagger_{0\mu}\vec{\sigma}_{\mu\nu}f_{0\nu} + \sum_{n=0\sigma}^{\infty} \lambda_n \left(f^\dagger_{n\sigma}f_{n+1\sigma} + f^\dagger_{n+1\sigma}f_{n\sigma}\right). \tag{6.3.24}$$

Now do some re-naming,

$$\begin{aligned} \frac{2}{1+\Lambda^{-1}}\mathcal{H}_K &= \frac{4}{1+\Lambda^{-1}}J\mathbf{S}\sum_{\mu\nu} f^\dagger_{0\mu}\vec{\sigma}_{\mu\nu}f_{0\nu} + \sum_{n=0\sigma}^{\infty}\Lambda^{-n/2}\xi_n \left(f^\dagger_{n\sigma}f_{n+1\sigma} + f^\dagger_{n+1\sigma}f_{n\sigma}\right) \\ \xi_n &\equiv \left[1-\Lambda^{-(n+1)}\right]\left[1-\Lambda^{-2n-1}\right]^{-1/2}\left[1-\Lambda^{-(2n+3)}\right]^{-1/2}. \end{aligned} \tag{6.3.25}$$

We write this as

$$\frac{2}{1+\Lambda^{-1}}\mathcal{H}_K = \lim_{N\to\infty}\tilde{H}_N \tag{6.3.26}$$

$$\tilde{H}_N \equiv H_0 + \sum_{n=0\sigma}^{N-1}\Lambda^{-n/2}\xi_n\left(f^\dagger_{n\sigma}f_{n+1\sigma} + f^\dagger_{n+1\sigma}f_{n\sigma}\right) \tag{6.3.27}$$

$$H_0 \equiv \tilde{J}\mathbf{S}\sum_{\mu\nu} f^\dagger_{0\mu}\vec{\sigma}_{\mu\nu}f_{0\nu}, \quad \tilde{J} \equiv \frac{4}{1+\Lambda^{-1}}J. \tag{6.3.28}$$

6.3.6 Comparison with Perturbation Theory

The sequence of Hamiltonians $\tilde{H}_N$ is now defined in a way where with each additional site on the Wilson chain acts as a small perturbation to all the previous sites on the chain: this is simply due to the *scaling factor* $\Lambda^{-n/2}$ in front of each additional term in the sum Eq. (6.3.26), i.e., in each step the additional term is a factor $\Lambda^{-1/2}$ smaller than the rest.

From a perturbation theory point of view, this way of arranging terms is similar to what one does in, e.g., hyperfine-structure calculations in atomic physics. Suppose we have a Hamiltonian of the form

$$H = H_a + H_b + H_c \tag{6.3.29}$$

with $H_a \gg H_b \gg H_c$, where the $\gg$ here has not to be taken literarily but shall just indicate that H_c is a small perturbation to H_b and H_b is a small perturbation to H_a.

The ‘right’ way of doing things is then not to diagonalize H directly, but to do the diagonalisation in three steps: First diagonalise H_a, this might be already very difficult. Say we can only obtain the lowest 1000 eigenstates of H_a to good accuracy. We take those and then write $H_a + H_b$ in the basis of those eigenstates, and then diagonalise $H_a + H_b$. This is much smarter then diagonalising $H_a + H_b$ straight away which in general will lead to large relative errors because H_b is much smaller than H_a, in particular if we wish to resolve very small energy differences at reliable accuracy. For example, if H_a has states with a degeneracy that is lifted by H_b, one has to proceed in this way - otherwise there is no chance to resolve the splitting of those degenerate states by H_b at sufficient accuracy. Similarly, in the next step one now uses the lowest eigenstates obtained from the diagonalisation after the first step and uses those to build the matrix $H_a + H_b + H_c$. In this way, the information from the previous step always fully remains as diagonal part, with the off-diagonal stemming from the (much smaller) next Hamiltonian.

6.3.7 Re-scaled Hamiltonians

It turns out to be convenient to work with a *re-scaled* series of Hamiltonians H_N,

$$H_N \equiv \Lambda^{(N-1)/2}\tilde{H}_N \tag{6.3.30}$$

instead of working with the $\tilde{H}_N$. With increasing N, the lowest energies of $\tilde{H}_N$ have finer and finer level spacings on an energy scale $\Lambda^{-(N-1)/2}$: with each additional site of the Wilson chain, additional states come in at an energy scale that is a factor $\Lambda^{-1/2}$ smaller than in the previous step.

In multiplying $\tilde{H}_N$ by $\Lambda^{(N-1)/2}$, we thus re-scale the re-fined energy spectrum: the re-scaled energies of the low-energy part of the spectrum are then numerically of the same order of magnitude in each step. It will in fact turn out that the re-scaled energies then actually converge to their fixed point values for large N.

Now, for the re-scaled Hamiltonians H_N one has a simple recursion (CHECK AS EXERCISE)

$$H_{N+1} = \sqrt{\Lambda} H_N + \sum_\sigma \xi_N \left(f^\dagger_{N\sigma} f_{N+1\sigma} + f^\dagger_{N+1\sigma} f_{N\sigma} \right). \tag{6.3.31}$$

Note that the ξ_n are all of the order of one.

The recursion Eq.(6.3.31) is the central ingredient to the calculation scheme that we discuss below. Some points:

- The recursion is a sequence of Hamiltonians, where H_{N+1} is obtained from the previous H_N by adding one additional site $N+1$ in the chain.
- Be careful with factors $\frac{1}{2}$ in the above derivation (definition of spin) !

- We have

$$\lim_{N\to\infty}\frac{1+\Lambda^{-1}}{2}\Lambda^{-(N-1)/2}H_N=\mathcal{H}_K. \tag{6.3.32}$$

6.4 Calculation Scheme

6.4.1 Starting Point

We first numerically diagonalise H_0,

$$H_0=U_0H_0^dU_0^T, \tag{6.4.1}$$

where H_0^d is diagonal. For the Kondo problem, H_0 is a $2^3\times 2^3$ matrix: 2 impurity spin states and 4 electron states (0, spin up, spin down, double). Explicitly, we have in the basis of four electron states at $n=0$, $e=0,\uparrow,\downarrow,\uparrow\downarrow$ times two impurity spin states u,d,

$$\begin{aligned} H_0 &= \tilde{J}\left[S^z\left(f_{0\uparrow}^\dagger f_{0\uparrow}-f_{0\downarrow}^\dagger f_{0\downarrow}\right)+S^+f_{0\downarrow}^\dagger f_{0\uparrow}+S^-f_{0\uparrow}^\dagger f_{0\downarrow}\right] && (6.4.2)\\ &= \dots && (6.4.3)\end{aligned}$$

(8 by 8 matrix), EXERCISE.

6.4.2 Adding the first sites

We add the first site $N=1$ of the Wilson chain

Construct the $2^{3+2}\times 2^{3+2}$ matrix H_1 using Eq.(6.3.31),

$$H_1=\sqrt{\Lambda}H_0+\sum_\sigma \xi_0\left(f_{0\sigma}^\dagger f_{1\sigma}+f_{1\sigma}^\dagger f_{0\sigma}\right). \tag{6.4.4}$$

This matrix has a tensor product structure. It is a four by four matrix (for the four electron states on site $N=1$) with elements which are $2^3\times 2^3$ matrices (from the coupling to the previous site). These elements are H_0 and $f_{0\uparrow}^\dagger$ etc. in the basis where H_0 is diagonal: all these $2^3\times 2^3$ matrices have to be transformed like H_0, i.e.

$$\begin{aligned} H_0 &\to U_0^TH_0U_0\equiv H_0^d && (6.4.5)\\ f_{0\uparrow} &\to U_0^Tf_{0\uparrow}U_0\equiv f_{0\uparrow}^d && (6.4.6)\end{aligned}$$

etc. Explicitly,

$$H_1=\begin{pmatrix} \sqrt{\Lambda}H_0^d & \xi_0(f_{0\uparrow}^d)^\dagger & \xi_0(f_{0\downarrow}^d)^\dagger & 0\\ \xi_0f_{0\uparrow}^d & \sqrt{\Lambda}H_0^d & 0 & \xi_0(f_{0\downarrow}^d)^\dagger\\ \xi_0f_{0\downarrow}^d & 0 & \sqrt{\Lambda}H_0^d & -\xi_0(f_{0\uparrow}^d)^\dagger\\ 0 & \xi_0f_{0\downarrow}^d & -\xi_0f_{0\uparrow}^d & \sqrt{\Lambda}H_0^d \end{pmatrix} \tag{6.4.7}$$

The electron annihilator $f_{0\uparrow}$ is a $2^3 \times 2^3$ matrix in the Hilbert space of the $N=0$ site, therefore $f^d_{0\uparrow}$ is again an 8×8 matrix. One has to take care with the minus signs in the matrices $f_{0\uparrow}$ etc. (fermions!). Denoting the diagonalized 8 by 8 matrix H^d_0 by $a_0(.,.)$, I get for the creation operators $(f^d_{0\sigma})^\dagger$ something like (CHECK!)

```
!!!!!!!!  Newly transformed creation operators (8 by 8 matrix)
          n = 8                       !!!! Size of first matrix
          DO 150 i=1,n
           DO 140 j=1,n
          f0up(i,j)   = a0(2,i)*a0(1,j) + a0(6,i)*a0(5,j)
     #                + a0(4,i)*a0(3,j) + a0(8,i)*a0(7,j)
          f0down(i,j) = a0(3,i)*a0(1,j) + a0(7,i)*a0(5,j)
     #                - a0(4,i)*a0(2,j) - a0(8,i)*a0(6,j)
 140      CONTINUE
 150      CONTINUE
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
```

Now diagonalise H_1,

$$H_1 = U_1 H^d_1 U^T_1. \tag{6.4.8}$$

We add the second site $N=2$ of the Wilson chain

Construct the $2^{3+2+2} \times 2^{3+2+2}$ matrix H_2 using Eq.(6.3.31). As before, this matrix has a tensor product structure as a four by four matrix (the four states for site $N=2$) with elements which are $2^{3+2} \times 2^{3+2}$ matrices from the coupling to the previous sites $N=0$ and $N=1$. These elements are H_1 and $f^\dagger_{1\uparrow}$ etc. in the basis where H_1 is diagonal: as before, these have to be transformed like H_1, i.e.

$$f_{1\uparrow} \quad \to \quad U^T_1 f_{1\uparrow} U_1 \equiv f^d_{0\uparrow} \tag{6.4.9}$$

etc. using the eigenvectors of the previous diagonalisation step.

For example, the electron annihilator $f_{1\uparrow}$ is a $2^{3+2} \times 2^{3+2}$ matrix in the Hilbert space of the first two sites $N=0,1$, therefore $f^d_{1\uparrow}$ is a 32×32 matrix. Again one has to take care with the minus signs in the matrices $f_{1\uparrow}$ etc. (fermions!).

Now diagonalise H_2,

$$H_2 = U_2 H^d_2 U^T_2. \tag{6.4.10}$$

Adding more and more sites of the Wilson chain

This works well for the first few sites which can be diagonalised exactly in this way. The matrix size, however, is increased by a factor of 4 in each step, i.e. H_N is a $2^{3+2N} \times 2^{3+2N}$ matrix. After adding a few sites, an exact diagonalisation of H_N is therefore completely out of the question even on big computers or with advanced algorithms. For example, for $N = 20$ the dimension of the matrix would be $\approx 8.8 \times 10^{12}$.

6.4.3 Truncation

Wilson's key idea was to make progress by *truncating* the Hilbert space such that one works with matrices that have manageable sizes. As a concrete example, consider the iteration after a few steps, say $N = 3$ with $dim(H_3) = 512$. The matrix H_4 in the next step would be $dim(H_3) = 512 \times 4 = 2048$ which one might decide to be too big (the actual number plays no role here, one could discuss this at larger N - the point is that it simply becomes *too* large beyond some N).

Now we decide that we only want to diagonalise up to 512×512 matrices. The *truncation* then leaves us with the lowest 128 eigenvalues from the diagonalisation of the previous H_3. These we take as the diagonal input in constructing the truncated matrix H_4. For the off-diagonals, we need the transformed f_3 operators which we first construct as 512×512 matrices and then truncate down to 128×128 when including them into H_4. In all the following steps we then work with dimension 512 but effectively truncate to dimension 128. Of course, these numbers are examples and one can do the scheme with keeping a larger number of eigenvalues.

6.4.4 Exploiting Symmetries

There are some conserved quantum numbers such as the total spin S or the total charge Q. Taking these into account renders the matrices as blockdiagonal and allows one to go to larger matrix sizes.

6.4.5 A First Look at the Results

A typical, still 'unpolished' result of a (small) numerical calculation looks like the one in Fig. (6.4.3).

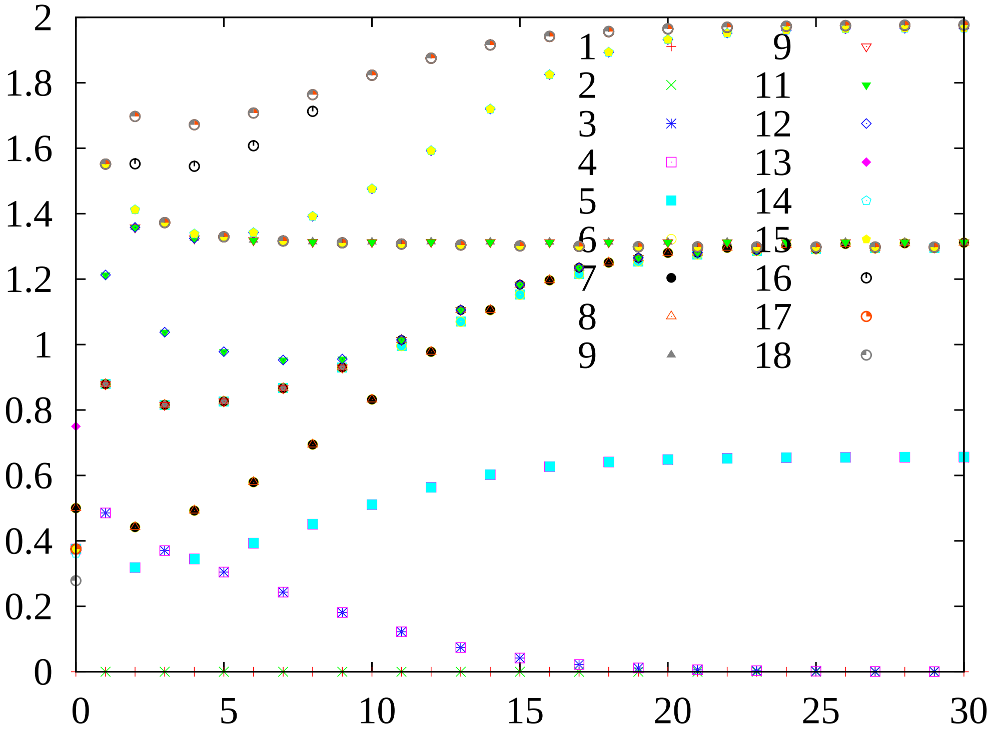


Figure 6.3: Excited state energies (y-axis, ground state energy subtracted) as a function of iterations N (x-axis) for the Kondo-model with parameters $\tilde{J} = 0.25$ and $\Lambda = 2$.

6.5 Understanding and Interpreting the Results

6.5.1 Wilsons 'Railroad track' Analogy

First let us consider two special cases: $J = 0$ (decoupled impurity) and $J = \infty$ (infinitely strongly coupled impurity). In these cases, the procedure described above leads to energy levels after n steps that fulfill a simple *scaling relation* to those after $n + 2$ steps (except very small n). In renormalisation group (RG) language, $J = 0$ and $J = \infty$ are *fixed points*, the corresponding fixed points Hamiltonians are denoted as

$$H_N^*(J = 0), \quad H_N^*(J = \infty). \tag{6.5.1}$$

Now we consider small positive $J > 0$ corresponding to weak anti-ferromagnetic coupling in our notation (Wilson defines his Kondo model with $-J$ with $J < 0$): in this case, the procedure leads (after a sufficiently large number n of iterations) to a cross-over from a spectrum that resembles the $J = 0$ case, to a spectrum that

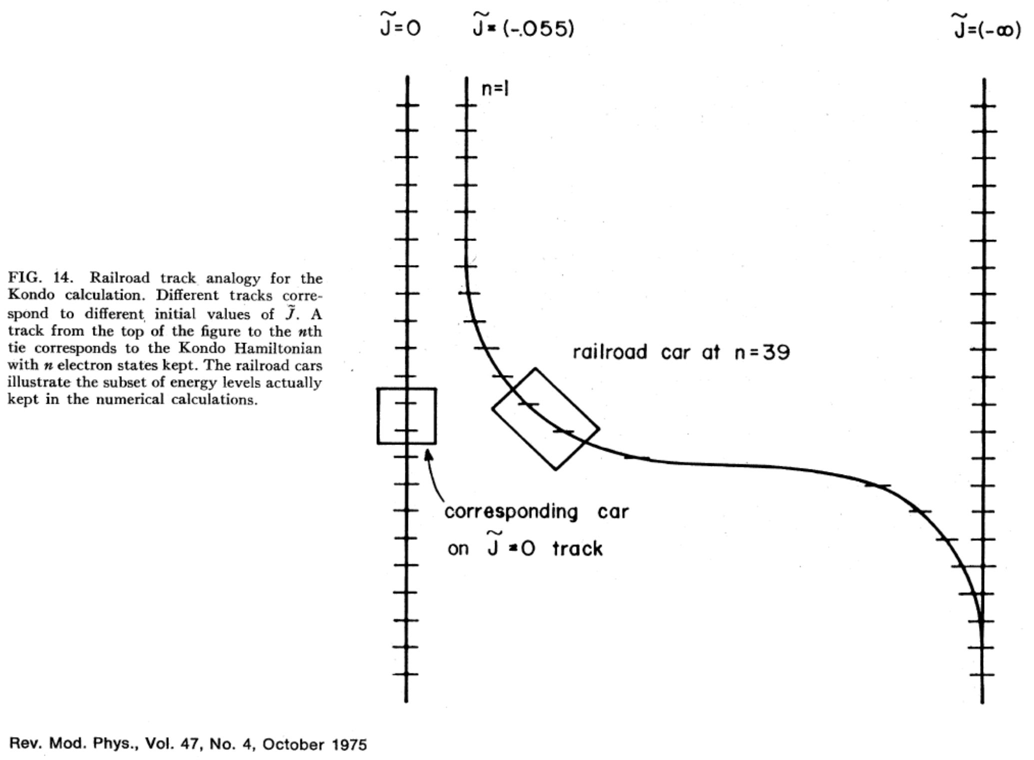


FIG. 14. Railroad track analogy for the Kondo calculation. Different tracks correspond to different initial values of $\tilde{J}$. A track from the top of the figure to the nth tie corresponds to the Kondo Hamiltonian with n electron states kept. The railroad cars illustrate the subset of energy levels actually kept in the numerical calculations.

Rev. Mod. Phys., Vol. 47, No. 4, October 1975

Figure 6.4: Wilsons 'Railroad track' analogy, from Wilson (1975).

(in its low-energy part) very much resembles the $J = \infty$ case. In RG language, the systems 'flows' from the $J = 0$ towards the $J = \infty$ fixed point.

The excitations about the ground state for the fixed point Hamiltonians are calculated by a simple (numerical) diagonalisation. For $J = 0$, one simply has the Wilson chain decoupled from the impurity. For large N and $\Lambda = 2$, the excitation energies then are (numerically) calculated as

$$0, \quad \pm\ 1.297, \quad \pm 2.827 ... \pm 2^{n-1}\sqrt{2}, \quad N \quad \text{even} \tag{6.5.2}$$

$$\pm\ 0.6555, \quad \pm 1.976 ... \pm 2^{n-1}, \quad N \quad \text{odd.} \tag{6.5.3}$$

For $J = \infty$, the impurity is coupled with the first site of the chain and both are effectively decoupled from the rest of the chain. The low energy excitations of $H_N(J = \infty)$ are therefore those of $H_{N-1}(J = 0)$.

6.5.2 Moving Along the Wilson Chain

The energy resolution in the N-th step of the iteration along the Wilson chain is $\propto \Lambda^{-(N-1)/2}$, i.e. increasing step by step. The sequence of Hamiltonians H_N are

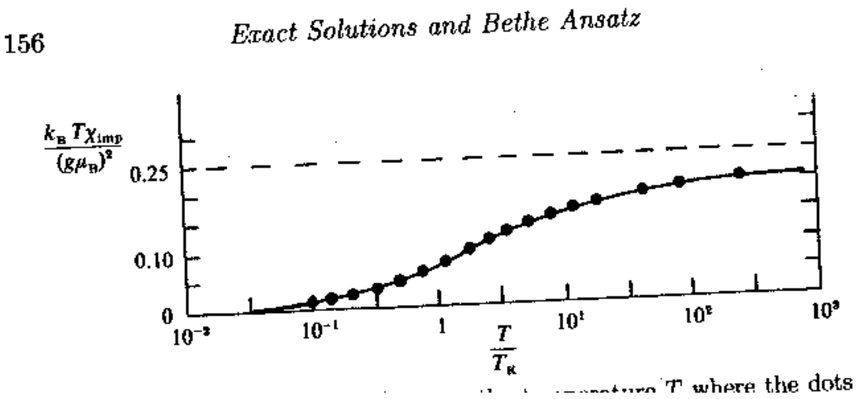


Figure 6.5: Magnetic impurity susceptibility for the Kondo model: comparison between the exact result (Bethe Ansatz, line) and the NRG calculation (dots). From the textbook by A. C. Hewson.

effective Hamiltonians that describe physical properties, derived from the spectrum of H_N, at a temperature scale k_BT or energy scale E with $k_BT, E \sim \Lambda^{-(N-1)/2}$.

When we fix the temperature T at a certain value, we have to terminate the iteration along the Wilson chain at that N that gives $k_BT \sim \Lambda^{-(N-1)/2}$. Any further step along the chain towards larger N would lead to an even finer energy resolution and, due to the truncation, to a loss of parts of the spectra in the subsequent H_{N+1} etc. which are important to describe the physics at k_BT. Conversely, terminating too early, i.e. at a too small N, means that we have not reached the necessary energy resolution yet.

In practice, one will do numerical runs along the chain and then use the data to evaluate quantities at different temperatures, or at different energies, for example in the *spectral function* $A(\omega)$.

As one example, the magnetic impurity susceptibility for the Kondo model is shown in Fig. 6.5.2, where results from an exact calculation (Bethe Ansatz) are compared with an NRG calculation (the exact solution was found later in the 1980s).

6.5.3 Outlook

We do not discuss further details here and just conclude this chapter by remarking that the Numerical Renormalisation Group has nowadays become an important theoretical tool in the analysis of complicated many-body problems, like the Kondo problem. It has been very successfully applied recently for calculations of, e.g., *quantum dots* at low temperatures. For further reading, cf. Wilson's original article, the textbook by A. C. Hewson, and recent research papers.

7. CLASSICAL ELECTROLYTES

7.1 Model

We consider a system of point charges, i.e. particles (ions) of charge q_α at position $\mathbf{r}_\alpha$, in a three-dimensional medium with dielectric constant $\epsilon(\mathbf{r})$. Here, α labels the particle species of which there are M. The system charge density $\rho_S(\mathbf{r})$ at position $\mathbf{r}$ (three-dimensional vector) is

$$\rho_S(\mathbf{r}) = \sum_{\alpha=1}^{M} \sum_{k_\alpha}^{N_\alpha} q_\alpha \delta(\mathbf{r} - \mathbf{r}_{k_\alpha}), \tag{7.1.1}$$

where N_α is the number of particles of species α. We also assume that there are additional, fixed particles at a density $\sigma(\mathbf{r})$ so that the total charge density $\rho(\mathbf{r})$ is

$$\rho(\mathbf{r}) = \sum_{\alpha=1}^{M} \sum_{k_\alpha=1}^{N_\alpha} q_\alpha \delta(\mathbf{r} - \mathbf{r}_{k_\alpha}) + \sigma(\mathbf{r}). \tag{7.1.2}$$

The total electrostatic (interaction) energy E of the system due to the Coulomb-interaction between the particles is given by

$$E = \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \phi(\mathbf{r}), \tag{7.1.3}$$

where the potential $\phi(\mathbf{r})$ obeys Poisson's equation: we use Maxwell's equation for the electric displacement $\mathbf{D}(\mathbf{r})$,

$$\nabla \mathbf{D}(\mathbf{r}) = 4\pi \rho(\mathbf{r}), \tag{7.1.4}$$

where we note that all charges are 'true' charges and not polarization charges. Then with $\mathbf{D}(\mathbf{r}) = \epsilon(\mathbf{r})\mathbf{E}(\mathbf{r})$ and the electric field $\mathbf{E}(\mathbf{r}) = -\nabla \phi(\mathbf{r})$, we find

$$-\nabla \epsilon(\mathbf{r}) \nabla \phi(\mathbf{r}) = 4\pi \rho(\mathbf{r}). \tag{7.1.5}$$

The associated Green's function to this problem fulfills

$$-\frac{1}{4\pi} \nabla \epsilon(\mathbf{r}) \nabla G_0(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \tag{7.1.6}$$

We obtain the potential, neglecting boundary terms,

$$\phi(\mathbf{r}) = \int d\mathbf{r}' G_0(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}'), \quad \textit{boundary terms neglected.} \tag{7.1.7}$$

(Neglecting the boundary terms is not quite without any problems, see below).

The energy of the electrostatic field can then be written entirely in terms of the charge distribution

$$E = \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\rho(\mathbf{r})G_0(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}') \tag{7.1.8}$$

The expression for the energy given above contains contribution from the interaction of each ion with itself — the self-energy. Subtracting this term from the energy, we write

$$E' = \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\rho(\mathbf{r})G_0(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}') - \frac{1}{2}\sum_{\alpha,k} q_\alpha^2 G_0(\mathbf{r}_{k_\alpha},\mathbf{r}_{k_\alpha}) \tag{7.1.9}$$

We also assume that there are external potentials $u_\alpha(\mathbf{r})$ acting on particles of type α. The total classical Hamilton function of the system is then

$$\mathcal{H} = \sum_{\alpha=1}^{M}\sum_{k_\alpha}^{N_\alpha}\left[\frac{\mathbf{p}_{k_\alpha}^2}{2m_\alpha} + u_\alpha(\mathbf{r}_{k_\alpha}) + E'\{\mathbf{r}_{k_\alpha}\}\right]. \tag{7.1.10}$$

7.2 Thermodynamics

7.2.1 Grand Partition Sum

Thermodynamical quantities of the system are best obtained from the grand partition sum Z_G in the grand-canonical ensemble at fixed temperature

$$k_B T \equiv \beta^{-1} \tag{7.2.1}$$

and chemical potentials μ_α for particles of type α. The grand partition sum Z_G is obtained from the partition sum $Z(N_1,...,N_M)$ of the canonical ensemble at fixed temperature and fixed particle numbers $N_1,...,N_M$ of species $\alpha = 1,...,M$,

$$Z_G = \sum_{N_1=0}^{\infty}\cdots\sum_{N_M=0}^{\infty}\prod_{\alpha=1}^{M} e^{\beta\mu_\alpha N_\alpha} Z(N_1,...,N_M). \tag{7.2.2}$$

In classical physics, the kinetic and potential energy terms in the Hamiltonian commute. The partition sum therefore contains the (trivial) contribution from the kinetic energy in the form of products of thermal wave lengths Λ_α, and the Gibbs correction factor in oder to account for the fact that particles of the same species are 'indistinguishable'. One therefore has

$$Z_G = \sum_{N_1=0}^{\infty} \cdots \sum_{N_M=0}^{\infty} \prod_{\alpha=1}^{M} \frac{e^{\beta\mu_\alpha N_\alpha}}{N_\alpha! \Lambda_\alpha^{3N_\alpha}} \int \prod_{\alpha=1}^{M} \prod_{k_\alpha=1}^{N_\alpha} d^3\mathbf{r}_{k_\alpha} e^{-\beta\left[\sum_{\alpha,k} u_\alpha(\mathbf{r}_{k_\alpha}) + E'\{\mathbf{r}_{k_\alpha}\}\right]}. \quad (7.2.3)$$

7.2.2 Hubbard-Stratonovich Transformation

The key idea now is to get rid of the term

$$e^{-\frac{1}{2}\beta \int d\mathbf{r}d\mathbf{r}'\rho(\mathbf{r})G_0(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')} \quad (7.2.4)$$

which comes from the interaction energy E', Eq. (7.1.9). This can be done at the expense of introducing additional Gaussian integrations over auxiliary fields, in very much the same way as we did in thermodynamics for the partition sum of the Ising model (see Lecture Notes), and in the chapter on Double Path Integrals in these Lecture Notes when we derived the function integral for the Fokker-Planck equation.

This Hubbard-Stratonovich transformation is best carried out by first 'discretizing'

$$\int d\mathbf{r}d\mathbf{r}'\rho(\mathbf{r})G_0(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}') \to \sum_{i,j}^{n} \rho_i G_{ij} \rho_j \quad (7.2.5)$$

and using the Gaussian identity

$$e^{-\frac{1}{2}\beta\varepsilon^2 \sum_{i,j}^{n} \rho_i G_{ij} \rho_j} = \left(\frac{\det(\beta G_0)^{-1}}{(2\pi)^n}\right)^{\frac{1}{2}} \int d\Psi_1 ... d\Psi_n e^{-\frac{1}{2\beta}\varepsilon^2 \sum_{i,j}^{n} \Psi_i \frac{1}{\varepsilon^2} G_{ij}^{-1} \Psi_j - i\varepsilon \sum_i \rho_i \Psi_i}. \quad (7.2.6)$$

In the limit $\varepsilon \to 0$, this yields

$$e^{-\frac{1}{2}\beta \int d\mathbf{r}d\mathbf{r}'\rho(\mathbf{r})G_0(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')} = \frac{1}{\sqrt{\det G_0}} \int D\Psi(\mathbf{r}) e^{-\frac{1}{2\beta}\int d\mathbf{r}d\mathbf{r}'\Psi(\mathbf{r})G_0^{-1}(\mathbf{r},\mathbf{r}')\Psi(\mathbf{r}') - i\int d\mathbf{r}\rho(\mathbf{r})\Psi(\mathbf{r})}. \quad (7.2.7)$$

Here, the path integral measure is defined as

$$D\Psi(\mathbf{r}) = \lim_{n\to\infty} (2\pi\beta)^{-n/2} d\Psi_1 ... d\Psi_n. \quad (7.2.8)$$

Now we insert this expression into the grand partition sum Z_G,

$$Z_G = \frac{1}{\sqrt{\det G_0}} \int D\Psi(\mathbf{r}) e^{-\frac{1}{2\beta}\int d\mathbf{r}d\mathbf{r}'\Psi(\mathbf{r})G_0^{-1}(\mathbf{r},\mathbf{r}')\Psi(\mathbf{r}')} e^{-i\int d\mathbf{r}\sigma(\mathbf{r})\Psi(\mathbf{r})} \tag{7.2.9}$$

$$\times \sum_{N_1=0}^{\infty} \cdots \sum_{N_M=0}^{\infty} \prod_{\alpha=1}^{M} \frac{e^{\beta\mu_\alpha N_\alpha}}{N_\alpha!\Lambda_\alpha^{3N_\alpha}} \int \prod_{\alpha=1}^{M} \prod_{k_\alpha=1}^{N_\alpha} d^3\mathbf{r}_{k_\alpha} e^{-\beta\sum_{\alpha,k}\left[u_\alpha(\mathbf{r}_{k_\alpha}) + \frac{i}{\beta}q_\alpha\Psi(\mathbf{r}_{k_\alpha}) - \frac{1}{2}q_\alpha^2 G_0(\mathbf{r}_{k_\alpha},\mathbf{r}_{k_\alpha})\right]} \tag{7.2.10}$$

The term $e^{-i\int d\mathbf{r}\sigma(\mathbf{r})\Psi(\mathbf{r})}$ comes from the fixed external charge density, $\sigma(\mathbf{r})$.

The second line can now be drastically simplified: consider that terms like

$$\int \prod_{k_1} d^3\mathbf{r}_{k_1} e^{-\beta\sum_{k_1=1}^{N_1} u_1(\mathbf{r}_{k_1})} = \left[\int d\mathbf{r} e^{-\beta u_1(\mathbf{r})}\right]^{N_1} \tag{7.2.11}$$

simply are powers of integrals over the coordinates of one particle. This means

$$\begin{aligned} \sum_{N_1=0}^{\infty} \cdots \sum_{N_M=0}^{\infty} \prod_{\alpha=1}^{M} \frac{e^{\beta\mu_\alpha N_\alpha}}{N_\alpha!\Lambda_\alpha^{3N_\alpha}} \int \prod_{\alpha=1}^{M} \prod_{k_\alpha=1}^{N_\alpha} d^3\mathbf{r}_{k_\alpha} e^{-\beta\sum_{\alpha,k} u_\alpha(\mathbf{r}_{k_\alpha})} &= \\ \sum_{N_1=0}^{\infty} \cdots \sum_{N_M=0}^{\infty} \prod_{\alpha=1}^{M} \frac{e^{\beta\mu_\alpha N_\alpha}}{N_\alpha!\Lambda_\alpha^{3N_\alpha}} \left[\int d\mathbf{r} e^{-\beta u_\alpha(\mathbf{r})}\right]^{N_\alpha} &= \\ \prod_{\alpha=1}^{M} \exp\left[\Lambda_\alpha^{-3}\int d\mathbf{r} e^{\beta\mu_\alpha - \beta u_\alpha(\mathbf{r})}\right] & \end{aligned} \tag{7.2.12}$$

This is actually nothing but the grand partition sum of a gas of M particle species $\alpha = 1, ..., M$ at chemical potential μ_α and inverse temperatur β in one-particle potentials $u_\alpha(\mathbf{r})$,

$$Z_G^{\mathrm{ref}}[\{\gamma_\alpha\}] \equiv \exp\left[\sum_{\alpha=1}^{M} \Lambda_\alpha^{-3}\int d\mathbf{r} e^{\gamma_\alpha(\mathbf{r})}\right], \quad \gamma_\alpha(\mathbf{r}) \equiv \beta\left[\mu_\alpha - u_\alpha(\mathbf{r})\right], \tag{7.2.13}$$

where the notation $\{\gamma_\alpha\}$ denotes a functional dependence on $\gamma_1(\mathbf{r}), ..., \gamma_M(\mathbf{r})$.

The full grand partition sum Z_G of the interacting system can now be written in a very elegant form,

$$Z_G = \frac{1}{\sqrt{\det G_0}} \int D\Psi(\mathbf{r}) e^{-\frac{1}{2\beta}\int d\mathbf{r}d\mathbf{r}'\Psi(\mathbf{r})G_0^{-1}(\mathbf{r},\mathbf{r}')\Psi(\mathbf{r}')} e^{-i\int d\mathbf{r}\sigma(\mathbf{r})\Psi(\mathbf{r})} \tag{7.2.14}$$

$$\tag{7.2.15}$$

$$\times \; Z_G^{\mathrm{ref}}[\{\gamma_\alpha - iq_\alpha\Psi + \frac{\beta q_\alpha^2}{2}G_0\}]. \tag{7.2.16}$$

This expression now also gives rise to a very intuitive interpretation: the interacting grand partition sum is an average over fields $\Psi(\mathbf{r})$ of the grand partition sum of a non-interacting gas of particles (M species) subject to a combination of the fixed, external chemical potentials μ_α and potentials u_α *and* the additional, fluctuating field $\Psi(\mathbf{r})$. The average is performed with a Gaussian weight factor (and the term $e^{-i\int d\mathbf{r}\sigma(\mathbf{r})\Psi(\mathbf{r})}$), and it is done in 'path-integral' form over all possible configurations of the fluctuating field.

7.2.3 Mean-Field Solution

This consists in replacing the functional integral for Z_G by the value of the integrand at an extremum $\bar{\Psi}(\mathbf{r})$,

$$Z_G^{\mathrm{MF}} = e^{-\frac{1}{2\beta}\int d\mathbf{r}d\mathbf{r}'\bar{\Psi}(\mathbf{r})G_0^{-1}(\mathbf{r},\mathbf{r}')\bar{\Psi}(\mathbf{r}')-i\int d\mathbf{r}\sigma(\mathbf{r})\bar{\Psi}(\mathbf{r})+\ln Z_G^{\mathrm{ref}}[\{\gamma_\alpha-iq_\alpha\bar{\Psi}\}]}, \tag{7.2.17}$$

where here and in the following we no longer include the self-interaction term $\frac{\beta q_\alpha^2}{2}G_0$ in Z_G^{ref}. The mean field solution, i.e. the extremum $\bar{\Psi}(\mathbf{r})$, is found by a functional derivative

$$\frac{\delta Z_G^{\mathrm{MF}}}{\delta\bar{\Psi}(\mathbf{r})} = 0, \tag{7.2.18}$$

which we find as

$$-\frac{1}{\beta}\int d\mathbf{r}'G_0^{-1}(\mathbf{r},\mathbf{r}')\bar{\Psi}(\mathbf{r}') + \frac{\delta\ln Z_G^{\mathrm{ref}}[\gamma_\alpha - iq_\alpha\bar{\Psi}]}{\delta\bar{\Psi}(\mathbf{r})} - i\sigma(\mathbf{r}) = 0. \tag{7.2.19}$$

For the derivative of $\ln Z_G^{\mathrm{ref}}$ we use its explicit form,

$$\begin{aligned}
\ln Z_G^{\mathrm{ref}}[\gamma_\alpha - iq_\alpha\bar{\Psi}] &= \sum_\alpha \Lambda_\alpha^{-3}\int d\mathbf{r}e^{\gamma_\alpha - iq_\alpha\bar{\Psi}} &\quad (7.2.20)\\
\rightsquigarrow \frac{\delta\ln Z_G^{\mathrm{ref}}[\gamma_\alpha - iq_\alpha\bar{\Psi}]}{\delta\bar{\Psi}(\mathbf{r})} &= -i\sum_\alpha \Lambda_\alpha^{-3}q_\alpha e^{\gamma_\alpha - iq_\alpha\bar{\Psi}(\mathbf{r})} &\quad (7.2.21)
\end{aligned}$$

In the following, we assume a constant dielectric functon,

$$\epsilon(\mathbf{r}) = \epsilon. \tag{7.2.22}$$

We then use

$$\int d\mathbf{r}''G_0^{-1}(\mathbf{r},\mathbf{r}'')G_0(\mathbf{r}'',\mathbf{r}) = \delta(\mathbf{r}-\mathbf{r}') \tag{7.2.23}$$

and the fact that G_0 solves Poisson's equation, which leads to (EXERCISE)

$$\Delta_{\mathbf{r}} i\bar{\Psi}(\mathbf{r}) = -\frac{4\pi}{\epsilon}\left[\sum_{\alpha} \Lambda_{\alpha}^{-3} q_{\alpha} e^{\gamma_{\alpha} - iq_{\alpha}\bar{\Psi}(\mathbf{r})} + \sigma(\mathbf{r})\right]. \tag{7.2.24}$$

Re-defining the imaginary potential Ψ into a real potential Φ,

$$\Phi(\mathbf{r}) \equiv \frac{i}{\beta}\bar{\Psi}(\mathbf{r}), \tag{7.2.25}$$

we finally obtain the desired mean-field equation,

$$\Delta_{\mathbf{r}} \Phi(\mathbf{r}) = -\frac{4\pi}{\epsilon}\left[\sum_{\alpha} \Lambda_{\alpha}^{-3} q_{\alpha} e^{\beta[\mu_{\alpha} - u_{\alpha}(\mathbf{r}) - q_{\alpha}\Phi(\mathbf{r})]} + \sigma(\mathbf{r})\right]. \tag{7.2.26}$$

This is the **Poisson-Boltzmann** equation: a second order PDE for the unknown potential $\Phi(\mathbf{r})$ due to a distribution of point charges in the grand-canonical ensemble at fixed inverse temperature β, chemical potentials μ_{α}, fixed external potentials u_{α}, and a fixed exernal charge density $\sigma(\mathbf{r})$. The term on the r.h.s of the Poisson-Boltzmann (minus $\sigma(\mathbf{r})$) is in fact just the charge density of a non-interacting gas of charges in a potential $u_{\alpha}(\mathbf{r}) + q_{\alpha}\Phi(\mathbf{r})$,

$$\bar{\rho}(\mathbf{r}) = \sum_{\alpha} \Lambda_{\alpha}^{-3} q_{\alpha} e^{\beta[\mu_{\alpha} - u_{\alpha}(\mathbf{r}) - q_{\alpha}\Phi(\mathbf{r})]}. \tag{7.2.27}$$

This density is, of course, nothing but a version of the barometric formula (barometrische Höhenformel).

The inhomogeneous term on the r.h.s. of the Poisson-Boltzmann is thus *non-linear* in $\Phi(\mathbf{r})$ which makes even the solution on mean field level non-trivial in general.

7.2.4 Expansion around Mean-Field

Before we discuss the Poisson-Boltzmann equation in the next section, some remarks:

- the Poisson-Boltzmann equation can be derived much easier in a phenomenological way, simply by inserting the thermodynamic equilibrium density $\bar{\rho}(\mathbf{r})$ of a gas in a potential $\phi(\mathbf{r})$ (given by the Boltzmann factors) into the Poisson equation: that is the origin of the name of that equation.
- however, the derivation via the *field theory* (functional integration, Hubbard-Stratonovich transformation) has the big advantage that one can calculate

corrections to mean field, i.e., corrections to the Poisson-Boltzmann equation. These come from fluctuations of the fields $\Psi(\mathbf{r})$ around their mean-field value $\bar{\Psi}(\mathbf{r})$. These fluctuations can be very important, e.g. in cases were the solution of the Poisson-Boltzmann equation is simply zero.

- The fluctuations can be calculated 'loop-wise' by expanding the functional integral around $\bar{\Psi}(\mathbf{r})$ in very much the same way as one does for the Gaussian fluctuations around Mean-Field theory for other models, e.g. the Ising Model (cf. lecture notes Thermodynamics).

7.3 Poisson-Boltzmann Theory

Here, we follow the Review Article by D. Andelman in 'Handbook of Biological Physics', Vol. 1, ed. R. Lipowsky and E. Sackmann (Elsevier, 1995).

We are concerned with solutions of the Poisson-Boltzmann equation

$$\Delta_{\mathbf{r}}\Phi(\mathbf{r}) = -\frac{4\pi}{\epsilon}\left[\sum_{\alpha}\Lambda_{\alpha}^{-3}q_{\alpha}e^{\beta[\mu_{\alpha}-u_{\alpha}(\mathbf{r})-q_{\alpha}\phi(\mathbf{r})]}+\sigma(\mathbf{r})\right] \tag{7.3.1}$$

that we derived in as mean-field approximation to the electrolyte problem in the previous section. Here, we are interested in situations involving boundaries in order to model, for example, membranes. The dielectric constant ϵ is the one for water if we are interested in a model for ion solutions in water, where the water just acts as a background medium.

7.3.1 Reference densities, classification for $M = 1$, $M = 2$

In the following, we consider $\sigma(\mathbf{r}) = 0$ and $u_{\alpha}(\mathbf{r}) = 0$ (no external charges, no external potentials). There is only the potential $\Phi(\mathbf{r})$ generated by the fluctuating ions. The Poisson-Boltzmann equation then reads

$$\Delta_{\mathbf{r}}\Phi(\mathbf{r}) = -\frac{4\pi}{\epsilon}\left[\sum_{\alpha}\Lambda_{\alpha}^{-3}q_{\alpha}e^{\beta[\mu_{\alpha}-q_{\alpha}\Phi(\mathbf{r})]}\right] \equiv -\frac{4\pi}{\epsilon}\sum_{\alpha}q_{\alpha}n_{\alpha}(\mathbf{r}), \tag{7.3.2}$$

where

$$n_{\alpha}(\mathbf{r}) = \Lambda_{\alpha}^{-3}e^{\beta[\mu_{\alpha}-q_{\alpha}\Phi(\mathbf{r})]} \tag{7.3.3}$$

are the mass densities of particle type α. We introduce the particle densities n_{α} (reference densities) at zero potential $\Phi(\mathbf{r}) = 0$,

$$n_{0,\alpha} \equiv \Lambda_{\alpha}^{-3}e^{\beta\mu_{\alpha}}, \tag{7.3.4}$$

which means that we can write

$$n_\alpha(\mathbf{r}) = n_{0,\alpha} e^{-\beta q_\alpha \Phi(\mathbf{r})} \tag{7.3.5}$$

and the Poisson-Boltzmann equation can be written as

$$\Delta_\mathbf{r} \Phi(\mathbf{r}) = -\frac{4\pi}{\epsilon} \sum_\alpha q_\alpha n_{0,\alpha} e^{-\beta q_\alpha \Phi(\mathbf{r})}. \tag{7.3.6}$$

Each ion mass density thus obeys a Boltzmann distribution with a potential $\Phi(\mathbf{r})$ determined by the Poisson-Boltzmann equation.

Classification $M = 1$

For $M = 1$, there is only one type of ions, e.g. positive ions such that

$$\Delta_\mathbf{r} \Phi(\mathbf{r}) = -\frac{4\pi}{\epsilon} q_+ n_{0,+} e^{-\beta q_+ \Phi(\mathbf{r})}. \tag{7.3.7}$$

Overall *charge neutrality* is usually guaranteed by charges on the boundaries of the system. For example, such a boundary can be a negatively charged membrane with an adjacent solution of positive ions. The positive ions are then called **counterions** because they counter-balance the charge of the membrane.

Classification $M = 2$, symmetric electrolyte $n_{0,+} = n_{0,-} = n_0$, $q_+ = -q_- = q > 0$

In this case, one has two types of ions (positive and negative) with charge neutrality

$$\sum_\alpha q_\alpha n_{0,\alpha} = 0 \tag{7.3.8}$$

guaranteed by all the ions themselves. The Poisson-Boltzmann equation then reads

$$\Delta_\mathbf{r} \Phi(\mathbf{r}) = -\frac{4\pi}{\epsilon} q n_0 \left[e^{-\beta q \Phi(\mathbf{r})} - e^{\beta q \Phi(\mathbf{r})} \right] = \frac{8\pi q n_0}{\epsilon} \sinh \beta q \Phi(\mathbf{r}) \tag{7.3.9}$$

7.3.2 Linearized symmetric case, Debye-Hückel length

This is obtained by linearising the $M = 2$ symmetric electrolyte Poisson-Boltzmann according to

$$\Delta_\mathbf{r} \Phi(\mathbf{r}) = \frac{8\pi q n_0}{\epsilon} \sinh \beta q \Phi(\mathbf{r}) \approx \frac{8\pi q n_0}{\epsilon} \beta q \Phi(\mathbf{r}), \quad \beta q \Phi(\mathbf{r}) \ll 1. \tag{7.3.10}$$

The r.h.s. of this equation then naturally defines a length scale,

$$\begin{aligned} \Delta_{\mathbf{r}}\Phi(\mathbf{r}) &= \lambda_D^{-2}\Phi(\mathbf{r}), \quad \beta q\Phi(\mathbf{r}) \ll 1 && (7.3.11)\\ \lambda_D &\equiv \left(\frac{8\pi n_0 q^2}{\epsilon k_B T}\right)^{-\frac{1}{2}}, \quad \textbf{Debye-Hückel length}. && (7.3.12)\end{aligned}$$

EXERCISE: check the numbers given by Andelman, i.e. $\lambda_D \approx 3\mathring{A}$ for 1M NaCl solution, and $\lambda_D \approx 1\mu m$ for pure water at pH 7 and room temperature.

7.3.3 Single, charged membrane and solution with $M = 1$ ion type

We consider a surface $z = 0$ with a constant negative surface charge density $\sigma < 0$, and a solution of positive ions with charge q_+ in the half space $z > 0$. The positive ions are called **counterions**.

There is no external potential;

$$\Delta_{\mathbf{r}}\Phi(\mathbf{r}) = -\frac{4\pi}{\epsilon}\Lambda_+^{-3} q_+ e^{\beta[\mu_+ - q_+\Phi(\mathbf{r})]}, \tag{7.3.13}$$

and as mentioned above the external charge density $\sigma(\mathbf{r})$ is not included here: instead, the negative surface charge density $\sigma < 0$ is regarded as part of the boundary. We write this equation as

$$\Delta_{\mathbf{r}}\Phi(\mathbf{r}) = -\frac{4\pi q_+}{\epsilon} n_0 e^{-\beta q_+ \phi(\mathbf{r})}, \quad n_0 \equiv \Lambda_+^{-3} q_+ e^{\beta\mu_+}, \tag{7.3.14}$$

where n_0 is the mass density of the ions at zero potential $\phi = 0$.

The geometry of the problem immediately shows that we only have to deal with a one-dimensional problem in z-direction,

$$\Phi''(z) = -\frac{4\pi q_+}{\epsilon} n_0 e^{-\beta q_+ \Phi(z)}, \tag{7.3.15}$$

because the potential must not depend on the x and the y direction. We then obviously need *two* boundary conditions in order to solve this equation as a boundary value problem. These conditions come from fixing the value of the electric field $E(z) = -\Phi'(z)$ (which points in z-direction),

$$\begin{aligned} E(z = \infty) &= 0 && (7.3.16)\\ E(z = 0) &= -\Phi'(z = 0) = \frac{4\pi}{\epsilon}\sigma. && (7.3.17)\end{aligned}$$

The last condition comes from applying Gauss' law on a box very closely around the plane $z = 0$ and the requirement that

$$E(z < 0) = 0, \tag{7.3.18}$$

which means that there is no electric field in the other half-space without ions (we could, e.g., demand that $z < 0$ consists of an infinitely thick metal).

We write an Ansatz

$$\Phi(z) = a\ln(z+b)+c \rightsquigarrow \Phi'(z) = \frac{a}{z+b} \rightsquigarrow \frac{a}{b} = -\frac{4\pi}{\epsilon}\sigma \qquad (7.3.19)$$

$$\rightsquigarrow \Phi''(z) = -\frac{a}{(z+b)^2} = -\frac{4\pi q_+}{\epsilon} n_0 e^{-\beta q_+(a\ln(z+b)+c)} \qquad (7.3.20)$$

$$= -\frac{4\pi q_+}{\epsilon} n_0 \left[e^{-\beta q_+ c}(z+b)^{-\beta q_+ a}\right] \qquad (7.3.21)$$

$$\rightsquigarrow -\frac{4\pi q_+}{\epsilon} n_0 e^{-\beta q_+ c} = -a, \quad \beta q_+ a = 2. \qquad (7.3.22)$$

This leads to the solution

$$\Phi(z) = \frac{2}{\beta q_+}\ln(z+b)+\Phi_0 \qquad (7.3.23)$$

$$b \equiv \frac{\epsilon}{2\pi|\sigma|\beta q_+}, \quad \textbf{Gouy-Chapman length} \qquad (7.3.24)$$

$$\Phi_0 \equiv \frac{-1}{\beta q_+}\ln\left[\frac{\epsilon}{2\pi q_+ n_0 \beta q_+}\right] \qquad (7.3.25)$$

We can re-write this as

$$\Phi(z) = \frac{2k_BT}{q_+}\ln\frac{z+b}{2\lambda_D} \qquad (7.3.26)$$

$$\lambda_D \equiv \left(\frac{8\pi n_0 q_+^2}{\epsilon k_B T}\right)^{-\frac{1}{2}}, \quad \textbf{Debye-Hückel length}. \qquad (7.3.27)$$

The counterion density $n_+(z)$ is obtained from the r.h.s. of the Poisson.Boltzmann equation,

$$\Phi''(z) = -\frac{4\pi q_+}{\epsilon} n(z), \quad n(z) \equiv n_0 e^{-\beta q_+ \Phi(z)} \qquad (7.3.28)$$

and thus by inserting

$$n(z) = n_0 e^{-\beta q_+ \frac{2}{\beta q_+}\ln\frac{z+b}{2\lambda_D}} = n_0 \frac{4\lambda_D^2}{(z+b)^2} = \frac{\epsilon k_B T}{2\pi q_+^2}\frac{1}{(z+b)^2} \qquad (7.3.29)$$

which again we re-write, introducing a third length-scale,

$$n(z) = \frac{1}{2\pi l}\frac{1}{(z+b)^2}, \quad l \equiv \frac{q_+^2}{\epsilon k_B T} = \frac{1}{8\pi n_0 \lambda_D^2}, \quad \textbf{Bjerrum length}. \qquad (7.3.30)$$

We just summarize these results,

$$\begin{aligned}
\Phi(z) &= \frac{2k_BT}{q_+}\ln\frac{z+b}{2\lambda_D} \quad \text{potential} && (7.3.31)\\
n(z) &= \frac{1}{2\pi l}\frac{1}{(z+b)^2} \quad \text{counterion density} && (7.3.32)\\
b &\equiv \frac{k_BT\epsilon}{2\pi|\sigma|q_+}, \quad \textbf{Gouy-Chapman length} && (7.3.33)\\
\lambda_D &\equiv \left(\frac{8\pi n_0 q_+^2}{\epsilon k_BT}\right)^{-\frac{1}{2}}, \quad \textbf{Debye-Hückel length} && (7.3.34)\\
l &\equiv \frac{q_+^2}{\epsilon k_BT} = \frac{1}{8\pi n_0\lambda_D^2}, \quad \textbf{Bjerrum length}. && (7.3.35)
\end{aligned}$$

7.3.4 Length scales in the Single-Surface Problem

Gouy-Chapman length

Consider the modulus of the electric field E_σ generated in both directions by an infinite plate with charge surface density σ embedded into a homogeneous medium with dielectric constant ϵ (no ions),

$$E_\sigma = \frac{2\pi|\sigma|}{\epsilon} \tag{7.3.36}$$

(again from Gauss' law). Then, the Gouy-Chapman length b is given by

$$bq_+E_\sigma = k_BT, \tag{7.3.37}$$

which is the length over which a point charge q_+ has to move in the constant field E_σ in order to aquire the energy k_BT.

Furthermore, the Gouy-Chapman length measures the thickness of the counterion layer close to the surface in the above single-membrane problem, where we have overall charge neutrality (EXERCISE). Then, the integrated counterion density (per area) attracted to the surface from $z = 0$ to $z = b$ is exactly $-\sigma/2$ (EXERCISE).

Bjerrum length

Consider the electrostatic potential ϕ_l generated by a single point charge q_+ at a distance r,

$$\phi_r = \frac{q_+}{\epsilon r}. \tag{7.3.38}$$

The Bjerrum length l is the distance $r = l$ such that the potential energy $q_+\phi_r$ of a second point charge q_+ equals $k_B T$,

$$\frac{q_+^2}{\epsilon l} = k_B T. \tag{7.3.39}$$

Note that the Bjerrum length is a ‘fixed’ quantity when q_+, T, and ϵ are regarded as fixed. In particular, there is no dependence on surface charges (as in the Gouy-Chapman length) and no ‘geometrical’ interpretation.