6 The The Quantum Master Equation in Energy Representation

we transform the QME into the energy (state) representation with respect to the system Hamiltonian; suppose we have solved the eigenvalue problem for $H_{\rm S}$

$$H_{\rm S}|a\rangle = E_a|a\rangle$$

the reduced density matrix (RDM) is given by

$$\rho_{ab}(t) = \langle a|\hat{\rho}(t)|b\rangle$$

the matrix elements of the system part of the system-reservoir coupling read

$$\langle a|K_u|b\rangle = K_{ab}^{(u)}$$

the energy representation offers the advantage that

$$U_{\rm S}(\tau)|a\rangle = e^{-iE_a\tau/\hbar}|a\rangle \equiv e^{-i\omega_a\tau}|a\rangle$$

we take respective matrix elements of the equation of motion for the RDO (note the introduction of transition frequencies $\omega_{ab} = \omega_a - \omega_b$)

$$\frac{\partial}{\partial t}\rho_{ab} = -i\omega_{ab}\rho_{ab} - \frac{i}{\hbar}\sum_c\sum_u \langle\Phi_u\rangle_{\rm R}(K_{ac}^{(u)}\rho_{cb} - \rho_{ac}K_{cb}^{(u)}) + \langle a|\left(\frac{\partial\hat{\rho}}{\partial t}\right)_{\rm diss}|b\rangle$$

the dissipative part is firstly considered in it's non–Markovian version

$$\langle a|\left(\frac{\partial\hat{\rho}}{\partial t}\right)_{\rm diss}|b\rangle = -\sum_{u,v}\int_0^{t-t_0} d\tau\Big\{C_{uv}(\tau)\Big(\langle a|K_u U_{\rm S}(\tau)K_v\hat{\rho}(t-\tau)U_{\rm S}^{+}(\tau) - U_{\rm S}(\tau)K_v\hat{\rho}(t-\tau)U_{\rm S}^{+}(\tau)K_u|b\rangle\Big)$$
$$-C_{vu}(-\tau)\Big(\langle a|K_u U_{\rm S}(\tau)\hat{\rho}(t-\tau)K_v U_{\rm S}^{+}(\tau)|b\rangle - \langle a|U_{\rm S}(\tau)\hat{\rho}(t-\tau)K_v U_{\rm S}^{+}(\tau)K_u|b\rangle\Big)\Big\}$$

introducing two times complete sets of system states results in

$$\langle a|\left(\frac{\partial\hat{\rho}}{\partial t}\right)_{\rm diss}|b\rangle \equiv \left(\frac{\partial\rho_{ab}}{\partial t}\right)_{\rm diss} = -\sum_{c,d}\sum_{u,v}\int_0^{t-t_0} d\tau\Big\{C_{uv}(\tau)\Big(K_{ac}^{(u)}e^{-i\omega_c\tau}K_{cd}^{(v)}\rho_{db}(t-\tau)e^{i\omega_b\tau}$$
$$-e^{-i\omega_a\tau}K_{ac}^{(v)}\rho_{cd}(t-\tau)e^{i\omega_d\tau}K_{db}^{(u)}\Big) - C_{vu}(-\tau)\Big(K_{ac}^{(u)}e^{-i\omega_c\tau}\rho_{cd}(t-\tau)K_{db}^{(v)}e^{i\omega_b\tau} - e^{-i\omega_a\tau}\rho_{ac}(t-\tau)K_{cd}^{(v)}e^{i\omega_d\tau}K_{db}^{(u)}\Big)\Big\}$$

a rearrangement of terms gives

$$\left(\frac{\partial\rho_{ab}}{\partial t}\right)_{\rm diss} = -\sum_{c,d}\sum_{u,v}\int_0^{t-t_0} d\tau\Big(C_{vu}(-\tau)K_{db}^{(u)}K_{cd}^{(v)}e^{i\omega_{da}\tau}\rho_{ac}(t-\tau) + C_{uv}(\tau)K_{ac}^{(u)}K_{cd}^{(v)}e^{i\omega_{bc}\tau}\rho_{db}(t-\tau)$$
$$-\{C_{vu}(-\tau)K_{ac}^{(u)}K_{db}^{(v)}e^{i\omega_{bc}\tau} + C_{uv}(\tau)K_{db}^{(u)}K_{ac}^{(v)}e^{i\omega_{da}\tau}\}\rho_{cd}(t-\tau)\Big)$$

a more compact notation of this equation is achieved by introducing the tetradic matrix called *memory matrix*

$$M_{ab,cd}(t) = \sum_{u,v} C_{uv}(t) K^{(u)}_{ab} K^{(v)}_{cd}$$

it satisfies the relation

$$M^{*}_{ab,cd}(t) = \sum_{u,v} C_{vu}(-t) K^{(u)}_{ba} K^{(v)}_{dc} = M_{dc,ba}(-t)$$

the dissipative part of the non-Markovian density matrix equation reads

$$\left(\frac{\partial \rho_{ab}}{\partial t}\right)_{\text{diss.}} = -\sum_{cd} \int_{0}^{t-t_0} d\tau \Big(M_{cd,db}(-\tau) e^{i\omega_{da}\tau} \rho_{ac}(t-\tau) + M_{ac,cd}(\tau) e^{i\omega_{bc}\tau} \rho_{db}(t-\tau)$$

$$- [M_{db,ac}(-\tau) e^{i\omega_{bc}\tau} + M_{db,ac}(\tau) e^{i\omega_{da}\tau}] \rho_{cd}(t-\tau) \Big)$$

one can proof that the total occupation probability of the different eigenstates of H_{S} are conserved, i.e. $\sum_a \partial \rho_{aa}/\partial t = 0$; since the reservoir is at temperature T the density matrix displays the limiting behavior

$$\lim_{t\to\infty} \rho_{ab}(t) = \delta_{a,b} e^{-E_a/k_{\text{B}}T} \Big/ \sum_c e^{-E_c/k_{\text{B}}T}$$

6.1 Multi-Level Redfield Equations

we carry out the Markov approximation

$$\rho_{ab}(t-\tau) = \langle a|\hat{\rho}(t-\tau)|b\rangle \approx \langle a|U_{\rm S}^{+}(\tau)\hat{\rho}(t)U_{\rm S}(\tau)|b\rangle = e^{i\omega_{ab}\tau}\rho_{ab}(t)$$

and obtain

$$\left(\frac{\partial\rho_{ab}}{\partial t}\right)_{\rm diss.} \approx -\sum_{cd}\int_{0}^{t-t_0} d\tau\Big(M_{cd,db}(-\tau)e^{i\omega_{da}\tau}e^{i\omega_{ac}\tau}\rho_{ac}(t) + M_{ac,cd}(\tau)e^{i\omega_{bc}\tau}e^{i\omega_{db}\tau}\rho_{db}(t)$$

$$-[M_{db,ac}(-\tau)e^{i\omega_{bc}\tau} + M_{db,ac}(\tau)e^{i\omega_{da}\tau}]e^{i\omega_{cd}\tau}\rho_{cd}(t)\Big)$$

and finally

$$\left(\frac{\partial\rho_{ab}}{\partial t}\right)_{\rm diss.} = -\sum_{cd}\int_{0}^{\infty} d\tau\Big(M_{cd,db}(-\tau)e^{i\omega_{dc}\tau}\rho_{ac}(t) + M_{ac,cd}(\tau)e^{i\omega_{dc}\tau}\rho_{db}(t)$$

$$[M_{db,ac}(-\tau)e^{i\omega_{bd}\tau} + M_{db,ac}(\tau)e^{i\omega_{ca}\tau}]\rho_{cd}(t)\Big)$$

the time integrals can be viewed as half–sided Fourier transforms of the memory functions;
these complex quantities define the dissipative part of the QME in the Markov approximation;
their real part describes an irreversible redistribution of the amplitudes contained in the various parts of reduced density matrix;
the imaginary part introduces terms which can be interpreted as a modification of the transition frequencies and the respective mean-field matrix elements;

they can be accounted for by changing the energy scale or adjusting the transition frequencies; therefore, we restrict ourselves to the discussion of the real part only leading to the following (damping) matrix

$$\Gamma_{ab,cd}(\omega) = \mathrm{Re}\int_0^\infty d\tau\; e^{i\omega\tau} M_{ab,cd}(\tau) = \mathrm{Re}\sum_{u,v} K_{ab}^{(u)} K_{cd}^{(v)} \int_0^\infty d\tau\; e^{i\omega\tau} C_{uv}(\tau)$$

the dissipative part of the QME in the state representation becomes

$$\left(\frac{\partial \rho_{ab}}{\partial t}\right)_{\mathrm{diss.}} = -\sum_{c,d} \Big(\Gamma_{bd,dc}(\omega_{cd})\rho_{ac}(t) + \Gamma_{ac,cd}(\omega_{dc})\rho_{db}(t) - [\Gamma_{ca,bd}(\omega_{db}) + \Gamma_{db,ac}(\omega_{ca})]\rho_{cd}(t) \Big)$$

we introduce the relaxation matrix

$$R_{ab,cd} = \delta_{a,c}\sum_e \Gamma_{be,ed}(\omega_{de}) + \delta_{b,d}\sum_e \Gamma_{ae,ec}(\omega_{ce}) - \Gamma_{ca,bd}(\omega_{db}) - \Gamma_{db,ac}(\omega_{ca})$$

the dissipative contribution to the reduced density matrix equations of motion can be finally written as

$$\left(\frac{\partial \rho_{ab}}{\partial t}\right)_{\mathrm{diss.}} = -\sum_{cd} R_{ab,cd}\rho_{cd}(t)$$

the tetradic relaxation matrix is frequently termed Redfield tensor after A. G. Redfield who introduced it in the theory of nuclear magnetic resonance spectroscopy in the early sixties;
since the density matrix elements can be distinguished as populations ($a = b$) and coherences ($a \neq b$) it is reasonable to discuss $R_{ab,cd}$ according to its effect on the dynamics of ρ_{aa} and ρ_{ab};

6.1.1 Population transfer: $a = b$, $c = d$

the respective matrix elements of the Redfield tensor can be written as

$$R_{aa,cc} = 2\delta_{a,c} \sum_e \Gamma_{ae,ea}(\omega_{ae}) - 2\Gamma_{ca,ac}(\omega_{ca}) = \delta_{a,c} \sum_e k_{a\to e} - k_{c\to a}$$

we introduced the rate $k_{a\to b}$ for the transition from state $|a\rangle$ to state $|b\rangle$ according to

$$k_{a\to b} = 2\Gamma_{ab,ba}(\omega_{ab}) = 2\mathrm{Re} \int_0^\infty d\tau e^{i\omega_{ab}\tau} M_{ab,ba}(\tau) = \int_0^\infty d\tau e^{i\omega_{ab}\tau} M_{ab,ba}(\tau) + \int_0^\infty d\tau e^{-i\omega_{ab}\tau} M^*_{ab,ba}(\tau)$$

the two terms on the last line can be combined to give

$$k_{a\to b} = \int d\tau \; e^{i\omega_{ab}\tau} M_{ab,ba}(\tau) \equiv M_{ab,ba}(\omega_{ab})$$

using the definition of the memory matrix we obtain an alternative expression for the energy relaxation rates

$$k_{a\to b} = \sum_{u,v} C_{uv}(\omega_{ab}) K^{(u)}_{ab} K^{(v)}_{ba}$$

the rate for a particular transition is determined by the matrix elements of the operators K_u and by the value of the correlation function taken at the respective transition frequency, $C_{uv}(\omega = \omega_{ab})$;
this last dependence can be viewed as a “probing” of the spectral density at this frequency;

in terms of the harmonic reservoir model this implies that there has to be a reservoir oscillator mode which can absorb or emit a reservoir quantum at the transition frequency of the system; since the transitions between the system states are therefore accompanied by energy dissipation into the reservoir, the rates are also called energy relaxation rates;

we can proof that the principle of detailed balance is fulfilled

$$k_{a\to b} = \sum_{u,v} C_{vu}(\omega_{ab}) K_{ab}^{(v)} K_{ba}^{(u)} = e^{\hbar\omega_{ab}/k_{\mathrm{B}}T} \sum_{u,v} C_{uv}(\omega_{ba}) K_{ba}^{(u)} K_{ab}^{(v)} = e^{\hbar\omega_{ab}/k_{\mathrm{B}}T} k_{b\to a}$$

6.1.2 **Coherence dephasing:** $a \neq b$**,** $a = c$**,** $b = d$

in this case we have

$$R_{ab,ab} \equiv \gamma_{ab} = \sum_e \left(\Gamma_{ae,ea}(\omega_{ae}) + \Gamma_{be,eb}(\omega_{be})\right) - \Gamma_{aa,bb}(0) - \Gamma_{bb,aa}(0)$$

the expression determines the damping of the off–diagonal elements of the reduced density matrix;
these are called coherences since they represent phase relations between different states;
the decay of coherences is known as the dephasing process, and the γ_{ab} are called dephasing rates;
we notice that the first part of the dephasing rate can be written as $\gamma_a + \gamma_b$ where γ_a and γ_b equals half of the relaxation rates;
within the present model energy relaxation is a source of coherence dephasing;
the second part denoted by $\gamma_{ab}^{(\mathrm{pd})}$ is defined by the reservoir correlation function at zero frequency, i.e., it represents an elastic type of collision where no energy is exchanged between system and reservoir;
these rates are usually named pure dephasing rates and we write

$$\gamma_{ab} = \frac{1}{2}\sum_e k_{a\to e} + \frac{1}{2}\sum_e k_{b\to e} + \gamma_{ab}^{(\mathrm{pd})}$$

with

$$\gamma_{ab}^{(\mathrm{pd})} = -\sum_{u,v} K_{aa}^{(u)} K_{bb}^{(v)} C_{uv}(\omega = 0)$$

6.1.3 Remaining Elements of $R_{ab,cd}$

we can distinguish the following transitions induced by $R_{ab,cd}$;
first coherences can be transferred between different pairs of states: $\rho_{ab} \rightarrow \rho_{cd}$ ($R_{ab,cd}$);

second, populations can change to coherences: $\rho_{aa} \rightarrow \rho_{cd}$ ($R_{aa,cd}$);

and finally, the coherences can be transformed into populations: $\rho_{ab} \rightarrow \rho_{cc}$ ($R_{ab,cc}$);

as a consequence there is a mixing between different types of reduced density matrix elements;

6.2 The Secular Approximation

in order to see under what conditions the mixing between population and coherence type density matrix elements can be neglected we change to the interaction representation

$$\left(\frac{\partial \rho_{ab}^{(\mathrm{I})}}{\partial t}\right)_{\mathrm{diss}} = -\sum_{cd} R_{ab,cd}\, e^{i(\omega_{ab}-\omega_{cd})(t-t_0)} \rho_{cd}^{(\mathrm{I})}(t)$$

the right–hand side contains various contributions which oscillate with the combined frequency $\omega_{ab} - \omega_{cd}$;

all contributions to the equations of motion where $1/|\omega_{ab} - \omega_{cd}|$ is much smaller than the time increment Δt for which the QME is solved will cancel each other upon integration of the equations of motion due to destructive interference;

let us suppose that we can neglect all those contributions to the dissipative part for which the condition $1/|\omega_{ab} - \omega_{cd}| \ll \Delta t$ is fulfilled;

there are at first glance two types of contributions which cannot be neglected since $|\omega_{ab} - \omega_{cd}| = 0$ holds;

these are related to those elements of $R_{ab,cd}$ which were discussed as cases (1) and (2) in the previous section;

however, for systems with degenerate transition frequencies such as a harmonic oscillator $|\omega_{ab} - \omega_{cd}| = 0$ can be fulfilled even if $R_{ab,cd}$ belongs to the category (3) of the previous section;

in general the approximation which builds upon the consideration of only those terms in the dissipative part of the QME for which $|\omega_{ab} - \omega_{cd}| = 0$ holds is called secular approximation; it is also often also termed
myred rotating wave approximation;

note that within the Markov approximation the smallest possible time step, Δt, is determined by the memory time $\tau_{\rm mem}$;
if, however, in systems with nearly degenerate transition frequencies the condition $1/|\omega_{ab} - \omega_{cd}| > \tau_{\rm mem}$ is realized the secular approximation determines the coarse graining of the time axis and therefore imposes a lower limit on the time resolution of the reduced density matrix;
thus, we have seen that even in the secular approximation there is a chance that populations and coherences are coupled via $R_{ab,cd}$; if we neglect this coupling, i.e. if we suppose that $|\omega_{ab} - \omega_{cd}| = 0$ holds only in the cases (1) and (2) of the previous section we are at the level of the so–called Bloch model

$$\left(\frac{\partial P_a}{\partial t}\right)_{\rm diss} = -\sum_c R_{aa,cc} P_c(t)$$

and

$$\left(\frac{\partial \rho_{ab}}{\partial t}\right)_{\rm diss} = -(1-\delta_{ab}) R_{ab,ab} \rho_{ab}$$

the Redfield tensor does not mix diagonal and off–diagonal elements of the reduced density matrix; we can consider the equations for the populations and the coherences separately;

6.3 State Expansion of the System-Reservoir Coupling

we introduce an expansion of $H_{\mathrm{S-R}}$ in the eigenstates of H_{S}:

$$H_{\mathrm{S-R}} = \sum_{a,b} \langle a|H_{\mathrm{S-R}}|b\rangle |a\rangle\langle b|$$

it is a special version of the factorized ansatz for the system–reservoir interaction Hamiltonian;
we have to identify the index u with (ab), K_u with $|a\rangle\langle b|$ (i.e. $K_{cd}^{(u)} = \delta_{c,a}\delta_{d,b}$), and Φ_u with $\langle a|H_{\mathrm{S-R}}|b\rangle$;
the K_u–operators do not represent Hermitian operators;
in a first step we set

$$\langle a|H_{\mathrm{S-R}}|b\rangle \equiv \Phi_{ab} = \sum_{\xi} \hbar\omega_\xi g_{ab}(\xi) Q_\xi$$

the (energy) relaxation rates are obtained as $k_{a\to b} = C_{ab,ba}(\omega_{ab})$
we get for the correlation function

$$C_{ab,cd}(\omega) = 2\pi\omega^2[1+n(\omega)]\,[J_{ab,cd}(\omega) - J_{ab,cd}(-\omega)]$$

where we introduced the generalized spectral density $J_{ab,cd}(\omega) = \sum_{\xi} g_{ab}(\xi) g_{cd}(\xi)\delta(\omega-\omega_\xi)$

the relaxation rates follow as (be aware of the relation $-n(-\omega) = 1+n(\omega)$)

$$k_{a\to b} = 2\pi\omega_{ab}^2\Big([1+n(\omega_{ab})]J_{ab,ba}(\omega_{ab}) + n(\omega_{ba})J_{ab,ba}(\omega_{ba})\Big)$$

finally, we demonstrate that in case of the Bloch model it is possible to change back from the energy representation to the following operator notation of the QME

$$\left(\frac{\partial\hat{\rho}(t)}{\partial t}\right)_{\text{diss}} = -\sum_{a,b}\left\{\frac{1}{2}\Big[k_{a\to b}|a\rangle\langle a|,\hat{\rho}(t)\Big]_{+} - k_{a\to b}|b\rangle\langle a|\hat{\rho}(t)|a\rangle\langle b|\right\} - \sum_{a,b}(1-\delta_{a,b})\gamma_{ab}^{(\text{pd})}|a\rangle\langle a|\hat{\rho}(t)|b\rangle\langle b|$$

the first sum including an anti–commutator is exclusively determined by the energy relaxation rate $k_{a\to b}$ whereas the second sum incorporates the pure dephasing part $\gamma_{ab}^{(\text{pd})}$;
once pure dephasing vanishes the whole dissipative part resembles what is often called the Lindblad form;
it is possible to derive this type of dissipative contribution to the equation of motion of the reduced density operator in a more formal way starting from the assumption that the diagonal elements of the reduced density operator have to be greater or equal to zero in any basis set;
this has been shown by Lindblad in the 1970s;
the advantage is that the condition $\rho_{aa}(t) \geq 0$ is guaranteed by construction in contrast to the case of the QME;

we proof the expression by changing to matrix elements

$$\langle a| \left(\frac{\partial \hat{\rho}}{\partial t}\right)_{\text{diss}} |b\rangle =$$

$$-\frac{1}{2}\langle a| \sum_{c,d} k_{c\to d}\Big\{ \Big[|c\rangle\langle c|, \hat{\rho}(t)\Big]_+ - 2|d\rangle\langle c|\hat{\rho}(t)|c\rangle\langle d|\Big\}|b\rangle - \langle a| \sum_{c,d}(1-\delta_{c,d})\gamma_{cd}^{(\text{pd})}|c\rangle\langle c|\hat{\rho}(t)|d\rangle\langle d||b\rangle$$

$$= -\frac{1}{2}\sum_d \big(k_{a\to d} + k_{b\to d}\big)\rho_{ab}(t) + \delta_{a,b}\sum_c k_{c\to a}\rho_{cc}(t) - (1-\delta_{a,b})\gamma_{ab}^{(\text{pd})}\rho_{ab}(t)$$

$$= -\delta_{a,b}\sum_c \Big(k_{a\to c}\rho_{aa}(t) - k_{c\to a}\rho_{cc}(t)\Big) - (1-\delta_{a,b})\Big(\sum_c \frac{1}{2}\big(k_{a\to c} + k_{b\to c}\big) + \gamma_{ab}^{(\text{pd})}\Big)\rho_{ab}(t)$$

6.4 Lindblad Form of Density Matrix Equations

in order to simplify the notation somewhat we assume $\gamma_{ab}^{(\mathrm{pd})} = 0$ and $H_{\mathrm{mf}} = 0$;
moreover we introduce so-called Lindblad operators as

$$\hat{L}_{ab}^{+} = |a\rangle\langle b|$$

as a result the full quantum master equation takes the form

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}\big[H_{\mathrm{S}}, \hat{\rho}(t)\big]_{-} - \frac{1}{2}\sum_{a,b} k_{a\to b}\Big(\big[\hat{L}_{ab}^{+}\hat{L}_{ab}, \hat{\rho}(t)\big]_{+} - 2\hat{L}_{ab}\hat{\rho}(t)\hat{L}_{ab}^{+}\Big)$$

finally, we demonstrate how this notation can be used to change from a density matrix equation to an equation of motion for a particular observable;
we introduce $\hat{O}$ as an operator representing a particular observable and being defined in the system state space;
it's expectation value is obtained as

$$O(t) = \mathrm{tr}_{\mathrm{S}}\{\hat{\rho}(t)\hat{O}\} =< \hat{O} > (t)$$

a related equation is immediately obtained as

$$\frac{\partial}{\partial t}O(t) = \mathrm{tr}_{\mathrm{S}}\{\frac{\partial}{\partial t}\hat{\rho}(t)\hat{O}\} = -\frac{i}{\hbar}\mathrm{tr}_{\mathrm{S}}\{\big[H_{\mathrm{S}}, \hat{\rho}(t)\big]_{-}\hat{O}\} - \frac{1}{2}\sum_{a,b} k_{a\to b}\mathrm{tr}_{\mathrm{S}}\{\big[\hat{L}_{ab}^{+}\hat{L}_{ab}, \hat{\rho}(t)\big]_{+} - 2\hat{L}_{ab}\hat{\rho}(t)\hat{L}_{ab}^{+}\hat{O}\}$$

we arrange the right–hand side somewhat and obtain

$$\frac{\partial}{\partial t}O(t) = \frac{i}{\hbar}\mathrm{tr_S}\Big\{\hat{\rho}(t)\big[H_{\mathrm{S}},\hat{O}\big]_-\} - \frac{1}{2}\sum_{a,b} k_{a\to b}\mathrm{tr_S}\{\hat{\rho}(t)\Big(\big[\hat{L}^+_{ab}\hat{L}_{ab},\hat{O}\big]_+ - 2\hat{L}^+_{ab}\hat{O}\hat{L}_{ab}\Big)\Big\}$$

this can be written in a more compact form as

$$\frac{\partial}{\partial t} < \hat{O} > (t) = \frac{i}{\hbar} < \big[H_{\mathrm{S}},\hat{O}\big]_- > (t) - \frac{1}{2}\sum_{a,b} k_{a\to b} < \big[\hat{L}^+_{ab}\hat{L}_{ab},\hat{O}\big]_+ - 2\hat{L}^+_{ab}\hat{O}\hat{L}_{ab} > (t)$$

the RDO is hidden in this notation what makes it ready for particular approximations (factorizations) of the bracket terms;