CHAPTER I

Density Operator Methods

1 The Nonequilibrium Statistical Operator and the Density Matrix

1.1 The Time-Dependent Schrödinger Equation

state vector notation of the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = H|\Psi(t)\rangle$$

the initial value of the state vector: $|\Psi_0\rangle \equiv |\Psi(t_0)\rangle$

if the Hamiltonian is time-independent a formal solution is given by

$$|\Psi(t)\rangle = e^{-iH(t-t_0)/\hbar}|\Psi_0\rangle$$

introduction of the time-evolution operator

$$U(t,t_0) \equiv U(t-t_0) = e^{-iH(t-t_0)/\hbar}$$

$U(t, t_0)$ is unitary and obeys the following equation of motion

$$i\hbar\frac{\partial}{\partial t}U(t, t_0) = HU(t, t_0)$$

with the initial condition $U(t_0, t_0) = 1$
the time-evolution operator has the important property that it can be decomposed as

$$U(t, t_0) = U(t, t_{N-1})U(t_{N-1}, t_{N-2})\ldots U(t_2, t_1)U(t_1, t_0)$$

where $t_1 \leq t_2 \ldots \leq t_{N-1}$ are arbitrary times in the interval $[t_0, t]$

if the solution of the stationary Schrödinger equation

$$H|\lambda\rangle = E_\lambda|\lambda\rangle$$

with eigenstates $|\lambda\rangle$ and eigenvalues E_λ is known, on can solve the time-dependent Schrödinger equation via an expansion with respect to the states $|\lambda\rangle$

$$|\Psi(t)\rangle = \sum_\lambda c_\lambda(t)|\lambda\rangle$$

$$c_\lambda(t) = \langle\lambda|e^{-iH(t-t_0)/\hbar}|\Psi_0\rangle = \langle\lambda|e^{-iE_\lambda(t-t_0)/\hbar}|\Psi_0\rangle = e^{-iE_\lambda(t-t_0)/\hbar}c_\lambda(t_0)$$

$$|\Psi(t)\rangle = \sum_\lambda c_\lambda(t_0)e^{-iE_\lambda(t-t_0)/\hbar}|\lambda\rangle$$

the superposition state is known as a *wave packet*

since the state vector $|\Psi(t)\rangle$ is given here as a superposition of (time-dependent) states $c_\lambda(t)|\lambda\rangle$, it is alternatively called *coherent* superposition state;

let us calculate the time-dependent expectation value of the operator $\hat{O}$:

$$O(t) = \langle\Psi(t)|\hat{O}|\Psi(t)\rangle = \sum_\lambda c_\lambda^*(t_0) e^{iE_\lambda(t-t_0)/\hbar} \langle\lambda|\hat{O} \sum_\kappa c_\kappa(t_0) e^{-iE_\kappa(t-t_0)/\hbar} |\kappa\rangle$$

$$= \sum_{\lambda,\kappa} c_\lambda^*(t_0) c_\kappa(t_0) \langle\lambda|\hat{O}|\kappa\rangle e^{i(E_\lambda - E_\kappa)(t-t_0)/\hbar}$$

the different time-dependent contributions are determined by *transition frequencies* $\omega_{\lambda\kappa} = (E_\lambda - E_\kappa)/\hbar$

1.2 The Density Operator

elementary quantum mechanics $\rightarrow$ a *complete description* of a system is only possible if a set of observables exists from which all physical quantities can be measured simultaneously;
a set of commuting operators $\{\hat{A}_\alpha\}$ has to exist, i.e., the following relation has to be fulfilled

$$\left[\hat{A}_\alpha, \hat{A}_{\alpha'}\right]_- = \hat{A}_\alpha\hat{A}_{\alpha'} - \hat{A}_{\alpha'}\hat{A}_\alpha = 0$$

if for the considered system the maximal number of such operators is known, a *complete* description can be accomplished; the system is described by a *pure state*;

if the complete measurement of all $\hat{A}_\alpha$ has not been carried out, for example, because the complete set of observables is principally unknown $\rightarrow$ the state of the quantum system has to be described as a *statistical mixture* of pure states $|\Psi_\nu\rangle$;
the probability for a single state to be in the mixture will be denoted by w_ν; the states $|\Psi_\nu\rangle$ are assumed to be ortho-normalized, and therefore the w_ν must satisfy the relation

$$\sum_\nu w_\nu = 1$$

the expectation value of an observable becomes

$$\langle\hat{O}\rangle = \sum_\nu w_\nu \langle\Psi_\nu|\hat{O}|\Psi_\nu\rangle$$

introduction of the *density operator* (the statistical operator)

$$\hat{W} = \sum_{\nu} w_{\nu} |\Psi_{\nu}\rangle\langle\Psi_{\nu}| = \hat{W}^{+}$$

simple notation of the expectation value of any observable using the *trace formula*

$$\langle\hat{O}\rangle = \text{tr}\{\hat{W}\hat{O}\}$$

the abbreviation "tr" is defined as the trace with respect to the matrix formed by all matrix elements which are determined in a complete orthonormal basis $|a\rangle$

$$\text{tr}\{\bullet\} = \sum_{a}\langle a| \bullet |a\rangle$$

therefore we have

$$\text{tr}\{\hat{W}\hat{O}\} = \sum_{a,\nu} w_{\nu}\langle a|\Psi_{\nu}\rangle\langle\Psi_{\nu}|\hat{O}|a\rangle = \sum_{a,\nu} w_{\nu}\langle\Psi_{\nu}|\hat{O}|a\rangle\langle a|\Psi_{\nu}\rangle = \sum_{\nu} w_{\nu}\langle\Psi_{\nu}|\hat{O}|\Psi_{\nu}\rangle$$

taking arbitrary operators $\hat{O}$, $\hat{P}$ and $\hat{Q}$ it is easy to proof the property called *cyclic invariance* of the operator arrangement

$$\text{tr}\{\hat{O}\hat{P}\} = \sum_{a}\langle a|\hat{O}\sum_{b}|b\rangle\langle b|\hat{P}|a\rangle = \sum_{b}\sum_{a}\langle b|\hat{P}|a\rangle\langle a|\hat{O}|b\rangle = \text{tr}\{\hat{P}\hat{O}\}$$

$$\text{tr}\{\hat{O}\hat{P}\hat{Q}\} = \text{tr}\{\hat{O}[\hat{P}\hat{Q}]\} = \text{tr}\{[\hat{P}\hat{Q}]\hat{O}\} = \text{tr}\{\hat{P}[\hat{Q}\hat{O}]\} = \text{tr}\{[\hat{Q}\hat{O}]\hat{P}\}$$

note also

$$\text{tr}\{\hat{W}\} = \sum_{a,\nu} w_{\nu}\langle a|\Psi_{\nu}\rangle\langle\Psi_{\nu}|a\rangle = \sum_{\nu} w_{\nu}\langle\Psi_{\nu}|\Psi_{\nu}\rangle = 1$$

example: the canonical density operator for thermal equilibrium

$$\hat{W}_{\mathrm{eq}} = \frac{1}{\mathcal{Z}} e^{-H/k_{\mathrm{B}}T} = \frac{1}{\mathcal{Z}} \sum_{\alpha} e^{-E_{\alpha}/k_{\mathrm{B}}T} |\alpha\rangle\langle\alpha|$$

$\mathcal{Z}$ is the partition function $\mathrm{tr}\{\exp(-H/k_{\mathrm{B}}T)\}$ ensuring proper normalization of $\hat{W}_{\mathrm{eq}}$;
the second part is obtained using the eigenenergies E_{α} and eigenstates $|\alpha\rangle$ of the Hamiltonian H;

density operator of a pure state $|\Psi\rangle$

$$\hat{W}_{\mathrm{pure}} = |\Psi\rangle\langle\Psi| = \hat{P}_{\Psi}$$

expansion of the state vector $|\Psi\rangle$ with respect to the complete orthogonal basis $|\alpha\rangle$:

$$|\Psi\rangle = \sum_{\alpha} c_{\alpha}|\alpha\rangle$$

introducing this expansion into the expression for the pure state density operator one obtains

$$\hat{W}_{\mathrm{pure}} = \sum_{\alpha,\bar{\alpha}} c_{\alpha} c_{\bar{\alpha}}^{*} |\alpha\rangle\langle\bar{\alpha}| \neq \sum_{\alpha} |c_{\alpha}|^{2} |\alpha\rangle\langle\alpha|$$

there exists a measure which tells us whether the state is a pure state or not: *degree of coherence*

$$C = \mathrm{tr}\{\hat{W}^2\}$$

it takes the value 1 for pure states since the statistical operator in this case is a projector

$$C_{\mathrm{pure}} = \mathrm{tr}\{\hat{W}_{\mathrm{pure}}^2\} = \mathrm{tr}\{\hat{P}_{\Psi}^2\} = \mathrm{tr}\{\hat{P}_{\Psi}\} = \mathrm{tr}\{\hat{W}_{\mathrm{pure}}\} = 1$$

where the projector property $P_{\Psi}^2 = P_{\Psi}$ has been used

for a mixed state it follows that

$$C_{\mathrm{mixed}} = \mathrm{tr}\{\hat{W}^2\} = \sum_{\mu,\nu} w_{\mu} w_{\nu} \, \mathrm{tr}\{\hat{P}_{\Psi_{\mu}} \hat{P}_{\Psi_{\nu}}\} = \sum_{\mu,\nu} \sum_{\alpha} w_{\mu} w_{\nu} \langle\alpha|\Psi_{\mu}\rangle \langle\Psi_{\mu}|\Psi_{\nu}\rangle \langle\Psi_{\nu}|\alpha\rangle$$

$$= \sum_{\mu} \sum_{\alpha} w_{\mu}^2 \langle\Psi_{\mu}|\alpha\rangle \langle\alpha|\Psi_{\mu}\rangle = \sum_{\mu} w_{\mu}^2 \; < \; 1$$

the degree of coherence becomes less than one

1.3 The Density Matrix

we consider a complete orthogonal basis of states $|a\rangle, |b\rangle, \ldots$
the density operator can be expanded as

$$\hat{W} = \sum_{a,b} \langle a|\hat{W}|b\rangle \; |a\rangle\langle b|$$

the expansion coefficients are called *density matrix* and denoted by

$$\rho_{ab} = \langle a|\hat{W}|b\rangle$$

the density matrix fulfills the relation

$$\rho_{ab} = \rho_{ba}^{*}$$

from which one simply deduces

$$\mathrm{Re}\ \rho_{ab} = \mathrm{Re}\ \rho_{ba} \qquad \mathrm{Im}\ \rho_{ab} = -\mathrm{Im}\ \rho_{ba}$$

the diagonal elements of the density matrix are real

$$\rho_{aa} = \mathrm{Re}\ \rho_{aa}$$

one may write

$$\rho_{aa} = \langle a|\hat{W}|a\rangle = \sum_\nu \langle a|w_\nu|\Psi_\nu\rangle\langle\Psi_\nu|a\rangle = \sum_\nu w_\nu |\langle a|\Psi_\nu\rangle|^2 \equiv \sum_\nu w_\nu |c_a(\nu)|^2$$

with the expansion coefficients $c_a(\nu) = \langle a|\Psi_\nu\rangle$;
it shows that ρ_{aa} gives us the probability for the state $|a\rangle$ being contained in the statistical mixture described by $\hat{W}$
taking the off-diagonal matrix elements of the density operator it follows

$$\rho_{ab} = \sum_\nu w_\nu c_a(\nu) c_b^*(\nu)$$

the density matrix ρ_{ab} describes an *incoherent* superposition of contributions from different pure states
depending on the basis set $\{|a\rangle\}$ the different terms on the right-hand side can cancel each other or give a finite ρ_{ab}
the off-diagonal density matrix are also called *coherences*
since the definition of the density matrix represents a quadratic form the Schwarz inequality is valid

$$\rho_{aa}\rho_{bb} \geq |\rho_{ab}|^2$$

the representation of the statistical operator via the density matrix introduced so far is frequently termed *state representation*

if eigenstates of some Hamiltonian are used it is also called *energy representation*

using eigenstates of the coordinate operator

$$|s\rangle = \prod_j |s_j\rangle$$

with coordinate s_j for the jth degree of freedom of the system, consequently, the *coordinate representation* of the statistical operator reads

$$\rho(s, \bar{s}) = \langle s|\hat{W}|\bar{s}\rangle$$

Equation of Motion for the Density Matrix

the probabilities w_ν represent our reduced knowledge about the state of the system;
the state vectors $|\Psi_\nu\rangle$ of the mixed state evolve in time according to the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\Psi_\nu\rangle = H|\Psi_\nu\rangle$$

although any individual state of the mixture changes in time there is no change whatsoever in the amount of our knowledge about the system;
the probabilities w_ν are constant $(w_\nu \neq w_\nu(t))$;
accordingly the time-dependent density operator has the following form

$$\hat{W}(t) = \sum_\nu w_\nu|\Psi_\nu(t)\rangle\langle\Psi_\nu(t)|$$

to derive an equation of motion we note

$$\hat{W}(t) = \sum_\nu w_\nu U(t, t_0)|\Psi_\nu(t_0)\rangle\langle\Psi_\nu(t_0)|U^+(t, t_0) = U(t, t_0)\hat{W}(t_0)U^+(t, t_0)$$

taking the time derivative of this expression it follows

$$\frac{\partial}{\partial t}\hat{W}(t) = -\frac{i}{\hbar}\Big(H\hat{W}(t) - \hat{W}(t)H\Big) \equiv -\frac{i}{\hbar}\Big[H, \hat{W}(t)\Big]_-$$

this equation of motion for the density operator $\hat{W}$ is called *Liouville-von Neumann equation* or *Quantum Liouville equation*; for its solution we have to establish an initial condition $\hat{W}(t_0) = \hat{W}_0$;

we give the Liouville-von Neumann equation in the state representation ($\langle a|H|b \rangle = H_{ab}$)

$$\frac{\partial}{\partial t}\rho_{ab} = -\frac{i}{\hbar}\sum_c \left(H_{ac}\rho_{cb} - H_{cb}\rho_{ac}\right) \equiv -i\frac{H_{aa} - H_{bb}}{\hbar}\rho_{ab} - \frac{i}{\hbar}\sum_{c\neq a} H_{ac}\rho_{cb} + \frac{i}{\hbar}\sum_{c\neq b} H_{cb}\rho_{ac}$$

the difference of the diagonal matrix elements of the Hamiltonian defines the transition frequencies $\omega_{ab} = (H_{aa} - H_{bb})/\hbar$, whereas the off-diagonal matrix elements describe the inter-state coupling

there exists an alternative notation of the Liouville-von Neumann equation using the concept of *superoperators*

$$\mathcal{L}\bullet = \frac{1}{\hbar}[H, \bullet]_-$$

we see that the Liouville-von Neumann equation can be written as

$$\frac{\partial}{\partial t}\hat{W}(t) = -i\mathcal{L}\hat{W}(t)$$

with the solution

$$\hat{W}(t) = e^{-i\mathcal{L}(t-t_0)}\,\hat{W}(t_0)$$

the exponential function of the superoperator is defined via the respective power expansion

one can introduce the *time-evolution superoperator* as follows:

$$\mathcal{U}(t, t_0) = e^{-i\mathcal{L}(t-t_0)}$$

it gives

$$\hat{W}(t) = \mathcal{U}(t, t_0)\hat{W}(t_0) = U(t, t_0)\hat{W}(t_0)U^+(t, t_0)$$

1.5 The Reduced Density Operator and the Reduced Density Matrix

the starting point will be the system-reservoir Hamiltonian

$$H = H_{\mathrm{S}} + H_{\mathrm{S-R}} + H_{\mathrm{R}}$$

a complete basis in the state space of the reservoir is written as $|\alpha\rangle$;
then the *reduced density operator* follows as

$$\hat{\rho}(t) = \sum_{\alpha} \langle \alpha | \hat{W}(t) | \alpha \rangle = \mathrm{tr}_{\mathrm{R}} \left\{ \hat{W}(t) \right\}$$

next we take a basis $|a\rangle$ in the state space of the system and define the *reduced density matrix*

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

the following relation has to be fulfilled

$$\mathrm{tr}_{\mathrm{S}} \{ \hat{\rho}(t) \} \equiv \sum_{a} \rho_{aa}(t) = 1$$

it is easily confirmed if we note that

$$\mathrm{tr}\{ \hat{W}(t) \} = 1 = \sum_{a,\alpha} \langle a | \langle \alpha | \hat{W}(t) | \alpha \rangle | a \rangle$$

an equation of motion for the reduced density matrix is derived by starting from the respective operator equation for the reduced density operator;
from the Liouville-von Neumann equation we obtain

$$\frac{\partial}{\partial t}\hat{\rho}(t) = \mathrm{tr_R}\left\{\frac{\partial}{\partial t}\hat{W}(t)\right\} = -\frac{i}{\hbar}\,\mathrm{tr_R}\left\{\left[H_\mathrm{S} + H_\mathrm{S-R} + H_\mathrm{R}, \hat{W}(t)\right]_-\right\}$$

$$= -\frac{i}{\hbar}\,[H_\mathrm{S}, \hat{\rho}(t)]_- - \frac{i}{\hbar}\,\mathrm{tr_R}\left\{\left[H_\mathrm{S-R} + H_\mathrm{R}, \hat{W}(t)\right]_-\right\}$$

the commutator notation for the reduced density operator is not possible for the contributions proportional to $H_\mathrm{S-R}$ and H_R;

to calculate the commutator with H_R we take into account the cyclic invariance of the trace; as a result the term proportional to H_R vanishes and the equation of motion for the reduced density operator follows as

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}\,[H_\mathrm{S}, \hat{\rho}(t)]_- - \frac{i}{\hbar}\mathrm{tr_R}\{\left[H_\mathrm{S-R}, \hat{W}(t)\right]_-\}$$

we realize that this is not yet a closed equation for the reduced density operator; because of the appearance of $H_\mathrm{S-R}$ in the commutator on the right-hand side it still contains the total density operator;

the effect of the environment can be accounted for by a superoperator $\mathcal{D}$ acting on the reduced density operator

$$-\frac{i}{\hbar}\mathrm{tr}_{\mathrm{R}}\{[H_{\mathrm{S-R}}, \hat{W}(t)]_-\} = -\mathcal{D}\hat{\rho}(t) \equiv -\hat{A}\hat{\rho}(t) - \hat{\rho}(t)\hat{B} - \sum_j \hat{C}_j\hat{\rho}(t)\hat{D}_j$$

the last part of this formula indicates the most general action of the superoperator when represented by different ordinary operators (acting from the left as well as from the right);
we introduce the density matrix where the states $|a\rangle$ are considered as eigenstates of H_{S} with energy $\hbar\omega_a$; the equation of motion can be written as ($\omega_{ab} = \omega_a - \omega_b$)

$$\frac{\partial}{\partial t}\rho_{ab}(t) = -i\omega_{ab}\rho_{ab}(t) - \sum_{c,d} R_{ab,cd}\rho_{cd}(t)$$

the action of the superoperator $\mathcal{D}$ is replaced by the so-called *Redfield tensor* $R_{ab,cd}$;

there exist several theories calculating $R_{ab,cd}$; we will quote the most simple version

$$\sum_{c,d} R_{ab,cd}\rho_{cd} = \delta_{a,b}\sum_c \left(k_{a\to c}\rho_{aa} - k_{c\to a}\rho_{cc}\right) + (1 - \delta_{a,b})\frac{1}{2}\sum_c \left(k_{a\to c} + k_{b\to c}\right)\rho_{ab}$$

it is based on a decoupling of diagonal and off-diagonal density matrix elements;

the diagonal elements obey a rate equation with transition rates $k_{a \to c}$ and $k_{c \to a}$;

the off-diagonal elements follow from an equation including transition frequencies as well as dephasing rates

$$\gamma_{ab} = \frac{1}{2} \sum_c \left(k_{a \to c} + k_{b \to c} \right)$$

they are responsible for the exponential decay of the off-diagonal density matrix elements (the coherences) with increasing time;

the transition rates and, thus, the dephasing rates can be calculated based on a concrete expression for the system-reservoir coupling $H_{\mathrm{S-R}}$;

1.6 The Phenomenon of Decoherence

to get some first insight into the time evolution of the density matrix, the total wave function (at time $t = 0$) is expanded with respect to a complete basis set ϕ_a of the system state space

$$\Psi(s, Z; t = 0) = \sum_a \phi_a(s)\chi_a(Z)$$

the χ_a are wave functions defined in the reservoir state space and follow from

$$\chi_a(Z) = \int ds \, \phi_a^*(s)\Psi(s, Z; t = 0)$$

the summation over the various χ_a can be interpreted as a manifestation of system-reservoir correlations;
the time evolution of the total wave function is determined by the related time-dependent Schrödinger equation, and the expansion similar to that at $t = 0$ reads

$$\Psi(s, Z; t) = \sum_a \phi_a(s)\chi_a(Z, t)$$

now including time dependent reservoir wave functions;

since the total wave function Ψ is normalized we may deduce

$$1 = \sum_a \int dZ \, \chi_a(Z, t)\chi_a^*(Z, t) = \sum_a \langle \chi_a(t)|\chi_a(t)\rangle \equiv \sum_a P_a(t)$$

$P_a(t)$ gives the probability that a particular system state ϕ_a is realized at time t;

the reduced density matrix follows as

$$\rho(s, \bar{s}; t) = \sum_{a,b} \langle \chi_b(t) | \chi_a(t) \rangle \phi_a(s) \phi_b^*(s) = \sum_{a} P_a(t) \phi_a(s) \phi_a^*(\bar{s}) + \sum_{\substack{a,b \\ a \neq b}} \langle \chi_b(t) | \chi_a(t) \rangle \phi_a(s) \phi_b^*(\bar{s})$$

the part proportional to the $P_a(t)$ is different from zero at all times;
the part determined by the overlap expressions $\langle \chi_b(t) | \chi_a(t) \rangle$ of reservoir wave functions belonging to different system states typically decays in time as

$$\langle \chi_b(t) | \chi_a(t) \rangle \sim \exp(-\gamma_{ab} t^r) \quad (r = 1, 2)$$

due to the different time evolution with respect to the two states;
this phenomenon is known as *decoherence*;
while the probabilities P_a to have the system state ϕ_a always sum up to one, interrelations between different system states ϕ_a and ϕ_b expressed by the part of the sum with $a \neq b$ decay;

going from a single system to an ensemble this type of decoherence is complemented by the destructive interference among observables belonging to different members of the ensemble in the course of the time evolution; this phenomenon is frequently termed *dephasing*;

Dynamics of Coupled Multi-Level Systems in a Heat Bath

as a first application of the density operator method we consider two coupled multi-level systems; in particular, a number of approximations are introduced which we will meet again later on;

each multilevel system is described by the energies E_a and E_β, respectively and the coupling between them is due to the matrix element $V_{a\beta}$; for both quantum numbers, i.e. a and β, we use the running indices μ, ν, etc. in the following;

the subject of the following consideration is to derive a closed set of equations of motion for the total population of the state manifold $\{|a\rangle\}$ (the initial state)

$$P_i(t) = \sum_a \rho_{aa}(t) \equiv \sum_a P_a(t)$$

and of the manifold $\{|\beta\rangle\}$ (the final state)

$$P_f(t) = \sum_\beta \rho_{\beta\beta}(t) \equiv \sum_\beta P_\beta(t)$$

the only assumption we will make is that the coupling to the heat bath is much stronger than the interstate coupling $V_{a\beta}$; the rates for transitions within the two manifolds, $k_{a \to a'}$ and $k_{\beta \to \beta'}$ are supposed to be much larger than those for interstate probability transfer;

as a consequence, the populations of the initial and final state can be assumed to be thermalized within the two manifolds on the time-scale of the inter-manifold transfer

$$P_a(t) = P_i(t)\, f_a \qquad P_\beta(t) = P_f(t)\, f_\beta$$

we search for equations of motion obeyed by the total populations P_i and P_f; since the coupling matrix element should be small, a perturbational treatment is appropriate;
we start with an equation of motion for the diagonal elements of the density matrix, $\rho_{\mu\mu} = P_\mu$,

$$\frac{\partial}{\partial t} P_\mu = -\frac{i}{\hbar} \sum_\kappa (V_{\mu\kappa}\rho_{\kappa\mu} - V_{\kappa\mu}\rho_{\mu\kappa}) \equiv \frac{2}{\hbar}\text{Im} \sum_\kappa V_{\mu\kappa}\rho_{\kappa\mu}$$

the off-diagonal density matrix elements which appear on the right-hand side obey

$$\frac{\partial}{\partial t}\rho_{\kappa\mu} = -i\omega_{\kappa\mu}\rho_{\kappa\mu} - \frac{i}{\hbar} \sum_\lambda (V_{\kappa\lambda}\rho_{\lambda\mu} - V_{\lambda\mu}\rho_{\kappa\lambda}) \approx -i\omega_{\kappa\mu}\rho_{\kappa\mu} - \frac{i}{\hbar}V_{\kappa\mu}(\rho_{\mu\mu} - \rho_{\kappa\kappa})$$

since we are looking for the lowest-order approximation in $V_{\mu\nu}$, off-diagonal density matrix elements have been neglected in the second line;
fixing the initial condition as $\rho_{a\beta}(0) = 0$ (absence of a superposition state between both subsystems), we obtain

$$\rho_{\kappa\mu}(t) = -\frac{i}{\hbar} V_{\kappa\mu} \int_0^t d\bar{t}\, e^{-i\omega_{\kappa\mu}(t-\bar{t})} [P_\mu(\bar{t}) - P_\kappa(\bar{t})]$$

inserting the result into the first equation yields (note the replacement of $\bar{t}$ by $t - \tau$)

$$\frac{\partial}{\partial t} P_\mu = -\frac{1}{\hbar^2} \sum_\kappa |V_{\mu\kappa}|^2 \, 2\mathrm{Re} \int_0^t d\tau \, e^{-i\omega_{\kappa\mu}\tau} \left[P_\mu(t - \tau) \; - \; P_\kappa(t - \tau) \right]$$

the total state populations P_i and P_f are obtained by making use of the thermalization condition

$$\frac{\partial}{\partial t} P_i = -\int_0^t d\tau \left[K_{i \to f}(\tau) \, P_i(t - \tau) - K_{f \to i}(\tau) \, P_f(t - \tau) \right]$$

with the integral kernel given by

$$K_{i \to f}(\tau) = \frac{2}{\hbar^2} \sum_{a,\beta} |V_{a\beta}|^2 \, f_a \, \cos(\omega_{a\beta}\tau)$$

the kernel referring to the reverse transition is obtained in replacing f_a by f_β;
interchanging i and f leads to the equation for $P_f(t)$;
the quantity $K_{i \to f}(\tau)$ is usually named *memory kernel*;
the state populations enter the equation at a time τ earlier than t; the system retains the *memory* of its past dynamics;

master equations which include memory effects are called *Generalized Master Equation*;

the time dependence of the memory kernel is determined by the structure of the energy spectrum related to the initial as well as the final state;
if these spectra are dense $K_{if}(\tau)$ would decay in a certain time interval τ_{mem} due to destructive interference;

if τ_{mem} is short compared to the characteristic time where the populations P_i and P_f change, the variation of both quantities within the interval $[t - \tau_{\mathrm{mem}}, t]$ can be neglected;
we can replace $P_i(t - \tau)$ and $P_f(t - \tau)$ by $P_i(t)$ and $P_f(t)$, respectively, in the integrand;
this corresponds to a coarse graining of the time axis; accordingly the populations P_i and P_f are only valid for times much larger than τ_{mem}; therefore, the result of the integration does not change if the upper limit is put to infinity

$$\frac{\partial}{\partial t} P_i = -k_{i \to f}\, P_i(t) + k_{f \to i}\, P_f(t)$$

the transition rates take the form

$$k_{i \to f} = \int_0^\infty dt\; K_{i \to f}(t) = \frac{2}{\hbar^2} \sum_{a,\beta} |V_{a\beta}|^2\, f_a\, \mathrm{Re} \int_0^\infty d\tau\; \exp(i\omega_{a\beta}\tau)$$

we note that $\mathrm{Re}z = (z + z^*)/2$ (where z is an arbitrary complex number) and replace the integral by one along the total time-axis;

using the Fourier representation of the δ-function

$$\delta(\omega) = \frac{1}{2\pi} \int\limits_{-\infty}^{\infty} dt \ e^{i\omega t}$$

we get

$$k_{i \to f} = \frac{2\pi}{\hbar} \sum_{a,\beta} f_a \left| V_{a\beta} \right|^2 \delta(E_a - E_\beta)$$

the derived rate formula is identical to the *Golden Rule* expression of transition rates

it is instructive to view the transition rates from a different perspective; we write

$$K_{i \to f}(t) = \frac{2}{\hbar^2} \operatorname{Re} \sum_{a,\beta} |V_{a\beta}|^2 f_a \, e^{i(E_a - E_\beta)t/\hbar} = \frac{2}{\hbar^2} \operatorname{Re} \sum_{a,\beta} f_a \langle a | e^{iE_a t/\hbar} V e^{-iE_\beta t/\hbar} | \beta \rangle \langle \beta | V | a \rangle$$

introducing the part

$$H_0 = \sum_a E_a |a\rangle \langle a| + \sum_\beta E_\beta |\beta\rangle \langle \beta|$$

of the total Hamiltonian we can replace the energies E_a and E_β by H_0 (the coupling part of the Hamiltonian is denoted by V);
using the completeness relation with respect to the state manifold $|\beta\rangle$ gives

$$K_{i \to f}(t) = \frac{2}{\hbar^2} \operatorname{Re} \sum_a \langle a | \hat{W}_{\mathrm{eq}}^{(i)} e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar} V | a \rangle = 2\operatorname{Re} C_{i \to f}(t)$$

the distribution f_a has been replaced by the equilibrium density operator of the initial state $\hat{W}_{\mathrm{eq}}^{(i)}$;
we introduced the correlation function

$$C_{i \to f}(t) = \frac{1}{\hbar^2} \operatorname{tr}_i \{ \hat{W}_{\mathrm{eq}}^{(i)} V^{(\mathrm{I})}(t) V^{(\mathrm{I})}(0) \}$$

it represents an *autocorrelation function* of the interstate coupling $V^{(\mathrm{I})}(t)$ written in the interaction representation and taken with respect to thermal equilibrium ($\operatorname{tr}_i\{...\}$ abbreviates $\sum_a \langle a|...|a\rangle$);
the memory kernel turns out to be proportional to the autocorrelation function of the inter-state coupling;
a short memory time thus implies a rapid decay of this correlation function;