CHAPTER IV

Non-Equilibrium Green's Function Technique

1 Introduction

we consider transitions between some state $|0\rangle$ with energy E_0 and a continuum of states $|\alpha\rangle$ with energies E_α;
the state $|0\rangle$ is supposed to be initially populated and the transitions into the states $|\alpha\rangle$ are due to some inter-state coupling expressed by $V_{0\alpha}$;
the total system is described by the Hamiltonian

$$H = E_0|0\rangle\langle 0| + \sum_\alpha \Big(E_\alpha|\alpha\rangle\langle\alpha| + V_{0\alpha}|0\rangle\langle\alpha| + V_{\alpha 0}|\alpha\rangle\langle 0| \Big)$$

our goal is to obtain an expression which tells us how the initially prepared state $|0\rangle$ decays into the set of states $|\alpha\rangle$;
this transfer of occupation probability can be characterized by looking at the population of state $|0\rangle$ which reads $P_0(t) = |\langle 0|e^{-iHt/\hbar}|0\rangle|^2$

instead of working with time evolution operator matrix elements we introduce

$$\hat{G}(t) = -i\theta(t)e^{-iHt/\hbar}$$

this quantity is known as the *Green's operator* let us write the Hamiltonian as

$$H = H_0 + H_1 + V$$

H_0 corresponds to level $|0\rangle$ and H_1 covers all levels $|\alpha\rangle$ and the coupling between them is V; the equation of motion for $\hat{G}(t)$ reads

$$i\hbar \frac{\partial}{\partial t} \hat{G}(t) = \hbar \delta(t) + H\hat{G}(t)$$

introducing the Fourier-transform

$$\hat{G}(\omega) = \int dt\ e^{i\omega t} \hat{G}(t)$$

translates the equation of motion into

$$(\omega - H/\hbar)\hat{G}(\omega) = 1$$

we may also compute the Fourier-transformed Green's operator directly which gives

$$\hat{G}(\omega) = -i \int_0^\infty dt\ e^{i\omega t} e^{-iHt/\hbar} = \frac{1}{\omega - H/\hbar + i\varepsilon}$$

the obtained expression has to be understood as the inverse of the operator $\omega - H/\hbar$ with a small imaginary contribution $i\varepsilon$ indicating the form of the solution for $\hat{G}(\omega)$ (it should have a pole below the real axis in the complex frequency plane) to get the time-dependence of the population of level $|0\rangle$ we have to compute

$$P_0(t) = |\langle 0|\hat{G}(t)|0\rangle|^2$$

the respective matrix elements of the Green's operator are deduced from its equation of motion by introducing projection operators;
the operator

$$\hat{\Pi}_0 = |0\rangle\langle 0|$$

projects on the single state $|0\rangle$ and the operator

$$\hat{\Pi}_1 = \sum_\alpha |\alpha\rangle\langle\alpha|$$

on the manifold of states $|\alpha\rangle$;
both projection operators enter the completeness relation

$$\hat{\Pi}_0 + \hat{\Pi}_1 = 1$$

which can be used, e.g., to write $\hat{\Pi}_1 = 1 - \hat{\Pi}_0$

the goal of the following derivation is to obtain an explicit expression for the population $P_0(t)$;
first, we determine the reduced Green's operator

$$\hat{G}_0(t) = \hat{\Pi}_0\hat{G}(t)\hat{\Pi}_0$$

instead of directly focusing on its matrix element with state $|0\rangle$

using the equation of motion for the Fourier-transformed Green's operator $\hat{G}(\omega)$ we may derive an equation for $\hat{G}_0(\omega)$;
by applying $\hat{\Pi}_0$ to the original equation from the left and from the right we get

$$\hat{\Pi}_0(\omega - H/\hbar)\left(\hat{\Pi}_0 + \hat{\Pi}_1\right)\hat{G}(\omega)\hat{\Pi}_0 = \hat{\Pi}_0$$

for further computations we note that

$$\hat{\Pi}_0 H \hat{\Pi}_0 = H_0$$
$$\hat{\Pi}_1 H \hat{\Pi}_1 = H_1$$

and

$$\hat{\Pi}_0 H \hat{\Pi}_1 = \hat{\Pi}_0 V \hat{\Pi}_1$$

it gives

$$(\omega - H_0/\hbar)\hat{G}_0 - \hat{\Pi}_0(V/\hbar)\hat{\Pi}_1 \times \hat{\Pi}_1\hat{G}(\omega)\hat{\Pi}_0 = \hat{\Pi}_0$$

the new quantity $\hat{\Pi}_1\hat{G}(\omega)\hat{\Pi}_0$ obeys

$$\hat{\Pi}_1(\omega - H/\hbar)\left(\hat{\Pi}_0 + \hat{\Pi}_1\right)\hat{G}(\omega)\hat{\Pi}_0 = \hat{\Pi}_1\hat{\Pi}_0 = 0$$

or

$$-\hat{\Pi}_1 V/\hbar\hat{\Pi}_0\hat{G}_0(\omega) + (\omega - H_1/\hbar)\hat{\Pi}_1\hat{G}(\omega)\hat{\Pi}_0 = 0$$

we define

$$[\hat{G}_1^{(0)}(\omega)]^{-1} = \omega - H_1/\hbar$$

what represents the inverse of a zeroth-order Green's operator (it is defined without the coupling V)

then, the equation for $\hat{\Pi}_1 \hat{G}(\omega) \hat{\Pi}_0$ can be rewritten as

$$\hat{\Pi}_1 \hat{G}(\omega) \hat{\Pi}_0 = \hat{G}_1^{(0)}(\omega) \hat{\Pi}_1 (V/\hbar) \hat{\Pi}_0 \hat{G}_0(\omega)$$

if inserted into the equation for $\hat{G}_0$ we obtain

$$\left(\omega - H_0/\hbar - \hat{\Pi}_0 (V/\hbar) \hat{\Pi}_1 \hat{G}_1^{(0)}(\omega) \hat{\Pi}_1 (V/\hbar) \hat{\Pi}_0\right) \hat{G}_0 = \hat{\Pi}_0$$

we analyze the extra term which depends on V and get

$$\hat{\Pi}_0 (V/\hbar) \hat{\Pi}_1 \hat{G}_1^{(0)}(\omega) \hat{\Pi}_1 (V/\hbar) \hat{\Pi}_0 = \frac{1}{\hbar^2} \sum_\alpha \frac{V_{0\alpha} V_{\alpha 0}}{\omega - E_\alpha/\hbar + i\varepsilon} \hat{\Pi}_0 \equiv \hat{\Sigma}(\omega)/\hbar$$

the operator $\hat{\Sigma}$ is the self-energy operator; its introduction gives for the reduced Green's operator

$$\hat{G}_0(\omega) = \frac{\hat{\Pi}_0}{\omega - H_0/\hbar - \hat{\Sigma}(\omega)/\hbar + i\varepsilon}$$

let us separate the self-energy operator into a Hermitian and an anti-Hermitian part

$$\hat{\Sigma}(\omega) = \frac{1}{2}\left(\hat{\Sigma}(\omega) + \hat{\Sigma}^+(\omega)\right) + \frac{1}{2}\left(\hat{\Sigma}(\omega) - \hat{\Sigma}^+(\omega)\right) \equiv \Delta H(\omega) - i\pi\hbar\hat{\Gamma}(\omega)$$

we can write the Hermitian part as

$$\Delta H(\omega) = \hbar \Delta\Omega(\omega) \hat{\Pi}_0$$

and the anti-Hermitian part as

$$\hat{\Gamma}(\omega) = \Gamma(\omega) \hat{\Pi}_0$$

or we write

$$\hat{\Sigma}(\omega) = \Sigma(\omega)\hat{\Pi}_0$$

with

$$\Sigma(\omega) \equiv \hbar\Delta\Omega(\omega) - i\hbar\Gamma(\omega) = \sum_\alpha \mathcal{P}\frac{|V_{0\alpha}|^2}{\hbar\omega - E_\alpha} - i\pi\sum_\alpha |V_{0\alpha}|^2\delta(\hbar\omega - E_\alpha)$$

if the energies E_α form a continuum the summation with respect to α has to be replaced by an integration;
in this case and provided that the coupling constant has no strong dependence on the quantum number α, the variation of the self-energy in the region where $\hbar\omega \approx E_0$ can be expected to be rather weak;
this means that the frequency dependence of $A_{00}(\omega)$ is dominated by the resonance at $\hbar\omega = E_0$;
since this will give the major contribution to the inverse Fourier transform we can approximately replace $\hbar\omega$ in $\Sigma(\omega)$ by E_0;
we note

$$P_0(t) = |\langle 0|\hat{G}(t)|0\rangle|^2 = \left|\langle 0|\int \frac{d\omega}{2\pi}e^{-i\omega t}\hat{G}_0(\omega)|0\rangle\right|^2$$

to carry out the inverse Fourier transformation we replace the quantity $\Sigma(\omega)$ by the frequency-independent value $\Sigma(E_0/\hbar)$ and obtain the desired state population $P_0(t)$ as

$$P_0(t) = \left|\int \frac{d\omega}{2\pi}e^{-i\omega t}\frac{i\hbar}{\hbar\omega - (E_0 + \hbar\Delta\Omega(E_0/\hbar)) + i\hbar\Gamma(E_0/\hbar)}\right|^2 = \theta(t)\ e^{-2\Gamma(E_0/\hbar)t}\ .$$

we will demonstrate an alternative way to introduce for a system-reservoir problem with Hamiltonian

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

the reservoir correlation function;
for this reason we will not ask in which manner the system is influenced by the reservoir but how the reservoir dynamics is modified by the system's motion;
to answer this question it will be sufficient to describe the action of the system on the reservoir via classical time-dependent fields $K_u(t)$;
therefore, we replace $H_{\rm S-R}$ by

$$H_{\rm ext}(t) = \sum_u K_u(t)\Phi_u$$

the Φ_u are the various reservoir operators;
the bath Hamiltonian becomes time-dependent too, and is denoted by

$$\mathcal{H}(t) = H_{\rm R} + H_{\rm ext}(t)$$

as a consequence of the action of the fields $K_u(t)$, the reservoir will be driven out of equilibrium;
but in the case where the actual non-equilibrium state deviates only slightly from the equilibrium this deviation can be linearized with respect to the external perturbations;

we argue that in this limit the expectation value of the reservoir operator Φ_u obeys the relation

$$\langle \Phi_u(t) \rangle = \sum_v \int\limits_{t_0}^{t} d\bar{t}\; \chi_{uv}(t, \bar{t}) K_u(\bar{t})$$

the functions $\chi_{uv}(t, \bar{t})$ are called *linear response functions* or *generalized linear susceptibilities*;

in order to derive an expression for χ_{uv} we start with the definition of the expectation value $\langle \Phi_u(t) \rangle$

$$\langle \Phi_u(t) \rangle = \mathrm{tr}_{\mathrm{R}}\{U(t - t_0)\hat{R}_{\mathrm{eq}} U^+(t - t_0)\Phi_u\}$$

the time-evolution of the reservoir statistical operator starting with the reservoir equilibrium density operator $\hat{R}_{\mathrm{eq}}$ has been explicitly indicated;
the time-evolution operator $U(t, t_0)$ does not depend on $t - t_0$ since the Hamiltonian $\mathcal{H}(t)$ is time-dependent;
to linearize this expression with respect to the external fields $U(t, t_0)$ is first separated into the free part $U_{\mathrm{R}}(t - t_0)$ defined by H_{R}, and the S-operator

$$S(t, t_0) = \hat{T} \exp\Big(-\frac{i}{\hbar} \int\limits_{t_0}^{t} d\tau\; U_{\mathrm{R}}^{+}(\tau - t_0) H_{\mathrm{ext}}(\tau) U_{\mathrm{R}}(\tau - t_0)\Big)$$

in a second step the S-operator is expanded up to first order in $H_{\rm ext}(\tau)$

$$\langle\Phi_u(t)\rangle_{\rm R} \approx {\rm tr}_{\rm R}\big\{\hat{R}_{\rm eq}\Phi_u^{(\rm I)}(t)\big\} - \frac{i}{\hbar}\int\limits_{t_0}^{t} d\bar{t}\;{\rm tr}_{\rm R}\big\{\hat{R}_{\rm eq}\big[\Phi_u^{(\rm I)}(t), \Phi_v^{(\rm I)}(\bar{t})\big]_{-}\big\}\;K_v(\bar{t})$$

here, the time dependence of the reservoir operators $\Phi_u^{(\rm I)}(t)$ is given in the interaction representation;

the linear response function can be identified as (we assume that the equilibrium expectation values of $\hat{\Phi}_u$ vanish)

$$\chi_{uv}(t,\bar{t}) = -\frac{i}{\hbar}\langle\big[\Phi_u^{(\rm I)}(t), \Phi_v^{(\rm I)}(\bar{t})\big]_{-}\rangle_{\rm R}$$

we notice that the right-hand side depends on the time difference $t-\bar{t}$ only, that is, $\chi_{uv}(t,\bar{t}) = \chi_{uv}(t-\bar{t})$; we also obtain $\chi_{uv}(t) = -iC_{uv}^{(-)}(t)/\hbar$;

if we assume $t_0 \to -\infty$ and if we extend $\chi_{uv}(t,\bar{t})$ by the prefactor $\theta(t-\bar{t})$ we may write

$$\langle\Phi_u(t)\rangle = \sum_v \int d\bar{t}\;\chi_{uv}(t,\bar{t})K_u(\bar{t})$$

with

$$\chi_{uv}(t,\bar{t}) = -\frac{i}{\hbar}\theta(t-\bar{t})\langle\big[\Phi_u^{(\rm I)}(t), \Phi_v^{(\rm I)}(\bar{t})\big]_{-}\rangle_{\rm R}$$

a so-called retardet Green's functions has been introduced;

3 Equilibrium Green's Functions

the retardet Green's function formed by two operators $\hat{A}$ and $\hat{B}$ is defined as

$$G_{AB}^{(\mathrm{ret})}(t,t') = -i\theta(t-t')\mathrm{tr}\{\hat{W}_{\mathrm{eq}}\big[\hat{A}(t),\hat{B}(t')\big]_-\}$$

note

$$\hat{W}_{\mathrm{eq}} = \frac{1}{\mathcal{Z}}e^{-iH/k_{\mathrm{B}}T} \qquad \hat{A}(t) = U^+(t)\hat{A}U(t) \qquad U(t) = e^{-iHt/\hbar}$$

it is obvious that

$$G_{AB}^{(\mathrm{ret})}(t,t') = G_{AB}^{(\mathrm{ret})}(t-t')$$

the advanced Green's function reads

$$G_{AB}^{(\mathrm{adv})}(t-t') = i\theta(t'-t)\mathrm{tr}\{\hat{W}_{\mathrm{eq}}\big[\hat{A}(t),\hat{B}(t')\big]_-\}$$

the causal Green's function takes the form

$$G_{AB}^{(\mathrm{cau})}(t-t') = -i\mathrm{tr}\{\hat{W}_{\mathrm{eq}}\hat{T}\hat{A}(t)\hat{B}(t')\}$$

$$= -i\theta(t-t')\mathrm{tr}\{\hat{W}_{\mathrm{eq}}\hat{A}(t)\hat{B}(t')\} - i\theta(t'-t)\mathrm{tr}\{\hat{W}_{\mathrm{eq}}\hat{B}(t')\hat{A}(t)\}$$

Fourier transformed retardet Green's function

$$G_{AB}^{(\mathrm{ret})}(\omega) = \int dt\; e^{i\omega t}G_{AB}^{(\mathrm{ret})}(t) \qquad G_{AB}^{(\mathrm{ret})}(t) = \frac{1}{2\pi}\int dt\; e^{-i\omega t}G_{AB}^{(\mathrm{ret})}(\omega)$$

we use the eigenstates $|a\rangle$ and eigen-energies E_a of H for a more detailed computation

$$G_{AB}^{(\mathrm{ret})}(\omega) = -i \int dt\ e^{i\omega t}\theta(t)\mathrm{tr}\{\hat{W}_{\mathrm{eq}}\big(\hat{A}(t)\hat{B}(0) - \hat{B}(0)\hat{A}(t)\big)\}$$

$$= -i \int dt\ e^{i\omega t}\theta(t) \sum_{a,b} f_a\big(\langle a|\hat{A}(t)|b\rangle\langle b|\hat{B}(0)|a\rangle - \langle a|\hat{B}(0)|b\rangle\langle b|\hat{A}(t)|a\rangle\big)$$

we interchange a and b in the second sum and get ($\omega_{ab} = (E_a - E_b)/\hbar$)

$$G_{AB}^{(\mathrm{ret})}(\omega) = -i \sum_{a,b} \int dt\ e^{i\omega t}\theta(t)(f_a - f_b)e^{i\omega_{ab}t}A_{ab}B_{ba}$$

note the relations

$$A_{ab} = \langle a|\hat{A}|b\rangle \qquad \int dt\ e^{i\omega t}\theta(t) = \frac{i}{\omega + i\epsilon}$$

after time-integration we obtain

$$G_{AB}^{(\mathrm{ret})}(\omega) = \sum_{a,b} \frac{(f_a - f_b)A_{ab}B_{ba}}{\omega_{ab} + i\epsilon}$$

expression is often called *spectral representation* of the Green's function;

the equation of motion reads

$$i\hbar\frac{\partial}{\partial t}G_{AB}^{(\mathrm{ret})}(t) = \hbar\delta(t)\mathrm{tr}\{\hat{W}_{\mathrm{eq}}\big[\hat{A},\hat{B}\big]_-\} - i\theta(t-t')\mathrm{tr}\{\hat{W}_{\mathrm{eq}}\big[-[H,\hat{A}(t)]_-,\hat{B}\big]_-\}$$

a new retardet Green's function has been originated; a perturbation theory can be established by deriving an additional equation of motion for this new function;

4 Zero-Temperature Green's Functions

the system is described by the Hamiltonian

$$H = H_0 + V$$

the ground-state shall be $|\psi_g\rangle$; a respective causal Green's function is defined as

$$G_{AB}^{(\mathrm{cau})}(t-t') = -i\langle\psi_g|\hat{T}\hat{A}(t)\hat{B}(t')|\psi_g\rangle$$

the time-evolution operator has the form

$$e^{-iHt/\hbar} = U(t) = U_0(t)S(t,0)$$

where

$$U_0(t) = e^{-iH_0t/\hbar}$$

the S-operator reads

$$S(t,t') = \hat{T}\exp\Big(-\frac{i}{\hbar}\int_{t'}^{t} d\tau V^{(\mathrm{I})}(\tau - t')\Big) = \hat{T}\exp\Big(-\frac{i}{\hbar}\int_{0}^{t-t'} d\tau' V^{(\mathrm{I})}(\tau')\Big)$$

we define the interaction picture

$$V^{(\mathrm{I})}(\tau) = U_0^{+}(\tau)VU_0(\tau)$$

the causal Green's function is rewritten as

$$G_{AB}^{(\mathrm{cau})}(t-t') = -i\langle\psi_g|\hat{T}S^+(t,0)U_0^+(t)\hat{A}U_0(t)S(t,0)S^+(t',0)U_0^+(t')\hat{B}U_0(t')S(t',0)|\psi_g\rangle$$
$$= -i\langle\psi_g|\hat{T}S^+(t,0)\hat{A}^{(\mathrm{I})}(t)S(t,0)S^+(t',0)\hat{B}^{(\mathrm{I})}(t')S(t',0)|\psi_g\rangle$$

the system ground-state is translated into an arbitrary state taken in the interaction representation

$$|\psi^{(\mathrm{I})}(t)\rangle = S(t,0)|\psi_g\rangle$$

the relation is inverted as

$$|\psi_g\rangle = S(0,t)|\psi^{(\mathrm{I})}(t)\rangle$$

if we replace V by $V(t) = V\exp(-\epsilon|t|)$ we can generate the complete ground-state from the zero-order ground-state $|\psi_g^{(0)}\rangle$ according to the relation (the coupling is switched on adiabatically)

$$|\psi_g\rangle = S(0,-\infty)|\psi_g^{(0)}\rangle$$

of course, at the end of all computations we have to take the limit $\epsilon \to 0$;

the Green's function can be written as

$$G_{AB}^{(\mathrm{cau})}(t-t') = -i\langle\psi_g^{(0)}|S^+(0,-\infty)\hat{T}S^+(t,0)\hat{A}^{(\mathrm{I})}(t)S(t,t')\hat{B}^{(\mathrm{I})}(t')S(t',0)S(0,-\infty)|\psi_g^{(0)}\rangle$$

in order to rewrite $\langle\psi_g^{(0)}|S^+(0,-\infty)$ into $\langle\psi_g^{(0)}|S(\infty,0)$ we consider

$$S(0,-\infty)|\psi_g^{(0)}\rangle = S(0,-\infty)S(-\infty,\infty)S(\infty,-\infty)|\psi_g^{(0)}\rangle = S(0,\infty)|\psi_g^{(0)}\rangle\langle\psi_g^{(0)}|S(\infty,-\infty)|\psi_g^{(0)}\rangle$$

since $S(\infty,-\infty)$ moves the zero-order ground-state back to itself (times a phase factor) it is correct to replace $S(-\infty,\infty)S(\infty,-\infty)$ by $S(-\infty,\infty)|\psi_g^{(0)}\rangle\langle\psi_g^{(0)}|S(\infty,-\infty)$;

since $\langle\psi_g^{(0)}|S(\infty,-\infty)|\psi_g^{(0)}\rangle$ is a phase factor it's inverse is identical with the conjugated complex expression; so we get

$$\langle\psi_g^{(0)}|S^+(0,-\infty) = \langle\psi_g^{(0)}|S(\infty,-\infty)|\psi_g^{(0)}\rangle^*\langle\psi_g^{(0)}|S^+(0,\infty) = \frac{\langle\psi_g^{(0)}|S(\infty,0)}{\langle\psi_g^{(0)}|S(\infty,-\infty)|\psi_g^{(0)}\rangle}$$

the causal Green's function takes the form

$$G_{AB}^{(\mathrm{cau})}(t-t') = -i\frac{\langle\psi_g^{(0)}|S(\infty,0)\hat{T}S(0,t)\hat{A}^{(\mathrm{I})}(t)S(t,t')\hat{B}^{(\mathrm{I})}(t')S(t',0)S(t_0,-\infty)|\psi_g^{(0)}\rangle}{\langle\psi_g^{(0)}|S(\infty,-\infty)|\psi_g^{(0)}\rangle}$$

we abbreviate $S=S(\infty,-\infty)$ and arrive finally at

$$G_{AB}^{(\mathrm{cau})}(t-t') = -i\frac{\langle\psi_g^{(0)}|\hat{T}S\hat{A}^{(\mathrm{I})}(t)\hat{B}^{(\mathrm{I})}(t')|\psi_g^{(0)}\rangle}{\langle\psi_g^{(0)}|S|\psi_g^{(0)}\rangle}$$

Green's Functions of an Electron Gas

electrons of a single band of a metal interacting via the Coulomb potential

$$H = \sum_{\mathbf{k},s} E_{\mathbf{k}} a^+_{\mathbf{k}s} a_{\mathbf{k}s} + \frac{1}{2} \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}} \sum_{s,s'} v_{\mathbf{k}\mathbf{k}'}(\mathbf{q}) a^+_{\mathbf{k}+\mathbf{q}s} a^+_{\mathbf{k}'-\mathbf{q}s'} a_{\mathbf{k}'s'} a_{\mathbf{k}s}$$

$$G^{(\mathrm{cau})}(\mathbf{k}st, \mathbf{k}'s't') = -i \frac{\langle \psi_g^{(0)} | \hat{T} S a^{(\mathrm{I})}_{\mathbf{k}s}(t) a^{(\mathrm{I})+}_{\mathbf{k}'s'}(t') | \psi_g^{(0)} \rangle}{\langle \psi_g^{(0)} | S | \psi_g^{(0)} \rangle}$$