

4 Quantum State Diffusion Method II: Coherent State Expansion

the approach is valid for reservoirs which are formed by decoupled harmonic oscillators

4.1 Coherent States of a Harmonic Oscillator

The Displacement Operator

Hamiltonian of a 1d harmonic oscillator $H = \frac{1}{2}(\hat{p}^2 + \omega^2 \hat{q}^2)$

annihilation operator

$$a = \sqrt{\frac{\omega}{2\hbar}} \hat{q} + \frac{i}{\sqrt{2\hbar\omega}} \hat{p} \quad \hat{q} = \sqrt{\frac{\hbar}{2\omega}} (a + a^\dagger) \quad \hat{p} = -i\sqrt{\frac{\hbar\omega}{2}} (a - a^\dagger)$$

oscillator eigenstate $|N\rangle = \frac{C^{+N}}{\sqrt{N!}} |0\rangle$

oscillator wave function $\chi_N(q) = \langle q|N\rangle$

displaced wave function

$$\chi_N(q - q_0) = \sum_{n=0}^{\infty} \frac{(-q_0)^n}{n!} \frac{d^n}{dq^n} \chi_N(q) = \exp\left(-\frac{i}{\hbar} q_0 \hat{p}\right) \chi_N(q)$$

displacement operator $D^+(\alpha) = \exp(\alpha(a - a^\dagger))$

Coherent States

Bargmann coherent states: not renormalized, α is a complex number,

$$|\alpha\rangle = e^{\alpha a^+} |0\rangle = \sum_n \frac{\alpha^n}{\sqrt{n!}} |n\rangle$$

states are eigenstates of the oscillator annihilation operator

$$a|\alpha\rangle = \sum_n \frac{\alpha^n}{\sqrt{(n-1)!}} |n-1\rangle = \alpha|\alpha\rangle$$

action of the creation operator

$$a^+|\alpha\rangle = \sum_n \frac{\alpha^n}{\sqrt{n!}} a^+ |n\rangle = \sum_n (n+1) \frac{\alpha^n}{\sqrt{(n+1)!}} |n+1\rangle = \frac{\partial}{\partial \alpha} \sum_n \frac{\alpha^{n+1}}{\sqrt{(n+1)!}} |n+1\rangle = \frac{\partial}{\partial \alpha} |\alpha\rangle$$

normalization

$$\langle \alpha | \beta \rangle = \sum_m \frac{\alpha^{*m}}{\sqrt{m!}} \sum_n \frac{\alpha^n}{\sqrt{n!}} \langle m | n \rangle = \sum_m \frac{(\alpha^* \beta)^m}{m!} = e^{\alpha^* \beta}$$

oscillator coordinate expectation value

$$\langle \alpha | \hat{q} | \alpha \rangle = \sqrt{\frac{\hbar}{2\omega}} \langle \alpha | a + a^+ | \alpha \rangle = \sqrt{\frac{\hbar}{2\omega}} \langle \alpha | \alpha + \alpha^* | \alpha \rangle = \sqrt{\frac{2\hbar}{\omega}} \operatorname{Re} \alpha e^{|\alpha|^2}$$

completeness relation

$$\frac{1}{\pi} \int d^2\alpha e^{-|\alpha|^2} |\alpha\rangle\langle\alpha| = 1$$

since the coherent states are not normalized the additional factor $1/\pi \times e^{-|\alpha|^2}$ appears;

$$\frac{1}{\pi} \int d^2\alpha e^{-|\alpha|^2} |\alpha\rangle\langle\alpha| = \frac{1}{\pi} \int d^2\alpha e^{-|\alpha|^2} \sum_m \frac{\alpha^{*m}}{\sqrt{m!}} |m\rangle \sum_n \frac{\alpha^n}{\sqrt{n!}} \langle n| = \sum_{m,n} |m\rangle\langle n| \frac{1}{\pi \sqrt{m!n!}} \int d^2\alpha e^{-|\alpha|^2} \alpha^{*m} \alpha^n$$

the α -integral is computed in changing to polar coordinates $|\alpha|$ and φ in the complex α -plane

$$\begin{aligned} \int d^2\alpha e^{-|\alpha|^2} \alpha^{*m} \alpha^n &= \int_0^\infty |\alpha| d|\alpha| \int_0^{2\pi} d\varphi e^{-|\alpha|^2} |\alpha|^{m+n} e^{-i\varphi(m-n)} \\ &= \delta_{m,n} 2\pi \int_0^\infty d|\alpha| e^{-|\alpha|^2} |\alpha|^{2n+1} = \delta_{m,n} 2\pi n! / 2 = \delta_{m,n} \pi n! \end{aligned}$$

it remains

$$\frac{1}{\pi} \int d^2\alpha e^{-|\alpha|^2} |\alpha\rangle\langle\alpha| = \sum_n |n\rangle\langle n| \frac{\pi n!}{\pi n!} = 1$$

Equilibrium Density Operator Expansion

$$\hat{R}_{\text{eq}} = e^{-H/k_{\text{B}}T} / \text{tr}\{e^{-H/k_{\text{B}}T}\}$$

state sum

$$\mathcal{Z} = \text{tr}\{e^{-H/k_{\text{B}}T}\} = 1 + n_{\text{BE}}(\omega)$$

Bose-Einstein distribution

$$n_{\text{BE}}(\omega) = \frac{1}{e^{\hbar\omega/k_{\text{B}}T} - 1}$$

we set $\hbar\omega/k_{\text{B}}T = x$ and consider

$$e^{-xa+a}|\alpha\rangle = e^{-xa+a} \sum_n \frac{\alpha^n}{\sqrt{n!}}|n\rangle = \sum_n \frac{\alpha^n}{\sqrt{n!}}e^{-xn}|n\rangle = \sum_n \frac{(\alpha e^{-x})^n}{\sqrt{n!}}|n\rangle = |\alpha e^{-x}\rangle$$

we may conclude

$$e^{-xa+a} = e^{-xa+a/2} \int \frac{d^2\alpha}{\pi} e^{-|\alpha|^2} |\alpha\rangle \langle \alpha| e^{-xa+a/2} = \int \frac{d^2\alpha}{\pi} e^{-|\alpha|^2} |\alpha e^{-x/2}\rangle \langle \alpha e^{-x/2}|$$

we introduce $\theta = e^{-x/2}$ and get for the complete equilibrium statistical operator

$$\frac{e^{-xa+a}}{\mathcal{Z}} = \int \frac{d^2\alpha}{\pi} e^{-|\alpha|^2} \frac{1}{\mathcal{Z}} |\theta\alpha\rangle \langle \theta\alpha|$$

4.2 Density Operator of a Quantum Particle Coupled to Phonons

The Model

quantum particle which moves across localization sites (charge migration in a molecular complex or disordered semiconductor)

$$H_S = \sum_{m,n} h_{mn} |\varphi_m\rangle \langle \varphi_n|$$

in the framework of an open quantum system approach the moving particle is considered as the active system;

the φ_m describe states localized at site m ;

the Hamiltonian matrix is

$$h_{mn} = \delta_{m,n} E_m + (1 - \delta_{m,n}) V_{mn}$$

expression covers site-energies E_m and inter-site transfer couplings V_{mn} ;

site-localized harmonic vibrations form the reservoir (heat bath)

$$H_R = \sum_{m,j} \hbar \omega_{mj} a_{mj}^+ a_{mj}$$

vibrations undergo a rearrangement if the particle arrives at a particular site;

if the vibrational frequencies are not affected and if only the normal modes become displaced we arrive at the following system-reservoir coupling

$$H_{S-R} = \sum_{m,j} K_{mj} (a_{mj} + a_{mj}^+) |\varphi_m\rangle \langle \varphi_m|$$

wave function defined in Schrödinger picture: $\Psi^{(S)}(t)$;
translation of the wave function in a particular interaction picture

$$|\Psi^{(S)}(t)\rangle = U_R(t)|\Psi(t)\rangle \equiv \exp(-iH_R t/\hbar)|\Psi(t)\rangle$$

related Hamiltonian follows as

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = U_R^\dagger(t) \left(-H_R + i\hbar \frac{\partial}{\partial t} \right) |\Psi^{(S)}(t)\rangle = H(t) |\Psi(t)\rangle$$

$$\begin{aligned} H(t) &= U_R^\dagger(t) (H_S + H_{S-R}) U_R(t) = \sum_{m,n} (h_{mn} + \delta_{m,n} \sum_j K_{mj} (a_{mj} e^{-i\omega_{mj}t} + a_{mj}^+ e^{i\omega_{mj}t})) |\varphi_m\rangle \langle \varphi_n| \\ &\equiv H_S + \hat{F}(t) \end{aligned}$$

generalized force operator

$$\hat{F}(t) = \sum_m \hat{F}_m(t) \hat{P}_m$$

$$\hat{F}_m(t) = \sum_j K_{mj} (a_{mj} e^{-i\omega_{mj}t} + a_{mj}^+ e^{i\omega_{mj}t})$$

time evolution operator $U(t)$ is introduced according to

$$i\hbar \frac{\partial}{\partial t} U(t) = H(t) U(t)$$

statistical operator

$$\hat{W}^{(S)}(t) = U_R(t)\hat{W}(t)U_R^+(t)$$

reduced statistical operator

$$\hat{\rho}(t) = \text{tr}_R\{\hat{W}(t)\} = \text{tr}_R\{U_R^+(t)\hat{W}^{(S)}(t)U_R(t)\} = \text{tr}_R\{\hat{W}^{(S)}(t)\}$$

generalization of the coherent states to the case of many vibrational modes

$$|\alpha\rangle = \prod_{m,j} |\alpha_{mj}\rangle$$

the completeness relation is understood as follows

$$\prod_{m,j} \frac{1}{\pi} \int d^2\alpha_{mj} e^{-|\alpha_{mj}|^2} |\alpha_{mj}\rangle\langle\alpha_{mj}| \equiv \int d\alpha e^{-|\alpha|^2} |\alpha\rangle\langle\alpha|$$

the expansion of an arbitrary state vector reads

$$|\Psi(t)\rangle = \int d\alpha e^{-|\alpha|^2} |\alpha\rangle |\psi_\alpha(t)\rangle$$

with

$$|\psi_\alpha(t)\rangle = \langle\alpha|\Psi(t)\rangle$$

Zero-Temperature Case for the Reservoir

we derive an expression for the reduced density operator;
the initial value of the complete statistical operator shall take the form

$$\hat{W}(t=0) = |\psi(0)\rangle\langle\psi(0)| \times |0\rangle\langle 0|$$

$|\psi(0)\rangle$ is the active system initial state and $|0\rangle$ denotes the overall reservoir oscillator ground-state

the reduced density operator can be rewritten

$$\begin{aligned}\hat{\rho}(t) &= \text{tr}_R\{\hat{W}(t)\} = \text{tr}_R\{U(t)|\psi(0)\rangle\langle\psi(0)| \times |0\rangle\langle 0|U^\dagger(t)\} \\ &= \int d\alpha e^{-|\alpha|^2} \langle\alpha|U(t)|0\rangle|\psi(0)\rangle\langle\psi(0)|\langle 0|U^\dagger(t)|\alpha\rangle = \int d\alpha e^{-|\alpha|^2} |\psi_\alpha(t)\rangle\langle\psi_\alpha(t)|\end{aligned}$$

with the state vector exclusively defined in the active system state space

$$|\psi_\alpha(t)\rangle = \langle\alpha|U(t)|0\rangle|\psi(0)\rangle$$

the reduced density operator is obtained as a superposition of time-dependent projectors $|\psi_\alpha(t)\rangle\langle\psi_\alpha(t)|$

Case of Finite Temperature for the Reservoir

the initial state is considered as a mixed state

$$\hat{W}(t=0) = |\psi(0)\rangle\langle\psi(0)|\hat{R}_{\text{eq}}$$

with thermal vibrational distribution

$$\hat{R}_{\text{eq}} = e^{-H_{\text{R}}/k_{\text{B}}T} / \text{tr}_{\text{R}}\{e^{-H_{\text{R}}/k_{\text{B}}T}\}$$

because of the harmonic model we get

$$\mathcal{Z} = \text{tr}_{\text{R}}\{e^{-H_{\text{R}}/k_{\text{B}}T}\} = \prod_{m,j} (1 + n_{\text{BE}}(\omega_{mj}))$$

with Bose-Einstein distribution

$$n_{\text{BE}}(\omega_{mj}) = \frac{1}{e^{\hbar\omega_{mj}/k_{\text{B}}T} - 1}$$

the reduced density operator follows as

$$\hat{\rho}(t) = \text{tr}_{\text{R}}\{U(t)|\psi(0)\rangle\langle\psi(0)|\hat{R}_{\text{eq}}U^+(t)\} = \int d\alpha e^{-|\alpha|^2} \int d\beta e^{-|\beta|^2} \langle\alpha|U(t)|\psi(0)\rangle\langle\psi(0)|\hat{R}_{\text{eq}}|\beta\rangle\langle\beta|U^+(t)|\alpha\rangle$$

we note

$$\begin{aligned} \int d\beta e^{-|\beta|^2} \hat{R}_{\text{eq}}|\beta\rangle\langle\beta| &= \frac{1}{\mathcal{Z}} \prod_{m,j} \left\{ \int \frac{d^2\beta_{mj}}{\pi} \exp(-|\beta_{mj}|^2) \times |\theta_{mj}\beta_{mj}\rangle\langle\theta_{mj}\beta_{mj}| \right\} \\ &= \frac{1}{\mathcal{Z}} \int d\beta e^{-|\beta|^2} |\theta\beta\rangle\langle\theta\beta| \end{aligned}$$

the reduced density operator takes the form

$$\begin{aligned}\hat{\rho}(t) &= \frac{1}{\mathcal{Z}} \int d\alpha d\beta e^{-|\alpha|^2 - |\beta|^2} \langle \alpha | U(t) | \theta \beta \rangle | \psi(0) \rangle \langle \psi(0) | \langle \theta \beta | U^\dagger(t) | \alpha \rangle \\ &= \int d\alpha d\beta e^{-|\alpha|^2 - |\beta|^2} | \psi(t; \alpha, \theta \beta) \rangle \langle \psi(t; \alpha, \theta \beta) | \end{aligned}$$

we again introduced state vectors which are only defined in the state-space of the active system

$$| \psi(t; \alpha, \theta \beta) \rangle = \frac{1}{\sqrt{\mathcal{Z}}} \langle \alpha | U(t) | \theta \beta \rangle | \psi(0) \rangle$$

to achieve an initial normalization we note $| \psi(t = 0; \alpha, \theta \beta) \rangle = \langle \alpha | \theta \beta \rangle / \sqrt{\mathcal{Z}} \times | \psi(0) \rangle$

4.3 Quantum State Diffusion

Zero-Temperature Case

we derive a Schrödinger equation for the state vectors $|\psi_\alpha(t)\rangle = \langle\alpha|U(t)|0\rangle|\psi(0)\rangle$ which define the reduced density operator;

it follows

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}|\psi_\alpha(t)\rangle &= \langle\alpha|H(t)U(t)|0\rangle|\psi(0)\rangle \\ &= \langle\alpha|\left(H_S + \sum_{m,j}\hat{P}_mK_{mj}(a_{mj}e^{-i\omega_{mj}t} + a_{mj}^+e^{i\omega_{mj}t})\right)U(t)|0\rangle|\psi(0)\rangle \\ &= \left(H_S + \sum_{m,j}\hat{P}_mK_{mj}\alpha_{mj}^*e^{i\omega_{mj}t}\right)\langle\alpha|U(t)|0\rangle|\psi(0)\rangle + \sum_{m,j}\hat{P}_mK_{mj}e^{-i\omega_{mj}t}\langle\alpha|a_{mj}U(t)|0\rangle|\psi(0)\rangle \end{aligned}$$

we may replace

$$\langle\alpha|a_{mj}U(t)|0\rangle = \left(\langle 0|U(t)a_{mj}^+|\alpha\rangle\right)^* = \frac{\partial}{\partial\alpha_{mj}^*}\langle\alpha|U(t)|0\rangle$$

we can also treat this term by replacing $a_{mj}U(t)$ by $U(t)a_{mj}(t)$ with $a_{mj}(t) = U^+(t)a_{mj}U(t)$ a time-derivative results in

$$i\hbar\frac{\partial}{\partial t}a_{mj}(t) = U^+(t)[a_{mj}, H(t)]_+U(t) = K_{mj}e^{i\omega_{mj}t}U^+(t)\hat{P}_mU(t)$$

we integrate

$$a_{mj}(t) = a_{mj} - \frac{i}{\hbar} \int_0^t d\tau K_{mj} e^{i\omega_{mj}\tau} U^+(\tau) \hat{P}_m U(\tau)$$

this expression indicates the vibrational displacement upon electronic excitation;
in a next step we get

$$\begin{aligned} \langle \alpha | U(t) a_{mj}(t) | 0 \rangle &= \langle \alpha | U(t) a_{mj} | 0 \rangle - \frac{i}{\hbar} \int_0^t d\tau K_{mj} e^{i\omega_{mj}\tau} \langle \alpha | U(t) U^+(\tau) \hat{P}_m U(\tau) | 0 \rangle \\ &= -\frac{i}{\hbar} \int_0^t d\tau K_{mj} e^{i\omega_{mj}\tau} \langle \alpha | U(t - \tau) \hat{P}_m U(\tau) | 0 \rangle \end{aligned}$$

a second-order description with respect to the system-reservoir coupling is achieved if we replace $U(t - \tau)$ by $U_S(t - \tau)$

$$\begin{aligned} \langle \alpha | U(t - \tau) \hat{P}_m U(\tau) | 0 \rangle | \psi(0) \rangle &\approx \langle \alpha | U_S(t - \tau) \hat{P}_m U(\tau) | 0 \rangle | \psi(0) \rangle + \langle \alpha | U(t - \tau) \hat{P}_m U_S(\tau) | 0 \rangle | \psi(0) \rangle \\ &= U_S(t - \tau) \hat{P}_m \langle \alpha | U(\tau) | 0 \rangle | \psi(0) \rangle + \langle \alpha | U(t - \tau) | 0 \rangle \hat{P}_m U_S(\tau) | \psi(0) \rangle \approx U_S(t - \tau) \hat{P}_m | \psi_\alpha(\tau) \rangle \end{aligned}$$

the Schrödinger equation follows as

$$i\hbar \frac{\partial}{\partial t} | \psi_\alpha(t) \rangle = \left(H_S + \sum_{m,j} \hat{P}_m K_{mj} \alpha_{mj}^* e^{i\omega_{mj}t} \right) | \psi_\alpha(t) \rangle - \frac{i}{\hbar} \sum_{m,j} \int_0^t d\tau K_{mj}^2 e^{-i\omega_{mj}(t-\tau)} \hat{P}_m U_S(t - \tau) \hat{P}_m | \psi_\alpha(\tau) \rangle$$

we note the definition of the spectral density (no separation of a frequency factor)

$$\sum_j K_{mj}^2 e^{-i\omega_{mj}t} = \hbar^2 \int d\omega e^{-i\omega t} J_m(\omega) = 2\pi\hbar^2 J_m(t)$$

and neglect memory effects

$$|\psi_\alpha(t)\rangle = U(t, \tau)|\psi_\alpha(\tau)\rangle \approx U_S(t - \tau)|\psi_\alpha(\tau)\rangle$$

the convolution-less Schrödinger equation follows as

$$i\hbar \frac{\partial}{\partial t} |\psi_\alpha(t)\rangle = \left(H_S + \sum_{m,j} \hat{P}_m K_{mj} \alpha_{mj}^* e^{i\omega_{mj}t} \right) |\psi_\alpha(t)\rangle - 2\pi i \hbar \sum_m \int_0^t d\tau J_m(t-\tau) \hat{P}_m U_S(t-\tau) \hat{P}_m U_S^+(t-\tau) |\psi_\alpha(t)\rangle$$

stochastic force

$$\mathcal{F}_m(t) = \sum_j K_{mj} \alpha_{mj}^* e^{i\omega_{mj}t}$$

interaction representation

$$\hat{P}_m^{(I)}(-t) = U_S(t) \hat{P}_m U_S^+(t)$$

final form of the Schrödinger equation ($\bar{t} = t - \tau$)

$$i\hbar \frac{\partial}{\partial t} |\psi_\alpha(t)\rangle = \left(H_S + \sum_m \mathcal{F}_m(t) \hat{P}_m \right) |\psi_\alpha(t)\rangle - 2\pi i \hbar \sum_m \int_0^t d\bar{t} J_m(\bar{t}) \hat{P}_m \hat{P}_m^{(I)}(-\bar{t}) |\psi_\alpha(t)\rangle$$

Realization of Complex Noise

zero-temperature correlation function

$$\begin{aligned} \hbar^2 C_m(t - \tau) &= \langle \mathcal{F}_m(t) \mathcal{F}_m^*(\tau) \rangle \equiv \int d\alpha e^{-|\alpha|^2} \sum_j K_{mj} \alpha_{mj}^* e^{i\omega_{mj}t} \sum_{j'} K_{mj'} \alpha_{mj'} e^{-i\omega_{mj'}\tau} \\ &= \int \frac{d^2\alpha_{mj}}{\pi} e^{-|\alpha_{mj}|^2} \sum_j K_{mj}^2 \alpha_{mj}^* \alpha_{mj} e^{i\omega_{mj}(t-\tau)} \equiv 2\pi\hbar^2 J_m(t) \end{aligned}$$

we consider the α -integration and change in a first step from $\alpha = \text{Re}\alpha + i\text{Im}\alpha$ to polar coordinates $|\alpha|$ and φ

$$\int \frac{d^2\alpha}{\pi} e^{-|\alpha|^2} \alpha^* \alpha \dots = \frac{1}{\pi} \int_0^\infty d|\alpha| |\alpha| \int_0^{2\pi} d\varphi e^{-|\alpha|^2} |\alpha| e^{-i\varphi} |\alpha| e^{i\varphi} \dots$$

new variables $A = \exp(-|\alpha|^2)$ and $B = \varphi/2\pi$ are introduced which both vary between zero and one;

we note $|\alpha| = \sqrt{-\ln A}$ and $dA = \exp(-|\alpha|^2) \times (-2|\alpha|)d|\alpha|$

$$\int \frac{d^2\alpha}{\pi} e^{-|\alpha|^2} \alpha^* \alpha \dots = \int_0^1 dA dB X^*(A, B) X(A, B)$$

we introduced $X(A, B) = \sqrt{-\ln A}(\cos 2\pi B + i \sin 2\pi B)$

we replace the summation with respect to the intramolecular vibrations by a frequency summation (with respect to a finite separation of the frequency axis)

$$\sum_j K_{mj}^2 e^{-i\omega_{mj}t} = \hbar^2 \int d\omega J_m(\omega) e^{-i\omega t} \approx \hbar^2 \sum_k \Delta\omega J_m(\omega_k) e^{-i\omega_k t}$$

the correlation function is rewritten according to

$$\begin{aligned} \langle \mathcal{F}_m(t) \mathcal{F}_m^*(\tau) \rangle &\equiv \int d\alpha e^{-|\alpha|^2} \sum_j K_{mj} \alpha_{mj}^* e^{i\omega_{mj}t} \sum_{j'} K_{mj'} \alpha_{mj'} e^{-i\omega_{mj'}\tau} \\ &= \prod_l \left(\int_0^1 dA_l dB_l \right) \hbar \sum_k \sqrt{\Delta\omega J_m(\omega_k)} X^*(A_k, B_k) e^{i\omega_k t} \times \hbar \sum_{k'} \sqrt{\Delta\omega J_m(\omega_{k'})} X(A_{k'}, B_{k'}) e^{-i\omega_{k'}\tau} \end{aligned}$$

this relation presents a way of determining the stochastic forces

$$\mathcal{F}_m(t) = \hbar \sum_k \sqrt{\Delta\omega J_m(\omega_k)} X^*(A_k, B_k) e^{i\omega_k t}$$

for every k (and m) the A_k and B_k are chosen randomly between zero and one

it results a particular realization η of the time-dependent function $\mathcal{F}_m(t)$

the solution of the time-dependent Schrödinger equation gives a particular wave function $|\psi_\eta(t)\rangle$

the density operator follows as

$$\hat{\rho}(t) = \frac{1}{N} \sum_\eta |\psi_\eta(t)\rangle \langle \psi_\eta(t)|$$