Chapter 8
Nonlinear system-bath interactions: A quantum Fokker-Planck approach

8.1 Introduction

Femtosecond nonlinear optical spectroscopies can provide valuable information on the dynamic characteristics of condensed phase systems [1-9]. Usually, these experiments are described by a response function formalism [6,10], which is based on a perturbative expansion of the optical polarization in powers of the applied electric field, as was briefly reviewed in Sec. 2.2. For the calculation of the (non)linear optical response functions one commonly assumes a certain functional form for the Hamiltonian of the medium, which allows for the derivation of closed form expressions. A typical example for this strategy is given in chapter 3 where the third- and fifth-order Raman response was calculated [11,12].

Dissipation and dephasing can be incorporated at different levels of sophistication. In vibrational spectroscopies population and phase relaxation are often modeled by phenomenological level-dependent decay rates [12-16], which can be included without major problems as was discussed in Sec. 3.4. However, these rates reflect the intermolecular dynamics in a rather indirect way. Frequency fluctuations with a finite correlation time can be described by the stochastic model of Anderson and Kubo, see Sec. 3.6 [17-22]. A microscopic description of the dissipation of energy was presented in Sec. 3.7 where the Brownian oscillator model was briefly reviewed [6,11,23-27].

In this chapter the nonlinear optical response is calculated by using the quantum Fokker-Planck equation [28-31], which has several advantages compared to the methods described above. To derive closed-form expressions for the response functions, one has to know the wavefunctions and transition matrix elements of the system Hamiltonian, cf. Sec. 3.2. Therefore, this strategy can be applied basically only to harmonic systems as was discussed in Sec. 3.3; the influence of small anharmonicities can then be treated by perturbation theory as was shown by Okumura and Tanimura [32-36]. The quantum Fokker-Planck equation, on the other hand, can be used for
potentials with an arbitrary shape and has been applied to Morse potentials [37] and displaced multistate systems [38].

Moreover, this method allows for a sophisticated description of relaxation phenomena. For a Gaussian-Markovian heat bath with a finite correlation time, a hierarchy of equations of motions can be obtained from the Fokker-Planck equation as was shown by Tanimura and Kubo [39,40]. This technique allows for the description of non-Markovian dynamics, but in contrast to the Kubo-Anderson model [17-21] the relaxation is now explicitly temperature dependent. Because it surpasses the traditional master equation approach, the hierarchy of equations of motions is often called doctor equation. Recently this method was applied to a harmonic oscillator and a double-well potential [41], tunneling of a quantum barrier in a dissipative system [42] and a three level system with Morse potential surfaces [43].

Up to now, the quantum Fokker-Planck approach has been applied only to systems, which were linearly coupled to a harmonic heat bath [28,29,37,39-43]. In this way it is possible to describe energy relaxation out of the system into the heat bath as was shown by Feynman and coworkers [23,24]. For harmonic potentials, linear coupling between the system and a continuous set of harmonic bath oscillators is, however, insufficient to induce pure dephasing. The loss of phase coherence can be achieved by anharmonic system or bath potentials, or by a nonlinear coupling mechanism [44]. In the latter case it is common to assume that the coupling of the system coordinate \( q \) and the \( j \)th bath oscillator \( x_j \) can be described by an interaction Hamiltonian 
\[
H_{sb} = -c q^2 x_j.
\]
This interaction leads to pure dephasing as can be understood qualitatively by considering a harmonic coordinate \( q \), which can be expressed in terms of the creation and annihilation operators \( a \) and \( a^\dagger \): The contributions proportional to \( aa^\dagger \) and \( a^\dagger a \) describe random fluctuations of the frequency leading to a net loss of phase coherence [45-49].

Very recently, this model was investigated by Okumura and Tanimura, who used the Feynman rule on the unified-time path to derive a perturbative expression for the third-order Raman response [50]. In the limit of weak coupling they predicted a Lorentzian line shape for the spontaneous Raman line; the width of the line should scale linearly with temperature. At strong system-bath coupling their treatment is expected to break down because of the \( a^2 \) and \( (a^\dagger)^2 \) terms, which describe higher-order energy exchange between the system and the bath. To further investigate the different relaxation processes due to this nonlinear system-bath interaction, we here calculate the third-, fifth- and seventh-order Raman response of a harmonic mode by solving the quantum Fokker-Planck equation.

In Sec. 8.2 the quantum Fokker-Planck equation for linear [28-30] and quadratic [51] coupling is presented. A derivation of this equation using the Vernon-Feynman path integral formalism [23-27] is given in the appendix. Calculational details of the simulations and examples for the wavepackets created in a fifth-order experiment are given in Sec. 8.3. The results for the third-, fifth- and seventh-order response function are presented in Sec. 8.4, and finally conclusions are formulated in Sec. 8.5.
8.2 The quantum Fokker-Planck equation

Since the early days of quantum mechanics [52] the description of dissipation and relaxation phenomena has attracted much attention. Quantum mechanical Langevin [53,54] and quantum master equations [21,55,56] have been applied to a large number of physical and chemical problems. However, these methods allow only for a perturbative treatment of the system-bath interaction and, therefore, they can be applied only in the limit of weak damping. In contrast to this, the functional integral description of dissipation, which was initiated by Vernon and Feynman [23,24], can be applied to quantum systems at arbitrary temperature and coupling strength [25].

In this section the quantum Fokker-Planck equation approach is introduced for the linear-linear coupling model (LL model) [28-30] and square-linear model (SL model) [51]. For both models the total Hamiltonian of the system and the bath can be written as:

\[
H = \frac{p^2}{2m} + U(q) + \sum_{j=1}^{N} \left[ \frac{p_j^2}{2m_j} + \frac{m_j \omega_j^2}{2} (x_j - \frac{F_j(q)}{m_j \omega_j^2})^2 \right].
\]  

(8.1)

Here, \(q, p, m\) and \(U(q)\) denote the effective coordinate, conjugated momentum, mass and the potential of the optically active degree of freedom, which is called the system. The coordinate, conjugated momentum, mass and frequency of the \(j\)th bath oscillator are given by \(x_j, p_j, m_j\) and \(\omega_j\) respectively. The coupling between the system and the \(j\)th bath oscillator is controlled by the function \(F_j(q)\) which is related to the system-bath interaction via: \(H_{SB} = -x_j F_j(q)\). In the LL model it is defined as \(F_j(q) = c_j q\) while in the SL model it reads \(F_j(q) = 1/2 g_j q^2\). Note that the Hamiltonian comprises a term proportional to \(F_j(q)^2\), which compensates for the coupling induced renormalization of the potential [57].

For the derivation of the quantum Fokker-Planck equation in the LL and the SL model one has to assume Gaussian white noise where the memory time of the heat bath is zero. The corresponding spectral density of the bath oscillators \(I(\omega)\) is then given by the Ohmic distribution:

\[
I_{LL}(\omega) = \pi \sum_{j=1}^{N} \frac{c_j^2}{2m_j \omega_j} \delta(\omega - \omega_j) = 4 m \gamma \pi \omega,
\]  

(8.2)

and:

\[
I_{SL}(\omega) = \pi \sum_{j=1}^{N} \frac{g_j^2}{8m_j \omega_j} \delta(\omega - \omega_j) = 4 m \zeta' \pi \omega.
\]  

(8.3)

It is further necessary to assume that the temperature of the bath is high, i.e., \(\hbar \omega_0 \beta \ll 1\) holds where \(\omega\) is the characteristic frequency of the system and \(\beta = 1/k_B T\).
The dynamics of the system and the bath can be described by the coordinate representation \( W(q,x,q_N^0|x_N^0;t) \) of the time dependent density operator \( W(t) \), where \( x \) denotes the coordinates of all \( N \) bath oscillators. The calculation of \( W(q,x,q_N^0|x_N^0;t) \) requires the exact knowledge of all degrees of freedom; for condensed phase systems this certainly has to be avoided. For the calculation of the system response due to, e.g., external optical fields, it is sufficient to know the time evolution of this subsystem only, which is given by:

\[
\rho(q,q',t) = \int dq x W(q,x,q',x;t).
\]

\[
\rho(q,q',t) = \int dq x W(q,x,q',x;t).
\]

In the appendix the quantum Fokker-Planck equation for the SL model is derived following the treatment of Caldeira and Leggett [28] who investigated the LL model. The treatment presented there partly follows their paper, but deviates in a number of details. In particular, we start with a renormalized Hamiltonian which comprises a term proportional to \([F(q)]^2\), and use modified effective coordinates to derive the equation of motion, see discussion below Eq. (8.35) of the appendix. For the derivation of the equation of motion the dynamics of the reduced density matrix has to be calculated. Therefore, it is necessary to average out the bath degrees of freedom. For a harmonic bath the integration over the environment can be done analytically as was shown by Grabert and coworkers for bilinear system-bath coupling [70]. It is straightforward to prove that this treatment is also possible for harmonic baths with system-bath interactions, which are linear in the bath coordinate, but nonlinear in the system coordinate. As shown by Grabert et al. [25] the system-bath interaction leads to a correlation between these two subsystems, even in thermal equilibrium. Initial conditions of the form \( W(q_o,x_o,q_N^0|x_N^0;t) = D(q_o,x_o,q_N^0|x_N^0;t) \) therefore, lead to unphysical results when the correlations are important, i.e., in the case of colored noise. Since we will restrict ourselves to the special case of Gaussian white noise here, these problems do not affect our treatment.

The numerical calculations presented in the subsequent sections are performed in the Wigner representation, which relates the coordinate representation of the density matrix \( D(q,q_N^0;t) \) to the phase space representation \( W(P,R;t) \) via [58-60]:

\[
W(P,R;t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dr e^{iPr/\hbar} \rho(R-r/2,R+r/2;t).
\]

As was shown by Wigner and coworkers [58,60] the variables \( P \) and \( R \) can be associated with the momentum and the coordinate of the system.

The equation of motion for both the LL and the SL model, i.e., the quantum Fokker-
Planck equation, can be written as [37,51]:

$$\frac{\partial}{\partial t} W = - \mathcal{Q}_s W + \Gamma W. \tag{8.7}$$

Here, the free (undamped) propagation of the system is governed by [37,61]:

$$- \mathcal{Q}_s W = - \frac{P}{m} \frac{\partial}{\partial R} W(P,R;t) - \frac{1}{\hbar} \int \frac{dP'}{2\pi\hbar} V(P - P',R) W(P',R;t), \tag{8.8}$$

where the Wigner transform $V(P,R)$ of the potential $U(q)$ is given by:

$$V(P,R) = 2 \int_{-\infty}^{\infty} d\rho \sin \rho \frac{r}{\hbar} [U(R + r/2) - U(R - r/2)]. \tag{8.9}$$

The relaxation in phase space is described by the damping operator, which in the LL model is given by [28-30,37]:

$$\Gamma_{LL} = \gamma \frac{\partial}{\partial P} \left( P + m \frac{\partial}{\partial P} \right), \tag{8.10}$$

while in the SL model it reads [51]:

$$\Gamma_{SL} = 8R^2 \zeta^* \frac{\partial}{\partial P} \left( P + m \frac{\partial}{\partial P} \right) + 2R \zeta \hbar^2 \frac{\partial^3}{\partial^2 P \partial R}. \tag{8.11}$$

In presence of two independent baths for the two relaxation processes the total relaxation operator is $\Gamma = \Gamma_{LL} + \Gamma_{SL}$.

When the system is subjected to electronically nonresonant optical fields and when contributions due to hyperpolarizabilities can be neglected, the third- and fifth-order Raman response function is entirely determined by the polarizability $\alpha$. As was shown in Sec. 2.4 and 2.5 these functions can be expressed by the polarizability operator $\alpha(q)$, its corresponding Liouville space operator $\alpha^\dagger(q)p \equiv \alpha(q)p - p\alpha(q)$ and the Liouville space Green function $G(\tau)$ [11,12]:

$$R^{(3)}(\tau) = \frac{i}{\hbar} \langle \alpha(q)G(\tau)\alpha^\dagger(q)p(-\infty) \rangle, \tag{8.12}$$

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and:

\[ R^{(5)}(\tau_2, \tau_1) = -\frac{1}{\hbar^2} \langle \alpha(q) G(\tau_2) \alpha^L(q) G(\tau_1) \alpha^L(q) \rho(-\infty) \rangle. \] (8.13)

It is straightforward to extend this treatment to obtain the seventh-order response function:

\[ R^{(7)}(\tau_3, \tau_2, \tau_1) = -\frac{i}{\hbar^3} \langle \alpha(q) G(\tau_3) \alpha^L(q) G(\tau_2) \alpha^L(q) G(\tau_1) \alpha^L(q) \rho(-\infty) \rangle. \] (8.14)

The processes corresponding to Eqs. (8.11) to (8.13) can be depicted by double sided Feynman diagrams as was discussed in Secs. 2.4 and 2.5 for the third- and fifth-order response, respectively. Initially the equilibrium density matrix \( D(\tau_4) \) is modified by the first interaction, which yields a wavepacket \( \rho_1 = \alpha^L(q) \rho(-\infty) \). This state is then propagated for a time \( \tau_1 \) by the Green function \( G(\tau_1) \). In higher-order experiments the propagated density matrix is then modified again by the interaction and subsequently propagated. Finally, the expectation value of the observable polarizability is obtained by calculating the trace of \( \alpha(q) \rho_n \) where \( \rho_n \) denotes the density matrix after the last propagation period.

This sequence of modifying and propagating the density matrix can be translated very conveniently in the Wigner representation. The modified wavepacket in phase space \( W_1 \), which corresponds to the density matrix \( \rho_1 \), is given by [37]:

\[ W_1 \equiv A^{LW_{eq}} \equiv \int \frac{dP'}{2\pi\hbar} A^{L(P-P',R)} W_{eq}(P',R;-\infty), \] (8.15)

where \( W_{eq} \) denotes the Wigner representation of the density matrix of the system in thermal equilibrium. The Wigner representation \( A^{L}(P,R) \) of the operator \( \alpha^L(q) \) is defined as:

\[ A^{L}(P,R) = 2 \int_{-\infty}^{\infty} dr \sin(iPr/\hbar) [\alpha(R-r/2) - \alpha(R+r/2)]. \] (8.16)

The time evolution of the resulting wavepacket is obtained by numerically integrating Eq. (8.6). For higher-order experiments the subsequent interactions are described by Eq. (8.14) where now \( W_{eq} \) has to be replaced by the propagated wavepacket just before the interaction. The expectation value of the polarizability, which yields the signal after all interactions and propagation periods, is then given by:
\[ tr[A(P,R)W_n(P,R)] = \int dP \int dR A(P,R) W_n(P,R), \]  

(8.17)

where \( W_n(P,R) \) denotes the wavepacket after the last propagation period. The Wigner transform \( A(P,R) \) of the polarizability operator \( \alpha(q) \) is given by:

\[ A(P,R) = i \int_{-\infty}^{\infty} dr \ e^{i P \cdot r} \alpha(R-r/2), \]  

(8.18)

Using these equations, it is now possible to numerically simulate the third-, fifth- and seventh-order response functions as will be explained in the next section.

### 8.3 Wavepacket dynamics in the Wigner representation

In this section some details of the numerical calculations are given together with a description of the wavepacket dynamics in the Wigner representation. The simulations presented in this chapter are performed for a harmonic mode with a frequency \( \omega = 38.7 \, \text{cm}^{-1} \), which is a typical value for low-frequency intermolecular motions, see Fig. 5.1.c. Although the Fokker-Planck approach can be applied to any potential, we restrict ourselves here to a harmonic coordinate. This system has been investigated for different system-bath interactions in great detail [6,11-16,23-30,44-49] and, moreover, it allows for a comparison with the results of the previous chapters. It is then in principle possible to solve the integral for the potential kernel [Eq. (8.8)] analytically: the second term in Eq. (8.6) then reduces to \( m \omega^2 R \partial W/\partial P \). During the numerical calculations it turned out that the differential expression is less stable compared to the integral expression; therefore, the latter was used.

The quantum Fokker-Planck equation [Eq. (8.6)] was numerically integrated on a discrete mesh in phase space using a second-order Runge-Kutta method. The mesh size was varied between 201×20 and 601×60 for mesh ranges between \(-10 < R < 10\), \(-20 < P < 20\) and \(-15 < R < 15\), \(-23 < P < 23\). The time steps for the finite difference expression \( \partial W/\partial t \) were between 0.5 and 0.0125 fs. The accuracy of the calculations was checked by changing the mesh size, mesh range and time step size. On the mesh linear difference operators such as \( \partial W/\partial R \) were approximated by \([W(P,R)_{r+1} - W(P,R)_{r-1}]/(2\Delta R)\), whereas quadratic difference operators like \( \partial^2 W/\partial R^2 \) were replaced by \([W(P,R)_{r+1} - 2W(P,R)_{r} + W(P,R)_{r-1}]/(\Delta R)^2\). The wavepacket \( W_q \) in thermal equilibrium was generated numerically by starting with an initial wavepacket \( W(P,R) = \exp[-\beta H_s(P,R)] \), where \( H_s(P,R) \) denotes the Wigner transform of the undamped system Hamiltonian. After a short propagation period of typically a few thousand steps this wavepacket becomes stable.

The evolution of the wavepacket in a 2D Raman experiment is depicted in Fig. 8.1. In thermal equilibrium the wavepacket is symmetric and bell shaped as is shown in part (a). In Fig.
Fig. 8.1: The time evolution of the wavepacket in a 2D Raman experiment is shown for thermal equilibrium (a), after the first interaction at $\tau_1=0$ (b) and 200 fs (c), and after the second interaction at $\tau_2=0$ (d) and 200 fs (e). Consult text for details.

interaction is depicted. For this calculation the polarizability operator $\alpha(R)$ is expanded in powers
of the coordinate up to second order, analogous to the treatment in chapters 3 and 7: 
\[ \alpha(R) = \alpha^{(1)} R + \alpha^{(2)} R^2. \]

The contribution due to the quadratic coordinate dependence of the polarizability is (almost) invisible since the coefficient of the linear contribution is chosen twenty times bigger than that of the quadratic contribution. Therefore, the distribution after the first interaction looks still symmetric in \( R \) but antisymmetric in \( P \). This is completely analogous to the classical situation where the interaction \( R \mathcal{W}_{eq} = [R, \mathcal{W}_{eq}] \) has to be replaced by \( \{ R, \mathcal{W}_{eq} \} = \partial R / \partial R \partial p_{eq} / \partial P \). Note that in contrast to the classical density in phase space, \( \rho(P,R) \), the Wigner distribution can be negative [58-60].

This nonequilibrium distribution then starts to evolve in time due to the free propagator \( \mathcal{L}_S \), which describes the periodic transfer of kinetic energy to potential energy and back: Those points in phase space with large positive (negative) momentum move in the positive (negative) \( R \)-direction while oscillators with zero momentum and a large positive (negative) deviation \( R \) turn back to acquire momentum. In other words, the wavepacket rotates in phase space with a frequency \( \omega \). In addition it changes its shape due to the damping operator \( \Gamma \), which for the simulation shown here is chosen so small that the changes for small propagation times are minor. A snapshot of the propagated wavepacket is depicted in Fig. 8.1.c for \( \tau = 200 \text{ fs} \) corresponding to approximately a quarter of a period. Note that the part of the wavepacket close to the origin is slightly distorted as can be seen at the grid lines along \( P \) for small \( R \), which already reflects the nonlinearity of the system-bath interactions. For the calculation of the third-order Raman response this propagated wavepacket has to be convoluted with the Wigner representation of the polarizability operator \( A(P,R) \) and integrated over the entire grid, cf. Eq. (8.16). In lowest order the third-order response is proportional to \( \alpha^{(1)} \). The contributions due to the nonlinear coordinate dependence of the polarizability are very small.

In a 2D Raman experiment the propagated phase space distribution such as shown in Fig. 8.1.c is modified by a second interaction operator \( A^L \). The resulting wavepacket for a first propagation time of 200 fs is shown in Fig. 8.1.d. Analogous to the first interaction the symmetry of the wavepacket along the \( R \)-direction is not changed but it is inverted along the \( P \)-axis. This phase space distribution then evolves in time in a similar way as described above; a snapshot after a propagation time \( \tau = 200 \text{ fs} \) is depicted in Fig. 8.1.e. Analogous to the calculation of the third-order Raman response the fifth-order response function is obtained by convoluting the propagated wavepacket after the second interaction with the Wigner representation of the polarizability operator \( A(P,R) \), see also Eq. (8.16). In contrast to the third-order response, which is governed by the entire wavepacket and proportional to \( \alpha^{(1)} \), the fifth-order signal is proportional to \( \alpha^{(1)} \alpha^{(2)} \). Therefore, the latter is determined by the deformation of the wavepacket due to the small quadratic contribution. For the calculation of the seventh-order response the above described procedure has to be extended by an additional interaction and propagation period.
8.4 Numerical results

In this section the third-, fifth- and seventh-order response functions of a harmonic oscillator in the SL model are presented for different temperatures and coupling strengths. The results are compared to the LL model, which for Gaussian white noise and a harmonic system can be solved analytically, cf. Sec. 3.7. In the LL model the line width is temperature-independent and there is no pure dephasing. The third- and fifth-order response function are then in lowest order given by [11,12]:

\[ R^{(3)}_{LL}(\tau) = e^{-\gamma \tau/2} \sin \Omega \tau, \]  

(8.19)

and:

\[ R^{(5)}_{LL}(\tau_2, \tau_1) = e^{-\gamma \tau_2/2} \sin \Omega \tau_2 [e^{-\gamma (\tau_2 + \tau_1)/2} \sin \Omega (\tau_2 + \tau_1) + e^{-\gamma \tau_1/2} \sin \Omega \tau_1]. \]  

(8.20)

Here, the reduced frequency \( \Omega \) is defined as \( \Omega = (\omega^2 - \gamma^2/4)^{1/2} \) and prefactors containing the polarizability coefficients \( \alpha^{(1)} \) and \( \alpha^{(2)} \), the mass and the reduced frequency are suppressed for simplicity. When the polarizability depends only linearly on the coordinate, the seventh-order response function vanishes in the LL model due to perfect destructive interference of the Liouville space pathways involved [11]. For level-dependent damping, however, this interference can be (partly) destroyed, resulting in a finite signal as was discussed by Fourkas and coworkers [15]. The third- and fifth-order response for phenomenological level-dependent damping were derived in chapter 3.

In the SL model it is possible to derive a perturbative expression for the third-order response in the limit of weak damping, as was shown recently by Okumura and Tanimura [50]. They obtained the spontaneous off-resonant Raman line shape function \( I(\omega) \), which looks similar to the one found in the LL model. The corresponding third-order response function is of the form of Eq. (8.18), but in the SL model the effective damping constant \( \gamma_{SL} \) and the overall intensity both scale linearly with the temperature. Because the calculations are quite complicated, the response for higher-order experiment has not been computed by this perturbation theory, yet.

In Fig. 8.2 the third-order results of the quantum Fokker-Planck simulation are compared to the predictions of the theory by Okumura and Tanimura [50]. The spectral density displayed in the figure is the imaginary part of the Fourier transform of the third-order response function, which is often used for the analysis of optically heterodyned detected optical Kerr effect data, see chapter 5 [62-64]. For weak coupling the line width increases linearly with temperature and the two methods agree very well. This temperature dependence is expected because of the nonlinear coordinate dependence of the damping operator \( \Gamma_{SL} \) [see Eq. (8.10)]: As the temperature is increased the wavepacket becomes broader and in particular the outer parts of the wavepacket
Fig. 8.2: The spectral density of the third-order Raman response of a harmonic mode in the SL-model for $T=150$, $300$ and $450$ K (bottom to top) calculated by the quantum Fokker-Planck equation (solid line) and by the perturbation theory of Okumura and Tanimura (dotted). The frequency of the undamped mode is $\omega=38.7$ cm$^{-1}$, the damping constant $\gamma$ was equal $0.1 \omega$.

Fig. 8.3: The spectral density of the third-order Raman response of a harmonic mode in the SL-model at $T=450$ K for $\gamma/\omega=0.1$ (dashed-dotted), $0.5$ (solid line) and $2.0$ (dashed).

are damped more strongly. With increasing damping the perturbation theory breaks down as is shown in Fig. 8.3. When $\zeta/2$ is bigger than $\omega$, the line shape becomes bimodal: In addition to a broad feature around $\omega$ there is a (nearly) Lorentzian peak close to zero frequency. In time domain this feature, which was also found in the OHD-OKE response (see Fig. 5.1) shows up as an exponential decay.

The physical origin of the bimodal structure at strong damping can be understood qualitatively from the form of the system-bath coupling $H_{sb}=c q^2 x$. When expressed in terms of the creation and annihilation operators of the system, $a$ and $a^\dagger$, one directly sees that next to pure dephasing due to the coupling terms proportional $aa^\dagger$ and $a^\dagger a$ there is also energy exchange
between the system and the bath via the terms $a^2$ and $[\hat{a} \hat{\jmath}]$. For strong damping the energy relaxation will lead to overdamped motion, analogous to the LL model.

In order to better distinguish the effects of population and phase relaxation it is instructive to investigate the fifth-order Raman response, which due to its temporally two-dimensional character provides additional insight. For weak coupling and low bath temperature the 2D Raman

![Graphical representation of the fifth-order response function in the SL-model.](image)

Fig. 8.4: The absolute value of the fifth-order response function $R^{(5)}(\tau_2,\tau_1)$ in the SL-model at $T=150$ K for $\zeta=0.1 \omega$. Consult text for details.

![Contour plot of the absolute value of the fifth-order response function.](image)

Fig. 8.5: Contour plot of the absolute value of the fifth-order response function in the SL-model. The left panel shows the same data as Fig. 8.4. In the right panel the response is displayed for $T=450$ K and $\zeta=2.0 \omega$. 
response function $R^{(5)}(\tau_2,\tau_1)$ exhibits clear oscillations with a frequency $\omega$ as is shown in Fig. 8.4. In a contour plot it becomes evident that neighboring peaks tend to form twins as is shown in Fig. 8.5. A similar feature is found in Fig. 3.7.c, which shows the fifth-order response of a harmonic oscillator in the fast fluctuation limit of the stochastic model. In this limit the dynamics is due to pure dephasing with a rate constant $\Gamma'=(\lambda-\mu)^2\Gamma''$ where $\lambda$ and $\mu$ are the quantum numbers of the involved states and $\Gamma''$ denotes the pure dephasing rate constant, cf. Sec. 3.6. This demonstrates that for small $\zeta'$ the SL model describes pure dephasing.

For large $\zeta'$ the fifth-order response is distinctly different as is shown in the right panel of Fig. 8.5: As function of the first delay time $T_1$ the fifth-order signal rapidly decays within a few hundred fs, while along $T_2$ it shows slow diffusive dynamics on a ps time scale. This asymmetry of the 2D Raman response can be understood by considering the involved Liouville space pathways: In all Liouville space pathways contributing to the fifth-order 2D Raman response the system first propagates in a coherence, which rapidly decays due to the strong coupling $\zeta'$. As was already discussed in Sec. 3.4, the fifth-order response comprises one contribution proportional to $\cos T_2$, which involves a population during the second propagation time. In the limit of pure dephasing this term does not decay at all and yields a plateau along $T_1$ for small $T_1$, cf. Figs. 3.3.c and 3.5. In the SL model, however, the signal does decay as function of $T_2$ when $\zeta'$ is large (see right panel of Fig. 8.5). The underlying population relaxation is induced by two quantum transitions between the system and the bath, which are due to the coupling terms proportional to $a^\dagger a$ and $[a^\dagger a]^2$.

The nonlinear character of the relaxation in the SL model becomes also evident in the seventh-order response. In the LL model the seventh-order response function vanishes when the polarizability depends only linearly on the coordinate because the different Liouville space pathways interfere destructively [11,15]. The LL model is a linear problem, which can be diagonalized and, therefore, there is no nonlinear response. When the damping is level-dependent, the interference can be partly destroyed and the seventh-order response is finite even for a linear

![Fig. 8.6](image-url)
coordinate dependence of the polarizability [15]. In the SL model the damping operator $\Gamma_{SL}$ has a large nonlinear contribution in $R$, see Eq. (8.10), and one therefore can expect a finite response. The impulsive seventh-order Raman response function [Eq. (8.13)] is temporally three-dimensional but up to now only temporally two-dimensional seventh-order experiments have been performed. In the Raman echo the second propagation time $\tau_2$ is zero whereas in the Raman pump probe experiment the time variable $\tau_1$ is zero [5,65-67]. Therefore, we here restrict ourselves to the Raman echo case. Note, however, that the seventh-order Raman experiments reported so far were done nonimpulsively on a two level system. Due to the anharmonicity of the probed molecular vibrations the transitions to higher vibrational states were not resonant with the applied ps pulse.

The numerical results in the two extreme cases of low temperature [68] and weak coupling, and high temperature and strong coupling are displayed in Fig. 8.6. Neither of the two plots shows an echo feature at the diagonal $T_1 = T_2$, which would be expected for an inhomogeneously broadened two-level system [69]. Since the spectral density $I(\omega)$ of Eq. (8.3) is chosen for the case of Gaussian white noise, one can indeed anticipate that the memory time of the system is zero and that there is no echo. The effect of a finite correlation time of the bath fluctuations can be described, in principle, by the theory of Tanimura and Kubo [39-43] but this approach has not been applied, yet, to the SL model.

In the limit of weak coupling the response shows clear oscillations with frequency $\omega$ that slowly decay. A similar behavior is found in the model of Fourkas and coworkers [15] who calculated the seventh-order response for level dependent population and phase relaxation. For strong coupling the response changes quite significantly: The signal decays more rapidly and the oscillation frequency becomes higher. Remember that in the LL model the reduced frequency $\Omega$ becomes smaller as the damping strength is increased. The physical origin of this phenomenon is not completely clear at the moment. Most likely it is caused by the beating between different levels, which due to the nonlinear damping operator $\Gamma_{SL}$ have different effective frequencies.

8.5 Conclusions

In this chapter the quantum Fokker-Planck equation is derived for a system that is nonlinearly coupled to a heat bath. For the so-called SL model studied here, it is assumed that the system-bath interaction is linear in the bath coordinate but quadratic in the system coordinate. The equation of motion for the wavepacket in Wigner space is solved numerically which allows one to calculate the third-, fifth- and seventh-order Raman response of a harmonic oscillator with (non)linear coordinate dependence of the polarizability. For weak coupling the third-order response function can be modeled by the perturbation theory of Okumura and Tanimura [50]. In the SL model the width of the third-order Raman line shape scales linearly with the temperature while it is temperature independent in the LL model. When the system and the bath are strongly coupled, the third-order response becomes bimodal: Next to the original line there is a Lorentzian line close to zero frequency, which is not present in the perturbation theory. This line is attributed to two-quantum energy transfer from the system to the bath, which is described by the coupling
terms proportional to \( a^2 \) and \([a^\dagger]^2\).

The combination of energy and phase relaxation also determines the fifth-order response. For weak coupling the neighboring maxima of the 2D Raman response form twins – a feature that was also found for level-dependent homogeneous pure dephasing. When the system and the bath are strongly coupled, the 2D Raman response becomes highly asymmetric. The signal decays rapidly as function of the first propagation time, which is assigned to very effective phase relaxation. Along the second time variable the decay is an order of magnitude slower which is attributed to a Liouville space pathway involving a population during the second propagation time. The impulsive 2D Raman response of \( \text{CS}_2 \) and benzene, presented in chapter 7, cannot be explained by this model. The tail in the experimental data is along the first propagation time whereas it is along the second propagation time in the simulations. The experimental signal is attributed to strong mode coupling, predominant contributions of \( \Gamma_{LL} \), and to other scattering mechanisms.

Due to the nonlinear coordinate dependence of the damping operator \( \Gamma_{SL} \), the population and phase relaxation becomes level-dependent in the SL model. Therefore, a finite seventh-order Raman echo response is predicted for a harmonic oscillator with linear coordinate dependence of the polarizability. In the LL model this response vanishes due to perfect destructive interference of the involved Liouville space pathways [15]. For weak coupling the response shows oscillations with the frequency of the unperturbed system while for strong coupling the frequency becomes higher. This effect is attributed to a level dependent effective frequency \( \Omega \).

For the calculations presented in this chapter it was assumed that the heat bath induces Gaussian white noise. Therefore, the memory time of the fluctuations is zero and there is no echo feature predicted, neither in the fifth- nor in the seventh-order Raman response. Memory effects can, in principle, be induced by a different spectral density \( I(\omega) \) of the heat bath. As was shown by Tanimura and coworkers [39-43] it is possible to derive a hierarchy of coupled equations of motion for a Gaussian-Markovian heat bath. Up to now this approach, which explicitly includes memory effects, has only been applied to the LL model. The extension of this so-called doctor equation to the SL model is very interesting since it allows for a direct comparison with the stochastic model by Anderson and Kubo [17-21]. In contrast to the latter case the damping operator in the SL model does depend explicitly on temperature and, therefore, partly bridges the gap between the stochastic and the dynamic theories. As demonstrated in this chapter the damping operator \( \Gamma_{SL} \) yields reasonable predictions of the third-, fifth- and seventh-order Raman response for the special case of Gaussian white noise; the extension to Gaussian-Markovian noise should be possible as well.
Appendix: Derivation of the quantum Fokker-Planck equation

For the derivation of the quantum Fokker-Planck equation in the SL model we first consider the time evolution of the reduced density matrix, which can then be represented by a functional integral [23-25,28,30]:

$$\rho(q,q';t) = \int dq_f \int dq_i^{'} \int Dq \int Dq^{'} \exp(\frac{i}{\hbar}(S[q]-S[q'])) F[q,q'] \rho(q,q';0), \quad (8.21)$$

where the two real time path integrals are over all paths $q(s)$, $q_N(s)$, $0 \leq s \leq t$ with $q(0)=q_i$, $q_N(0)=q_{N,i}$ $q(t)=q_i$ and $q_{N}(t)=q_{i}^{'}$ while the outer two integrals are over all possible coordinates of the initial system state $q_i$ and $q_{i,N}$. The path probability is weighted not only by the usual action $S[q]$ given by:

$$S[q] = \int_0^t ds \left( \frac{m}{2} \dot{q}^2 - V(q) \right), \quad (8.22)$$

but also by the Vernon-Feynman influence functional $F[q,q_N]$, which accounts for the bath-induced relaxation. For both the LL and the SL model this quantity can be expressed in terms of the influence phase $\Phi[q,q_N]$:

$$F[q,q'] = \exp\left\{ -\frac{1}{\hbar} \Phi[q,q'] \right\}, \quad (8.23)$$

which in the SL model is given by:

$$\Phi[q,q'] = \int_0^t ds \int_0^s du \left[ q^2(s) - q^{'2}(s) \right] \left[ q^2(u) - q^{'2}(u) \right] K'(s-u) + i \int_0^t ds \int_0^s du \left[ q^2(s) - q^{'2}(s) \right] \left[ q^2(u) + q^{'2}(u) \right] K''(s-u) + i \int_0^t ds \int_0^s du \left[ q^4(s) - q^{'4}(s) \right] \frac{\hbar}{2} \quad (8.24)$$
The influence of the environment is completely determined by the spectral density \( I(\omega) \) of the bath oscillators [71]:

\[
I(\omega) = \pi \sum_{j=1}^{N} \frac{g_j^2}{8m_j \omega_j} \delta(\omega - \omega_j). 
\] (8.25)

The complex kernel \( K(s) = K_N(s) + iK_O(s) \) can be expressed in terms of \( I(\omega) \) via:

\[
K'(s) = \int_{0}^{\infty} \frac{d\omega}{\pi} I(\omega) \coth \frac{\omega \beta}{2} \cos \omega s, 
\] (8.26)

and:

\[
K''(s) = -\int_{0}^{\infty} \frac{d\omega}{\pi} I(\omega) \sin \omega s. 
\] (8.27)

The auxiliary constant \( \mu \) in the last term of Eq. (8.23), which originates from the potential renormalization, is related to \( I(\omega) \) via:

\[
\mu = \int_{0}^{\infty} \frac{d\omega}{\pi} I(\omega) \frac{2}{\omega}. 
\] (8.28)

In the LL model the influence phase \( \Phi \) and the spectral density \( I(\omega) \) have to be slightly changed: all \( q^2 \) in Eq. (8.23) and \( \frac{1}{2}g \) in Eq. (8.24) have to be replaced by \( q \) and \( c_j \), respectively.

For the derivation of the quantum Fokker-Planck equation let us consider Eq. (8.20) at a small time instant \( \epsilon \) later, where the system propagated from \( q \) and \( q^N \) to \( q' \) and \( q'^N \), respectively:

\[
\rho(q,q',t+\epsilon) = \int dq_{i}^{\prime} \int dq_{i}^{\prime} \int Dq_{i}^{\prime} \int Dq_{i} \exp \left( \frac{i}{\hbar} (S[q] - S[q']) \right) F(q,q') \rho(q,q_{i}^{\prime};0). 
\] (8.29)

Note that now the integrals in the expression for the action [Eq. (8.21)] and for the influence phase [Eq. (8.23)] also run to \( t+\epsilon \) instead of \( t \).

For small \( \epsilon \) the last part of the path integrals, which run from \( q \) to \( q' \) and from \( q^N \) to \( q'^N \) can be split and approximated by a straight line times a normalization constant \( C \) [72,73]. Similarly, the integrals from 0 to \( t+\epsilon \) can be split into two integrals running from 0 to \( t \) and from
\( t \) to \( t+\epsilon \), respectively. The latter integrals can be approximated by \( \epsilon \) times the integrand at \( t+\epsilon \); moreover, it is a good approximation to replace derivatives around \( t+\epsilon \) by finite differences, e.g., \( \partial q/\partial t \) by \((q-q_i)/\epsilon \). The last equation can then be rewritten as:

\[
\rho(q,q';t+\epsilon) = \frac{1}{C^2} \int dq_1 \int dq_2 \int dq_3 \int dq_4 \int Dq' \int Dq \times \exp \left[ \frac{i}{2 \hbar} \{ (q-q_r)^2 - (q'-q'_r)^2 \} \right] \exp\left[ -\frac{i \epsilon}{\hbar} \{ V(q) - V(q') \} \right]
\]

\[
\exp\left[ -\frac{\epsilon}{\hbar} (q^2 - q'^2) \right] \int ds \left[ q^2(s) - q'^2(s) \right] K'(t+\epsilon - s)
\]

\[
\exp\left[ -\frac{i \epsilon}{\hbar} (q^2 - q'^2) \right] \int ds \left[ q^2(s) + q'^2(s) \right] K''(t+\epsilon - s)
\]

\begin{align}
\exp\left[ -\frac{i \epsilon}{\hbar} (q^4 - q'^4) \right] & \frac{1}{2} \mu \exp \left[ \frac{i}{\hbar} \int ds \left( m(q^2 - q'^2) - (V(q) - V(q')) \right) \right] \\
\exp\left[ -\frac{1}{\hbar} \int ds \left[ q^2(s) - q'^2(s) \right] [q^2(u) - q'^2(u)] K'(s-u) \right] \\
\exp\left[ -\frac{i}{\hbar} \int ds \int du \left[ q^2(s) - q'^2(s) \right] [q^2(u) + q'^2(u)] K''(s-u) \right] \\
\exp\left[ -\frac{i}{\hbar} \int ds \int du \left[ q^4(s) - q'^4(s) \right] \frac{\mu}{2} \rho(q,q';0) \right].
\end{align}

For small \( \epsilon \) almost all exponents are expanded up to first order in \( \epsilon \) – except the first exponent, which rapidly oscillates as \( \epsilon \to 0 \). It can be shown [28] that only the parts with \( q! q_r \sim \epsilon^{1/2} \) and \( qN q_r N \sim \epsilon^{1/2} \) will yield a finite contribution since the exponent hardly changes in this range:
\[
\rho(q,q';t+\epsilon) = \frac{1}{C^2} \int dq_0 \int dq_{0'} \int dq \int dq_{0'} \int Dq \int Dq_{0'} \ x \exp\left[\frac{i m}{2\hbar\epsilon}((q-q')^2-(q'-q''))\right] \\
\times \exp\left[-\frac{i}{\hbar} \left[ V(q) - V(q') \right] - \frac{2}{\hbar} (q^2 - q'^2) \int_0^{t+\epsilon} ds \left[ q^2(s) - q'^2(s) \right] K''(t+\epsilon-s) \right) \right] \\
\times \left[ 1 - \frac{i}{\hbar} \left[ V(q) - V(q') \right] - \frac{2}{\hbar} (q^2 - q'^2) \int_0^{t+\epsilon} ds \left[ q^2(s) - q'^2(s) \right] K''(t+\epsilon-s) \right) \right] \\
\times \exp\left[ \frac{i}{\hbar} \int_0^s ds \left[ \frac{m}{2} (\dot{q}^2 - \dot{q}'^2) - (V(q) - V(q')) \right] \right] \\
\times \exp\left[ -\frac{i}{\hbar} \int_0^s du \left[ q^2(s) - q'^2(s) \right] \left[ q^2(u) - q'^2(u) \right] K'(s-u) \right] \\
\times \exp\left[ -\frac{i}{\hbar} \int_0^s du \left[ q^2(s) - q'^2(s) \right] \left[ q^2(u) + q'^2(u) \right] K''(s-u) \right] \\
\times \exp\left[ -\frac{i}{\hbar} \int_0^s du \left[ q^4(s) - q'^4(s) \right] \frac{\mu}{2} \rho(q,q';0) \right].
\]

The last two terms in the big squared brackets can be rearranged by introducing the function \(\eta(s)\) which is defined as:

\[
\eta(s) = 2 \int_0^\infty \frac{d\omega}{\pi} \frac{I(\omega)}{\omega} \cos \omega s.
\] (8.32)

This function is proportional to the correlation function of the collective bath coordinate \[28\]. From the definition of \(K''(s)\) in Eq. (8.26) it is directly evident that \(d\gamma/ds = K''(s)\) holds. Using this identity and the relation \(\eta(0) = \mu\) the last two terms in the big squared brackets of Eq. (8.30) can be replaced by:
\[-\frac{i\epsilon}{2\hbar} (q^2 - q'^2) \frac{d}{d(t+\epsilon)} \int_0^{t+\epsilon} ds \left[ q^2(s) + q'^2(s) \right] \eta(t+\epsilon-s).\]

For Gaussian white noise the spectral density $I(\omega)$ is given by Eq. (8.3), the corresponding correlation function of the collective bath coordinate is proportional to a delta function:

$$\eta(s) = 4m\zeta' \delta(s).$$  \hspace{1cm} (8.34)

In the high temperature limit $\coth(\hbar\beta\omega/2) = 2/\hbar\beta \omega$ and the real part of the kernel $K'(s)$ is now given by, cf. the definition Eq. (8.25):

$$K'(s) = \frac{4m\zeta'}{\beta\hbar} \delta(s).$$  \hspace{1cm} (8.35)

Using the above relations the expression for $\rho(q,q',t+\epsilon)$ can be simplified to:

$$\rho(q,q',t+\epsilon) = \frac{1}{C^2} \int dq dq' \exp \left[ \frac{i}{2\hbar\epsilon} \left[ (q-q')^2 - (q'-q')^2 \right] \right]$$

$$\times \left[ -\frac{i\epsilon}{\hbar} [V(q) - V(q')] - \frac{2m\zeta'}{\hbar^2} (q^2 - q'^2) \right.$$  \hspace{1cm} (8.36)

$$\left. - \frac{2m\zeta'\epsilon}{\hbar} (q^2 - q'^2)(q\dot{q} + q'\dot{q}') \right] \rho(q,q',t).$$

Now introduce the new variables $x = q! q$ and $x' = q'! q'$ and use the approximations $\partial q / \partial t = x / \epsilon$ and $\partial q' / \partial t = x' / \epsilon$. The integrals over $q_j$ and $q_j'$ can be transformed into integrals over $x$ and $x'$. The density matrices $\rho(q,q',t+\epsilon)$ and $\rho(q,q',t) = \rho(q!,x,q',t)$ are also expanded up to first order in $\epsilon$. Remember that $x$ and $x'$ are of the order $\epsilon^{1/2}$ as was explained above. In zeroth order of epsilon the last equation yields the normalization constant $C^2 = 2\pi \epsilon \hbar / m$. In first order we find the equation of motion for the reduced density matrix in coordinate representation:
\[
\frac{\partial \hat{p}}{\partial t} = -\frac{\hbar}{2m} \left( \frac{\partial^2 \hat{p}}{\partial q^2} - \frac{\partial^2 \hat{p}}{\partial q'^2} \right) - \frac{i}{\hbar} \{V(q) - V(q')\}
\]

\[
- \frac{2m \zeta'}{\hbar^2 \beta} (q^2 - q'^2)^2 - 2 \zeta'(q^2 - q'^2) \left( \frac{q}{\partial q} - q' \frac{q}{\partial q'} \right)
\]

In an operator representation this equation reads:

\[
\frac{\partial \hat{p}}{\partial t} = -\frac{i}{\hbar} \left[ \frac{1}{2m} \hat{p}^2 + V(q), \hat{p} \right] - \frac{2i \gamma}{\hbar} (\hat{q}^2 \hat{\hat{p}} \hat{\hat{p}} + \hat{q}^2 (\hat{\hat{p}} \hat{\hat{p}} \hat{q} - \hat{q} \hat{\hat{p}} \hat{\hat{p}} \hat{q}^2 - (\hat{\hat{p}} \hat{\hat{p}}) \hat{q}^2)
\]

\[
- \frac{2m \gamma}{\hbar^2} [\hat{q}^2, [\hat{q}^2, \hat{\hat{p}}]].
\]

Finally, this expression is transformed into the Wigner representation, which was introduced in Sec. 8.2, see in particular Eq. (8.5). The action of a function of operators onto the density matrix is transformed to the corresponding Wigner space expression via the relations [59]:

\[
A(\hat{p}, \hat{q}) \hat{\hat{p}} \rightarrow A(P + \frac{\hbar}{2i} \frac{\partial}{\partial R} R - \frac{\hbar}{2i} \frac{\partial}{\partial P} P) W(P,R),
\]

\[
\hat{\hat{p}} A(\hat{p}, \hat{q}) \rightarrow A(P - \frac{\hbar}{2i} \frac{\partial}{\partial R} R + \frac{\hbar}{2i} \frac{\partial}{\partial P} P) W(P,R),
\]

which directly results in the quantum Fokker-Planck equation, see Eq. (8.6) with the damping operator as defined in Eq. (8.10).
References

[57] See Sec. 4.1 of reference 25.
[68] The temperature is still high enough to fulfill the condition $S T \ll 1$.
[70] See Appendix A of reference 25.
[71] In order to introduce irreversible relaxation it is necessary to have a continuous spectrum of bath oscillators; a discrete set would lead to periodic beating phenomena.