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Perturbation theory for the spin-phonon model

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Abstract. The reduced time evolution operator for the spin-boson model with a cubic bath spectrum is expanded in terms of the spin-phonon coupling parameter. The contributions of first and second order to the damping rate are calculated explicitly. The second-order term constitutes a novel result and yields a rigorous criterion for the validity of various previous theories.

1. Introduction

Quantum tunnelling of localized defects between degenerate states is a ubiquitous phenomenon in solid state physics. In many cases the defect coordinate may be reduced to a two-state variable which accounts for the ground states in a double-well potential. Such effective two-state systems have been observed in oxide glasses [1, 2], submicrometre metallic wires [3, 4], amorphous metals [5] and polycrystalline metals [6], impurity ions in various alkali halides [7, 8], and interstitial hydrogen in niobium [9].

The ground states in the left and right wells, $|L\rangle$ and $|R\rangle$, give rise to four quantum mechanical operators; it turns out to be convenient to choose Pauli matrices

$$\sigma_z \equiv |L\rangle\langle L| - |R\rangle\langle R| \qquad \sigma_x \equiv |R\rangle\langle L| + |L\rangle\langle R| \tag{1.1}$$

and $\sigma_y = \mathrm{i}\sigma_x\sigma_z$, and the identity operator $\sigma_0 = |L\rangle\langle L| + |R\rangle\langle R|$. Here, the reduced coordinate $\sigma_z = \pm 1$ describes the particle dwelling in the left or in the right well.

The dynamics of the isolated defect is described by the off-diagonal matrix element of the Hamiltonian, defining a tunnel frequency Δ_b. Dissipation arises from the coupling of the defect coordinate σ_z to collective modes of the host solid. Quite generally, the heat bath may be reduced to a set of harmonic oscillators with linear coupling to σ_z [10],

$$H = \frac{1}{2}\hbar\Delta_\mathrm{b}\sigma_x + \frac{1}{2}\sigma_z\sum_k \hbar\lambda_k\left(b_k + b_k^\dagger\right) + \sum_k \hbar\omega_k b_k^\dagger b_k \tag{1.2}$$

where the bath operators obey Bose commutation relations, $[b_k, b_{k'}^\dagger] = \delta_{kk'}$.

For sufficiently dilute defects, the time evolution of the boson operators is not affected by the pseudospins, and the heat bath is entirely characterized by the coupled density of states

$$J(\omega) = \frac{\pi}{2}\sum_k \lambda_k^2\delta(\omega - \omega_k). \tag{1.3}$$

For tunnelling of atoms, the frequency Δ_b is small; the quantity $\hbar\Delta_\mathrm{b}/k_\mathrm{B}$ does not exceed a few Kelvin. Thus the low-energy bath excitations are most important, and the spectral density $J(\omega)$ obeys a simple power law behaviour that is determined by the density of states

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$\sum_k \delta(\omega-\omega_k)$ and the frequency dependence of the coupling energies $\hbar\lambda_k$. We briefly discuss the two most relevant cases, which arise from the interaction with conduction electrons in metals and with elastic waves; they are described by linear and cubic spectral functions, respectively.

1.1. Ohmic damping

Low-energy electron–hole excitations in metallic materials may be replaced by effective bosons with a linear spectral density $J(\omega) = \pi K\omega$. As a particular feature, the resulting damping function is constant at low frequency, which is the criterion for 'ohmic' dissipation. The ohmic damping model describes both interstitial hydrogen impurities in metals and tunnelling defects in metallic glasses. The effects on the impurity dynamics are governed by a logarithmic infrared singularity, which is found in any order of perturbation theory. Kondo performed a partial summation of singular terms in the perturbation series, and found a power law for the dependence of the tunnel frequency on temperature, $\tilde{\Delta}_0 \propto T^K$ [11]. Subsequently, much work was devoted to the ohmic damping model [10, 12, 13]. As a most striking result, a cross-over from damped oscillations to overdamped motion was found; for weak coupling $K \ll 1$, the incoherent relaxation rate decreases with rising temperature, according to $\Gamma \propto T^{2K-1}$.

1.2. Phonon damping

In insulating materials, low-frequency elastic waves provide the most efficient damping mechanism. The dispersion relation $\omega_{s\boldsymbol{k}} = v_s|\boldsymbol{k}|$, where s labels transverse and longitudinal polarization, gives rise to the quadratic Debye density of phonon states. Moreover, taking into account the frequency dependence $\lambda_k \propto \sqrt{\omega_k}$, and subsuming the wave vector $\boldsymbol{k}$ and the branch index s in the label k, we obtain the well known cubic law

$$J(\omega) = \left(\frac{\gamma_\mathrm{l}^2}{v_\mathrm{l}^5} + \frac{2\gamma_\mathrm{t}^2}{v_\mathrm{t}^5}\right)\frac{\omega^3}{2\pi\hbar\varrho} \equiv \frac{3\gamma^2\omega^3}{2\pi\hbar\varrho v^5}. \tag{1.4}$$

We have replaced the sound velocities v_t and v_l and the deformation potentials γ_t and γ_l by appropriate average values v and γ. For later convenience we rewrite the spectral density as

$$J(\omega) = \pi\alpha\omega^3 \equiv \pi\tilde{\alpha}(\hbar^2/k_\mathrm{B}^2)\omega^3 \tag{1.5}$$

where the dimension of the coupling parameter α is (frequency)$^{-2}$, and that of $\tilde{\alpha}$ is (temperature)$^{-2}$. (For $\hbar = k_\mathrm{B}$, one has $\alpha = \tilde{\alpha}$.) In terms of the material constants, α reads $\alpha = (3\gamma^2/2\pi^2\hbar\varrho v^5)$.

For a solid consisting of N atoms in a volume V, the Debye temperature Θ_s and the corresponding frequency cut-off $k_\mathrm{B}\Theta_s/\hbar$ for the phonon branch s are given by the sound velocity $v_s k_\mathrm{D}$ according to $k_\mathrm{B}\Theta_s = \hbar v_s(6\pi^2 N/V)^{1/3}$. Following [14], we define an effective Debye temperature by the average value $3/\Theta^3 = 1/\Theta_\mathrm{l}^3 + 2/\Theta_\mathrm{t}^3$.

This paper is restricted to tunnelling of atomic defects which are coupled to a phonon heat bath with a cubic spectral function. There are four parameters, the tunnel frequency Δ_b, temperature T, the Debye temperature Θ, and the coupling strength $\tilde{\alpha}$. The latter may vary from $\tilde{\alpha} \approx 10^{-5}$ K^{-2} for Li impurities in potassium chloride to $\tilde{\alpha} \approx 10^{-2}$ K^{-2} for tunnelling defects in oxide glasses. The quantity $\hbar\Delta_\mathrm{b}/k_\mathrm{B}$ hardly exceeds 1 K, and one finds that most real systems satisfy the condition of small tunnel frequency,

$$\alpha\Delta_\mathrm{b}^2 \ll 1. \tag{1.6}$$

This relation simplifies significantly the analysis of the perturbation series; we will refer to it later on. The two-state approximation applies only for temperatures well below the vibrational levels in the double-well potential. For most cases this implies that the validity of the present model is restricted to $T \ll \Theta$.

There are various approaches to the dissipative dynamics of a two-state system coupled to a phonon heat bath, using functional integral methods [10, 15], diagrammatic perturbation theory [16], mode-coupling theory [17, 18, 19, 20], and, more recently, strong-coupling perturbation theory for the pseudo-spin propagator matrix [22]. These works agree on the behaviour at very low temperature, where both damping and relaxation rates are governed by the direct or one-phonon process, resulting in weakly damped oscillations.

Discrepancies arise, however, at higher temperature, where the first-order approximation for the perturbation series breaks down, and where multi-phonon processes contribute significant corrections to the rate. In each of the works above cited, a different high-temperature law has been reported (cf. the discussion in [22]). Since already for the lowest-order correction to the direct process, i.e., for the term proportional to $\tilde{\alpha}^2$, there is a manifest disagreement, a rigorous evaluation of this term would provide a proper criterion for the validity of the cited approaches. The purpose of the present paper is to derive such a criterion.

General aspects of the spin-phonon model have been discussed in detail by Leggett *et al* in [10] which we will frequently refer to. In the present work we use a perturbation expansion in terms of a four-dimensional propagator matrix, which was developed in [22], yet with a different choice for the 'unperturbed' problem. The expansion in [22] starts from small-polaron types of state, whereas here we use the form (1.2) and treat the linear coupling term as a perturbation. Accordingly, both the dressed tunnel frequency and the lowest-order damping rate obtained in [22] contain terms of any order in the coupling parameter $\tilde{\alpha}$. This implicit partial resummation of powers of $\tilde{\alpha}$ is supposed to provide a proper strong-coupling theory; yet since it is not based on a series in terms of a well defined small parameter, its validity is not easily assessed.

By means of a perturbation theory in terms of the phonon coupling potential, we derive a reduced pseudo-spin propagator whose self-energy is expanded in powers of the coupling parameter $\tilde{\alpha}$. (According to (1.3) and (1.4), $\tilde{\alpha}$ is quadratic in the coupling energy $\hbar\lambda_k$.) Then we calculate the first two terms of the series for the damping rate. The lowest-order contribution is identical to the well known one-phonon rate [1]. The next-order correction is a novel result; it provides a rigorous criterion for the validity of the various strong-coupling approaches mentioned above, and it permits us to settle the question of the existence of an incoherent regime.

2. Dynamic quantities

Time evolution of quantum mechanical operators is determined by the von Neumann equation, $\dot{\sigma}_\alpha = (\mathrm{i}/\hbar)[H, \sigma_\alpha] \equiv \mathrm{i}\mathcal{L}\sigma_\alpha$, whose formal integral may be written in terms of the quantum Liouville operator $\mathcal{L}$ as

$$\sigma_\alpha(t) = \mathrm{e}^{\mathrm{i}\mathcal{L}(t-t')}\sigma_\alpha(t'). \tag{2.1}$$

Moreover we need to define the initial state at $t = 0$. It turns out to be convenient to consider a particle initially localized in the left well evolving in time according to (2.1) [10]. The corresponding statistical operator factorizes at $t = 0$,

$$\rho = \rho_{\mathrm{S}}\rho_{\mathrm{B}}. \tag{2.2}$$

Here, ρ_S projects on the quantum state $|L\rangle$, and the remaining factor, $\rho_B = e^{-\beta H_B}/\mathrm{Tr}(e^{-\beta H_B})$, describes the heat bath in thermal equilibrium, with $H_B = \sum_k \hbar\omega_k b_k^\dagger b_k$. The average with respect to (2.2) is denoted by angular brackets,

$$\langle \cdots \rangle = \mathrm{Tr}(\rho \cdots). \tag{2.3}$$

Since ρ factorizes with respect to spin and bath degrees of freedom, the trace in the average (2.3) may be performed in two steps, accordingly. Thus the time-dependent spin polarization

$$\langle \sigma_\alpha(t) \rangle = \langle \mathcal{U}(t)\sigma_\alpha \rangle \tag{2.4}$$

may be written in terms of the reduced time evolution operator

$$\mathcal{U}(t) = \langle e^{i\mathcal{L}t} \rangle_B \tag{2.5}$$

where the subscript B indicates a partial trace over bath coordinates, $\langle \cdots \rangle_B = \mathrm{Tr}_B(\rho_B \cdots)$. (The trace in (2.4) involves only spin degrees of freedom.)

As discussed in [22], the time-dependent expectation values of σ_z and σ_x determine the dissipative two-state dynamics entirely. According to the definition of the statistical operator in (2.2), the time-dependent expectation value of the two-state coordinate,

$$P(t) = \langle \sigma_z(t) \rangle \tag{2.6}$$

satisfies the the initial condition $P(t = 0) = 1$. In the limit of zero coupling, $\lambda_k \to 0$, $P(t)$ oscillates with the tunnel frequency Δ_b, while finite phonon coupling results in reduction of the tunnel frequency and an exponential loss of phase coherence.

Whereas the damping of $P(t)$ describes the loss of phase memory, the energy dissipation between even and odd pseudospin eigenstates is accounted for by the relaxation function

$$R(t) = \langle \sigma_x(t) \rangle. \tag{2.7}$$

Since σ_x is diagonal in the energy eigenstates of the uncoupled system, for $\lambda_k \to 0$ we find $R(t) = 0$ for all times. For the coupled system, i.e. finite λ_k, the function $R(t)$ tends towards the equilibrium occupation. The time scale of this relaxation process gives the energy dissipation rate.

3. Perturbation series

The Hamiltonian may be separated into spin and bath parts $H_S = \frac{1}{2}\hbar\Delta_b\sigma_x$ and H_B, and an interaction term $H_1 = \frac{1}{2}\hbar f\sigma_z$. Accordingly the Liouville operator consists of three terms $\mathcal{L} = \mathcal{L}_S + \mathcal{L}_B + \mathcal{L}_1$, which are defined by $\hbar\mathcal{L}_S A = [H_S, A]$, etc. Here A is an arbitrary composite operator which, in general, involves both spin and bath degrees of freedom.

Despite the formal similarity of the present perturbation theory to that of [22], the above choice for the perturbation H_1 leads to a basically different series expansion which, in turn, requires approximations unlike those of [22]. This becomes obvious when noting the equation of motion,

$$\dot\sigma_x = -f\sigma_y \qquad \dot\sigma_y = f\sigma_x - \Delta_b\sigma_z \qquad \dot\sigma_z = \Delta_b\sigma_y \tag{3.1}$$

where we have defined the phonon coupling potential

$$f = \sum_k \lambda_k(b_k + b_k^\dagger). \tag{3.2}$$

In contrast to the present case, both the perturbation potential H_1 and the equation of motion in [22] depend exponentially on the coupling constants λ_k.

The perturbation series for $\mathcal{U}(t)$ in terms of λ_k^2 is set up by putting $\mathcal{L}_0 = \mathcal{L}_S + \mathcal{L}_B$, expanding the time evolution operator in powers of $\mathcal{L}_1$,

$$e^{i\mathcal{L}t} = e^{i\mathcal{L}_0 t} + i\int_0^t d\tau\, e^{i\mathcal{L}_0(t-\tau)}\mathcal{L}_1 e^{i\mathcal{L}_0\tau} + i^2\int_0^t d\tau \int_0^\tau d\tau'\, e^{i\mathcal{L}_0(t-\tau)}\mathcal{L}_1 e^{i\mathcal{L}_0(\tau-\tau')}\mathcal{L}_1 e^{i\mathcal{L}_0\tau'} + \cdots \tag{3.3}$$

and performing the partial trace over bath coordinates. By definition, the unperturbed time evolution factorizes into spin and bath parts,

$$e^{i\mathcal{L}_0 t} = e^{i\mathcal{L}_S t}\, e^{i\mathcal{L}_B t}. \tag{3.4}$$

Following [22], we represent each factor in the series (3.3) as a 4×4 matrix on the space spanned by the identity operator σ_0 and the three Pauli matrices σ_x, σ_y, σ_z. While $\mathcal{L}_S$ and $\mathcal{L}_B$ act on either spin or bath degrees of freedom, the interaction part $\mathcal{L}_1$ is defined as the commutator of a composite operator, $\frac{1}{2}\sigma_z f$, with the operator to its right.

We start with the left-hand side of (3.3). After performing the bath average, we define the matrix

$$\mathcal{U}_{ij}(t) = \tfrac{1}{2}\,\mathrm{Tr}(\sigma_i \mathcal{U}(t)\sigma_j) \tag{3.5}$$

with $i, j = 0, x, y, z$. (We need to retain the element σ_0 in order to obtain a closed algebra with respect to multiplication.) Regarding the right-hand side of (3.3), we first consider the spin factor of the unperturbed time evolution (3.4),

$$\breve{\mathcal{U}}_{ij}(t) = \tfrac{1}{2}\,\mathrm{Tr}(\sigma_i\, e^{i\mathcal{L}_S t}\sigma_j). \tag{3.6}$$

Since it does not involve bath degrees of freedom, it is easily integrated; in the matrix notation defined above it reads

$$\breve{\mathcal{U}}(t) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \cos(\Delta_b t) & -\sin(\Delta_b t) \\ 0 & 0 & \sin(\Delta_b t) & \cos(\Delta_b t) \end{pmatrix}. \tag{3.7}$$

The bath part of (3.3) results in the usual time evolution of Bose operators

$$b_k^\dagger(t) = e^{i\omega_k t} b_k^\dagger \qquad b_k(t) = e^{-i\omega_k t} b_k. \tag{3.8}$$

Involving composite operators, the matrix representation of the factors $\mathcal{L}_1$ in (3.3) proves to be more complicated. The spin parts develop according to (3.6) and bath parts according to (3.8). Yet each factor $\mathcal{L}_1$, acting as a commutator with the whole object to its right, gives rise to a subtlety with respect to the time ordering of the bath operators.

This becomes obvious when evaluating the action of $\mathcal{L}_1$ on a composite operator $\sigma_i B$, where B depends on the bath operators b_k and $b_k^\dagger$ and may include a time-dependent phase factor. With $[\sigma_i, B] = 0$ and the well known algebra of Pauli matrices we define operators $\mathcal{F}_i$ through

$$\mathcal{L}_1 \sigma_i B = \sigma_z \sigma_i \mathcal{F}_i B \tag{3.9}$$

where, with $i = 0, x, y, z$, the action of $\mathcal{F}_i$ on the bath operator B is given either by the commutator or the anticommutator with the elastic strain f,

$$\mathcal{F}_0 B = \mathcal{F}_z B = \tfrac{1}{2}(fB - Bf) \tag{3.10}$$

$$\mathcal{F}_x B = \mathcal{F}_y B = \tfrac{1}{2}(fB + Bf). \tag{3.11}$$

Equations (3.9)–(3.11) are just a special case of a more general commutation relation for composite operators A_iB_i with $[A_i, B_j] = 0$, namely [23]

$$[A_1B_1, A_2B_2] = \tfrac{1}{2}[A_1, A_2]\{B_1, B_2\} + \tfrac{1}{2}\{A_1, A_2\}[B_1, B_2] \tag{3.12}$$

where square brackets denote the commutator, and curly brackets the anticommutator. Putting $A_1 = \sigma_z$, $B_1 = f$, $A_2 = \sigma_i$, and $B_2 = B$, one easily recovers (3.9). Accordingly, the perturbation theory can be written in terms of correlation operators $\mathcal{A}_C. = \{A, .\}$ and response operators $\mathcal{A}_R. = [A, .]$. In [22] a more explicit use of the form (3.12) turned out to be necessary, because of the more complicated perturbation chosen there.

According to (3.9), the algebra of Pauli matrices determines the action of $\mathcal{L}_1$ on the spin degrees of freedom. With

$$\Lambda_{ij} = \tfrac{1}{2}\,\mathrm{Tr}(\sigma_i\sigma_z\sigma_j) \tag{3.13}$$

we calculate the matrix representation for the operator σ_z,

$$\mathbf{\Lambda} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -\mathrm{i} & 0 \\ 0 & \mathrm{i} & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}. \tag{3.14}$$

The action on the bath degrees of freedom is accounted for by multiplying Λ_{ij} by $\mathcal{F}_j$; with (3.9) and (3.13) we have

$$\tfrac{1}{2}\,\mathrm{Tr}_S(\sigma_i\mathcal{L}_1\sigma_j) = \Lambda_{ij}\mathcal{F}_j. \tag{3.15}$$

Now we are ready to insert the matrices (3.7) and (3.15) in the series (3.3). After taking the thermal average with respect to the bath we obtain a series for the time evolution operator $\mathcal{U}(t)$,

$$\begin{aligned}\mathcal{U}_{ij}(t) = \breve{\mathcal{U}}_{ij}(t) &+ \mathrm{i}\int_0^t \mathrm{d}\tau\, \breve{\mathcal{U}}_{ik}(t-\tau)\Lambda_{kl}\breve{\mathcal{U}}_{lj}(\tau)\varphi_l(\tau) \\ &+ \mathrm{i}^2\int_0^t \mathrm{d}\tau \int_0^\tau \mathrm{d}\tau'\, \breve{\mathcal{U}}_{ik}(t-\tau)\Lambda_{kl}\breve{\mathcal{U}}_{lm}(\tau-\tau')\Lambda_{mn}\breve{\mathcal{U}}_{nj}(\tau')\varphi_{ln}(\tau,\tau') \\ &+ \cdots\end{aligned} \tag{3.16}$$

where the summation labels $k, l, m, \ldots$ run over $0, x, y, z$. The influence of the heat bath is accounted for by the correlation functions

$$\varphi_{i\ldots j}(\tau_i, \ldots, \tau_j) = \langle \mathcal{F}_i(\tau_i)\cdots\mathcal{F}_j(\tau_j)\rangle_B. \tag{3.17}$$

Equation (3.16) constitutes the formal solution for the time evolution of the initial state (2.2). The subsequent perturbation theory relies on a cumulant expansion of the bath correlations (3.17). First note that, because the operators $\mathcal{F}_i$ are linear in b_k and $b_k^\dagger$, the correlations with an odd number of arguments vanish,

$$0 = \varphi_i(\tau_i) = \varphi_{ijk}(\tau_i, \tau_j, \tau_k) = \cdots. \tag{3.18}$$

In order to put the series (3.16) in a form that permits partial re-summation, we decompose the bath correlations of even order in terms of particular cumulants. Starting from the second-order correlation

$$\phi_{ij}(\tau_i, \tau_j) = \langle \mathcal{F}_i(\tau_i)\mathcal{F}_j(\tau_j)\rangle_B \equiv \varphi_{ij}(\tau_i, \tau_j) \tag{3.19}$$

we define cumulants $\phi_{i\ldots j}$ according to

$$\varphi_{ijkl} = \phi_{ij}\phi_{kl} + \phi_{ijkl} \tag{3.20}$$

$$\varphi_{ijklmn} = \phi_{ij}\phi_{kl}\phi_{mn} + \phi_{ijkl}\phi_{mn} + \phi_{ij}\phi_{klmn} + \phi_{ijklmn} \tag{3.21}$$

and so forth. Because of the time ordering $\tau_i > \tau_j > \tau_k > \cdots$, the cumulants ϕ_{ij}, ϕ_{ijkl}, ϕ_{ijklmn},... contain irreducible terms with 1, 2, 3,... phonon lines.

Insertion in (3.16) and rearranging the terms yields an integral equation for the time evolution operator,

$$\mathcal{U}_{ij}(t) = \breve{\mathcal{U}}_{ij}(t) - \sum_{kl} \int_0^t \mathrm{d}\tau \int_0^\tau \mathrm{d}\tau' \breve{\mathcal{U}}_{ik}(t-\tau)\Sigma_{kl}(\tau-\tau')\mathcal{U}_{lj}(\tau') \tag{3.22}$$

where the self-energy is given in terms of a series

$$\Sigma_{ij}(t) = \Sigma_{ij}^{(1)}(t) + \Sigma_{ij}^{(2)}(t) + \cdots \tag{3.23}$$

whose nth-order contribution involves the cumulant with $2n$ indices, $\phi_{i_1 \ldots i_{2n}}$. We give explicitly the first two terms

$$\Sigma_{ij}^{(1)}(t-t') = \textstyle\sum_{kl} \Lambda_{ik}\breve{\mathcal{U}}_{kl}(t-t')\Lambda_{lj}\phi_{kj}(t,t') \tag{3.24}$$

$$\begin{aligned}\Sigma_{ij}^{(2)}(t-t') = -\sum_{k\cdots q} \int_{t'}^t \mathrm{d}\tau \int_{t'}^\tau \mathrm{d}\tau' \Lambda_{ik}\breve{\mathcal{U}}_{kl}(t-\tau)\Lambda_{lm}\breve{\mathcal{U}}_{mn}(\tau-\tau') \\ \times \Lambda_{np}\breve{\mathcal{U}}_{pq}(\tau'-t')\Lambda_{qj}\phi_{kmpj}(t,\tau,\tau',t').\end{aligned} \tag{3.25}$$

(The self-energy depends only on the difference $(t-t')$, since the bath correlations are invariant under translation in time, e.g., $\phi_{ij}(t,t') = \phi_{ij}(t+\tau, t'+\tau)$; this property has already been used when writing (3.22) as a double convolution.)

We mention two general properties of the self-energy matrix $\mathbf{\Sigma}$, which will considerably simplify the evaluation of the perturbation series (3.23). *First*, from (3.17)–(3.26) it follows that in any order $\Sigma_{ij}(t)$ involves a bath correlation whose first element from the right reads $\mathcal{F}_j(0)$; according to the definition of the thermal average, there is no bath operator to its right. As both $\mathcal{F}_0$ and $\mathcal{F}_z$ yield zero when acting on identity, the corresponding entries of the self-energy vanish,

$$\Sigma_{i0}(t) = 0 = \Sigma_{iz}(t) \qquad \text{for } i = 0, x, y, z. \tag{3.26}$$

(Thus Σ is not symmetric; when choosing $\mathrm{tr}_\mathrm{B}(\cdots\rho_\mathrm{B})$ for the thermal average, (3.26) would be valid for the adjoint matrix $\Sigma^\dagger$.)

Second, the Hamiltonian (1.2) is invariant under the canonical transformation

$$\sigma_z \to -\sigma_z \qquad \sigma_y \to -\sigma_y \qquad b_k \to -b_k. \tag{3.27}$$

As a consequence any correlation function involving an odd number of these operators vanishes; in terms of the self-energy this condition requires

$$\Sigma_{ij}(t) = 0 = \Sigma_{ji}(t) \qquad \text{for } i = 0, x \text{ and } j = y, z. \tag{3.28}$$

Thus the self-energy matrix splits in two 2×2 blocks; taking into account both (3.26) and (3.28) we have

$$\mathbf{\Sigma}(t) = \begin{pmatrix} 0 & \Sigma_{0x}(t) & 0 & 0 \\ 0 & \Sigma_{xx}(t) & 0 & 0 \\ 0 & 0 & \Sigma_{yy}(t) & 0 \\ 0 & 0 & \Sigma_{zy}(t) & 0 \end{pmatrix}. \tag{3.29}$$

In the following we will calculate the first two terms of the perturbation series for these entries according to (3.24) and (3.26).

4. Bath correlations

According to the definition of the operators $\mathcal{F}_i$, all bath correlations can be expressed in terms of

$$\chi(t-t') = \tfrac{1}{2}\langle f(t)f(t') - f(t')f(t)\rangle \tag{4.1}$$

$$\psi(t-t') = \tfrac{1}{2}\langle f(t)f(t') + f(t')f(t)\rangle. \tag{4.2}$$

After inserting (3.10) and (3.11), we find eight finite functions of second order,

$$\phi_{0x}(t,t') = \phi_{0y}(t,t') = \phi_{zx}(t,t') = \phi_{zy}(t,t') \equiv \chi(t-t') \tag{4.3}$$

$$\phi_{xx}(t,t') = \phi_{xy}(t,t') = \phi_{yy}(t,t') = \phi_{yx}(t,t') \equiv \psi(t-t'). \tag{4.4}$$

Since both $\mathcal{F}_0$ and $\mathcal{F}_z$ yield zero when acting on identity, the remaining terms vanish:

$$\phi_{i0}(t) = 0 = \phi_{iz}(t). \tag{4.5}$$

Regarding the fourth-order correlations, we use (3.20) and the well known expansion in terms of two-times correlation functions, and thus obtain

$$\phi_{ijkl}(\tau_i,\tau_j,\tau_k,\tau_l) = \phi_{ik}(\tau_i,\tau_k)\phi_{jl}(\tau_j,\tau_l) + \phi_{il}(\tau_i,\tau_l)\phi_{jk}(\tau_j,\tau_k). \tag{4.6}$$

Because of the relations (4.5), certain correlations vanish,

$$\phi_{ijkl} = 0 \qquad \text{for } k = 0, z \text{ or } l = 0, z. \tag{4.7}$$

Here we note explicitly those functions which will be needed later,

$$\begin{aligned}\phi_{xyxy}(t,\tau,\tau',t') &= \phi_{yxyx}(t,\tau,\tau',t') \\ &= \psi(t-t')\psi(\tau-\tau') + \psi(t-\tau')\psi(\tau-t')\end{aligned} \tag{4.8}$$

$$\phi_{zxyx}(t,\tau,\tau',t') = \chi(t-t')\psi(\tau-\tau') + \chi(t-\tau')\psi(\tau-t') \tag{4.9}$$

$$\phi_{0zxy}(t,\tau,\tau',t') = \chi(t-t')\chi(\tau-\tau') + \chi(t-\tau')\chi(\tau-t'). \tag{4.10}$$

For further use we calculate the phonon propagators

$$\psi(t) = \sum_k \lambda_k^2(1+2n_k)\cos(\omega_k t) \qquad \chi(t) = -\mathrm{i}\sum_k \lambda_k^2 \sin(\omega_k t) \tag{4.11}$$

and their Laplace transforms,

$$\psi(z) = -\sum_k \lambda_k^2(1+2n_k)\frac{z}{z^2-\omega_k^2} \tag{4.12}$$

$$\chi(z) = -\sum_k \lambda_k^2 \frac{\omega_k}{z^2-\omega_k^2} \tag{4.13}$$

with Bose occupation numbers $n_k = [\mathrm{e}^{\beta\hbar\omega_k} - 1]^{-1}$.

4.1. Pole approximation

Besides the perturbation expansion, we need to apply a Markov approximation. Since the latter is obtained naturally in frequency space, we note the Laplace transform of the propagator matrix $\mathcal{U}(t)$. Applying the convolution theorem to (3.22) and solving for $\mathcal{U}(z)$, we obtain

$$\mathcal{U}(z) = \frac{-1}{-\breve{\mathcal{U}}(z)^{-1} + \Sigma(z)} \tag{4.14}$$

where the uncoupled spin dynamics is given by

$$-\breve{\mathcal{U}}(z)^{-1} = \begin{pmatrix} z & 0 & 0 & 0 \\ 0 & z & 0 & 0 \\ 0 & 0 & z & -\mathrm{i}\Delta_\mathrm{b} \\ 0 & 0 & \mathrm{i}\Delta_\mathrm{b} & z \end{pmatrix}. \tag{4.15}$$

From the determinant

$$\det\bigl(\breve{\mathcal{U}}(z)^{-1}\bigr) = -z^2\bigl(z^2 - \Delta_\mathrm{b}^2\bigr) \tag{4.16}$$

one finds that the uncoupled propagator exhibits a double pole at $z = 0$ and a pair of poles at $z = \pm\Delta_\mathrm{b}$.

The entries of the self-energy matrix are smooth functions of frequency. In order to calculate the resonance frequencies z_0 of $\mathcal{U}(z)$, we expand the self-energy $\Sigma(z)$ in a power series about z_0,

$$\Sigma(z) = \Sigma(z_0) + (z - z_0)\left[\frac{\mathrm{d}\Sigma(z)}{\mathrm{d}z}\right]_{z=z_0} + \cdots \tag{4.17}$$

and we truncate after the linear term. After inserting this approximate expression in (4.14), one finds that the determinant of $\mathcal{U}(z)^{-1}$ is given by a fourth-order polynomial in z. Each root of this polynomial provides a resonance, which requires an imaginary part after evaluating the dissipative terms of Σ at the corresponding frequency.

Since both $\breve{\mathcal{U}}$ and Σ are block-diagonal, the full propagator may be written as

$$\boldsymbol{\mathcal{U}}(z) = \begin{pmatrix} \mathcal{V}(z) & 0 \\ 0 & \mathcal{W}(z) \end{pmatrix} \tag{4.18}$$

with 2×2 matrices $\mathcal{V}$ and $\mathcal{W}$, where $\mathcal{V}$ acts on the subspace labelled by 0 and x, and $\mathcal{W}$ on that spanned by y and z. This particular form of the propagator follows directly from (3.6) and the invariance under the canonical transformation (3.27). Owing to the fact that $\mathcal{U}(z)$ is block-diagonal, the submatrices $\mathcal{V}$ and $\mathcal{W}$ may be dealt with separately. We start with $\mathcal{W}$.

5. Phase relaxation: $\mathcal{W}(z)$

The submatrix $\mathcal{W}$ describes tunnelling oscillations with the bare frequency Δ_b. Phonon coupling affects this motion in two respects. First, it results in renormalization of the tunnel frequency and, second, it destroys the phase coherence. These two effects will be accounted for by a reduced tunnel frequency $\tilde{\Delta}_0$ and a damping rate Γ_t.

In order to properly perform the pole approximation, we insert the expansion (4.17) in the secular equation

$$0 = \det\bigl(-\mathcal{W}(z)^{-1}\bigr) = \det\begin{pmatrix} z + \Sigma_{yy}(z) & -\mathrm{i}\Delta_\mathrm{b} \\ \mathrm{i}\Delta_\mathrm{b} + \Sigma_{zy}(z) & z \end{pmatrix}. \tag{5.1}$$

First we determine the reduced tunnel frequency $\tilde{\Delta}_0$ by calculating the reactive part of the self-energy. In a second step we evaluate the dissipative part of Σ at the effective tunnel frequency $\tilde{\Delta}_0$.

5.1. The self-energy

After inserting the bath correlations (4.3)–(4.5), one easily finds that there is a single first-order term,

$$\Sigma^{(1)}_{yy}(t) = \breve{\mathcal{U}}_{xx}(t)\psi(t); \tag{5.2}$$

the remaining entries vanish. Since $\breve{\mathcal{U}}_{xx}(t)$ is equal to unity, the Laplace transform of (5.2) reads as

$$\Sigma^{(1)}_{yy}(z) = \psi(z); \tag{5.3}$$

derivation with respect to frequency gives

$$\frac{\mathrm{d}}{\mathrm{d}z}\Sigma^{(1)}_{yy}(z) = \sum_k \lambda_k^2(1+2n_k)\frac{\omega_k^2+z^2}{(\omega_k^2-z^2)^2}. \tag{5.4}$$

Owing to the cubic phonon spectral function, the integral is dominated by high frequencies; hence we may drop the terms z^2. Then the derivative is independent of frequency,

$$\frac{\mathrm{d}}{\mathrm{d}z}\Sigma^{(1)}_{yy} = \sum_k \lambda_k^2(1+2n_k)\omega_k^{-2} \equiv \delta_1. \tag{5.5}$$

Now we turn to the second-order contributions. From the selection rule (4.7), we obtain two finite entries

$$\Sigma^{(2)}_{yy}(t) = -\int_0^t \mathrm{d}\tau \int_0^\tau \mathrm{d}\tau' \breve{\mathcal{U}}_{xx}(t-\tau)\breve{\mathcal{U}}_{yy}(\tau-\tau')\breve{\mathcal{U}}_{xx}(\tau')\phi_{xyxy} \tag{5.6}$$

$$\Sigma^{(2)}_{zy}(t) = -\int_0^t \mathrm{d}\tau \int_0^\tau \mathrm{d}\tau' \breve{\mathcal{U}}_{00}(t-\tau)\breve{\mathcal{U}}_{zy}(\tau-\tau')\breve{\mathcal{U}}_{xx}(\tau')\phi_{0zxy}. \tag{5.7}$$

In a diagrammatic representation, the second-order phonon correlations comprise a part where the two phonon lines cross ('crossing diagram') and a part where they do not ('rainbow diagram'); accordingly we separate the self-energy

$$\Sigma^{(2)}_{yy}(t) = Y_{\mathrm{C}}(t) + Y_{\mathrm{R}}(t) \qquad \Sigma^{(2)}_{zy}(t) = Z_{\mathrm{C}}(t) + Z_{\mathrm{R}}(t). \tag{5.8}$$

We start with Σ_{yy}. After decomposing the cosine functions according to $\cos(x) = \frac{1}{2}(\mathrm{e}^{\mathrm{i}x} + \mathrm{e}^{-\mathrm{i}x})$, the time dependence involves exponentials only. Defining

$$\tilde{\lambda}_k^2 = \lambda_k^2(1+2n_k) \tag{5.9}$$

and performing the double integrals, we find the contribution arising from the rainbow diagram

$$Y_{\mathrm{R}}(t) = \frac{1}{8}\sum_{k,k'}\tilde{\lambda}_k^2\tilde{\lambda}_{k'}^2\sum_{\{\pm\}}\left[\frac{-\mathrm{i}t\,\mathrm{e}^{\pm\mathrm{i}\omega_k t}}{\pm\omega_{k'}\pm\Delta_{\mathrm{b}}} + \frac{\mathrm{e}^{\mathrm{i}(\pm\omega_k\pm\omega_{k'}\pm\Delta_{\mathrm{b}})t} - \mathrm{e}^{\pm\mathrm{i}\omega_k t}}{(\pm\omega_{k'}\mp\Delta_{\mathrm{b}})^2}\right] \tag{5.10}$$

and from the crossing diagram

$$Y_{\mathrm{C}}(t) = \frac{1}{8}\sum_{k,k'}\tilde{\lambda}_k^2\tilde{\lambda}_{k'}^2\sum_{\{\pm\}}\left[\frac{\mathrm{e}^{\pm\mathrm{i}\omega_k t} - \mathrm{e}^{\pm\mathrm{i}\omega_{k'} t}}{(\pm\omega_{k'}\mp\omega_k)(\pm\omega_k\pm\Delta_{\mathrm{b}})} + \frac{\mathrm{e}^{\mathrm{i}(\pm\omega_k\pm\omega_{k'}\pm\Delta_{\mathrm{b}})t} - \mathrm{e}^{\pm\mathrm{i}\omega_k t}}{(\pm\omega_{k'}\mp\Delta_{\mathrm{b}})(\pm\omega_k\mp\Delta_{\mathrm{b}})}\right]. \tag{5.11}$$

The sums over the signs of Δ_{b}, ω_k, and $\omega_{k'}$ are independent of each other and give rise to eight terms.

Since it involves exponential functions only, the Laplace transform $\Sigma^{(2)}_{yy}(z)$ is easily calculated. The first term in brackets in (5.10) vanishes when summing over the signs, whereas the second one gives a finite contribution,

$$Y_{\mathrm{R}}(z) = -\frac{1}{8}\sum_{kk'\{\pm\}}\tilde{\lambda}_k^2\tilde{\lambda}_{k'}^2\frac{-(\pm\omega_{k'}\pm\Delta_{\mathrm{b}})}{(z\pm\omega_k\pm\omega_{k'}\pm\Delta_{\mathrm{b}})(z\pm\omega_k)}\frac{1}{(\pm\omega_{k'}\mp\Delta_{\mathrm{b}})^2}. \tag{5.12}$$

An analogous expression for $Y_{\mathrm{C}}(z)$ is obtained from (5.11).

At frequencies small compared with $k_{\mathrm{B}}T/\hbar$, the real part is much larger than the imaginary one. When expanding $\Re Y_{\mathrm{R}}(z)$ and $\Re Y_{\mathrm{C}}(z)$ in powers of z, we find the linear term prevails. A straightforward calculation gives

$$\frac{\mathrm{d}}{\mathrm{d}z}\Re\Sigma^{(2)}_{yy}(z) = \mathcal{P}\sum_{k,k'}\tilde{\lambda}^2_k\tilde{\lambda}^2_{k'}\frac{1}{(\omega^2_k-\Delta^2_{\mathrm{b}})(\omega^2_{k'}-\omega^2_k)} \equiv \delta_2 \tag{5.13}$$

where we have discarded insignificant corrections of the order $(\hbar\Delta_{\mathrm{b}}/k_{\mathrm{B}}T)$ and where $\mathcal{P}$ denotes the principal value.

Evaluation of the off-diagonal element $\Sigma^{(2)}_{zy}$ runs along the same lines. When proceeding as for $Y_{\mathrm{R}}(t)$ we find

$$Z_{\mathrm{R}}(t) = -\frac{\mathrm{i}}{8}\sum_{k,k'}\lambda^2_k\lambda^2_{k'}\sum_{s,s',\sigma}ss'\sigma\frac{\mathrm{e}^{\mathrm{i}(s\omega_k+s'\omega_{k'}+\sigma\Delta_{\mathrm{b}})t}-\mathrm{e}^{\mathrm{i}s\omega_k t}}{(s'\omega_{k'}-\sigma\Delta_{\mathrm{b}})^2} \tag{5.14}$$

where we have defined the sign variables $s, s', \sigma = \pm$. The sine functions in the propagators $\mathcal{U}_{zy}(t)$ and $\chi(t)$ result in the additional factor $ss'\sigma$, as compared with Y_{R}.

Because of our definition of off-diagonal matrix elements, Σ_{zy} carries an additional factor i, and thus $\Re\Sigma_{zy}$ is the dissipative part, and $\Im\Sigma_{zy}$ the reactive one. (Note the factor i of the tunnel frequency Δ_{b} in (4.15) and (5.1).) With the same approximations as above, we find that the reactive part is small and its derivative negligible at small frequencies,

$$(\mathrm{d}\,\Im\Sigma^{(2)}_{zy}/\mathrm{d}z) = 0. \tag{5.15}$$

5.2. The reduced tunnel frequency

Now we are going to calculate the reduced tunnel frequency from (5.1). For frequencies much smaller than $k_{\mathrm{B}}T/\hbar$, $\Re\Sigma_{yy}$ is well approximated by its term linear in z; therefore

$$(z-z_0)\partial_z\,\Re\Sigma_{yy}(z_0) + \Re\Sigma_{yy}(z_0) = z\,\partial_z\,\Re\Sigma_{yy} = z(\delta_1+\delta_2). \tag{5.16}$$

Discarding for the moment the dissipative parts of Σ, we have

$$\det\bigl(\mathcal{W}(z)^{-1}\bigr) = z^2(1+\delta_1+\delta_2) - \Delta^2_{\mathrm{b}} = \mathcal{Z}^{-1}[z^2-\tilde{\Delta}^2_0] \tag{5.17}$$

with the renormalized tunnel frequency

$$\tilde{\Delta}^2_0 = \mathcal{Z}\Delta^2_{\mathrm{b}} \tag{5.18}$$

and the reduction factor

$$\mathcal{Z} = [1+\delta_1+\delta_2]^{-1}. \tag{5.19}$$

5.3. The damping rate

With (5.16) and when taking into account the dissipative parts of the self-energy, we obtain the characteristic equation

$$\det\bigl(\mathcal{W}(z)^{-1}\bigr) = z^2(1+\delta_1+\delta_2) - \Delta^2_{\mathrm{b}} + \mathrm{i}z\Gamma(z) \tag{5.20}$$

with the dissipation kernel

$$\Gamma(z) = \Im\Sigma_{yy}(z) + (\Delta_{\mathrm{b}}/z)\,\Re\Sigma_{zy}(z). \tag{5.21}$$

We note that $\Gamma(z)$ is a symmetric function of z, since $\Im\Sigma_{yy}(z)$ is symmetric and $\Re\Sigma_{zy}(z)$ antisymmetric. Solving the quadratic equation (5.20) and evaluating the damping function $\Gamma(z)$ at the tunnel frequency $\tilde{\Delta}_0$ leads to the rate

$$\Gamma_{\mathrm{t}} = \tfrac{1}{2}\mathcal{Z}\Gamma(\tilde{\Delta}_0) \tag{5.22}$$

and to the effective resonance frequency

$$\omega_{\rm t}^2 = \tilde{\Delta}_0^2 - \tfrac{1}{4}\mathcal{Z}^2\big[\Im\Sigma_{yy}(\tilde{\Delta}_0)\big]^2. \tag{5.23}$$

After matrix inversion and dropping an insignificant term Σ_{zy} in the residue, we find

$$\mathcal{W}(z) = -\frac{1}{(z+{\rm i}\Gamma_{\rm t})^2 - \omega_{\rm t}^2}\begin{pmatrix} \mathcal{Z}z & -{\rm i}\mathcal{Z}\Delta_{\rm b} \\ {\rm i}\mathcal{Z}\Delta_{\rm b} & z+2{\rm i}\Gamma_{\rm t}\end{pmatrix}. \tag{5.24}$$

Now we are going to evaluate the dissipative entries of the self-energy $\Im\Sigma_{yy}$ and $\Re\Sigma_{zy}$. The first-order term of the transverse rate is given by

$$\Im\Sigma_{yy}^{(1)}(z) = \pi\alpha z^3\coth(\hbar z/2k_{\rm B}T) \tag{5.25}$$

for z real. According to (5.8), the second-order contribution $\Sigma_{yy}^{(2)}$ comprises two terms,

$$Y_{\rm R}''(z) = \frac{\pi}{8}\sum_{k,k'}\tilde{\lambda}_k^2\tilde{\lambda}_{k'}^2\sum_{\{\pm\}}\frac{\delta(z\pm\omega_k\pm\omega_{k'}\pm\Delta_{\rm b})-\delta(z\pm\omega_k)}{(\pm\omega_{k'}\pm\Delta_{\rm b})^2} \tag{5.26}$$

$$\begin{aligned} Y_{\rm C}''(z) = \frac{\pi}{8}\sum_{k,k'}\tilde{\lambda}_k^2\tilde{\lambda}_{k'}^2\sum_{\{\pm\}}\Bigg[&\frac{\delta(z\pm\omega_k)-\delta(z\pm\omega_{k'})}{(\pm\omega_{k'}\mp\omega_k)(\pm\omega_k\pm\Delta_{\rm b})} \\ &+\frac{\delta(z\pm\omega_k\pm\omega_{k'}\pm\Delta_{\rm b})-\delta(z\pm\omega_k)}{(\pm\omega_{k'}\pm\Delta_{\rm b})(\pm\omega_k\pm\Delta_{\rm b})}\Bigg]. \end{aligned} \tag{5.27}$$

Those terms in (5.26) and (5.27) which involve a delta function of a single phonon frequency are easily calculated, since the integrand factorizes with respect to ω_k and $\omega_{k'}$. When keeping the leading term only, we find

$$\frac{\pi}{2}\sum_{k,k'}\tilde{\lambda}_k^2\tilde{\lambda}_{k'}^2\delta(z-\omega_k)\omega_{k'}^{-2} = \delta_1\,\Im\Sigma_{yy}^{(1)}(z). \tag{5.28}$$

Now we consider the contributions involving a delta function with two frequency arguments, $\delta(z\pm\omega_k\pm\omega_{k'}\pm\Delta_{\rm b})$. After inserting the spectral density (1.4) and removing one frequency integration by means of the delta function, we expand the integral in powers of the small quantities z and $\Delta_{\rm b}$. Note that this expansion involves the temperature factors $\coth(\hbar\omega_k/2k_{\rm B}T)$, the spectral function $J(\omega)$, and the factors given explicitly in (5.27). (We note the derivative $\partial_x\coth(x) = -\sinh(x)^{-2}$.) The first two terms of this power series cancel; after calculating the quadratic term and using (5.28), we have

$$\begin{aligned} \Im\Sigma_{yy}^{(2)}(z) = \delta_1\,\Im\Sigma_{yy}^{(1)}(z) &+ z^2 2\pi\alpha^2\int_0^{\omega_{\rm D}}{\rm d}\omega\,\omega^2\coth(\beta\hbar\omega/2)^2 \\ &+(z^2-\Delta_{\rm b}^2)2\pi\alpha^2\int_0^{\omega_{\rm D}}{\rm d}\omega\,\omega^2\frac{\coth(\beta\hbar\omega/2)}{\sinh(\beta\hbar\omega/2)^2}. \end{aligned} \tag{5.29}$$

Evaluation of the off-diagonal entry $\Re\Sigma_{zy}$ runs along the same lines. When expanding in powers of z and $\Delta_{\rm b}$, we find after some algebra the quadratic term

$$\Re\Sigma_{zy}^{(2)}(z) = -2\pi\alpha^2 z\Delta_{\rm b}\int_0^{\omega_{\rm D}}{\rm d}\omega\,\omega^2. \tag{5.30}$$

Finally we calculate the damping function $\Gamma(\tilde{\Delta}_0)$ according to (5.22). For this purpose we evaluate the self-energy (5.25), (5.29), (5.30) at the reduced tunnel frequency $\tilde{\Delta}_0$. In order to obtain meaningful results, we retain only those contributions to $\Gamma(\tilde{\Delta}_0)$ that are linear or quadratic in the coupling parameter $\tilde{\alpha}$. Thus we find from (5.25)

$$\Im\Sigma_{yy}^{(1)}(\tilde{\Delta}_0) = 2\pi\alpha\Delta_{\rm b}^2(k_{\rm B}T/\hbar)\,[1-\delta_1] + {\rm O}(\alpha^3). \tag{5.31}$$

The second-order term (5.29) is already quadratic in α. Hence the corrections arising from its argument $\tilde{\Delta}_0$ are to be discarded; accordingly we put $z = \Delta_b$. Then the first term in (5.29) cancels the correction proportional to δ_1 in (5.31), and the third term on the r.h.s. of (5.29) disappears. In view of (5.21) we combine the second term of (5.29) with (5.30); for $k_B T \ll \hbar\omega_D$ we may replace the upper bound of the resulting integral by infinity and thus obtain

$$\int_0^\infty d\omega\, \omega^2 [\coth(\hbar\omega/2k_B T)^2 - 1] = (2k_B T/\hbar)^3 \frac{\pi^2}{6}. \tag{5.32}$$

Rearranging the remaining terms and using (1.5), we find

$$\Gamma(\tilde{\Delta}_0) = 2\pi\alpha\Delta_b^2 (k_B T/\hbar)\left[1 + \tfrac{4}{3}\pi^2 \tilde{\alpha} T^2 + O(\tilde{\alpha}^2 T^4)\right]. \tag{5.33}$$

6. Energy relaxation: $\mathcal{V}(z)$

For zero phonon coupling, $\mathcal{V}$ has two undamped poles at zero frequency. When expanding Σ_{xx} and Σ_{0x} about $z_0 = 0$ and inverting the 2×2 matrix, it acquires one damped pole,

$$\mathcal{V}(z) = \frac{-1}{z[z(1+\Sigma'_{xx}) + \Sigma_{xx}]} \begin{pmatrix} z(1+\Sigma'_{xx}) + \Sigma_{xx} & -\Sigma_{0x} - z\Sigma'_{0x} \\ 0 & z \end{pmatrix}. \tag{6.1}$$

(We use the shorthand notation for the derivative $\Sigma' = (d\Sigma/dz)$.)

6.1. The self-energy Σ_{xx}

When taking into account (4.5), we easily we find from (3.24) the finite first-order terms

$$\Sigma^{(1)}_{0x}(t) = i\breve{\mathcal{U}}_{zy}(t)\chi(t) \tag{6.2}$$

$$\Sigma^{(1)}_{xx}(t) = \breve{\mathcal{U}}_{yy}(t)\psi(t). \tag{6.3}$$

Since these entries are products of the uncoupled spin propagator $\breve{\mathcal{U}}(t)$ and the phonon propagators $\chi(t)$ and $\psi(t)$, their Laplace transforms are given as convolutions, e.g.,

$$\Sigma^{(1)}_{xx}(z) = -\frac{1}{2\pi i}\int dz'\, \breve{\mathcal{U}}_{yy}(z')\psi(z - z'). \tag{6.4}$$

After closing the integration contour at infinity, we obtain

$$\Sigma^{(1)}_{xx}(z) = \tfrac{1}{2}\big[\psi(z - \Delta_b) + \psi(z + \Delta_b)\big] \tag{6.5}$$

$$\Sigma^{(1)}_{0x}(z) = \tfrac{1}{2}\big[\chi(z - \Delta_b) - \chi(z + \Delta_b)\big]. \tag{6.6}$$

At zero frequency both functions are purely imaginary,

$$\Sigma^{(1)}_{0x}(0) = i\frac{\pi}{2}\sum_k \lambda_k^2 \delta(\omega_k - \Delta_b) \equiv i\gamma_0 \tag{6.7}$$

$$\Sigma^{(1)}_{xx}(0) = i\gamma_0 \coth(\hbar\Delta_b/2k_B T) \tag{6.8}$$

whereas their derivatives at $z = 0$ are real. For $k_B T \gg \hbar\Delta_b$, the derivatives with respect to z are dominated by thermal phonon frequencies $\omega_k \gg \Delta_b$. Thus we may drop the tunnel frequency in the denominator, and we find with (5.4)

$$(d\Sigma^{(1)}_{xx}/dz) = \delta_1 \qquad (d\Sigma^{(1)}_{0x}/dz) \ll \delta_1; \tag{6.9}$$

accordingly we drop $(d\Sigma^{(1)}_{0x}/dz)$ and keep $(d\Sigma^{(1)}_{xx}/dz)$ only.

We will not derive the second-order contributions in detail, but merely note two particular features. First, the derivative of the real part is equal to that of $\Sigma^{(2)}_{yy}$,

$$(\mathrm{d}\Sigma^{(2)}_{xx}/\mathrm{d}z)|_{z=0} = \delta_2. \tag{6.10}$$

This is not surprising, since both $\Sigma^{(2)}_{yy}(t)$ and $\Sigma^{(2)}_{yy}(t)$ involve the same phonon correlation, and the spin propagator is of little significance for the derivatives. Thus we have with (6.9), (6.10) and (5.23)

$$1 + \partial_z \Sigma_{xx} = \mathcal{Z}^{-1}. \tag{6.11}$$

A second remark concerns the dissipative part $\Im\Sigma^{(2)}_{xx}(z)$. A detailed calculation shows that there is no proper second-order contribution like (5.32); one rather finds a renormalization of the first-order term, $\Im\Sigma^{(2)}_{xx}(z) = \delta_1 \Im\Sigma^{(1)}_{xx}(z)$, similar to the first term in (5.29).

The following discussion of the relaxation part of the propagator $\mathcal{U}$ will be restricted to the first order with respect to the coupling parameter α.

6.2. The relaxation rate

Because of (6.9) we may discard $\partial_z \Sigma_{0x}$ in (6.1). Using (6.7), (6.11) and the rate

$$\Gamma_\mathrm{l} = \mathcal{Z}\Sigma_{xx}(z=0) \tag{6.12}$$

and separating the two poles, we obtain for (6.1)

$$\mathcal{V}(z) = -\frac{1}{z}\begin{pmatrix} 1 & -\mathcal{Z}\gamma_0/\Gamma_\mathrm{l} \\ 0 & 0 \end{pmatrix} - \frac{1}{z + \mathrm{i}\Gamma_\mathrm{l}}\begin{pmatrix} 0 & \mathcal{Z}\gamma_0/\Gamma_\mathrm{l} \\ 0 & \mathcal{Z} \end{pmatrix}. \tag{6.13}$$

7. Time propagation

7.1. Damped oscillations

The propagator $\mathcal{U}(t)$ results from Laplace back-transformation of both $\mathcal{V}(z)$ and $\mathcal{W}(z)$. With (2.4) we find the transverse spin polarization (2.6) to be given by the lower diagonal element of $\mathcal{U}(t)$,

$$P(t) = \mathcal{U}_{zz}(t). \tag{7.1}$$

Upon Laplace back-transformation of (5.24) we find

$$\mathcal{U}_{zz}(t) = \mathrm{e}^{-\Gamma_\mathrm{t} t}\cos(\omega_\mathrm{t} t + \delta)/\cos(\delta) \tag{7.2}$$

with $\tan(\delta) = \Gamma_\mathrm{t}/\omega_\mathrm{t}$.

7.2. Relaxation to the stationary state

From (6.13) we obtain the time evolution in the subspace spanned by σ_0 and σ_x,

$$\mathcal{V}(t) = \begin{pmatrix} 1 & -\mathcal{Z}\gamma_0/\Gamma_\mathrm{l} \\ 0 & 0 \end{pmatrix} + \mathrm{e}^{-\Gamma_\mathrm{l} t}\begin{pmatrix} 0 & \mathcal{Z}\gamma_0/\Gamma_\mathrm{l} \\ 0 & \mathcal{Z} \end{pmatrix}. \tag{7.3}$$

Note that $\mathcal{V}(t)$ is equal to identity at $t = 0$; in the long-time limit $t \to \infty$ the second term in (7.3) disappears.

Inserting the phonon spectral density, we find the rates

$$\Gamma_\mathrm{l} = \mathcal{Z}\pi\alpha\Delta_\mathrm{b}^3 \coth(\hbar\Delta_\mathrm{b}/2k_\mathrm{B}T) \qquad \gamma_0 = \pi\alpha\Delta_\mathrm{b}^3. \tag{7.4}$$

With (2.6) and the average (2.3) we find $R(t) = \mathcal{U}_{0x}(t)$ and, after inserting (7.3),

$$R(t) = \tanh(\hbar\Delta_\mathrm{b}/2k_\mathrm{B}T)[1 - \mathrm{e}^{-\Gamma_\mathrm{l} t}]. \tag{7.5}$$

The spin polarization in thermal equilibrium, $\langle\sigma_x\rangle_{\rm eq}$, is given by the long-time limit

$$\langle\sigma_x\rangle_{\rm eq} = \lim_{t\to\infty} R(t) = \tanh(\hbar\Delta_{\rm b}/2k_{\rm B}T). \tag{7.6}$$

Finally we note the statistical operator in thermal equilibrium

$$\rho_{\rm S}^{\rm eq} = \tfrac{1}{2}[\sigma_0 - \tanh(\hbar\Delta_{\rm b}/2k_{\rm B}T)\sigma_x]. \tag{7.7}$$

7.3. Temperature dependence

Here we evaluate the reduced tunnel frequency and the rates, the main issue being the variation with temperature. We start with the factor $\mathcal{Z} = (1+\delta_1+\delta_2)^{-1}$. When inserting the spectral density in (6.9), we obtain

$$\delta_1 = \tilde{\alpha}\Theta^2 + \tfrac{2}{3}\pi^2\tilde{\alpha}T^2. \tag{7.8}$$

The second term δ_2 involves more complicated integrals, which cannot be performed analytically. Since we will consider lowest-order corrections to the one-phonon rate only, we will not need δ_2.

Noting $\delta_n \propto \tilde{\alpha}^n$, we find that an expansion of the reduced tunnel frequency in terms of δ_1 and δ_2,

$$\tilde{\Delta}_0^2 = \mathcal{Z}\Delta_{\rm b}^2 = \Delta_{\rm b}^2[1-\delta_1-\delta_2+\tfrac{1}{2}\delta_1^2+\cdots] \tag{7.9}$$

constitutes a series in powers of the coupling parameter $\tilde{\alpha}$. According to the definitions of δ_1 and δ_2, the renormalization of the tunnel frequency involves both a static part in terms of $\tilde{\alpha}\Theta^2$ and a temperature-dependent one in powers of $\tilde{\alpha}T^2$. The above expressions for δ_1 and δ_2 are valid for $T \ll \Theta$ only.

In the limit of vanishing coupling the factor $\mathcal{Z}$ is unity; the rates are given by the first-order terms and fulfil the well known relation

$$\Gamma_{\rm l} = 2\Gamma_{\rm t} = \pi\alpha\Delta_{\rm b}^3\coth(\hbar\Delta_{\rm b}/2k_{\rm B}T) \qquad \text{for } \delta_2 \ll \delta_1 \ll 1. \tag{7.10}$$

Yet this law does not hold true for higher-order contributions. The terms of higher order in $\tilde{\alpha}$ are relevant at higher temperatures $k_{\rm B}T \gg \hbar\Delta_{\rm b}$, where we may replace the coth function by its inverse argument. As mentioned above without derivation, the second-order terms of the longitudinal rate vanish.

The transverse damping rate $\Gamma_{\rm t}$ describes the loss of phase memory of the tunnelling oscillations. When inserting (5.33) and the definition of the reduced tunnel frequency $\tilde{\Delta}_0$ in (5.22), we obtain

$$\Gamma_{\rm t} = \pi\alpha\tilde{\Delta}_0^2(k_{\rm B}T/\hbar)\left[1+\tfrac{4}{3}\pi^2\tilde{\alpha}T^2+{\rm O}(\tilde{\alpha}^2T^4)\right]. \tag{7.11}$$

Yet the rate $\Gamma_{\rm t}$ involves the reduced tunnel frequency $\tilde{\Delta}_0 = \tilde{\Delta}_0(T)$ which depends on temperature through the factor $\mathcal{Z}$. Inserting (7.9) and expanding the tunnel frequency in terms of $\tilde{\alpha}T^2$ about its zero-temperature value, $\Delta_0 = \tilde{\Delta}_0(T=0)$, we find

$$\Gamma_{\rm t} = \pi\alpha\Delta_0^2(k_{\rm B}T/\hbar)\left[1+\tfrac{2}{3}\pi^2\tilde{\alpha}T^2+{\rm O}(\tilde{\alpha}^2T^4)\right]. \tag{7.12}$$

(To lowest order we have $\Delta_0^2 = \Delta_{\rm b}^2[1-\tilde{\alpha}\Theta^2]$.) As a consequence of the temperature dependence of $\tilde{\Delta}_0$, the linear and quadratic terms in brackets differ by a factor $\frac{4}{3}\pi^2\tilde{\alpha}T^2$ in (7.11) and by $\frac{2}{3}\pi^2\tilde{\alpha}T^2$ in (7.12). These expressions for the transverse rate constitute a main result of this paper.

8. Discussion

8.1. Validity of the perturbation expansion

From the above results it is clear that truncation of the perturbation series at first or second order yields proper results as long as the quantities δ_1 and δ_2 are much smaller than unity; in terms of temperature T, Debye temperature Θ, and coupling constant $\tilde{\alpha}$, this condition reads

$$\tilde{\alpha}T^2 \ll 1 \qquad \tilde{\alpha}\Theta^2 \ll 1. \tag{8.1}$$

Thus the perturbative regime is characterized by weak coupling and low temperature. The opposite case requires a strong-coupling approach as discussed in [21, 22].

As is clear from (7.12), the quantity $\tilde{\alpha}T^2$ is the most relevant small parameter for the perturbation expansion. Violation of the second inequality, $\tilde{\alpha}\Theta^2 \geqslant 1$, is a less serious problem, since formally the corresponding reduction factor may be absorbed in the zero-temperature tunnel frequency Δ_0.

From the form of the perturbation series one expects that higher-order corrections to the rate involve factors $(\tilde{\alpha}T^2)^n$ with $n = 2, 3, \ldots$. Thus it might seem that the expansion (7.12) is of little practical use, since terms of any order become important as soon as $\tilde{\alpha}T^2$ approaches unity.

Yet (7.11) and (7.12) constitute the only rigorous result for the damping rate beyond the first-order term available up to now. They provide a thorough criterion for the validity of any strong-coupling theory. In the remainder of this section, we compare our findings with those from previous approaches.

8.2. Comparison to previous work

Except for the mode-coupling approximation in [20], most works on the spin-boson model start from a small-polaron type formulation for the Hamiltonian (1.2) [10, 16, 21, 22]. Here we discuss their results for the transverse rate in view of (7.11). Since the rate is usually written in terms of a temperature-dependent tunnel frequency whose lowest-order corrections are identical to those of our $\tilde{\Delta}_0$, we use (7.11) rather than (7.12).

In the framework of a functional-integral formulation for $P(t)$, Leggett *et al* have evaluated the two-state dynamics in terms of the *non-interacting blip approximation* (NIBA). For the cubic bath spectral density (1.5), their rate, (6.36) of [10], reads in our notation as $(\pi/2)\alpha\tilde{\Delta}_0^3 \coth(\hbar\tilde{\Delta}_0/2k_BT)$. From the absence of higher-order terms these authors conclude that the coupling to phonons does not lead to overdamped, or incoherent, motion of the two-state system. It turns out, however, that the result of [10] has been derived with an additional approximation which, in terms of (7.11), amounts to neglecting the corrections in brackets. Clearly, this approximation is valid at low temperatures, $\tilde{\alpha}T^2 \ll 1$, but it breaks down for $\tilde{\alpha}T^2$ approaching unity.

Pirc and Gosar have developed a diagrammatic perturbation theory for the spin-boson model [16]. Their rate contains higher-order terms, but of odd order only, i.e., it fails in view of the quadratic contribution to (7.11).

Starting from the equation of motion for the pseudo-spin operators in the small-polaron picture, the present author has evaluated the transverse rate in NIBA and calculated lowest-order corrections (cf. [21] or chapter 8 of [8]). The transverse rate increases exponentially with temperature for $\tilde{\alpha}T^2 \gg 1$. The result in NIBA, Eq. (27) of [21], gives one half of the second-order term in (7.11). Yet when taking into account the corrections to NIBA, the second-order term of (34) of [21] agrees with the exact result (7.11).

Finally we compare (7.11) with the rate obtained from a mode-coupling approximation (MCA), which reads in our notation $\pi\alpha\tilde{\Delta}_0^2(k_BT/\hbar)+\pi^5\alpha^2(k_BT/\hbar)^5$ for $\tilde{\alpha}T^2 \ll 1$; cf. (3.32) of [20]. The discrepancy with respect to the correction term in (7.11) may be understood by noting that MCA corresponds to retaining in the perturbation series non-crossing diagrams only. When dropping the crossing part of (5.8), and evaluating the rainbow diagram (5.12), the present perturbation theory yields, up to an insignificant numerical constant, the result from MCA. Yet the subtle cancellation of the leading terms of crossing and rainbow diagrams leads us to the conclusion that MCA does not provide an appropriate approximation scheme for the spin-boson model.

9. Summary and conclusion

We have applied a perturbation expansion in terms of the Liouville operator to the self-energy matrix of the pseudo-spin propagator. Although formally very similar to the strong-coupling theory of [22], the present approach requires different approximations and, accordingly, yields complementary results. Its basic feature consists in a systematic expansion of the self-energy in powers of the coupling parameter $\tilde{\alpha}$.

The transverse damping rate (7.11) constitutes the main results of this paper. In terms of the coupling parameter $\tilde{\alpha}$, it shows a positive second-order contribution. This rigorous result settles the question of the existence of higher-order contributions to the damping rate. Thereby, it invalidates various previous statements on that issue and, in particular, the claim of [10] that a phonon heat bath would not drive a cross-over to incoherent tunnelling.

Together with a recent small-polaron approach [8, 21], the correction factor in (7.11) permits us to conclude on the validity of the high-temperature rate obtained there. The factor $\frac{4}{3}\pi^2\tilde{\alpha}T^2$ in (7.11) proves that NIBA is not a controlled approximation for the cubic bath spectral density. On the other hand, our result confirms the rate which has been obtained previously by calculating lowest-order corrections to NIBA [21]. Regarding the strong-coupling theory of [22], we find that it gives the correct linear and quadratic contributions to the rate. In view of the present findings, that approach provides the most suitable treatment for the spin-phonon model in the temperature range where multi-phonon contributions are not negligible.

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