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Density Matrix Equation for a Bathed Small System and its Application to Molecular Magnets

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The technique of density matrix equation (DME) for a small system interacting with a bath is explained in detail. Special attention is given to the nonsecular DME that is needed in the vicinity of overdamped tunnelling resonances in molecular magnets (MM). The relaxation terms of the DME for MM are represented in the universal form that does not employ any unknown spin-lattice coupling constants and absorbs the information about the spin Hamiltonian in the exact basis states and transition frequencies. This makes adding new types of anisotropy easy and error-free. The Mathematica code is available from the author.

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I. GENERAL THEORY

Density matrix is used to describe properties of a system that is a part of a larger system with which it interacts. Whereas isolated systems (such as the above mentioned larger system) can be described by a Schrödinger equation, systems which interact with their environments cannot. Starting from the Schrödinger equation for the isolated whole system, small system + environment (or *bath*), and eliminating the environmental variables, one can, in principle, construct an object that can be used to calculate observables of the small system in a short way. This object is the density matrix of the small system. Of course, integrating or taking matrix elements in two steps, at first over the environment and then over the small system is not a big simplification. This approach becomes really useful if one obtains a closed equation of motion for the density matrix of the small system, the density matrix equation (DME). This is possible if the interaction between the small system and its environment is small and can be considered as a perturbation, and the small system does not strongly perturb the state of the environment. The derivation of the DME for a bathed small system will be presented in Sec. II. Here the necessary components of the formalism will be introduced.

A. From the wave function to the density matrix

The general wave function or state $|\psi\rangle$ of an isolated quantum system can be expanded over a set of complete basis states $|\Psi_m\rangle$ as

$$|\Psi\rangle = \sum_m c_m |\Psi_m\rangle. \quad (1)$$

The coefficients c_m completely characterize the state $|\Psi\rangle$ and can be used to calculate physical quantities A described by corresponding operators \hat{A} :

$$A \equiv \langle \hat{A} \rangle \equiv \langle \Psi | \hat{A} | \Psi \rangle = \sum_{mn} c_m c_n^* \langle \Psi_n | \hat{A} | \Psi_m \rangle = \sum_{mn} c_m c_n^* A_{nm}. \quad (2)$$

One can define the *density matrix* ρ corresponding to quantum-mechanical states (pure states) of our small system by its matrix elements as

$$\{\rho\}_{mn} = \rho_{mn} = c_m c_n^*, \quad (3)$$

then Eq. (2) becomes

$$A = \sum_{mn} \rho_{mn} A_{nm}. \quad (4)$$

The density matrix satisfies the normalization condition

$$\text{Tr} \{\rho\} \equiv \sum_m \rho_{mm} = 1. \quad (5)$$

This condition follows from Eq. (3) for the pure states but it holds in general, too, since the average of the unity operator $A_{mn} = \delta_{mn}$ should be 1. Additionally, the condition

$$\sum_{mn} |\rho_{mn}|^2 = 1 \quad (6)$$

is satisfied for the density matrix of pure states, Eq. (3).

For systems interacting with their environment, observables A still are given by Eq. (4), although the coefficients ρ_{nm} in general do not reduce to products as in Eq. (3). For the whole system including the environment, one can use basis states that are direct products of those of the small system $|\psi_m\rangle$ and those of the environment $|\phi_\varpi\rangle$:

$$|\Psi_{m\varpi}\rangle = |\psi_m\rangle \otimes |\phi_\varpi\rangle \equiv |\psi_m \phi_\varpi\rangle. \quad (7)$$

The quantum mechanical states of the whole system (considered as isolated) can be written, similarly to Eq. (1), in the form

$$|\Psi\rangle = \sum_{m\varpi} C_{m\varpi} |\Psi_{m\varpi}\rangle. \quad (8)$$

The expression for the observable A of the small system becomes

$$A = \langle \Psi | \hat{A} | \Psi \rangle = \sum_{m\varpi, n\varpi'} C_{m\varpi}^* C_{n\varpi'} \langle \Psi_{m\varpi} | \hat{A} | \Psi_{n\varpi'} \rangle = \sum_{m\varpi, n\varpi'} C_{m\varpi}^* C_{n\varpi'} \langle \psi_m | \hat{A} | \psi_n \rangle \langle \phi_\varpi | \phi_{\varpi'} \rangle. \quad (9)$$

For the orthonormal set of $|\phi_\varpi\rangle$ this can be rewritten in the form of Eq. (4) with $\rho_{mn} \Rightarrow \rho_{mn}^s$, where ρ_{mn}^s is the reduced density matrix of the subsystem given by

$$\rho_{mn}^s = \sum_{\varpi} C_{m\varpi} C_{n\varpi}^* \equiv \sum_{\varpi} \rho_{m\varpi, n\varpi}. \quad (10)$$

Since, in general, $C_{m\varpi}$ do not split into the factors depending on m and ϖ , the reduced DM ρ_{mn}^s is not a product of its wave-function coefficients, $\rho_{mn}^s \neq c_m c_n^*$. Obviously ρ_{mn}^s in Eq. (10) depends on the state of the whole system. One can check that it satisfies the normalization, Eq. (5). On the other hand, Eq. (6) is not satisfied, in general.

B. Entangled states and quantum statistics

It would be wrong to think that when the interaction between the small system and the environment becomes very weak, the density matrix of the small system, Eq. (10), simplifies to Eq. (3). If the coupling is vanishingly weak, quantum states of both the small system and the environment are well defined. Thus both the small system and the environment could be in their pure quantum mechanical states. However, there are pure states of the whole system that do not consist of pure states of the two subsystems. Such states can be called *entangled*. For instance, if both subsystems are two-level systems with the states $|\psi_1\rangle, |\psi_2\rangle$ and $|\phi_1\rangle, |\phi_2\rangle$, respectively, and the whole system is in the state

$$|\Psi\rangle = C_{11} |\psi_1 \phi_1\rangle + C_{22} |\psi_2 \phi_2\rangle \quad (11)$$

with $|C_{11}|^2 + |C_{22}|^2 = 1$, Eq. (10) with $C_{m\varpi} = C_{mm} \delta_{m\varpi}$ yields the diagonal density matrix

$$\rho_{mn}^s = |C_{mm}|^2 \delta_{mn}. \quad (12)$$

This density matrix satisfies Eq. (5). On the other hand, diagonal ρ_{mn}^s does not correspond to any pure state, cf. Eq. (3). Thus Eq. (6) is not satisfied,

$$\sum_{mn} |\rho_{mn}^s|^2 = \sum_m |C_{mm}|^4 \leq 1. \quad (13)$$

In particular, for $|C_{11}|^2 = |C_{22}|^2 = 1/2$ the result is $1/2$ instead of 1. This is unrelated to the interaction between the two subsystems and it alone mandates using the density matrix rather than the wave function for a subsystem in the general case.

In a non-entangled state, in the absence of interaction, the wave function of the whole system factorizes:

$$|\Psi\rangle = |\psi\rangle \otimes |\phi\rangle = \sum_m c_m |\psi_m\rangle \sum_{\varpi} d_{\varpi} |\phi_{\varpi}\rangle. \quad (14)$$

If the whole system and both subsystems are described by density matrices, the total density matrix under the above conditions factorizes such as

$$\rho_{m\varpi, n\varpi'} = \rho_{mn}^s \rho_{\varpi\varpi'}^b \quad (15)$$

for a small system and the bath. This factorization means that both subsystems are completely independent. If they are prepared at the initial moment independently from each other, one cannot expect their entanglement that requires a special care. As the time goes, interaction between the subsystems can cause some entanglement that, however, should remain small if the interaction is weak. The measure of entanglement is the mismatch in Eq. (15), where ρ_{mn}^s is defined by Eq. (10) and $\rho_{\varpi\varpi'}^b$ is defined by similar tracing out the variables of the small system. Note that both

rhs and lhs of Eq. (15) are properly normalized according to Eq. (5) and its variants. As a number measuring the entanglement, one can use, e.g.,

$$\text{Ent} = \frac{n^2}{n^2 - 1} \left[1 - \frac{\sum_{mn} |\rho_{mn}^s|^2 \sum_{\varpi\varpi'} |\rho_{\varpi\varpi'}^b|^2}{\sum_{m\varpi, n\varpi'} |\rho_{m\varpi, n\varpi'}|^2} \right] \quad (16)$$

that is related to Eq. (6). Here n is the number of states of each subsystem that is assumed to be common. If the whole system is in a pure state, the denominator is equal to 1. In particular, for Ψ given by Eq. (11), $n = 2$, one has ρ_{mn}^s given by Eq. (12) and similarly $\rho_{\varpi\varpi'}^b = |C_{\varpi\varpi}|^2 \delta_{\varpi\varpi'}$, so that

$$\text{Ent} = \frac{4}{3} \left[1 - \left(|C_{11}|^4 + |C_{22}|^4 \right)^2 \right]. \quad (17)$$

In the case $|C_{11}|^2 = |C_{22}|^2 = 1/2$ entanglement reaches its maximal value 1.

The coupling between subsystems also results in impossibility to describe them in terms of wave functions. The coupling causes slow transitions between energy levels, so that the total energy of the whole system is conserved. For the small system this means that it spends time in its different quantum mechanical states (in the interaction is weak and they are well defined), so that over a large time its state is a mixture of different states rather than a pure quantum mechanical state. Alternatively one can think about an ensemble of bathed small systems being in different pure states. An example of a mixture state is the thermal-equilibrium state

$$\rho_{mn} = \frac{1}{Z_s} \exp\left(-\frac{E_m}{k_B T}\right) \delta_{mn}, \quad (18)$$

where $Z_s = \sum_m e^{-E_m/(k_B T)}$ is the partition function. This formula holds if the basis states $|\psi_m\rangle$ are eigenfunctions of the small-system's Hamiltonian \hat{H}_s , that is a natural choice. We will see below that in the course of temporal evolution described by the DME, the initial density matrix approaches the form above.

In fact, the environment of the small system also can be weakly coupled to some *super-bath*, so that the small system + environment is not an isolated system and it also should be described by the density matrix instead of the wave function. The role of the super-bath is just to ensure that the whole system is not in a pure quantum state but in a mixture state, whereas the coupling between the bath and super-bath is assumed to be very weak and is never considered explicitly. In most cases the state of the environment (bath) is the thermal equilibrium that is described by the density matrix similar to Eq. (18). Since the bath is much larger than the small system, the weak coupling to the latter won't drive it out of the equilibrium.

C. Density matrix as an operator

The formalism of quantum mechanics allows one to consider the density matrix as an operator. More precisely, one can introduce the density operator

$$\hat{\rho} = \sum_{mn} \rho_{mn} |\psi_m\rangle \langle \psi_n|, \quad (19)$$

where $|\psi_m\rangle$ is a complete orthogonal set of states. The density matrix consists of matrix elements of the density operator:

$$\rho_{mn} = \langle \psi_m | \hat{\rho} | \psi_n \rangle, \quad (20)$$

so that both DM and DO contain the same information and are equivalent. Using the density operator allows one to put formulas in a more compact form without subscripts.

In particular, the expectation value of an operator \hat{A} can be obtained as a trace of $\hat{A}\hat{\rho}$ over any complete orthogonal set of states $|\psi_n\rangle$. The calculation is especially simple if one uses the set of states in the definition of $\hat{\rho}$:

$$\langle \hat{A} \rangle = \text{Tr} \left\{ \hat{A} \hat{\rho} \right\} = \sum_n \langle \psi_n | \hat{A} \hat{\rho} | \psi_n \rangle = \sum_{mn} \langle \psi_n | \hat{A} | \psi_m \rangle \langle \psi_m | \hat{\rho} | \psi_n \rangle = \sum_{mn} A_{nm} \rho_{mn}, \quad (21)$$

and the result coincides with Eq. (4). It can be proven that the trace of an operator is independent of the choice of the basis in $\text{Tr} \{ \dots \}$ and operators can be cyclically permuted under the trace symbol, so that $\text{Tr} \left\{ \hat{A} \hat{\rho} \right\} = \text{Tr} \left\{ \hat{\rho} \hat{A} \right\}$.

If the system interacts with its environment described by the basis $|\phi_{\varpi}\rangle$, the total DO has the form

$$\hat{\rho} = \sum_{m\varpi, n\varpi'} \rho_{m\varpi, n\varpi'} |\psi_m \phi_{\varpi}\rangle \langle \psi_n \phi_{\varpi'}| \equiv \sum_{m\varpi, n\varpi'} \rho_{m\varpi, n\varpi'} |\psi_m\rangle \langle \psi_n| \otimes |\phi_{\varpi}\rangle \langle \phi_{\varpi'}|. \quad (22)$$

Calculating any observable A that corresponds to the small system can be done in two steps: First calculating the trace over the variables of the bath and then calculating the trace over the basis states of the small system using Eq. (21). The first step yields the reduced density operator for the small system

$$\hat{\rho}^s = \text{Tr}_b \hat{\rho} \equiv \text{Tr}_{\varpi} \hat{\rho} \quad (23)$$

that has the form of Eq. (19) with

$$\rho_{mn}^s = \sum_{\varpi} \rho_{m\varpi, n\varpi}. \quad (24)$$

If the whole system is in a pure state, this formula coincides with Eq. (10).

The density operator corresponding to the thermal equilibrium of the small subsystem in contact with the bath has the beautiful form

$$\hat{\rho}^{\text{s,eq}} = \frac{1}{Z_s} \exp\left(-\frac{\hat{H}_s}{k_B T}\right). \quad (25)$$

Because of applications in quantum statistics density operator is also called *statistical operator*. Defining the density matrix ρ_{mn}^s with respect to the basis of eigenstates of \hat{H} in Eq. (20), one arrives at Eq. (18). The eigenstate basis is the most convenient for calculating thermal averages of physical quantities. However, as pointed out above, this could be done with the help of any other basis. If the whole system consisting of the small subsystem and the bath is in contact with a super-bath, the equilibrium statistical operator of the whole system has the form similar to Eq. (25).

For a system in a pure state, the density operator defined by Eq. (19) can be with the help of Eqs. (3) and (1) rewritten in the form

$$\hat{\rho} = |\psi\rangle \langle \psi|. \quad (26)$$

D. Temporal evolution and interaction representation

Temporal evolution of the DM or DO of an isolated system such as the small system + bath obeys the equation that follows from the Schrödinger equation. If, for instance, the whole system is in a pure state $|\Psi\rangle$, its density operator is given by

$$\hat{\rho} = |\Psi\rangle \langle \Psi| \quad (27)$$

c.f. Eq. (26). Then with the help of the Schrödinger equation and its conjugate

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle, \quad -i\hbar \frac{\partial}{\partial t} \langle \Psi| = \langle \Psi| \hat{H} \quad (28)$$

one obtains the quantum Liouville equation

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}]. \quad (29)$$

It should be noted that this equation is *not* an equation of motion for an operator in the Heisenberg representation that has another sign. The DO consists of states that have their *own* time dependence, unlike Heisenberg operators whose time dependence is *borrowed* from the states. In the presence of the super-bath the system is not in a pure state but rather in a mixture of different states $|\Psi\rangle$,

$$\hat{\rho} = \sum_{\Psi} A_{\Psi} |\Psi\rangle \langle \Psi|. \quad (30)$$

Fortunately, Eq. (29) is valid also in this case. Remember that Eq. (29) describes the whole system, small system + bath, although we dropped the index “tot” for brevity. Our final aim is, however, to obtain a density matrix equation (DME) for the density matrix of the small system alone with the bath degrees of freedom eliminated.

Let us break up the Hamiltonian of the system into a “simple” Hamiltonian \hat{H}_0 and perturbation or interaction \hat{V} :

$$\hat{H} = \hat{H}_0 + \hat{V}. \quad (31)$$

In the absence of \hat{V} , evolution of quantum states $|\Psi\rangle$ is described by the unitary evolution operator $\hat{U}_0(t)$:

$$|\Psi\rangle_t = \hat{U}_0(t)|\Psi\rangle_0, \quad \langle\Psi|_t = \langle\Psi|_0\hat{U}_0^\dagger(t), \quad (32)$$

where $|\Psi\rangle_0$ corresponds to the starting moment $t = 0$. We call $\hat{U}_0(t)$ *bare* evolution operator. From the Schrödinger equation (28) the equations of motion for \hat{U}_0 and its conjugate follow :

$$i\hbar\frac{\partial}{\partial t}\hat{U}_0 = \hat{H}_0\hat{U}_0, \quad -i\hbar\frac{\partial}{\partial t}\hat{U}_0^\dagger = \hat{U}_0^\dagger\hat{H}_0, \quad \hat{U}_0^\dagger(t) = \hat{U}_0^{-1}(t). \quad (33)$$

If \hat{H}_0 is time independent, the solution of these equations is

$$\hat{U}_0(t) = e^{-i\hat{H}_0 t/\hbar}, \quad \hat{U}_0^\dagger(t) = e^{i\hat{H}_0 t/\hbar}. \quad (34)$$

Of course, one can write similar formulas with the total Hamiltonian \hat{H} as well, $\hat{U}(t)$ being the full evolution operator. The idea of using $\hat{U}_0(t)$ is to split the nontrivial part of the evolution due to the perturbation \hat{V} from the trivial evolution due to \hat{H}_0 . To effectuate this, one can introduce the density matrix in the *interaction representation*

$$\hat{\rho}(t)_I = \hat{U}_0^\dagger(t)\hat{\rho}(t)\hat{U}_0(t). \quad (35)$$

The equation of motion for $\hat{\rho}(t)_I$ follows from Eqs. (29) and (33):

$$\begin{aligned} i\hbar\frac{\partial\hat{\rho}_I}{\partial t} &= i\hbar\frac{\partial\hat{U}_0^\dagger(t)}{\partial t}\hat{\rho}(t)\hat{U}_0(t) + \hat{U}_0^\dagger(t)i\hbar\frac{\partial\hat{\rho}}{\partial t}\hat{U}_0(t) + \hat{U}_0^\dagger(t)\hat{\rho}(t)i\hbar\frac{\partial\hat{U}_0(t)}{\partial t} \\ &= -\hat{U}_0^\dagger\hat{H}_0\hat{\rho}(t)\hat{U}_0(t) + \hat{U}_0^\dagger(t)\left[\hat{H}, \hat{\rho}\right]\hat{U}_0(t) + \hat{U}_0^\dagger(t)\hat{\rho}(t)\hat{H}_0\hat{U}_0 \\ &= \hat{U}_0^\dagger(t)\left[\hat{V}, \hat{\rho}\right]\hat{U}_0(t). \end{aligned} \quad (36)$$

Inserting $\hat{U}_0(t)\hat{U}_0^\dagger(t) = 1$ [see Eq. (33)] between the operators and defining

$$\hat{V}_I(t) \equiv \hat{U}_0^\dagger(t)\hat{V}\hat{U}_0(t), \quad (37)$$

this equation can be brought into the form

$$i\hbar\frac{\partial\hat{\rho}_I}{\partial t} = \left[\hat{V}_I, \hat{\rho}_I\right]. \quad (38)$$

One can see that the temporal evolution of the density matrix in the interaction representation is governed by the interaction only. This facilitates constructing the perturbation theory in \hat{V} .

II. THE DENSITY MATRIX EQUATION

A. From the full to reduced DOE

In this section the equation of motion for the reduced density operator of a small system s weakly interacting with a bath will be obtained. We will be following the method of Karl Blum [1] that is most practical, although not rigorous. Rigorous methods using the projection operator technique [2, 3] lead to the same result with much greater efforts.

The Hamiltonian can be written in the form

$$\hat{H} = \hat{H}_0 + \hat{V}, \quad \hat{H}_0 \equiv \hat{H}_s + \hat{H}_b, \quad \hat{V} \equiv \hat{H}_{s-b}. \quad (39)$$

Eq. (38) for the DO of the whole system can be integrated over the time resulting in the integral equation

$$\hat{\rho}(t)_I = \hat{\rho}(0)_I - \frac{i}{\hbar} \int_0^t dt' [\hat{V}(t')_I, \hat{\rho}(t')_I]. \quad (40)$$

Inserting it back into Eq. (38) one obtains the integro-differential equation

$$i\hbar \frac{d}{dt} \hat{\rho}(t)_I = [\hat{V}(t)_I, \hat{\rho}(0)_I] - \frac{i}{\hbar} \int_0^t dt' [\hat{V}(t)_I, [\hat{V}(t')_I, \hat{\rho}(t')_I]] \quad (41)$$

which is still an exact relation. Although this equation seems to be more complicated than the initial equation (38), it is convenient for perturbative treatment of the interaction \hat{V} . If the small system is not entangled with the bath in the initial state, that is a natural assumption, a small interaction cannot cause a significant entanglement as well. Thus the density operator of the whole system nearly factorizes, see Eq. (15). Here we additionally use that the bath is at thermal equilibrium that cannot be noticeably distorted by a weak interaction with the small subsystem:

$$\hat{\rho}(t)_I \cong \hat{\rho}_s(t)_I \hat{\rho}_b^{\text{eq}} = \hat{\rho}_s(t) \frac{1}{Z_b} \exp\left(-\frac{\hat{H}_b}{k_B T}\right) \quad (42)$$

Note that this approximation cannot be done in Eq. (40) since it leads to disappearance of the effect of interaction. To properly describe this effect, one has then to account for the corrections to Eq. (42) in the first order in \hat{V} . This way is inconvenient. To the contrary, Eq. (41) already contains quadratic \hat{V} terms that capture the main effect of interaction. Here taking into account small corrections to Eq. (42) can bring only irrelevant small terms. Now using Eq. (42) one can transform Eq. (41) into the density operator equation for the small system by making a trace over the bath variables according to Eq. (23):

$$\frac{d}{dt} \hat{\rho}_s(t)_I = \frac{i}{\hbar} \text{Tr}_b [\hat{V}(t)_I, \hat{\rho}_s(0)_I \hat{\rho}_b^{\text{eq}}] - \frac{1}{\hbar^2} \int_0^t dt' \text{Tr}_b [\hat{V}(t)_I, [\hat{V}(t')_I, \hat{\rho}_s(t')_I \hat{\rho}_b^{\text{eq}}]] \quad (43)$$

For the couplings \hat{V} we consider here, the first linear- \hat{V} term disappears.

The equation above is an integro-differential equation with integration over preceding times, $t' \leq t$, in the rhs. Such equations are called equations with memory and they are difficult to solve directly. In our case, however, the problem simplifies. The time evolution of $\hat{\rho}_s(t)_I$ in Eq. (43) is slow since it is governed by the weak interaction between the system and the bath. On the other hand, t' dependences of the other terms in the integrand (the kernel) are governed by \hat{H}_0 and thus they are fast at the scale of $\hat{\rho}_s(t)_I$. The analysis shows that the kernel in Eq. (43) is localized in the region $|t - t'| \lesssim 1/\omega_{\text{max}}$, where ω_{max} is the maximal frequency of the bath excitations. Thus in the integral over t' one can make the short-memory approximation $\hat{\rho}_s(t')_I \Rightarrow \hat{\rho}_s(t)_I$ after which the time integral can be calculated explicitly.

Returning to the original reduced density operator

$$\hat{\rho}_s(t) = \hat{U}_0(t) \hat{\rho}_s(t)_I \hat{U}_0^\dagger(t), \quad (44)$$

c.f. Eq. (35), and computing the derivative with the help of Eq. (33),

$$\frac{d}{dt} \hat{\rho}_s(t) = -\frac{i}{\hbar} [\hat{H}_s, \hat{\rho}_s(t)] + \hat{U}_0(t) \left(\frac{d}{dt} \hat{\rho}_s(t)_I \right) \hat{U}_0^\dagger(t), \quad (45)$$

one obtains

$$\frac{d}{dt} \hat{\rho}_s(t) = -\frac{i}{\hbar} [\hat{H}_s, \hat{\rho}_s(t)] - \frac{1}{\hbar^2} \int_0^t dt' \text{Tr}_b [\hat{V}, [\hat{V}(t' - t)_I, \hat{\rho}_s(t) \hat{\rho}_b^{\text{eq}}]] \quad (46)$$

or, with $\tau \equiv t - t'$ and dropping the subscript s, $\hat{\rho}^s(t) \Rightarrow \hat{\rho}(t)$,

$$\frac{d}{dt}\hat{\rho}(t) = -\frac{i}{\hbar} \left[\hat{H}_s, \hat{\rho}(t) \right] + \hat{R}\hat{\rho}(t), \quad (47)$$

where the first term with commutator is the conservative term and

$$\hat{R}\hat{\rho}(t) \equiv -\frac{1}{\hbar^2} \int_0^t d\tau \frac{1}{Z_b} \text{Tr}_b \left[\hat{V}, \left[\hat{V}(-\tau)_I, \hat{\rho}(t) \exp\left(-\frac{\hat{H}_b}{k_B T}\right) \right] \right] \quad (48)$$

describes the relaxation of the small system. Here, for time-independent problems,

$$\hat{V}(\tau)_I = \hat{U}_0^\dagger(\tau) \hat{V} \hat{U}_0(\tau) = e^{i\hat{H}_0\tau} \hat{V} e^{-i\hat{H}_0\tau}. \quad (49)$$

If the Hamiltonian of the small system \hat{H}_s depends on time, this time dependence is typically slow in comparison to the frequency of the bath excitations ω_{\max} , so that during the short times $\tau \sim 1/\omega_{\max}$ the change of \hat{H}_s is negligibly small. Thus one can simply use Eq. (49) with $\hat{H}_s = \hat{H}_s(t)$.

B. From the DOE to DME

Now one can go over from the density operator $\hat{\rho}$ to the density matrix ρ_{mn} using Eq. (20) and the notations

$$H_{s,mn} \equiv \langle \psi_m | \hat{H}_s | \psi_n \rangle, \quad V_{m\varpi, n\varpi'} \equiv \langle \psi_m \phi_\varpi | \hat{V} | \psi_n \phi_{\varpi'} \rangle, \quad (50)$$

where $|\phi_\varpi\rangle$ are eigenfunctions of \hat{H}_b . Then the partition function of the bath becomes

$$Z_b = \sum_{\varpi} \langle \phi_\varpi | e^{-\hat{H}_b/(k_B T)} | \phi_\varpi \rangle = \sum_{\varpi} e^{-E_{\varpi}/(k_B T)}. \quad (51)$$

The conservative term of the resulting DME has three different forms in three different cases. If the small-system states $|\psi_m\rangle$ are time independent and form a so-called *natural basis* unrelated to \hat{H}_s , the DME has the form

$$\frac{d}{dt}\rho_{mn} = -\frac{i}{\hbar} \sum_l (H_{s,ml}\rho_{ln} - \rho_{ml}H_{s,ln}) + \langle \psi_m | \hat{R}\hat{\rho} | \psi_n \rangle. \quad (52)$$

The natural basis is inconvenient for the evaluation of the relaxation term since the relaxation of the small system takes place not between the states $|\psi_m\rangle$ but between the eigenstates of \hat{H}_s :

$$\hat{H}_s |\chi_\alpha\rangle = \varepsilon_\alpha |\chi_\alpha\rangle, \quad e^{-i\hat{H}_s\tau/\hbar} |\chi_\alpha\rangle = e^{-i\varepsilon_\alpha\tau/\hbar} |\chi_\alpha\rangle. \quad (53)$$

The basis of $|\chi_\alpha\rangle$ will be called *diagonal basis* since the Hamiltonian matrix $\langle \chi_\alpha | \hat{H}_s | \chi_\beta \rangle = \varepsilon_\alpha \delta_{\alpha\beta}$ is diagonal. In the diagonal basis the DME has the form

$$\frac{d}{dt}\rho_{\alpha\beta} = -i\omega_{\alpha\beta}\rho_{\alpha\beta} + \langle \chi_\alpha | \hat{R}\hat{\rho} | \chi_\beta \rangle, \quad (54)$$

where $\omega_{\alpha\beta}$ are transition frequencies between the energy levels of the small system,

$$\hbar\omega_{\alpha\beta} \equiv \varepsilon_\alpha - \varepsilon_\beta, \quad (55)$$

and the relaxation term can be conveniently evaluated (see next section). If \hat{H}_s depends on time, one can use the *adiabatic basis* of the states $|\chi_\alpha(t)\rangle$ defined as

$$\hat{H}_s(t) |\chi_\alpha(t)\rangle = \varepsilon_\alpha(t) |\chi_\alpha(t)\rangle. \quad (56)$$

In this basis $\dot{\rho}_{\alpha\beta}$ acquires additional *non-adiabatic* terms:

$$\frac{d}{dt}\rho_{\alpha\beta} = \frac{d}{dt} \langle \chi_\alpha | \hat{\rho} | \chi_\beta \rangle = \langle \dot{\chi}_\alpha | \hat{\rho} | \chi_\beta \rangle + \langle \chi_\alpha | \hat{\rho} | \dot{\chi}_\beta \rangle - \frac{i}{\hbar} \langle \chi_\alpha | [\hat{H}_s, \hat{\rho}] | \chi_\beta \rangle + \langle \chi_\alpha | \hat{R}\hat{\rho} | \chi_\beta \rangle \quad (57)$$

i.e.,

$$\frac{d}{dt}\rho_{\alpha\beta} = \sum_\gamma (\langle \dot{\chi}_\alpha | \chi_\gamma \rangle \rho_{\gamma\beta} + \rho_{\alpha\gamma} \langle \chi_\gamma | \dot{\chi}_\beta \rangle) - i\omega_{\alpha\beta}\rho_{\alpha\beta} + \langle \chi_\alpha | \hat{R}\hat{\rho} | \chi_\beta \rangle. \quad (58)$$

As argued at the end of the preceding section, calculation of the relaxation term $\langle \chi_\alpha | \hat{R}\hat{\rho} | \chi_\beta \rangle$ is not complicated by the time dependence of \hat{H}_s . This calculation will be done in the next section where Eq. (54) will be used for brevity. The terms due to the time dependence of \hat{H}_s in Eq. (58) can be added if needed.

C. DME in the diagonal basis

Using Eqs. (54) and (48) and inserting summation over intermediate states yields

$$\begin{aligned} \frac{d}{dt}\rho_{\alpha\beta} &= -i\omega_{\alpha\beta}\rho_{\alpha\beta} - \frac{1}{\hbar^2} \int_0^t d\tau \frac{1}{Z_b} \sum_{\alpha'\beta'\varpi\varpi''} \\ &\left\{ \langle \chi_{\alpha}\phi_{\varpi} | \hat{V} | \chi_{\alpha'}\phi_{\varpi'} \rangle \langle \chi_{\alpha'}\phi_{\varpi'} | e^{-i\hat{H}_0\tau/\hbar} \hat{V} e^{i\hat{H}_0\tau/\hbar} | \chi_{\beta'}\phi_{\varpi''} \rangle \langle \chi_{\beta'}\phi_{\varpi''} | \hat{\rho} e^{-\hat{H}_b/(k_B T)} | \chi_{\beta}\phi_{\varpi} \rangle \right. \\ &- \langle \chi_{\alpha}\phi_{\varpi} | \hat{V} | \chi_{\alpha'}\phi_{\varpi'} \rangle \langle \chi_{\alpha'}\phi_{\varpi'} | \hat{\rho} e^{-\hat{H}_b/(k_B T)} | \chi_{\beta'}\phi_{\varpi''} \rangle \langle \chi_{\beta'}\phi_{\varpi''} | e^{-i\hat{H}_0\tau/\hbar} \hat{V} e^{i\hat{H}_0\tau/\hbar} | \chi_{\beta}\phi_{\varpi} \rangle \\ &- \langle \chi_{\alpha}\phi_{\varpi} | e^{-i\hat{H}_0\tau/\hbar} \hat{V} e^{i\hat{H}_0\tau/\hbar} | \chi_{\alpha'}\phi_{\varpi'} \rangle \langle \chi_{\alpha'}\phi_{\varpi'} | \hat{\rho} e^{-\hat{H}_b/(k_B T)} | \chi_{\beta'}\phi_{\varpi''} \rangle \langle \chi_{\beta'}\phi_{\varpi''} | \hat{V} | \chi_{\beta}\phi_{\varpi} \rangle \\ &\left. + \langle \chi_{\alpha}\phi_{\varpi} | \hat{\rho} e^{-\hat{H}_b/(k_B T)} | \chi_{\alpha'}\phi_{\varpi'} \rangle \langle \chi_{\alpha'}\phi_{\varpi'} | e^{-i\hat{H}_0\tau/\hbar} \hat{V} e^{i\hat{H}_0\tau/\hbar} | \chi_{\beta'}\phi_{\varpi''} \rangle \langle \chi_{\beta'}\phi_{\varpi''} | \hat{V} | \chi_{\beta}\phi_{\varpi} \rangle \right\}. \quad (59) \end{aligned}$$

Since the states are eigenfunctions of \hat{H}_s and \hat{H}_b , this simplifies to

$$\begin{aligned} \frac{d}{dt}\rho_{\alpha\beta} &= -i\omega_{\alpha\beta}\rho_{\alpha\beta} - \frac{1}{\hbar^2} \int_0^t d\tau \frac{1}{Z_b} \sum_{\alpha'\beta'\varpi\varpi''} \\ &\left\{ e^{i(-\varepsilon_{\alpha'} - E_{\varpi'} + \varepsilon_{\beta'} + E_{\varpi})\tau/\hbar} e^{-E_{\varpi}/(k_B T)} V_{\alpha\varpi, \alpha'\varpi'} V_{\alpha'\varpi', \beta'\varpi''} \rho_{\beta'\varpi''} \delta_{\varpi\varpi''} \right. \\ &- e^{i(-\varepsilon_{\beta'} - E_{\varpi''} + \varepsilon_{\beta} + E_{\varpi})\tau/\hbar} e^{-E_{\varpi''}/(k_B T)} V_{\alpha\varpi, \alpha'\varpi'} \rho_{\alpha'\beta'} \delta_{\varpi\varpi''} V_{\beta'\varpi'', \beta\varpi} \\ &- e^{i(-\varepsilon_{\alpha} - E_{\varpi} + \varepsilon_{\alpha'} + E_{\varpi'})\tau/\hbar} e^{-E_{\varpi''}/(k_B T)} V_{\alpha\varpi, \alpha'\varpi'} \rho_{\alpha'\beta'} \delta_{\varpi\varpi''} V_{\beta'\varpi'', \beta\varpi} \\ &\left. + e^{i(-\varepsilon_{\alpha'} - E_{\varpi'} + \varepsilon_{\beta'} + E_{\varpi})\tau/\hbar} e^{-E_{\varpi'}/(k_B T)} \rho_{\alpha\alpha'} \delta_{\varpi\varpi'} V_{\alpha'\varpi', \beta'\varpi''} V_{\beta'\varpi'', \beta\varpi} \right\} \quad (60) \end{aligned}$$

and further to

$$\begin{aligned} \frac{d}{dt}\rho_{\alpha\beta} &= -i\omega_{\alpha\beta}\rho_{\alpha\beta} - \frac{1}{\hbar^2} \int_0^t d\tau \frac{1}{Z_b} \sum_{\alpha'\beta'\varpi\varpi'} \\ &\left\{ e^{i(-\varepsilon_{\alpha'} - E_{\varpi'} + \varepsilon_{\beta'} + E_{\varpi})\tau/\hbar} e^{-E_{\varpi}/(k_B T)} V_{\alpha\varpi, \alpha'\varpi'} V_{\alpha'\varpi', \beta'\varpi} \rho_{\beta'\varpi} \right. \\ &- e^{i(-\varepsilon_{\beta'} - E_{\varpi'} + \varepsilon_{\beta} + E_{\varpi})\tau/\hbar} e^{-E_{\varpi'}/(k_B T)} V_{\alpha\varpi, \alpha'\varpi'} \rho_{\alpha'\beta'} V_{\beta'\varpi', \beta\varpi} \\ &- e^{i(-\varepsilon_{\alpha} - E_{\varpi} + \varepsilon_{\alpha'} + E_{\varpi'})\tau/\hbar} e^{-E_{\varpi'}/(k_B T)} V_{\alpha\varpi, \alpha'\varpi'} \rho_{\alpha'\beta'} V_{\beta'\varpi', \beta\varpi} \\ &\left. + e^{i(-\varepsilon_{\alpha'} - E_{\varpi'} + \varepsilon_{\beta'} + E_{\varpi})\tau/\hbar} e^{-E_{\varpi}/(k_B T)} \rho_{\alpha\alpha'} V_{\alpha'\varpi', \beta'\varpi} V_{\beta'\varpi', \beta\varpi} \right\}. \quad (61) \end{aligned}$$

Since the time kernel is sharply localized, the integration over τ can be extended to the interval $(0, \infty)$. Further, the relaxation of the small system that we are mainly interested in is due to the real part of the bath coupling term in Eq. (61). Its imaginary part is in most cases only a small correction to the first (conservative) term in this equation. Thus taking into account the time symmetry of $F_{ij}(\tau)$ one can replace

$$\int_0^t d\tau e^{i(-\varepsilon_{\alpha'} - E_{\varpi'} + \varepsilon_{\beta'} + E_{\varpi})\tau/\hbar} \Rightarrow \hbar\pi\delta(-\varepsilon_{\alpha'} - E_{\varpi'} + \varepsilon_{\beta'} + E_{\varpi}) \quad (62)$$

etc. After renaming indices in Eq. (61) ($\alpha' \Rightarrow \lambda$, $\beta' \Rightarrow \alpha'$ in the first term and $\beta' \Rightarrow \lambda$, $\alpha' \Rightarrow \beta'$ in the fourth term) one obtains the DME in the form

$$\frac{d}{dt}\rho_{\alpha\beta} = -i\omega_{\alpha\beta}\rho_{\alpha\beta} + \sum_{\alpha'\beta'} R_{\alpha\beta, \alpha'\beta'} \rho_{\alpha'\beta'}, \quad (63)$$

where

$$\begin{aligned} R_{\alpha\beta, \alpha'\beta'} &= \frac{\pi}{\hbar Z_b} \sum_{\varpi\varpi'} \left\{ - \sum_{\gamma} e^{-E_{\varpi}/(k_B T)} \delta(\varepsilon_{\alpha} - \varepsilon_{\gamma} + E_{\varpi} - E_{\varpi'}) V_{\alpha\varpi, \gamma\varpi'} V_{\gamma\varpi', \alpha'\varpi} \delta_{\beta'\varpi} \right. \\ &- \sum_{\gamma} e^{-E_{\varpi}/(k_B T)} \delta(\varepsilon_{\beta'} - \varepsilon_{\gamma} + E_{\varpi} - E_{\varpi'}) \delta_{\alpha\alpha'} V_{\beta'\varpi, \gamma\varpi'} V_{\gamma\varpi', \beta\varpi} \\ &\left. + e^{-E_{\varpi'}/(k_B T)} [\delta(\varepsilon_{\beta} - \varepsilon_{\beta'} + E_{\varpi} - E_{\varpi'}) + \delta(\varepsilon_{\alpha} - \varepsilon_{\alpha'} + E_{\varpi} - E_{\varpi'})] V_{\alpha\varpi, \alpha'\varpi'} V_{\beta'\varpi', \beta\varpi} \right\}. \quad (64) \end{aligned}$$

Eq. (63) can be written in a more compact form

$$\frac{d}{dt}\rho_{\alpha\beta} = \sum_{\alpha'\beta'} \Phi_{\alpha\beta,\alpha'\beta'} \rho_{\alpha'\beta'}, \quad (65)$$

where

$$\Phi_{\alpha\beta,\alpha'\beta'} \equiv -i\omega_{\alpha\beta}\delta_{\alpha\alpha'}\delta_{\beta\beta'} + R_{\alpha\beta,\alpha'\beta'}. \quad (66)$$

In the case of time-dependent Hamiltonian one has to add the non-adiabatic terms from Eq. (58) to the above DME. The asymptotic solution of Eq. (63) is

$$\rho_{\alpha\beta}^{\text{eq}} = \frac{1}{Z_s} \exp\left(-\frac{\varepsilon_{\alpha}}{k_B T}\right) \delta_{\alpha\beta} \quad (67)$$

that describes thermal equilibrium. This will be shown in Sec. II E.

D. Secular approximation and Fermi golden rule

One can transform Eq. (63) back into the interaction representation using Eqs. (35) and (20). In the diagonal basis, the relation between $\rho_{\alpha\beta}(t)$ and $\rho_{\alpha\beta}(t)_I$ has the simple form

$$\rho_{\alpha\beta}(t)_I = \langle \chi_{\alpha} | e^{i\hat{H}_s t/\hbar} \hat{\rho}(t) e^{-i\hat{H}_s t/\hbar} | \chi_{\beta} \rangle = e^{i\omega_{\alpha\beta} t} \rho_{\alpha\beta}(t). \quad (68)$$

Computing the time derivative of $\rho_{\alpha\beta}(t)_I$ and using Eq. (63), one arrives at the equation

$$\frac{d}{dt}\rho_{\alpha\beta}(t)_I = \sum_{\alpha'\beta'} e^{i(\omega_{\alpha\beta} - \omega_{\alpha'\beta'})t} R_{\alpha\beta,\alpha'\beta'} \rho_{\alpha'\beta'}(t)_I, \quad (69)$$

where the conservative term disappeared and the relaxation term has an explicit time dependence. While the change of the density matrix due to the relaxation is slow, the oscillation in the terms with $\omega_{\alpha\beta} \neq \omega_{\alpha'\beta'}$ are generally fast. These fast oscillating terms average out and make a negligible contribution into the dynamics of the small system. In general, all transition frequencies are nondegenerate, so that one can drop all terms with $\alpha \neq \alpha'$ and $\beta \neq \beta'$, if $\alpha \neq \beta$. In the equations for the diagonal terms $\rho_{\alpha\alpha}(t)_I$ one can keep only diagonal terms with $\alpha' = \beta'$. This is the *secular approximation* that tremendously simplifies the DME. In the secular approximation one has

$$\begin{aligned} \frac{d}{dt}\rho_{\alpha\beta}(t)_I &= \delta_{\alpha\beta} \sum_{\alpha'} R_{\alpha\alpha,\alpha'\alpha'} \rho_{\alpha'\alpha'}(t)_I + (1 - \delta_{\alpha\beta}) R_{\alpha\beta,\alpha\beta} \rho_{\alpha\beta}(t)_I \\ &= \delta_{\alpha\beta} \sum_{\alpha' \neq \alpha} R_{\alpha\alpha,\alpha'\alpha'} \rho_{\alpha'\alpha'}(t)_I + R_{\alpha\beta,\alpha\beta} \rho_{\alpha\beta}(t)_I. \end{aligned} \quad (70)$$

Simplifying Eq. (64) and using the Hermiticity

$$V_{\alpha'\varpi',\alpha\varpi} = V_{\alpha\varpi,\alpha'\varpi'}^* \quad (71)$$

one obtains

$$R_{\alpha\alpha,\alpha'\alpha'}|_{\alpha' \neq \alpha} = \frac{2\pi}{\hbar Z_b} \sum_{\varpi\varpi'} e^{-E_{\varpi'}/(k_B T)} \delta(\varepsilon_{\alpha} - \varepsilon_{\alpha'} + E_{\varpi} - E_{\varpi'}) |V_{\alpha\varpi,\alpha'\varpi'}|^2 \equiv \Gamma_{\alpha\alpha'} \quad (72)$$

and

$$\begin{aligned} R_{\alpha\beta,\alpha\beta} &= \frac{\pi}{\hbar Z_b} \sum_{\varpi\varpi'} \left\{ - \sum_{\gamma} e^{-E_{\varpi}/(k_B T)} \delta(\varepsilon_{\alpha} - \varepsilon_{\gamma} + E_{\varpi} - E_{\varpi'}) |V_{\alpha\varpi,\gamma\varpi'}|^2 \right. \\ &\quad - \sum_{\gamma} e^{-E_{\varpi}/(k_B T)} \delta(\varepsilon_{\beta} - \varepsilon_{\gamma} + E_{\varpi} - E_{\varpi'}) |V_{\beta\varpi,\gamma\varpi'}|^2 \\ &\quad \left. + 2 e^{-E_{\varpi'}/(k_B T)} \delta(E_{\varpi} - E_{\varpi'}) V_{\alpha\varpi,\alpha\varpi'} V_{\beta\varpi',\beta\varpi} \right\}. \end{aligned} \quad (73)$$

Rearranging the terms one obtains

$$R_{\alpha\beta,\alpha\beta} = -\tilde{\Gamma}_{\alpha\beta}, \quad (74)$$

where

$$\tilde{\Gamma}_{\alpha\beta} = \bar{\Gamma}_{\alpha\beta} + \frac{1}{2} \left(\sum_{\alpha' \neq \alpha} \Gamma_{\alpha'\alpha} + \sum_{\beta' \neq \beta} \Gamma_{\beta'\beta} \right). \quad (75)$$

Here $\Gamma_{\alpha'\alpha}$ is defined by Eq. (72) and

$$\bar{\Gamma}_{\alpha\beta} = \frac{\pi}{\hbar Z_b} \sum_{\varpi\varpi'} e^{-E_{\varpi}/(k_B T)} \delta(E_{\varpi} - E_{\varpi'}) |V_{\alpha\varpi,\alpha\varpi'} - V_{\beta\varpi',\beta\varpi}|^2. \quad (76)$$

Using these results in Eq. (70) and changing to $\rho_{\alpha\beta}$, one obtains the secular DME in the diagonal basis in the form

$$\frac{d}{dt} \rho_{\alpha\beta} = - \left(i\omega_{\alpha\beta} + \tilde{\Gamma}_{\alpha\beta} \right) \rho_{\alpha\beta} + \delta_{\alpha\beta} \sum_{\alpha' \neq \alpha} \Gamma_{\alpha\alpha'} \rho_{\alpha'\alpha}. \quad (77)$$

In Eq. (72), $\Gamma_{\alpha\alpha'}$ is the rate of quantum transitions $\alpha' \rightarrow \alpha$ in the small system, accompanied by an appropriate transition in the bath so that the total energy is conserved. To the contrary, $\Gamma_{\alpha'\alpha}$ in Eq. (74) is the rate of quantum transitions $\alpha \rightarrow \alpha'$ in the small system. One can relate both rates as

$$\begin{aligned} \Gamma_{\alpha'\alpha} &= \frac{\pi}{\hbar Z_b} \sum_{\varpi\varpi'} e^{-E_{\varpi}/(k_B T)} \delta(\varepsilon_{\alpha} - \varepsilon_{\alpha'} + E_{\varpi} - E_{\varpi'}) |V_{\alpha\varpi,\alpha'\varpi'}|^2 \\ &= \frac{\pi}{\hbar Z_b} \sum_{\varpi\varpi'} e^{(-E_{\varpi'} + \varepsilon_{\alpha} - \varepsilon_{\alpha'})/(k_B T)} \delta(\varepsilon_{\alpha} - \varepsilon_{\alpha'} + E_{\varpi} - E_{\varpi'}) |V_{\alpha\varpi,\alpha'\varpi'}|^2 \end{aligned} \quad (78)$$

or

$$\Gamma_{\alpha'\alpha} = e^{(\varepsilon_{\alpha} - \varepsilon_{\alpha'})/(k_B T)} \Gamma_{\alpha\alpha'}. \quad (79)$$

This is the so-called *detailed-balance relation* that ensures that asymptotically the small system reaches the thermal equilibrium described by Eq. (67). If $\varepsilon_{\alpha} < \varepsilon_{\alpha'}$, then at low temperatures the rate of transitions $\alpha \rightarrow \alpha'$ (with increasing energy) is exponentially small. Note that the transition rates $\Gamma_{\alpha'\alpha}$ and $\Gamma_{\alpha\alpha'}$ correspond to the Fermi golden rule.

The quantity $\bar{\Gamma}_{\alpha\beta}$ of Eq. (76) is the dephasing rate that turns to zero for the diagonal elements of the density matrix

$$n_{\alpha} \equiv \rho_{\alpha\alpha}, \quad (80)$$

the populations of states α . The dephasing rate is not related to any transitions of the small system. Its origin is modulating its transition frequencies $\omega_{\alpha\beta}$ by fluctuations of the bath.

One can see that in the decoupled equations for nondiagonal terms of the density matrix $\alpha \neq \beta$ in Eq. (77) there are only outgoing terms, so that the nondiagonal terms tend to zero asymptotically. The diagonal terms of the DME satisfy the system of rate equations

$$\frac{d}{dt} n_{\alpha} = \sum_{\alpha' \neq \alpha} (\Gamma_{\alpha\alpha'} n_{\alpha'} - \Gamma_{\alpha'\alpha} n_{\alpha}). \quad (81)$$

The asymptotic solution satisfies

$$\frac{n_{\alpha'}}{n_{\alpha}} = \frac{\Gamma_{\alpha'\alpha}}{\Gamma_{\alpha\alpha'}} = \frac{e^{-\varepsilon_{\alpha'}/(k_B T)}}{e^{-\varepsilon_{\alpha}/(k_B T)}} \quad (82)$$

that corresponds to the thermal equilibrium. The equation for nondiagonal elements can be written in the form

$$\frac{d}{dt} \rho_{\alpha\beta} = - \left(i\omega_{\alpha\beta} + \tilde{\Gamma}_{\alpha\beta} \right) \rho_{\alpha\beta} \quad (83)$$

with $\tilde{\Gamma}_{\alpha\beta}$ given by Eq. (75).

E. Analysis of the non-secular DME

We have seen above that within the secular approximation nondiagonal DM elements are decoupled from diagonal ones and oscillate with decay independently of each other. In the full DME of Eq. (63), nondiagonal DM elements are coupled to the diagonal elements. Nevertheless, they approach zero at equilibrium, in spite of diagonal elements being nonzero. This points at an interesting feature of the full DME that has to be worked out in more detail. Separating diagonal and nondiagonal elements in the relaxation term of Eq. (63), one obtains

$$\begin{aligned}
\frac{d}{dt}\rho_{\alpha\beta} &= -i\omega_{\alpha\beta}\rho_{\alpha\beta} + \sum_{\alpha'\beta'} R_{\alpha\beta,\alpha'\beta'} (1 - \delta_{\alpha'\beta'}) \rho_{\alpha'\beta'} + \sum_{\alpha'} R_{\alpha\beta,\alpha'\alpha'} \rho_{\alpha'\alpha'} \\
&= -i\omega_{\alpha\beta}\rho_{\alpha\beta} + \sum_{\alpha'\beta'} R_{\alpha\beta,\alpha'\beta'} (1 - \delta_{\alpha'\beta'}) \rho_{\alpha'\beta'} \\
&\quad + \frac{\pi}{\hbar Z_b} \sum_{\varpi\varpi'} \left\{ - \sum_{\gamma} e^{-E_{\varpi}/(k_B T)} \delta(\varepsilon_{\beta} - \varepsilon_{\gamma} + E_{\varpi} - E_{\varpi'}) V_{\alpha\varpi,\gamma\varpi'} V_{\gamma\varpi',\beta\varpi} \rho_{\beta\beta} \right. \\
&\quad - \sum_{\gamma} e^{-E_{\varpi}/(k_B T)} \delta(\varepsilon_{\alpha} - \varepsilon_{\gamma} + E_{\varpi} - E_{\varpi'}) V_{\alpha\varpi,\gamma\varpi'} V_{\gamma\varpi',\beta\varpi} \rho_{\alpha\alpha} \\
&\quad + \sum_{\gamma} e^{-E_{\varpi'}/(k_B T)} \delta(\varepsilon_{\beta} - \varepsilon_{\gamma} + E_{\varpi} - E_{\varpi'}) V_{\alpha\varpi,\gamma\varpi'} V_{\gamma\varpi',\beta\varpi} \rho_{\gamma\gamma} \\
&\quad \left. + \sum_{\gamma} e^{-E_{\varpi'}/(k_B T)} \delta(\varepsilon_{\alpha} - \varepsilon_{\gamma} + E_{\varpi} - E_{\varpi'}) V_{\alpha\varpi,\gamma\varpi'} V_{\gamma\varpi',\beta\varpi} \rho_{\gamma\gamma} \right\}. \tag{84}
\end{aligned}$$

With the use of the energy conservation this can be rewritten as

$$\begin{aligned}
\frac{d}{dt}\rho_{\alpha\beta} &= -i\omega_{\alpha\beta}\rho_{\alpha\beta} + \sum_{\alpha'\beta'} R_{\alpha\beta,\alpha'\beta'} (1 - \delta_{\alpha'\beta'}) \rho_{\alpha'\beta'} \\
&\quad + \frac{\pi}{\hbar Z_b} \sum_{\gamma} \sum_{\varpi\varpi'} e^{-E_{\varpi'}/(k_B T)} V_{\alpha\varpi,\gamma\varpi'} V_{\gamma\varpi',\beta\varpi} \\
&\quad \times \left[\delta(\varepsilon_{\beta} - \varepsilon_{\gamma} + E_{\varpi} - E_{\varpi'}) \left(\rho_{\gamma\gamma} - e^{(\varepsilon_{\beta} - \varepsilon_{\gamma})/(k_B T)} \rho_{\beta\beta} \right) \right. \\
&\quad \left. + \delta(\varepsilon_{\alpha} - \varepsilon_{\gamma} + E_{\varpi} - E_{\varpi'}) \left(\rho_{\gamma\gamma} - e^{(\varepsilon_{\alpha} - \varepsilon_{\gamma})/(k_B T)} \rho_{\alpha\alpha} \right) \right]. \tag{85}
\end{aligned}$$

One can see that as the diagonal DM elements approach their equilibrium values, they cease to drive nondiagonal elements because of the detailed balance relation. Thus the equilibrium solution of the full DME is Eq. (67).

F. Semi-secular approximation

While the secular approximation neglects the interaction between diagonal and slow nondiagonal DM elements, the full non-secular formalism involves a big $N^2 \times N^2$ matrix that has to be diagonalized. In important particular cases such as thermal activation over a barrier or tunneling, the eigenvalues of the DM span a broad range from very fast to very slow, the latter being of a primary importance in relaxation. Because of this, one has to do numerical calculations with increased precision that makes them very slow. This difficulty can be overcome with the help of the semi-secular approximation that considers coupled equations for diagonal and slow nondiagonal DM elements plus decoupled equations for the fast DM elements. The easiest way to implement it is to include the diagonal and subdiagonal terms $\rho_{\alpha\alpha}$ and $\rho_{\alpha,\alpha\pm 1}$ into the slow group, because in most situations there are only two levels that come close to each other, making $\rho_{\alpha,\alpha+1}$ or $\rho_{\alpha,\alpha-1}$ slow. Implementation of the semi-secular DME in the case of time-independent \hat{H}_s will be done in Sec. III A 3.

G. Transformation to the natural basis

One can transform the DME, Eq. (77) to the natural basis using Eqs. (20) and (19) in the form

$$\rho_{mn} = \langle \psi_m | \hat{\rho} | \psi_n \rangle = \sum_{\alpha\beta} \langle \psi_m | \chi_{\alpha} \rangle \rho_{\alpha\beta} \langle \chi_{\beta} | \psi_n \rangle. \tag{86}$$

The inverse transformation has the form

$$\rho_{\alpha\beta} = \langle \chi_\alpha | \hat{\rho} | \chi_\beta \rangle = \sum_{mn} \langle \chi_\alpha | \psi_m \rangle \rho_{mn} \langle \psi_n | \chi_\beta \rangle. \quad (87)$$

The general DME in the diagonal basis, Eq. (63), can be transformed to the natural basis with the help of Eq. (86) as follows

$$\begin{aligned} \frac{d}{dt} \rho_{mn} &= \sum_{\alpha\beta} \langle \psi_m | \chi_\alpha \rangle \frac{d}{dt} \rho_{\alpha\beta} \langle \chi_\beta | \psi_n \rangle \\ &= -\frac{i}{\hbar} \sum_{\alpha\beta} \langle \psi_m | \chi_\alpha \rangle (\varepsilon_\alpha - \varepsilon_\beta) \rho_{\alpha\beta} \langle \chi_\beta | \psi_n \rangle + \sum_{\alpha\beta} \langle \psi_m | \chi_\alpha \rangle \sum_{\alpha'\beta'} R_{\alpha\beta, \alpha'\beta'} \rho_{\alpha'\beta'} \langle \chi_\beta | \psi_n \rangle \\ &= -\frac{i}{\hbar} \sum_{m'n'} \sum_{\alpha\beta} \langle \psi_m | \chi_\alpha \rangle \varepsilon_\alpha \langle \chi_\alpha | \psi_{m'} \rangle \rho_{m'n'} \langle \psi_{n'} | \chi_\beta \rangle \langle \chi_\beta | \psi_n \rangle \\ &\quad + \frac{i}{\hbar} \sum_{m'n'} \sum_{\alpha\beta} \langle \psi_m | \chi_\alpha \rangle \langle \chi_\alpha | \psi_{m'} \rangle \rho_{m'n'} \langle \psi_{n'} | \chi_\beta \rangle \varepsilon_\beta \langle \chi_\beta | \psi_n \rangle \\ &\quad + \sum_{m'n'} \sum_{\alpha\beta} \langle \psi_m | \chi_\alpha \rangle \sum_{\alpha'\beta'} R_{\alpha\beta, \alpha'\beta'} \langle \chi_{\alpha'} | \psi_{m'} \rangle \rho_{m'n'} \langle \psi_{n'} | \chi_{\beta'} \rangle \langle \chi_\beta | \psi_n \rangle. \end{aligned} \quad (88)$$

This yields

$$\frac{d}{dt} \rho_{mn} = -\frac{i}{\hbar} \sum_{m'} H_{s, mm'} \rho_{m'n} + \frac{i}{\hbar} \sum_{n'} \rho_{mn} H_{s, n'n} + \sum_{m'n'} R_{mn, m'n'} \rho_{m'n'}, \quad (89)$$

where $H_{s, mm'} \equiv \langle \psi_m | \hat{H}_s | \psi_{m'} \rangle$ and

$$R_{mn, m'n'} \equiv \sum_{\alpha\beta, \alpha'\beta'} T_{mn, m'n'; \alpha\beta, \alpha'\beta'} R_{\alpha\beta, \alpha'\beta'}, \quad (90)$$

where

$$T_{mn, m'n'; \alpha\beta, \alpha'\beta'} \equiv \langle \psi_m | \chi_\alpha \rangle \langle \chi_\beta | \psi_n \rangle \langle \chi_{\alpha'} | \psi_{m'} \rangle \langle \psi_{n'} | \chi_{\beta'} \rangle. \quad (91)$$

Additionally, the matrix elements in the Fermi-golden-rule transition rate, Eq. (72), that are defined with respect to the diagonal basis, can be expressed through those with respect to the natural basis. Similarly to Eq. (87) one obtains

$$V_{\alpha\varpi, \alpha'\varpi'} = \sum_{mm'} \langle \chi_\alpha | \psi_m \rangle V_{m\varpi, m'\varpi'} \langle \psi_{m'} | \chi_{\alpha'} \rangle. \quad (92)$$

III. TIME-DEPENDENT PROBLEMS

In this section we consider the DME and its solution in three important cases: i) free evolution for time-independent \hat{H}_s ; ii) fast resonance perturbation and iii) periodic or nonperiodic slow perturbation. In the second case it is sufficient to keep the perturbation in the conservative part of the DME only, while in the third case modification of the relaxation terms is required, as well. In all these cases the solution can be obtained by matrix algebra. To the contrast, problems with a large temporal change of \hat{H}_s cannot be solved by matrix algebra. The secular, non-secular, and semi-secular versions of the DME yield the same results except for the case of anomalously close energy levels (e.g., tunnel split levels). In the latter case the semi-secular DME is preferred, while in general the fastest and easiest secular DME is the best choice.

A. Free evolution

1. Non-secular DME

The solution of time-independent DME, Eq. (63), that can be rewritten as

$$\frac{d}{dt}\rho_{\alpha\beta} = \sum_{\alpha'\beta'} \Phi_{\alpha\beta,\alpha'\beta'} \rho_{\alpha'\beta'}, \quad \Phi_{\alpha\beta,\alpha'\beta'} = -i\omega_{\alpha\beta}\delta_{\alpha\alpha'}\delta_{\beta\beta'} + R_{\alpha\beta,\alpha'\beta'}, \quad (93)$$

is a linear combination of time exponentials with exponents being eigenvalues of the matrix Φ building the DME. To bring the DME into a standard form, it is convenient to introduce the compound index a defined by

$$a = \alpha + N(\beta - 1), \quad (94)$$

where N is the size of the density matrix, i.e., $\alpha, \beta = 1, 2, \dots, N$. Then $a = 1, 2, \dots, N^2$. Inversion of Eq. (94) yields

$$\alpha = 1 + N \text{Frac} \left(\frac{a-1}{N} \right), \quad \beta = 1 + \text{Int} \left(\frac{a-1}{N} \right). \quad (95)$$

With the index a , the density matrix $\rho_{\alpha\beta}$ becomes a vector with the components ρ_a while $\Phi_{\alpha\beta,\alpha'\beta'}$ becomes a matrix with the elements $\Phi_{aa'}$:

$$\frac{d}{dt}\boldsymbol{\rho} = \Phi \cdot \boldsymbol{\rho}, \quad \frac{d}{dt}\rho_a = \sum_{a'} \Phi_{aa'} \rho_{a'}. \quad (96)$$

The eigenvalue problem for the DME can be written as

$$\Phi \cdot \mathbf{R}_\mu = -\Lambda_\mu \mathbf{R}_\mu, \quad \Lambda_\mu = \Gamma_\mu + i\Omega_\mu, \quad (97)$$

where \mathbf{R}_μ is the right eigenvector corresponding to the eigenvalue Λ_μ and $\mu = 1, 2, \dots, (2S+1)^2$. Since Φ is a non-Hermitian matrix, right eigenvectors differ from left eigenvectors that satisfy $\mathbf{L}_\mu \cdot \Phi = -\Lambda_\mu \mathbf{L}_\mu$. Left and right eigenvectors satisfy orthonormality and completeness relations

$$\sum_a L_{\mu a} R_{\nu a} = \delta_{\mu\nu}, \quad \sum_\mu L_{\mu a} R_{\mu a'} = \delta_{aa'}. \quad (98)$$

In general, \mathbf{L}_μ and \mathbf{R}_μ are not Hermitian conjugate, see, e.g., Eq. (103). All real parts of the eigenvalues are positive, $\Gamma_\mu > 0$. There are N purely real eigenvalues, one of which is zero and corresponds to thermal equilibrium. We assign the zero eigenvalue the index $\mu = 1$. Complex eigenvalues occur in complex conjugate pairs.

The solution of the DME with the initial conditions can be written in the form

$$\boldsymbol{\rho}(t) = \sum_\mu \mathbf{R}_\mu e^{-\Lambda_\mu t} \mathbf{L}_\mu \cdot \boldsymbol{\rho}(0). \quad (99)$$

The fully vectorized form of this equation is

$$\boldsymbol{\rho}(t) = \mathbf{E} \cdot \mathbf{W}(t) \cdot \mathbf{E}^{-1} \cdot \boldsymbol{\rho}(0), \quad (100)$$

where \mathbf{E} is right-eigenvector matrix composed of all eigenvectors \mathbf{R}_μ standing vertically, \mathbf{E}^{-1} is the left-eigenvector matrix, composed of all left eigenvectors lying horizontally, and $\mathbf{W}(t)$ is the diagonal matrix with the elements $e^{-\Lambda_\mu t}$. In fact,

$$\mathbf{E} \cdot \mathbf{W}(t) \cdot \mathbf{E}^{-1} = \exp(\Phi t). \quad (101)$$

The asymptotic value of $\rho(t)$ is described by the zero eigenvalue $\Lambda_1 = 0$,

$$\rho(\infty) = \mathbf{R}_1 (\mathbf{L}_1 \cdot \rho(0)). \quad (102)$$

Here $\rho(\infty) = \rho^{\text{eq}}$ should be satisfied, where ρ^{eq} follows from Eq. (67), and this result should be independent of $\rho(0)$. Thus one concludes that

$$L_{1a} = \delta_{\alpha(a)\beta(a)}, \quad R_{1a} = \frac{1}{Z_s} \exp\left(-\frac{\varepsilon_{\alpha(a)}}{k_B T}\right) \delta_{\alpha(a)\beta(a)}, \quad (103)$$

where $\alpha(a)$ and $\beta(a)$ are given by Eq. (95). This means that \mathbf{L}_1 is related to the normalization of the DM while \mathbf{R}_1 contains the information about the equilibrium state. One obtains

$$\mathbf{L}_1 \cdot \rho(0) = \sum_a L_{1a} \rho_a(0) = \sum_{\alpha\beta} \delta_{\alpha\beta} \rho_{\alpha\beta}(0) = \sum_{\alpha} \rho_{\alpha\alpha}(0) = 1 \quad (104)$$

and $\rho(\infty) = \mathbf{R}_1 = \rho^{\text{eq}}$, as it should be. Note that \mathbf{R}_1 and \mathbf{L}_1 satisfy the orthonormality condition in Eq. (98),

$$\sum_a L_{1a} R_{1a} = \frac{1}{Z_s} \sum_a \exp\left(-\frac{\varepsilon_{\alpha(a)}}{k_B T}\right) \delta_{\alpha(a)\beta(a)} = \frac{1}{Z_s} \sum_{\alpha\beta} \exp\left(-\frac{\varepsilon_{\alpha}}{k_B T}\right) \delta_{\alpha\beta} = 1. \quad (105)$$

The time dependence of any physical quantity A is given by Eq. (4) that can be rewritten in the form

$$A(t) = \sum_{\alpha\beta} A_{\beta\alpha} \rho_{\alpha\beta}(t) = \sum_a A_a \rho_a(t), \quad (106)$$

where

$$A_a \equiv A_{\beta(a)\alpha(a)}, \quad A_{\beta\alpha} \equiv \langle \beta | \hat{A} | \alpha \rangle. \quad (107)$$

Writing Eq. (106) in the vector form as $A(t) = \mathbf{A} \cdot \rho(t)$ one obtains

$$A(t) = \sum_{\mu} \mathbf{A} \cdot \mathbf{R}_\mu e^{-\Lambda_\mu t} \mathbf{L}_\mu \cdot \rho(0) \quad (108)$$

or, in the fully vectorized form,

$$A(t) = \mathbf{A} \cdot \mathbf{E} \cdot \mathbf{W}(t) \cdot \mathbf{E}^{-1} \cdot \rho(0). \quad (109)$$

Since the time dependence of observables in the course of evolution of the density matrix is described by more than one exponential, one needs an appropriate definition of the relaxation rate or relaxation time. A convenient way is to use the integral relaxation time defined as the area under the relaxation curve

$$\tau_{\text{int}} \equiv \frac{\int_0^\infty dt [A(t) - A(\infty)]}{A(0) - A(\infty)}. \quad (110)$$

One can check that in the case of a single exponential, $A(t) = A(\infty) + [A(0) - A(\infty)] e^{-\Gamma t}$, the result is $\tau_{\text{int}} = 1/\Gamma$. From Eq. (108) one obtains

$$A(t) - A(\infty) = \sum_{\mu \neq 1} \mathbf{A} \cdot \mathbf{R}_\mu e^{-\Lambda_\mu t} \mathbf{L}_\mu \cdot \rho(0) \quad (111)$$

and thus

$$\tau_{\text{int}} = \frac{\sum_{\mu=2}^{N^2} (\mathbf{A} \cdot \mathbf{R}_\mu) \Lambda_\mu^{-1} (\mathbf{L}_\mu \cdot \rho(0))}{\sum_{\mu=2}^{N^2} (\mathbf{A} \cdot \mathbf{R}_\mu) (\mathbf{L}_\mu \cdot \rho(0))}. \quad (112)$$

This formula cannot be fully vectorized since summation skips the static eigenvalue $\mu = 1$.

2. Secular DME

Within the secular approximation, one has to consider the dynamics of diagonal and nondiagonal components of the density matrix separately. The former is described by Eqs. (96)–(102) where the vector $\boldsymbol{\rho}$ is replaced by the vector of the diagonal components $\mathbf{n} = \{n_\alpha\} = \{\rho_{\alpha\alpha}\}$ and the $(N)^2 \times (N)^2$ matrix $\boldsymbol{\Phi}$ is replaced by the $(N) \times (N)$ matrix $\boldsymbol{\Phi}^{\text{sec}}$ having matrix elements

$$\Phi_{\alpha\alpha'}^{\text{sec}} = (1 - \delta_{\alpha\alpha'}) \Gamma_{\alpha\alpha'} - \delta_{\alpha\alpha'} \sum_{\gamma} \Gamma_{\gamma\alpha}, \quad (113)$$

as follows from Eqs. (77) or (81). All eigenvalues of $\boldsymbol{\Phi}^{\text{sec}}$ are positive reals, except for one zero eigenvalue, $\Lambda_1 = 0$. Eq. (103) becomes simply

$$L_{1\alpha} = 1, \quad R_{1\alpha} = \frac{1}{Z_s} \exp\left(-\frac{\varepsilon_\alpha}{k_B T}\right). \quad (114)$$

If the initial condition is a diagonal matrix, the non-diagonal elements do not arise dynamically and hence they can be dropped. Then the time dependence of any quantity A is described by

$$A(t) = \sum_{\alpha} A_{\alpha\alpha} n_{\alpha}(t) = \mathbf{A} \cdot \mathbf{E} \cdot \mathbf{W}(t) \cdot \mathbf{E}^{-1} \cdot \mathbf{n}(0), \quad (115)$$

c.f. Eqs. (106)–(109). For the integral relaxation time in the case of a purely diagonal evolution one obtains

$$\tau_{\text{int}} = \frac{\sum_{\mu=2}^N (\mathbf{A} \cdot \mathbf{R}_{\mu}) \Lambda_{\mu}^{-1} (\mathbf{L}_{\mu} \cdot \mathbf{n}(0))}{\sum_{\mu=2}^N (\mathbf{A} \cdot \mathbf{R}_{\mu}) (\mathbf{L}_{\mu} \cdot \mathbf{n}(0))}, \quad (116)$$

c.f. Eq. (112).

If the initial state is a non-diagonal density matrix, one has to add the corresponding trivial terms following from Eq. (83),

$$A(t) = \mathbf{A} \cdot \mathbf{E} \cdot \mathbf{W}(t) \cdot \mathbf{E}^{-1} \cdot \mathbf{n}(0) + \sum_{\alpha \neq \beta} A_{\beta\alpha} \rho_{\alpha\beta}(0) e^{-(i\omega_{\alpha\beta} + \tilde{\Gamma}_{\alpha\beta})t}. \quad (117)$$

Then Eq. (116) is generalized to

$$\tau_{\text{int}} = \frac{\sum_{\mu=2}^N (\mathbf{A} \cdot \mathbf{R}_{\mu}) \Lambda_{\mu}^{-1} (\mathbf{L}_{\mu} \cdot \mathbf{n}(0)) + \sum_{\alpha \neq \beta} A_{\beta\alpha} \rho_{\alpha\beta}(0) (i\omega_{\alpha\beta} + \tilde{\Gamma}_{\alpha\beta})^{-1}}{\sum_{\mu=2}^N (\mathbf{A} \cdot \mathbf{R}_{\mu}) (\mathbf{L}_{\mu} \cdot \mathbf{n}(0)) + \sum_{\alpha \neq \beta} A_{\beta\alpha} \rho_{\alpha\beta}(0)}. \quad (118)$$

Obviously this expression is real.

3. Semi-secular DME

Within the semisecular approximation introduced in Sec. IIF, the slow group being formed by diagonal and subdiagonal DM elements, $|\alpha - \beta| \leq 1$, the equations of motion for the latter have the form

$$\frac{d}{dt} \rho_{\alpha\beta} = \sum_{\alpha'} (\Phi_{\alpha\beta;\alpha',\alpha'-1} \rho_{\alpha',\alpha'-1} + \Phi_{\alpha\beta;\alpha',\alpha'} \rho_{\alpha',\alpha'} + \Phi_{\alpha\beta;\alpha',\alpha'+1} \rho_{\alpha',\alpha'+1}) \quad (119)$$

that is a subset of Eq. (93). In labeling matrix elements, one can introduce the compound index

$$a = 2(\alpha - 1) + \beta. \quad (120)$$

Here $\alpha = 1, 2, \dots, N$ and $\beta = \alpha - 1, \alpha, \alpha + 1$, so that a takes the values $a = 1, \dots, 3N - 2$. In terms of a one has

$$\alpha = 1 + \text{Int}\left(\frac{a}{3}\right), \quad \beta = \alpha - 1 + 3\text{Frac}\left(\frac{a}{3}\right), \quad (121)$$

and Eq. (119) can be rewritten as

$$\frac{d}{dt}\rho_a^{\text{slow}} = \sum_{a'} \tilde{\Phi}_{aa'} \rho_{a'}^{\text{slow}}, \quad (122)$$

where $\tilde{\Phi}_{aa'} = \Phi_{\alpha(a),\beta(a);\alpha(a'),\beta(a')}$.

The solution of Eq. (122) is similar to that of Eq. (96). On the other hand, there are uncoupled DM elements with $|\alpha - \beta| \geq 2$, like in the secular approximation. Instead of Eq. (117) one has

$$A(t) = \mathbf{A} \cdot \mathbf{E} \cdot \mathbf{W}(t) \cdot \mathbf{E}^{-1} \cdot \boldsymbol{\rho}^{\text{slow}}(0) + \sum_{|\alpha-\beta|>1} A_{\beta\alpha} \rho_{\alpha\beta}(0) e^{-(i\omega_{\alpha\beta} + \tilde{\Gamma}_{\alpha\beta})t} \quad (123)$$

and instead of Eq. (118) one has

$$\tau_{\text{int}} = \frac{\sum_{\mu=2}^{3N-2} (\mathbf{A} \cdot \mathbf{R}_{\mu}) \Lambda_{\mu}^{-1} (\mathbf{L}_{\mu} \cdot \boldsymbol{\rho}^{\text{slow}}(0)) + \sum_{|\alpha-\beta|>1} A_{\beta\alpha} \rho_{\alpha\beta}(0) (i\omega_{\alpha\beta} + \tilde{\Gamma}_{\alpha\beta})^{-1}}{\sum_{\mu=2}^{3N-2} (\mathbf{A} \cdot \mathbf{R}_{\mu}) (\mathbf{L}_{\mu} \cdot \boldsymbol{\rho}^{\text{slow}}(0)) + \sum_{|\alpha-\beta|>1} A_{\beta\alpha} \rho_{\alpha\beta}(0)}. \quad (124)$$

B. Resonant perturbation

Let \hat{H}_s contain a periodic perturbation

$$\hat{V}(t) = \hat{V}_0 e^{-i\omega t} + \hat{V}_0^{\dagger} e^{i\omega t} \quad (125)$$

with the frequency $\omega > 0$ close to one of transition frequencies $\omega_{\eta\eta'} > 0$. For the resonance to occur, the latter should exceed the relaxation rates, so that one can use the secular DME, Eq. (77). Since \hat{V}_0 is small, one can disregard it in the relaxation terms and use the diagonal basis corresponding to the time-independent part of \hat{H}_s . Combining Eqs. (52) and (77), one obtains

$$\begin{aligned} \frac{d}{dt}\rho_{\alpha\beta} &= -\frac{i}{\hbar} \left(\sum_{\alpha'} V(t)_{\alpha\alpha'} \rho_{\alpha'\beta} - \sum_{\beta'} \rho_{\alpha\beta'} V(t)_{\beta'\beta} \right) \\ &\quad - (i\omega_{\alpha\beta} + \tilde{\Gamma}_{\alpha\beta}) \rho_{\alpha\beta} + \delta_{\alpha\beta} \sum_{\gamma \neq \alpha} \Gamma_{\alpha\gamma} \rho_{\gamma\gamma}. \end{aligned} \quad (126)$$

Here one should drop all nondiagonal DM elements but $\rho_{\eta\eta'}$ and $\rho_{\eta'\eta}$ since the former are not excited by the resonance perturbation and vanish with time. As a result, one obtains a coupled system of equations for the diagonal elements $\rho_{\alpha\alpha}$ and the elements $\rho_{\eta\eta'}$ and $\rho_{\eta'\eta} = \rho_{\eta\eta'}^*$ of the form

$$\begin{aligned} \frac{d}{dt}\rho_{\eta\eta'} &= -\frac{i}{\hbar} (e^{-i\omega t} V_{0,\eta\eta'} \rho_{\eta'\eta'} - e^{-i\omega t} \rho_{\eta\eta} V_{0,\eta\eta'}) - (i\omega_{\eta\eta'} + \tilde{\Gamma}_{\eta\eta'}) \rho_{\eta\eta'} \\ \frac{d}{dt}\rho_{\eta\eta} &= -\frac{i}{\hbar} \left(e^{-i\omega t} V_{0,\eta\eta'} \rho_{\eta'\eta} - e^{i\omega t} \rho_{\eta\eta'} (\hat{V}_0^{\dagger})_{\eta'\eta} \right) + \sum_{\gamma \neq \eta} (\Gamma_{\eta\gamma} \rho_{\gamma\gamma} - \Gamma_{\gamma\eta} \rho_{\eta\eta}) \\ \frac{d}{dt}\rho_{\eta'\eta'} &= -\frac{i}{\hbar} \left(e^{i\omega t} (\hat{V}_0^{\dagger})_{\eta'\eta} \rho_{\eta\eta'} - e^{-i\omega t} \rho_{\eta'\eta} V_{0,\eta\eta'} \right) + \sum_{\gamma \neq \eta'} (\Gamma_{\eta'\gamma} \rho_{\gamma\gamma} - \Gamma_{\gamma\eta'} \rho_{\eta'\eta'}), \end{aligned} \quad (127)$$

plus Eq. (81) for all diagonal elements with $\alpha \neq \eta, \eta'$. Also terms such as $e^{i\omega t} (\hat{V}_0^{\dagger})_{\eta\eta'} \rho_{\eta'\eta} \sim e^{i(\omega + \omega_{\eta\eta'})t}$ in the second equation have been dropped. Neglecting such terms that oscillate out is the so-called rotating-wave approximation that is similar to the secular approximation. It is convenient to introduce the slow nondiagonal elements $\tilde{\rho}_{\eta\eta'}$ and $\tilde{\rho}_{\eta'\eta}$ via

$$\rho_{\eta\eta'} = \tilde{\rho}_{\eta\eta'} e^{-i\omega t}, \quad \rho_{\eta'\eta} = \tilde{\rho}_{\eta'\eta} e^{i\omega t}. \quad (128)$$

With the use of $(\hat{V}_0^\dagger)_{\eta'\eta} = V_{0,\eta\eta'}^*$ the DME acquires the form

$$\begin{aligned}
\frac{d}{dt}\tilde{\rho}_{\eta\eta'} &= -\frac{i}{\hbar}V_{0,\eta\eta'}(\rho_{\eta'\eta'} - \rho_{\eta\eta}) + \left[i(\omega - \omega_{\eta\eta'}) - \tilde{\Gamma}_{\eta\eta'} \right] \tilde{\rho}_{\eta\eta'} \\
\frac{d}{dt}\rho_{\eta\eta} &= -\frac{2}{\hbar}\text{Im}(\tilde{\rho}_{\eta\eta'}V_{0,\eta\eta'}^*) + \sum_{\gamma \neq \eta} (\Gamma_{\eta\gamma}\rho_{\gamma\gamma} - \Gamma_{\gamma\eta}\rho_{\eta\eta}) \\
\frac{d}{dt}\rho_{\eta'\eta'} &= \frac{2}{\hbar}\text{Im}(\tilde{\rho}_{\eta\eta'}V_{0,\eta\eta'}^*) + \sum_{\gamma \neq \eta'} (\Gamma_{\eta'\gamma}\rho_{\gamma\gamma} - \Gamma_{\gamma\eta'}\rho_{\eta'\eta'}) \\
\frac{d}{dt}\rho_{\alpha\alpha} &= \sum_{\gamma \neq \alpha} (\Gamma_{\alpha\gamma}\rho_{\gamma\gamma} - \Gamma_{\gamma\alpha}\rho_{\alpha\alpha}), \quad \alpha \neq \eta, \eta'.
\end{aligned} \tag{129}$$

Here $\tilde{\Gamma}_{\eta\eta'}$ is given by Eq. (75).

In the strong-dephasing case $\tilde{\Gamma}_{\eta\eta'} \gg \Gamma_{\eta\eta'}$, $\hat{V}_{0,\eta\eta'}$, the nondiagonal element $\tilde{\rho}_{\eta\eta'}$ quickly reaches its quasistationary value that can be obtained from the first equation of Eq. (129) by setting $d\tilde{\rho}_{\eta\eta'}/dt = 0$. This results in

$$\tilde{\rho}_{\eta\eta'} = \frac{1}{\hbar} \frac{V_{0,\eta\eta'}(\rho_{\eta'\eta'} - \rho_{\eta\eta})}{\omega - \omega_{\eta\eta'} + i\tilde{\Gamma}_{\eta\eta'}}. \tag{130}$$

Substituting this into the equations for the diagonal DM elements, one obtains

$$\begin{aligned}
\frac{d}{dt}\rho_{\eta\eta} &= \frac{|\hat{V}_{0,\eta\eta'}|^2}{\hbar^2} (\rho_{\eta'\eta'} - \rho_{\eta\eta}) \frac{2\tilde{\Gamma}_{\eta\eta'}}{(\omega - \omega_{\eta\eta'})^2 + \tilde{\Gamma}_{\eta\eta'}^2} + \sum_{\gamma \neq \eta} (\Gamma_{\eta\gamma}\rho_{\gamma\gamma} - \Gamma_{\gamma\eta}\rho_{\eta\eta}) \\
\frac{d}{dt}\rho_{\eta'\eta'} &= -\frac{|\hat{V}_{0,\eta\eta'}|^2}{\hbar^2} (\rho_{\eta'\eta'} - \rho_{\eta\eta}) \frac{2\tilde{\Gamma}_{\eta\eta'}}{(\omega - \omega_{\eta\eta'})^2 + \tilde{\Gamma}_{\eta\eta'}^2} + \sum_{\gamma \neq \eta'} (\Gamma_{\eta'\gamma}\rho_{\gamma\gamma} - \Gamma_{\gamma\eta'}\rho_{\eta'\eta'}) \\
\frac{d}{dt}\rho_{\alpha\alpha} &= \sum_{\gamma \neq \alpha} (\Gamma_{\alpha\gamma}\rho_{\gamma\gamma} - \Gamma_{\gamma\alpha}\rho_{\alpha\alpha}), \quad \alpha \neq \eta, \eta'.
\end{aligned} \tag{131}$$

Note that the absorbed power of the field acting on the system is given by

$$P = \hbar\omega_{\eta\eta'} \frac{|\hat{V}_{0,\eta\eta'}|^2}{\hbar^2} (\rho_{\eta'\eta'} - \rho_{\eta\eta}) \frac{2\tilde{\Gamma}_{\eta\eta'}}{(\omega - \omega_{\eta\eta'})^2 + \tilde{\Gamma}_{\eta\eta'}^2}, \tag{132}$$

since every transition $|\eta'\rangle \rightarrow |\eta\rangle$ absorbs the quant of energy equal to $\hbar\omega_{\eta\eta'}$. Eq. (131) can be simplified by introducing the experimentally measured power P and thus eliminating the matrix element $\hat{V}_{0,\eta\eta'}$ and the dephasing rate $\tilde{\Gamma}_{\eta\eta'}$. Still the equations are rather complicated so that one cannot find a simple general solution even for the stationary state.

Let us consider at first the model with only two levels, η and η' . Here with $\rho_{\eta\eta} = 1 - \rho_{\eta'\eta'}$ and the induced-transition rate

$$\Lambda \equiv \frac{|\hat{V}_{0,\eta\eta'}|^2}{\hbar^2} \frac{2\tilde{\Gamma}_{\eta\eta'}}{(\omega - \omega_{\eta\eta'})^2 + \tilde{\Gamma}_{\eta\eta'}^2} \tag{133}$$

Eq. (131) reduces to a single equation

$$\begin{aligned}
\frac{d}{dt}\rho_{\eta'\eta'} &= -\Lambda(\rho_{\eta'\eta'} - \rho_{\eta\eta}) + \Gamma_{\eta'\eta}\rho_{\eta\eta} - \Gamma_{\eta\eta'}\rho_{\eta'\eta'} \\
&= -\Lambda(2\rho_{\eta'\eta'} - 1) + \Gamma_{\eta'\eta} - (\Gamma_{\eta'\eta} + \Gamma_{\eta\eta'})\rho_{\eta'\eta'} \\
&= \Lambda + \Gamma_{\eta'\eta} - (2\Lambda + \Gamma_{\eta'\eta} + \Gamma_{\eta\eta'})\rho_{\eta'\eta'}
\end{aligned} \tag{134}$$

that describes relaxation with the rate $2\Lambda + \Gamma_{\eta'\eta} + \Gamma_{\eta\eta'}$ towards the stationary state described by

$$\rho_{\eta'\eta'} = \frac{\Lambda + \Gamma_{\eta'\eta}}{2\Lambda + \Gamma_{\eta'\eta} + \Gamma_{\eta\eta'}}, \quad \Gamma_{\eta\eta'} = \Gamma_{\eta'\eta} \exp\left(-\frac{\hbar\omega_{\eta\eta'}}{k_B T}\right) \tag{135}$$

for the ground-state population. The limiting cases of this formula are

$$\rho_{\eta'\eta'} = \begin{cases} \rho_{\eta'\eta'}^{(\text{eq})} = \left[1 + \exp\left(-\frac{\hbar\omega_{\eta\eta'}}{k_B T}\right)\right]^{-1}, & \Lambda = 0 \\ 1/2, & \Lambda \rightarrow \infty, \end{cases} \quad (136)$$

as it should be. For the population difference from Eq. (135) one obtains

$$\rho_{\eta'\eta'} - \rho_{\eta\eta} = 2\rho_{\eta'\eta'} - 1 = \frac{\Gamma_{\eta'\eta} - \Gamma_{\eta\eta'}}{2\Lambda + \Gamma_{\eta'\eta} + \Gamma_{\eta\eta'}} = \frac{\rho_{\eta'\eta'}^{(\text{eq})} - \rho_{\eta\eta}^{(\text{eq})}}{1 + 2\Lambda/(\Gamma_{\eta'\eta} + \Gamma_{\eta\eta'})}. \quad (137)$$

One can see that the population difference is reduced by the resonance perturbation. The absorbed power is then given by

$$P = \hbar\omega_{\eta\eta'} (\rho_{\eta'\eta'} - \rho_{\eta\eta}) \Lambda = \frac{\hbar\omega_{\eta\eta'} (\rho_{\eta'\eta'}^{(\text{eq})} - \rho_{\eta\eta}^{(\text{eq})}) \Lambda}{1 + 2\Lambda/(\Gamma_{\eta'\eta} + \Gamma_{\eta\eta'})}. \quad (138)$$

It increases with Λ and reaches an asymptotic maximal value.

To relate the populations directly to the measured absorbed power P , it is most convenient to rewrite Eq. (131) for the two-level system in the form

$$\begin{aligned} \frac{d}{dt}\rho_{\eta'\eta'} &= -\frac{P}{\hbar\omega_{\eta\eta'}} + \Gamma_{\eta'\eta}\rho_{\eta\eta} - \Gamma_{\eta\eta'}\rho_{\eta'\eta'} \\ &= -\frac{P}{\hbar\omega_{\eta\eta'}} + \Gamma_{\eta'\eta} - (\Gamma_{\eta'\eta} + \Gamma_{\eta\eta'})\rho_{\eta'\eta'}. \end{aligned} \quad (139)$$

This equation has a stationary solution

$$\rho_{\eta'\eta'} = \frac{\Gamma_{\eta'\eta} - P/(\hbar\omega_{\eta\eta'})}{\Gamma_{\eta'\eta} + \Gamma_{\eta\eta'}} = \rho_{\eta'\eta'}^{(\text{eq})} - \frac{P/(\hbar\omega_{\eta\eta'})}{\Gamma_{\eta'\eta} + \Gamma_{\eta\eta'}}. \quad (140)$$

Note that the maximal absorbed power corresponds to the saturation, $\rho_{\eta'\eta'} = \rho_{\eta\eta}$, i.e., $\rho_{\eta'\eta'} = 1/2$, wherefrom follows

$$P_{\text{max}} = \frac{\hbar\omega_{\eta\eta'}}{2} (\Gamma_{\eta'\eta} - \Gamma_{\eta\eta'}) = \frac{\hbar\omega_{\eta\eta'}}{2} \Gamma_{\eta'\eta} \left[1 - \exp\left(-\frac{\hbar\omega_{\eta\eta'}}{k_B T}\right)\right] \quad (141)$$

that also can be obtained from Eq. (138).

Consider now a physical quantity \hat{A} that has the expectation value given by Eq. (4). The contributions from the nondiagonal DM elements oscillate in time and thus average out. The result is due to the diagonal elements only,

$$A = A_{\eta\eta}\rho_{\eta\eta} + A_{\eta'\eta'}\rho_{\eta'\eta'} = A_{\eta\eta} + (A_{\eta'\eta'} - A_{\eta\eta})\rho_{\eta'\eta'} \quad (142)$$

With the help of Eq. (140) it can be rewritten as

$$A = A^{(\text{eq})} + \Delta A, \quad (143)$$

where

$$A^{(\text{eq})} = A_{\eta\eta} + (A_{\eta'\eta'} - A_{\eta\eta})\rho_{\eta'\eta'}^{(\text{eq})} = \frac{A_{\eta'\eta'} + A_{\eta\eta} \exp\left(-\frac{\hbar\omega_{\eta\eta'}}{k_B T}\right)}{1 + \exp\left(-\frac{\hbar\omega_{\eta\eta'}}{k_B T}\right)} \quad (144)$$

is the equilibrium value and the deviation from the equilibrium is given by

$$\Delta A = -\frac{A_{\eta'\eta'} - A_{\eta\eta}}{\Gamma_{\eta'\eta} + \Gamma_{\eta\eta'}} \frac{P}{\hbar\omega_{\eta\eta'}}. \quad (145)$$

Thus the total relaxation rate between the states $|\eta\rangle$ and $|\eta'\rangle$ can be expressed by the formula

$$\Gamma = \Gamma_{\eta'\eta} + \Gamma_{\eta\eta'} = \frac{A_{\eta\eta} - A_{\eta'\eta'}}{\Delta A} \frac{P}{\hbar\omega_{\eta\eta'}} \quad (146)$$

through the measured P and ΔA .

If the system has more than two levels but the levels η and η' are the lowest two levels and the temperature is low, so that the populations of all other levels are small, one can still consider an effective two-level model in which relaxation between η and η' can be assisted by the upper levels. Instead of the direct relaxation $|\eta\rangle \rightarrow |\eta'\rangle$ (that can have a small rate) the system can be thermally excited from $|\eta\rangle$ to some high level $|\alpha\rangle$ and then fall down to $|\eta'\rangle$. This is the Orbach mechanism that has the characteristic Arrhenius temperature dependence of the rate. Using the effective two-level model is justified by the fact that the upper levels do not contribute to physical quantities A at low temperatures.

C. Linear response

In this section we consider a small harmonic perturbation of Eq. (125) acting on the small system, similarly to the preceding section. However, the frequency ω of the perturbation does not need to be close to the resonance with any transition $\omega_{\alpha\beta}$. If $\omega \ll \omega_{\alpha\beta}$ for all α, β , the response of the small system is due to the relaxation and it depends on the relation between ω and the relaxation rate Γ . To make an account of this effect, one has to include $\hat{V}(t)$ into the relaxation terms of the density-matrix equation. Temporal change of $\hat{V}(t)$ changes the instantaneous equilibrium to which the system relaxes that gives rise to a dissipative dynamics. On the other hand, one has to include $\hat{V}(t)$ into the conservative term of the DME as well, where it can work as a resonance perturbation. The secular approximation will be used below for simplicity.

Using the adiabatic basis of Eq. (56) and combining Eq. (58) with Eqs. (81) and (83), one can write the secular DME in the form

$$\frac{d}{dt}\rho_{\alpha\alpha} = \sum_{\gamma} (\langle \dot{\chi}_{\alpha} | \chi_{\gamma} \rangle \rho_{\gamma\alpha} + \rho_{\alpha\gamma} \langle \chi_{\gamma} | \dot{\chi}_{\alpha} \rangle) + \sum_{\alpha' \neq \alpha} \Gamma_{\alpha'\alpha} \left(e^{(\varepsilon_{\alpha'} - \varepsilon_{\alpha})/(k_B T)} \rho_{\alpha'\alpha} - \rho_{\alpha\alpha} \right) \quad (147)$$

for diagonal terms and

$$\frac{d}{dt}\rho_{\alpha\beta} = \sum_{\gamma} (\langle \dot{\chi}_{\alpha} | \chi_{\gamma} \rangle \rho_{\gamma\beta} + \rho_{\alpha\gamma} \langle \chi_{\gamma} | \dot{\chi}_{\beta} \rangle) - (i\omega_{\alpha\beta} + \tilde{\Gamma}_{\alpha\beta}) \rho_{\alpha\beta} \quad (148)$$

for nondiagonal terms. If time derivatives of the adiabatic states are small, the density matrix in the adiabatic basis $\rho_{\alpha\beta}$ is close to its instantaneous quasiequilibrium form given by Eq. (67). The time dependence of the adiabatic states drives the DM out of the instantaneous equilibrium, $\rho_{\alpha\beta}$ lagging behind time-dependent $\rho_{\alpha\beta}^{\text{eq}}$. On the other hand, since $\hat{V}(t)$ is a small perturbation, $\rho_{\alpha\beta}^{\text{eq}}$ deviates from the full equilibrium $\rho_{\alpha\beta}^{(0)\text{eq}}$ in the absence of $\hat{V}(t)$ at linear order in $\hat{V}(t)$. Thus the deviation from the full equilibrium,

$$\delta\rho_{\alpha\beta} \equiv \rho_{\alpha\beta} - \rho_{\alpha\beta}^{(0)\text{eq}} \quad (149)$$

is also linear in $\hat{V}(t)$. Since the difference $e^{(\varepsilon_{\alpha'} - \varepsilon_{\alpha})/(k_B T)} \rho_{\alpha'\alpha} - \rho_{\alpha\alpha}$ and the nondiagonal elements $\rho_{\alpha\beta}$ are small, one does not have to expand $\omega_{\alpha\beta}$ and the relaxation rates. The only term to expand is $e^{(\varepsilon_{\alpha'} - \varepsilon_{\alpha})/(k_B T)}$, where one can use, at linear order in $\hat{V}(t)$,

$$\varepsilon_{\alpha}(t) = \varepsilon_{\alpha}^{(0)} + \delta\varepsilon_{\alpha}^{(0)}(t), \quad \delta\varepsilon_{\alpha}(t) = \langle \chi_{\alpha}^{(0)} | \hat{V}(t) | \chi_{\alpha}^{(0)} \rangle = V(t)_{\alpha\alpha}^{(0)}. \quad (150)$$

Thus

$$e^{(\varepsilon_{\alpha'} - \varepsilon_{\alpha})/(k_B T)} \cong e^{(\varepsilon_{\alpha'}^{(0)} - \varepsilon_{\alpha}^{(0)})/(k_B T)} \left(1 + \frac{V(t)_{\alpha'\alpha}^{(0)} - V(t)_{\alpha\alpha}^{(0)}}{k_B T} \right). \quad (151)$$

The driving term expands as follows:

$$\begin{aligned} & \sum_{\gamma} (\langle \dot{\chi}_{\alpha} | \chi_{\gamma} \rangle \rho_{\gamma\beta} + \rho_{\alpha\gamma} \langle \chi_{\gamma} | \dot{\chi}_{\beta} \rangle) \\ & \cong \sum_{\gamma} (\langle \dot{\chi}_{\alpha} | \chi_{\gamma} \rangle \rho_{\gamma\beta}^{(0)\text{eq}} + \rho_{\alpha\gamma}^{(0)\text{eq}} \langle \chi_{\gamma} | \dot{\chi}_{\beta} \rangle) \\ & = \langle \dot{\chi}_{\alpha} | \chi_{\beta} \rangle \rho_{\beta\beta}^{(0)\text{eq}} + \rho_{\alpha\alpha}^{(0)\text{eq}} \langle \chi_{\alpha} | \dot{\chi}_{\beta} \rangle = \langle \chi_{\alpha} | \dot{\chi}_{\beta} \rangle \left(\rho_{\alpha\alpha}^{(0)\text{eq}} - \rho_{\beta\beta}^{(0)\text{eq}} \right), \end{aligned} \quad (152)$$

where $\langle \chi_\alpha | \chi_\beta \rangle = \delta_{\alpha\beta}$ was used. One can see that in the diagonal equations this term disappears. Thus for the diagonal equations the linearized DME has the form

$$\begin{aligned} \frac{d}{dt} \delta \rho_{\alpha\alpha} &= \sum_{\alpha' \neq \alpha} \Gamma_{\alpha'\alpha} \left(e^{(\varepsilon_{\alpha'}^{(0)} - \varepsilon_\alpha^{(0)}) / (k_B T)} \delta \rho_{\alpha'\alpha'} - \delta \rho_{\alpha\alpha} \right) \\ &+ \sum_{\alpha' \neq \alpha} \Gamma_{\alpha'\alpha} e^{(\varepsilon_{\alpha'}^{(0)} - \varepsilon_\alpha^{(0)}) / (k_B T)} \rho_{\alpha'\alpha'}^{(0)\text{eq}} \frac{V(t)_{\alpha'\alpha'}^{(0)} - V(t)_{\alpha\alpha}^{(0)}}{k_B T} \end{aligned} \quad (153)$$

or

$$\frac{d}{dt} \rho_{\alpha\alpha} = \sum_{\alpha'} (\Gamma_{\alpha\alpha'} \rho_{\alpha'\alpha'} - \Gamma_{\alpha'\alpha} \rho_{\alpha\alpha}) + f_{\alpha\alpha}, \quad (154)$$

where

$$f_{\alpha\alpha} \equiv \frac{e^{-\varepsilon_\alpha^{(0)} / (k_B T)}}{Z_s} \sum_{\alpha'} \Gamma_{\alpha'\alpha} \frac{V(t)_{\alpha'\alpha'}^{(0)} - V(t)_{\alpha\alpha}^{(0)}}{k_B T}. \quad (155)$$

Linearization of nondiagonal equations yields

$$\frac{d}{dt} \rho_{\alpha\beta} = - \left(i\omega_{\alpha\beta} + \tilde{\Gamma}_{\alpha\beta} \right) \rho_{\alpha\beta} + f_{\alpha\beta}, \quad (156)$$

where

$$f_{\alpha\beta} \equiv \langle \chi_\alpha | \dot{\chi}_\beta \rangle \left(\rho_{\alpha\alpha}^{(0)\text{eq}} - \rho_{\beta\beta}^{(0)\text{eq}} \right). \quad (157)$$

One can see that within the secular approximation the driving term is conservative in the nondiagonal equations and dissipative in the diagonal equations.

The density matrix $\rho_{\alpha\beta}$ in the equations above is still defined with respect to the adiabatic basis $|\chi_\alpha\rangle$, although the relaxation term is already expanded around the unperturbed states $|\chi_\alpha^{(0)}\rangle$. Let us now make transformation to $\rho_{\alpha\beta}^{(0)}$ defined with respect to the unperturbed diagonal basis $|\chi_\alpha^{(0)}\rangle$. The relations between the two density matrices have the form

$$\rho_{\alpha\beta}^{(0)} = \sum_{\alpha'\beta'} \langle \chi_\alpha^{(0)} | \chi_{\alpha'} \rangle \rho_{\alpha'\beta'} \langle \chi_{\beta'} | \chi_\beta^{(0)} \rangle, \quad (158)$$

c.f. Eq. (86), and

$$\rho_{\alpha\beta} = \sum_{\alpha'\beta'} \langle \chi_\alpha | \chi_{\alpha'}^{(0)} \rangle \rho_{\alpha'\beta'}^{(0)} \langle \chi_{\beta'}^{(0)} | \chi_\beta \rangle. \quad (159)$$

Differentiating the first equation over time one obtains, at linear order in $\hat{V}(t)$,

$$\begin{aligned} \frac{d}{dt} \rho_{\alpha\beta}^{(0)} &= \sum_{\alpha'\beta'} \langle \chi_\alpha^{(0)} | \dot{\chi}_{\alpha'} \rangle \rho_{\alpha'\beta'} \langle \chi_{\beta'} | \chi_\beta^{(0)} \rangle + \sum_{\alpha'\beta'} \langle \chi_\alpha^{(0)} | \chi_{\alpha'} \rangle \rho_{\alpha'\beta'} \langle \dot{\chi}_{\beta'} | \chi_\beta^{(0)} \rangle + \sum_{\alpha'\beta'} \langle \chi_\alpha^{(0)} | \chi_{\alpha'} \rangle \dot{\rho}_{\alpha'\beta'} \langle \chi_{\beta'} | \chi_\beta^{(0)} \rangle \\ &\cong \sum_{\alpha'} \langle \chi_\alpha^{(0)} | \dot{\chi}_{\alpha'} \rangle \rho_{\alpha'\beta}^{(0)\text{eq}} + \sum_{\beta'} \rho_{\alpha\beta'}^{(0)\text{eq}} \langle \dot{\chi}_{\beta'} | \chi_\beta^{(0)} \rangle + \sum_{\alpha'\beta'} \langle \chi_\alpha^{(0)} | \chi_{\alpha'} \rangle \dot{\rho}_{\alpha'\beta'} \langle \chi_{\beta'} | \chi_\beta^{(0)} \rangle \\ &= - \langle \chi_\alpha^{(0)} | \dot{\chi}_\beta \rangle \left(\rho_{\alpha\alpha}^{(0)\text{eq}} - \rho_{\beta\beta}^{(0)\text{eq}} \right) + \sum_{\alpha'\beta'} \langle \chi_\alpha^{(0)} | \chi_{\alpha'} \rangle \dot{\rho}_{\alpha'\beta'} \langle \chi_{\beta'} | \chi_\beta^{(0)} \rangle. \end{aligned} \quad (160)$$

For $\alpha = \beta$ the first term in this equation disappears and for $\alpha \neq \beta$ it cancels a similar term in Eq. (156). Thus Eq. (156) with $\alpha \neq \beta$ transforms as

$$\begin{aligned} \frac{d}{dt} \rho_{\alpha\beta}^{(0)} &= - \sum_{\alpha'\beta'} \langle \chi_\alpha^{(0)} | \chi_{\alpha'} \rangle \left(i\omega_{\alpha'\beta'} + \tilde{\Gamma}_{\alpha'\beta'} \right) \rho_{\alpha'\beta'} \langle \chi_{\beta'} | \chi_\beta^{(0)} \rangle \\ &= - \sum_{\alpha'\beta'} \sum_{\alpha''\beta''} \langle \chi_\alpha^{(0)} | \chi_{\alpha'} \rangle \left(i\omega_{\alpha'\beta'} + \tilde{\Gamma}_{\alpha'\beta'} \right) \langle \chi_{\alpha'} | \chi_{\alpha''}^{(0)} \rangle \rho_{\alpha''\beta''}^{(0)} \langle \chi_{\beta''}^{(0)} | \chi_{\beta'} \rangle \langle \chi_{\beta'} | \chi_\beta^{(0)} \rangle. \end{aligned}$$

In this expression the projectors such as $\langle \chi_\alpha^{(0)} | \chi_{\alpha'} \rangle$ are linear in $\hat{V}(t)$, if the indices do not coincide. Thus there are two types of contributions: (i) All indices pairwise coincide and thus $\rho_{\alpha''\beta''}^{(0)} \rightarrow \rho_{\alpha\beta}^{(0)} \sim \hat{V}(t)$ or (ii) $\alpha'' = \beta''$ so that $\rho_{\alpha''\beta''}^{(0)} \rightarrow \rho_{\alpha''\alpha''}^{(0)\text{eq}}$ and one of the pair of indices in projectors do not coincide. This yields

$$\begin{aligned}
\frac{d}{dt}\rho_{\alpha\beta}^{(0)} &\cong - \left(i\omega_{\alpha'\beta'}^{(0)} + \tilde{\Gamma}_{\alpha'\beta'}^{(0)} \right) \rho_{\alpha\beta}^{(0)} \\
&\quad - \sum_{\alpha'\beta'} \langle \chi_\alpha^{(0)} | \chi_{\alpha'} \rangle \left(i\omega_{\alpha'\beta'}^{(0)} + \tilde{\Gamma}_{\alpha'\beta'}^{(0)} \right) \rho_{\alpha'\alpha'}^{(0)\text{eq}} \langle \chi_{\alpha'}^{(0)} | \chi_{\beta'} \rangle \langle \chi_{\beta'} | \chi_\beta^{(0)} \rangle \\
&\quad - \sum_{\alpha'\beta'} \langle \chi_\alpha^{(0)} | \chi_{\alpha'} \rangle \left(i\omega_{\alpha'\beta'}^{(0)} + \tilde{\Gamma}_{\alpha'\beta'}^{(0)} \right) \langle \chi_{\alpha'} | \chi_{\beta'}^{(0)} \rangle \rho_{\beta'\beta'}^{(0)\text{eq}} \langle \chi_{\beta'} | \chi_\beta^{(0)} \rangle \\
&\cong - \left(i\omega_{\alpha'\beta'}^{(0)} + \tilde{\Gamma}_{\alpha'\beta'}^{(0)} \right) \rho_{\alpha\beta}^{(0)} \\
&\quad - \langle \chi_\alpha^{(0)} | \chi_\beta \rangle \tilde{\Gamma}_{\beta\beta} \rho_{\beta\beta}^{(0)\text{eq}} - \tilde{\Gamma}_{\alpha\alpha} \rho_{\alpha\alpha}^{(0)\text{eq}} \langle \chi_\alpha | \chi_\beta^{(0)} \rangle - \left(i\omega_{\alpha\beta} + \tilde{\Gamma}_{\alpha\beta} \right) \rho_{\alpha\alpha}^{(0)\text{eq}} \langle \chi_\alpha^{(0)} | \chi_\beta \rangle \\
&\quad - \langle \chi_\alpha^{(0)} | \chi_\beta \rangle \tilde{\Gamma}_{\beta\beta} \rho_{\beta\beta}^{(0)\text{eq}} - \tilde{\Gamma}_{\alpha\alpha} \rho_{\alpha\alpha}^{(0)\text{eq}} \langle \chi_\alpha | \chi_\beta^{(0)} \rangle - \left(i\omega_{\alpha\beta} + \tilde{\Gamma}_{\alpha\beta} \right) \langle \chi_\alpha | \chi_\beta^{(0)} \rangle \rho_{\beta\beta}^{(0)\text{eq}}, \tag{161}
\end{aligned}$$

i.e.,

$$\begin{aligned}
\frac{d}{dt}\rho_{\alpha\beta}^{(0)} &\cong - \left(i\omega_{\alpha'\beta'}^{(0)} + \tilde{\Gamma}_{\alpha'\beta'}^{(0)} \right) \rho_{\alpha\beta}^{(0)} \\
&\quad - 2 \langle \chi_\alpha^{(0)} | \chi_\beta \rangle \tilde{\Gamma}_{\beta\beta} \rho_{\beta\beta}^{(0)\text{eq}} - 2 \langle \chi_\alpha | \chi_\beta^{(0)} \rangle \tilde{\Gamma}_{\alpha\alpha} \rho_{\alpha\alpha}^{(0)\text{eq}} \\
&\quad - \left(i\omega_{\alpha\beta} + \tilde{\Gamma}_{\alpha\beta} \right) \left(\langle \chi_\alpha^{(0)} | \chi_\beta \rangle \rho_{\alpha\alpha}^{(0)\text{eq}} + \langle \chi_\alpha | \chi_\beta^{(0)} \rangle \rho_{\beta\beta}^{(0)\text{eq}} \right). \tag{162}
\end{aligned}$$

The small projections $\langle \chi_\alpha^{(0)} | \chi_\beta \rangle$ can be calculated with the help of the perturbative expansion

$$|\chi_\alpha \rangle \cong |\chi_\alpha^{(0)} \rangle + \sum_{\alpha'} |\chi_{\alpha'}^{(0)} \rangle \frac{\langle \chi_{\alpha'}^{(0)} | \hat{V}(t) | \chi_\alpha^{(0)} \rangle}{\varepsilon_\alpha^{(0)} - \varepsilon_{\alpha'}^{(0)}}, \tag{163}$$

that yields

$$\begin{aligned}
\langle \chi_\alpha^{(0)} | \chi_\beta \rangle &\cong \frac{\langle \chi_\alpha^{(0)} | \hat{V}(t) | \chi_\beta^{(0)} \rangle}{\varepsilon_\beta^{(0)} - \varepsilon_\alpha^{(0)}} = - \frac{V(t)_{\alpha\beta}^{(0)}}{\hbar\omega_{\alpha\beta}^{(0)}} \\
\langle \chi_\alpha | \chi_\beta^{(0)} \rangle &\cong \frac{\langle \chi_\alpha^{(0)} | \hat{V}(t) | \chi_\beta^{(0)} \rangle}{\varepsilon_\alpha^{(0)} - \varepsilon_\beta^{(0)}} = \frac{V(t)_{\alpha\beta}^{(0)}}{\hbar\omega_{\alpha\beta}^{(0)}}. \tag{164}
\end{aligned}$$

Thus the DME for nondiagonal components has the form

$$\frac{d}{dt}\rho_{\alpha\beta}^{(0)} = - \left(i\omega_{\alpha\beta}^{(0)} + \tilde{\Gamma}_{\alpha\beta}^{(0)} \right) \rho_{\alpha\beta}^{(0)} + f_{\alpha\beta}^{(0)}, \tag{165}$$

where

$$f_{\alpha\beta}^{(0)} \equiv \left[\left(i + \frac{\tilde{\Gamma}_{\alpha\beta}^{(0)}}{\omega_{\alpha\beta}^{(0)}} \right) \left(\rho_{\alpha\alpha}^{(0)\text{eq}} - \rho_{\beta\beta}^{(0)\text{eq}} \right) - 2 \frac{\tilde{\Gamma}_{\alpha\alpha} \rho_{\alpha\alpha}^{(0)\text{eq}} - \tilde{\Gamma}_{\beta\beta} \rho_{\beta\beta}^{(0)\text{eq}}}{\omega_{\alpha\beta}^{(0)}} \right] \frac{V(t)_{\alpha\beta}^{(0)}}{\hbar}. \tag{166}$$

As the secular approximation implies $\Gamma_{\alpha\beta} \ll \omega_{\alpha\beta}$, relaxation terms in this equation can be neglected,

$$f_{\alpha\beta}^{(0)} \equiv i \left(\rho_{\alpha\alpha}^{(0)\text{eq}} - \rho_{\beta\beta}^{(0)\text{eq}} \right) V(t)_{\alpha\beta}^{(0)} / \hbar. \tag{167}$$

The conservative part of this driving term could actually be transformed exactly using the relation between the two

bases, Eqs. (52) and (58). Transformation of the diagonal Eq. (154) is as follows:

$$\begin{aligned}
\frac{d}{dt}\rho_{\alpha\alpha}^{(0)} &\cong \sum_{\alpha'} \langle \chi_{\alpha}^{(0)} | \chi_{\alpha'} \rangle \dot{\rho}_{\alpha'\alpha'} \langle \chi_{\alpha'} | \chi_{\alpha}^{(0)} \rangle \\
&= \sum_{\alpha'} \langle \chi_{\alpha}^{(0)} | \chi_{\alpha'} \rangle \left[\sum_{\alpha''} (\Gamma_{\alpha'\alpha''} \rho_{\alpha''\alpha'} - \Gamma_{\alpha''\alpha'} \rho_{\alpha'\alpha''}) + f_{\alpha'\alpha'} \right] \langle \chi_{\alpha'} | \chi_{\alpha}^{(0)} \rangle \\
&= \sum_{\alpha'} (\Gamma_{\alpha\alpha'} \rho_{\alpha'\alpha'} - \Gamma_{\alpha'\alpha} \rho_{\alpha\alpha}) + f_{\alpha\alpha} \\
&\cong \sum_{\alpha'} \left(\Gamma_{\alpha\alpha'} \sum_{\alpha''\beta''} \langle \chi_{\alpha'} | \chi_{\alpha''} \rangle \rho_{\alpha''\beta''}^{(0)} \langle \chi_{\beta''} | \chi_{\alpha'} \rangle - \Gamma_{\alpha'\alpha} \sum_{\alpha''\beta''} \langle \chi_{\alpha} | \chi_{\alpha''} \rangle \rho_{\alpha''\beta''}^{(0)} \langle \chi_{\beta''} | \chi_{\alpha} \rangle \right) + f_{\alpha\alpha}^{(0)} \\
&\cong \sum_{\alpha'} \left(\Gamma_{\alpha\alpha'} \rho_{\alpha'\alpha'}^{(0)} - \Gamma_{\alpha'\alpha} \rho_{\alpha\alpha}^{(0)} \right) + f_{\alpha\alpha}^{(0)}.
\end{aligned} \tag{168}$$

Since there are no corrections to $\Gamma_{\alpha\alpha'}$ linear in $V(t)$, this finally yields

$$\frac{d}{dt}\rho_{\alpha\alpha}^{(0)} = \sum_{\alpha'} \left(\Gamma_{\alpha\alpha'}^{(0)} \rho_{\alpha'\alpha'}^{(0)} - \Gamma_{\alpha'\alpha}^{(0)} \rho_{\alpha\alpha}^{(0)} \right) + f_{\alpha\alpha}^{(0)} \tag{169}$$

where

$$f_{\alpha\alpha}^{(0)} \equiv \frac{e^{-\varepsilon_{\alpha}^{(0)}/(k_{\text{B}}T)}}{Z_{\text{s}}} \sum_{\alpha' \neq \alpha} \Gamma_{\alpha'\alpha}^{(0)} \frac{V(t)_{\alpha'\alpha'}^{(0)} - V(t)_{\alpha\alpha}^{(0)}}{k_{\text{B}}T}. \tag{170}$$

One can see that this transformation was trivial. In the sequel we will drop the superscript (0).

Let us now solve Eqs. (165)–(170). Similarly to Sec. III A 2, one can write Eq. (169) in the vectorized form

$$\frac{d}{dt}\delta\mathbf{n} = \mathbf{\Phi}^{\text{sec}} \cdot \delta\mathbf{n} + \mathbf{f}^{\text{diag}}, \tag{171}$$

where $(\delta\mathbf{n})_{\alpha} \equiv \delta\rho_{\alpha\alpha}$ and the elements of $\mathbf{\Phi}^{\text{sec}}$ are given by Eq. (113). Since \mathbf{f} contains positively- and negatively-rotating terms, the stationary solution of this equation has the form

$$\pm i\omega\delta\mathbf{n}^{(\pm)} = \mathbf{\Phi}^{\text{sec}} \cdot \delta\mathbf{n}^{(\pm)} + \mathbf{f}^{\text{diag},(\pm)} \tag{172}$$

with

$$f_{\alpha\alpha}^{(\pm)} = \frac{e^{-\varepsilon_{\alpha}/(k_{\text{B}}T)}}{Z_{\text{s}}} \sum_{\alpha' \neq \alpha} \Gamma_{\alpha'\alpha} \frac{V_{\alpha'\alpha'}^{(\pm)} - V_{\alpha\alpha}^{(\pm)}}{k_{\text{B}}T}. \tag{173}$$

Here $V_{0,\alpha\gamma}^{(+)} \equiv V_{0,\alpha\gamma}$ and $V_{0,\alpha\gamma}^{(-)} \equiv (\hat{V}_0^{\dagger})_{\alpha\gamma} = V_{0,\gamma\alpha}^*$. The solution of this equation can be expanded over the set of right eigenvectors defined by an equation similar to Eq. (97),

$$\delta\mathbf{n}^{(\pm)} = \sum_{\mu} C_{\mu}^{(\pm)} \mathbf{R}_{\mu}. \tag{174}$$

Inserting this into Eq. (172), multiplying from left by the left eigenvector \mathbf{L}_{ν} and using orthogonality in Eq. (98), one obtains

$$\pm i\omega C_{\nu}^{(\pm)} = -\Lambda_{\nu} C_{\nu}^{(\pm)} + \mathbf{L}_{\nu} \cdot \mathbf{f}^{\text{diag},(\pm)} \tag{175}$$

and

$$C_{\nu}^{(\pm)} = \frac{\mathbf{L}_{\nu} \cdot \mathbf{f}^{\text{diag},(\pm)}}{\Lambda_{\nu} \pm i\omega}. \tag{176}$$

Now the final result for the populations is

$$\delta\mathbf{n}^{(\pm)} = \sum_{\mu} \frac{\mathbf{L}_{\mu} \cdot \mathbf{f}^{\text{diag},(\pm)}}{\Lambda_{\mu} \pm i\omega} \mathbf{R}_{\mu}. \tag{177}$$

At equilibrium, $\omega = 0$, this expression should reduce to the static result

$$\delta n_\alpha = \sum_{\pm} \sum_{\mu} \frac{\mathbf{L}_\mu \cdot \mathbf{f}^{\text{diag},(\pm)}}{\Lambda_\mu} R_{\mu\alpha} = -\frac{e^{-\varepsilon_\alpha/(k_B T)}}{Z_s} \left(\frac{\delta \varepsilon_\alpha}{k_B T} + \frac{\delta Z_s}{Z_s} \right) \quad (178)$$

that can be proven to satisfy Eq. (169) in the static case. Using Eq. (173) and $\sum_{\pm} V_{\alpha\alpha}^{(\pm)} = \delta \varepsilon_\alpha$, one obtains the identity

$$\sum_{\mu} \frac{R_{\mu\alpha}}{\Lambda_\mu} \sum_{\alpha'\alpha''} \Gamma_{\alpha''\alpha'} \frac{\delta \varepsilon_{\alpha''} - \delta \varepsilon_{\alpha'}}{k_B T} L_{\mu\alpha'} = -\frac{\delta \varepsilon_\alpha}{k_B T} - \frac{\delta Z_s}{Z_s} \quad (179)$$

that should be satisfied by the matrix solution and can be used for checking. Nondiagonal components of the DME satisfy the equations

$$\pm i\omega \delta \rho_{\alpha\beta}^{(\pm)} = -\left(i\omega_{\alpha\beta} + \tilde{\Gamma}_{\alpha\beta} \right) \delta \rho_{\alpha\beta}^{(\pm)} + f_{\alpha\beta}^{(\pm)}, \quad (180)$$

where

$$f_{\alpha\beta}^{(\pm)} \equiv -\frac{1}{\hbar} \left(i + \frac{\tilde{\Gamma}_{\alpha\beta}}{\omega_{\alpha\beta}} \right) V_{\alpha\beta}^{(\pm)} \left(\rho_{\alpha\alpha}^{\text{eq}} - \rho_{\beta\beta}^{\text{eq}} \right). \quad (181)$$

These equations have the solution

$$\delta \rho_{\alpha\beta}^{(\pm)} = \frac{f_{\alpha\beta}^{(\pm)}}{\tilde{\Gamma}_{\alpha\beta} + i\omega_{\alpha\beta} \pm i\omega}. \quad (182)$$

For a physical quantity \hat{A} the linear response has the form

$$A(t) = e^{i\omega t} A^{(+)}(\omega) + e^{-i\omega t} A^{(-)}(\omega), \quad (183)$$

where

$$A^{(\pm)}(\omega) = \sum_{\mu=2}^N \frac{(\mathbf{A} \cdot \mathbf{R}_\mu) (\mathbf{L}_\mu \cdot \mathbf{f}^{\text{diag},(\pm)})}{\Lambda_\mu \pm i\omega} + \sum_{\alpha \neq \beta} \frac{A_{\beta\alpha} f_{\alpha\beta}^{(\pm)}}{\tilde{\Gamma}_{\alpha\beta} + i\omega_{\alpha\beta} \pm i\omega} \quad (184)$$

c.f. Eq. (118). Here $(\mathbf{A})_\alpha = A_{\alpha\alpha}$. The zero eigenvalue, $\mu = 1$ and $\Lambda_1 = 0$, does not make a contribution to this formula since \mathbf{L}_1 given by Eq. (114) is orthogonal to $\mathbf{f}^{\text{diag},(\pm)}$ defined by Eq. (173). Physically relevant are real and imaginary parts of the linear response

$$\begin{aligned} A'(\omega) &= \text{Re} A^{(+)}(\omega) + \text{Re} A^{(-)}(\omega) \\ A''(\omega) &= -\text{Im} A^{(+)}(\omega) + \text{Im} A^{(-)}(\omega). \end{aligned} \quad (185)$$

IV. APPLICATION TO MOLECULAR MAGNETS

A. The model

Let us consider, as an example, a magnetic molecule (MM) described as a large spin S with the Hamiltonian

$$\hat{H}_s = \hat{H}_S = \hat{H}_A + \hat{H}_Z, \quad (186)$$

where \hat{H}_A is the crystal-field Hamiltonian and \hat{H}_Z is the Zeeman Hamiltonian, $\hat{H}_Z = -g\mu_B \mathbf{H} \cdot \mathbf{S}$. The crystal field \hat{H}_A is usually dominated by the uniaxial anisotropy,

$$\hat{H}_A = -DS_z^2 - BS_z^4 + \hat{H}'_A, \quad (187)$$

whereas \hat{H}'_A contains smaller terms that do not commute with S_z . In the absence of the latter and of the transverse field, the eigenstates of the spin are $|m\rangle$, $m = -S, \dots, S$. The energy levels of the magnetic molecule are given by

$$\varepsilon_m = -Dm^2 - Bm^4 - gm_B H_z m. \quad (188)$$

The transition frequency for a pair of levels is

$$\hbar\omega_{mm'} = \varepsilon_m - \varepsilon_{m'} = -(m - m') \{ (m + m') [D + (m^2 + m'^2) B] + gm_B H_z \} \quad (189)$$

Condition $\hbar\omega_{mm'} = 0$ for $m \neq m'$ (levels on different sides of the barrier created by the uniaxial anisotropy) defines the resonance values of the longitudinal field H_z . For the generic model of molecular magnets with $B = 0$ the latter are given by

$$gm_B H_z = kD, \quad k = 0, \pm 1, \pm 2, \dots \quad (190)$$

For these fields *all* levels in the right well

$$m' = -m - k \quad (191)$$

are at resonance with the corresponding levels in the left well $m < 0$. For the realistic model with $B > 0$, the field creating resonances between low-lying levels with large $m^2 + m'^2$ is greater than the resonance fields for high levels. Transverse anisotropy and transverse field H_x that enter \hat{H}'_A result in the tunneling under the barrier and tunneling splitting of the resonant levels m, m' .

For Mn_{12} used in illustrations below we adopt the values $D/k_B = 0.548$ K and $B/k_B = 1.1 \times 10^{-3}$ K (Refs. [4, 5, 6]) that makes up the barrier of 66 K. \hat{H}'_A in Eq. (187) can contain second- and fourth order transverse anisotropy,

$$\hat{H}'_A = E (S_x^2 - S_y^2) + C(S_+^4 + S_-^4). \quad (192)$$

For Mn_{12} $C/k_B = 3 \times 10^{-5}$ K (Refs. [4, 5, 6]), whereas $E = 0$ in the ideal case because of the tetragonal symmetry of the crystal. However, it was shown [6] that *local* molecular environments of Mn_{12} molecules have a two-fold symmetry and rotated by 90° for different molecules. Although on average the four-fold symmetry of the crystal is preserved, it gives rise to nonzero E that will be set to $E/k_B = 2.5 \times 10^{-3}$ K.

The spin Hamiltonian of molecular magnets can be easily numerically diagonalized to yield eigenstates $|\alpha\rangle$ and transition frequencies $\omega_{\alpha\beta}$, $\alpha, \beta = 1, \dots, 2S + 1$. The terms non-commuting with S_z such as \hat{H}'_A and the transverse magnetic field cause hybridization of the spin states in the two wells that leads to spin tunneling.

B. Spin-phonon interaction

The magnetic molecule is embedded in the elastic matrix described by the harmonic-phonon Hamiltonian

$$\hat{H}_b = \hat{H}_{\text{ph}} = \sum_{\mathbf{k}\lambda} \hbar\omega_{\mathbf{k}\lambda} a_{\mathbf{k}\lambda}^\dagger a_{\mathbf{k}\lambda}. \quad (193)$$

Describing the spin-phonon interaction, we will follow the approach developed in Refs. [7, 8] that allows to avoid using unknown spin-phonon coupling constants and to greatly simplify the formalism. As a magnetic molecule is more rigid

than its ligand environment, a good approximation is to consider this molecule rotated by transverse phonons without distortion of its crystal field. This leads to the spin-phonon interaction

$$\hat{V} = \hat{H}_{\text{s-ph}} = \hat{R}\hat{H}_A\hat{R}^{-1} - \hat{H}_A, \quad \hat{R} = e^{-i\mathbf{S}\cdot\delta\phi}, \quad (194)$$

where $\delta\phi$ is a small rotation angle given by

$$\delta\phi = \frac{1}{2}\nabla \times \mathbf{u}(\mathbf{r}), \quad (195)$$

$\mathbf{u}(\mathbf{r})$ being the lattice displacement due to phonons. Expanding Eq. (194) up to the second order in $\delta\phi$ components yields

$$\hat{V} = \hat{V}^{(1)} + \hat{V}^{(2)}, \quad (196)$$

where

$$\hat{V}^{(1)} = i \left[\hat{H}_A, \mathbf{S} \right] \cdot \delta\phi \quad (197)$$

and

$$\hat{V}^{(2)} = \frac{i^2}{2!} \left[\left[\hat{H}_A, S_\xi \right], S_{\xi'} \right] \delta\phi_\xi \delta\phi_{\xi'}, \quad \xi, \xi' = x, y, z \quad (198)$$

with summation over repeated indices. We use canonical quantization of phonons,

$$\mathbf{u} = \sqrt{\frac{\hbar}{2MN}} \sum_{\mathbf{k}\lambda} \frac{\mathbf{e}_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\omega_{\mathbf{k}\lambda}}} \left(a_{\mathbf{k}\lambda} + a_{-\mathbf{k}\lambda}^\dagger \right), \quad (199)$$

where M is the mass of the unit cell, N is the number of cells in the crystal, $\mathbf{e}_{\mathbf{k}\lambda}$ are unit polarization vectors, $\lambda = t_1, t_2, l$ denotes polarization, and $\omega_{k\lambda} = v_\lambda k$ is the phonon frequency. The operator $\delta\phi$ that follows from Eq. (195) is given by

$$\delta\phi = \frac{1}{2} \sqrt{\frac{\hbar}{2MN}} \sum_{\mathbf{k}\lambda} \frac{[i\mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}] e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\omega_{\mathbf{k}\lambda}}} \left(a_{\mathbf{k}\lambda} + a_{-\mathbf{k}\lambda}^\dagger \right). \quad (200)$$

Only transverse phonons, $\mathbf{e}_{\mathbf{k}\lambda} \perp \mathbf{k}$, survive in this formula. Whereas $\hat{V}^{(1)}$ is linear in phonon operators and describes direct phonon processes, $\hat{V}^{(2)}$ is quadratic and describes Raman processes. Relaxation rates due to Raman processes are generally much smaller than that due to the direct processes since they are the next order in the spin-phonon interaction. However, the rates of direct processes can be small for special reasons, then Raman processes become important. Processes of orders higher than Raman can be always neglected.

It is important that the spin-phonon interaction above does not include any poorly known spin-lattice coupling coefficients and it is entirely represented by the crystal field \hat{H}_A . Moreover, the relaxation terms in the DME can be represented in the form that does not explicitly contain \hat{H}_A , the information about it being absorbed in the spin eigenstates $|\alpha\rangle$ and transition frequencies $\omega_{\alpha\beta}$ that can be found by numerical diagonalization of \hat{H}_S . This can be achieved either by changing from the laboratory frame to the local lattice frame in which \hat{H}_A remains constant but an effective rotation-generated magnetic field arises[7, 8, 9] or by manipulating matrix elements of the spin-phonon interaction with respect to spin states, $\langle \alpha | \hat{V} | \beta \rangle$, Ref. [8]. Both methods are mathematically equivalent [8]. In particular, for $\hat{V}^{(1)}$ one can use

$$\left[\hat{H}_A, \mathbf{S} \right] = \left[\left(\hat{H}_S - \hat{H}_Z \right), \mathbf{S} \right] = \left[\hat{H}_S, \mathbf{S} \right] + i\mathbf{S} \times g\mu_B \mathbf{H} \quad (201)$$

and the fact that $|\alpha\rangle$ are eigenstates of \hat{H}_S to obtain the spin matrix element

$$\Xi_{\alpha\beta}^{(1)} \equiv i \langle \alpha | \left[\hat{H}_A, \mathbf{S} \right] | \beta \rangle = i\hbar\omega_{\alpha\beta} \langle \alpha | \mathbf{S} | \beta \rangle - \langle \alpha | \mathbf{S} | \beta \rangle \times g\mu_B \mathbf{H}. \quad (202)$$

For $\hat{V}^{(2)}$ one writes [10]

$$\begin{aligned} \left[\left[\hat{H}_A, S_\xi \right], S_{\xi'} \right] &= \left[\left[\left(\hat{H}_S - \hat{H}_Z \right), S_\xi \right], S_{\xi'} \right] \\ &= \left[\left[\hat{H}_S, S_\xi \right], S_{\xi'} \right] - g\mu_B \left(H_{\xi'} S_\xi - \delta_{\xi\xi'} \sum_{\xi''} H_{\xi''} S_{\xi''} \right). \end{aligned} \quad (203)$$

Here the first term can be transformed as follows

$$\begin{aligned}
\langle \alpha | \left[\left[\hat{H}_S, S_\xi \right], S_{\xi'} \right] | \beta \rangle &= \langle \alpha | \left[\hat{H}_S S_\xi S_{\xi'} - S_\xi \hat{H}_S S_{\xi'} - S_{\xi'} \hat{H}_S S_\xi + S_{\xi'} S_\xi \hat{H}_S \right] | \beta \rangle \\
&= \sum_\gamma [(\varepsilon_\alpha - \varepsilon_\gamma) \langle \alpha | S_\xi | \gamma \rangle \langle \gamma | S_{\xi'} | \beta \rangle + (\varepsilon_\beta - \varepsilon_\gamma) \langle \alpha | S_{\xi'} | \gamma \rangle \langle \gamma | S_\xi | \beta \rangle] \\
&\Rightarrow \sum_\gamma (\varepsilon_\alpha + \varepsilon_\beta - 2\varepsilon_\gamma) \langle \alpha | S_\xi | \gamma \rangle \langle \gamma | S_{\xi'} | \beta \rangle,
\end{aligned} \tag{204}$$

where on the last step the symmetry properties of Eq. (198) were used. Finally one obtains

$$\begin{aligned}
\Xi_{\alpha\beta, \xi\xi'}^{(2)} &\equiv i^2 \langle \alpha | \left[\left[\hat{H}_A, S_\xi \right], S_{\xi'} \right] | \beta \rangle = - \sum_\gamma (\varepsilon_\alpha + \varepsilon_\beta - 2\varepsilon_\gamma) \langle \alpha | S_\xi | \gamma \rangle \langle \gamma | S_{\xi'} | \beta \rangle \\
&\quad + g\mu_B \left(H_{\xi'} \langle \alpha | S_\xi | \beta \rangle - \delta_{\xi\xi'} \sum_{\xi''} H_{\xi''} \langle \alpha | S_{\xi''} | \beta \rangle \right).
\end{aligned} \tag{205}$$

Eqs. (202) and (205) provide a great simplification of the formalism, since otherwise one would have to derive different forms of the relaxation part of the DME for each particular \hat{H}_A .

C. DME for molecular magnets

1. Secular vs non-secular

Most of numerical work on molecular magnets used the secular form of the DME, in fact reduced to the system of rate equations for the populations. However, tunneling resonances can make the secular approximation invalid. Indeed, if two levels α and α' of the small system have very close energies, the density matrix element $\rho_{\alpha\alpha'}$ is oscillating with a very small frequency $\omega_{\alpha\alpha'}$ in the absence of the coupling to the bath, see Eq. (63). If $\omega_{\alpha\alpha'}$ is smaller than the relaxation rate between the neighboring energy levels, $\rho_{\alpha\alpha'}$ does not decouple from the diagonal elements $\rho_{\alpha\alpha}$ and $\rho_{\alpha'\alpha'}$, and the secular approximation breaks down. It is easy to demonstrate that the failure of the secular approximation at resonance may lead to unphysically high escape rates out of the metastable state. Consider a MM exactly at k th resonance with $k > 0$ and a very small \hat{H}'_A and the transverse field, so that the metastable ground state $| -S \rangle$ is at resonance with the excited state $| S - k \rangle$ in the right well. The latter can decay into the lower-lying state $| S - k + 1 \rangle$ with the rate $\Gamma_{S-k+1, S-k}$. Since the exact eigenstates at the tunneling resonance are $|\pm\rangle$ that are linear combinations of $| -S \rangle$ and $| S - k \rangle$ (see Sec. IV E), both of these eigenstates are damped with the rate of order $\Gamma_{S-k+1, S-k}$ (in fact, half of it). The secular DME uses rate equations for ρ_{++} , ρ_{--} , etc., and the initial condition spin in the state $| -S \rangle$ gives rise to the initial conditions $\rho_{++}(0) = \rho_{--}(0) = 1/2$. Since both ρ_{++} and ρ_{--} relax with a rate of order $\Gamma_{S-k+1, S-k}$, the spin quickly leaves the metastable state, even in the case of a vanishing tunnel splitting, $\Delta \rightarrow 0$. Indeed, such an unphysical behavior follows from the analytical and numerical solution of the secular DME at weak tunneling resonances. In contrast, coupling of ρ_{++} and ρ_{--} to the slow non-diagonal DM elements ρ_{+-} and ρ_{-+} in the non-secular DME leads to the physically expected vanishing of the escape rate in the limit $\Delta \rightarrow 0$ and $T \rightarrow 0$.

Below the non-secular DME, Eq. (63), will be used in the development of the formalism. The secular and semi-secular reductions of it can be obtained later. The relaxation tensor $R_{\alpha\beta, \alpha'\beta'}$ is a sum of two contributions,

$$R_{\alpha\beta, \alpha'\beta'} = R_{\alpha\beta, \alpha'\beta'}^{(1)} + R_{\alpha\beta, \alpha'\beta'}^{(2)}, \tag{206}$$

that are due to the first- and second-order phonon processes. These contributions will be calculated separately below.

2. Initial condition for free relaxation

Let us consider the question of the initial state of the spin in the case of free evolution. In resonance experiments it is, typically, the first excited state. Although, practically, in these experiments only a small portion of the population is being transferred from the ground state to the excited state, one can consider the system prepared fully in the excited state because of the linearity of the DME. Preparing the spin in the metastable energy minimum, one can study its thermal activation over the barrier and tunneling under the barrier. In general, it is not easy to find the quantum-mechanical state realizing or approximating this classical state, and in the case of a tunneling resonance such

a state does not exist. A good practical way to create such an initial condition is to prepare the spin in the coherent state $|\mathbf{n}(\theta, \varphi)\rangle$ pointing in the direction of the metastable minimum found classically. The spin coherent state is given by

$$|\mathbf{n}(\theta, \varphi)\rangle = \sum_{m=-S}^S C_m |m\rangle, \quad (207)$$

where

$$C_m = \binom{2S}{S+m}^{1/2} \left(\cos \frac{\theta}{2}\right)^{S+m} \left(\sin \frac{\theta}{2}\right)^{S-m} e^{-im\varphi}. \quad (208)$$

3. Direct processes

To compute matrix elements $V_{\alpha\varpi, \gamma\varpi'}^{(1)}$, etc., in Eq. (64) with respect to the phonon bath, one can label the state $|\phi_{\varpi}\rangle$ by the numbers of phonons $\nu_{\mathbf{k}\lambda} = 0, 1, 2, \dots$ in each phonon mode $\mathbf{k}\lambda$

$$|\phi_{\varpi}\rangle = |\dots, \nu_{\mathbf{k}\lambda}, \dots\rangle \Rightarrow |\nu_{\mathbf{k}\lambda}\rangle. \quad (209)$$

In the direct processes, the state $|\phi_{\varpi'}\rangle$ is not independent and it differs from $|\phi_{\varpi}\rangle$ by creation or annihilation of one phonon, according to Eq. (200). We will make use of the phonon matrix elements

$$\mathbf{M}_{\pm}(\mathbf{k}) = \langle \nu_{\mathbf{k}\lambda} \pm 1 | \delta\phi | \nu_{\mathbf{k}\lambda} \rangle \quad (210)$$

and their conjugates. From Eq. (200) one obtains

$$\begin{aligned} \mathbf{M}_-(\mathbf{k}) &= \left\langle \nu_{\mathbf{k}\lambda} - 1 \left| \frac{1}{2} \sqrt{\frac{\hbar}{2MN}} \frac{[i\mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}] e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\omega_{\mathbf{k}}}} a_{\mathbf{k}\lambda} \right| \nu_{\mathbf{k}\lambda} \right\rangle = \frac{1}{2} \sqrt{\frac{\hbar}{2MN}} \frac{[i\mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}] e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\omega_{\mathbf{k}}}} \sqrt{\nu_{\mathbf{k}\lambda}} \\ \mathbf{M}_-^*(\mathbf{k}) &= \left\langle \nu_{\mathbf{k}\lambda} \left| \frac{1}{2} \sqrt{\frac{\hbar}{2MN}} \frac{[-i\mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}] e^{-i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\omega_{\mathbf{k}}}} a_{\mathbf{k}\lambda}^\dagger \right| \nu_{\mathbf{k}\lambda} - 1 \right\rangle = \frac{1}{2} \sqrt{\frac{\hbar}{2MN}} \frac{[-i\mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}] e^{-i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\omega_{\mathbf{k}}}} \sqrt{\nu_{\mathbf{k}\lambda}} \\ \mathbf{M}_+(\mathbf{k}) &= \left\langle \nu_{\mathbf{k}\lambda} + 1 \left| \frac{1}{2} \sqrt{\frac{\hbar}{2MN}} \frac{[-i\mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}] e^{-i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\omega_{\mathbf{k}}}} a_{\mathbf{k}\lambda}^\dagger \right| \nu_{\mathbf{k}\lambda} \right\rangle = \frac{1}{2} \sqrt{\frac{\hbar}{2MN}} \frac{[-i\mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}] e^{-i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\omega_{\mathbf{k}}}} \sqrt{\nu_{\mathbf{k}\lambda} + 1} \\ \mathbf{M}_+^*(\mathbf{k}) &= \left\langle \nu_{\mathbf{k}\lambda} \left| \frac{1}{2} \sqrt{\frac{\hbar}{2MN}} \frac{[i\mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}] e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\omega_{\mathbf{k}}}} a_{\mathbf{k}\lambda} \right| \nu_{\mathbf{k}\lambda} + 1 \right\rangle = \frac{1}{2} \sqrt{\frac{\hbar}{2MN}} \frac{[i\mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}] e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\omega_{\mathbf{k}}}} \sqrt{\nu_{\mathbf{k}\lambda} + 1}. \end{aligned} \quad (211)$$

In Eq. (64) one has, e.g.,

$$\begin{aligned} &\frac{\pi}{\hbar Z_b} \sum_{\varpi\varpi'} e^{-E_{\varpi}/(k_B T)} \delta(\varepsilon_{\alpha'} - \varepsilon_{\gamma} + E_{\varpi} - E_{\varpi'}) V_{\alpha\varpi, \gamma\varpi'}^{(1)} V_{\gamma\varpi', \alpha'\varpi}^{(1)} \\ &= \sum_{\mathbf{k}\lambda} \frac{\pi}{\hbar Z_b} \sum_{\nu_{\mathbf{k}\lambda}, \dots} e^{-E_{\nu_{\mathbf{k}\lambda}, \dots}/(k_B T)} \delta(\varepsilon_{\alpha'} - \varepsilon_{\gamma} + \hbar\omega_{\mathbf{k}}) \left(\boldsymbol{\Xi}_{\alpha\gamma}^{(1)} \cdot \mathbf{M}_-^*(\mathbf{k}) \right) \left(\boldsymbol{\Xi}_{\gamma\alpha'}^{(1)} \cdot \mathbf{M}_-(\mathbf{k}) \right) \\ &\quad + \sum_{\mathbf{k}\lambda} \frac{\pi}{\hbar Z_b} \sum_{\nu_{\mathbf{k}\lambda}, \dots} e^{-E_{\nu_{\mathbf{k}\lambda}, \dots}/(k_B T)} \delta(\varepsilon_{\alpha'} - \varepsilon_{\gamma} - \hbar\omega_{\mathbf{k}}) \left(\boldsymbol{\Xi}_{\alpha\gamma}^{(1)} \cdot \mathbf{M}_+^*(\mathbf{k}) \right) \left(\boldsymbol{\Xi}_{\gamma\alpha'}^{(1)} \cdot \mathbf{M}_+(\mathbf{k}) \right). \end{aligned} \quad (212)$$

After averaging over phonon populations,

$$\frac{1}{Z_b} \sum_{\nu_{\mathbf{k}\lambda}, \dots} e^{-E_{\nu_{\mathbf{k}\lambda}, \dots}/(k_B T)} \nu_{\mathbf{k}\lambda} \equiv \langle \nu_{\mathbf{k}\lambda} \rangle = n_{\mathbf{k}\lambda} = n_{\mathbf{k}} = \frac{1}{e^{\hbar\omega_{\mathbf{k}}/(k_B T)} - 1}, \quad (213)$$

this becomes

$$\begin{aligned} &\frac{\pi}{8MN} \sum_{\mathbf{k}\lambda} \left[\left(\boldsymbol{\Xi}_{\alpha\gamma}^{(1)} \cdot \frac{[\mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}]}{\sqrt{\omega_{\mathbf{k}}}} \right) \left(\boldsymbol{\Xi}_{\gamma\alpha'}^{(1)} \cdot \frac{[\mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}]}{\sqrt{\omega_{\mathbf{k}}}} \right) \delta(\varepsilon_{\alpha'} - \varepsilon_{\gamma} + \hbar\omega_{\mathbf{k}}) n_{\mathbf{k}} \right. \\ &\quad \left. + \left(\boldsymbol{\Xi}_{\alpha\gamma}^{(1)} \cdot \frac{[\mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}]}{\sqrt{\omega_{\mathbf{k}}}} \right) \left(\boldsymbol{\Xi}_{\gamma\alpha'}^{(1)} \cdot \frac{[\mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}]}{\sqrt{\omega_{\mathbf{k}}}} \right) \delta(\varepsilon_{\alpha'} - \varepsilon_{\gamma} - \hbar\omega_{\mathbf{k}}) (n_{\mathbf{k}} + 1) \right]. \end{aligned} \quad (214)$$

This can be further simplified using

$$[\mathbf{k} \times \mathbf{e}_{\mathbf{k}t_1}] = \pm k \mathbf{e}_{\mathbf{k}t_2} \quad (215)$$

and, for the summation over the two transverse polarizations,

$$\sum_{t=t_1, t_2} (\mathbf{e}_{\mathbf{k}t} \cdot \mathbf{a}) (\mathbf{e}_{\mathbf{k}t} \cdot \mathbf{b}) = (\mathbf{a} \cdot \mathbf{b}) - \frac{(\mathbf{k} \cdot \mathbf{a})(\mathbf{k} \cdot \mathbf{b})}{k^2} \quad (216)$$

with $\mathbf{a} = \mathbf{b} = \mathbf{e}_x$, and then \mathbf{e}_y . Averaging over the directions of the vector \mathbf{k} :

$$\langle (\mathbf{k} \cdot \mathbf{a})(\mathbf{k} \cdot \mathbf{b}) \rangle = \frac{k^2}{3} (\mathbf{a} \cdot \mathbf{b}) \quad (217)$$

one obtains

$$\begin{aligned} & \left(\Xi_{\alpha\gamma}^{(1)} \cdot \Xi_{\gamma\alpha'}^{(1)} \right) \frac{\pi}{12MN} \sum_{\mathbf{k}} \frac{k^2}{\omega_{\mathbf{k}}} [\delta(\varepsilon_{\alpha'} - \varepsilon_{\gamma} + \hbar\omega_{\mathbf{k}}) n_{\mathbf{k}} + \delta(\varepsilon_{\alpha'} - \varepsilon_{\gamma} - \hbar\omega_{\mathbf{k}}) (n_{\mathbf{k}} + 1)] \\ &= \left(\Xi_{\alpha\gamma}^{(1)} \cdot \Xi_{\gamma\alpha'}^{(1)} \right) \frac{\pi}{12\hbar MN} \sum_{\mathbf{k}} \frac{k^2}{\omega_{\mathbf{k}}} [\delta(\omega_{\alpha'\gamma} + \omega_{\mathbf{k}}) n_{\mathbf{k}} + \delta(\omega_{\alpha'\gamma} - \omega_{\mathbf{k}}) (n_{\mathbf{k}} + 1)]. \end{aligned} \quad (218)$$

Now recalling Eq. (64) one obtains

$$\begin{aligned} R_{\alpha\beta, \alpha'\beta'}^{(1)} &= \frac{\pi D^2}{12\hbar MN} \sum_{\mathbf{k}} \frac{k^2}{\omega_{\mathbf{k}}} \\ & \left\{ - \sum_{\gamma} Q_{\alpha\alpha', \gamma\gamma}^{(1)} [\delta(\omega_{\alpha'\gamma} + \omega_{\mathbf{k}}) n_{\mathbf{k}} + \delta(\omega_{\alpha'\gamma} - \omega_{\mathbf{k}}) (n_{\mathbf{k}} + 1)] \delta_{\beta'\beta} \right. \\ & - \delta_{\alpha\alpha'} \sum_{\gamma} Q_{\beta'\beta, \gamma\gamma}^{(1)} [\delta(\omega_{\beta'\gamma} + \omega_{\mathbf{k}}) n_{\mathbf{k}} + \delta(\omega_{\beta'\gamma} - \omega_{\mathbf{k}}) (n_{\mathbf{k}} + 1)] \\ & \left. + Q_{\alpha\beta, \alpha'\beta'}^{(1)} [\delta(\omega_{\alpha\alpha'} + \omega_{\mathbf{k}}) (n_{\mathbf{k}} + 1) + \delta(\omega_{\alpha\alpha'} - \omega_{\mathbf{k}}) n_{\mathbf{k}} + (\alpha \rightarrow \beta)] \right\}, \end{aligned} \quad (219)$$

where

$$Q_{\alpha\beta, \alpha'\beta'}^{(1)} \equiv \left(\Xi_{\alpha\alpha'}^{(1)} \cdot \Xi_{\beta'\beta}^{(1)} \right) / D^2 \quad (220)$$

is a dimensionless combination that characterizes the spin. Next, it is convenient to go over from summation to integration,

$$\frac{1}{N} \sum_{\mathbf{k}} \dots \Rightarrow v_0 \int \frac{d^3k}{(2\pi)^3} \dots \quad (221)$$

where v_0 is the unit-cell volume. Using $v_0/M = 1/\rho$ and $\omega_{\mathbf{k}} = v_t k$ one can introduce the characteristic frequency Ω_t and the corresponding energy E_t of the spin-phonon interaction

$$\Omega_t \equiv \left(\frac{\rho v_t^5}{\hbar} \right)^{1/4}, \quad E_t \equiv (\rho v_t^5 \hbar^3)^{1/4}. \quad (222)$$

As a result one obtains the characteristic relaxation rate

$$\frac{\pi D^2}{12\hbar MN} \sum_{\mathbf{k}} \frac{k^2}{\omega_{\mathbf{k}}} \delta(\omega_{\mathbf{k}} - \omega_0) = \frac{\omega_0^3 D^2}{24\pi \hbar^2 \Omega_t^4} \theta(\omega_0) \equiv \Gamma^{(1)}(\omega_0), \quad (223)$$

where

$$\theta(\omega) = \begin{cases} 0, & \omega \leq 0 \\ 1, & \omega > 0. \end{cases} \quad (224)$$

that enters the relaxation terms. In terms of $\Gamma^{(1)}(\omega_0)$ and

$$n_\omega \equiv \frac{1}{e^{\hbar\omega/(k_B T)} - 1} \quad (225)$$

one obtains

$$\begin{aligned} R_{\alpha\beta,\alpha'\beta'}^{(1)} &= -\sum_\gamma Q_{\alpha\alpha',\gamma\gamma}^{(1)} \left[\Gamma^{(1)}(\omega_{\gamma\alpha'}) n_{\omega_{\gamma\alpha'}} + \Gamma^{(1)}(\omega_{\alpha'\gamma}) (n_{\omega_{\alpha'\gamma}} + 1) \right] \delta_{\beta'\beta} \\ &\quad -\delta_{\alpha\alpha'} \sum_\gamma Q_{\beta'\beta,\gamma\gamma}^{(1)} \left[\Gamma^{(1)}(\omega_{\gamma\beta'}) n_{\omega_{\gamma\beta'}} + \Gamma^{(1)}(\omega_{\beta'\gamma}) (n_{\omega_{\beta'\gamma}} + 1) \right] \\ &\quad + Q_{\alpha\beta,\alpha'\beta'}^{(1)} \left[\Gamma^{(1)}(\omega_{\alpha'\alpha}) (n_{\omega_{\alpha'\alpha}} + 1) + \Gamma^{(1)}(\omega_{\alpha\alpha'}) n_{\omega_{\alpha\alpha'}} + (\alpha \rightarrow \beta) \right]. \end{aligned} \quad (226)$$

Remember that here all $\Gamma^{(1)}(\omega)$ with $\omega < 0$ are zero. Here $Q_{\alpha\beta,\alpha'\beta'}^{(1)}$ is defined by Eqs. (220) and (202).

Within the secular approximation, all relaxation terms in the DME are defined by $\Gamma_{\alpha\alpha'} = R_{\alpha\alpha,\alpha'\alpha'}|_{\alpha' \neq \alpha}$, see Eqs. (72), (75), and (77), whereas for the direct processes considered here one has $\bar{\Gamma}_{\alpha\beta}^{(1)} = 0$. For $\Gamma_{\alpha\alpha'}^{(1)}$ from Eq. (226) one obtains

$$\Gamma_{\alpha\alpha'}^{(1)} = 2 \frac{|\Xi_{\alpha\alpha'}^{(1)}|^2}{D^2} \left[\Gamma^{(1)}(\omega_{\alpha'\alpha}) (n_{\omega_{\alpha'\alpha}} + 1) + \Gamma^{(1)}(\omega_{\alpha\alpha'}) n_{\omega_{\alpha\alpha'}} \right], \quad (227)$$

where we used

$$\left(\Xi_{\alpha\alpha'}^{(1)} \cdot \Xi_{\alpha'\alpha}^{(1)} \right) = \left(\Xi_{\alpha\alpha'}^{(1)} \cdot \Xi_{\alpha\alpha'}^{(1)*} \right) = \left| \Xi_{\alpha\alpha'}^{(1)} \right|^2. \quad (228)$$

To compute the matrix elements of the spin operator components above, one uses

$$\begin{aligned} S_\pm &\equiv S_x \pm iS_y, & S_x &= \frac{1}{2} (S_- + S_+), & S_y &= \frac{i}{2} (S_- - S_+) \\ S_- &= \sum_{m=-S}^{S-1} |m\rangle l_{m,m+1} \langle m+1|, & S_+ &= \sum_{m=-S}^{S-1} |m+1\rangle l_{m+1,m} \langle m|, & S_z &= \sum_{m=-S}^S |m\rangle m \langle m|, \end{aligned} \quad (229)$$

where $l_{m,m'} = \sqrt{S(S+1) - mm'}$. Thus one obtains

$$\begin{aligned} \langle \alpha | S_z | \alpha' \rangle &= \sum_{m=-S}^S \langle \alpha | m \rangle m \langle m | \alpha' \rangle \\ \langle \alpha | S_x | \alpha' \rangle &= \frac{1}{2} \sum_{m=-S}^{S-1} (\langle \alpha | m \rangle l_{m,m+1} \langle m+1 | \alpha' \rangle + \langle \alpha | m+1 \rangle l_{m+1,m} \langle m | \alpha' \rangle) \\ \langle \alpha | S_y | \alpha' \rangle &= \frac{i}{2} \sum_{m=-S}^{S-1} (\langle \alpha | m \rangle l_{m,m+1} \langle m+1 | \alpha' \rangle - \langle \alpha | m+1 \rangle l_{m+1,m} \langle m | \alpha' \rangle). \end{aligned} \quad (230)$$

4. Raman processes

Raman processes arise due to $V^{(2)}$ in Eq. (196), as well as due to $V^{(1)}$ in the second order of the perturbation theory (details can be found in Ref. [10]). The latter terms are nonessential at higher temperatures where Raman processes can become non-negligible since they contain a large thermal phonon frequency in the denominator. In Raman processes a phonon \mathbf{k} is absorbed and a phonon \mathbf{q} is emitted or vice versa. Processes with emission or absorption of two phonons make a small contribution and they will be ignored here. Thus the relevant phonon matrix elements are of the form

$$\begin{aligned} &\langle \nu_{\mathbf{k}\lambda} - 1, \nu_{\mathbf{q}\lambda} + 1 | \delta\phi_\xi \delta\phi_{\xi'} | \nu_{\mathbf{k}\lambda}, \nu_{\mathbf{q}\lambda} \rangle \\ &= \langle \nu_{\mathbf{q}\lambda} + 1 | \delta\phi_\xi | \nu_{\mathbf{q}\lambda} \rangle \langle \nu_{\mathbf{k}\lambda} - 1 | \delta\phi_{\xi'} | \nu_{\mathbf{k}\lambda} \rangle + \langle \nu_{\mathbf{k}\lambda} - 1 | \delta\phi_\xi | \nu_{\mathbf{k}\lambda} \rangle \langle \nu_{\mathbf{q}\lambda} + 1 | \delta\phi_{\xi'} | \nu_{\mathbf{q}\lambda} \rangle \\ &= M_{-,\xi'}(\mathbf{k}) M_{+,\xi}(\mathbf{q}) + M_{-,\xi}(\mathbf{k}) M_{+,\xi'}(\mathbf{q}) \equiv 2\tilde{M}_{\xi\xi'}(\mathbf{k}, \mathbf{q}), \end{aligned} \quad (231)$$

where the matrix elements $M(\mathbf{k})$ are defined by Eq. (211). Similarly to Eq. (212), for one of the parts of $R_{\alpha\beta,\alpha'\beta'}^{(2)}$ one obtains

$$\begin{aligned}
& \frac{\pi}{\hbar Z_b} \sum_{\varpi\varpi'} e^{-E_{\varpi}/(k_B T)} \delta(\varepsilon_{\alpha'} - \varepsilon_{\gamma} + E_{\varpi} - E_{\varpi'}) V_{\alpha\varpi,\gamma\varpi'}^{(2)} V_{\gamma\varpi',\alpha'\varpi}^{(2)} \\
&= \sum_{\mathbf{k}\lambda,\mathbf{q}\lambda} \frac{\pi}{\hbar Z_b} \sum_{\nu_{\mathbf{k}\lambda},\nu_{\mathbf{q}\lambda},\dots} e^{-E_{\nu_{\mathbf{k}\lambda},\nu_{\mathbf{q}\lambda},\dots}/(k_B T)} \delta(\varepsilon_{\alpha'} - \varepsilon_{\gamma} + \hbar\omega_{\mathbf{q}} - \hbar\omega_{\mathbf{k}}) \\
&\quad \times \left(\Xi_{\alpha\gamma,\xi\xi'}^{(2)} \tilde{M}_{\xi\xi'}^*(\mathbf{k}, \mathbf{q}) \right) \left(\Xi_{\gamma\alpha',\zeta\zeta'}^{(2)} \tilde{M}_{\zeta\zeta'}(\mathbf{k}, \mathbf{q}) \right) \\
&= \frac{\pi}{\hbar} \sum_{\mathbf{k}\lambda,\mathbf{q}\lambda} \delta(\varepsilon_{\alpha'} - \varepsilon_{\gamma} + \hbar\omega_{\mathbf{q}} - \hbar\omega_{\mathbf{k}}) \Xi_{\alpha\gamma,\xi\xi'}^{(2)} \frac{1}{2} (M_{-, \xi'}^*(\mathbf{k}) M_{+, \xi}^*(\mathbf{q}) + M_{-, \xi}^*(\mathbf{k}) M_{+, \xi'}^*(\mathbf{q})) \\
&\quad \times \Xi_{\gamma\alpha',\zeta\zeta'}^{(2)} \frac{1}{2} (M_{-, \zeta'}(\mathbf{k}) M_{+, \zeta}(\mathbf{q}) + M_{-, \zeta}(\mathbf{k}) M_{+, \zeta'}(\mathbf{q})) \\
&= \frac{\pi}{\hbar} \sum_{\mathbf{k}\lambda,\mathbf{q}\lambda} \delta(\varepsilon_{\alpha'} - \varepsilon_{\gamma} + \hbar\omega_{\mathbf{q}} - \hbar\omega_{\mathbf{k}}) \Xi_{\alpha\gamma,\xi\xi'}^{(2)} M_{-, \xi}^*(\mathbf{k}) M_{+, \xi'}^*(\mathbf{q}) \Xi_{\alpha\gamma,\xi\xi'}^{(2)} M_{-, \zeta}(\mathbf{k}) M_{+, \zeta'}(\mathbf{q}), \tag{232}
\end{aligned}$$

where

$$\Xi_{\alpha\gamma,\xi\xi'}^{(2)} = \frac{1}{2} \left(\Xi_{\alpha\gamma,\xi\xi'}^{(2)} + \Xi_{\alpha\gamma,\xi'\xi}^{(2)} \right) \tag{233}$$

and M are averaged over the phonon populations, $\nu_{\mathbf{k}\lambda} \rightarrow n_{\mathbf{k}\lambda}$, see Eq. (213). Substituting the expressions for M from Eq. (211), one obtains

$$\begin{aligned}
& \frac{\pi}{\hbar} \left(\frac{\hbar}{8MN} \right)^2 \sum_{\mathbf{k}\lambda,\mathbf{q}\lambda} \delta(\varepsilon_{\alpha'} - \varepsilon_{\gamma} + \hbar\omega_{\mathbf{q}} - \hbar\omega_{\mathbf{k}}) n_{\mathbf{k}} (n_{\mathbf{q}} + 1) \Xi_{\alpha\gamma,\xi\xi'}^{(2)} \Xi_{\gamma\alpha',\zeta\zeta'}^{(2)} \\
&\quad \times \frac{[\mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}]_{\xi} [\mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}]_{\zeta} [\mathbf{q} \times \mathbf{e}_{\mathbf{q}\lambda}]_{\xi'} [\mathbf{q} \times \mathbf{e}_{\mathbf{q}\lambda}]_{\zeta'}}{\omega_{\mathbf{k}} \omega_{\mathbf{q}}}. \tag{234}
\end{aligned}$$

Now, using Eqs. (215)–(217), one can simplify this result to

$$\begin{aligned}
& \frac{\pi}{(8MN)^2} \sum_{\mathbf{k}\lambda,\mathbf{q}\lambda} \delta(\omega_{\alpha'\gamma} + \omega_{\mathbf{q}} - \omega_{\mathbf{k}}) n_{\mathbf{k}} (n_{\mathbf{q}} + 1) \Xi_{\alpha\gamma,\xi\xi'}^{(2)} \Xi_{\gamma\alpha',\zeta\zeta'}^{(2)} \left(\frac{2}{3} \right)^2 \frac{k^2 q^2}{\omega_{\mathbf{k}} \omega_{\mathbf{q}}} \delta_{\xi\xi'} \delta_{\xi'\zeta'} \\
&= \frac{\pi}{(12MN)^2} \Xi_{\alpha\gamma,\xi\xi'}^{(2)} \Xi_{\gamma\alpha',\xi\xi'}^{(2)} \sum_{\mathbf{k}\mathbf{q}} \frac{k^2 q^2}{\omega_{\mathbf{k}} \omega_{\mathbf{q}}} \delta(\omega_{\alpha'\gamma} + \omega_{\mathbf{q}} - \omega_{\mathbf{k}}) n_{\mathbf{k}} (n_{\mathbf{q}} + 1). \tag{235}
\end{aligned}$$

Now recalling Eq. (64) one obtains

$$\begin{aligned}
R_{\alpha\beta,\alpha'\beta'}^{(2)} &= \frac{\pi D^2}{(12MN)^2} \sum_{\mathbf{k}\mathbf{q}} \frac{k^2 q^2}{\omega_{\mathbf{k}} \omega_{\mathbf{q}}} n_{\mathbf{k}} (n_{\mathbf{q}} + 1) \\
&\quad \times \left\{ - \sum_{\gamma} Q_{\alpha\alpha',\gamma\gamma}^{(2)} \delta(\omega_{\alpha'\gamma} + \omega_{\mathbf{q}} - \omega_{\mathbf{k}}) \delta_{\beta'\beta} - \delta_{\alpha\alpha'} \sum_{\gamma} Q_{\beta'\beta,\gamma\gamma}^{(2)} \delta(\omega_{\beta'\gamma} + \omega_{\mathbf{q}} - \omega_{\mathbf{k}}) \right. \\
&\quad \left. + Q_{\alpha\beta,\alpha'\beta'}^{(2)} [\delta(\omega_{\beta\beta'} + \omega_{\mathbf{q}} - \omega_{\mathbf{k}}) + \delta(\omega_{\alpha\alpha'} + \omega_{\mathbf{q}} - \omega_{\mathbf{k}})] \right\}, \tag{236}
\end{aligned}$$

where

$$Q_{\alpha\beta,\alpha'\beta'}^{(2)} \equiv \frac{1}{D^2} \sum_{\xi\xi'} \Xi_{\alpha\alpha',\xi\xi'}^{(2)} \Xi_{\beta'\beta,\xi\xi'}^{(2)}, \tag{237}$$

similarly to Eq. (220). Since Raman processes can become important only at high temperatures, one can drop spin transition frequencies in the energy δ -functions. Next, one can replace summation by integration with the help of Eq. (221) and introduce the characteristic Raman rate

$$\Gamma^{(2)} = \frac{D^2}{24^2 \pi^3 \hbar^2 \Omega_i^8} \int d\omega_{\mathbf{k}} \omega_{\mathbf{k}}^6 n_{\mathbf{k}} (n_{\mathbf{k}} + 1). \tag{238}$$

Then $R_{\alpha\beta,\alpha'\beta'}^{(2)}$ can be written in the form

$$R_{\alpha\beta,\alpha'\beta'}^{(2)} = \Gamma^{(2)} \left(- \sum_{\gamma} Q_{\alpha\alpha',\gamma\gamma}^{(2)} \delta_{\beta'\beta} - \delta_{\alpha\alpha'} \sum_{\gamma} Q_{\beta'\beta,\gamma\gamma}^{(2)} + 2Q_{\alpha\beta,\alpha'\beta'}^{(2)} \right). \quad (239)$$

In the secular approximation one needs the rate

$$\begin{aligned} \Gamma_{\alpha\alpha'}^{(2)} &= R_{\alpha\alpha,\alpha'\alpha'}^{(2)} \Big|_{\alpha' \neq \alpha} = 2\Gamma^{(2)} Q_{\alpha\alpha,\alpha'\alpha'}^{(2)} = \frac{2\Gamma^{(2)}}{D^2} \sum_{\xi\xi'} \bar{\Xi}_{\alpha\alpha',\xi\xi'}^{(2)} \bar{\Xi}_{\alpha'\alpha,\xi\xi'}^{(2)} \\ &= \frac{2\Gamma^{(2)}}{D^2} \sum_{\xi\xi'} \bar{\Xi}_{\alpha\alpha',\xi\xi'}^{(2)} \bar{\Xi}_{\alpha\alpha',\xi\xi'}^{(2)*} = \frac{2\Gamma^{(2)}}{D^2} \sum_{\xi\xi'} \left| \bar{\Xi}_{\alpha\alpha',\xi\xi'}^{(2)} \right|^2, \end{aligned} \quad (240)$$

where from Eqs. (205) and (233) follows

$$\begin{aligned} \bar{\Xi}_{\alpha\beta,\xi\xi'}^{(2)} &\equiv -\frac{1}{2} \sum_{\gamma} (\varepsilon_{\alpha} + \varepsilon_{\beta} - 2\varepsilon_{\gamma}) (\langle \alpha | S_{\xi} | \gamma \rangle \langle \gamma | S_{\xi'} | \beta \rangle + \langle \alpha | S_{\xi'} | \gamma \rangle \langle \gamma | S_{\xi} | \beta \rangle) \\ &\quad + \frac{1}{2} g\mu_B (H_{\xi'} \langle \alpha | S_{\xi} | \beta \rangle + H_{\xi} \langle \alpha | S_{\xi'} | \beta \rangle) - \delta_{\xi\xi'} \sum_{\xi''} g\mu_B H_{\xi''} \langle \alpha | S_{\xi''} | \beta \rangle. \end{aligned} \quad (241)$$

Integration in Eq. (238) is limited by the Brillouin zone, so that $\omega_{\mathbf{k}}$ does not exceed some maximal value. We will use the Debye model in which the phonon spectrum continues in the same form up to the Debye frequency Ω_D that is the upper bound of integration. Thus Eq. (238) can be represented in the form

$$\Gamma^{(2)} = \frac{D^2}{24^2 \pi^3 \hbar} \frac{(k_B T)^7}{E_t^8} G_6 \left(\frac{\Theta_D}{T} \right), \quad (242)$$

where

$$G_n(y) \equiv \int_0^y dx \frac{x^n e^x}{(e^x - 1)^2}. \quad (243)$$

For $T \ll \Theta_D$ the integration can be extended to infinity. Using $G_6(\infty) = 16\pi^6/21$, one obtains

$$\Gamma^{(2)} = \frac{\pi^3 D^2 (k_B T)^7}{756 \hbar E_t^8}. \quad (244)$$

On the contrary, for $T \gg \Theta_D$ one can use $G_6(y) \cong y^5/5$ that yields

$$\Gamma^{(2)} = \frac{D^2}{2880 \pi^3 \hbar} \frac{(k_B \Theta_D)^5 (k_B T)^2}{E_t^8}. \quad (245)$$

The transition between these two regimes takes place at $T/\Theta_{D,1} = 1/y \approx [21/(5 \times 16\pi^6)]^{1/5} \approx 0.2$, i.e., much lower than the Debye temperature. For this reason the contribution of Raman processes is small in comparison to that of direct processes up to very high temperatures. Indeed, the contribution of Eq. (244) could become essential at high temperatures but long before it could happen the growth slows down to Eq. (245). Then from Eqs. (245) and (223) one obtains the ratio

$$\eta = \frac{\Gamma^{(2)}}{\Gamma^{(1)} \coth \frac{\hbar\omega_0}{2k_B T}} \cong \frac{1}{240\pi^2} \frac{(k_B \Theta_D)^5 (k_B T)}{(\hbar\omega_0)^2 E_t^4}. \quad (246)$$

For Mn_{12} with $\Theta_D \simeq 30$ K, $E_t/k_B \simeq 150$ K, and $\hbar\omega_0/k_B \simeq D \simeq 0.66$ K (near the top of the barrier) the ratio $\eta = 1$ requires $T = 2 \times 10^4$ K.

D. The realistic phonon spectrum

In the above derivations we have assumed that the crystal lattice possesses two degenerate transverse phonon modes that contribute to the spin-lattice relaxation. This is only the case for isotropic elastic bodies. In real crystals all

three acoustic phonon branches are different and they are neither fully longitudinal nor fully transverse. Fitting the heat capacity data for Mn_{12} to the *extended Debye model* of Ref. [11] has shown three acoustic modes with speeds $v_1 = 1541$ m/s, $v_2 = 2488$ m/s, and $v_3 = 3176$ m/s. Since $\Gamma^{(1)} \propto \nu_t^{-5}$, only the mode with the lowest speed should be taken into account. This mode can be considered as approximately transverse. Thus we introduce the factor 1/2 in Eq. (223) and in all other formulas for the spin-lattice rate due to direct processes. Similarly, the factor 1/4 must be introduced in Eq. (238) and in all subsequent formulas for Raman processes. The values of Θ_D and E_t quoted below Eq. (246) correspond to v_1 .

E. Ground-state tunneling and relaxation

1. The two-level model

Consider the case in which H_x and H_y in Eq. (186) are small, so that, in the absence of tunneling, the spin eigenstates $|\alpha\rangle$ are basically $|m\rangle$ that are only weakly hybridized with the states in the same well. We will denote these states by

$$|\psi_m\rangle = \sum_{m''=-S}^S c_{mm''} |m''\rangle, \quad (247)$$

where $|c_{mm}| \cong 1$ and all other coefficients are small. Near tunneling resonances, these states are strongly hybridized with resonant states in the other well. Hybridization of the states $|\psi_m\rangle$ and $|\psi_{m'}\rangle$ can be taken into account in the framework of the two-state model

$$\begin{aligned} \langle \psi_{m_i} | \hat{H}_S | \psi_{m_i} \rangle &= \varepsilon_{m_i}, \quad m_i = m, m' \\ \langle \psi_m | \hat{H}_S | \psi_{m'} \rangle &= \frac{1}{2} \Delta e^{i\varphi}, \end{aligned} \quad (248)$$

where Δ is the tunnel splitting of the levels m and m' that can be calculated from the exact spin Hamiltonian \hat{H}_S or determined experimentally and φ is a phase. Since one can multiply the basis functions $|\psi_m\rangle$ by arbitrary phase factors, we will set $\varphi = \pi$ for convenience. This will result in a simpler form of the wave functions than in Ref. [8], whereas all physical results remain the same. Then the model above can be formulated as the pseudospin model

$$\hat{H}_{\text{eff}} = -\frac{1}{2} \hat{\boldsymbol{\sigma}} \cdot \mathbf{A} + \frac{1}{2} (\varepsilon_m + \varepsilon_{m'}), \quad (249)$$

where components of $\hat{\boldsymbol{\sigma}}$ are Pauli matrices,

$$\mathbf{A} \equiv \Delta \mathbf{e}_x + W \mathbf{e}_z, \quad (250)$$

is the effective field, and W is the energy bias or resonance detuning

$$W = \varepsilon_m - \varepsilon_{m'}, \quad (251)$$

defined by Eq. (189). We will need the direction angle θ of \mathbf{A} ,

$$\cos \theta = \frac{W}{\sqrt{W^2 + \Delta^2}}. \quad (252)$$

The pseudospin acts on the states as

$$\begin{aligned} \hat{\sigma}_z |\psi_m\rangle &= -|\psi_m\rangle, & \hat{\sigma}_z |\psi_{m'}\rangle &= |\psi_{m'}\rangle \\ \hat{\sigma}_x |\psi_m\rangle &= |\psi_{m'}\rangle, & \hat{\sigma}_x |\psi_{m'}\rangle &= |\psi_m\rangle. \end{aligned} \quad (253)$$

Of course, one also can calculate matrix elements of the physical spin \mathbf{S} with respect to this basis.

Eigenstates of \hat{H}_{eff} are the states polarized parallel and antiparallel to \mathbf{A} , and the eigenvalues are given by

$$\varepsilon_\alpha = \frac{1}{2} \left(\varepsilon_m + \varepsilon_{m'} + \alpha \sqrt{W^2 + \Delta^2} \right), \quad \alpha = \pm. \quad (254)$$

The transition frequency ω_0 between the levels is defined by

$$\varepsilon_+ - \varepsilon_- \equiv \hbar\omega_0 \equiv \sqrt{W^2 + \Delta^2}. \quad (255)$$

The eigenstates of \hat{H}_{eff} can be expanded over the natural basis as

$$|\alpha\rangle \equiv |\chi_\alpha\rangle = \frac{1}{\sqrt{2}} (C_\alpha |\psi_m\rangle - \alpha C_{-\alpha} |\psi_{m'}\rangle), \quad (256)$$

where

$$C_\alpha = \sqrt{1 + \alpha \cos \theta}. \quad (257)$$

One can directly check $\hat{H}_{\text{eff}} |\chi_\alpha\rangle = \varepsilon_\alpha |\chi_\alpha\rangle$. The coefficients C_α satisfy $1/C_\alpha = C_{-\alpha}/\sin \theta$.

Let us prepare the system in the state $|\psi_{-S}\rangle$, the ground state in the left well that can be at resonance with the ground or excited state in the right well, $|\psi_{m'}\rangle$ with $m' \leq S$. Near the resonance these states hybridize into $|\psi_\pm\rangle$. At low temperatures, all levels above $|\psi_{-S}\rangle$ are unpopulated and do not contribute to relaxation. The only relaxation processes are between $|\psi_\pm\rangle$ and the levels in the right well below $|\psi_{m'}\rangle$. Again, since the levels are only weakly hybridized inside the wells, here the dominant process is decay $|\psi_{m'}\rangle \rightarrow |\psi_{m'+1}\rangle$. The inverse process can be neglected at low temperatures. In the case of the ground-state resonance, $|\psi_{-S}\rangle$ with $|\psi_S\rangle$, this decay process is, of course, absent. The full description of both ground-ground and ground-excited resonances at low temperatures includes only two levels $|\chi_\pm\rangle$, so that the effective DM is a 2×2 matrix. The DME in the general case of time-dependent spin Hamiltonians is Eq. (63) with non-adiabatic terms from Eq. (58) added, i.e.,

$$\frac{d}{dt} \rho_{\alpha\beta} = \sum_\gamma (\langle \dot{\chi}_\alpha | \chi_\gamma \rangle \rho_{\gamma\beta} + \rho_{\alpha\gamma} \langle \chi_\gamma | \dot{\chi}_\beta \rangle) - i\omega_{\alpha\beta} \rho_{\alpha\beta} + \sum_{\alpha'\beta'} R_{\alpha\beta, \alpha'\beta'} \rho_{\alpha'\beta'}, \quad (258)$$

where all indices take the values \pm . If $|\psi_{m'}\rangle$ is an excited state, in general one cannot use the secular approximation because ω_0 can be comparable with the relaxation rate.

Let us work out the non-adiabatic terms in Eq. (258). Calculating the time derivative of C_α in Eq. (256),

$$\dot{C}_\alpha = \frac{\alpha}{2C_\alpha} \frac{d}{dt} \cos \theta = -\frac{\alpha}{2C_\alpha} \sin \theta \dot{\theta} = -\alpha C_{-\alpha} \frac{\dot{\theta}}{2}, \quad (259)$$

one obtains

$$|\dot{\chi}_\alpha\rangle = \frac{1}{\sqrt{2}} (\dot{C}_\alpha |\psi_{-S}\rangle - \alpha \dot{C}_{-\alpha} |\psi_{m'}\rangle) = -\frac{\alpha}{\sqrt{2}} (C_{-\alpha} |\psi_{-S}\rangle + \alpha C_\alpha |\psi_{m'}\rangle) \frac{\dot{\theta}}{2} = -\alpha |\chi_{-\alpha}\rangle \frac{\dot{\theta}}{2}. \quad (260)$$

Thus in Eq. (258) the scalar products are

$$\langle \dot{\chi}_\alpha | \chi_\beta \rangle = -\alpha \frac{\dot{\theta}}{2} \langle \chi_{-\alpha} | \chi_\beta \rangle = -\alpha \delta_{-\alpha, \beta} \frac{\dot{\theta}}{2}. \quad (261)$$

and

$$\sum_\gamma (\langle \dot{\chi}_\alpha | \chi_\gamma \rangle \rho_{\gamma\beta} + \rho_{\alpha\gamma} \langle \chi_\gamma | \dot{\chi}_\beta \rangle) = -(\alpha \rho_{-\alpha, \beta} + \beta \rho_{\alpha, -\beta}) \frac{\dot{\theta}}{2}. \quad (262)$$

The density operator in the initial state typically is

$$\hat{\rho}(0) = |\psi_{-S}\rangle \langle \psi_{-S}|, \quad (263)$$

so that the density matrix in the diagonal basis is given by

$$\rho_{\alpha\beta}(0) = \langle \alpha | \hat{\rho}(0) | \beta \rangle = \langle \alpha | \psi_{-S} \rangle \langle \psi_{-S} | \beta \rangle = \frac{1}{2} C_\alpha C_\beta, \quad (264)$$

where Eq. (256) with $m = -S$ was used. In particular,

$$\begin{aligned} \rho_{++}(0) &= \frac{1}{2} (1 + \cos \theta), & \rho_{--}(0) &= \frac{1}{2} (1 - \cos \theta) \\ \rho_{+-}(0) &= \rho_{-+}(0) = \frac{1}{2} \sin \theta. \end{aligned} \quad (265)$$

2. Ground-ground state resonance

The results obtained above already allow to consider the dynamics at the ground-state resonance, $m' = S$. In this case the relaxation terms in Eq. (258) contain only $\Gamma(\omega_0) \ll \omega_0$, so that the secular approximation is applicable. Dropping nonsecular terms in Eq. (258) one obtains

$$\begin{aligned}\frac{d}{dt}\rho_{++} &= -(\rho_{+-} + \rho_{-+})\frac{\dot{\theta}}{2} + R_{++,+}\rho_{++} + R_{++,-}\rho_{--} \\ \frac{d}{dt}\rho_{+-} &= -(\rho_{--} - \rho_{++})\frac{\dot{\theta}}{2} - i\omega_0\rho_{+-} + R_{+,-,+}\rho_{+-},\end{aligned}\quad (266)$$

whereas

$$\rho_{--} = 1 - \rho_{++}, \quad \rho_{-+} = (\rho_{+-})^*.\quad (267)$$

Using Eq. (226), one obtains

$$\begin{aligned}R_{++,+} &= -2Q_{++,-}\Gamma(\omega_0)(n_{\omega_0} + 1) \equiv -\Gamma_{-+} \\ R_{--,-} &= -2Q_{--,+}\Gamma(\omega_0)n_{\omega_0} = -\Gamma_{+-} = -e^{-\hbar\omega_0/(k_B T)}\Gamma_{-+} \\ R_{++,-} &= 2Q_{++,-}\Gamma(\omega_0)n_{\omega_0} = \Gamma_{+-} = e^{-\hbar\omega_0/(k_B T)}\Gamma_{-+} \\ R_{-,-,+} &= 2Q_{-,-,+}\Gamma(\omega_0)(n_{\omega_0} + 1) = \Gamma_{-+}\end{aligned}\quad (268)$$

and

$$R_{+,-,+} = -Q_{++,-}\Gamma(\omega_0)(n_{\omega_0} + 1) - Q_{--,+}\Gamma(\omega_0)n_{\omega_0} = -\frac{1}{2}(\Gamma_{-+} + \Gamma_{+-})\quad (269)$$

etc. Thus Eq. (266) takes the form

$$\begin{aligned}\dot{\rho}_{++} &= -(\rho_{+-} + \rho_{-+})\frac{\dot{\theta}}{2} - \Gamma_{-+}\rho_{++} + \Gamma_{+-}\rho_{--} \\ \dot{\rho}_{+-} &= (\rho_{++} - \rho_{--})\frac{\dot{\theta}}{2} - \left[i\omega_0 + \frac{1}{2}(\Gamma_{-+} + \Gamma_{+-}) \right] \rho_{+-}.\end{aligned}\quad (270)$$

This system of equations can be rewritten as

$$\begin{aligned}\dot{\rho}_{++} &= -\dot{\theta} \text{Re} \rho_{+-} - \Gamma(\rho_{++} - \rho_{++}^{\text{eq}}) \\ \dot{\rho}_{+-} &= \dot{\theta}(\rho_{++} - 1/2) - (i\omega_0 + \Gamma/2)\rho_{+-},\end{aligned}\quad (271)$$

where

$$\Gamma \equiv \Gamma_{-+} + \Gamma_{+-}\quad (272)$$

is the total relaxation rate between the \pm states and

$$\rho_{++}^{\text{eq}} = \frac{\Gamma_{+-}}{\Gamma_{-+} + \Gamma_{+-}} = \frac{e^{-\hbar\omega_0/(k_B T)}}{1 + e^{-\hbar\omega_0/(k_B T)}}\quad (273)$$

is the equilibrium population of the upper level.

3. Dynamics of the ground-ground state resonance via effective classical spin

The DME for the ground-ground state resonance, Eq. (270), can be conveniently formulated in terms of the averages the pseudospin $\hat{\sigma}$ with the density operator. Using Eq. (4) one can write

$$\sigma \equiv \langle \hat{\sigma} \rangle = \sum_{\alpha\beta} \rho_{\alpha\beta} \langle \chi_\beta | \hat{\sigma} | \chi_\alpha \rangle.\quad (274)$$

Directing the axis z' along the total field \mathbf{A} , one has

$$\begin{aligned}\hat{\boldsymbol{\sigma}} &\equiv (\hat{\sigma}_- + \hat{\sigma}_+) \mathbf{e}_{x'} + i(\hat{\sigma}_- - \hat{\sigma}_+) \mathbf{e}_{y'} + \hat{\sigma}_{z'} \mathbf{e}_{z'} \\ &= (|\chi_+\rangle\langle\chi_-| + |\chi_-\rangle\langle\chi_+|) \mathbf{e}_{x'} + i(|\chi_+\rangle\langle\chi_-| - |\chi_-\rangle\langle\chi_+|) \mathbf{e}_{y'} + (|\chi_-\rangle\langle\chi_-| - |\chi_+\rangle\langle\chi_+|) \mathbf{e}_{z'}.\end{aligned}\quad (275)$$

Then one obtains

$$\begin{aligned}\sigma_{x'} &= \rho_{+-} \langle\chi_-|\hat{\sigma}_{x'}|\chi_+\rangle + \rho_{-+} \langle\chi_+|\hat{\sigma}_{x'}|\chi_-\rangle = \rho_{-+} + \rho_{+-} = 2\text{Re}\rho_{-+} \\ \sigma_{y'} &= \rho_{+-} \langle\chi_-|\hat{\sigma}_{y'}|\chi_+\rangle + \rho_{-+} \langle\chi_+|\hat{\sigma}_{y'}|\chi_-\rangle = i(\rho_{-+} - \rho_{+-}) = 2\text{Im}\rho_{-+} \\ \sigma_{z'} &= \rho_{++} \langle\chi_+|\hat{\sigma}_{z'}|\chi_+\rangle + \rho_{--} \langle\chi_-|\hat{\sigma}_{z'}|\chi_-\rangle = \rho_{--} - \rho_{++} = 1 - 2\rho_{++}.\end{aligned}\quad (276)$$

Now Eq. (270) can be transformed as

$$\begin{aligned}\dot{\sigma}_{x'} &= \dot{\rho}_{-+} + \dot{\rho}_{+-} = (\rho_{++} - \rho_{--})\dot{\theta} + i\omega_0(\rho_{-+} - \rho_{+-}) + R_{x'} = -\dot{\theta}\sigma_{z'} + \omega_0\sigma_{y'} + R_{x'} \\ \dot{\sigma}_{y'} &= i(\dot{\rho}_{-+} - \dot{\rho}_{+-}) = i(i\omega_0\rho_{-+} + i\omega_0\rho_{+-}) + R_{y'} = -\omega_0\sigma_{x'} + R_{y'} \\ \dot{\sigma}_{z'} &= (\rho_{+-} + \rho_{-+})\dot{\theta} + R_{z'} = \dot{\theta}\sigma_{x'} + R_{z'}\end{aligned}\quad (277)$$

or

$$\dot{\boldsymbol{\sigma}} = [\boldsymbol{\sigma} \times (\boldsymbol{\omega}_0 + \boldsymbol{\Omega})] + \mathbf{R}, \quad \boldsymbol{\omega}_0 = \omega_0 \mathbf{e}_{z'}, \quad \boldsymbol{\Omega} = \dot{\theta} \mathbf{e}_{y'}.\quad (278)$$

This is a Larmor equation for the classical vector $\boldsymbol{\sigma}$ in the frame rotating with frequency $\boldsymbol{\Omega}$ due to the time dependence of the spin Hamiltonian. The relaxation vector is given by

$$\begin{aligned}\mathbf{R} &= -\frac{1}{2}(\Gamma_{-+} + \Gamma_{+-})\sigma_{x'}\mathbf{e}_{x'} - \frac{1}{2}(\Gamma_{-+} + \Gamma_{+-})\sigma_{y'}\mathbf{e}_{y'} - 2(-\Gamma_{-+}\rho_{++} + \Gamma_{+-}\rho_{--})\mathbf{e}_{z'} \\ &= -\frac{1}{2}(\Gamma_{-+} + \Gamma_{+-})\sigma_{x'}\mathbf{e}_{x'} - \frac{1}{2}(\Gamma_{-+} + \Gamma_{+-})\sigma_{y'}\mathbf{e}_{y'} - [-\Gamma_{-+}(1 - \sigma_{z'}) + \Gamma_{+-}(1 + \sigma_{z'})]\mathbf{e}_{z'} \\ &= -\frac{1}{2}(\Gamma_{-+} + \Gamma_{+-})\sigma_{x'}\mathbf{e}_{x'} - \frac{1}{2}(\Gamma_{-+} + \Gamma_{+-})\sigma_{y'}\mathbf{e}_{y'} - [(\Gamma_{-+} + \Gamma_{+-})\sigma_{z'} - (\Gamma_{-+} - \Gamma_{+-})]\mathbf{e}_{z'}\end{aligned}\quad (279)$$

or

$$\mathbf{R} = -\frac{\Gamma}{2} \left(\boldsymbol{\sigma} - \frac{\boldsymbol{\omega}_0 \cdot \boldsymbol{\sigma}}{\omega_0^2} \boldsymbol{\omega}_0 \right) - \Gamma \frac{\boldsymbol{\omega}_0}{\omega_0} \left(\frac{\boldsymbol{\omega}_0 \cdot \boldsymbol{\sigma}}{\omega_0} - \sigma^{\text{eq}} \right),\quad (280)$$

where Γ is given by Eq. (272) and

$$\sigma^{\text{eq}} = \frac{\Gamma_{-+} - \Gamma_{+-}}{\Gamma_{-+} + \Gamma_{+-}} = \tanh \frac{\hbar\omega_0}{2k_B T}\quad (281)$$

is the equilibrium spin polarization.

Eq. (278) can describe, in particular, the Landau-Zener effect of transition between the energy levels of a two-level system as the energy bias W is swept through the resonance, $W = 0$. It is remarkable that this essentially quantum phenomenon can be described by a classical language. Studying the dynamical behavior of the classical spin $\boldsymbol{\sigma}$ helps a lot understanding the LZ effect. In particular, if the sweep is slow, the non-adiabatic term $\boldsymbol{\Omega}$ in Eq. (278) is small and the spin remains nearly collinear to $\boldsymbol{\omega}_0$ at all times. In the adiabatic frame $\boldsymbol{\omega}_0 = \text{const}$ and the spin vector in the laboratory frame (i.e., in the natural basis) can be obtained by a rotational transformation. One also can rewrite Eq. (278) in the laboratory frame by simply dropping $\boldsymbol{\Omega}$ and making $\boldsymbol{\omega}_0$ time dependent according to Eq. (250), $\hbar\boldsymbol{\omega}_0 = \mathbf{A}$. Because of the vector form of the equation of motion, its transformation between the frames is easy, in contrast to the transformation of the DME between the natural basis and the diagonal (adiabatic) basis described in Sec. II G. As the vector \mathbf{A} is rotating, $\boldsymbol{\sigma}$ is lagging behind it, depending on the sweep rate. For a slow sweep rate it nearly follows the direction of \mathbf{A} while for a fast sweep it nearly remains in the initial state.

4. Coherence in the ground-ground state resonance

Let us consider the time evolution of a two-level system in the case of time-independent spin Hamiltonian, $\dot{\theta} = 0$. This can be done using either Eq. (271) or Eq. (278). In particular, the solution of Eq. (271) with the initial

conditions of Eq. (265) is

$$\begin{aligned}\rho_{++}(t) &= \rho_{++}^{\text{eq}} + [\rho_{++}(0) - \rho_{++}^{\text{eq}}] e^{-\Gamma t} = \rho_{++}^{\text{eq}} + \left[\frac{1}{2} \left(1 + \frac{W}{\sqrt{W^2 + \Delta^2}} \right) - \rho_{++}^{\text{eq}} \right] e^{-\Gamma t} \\ \rho_{+-}(t) &= \rho_{+-}(0) e^{-(i\omega_0 + \Gamma/2)t} = \frac{1}{2} \frac{\Delta}{\sqrt{W^2 + \Delta^2}} e^{-(i\omega_0 + \Gamma/2)t}.\end{aligned}\quad (282)$$

Transformation back to the natural basis is done using Eq. (86). The probability to remain in the initial state $|\psi_{-S}\rangle$ is

$$\begin{aligned}\rho_{-S,-S}(t) &= \sum_{\alpha\beta} \langle \psi_{-S} | \alpha \rangle \rho_{\alpha\beta}(t) \langle \beta | \psi_{-S} \rangle = \frac{1}{2} \sum_{\alpha\beta} C_\alpha C_\beta \rho_{\alpha\beta}(t) \\ &= \frac{1}{2} \left(1 + \frac{W}{\sqrt{W^2 + \Delta^2}} \right) \rho_{++}(t) + \frac{1}{2} \left(1 - \frac{W}{\sqrt{W^2 + \Delta^2}} \right) [1 - \rho_{++}(t)] + \frac{\Delta}{\sqrt{W^2 + \Delta^2}} \text{Re} \rho_{+-}(t) \\ &= \frac{1}{2} \left(1 - \frac{W}{\sqrt{W^2 + \Delta^2}} \right) + \frac{W}{\sqrt{W^2 + \Delta^2}} \rho_{++}(t) + \frac{\Delta}{\sqrt{W^2 + \Delta^2}} \text{Re} \rho_{+-}(t) \\ &= \frac{1}{2} \left(1 - \frac{W}{\sqrt{W^2 + \Delta^2}} \right) + \frac{W}{\sqrt{W^2 + \Delta^2}} \left\{ \rho_{++}^{\text{eq}} + \left[\frac{1}{2} \left(1 + \frac{W}{\sqrt{W^2 + \Delta^2}} \right) - \rho_{++}^{\text{eq}} \right] e^{-\Gamma t} \right\} \\ &\quad + \frac{1}{2} \frac{\Delta^2}{W^2 + \Delta^2} e^{-(\Gamma/2)t} \cos(\omega_0 t)\end{aligned}\quad (283)$$

or

$$\begin{aligned}\rho_{-S,-S}(t) &= \frac{1}{2} \left[\frac{W^2}{W^2 + \Delta^2} e^{-\Gamma t} + \frac{\Delta^2}{W^2 + \Delta^2} e^{-(\Gamma/2)t} \cos(\omega_0 t) + 1 - \frac{W}{\sqrt{W^2 + \Delta^2}} (1 - e^{-\Gamma t}) \right] \\ &\quad + \frac{W}{\sqrt{W^2 + \Delta^2}} \rho_{++}^{\text{eq}} (1 - e^{-\Gamma t}).\end{aligned}\quad (284)$$

The time evolution described by this formula is a combination of relaxation with rate Γ and oscillations of frequency ω_0 damped with rate $\Gamma/2$. It should be noted, however, that the ground-state tunnel splitting Δ is typically very small, so that it is very difficult to experimentally realize $|W| \lesssim \Delta$ to see coherent oscillations of the spin between the two states.

5. Relaxation rate between two tunnel-split states

The relaxation rate Γ_{-+} for the ground-state doublet can be found analytically [8]. In particular, for the uniaxial model in the presence of transverse field along the x axis, with the help of the high-order perturbation theory one obtains

$$\begin{aligned}\langle \psi_- | S_z | \psi_+ \rangle &= -\frac{\Delta}{\sqrt{W^2 + \Delta^2}} \frac{m' - m}{2} \\ \langle \psi_- | S_x | \psi_+ \rangle &= \frac{\Delta}{g\mu_B H_x} \frac{W}{\sqrt{W^2 + \Delta^2}} \frac{m' - m}{2} \\ \langle \psi_- | S_y | \psi_+ \rangle &= -i \frac{\Delta}{g\mu_B H_x} \frac{m' - m}{2}.\end{aligned}\quad (285)$$

Then from Eq. (202) in components,

$$\begin{aligned}\Xi_{-,x} &= -i\hbar\omega_0 \langle \psi_- | S_x | \psi_+ \rangle - \langle \psi_- | S_y | \psi_+ \rangle g\mu_B H_z + \langle \psi_- | S_z | \psi_+ \rangle g\mu_B H_y \\ \Xi_{-,y} &= -i\hbar\omega_0 \langle \psi_- | S_y | \psi_+ \rangle - \langle \psi_- | S_z | \psi_+ \rangle g\mu_B H_x + \langle \psi_- | S_x | \psi_+ \rangle g\mu_B H_z \\ \Xi_{-,z} &= -i\hbar\omega_0 \langle \psi_- | S_z | \psi_+ \rangle - \langle \psi_- | S_x | \psi_+ \rangle g\mu_B H_y + \langle \psi_- | S_y | \psi_+ \rangle g\mu_B H_x,\end{aligned}\quad (286)$$

with $H_y = 0$ one obtains

$$\begin{aligned}\Xi_{-,z} &= 0 \\ \Xi_{-,x} &= -i \frac{\Delta}{g\mu_B H_x} \frac{m' - m}{2} (W - g\mu_B H_z) \\ \Xi_{-,y} &= \frac{\Delta}{\sqrt{W^2 + \Delta^2}} \frac{m' - m}{2} g\mu_B H_x \left(1 - \frac{\Delta^2}{(g\mu_B H_x)^2} - \frac{W(W - g\mu_B H_z)}{(g\mu_B H_x)^2} \right).\end{aligned}\quad (287)$$

Taking into account $\Delta \ll g\mu_B H_x$ and using $W = (m' - m)g\mu_B H_z$ yields

$$\begin{aligned} |\Xi_{-+}|^2 &= |\Xi_{-+,x}|^2 + |\Xi_{-+,y}|^2 \\ &= \left(\frac{m' - m}{2}\right)^2 \Delta^2 \left[(m' - m - 1)^2 \frac{H_z^2}{H_x^2} + \frac{(g\mu_B H_x)^2}{W^2 + \Delta^2} \left(1 - (m' - m)(m' - m - 1) \frac{H_z^2}{H_x^2}\right)^2 \right]. \end{aligned} \quad (288)$$

Now, from Eqs. (268), (220), and (223) one obtains

$$\begin{aligned} \Gamma_{-+} &= 2Q_{--,++}\Gamma(\omega_0) = |\Xi_{-+}|^2 \frac{\omega_0^3}{12\pi\hbar^2\Omega_t^4} \\ &= \left(\frac{m' - m}{2}\right)^2 \frac{\Delta^2\omega_0(g\mu_B H_x)^2}{12\pi E_t^4} \left[\frac{W^2 + \Delta^2}{(g\mu_B H_x)^2} (m' - m - 1)^2 \frac{H_z^2}{H_x^2} + \left(1 - (m' - m)(m' - m - 1) \frac{H_z^2}{H_x^2}\right)^2 \right] \end{aligned} \quad (289)$$

Dropping again the small Δ^2 term in the square brackets one obtains

$$\Gamma_{-+} = \left(\frac{m' - m}{2}\right)^2 \frac{\Delta^2\omega_0(g\mu_B H_x)^2}{12\pi E_t^4} Q, \quad (290)$$

where

$$\begin{aligned} Q &= \xi^4 + (1 - \xi^2)^2 = 1 - 2\xi^2 + 2\xi^4, \\ \xi &\equiv \sqrt{(m' - m)(m' - m - 1)} \frac{H_z}{H_x}. \end{aligned} \quad (291)$$

In particular, for the ground-state resonance, $m = -S$, $m' = S$, one has $\xi = \sqrt{2S(2S - 1)}H_z/H_x$. One can see that Q begins to deviate from 1 only for $SH_z \gtrsim H_x$ that requires $W \gg \Delta$. For such a strong bias, the dependence of Γ_{-+} on the bias has the form

$$\Gamma_{-+} \propto f(\xi) = \xi Q = \xi(1 - 2\xi^2 + 2\xi^4). \quad (292)$$

The function $f(\xi)$ monotonically increases but its slope initially decreases from 1, attaining the minimal value $f'(\xi_0) = 1/10$ at $\xi_0 = \sqrt{3/10} \simeq 0.5477$. At this point $f(\xi_0) = \sqrt{3/10}(29/50) \simeq 0.3177$. After that the slope of $f(\xi)$ begins strongly to increase, so that $\Gamma_{-+} \sim \xi^5 \sim H_z^5$.

6. Ground-excited state resonance

Let us consider the tunneling resonance between $|\psi_{-S}\rangle$ and $|\psi_{m'}\rangle$ with $m' < S$. The hybridized states $|\psi_{\pm}\rangle$ decay, predominantly, into $|\psi_{m'+1}\rangle$. The corresponding relaxation rate is large, so that we will neglect the rate of transitions between $|\psi_{\pm}\rangle$ that is small near the resonance. At low temperatures one can neglect the energy-up processes $|\psi_{m'+1}\rangle \rightarrow |\psi_{\pm}\rangle$. Thus, as in the case of the ground-ground state resonance, it is sufficient to consider the 2×2 DME for the states $|\psi_{\pm}\rangle$. In this case, however, the normalization of the effective DM of the two-level system is not conserved because of the decay to the lower states.

The DME for the states $|\psi_{\pm}\rangle$ can be obtained from the general formalism, as above, but this way is lengthy and the final results can be written without any calculations. In fact, the system obeys the damped Schrödinger equation in the natural basis that is simpler than the DME and has the form

$$\begin{aligned} \frac{d}{dt}c_{-S} &= -\frac{i}{2} \frac{W}{\hbar} c_{-S} - \frac{i}{2} \frac{\Delta}{\hbar} c_{m'} \\ \frac{d}{dt}c_{m'} &= \left(\frac{i}{2} \frac{W}{\hbar} - \frac{1}{2}\Gamma_{m'+1,m'}\right) c_{m'} - \frac{i}{2} \frac{\Delta}{\hbar} c_{-S}, \end{aligned} \quad (293)$$

where the level m' is damped and the level $-S$ is undamped. The decay rate between the adjacent m -states in the generic MM model is given by Eq. (A9) of Ref. [8] that can be rewritten as

$$\Gamma_{m+1,m} = \frac{(2m+1)^2 l_{m+1,m}^2 (D/\hbar)^2 |\omega_{m+1,m}|^3}{24\pi \Omega_t^4}. \quad (294)$$

Here $l_{m+1,m}$ is defined below Eq. (229) and Ω_t is defined by Eq. (222). In the case $m = S - 1$ and $m + 1 = S$, Eq. (294) simplifies to the elegant form

$$\Gamma_{S,S-1} = \frac{S^2}{12\pi} \frac{\omega_{S-1,S}^5}{\Omega_t^4}, \quad (295)$$

where $\hbar\omega_{S-1,S} = (2S - 1)D$.

The DME can be obtained from Eq. (293) by setting

$$\rho_{-S,-S} = c_{-S}c_{-S}^*, \quad \rho_{m',m'} = c_{m'}c_{m'}^*, \quad \rho_{-S,m'} = c_{-S}c_{m'}^* \quad (296)$$

and calculating time derivatives. It has the form

$$\begin{aligned} \frac{d}{dt}\rho_{-S,-S} &= \frac{i}{2} \frac{\Delta}{\hbar} (\rho_{-S,m'} - \rho_{m',-S}) \\ \frac{d}{dt}\rho_{m',m'} &= -\Gamma_{m'+1,m'}\rho_{m',m'} - \frac{i}{2} \frac{\Delta}{\hbar} (\rho_{-S,m'} - \rho_{m',-S}) \\ \frac{d}{dt}\rho_{-S,m'} &= \left(-i\frac{W}{\hbar} - \frac{1}{2}\Gamma_{m'+1,m'}\right)\rho_{-S,m'} + \frac{i}{2} \frac{\Delta}{\hbar} (\rho_{-S,-S} - \rho_{m',m'}) \end{aligned} \quad (297)$$

that coincides with the results of Ref. [12] (In the latter the precession goes in the wrong direction, however). It should be stressed once more that this tunneling DME is non-secular.

Of course Eq. (293) is easier to solve than Eq. (297). We search for the solution of Eq. (293) in the form $e^{-\lambda t}$. Eigenvalues λ of Eq. (293) satisfy the equation

$$\begin{vmatrix} -\lambda + \frac{i}{2} \frac{W}{\hbar} & -\lambda - \frac{i}{2} \frac{W}{\hbar} + \frac{i}{2} \frac{\Delta}{\hbar} \Gamma_{m'+1,m'} \\ \frac{i}{2} \frac{\Delta}{\hbar} & -\lambda - \frac{i}{2} \frac{W}{\hbar} + \frac{1}{2} \Gamma_{m'+1,m'} \end{vmatrix} = 0 \quad (298)$$

or, with the use of Eq. (255),

$$\begin{aligned} 0 &= \left(-\lambda + \frac{i}{2} \frac{W}{\hbar}\right) \left(-\lambda - \frac{i}{2} \frac{W}{\hbar} + \frac{1}{2} \Gamma_{m'+1,m'}\right) + \frac{1}{4} \left(\frac{\Delta}{\hbar}\right)^2 \\ &= \lambda^2 - \frac{1}{2} \Gamma_{m'+1,m'} \lambda + \frac{1}{4} \omega_0^2 + \frac{i}{4} \frac{W}{\hbar} \Gamma_{m'+1,m'} \end{aligned} \quad (299)$$

that yields

$$\begin{aligned} \lambda_{\pm} &= \frac{1}{2} \left(\frac{1}{2} \Gamma_{m'+1,m'} \pm \sqrt{\frac{1}{4} \Gamma_{m'+1,m'}^2 - \omega_0^2 - i \frac{W}{\hbar} \Gamma_{m'+1,m'}} \right) \\ &= \frac{1}{2} \left(\frac{1}{2} \Gamma_{m'+1,m'} \pm i \sqrt{-\frac{1}{4} \Gamma_{m'+1,m'}^2 + \omega_0^2 + i \frac{W}{\hbar} \Gamma_{m'+1,m'}} \right). \end{aligned} \quad (300)$$

The solution of Eq. (293) has the form

$$\begin{aligned} c_{-S}(t) &= a_{-S}^{(+)} e^{-\lambda_+ t} + a_{-S}^{(-)} e^{-\lambda_- t} \\ c_{m'}(t) &= a_{m'}^{(+)} e^{-\lambda_+ t} + a_{m'}^{(-)} e^{-\lambda_- t}. \end{aligned} \quad (301)$$

The eigenvectors $(a_{-S}^{(\pm)}, a_{m'}^{(\pm)})$ follow from Eq. (293):

$$-\lambda_{\pm} a_{-S}^{(\pm)} = -\frac{i}{2} \frac{W}{\hbar} a_{-S}^{(\pm)} - \frac{i}{2} \frac{\Delta}{\hbar} a_{m'}^{(\pm)}, \quad (302)$$

i.e.,

$$a_{m'}^{(\pm)} = -\frac{\hbar}{\Delta} \left(\frac{W}{\hbar} + 2i\lambda_{\pm} \right) a_{-S}^{(\pm)}. \quad (303)$$

Thus Eq. (301) can be rewritten as

$$\begin{aligned} c_{-S}(t) &= a_{-S}^{(+)} e^{-\lambda_+ t} + a_{-S}^{(-)} e^{-\lambda_- t} \\ c_{m'}(t) &= -a_{-S}^{(+)} \frac{W/\hbar + 2i\lambda_+}{\Delta/\hbar} e^{-\lambda_+ t} - a_{-S}^{(-)} \frac{W/\hbar + 2i\lambda_-}{\Delta/\hbar} e^{-\lambda_- t}. \end{aligned} \quad (304)$$

From the initial conditions $c_{-S}(0) = 1$ and $c_{m'}(0) = 0$ one obtains

$$\begin{aligned} a_{-S}^{(+)} + a_{-S}^{(-)} &= 1 \\ a_{-S}^{(+)} (W/\hbar + 2i\lambda_+) + a_{-S}^{(-)} (W/\hbar + 2i\lambda_-) &= 0 \end{aligned} \quad (305)$$

that yields

$$\begin{aligned} a_{-S}^{(+)} &= \frac{1}{1 - \frac{W/\hbar + 2i\lambda_+}{W/\hbar + 2i\lambda_-}} = \frac{W/\hbar + 2i\lambda_-}{2i(\lambda_- - \lambda_+)} = \frac{iW/(2\hbar) - \lambda_-}{\lambda_+ - \lambda_-} \\ a_{-S}^{(-)} &= \frac{iW/(2\hbar) - \lambda_+}{\lambda_- - \lambda_+} \end{aligned} \quad (306)$$

and, from Eq. (303),

$$\begin{aligned} a_{m'}^{(+)} &= 2i \frac{\hbar}{\Delta} \frac{(iW/(2\hbar) - \lambda_+)(iW/(2\hbar) - \lambda_-)}{\lambda_+ - \lambda_-} \\ a_{m'}^{(-)} &= -a_{m'}^{(+)}. \end{aligned} \quad (307)$$

Finally one obtains

$$\begin{aligned} c_{-S}(t) &= \frac{1}{\lambda_+ - \lambda_-} \left[\left(\frac{iW}{2\hbar} - \lambda_- \right) e^{-\lambda_+ t} - \left(\frac{iW}{2\hbar} - \lambda_+ \right) e^{-\lambda_- t} \right] \\ c_{m'}(t) &= \frac{2i}{\lambda_+ - \lambda_-} \frac{\hbar}{\Delta} \left(\frac{iW}{2\hbar} - \lambda_+ \right) \left(\frac{iW}{2\hbar} - \lambda_- \right) (e^{-\lambda_+ t} - e^{-\lambda_- t}). \end{aligned} \quad (308)$$

Now the components of the density matrix are given by

$$\begin{aligned} \rho_{-S,-S} &= \frac{1}{|\lambda_+ - \lambda_-|^2} \left[\left(\frac{iW}{2\hbar} - \lambda_- \right) e^{-\lambda_+ t} - \left(\frac{iW}{2\hbar} - \lambda_+ \right) e^{-\lambda_- t} \right] \\ &\quad \times \left[\left(-\frac{iW}{2\hbar} - \lambda_-^* \right) e^{-\lambda_+^* t} - \left(-\frac{iW}{2\hbar} - \lambda_+^* \right) e^{-\lambda_-^* t} \right] \\ &= \frac{1}{|\lambda_+ - \lambda_-|^2} \left\{ \left| \frac{iW}{2\hbar} - \lambda_- \right|^2 e^{-2\text{Re}(\lambda_+)t} + \left| \frac{iW}{2\hbar} - \lambda_+ \right|^2 e^{-2\text{Re}(\lambda_-)t} \right. \\ &\quad \left. - 2\text{Re} \left[\left(\frac{iW}{2\hbar} - \lambda_- \right) \left(-\frac{iW}{2\hbar} - \lambda_+^* \right) e^{-(\lambda_+ + \lambda_-^*)t} \right] \right\} \end{aligned} \quad (309)$$

and

$$\rho_{m'm'} = \left(\frac{\hbar}{\Delta} \right)^2 \frac{4 \left| \frac{iW}{2\hbar} - \lambda_- \right|^2 \left| \frac{iW}{2\hbar} - \lambda_+ \right|^2}{|\lambda_+ - \lambda_-|^2} \left[e^{-2\text{Re}(\lambda_+)t} + e^{-2\text{Re}(\lambda_-)t} - 2\text{Re} \left(e^{-(\lambda_+ + \lambda_-^*)t} \right) \right]. \quad (310)$$

One can see that the relaxation is described by three relaxation rates, $2\text{Re}(\lambda_{\pm})$ and $\text{Re}(\lambda_+ + \lambda_-)$. In addition, there are oscillations with the frequency $\text{Im}(\lambda_+ - \lambda_-)$ corresponding to quantum transitions $|-S\rangle \rightleftharpoons |m'\rangle$.

Spin polarization in our low-temperature tunneling process is given by

$$\langle S_z \rangle = -S\rho_{-S,-S} + \sum_{m=m'}^S m\rho_{mm}. \quad (311)$$

As the states with $m = m' + 1, \dots, S - 1$ decay faster than $|m'\rangle$, their contribution can be neglected. Then one can write

$$\begin{aligned} \langle S_z \rangle &= -S\rho_{-S,-S} + m'\rho_{m'm'} + S\rho_{SS} \\ &= -S\rho_{-S,-S} + m'\rho_{m'm'} + S(1 - \rho_{-S,-S} - \rho_{m'm'}) \\ &= S - 2S\rho_{-S,-S} - (S - m')\rho_{m'm'}. \end{aligned} \quad (312)$$

As both $\rho_{-S,-S}$ and $\rho_{m'm'}$ go asymptotically to zero, the magnetization change in the process is $\langle S_z \rangle_0 - \langle S_z \rangle_\infty = -2S$, and

$$\langle S_z \rangle_t - \langle S_z \rangle_\infty = -2S\rho_{-S,-S} - (S - m')\rho_{m'm'}. \quad (313)$$

Thus the integral relaxation time is given by

$$\tau_{\text{int}} = \frac{\int_0^\infty dt (\langle S_z \rangle_t - \langle S_z \rangle_\infty)}{\langle S_z \rangle_0 - \langle S_z \rangle_\infty} = \int_0^\infty dt \left(\rho_{-S,-S}(t) + \frac{S - m'}{2S} \rho_{m'm'}(t) \right). \quad (314)$$

For a small bias, say, $m' = S - 1$ and large spin, the contribution of the second term is small. Using Eq. (309), one obtains

$$\int_0^\infty dt \rho_{-S,-S}(t) = \frac{1}{|\lambda_+ - \lambda_-|^2} \left\{ \frac{|\frac{iW}{2\hbar} - \lambda_-|^2}{2\text{Re}(\lambda_+)} + \frac{|\frac{iW}{2\hbar} - \lambda_+|^2}{2\text{Re}(\lambda_-)} - 2\text{Re} \frac{(\frac{iW}{2\hbar} - \lambda_-)(-\frac{iW}{2\hbar} - \lambda_+^*)}{\lambda_+ + \lambda_-^*} \right\} \quad (315)$$

and

$$\int_0^\infty dt \rho_{m'm'}(t) = \left(\frac{\hbar}{\Delta} \right)^2 \frac{4|\frac{iW}{2\hbar} - \lambda_-|^2 |\frac{iW}{2\hbar} - \lambda_+|^2}{|\lambda_+ - \lambda_-|^2} \left\{ \frac{1}{2\text{Re}(\lambda_+)} + \frac{1}{2\text{Re}(\lambda_-)} - \text{Re} \frac{2}{\lambda_+ + \lambda_-^*} \right\}. \quad (316)$$

Mathematica-aided simplification yields

$$\int_0^\infty dt \rho_{-S,-S}(t) = \frac{4W + \Delta^2 + \Gamma_{m'+1,m'}^2}{\Gamma_{m'+1,m'} \Delta^2} \quad (317)$$

and

$$\int_0^\infty dt \rho_{m'm'}(t) = \frac{1}{\Gamma_{m'+1,m'}}. \quad (318)$$

Then from Eq. (314) one obtains

$$\tau_{\text{int}} = \frac{4W + \Delta^2 + \Gamma_{m'+1,m'}^2}{\Gamma_{m'+1,m'} \Delta^2} + \frac{S - m'}{2S} \frac{1}{\Gamma_{m'+1,m'}} = \frac{4W + \left(1 + \frac{S - m'}{2S}\right) \Delta^2 + \Gamma_{m'+1,m'}^2}{\Gamma_{m'+1,m'} \Delta^2}. \quad (319)$$

The corresponding rate can be written as

$$\Gamma_{\text{int}} = \frac{\Delta^2}{2\hbar^2} \frac{\Gamma_{m'+1,m'}/2}{\Omega^2 + (\Gamma_{m'+1,m'}/2)^2}, \quad (\hbar\Omega)^2 \equiv W^2 + \frac{1}{4} \left(1 + \frac{S - m'}{2S}\right) \Delta^2. \quad (320)$$

In comparison to the overdamped result of Ref. [12], this formula contains an additional term $\sim \Delta^2$ in the denominator. In the underdamped case $\Delta \gg \hbar\Gamma_{m'+1,m'}$ at resonance $W = 0$, the rate is given by

$$\Gamma_{\text{int}} = \Gamma_{m'+1,m'} / \left(1 + \frac{S - m'}{2S}\right) \quad (321)$$

that is of the order of thermal activation rate at high temperatures. This means that the barrier is completely cut at resonance and the relaxation rate does not significantly increase with temperature. Condition $\Delta \gg \hbar\Gamma_{m'+1,m'}$ makes the secular approximation valid, unlike the overdamped case $\Delta \lesssim \hbar\Gamma_{m'+1,m'}$, where the secular approximation leads to unphysically large relaxation rates at resonance.

F. Numerical implementation and illustrations

In this section some representative results of the numerical solution of the DME for molecular magnets are shown. The code implemented in Wolfram Mathematica is available from the author. It is based on the diagonalization of the dynamical matrix Φ of the DME for the free-evolution problem, as described in Sec. III A. Linear dynamical susceptibility, Sec. III C, can also be obtained on this way. As the tunnel splitting Δ can be very small, especially in Mn_{12} ($S = 10$) at small transverse fields, matrix algebra requires using a high custom precision, typically 100 significant

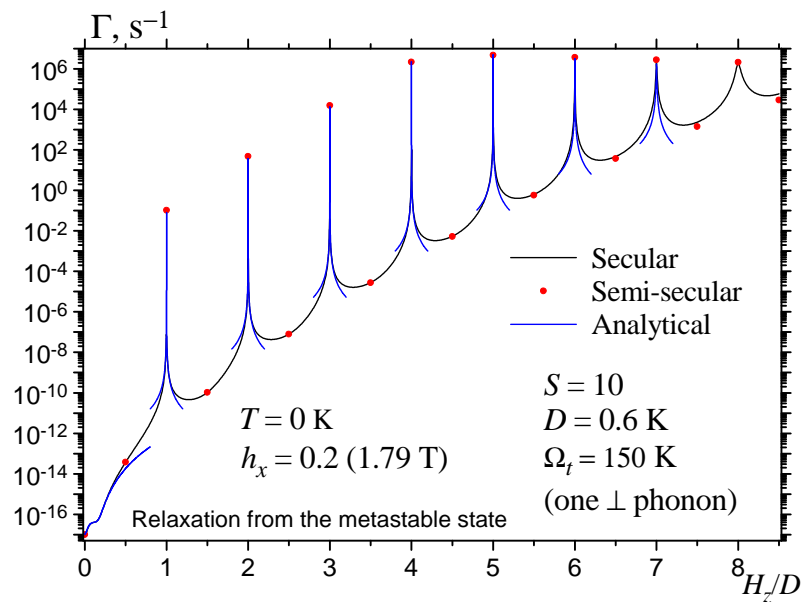


FIG. 1: Zero-temperature escape rate from the metastable state vs the bias field in the generic model of MM.

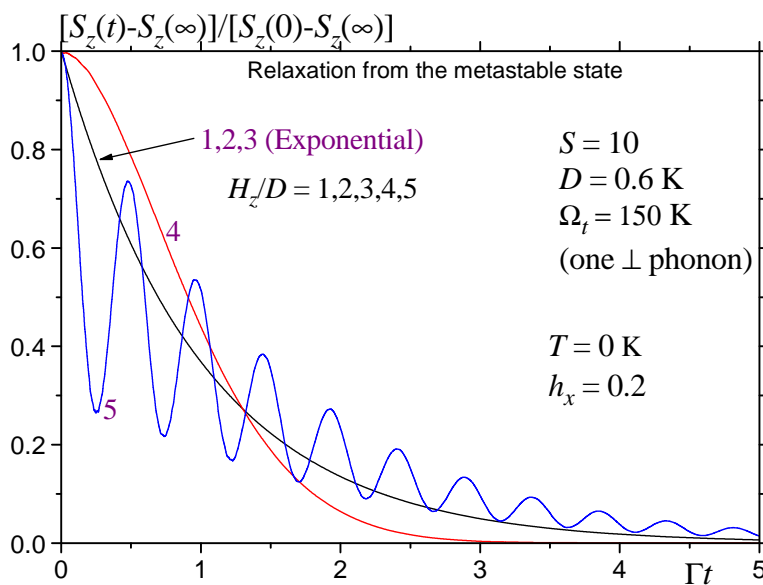


FIG. 2: Time evolution of $\langle S_z \rangle$ at over- and underdamped tunneling resonances in previous figure.

figures. For Ni_4 ($S = 4$) standard precision is sufficient. Custom precision makes computation slower. Still, the DME in the secular approximation involving the $(2S + 1) \times (2S + 1)$ dynamical matrix solves fast enough on a standard PC. Solution of the full non-secular DME is very slow for $S = 10$ because of the big size $(2S + 1)^2 \times (2S + 1)^2$ of the dynamical matrix. It is very important to use the semi-secular DME that is no less accurate than the full non-secular DME but has the dynamical matrix of the size $(6S + 1) \times (6S + 1)$. As a result, the solution, although slower than that of the secular DME, is still realistically fast. The difference between the secular and semi-secular versions of the method is confined to the close vicinity of the overdamped tunneling resonances, $\Delta \lesssim \hbar \Gamma_{m'+1, m'}$, while everywhere else the numerical results are the same.

Numerical solution shows that the dynamical matrix Φ of the non-secular DME has exactly $2S + 1$ real eigenvalues out of the total $(2S + 1)^2$ eigenvalues. One of real eigenvalues is zero and corresponds to the thermal equilibrium. Complex eigenvalues occur in complex conjugate pairs. This behavior is similar to that of the secular DME and

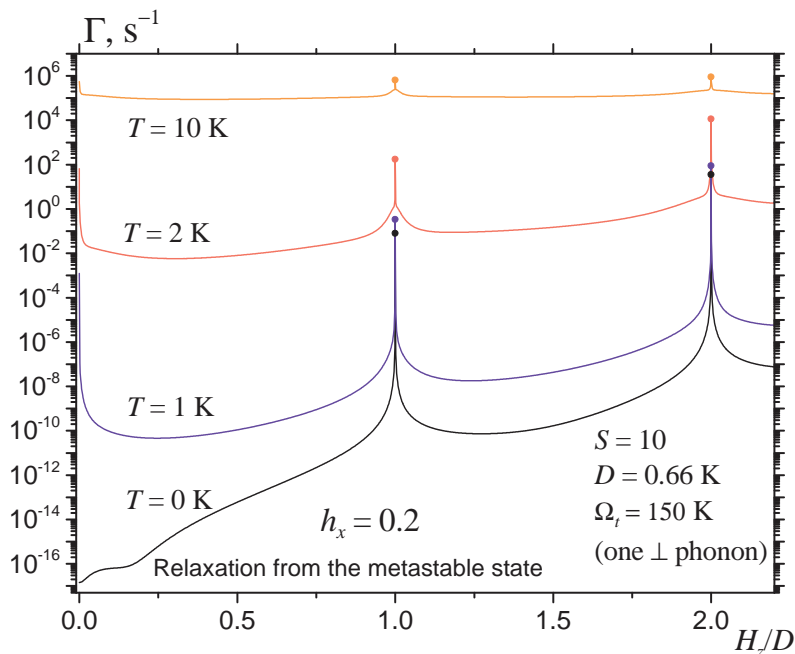


FIG. 3: Escape rate vs bias field in the generic model of MM at different temperatures.

requires explanation. At low temperatures in the regime of thermal activation and weak tunneling (overdamped resonances) there is one nonzero real eigenvalue that is much smaller than all other real eigenvalues and real parts of complex eigenvalues. In the case of underdamped resonances, there are three eigenvalues, one real and two complex, that describe the slow dynamics.

Fig. 1 shows the zero-temperature escape rate vs the bias field H_z in the generic MM model with $B = 0$ in Eq. (188). The striking feature is the spin tunneling at resonance fields that leads to the increase of the escape rate by many orders of magnitude. Most of the points have been obtained from the secular DME, the points at resonances and between them have been obtained from the semi-secular DME, and the analytical result of Eq. (320) is drawn in the vicinity of resonances. Near the zero-field resonance, Eq. (290) is shown. The characteristic “shoulder” described by this equation is well reproduced by the numerical result. As mentioned above, the secular approximation can yield unphysically high escape rates at resonances but the resonances are narrow and there are no secular points that hit them. Resonances with $k = 1, 2$, and 3 are overdamped and can be approximately described by the DME solution based on effective resistances method of Ref. [12]. As explained in Ref. [12], the barrier at resonances is lower than the full classical barrier, and its height corresponds to the so-called *blocking level* for which $\Delta_{mm'} \sim \hbar(\Gamma_{m'+1,m'} + \Gamma_{m-1,m})$. Resonances with $k \geq 4$ in Fig. 1 are underdamped, so that the blocking level is the ground state and the barrier is reduced to zero. Accordingly, the escape rate at these resonances is of order $\Gamma \sim 3 \times 10^6 \text{ s}^{-1}$ and it coincides with the spin-phonon rate between the adjacent levels that is the highest possible rate achievable off resonance at temperatures exceeding the energy barrier.

Fig. 2 shows the time dependence of spin polarization $\langle S_z \rangle$ at different resonances in Fig. 1. The relaxation is exponential for the overdamped resonances, as well as off resonance (not shown). To the contrast, at underdamped resonances with $k \geq 5$ there are damped oscillations described by three different relaxation rates in Eq. (309). In the case of exponential relaxation, it is sufficient to identify the escape rate with the smallest real eigenvalue of the dynamical matrix. In the case of underdamped resonances there are three slow eigenvalues, and obtaining the correct value of the escape rate requires using the integral relaxation time.

Escape rate vs the bias field at different temperatures in the generic model is shown in Fig. 3. All data were obtained from the numerical solution of the semi-secular DME. The anisotropy value $D = 0.66 \text{ K}$ has been chosen to fit the barrier height in Mn_{12} (see below). As expected, the escape rate increases with temperature, faster off resonance than on resonance. One can see (especially clear for $T = 2 \text{ K}$ and $k = 1$) that at nonzero temperatures the tunneling peak may consist of several peaks of different width on the top of each other [12]. Broad peaks correspond to tunneling at high energy with a large splitting Δ while narrow peaks correspond to tunneling via a low-lying resonant pair of levels with small Δ . At zero temperatures the zero-bias tunneling peak is very narrow because of the anomalously small damping of the ground-state levels and it is not seen in the plot. However, for nonzero temperatures this peak becomes broad as all other peaks because of tunneling via excited levels that are regularly damped via decay to the

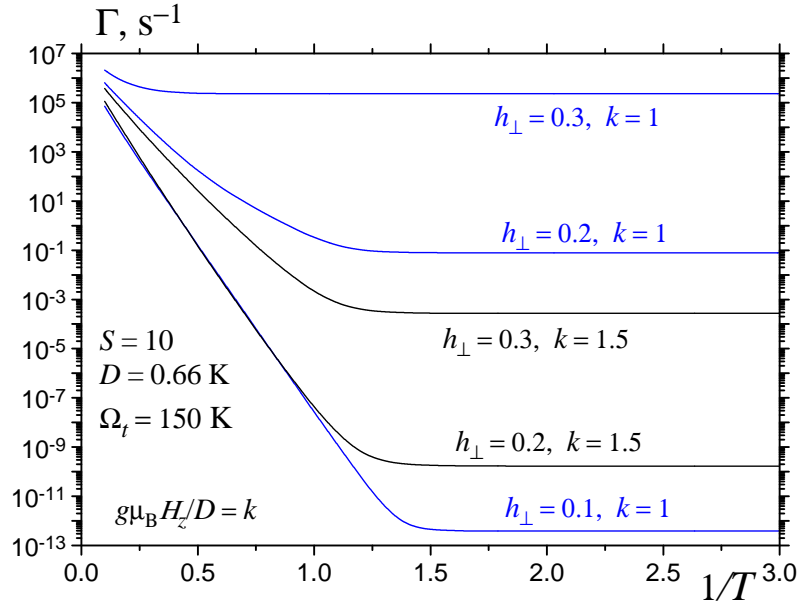


FIG. 4: Temperature dependence of the escape rate in the generic model on and off resonance.

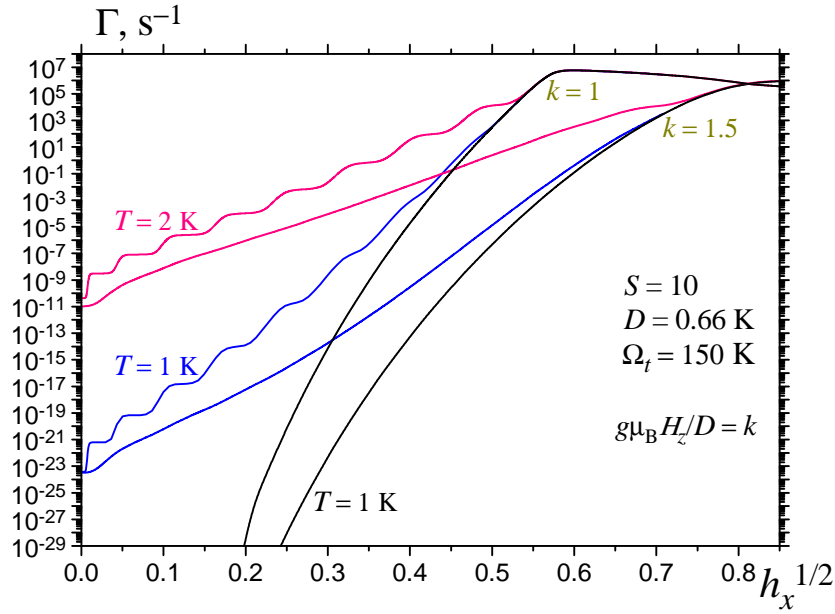


FIG. 5: Escape rate vs transverse field in the generic model of MM at different temperatures, on and off resonance.

lower-lying levels.

Arrhenius plot in Fig. 4 shows transition between the thermal-activation and ground-state-tunneling regimes on and off resonance for different transverse fields parametrized by $h_x = g\mu_B H_x / (2SD)$. For small transverse fields, the resonances are overdamped and ground-state tunneling is small. In this case the activation part of the plot is nearly a straight line with the slope corresponding to a particular effective barrier. The transition to the horizontal line describing the ground-state tunneling has little rounding. This is the so-called first-order transition between thermal activation and ground-state tunneling, the two competing channels [12, 13]. For $h_x = 0.2$ at resonance, the activation part of the plot is noticeably curved. This is a manifestation of the second-order transition in which the dominating tunneling level gradually moves down with lowering temperature, effectively decreasing the barrier height and the slope of the curve. For $h_x = 0.3$ at resonance, the barrier is reduced to nearly zero and the ground-state tunneling is very strong.

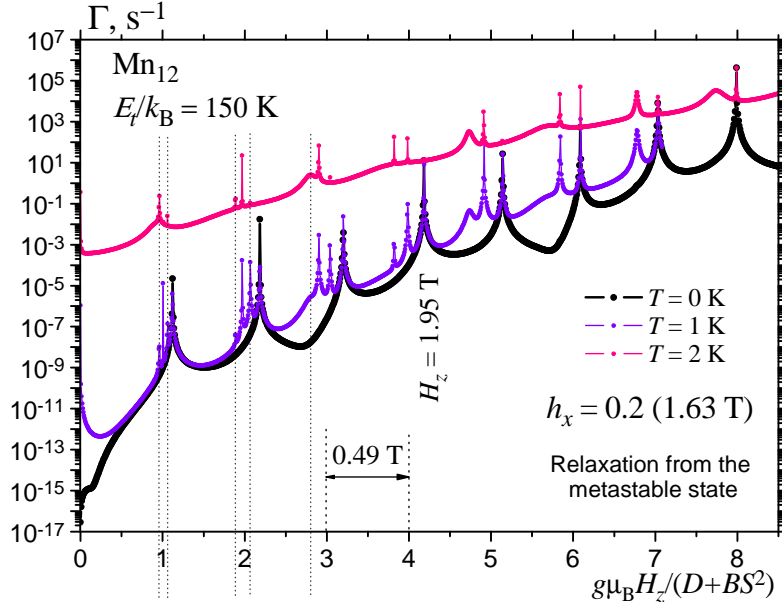


FIG. 6: Escape rate vs bias field in Mn_{12} at different temperatures.

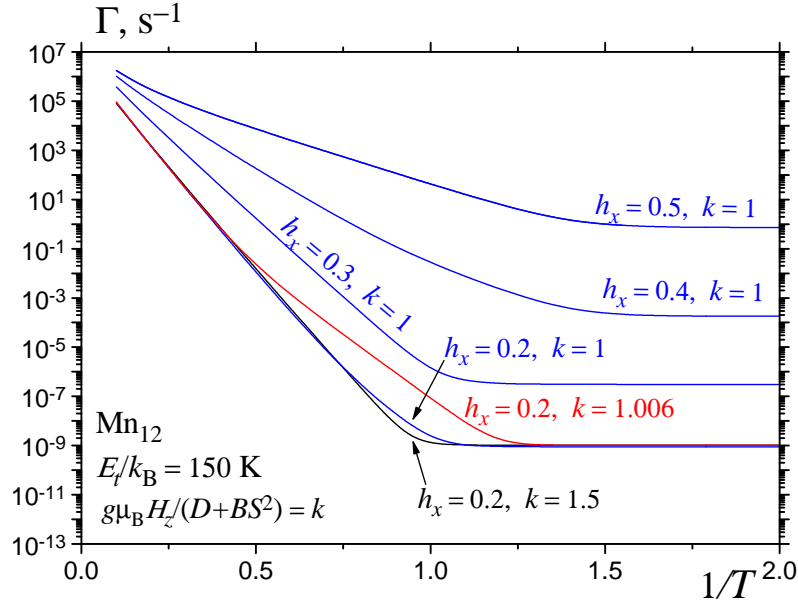


FIG. 7: Temperature dependence of the escape rate in Mn_{12} .

Fig. 5 shows the dependence of the escape rate on the transverse field h_x at different temperatures on and off resonance. On resonance at nonzero temperatures, there are characteristic steps arising as a result of moving the blocking level up or down the energy [12]. This phenomenon can be seen in Fig. 5 of Ref. [12], obtained by the effective resistances method. One can see that on resonance, $k = 1$, the barrier goes to zero with increasing h_x , so that above some critical value of h_x curves corresponding to different temperatures merge at the level of the highest possible rate. At these transverse fields the barrier off resonance still exists since the curves corresponding to different temperatures merge at higher values of h_x .

Next figures show the numerical results for Mn_{12} . Because of the quartic uniaxial anisotropy B , tunneling peaks in Fig. 6 are split, as explained in the comment after Eq. (191). The rightmost big peaks correspond to the ground-state tunneling, and smaller peaks to the left of them, seen at nonzero temperatures, are due to tunneling via excited states. Graphed results of earlier calculations of this kind for Mn_{12} can be found in Refs. [14, 15]. In comparison to the

results for the generic model with the same barrier 66 K in Fig. 4, Mn_{12} shows ground-state tunneling up to higher temperatures.

Temperature dependences of the escape rate in Fig. 7 are different for different bias fields. If for a given H_z there is a tunneling resonance at some energy between the top of the classical barrier and the ground-state, thermally activated tunneling via this resonant pair is a relaxation channel competing with the two channels considered above. As a result, there are two different slopes in the Arrhenius part of the plot, such as for $k = 1.006$. This value of k corresponds to the high blue peak in Fig. 6 that disappears at $T = 0$.

G. Discussion

Existing work on molecular magnets using the density matrix equation can be split up into two groups: (i) using the natural or m -basis and (ii) using the diagonal basis. In all known cases the DME is reduced to the system of rate equations for the diagonal DM elements, the level populations. Using the natural basis is justified if the terms in the spin Hamiltonian that are non-commuting with S_z are a small perturbation. However, even a small non-commuting perturbation can severely distort the levels near the top of the barrier that are mostly important in thermal activation. On the other hand, tunneling via robust low-lying levels at low temperatures can be well described perturbatively in the m -basis.

In Ref. [16] the thermal activation rate of a generic MM was calculated in the m -basis *in the absence of tunneling* via the *integral relaxation time*. Tunneling has been taken into account in Ref. [12] by adiabatically eliminating fast nondiagonal DM elements that amounts to using the high-order perturbation theory in calculating tunnel splittings [17]. The resulting system of rate equations with resonance tunneling was solved by the method of *effective resistances* [12] using the idea of the solution of the Fokker-Planck equation at low temperatures in the classical case. Later the system of rate equations in the m -basis was employed in Refs. [15, 18, 19].

In particular, Ref. [15] repeats the steps of Ref. [12] using the realistic model of Mn_{12} with $B \neq 0$ in Eq. (187). A new element of Ref. [15] is the erroneous consideration of spin-phonon interactions leading to the spin-phonon coupling of the type $D(S_+^2 + S_-^2)(\epsilon_{xx} - \epsilon_{yy})$, $\epsilon_{\alpha\alpha}$ being components of the deformation tensor, because of tilting the easy axis by transverse phonons at *second* order in small tilting angle $\delta\varphi$. This leads to nonexistent direct processes with changing m by 2. In fact, as we have seen above, second-order terms in $\delta\varphi$, Eq. (198), give rise to Raman processes rather than to direct processes. The error made in Ref. [15], neglect of a part of $\delta\varphi^2$ terms that cancel the result, has been explained in Ref. [20]. Nevertheless, the appeal of $\Delta m = 2$ direct processes has been remaining strong, so that the relevance of Eq. (A12) of Ref. [15] for explanation of experiments on molecular magnets is still disputable. The recent examples are experimental works on Fe_8 , Refs. [21, 22]. Whereas in Ref. [21] Eq. (A12) of Ref. [15] is used with success, Ref. [22] states that direct processes with $\Delta m = 2$ do not fit the data. On the other hand, for Fe_8 these processes were shown to arise from rotations around the easy axis, the corresponding coupling constant being the transverse anisotropy E , see Eq. (B5) of Ref. [8].

Moving to the universal form of the DME proposed here can help to end the confusion about what to include into the relaxation terms, since the latter automatically follow from the spin Hamiltonian and there is no freedom to make a mistake. Moreover, in the diagonal basis used in the universal DME there are phonon-induced transitions between *all* exact energy levels, not only between the nearest or second-nearest neighbors. An example is the relaxation rate between the levels of the ground-state doublet, Eq. (290) and Eq. (69) of Ref. [8].

Among the works using the DME in the natural basis, in the secular approximation, are Refs. [14, 22]. The authors say that the advantage of this method is that spin tunneling is absorbed in the exact basis states. This is overall true, although the full dynamical description requires taking into account the decoupled nondiagonal DM elements, in addition to the system of rate equations that was used. Also in the case of weak tunneling (overdamped tunneling resonances) the secular approximation fails and results in unphysically large escape rates at resonances. This was explained at the beginning of Sec. IV C, as well as in the comments below Eq. (19) of Ref. [14] and above Eq. (2) of Ref. [22]. Certainly something is missing if spin tunneling is automatically incorporated into the exact basis states but, in spite of it, one cannot approach tunneling resonances. The solution is to use the non-secular or better semi-secular DME that takes into account the dynamical coupling between the diagonal and slow nondiagonal DM elements and is thus valid everywhere. It should be stressed that the system of rate equations with tunneling in the m -basis is essentially non-secular and for this reason it does not fail at resonances.

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