Journal of Statistical Physics, Vol. 114, Nos. 1/2, January 2004 (© 2004)

Coherent and Dissipative Spin Dynamics in *N*-Electron Systems

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Received January 4, 2002; accepted March 12, 2003

We investigate the ensemble averaged evolution of *N*-electron systems dynamically coupled to a statistical environment. The electrons are characterized by their spatial and by their spin properties. While the Hilbert space for single electrons is given by the tensor product of the Hilbert spaces associated with both properties, the corresponding Hilbert space for *N*-electron systems cannot be factorized. Consequently, quantum correlations between spatial and spin properties become extremely important. We assume that the evolution of the spin properties is controlled by spin-orbit interaction and that the spatial properties take the part of a bath held near some equilibrium. This description is appropriate for magnetic systems where the electronic states near the ground state correspond to different spin configurations, whereas electronic states with large excitation energies belong to different spatial-orbital configurations. In order to determine the coarse grained evolution of the spin properties, we have to know the evolution of the *N*-electron system over time intervals larger than the bath-correlation time. This is obtained from the first- and second-order contributions in the interaction picture. We show that, in spite of the strong quantum correlations between spin properties and spatial properties, the coarse grained statistical evolution of the electronic spin properties may be described by a set of coupled master equations.

KEY WORDS: Master equations; Fermion systems; relaxation.

1. INTRODUCTION

The description of the evolution of quantum systems interacting with a statistical environment is a rather challenging theoretical problem. This is

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0022-4715/04/0100-0361/0

particularly true, if the system is formed by indistinguishable particles and if only the evolution of certain selected degrees of freedom of the system is of interest, whereas the remaining degrees of freedom constitute the statistical environment. Such a situation is encountered, if one considers the evolution of the electronic spins in an ensemble of electrons, where the spatial degrees of freedom play the role of the statistical environment or eventually of the bath. This kind of approach would be adequate to describe the magnetic properties of a molecule or cluster, which are determined by the electronic spins. In these systems, the direct interaction between the nuclei and the electronic spins is in general negligible, so that the evolution of the electron spins is driven by spin-orbit coupling and by external magnetic fields. We may thus relate the bath directly with the spatial degrees of freedom. Dealing with such a problem, the principal difficulty to cope with is due to the presence of strong quantum correlations between the considered degrees of freedom and the statistical environment. This becomes most evident for the above example. In this case, the quantum correlations between the electronic spins and the orbital degrees of freedom are due to the fermionic character of the electrons. The presently considered situation is thus completely different from the conventional quantum statistical approach to the evolution of fermionic systems, where bath and evolving physical system correspond to subsystems of the physical system, both being associated with different particles. In this case, the states constituting the statistical ensemble may in a first approximation be assumed to be quantically uncorrelated with the bath subsystem (see, e.g., ref. 1). In the present article we will show that, in spite of the abovementioned problems, the coarse grained evolution of a sub-ensemble of degrees of freedom in a fermionic system may still be described in terms of master equations. For our convenience, we will in the following refer to the chosen degrees of freedom as a subsystem, thus generalizing the usual notion of this term.

Open quantum systems have been the object of intense theoretical research since the early beginnings of quantum mechanics. The fundamental concept of density matrices allowing for a statistical description of quantum systems was already introduced in the early thirties of the last century.[2, 3] Different methods have been proposed to study the evolution of subsystems embedded in their environment. The path-integral method,[4–6] which has become popular during the last 15 years, offers a practical scheme for the calculation of density matrices describing such subsystems.[7, 8] Considering the particular problem of nuclear-spin relaxation in a solid, Bloch, Wangsness, and Redfield have developed a phenomenological approach, in which the coarse grained evolution of the reduced density matrix associated with the nuclear spin subsystem is

governed by a master equation of Markovian type.[9–11] Based on the same ideas, similar methods have been worked out later on to describe dissipation phenomena in quantum optics.[12, 13] The coarse grained density matrix, which is the central quantity in these approaches, satisfies the von Neumann conditions of hermiticity and trace preservation, but not that of positivity. Thus, strictly speaking, it is no longer a density matrix. It is important to note that in spite of this it allows a correct description of the coarse grained evolution of observables characterizing the considered subsystem. More recently, it was shown that the evolution of the reduced density matrix associated with a subsystem can be described in a way that the latter obeys strictly all the von Neumann conditions at all times.[14–23] In the limit of weak interaction and correspondingly long time scales, the evolution of the density matrix describing the quantum mechanical subsystem becomes again strictly Markovian leading to a quantum dynamical semigroup.[15, 17–23] This approach was generalized later on. In fact, a Markovian evolution of an open quantum system weakly interacting with a bath subsystem is expected on time scales for which memory effects can be neglected.[22, 23] The most general form of a generator corresponding to a Markovian evolution of the density matrix of the subsystem has been given by Lindblad.[16] The results presented in refs. 14–23 are very important, since they ensure that a Markovian evolution of a finite subsystem is compatible with a quantum statistical description of the full system. They offer a more profound justification of the physical hypotheses underlying the Bloch–Wangsness–Redfield approach. Thus, for practical applications, both methods can be considered to be equivalent.

Presently we will adopt the phenomenological approach of refs. 9–13, which not only is physically more transparent, but it is also more adequate to deal with our particular situation. In fact, internal and spatial degrees of freedom of our fermionic system being associated with the same particles, it is impossible to follow directly the approach of refs. 15, and 17–23, and to perform the thermodynamic limit for the spatial degrees of freedom constituting the bath subsystem without changing the subsystem associated with the internal degrees of freedom at the same time. This does of course not mean that a description of the evolution of the bathed subsystem in terms of density matrices rather than coarse grained density matrices is principally impossible.

The master equations for the evolution of the subsystem are obtained under certain additional assumptions, which are physically equivalent to the ones invoked in the standard approach. In particular, we have to assume that the internal dynamics of the chosen subsystem is sufficiently slow with respect to the memory time of the bath, which depends in particular on its coupling to the further environment. This requirement is

usually satisfied for weakly excited magnetic systems, where the electronic spin-relaxation times for temperatures of the order of the Curie temperature are by two to three orders of magnitude larger than the typical times for electronic energy relaxation due to electron-phonon coupling.[24–26] We thus expect that the here proposed approach is a good starting point for the understanding of the relaxation dynamics of superparamagnetic clusters[27] and of individual single-domain ferromagnetic particles.[28, 29]

The present work is divided into two main parts. In Section 2 we develop the approach for arbitrary fermions. The specific case of N-electron systems is discussed in Section 3. Our approach relies heavily on the theory of representations of the permutation group S_N. For readers who are not familiar with this subject we give a list of some recommendable books on this subject in refs. 30–37.

The general mathematical framework is established in Section 2.1, where we introduce the Hilbert space that describes the spatial and the internal properties of the N-fermion system, the partial Hamiltonians connected with the spatial and the internal dynamical properties of the system, and the interaction Hamiltonian. We start from the Hilbert space $\mathscr{H}$ that is given by the tensor product of the N one-particle Hilbert spaces or, alternatively, by the tensor product of the Hilbert space associated with the internal properties and the Hilbert space associated with the spatial properties of the N fermions. In both Hilbert spaces we introduce an orthonormal basis. The basis vectors are chosen to be simultaneously eigenvectors of the partial Hamiltonians acting in the respective Hilbert space. Thus they transform according to the irreducible representations of the permutation group S_N. The physical states of a fermionic system are described by the rays of the subspace of antisymmetric tensors in $\mathscr{H}$. The tensor products of the above basis vectors form an orthonormal basis in $\mathscr{H}$. They are used to construct an orthonormal basis of the subspace of antisymmetric tensors. The antisymmetry implies that the two basis vectors involved in the tensor products, which are associated with the internal and the spatial degrees of freedom, must transform according to dual irreducible representations of the permutation group S_N.

Our principal aim being to reveal the interplay between quantum correlations and dynamical coupling, it is crucial to decompose the interaction Hamiltonian in a way that allows us to follow its action in the Hilbert spaces associated with the internal and the spatial properties. This is also done in Section 2.1. The procedure is similar to the above construction of the fermionic Hilbert space. In a first step, we introduce a basis in the vector space of linear operators acting in the Hilbert space associated with the internal properties. Similarly, we introduce a basis in the vector space of linear operators acting in the Hilbert space associated with the spatial

properties. The chosen basis vectors transform as irreducible tensor operators under the action of the permutation group S_N. In a second step, we use these basis vectors to construct an operator basis acting in $\mathscr{H}$. The resulting basis is given by the tensor products of the basis operators obtained in the first step, where the two operators act in different spaces. The interaction Hamiltonian is then written as a linear combination of these basis operators. It must be invariant under the action of the permutation group S_N. This implies that the basis vectors correspond to tensor products, where both operators transform according to the same irreducible representation of the permutation group S_N.

In Section 2.2, we discuss the properties of the density matrix, which gives access to the statistical properties of the ensemble. We further introduce the relevant partial trace operations, which correspond to projections of the density matrix describing the whole system onto the spatial or onto the spin properties. These operations are discussed in detail in the following Sections 2.3 and 2.4. In Section 2.3 we consider first the hypothetical situation of statistically uncorrelated subsystems. The case of correlated subsystems is discussed in Section 2.4.

In order to reveal the effects of the dynamical interaction, it is indicated to adopt the interaction picture rather than the Schrödinger picture used in Sections 2.2 to 2.4. In Section 2.5, we therefore restate our preceding results in the interaction picture. We then derive the evolution of the N-fermion system during a time interval Δt in Section 2.6. Assuming weak dynamical coupling and weak statistical correlation between the internal and the spatial properties, the evolution is described up to second-order in the dynamical interaction.

Knowing the evolution over a finite time interval, we come back to our actual problem and determine the statistical evolution of the internal properties of the fermions. This is done in Sections 2.7 and 2.8. Here we assume that the spatial degrees of freedom of the fermions constitute the bath, which fluctuates around some statistical equilibrium. We define appropriate correlation functions, which take care of the fact that, due to the interaction of the bath with the environment, the fluctuations become uncorrelated for times exceeding a given correlation time. This loss of memory is crucial to avoid the appearance of Poincaré cycles.[38] In Section 2.9 we make the additional assumption that the bath-correlation time is much smaller than the typical dynamical time scale characterizing the dynamics of the internal properties. This allows us to describe the coarse grained evolution by a set of master equations. The particular structure of these equations is discussed in Section 2.10.

In Section 3 we specify our approach for the case of N-electron systems, where the internal properties of the fermions are given by the

electron spins. In this situation, the total spin S, besides determining the operator of the spatial rotations, defines also the isotypic subspaces with respect to the action of the permutation group S_N. This feature allows us to construct an explicit basis in the Hilbert space associated with the spin properties. The spin-orbit like interaction Hamiltonian defining the dynamical interaction between spin properties and spatial properties is discussed in Sections 3.1 to 3.3. In Section 3.4 we show that the first-order interactions between the spin properties and the bath lead to a polarizaton of the spin subsystem. The master equations describing the evolution of the spin properties are presented in Section 3.5. Our final conclusions are drawn in Section 4.

2. GENERAL *N*-FERMION SYSTEMS

2.1. Mathematical Framework

We consider a system of N fermions. The Hilbert space describing such a system, which will be called $\mathscr{H}_{A+B}$ for reasons that will become clear later, may be constructed from the Hilbert space $\mathscr{H}_{\text{fermion}}$ describing the properties of a single fermion. It is given by the subspace of the antisymmetric tensors of $\mathscr{H} \equiv \mathscr{H}_{\text{fermion}}^{\otimes N}$. Thus, to obtain $\mathscr{H}_{A+B}$, we have first to consider the natural action of the permutation group S_N on $\mathscr{H}$, which is specified by the unitary operators $U(s), s \in S_N$. In order to define these operators $U(s)$, we choose a basis set of orthonormal vectors $|v\rangle, v \in \mathscr{N}$ in $\mathscr{H}_{\text{fermion}}$. Then $|v_1,\ldots, v_N\rangle \equiv |v_1\rangle \otimes |v_2\rangle \otimes \cdots \otimes |v_N\rangle$ with $v_1, v_2,\ldots, v_N \in \mathscr{N}$ is a basis of orthonormal vectors in $\mathscr{H}$. The action of S_N on $\mathscr{H}$ is described by

$$U(s)\,|v_1,\ldots, v_N\rangle = |v_{s^{-1}(1)},\ldots, v_{s^{-1}(N)}\rangle, \qquad \forall v_1,\ldots, v_N \in \mathscr{N}, \tag{2.1.1}$$

which implies

$$U(s_1)\,U(s_2) = U(s_1 s_2), \qquad \forall s_1, s_2 \in S_N. \tag{2.1.2}$$

Thus, the correspondence $s \mapsto U(s)$ constitutes a unitary representation of S_N in the group of the automorphisms of $\mathscr{H}$.

The Hilbert space $\mathscr{H}_{A+B}$ describing the N-fermion system is

$$\mathscr{H}_{A+B} = P^{[1^N]}\mathscr{H}, \tag{2.1.3}$$

where

$$P^{[1^N]} = \frac{1}{N!}\sum_{s \in S_N} \sigma(s)\,U(s) \tag{2.1.4}$$

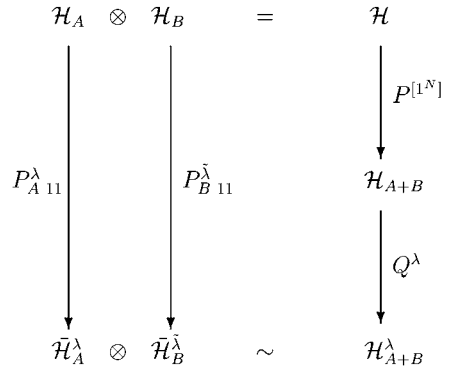

Fig. 1. The diverse considered subspaces of the Hilbert space $\mathscr{H} = \mathscr{H}_A \otimes \mathscr{H}_B$. The corresponding orthogonal projection operators are defined by the expressions (2.1.4), (2.1.20) and its correspondent, and (2.6.9).

is the orthogonal projection operator of $\mathscr{H}$ onto the subspace of antisymmetric tensors (see Fig. 1). The symbol $\sigma(s) \in \{+1, -1\}$ denotes the signature of the permutation s of S_N, and we have

$$\sigma(s_1)\,\sigma(s_2) = \sigma(s_1 s_2), \qquad \forall s_1, s_2 \in S_N. \tag{2.1.5}$$

In the following we label the different types of the irreducible representations of S_N by λ. The dimension of the irreducible representations of type λ will be denoted d_λ. The set of all types of irreducible representations will be denoted Λ. It may be identified by the set of partitions of N. Then each type λ is labeled by $p \leqslant N$ strictly positive integers λ_i, $i = 1,\ldots, p$ such that

$$\lambda_1 \geqslant \lambda_2 \geqslant \cdots \geqslant \lambda_p > 0 \qquad \text{with} \quad \lambda_1 + \lambda_2 + \cdots + \lambda_p = N. \tag{2.1.6}$$

The partitions are represented graphically by the so-called Young diagrams in which boxes are arranged in rows and columns with λ_i boxes in the ith row.[30–33, 37]

For example, the symbol $[1^N] = [1, 1,\ldots, 1]$ corresponds to a column of N boxes. It denotes the type of the one-dimensional (irreducible) representation provided by the mapping $S_N \ni s \mapsto \sigma(s)$. In Eqs. (2.1.3) and (2.1.4), the symbol $[1^N]$ means that $P^{[1^N]}$ projects $\mathscr{H}$ onto a subspace carrying irreducible representations of this type. In other words, $\mathscr{H}_{A+B}$ is the isotypic component of type $[1^N]$ of $\mathscr{H}$ with respect to the representation U, i.e.,

$$U(s)\,|\psi\rangle = \sigma(s)\,|\psi\rangle, \qquad \forall s \in S_N \quad \text{and} \quad |\psi\rangle \in \mathscr{H}_{A+B}. \tag{2.1.7}$$

In the following we suppose that each fermion possesses spatial as well as internal properties being compatible which each other. In this case, the single fermion is described by the Hilbert-space-tensor product

$$\mathscr{H}_{\text{fermion}} = \mathscr{H}_{\text{internal}} \otimes \mathscr{H}_{\text{spatial}}, \tag{2.1.8}$$

where $\mathscr{H}_{\text{spatial}}$ and $\mathscr{H}_{\text{internal}}$ describe the spatial and the internal properties of the fermion, respectively. For example, in the particular case of an electron, $\mathscr{H}_{\text{spatial}}$ is given by $L^2(\mathbb{R}^3, d^3\mathbf{x})$, and $\mathscr{H}_{\text{internal}} = \mathbb{C}^2$ describes the internal properties associated with the spin $1/2$. More generally, for massive fermions with spin S the subspace $\mathscr{H}_{\text{internal}}$ would be given by $(\mathbb{C}^{2S+1})$.

With Eq. (2.1.8), we obtain for the N-fermion system

$$\mathscr{H} = \mathscr{H}_A \otimes \mathscr{H}_B \qquad \text{with} \quad \mathscr{H}_A = \mathscr{H}_{\text{internal}}^{\otimes N}, \quad \mathscr{H}_B = \mathscr{H}_{\text{spatial}}^{\otimes N}. \tag{2.1.9}$$

Accordingly, the unitary representation $U(s)$ of S_N in $\mathscr{H}$ decomposes in $\mathscr{H}_A$ and $\mathscr{H}_B$, so that

$$U(s) = U_A(s) \otimes U_B(s), \qquad \forall s \in S_N. \tag{2.1.10}$$

Any observable of the system may be described by a self-adjoint operator O, which necessarily commutes with the representation U of S_N in the full space $\mathscr{H}$,

$$[O, U(s)] = 0, \qquad \forall s \in S_N. \tag{2.1.11}$$

An observable of the subsystem A is described by an operator of the form $O_A \otimes \mathbb{1}_B$, with a self-adjoint operator O_A acting in $\mathscr{H}_A$. O_A commutes with the action of S_N in $\mathscr{H}_A$, which implies

$$[O_A, U_A(s)] = 0, \qquad \forall s \in S_N. \tag{2.1.12}$$

Similarly, an observable of the subsystem B is described by an operator of the form $\mathbb{1}_A \otimes O_B$ with

$$[O_B, U_B(s)] = 0, \qquad \forall s \in S_N. \tag{2.1.13}$$

In the following we assume that the dynamical evolution of the system is determined by a time-independent Hamiltonian of the form

$$H = H_A \otimes \mathbb{1}_B + \mathbb{1}_A \otimes H_B + H_{\text{int}}, \tag{2.1.14}$$

where the Hamiltonians H_A and H_B govern the free evolution of the respective subsystems A and B. The term H_{int} describes the interaction

between the two subsystems. The operators H_A, H_B, and H_{int} satisfy the commutation relations

$$[H_A, U_A(s)] = 0, \qquad \forall s \in S_N, \tag{2.1.15}$$

$$[H_B, U_B(s)] = 0, \qquad \forall s \in S_N, \tag{2.1.16}$$

$$[H_{\text{int}}, U(s)] = 0, \qquad \forall s \in S_N. \tag{2.1.17}$$

For the following it is convenient to introduce orthonormal basis sets in $\mathscr{H}_A$ and $\mathscr{H}_B$, which are associated with the representations U_A and U_B of the group S_N. The vectors forming such an orthonormal basis set in $\mathscr{H}_A$ will be denoted $|a, \lambda, i\rangle$. The symbol $\lambda \in \Lambda$ labels the different types of the irreducible components of U_A, and $i = 1,..., d_\lambda$. The index a runs from 1 to n_A^λ, where n_A^λ denotes the multiplicity of the irreducible components of type λ. To get rid of the non-contributing irreducible representations, we define the subset $\Lambda_A \subset \Lambda$

$$\Lambda_A = \{\lambda \in \Lambda \,|\, n_A^\lambda > 0\}. \tag{2.1.18}$$

The subset of vectors $\{|a, \lambda, i\rangle, i = 1,..., d_\lambda\}$ generates an invariant subspace of $\mathscr{H}_A$ carrying an irreducible representation of S_N of type λ. Except for the trivial case of a one-dimensional space $\mathscr{H}_A$, this basis set is not uniquely determined. It can be chosen such that the vectors $|a, \lambda, i\rangle$ transform as

$$U_A(s)\,|a, \lambda, k\rangle = \sum_{i=1}^{d_\lambda} |a, \lambda, i\rangle\, d^\lambda_{i\,k}(s) \tag{2.1.19}$$

for all $s \in S_N$, $\lambda \in \Lambda_A$, and $a = 1,..., n_A^\lambda$. In this relation, $d^\lambda_{ik}(s)$, $s \in S_N$, $i, k = 1,..., d_\lambda$, denote the matrix elements of an irreducible representation of S_N of type λ chosen once and for all in the class of equivalence of the irreducible representations of S_N of this type. Such an irreducible representation is usually referred to as "standard representation" of type λ. In the case of the group S_N, this representation can be chosen such that the matrix elements $d^\lambda_{ik}(s)$ are real.[39] In order to avoid any confusion, we will nevertheless quote the group theoretical results in their general formulation without using this feature.

According to Eq. (2.1.15) the basis vectors associated with the representation U_A may be chosen to be simultaneously eigenvectors of H_A. For an explicit construction of the basis, we introduce the operators[40]

$$P^\lambda_{A\,ik} = \frac{d_\lambda}{N!} \sum_{s \in S_N} d^\lambda_{ik}(s)^\star\, U_A(s) \tag{2.1.20}$$

for $\lambda \in \Lambda_A$ and $i, k = 1,\ldots, d_\lambda$. For $i \neq k$ these operators are partially isometric, otherwise they are commuting orthogonal projectors providing a decomposition of the Hilbert space $\mathscr{H}_A$ into orthogonal subspaces (see also Fig. 1). From the theory of linear complex representations of finite groups the operators $P^{\lambda}_{A\,ik}$ are known to satisfy the relations

$$\begin{aligned} P^{\lambda\,\dagger}_{A\,ik} &= P^{\lambda}_{A\,ki}, \\ P^{\lambda}_{A\,ij} P^{\lambda'}_{A\,kl} &= \delta_{\lambda\lambda'} \delta_{jk} P^{\lambda}_{A\,il}. \end{aligned} \tag{2.1.21}$$

The operator

$$P^{\lambda}_{A} \equiv \sum_{i=1}^{d_\lambda} P^{\lambda}_{A\,ii} = \frac{d_\lambda}{N!} \sum_{s \in S_N} \chi_\lambda(s)^\star\, U_A(s) \tag{2.1.22}$$

is the projector of $\mathscr{H}_A$ onto its isotypic component of type λ. The symbol $\chi_\lambda(s)$ denotes the character of the irreducible representation of type λ, i.e.,

$$\chi_\lambda(s) = \sum_{i=1}^{d_\lambda} d^{\lambda}_{ii}(s). \tag{2.1.23}$$

According to Eq. (2.1.15) the operators $P^{\lambda}_{A\,ik}$ and H_A commute, i.e.,

$$[H_A, P^{\lambda}_{A\,ik}] = 0, \qquad \forall \lambda \in \Lambda_A \quad \text{and} \quad \forall i, k = 1,\ldots, d_\lambda. \tag{2.1.24}$$

From Eq. (2.1.19) it follows that

$$P^{\lambda}_{A\,ik}\, |a, \lambda, k\rangle = |a, \lambda, i\rangle. \tag{2.1.25}$$

Thus, starting from one of the eigenvectors of H_A with the eigenvalue E^{λ}_{a} associated with an irreducible representation of type λ, the other $d_\lambda - 1$ eigenvectors within the same subspace and with the same energy eigenvalue are obtained from

$$P^{\lambda}_{A\,k1}\, |a, \lambda, 1\rangle = |a, \lambda, k\rangle, \qquad \forall k. \tag{2.1.26}$$

They satisfy Eq. (2.1.19), as well as

$$H_A\, |a, \lambda, k\rangle = E^{\lambda}_{a}\, |a, \lambda, k\rangle, \qquad \forall k, \tag{2.1.27}$$

assuming the spectrum of the operator H_A to be discrete. The degeneracy of the eigenvalue E^{λ}_{a} is at least equal to d_λ.

The B subsystem is described in the same manner. The basis vectors of $\mathscr{H}_B$ are denoted $|b, \lambda, i\rangle$. The subset Λ_B

$$\Lambda_B = \{\lambda \in \Lambda \,|\, n_B^\lambda > 0\} \tag{2.1.28}$$

selects the type of irreducible representations of S_N carried by $\mathscr{H}_B$. The basis vectors $|b, \lambda, i\rangle$, $\lambda \in \Lambda_B$, with $i = 1,\ldots, d_\lambda$ and $b = 1,\ldots, n_B^\lambda$, satisfy the relations

$$U_B(s)\,|b, \lambda, k\rangle = \sum_{i=1}^{d_\lambda} |b, \lambda, i\rangle\, d^\lambda_{i\,k}(s), \qquad \forall s \in S_N \tag{2.1.29}$$

and

$$H_B\,|b, \lambda, k\rangle = E_b^\lambda\,|b, \lambda, k\rangle, \qquad \forall k. \tag{2.1.30}$$

The tensors

$$|a, \lambda, k\rangle \otimes |b, \mu, j\rangle \qquad \lambda \in \Lambda_A, \quad \mu \in \Lambda_B \tag{2.1.31}$$

form an orthonormal basis of the Hilbert space $\mathscr{H} = \mathscr{H}_A \otimes \mathscr{H}_B$. The fermionic character of the system implies that the physical states are described by antisymmetric tensors $|\psi\rangle \in \mathscr{H}_{A+B} \subset \mathscr{H}$, i.e.,

$$U(s)\,|\psi\rangle = \sigma(s)\,|\psi\rangle, \qquad \forall s \in S_N. \tag{2.1.32}$$

We therefore have to find the linear combinations of the basis vectors (2.1.31) obeying the antisymmetry condition (2.1.32) and thus belonging to the subspace $\mathscr{H}_{A+B}$. For fixed λ, a and μ, b a non-zero vector can only be obtained if and only if the irreducible antisymmetric representation (denoted $\rho = [1^N]$) has a non-zero multiplicity in the decomposition

$$D^{(\lambda)} \otimes D^{(\mu)} \sim \bigoplus_{\rho \in \Lambda} a_\rho D^{(\rho)}. \tag{2.1.33}$$

Due to the fact that the representation of type $[1^N]$ is one-dimensional, the tensor product with an irreducible representation of type λ is itself irreducible. Using the orthogonality relation for the characters of the irreducible representations[30–37] we get

$$a_{[1^N]} = \frac{1}{N!} \sum_{s \in S_N} \chi_{[1^N]}(s)^\star\, \chi_\lambda(s)\, \chi_\mu(s) = \begin{cases} 1 & \text{if} \quad \mu = \tilde{\lambda} \\ 0 & \text{otherwise.} \end{cases} \tag{2.1.34}$$

Here $\tilde{\lambda}$ stands for the type of representation that is dual with respect to λ. We recall that there is a one-to-one correspondence between the different Young diagrams specifying the partitions of the integer N, and the irreducible representations of the S_N group. The dual representation corresponds to the transposed Young diagram, which is obtained after exchanging lines and columns of the Young scheme associated with the reference representation. According to Eq. (2.1.34), the linear combination of tensors (2.1.31) with fixed $\lambda \in \Lambda_A$, a and $\mu \in \Lambda_B$, b carries a one-dimensional subspace satisfying the condition (2.1.32) if and only if $\tilde{\lambda} = \mu \in \Lambda_B$. In other words, only the non-zero linear combination

$$|a, b, \lambda\rangle \equiv \sum_{i,k=1}^{d_\lambda} c_{i\,k\,1}^{\lambda\,\tilde{\lambda}\,[1^N]} |a, \lambda, i\rangle \otimes |b, \tilde{\lambda}, k\rangle \tag{2.1.35}$$

describes a physical state and only one. In this expression $c_{i\,k\,1}^{\lambda\,\tilde{\lambda}\,[1^N]}$ stands for the Clebsch–Gordan coefficients associated with the isotypic components of $[1^N]$ type in the tensor product representation $D^{(\lambda)} \otimes D^{(\tilde{\lambda})}$. These coefficients can be supposed to be real since the standard irreducible representations are real. Note also that d_λ and $d_{\tilde{\lambda}}$ are always equal, and that the resulting vector $|a, b, \lambda\rangle$ is non-zero if and only if $\lambda \in \Lambda_{AB}$, with

$$\Lambda_{AB} = \{\lambda \mid \lambda \in \Lambda_A \text{ and } \tilde{\lambda} \in \Lambda_B\}. \tag{2.1.36}$$

Finally, it is easy to verify that the vectors $|a, b, \lambda\rangle$, $\lambda \in \Lambda_{AB}$, $a = 1,\ldots, n_A^\lambda$, and $b = 1,\ldots, n_B^{\tilde{\lambda}}$ constitute an orthonormalized basis set of the Hilbert space $\mathscr{H}_{A+B}$ describing the composed system $A+B$, i.e., we have

$$\langle a', b', \lambda' \mid a, b, \lambda\rangle = \delta_{a'a}\delta_{b'b}\delta_{\lambda'\lambda}. \tag{2.1.37}$$

We will also use the relation

$$\sum_{i,k=1}^{d_\lambda} c_{i\,k\,1}^{\lambda\,\tilde{\lambda}\,[1^N]\star} c_{i\,k\,1}^{\lambda\,\tilde{\lambda}\,[1^N]} = 1, \tag{2.1.38}$$

which follows from the fact that the Clebsch–Gordan coefficients are matrix elements of a unitary (orthogonal) transformation.

Following essentially the same procedure, we can also decompose the interaction Hamiltonian into a linear combination of tensor products of operators acting in $\mathscr{H}_A$ and $\mathscr{H}_B$. Let $\mathscr{L}(\mathscr{H}_A)$ be the vector space of the linear operators acting in $\mathscr{H}_A$ supplied with the Hilbert–Schmidt scalar product $\langle O_A \mid O'_A\rangle = \mathrm{Tr}(O_A^\dagger O'_A)$. Consider the linear mapping

$$\mathscr{U}_A(s)\colon \mathscr{L}(\mathscr{H}_A) \to \mathscr{L}(\mathscr{H}_A), \qquad s \in S_N \tag{2.1.39}$$

defined by the correspondence

$$\mathscr{L}(\mathscr{H}_A) \ni O_A \mapsto U_A(s)\, O_A U_A(s)^{-1}. \tag{2.1.40}$$

The operator $\mathscr{U}_A(s)$ is unitary relatively to the Hilbert–Schmidt scalar product in $\mathscr{L}(\mathscr{H}_A)$. The correspondence

$$S_N \ni s \mapsto \mathscr{U}_A(s) \tag{2.1.41}$$

yields a unitary representation of S_N in the space of linear operators acting in $\mathscr{L}(\mathscr{H}_A)$. We thus can choose an orthogonal basis in $\mathscr{L}(\mathscr{H}_A)$ associated to this last representation. Let $A^\lambda_{\alpha i}$, $\lambda \in \Lambda$, $i = 1,\ldots, d_\lambda$ and $\alpha = 1,\ldots, N^\lambda_A$ be the basis vectors, where N^λ_A stands for the multiplicity of the irreducible representation of type λ, and where the index λ labels representations with $N^\lambda_A > 0$. We define the corresponding subset

$$\Lambda^{\mathscr{L}}_A = \{\lambda \in \Lambda \mid N^\lambda_A > 0\}. \tag{2.1.42}$$

The $A^\lambda_{\alpha i}$ operators transform as irreducible tensor operators, i.e.,

$$\mathscr{U}_A(s)\, A^\lambda_{\alpha k} \equiv U_A(s)\, A^\lambda_{\alpha k} U_A(s)^{-1} = \sum_{i=1}^{d_\lambda} A^\lambda_{\alpha i} d^\lambda_{ik}(s), \qquad \forall s \in S_N. \tag{2.1.43}$$

The matrix elements $d^\lambda_{ik}(s)$ being real for $\forall s \in S_N$, the operators (basis vectors) $A^\lambda_{\alpha i}$ can be chosen to be self-adjoint operators. Thus we may assume

$$(A^\lambda_{\alpha i})^\dagger = A^\lambda_{\alpha i}. \tag{2.1.44}$$

The operators $A^\lambda_{\alpha i}$ form a basis of the isotypic component of type λ of $\mathscr{L}(\mathscr{H}_A)$ relatively to the representation $\mathscr{U}_A(s)$. In accordance with the expressions (2.1.20) and (2.1.22), the corresponding orthogonal projector $\mathscr{P}^\lambda_A$ of $\mathscr{L}(\mathscr{H}_A)$ onto the isotypic component $\mathscr{L}_\lambda(\mathscr{H}_A)$ of type λ is (see Fig. 2)

$$\mathscr{P}^\lambda_A = \sum_{i=1}^{d_\lambda} \mathscr{P}^\lambda_{A\,ii} \tag{2.1.45}$$

with

$$\mathscr{P}^\lambda_{A\,ii} = \frac{d_\lambda}{N!} \sum_{s \in S_N} d^\lambda_{ii}(s)^\star\, \mathscr{U}_A(s).$$

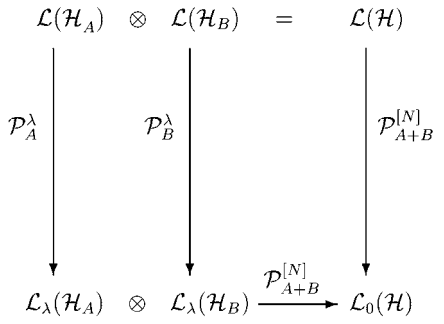

Fig. 2. The diverse subspaces of the space of linear operators $\mathscr{L}(\mathscr{H}) = \mathscr{L}(\mathscr{H}_A) \otimes \mathscr{L}(\mathscr{H}_B)$. The corresponding projection operators are defined by the expression (2.1.45) and its correspondents.

Similar notions can be introduced for the subsystem B as well as for the full system $A+B$. Let $\Lambda_B^{\mathscr{L}}$ be the analog of $\Lambda_A^{\mathscr{L}}$ for B. In the space of operators $\mathscr{L}(\mathscr{H}_B)$ we choose a basis of irreducible tensor operators $B_{\beta k}^\lambda$

$$B_{\beta k}^\lambda, \qquad \lambda \in \Lambda_B^{\mathscr{L}}, \quad \beta = 1,\ldots, N_B^\lambda, \quad k = 1,\ldots, d_\lambda. \tag{2.1.46}$$

Since

$$\mathscr{L}(\mathscr{H}_A \otimes \mathscr{H}_B) = \mathscr{L}(\mathscr{H}_A) \otimes \mathscr{L}(\mathscr{H}_B), \tag{2.1.47}$$

the tensor products $A_{\alpha k}^\lambda \otimes B_{\beta j}^\mu$, $\lambda \in \Lambda_A^{\mathscr{L}}$, $\mu \in \Lambda_B^{\mathscr{L}}$, etc., constitute an orthonormalized basis of linear operators acting in $\mathscr{H} = \mathscr{H}_A \otimes \mathscr{H}_B$. In consequence, the interaction Hamiltonian H_{int} in Eq. (2.1.14) can be decomposed in a linear combination of operators of the form $A_{\alpha k}^\lambda \otimes B_{\beta j}^\mu$. We thus have to determine the non-trivial linear combinations for which the condition (2.1.17) is satisfied. Note that this condition is equivalent to the affirmation that H_{int} is an operator of trivial type $[N]$ for the representation

$$\mathscr{U}(s) \equiv \mathscr{U}_A(s) \otimes \mathscr{U}_B(s) \tag{2.1.48}$$

of S_N in $\mathscr{L}(\mathscr{H})$. The symbol $[N]$ corresponds to a row of N boxes in the graphical representation by Young diagrams.

Considering the linear combinations of vectors $A_{\alpha k}^\lambda \otimes B_{\beta j}^\mu$ with λ, α and μ, β fixed, it is obvious that the condition (2.1.17) is satisfied if and only if the irreducible representation of trivial type $[N]$ appears with a non-zero multiplicity in the decomposition

$$D^{(\lambda)} \otimes D^{(\mu)} \sim \bigoplus_{\rho \in \Lambda} a_\rho D^{(\rho)}, \tag{2.1.49}$$

or in other words, if $a_{[N]} > 0$. Since the characters $\chi_\lambda(s)$ (2.1.23) of the irreducible representations are always real and since also $\chi_{[N]}(s) = 1$, $\forall s \in S_N$, the orthogonality relations for the characters of the irreducible representations[41] imply that

$$a_{[N]} = \frac{1}{N!} \sum_{s \in S_N} \chi_{[N]}(s)^\star \, \chi_\lambda(s) \, \chi_\mu(s) = \delta_{\lambda\mu}. \tag{2.1.50}$$

The linear combination corresponding to the decomposition is unique. It follows that the interaction Hamiltonian H_{int} can always be written as a linear combination of the operators

$$H^\lambda_{\alpha\beta} = \sum_{k,j=1}^{d_\lambda} c^{\lambda\,\lambda\,[N]}_{k\,j\,1} A^\lambda_{\alpha k} \otimes B^\lambda_{\beta j} \tag{2.1.51}$$

with

$$\lambda \in \Lambda^{\mathscr{L}}_A \cap \Lambda^{\mathscr{L}}_B \equiv \Lambda^{\mathscr{L}}_{AB}. \tag{2.1.52}$$

We further note that

$$c^{\lambda\,\lambda\,[N]}_{k\,j\,1} = \frac{1}{\sqrt{d_\lambda}} \delta_{kj}. \tag{2.1.53}$$

The operators $H^\lambda_{\alpha\beta}$ are self-adjoint. It can easily be verified that they constitute an orthogonal basis for the isotypic component of trivial type of $\mathscr{L}(\mathscr{H})$ for the representation $\mathscr{U}(s)$, $\forall s \in S_N$, which is denoted $\mathscr{L}_o(\mathscr{H})$. Thus we have

$$\mathscr{U}(s) \, H^\lambda_{\alpha\beta} \equiv U(s) \, H^\lambda_{\alpha\beta} U(s)^{-1} = H^\lambda_{\alpha\beta}, \tag{2.1.54}$$

$$(H^\lambda_{\alpha\beta})^\dagger = H^\lambda_{\alpha\beta}, \tag{2.1.55}$$

and the most general form of the interaction Hamiltonian H_{int} can be written

$$H_{\text{int}} = \sum_{\lambda \in \Lambda^{\mathscr{L}}_{AB}} \sum_{\alpha=1}^{N^\lambda_A} \sum_{\beta=1}^{N^\lambda_B} g^\lambda_{\alpha\beta} H^\lambda_{\alpha\beta} \tag{2.1.56}$$

with $g^\lambda_{\alpha\beta} \in \mathbb{R}$.

2.2. Density Matrix and Partial Trace Operations

We are now prepared to describe the physical system under consideration. Let us first note that the corresponding density matrix is an operator ρ acting on $\mathscr{H}$, which belongs to the trivial isotypic component $\mathscr{L}_o(\mathscr{H})$ of the space of linear operators $\mathscr{L}(\mathscr{H})$, i.e., it remains unchanged under the action of S_N generated by the unitary representation $\mathscr{U} = \mathscr{U}_A \otimes \mathscr{U}_B$. More precisely, the operator ρ satisfies the conditions

$$\rho^\dagger = \rho \qquad \rho^2 \leqslant \rho \qquad \mathrm{Tr}(\rho) = 1 \tag{2.2.1}$$

and

$$[U(s), \rho] = 0, \qquad \forall s \in S_N. \tag{2.2.2}$$

Accordingly, ρ commutes with the projectors

$$P^\lambda = \frac{d_\lambda}{N!} \sum_{s \in S_N} \chi_\lambda(s)^\star U(s), \qquad \lambda \in \Lambda \tag{2.2.3}$$

of the Hilbert space $\mathscr{H}$ onto its isotypic components with respect to the action of S_N on $\mathscr{H}$ provided by the unitary representation U. Thus, the isotypic components are stable under the action of the density matrix ρ. This holds in particular for the isotypic component of the type $\lambda = [1^N]$, which corresponds to the Hilbert space describing the physical system $A+B$. In fact, taking into account the definition of the density matrix, the operator ρ acts non-trivially only on $\mathscr{H}_{A+B}$, i.e.,

$$P^\lambda \rho = \rho P^\lambda = \begin{cases} \rho & \text{if} \quad \lambda = [1^N], \\ 0 & \text{otherwise.} \end{cases} \tag{2.2.4}$$

As a direct consequence of the previous considerations, the mean value of an observable characterized by a self-adjoint operator O satisfying the condition (2.1.11) is given by the trace operation

$$\langle O \rangle = \mathrm{Tr}(\rho O) \tag{2.2.5}$$

performed on the whole space $\mathscr{H}$ or restricted to $\mathscr{H}_{A+B}$.

For our present purposes we still need a statistical description of the subsystems. This can be obtained by a natural generalization of the above relation using a so-called "partial trace operation." We consider an observable of the subsystem A. It is characterized by a self-adjoint operator

O_A that commutes with the unitary representation U_A of S_N in the Hilbert space $\mathscr{H}_A$,

$$[O_A, U_A(s)] = 0, \qquad \forall s \in S_N.$$

These commutation relations impose important restrictions on the values of the matrix elements of the operator O_A taken between the basis vectors $|a, \lambda, i\rangle$. Actually, the operator O_A commutes with the operators $P^{\lambda}_{A\,ik}$ defined by Eq. (2.1.20), i.e.,

$$[O_A, P^{\lambda}_{A\,ik}] = 0, \qquad \forall \lambda \in \Lambda_A \quad \text{and} \quad \forall i, k = 1,\ldots, d_\lambda. \tag{2.2.6}$$

From Eq. (2.1.25) it follows that $P^{\lambda}_{A\,ik}$ may be used to generate the basis vectors of $\mathscr{H}_A$. One can easily show that the matrix elements $\langle a', \lambda', i'| O_A |a, \lambda, i\rangle$ vanish for $\lambda \neq \lambda'$ or for $i \neq i'$, and that the values of the matrix elements $\langle a', \lambda, i| O_A |a, \lambda, i\rangle$ do not depend on the index $i = 1,\ldots, d_\lambda$. This may be expressed formally as

$$\langle a', \lambda', i'| O_A |a, \lambda, i\rangle = \delta_{\lambda'\lambda}\delta_{i'i}\langle a', \lambda, i_o| O_A |a, \lambda, i_o\rangle, \tag{2.2.7}$$

where i_o denotes an arbitrary integer $i_o = 1,\ldots, d_\lambda$. In the following we assume $i_o = 1$. In order to prove Eq. (2.2.7) we use Eqs. (2.1.21) and (2.1.26), from which we get

$$\begin{aligned}
\langle a', \lambda', i'| O_A |a, \lambda, i\rangle &= \langle a', \lambda', 1| P^{\lambda'}_{A\,1i'} O_A P^{\lambda}_{A\,i1} |a, \lambda, 1\rangle \\
&= \langle a', \lambda', 1| P^{\lambda'}_{A\,1i'} P^{\lambda}_{A\,i1} O_A |a, \lambda, 1\rangle \\
&= \delta_{\lambda'\lambda}\delta_{i'i}\langle a', \lambda, 1| P^{\lambda}_{A\,11} O_A |a, \lambda, 1\rangle \\
&= \delta_{\lambda'\lambda}\delta_{i'i}\langle a', \lambda, 1| O_A |a, \lambda, 1\rangle.
\end{aligned}$$

Adopting the notation $|a, \lambda\rangle \equiv |a, \lambda, 1\rangle$, we have

$$O_A |a, \lambda, i\rangle = \sum_{a'=1}^{n^{\lambda}_A} |a', \lambda, i\rangle\langle a', \lambda| O_A |a, \lambda\rangle, \tag{2.2.8}$$

and consequently, with Eq. (2.1.35),

$$(O_A \otimes \mathbb{1}_B)\,|a, b, \lambda\rangle = \sum_{a'=1}^{n^{\lambda}_A} |a', b, \lambda\rangle\langle a', \lambda| O_A |a, \lambda\rangle. \tag{2.2.9}$$

Following the same arguments, we get a similar relation for the operators O_B commuting with the unitary representation U_B of S_N in the Hilbert space $\mathscr{H}_B$,

$$(\mathbb{1}_A \otimes O_B)\,|a, b, \lambda\rangle = \sum_{b'=1}^{n_B^{\tilde{\lambda}}} |a, b', \lambda\rangle\langle b', \tilde{\lambda}|\, O_B\, |b, \tilde{\lambda}\rangle. \tag{2.2.10}$$

The mean value of an observable in the subsystem A defined by a self-adjoint operator O_A is obtained from a "partial trace" operation. Using Eq. (2.2.9), one gets

$$\begin{aligned}\langle O_A\rangle &= \mathrm{Tr}(\rho(O_A \otimes \mathbb{1}_B)) \\ &= \sum_{\lambda \in \Lambda_{AB}} \sum_{a=1}^{n_A^{\lambda}} \sum_{b=1}^{n_B^{\tilde{\lambda}}} \langle a, b, \lambda|\, \rho(O_A \otimes \mathbb{1}_B)\, |a, b, \lambda\rangle \\ &= \sum_{\lambda \in \Lambda_{AB}} \sum_{a=1}^{n_A^{\lambda}} \sum_{a'=1}^{n_A^{\lambda}} \rho^{\lambda}_{A\, aa'} \langle a', \lambda|\, O_A\, |a, \lambda\rangle\end{aligned}$$

with

$$\rho^{\lambda}_{A\, aa'} = \sum_{b=1}^{n_B^{\tilde{\lambda}}} \langle a, b, \lambda|\, \rho\, |a', b, \lambda\rangle. \tag{2.2.11}$$

In order to write the partial trace operation in a more compact form, it is convenient to introduce some further definitions. First we define the subspaces of $\mathscr{H}_A$ generated by the vectors $|a, \lambda\rangle \equiv |a, \lambda, 1\rangle$, $\lambda \in \Lambda_A$. The subspace generated by the vectors $|a, \lambda\rangle$ for fixed λ will be denoted $\bar{\mathscr{H}}_A^{\lambda}$, and the one generated by the full ensemble of vectors by $\bar{\mathscr{H}}_A$, i.e., we have

$$\bar{\mathscr{H}}_A^{\lambda} = P^{\lambda}_{A\,11}\mathscr{H}_A \qquad \text{and} \qquad \bar{\mathscr{H}}_A = \bigoplus_{\lambda} \bar{\mathscr{H}}_A^{\lambda}. \tag{2.2.12}$$

Next, we introduce the operator Tr_B, which describes the linear mapping

$$\mathrm{Tr}_B\colon \mathscr{L}_o(\mathscr{H}) \mapsto \mathscr{L}(\bar{\mathscr{H}}_A) \tag{2.2.13}$$

defined by

$$\langle a', \lambda'|\, \mathrm{Tr}_B(O)\, |a, \lambda\rangle = \delta_{\lambda'\lambda} O^{\lambda}_{A\, a'a} \tag{2.2.14}$$

with

$$O^{\lambda}_{A\, a'a} = \sum_{b=1}^{n_B^{\tilde{\lambda}}} \langle a', b, \lambda|\, O\, |a, b, \lambda\rangle, \tag{2.2.15}$$

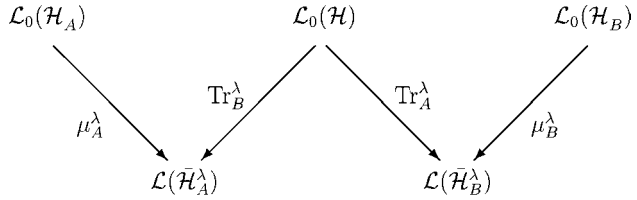

Fig. 3. Mapping relations for the trivial isotypic components of the spaces of linear operators acting in $\mathscr{H}$, $\mathscr{H}_A$, and $\mathscr{H}_B$. The mappings are defined by the relations (2.2.16), (2.2.22), and their correspondents.

where $O \in \mathscr{L}_o(\mathscr{H})$, $\lambda \in \Lambda_{AB}$, and a', $a = 1,\ldots, n_A^\lambda$. For later purposes, we also introduce three further linear mappings. The first mapping (see Fig. 3)

$$\mathrm{Tr}_B^\lambda \colon \mathscr{L}_o(\mathscr{H}) \mapsto \mathscr{L}(\bar{\mathscr{H}}_A^\lambda) \tag{2.2.16}$$

is defined by

$$\langle a', \lambda |\, \mathrm{Tr}_B^\lambda(O)\, | a, \lambda \rangle = O^\lambda_{A\, a'a}. \tag{2.2.17}$$

The second mapping from the trivial isotypic component of $\mathscr{L}(\mathscr{H}_A)$ into $\mathscr{L}(\bar{\mathscr{H}}_A)$

$$\mu_A \colon \mathscr{L}_o(\mathscr{H}_A) \mapsto \mathscr{L}(\bar{\mathscr{H}}_A) \tag{2.2.18}$$

is given by

$$\mu_A \colon \mathscr{L}_o(\mathscr{H}_A) \ni O_A \mapsto P_{A\,11} O_A P_{A\,11} \in \mathscr{L}(\bar{\mathscr{H}}_A), \tag{2.2.19}$$

where $P_{A\,11}$ denotes the projector of $\mathscr{H}_A$ onto $\bar{\mathscr{H}}_A$

$$P_{A\,11} = \sum_{\lambda \in \Lambda_A} P^\lambda_{A\,11}. \tag{2.2.20}$$

Finally, the third mapping

$$\mu_A^\lambda \colon \mathscr{L}_o(\mathscr{H}_A) \mapsto \mathscr{L}(\bar{\mathscr{H}}_A^\lambda) \tag{2.2.21}$$

is defined by (see Fig. 3)

$$\mu_A^\lambda \colon \mathscr{L}_o(\mathscr{H}_A) \ni O_A \mapsto P^\lambda_{A\,11} O_A P^\lambda_{A\,11} \in \mathscr{L}(\bar{\mathscr{H}}_A^\lambda). \tag{2.2.22}$$

Obviously, the mappings μ_A and μ_A^λ are homomorphisms of algebra, i.e., for any O_A, $O'_A \in \mathscr{L}_o(\mathscr{H}_A)$ they satisfy the relations

$$\begin{aligned} \mu_A(O_A O'_A) &= \mu_A(O_A)\, \mu_A(O'_A), \\ \mu_A(\alpha O_A + \alpha' O'_A) &= \alpha \mu_A(O_A) + \alpha' \mu_A(O'_A) \end{aligned} \tag{2.2.23}$$

and

$$\mu_A^\lambda(O_A O'_A) = \mu_A^\lambda(O_A)\,\mu_A^\lambda(O'_A),$$
$$\mu_A^\lambda(\alpha O_A + \alpha' O'_A) = \alpha\mu_A^\lambda(O_A) + \alpha'\mu_A^\lambda(O'_A) \tag{2.2.24}$$

for every $\lambda \in \Lambda_A$ and for arbitrary coefficients α, α'. In fact, the mapping μ_A corresponds to an isomorphism between $\mathscr{L}_o(\mathscr{H}_A)$ and $\mathscr{L}(\bar{\mathscr{H}}_A)$, i.e., there exists a one-to-one correspondence between operators O_A in $\mathscr{L}_o(\mathscr{H}_A)$ and the associated operators $\bigoplus_\lambda \mu_A^\lambda(O_A)$ in $\mathscr{L}(\bar{\mathscr{H}}_A)$. This follows immediately from Eq. (2.2.7), which shows that the matrix corresponding to an operator $O_A \in \mathscr{L}_o(\mathscr{H}_A)$ is block-diagonal with respect to the index λ denoting the types of the representations. In addition, the blocks associated with different types λ are themselves block-diagonal, where the d_λ subblocks labeled by $i = 1,\ldots, d_\lambda$ are all identically the same. Then, each subblock of type λ in $\mathscr{L}_o(\mathscr{H}_A)$ associated with the operator O_A, which is well defined since the transformation $U_A(s)$, $s \in S_N$ leaves the subspaces $\mathscr{H}_A^\lambda$ unchanged, is associated with one and only one subblock with indices λ and $i = 1$ in $\mathscr{L}(\bar{\mathscr{H}}_A)$. For each irreducible representation of type λ we have thus an isomorphism between $\mathscr{L}_o(\mathscr{H}_A^\lambda)$ and $\mathscr{L}(\bar{\mathscr{H}}_A^\lambda)$, and consequently also between $\mathscr{L}_o(\mathscr{H}_A)$ and $\mathscr{L}(\bar{\mathscr{H}}_A)$.

The above definitions allow us to keep the mathematical formalism on a concise level. In particular, the mean values of observables, which are characterized by the self-adjoint operators O_A, become

$$\langle O_A \rangle = \mathrm{Tr}(\bar{\rho}_A \bar{O}_A) \tag{2.2.25}$$

where

$$\bar{\rho}_A = \mathrm{Tr}_B(\rho) \tag{2.2.26}$$

and

$$\bar{O}_A = \mu_A(O_A). \tag{2.2.27}$$

Corresponding relations hold for the subsystem B.

We note that the operator $\bar{\rho}_A$ possesses all the mathematical properties required for a density matrix, i.e.,

$$\bar{\rho}_A^\dagger = \bar{\rho}_A \qquad \mathrm{Tr}(\bar{\rho}_A) = 1 \qquad \bar{\rho}_A^2 \leqslant \bar{\rho}_A. \tag{2.2.28}$$

The first two properties follow immediately from the definition of $\bar{\rho}_A$. Here we will prove the third relation usually referred to as positivity condition, which may also be expressed as $\langle\psi|\,\bar{\rho}_A^2\,|\psi\rangle \leqslant \langle\psi|\,\bar{\rho}_A\,|\psi\rangle$, $\forall|\psi\rangle \in \bar{\mathscr{H}}_A$. With

$$\begin{aligned}\langle\psi|\,\bar{\rho}_A^2\,|\psi\rangle &= \sum_{\lambda}\sum_{a=1}^{n_A^\lambda}\langle\psi|\,\bar{\rho}_A\,|a,\lambda\rangle\langle a,\lambda|\,\bar{\rho}_A\,|\psi\rangle \\ &= \sum_{\lambda}\sum_{a=1}^{n_A^\lambda}|\langle a,\lambda|\,\bar{\rho}_A\,|\psi\rangle|^2 \\ &\leqslant \langle\psi|\,\bar{\rho}_A\,|\psi\rangle\sum_{\lambda}\sum_{a=1}^{n_A^\lambda}\langle a,\lambda|\,\bar{\rho}_A\,|a,\lambda\rangle \\ &= \langle\psi|\,\bar{\rho}_A\,|\psi\rangle, \end{aligned} \tag{2.2.29}$$

where the last two lines are obtained from the Schwarz inequality and from the second property in Eq. (2.2.28), respectively, we prove the desired property.

The partial traces (2.2.13), (2.2.14), and (2.2.15) generalize the partial trace operations employed in the standard quantum statistical approach. Applied to the density matrix ρ they provide the statistical state of the subsystem associated with the internal degrees of freedom of our fermionic system. In contrast with the standard situation, where the reduction associated with the partial trace operation corresponds to the reduction $\mathscr{L}(\mathscr{H}) \mapsto \mathscr{L}(\mathscr{H}_A)$, we have presently a reduction of $\mathscr{L}_o(\mathscr{H})$ onto the subspace $\mathscr{L}(\bar{\mathscr{H}}_A)$, where $\bar{\mathscr{H}}_A$ is strictly included in $\mathscr{H}_A$. This generalization with respect to the standard case is a consequence of the indistinguishability of the particles forming the system $A+B$. It implies the use of a more elaborate mathematical scheme. In the following we will show that the standard approach of quantum statistics can be generalized to cope with this situation.

2.3. Statistically Uncorrelated Subsystems

In spite of the fact that quantum correlations are unavoidable for fermionic systems, it is appropriate to consider first statistically uncorrelated subsystems A and B. This corresponds to the assumption that the density matrix ρ describing the statistical state of the system takes the form of a tensor product

$$\rho = \rho_A \otimes \rho_B, \tag{2.3.1}$$

where $\rho_A \in \mathscr{L}_o(\mathscr{H}_A)$ and $\rho_B \in \mathscr{L}_o(\mathscr{H}_B)$ are self-adjoint positive operators satisfying the commutation relations

$$[\rho_A, U_A(s)] = 0 \quad \text{and} \quad [\rho_B, U_B(s)] = 0, \qquad \forall s \in S_N. \tag{2.3.2}$$

It should be noted that the above form of the density matrix is preserved during its evolution when the subsystems A and B are not dynamically coupled, that is to say when $H_{\text{int}} \equiv 0$ in Eq. (2.1.14). The above definition is also conform with the theory of the canonical ensemble, since for $H_{\text{int}} \equiv 0$ we have

$$\rho = \frac{1}{Z_A} e^{-H_A/k_B T} \otimes \frac{1}{Z_B} e^{-H_B/k_B T}$$

with $Z_A = \text{Tr}(e^{-H_A/k_B T})$ and $Z_B = \text{Tr}(e^{-H_B/k_B T})$, and where T is the system temperature and k_B denotes the Boltzmann constant. The partial trace $\text{Tr}_B(\rho)$ of the density matrix (2.3.1) can be easily calculated. From the definitions (2.2.14), (2.2.15) and the relations (2.2.9), (2.2.10) we obtain

$$\begin{aligned}
&\langle a', \lambda' | \, \text{Tr}_B(O_A \otimes O_B) \, | a, \lambda \rangle \\
&\quad = \delta_{\lambda'\lambda} \sum_{b=1}^{n_B^{\tilde{\lambda}}} \sum_{a''=1}^{n_A^{\lambda}} \sum_{b''=1}^{n_B^{\tilde{\lambda}}} \langle a', b, \lambda \, | \, a'', b'', \lambda \rangle \langle a'', \lambda | \, O_A \, | a, \lambda \rangle \langle b'', \tilde{\lambda} | \, O_B \, | b, \tilde{\lambda} \rangle \\
&\quad = \delta_{\lambda'\lambda} \langle a', \lambda | \, O_A \, | a, \lambda \rangle \sum_{b=1}^{n_B^{\tilde{\lambda}}} \langle b, \tilde{\lambda} | \, O_B \, | b, \tilde{\lambda} \rangle \\
&\qquad (\equiv \delta_{\lambda'\lambda} \langle a', \lambda | \, \text{Tr}_B^{\lambda}(O_A \otimes O_B) \, | a, \lambda \rangle).
\end{aligned}$$

This can be summarized as

$$\bar{O}_A^{\lambda} \equiv \text{Tr}_B^{\lambda}(O_A \otimes O_B) = \mu_A^{\lambda}(O_A) \, \text{Tr}(\mu_B^{\tilde{\lambda}}(O_B)). \tag{2.3.3}$$

Exchanging the role of subsystems A and B we obtain similarly

$$\bar{O}_B^{\tilde{\lambda}} \equiv \text{Tr}_A^{\tilde{\lambda}}(O_A \otimes O_B) = \text{Tr}(\mu_A^{\lambda}(O_A)) \, \mu_B^{\tilde{\lambda}}(O_B). \tag{2.3.4}$$

For the particular choice $O_A = \rho_A$ and $O_B = \rho_B$, the last two equations become

$$\bar{\rho}_A^{\lambda} \equiv \text{Tr}_B^{\lambda}(\rho_A \otimes \rho_B) = \mu_A^{\lambda}(\rho_A) \, \text{Tr}(\mu_B^{\tilde{\lambda}}(\rho_B)) \tag{2.3.5}$$

and

$$\bar{\rho}_B^{\tilde{\lambda}} \equiv \text{Tr}_A^{\tilde{\lambda}}(\rho_A \otimes \rho_B) = \mu_B^{\tilde{\lambda}}(\rho_B) \, \text{Tr}(\mu_A^{\lambda}(\rho_A)). \tag{2.3.6}$$

2.4. Statistically Correlated Subsystems

Even in the case of statistically correlated subsystems A and B, we may still try to decompose the full density matrix ρ into parts associated with the subsystems A and B. We first note that any density matrix ρ can be decomposed as

$$\rho = \rho_A \otimes \rho_B + \eta_{AB}. \tag{2.4.1}$$

This decomposition is of course not unique. In order to get rid of this ambiguity, we will impose further conditions on ρ_A, ρ_B, and η_{AB}. Motivated by the preceding description of uncorrelated systems, we attempt the choice

$$\mathrm{Tr}_B^{\lambda}(\rho) = \mu_A^{\lambda}(\rho_A)\,\mathrm{Tr}(\mu_B^{\tilde{\lambda}}(\rho_B)), \tag{2.4.2}$$

$$\mathrm{Tr}_A^{\tilde{\lambda}}(\rho) = \mathrm{Tr}(\mu_A^{\lambda}(\rho_A))\,\mu_B^{\tilde{\lambda}}(\rho_B), \tag{2.4.3}$$

and

$$\mathrm{Tr}_B^{\lambda}(\eta_{AB}) = 0 \qquad \text{and} \qquad \mathrm{Tr}_A^{\tilde{\lambda}}(\eta_{AB}) = 0, \tag{2.4.4}$$

with $\rho_A \in \mathscr{L}_o(\mathscr{H}_A)$ and $\rho_B \in \mathscr{L}_o(\mathscr{H}_B)$ and for every $\lambda \in \Lambda_{AB}$.

In order to prove the existence of the above decomposition, we first define

$$p_{\lambda} = \mathrm{Tr}(\mathrm{Tr}_B^{\lambda}(\rho)) \equiv \mathrm{Tr}(\mathrm{Tr}_A^{\tilde{\lambda}}(\rho)), \tag{2.4.5}$$

where $0 \leqslant p_{\lambda} \leqslant 1$ is the probability of occurrence of the physical property corresponding to λ. Exploiting the isomorphism between $\mathscr{L}_o(\mathscr{H}_A^{\lambda})$ $(\mathscr{L}_o(\mathscr{H}_B^{\lambda}))$ and $\mathscr{L}(\overline{\mathscr{H}}_A^{\lambda})$ $(\mathscr{L}(\overline{\mathscr{H}}_B^{\lambda}))$, we can choose ρ_A (ρ_B) such that

$$\mathrm{Tr}_B^{\lambda}(\rho) = a_{\lambda}\mu_A^{\lambda}(\rho_A), \qquad \forall \lambda \in \Lambda_{AB} \tag{2.4.6}$$

$$\mathrm{Tr}_A^{\tilde{\lambda}}(\rho) = b_{\tilde{\lambda}}\mu_B^{\tilde{\lambda}}(\rho_B), \qquad \forall \lambda \in \Lambda_{AB} \tag{2.4.7}$$

for arbitrary positive real numbers a_{λ}, $b_{\tilde{\lambda}}$. Tracing the above equations (2.4.6), (2.4.7) and using the definition (2.4.5), we find

$$a_{\lambda} = \frac{p_{\lambda}}{\mathrm{Tr}(\mu_A^{\lambda}(\rho_A))}, \qquad b_{\tilde{\lambda}} = \frac{p_{\lambda}}{\mathrm{Tr}(\mu_B^{\tilde{\lambda}}(\rho_B))}.$$

Imposing now

$$a_{\lambda}b_{\tilde{\lambda}} = p_{\lambda} \qquad \text{with} \quad a_{\lambda} > 0, \quad b_{\tilde{\lambda}} > 0,$$

we get that Eqs. (2.4.6), (2.4.7) and Eqs. (2.4.2), (2.4.3) become identically the same. Then Eqs. (2.4.4) are also satisfied. In fact, using Eqs. (2.3.3) and (2.4.6) we get

$$\mathrm{Tr}_B^{\lambda}(\eta_{AB}) = \mathrm{Tr}_B^{\lambda}(\rho - \rho_A \otimes \rho_B) = \mathrm{Tr}_B^{\lambda}(\rho) - \frac{a_\lambda \, \mathrm{Tr}_B^{\lambda}(\rho)}{a_\lambda} = 0,$$

and similarly from Eqs. (2.3.4) and (2.4.7)

$$\mathrm{Tr}_A^{\tilde{\lambda}}(\eta_{AB}) = \mathrm{Tr}_A^{\tilde{\lambda}}(\rho - \rho_A \otimes \rho_B) = \mathrm{Tr}_A^{\tilde{\lambda}}(\rho) - \frac{b_{\tilde{\lambda}} \, \mathrm{Tr}_A^{\tilde{\lambda}}(\rho)}{b_{\tilde{\lambda}}} = 0,$$

which proves that the decomposition described by Eqs. (2.4.1)–(2.4.4) is always possible.

2.5. Interaction Picture

The time dependence of a density matrix ρ describing the evolution of the system $A+B$ in the Schrödinger picture is given by

$$\rho(t) = e^{-iHt/\hbar} \rho(0) \, e^{iHt/\hbar}, \tag{2.5.1}$$

where the Hamiltonian H has been defined in Eq. (2.1.14). In the interaction picture the density matrix reads

$$\rho^I(t) = e^{iH_0 t/\hbar} \rho(t) \, e^{-iH_0 t/\hbar}, \tag{2.5.2}$$

where H_0 is the free Hamiltonian

$$H_0 = H_A \otimes \mathbb{1}_B + \mathbb{1}_A \otimes H_B.$$

The evolution of the density matrix in the interaction picture is obtained by taking the derivative of the relation (2.5.2) with respect to the time and using Eq. (2.5.1). We then get

$$\frac{d}{dt} \rho^I(t) = \frac{i}{\hbar} [\rho^I(t), H_{\mathrm{int}}^I(t)], \tag{2.5.3}$$

where $H_{\mathrm{int}}^I(t)$ describes the interaction in the interaction picture

$$H_{\mathrm{int}}^I(t) = e^{iH_0 t/\hbar} H_{\mathrm{int}} e^{-iH_0 t/\hbar}. \tag{2.5.4}$$

For the following it is useful to introduce $\mathrm{Tr}_B(\rho^I(t)) \in \mathscr{L}(\bar{\mathscr{H}}_A)$ and $\mathrm{Tr}_B^{\lambda}(\rho^I(t)) \in \mathscr{L}(\bar{\mathscr{H}}_A^{\lambda})$. According to Eqs. (2.2.14) and (2.2.17) we have

$$\begin{aligned}\langle a', \lambda'| \mathrm{Tr}_B(\rho^I(t))\, |a'', \lambda''\rangle &= \delta_{\lambda'\lambda''} \langle a', \lambda'| \mathrm{Tr}_B^{\lambda'}(\rho^I(t))\, |a'', \lambda'\rangle \\ &= \delta_{\lambda'\lambda''} \sum_{b=1}^{n_B^{\lambda}} \langle a', b, \lambda'|\, \rho^I(t)\, |a'', b, \lambda'\rangle \\ &= \delta_{\lambda'\lambda''} \sum_{b=1}^{n_B^{\lambda}} \langle a', b, \lambda'|\, e^{iH_0 t/\hbar} \rho(t)\, e^{-iH_0 t/\hbar}\, |a'', b, \lambda'\rangle.\end{aligned}$$

From Eqs. (2.1.27), (2.1.30), and (2.1.35) we get

$$e^{-iH_0 t/\hbar}\, |a, b, \lambda\rangle = e^{-i(E_a^{\lambda} + E_b^{\tilde{\lambda}})\, t/\hbar}\, |a, b, \lambda\rangle,$$

and consequently

$$\langle a', \lambda'| \mathrm{Tr}_B(\rho^I(t))\, |a'', \lambda''\rangle = e^{iE_{a'}^{\lambda'} t/\hbar} \langle a', \lambda'| \mathrm{Tr}_B(\rho(t))\, |a'', \lambda''\rangle\, e^{-iE_{a''}^{\lambda''} t/\hbar}.$$

Defining $\bar{H}_A$ as the self-adjoint operator $\mu_A(H_A)$ acting in $\bar{\mathscr{H}}_A$ we have

$$\bar{H}_A\, |a, \lambda\rangle = E_a^{\lambda}\, |a, \lambda\rangle, \tag{2.5.5}$$

and finally

$$\mathrm{Tr}_B(\rho^I(t)) = e^{i\bar{H}_A t/\hbar}\, \mathrm{Tr}_B(\rho(t))\, e^{-i\bar{H}_A t/\hbar}, \tag{2.5.6}$$

or equivalently,

$$\bar{\rho}_A^I(t) = e^{i\bar{H}_A t/\hbar} \bar{\rho}_A(t)\, e^{-i\bar{H}_A t/\hbar}. \tag{2.5.7}$$

Thus the transformation from the Schrödinger picture to the interaction picture commutes with the partial trace operation Tr_B. The same holds also for the partial trace Tr_A as well as for Tr_B^{λ} and $\mathrm{Tr}_A^{\tilde{\lambda}}$.

2.6. Statistical Evolution of the Subsystems *A* and *B* for Weak Dynamical Coupling and Weak Statistical Correlation

We will now investigate the time evolution of the density matrix, or more precisely of $\mathrm{Tr}_B^{\lambda}(\rho(t))$ or $\mathrm{Tr}_A^{\tilde{\lambda}}(\rho(t))$, assuming that the dynamical coupling H_{int} (see Eq. (2.1.14)) between the subsystems A and B is weak and that the mutual statistical correlation given by η_{AB} (see Eq. (2.4.1)) remains small during the considered time interval. Under these conditions we can describe the variation $\mathrm{Tr}_B^{\lambda}(\rho(t) - \rho(t_0))$ within second-order perturbation theory. We note that a first-order approach would lead to a

rather trivial result, since in this case the most relevant contributions to the energy transfer between the subsystems would be suppressed. The proposed second-order approach is of course only valid for sufficiently small $\Delta t = t - t_0$. Actually, we will determine the reliable time interval from the dynamical properties of the subsystems A and B, in agreement with the hypothesis of weak dynamical coupling. This point will be discussed later in more detail.

The hypothesis of weak statistical correlations between the subsystems A and B relies partly on their presupposed weak dynamical coupling. In fact, our approach is based on the hypothesis that the statistical correlation between both subsystems is caused solely by their mutual dynamical interaction. The correlation η_{AB} is supposed to be of first order with respect to the dynamical interaction H_{int}. More precisely, we postulate the existence of a past time t_{00} with $t_{00} < t_0 \leqslant t$, at which the two considered subsystems were statistically uncorrelated. We then assume that the initially uncorrelated subsystems start to interact dynamically at time t_{00}.

Integration of Eq. (2.5.3) from t_0 to $t = t_0 + \Delta t$ yields

$$\rho^I(t) = \rho^I(t_0) + \frac{i}{\hbar}\int_{t_0}^{t} dt' [\rho^I(t'), H^I_{\text{int}}(t')]. \tag{2.6.1}$$

This equation can be solved by an iteration procedure. Replacing successively $\rho^I(t')$ on the right-hand side by the above expression (2.6.1), we obtain

$$\rho^I(t) = \rho^I(t_0) + \frac{i}{\hbar}\int_{t_0}^{t} dt' [\rho^I(t_0), H^I_{\text{int}}(t')] + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' [[\rho^I(t_0), H^I_{\text{int}}(t'')], H^I_{\text{int}}(t')] + \cdots, \tag{2.6.2}$$

which relates $\rho^I(t)$ to the initial density matrix $\rho^I(t_0)$. The density matrix $\text{Tr}^{\lambda}_B(\rho(t))$, $\lambda \in \Lambda_{AB}$, which provides the statistical description of the subsystem A, becomes

$$\text{Tr}^{\lambda}_B(\rho^I(t)) = \text{Tr}^{\lambda}_B(\rho^I(t_0)) + \frac{i}{\hbar}\int_{t_0}^{t} dt' \, \text{Tr}^{\lambda}_B([\rho^I(t_0), H^I_{\text{int}}(t')]) + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \, \text{Tr}^{\lambda}_B([[\rho^I(t_0), H^I_{\text{int}}(t'')], H^I_{\text{int}}(t')]) + \cdots. \tag{2.6.3}$$

A similar expression can be obtained for $\text{Tr}^{\tilde{\lambda}}_A(\rho(t))$.

Following our introductory remarks at the beginning of this subsection, we keep only terms up to second order in H_{int}. Moreover, in order to control the degree of correlation between the subsystems, we replace $\rho^I(t_0)$ in expressions (2.6.2) and (2.6.3) by

$$\rho^I(t_0) = \rho_A^I(t_0) \otimes \rho_B^I(t_0) + \eta_{AB}^I(t_0),$$

which is the correspondent of Eq. (2.4.1) in the interaction picture. Furthermore, according to our second hypothesis, we allow only for weak statistical correlations $\eta_{AB}^I(t)$ corresponding to the first-order contribution with respect to the dynamical interaction H_{int}. Considering the right-hand side of Eqs. (2.6.2) and (2.6.3), we see that $\eta_{AB}^I(t_0)$ gives rise to a second-order contribution in the second term, and a third-order contribution in the third term. Keeping only the terms up to second order, we thus obtain

$$\begin{aligned}\rho^I(t) = \rho^I(t_0) &+ \frac{i}{\hbar}\int_{t_0}^{t} dt' [\rho_A^I(t_0) \otimes \rho_B^I(t_0), H_{\text{int}}^I(t')] \\ &+ \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' [[\rho_A^I(t_0) \otimes \rho_B^I(t_0), H_{\text{int}}^I(t'')], H_{\text{int}}^I(t')] \\ &+ \frac{i}{\hbar}\int_{t_0}^{t} dt' [\eta_{AB}^I(t_0), H_{\text{int}}^I(t')], \end{aligned} \tag{2.6.4}$$

and consequently

$$\begin{aligned}\text{Tr}_B^{\lambda}(\rho^I(t)) = \text{Tr}_B^{\lambda}(\rho^I(t_0)) &+ \frac{i}{\hbar}\int_{t_0}^{t} dt' \, \text{Tr}_B^{\lambda}([\rho_A^I(t_0) \otimes \rho_B^I(t_0), H_{\text{int}}^I(t')]) \\ &+ \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \, \text{Tr}_B^{\lambda}([[\rho_A^I(t_0) \otimes \rho_B^I(t_0), H_{\text{int}}^I(t'')], H_{\text{int}}^I(t')]) \\ &+ \frac{i}{\hbar}\int_{t_0}^{t} dt' \, \text{Tr}_B^{\lambda}([\eta_{AB}^I(t_0), H_{\text{int}}^I(t')]). \end{aligned} \tag{2.6.5}$$

A similar expression holds for $\text{Tr}_A^{\tilde{\lambda}}(\rho^I(t))$.

Now we need an evaluation of $\eta_{AB}^I(t_0)$ limited to the first-order contribution of the interaction H_{int}. Keeping only the first-order terms in Eq. (2.6.4), we get

$$\begin{aligned}&\rho_A^I(t) \otimes \rho_B^I(t) + \eta_{AB}^I(t) \\ &\quad = \rho_A^I(t_0) \otimes \rho_B^I(t_0) + \eta_{AB}^I(t_0) + \frac{i}{\hbar}\int_{t_0}^{t} dt' [\rho_A^I(t_0) \otimes \rho_B^I(t_0), H_{\text{int}}^I(t')]. \end{aligned}$$

Using our previous assumption that $\eta^I_{AB}(t)$ vanishes at time $t = t_{00}$, the above relation implies

$$\eta^I_{AB}(t_0) = \rho^I_A(t_{00}) \otimes \rho^I_B(t_{00}) - \rho^I_A(t_0) \otimes \rho^I_B(t_0) - \frac{i}{\hbar}\int_{t_0}^{t_{00}} dt' [\rho^I_A(t_0) \otimes \rho^I_B(t_0), H^I_{\text{int}}(t')]. \tag{2.6.6}$$

Insertion of the above expression for $\eta^I_{AB}(t_0)$ into Eq. (2.6.5) yields

$$\begin{aligned}\text{Tr}^\lambda_B(\rho^I(t)) = \text{Tr}^\lambda_B(\rho^I(t_0)) &+ \frac{i}{\hbar}\int_{t_0}^{t} dt'\, \text{Tr}^\lambda_B([\rho^I_A(t_0) \otimes \rho^I_B(t_0), H^I_{\text{int}}(t')]) \\ &+ \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_{00}}^{t'} dt''\, \text{Tr}^\lambda_B([[\rho^I_A(t_0) \otimes \rho^I_B(t_0), H^I_{\text{int}}(t'')], H^I_{\text{int}}(t')]) \\ &+ \frac{i}{\hbar}\int_{t_0}^{t} dt'\, \text{Tr}^\lambda_B([\rho^I_A(t_{00}) \otimes \rho^I_B(t_{00}) - \rho^I_A(t_0) \otimes \rho^I_B(t_0), H^I_{\text{int}}(t')]).\end{aligned} \tag{2.6.7}$$

Our aim is to express $\text{Tr}^\lambda_B(\rho^I(t))$ in terms of the density matrices $\rho^I_A(t_0)$ and $\rho^I_B(t_0)$. Thus, we have to reconsider the dependence on $\rho^I_A(t_{00}) \otimes \rho^I_B(t_{00})$ appearing in the last integral. We start from the identity

$$\text{Tr}^\lambda_B([\rho^I_A(t) \otimes \rho^I_B(t), H^I_{\text{int}}(t')]) = [\mu^\lambda_A(\rho^I_A(t)), \text{Tr}^\lambda_B((\mathbb{1}_A \otimes \rho^I_B(t))\, H^I_{\text{int}}(t'))], \tag{2.6.8}$$

which is obtained from the definition (2.2.17) and the relations (2.2.9) and (2.2.11) according to

$$\begin{aligned}&\langle a, \lambda|\, \text{Tr}^\lambda_B((\rho_A \otimes \rho_B)\, H_{\text{int}})\, |a', \lambda\rangle \\ &= \sum_b \sum_{a''b''\lambda''} \langle a, b, \lambda|\, \rho_A \otimes \rho_B\, |a'', b'', \lambda''\rangle\langle a'', b'', \lambda''|\, H_{\text{int}}\, |a', b, \lambda\rangle \\ &= \sum_b \sum_{a''b''} \langle a, \lambda|\, \mu_A(\rho_A)\, |a'', \lambda\rangle\langle b, \tilde{\lambda}|\, \mu_B(\rho_B)\, |b'', \tilde{\lambda}\rangle\langle a'', b'', \lambda|\, H_{\text{int}}\, |a', b, \lambda\rangle \\ &= \sum_{a''} \langle a, \lambda|\, \mu_A(\rho_A)\, |a'', \lambda\rangle\langle a'', \lambda|\, \text{Tr}^\lambda_B((\mathbb{1}_A \otimes \rho_B)\, H_{\text{int}})\, |a', \lambda\rangle,\end{aligned}$$

and the corresponding expression for the reversed order of operators $H_{\text{int}}(\rho_A \otimes \rho_B)$.

Let now Q^{λ}, $\lambda \in \Lambda_{AB}$ be the orthogonal projectors of the Hilbert space $\mathscr{H}_{A+B}$ onto the subspaces $\mathscr{H}^{\lambda}_{A+B}$, which are generated by the vectors $|a, b, \lambda\rangle$ for $a = 1,\ldots, n^{\lambda}_{A}$ and $b = 1,\ldots, n^{\tilde{\lambda}}_{B}$ (see Fig. 1). We have

$$Q^{\lambda} = \sum_{a=1}^{n^{\lambda}_{A}} \sum_{b=1}^{n^{\tilde{\lambda}}_{B}} |a, b, \lambda\rangle\langle a, b, \lambda| \tag{2.6.9}$$

with

$$\sum_{\lambda \in \Lambda_{AB}} Q^{\lambda} = P^{[1^N]} \quad \text{and} \quad Q^{\lambda}Q^{\lambda'} = \delta_{\lambda\lambda'}Q^{\lambda}, \qquad \forall \lambda, \lambda' \in \Lambda_{AB}. \tag{2.6.10}$$

The projectors Q^{λ} commute with the non-interacting part of the Hamiltonian (2.1.14), i.e.,

$$[Q^{\lambda}, H_A \otimes \mathbb{1}_B + \mathbb{1}_A \otimes H_B] = 0. \tag{2.6.11}$$

The decomposed interaction Hamiltonian H_{int} is given by Eqs. (2.1.51) and (2.1.56). The matrix elements of the operators $H^{\mu}_{\alpha\beta}$, acting in the subspace $\mathscr{H}_{A+B}$ generated by the vectors $|a, b, \lambda\rangle$, $\lambda \in \Lambda_{AB}$, can be written as

$$\langle a, b, \lambda|\, H^{\mu}_{\alpha\beta}\, |a', b', \lambda'\rangle = \sum_{\gamma=1}^{a_{\lambda}} \sum_{\delta=1}^{b_{\tilde{\lambda}}} h^{\lambda\mu\lambda'}_{\gamma\delta} \langle a, \lambda \| \mathbf{A}^{\mu}_{\alpha} \| a', \lambda'\rangle_{\gamma} \langle b, \tilde{\lambda} \| \mathbf{B}^{\mu}_{\beta} \| b', \tilde{\lambda}'\rangle_{\delta}, \tag{2.6.12}$$

where $\langle a, \lambda \| \mathbf{A}^{\mu}_{\alpha} \| a', \lambda'\rangle_{\gamma}$ and $\langle b, \tilde{\lambda} \| \mathbf{B}^{\mu}_{\beta} \| b', \tilde{\lambda}'\rangle_{\delta}$ denote the reduced matrix elements of the operators $A^{\mu}_{\alpha k}$ and $B^{\mu}_{\beta l}$, respectively. The coefficients a_{λ} and $b_{\tilde{\lambda}}$ denote the multiplicities of the irreducible representations of types λ and $\tilde{\lambda}$ in the tensor products $D^{(\mu)} \otimes D^{(\lambda')}$ and $D^{(\mu)} \otimes D^{(\tilde{\lambda}')}$, i.e.,

$$D^{(\mu)} \otimes D^{(\lambda')} \sim \bigoplus_{\lambda} a_{\lambda} D^{(\lambda)} \tag{2.6.13}$$

and

$$D^{(\mu)} \otimes D^{(\tilde{\lambda}')} \sim \bigoplus_{\tilde{\lambda}} b_{\tilde{\lambda}} D^{(\tilde{\lambda})}. \tag{2.6.14}$$

Obviously, we have

$$b_{\tilde{\lambda}} = a_{\lambda}, \qquad \forall \lambda \in \Lambda_{AB}. \tag{2.6.15}$$

Equation (2.6.12) is obtained by evaluating the matrix elements of the irreducible tensor operators $A^{\mu}_{\alpha k}$ and $B^{\mu}_{\beta l}$ using the Wigner–Eckart theorem. We get

$$\langle a, \lambda, i|\, A^{\mu}_{\alpha k}\, |a', \lambda', i'\rangle = \sum_{\gamma=1}^{a_\lambda} c^{\lambda' \mu\ \lambda}_{i' k\ (i,\gamma)} \langle a, \lambda \| \mathbf{A}^{\mu}_{\alpha} \| a', \lambda' \rangle_{\gamma} \tag{2.6.16}$$

and

$$\langle b, \tilde{\lambda}, j|\, B^{\mu}_{\beta l}\, |b', \tilde{\lambda}', j'\rangle = \sum_{\delta=1}^{b_{\tilde{\lambda}}} c^{\tilde{\lambda}' \mu\ \tilde{\lambda}}_{j' l\ (j,\delta)} \langle b, \tilde{\lambda} \| \mathbf{B}^{\mu}_{\beta} \| b', \tilde{\lambda}' \rangle_{\delta}, \tag{2.6.17}$$

where the coefficients $c^{\lambda' \mu\ \lambda}_{i' k\ (i,\gamma)}$ and $c^{\tilde{\lambda}' \mu\ \tilde{\lambda}}_{j' l\ (j,\delta)}$ are the Clebsch–Gordan coefficients associated with the decompositions (2.6.13) and (2.6.14).

Finally, together with the relation (2.1.35) for the orthonormal basis vectors in $\mathscr{H}_{A+B}$, we obtain for the real coefficients $h^{\lambda\mu\lambda'}_{\gamma\delta}$ in Eq. (2.6.12)

$$h^{\lambda\mu\lambda'}_{\gamma\delta} = h^{\lambda'\mu\lambda}_{\gamma\delta} = \frac{1}{\sqrt{d_\mu}} \sum_{i,j=1}^{d_\lambda} \sum_{i',j'=1}^{d_{\lambda'}} \sum_{k=1}^{d_\mu} c^{\lambda\ \tilde{\lambda}\ [1^N]}_{i\ j\ \ 1} c^{\lambda' \mu\ \lambda}_{i' k\ (i,\gamma)} c^{\tilde{\lambda}' \mu\ \tilde{\lambda}}_{j' k\ (j,\delta)} c^{\lambda'\ \tilde{\lambda}'\ [1^N]}_{i'\ j'\ \ 1}. \tag{2.6.18}$$

Making use of the isomorphism between the subspaces $\mathscr{H}^{\lambda}_{A+B} = Q^{\lambda}\mathscr{H}_{A+B}$ and $\bar{\mathscr{H}}^{\lambda}_{A} \otimes \bar{\mathscr{H}}^{\tilde{\lambda}}_{B}$,

$$\mathscr{H}^{\lambda}_{A+B} \sim \bar{\mathscr{H}}^{\lambda}_{A} \otimes \bar{\mathscr{H}}^{\tilde{\lambda}}_{B}, \tag{2.6.19}$$

we define the linear operators

$$A^{\lambda\mu\lambda'}_{\gamma\alpha} : \bar{\mathscr{H}}^{\lambda'}_{A} \mapsto \bar{\mathscr{H}}^{\lambda}_{A} \tag{2.6.20}$$

and

$$B^{\tilde{\lambda}\mu\tilde{\lambda}'}_{\delta\beta} : \bar{\mathscr{H}}^{\tilde{\lambda}'}_{B} \mapsto \bar{\mathscr{H}}^{\tilde{\lambda}}_{B} \tag{2.6.21}$$

by

$$\langle a, \lambda|\, A^{\lambda\mu\lambda'}_{\gamma\alpha}\, |a', \lambda'\rangle = \langle a, \lambda \| \mathbf{A}^{\mu}_{\alpha} \| a', \lambda' \rangle_{\gamma} \tag{2.6.22}$$

and

$$\langle b, \tilde{\lambda}|\, B^{\tilde{\lambda}\mu\tilde{\lambda}'}_{\delta\beta}\, |b', \tilde{\lambda}'\rangle = \langle b, \tilde{\lambda} \| \mathbf{B}^{\mu}_{\beta} \| b', \tilde{\lambda}' \rangle_{\delta}. \tag{2.6.23}$$

As can immediately be seen from their definition, they satisfy the relations

$$(A^{\lambda\mu\lambda'}_{\gamma\alpha})^{\dagger} = A^{\lambda'\mu\lambda}_{\gamma\alpha} \tag{2.6.24}$$

and

$$(B_{\delta\beta}^{\tilde{\lambda}\mu\tilde{\lambda}'})^{\dagger} = B_{\delta\beta}^{\tilde{\lambda}'\mu\tilde{\lambda}}. \tag{2.6.25}$$

It should be noted that the operators $A_{\gamma\alpha}^{\lambda\mu\lambda'}$ and $B_{\delta\beta}^{\tilde{\lambda}\mu\tilde{\lambda}'}$ act in the subspaces $\mathscr{H}_A$ and $\mathscr{H}_B$, respectively. This allows us to describe the interaction operator (2.1.56) in the space $\bigoplus_{\lambda\in\Lambda_{AB}} \mathscr{H}_A^{\lambda} \otimes \mathscr{H}_B^{\tilde{\lambda}}$ rather than in $\mathscr{H}_{A+B}$. From Eq. (2.1.56) and the Definitions (2.6.22) and (2.6.23) we get

$$H_{\text{int}}^{\lambda\lambda'} = \sum_{\mu} \sum_{\alpha\beta} g_{\alpha\beta}^{\mu} \sum_{\gamma=1}^{a_\lambda} \sum_{\delta=1}^{b_{\tilde{\lambda}}} h_{\gamma\delta}^{\lambda\mu\lambda'} A_{\gamma\alpha}^{\lambda\mu\lambda'} \otimes B_{\delta\beta}^{\tilde{\lambda}\mu\tilde{\lambda}'}, \tag{2.6.26}$$

which corresponds to

$$Q^{\lambda} H_{\text{int}} Q^{\lambda'} \colon \mathscr{H}_{A+B}^{\lambda'} \to \mathscr{H}_{A+B}^{\lambda}.$$

This form is rather convenient and will be used in the following.

The above definitions can be straightforwardly translated into the interaction picture. We then have

$$A^{I}{}_{\gamma\alpha}^{\lambda\mu\lambda'}(t) = e^{i\bar{H}_A^{\lambda}t/\hbar} A_{\gamma\alpha}^{\lambda\mu\lambda'} e^{-i\bar{H}_A^{\lambda'}t/\hbar} \tag{2.6.27}$$

and

$$B^{I}{}_{\delta\beta}^{\tilde{\lambda}\mu\tilde{\lambda}'}(t) = e^{i\bar{H}_B^{\tilde{\lambda}}t/\hbar} B_{\delta\beta}^{\tilde{\lambda}\mu\tilde{\lambda}'} e^{-i\bar{H}_B^{\tilde{\lambda}'}t/\hbar} \tag{2.6.28}$$

with

$$\bar{H}_A^{\lambda} \equiv \mu_A^{\lambda}(H_A) \qquad \text{and} \qquad \bar{H}_B^{\tilde{\lambda}} \equiv \mu_B^{\tilde{\lambda}}(H_B), \tag{2.6.29}$$

and the interaction Hamiltonian (2.6.26) can be expressed in terms of the block operators

$$H_{\text{int}}^{I\,\lambda\lambda'}(t) = \sum_{\mu} \sum_{\alpha\beta} g_{\alpha\beta}^{\mu} \sum_{\gamma=1}^{a_\lambda} \sum_{\delta=1}^{b_{\tilde{\lambda}}} h_{\gamma\delta}^{\lambda\mu\lambda'} A^{I}{}_{\gamma\alpha}^{\lambda\mu\lambda'}(t) \otimes B^{I}{}_{\delta\beta}^{\tilde{\lambda}\mu\tilde{\lambda}'}(t). \tag{2.6.30}$$

In the following we group the index pairs $\gamma\alpha$ and $\delta\beta$ into one, i.e., we replace $A_{\gamma\alpha}^{\lambda\mu\lambda'}$ by $A_{\alpha}^{\lambda\mu\lambda'}$ and $B_{\delta\beta}^{\tilde{\lambda}\mu\tilde{\lambda}'}$ by $B_{\beta}^{\tilde{\lambda}\mu\tilde{\lambda}'}$. With this convention Eq. (2.6.30) becomes

$$H_{\text{int}}^{I\,\lambda\lambda'}(t) = \sum_{\mu} \sum_{\alpha\beta} g_{\alpha\beta}^{\lambda\mu\lambda'} A^{I}{}_{\alpha}^{\lambda\mu\lambda'}(t) \otimes B^{I}{}_{\beta}^{\tilde{\lambda}\tilde{\mu}\tilde{\lambda}'}(t) \tag{2.6.31}$$

with

$$g_{\alpha\beta}^{\lambda\mu\lambda'} = g_{\alpha\beta}^{\lambda'\mu\lambda} \equiv g_{\alpha\beta}^{\mu} h_{\gamma\delta}^{\lambda\mu\lambda'}. \tag{2.6.32}$$

Inserting (2.6.31) into Eq. (2.6.8), we get

$$\begin{aligned}&\mathrm{Tr}_B^{\lambda}([\rho_A^I(t)\otimes\rho_B^I(t), H_{\mathrm{int}}^I(t')])\\&\quad=\sum_{\mu\alpha}[\mu_A^{\lambda}(\rho_A^I(t)), A^{I}{}_{\alpha}^{\lambda\mu\lambda}(t')]\sum_{\beta} g_{\alpha\beta}^{\lambda\mu\lambda}\,\mathrm{Tr}(\mu_B^{\tilde{\lambda}}(\rho_B^I(t))\,B^{I}{}_{\beta}^{\tilde{\lambda}\mu\tilde{\lambda}}(t')),\end{aligned}\tag{2.6.33}$$

where we have used the identity

$$\mathrm{Tr}_B^{\lambda}((\mathbb{1}_A\otimes\rho_B^I(t))\,H_{\mathrm{int}}^I(t'))=\sum_{\mu\alpha}A^{I}{}_{\alpha}^{\lambda\mu\lambda}(t')\sum_{\beta}g_{\alpha\beta}^{\lambda\mu\lambda}\,\mathrm{Tr}(\mu_B^{\tilde{\lambda}}(\rho_B^I(t))\,B^{I}{}_{\beta}^{\tilde{\lambda}\mu\tilde{\lambda}}(t')),$$

which follows directly from the relation (2.3.3). With the corresponding of relation (2.3.5) in the interaction picture

$$\mathrm{Tr}(\mu_B^{\tilde{\lambda}}(\rho_B^I(t)))\,\mu_A^{\lambda}(\rho_A^I(t))=\mathrm{Tr}_B^{\lambda}(\rho^I(t))=\bar{\rho}_A^{I\,\lambda}(t),$$

Eq. (2.6.33) can be written in the compact form

$$\mathrm{Tr}_B^{\lambda}([\rho_A^I(t)\otimes\rho_B^I(t), H_{\mathrm{int}}^I(t')])=\sum_{\mu\alpha}[\bar{\rho}_A^{I\,\lambda}(t), A^{I}{}_{\alpha}^{\lambda\mu\lambda}(t')]\,b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t,t').\tag{2.6.34}$$

The coefficients

$$b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t,t')=\sum_{\beta}g_{\alpha\beta}^{\lambda\mu\lambda}\frac{\mathrm{Tr}(\bar{\rho}_B^{I\,\tilde{\lambda}}(t)\,B^{I}{}_{\beta}^{\tilde{\lambda}\mu\tilde{\lambda}}(t'))}{\mathrm{Tr}(\bar{\rho}_B^{I\,\tilde{\lambda}}(t))}\tag{2.6.35}$$

are real numbers, as can be seen immediately from Eq. (2.6.25).

We now come back to our actual problem, which was the transformation of expression (2.6.7) for $\mathrm{Tr}_B^{\lambda}(\rho^I(t))$. With Eq. (2.6.34) we obtain for the first-order contribution

$$\begin{aligned}\bar{\rho}_A^{I\,\lambda}(t)&=\mathrm{Tr}_B^{\lambda}(\rho^I(t))\\&\simeq\mathrm{Tr}_B^{\lambda}(\rho^I(t_0))+\frac{i}{\hbar}\int_{t_0}^{t}dt'\sum_{\mu\alpha}[\bar{\rho}_A^{I\,\lambda}(t_0), A^{I}{}_{\alpha}^{\lambda\mu\lambda}(t')]\,b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t_0,t').\end{aligned}\tag{2.6.36}$$

Similarly, the integrand in the last integral of Eq. (2.6.7) becomes

$$\begin{aligned}&\mathrm{Tr}_B^{\lambda}([\rho_A^I(t_{00})\otimes\rho_B^I(t_{00})-\rho_A^I(t_0)\otimes\rho_B^I(t_0), H_{\mathrm{int}}^I(t')])\\&\quad=\sum_{\mu\alpha}[\bar{\rho}_A^{I\,\lambda}(t_{00}), A^{I}{}_{\alpha}^{\lambda\mu\lambda}(t')]\,b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t_{00},t')-\sum_{\mu\alpha}[\bar{\rho}_A^{I\,\lambda}(t_0), A^{I}{}_{\alpha}^{\lambda\mu\lambda}(t')]\,b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t_0,t').\end{aligned}\tag{2.6.37}$$

Equation (2.6.7) treats the interaction term up to second order. We have thus to look for a first-order approximation to $\bar{\rho}_A^{I\,\lambda}(t_{00})$. This is obtained by evaluating Eq. (2.6.36) at $t = t_{00}$, which yields

$$\bar{\rho}_A^{I\,\lambda}(t_{00}) = \bar{\rho}_A^{I\,\lambda}(t_0) + \frac{i}{\hbar}\int_{t_0}^{t_{00}} dt'' \sum_{\mu'\alpha'} [\bar{\rho}_A^{I\,\lambda}(t_0), A^{I\,\lambda\mu'\lambda}_{\alpha'}(t'')]\, b^{\tilde{\lambda}\mu'\tilde{\lambda}}_{\alpha'}(t_0, t''). \tag{2.6.38}$$

Inserting this first-order relation into Eq. (2.6.37), we get after integration

$$\begin{aligned}
&\frac{i}{\hbar}\int_{t_0}^{t} dt'\, \mathrm{Tr}_B^{\lambda}([\rho_A^I(t_{00}) \otimes \rho_B^I(t_{00}) - \rho_A^I(t_0) \otimes \rho_B^I(t_0), H_{\mathrm{int}}^I(t')]) \\
&\quad = \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \sum_{\mu\alpha} \int_{t_0}^{t_{00}} dt'' \sum_{\mu'\alpha'} [[\bar{\rho}_A^{I\,\lambda}(t_0), A^{I\,\lambda\mu'\lambda}_{\alpha'}(t'')], A^{I\,\lambda\mu\lambda}_{\alpha}(t')] \\
&\qquad \times b^{\tilde{\lambda}\mu'\tilde{\lambda}}_{\alpha'}(t_0, t'')\, b^{\tilde{\lambda}\mu\tilde{\lambda}}_{\alpha}(t_{00}, t') \\
&\qquad + \frac{i}{\hbar}\int_{t_0}^{t} dt' \sum_{\mu\alpha} [\bar{\rho}_A^{I\,\lambda}(t_0), A^{I\,\lambda\mu\lambda}_{\alpha}(t')](b^{\tilde{\lambda}\mu\tilde{\lambda}}_{\alpha}(t_{00}, t') - b^{\tilde{\lambda}\mu\tilde{\lambda}}_{\alpha}(t_0, t')).
\end{aligned} \tag{2.6.39}$$

In the first term on the right-hand side we can replace $b^{\tilde{\lambda}\mu\tilde{\lambda}}_{\alpha}(t_{00}, t')$ by $b^{\tilde{\lambda}\mu\tilde{\lambda}}_{\alpha}(t_0, t')$, since this change corresponds to a third-order correction in Eq. (2.6.39).

We now consider the last term in Eq. (2.6.39). With the definitions (2.6.35) and (2.4.5) we obtain

$$b^{\tilde{\lambda}\mu\tilde{\lambda}}_{\alpha}(t_{00}, t') - b^{\tilde{\lambda}\mu\tilde{\lambda}}_{\alpha}(t_0, t') = \sum_{\beta} g^{\lambda\mu\lambda}_{\alpha\beta}\, \mathrm{Tr}\left(\left(\frac{\bar{\rho}_B^{I\,\tilde{\lambda}}(t_{00})}{p_\lambda(t_{00})} - \frac{\bar{\rho}_B^{I\,\tilde{\lambda}}(t_0)}{p_\lambda(t_0)}\right) B^{I\,\tilde{\lambda}\mu\tilde{\lambda}}_{\beta}(t')\right). \tag{2.6.40}$$

Interchanging the roles of the subsystems A and B in Eq. (2.6.38), we get the first-order expression for the subsystem B

$$\bar{\rho}_B^{I\,\tilde{\lambda}}(t_{00}) = \bar{\rho}_B^{I\,\tilde{\lambda}}(t_0) + \frac{i}{\hbar}\int_{t_0}^{t_{00}} dt'' \sum_{\mu'\beta'} [\bar{\rho}_B^{I\,\tilde{\lambda}}(t_0), B^{I\,\tilde{\lambda}\mu'\tilde{\lambda}}_{\beta'}(t'')]\, a^{\lambda\mu'\lambda}_{\beta'}(t_0, t''), \tag{2.6.41}$$

where the coefficients $a^{\lambda\mu\lambda}_{\beta}(t, t')$ are given by the correspondent of Eq. (2.6.35)

$$a^{\lambda\mu\lambda}_{\beta}(t, t') = \sum_{\alpha} g^{\lambda\mu\lambda}_{\alpha\beta} \frac{\mathrm{Tr}(\bar{\rho}_A^{I\,\lambda}(t)\, A^{I\,\lambda\mu\lambda}_{\alpha}(t'))}{\mathrm{Tr}(\bar{\rho}_A^{I\,\lambda}(t))}. \tag{2.6.42}$$

From the definition (2.4.5) of p_λ and the equivalent of Eq. (2.2.11) for the subsystem B we find that

$$p_\lambda(t) = \mathrm{Tr}(\bar{\rho}_B^{I\,\tilde{\lambda}}(t)).$$

Tracing Eq. (2.6.41) and using the fact that the trace over the second term containing a commutator is zero, we get the first-order relation

$$p_\lambda(t_{00}) = \mathrm{Tr}(\bar{\rho}_B^{I\,\tilde{\lambda}}(t_{00})) = \mathrm{Tr}(\bar{\rho}_B^{I\,\tilde{\lambda}}(t_0)) = p_\lambda(t_0).$$

We may thus rewrite Eq. (2.6.40) as

$$\begin{aligned} & b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t_{00}, t') - b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t_0, t') \\ &= \sum_{\beta} g_{\alpha\beta}^{\lambda\mu\lambda}\, \mathrm{Tr}\left(\frac{i}{\hbar} \int_{t_0}^{t_{00}} dt'' \sum_{\mu'\beta'} \frac{a_{\beta'}^{\lambda\mu'\lambda}(t_0, t'')}{p_\lambda(t_0)} [\bar{\rho}_B^{I\,\tilde{\lambda}}(t_0), B^{I\,\tilde{\lambda}}_{\beta'}(t'')]\, B^{I\,\tilde{\lambda}\mu\tilde{\lambda}}_{\beta}(t') \right) \\ &= \frac{i}{\hbar} \int_{t_0}^{t_{00}} dt'' \sum_{\mu'\alpha'} (b_{\alpha'\alpha}^{\tilde{\lambda}\mu'\tilde{\lambda}\mu\tilde{\lambda}}(t_0, t'', t') - b_{\alpha\alpha'}^{\tilde{\lambda}\mu\tilde{\lambda}\mu'\tilde{\lambda}}(t_0, t', t''))\, a_{\alpha'}^{\lambda\mu'}(t_0, t''), \end{aligned} \tag{2.6.43}$$

where the coefficients $b_{\alpha\alpha'}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}(t_0, t', t'')$ and $a_{\alpha}^{\lambda\mu}(t_0, t')$ are defined as

$$b_{\alpha\alpha'}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}(t_0, t', t'') = \sum_{\beta\beta'} g_{\alpha\beta}^{\lambda\mu\rho} g_{\alpha'\beta'}^{\rho\mu'\lambda} \frac{\mathrm{Tr}(\bar{\rho}_B^{I\,\tilde{\lambda}}(t_0)\, B^{I\tilde{\lambda}\mu\tilde{\rho}}_{\beta}(t')\, B^{I\tilde{\rho}\mu'\tilde{\lambda}}_{\beta'}(t''))}{\mathrm{Tr}(\bar{\rho}_B^{I\,\tilde{\lambda}}(t_0))} \tag{2.6.44}$$

and

$$a_{\alpha}^{\lambda\mu}(t_0, t') = \frac{\mathrm{Tr}(\bar{\rho}_A^{I\,\lambda}(t_0)\, A_{\alpha}^{I\lambda\mu\lambda}(t'))}{\mathrm{Tr}(\bar{\rho}_A^{I\,\lambda}(t_0))}. \tag{2.6.45}$$

Inserting (2.6.43) we get finally for expression (2.6.39)

$$\begin{aligned} & \frac{i}{\hbar} \int_{t_0}^{t} dt'\, \mathrm{Tr}_B^{\lambda}([\rho_A^I(t_{00}) \otimes \rho_B^I(t_{00}) - \rho_A^I(t_0) \otimes \rho_B^I(t_0), H_{\mathrm{int}}^I(t')]) \\ &= \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \sum_{\mu\alpha} \int_{t_0}^{t_{00}} dt'' \\ &\quad \times \sum_{\mu'\alpha'} ([[\bar{\rho}_A^{I\,\lambda}(t_0), A^{I\lambda\mu'\lambda}_{\alpha'}(t'')], A_{\alpha}^{I\lambda\mu\lambda}(t')]\, b_{\alpha'}^{\tilde{\lambda}\mu'\tilde{\lambda}}(t_0, t'')\, b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t_0, t') \\ &\quad + [\bar{\rho}_A^{I\,\lambda}(t_0), A_{\alpha}^{I\lambda\mu\lambda}(t')](b_{\alpha'\alpha}^{\tilde{\lambda}\mu'\tilde{\lambda}\mu\tilde{\lambda}}(t_0, t'', t') - b_{\alpha\alpha'}^{\tilde{\lambda}\mu\tilde{\lambda}\mu'\tilde{\lambda}}(t_0, t', t''))\, a_{\alpha'}^{\lambda\mu'}(t_0, t'')). \end{aligned} \tag{2.6.46}$$

We now consider the third term in Eq. (2.6.7), which contains the commutator expression

$$\begin{aligned}
&\mathrm{Tr}_B^{\lambda}([[\rho_A^I(t_0)\otimes\rho_B^I(t_0), H_{\mathrm{int}}^I(t'')], H_{\mathrm{int}}^I(t')]) \\
&\quad = \mathrm{Tr}_B^{\lambda}((\rho_A^I(t_0)\otimes\rho_B^I(t_0))\, H_{\mathrm{int}}^I(t'')\, H_{\mathrm{int}}^I(t')) \\
&\qquad - \mathrm{Tr}_B^{\lambda}(H_{\mathrm{int}}^I(t'')(\rho_A^I(t_0)\otimes\rho_B^I(t_0))\, H_{\mathrm{int}}^I(t')) \\
&\qquad - \mathrm{Tr}_B^{\lambda}(H_{\mathrm{int}}^I(t')(\rho_A^I(t_0)\otimes\rho_B^I(t_0))\, H_{\mathrm{int}}^I(t'')) \\
&\qquad + \mathrm{Tr}_B^{\lambda}(H_{\mathrm{int}}^I(t')\, H_{\mathrm{int}}^I(t'')(\rho_A^I(t_0)\otimes\rho_B^I(t_0))).
\end{aligned} \tag{2.6.47}$$

This relation can still be simplified. As an example, we take the first term on the right-hand side. According to the definition (2.2.15) of the partial trace operation, its matrix elements in $\bar{\mathscr{H}}_A^{\lambda}$ can be written

$$\begin{aligned}
&\langle a, \lambda|\, \mathrm{Tr}_B^{\lambda}(\rho_A^I(t_0)\otimes\rho_B^I(t_0)\, H_{\mathrm{int}}^I(t'')\, H_{\mathrm{int}}^I(t'))\, |a', \lambda\rangle \\
&\quad = \sum_b \sum_{a''b''} \sum_{a'''b'''\rho} \langle a, b, \lambda|\, \rho_A^I(t_0)\otimes\rho_B^I(t_0)\, |a'', b'', \lambda\rangle \\
&\qquad \times \langle a'', b'', \lambda|\, H_{\mathrm{int}}^I(t'')\, |a''', b''', \rho\rangle\langle a''', b''', \rho|\, H_{\mathrm{int}}^I(t')\, |a', b, \lambda\rangle,
\end{aligned}$$

where we have used the fact that $\rho_A^I(t_0)$ and $\rho_B^I(t_0)$ commute with the representations U_A and U_B of S_N in $\mathscr{H}_A$ and $\mathscr{H}_B$, respectively. Using Eqs. (2.1.35), (2.1.37), (2.1.38), and (2.2.7), we obtain

$$\begin{aligned}
&\langle a, b, \lambda|\, \rho_A^I(t_0)\otimes\rho_B^I(t_0)\, |a'', b'', \lambda\rangle \\
&\quad = \langle a, \lambda|\, \mu_A^{\lambda}(\rho_A^I(t_0))\, |a'', \lambda\rangle\langle b, \tilde{\lambda}|\, \mu_B^{\tilde{\lambda}}(\rho_B^I(t_0))\, |b'', \tilde{\lambda}\rangle.
\end{aligned}$$

With Eq. (2.6.12), the matrix elements of the interaction Hamiltonian (2.6.26) become

$$\begin{aligned}
&\langle a'', b'', \lambda|\, H_{\mathrm{int}}^I(t'')\, |a''', b''', \rho\rangle \\
&\quad = \sum_{\mu'} \sum_{\alpha'\beta'} g_{\alpha'\beta'}^{\mu'} \sum_{\gamma'\delta'} h_{\gamma'\delta'}^{\lambda\mu'\rho} \langle a'', \lambda\|\, \mathbf{A}_{\alpha'}^{I\mu'}(t'')\, \|a''', \rho\rangle_{\gamma'}\, \langle b'', \tilde{\lambda}\|\, \mathbf{B}_{\beta'}^{I\mu'}(t'')\, \|b''', \tilde{\rho}\rangle_{\delta'}
\end{aligned}$$

and

$$\begin{aligned}
&\langle a''', b''', \rho|\, H_{\mathrm{int}}^I(t')\, |a', b, \lambda\rangle \\
&\quad = \sum_{\mu} \sum_{\alpha\beta} g_{\alpha\beta}^{\mu} \sum_{\gamma\delta} h_{\gamma\delta}^{\rho\mu\lambda} \langle a''', \rho\|\, \mathbf{A}_{\alpha}^{I\mu}(t')\, \|a', \lambda\rangle_{\gamma}\, \langle b''', \tilde{\rho}\|\, \mathbf{B}_{\beta}^{I\mu}(t')\, \|b, \tilde{\lambda}\rangle_{\delta}.
\end{aligned}$$

Altogether, we get for the first term on the right-hand side of (2.6.47)

$$
\begin{aligned}
&\mathrm{Tr}_B^{\lambda}(\rho_A^I(t_0)\otimes\rho_B^I(t_0)\,H_{\mathrm{int}}^I(t'')\,H_{\mathrm{int}}^I(t')) \\
&\quad=\sum_{\rho}\sum_{\mu'}\sum_{\alpha'\beta'} g_{\alpha'\beta'}^{\mu'}\sum_{\gamma'\delta'} h^{\lambda\mu'\rho}_{\gamma'\delta'}\sum_{\mu}\sum_{\alpha\beta} g_{\alpha\beta}^{\mu}\sum_{\gamma\delta} h^{\rho\mu\lambda}_{\gamma\delta} \\
&\qquad\times\mu_A^{\lambda}(\rho_A^I(t_0))\,A^{I\lambda\mu'\rho}_{\gamma'\alpha'}(t'')\,A^{I\rho\mu\lambda}_{\gamma\alpha}(t')\,\mathrm{Tr}(\mu_B^{\tilde{\lambda}}(\rho_B^I(t_0))\,B^{I\tilde{\lambda}\mu'\tilde{\rho}}_{\delta'\beta'}(t'')\,B^{I\tilde{\rho}\mu\tilde{\lambda}}_{\delta\beta}(t'))
\end{aligned}
$$

where we have used the definitions (2.6.22) and (2.6.23). Adopting the short-hand notation introduced in Eqs. (2.6.31) and (2.6.32), and remembering that according to Eq. (2.4.2)

$$
\mu_A^{\lambda}(\rho_A^I(t_0))=\frac{\bar{\rho}_A^{I\,\lambda}(t_0)}{\mathrm{Tr}(\mu_B^{\tilde{\lambda}}(\rho_B^I(t_0)))},
$$

we obtain

$$
\begin{aligned}
&\mathrm{Tr}_B^{\lambda}(\rho_A^I(t_0)\otimes\rho_B^I(t_0)\,H_{\mathrm{int}}^I(t'')\,H_{\mathrm{int}}^I(t')) \\
&\quad=\sum_{\rho}\sum_{\mu\mu'}\sum_{\alpha\alpha'}\bar{\rho}_A^{I\,\lambda}(t_0)\,A^{I\lambda\mu'\rho}_{\alpha'}(t'')\,A^{I\rho\mu\lambda}_{\alpha}(t')\,b^{\tilde{\lambda}\mu'\tilde{\rho}\mu\tilde{\lambda}}_{\alpha'\alpha}(t_0,t'',t'),
\end{aligned}
\tag{2.6.48}
$$

where the coefficients $b^{\tilde{\lambda}\mu'\tilde{\rho}\mu\tilde{\lambda}}_{\alpha'\alpha}(t_0,t'',t')$ are defined in Eq. (2.6.44).

The other terms on the right-hand side of Eq. (2.6.47) can be simplified following the same procedure. With Eqs. (2.6.34), (2.6.46), (2.6.48) and its correspondents, the partial trace (2.6.7) finally becomes

$$
\begin{aligned}
&\mathrm{Tr}_B^{\lambda}(\rho^I(t)) \\
&\equiv\bar{\rho}_A^{I\,\lambda}(t)\simeq\bar{\rho}_A^{I\,\lambda}(t_0)+\frac{i}{\hbar}\int_{t_0}^{t}dt'\sum_{\mu\alpha}[\bar{\rho}_A^{I\,\lambda}(t_0),A^{I\lambda\mu\lambda}_{\alpha}(t')]\,b^{\tilde{\lambda}\mu\tilde{\lambda}}_{\alpha}(t_0,t') \\
&\quad+\left(\frac{i}{\hbar}\right)^2\int_{t_0}^{t}dt'\sum_{\mu\alpha}\int_{t_0}^{t_{00}}dt'' \\
&\quad\times\sum_{\mu'\alpha'}([[\bar{\rho}_A^{I\,\lambda}(t_0),A^{I\lambda\mu'\lambda}_{\alpha'}(t'')],A^{I\lambda\mu\lambda}_{\alpha}(t')]\,b^{\tilde{\lambda}\mu'\tilde{\lambda}}_{\alpha'}(t_0,t'')\,b^{\tilde{\lambda}\mu\tilde{\lambda}}_{\alpha}(t_0,t') \\
&\quad+[\bar{\rho}_A^{I\,\lambda}(t_0),A^{I\lambda\mu\lambda}_{\alpha}(t')]\,a^{\lambda\mu'}_{\alpha'}(t_0,t'')(b^{\tilde{\lambda}\mu'\tilde{\lambda}\mu\tilde{\lambda}}_{\alpha'\alpha}(t_0,t'',t')-b^{\tilde{\lambda}\mu\tilde{\lambda}\mu'\tilde{\lambda}}_{\alpha\alpha'}(t_0,t',t'))) \\
&\quad+\left(\frac{i}{\hbar}\right)^2\int_{t_0}^{t}dt'\sum_{\mu\alpha}\int_{t_{00}}^{t'}dt''\sum_{\mu'\alpha'}\sum_{\rho}(\bar{\rho}_A^{I\,\lambda}(t_0)\,A^{I\lambda\mu'\rho}_{\alpha'}(t'')\,A^{I\rho\mu\lambda}_{\alpha}(t')\,b^{\tilde{\lambda}\mu'\tilde{\rho}\mu\tilde{\lambda}}_{\alpha'\alpha}(t_0,t'',t') \\
&\quad-A^{I\lambda\mu'\rho}_{\alpha'}(t'')\,\bar{\rho}_A^{I\,\rho}(t_0)\,A^{I\rho\mu\lambda}_{\alpha}(t')\,b^{\tilde{\rho}\mu\tilde{\lambda}\mu'\tilde{\rho}}_{\alpha\alpha'}(t_0,t',t'') \\
&\quad-A^{I\lambda\mu\rho}_{\alpha}(t')\,\bar{\rho}_A^{I\,\rho}(t_0)\,A^{I\rho\mu'\lambda}_{\alpha'}(t'')\,b^{\tilde{\rho}\mu'\tilde{\lambda}\mu\tilde{\rho}}_{\alpha'\alpha}(t_0,t'',t') \\
&\quad+A^{I\lambda\mu\rho}_{\alpha}(t')\,A^{I\rho\mu'\lambda}_{\alpha'}(t'')\,\bar{\rho}_A^{I\,\lambda}(t_0)\,b^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}_{\alpha\alpha'}(t_0,t',t'')).
\end{aligned}
\tag{2.6.49}
$$

The above relation describes the time evolution of the subsystem A of a fermionic system $A+B$ up to second order in the interaction H_{int} with the subsystem B. The resulting diagonal blocks $\bar{\rho}_A^{I\,\lambda}(t)$, $\lambda \in \Lambda_{AB}$ of the density matrix $\bar{\rho}_A^I(t)$ determine the "statistical state" of the subsystem A at time t. They depend on the initial statistical states of both subsystems at time t_0 described by $\bar{\rho}_A^I(t_0)$ and $\bar{\rho}_B^I(t_0)$, and also on the time t_{00} at which both subsystems were supposed to be statistically uncorrelated. The influence of the subsystem B on the behavior of the subsystem A enters Eq. (2.6.49) through the functions $b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t_0, t)$ and $b_{\alpha\,\alpha'}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}(t_0, t', t'')$, which depend only on $\bar{\rho}_B^I(t_0)$.

Relations similar to (2.6.49) hold also for the density matrix $\bar{\rho}_B^I(t)$. In this case, the subsystems A and B are exchanged, and the respective relations can easily be obtained using this formal analogy.

2.7. Statistical Evolution of the Subsystem *A* for a Subsystem *B* Fluctuating around Some Statistical Equilibrium

We consider again the situation discussed in the previous subsection, where the two dynamically coupled subsystems A and B were supposed to be only weakly statistically correlated. For the following, it is now important to note that even though our description of the evolution of the system was based on Eq. (2.5.3), which assumes the physical system $A+B$ to be isolated or closed, the above relation (2.6.49) can be used also in the more general situation, where the physical system $A+B$ interacts with its environment. This follows from the fact that the influence of the rest of the system on the subsystem A is completely included in the functions $b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t_0, t)$ and $b_{\alpha\,\alpha'}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}(t_0, t', t'')$. Thus, it is only necessary to assume that the dynamical coupling of the subsystem A to the rest of the system, whether open or not, is solely determined by the interaction with the subsystem B. In other words, the subsystem B can be limited to the most important degrees of freedom in the rest of the system that govern the time evolution over time intervals compatible with second-order perturbation theory. In the following we will use Eq. (2.6.49) to study the time evolution in the subsystem A interacting with an open environment, assuming that the dynamical coupling of subsystem A with its environment can be described by the coupling to an adequately chosen finite subsystem B.

We first discuss the statistical evolution of a subsystem A that interacts with a subsystem B, which is maintained near some statistical equilibrium but which still fluctuates due to its dynamical coupling with the subsystem A. Expressed in the Schrödinger picture, the corresponding density matrix of the subsystem B reads

$$\mathrm{Tr}_A^{\tilde{\lambda}}(\rho(t)) = \bar{\rho}_B^{\tilde{\lambda}}(t) = \bar{\rho}_B^{\tilde{\lambda}\,0} + \delta\bar{\rho}_B^{\tilde{\lambda}}(t), \tag{2.7.1}$$

where $\bar{\rho}_B^{\tilde{\lambda}\,0}$ describes the imposed statistical equilibrium in the subsystem B with

$$[\bar{\rho}_B^{\tilde{\lambda}\,0}, \bar{H}_B^{\tilde{\lambda}}] = 0. \tag{2.7.2}$$

The fluctuations $\delta\bar{\rho}_B^{\tilde{\lambda}}(t)$ being generated by the dynamical interaction H_{int}, they depend at least in first order on H_{int}.

Actually, as in Section 2.6, we postulate the absence of fluctuations at a time t_{00} preceding the considered time interval from t_0 to t, i.e., we suppose that before the time t_{00} the system dynamics is described by two independent and statistically uncorrelated subsystems A and B.

From Eqs. (2.4.1), (2.5.3), and (2.6.34) we find

$$\begin{aligned}\frac{d}{dt}\bar{\rho}_A^{I\,\lambda}(t) &\equiv \mathrm{Tr}_B^{\lambda}\left(\frac{d\rho^I(t)}{dt}\right)\\ &= \frac{i}{\hbar}\,\mathrm{Tr}_B^{\lambda}([\rho^I(t), H_{\text{int}}^I(t)])\\ &= \frac{i}{\hbar}\left[\bar{\rho}_A^{I\,\lambda}(t), \sum_{\mu\alpha} b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t,t)\, A_{\alpha}^{I\lambda\mu\lambda}(t)\right] + \frac{i}{\hbar}\,\mathrm{Tr}_B^{\lambda}([\eta_{AB}^I(t), H_{\text{int}}^I(t)]).\end{aligned} \tag{2.7.3}$$

In a first rough approximation we will neglect the influence of the fluctuations $\delta\bar{\rho}_B^I(t)$ on the evolution of the subsystem A. In the same spirit, we will also neglect the influence of the statistical correlations $\eta_{AB}^I(t)$. This is equivalent to a first-order approach with regard to the interaction H_{int}. Then, Eq. (2.7.3) simplifies to

$$\frac{d}{dt}\bar{\rho}_A^{I\,\lambda}(t) \simeq \frac{i}{\hbar}[\bar{\rho}_A^{I\,\lambda}(t), \bar{H}_{A\,\text{pol}}^{I\,\lambda}(t)], \tag{2.7.4}$$

where, in accordance with Eq. (2.6.35), we have introduced the operator

$$\bar{H}_{A\,\text{pol}}^{I\,\lambda}(t) = \sum_{\mu}\sum_{\alpha\beta} g^{\lambda\mu\lambda} b_{\beta}^{\tilde{\lambda}\mu\tilde{\lambda}0} A_{\alpha}^{I\lambda\mu\lambda}(t) \tag{2.7.5}$$

with the coefficients

$$b_{\beta}^{\tilde{\lambda}\mu\tilde{\lambda}\,0} = \frac{\mathrm{Tr}(\bar{\rho}_B^{\tilde{\lambda}\,0} B_{\beta}^{I\tilde{\lambda}\mu\tilde{\lambda}}(t))}{\mathrm{Tr}(\bar{\rho}_B^{\tilde{\lambda}\,0})} = \frac{\mathrm{Tr}(\bar{\rho}_B^{\tilde{\lambda}\,0} B_{\beta}^{\tilde{\lambda}\mu\tilde{\lambda}})}{\mathrm{Tr}(\bar{\rho}_B^{\tilde{\lambda}\,0})}. \tag{2.7.6}$$

The second equality in the above relation implying the time independence of $b_{\beta}^{\tilde{\lambda}\mu\tilde{\lambda}\,0}$ follows from

$$B_{\beta}^{I\tilde{\lambda}\mu\tilde{\lambda}}(t) = e^{i\,\bar{H}_B^{\tilde{\lambda}}t/\hbar} B_{\beta}^{\tilde{\lambda}\mu\tilde{\lambda}} e^{-i\,\bar{H}_B^{\tilde{\lambda}}t/\hbar}$$

and the fact that $\bar{\rho}_B^{\tilde{\lambda}\,0}$ commutes with $\bar{H}_B^{\tilde{\lambda}}$. Going back to the Schrödinger picture, this means that, keeping only the lowest-order interaction terms, the presence of the subsystem B can be described by an additional time-independent "external force." In other words, the first-order contributions can be removed by including them in the free Hamiltonian H_A that characterizes the internal dynamics of the subsystem A. To state this more precisely, we first write the Hamiltonian H in the Schrödinger picture in the form

$$H = (H_A + H_{A\,\mathrm{pol}}) \otimes \mathbb{1}_B + \mathbb{1}_A \otimes H_B + (H_{\mathrm{int}} - H_{A\,\mathrm{pol}} \otimes \mathbb{1}_B),$$

where $H_{A\,\mathrm{pol}}$ is determined by the relations

$$\mu_A^{\lambda}(H_{A\,\mathrm{pol}}) = \sum_{\mu} \sum_{\alpha\beta} g_{\alpha\beta}^{\lambda\mu\lambda} b_{\beta}^{\tilde{\lambda}\mu\tilde{\lambda}\,0} A_{\alpha}^{\lambda\mu\lambda}$$

for all λ. The uniqueness of $H_{A\,\mathrm{pol}}$ is ensured in view of the isomorphism between $\mathscr{L}_o(\mathscr{H}_A^{\lambda})$ and $\mathscr{L}(\bar{\mathscr{H}}_A^{\lambda})$ discussed in Section 2.2. Then, according to

$$H_{\mathrm{int}}^{\lambda\lambda'} - H_{A\,\mathrm{pol}}^{\lambda}\delta_{\lambda\lambda'} \otimes \mathbb{1}_B^{\tilde{\lambda}} = \sum_{\mu} \sum_{\alpha\beta} g_{\alpha\beta}^{\lambda\mu\lambda'} A_{\alpha}^{\lambda\mu\lambda'} \otimes (B_{\beta}^{\tilde{\lambda}\mu\tilde{\lambda}'} - \delta_{\tilde{\lambda}\,\tilde{\lambda}'} b_{\beta}^{\tilde{\lambda}\mu\tilde{\lambda}\,0} \mathbb{1}_B^{\tilde{\lambda}})$$

it is convenient to make the substitutions

$$\begin{aligned} H_A + H_{A\,\mathrm{pol}} &\to H_A \\ B_{\beta}^{\tilde{\lambda}\mu\tilde{\lambda}'} - \delta_{\tilde{\lambda}\,\tilde{\lambda}'} b_{\beta}^{\tilde{\lambda}\mu\tilde{\lambda}\,0} \mathbb{1}_B^{\tilde{\lambda}} &\to B_{\beta}^{\tilde{\lambda}\mu\tilde{\lambda}'}. \end{aligned} \tag{2.7.7}$$

The redefined hamiltonian operator H_A includes the polarization of the subsystem A in presence of the subsystem B. Adopting the redefined operators $B_{\beta}^{\tilde{\lambda}\mu\tilde{\lambda}'}$ and using Eqs. (2.7.2) and (2.7.6) we find

$$\mathrm{Tr}(\bar{\rho}_B^{\tilde{\lambda}\,0} B_{\beta}^{I\tilde{\lambda}\mu\tilde{\lambda}}(t)) \equiv 0, \tag{2.7.8}$$

and Eq. (2.6.35) yields

$$b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t_0, t') \equiv 0, \tag{2.7.9}$$

which is valid to first order in H_{int}. Thus, the above substitution leads to a vanishing first-order contribution in Eq. (2.6.49). Expressed in more

physical terms this means that, neglecting the effects of the fluctuations of the subsystem B and of the statistical correlation $\eta_{AB}(t)$, the time evolution of the subsystem A is trivially described by

$$\frac{d\bar{\rho}_A^{I\,\lambda}(t)}{dt} = 0.$$

In order to catch the non-trivial part of the dynamics that is induced in the subsystem A by its interaction with the subsystem B, we have to consider the effects of the fluctuations $\delta\bar{\rho}_B^I(t)$ as well as of the statistical correlation $\eta_{AB}(t)$ between both subsystems. In the following we will work with the new operators H_A and $B_\beta^{\tilde{\lambda}\tilde{\lambda}'}$, which are obtained after the substitution (2.7.7). Then Eq. (2.7.8) is valid, and all first-order terms vanish.

Let us first consider the functions $b_{\alpha\,\alpha'}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}'}(t_0, t', t'')$ defined in Eq. (2.6.44), which depend on the reduced density matrix

$$\bar{\rho}_B^{I\,\tilde{\lambda}}(t) = \bar{\rho}_B^{\tilde{\lambda}\,0} + \delta\bar{\rho}_B^{I\,\tilde{\lambda}}(t). \tag{2.7.10}$$

The changes of $b_{\alpha\,\alpha'}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}'}(t_0, t', t'')$ due to the fluctuations $\delta\bar{\rho}_B^{I\,\tilde{\lambda}}(t)$ lead to contributions of at least third order in the relation (2.6.49), which can be neglected in our present second-order approach. This means that we can replace the functions $b_{\alpha\,\alpha'}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}(t_0, t', t'')$ in Eq. (2.6.49) by

$$c_{\alpha\,\alpha'}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}(t'-t'') = \sum_{\beta\beta'} g_{\alpha\beta}^{\lambda\mu\rho}\, g_{\alpha'\beta'}^{\rho\mu'\lambda}\, \frac{\mathrm{Tr}(\bar{\rho}_B^{\tilde{\lambda}\,0} B^{I\tilde{\lambda}\mu\tilde{\rho}}_\beta(t')\, B^{I\tilde{\rho}\mu'\tilde{\lambda}}_{\beta'}(t''))}{\mathrm{Tr}(\bar{\rho}_B^{\tilde{\lambda}\,0})}. \tag{2.7.11}$$

They depend only on the time interval $t'-t''$, since the operators $\bar{\rho}_B^{\tilde{\lambda}\,0}$ commute with $\bar{H}_B^{\tilde{\lambda}}$ (see Eq. (2.7.2)) and thus

$$\begin{aligned}\mathrm{Tr}(\bar{\rho}_B^{\tilde{\lambda}\,0} B^{I\tilde{\lambda}\mu\tilde{\rho}}_\beta(t')\, B^{I\tilde{\rho}\mu'\tilde{\lambda}}_{\beta'}(t'')) &= \mathrm{Tr}(\bar{\rho}_B^{\tilde{\lambda}\,0} e^{i\bar{H}_B^{\tilde{\lambda}}t'/\hbar} B^{\tilde{\lambda}\mu\tilde{\rho}}_\beta e^{-i\bar{H}_B^{\tilde{\beta}}(t'-t'')/\hbar} B^{\tilde{\rho}\mu'\tilde{\lambda}}_{\beta'} e^{-i\bar{H}_B^{\tilde{\lambda}}t''/\hbar}) \\ &= \mathrm{Tr}(\bar{\rho}_B^{\tilde{\lambda}\,0} e^{i\bar{H}_B^{\tilde{\lambda}}(t'-t'')/\hbar} B^{\tilde{\lambda}\mu\tilde{\rho}}_\beta e^{-i\bar{H}_B^{\tilde{\beta}}(t'-t'')/\hbar} B^{\tilde{\rho}\mu'\tilde{\lambda}}_{\beta'}).\end{aligned}$$

From the symmetry properties of the functions $b_{\alpha\,\alpha'}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}(t_0, t', t'')$ we get immediately

$$c_{\alpha\,\alpha'}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}(t'-t'')^\star = c_{\alpha'\,\alpha}^{\tilde{\lambda}\mu'\tilde{\rho}\mu\tilde{\lambda}}(t''-t'). \tag{2.7.12}$$

The functions $c_{\alpha\,\alpha'}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}(t'-t'')$ are the so-called correlation functions of the "observables" associated with the operators $B_\alpha^{I\tilde{\lambda}\mu\tilde{\rho}}(t')$ and $B_{\alpha'}^{I\tilde{\rho}\mu'\tilde{\lambda}}(t'')$ in the subsystem B. They depend explicitly on the statistical equilibrium described by the density matrix $\bar{\rho}_B^0$.

The remaining second-order contributions in Eq. (2.6.49) are generated by the functions $b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t_0, t)$, which are defined in (2.6.35). After the substitution (2.7.7), the dependence of the functions $b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t_0, t')$ on the interaction H_{int} is given by second- and higher-order terms. Consequently, the third term in Eq. (2.6.49), which contains the product of these functions, describes contributions of at least fourth order in the interaction, and thus it has to be neglected in our present second-order approach. It follows that only the second term in Eq. (2.6.49) can still contribute to second order in the interaction. For its evaluation we first rewrite the definition (2.6.35) of $b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t_0, t')$ by using Eqs. (2.7.1) and (2.7.8). We then get

$$b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t_0, t') = \sum_{\beta} g_{\alpha\beta}^{\lambda\mu\lambda} \frac{\mathrm{Tr}(\delta\bar{\rho}_B^{I\,\tilde{\lambda}}(t_0)\, B^{I\tilde{\lambda}\mu\tilde{\lambda}}_{\beta}(t'))}{\mathrm{Tr}(\bar{\rho}_B^{\tilde{\lambda}\,0} + \delta\bar{\rho}_B^{I\,\tilde{\lambda}}(t_0))}. \tag{2.7.13}$$

Obviously, the second-order contribution to $b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t_0, t')$ is determined by the first-order contribution to $\delta\bar{\rho}_B^{I\,\tilde{\lambda}}(t_0)$. According to our general assumptions, the subsystems A and B are statistically uncorrelated at time t_{00}, i.e., we have

$$\delta\bar{\rho}_B^{I\,\tilde{\lambda}}(t_{00}) = 0. \tag{2.7.14}$$

Thus, from Eq. (2.6.41) and with the definitions (2.6.42) and (2.6.45) we get the first-order expression

$$\delta\bar{\rho}_B^{I\,\tilde{\lambda}}(t_0) = -\frac{i}{\hbar}\int_{t_0}^{t_{00}} dt'' \sum_{\mu'\beta'\alpha'} g_{\alpha'\beta'}^{\lambda\mu'\lambda}[\bar{\rho}_B^{\tilde{\lambda}\,0}, B^{I\tilde{\lambda}\mu'\tilde{\lambda}}_{\beta'}(t'')]\, a_{\alpha'}^{\lambda\mu'}(t_0, t''). \tag{2.7.15}$$

This relation for $\delta\bar{\rho}_B^{I}(t_0)$ describes the linear response of the subsystem B to the "external forces" $a_{\alpha}^{\lambda\mu'}(t_0, t'')$, which represent the interaction with the subsystem A over the time interval from t_{00} to t_0. Inserting the above expression for $\delta\bar{\rho}_B^{I\,\tilde{\lambda}}(t_0)$ into Eq. (2.7.13) and using the definition (2.7.11), we obtain finally the desired second-order relation

$$\begin{aligned} b_{\alpha}^{\tilde{\lambda}\mu\tilde{\lambda}}(t_0, t') &\simeq \sum_{\beta} g_{\alpha\beta}^{\lambda\mu\lambda} \frac{\mathrm{Tr}(\delta\bar{\rho}_B^{I\,\tilde{\lambda}}(t_0)\, B^{I\tilde{\lambda}\mu\tilde{\lambda}}_{\beta}(t'))}{\mathrm{Tr}(\bar{\rho}_B^{\tilde{\lambda}\,0})} \\ &= -\frac{i}{\hbar}\int_{t_0}^{t_{00}} dt'' \sum_{\alpha'\mu'} \sum_{\beta\beta'} g_{\alpha\beta}^{\lambda\mu\lambda} g_{\alpha'\beta'}^{\lambda\mu'\lambda} \frac{\mathrm{Tr}([\bar{\rho}_B^{\tilde{\lambda}\,0}, B^{I\tilde{\lambda}\mu'\tilde{\lambda}}_{\beta'}(t'')]\, B^{I\tilde{\lambda}\mu\tilde{\lambda}}_{\beta}(t'))}{\mathrm{Tr}(\bar{\rho}_B^{\tilde{\lambda}\,0})} a_{\alpha'}^{\lambda\mu'}(t_0, t'') \\ &= -\frac{i}{\hbar}\int_{t_0}^{t_{00}} dt'' \sum_{\alpha'\mu'} (c_{\alpha'\alpha}^{\tilde{\lambda}\mu'\tilde{\lambda}\mu\tilde{\lambda}}(t''-t') - c_{\alpha\alpha'}^{\tilde{\lambda}\mu\tilde{\lambda}\mu'\tilde{\lambda}}(t'-t''))\, a_{\alpha'}^{\lambda\mu'}(t_0, t''). \end{aligned}$$

With the definition and the symmetry property of the susceptibility

$$\begin{aligned}\chi^{\tilde{\lambda}\mu\mu'}_{\alpha\ \alpha'}(\tau) &= \frac{2}{\hbar}\,\mathrm{Im}(c^{\tilde{\lambda}\mu\tilde{\lambda}\mu'\tilde{\lambda}}_{\alpha\ \alpha'}(\tau)),\\ \chi^{\tilde{\lambda}\mu\mu'}_{\alpha\ \alpha'}(\tau) &= -\chi^{\tilde{\lambda}\mu'\mu}_{\alpha'\ \alpha}(-\tau),\end{aligned} \tag{2.7.16}$$

the above equation becomes

$$b^{\tilde{\lambda}\mu\tilde{\lambda}}_{\alpha}(t_0, t') = \sum_{\alpha'\mu'} \int_{t_{00}}^{t_0} dt''\ \chi^{\tilde{\lambda}\mu\mu'}_{\alpha\ \alpha'}(t'-t'')\, a^{\lambda\mu'}_{\alpha'}(t_0, t''). \tag{2.7.17}$$

As was already mentioned above, the functions $b^{\tilde{\lambda}\mu\tilde{\lambda}\mu'\tilde{\lambda}}_{\alpha\ \alpha'}(t_0, t', t'')$ and $c^{\tilde{\lambda}\mu\tilde{\lambda}\mu'\tilde{\lambda}}_{\alpha\ \alpha'}(t'-t'')$ differ from each other by contributions of at least third order in the interaction. We emphasize that the correlation functions depend only on the time difference $t'-t''$ and, in particular, do not depend on t_{00}. Keeping only terms up to second order, we thus find that the second and the fourth term in Eq. (2.6.49) cancel each other, so that finally, under the additional initial conditions discussed at the beginning of this subsection, only the first and the fifth terms of Eq. (2.6.49) contribute to the corresponding second-order expression. The influence of the subsystem B on the evolution of the subsystem A is then given by

$$\begin{aligned}\bar{\rho}^{I\ \lambda}_{A}(t) = \bar{\rho}^{I\ \lambda}_{A}(t_0) + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \sum_{\mu\alpha} \int_{t_{00}}^{t'} dt''\\ \times \sum_{\mu'\alpha'} \sum_{\rho} (\bar{\rho}^{I\ \lambda}_{A}(t_0)\, A^{I\lambda\mu'\rho}_{\alpha'}(t'')\, A^{I\rho\mu\lambda}_{\alpha}(t')\, c^{\tilde{\lambda}\mu'\tilde{\rho}\mu\tilde{\lambda}}_{\alpha'\ \alpha}(t''-t')\\ - A^{I\lambda\mu'\rho}_{\alpha'}(t'')\, \bar{\rho}^{I\ \rho}_{A}(t_0)\, A^{I\rho\mu\lambda}_{\alpha}(t')\, c^{\tilde{\rho}\mu\tilde{\lambda}\mu'\tilde{\rho}}_{\alpha\ \alpha'}(t'-t'')\\ - A^{I\lambda\mu\rho}_{\alpha}(t')\, \bar{\rho}^{I\ \rho}_{A}(t_0)\, A^{I\rho\mu'\lambda}_{\alpha'}(t'')\, c^{\tilde{\rho}\mu'\tilde{\lambda}\mu\tilde{\rho}}_{\alpha'\ \alpha}(t''-t')\\ + A^{I\lambda\mu\rho}_{\alpha}(t')\, A^{I\rho\mu'\lambda}_{\alpha'}(t'')\, \bar{\rho}^{I\ \lambda}_{A}(t_0)\, c^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}_{\alpha\ \alpha'}(t'-t'')).\end{aligned} \tag{2.7.18}$$

The above equation describes the situation, where the subsystem B is held near some statistical equilibrium but still fluctuates. We see that, apart from an explicit dependence on the time t_{00}, the resulting evolution of the subsystem A is fully determined by the correlation functions $c^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}_{\alpha\ \alpha'}(t'-t'')$.

As a particular example, let us consider the case where the density matrix of the bath subsystem B is described by the canonical ensemble

$$\bar{\rho}^{\tilde{\lambda}\,0}_{B} = \frac{1}{Z_B}\, e^{-\beta \bar{H}^{\tilde{\lambda}}_{B}}, \qquad \beta = \frac{1}{k_B T}.$$

Inserting the formal identity

$$\begin{aligned}
&\mathrm{Tr}(\bar{\rho}_B^{\tilde{\lambda}\,0} B_\beta^{I\tilde{\lambda}\mu\tilde{\rho}}(t')\, B_{\beta'}^{I\tilde{\rho}\mu'\tilde{\lambda}}(t'')) \\
&\quad = \frac{1}{Z_B}\,\mathrm{Tr}(e^{i\bar{H}_B^{\tilde{\lambda}}(t'+i\hbar\beta-t'')/\hbar} B_\beta^{\tilde{\lambda}\mu\tilde{\rho}} e^{-i\bar{H}_B^{\tilde{\rho}}(t'+i\hbar\beta-t'')/\hbar} e^{-\beta\bar{H}_B^{\tilde{\rho}}} B_{\beta'}^{\tilde{\rho}\mu'\tilde{\lambda}}) \\
&\quad = \mathrm{Tr}(\bar{\rho}_B^{\tilde{\rho}\,0} e^{-i\bar{H}_B^{\tilde{\rho}}(t'+i\hbar\beta-t'')/\hbar} B_{\beta'}^{\tilde{\rho}\mu'\tilde{\lambda}} e^{i\bar{H}_B^{\tilde{\lambda}}(t'+i\hbar\beta-t'')/\hbar} B_\beta^{\tilde{\lambda}\mu\tilde{\rho}}) \\
&\quad = \mathrm{Tr}(\bar{\rho}_B^{\tilde{\rho}\,0} B_{\beta'}^{I\tilde{\rho}\mu'\tilde{\lambda}}(t'')\, B_\beta^{I\tilde{\lambda}\mu\tilde{\rho}}(t'+i\hbar\beta))
\end{aligned}$$

into the definition (2.7.11) for the correlation functions, we get the symmetry property

$$\begin{aligned}
p_\lambda^0 c_{\alpha\,\alpha'}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}(\tau) &= \sum_{\beta\beta'} g_{\alpha\beta}^{\lambda\mu\rho} g_{\alpha'\beta'}^{\rho\mu'\lambda}\,\mathrm{Tr}(\bar{\rho}_B^{\tilde{\rho}\,0} B_{\beta'}^{I\tilde{\rho}\mu'\tilde{\lambda}}(t'')\, B_\beta^{I\tilde{\lambda}\mu\tilde{\rho}}(t'+i\hbar\beta)) \\
&= p_\rho^0 c_{\alpha'\,\alpha}^{\tilde{\rho}\mu'\tilde{\lambda}\mu\tilde{\rho}}(-\tau-i\hbar\beta)
\end{aligned} \tag{2.7.19}$$

with $p_\lambda^0 = \mathrm{Tr}(\bar{\rho}_B^{\tilde{\lambda}\,0})$, which will be used later on.

2.8. Statistical Evolution of the Subsystem *A* for a Subsystem *B* Acting as a Bath

We now come back to our original problem, which was the description of the statistical evolution of the subsystem A coupled to a bath subsystem B. As before, we assume weak dynamical coupling and weak statistical correlations between both subsystems. The bath character of the subsystem B imposes certain constraints. First, we have to assume that the subsystem B fluctuates around a statistical equilibrium, which is described by a density matrix $\bar{\rho}_B^0$ that commutes with the free hamiltonian operator $\bar{H}_B$, the fluctuations becoming uncorrelated for times larger than the "correlation time" τ_B^{corr}. Secondly, the evolution of the subsystem A must be slow on the time scale τ_B^{corr}, i.e., the correlation time τ_B^{corr} has to be much smaller than the typical "evolution time" τ_A^{evol} of the subsystem A.

The second condition requires some additional comments. While the meaning of the correlation time τ_B^{corr} is rather self-explanatory—it defines the time interval $|t'-t''|$ over which the correlation functions $c_{\alpha\alpha'}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}(t'-t'')$ differ significantly from zero—the notion of the evolution time τ_A^{evol} is much more subtle. This time will be defined properly in the next subsection. For the moment it is sufficient to say that the "evolution time" τ_A^{evol} can be seen as a measure of the coupling strength, which increases with decreasing strength of H_{int}. Roughly speaking, for electrons in a "frozen" molecule, τ_A^{evol} would correspond to the fine-structure splitting of the energy levels.

It is easily seen that—in principle—a small correlation time τ_B^{corr} is only compatible with a broad continuous (or at least quasi-continuous) energy spectrum of the subsystem B and a statistical state $\bar{\rho}_B^0$ corresponding to wide-spread occupation probabilities on this energy spectrum. At first sight, this seems to be in conflict with our actual description, where the subsystem B is associated with a Hilbert space $\mathcal{H}_B$ of finite dimension. In a completely closed system this would lead to Poincaré cycles for the correlation functions of the subsystem B on long time scales.[38] This is obviously not the situation considered here, where we have characterized the bath subsystem B by the mean density matrix $\bar{\rho}_B^0$ and the correlation functions $c_{\alpha\,\alpha'}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\lambda}(t'-t'')$, which become zero for large time intervals $t'-t''$. In order to solve this puzzle, let us first recall that, according to the remarks at the beginning of Section 2.7, the relation (2.7.18) is still valid for subsystems B interacting with the external world containing an infinite number of degrees of freedom and a continuous infinite spectrum. In this case, the statistical properties of the subsystem B and in particular the correlation functions $c_{\alpha\,\alpha'}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\lambda}(t'-t'')$ are determined by its interaction with the subsystem A as well as by its interaction with the external world. In our present description we assume that the latter interaction prohibits the appearance of Poincaré cycles, and that it is responsible for the required small correlation time τ_B^{corr}. Thus, τ_B^{corr} is a phenomenological parameter that accounts for the effective openness of the considered $A+B$ system due to its interaction with the infinite external world.

Our present aim is to describe the evolution of the subsystem A during a time interval $\Delta t \equiv t-t_0$ that is much larger than the correlation time τ_B^{corr}, i.e., we suppose

$$t-t_0 \equiv \Delta t \gg \tau_B^{\text{corr}}.$$

The above restriction allows us to simplify the corresponding relation (2.7.18). As can be seen from this equation, the influence of the bath subsystem B on the evolution of the subsystem A is completely determined by the correlation functions $c_{\alpha\alpha'}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\lambda}(t'-t'')$. The latter are only significantly different from zero if their argument $|t'-t''|$ is of the same order of magnitude or smaller than the correlation time τ_B^{corr}. Accordingly, the integration area for the double integrals with respect to t' and t'' in Eq. (2.7.18) can be restricted to a narrow strip close to the line $|t'-t''|=0$. This suggests to replace t'' in Eq. (2.7.18) by the new variable of integration $\tau = t'-t''$. Then the double integration can be rewritten as

$$\int_{t_0}^{t} dt' \int_{t_{00}}^{t'} dt'' \cdots = -\int_{t_0}^{t} dt' \int_{t'-t_{00}}^{0} d\tau \cdots = \int_{t_0}^{t} dt' \int_{0}^{t'-t_{00}} d\tau \cdots \simeq \int_{t_0}^{t} dt' \int_{0}^{\infty} d\tau \cdots .$$

For the last approximate equality we have used the fact that the correlation functions $c^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}_{\alpha\alpha'}(\tau)$ vanish for $\tau \geqslant t' - t_{00} \geqslant t_0 - t_{00} \geqslant \tau_B^{\text{corr}}$. Thus, expression (2.7.18) can be replaced by

$$\begin{aligned}
\bar{\rho}_A^{I\,\lambda}(t) = \bar{\rho}_A^{I\,\lambda}(t_0) + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \sum_{\mu\alpha} \int_0^{\infty} d\tau \\
\times \sum_{\mu'\alpha'} \sum_{\rho} (\bar{\rho}_A^{I\,\lambda}(t_0)\, A^{I\lambda\mu'\rho}_{\alpha'}(t'-\tau)\, A^{I\rho\mu\lambda}_{\alpha}(t')\, c^{\tilde{\lambda}\mu'\tilde{\rho}\mu\tilde{\lambda}}_{\alpha'\alpha}(-\tau) \\
- A^{I\lambda\mu'\rho}_{\alpha'}(t'-\tau)\, \bar{\rho}_A^{I\,\rho}(t_0)\, A^{I\rho\mu\lambda}_{\alpha}(t')\, c^{\tilde{\rho}\mu\tilde{\lambda}\mu'\tilde{\rho}}_{\alpha\alpha'}(\tau) \\
- A^{I\lambda\mu\rho}_{\alpha}(t')\, \bar{\rho}_A^{I\,\rho}(t_0)\, A^{I\rho\mu'\lambda}_{\alpha'}(t'-\tau)\, c^{\tilde{\rho}\mu'\tilde{\lambda}\mu\tilde{\rho}}_{\alpha'\alpha}(-\tau) \\
+ A^{I\lambda\mu\rho}_{\alpha}(t')\, A^{I\rho\mu'\lambda}_{\alpha'}(t'-\tau)\, \bar{\rho}_A^{I\,\lambda}(t_0)\, c^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}_{\alpha\alpha'}(\tau)).
\end{aligned} \tag{2.8.1}$$

We emphasize that the above relation does no longer depend on the time t_{00}. It is homogeneous with respect to the time. This is a consequence of the fact that the bath subsystem B has a finite temporal memory, which implies that it cannot store any information about its interaction with the subsystem A over times larger than τ_B^{corr}. Thus, the introduction of the time t_{00} is just a formal step, which does not lead to any further limitations concerning the validity of the present approach. The influence of the bath B on the behavior of the subsystem A is completely determined by the statistical correlations which are "born" during the time interval from t_0 to t. These correlations are maintained over times, which are of the order of τ_B^{corr}, and thus much shorter than the considered time interval.

To write Eq. (2.8.1) in a more explicit form, we refer to the orthonormal basis vectors in the Hilbert space $\bar{\mathscr{H}}_A$, which were introduced in Section 2.2. Let us briefly recall the basic facts. The orthonormal basis of the Hilbert space $\bar{\mathscr{H}}_A$ is given by the vectors $|a, \lambda\rangle \equiv |a, \lambda, 1\rangle$, $a = 1,\ldots, n_A^{\lambda}$ and $\lambda \in \Lambda_{AB}$. According to Eq. (2.5.5), these vectors are eigenvectors of the Hamiltonian $\bar{H}_A$, i.e., they satisfy

$$\bar{H}_A\, |a, \lambda\rangle = E_a^{\lambda}\, |a, \lambda\rangle. \tag{2.8.2}$$

We have

$$\langle a', \lambda'|\, A^{I\lambda\mu\rho}_{\alpha}(t)\, |a'', \rho'\rangle = 0 \qquad \text{if} \quad \lambda' \neq \lambda \quad \text{or} \quad \rho' \neq \rho, \tag{2.8.3}$$

and otherwise

$$\langle a', \lambda|\, A^{I\lambda\mu\rho}_{\alpha}(t)\, |a'', \rho\rangle = \langle a', \lambda|\, A^{\lambda\mu\rho}_{\alpha}\, |a'', \rho\rangle\, e^{i\,\omega^{\lambda\ \rho}_{a'\ a''}\, t} \tag{2.8.4}$$

with

$$\omega_{a'\,a''}^{\lambda\ \rho} = \frac{E_{a'}^{\lambda} - E_{a''}^{\rho}}{\hbar}. \tag{2.8.5}$$

Thus, using the above basis of $\bar{\mathscr{H}}_A$, we know the explicit time dependence of the matrix elements of the operators occurring in Eq. (2.8.1). This allows us to write the corresponding relations for the matrix elements of the density matrix $\bar{\rho}_A^{I\,\lambda}(t)$ in a rather compact form. Inserting the matrix elements (2.8.3)–(2.8.5) into the matrix equation corresponding to Eq. (2.8.1), we obtain

$$\begin{aligned}
&\langle a_1, \lambda|\, \bar{\rho}_A^{I\,\lambda}(t)\, |a_2, \lambda\rangle \\
&= \langle a_1, \lambda|\, \bar{\rho}_A^{I\,\lambda}(t_0)\, |a_2, \lambda\rangle \\
&\quad + \sum_{\rho} \sum_{a_1', a_2'} \Gamma_{\lambda\ a_1 a_2}^{\rho\ a_1' a_2'} \langle a_1', \rho|\, \bar{\rho}_A^{I\,\rho}(t_0)\, |a_2', \rho\rangle \int_{t_0}^{t} \exp(i(\omega_{a_1 a_2}^{\lambda\ \lambda} - \omega_{a_1' a_2'}^{\rho\ \rho})\, t')\, dt'
\end{aligned} \tag{2.8.6}$$

with

$$\Gamma_{\lambda\ a_1 a_2}^{\rho\ a_1' a_2'} = \left(F_{\lambda\ a_1 a_2}^{\rho\ a_1' a_2'} + F_{\lambda\ a_2 a_1}^{\rho\ a_2' a_1'\,\star} - \delta_{\lambda\rho} \left(\delta_{a_1}^{a_1'} \sum_{a,\nu} F_{\nu a a}^{\lambda a_2 a_2'} + \delta_{a_2}^{a_2'} \sum_{a,\nu} F_{\nu a a}^{\lambda a_1 a_1'\,\star} \right) \right) \tag{2.8.7}$$

and

$$F_{\lambda\ a_1 a_2}^{\rho\ a_1' a_2'} = \frac{1}{\hbar^2} \sum_{\mu\alpha} \sum_{\mu'\alpha'} \langle a_1, \lambda|\, A_{\alpha}^{\lambda\mu\rho}\, |a_1', \rho\rangle \langle a_2', \rho|\, A_{\alpha'}^{\rho\mu'\lambda}\, |a_2, \lambda\rangle \int_{-\infty}^{0} c_{\alpha'\alpha}^{\tilde{\rho}\mu'\tilde{\lambda}\mu\tilde{\rho}}(\tau)\, e^{i\, \omega_{a_2' a_2}^{\rho\ \lambda} \tau}\, d\tau. \tag{2.8.8}$$

From the above expression of the coefficients $\Gamma_{\lambda\ a_1 a_2}^{\rho\ a_1' a_2'}$ we get immediately the symmetry relations

$$\Gamma_{\lambda\ a_1 a_2}^{\rho\ a_1' a_2'\,\star} = \Gamma_{\lambda\ a_2 a_1}^{\rho\ a_2' a_1'} \tag{2.8.9}$$

and the sum rule

$$\sum_{\lambda} \sum_{a} \Gamma_{\lambda\ a a}^{\rho\ a_1' a_2'} = 0. \tag{2.8.10}$$

The proof of the relations (2.8.6) and (2.8.7) is straightforward even though rather laborious, and it does not present any major mathematical difficulties. After integration with respect to t' in Eq. (2.8.6), we obtain the

following expression for the matrix elements of the reduced density matrix $\bar{\rho}_A^I(t)$

$$\begin{aligned}\langle a_1, \lambda|\, \bar{\rho}_A^{I\,\lambda}(t)\, |a_2, \lambda\rangle &= \langle a_1, \lambda|\, \bar{\rho}_A^{I\,\lambda}(t_0)\, |a_2, \lambda\rangle + \Delta t \sum_{\rho} \sum_{a_1' a_2'} \Gamma^{\rho\, a_1' a_2'}_{\lambda\, a_1 a_2} \langle a_1', \rho|\, \bar{\rho}_A^{I\,\rho}(t_0)\, |a_2', \rho\rangle \\ &\times g((\omega^{\lambda\,\lambda}_{a_1 a_2} - \omega^{\rho\,\rho}_{a_1' a_2'})\, \Delta t) \exp(i(\omega^{\lambda\,\lambda}_{a_1 a_2} - \omega^{\rho\,\rho}_{a_1' a_2'})\, \bar{t}) \end{aligned} \tag{2.8.11}$$

with

$$\Delta t = t - t_0 \qquad \text{and} \qquad \bar{t} = t_0 + \frac{\Delta t}{2}, \tag{2.8.12}$$

and where g denotes the real function

$$g(x) = \frac{\sin(x/2)}{x/2}, \qquad x \in \mathbb{R}. \tag{2.8.13}$$

Equation (2.8.11) gives us the desired time dependence of the statistical state of the subsystem A interacting with the bath subsystem B. It is the basis for our following derivation of the so-called master equations, which govern the "coarse grained" evolution of the subsystem A.

The absolute values of the exact matrix elements $\langle a_1, \lambda|\, \bar{\rho}_A^{I\,\lambda}(t)\, |a_2, \lambda\rangle$ are bounded by 1. This follows from Eq. (2.2.28), which implies that

$$\sum_{\lambda} \sum_{a_1, a_2 = 1}^{n_A^{\lambda}} |\langle a_1, \lambda|\, \bar{\rho}_A\, |a_2, \lambda\rangle|^2 \equiv \mathrm{Tr}((\bar{\rho}_A)^2) \leqslant \mathrm{Tr}(\bar{\rho}_A) = 1.$$

In order to prevent violation of this condition when using the approximative relations (2.8.11), we have to keep the time interval Δt small enough. This means that the relations (2.8.11) are only valid within a time interval, which on the one hand satisfies $\Delta t \gg \tau_B^{\mathrm{corr}}$, and which on the other hand is small enough to ensure that the operator $\bar{\rho}_A^I(t)$ provided by (2.8.11) satisfies the second condition (2.2.28). It should be noted that the two further conditions listed in (2.2.28) are automatically satisfied by the approximated reduced density matrix, since the relations (2.8.11) together with the properties (2.8.9) and (2.8.10) yield a self-adjoint density matrix $\bar{\rho}_A^I(t)$ with unit trace for arbitrary t and t_0.

2.9. Coarse Grained Statistical Evolution of the Subsystem *A*

In the following we will assume that the ensemble of difference frequencies $\omega^{\lambda\,\lambda}_{a_1 a_2} - \omega^{\rho\,\rho}_{a_1' a_2'} \neq 0$ in Eq. (2.8.11) does not have an accumulation

point at zero frequency, or in other words, that the spectrum of all transition frequencies $\omega^{\lambda\,\lambda}_{a_1 a_2}$ possesses a minimal non-zero splitting frequency $\Delta\omega_A$,

$$\Delta\omega_A = \inf |\omega^{\lambda\,\lambda}_{a_1 a_2} - \omega^{\rho\,\rho}_{a'_1 a'_2}| \neq 0,$$

with a_1 and $a_2 = 1,\ldots, n^{\lambda}_A$, a'_1 and $a'_2 = 1,\ldots, n^{\rho}_A$ and $\lambda, \rho \in \Lambda_A$. This condition is satisfied in the presently considered situation of a Hilbert space $\mathscr{H}_A$ of finite dimension where one has a finite number of frequencies.

Our present purpose is to obtain a system of equations governing the so-called "coarse grained" evolution. In other words, we are looking for the equations, which govern the time evolution of a "time-averaged" density matrix $\bar{\rho}^I_A(t)$, where the time averaging suppresses the oscillations generated by the bath. We define the time-averaged density matrix $D^I_R(\bar{t})$ by

$$D^I_R(\bar{t}) = \frac{1}{\Delta t} \int_{\bar{t}-\Delta t/2}^{\bar{t}+\Delta t/2} \bar{\rho}^I_A(t')\, dt' \tag{2.9.1}$$

with

$$\tau^{\mathrm{corr}}_B \ll \Delta t \ll \pi/\omega_{\max} < 2\pi/\Delta\omega_A, \tag{2.9.2}$$

where

$$\omega_{\max} = \max\{|\omega^{\lambda\,\lambda}_{a_1 a_2}|\}, \qquad a_1, a_2 = 1,\ldots, n^{\lambda}_A, \quad \lambda \in \Lambda_{AB}$$

denotes the maximal transition frequency. Similar to $\bar{\rho}^I_A(t')$, the operator $D^I_R(\bar{t})$ (2.9.1) is self-adjoint with unit trace. We note, however, that the time-averaged density matrix $D^I_R(\bar{t})$ does not strictly satisfy the positivity condition (2.2.28).

Equation (2.9.2) allows us to use the approximate identity

$$g((\omega^{\lambda\,\lambda}_{a_1 a_2} - \omega^{\rho\,\rho}_{a'_1 a'_2})\, \Delta t) = 1. \tag{2.9.3}$$

Then, according to the relations (2.8.11), the evolution of the restricted density matrix $\bar{\rho}^{I\,\lambda}_A(t)$ is basically governed by two different types of behavior. On the one hand, terms with $\omega^{\lambda\,\lambda}_{a_1 a_2} - \omega^{\rho\,\rho}_{a'_1 a'_2} \simeq 0$ lead to a change increasing linearly with time. On the other hand, terms corresponding to difference frequencies significantly different from zero give rise to oscillating contributions. Obviously, a clear cut separation between the two types of behavior is only possible if both contributions act on different time scales. The time scale for the the slowest oscillations is given by $2\pi/\Delta\omega_A$.

The typical time scale for the linear change of the reduced density matrix $\bar{\rho}_A^I(t)$ is given by the inverse of the "evolution time" τ_A^{evol}, which was introduced in Section 2.8. Starting from Eq. (2.8.11), we define τ_A^{evol} as the time interval, which would correspond to a change of order unity of the matrix element $\langle a_1, \lambda| \bar{\rho}_A^{I\,\lambda}(t) |a_2, \lambda\rangle$ with the fastest linear increase, i.e.,

$$\frac{1}{\tau_A^{\text{evol}}} = \sup_{(\lambda, a_1, a_2) \in \mathscr{D}} \left| \sum_{\rho} \sum_{a_1' a_2'} \Gamma^{\rho\ a_1' a_2'}_{\lambda\ a_1 a_2} \langle a_1', \rho| \bar{\rho}_A^{I\,\rho}(t_0) |a_2', \rho\rangle \right|$$

with

$$\mathscr{D} = \{(\lambda, a_1, a_2) \mid \lambda \in \Lambda_{AB}, a_1, a_2 = 1,\ldots, n_A^{\lambda}\}.$$

The term $|\cdots|$ specifies the speed of the linear change for the matrix element $\langle a_1, \lambda| \bar{\rho}_A^{I\,\lambda}(t_0) |a_2, \lambda\rangle$. Consequently, linear and oscillatory contributions are well distinguished if

$$2\pi/\Delta\omega_A \ll \tau_A^{\text{evol}}. \tag{2.9.4}$$

This condition is an alternative way to express our initial assumption of a weak dynamical coupling. Putting the conditions (2.9.2) and (2.9.4) together we have

$$\tau_B^{\text{corr}} \ll \Delta t \ll \pi/\omega_{\max} < 2\pi/\omega_A \ll \tau_A^{\text{evol}}.$$

From the definition (2.9.1) it follows that

$$\frac{dD_R^I(\bar{t})}{d\bar{t}} = \frac{\bar{\rho}_A^I(t) - \bar{\rho}_A^I(t_0)}{t - t_0}.$$

Thus, making use of Eq. (2.9.3), we get from Eq. (2.8.11)

$$\frac{d}{d\bar{t}} \langle a_1, \lambda| D_R^I(\bar{t}) |a_2, \lambda\rangle = \sum_{\rho} \sum_{a_1', a_2'} \Gamma^{\rho\ a_1' a_2'}_{\lambda\ a_1 a_2} \langle a_1', \rho| \bar{\rho}_A^{I\,\rho}(t_0) |a_2', \rho\rangle\, e^{i(\omega_{a_1 a_2}^{\lambda\ \lambda} - \omega_{a_1' a_2'}^{\rho\ \rho})\bar{t}}. \tag{2.9.5}$$

For the considered time intervals satisfying the condition (2.9.2), the matrix elements of $\bar{\rho}_A^I(t_0)$ on the right-hand side of the relations (2.9.5) can be replaced by the respective matrix elements of the operator $D_R^I(\bar{t})$. We then get the Redfield equations[9–11]

$$\frac{d}{d\bar{t}} \langle a_1, \lambda| D_R^I(\bar{t}) |a_2, \lambda\rangle = \sum_{\rho, a_1', a_2'} \Gamma^{\rho\ a_1' a_2'}_{\lambda\ a_1 a_2} \langle a_1', \rho| D_R^I(\bar{t}) |a_2', \rho\rangle\, e^{i(\omega_{a_1 a_2}^{\lambda\ \lambda} - \omega_{a_1' a_2'}^{\rho\ \rho})\bar{t}}. \tag{2.9.6}$$

When considering the effects of external forces, it is convenient to change to a Schrödinger-like picture, in order to get rid of the spurious time-dependence introduced by the change to the interaction picture. We then have to consider the evolution of the matrix

$$D_R(\bar{t}) = e^{-i\bar{H}_A\bar{t}/\hbar} D_R^I(\bar{t})\, e^{+i\bar{H}_A\bar{t}/\hbar}. \tag{2.9.7}$$

From Eq. (2.9.6) we find

$$\frac{d}{d\bar{t}} \langle a_1, \lambda |\, D_R(\bar{t})\, | a_2, \lambda \rangle$$

$$= \frac{i}{\hbar} \langle a_1, \lambda |\, [D_R(\bar{t}), \bar{H}_A]\, | a_2, \lambda \rangle + \sum_{\rho, a_1', a_2'} \Gamma_{\lambda\, a_1 a_2}^{\rho\, a_1' a_2'} \langle a_1', \rho |\, D_R(\bar{t})\, | a_2', \rho \rangle. \tag{2.9.8}$$

The above "master equations" Eq. (2.9.6) or Eq. (2.9.8) govern the coarse grained evolution of the time-averaged reduced density matrix of the subsystem A interacting with the bath B, where the subsystems A and B represent parts of a fermionic system. It should be noted that, as a direct consequence of Eq. (2.2.14), the matrices $D_R^I(\bar{t})$ and $D_R(\bar{t})$ are block-diagonal with respect to the type λ. Dynamical coupling between different diagonal blocks λ and ρ is generated by the bath subsystem B through the coefficients $\Gamma_{\lambda\, a_1 a_2}^{\rho\, a_1' a_2'}$. Consequently, Eqs. (2.9.6) and (2.9.8) constitute systems of coupled master equations.

In many situations the oscillatory contributions to the Redfield equations (2.9.6) are irrelevant. Then the evolution of the time-averaged density matrix becomes Markovian, i.e., we get

$$\frac{d}{d\bar{t}} \langle a_1, \lambda |\, D^I(\bar{t})\, | a_2, \lambda \rangle = \sum_{\{\rho, a_1', a_2' \,|\, \omega_{a_1' a_2'}^{\rho\,\rho} = \omega_{a_1 a_2}^{\lambda\,\lambda}\}} \Gamma_{\lambda\, a_1 a_2}^{\rho\, a_1' a_2'} \langle a_1', \rho |\, D^I(\bar{t})\, | a_2', \rho \rangle. \tag{2.9.9}$$

In order to simplify our terminology, we will from now on refer to these equations as the master equations governing the Markovian coarse-grained evolution or the Markovian master equations. Switching to the Schrödinger picture, we get in full analogy with Eqs. (2.9.7) and (2.9.8)

$$D(\bar{t}) = e^{-i\bar{H}_A\bar{t}/\hbar} D^I(\bar{t})\, e^{+i\bar{H}_A\bar{t}/\hbar}$$

and

$$\frac{d}{d\bar{t}}\langle a_1, \lambda|\, D(\bar{t})\,|a_2, \lambda\rangle = \frac{i}{\hbar}\langle a_1, \lambda|\,[D(\bar{t}), \bar{H}_A]\,|a_2, \lambda\rangle + \sum_{\{\rho, a_1', a_2'\,|\,\omega^{\rho\,\rho}_{a_1' a_2'} = \omega^{\lambda\,\lambda}_{a_1 a_2}\}} \Gamma^{\rho\; a_1' a_2'}_{\lambda\; a_1 a_2}\langle a_1', \rho|\, D(\bar{t})\,|a_2', \rho\rangle. \tag{2.9.10}$$

In Section 3 we will discuss the Markovian master equations (2.9.9) and (2.9.10) for the particular situation, where the physical system is provided by N electrons. We will see that in this situation the spin part of the electrons takes the part of the subsystem A, whereas the spatial degrees of freedom, i.e., positions and momenta, take the part of the subsystem B. Furthermore, there is a one-to-one correspondence between the type λ and the quantum number specifying the total spin of the electrons.

The master equations (2.9.6) and (2.9.9) show that the evolution of the subsystem A associated with the internal degrees of freedom is determined by the coefficients $\Gamma^{\rho\; a_1' a_2'}_{\lambda\; a_1 a_2}$. In the following we will focus on the structure of these coefficients and on their physical interpretation.

2.10. Structure of the Master Equations

In this subsection we will rearrange the master equations (2.9.9) to obtain a better understanding of the physical mechanisms, which govern the Markovian coarse grained evolution of a subsystem A of a fermionic system. This evolution is of course completely determined by the coefficients $\Gamma^{\rho\; a_1' a_2'}_{\lambda\; a_1 a_2}$. In fact, due to the restriction of the summation in Eq. (2.9.9) we need only to consider the coefficients corresponding to $\omega^{\rho\,\rho}_{a_1' a_2'} = \omega^{\lambda\,\lambda}_{a_1 a_2}$. Thus, without loss of generality we can assume

$$\Gamma^{\rho\; a_1' a_2'}_{\lambda\; a_1 a_2} = 0 \qquad \text{if} \quad \omega^{\lambda\,\lambda}_{a_1 a_2} \neq \omega^{\rho\,\rho}_{a_1' a_2'}. \tag{2.10.1}$$

Starting from the definition (2.8.7), we first rewrite the coefficients as

$$\Gamma^{\rho\; a_1' a_2'}_{\lambda\; a_1 a_2} = \Gamma_0{}^{\rho\; a_1' a_2'}_{\lambda\; a_1 a_2} + \frac{i}{\hbar}\,\delta_{\lambda\rho}(\delta_{a_1 a_1'}(H^{\lambda}_{a_2' a_2} + iG^{\lambda}_{a_2' a_2}) - (H^{\lambda}_{a_1 a_1'} - iG^{\lambda}_{a_1 a_1'})\,\delta_{a_2 a_2'}) \tag{2.10.2}$$

with

$$\Gamma_{0\ \lambda\ a_1 a_2}^{\rho\ a_1' a_2'} = F_{\lambda a_1 a_2}^{\rho a_1' a_2'} + F_{\lambda a_2 a_1}^{\rho a_2' a_1'\star}$$

$$G_{aa'}^{\lambda} = \frac{\hbar}{2} \sum_{\nu a''} (F_{\nu a'' a''}^{\lambda a' a} + F_{\nu a'' a''}^{\lambda a a'\star}) \tag{2.10.3}$$

$$H_{aa'}^{\lambda} = i \frac{\hbar}{2} \sum_{\nu a''} (F_{\nu a'' a''}^{\lambda a' a} - F_{\nu a'' a''}^{\lambda a a'\star}).$$

The new coefficients satisfy the symmetry relations

$$\Gamma_{0\ \lambda\ a_1 a_2}^{\rho\ a_1' a_2'\star} = \Gamma_{0\ \lambda\ a_2 a_1}^{\rho\ a_2' a_1'} \qquad G_{aa'}^{\lambda\star} = G_{a'a}^{\lambda} \qquad H_{aa'}^{\lambda\star} = H_{a'a}^{\lambda}. \tag{2.10.4}$$

From the definition (2.8.8), the symmetry property (2.7.12), the relation (2.6.24), and exploiting the fact that presently we have $\omega_{a_1' a_1}^{\rho\ \lambda} = \omega_{a_2' a_2}^{\rho\ \lambda}$, we get

$$\Gamma_{0\ \lambda\ a_1 a_2}^{\rho\ a_1' a_2'} = \frac{1}{\hbar} \sum_{\mu\alpha} \sum_{\mu'\alpha'} \chi_{\alpha\alpha'}^{\tilde{\rho}\mu\tilde{\lambda}\mu'\tilde{\rho}}(\omega_{a_1' a_1}^{\rho\ \lambda}) \langle a_1, \lambda | A_{\alpha'}^{\lambda\mu'\rho} | a_1', \rho \rangle \langle a_2', \rho | A_{\alpha}^{\rho\mu\lambda} | a_2, \lambda \rangle \tag{2.10.5}$$

where

$$\chi_{\alpha\alpha'}^{\tilde{\rho}\mu\tilde{\lambda}\mu'\tilde{\rho}}(\omega) = \frac{1}{\hbar} \int_{-\infty}^{+\infty} c_{\alpha\ \alpha'}^{\tilde{\rho}\mu\tilde{\lambda}\mu'\tilde{\rho}}(\tau)\, e^{i\omega\tau}\, d\tau. \tag{2.10.6}$$

Due to the symmetry property (2.7.12) we have also

$$\chi_{\alpha\alpha'}^{\tilde{\rho}\mu\tilde{\lambda}\mu'\tilde{\rho}}(\omega)^{\star} = \chi_{\alpha'\alpha}^{\tilde{\rho}\mu'\tilde{\lambda}\mu\tilde{\rho}}(\omega). \tag{2.10.7}$$

This can be used to rewrite the expression for $G_{aa'}^{\lambda}$ defined in (2.10.3). For simplicity, we will assume in the following that $\omega_{a_1 a_2}^{\lambda\ \lambda} = \omega_{a_1' a_2'}^{\rho\ \rho}$ is only possible for $a_1 = a_2$ and $a_1' = a_2'$. For $E_a^{\lambda} = E_{a'}^{\lambda}$, which then corresponds to our condition (2.10.1), we get

$$G_{aa'}^{\lambda} = \frac{\hbar}{2} \sum_{\nu a''} \Gamma_{0\ \nu\ a'' a''}^{\lambda\ a' a}$$

$$= \frac{1}{2} \sum_{\nu a''} \sum_{\mu\alpha} \sum_{\mu'\alpha'} \chi_{\alpha\alpha'}^{\tilde{\lambda}\mu\tilde{\nu}\mu'\tilde{\lambda}}(\omega_{aa''}^{\lambda\nu}) \langle a, \lambda | A_{\alpha}^{\lambda\mu\nu} | a'', \nu \rangle \langle a'', \nu | A_{\alpha'}^{\nu\mu'\lambda} | a', \lambda \rangle. \tag{2.10.8}$$

Again, the definition for $H^{\lambda}_{aa'}$ in (2.10.3) becomes for $E^{\lambda}_{a} = E^{\lambda}_{a'}$

$$H^{\lambda}_{aa'} = -\tfrac{1}{2} \sum_{\nu a''} \sum_{\mu\alpha} \sum_{\mu'\alpha'} \bar{\chi}^{\tilde{\lambda}\mu\tilde{\nu}\mu'\tilde{\lambda}}_{\alpha\alpha'}(\omega^{\lambda\nu}_{aa''}) \langle a, \lambda | A^{\lambda\mu\nu}_{\alpha} | a'', \nu \rangle \langle a'', \nu | A^{\nu\mu'\lambda}_{\alpha'} | a', \lambda \rangle \tag{2.10.9}$$

with

$$\bar{\chi}^{\tilde{\lambda}\mu\tilde{\nu}\mu'\tilde{\lambda}}_{\alpha\alpha'}(\omega) = \frac{i}{\hbar} \int_{-\infty}^{\infty} c^{\tilde{\lambda}\mu\tilde{\nu}\mu'\tilde{\lambda}}_{\alpha\alpha'}(\tau)\, \epsilon(\tau)\, e^{i\omega\tau}\, d\tau. \tag{2.10.10}$$

For $E^{\lambda}_{a} \neq E^{\lambda}_{a'}$ we have $G^{\lambda}_{aa'} = H^{\lambda}_{aa'} = 0$.

The function $\epsilon(\tau)$ in Eq. (2.10.10) represents the Heaviside function

$$\epsilon(\tau) = \begin{cases} 1 & \text{if} \quad \tau > 0 \\ 0 & \text{if} \quad \tau = 0 \\ -1 & \text{if} \quad \tau < 0. \end{cases} \tag{2.10.11}$$

Note that, similar to Eq. (2.10.7), the symmetry relation (2.7.12) implies also that

$$\bar{\chi}^{\tilde{\lambda}\mu\tilde{\rho}\mu'\tilde{\lambda}}_{\alpha\alpha'}(\omega)^{\star} = \bar{\chi}^{\tilde{\lambda}\mu'\tilde{\rho}\mu\tilde{\lambda}}_{\alpha'\alpha}(\omega). \tag{2.10.12}$$

The coefficients $H^{\lambda}_{aa'}$ define a self-adjoint operator acting in the Hilbert space $\bar{\mathscr{H}}_A$, which will be denoted $\Delta\bar{H}_A$ in the following. Its matrix elements in the full space $\bar{\mathscr{H}}_A$ read

$$\langle a, \lambda | \Delta\bar{H}_A | a', \rho \rangle = \delta_{\lambda\rho} H^{\lambda}_{aa'}. \tag{2.10.13}$$

Since $H^{\lambda}_{aa'}$ is non-zero only if $E^{\lambda}_{a} = E^{\lambda}_{a'}$, the operator $\Delta\bar{H}_A$ commutes with the hamiltonian operator $\bar{H}_A$, i.e., we have

$$[\bar{H}_A, \Delta\bar{H}_A] = 0. \tag{2.10.14}$$

Similarly, based on the coefficients $G^{\lambda}_{aa'}$ defined in Eq. (2.10.6), we can define self-adjoint operators $\bar{G}_A$ by their matrix elements

$$\langle a, \lambda | \bar{G}_A | a', \rho \rangle = \delta_{\lambda\rho} G^{\lambda}_{aa'}. \tag{2.10.15}$$

The operator $\bar{G}_A$ commutes again with the free hamiltonian operator $\bar{H}_A$

$$[\bar{H}_A, \bar{G}_A] = 0. \tag{2.10.16}$$

In addition, the self-adjoint operator $\bar{G}_A$ is positive, i.e.,

$$\bar{G}_A \geqslant 0. \tag{2.10.17}$$

This is obviously true when all eigenvalues of the matrices $G^{\lambda}_{aa'}$ are positive or zero. According to Eq. (2.10.16), the eigenvectors $|a, \lambda\rangle$ of $\bar{H}_A$, which span the subspace $\bar{\mathscr{H}}_A$, can be supposed to be simultaneously eigenvectors of the operator $\bar{G}_A$. Thus, we have only to prove that the coefficients G^{λ}_{aa} are positive or zero. Actually, this property is a direct consequence of the more fundamental fact that the coefficients $\Gamma^{\rho a' a'}_{0\lambda aa}$ are real and positive. The reality of these coefficients is a direct consequence of the symmetry properties (2.10.4). To prove the positivity, let us first note that the symmetry properties (2.10.7) imply that the expression

$$\sum_{\mu\alpha\mu'\alpha'} x^{\mu}_{\alpha} \chi^{\tilde{\rho}\mu\tilde{\lambda}\mu'\tilde{\rho}}_{\alpha\ \alpha'}(\omega)(x^{\mu'}_{\alpha'})^{\star} \tag{2.10.18}$$

is real for $\omega \in \mathbb{R}$, $\forall x^{\mu}_{\alpha} \in \mathbb{C}$, and for arbitrary $\tilde{\rho}$, $\tilde{\lambda}$. Moreover, this expression is positive. In order to prove this, we start from the definition (2.7.11). According to the commutation relation (2.7.2), the eigenvectors $|b, \tilde{\lambda}\rangle$ of the Hamiltonian $\bar{H}_B$ defining the subspace $\bar{\mathscr{H}}_B$ are also eigenvectors of the density matrix $\bar{\rho}^0_B$, so that

$$\bar{H}_B\,|b, \tilde{\lambda}\rangle = E^{\tilde{\lambda}}_b\,|b, \tilde{\lambda}\rangle \qquad \text{and} \qquad \bar{\rho}^0_B\,|b, \tilde{\lambda}\rangle = p^{\tilde{\lambda}}_b\,|b, \tilde{\lambda}\rangle$$

with

$$p^{\tilde{\lambda}}_b \geqslant 0 \qquad \text{and} \qquad \sum_{\tilde{\lambda} \in \Lambda_B} \sum_{b=1}^{n^{\tilde{\lambda}}_B} p^{\tilde{\lambda}}_b = 1.$$

Consequently, taking account of the symmetry properties (2.6.25) as well as of Eq. (2.7.11), we get for the expression (2.10.18)

$$\frac{1}{\mathrm{Tr}(\bar{\rho}^{\tilde{\rho}\,0}_B)} \int_{-\infty}^{\infty} \mathrm{Tr}(\bar{\rho}^{\tilde{\rho}\,0}_B e^{i\bar{H}^{\tilde{\rho}}_B \tau/\hbar} B^{\tilde{\rho}\tilde{\lambda}} e^{-i\bar{H}^{\tilde{\lambda}}_B \tau/\hbar} (B^{\tilde{\rho}\tilde{\lambda}})^{\dagger})\, e^{i\omega\tau}\, d\tau$$

$$= \frac{2\pi}{p^0_{\rho}} \sum_{b,\,b'} p^{\tilde{\rho}}_b \langle b, \tilde{\rho}|\, B^{\tilde{\rho}\tilde{\lambda}}\, |b', \tilde{\lambda}\rangle\langle b', \tilde{\lambda}|\, (B^{\tilde{\rho}\tilde{\lambda}})^{\dagger}\, |b, \tilde{\rho}\rangle\, \delta(\omega + \omega^{\tilde{\rho}\tilde{\lambda}}_{bb'}) \geqslant 0,$$

with the operators

$$B^{\tilde{\rho}\tilde{\lambda}} = \sum_{\mu\alpha} x^{\mu}_{\alpha} \sum_{\beta} g^{\rho\mu\lambda}_{\alpha\beta} B^{\tilde{\rho}\mu\tilde{\lambda}}_{\beta},$$

$$(B^{\tilde{\rho}\tilde{\lambda}})^{\dagger} = \sum_{\mu\alpha} x^{\mu\,\star}_{\alpha} \sum_{\beta} g^{\lambda\mu\rho}_{\alpha\beta} B^{\tilde{\lambda}\mu\tilde{\rho}}_{\beta},$$

which satisfy the relation

$$\langle b', \tilde{\lambda}| \, (B^{\tilde{\rho}\tilde{\lambda}})^{\dagger} \, |b, \tilde{\rho}\rangle = \langle b, \tilde{\rho}| \, B^{\tilde{\rho}\tilde{\lambda}} \, |b', \tilde{\lambda}\rangle^{\star}.$$

Now, putting

$$x_{\alpha}^{\mu} = \langle a', \rho| \, A_{\alpha}^{\rho\mu\lambda} \, |a, \lambda\rangle,$$

which implies also

$$x_{\alpha}^{\mu\star} = \langle a, \lambda| \, A_{\alpha}^{\lambda\mu\rho} \, |a', \rho\rangle,$$

we see that the positive expression (2.10.18) agrees with the expression (2.10.5) for $\Gamma_{0\lambda aa}^{\rho a' a'}$, apart from a factor $1/\hbar$. Consequently, we have

$$\Gamma_{0\lambda aa}^{\rho a' a'} > 0, \qquad \forall(\lambda, a) \quad \text{and} \quad \forall(\rho, a'), \tag{2.10.19}$$

which implies (2.10.17).

Written in terms of the new coefficients defined in Eq. (2.10.2), the Markovian master equations (2.9.9) become

$$\frac{dD^{I}(\bar{t})}{d\bar{t}} = \Gamma_0(D^{I}(\bar{t})) + \frac{i}{\hbar}\,(D^{I}(\bar{t})(\Delta\bar{H}_A + i\bar{G}_A) - (\Delta\bar{H}_A - i\bar{G}_A)\, D^{I}(\bar{t})), \tag{2.10.20}$$

where Γ_0 denotes the linear mapping

$$\Gamma_0 \colon \mathscr{L}(\bar{\mathscr{H}}_A) \longmapsto \mathscr{L}(\bar{\mathscr{H}}_A), \tag{2.10.21}$$

which transforms a linear operator O of $\bar{\mathscr{H}}_A$ into a new linear operator O' of $\bar{\mathscr{H}}_A$ such that

$$\langle a_1, \lambda| \, O' \, |a_2, \mu\rangle = \delta_{\lambda\mu} \sum_{\rho a_1' a_2'} \Gamma_{0\,\lambda\, a_1 a_2}^{\rho\, a_1' a_2'} \langle a_1', \rho| \, O \, |a_2', \rho\rangle. \tag{2.10.22}$$

It should be recognized that the term $\Gamma_0(D^{I}(\bar{t}))$ plays a rather particular role in the master equations (2.10.20). This results from the fact that the time-averaged density matrix $D^{I}(\bar{t})$ is block diagonal, whereas $\Gamma_0(D^{I}(\bar{t}))$ is a full matrix! This important feature is a consequence of the indistinguishability of the particles constituting the $A+B$ system and the related symmetry properties. Consequently, coupling between different diagonal blocks is possible only through the term $\Gamma_0(D^{I}(\bar{t}))$! This resembles the situation of a superselection rule in quantum mechanics, the only difference being that the quantum states are presently replaced by statistical states. As will be shown in Section 3, in the case of electrons the types λ define

the total electronic spin. Thus, in a statistical ensemble of electrons, the total spin S plays a role similar to that of a classical variable. In order to characterize this particular behavior we may say that in a statistical ensemble the total electron spin S satisfies a "statistical superselection rule."

The new form of the master equations (2.10.20) allows us to identify the different concurring contributions to the evolution of the reduced density matrix of the subsystem A, which are induced by the interaction with the bath subsystem B. Formally, the second term describes the effect of the interaction with an "effective Hamiltonian" $\Delta\bar{H}_A + i\bar{G}_A$, which is described by a non-self-adjoint linear operator. The two constituting operators $\Delta\bar{H}_A$ and $\bar{G}_A$ being self-adjoint, it is easily seen that both play completely different roles for the evolution of the subsystem A. Whereas the "self-energy operator" $\Delta\bar{H}_A$ just changes the eigenenergies of the subsystem A, the operator $\bar{G}_A$ gives rise to dissipation. Let us recall that the "effective Hamiltonian" $\Delta\bar{H}_A + i\bar{G}_A$ does not couple between different subspaces $\mathscr{H}_A^{\lambda}$. This type of coupling is only provided by the first term in Eq. (2.10.20), which describes again dissipative (or irreversible) contributions to the evolution. The operator Γ_0 is thus responsible for the transfer of populations between states corresponding to different quantum numbers λ.

Let us now discuss the particular situation of a thermal equilibrium at a temperature corresponding to $\beta = 1/k_B T$. From Eq. (2.7.19) we get

$$\begin{aligned} p_\rho^0 \chi_{\alpha\alpha'}^{\tilde{\rho}\mu\tilde{\lambda}\mu'\tilde{\rho}}(\omega) &= \frac{p_\lambda^0}{\hbar}\int_{-\infty}^{\infty} c_{\alpha'\alpha}^{\tilde{\lambda}\mu'\tilde{\rho}\mu\tilde{\lambda}}(-\tau - i\hbar\beta)\, e^{i\omega\tau}\, d\tau \\ &= \frac{p_\lambda^0}{\hbar}\int_{-\infty+i\hbar\beta}^{\infty+i\hbar\beta} c_{\alpha'\alpha}^{\tilde{\lambda}\mu'\tilde{\rho}\mu\tilde{\lambda}}(\tau)\, e^{-i\omega(\tau+i\hbar\beta)}\, d\tau \\ &= p_\lambda^0 e^{\beta\hbar\omega}\chi_{\alpha'\alpha}^{\tilde{\lambda}\mu'\tilde{\rho}\mu\tilde{\lambda}}(-\omega). \end{aligned}$$

We then find

$$\begin{aligned} p_\rho^0 \Gamma_{0\ \lambda\ a_1 a_2}^{\ \rho\ a_1' a_2'} &= \frac{p_\lambda^0}{\hbar}\, e^{\beta\hbar\omega_{a_1' a_1}^{\rho\ \lambda}} \sum_{\mu\alpha}\sum_{\mu'\alpha'} \chi_{\alpha'\alpha}^{\tilde{\lambda}\mu'\tilde{\rho}\mu\tilde{\lambda}}(-\omega_{a_1' a_1}^{\rho\ \lambda}) \\ &\quad \times \langle a_1, \lambda|\, A_{\alpha'}^{\lambda\mu'\rho}\, |a_1', \rho\rangle\langle a_2', \rho|\, A_{\alpha}^{\rho\mu\lambda}\, |a_2, \lambda\rangle \\ &= p_\lambda^0 e^{\beta\hbar\omega_{a_1' a_1}^{\rho\ \lambda}} \Gamma_{0\ \rho\ a_2' a_1'}^{\ \lambda\ a_2 a_1}. \end{aligned}$$

The last equality is obtained using the relation $-\omega_{a_1' a_1}^{\rho\ \lambda} = \omega_{a_2 a_2'}^{\lambda\ \rho}$. Finally we get

$$p_\rho^0 e^{-\beta E_{a_1'}^{\rho}} \Gamma_{0\ \lambda\ a_1 a_2}^{\ \rho\ a_1' a_2'} = p_\lambda^0 e^{-\beta E_{a_1}^{\lambda}} \Gamma_{0\ \rho\ a_2' a_1'}^{\ \lambda\ a_2 a_1}. \tag{2.10.23}$$

Note that the corresponding energies satisfy the relation $E^{\rho}_{a'_1} - E^{\rho}_{a'_2} = E^{\lambda}_{a_1} - E^{\lambda}_{a_2}$.

For the discussion of the effects of external forces, it is often more convenient to change to a Schrödinger-like picture. Using the fact that $\bar{H}_A$ commutes with the operators $\Delta\bar{H}_A$ and $\bar{G}_A$, we get from Eq. (2.9.10)

$$\frac{dD(\bar{t})}{d\bar{t}} = \Gamma_0(D(\bar{t})) + \frac{i}{\hbar}[D(\bar{t}), \bar{H}_A + \Delta\bar{H}_A] - \frac{1}{\hbar}\{D(\bar{t}), \bar{G}_A\}, \qquad (2.10.24)$$

where $\{\ldots,\ldots\}$ denotes the anti-commutator. This equation, together with the definitions (2.10.5), (2.10.8), and (2.10.9) of the relevant operators Γ_0, $\bar{G}_A$ and $\Delta\bar{H}_A$, constitutes the basis for our following discussions. In particular, it will allow us to investigate the influence of external "forces" on the subsystem A, provided that the following two conditions are satisfied. First, one has to ensure that the external "forces" do not act directly on the bath. Secondly, the time dependence of the external "forces" must be sufficiently slow. More precisely, the change of the external "forces" during a time interval Δt must be negligible on the time scale τ_A^{evol}. Under the above two conditions one may describe the external "forces" by adding an additional hamiltonian-like term $\bar{H}_{A\,\text{ext}}(\bar{t})$ that is derived from the corresponding $H_{A\,\text{ext}}(t)$ acting in the Hilbert space $\mathscr{H}_A$. The term $\bar{H}_{A\,\text{ext}}(\bar{t})$ acting in $\bar{\mathscr{H}}_A$ can then be obtained by exploiting the homomorphism μ_A (see Eq. (2.2.19)) as described in Section 2.2. We just recall the commutation relations

$$[H_{A\,\text{ext}}(t), U_A(s)] = 0, \qquad s \in S_N, \qquad (2.10.25)$$

which result from the fermionic character of the system. Moreover, according to the above remarks, we have

$$\bar{H}_{A\,\text{ext}}(\bar{t}) = \mu_A(H_{A\,\text{ext}}(\bar{t})). \qquad (2.10.26)$$

The resulting equation governing the evolution in the presence of external forces reads

$$\frac{dD(\bar{t})}{d\bar{t}} = \Gamma_0(D(\bar{t})) + \frac{i}{\hbar}[D(\bar{t}), \bar{H}_A + \Delta\bar{H}_A + \bar{H}_{A\,\text{ext}}(\bar{t})] - \frac{1}{\hbar}\{D(\bar{t}), \bar{G}_A\}. \qquad (2.10.27)$$

This equation would for example be adequate to describe the effect of an external magnetic field on the spin dynamics in a molecule with N electrons, provided that the magnetic field is sufficiently weak, so that its influence on the spatial degrees of freedom can be neglected.

3. APPLICATION TO *N*-ELECTRON SYSTEMS

3.1. Description of the Electronic Spin Subsystem

We now come back to our original problem, which is the description of the coherent and dissipative spin dynamics in finite N electron systems. Following the general ideas of Section 2.1, we assume that the spin properties correspond to the subsystem A whereas the bath subsystem B is associated with the spatial properties. In this case the Hilbert space $\mathscr{H}_A$ is given by the tensor product $(\mathbb{C}^2)^{\otimes N}$ supplied with the scalar product induced by the usual scalar product in $\mathbb{C}^2$, and the non-trivial isotypic components of $\mathscr{H}_A$ are associated with types $\lambda = [\lambda_1, \lambda_2]$. It is a well-known result of the theory of linear representations of the group S_N that then the isotypic component λ coincides with the eigensubspace of spins $S = \frac{\lambda_1 - \lambda_2}{2}$, so that

$$\lambda = [\lambda_1, \lambda_2], \qquad \lambda_1 = \frac{N}{2} + S, \qquad \lambda_2 = \frac{N}{2} - S. \tag{3.1.1}$$

The corresponding dimensions of the above irreducible representations of λ type of the group S_N are

$$d_\lambda = (\lambda_1 + 1 - \lambda_2) \frac{N!}{(\lambda_1 + 1)!\, \lambda_2!}. \tag{3.1.2}$$

The proof of the above relations is given in ref. 42. The multiplicity of the irreducible representation of type λ is $2S+1$.[43] The type S is associated with λ by Eq. (3.1.1). Thus the vectors $|a, \lambda, i\rangle$ will be denoted $|M, S, i\rangle$ in the following, where $M = -S, -S+1, \ldots, S$ and $i = 1, \ldots, d_\lambda$. Moreover, n_A^λ is replaced by $n_A^S = 2S+1$ with $S = N/2, (N-2)/2, \ldots, 0$ or $1/2$, depending on whether N is even or odd. Here it is important to realize that the vectors $|M, S, i\rangle$ are not yet known and that they have still to be determined. In particular, at the present stage the index M just labels the $2S+1$ irreducible subspaces associated with the type λ (or S), and it has yet no physical interpretation.

Accordingly, the vectors $|a, b, \lambda\rangle$ of the general theory become $|M, b, S\rangle$. The subspace generated by $|M, b, S\rangle$ for fixed S, corresponding to $\mathscr{H}_{A+B}^\lambda$ in Section 2, is denoted $\mathscr{H}_{A+B}^S$. The choice of a basis satisfying the conditions (2.1.19) and (2.1.27) requires the knowledge of H_A, H_{int}, and of the density matrix $\bar{\rho}_B^0$ describing the statistical equilibrium of the bath subsystem B. This basis will be determined in Section 3.4. For the moment it is fully sufficient to suppose the existence of such a basis.

We describe the interaction between spatial degrees of freedom and spin degrees of freedom in terms of the spin-orbit like coupling term

$$H_{\text{int}} = \sum_{j=1}^{N} \boldsymbol{\sigma}^j \otimes \mathscr{B}^j(\mathbf{p}^1,\ldots, \mathbf{p}^N; \mathbf{q}^1,\ldots, \mathbf{q}^N), \tag{3.1.3}$$

where $\mathbf{p}^j$ and $\mathbf{q}^j$ refer to the electronic momentum and position operators, respectively. For simplicity reasons we include the coupling constant in the definition of $\mathscr{B}^j(\cdots)$. The operators $\boldsymbol{\sigma}^j$ in Eq. (3.1.3) act in $(\mathbb{C}^2)^{\otimes N}$. They are given by the tensor product

$$\boldsymbol{\sigma}^j = \mathbb{1} \otimes \mathbb{1} \otimes \cdots \otimes \boldsymbol{\sigma} \otimes \cdots \otimes \mathbb{1}, \tag{3.1.4}$$

where $\boldsymbol{\sigma}$ is the spin operator, which is defined as $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$, with the Pauli matrices σ_i, $i = 1, 2, 3$. In the definition (3.1.4) the spin operator $\boldsymbol{\sigma}$ defines the jth factor, the remaining factors are given by the identity operator in $\mathbb{C}^2$. The Hilbert space $\mathscr{H}_A$ is supplied by an orthonormal set of basis vectors. The latter are eigenvectors of the operators σ_3^j for $j = 1,\ldots, N$ with

$$\tfrac{1}{2}\sigma_3^j \,|m_1,\ldots, m_N\rangle = m_j \,|m_1,\ldots, m_N\rangle \tag{3.1.5}$$

and $m_j = \pm 1/2$, $j = 1,\ldots, N$. The representation U_A of the group S_N in $\mathscr{H}_A$ is generated by

$$U_A(s) \,|m_1,\ldots, m_N\rangle = |m_{s^{-1}(1)},\ldots, m_{s^{-1}(N)}\rangle, \qquad \forall s \in S_N, \tag{3.1.6}$$

which implies that

$$\mathscr{U}_A(s)\, \boldsymbol{\sigma}^j \equiv U_A(s)\, \boldsymbol{\sigma}^j U_A(s)^{-1} = \boldsymbol{\sigma}^{s(j)} \tag{3.1.7}$$

for $j = 1,\ldots, N$ and for every $s \in S_N$.

The above relations allow us to redraft the general theory in a simpler and more transparent form. From Eq. (3.1.7) together with

$$\mathscr{U}_B(s)\, \mathscr{B}^j(\cdots) \equiv U_B(s)\, \mathscr{B}^j(\cdots)\, U_B(s)^{-1} = \mathscr{B}^{s(j)}(\cdots) \tag{3.1.8}$$

we see that the interaction term (3.1.3) commutes in fact with the action of the group S_N in the Hilbert space $\mathscr{H}_A \otimes \mathscr{H}_B$. Seeking for the decomposition of the operator H_{int} corresponding to Eq. (2.1.56), we first decompose the operators $\boldsymbol{\sigma}^j$ acting in $\mathscr{H}_A$ into their isotypic components $\mathscr{L}_\mu(\mathscr{H}_A)$. The correspondent projector from $\mathscr{L}(\mathscr{H}_A)$ onto $\mathscr{L}_\mu(\mathscr{H}_A)$ is

$$\mathscr{P}_A^\mu = \frac{d_\mu}{N!} \sum_{s \in S_N} \chi_\mu(s)^\star\, \mathscr{U}_A(s). \tag{3.1.9}$$

With Eq. (3.1.7), and remembering that the characters $\chi_\mu(s)$ are real, we get

$$\boldsymbol{\sigma}^{\mu j} \equiv \mathscr{P}_A^\mu \boldsymbol{\sigma}^j \equiv \frac{d_\mu}{N!} \sum_{s \in S_N} \chi_\mu(s)\, \boldsymbol{\sigma}^{s(j)}, \tag{3.1.10}$$

which can be rewritten as

$$\boldsymbol{\sigma}^{\mu j} = \sum_{n=1}^{N} a_{jn}^\mu \boldsymbol{\sigma}^n \tag{3.1.11}$$

with

$$a_{jn}^\mu \equiv \frac{d_\mu}{N!} \sum_{\{s \in S_N \mid s(j)=n\}} \chi_\mu(s) = \begin{cases} \frac{1}{N} & \text{if} \quad \mu = [N] \\ \delta_{jn} - \frac{1}{N} & \text{if} \quad \mu = [N-1, 1] \\ 0 & \text{otherwise.} \end{cases} \tag{3.1.12}$$

This relation is proven in Appendix A. From Eqs. (3.1.11) and (3.1.12) we obtain finally

$$\boldsymbol{\sigma}^{\mu j} = \begin{cases} \sum_{n=1}^N \boldsymbol{\sigma}^n / N & \text{if} \quad \mu = [N] \\ \boldsymbol{\sigma}^j - \sum_{n=1}^N \boldsymbol{\sigma}^n / N & \text{if} \quad \mu = [N-1, 1] \\ 0 & \text{otherwise.} \end{cases} \tag{3.1.13}$$

The decomposition of the operators $\mathscr{B}^j(\cdots)$

$$\mathscr{B}^{\mu j} = \mathscr{P}_B^\mu \mathscr{B}^j(\cdots) \tag{3.1.14}$$

is found in a similar way. From Eq. (3.1.8) we get

$$\mathscr{B}^{\mu j} = \begin{cases} \sum_{n=1}^N \mathscr{B}^n(\cdots)/N & \text{if} \quad \mu = [N] \\ \mathscr{B}^j(\cdots) - \sum_{n=1}^N \mathscr{B}^n(\cdots)/N & \text{if} \quad \mu = [N-1, 1] \\ 0 & \text{otherwise.} \end{cases} \tag{3.1.15}$$

The interaction Hamiltonian H_{int} (3.1.3) can be decomposed according to Eqs. (2.1.51) and (2.1.56). With Eqs. (3.1.11) and (3.1.12) it reduces to

$$H_{\text{int}} = \sum_{\alpha,\,\beta=1}^{3} g_{\alpha\beta}^{[N]} H_{\alpha\beta}^{[N]} + g_{\alpha\beta}^{[N-1,1]} H_{\alpha\beta}^{[N-1,1]}, \tag{3.1.16}$$

where

$$g_{\alpha\beta}^{[N]} = g_{\alpha\beta}^{[N-1,1]} = \delta_{\alpha\beta}$$

and

$$H_{\alpha\beta}^{[N]} = \Sigma_{\alpha}^{[N]} \otimes B_{\beta}^{[N]}, \tag{3.1.17}$$

$$H_{\alpha\beta}^{[N-1,1]} = \sum_{l=1}^{d_{[N-1,1]}} \Sigma_{\alpha l}^{[N-1,1]} \otimes B_{\beta l}^{[N-1,1]}, \tag{3.1.18}$$

with

$$\mathbf{\Sigma}^{[N]} = \sum_{n=1}^{N} \boldsymbol{\sigma}^n \qquad \mathbf{B}^{[N]} = \frac{1}{N} \sum_{n=1}^{N} \mathscr{B}^n(\cdots), \tag{3.1.19}$$

$$\mathbf{\Sigma}_l^{[N-1,1]} = \sqrt{N} \sum_{n=1}^{N} a_l^n \boldsymbol{\sigma}^n \qquad \mathbf{B}_l^{[N-1,1]} = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} a_l^n \mathscr{B}^n(\cdots), \tag{3.1.20}$$

and $l = 1,\ldots, d_{[N-1,1]} = N-1$. The real coefficients a_l^n define $N-1$ orthonormal basis vectors that span the vector subspace of dimension $N-1$ corresponding to the isotypic component of type $\mu = [N-1, 1]$. They thus satisfy the orthogonality relations

$$\sum_{n=1}^{N} a_l^n = 0 \qquad \sum_{n=1}^{N} a_l^n a_k^n = \delta_{lk}, \tag{3.1.21}$$

where the first equation is a consequence of the orthogonality of the isotypic components of types $[N-1, 1]$ and $[N]$. Consequently, we have also

$$\sum_{l=1}^{d_{[N-1,1]}} a_l^n a_l^m = \delta^{nm} - \frac{1}{N}. \tag{3.1.22}$$

The operators $\mathbf{\Sigma}_l^{[N-1,1]}$ and $\mathbf{B}_l^{[N-1,1]}$ transform as

$$\begin{aligned} U_A(s)\, \mathbf{\Sigma}_l^{[N-1,1]} U_A(s)^{-1} &= \sum_{k=1}^{d_{[N-1,1]}} \mathbf{\Sigma}_k^{[N-1,1]} d_{kl}^{[N-1,1]}(s), \\ U_B(s)\, \mathbf{B}_l^{[N-1,1]} U_B(s)^{-1} &= \sum_{k=1}^{d_{[N-1,1]}} \mathbf{B}_k^{[N-1,1]} d_{kl}^{[N-1,1]}(s). \end{aligned} \tag{3.1.23}$$

After insertion of the definitions (3.1.19) and (3.1.20), and using also Eq. (3.1.7) we find

$$d_{kl}^{[N-1,1]}(s) = \sum_{n=1}^{N} a_k^{s(n)} a_l^n. \tag{3.1.24}$$

Comparing the decomposition (3.1.16) with the corresponding equation (2.1.56) of the general theory of Section 2.1, we note that presently only two isotypic components of types $\mu = [N], [N-1, 1]$ contribute and that the operators $H_{\text{int}}^{[N]}$ and $H_{\text{int}}^{[N-1,1]}$ replace the operators $H_{\alpha\beta}^{\lambda}$ in Eq. (2.1.56). Further comparison between the definitions (3.1.17), (3.1.18), and (2.1.51) shows that the operators $\mathbf{\Sigma}^{[N]}$ and $\mathbf{\Sigma}_l^{[N-1,1]}$, $l = 1,\ldots, d_{[N-1,1]} = N-1$ take the part of the operators $A_{\alpha l}^{\mu}$, $l = 1,\ldots, d_{\mu}$, whereas the operators $\mathbf{B}^{[N]}$ and $\mathbf{B}_l^{[N-1,1]}$ replace the operators $B_{\beta l}^{\mu}/\sqrt{d_{\mu}}$. Moreover, we note that the indices α and β in Eq. (2.1.56) correspond to the spatial components of the axial vectors $\mathbf{B}$ and $\mathbf{\Sigma}$ defined in Eqs. (3.1.19) and (3.1.20), and thus we have presently $\alpha = 1, 2, 3$ and $\beta = 1, 2, 3$.

3.2. Electronic Spins and Spatial Rotations

We will now take into account the action of spatial rotations in the Hilbert space $\mathscr{H}_A$ and in $\mathscr{L}(\mathscr{H}_A)$. The action in $\mathscr{H}_A$ of a rotation $R(\boldsymbol{\omega})$ characterized by an axial vector of rotation $\boldsymbol{\omega}$ is described by the unitary operator

$$V_A(\boldsymbol{\omega}) = \exp(-i\boldsymbol{\omega}\cdot\mathbf{S}), \qquad \mathbf{S} = \mathbf{\Sigma}^{[N]}/2, \tag{3.2.1}$$

where the self-adjoint operators $\mathbf{\Sigma}^{[N]}$ are defined in Eq. (3.1.19). Actually, the correspondence $R(\boldsymbol{\omega}) \longmapsto V_A(\boldsymbol{\omega})$ defines a unitary ray representation of the rotation group $SO(3)$ in the group of unitary operators in $\mathscr{L}(\mathscr{H}_A)$. From the above definition and from the commutation relations of the operators σ_{α}^{j} introduced in (3.1.4) we obtain the transformation rules

$$V_A(\boldsymbol{\omega})\, \sigma_{\alpha}^{j} V_A(\boldsymbol{\omega})^{-1} = \sum_{\beta=1}^{3} \sigma_{\beta}^{j} R_{\alpha}^{\beta}(\boldsymbol{\omega}), \qquad j = 1,\ldots, N, \tag{3.2.2}$$

where the matrix $(R_{\alpha}^{\beta}(\boldsymbol{\omega}))$ describes the rotation in cartesian coordinates. With the definitions (3.1.19) and (3.1.20) we get

$$V_A(\boldsymbol{\omega})\, \Sigma_{\alpha l}^{\mu} V_A(\boldsymbol{\omega})^{-1} = \sum_{\beta=1}^{3} \Sigma_{\beta l}^{\mu} R_{\alpha}^{\beta}(\boldsymbol{\omega}), \qquad l = 1,\ldots, d_{\mu}. \tag{3.2.3}$$

Equations (3.2.2) and (3.2.3) describe the action of the rotation group on the operators $\mathbf{\Sigma}_l^{\mu}$. They play a similar role as the relations (3.1.23). Now, according to Eq. (3.1.7) and to the definition (3.1.19), the unitary operators $U_A(s)$, $s \in S_N$ commute with the generators $\mathbf{S}$. Therefore the representations of the group S_N and of the rotation group in $\mathscr{L}(\mathscr{H}_A)$ commute, i.e.,

$$[V_A(\boldsymbol{\omega}), U_A(s)] = 0, \qquad \forall \boldsymbol{\omega}, s. \tag{3.2.4}$$

These commutation relations imply that the operator $V_A(\boldsymbol{\omega})$ commutes also with the partially isometric operators P^{λ}_{Aik} given by Eq. (2.1.20). For our convenience, we will from now on use the relation (3.1.1) to switch between the two notations $\lambda \leftrightarrow S$ associated with the group S_N. Thus, each subspace $\mathscr{H}^S_{Ai}$ generated by the vectors $|M, S, i\rangle$, $M = -S,\ldots, +S$ for fixed S and i, is invariant with respect to the representation $V_A(\boldsymbol{\omega})$ of the rotation group, so that

$$V_A(\boldsymbol{\omega})\, \mathscr{H}^S_{Ai} = \mathscr{H}^S_{Ai}, \qquad \forall \boldsymbol{\omega}, S, i. \tag{3.2.5}$$

According to Eq. (2.1.25), which reads in the new notation

$$P^S_{Aik}\, |M, S, k\rangle = |M, S, i\rangle, \tag{3.2.6}$$

we have

$$V_A(\boldsymbol{\omega})\, |M, S, i\rangle = \sum_{M'=-S}^{S} |M', S, i\rangle\, r^S_{M'M}(\boldsymbol{\omega}), \tag{3.2.7}$$

where $r^S_{M'M}(\boldsymbol{\omega})$ are the matrix elements of a standard representation of the rotation group of type S. Their elements are independent of $i = 1,\ldots, d_\lambda$.

For our further considerations, it is convenient to introduce the direct product G of the permutation group S_N and the group of rotations $SO(3)$

$$G = S_N \times SO(3). \tag{3.2.8}$$

The correspondence

$$W_A\colon G \ni (s, \boldsymbol{\omega}) \longmapsto U_A(s)\, V_A(\boldsymbol{\omega}) = W_A(s, \boldsymbol{\omega}) \tag{3.2.9}$$

defines a unitary ray representation of the group G in $\mathscr{L}(\mathscr{H}_A)$. Clearly, the isotypic components $\mathscr{H}^S_A$ of $\mathscr{H}_A$ relatively to U_A and V_A are also irreducible with respect to the representation W_A of G. Thus we can write

$$W_A(s, \boldsymbol{\omega})\, |M, S, i\rangle = \sum_{i'=1}^{d_\lambda} \sum_{M'=-S}^{S} D^S_{(M', i')(M, i)}(s, \boldsymbol{\omega})\, |M', S, i'\rangle. \tag{3.2.10}$$

The coefficients

$$D^S_{(M', i')(M, i)}(s, \boldsymbol{\omega}) = d^{\lambda}_{i'i}(s)\, r^S_{M', M}(\boldsymbol{\omega}) \tag{3.2.11}$$

denote the matrix elements of the irreducible representation of G carried by the isotypic component $\mathscr{H}_A^S$. We now have the transformation rules

$$W_A(s, \omega)\, \sigma_\alpha^j W_A(s, \omega)^{-1} = \sum_{\beta=1}^{3} \sigma_\beta^{s(j)} R_\alpha^\beta(\omega), \tag{3.2.12}$$

and consequently

$$W_A(s, \omega)\, \Sigma_{\alpha l}^\mu W_A(s, \omega)^{-1} = \sum_{k=1}^{d_\mu} \sum_{\beta=1}^{3} \Sigma_{\beta k}^\mu d_{kl}^\mu(s)\, R_\alpha^\beta(\omega). \tag{3.2.13}$$

The operators $\Sigma_{\alpha l}^\mu$ for fixed μ are the components of an irreducible tensor operator of type $(\mu, 1)$ with respect to the representation W_A of G. Using the Wigner–Eckart theorem, we can write the matrix element of these operators as

$$\langle M', S', i' |\, \Sigma_{\alpha l}^\mu \,| M, S, i \rangle = \sum_{\gamma=1}^{a_{\lambda'}} c_{l\, i\, (i', \gamma)}^{\mu\, \lambda\, \lambda'} C_{\alpha M M'}^{1 S S'} \langle S' \|\, \mathbf{\Sigma}^\mu \,\| S \rangle_\gamma. \tag{3.2.14}$$

In this expression, the symbols $c_{l\, i\, (i', \gamma)}^{\mu\, \lambda\, \lambda'}$ denote the Clebsch–Gordan coefficients associated with the decomposition of the tensor product of irreducible representations of S_N of types λ and μ. Let us recall that the types λ, λ' are associated with S, S' according to Eq. (3.1.1), and that the multiplicity of the irreducible components of type λ' in the above tensor product of representations is given by $a_{\lambda'}$. The symbols $C_{\alpha M M'}^{1\, S\, S'}$ denote the Clebsch–Gordan coefficients associated with the decomposition of the tensor product of the irreducible ray representations of $SO(3)$ of types S and 1.[44] As a direct consequence of Eq. (3.2.14), we obtain the selection rule

$$\langle M', S', i' |\, \Sigma_{\alpha l}^\mu \,| M, S, i \rangle = 0 \qquad \text{if} \quad |S - S'| > 1 \quad \text{or if } S = S' = 0. \tag{3.2.15}$$

3.3. Decomposition of the Interaction Hamiltonian

We search for the correspondent of the decomposition (2.6.26) of the interaction operator H_{int}. Exploiting the isomorphism (2.6.19), we will describe the action of H_{int} in the space

$$\bigoplus_{\lambda \in \Lambda_{AB}} \mathscr{H}_A^\lambda \otimes \mathscr{H}_B^{\tilde{\lambda}}.$$

The operator H_{int} is presently given by Eqs. (3.1.16)–(3.1.18). Expressed in the form of Eq. (2.1.56), it reads

$$H_{\text{int}} = H_{\text{int}}^{[N]} + H_{\text{int}}^{[N-1,1]}, \tag{3.3.1}$$

where the operators $H_{\text{int}}^{[N]}$ and $H_{\text{int}}^{[N-1,1]}$ are given by

$$H_{\text{int}}^{[N]} = \sum_{\alpha} \Sigma_{\alpha}^{[N]} \otimes B_{\alpha}^{[N]} \tag{3.3.2}$$

and

$$H_{\text{int}}^{[N-1,1]} = \sum_{l=1}^{d^{[N-1,1]}} \sum_{\alpha} \Sigma_{\alpha l}^{[N-1,1]} \otimes B_{\alpha l}^{[N-1,1]}. \tag{3.3.3}$$

Equations (3.3.2) and (3.3.3) are a convenient starting point to calculate the matrix elements $\langle M, b, S| H_{\text{int}} |M', b', S'\rangle$. For the operators $H_{\text{int}}^{[N]}$ the result is immediate. In this case, the operators $\Sigma_{\alpha}^{[N]}$ and $B_{\beta}^{[N]}$ commute with the unitary representation U_A and U_B of S_N in the corresponding Hilbert spaces $\mathscr{H}_A$ and $\mathscr{H}_B$, and the calculation of the reduced matrix elements of these operators relatively to the action of the group S_N becomes trivial. We obtain

$$\begin{aligned} \langle M, S, i| \Sigma_{\alpha}^{[N]} |M', S', i'\rangle &= \delta_{SS'}\delta_{ii'}\langle M, S\| \mathbf{\Sigma}_{\alpha}^{[N]} \|M', S\rangle, \\ \langle b, \tilde{S}, k| B_{\beta}^{[N]} |b', \tilde{S}', k'\rangle &= \delta_{SS'}\delta_{kk'}\langle b, \tilde{S}\| \mathbf{B}_{\beta}^{[N]} \|b', \tilde{S}\rangle. \end{aligned} \tag{3.3.4}$$

In the last equation, $\tilde{S}$ denotes the dual $\tilde{\lambda}$ of the type λ, which is related with the spin S via the correspondence (3.1.1).

We are now in the position to write the corresponding of the expression (2.6.12) for $H_{\alpha\beta}^{[N]}$. Presently, $\mu = [N]$ corresponds to the trivial representation of S_N, and $a_\lambda = b_{\tilde{\lambda}} = 1$, the type λ corresponding to S. The coefficient $h_{\gamma\delta}^{\lambda\mu\lambda'}$ in Eq. (2.6.12) is then replaced by $\delta_{SS'}$, and the summation indices γ and δ can be omitted. We thus find

$$\langle M, b, S| H_{\alpha\beta}^{[N]} |M', b', S'\rangle = \delta_{SS'}\langle M, S\| \mathbf{\Sigma}_{\alpha}^{[N]} \|M', S\rangle\langle b, \tilde{S}\| \mathbf{B}_{\beta}^{[N]} \|b', \tilde{S}\rangle. \tag{3.3.5}$$

We note that the interaction terms $H_{\alpha\beta}^{[N]}$ cannot generate a change of the total spin of the subsystem A.

The correspondents of the operators $A_{\gamma\alpha}^{\lambda\mu\lambda'}$ and $B_{\delta\beta}^{\tilde{\lambda}\mu\tilde{\lambda}'}$ defined in Eqs. (2.6.22) and (2.6.23) will be replaced by $\Sigma_{\alpha}^{S[N]S'}$ and $B_{\beta}^{S[N]S'}/\sqrt{d_\lambda}$, respectively.

According to their definitions, the matrix elements of $\Sigma_\alpha^{S[N]\,S'}$ and $B_\beta^{S[N]\,S'}$ read

$$\begin{aligned}\langle M, S|\, \Sigma_\alpha^{S[N]\,S'}\, |M', S'\rangle &= \langle M, S\|\, \mathbf{\Sigma}_\alpha^{[N]}\, \|M', S'\rangle,\\ \langle b, \tilde{S}|\, B_\beta^{S[N]\,S'}\, |b', \tilde{S}'\rangle\ &= \langle b, \tilde{S}\|\, \mathbf{B}_\beta^{[N]}\, \|b', \tilde{S}'\rangle.\end{aligned} \tag{3.3.6}$$

As an immediate consequence of Eq. (3.2.14), the reduced matrix elements can be written as

$$\langle M, S\|\, \mathbf{\Sigma}_\alpha^{[N]}\, \|M', S'\rangle = C_{\alpha\, M'\, M}^{1\;\; S'\;\; S} \langle S\|\, \mathbf{\Sigma}^{[N]}\, \|S'\rangle. \tag{3.3.7}$$

Here $C_{\alpha\, M'\, M}^{1\;\; S'\;\; S}$ denotes the Clebsch–Gordan coefficients associated with the rotation group, and $\langle S\|\, \mathbf{\Sigma}^{[N]}\, \|S'\rangle$ denotes the reduced matrix elements with respect to the action of the full group $G = S_N \times SO(3)$.

The handling of the operators $H_{\alpha\beta}^{[N-1,\,1]}$ is somewhat more complicated. To discuss the matrix elements of these terms, we have first to determine the selection rules for the irreducible tensor operators $\Sigma_{\alpha l}^{[N-1,\,1]}$ defined in Eq. (3.1.20). Some of them are already provided by Eq. (3.2.15). However, to get more insight of the situation we have to determine the Clebsch–Gordan series corresponding to the tensor product of the irreducible representations of types $[N-1, 1]$ and $[N/2+S, N/2-S]$ of the group S_N

$$D^{[N-1,\,1]} \otimes D^{[N/2+S,\,N/2-S]} = \bigoplus_{\lambda'} a_{\lambda'} D^{(\lambda')}. \tag{3.3.8}$$

The multiplicities of the irreducible representations of type λ' contributing to the decomposition are denoted $a_{\lambda'}$. Since presently we only need to consider irreducible representations of types $\lambda' = [N/2+S', N/2-S']$, we have to evaluate

$$a_{[N/2+S',\,N/2-S']} = \frac{1}{N!} \sum_{s \in S_N} \chi_{[N/2+S',\,N/2-S']}(s)^\star\, \chi_{[N-1,\,1]}(s)\, \chi_{[N/2+S,\,N/2-S]}(s). \tag{3.3.9}$$

In Appendix B it is shown that

$$a_{[\frac{N}{2}+S',\,\frac{N}{2}-S']} = \begin{cases} 1 & \text{if} \quad |S-S'| \leqslant 1 \quad \text{and if} \quad (S', S) \neq (N/2, N/2) \\ 0 & \text{otherwise.} \end{cases} \tag{3.3.10}$$

We thus see that the multiplicity $a_{[\frac{N}{2}+S', \frac{N}{2}-S']}$ cannot exceed 1. Consequently, we get from the Wigner–Eckart theorem

$$\langle M, S, i| \Sigma_{\alpha l}^{[N-1,1]} |M', S', i'\rangle = c^{[N-1,1]\ \lambda' \lambda}_{l\ i' i} \langle M, S\| \mathbf{\Sigma}_{\alpha}^{[N-1,1]} \|M', S'\rangle, \tag{3.3.11}$$

where the prefactor $c^{[N-1,1]\ \lambda' \lambda}_{l\ i' i}$ denotes the Clebsch–Gordan coefficients associated with the decomposition (3.3.8). In analogy with Eq. (3.3.7) we have

$$\langle M, S\| \mathbf{\Sigma}_{\alpha}^{[N-1,1]} \|M', S'\rangle = C^{1\ S'\ S}_{\alpha\ M'\ M} \langle S\| \mathbf{\Sigma}^{[N-1,1]} \|S'\rangle, \tag{3.3.12}$$

where $\langle S\| \mathbf{\Sigma}^{[N-1,1]} \|S'\rangle$ denotes the reduced matrix elements with respect to the action of the full group $G = S_N \times SO(3)$.

Similar results can be derived for the operators $B_{\beta l}^{[N-1,1]}$. Exploiting the irreducible tensor character of these operators, we find from the Wigner–Eckart theorem

$$\langle b, \tilde{S}, k| B_{\beta l}^{[N-1,1]} |b', \tilde{S}', k'\rangle = c^{[N-1,1]\ \tilde{\lambda}' \tilde{\lambda}}_{l\ k' k} \langle b, \tilde{S}\| \mathbf{B}_{\beta}^{[N-1,1]} \|b', \tilde{S}'\rangle. \tag{3.3.13}$$

In the above expression, the Clebsch–Gordan coefficient $c^{[N-1,1]\ \tilde{\lambda}' \tilde{\lambda}}_{l\ k' k}$ corresponds to the decomposition

$$D^{[N-1,1]} \otimes D^{\tilde{\lambda}} = \bigoplus_{\lambda'} b_{\lambda'} D^{(\lambda')}, \tag{3.3.14}$$

where $\tilde{\lambda}$ is dual with respect to the type $\lambda = [\frac{N}{2}+S, \frac{N}{2}-S]$. Actually, since

$$\chi_{\tilde{\lambda}}(s) = \sigma(s)\, \chi_{\lambda}(s), \qquad \forall s \in S_N,$$

we have

$$b_{\tilde{\lambda}'} = a_{\lambda'}, \qquad \forall \lambda'. \tag{3.3.15}$$

We are now in the position to specify the correspondent of the relation (2.6.12) for the operators $H_{\alpha\beta}^{[N-1,1]}$. It reads

$$\begin{aligned} &\langle M, b, S| H_{\alpha\beta}^{[N-1,1]} |M', b', S'\rangle \\ &\quad = g_{SS'} \langle M, S\| \mathbf{\Sigma}_{\alpha}^{[N-1,1]} \|M', S'\rangle \langle b, \tilde{S}\| \mathbf{B}_{\beta}^{[N-1,1]} \|b', \tilde{S}'\rangle, \end{aligned} \tag{3.3.16}$$

where

$$g_{SS'} = \sum_{i,j=1}^{d_\lambda} \sum_{i',j'=1}^{d_{\lambda'}} \sum_{k=1}^{d_\mu} c^{\lambda\ \tilde{\lambda}\ [1^N]}_{i\ j\ 1}\, c^{\lambda'\ \mu\ \lambda}_{i'\ k\ (i,\gamma)}\, c^{\tilde{\lambda}'\ \mu\ \tilde{\lambda}}_{j'\ k\ (j,\delta)}\, c^{\lambda'\ \tilde{\lambda}'\ [1^N]}_{i'\ j'\ 1} \tag{3.3.17}$$

replaces the coefficients $h_{\gamma\delta}^{\lambda\mu\lambda'}$ of Eq. (2.6.18). Presently, the indices γ (= 1), δ (= 1), and μ (= [$N-1$, 1]) are fixed. They will be omitted in the following. The other parameters are

$$\lambda = [N/2+S, N/2-S] \qquad \lambda' = [N/2+S', N/2-S']$$
$$d_\lambda = d_{\tilde{\lambda}} \qquad d_{\lambda'} = d_{\tilde{\lambda}'}.$$

The correspondents of the operators $A_{\gamma\alpha}^{\lambda\mu\lambda'}$ and $B_{\delta\beta}^{\tilde{\lambda}\mu\tilde{\lambda}'}/\sqrt{d_\mu}$ for $\mu = [N-1, 1]$ defined in Eqs. (2.6.22) and (2.6.23) will be denoted $\Sigma_\alpha^{S[N-1,1]S'}$ and $B_\beta^{\tilde{S}[N-1,1]\tilde{S}'}$, respectively. From the definitions we get immediately

$$\begin{aligned} \langle M, S|\, \Sigma_\alpha^{S[N-1,1]S'}\, |M', S'\rangle &= \langle M, S\|\, \mathbf{\Sigma}_\alpha^{[N-1,1]}\, \|M', S'\rangle, \\ \langle b, \tilde{S}|\, B_\beta^{S[N-1,1]S'}\, |b', \tilde{S}'\rangle &= \langle b, \tilde{S}\|\, \mathbf{B}_\beta^{[N-1,1]}\, \|b', \tilde{S}'\rangle. \end{aligned} \tag{3.3.18}$$

Summarizing our results, and taking into account the definitions (3.3.6) and (3.3.18), we get finally for the block operators $H_{\text{int}}^{SS'}$

$$H_{\text{int}}^{SS'} = \sum_{\alpha=1}^{3} (\delta_{SS'} \Sigma_\alpha^{S[N]S} \otimes B_\alpha^{\tilde{S}[N]\tilde{S}} + g_{SS'} \Sigma_\alpha^{S[N-1,1]S'} \otimes B_\alpha^{\tilde{S}[N-1,1]\tilde{S}'}), \tag{3.3.19}$$

where we have implicitly used the isomorphism (2.6.19) between $\mathscr{H}_{A+B}^S$ and the tensor product $\bar{\mathscr{H}}_A^S \otimes \bar{\mathscr{H}}_B^{\tilde{S}}$.

To complete the above result, we still mention some direct consequences of Eq. (3.2.15), which are obtained using the definitions (3.3.6) and (3.3.11). We have

$$\Sigma_\alpha^{S[N]S'} = 0 \qquad \text{if} \quad S \neq S', \tag{3.3.20}$$

and for $\mu \neq [N]$

$$\Sigma_\alpha^{S\mu S'} = 0 \qquad \text{if} \quad |S-S'| > 1, \tag{3.3.21}$$

and consequently,

$$H_{\text{int}}^{SS'} = 0 \qquad \text{if} \quad |S-S'| > 1, \tag{3.3.22}$$

i.e., the interaction couples only between states with total spins differing at most by 1.

3.4. Polarization of the Spin Subsystem

Following the general ideas of Section 2.7, we will now discuss the influence of the subsystem B on the spin-system A. According to our

general assumptions, the subsystem B, which presently represents the spatial degrees of freedom of the electrons, fluctuates around a given statistical equilibrium. The latter is described by a density matrix $\bar{\rho}_B^0$ composed of blocks $\bar{\rho}_B^{\tilde{S}\,0}$, each block $\bar{\rho}_B^{\tilde{S}\,0}$ satisfying the commutation relations (2.7.2). In Section 2.7 we have already shown that the first-order contribution of the interaction between both subsystems gives rise to a polarization of the spin system A. It corresponds to the presence of a time-independent external force, the latter being determined by the mean values (2.7.6). Presently, Eq. (2.7.6) reads

$$b_{\beta}^{\tilde{S}\mu\tilde{S}\,0} = \frac{\mathrm{Tr}(\bar{\rho}_B^{\tilde{S}\,0} B_{\beta}^{\tilde{S}\mu\tilde{S}})}{\mathrm{Tr}(\bar{\rho}_B^{\tilde{S}\,0})} \qquad \text{with} \quad \mu = [N], [N-1, 1]. \tag{3.4.1}$$

Comparing the expressions (3.3.19) and (2.6.31) we see that we have now

$$g_{\alpha\beta}^{S[N]\,S'} = \delta_{SS'}\delta_{\alpha\beta},$$
$$g_{\alpha\beta}^{S[N-1,\,1]\,S'} = g_{SS'}\delta_{\alpha\beta},$$

so that the Hamiltonian (2.7.5) describing the dynamical effect of this force on the spin system A becomes in the Schrödinger picture

$$\bar{H}_{A\,\mathrm{pol}}^{S} = \sum_{\alpha} (b_{\alpha}^{\tilde{S}[N]\,\tilde{S}\,0} \Sigma_{\alpha}^{S[N]\,S} + g_{SS} b_{\alpha}^{\tilde{S}[N-1,\,1]\,\tilde{S}\,0} \Sigma_{\alpha}^{S[N-1,\,1]\,S}). \tag{3.4.2}$$

From the definitions (3.3.6), (3.3.18) and the relations (3.3.7), (3.3.12) we get

$$\Sigma_{\alpha}^{S[N-1,\,1]\,S} = f_S^N \Sigma_{\alpha}^{S[N]\,S} \tag{3.4.3}$$

with the numerical factor

$$f_S^N = \frac{\langle S \| \mathbf{\Sigma}^{[N-1,\,1]} \| S \rangle}{\langle S \| \mathbf{\Sigma}^{[N]} \| S \rangle}. \tag{3.4.4}$$

Accordingly, we may write

$$\bar{H}_{A\,\mathrm{pol}}^{S} = \sum_{\alpha=1}^{3} \Omega_{\alpha}^{S} \Sigma_{\alpha}^{S[N]\,S} \tag{3.4.5}$$

where

$$\Omega_{\alpha}^{S} = b_{\alpha}^{\tilde{S}[N]\,\tilde{S}\,0} + g_{SS} f_S^N b_{\alpha}^{\tilde{S}[N-1,\,1]\,\tilde{S}\,0}. \tag{3.4.6}$$

The above operators $\bar{H}^S_{A\,\mathrm{pol}}$ are the constituents of the hamiltonian term $\bar{H}_{A\,\mathrm{pol}}$ acting in $\bar{\mathscr{H}}_A$. The operator $\bar{H}_{A\,\mathrm{pol}}$ is diagonal with respect to the total spin S, i.e., it has a block structure. In Section 2.7 we have shown that there is a one-to-one correspondence between $\bar{H}_{A\,\mathrm{pol}}$ and the Hamiltonian $H_{A\,\mathrm{pol}}$ acting in $\mathscr{H}_A$, both being related by the mapping (2.2.18)

$$\mu_A(H_{A\,\mathrm{pol}}) = \bar{H}_{A\,\mathrm{pol}}. \tag{3.4.7}$$

We have further seen that the Hamiltonian H_A governing the free evolution of the subsystem A can be redefined to include the polarization due to the subsystem B. Since presently our initial Hamiltonian H_A is trivial, the new Hamiltonian, which will again be denoted H_A, is

$$H_A = \mu_A^{-1}(\bar{H}_A) \qquad \text{with} \quad \bar{H}_A = \bar{H}_{A\,\mathrm{pol}}. \tag{3.4.8}$$

We note that both, $\bar{H}_A$ and H_A, are completely determined by Eq. (3.3.2). The redefined interaction term now reads

$$H_{\mathrm{int}} - H_{A\,\mathrm{pol}} \otimes \mathbb{1}_B.$$

It will again be denoted H_{int} in the following. We further make the replacement

$$B^{\tilde{S}\mu\tilde{S}'}_{\beta} - b^{\tilde{S}\mu\tilde{S}\,0}_{\beta}\,\mathbb{1}^{\tilde{S}}_{B}\delta_{\tilde{S}\tilde{S}'} \longrightarrow B^{\tilde{S}\mu\tilde{S}'}_{\beta} \tag{3.4.9}$$

for $\mu = [N]$ and $[N-1, 1]$, which does of course not affect the validity of the expressions (3.3.19). After the above redefinitions, we get

$$\mathrm{Tr}(\bar{\rho}^{\tilde{S}\,0}_B B^{I\tilde{S}\mu\tilde{S}}_{\beta}(t)) \equiv 0, \tag{3.4.10}$$

which is the correspondent of Eq. (2.7.8).

Thus prepared, we can now specify the basis vectors $|M, S, i\rangle$. According to our conventions expressed in Eqs. (2.1.19) and (2.1.27), we have

$$U_A(s)\,|M, S, i\rangle = \sum_{k=1}^{d_\lambda} |M, S, k\rangle\, d^{\lambda}_{ki}(s) \tag{3.4.11}$$

and

$$H_A\,|M, S, i\rangle = E^S_M\,|M, S, i\rangle \tag{3.4.12}$$

with $\lambda = [N/2+S, N/2-S]$. The spin Hamiltonian $\bar{H}_A$ defined in (3.4.8), which governs the free evolution of the spin system, corresponds to the diagonal block operators

$$\bar{H}_A^S = \sum_{\alpha=1}^{3} \Omega_\alpha^S \Sigma_\alpha^{S[N]S}, \tag{3.4.13}$$

where the parameters Ω_α^S are defined in Eq. (3.4.6).

Thus prepared, we now look for the solution of Eq. (3.4.12), where the spin Hamiltonian $\bar{H}_A^S$ is given by Eq. (3.4.13). For convenience, we first perform a rotation such that the vector $\mathbf{\Omega}^S$ coincides with the z-axis. According to Eq. (3.2.1), the action of a rotation corresponding to an axial rotation vector $\boldsymbol{\omega}^S$ in $\bar{\mathscr{H}}_A^S$ is described by

$$\bar{V}_A^S(\boldsymbol{\omega}^S) = \exp(-i\boldsymbol{\omega}^S \cdot \mathbf{S}^{SS}) \tag{3.4.14}$$

with

$$\boldsymbol{\omega}^S \cdot \mathbf{\Omega}^S = 0, \qquad \boldsymbol{\omega}^S \cdot \mathbf{e}_3 = 0, \qquad \text{and} \qquad R(\boldsymbol{\omega}^S)\, \mathbf{\Omega}^S = \|\mathbf{\Omega}^S\|\, \mathbf{e}_3, \tag{3.4.15}$$

where $\mathbf{S}^{SS}$ is the operator $\mathbf{S}$ (3.2.1) restricted to the subspace of the irreducible representation of type S. These operators are the irreducible generators of a representation of the rotation group with the dimension $2S+1$. We have

$$\bar{V}_A^S(\boldsymbol{\omega}^S)\, \bar{H}_A^S \bar{V}_A^S(\boldsymbol{\omega}^S)^{-1} = \|\mathbf{\Omega}^S\|\, \Sigma_3^{S[N]S}. \tag{3.4.16}$$

The eigenvalues of the operator $\bar{H}_A^S$ are thus non-degenerate and real. According to Eq. (3.4.16), they are directly related with the eigenvalues of $\Sigma_3^{S[N]S}$, and we have

$$E_M^S = 2M\, \|\mathbf{\Omega}^S\|, \qquad M = -S,\ldots, +S. \tag{3.4.17}$$

Similarly, as can be seen from Eq. (3.4.16), the corresponding eigenvectors of $\bar{H}_A^S$ in the unrotated system $\bar{\mathscr{H}}_A^S$ satisfy the relation

$$|M, S\rangle = \bar{V}_A^S(\boldsymbol{\omega}^S)^{-1}\, |M, S, 1\rangle, \tag{3.4.18}$$

where

$$\Sigma_3^{S[N]S}\, |M, S, 1\rangle = 2M\, |M, S, 1\rangle. \tag{3.4.19}$$

Finally, the whole set of basis vectors $|M, S, i\rangle$ may be generated from the vectors $|M, S, 1\rangle$ using the correspondents of the partially isometric operators (2.1.20) in Eq. (2.1.26)

$$P^{S}_{A\,i\,1}\,|M, S, 1\rangle = |M, S, i\rangle. \tag{3.4.20}$$

We are now in the position to complete the selection rules (3.3.20) and (3.3.21). From Eq. (3.4.19), the relations (3.2.14), and the well-known properties of the Clebsch–Gordan coefficients associated with the group of rotations we obtain

$$\langle M', S, i'|\,\Sigma^{\mu}_{\alpha l}\,|M, S, i\rangle = 0 \qquad \text{if} \quad |M - M'| > 1. \tag{3.4.21}$$

Together with the definitions (3.3.6) and (3.3.11) we get the selection rules

$$\langle M, S|\,\Sigma^{S\mu S}_{\alpha}\,|M', S\rangle = 0 \qquad \text{if} \quad |M - M'| > 1, \tag{3.4.22}$$

which hold for any μ.

3.5. Master Equations

We now come back to the Markovian master equations (2.9.9), which are determined by the coefficients $\Gamma^{\rho\ a'_1 a'_2}_{\lambda\ a_1 a_2}$. Adopting the notation based on the bijective correspondence (3.1.1) between the total spin S and the type λ of the irreducible representations, the expression (2.10.2) for these coefficients reads

$$\Gamma^{S'M'_1M'_2}_{SM_1M_2} = \Gamma^{\ S'M'_1M'_2}_{0\ SM_1M_2} + \frac{i}{\hbar}\,(\delta_{SS'}(\delta_{M_1M'_1}(H^{S}_{M'_2M_2} + iG^{S}_{M'_2M_2}) - (H^{S}_{M_1M'_1} - iG^{S}_{M_1M'_1})\,\delta_{M_2M'_2})). \tag{3.5.1}$$

In Section 2.10 we have already seen that $\Gamma^{\rho\ a'_1 a'_2}_{\lambda\ a_1 a_2}$ can be set to zero when the transition energies are different. Thus, as in Eq. (2.10.1), we may assume

$$\Gamma^{S'M'_1M'_2}_{SM_1M_2} = 0 \qquad \text{if} \quad \omega^{S\ S}_{M_1M_2} \neq \omega^{S'\ S'}_{M'_1M'_2}. \tag{3.5.2}$$

Equation (3.4.17) yields

$$\omega^{S\ S}_{M_1M_2} = \frac{2}{\hbar}\,\|\Omega^{S}\|\,(M_1 - M_2), \tag{3.5.3}$$

and Eq. (2.10.5) becomes

$$\Gamma_{0\ SM_1M_2}^{\ S'M_1'M_2'} = \frac{1}{\hbar} \sum_{\mu\alpha} \sum_{\mu'\alpha'} \chi_{\ \alpha\ \alpha'}^{\tilde{S}'\mu\tilde{S}\mu'\tilde{S}'}(\omega_{M_1'M_1}^{S'\ S}) \times \langle M_1, S|\, \Sigma_{\alpha'}^{S\mu'S'}\, |M_1', S'\rangle \langle M_2', S'|\, \Sigma_{\alpha}^{S'\mu S}\, |M_2, S\rangle, \tag{3.5.4}$$

where

$$\chi_{\ \alpha\ \alpha'}^{\tilde{S}'\mu\tilde{S}\mu'\tilde{S}'}(\omega) = \frac{1}{\hbar} \int_{-\infty}^{\infty} c_{\ \alpha\ \alpha'}^{\tilde{S}'\mu\tilde{S}\mu'\tilde{S}'}(\tau)\, e^{i\omega\tau}\, d\tau \tag{3.5.5}$$

with

$$c_{\ \alpha\ \alpha'}^{\tilde{S}'\mu\tilde{S}\mu'\tilde{S}'}(\tau) = \frac{\mathrm{Tr}(\bar{\rho}_B^{\tilde{S}'\,0} B_{\alpha}^{I\tilde{S}'\mu\tilde{S}}(t')\, B_{\alpha'}^{I\tilde{S}\mu'\tilde{S}'}(t''))}{\mathrm{Tr}(\bar{\rho}_B^{\tilde{S}'\,0})}. \tag{3.5.6}$$

In accordance with Eq. (2.10.7), the susceptibility satisfies

$$\chi_{\ \alpha\ \alpha'}^{\tilde{S}'\mu\tilde{S}\mu'\tilde{S}'}(\omega)^{\star} = \chi_{\ \alpha'\ \alpha}^{\tilde{S}'\mu'\tilde{S}\mu\tilde{S}'}(\omega). \tag{3.5.7}$$

As before, the types μ or μ' can be identified with the partitions $[N]$ and $[N-1, 1]$. Now, from Eq. (3.3.20) we know that

$$\Sigma_{\alpha}^{S[N]\,S'} = 0 \qquad \text{if} \quad S \neq S'. \tag{3.5.8}$$

Moreover, inserting the definitions (3.3.18) into the relation (3.3.12), we have already seen that

$$\Sigma_{\alpha}^{S[N-1,\,1]\,S} = f_S^N \Sigma_{\alpha}^{S[N]\,S}, \tag{3.5.9}$$

where the numerical factor f_S^N is given by Eq. (3.4.4). Thus, evaluating Eq. (3.5.4) for $S = S'$, we obtain

$$\Gamma_{0\ SM_1M_2}^{\ SM_1'M_2'} = \frac{1}{\hbar} \sum_{\alpha,\,\alpha'=1}^{3} \chi_{\alpha\alpha'}^{S}(\omega_{M_1'M_1}^{S\ S}) \times \langle M_1, S|\, \Sigma_{\alpha'}^{S[N]\,S}\, |M_1', S\rangle \langle M_2', S|\, \Sigma_{\alpha}^{S[N]\,S}\, |M_2, S\rangle, \tag{3.5.10}$$

where

$$\chi_{\alpha\alpha'}^{S}(\omega) = \chi_{\ \alpha\ \alpha'}^{\tilde{S}[N]\tilde{S}[N]\tilde{S}}(\omega) + f_S^N(\chi_{\ \alpha\ \alpha'}^{\tilde{S}[N]\tilde{S}[N-1,\,1]\tilde{S}}(\omega) + \chi_{\ \alpha\ \alpha'}^{\tilde{S}[N-1,\,1]\tilde{S}[N]\tilde{S}}(\omega)) + (f_S^N)^2\, \chi_{\ \alpha\ \alpha'}^{\tilde{S}[N-1,\,1]\tilde{S}[N-1,\,1]\tilde{S}}(\omega). \tag{3.5.11}$$

The factor f_S^N being real, Eq. (3.5.7) implies also that

$$\chi^S_{\alpha\alpha'}(\omega)^\star = \chi^S_{\alpha'\alpha}(\omega). \tag{3.5.12}$$

From the properties (3.4.22) we find that

$$\Gamma_{0\ SM_1M_2}^{\ SM_1'M_2'} = 0 \qquad \text{if} \quad |M_1 - M_1'| > 1 \quad \text{or} \quad |M_2 - M_2'| > 1. \tag{3.5.13}$$

Similarly, we get for $S \neq S'$

$$\Gamma_{0\ SM_1M_2}^{\ S'M_1'M_2'} = \frac{1}{\hbar} \sum_{\alpha,\,\alpha'=1}^{3} \chi^{S(\pm)}_{\alpha\alpha'}(\omega^{S'\ S}_{M_1'M_1}) \times \langle M_1, S|\, \Sigma_{\alpha'}^{S[N-1,\,1]\,S'}\, |M_1', S'\rangle \langle M_2', S'|\, \Sigma_{\alpha}^{S'[N-1,\,1]\,S}\, |M_2, S\rangle, \tag{3.5.14}$$

where we have introduced the short-hand notation

$$\chi^{S(\pm)}_{\alpha\alpha'}(\omega) = \chi^{\tilde{S}'[N-1,\,1]\,\tilde{S}[N-1,\,1]\,\tilde{S}'}_{\alpha\ \ \alpha'}(\omega) \tag{3.5.15}$$

for $S' = S \pm 1$. By virtue of Eq. (3.5.7) we have

$$\chi^{S(\pm)}_{\alpha\alpha'}(\omega)^\star = \chi^{S(\pm)}_{\alpha'\alpha}(\omega). \tag{3.5.16}$$

From the properties (3.2.15) we further get that

$$\Gamma_{0\ SM_1M_2}^{\ S'M_1'M_2'} = 0 \qquad \text{if} \quad |S - S'| > 1. \tag{3.5.17}$$

Let us now have a look at the matrix elements of the operators $\bar{G}_A$ and $\Delta\bar{H}_A$ introduced in Section 2.10. From the definition (2.10.15) we get immediately that the matrix elements of $\bar{G}_A$ are equal to zero for states with different spins. Moreover, according to Eq. (2.10.1) and to the definition (2.10.3), they are also zero for states with different energies. We thus have

$$G^S_{MM'} = 0 \qquad \text{if} \quad \omega^{S\ S}_{MM'} \neq 0, \tag{3.5.18}$$

and otherwise, for $S \geqslant 1$,

$$G^S_{MM'} = \frac{\hbar}{2}\left(\sum_{M''=-S}^{S} \Gamma_{0\ SM''M''}^{\ SM'M} + \sum_{M''=-S+1}^{S-1} \Gamma_{0\ S-1M''M''}^{\ SM'M} + \sum_{M''=-S-1}^{S+1} \Gamma_{0\ S+1M''M''}^{\ SM'M} \right). \tag{3.5.19}$$

Similar relations hold for the matrix elements of the operator $\Delta\bar{H}_A$ defined by Eq. (2.10.13). From the definitions (2.10.1) and (2.10.3) it is easily seen

that they are zero for states with different spins as well as for states with different energies, i.e., we have in particular

$$H^S_{MM'} = 0 \qquad \text{if} \quad \omega^{S\,S}_{MM'} \neq 0, \tag{3.5.20}$$

and otherwise, by virtue of Eqs. (2.10.9) and (3.5.4),

$$H^S_{MM'} = -\tfrac{1}{2} \sum_{\mu\alpha} \sum_{\mu'\alpha'} \sum_{S''M''} \bar{\chi}^{\tilde{S}\mu\tilde{S}''\mu'\tilde{S}}_{\alpha\ \alpha'}(\omega^{S\ S''}_{M'M''}) \times \langle M, S| \Sigma^{S\mu S''}_{\alpha} |M'', S''\rangle \langle M'', S''| \Sigma^{S''\mu' S}_{\alpha'} |M', S\rangle, \tag{3.5.21}$$

where $\bar{\chi}^{\tilde{S}\mu\tilde{S}''\mu'\tilde{S}}_{\alpha\ \alpha'}(\omega)$ is the Fourier transform of $\epsilon(\tau)\, c^{\tilde{S}\mu\tilde{S}''\mu'\tilde{S}}_{\alpha\ \alpha'}(\tau)$, the function $c^{\tilde{S}\mu\tilde{S}''\mu'\tilde{S}}_{\alpha\ \alpha'}(\tau)$ being defined by Eq. (3.5.6). As we have seen before, the types μ and μ' can be identified with the partitions $[N]$ and $[N-1, 1]$. In this particular situation we have also

$$\bar{\chi}^{\tilde{S}\mu\tilde{S}''\mu'\tilde{S}}_{\alpha\ \alpha'}(\omega)^{\star} = \bar{\chi}^{\tilde{S}\mu'\tilde{S}''\mu\tilde{S}}_{\alpha'\ \alpha}(\omega). \tag{3.5.22}$$

Taking account of the properties (3.5.8) and (3.5.9), the matrix elements $H^S_{MM'}$ can be written as

$$H^S_{MM'} = H^{(0)\,S}_{MM'} + H^{(-)\,S}_{MM'} + H^{(+)\,S}_{MM'} \tag{3.5.23}$$

with

$$H^{(0)\,S}_{MM'} = -\tfrac{1}{2} \sum_{\alpha,\,\alpha'=1}^{3} \sum_{M''=-S}^{S} \bar{\chi}^{(0)\,S}_{\alpha\ \alpha'}(\omega^{S\ S}_{MM'}) \times \langle M, S| \Sigma^{S[N]\,S}_{\alpha} |M'', S\rangle \langle M'', S| \Sigma^{S[N]\,S}_{\alpha'} |M', S\rangle, \tag{3.5.24}$$

$$H^{(\pm)\,S}_{MM'} = -\tfrac{1}{2} \sum_{\alpha,\,\alpha'=1}^{3} \sum_{M''=-S''}^{S''} \bar{\chi}^{(\pm)\,S}_{\alpha\ \alpha'}(\omega^{S\ S''}_{MM'}) \times \langle M, S| \Sigma^{S[N-1,\,1]\,S''}_{\alpha} |M'', S''\rangle \langle M'', S''| \Sigma^{S''[N-1,\,1]\,S}_{\alpha'} |M', S\rangle, \tag{3.5.25}$$

and $S'' = S \pm 1$. In the above expressions we have introduced the shorthand notations

$$\bar{\chi}^{(0)\,S}_{\alpha\ \alpha'}(\omega) = \bar{\chi}^{\tilde{S}[N]\,\tilde{S}[N]\,\tilde{S}}_{\alpha\ \alpha'}(\omega) + f^N_S(\bar{\chi}^{\tilde{S}[N]\,\tilde{S}[N-1,\,1]\,\tilde{S}}_{\alpha\ \alpha'}(\omega) + \bar{\chi}^{\tilde{S}[N-1,\,1]\,\tilde{S}[N]\,\tilde{S}}_{\alpha\ \alpha'}(\omega)) + (f^N_S)^2\, \bar{\chi}^{\tilde{S}[N-1,\,1]\,\tilde{S}[N-1,\,1]\,\tilde{S}}_{\alpha\ \alpha'}(\omega) \tag{3.5.26}$$

and

$$\bar{\chi}^{(\pm)\,S}_{\alpha\ \alpha'}(\omega) = \bar{\chi}^{\tilde{S}[N-1,\,1]\,\tilde{S}''[N-1,\,1]\,\tilde{S}}_{\alpha\ \alpha'}(\omega), \qquad S'' = S \pm 1. \tag{3.5.27}$$

According to Eq. (3.5.22) we have

$$\begin{aligned}\bar{\chi}^{(0)\,S}_{\alpha\,\alpha'}(\omega)^{\star} &= \bar{\chi}^{(0)\,S}_{\alpha'\,\alpha}(\omega),\\ \bar{\chi}^{(\pm)\,S}_{\alpha\,\alpha'}(\omega)^{\star} &= \bar{\chi}^{(\pm)\,S}_{\alpha'\,\alpha}(\omega).\end{aligned} \tag{3.5.28}$$

We are now prepared to discuss the Markovian master equations governing the evolution of the spin system. The general form of these equations in the Schrödinger picture is given by the relation (2.10.27). Presently, the time averaged density matrix $D(\bar{t})$ consists of diagonal blocks $D^S_{MM'}(\bar{t})$ acting in $\bar{\mathscr{H}}^S_A$. The operators $\Delta\bar{H}_A$ and $\bar{G}_A$ have the same structure. The diagonal blocks $\Delta\bar{H}^S_A$ are determined by the relations (3.5.21) for the matrix elements. Similarly, the diagonal blocks $\bar{G}^S_A$ are obtained from Eq. (3.5.19). Exploiting this block structure, the master equations (2.10.27) can be rewritten in the more explicit form

$$\begin{aligned}\frac{dD^S(\bar{t})}{d\bar{t}} &= \frac{i}{\hbar}\left[D^S(\bar{t}),\, \bar{H}^S_A + \Delta\bar{H}^S_A + \bar{H}^S_{A\,\mathrm{ext}}(\bar{t})\right]\\ &\quad + \Gamma^S_0(D^S(\bar{t})) - \frac{1}{\hbar}\left\{D^S(\bar{t}),\, \bar{G}^S_A\right\}\\ &\quad + \Gamma^S_+(D^{S+1}(\bar{t})) + \Gamma^S_-(D^{S-1}(\bar{t})),\end{aligned} \tag{3.5.29}$$

where the mappings

$$\begin{aligned}\Gamma^S_0 &: \mathscr{L}(\bar{\mathscr{H}}^S_A) \longmapsto \mathscr{L}(\bar{\mathscr{H}}^S_A)\\ \Gamma^S_\pm &: \mathscr{L}(\bar{\mathscr{H}}^{S\pm1}_A) \longmapsto \mathscr{L}(\bar{\mathscr{H}}^S_A)\end{aligned} \tag{3.5.30}$$

are defined according to Eqs. (2.10.21) and (2.10.22),

$$\begin{aligned}\Gamma^S_0(D^S(\bar{t}))_{M_1M_2} &= \sum_{M'_1,\,M'_2=-S}^{S} \Gamma_{0\;SM'_1M'_2}^{\;\;SM_1M_2} D^S(\bar{t})_{M'_1M'_2},\\ \Gamma^S_\pm(D^{S\pm1}(\bar{t}))_{M_1M_2} &= \sum_{M'_1,\,M'_2=-(S\pm1)}^{S\pm1} \Gamma_{0\;\;S\;M'_1M'_2}^{\;\;S\pm1\;\;M_1M_2} D^{S\pm1}(\bar{t})_{M'_1M'_2}.\end{aligned} \tag{3.5.31}$$

Clearly, in Eq. (3.5.29) $D^S(\bar{t})$ denotes the block operator associated with the subspace $\bar{\mathscr{H}}^S_A$. The first term, given by the commutator on the right-hand side, describes the reversible part of the evolution. The free Hamiltonian $\bar{H}^S_A$ is modified by the self-energy $\Delta\bar{H}^S_A$, which is due to the interaction with the bath. The term $\bar{H}^S_{A\,\mathrm{ext}}$ describes the effect of an external force. It was already discussed at the end of Section 2.10. Presently we will consider

the situation where the external force corresponds to a spatially uniform magnetic field slowly varying with time. This is adequate to describe an electromagnetic field in the limit of long wavelengths. In this case the external Hamiltonian reads

$$\bar{H}^{S}_{A\,\mathrm{ext}}(\bar{t}) = -g\frac{\mu_B}{2}\,\mathbf{B}(\bar{t})\cdot\mathbf{\Sigma}^{S[N]\,S}, \tag{3.5.32}$$

where $\mathbf{B}(\bar{t})$ denotes the external magnetic field, g is a coupling constant, and $\mu_B = e\hbar/2m$ is the magnetic moment of the electron. The terms of the second line in Eq. (3.5.29) represent the dissipative effect of the bath on the "states" of spin S. The two terms of the third line describe the transfer driven between a "state" with spin S and "states" of spins $S+1$ and $S-1$, which is induced by the interaction of the spin subsystem with the bath.

Let us now briefly discuss the particular situation, where the statistical equilibrium of the bath is described by the canonical ensemble for a fixed temperature T. From the general results presented in Section 2.7 we know already that

$$p^0_{S'}\,e^{-\beta E^{S'}_{M'_1}}\Gamma_{0\;S\,M_1M_2}^{\;\;S'M'_1M'_2} = p^0_S\,e^{-\beta E^{S}_{M_1}}\Gamma_{0\;S'\,M'_2M'_1}^{\;\;S\;\;M_2M_1}, \tag{3.5.33}$$

where

$$p^0_S = \frac{1}{Z_B}\,\mathrm{Tr}(e^{-\beta\bar{H}^{\bar{S}}_B}) \tag{3.5.34}$$

denotes the probability of the bath to be in a statistical state compatible with the spin S. From the above relation we get the important results

$$e^{-\beta E^{S}_{M'_1}}\Gamma_{0\;S\,M_1M_2}^{\;\;S\;M'_1M'_2} = e^{-\beta E^{S}_{M_1}}\Gamma_{0\;S\,M'_2M'_1}^{\;\;S\;M_2M_1} \tag{3.5.35}$$

and

$$p^0_{S+1}\,e^{-\beta E^{S+1}_{M'_1}}\Gamma_{0\;\;S\;\;M_1M_2}^{\;\;S+1\;M'_1M'_2} = p^0_S\,e^{-\beta E^{S}_{M_1}}\Gamma_{0\;S+1\;M'_2M'_1}^{\;\;S\;\;\;M_2M_1}. \tag{3.5.36}$$

We now return to the general discussion of the Markovian master equation (3.5.29). According to Eq. (2.10.14), the self-energy hamiltonian term commutes with $\bar{H}_A$. Therefore, this term can be included in the free Hamiltonian $\bar{H}_A$. It can formally be removed from Eq. (3.5.29), provided that this self-energy term does not affect the change from the Schrödinger picture to the interaction picture. This is the case in most situations of physical interest. We further suppose that the term $\|\mathbf{\Omega}^S\|$ in Eq. (3.5.3)

differs for different S. Under this assumption the energy levels of the unperturbed spin system satisfy the conditions

$$\omega^{S\ S}_{M_1 M_2} = \omega^{S'\ S'}_{M'_1 M'_2} \qquad \text{if and only if} \quad \begin{cases} S = S' \text{ and } M_1 - M_2 = M'_1 - M'_2 \\ \qquad \text{or} \\ S \neq S' \text{ and } M_1 = M_2 \text{ and } M'_1 = M'_2. \end{cases} \tag{3.5.37}$$

Now, condition (3.5.20) implies that the self-energy term, which according to the commutation relation (2.10.14) can only couple between states having the same total spin S, just changes the energy levels of the Hamiltonian $\bar{H}_A$ according to

$$(\bar{H}_A + \Delta\bar{H}_A)\,|M, S\rangle = (E^S_M + \Delta E^S_M)\,|M, S\rangle. \tag{3.5.38}$$

The master equations (3.5.29) determine in particular the evolution of the diagonal elements of the density matrix

$$p^S_M(\bar{t}) = D^S_{MM}(\bar{t}), \tag{3.5.39}$$

which are usually referred to as "populations." Together with the conditions (3.5.37) we obtain

$$\begin{aligned} \frac{dp^S_M(\bar{t})}{d\bar{t}} = & \sum_{M'=M-1}^{M+1} (\Gamma^{S\to S}_{M'\to M} p^S_{M'}(\bar{t}) - \Gamma^{S\to S}_{M\to M'} p^S_M(\bar{t})) \\ & + \sum_{M'=-(S+1)}^{S+1} (\Gamma^{S+1\to S}_{M'\to M} p^{S+1}_{M'}(\bar{t}) - \Gamma^{S\to S+1}_{M\to M'} p^S_M(\bar{t})) \\ & + \sum_{M'=-(S-1)}^{S-1} (\Gamma^{S-1\to S}_{M'\to M} p^{S-1}_{M'}(\bar{t}) - \Gamma^{S\to S-1}_{M\to M'} p^S_M(\bar{t})) \\ & - i\{(\gamma^{(+)S}_M(\bar{t})\, D^S_{MM+1}(\bar{t}) - \gamma^{(+)S}_{M-1}(\bar{t})\, D^S_{M-1M}(\bar{t})) \\ & - (\gamma^{(-)S}_{M+1}(\bar{t})\, D^S_{M+1M}(\bar{t}) - \gamma^{(-)S}_M(\bar{t})\, D^S_{MM-1}(\bar{t}))\} \end{aligned} \tag{3.5.40}$$

with

$$\Gamma^{S'\to S}_{M'\to M} = \Gamma_{0\,S\,M\,M'\,M'}, \tag{3.5.41}$$

which are real numbers according to Eqs. (2.10.19). The coefficients

$$\gamma_M^{(\pm)S}(\bar{t}) = g\frac{\mu_B}{2\hbar}\langle M\pm 1, S|\,\mathbf{B}(\bar{t})\cdot\mathbf{\Sigma}^{S[N]S}\,|M,S\rangle$$

$$= g\frac{\mu_B}{2\hbar}\sqrt{S(S+1)-M(M\pm 1)}\,(B_1(\bar{t})\mp iB_2(\bar{t})) \quad (3.5.42)$$

are associated with the external Hamiltonian, Eq. (3.5.32). They satisfy the symmetry relations

$$\gamma_M^{(+)S}(\bar{t})^\star = \gamma_{M+1}^{(-)S}(\bar{t}). \quad (3.5.43)$$

Equations (3.5.40) govern the evolution of the spin populations. The first sum on the right-hand side describes the population transfer between states of the same total spin S but with $M' = M\pm 1$. The second and the third sums describe the population transfer between the state $|S, M\rangle$ and the states $|S\pm 1, M'\rangle$. The last two lines depending on $\gamma_M^{(\pm)S}(\bar{t})$ account for the influence of the external magnetic field $\mathbf{B}(\bar{t})$ on the evolution of the populations. We note that they introduce a coupling between the diagonal and the off-diagonal matrix elements of the density matrix $D^S(\bar{t})$. These off-diagonal elements are also often denoted "coherences."

In the particular situation, where the statistical equilibrium of the bath subsystem is given by the canonical ensemble corresponding to a temperature $T > 0$, the resulting statistical equilibrium of the spin subsystem satisfies the detailed-balance relations. Actually, referring to the relations (3.5.33) we have

$$p_{0\,M'}^{\,S'}\,\Gamma_{M'\to M}^{S'\to S} = p_{0\,M}^{\,S}\,\Gamma_{M\to M'}^{S\to S'}, \quad (3.5.44)$$

with

$$p_{0\,M}^{\,S} = \frac{1}{Z_A}\,p_S^0\,e^{-\beta E_M^S} \quad (3.5.45)$$

and

$$Z_A = \sum_S p_S^0 Z_A^S \qquad \text{with} \quad Z_A^S = \sum_{M=-S}^{S} e^{-\beta E_M^S}. \quad (3.5.46)$$

We now return to the general case. From Eq. (3.5.40) we can derive the equations governing the evolution of the populations for a given total spin S

$$p^S(\bar{t}) = \sum_{M=-S}^{S} p_M^S(\bar{t}). \tag{3.5.47}$$

We get

$$\begin{aligned}\frac{dp^S(\bar{t})}{d\bar{t}} = &\sum_{M'=-(S+1)}^{S+1} \Gamma_{M'}^{S+1\to S} p_{M'}^{S+1}(\bar{t}) - \sum_{M'=-S}^{S} \Gamma_{M'}^{S\to S+1} p_{M'}^{S}(\bar{t}) \\ &+ \sum_{M'=-(S-1)}^{S-1} \Gamma_{M'}^{S-1\to S} p_{M'}^{S-1}(\bar{t}) - \sum_{M'=-S}^{S} \Gamma_{M'}^{S\to S-1} p_{M'}^{S}(\bar{t})\end{aligned} \tag{3.5.48}$$

with

$$\Gamma_M^{S\to S'} = \sum_{M'=-S'}^{S'} \Gamma_{M\to M'}^{S\to S'}. \tag{3.5.49}$$

The equations governing the evolution of the non-diagonal elements of the density matrix, the so-called " coherences," read

$$\begin{aligned}\frac{d}{d\bar{t}} D_{MM'}^S(\bar{t}) = &-\frac{1}{\hbar}(G_{MM}^S + G_{M'M'}^S + i(E_M^S - E_{M'}^S) + \Gamma_{0\,SMM'}^{\;\;SMM'})\, D_{MM'}^S(\bar{t}) \\ &+ \Gamma_{0\,SMM'}^{\;\;SM-1M'-1} D_{M-1M'-1}^S(\bar{t}) + \Gamma_{0\,SMM'}^{\;\;SM+1M'+1} D_{M+1M'+1}^S(\bar{t}) \\ &+ i(\gamma_M^{(0)\,S}(\bar{t}) - \gamma_{M'}^{(0)\,S}(\bar{t}))\, D_{MM'}^S(\bar{t}) \\ &- i\{(\gamma_{M'}^{(+)\,S}(\bar{t})\, D_{MM'+1}^S(\bar{t}) - \gamma_{M-1}^{(+)\,S}(\bar{t})\, D_{M-1M'}^S(\bar{t})) \\ &- (\gamma_{M+1}^{(-)\,S}(\bar{t})\, D_{M+1M'}^S(\bar{t}) - \gamma_{M'}^{(-)\,S}(\bar{t})\, D_{MM'-1}^S(\bar{t}))\}\end{aligned} \tag{3.5.50}$$

for $M \neq M'$, and where

$$\gamma_M^{(0)\,S}(\bar{t}) = g\frac{\mu_B}{2\hbar}\langle M, S|\, \mathbf{B}(\bar{t})\cdot \mathbf{\Sigma}^{S[N]\,S}\, |M, S\rangle = g\frac{\mu_B}{\hbar} M B_3(\bar{t}). \tag{3.5.51}$$

Let us briefly discuss the role of the different terms on the right-hand side of Eq. (3.5.50). The first line contains the self-interaction of $D_{MM'}^S(\bar{t})$ to the coherent as well as to the dissipative evolution. The second line accounts for the coupling with the other coherences corresponding to the same S and the same difference of the M values. The last three lines describe the additional couplings in presence of an external magnetic field.

Inspection of the above equations shows that populations and coherences are not coupled in absence of an external time-dependent magnetic field $\mathbf{B}(t)$. This rather particular feature is a consequence of the assumptions (3.5.37), which exclude accidental degeneracies between the energy levels. It suggests that the evolution of a fermionic system may be drastically changed in presence of a slowly time-varying electromagnetic field.

Eq. (3.5.50) further shows that the coherences within a given block S do not couple directly with the coherences associated with other spin values. In this case we have a coupling between the coherences and the populations belonging to the same spin S, which is described by the term $\{\cdots\}$ in Eq. (3.5.50). These populations are themselves coupled to the populations corresponding to other spin values S' by virtue of the second and the third term in Eq. (3.5.40).

Coupling between blocks corresponding to different total spins is only provided by the coefficients $\Gamma_{0\,SMM}^{S'M'M'}\, p_{M'}^{S'}$ on the right-hand side of Eq. (3.5.40). Thus, these terms are the only responsible for the spin relaxation of the system. We also note that, according to Eq. (3.5.17), only adjacent blocks S and S' with $S' = S \pm 1$ are coupled.

4. SUMMARY AND CONCLUSIONS

We have presented a quantum statistical description of the ensemble-averaged coarse grained evolution of the electronic spin properties in N-electron systems embedded in a statistical environment. Let us here recall the principal physical ideas and assumptions underlying our approach. Starting from the fact that any quantum system of identical particles is characterized by its spatial and internal properties, we have introduced the Hilbert space $\mathscr{H} = \mathscr{H}_A \otimes \mathscr{H}_B$, where $\mathscr{H}_A$ and $\mathscr{H}_B$ describe the internal and the spatial properties, respectively. The Hilbert space for a N-fermion system is then provided by $\mathscr{H}_{A+B}$, the subspace of antisymmetric tensors in $\mathscr{H}$. The statistical evolution of an ensemble of N-fermion systems was obtained from the time-dependence of the associated density matrix. In order to determine its temporal behavior we had to delimit the considered physical situation. Thus, we have supposed that the considered system is quasi-degenerate with respect to changes of the internal properties, so that changes of the internal properties are possible with only small changes of the energy of the N-fermion system. The bath was associated with the spatial degrees of freedom. Due to the symmetry properties induced by the indistinguishability of the electrons, the properties of the subsystem A are described by the Hilbert subspaces $\bar{\mathscr{H}}_A^{\lambda}$, which are strictly included in $\mathscr{H}_A^{\lambda}$, rather than in the factor subspace $\mathscr{H}_A$. We have shown

that the standard quantum statistical approach can be adapted to this situation. Following this approach, we have obtained the coupled Markovian master equations (2.10.20). These equations can be generalized to cover the evolution in presence of external forces, provided that the latter can be considered to be constant on a time scale of the order of τ_A^{evol} (see Eq. (2.10.27)).

The above results of Section 2 were obtained without referring to a particular subspace $\mathscr{H}_A$, i.e., they apply to arbitrary fermions. In Section 3 we have considered the particular situation of N-electron systems, which is clearly the most interesting from the physical point of view. In this case, the internal fermionic properties are represented by the electronic spins, the Hilbert space $\mathscr{H}_A$ is given by the tensor product $(\mathbb{C}^2)^{\otimes N}$, and the total spin S labels the irreducible representations of the permutation group carried by $\mathscr{H}_A$. We have shown that the time-averaged density matrix describing the evolution of the spin subsystem remains block-diagonal, each single block corresponding to a different total spin S. Consequently, a statistical state describing the spin subsystem is always compatible with the other observables associated with this subsystem. Accordingly, the total spin in a quantum statistical ensemble gets a status similar to that of a classical observable. We have expressed this feature by saying that the total electron spin S satisfies a " statistical superselection rule."

In Section 3.3 we have shown that the interaction operator couples only between blocks corresponding to total spins S and S' differing at most by 1. The first-order interaction terms give rise to a polarization of the spin subsystem. Thus, similar to the effect of a time-independent external force, the interaction with the bath leads to a fine-structure splitting. For convenience, we have included the first-order terms in the Hamiltonian H_A describing the internal degrees of freedom. Exploiting the fact that the total-spin operator generates the representation of the spatial rotations in $\mathscr{H}_A$, we have obtained the required explicit basis in $\mathscr{H}_A$, by diagonalizing the redefined Hamiltonian H_A. Following the general approach of Section 2, we have then obtained the Markovian master equations (3.5.29), which describe the evolution of the spin subsystem. Analysis of these equations shows that the above-mentioned restricted coupling of the interaction Hamiltonian between blocks associated with different total spins S puts severe constraints on the evolution of the spin subsystem. In fact, we can distinguish between three different types of evolution, (i) a reversible evolution involving the electronic states associated with a given total spin S, (ii) an irreversible evolution among the same states, and (iii) an irreversible evolution corresponding to changes of the total spin S in steps of 1 and arbitrary changes of the magnetic numbers M. We find in particular that global changes of the total spin S are always irreversible. The evolution of

the electronic spin properties may thus be described as an irreversible cascade process with steps $\Delta S = 1$. We expect different kinds of behavior, depending on the relative importance of the three types of contribution. The evolution (3.5.29) is determined by the coefficients $\Gamma_{0\,SM_1M_2}^{S'M'_1M'_2}$ (3.5.4). At the present stage, it is rather impossible to delimit the range of parameters, which is adequate to describe real physical systems. For a given physical system, the coefficients $\Gamma_{0\,SM_1M_2}^{S'M'_1M'_2}$ may be changed in principle by changing the imposed statistical equilibrium of the bath. It should be interesting to look whether, besides the above-mentioned expected changes of the fine-structure splittings, this dependence could be used to slow down the irreversible evolution and thus to increase the time domain for the coherent evolution of type (i).

An important step in our approach was the exploitation of the isomorphism (2.6.19) and the resulting decomposition of the action of the interaction operator H_{int} in the Hilbert space $\mathscr{H} = \mathscr{H}_A \otimes \mathscr{H}_B$ presented in Sections 2.1, 2.6, and 3.3. This description of H_{int} will also be crucial for future extensions, which may be necessary to get a satisfactory description of specific physical systems. In the present work, we have focused our attention on the electronic degrees of freedom. This was sufficient to understand the general aspects of the fermionic evolution. However, other degrees of freedom may come into play in real physical systems. For example, to study the dynamic magnetic response of a molecule deposited on a substrate, it will possibly be adequate to account for eventual structural changes as a function of the substrate temperature, and thus to include the vibrational degrees of freedom.

Further generalizations of our approach may be envisaged. Thus one may want to treat situations, where our assumptions concerning the dynamical behavior of the electronic spins and the electronic orbitals are not satisfied. In our present approach, we have assumed that the typical time scales for the evolution of the spins and for the evolution of the orbitals are different, and that the bath correlation time τ_B^{corr} is much smaller than the typical evolution time of the spin properties τ_A^{evol}. This restriction was necessary to obtain a description of the spin evolution in terms of a set of master equations. Obviously, short bath-correlation times τ_B^{corr} require a sufficiently large effective dynamical coupling of the orbitals with the infinite statistical environment. Depending on the physical situation, it is thus quite possible that the above condition is not satisfied and that memory effects have to be considered. The corresponding extension of the present approach can be obtained following the lines discussed in refs. 14–23.

Finally, it should be noted that the master equations (3.5.29) may be used in different manners. They offer a quantum statistically correct description of the global evolution of the spin properties. Thus, without

any further restrictions, the free parameters entering Eq. (3.5.29) may either be taken as phenomenological parameters, to describe the experimentally observed dynamical behavior of a given system, or they may be determined from a microscopic description of the considered system.

APPENDIX A. PROOF OF THE RELATION (3.1.12)

We have to evaluate

$$a^{\lambda}_{jn} = \frac{d_\lambda}{N!} \sum_{\{s \in S_N \mid s(j) = n\}} \chi_\lambda(s), \qquad j \text{ and } n \in \{1,\ldots, N\}, \tag{A.1}$$

where λ denotes the character of an irreducible representation of the group S_N. From Eq. (A.1) we get immediately

$$a^{\lambda}_{t(j)\, t(n)} = a^{\lambda}_{jn}, \qquad \forall j \text{ and } n, \quad \forall t \in S_N, \tag{A.2}$$

since

$$a^{\lambda}_{t(j)\, t(n)} = \frac{d_\lambda}{N!} \sum_{\{s \in S_N \mid st(j) = t(n)\}} \chi_\lambda(s) = \frac{d_\lambda}{N!} \sum_{\{s \in S_N \mid t^{-1}st(j) = n\}} \chi_\lambda(t^{-1}st) = a^{\lambda}_{jn},$$

where we have also used the fact that $\chi_\lambda(t^{-1}st) = \chi_\lambda(s)$. Equation (A.2) implies

$$a^{\lambda}_{11} = a^{\lambda}_{22} = \cdots = a^{\lambda}_{NN} \qquad \text{and} \qquad a^{\lambda}_{jn} = a^{\lambda}_{12}, \quad \forall j \neq n. \tag{A.3}$$

In addition, because of the orthogonality of the characters and since $\chi_{[N]}(s) = 1$, $\forall s$, we get from Eq. (A.1)

$$\sum_{n=1}^{N} a^{\lambda}_{jn} = \frac{d_\lambda}{N!} \sum_{s \in S_N} \chi_\lambda(s) = \delta^{[N]}_{\lambda}. \tag{A.4}$$

Insertion of Eqs. (A.3) into Eq. (A.4) gives

$$a^{\lambda}_{11} + (N-1)\, a^{\lambda}_{12} = \delta^{\lambda}_{[N]}. \tag{A.5}$$

For $\lambda = [N]$ we obtain from Eq. (A.1) and from the dimensions (3.1.2)

$$a^{[N]}_{ij} = \frac{1}{N}, \qquad \forall i, j = 1,\ldots, N. \tag{A.6}$$

The characters $\chi_\lambda(s)$ associated with the isotypic components of type λ of the group S_N are obtained from

$$\chi_\lambda(s) = \frac{d_\lambda}{N!} \sum_{g \in S_N} \sum_{p \in P_{T[\lambda]}} \sum_{q \in Q_{T[\lambda]}} \sigma(q)\, \epsilon_g(s^{-1} g q^{-1} p^{-1}), \tag{A.7}$$

where $P_{T[\lambda]}$ ($Q_{T[\lambda]}$) denotes the subgroup of horizontal (vertical) permutations, which is associated with a Young tableau $T[\lambda]$ corresponding to a partition λ of N.[45] The symbol $\sigma(q)$ denotes the signature of the permutation q, and $\epsilon_g(g')$ is defined as

$$\epsilon_g(g') = \begin{cases} 1 & \text{if} \quad g' = g \\ 0 & \text{otherwise.} \end{cases}$$

Using the expression (A.7), we obtain from Eq. (A.1)

$$\begin{aligned} a^\lambda_{11} &= \frac{d_\lambda}{N!} \sum_{\{s \in S_N \,|\, s(1)=1\}} \chi_\lambda(s) \\ &= \frac{d_\lambda^2}{(N!)^2} \sum_{\{s \in S_N \,|\, s(1)=1\}} \sum_{g \in S_N} \sum_{p \in P_{T[\lambda]}} \sum_{q \in Q_{T[\lambda]}} \sigma(q)\, \epsilon_g(s^{-1} g q p) \\ &= \frac{d_\lambda^2}{(N!)^2} \sum_{g \in S_N} \sum_{p \in P_{T[\lambda]}} \sum_{q \in Q_{T[\lambda]}} \sigma(q)\, \delta^1_{gqpg^{-1}(1)} \\ &= \frac{d_\lambda^2}{(N!)^2} \sum_{j=1}^{N} (N-1)! \sum_{p \in P_{T[\lambda]}} \sum_{q \in Q_{T[\lambda]}} \sigma(q)\, \delta^j_{qp(j)} \\ &= \frac{d_\lambda^2}{N!} \frac{1}{N} \sum_{j=1}^{N} \left(\sum_{p \in P_{T[\lambda]}} \delta^j_{p(j)} \right) \left(\sum_{q \in Q_{T[\lambda]}} \sigma(q)\, \delta^j_{q(j)} \right). \end{aligned}$$

For $\lambda \neq [N]$, the last factor in the previous expression is nonzero only if $\lambda = [N-1, 1]$ and if j is included in the first column of $T[\lambda]$. In this case we get

$$\sum_{\{q \in Q_{T[\lambda]} \,|\, q(j)=j\}} \sigma(q) = 1.$$

If j is also included in the first row, we have

$$\sum_{p \in P_{T[\lambda]}} \delta^j_{p(j)} = (N-2)!,$$

and if it is included in the second row

$$\sum_{p \in P_{T[\lambda]}} \delta^{j}_{p(j)} = (N-1)!.$$

Thus, with the dimensions d_λ obtained from Eq. (3.1.2), we get

$$a^{\lambda}_{11} = \frac{d^2_\lambda}{N!}\frac{1}{N}((N-1)!+(N-2)!) = \frac{d^2_\lambda}{N!}(N-2)! = \frac{(N-1)^2}{N!}(N-2)! = 1-\frac{1}{N}$$

and finally from Eqs. (A.6), (A.3), and (A.4)

$$a^{\lambda}_{jn} = \delta^{[N-1,1]}_{\lambda}\left(\delta_{jn}-\frac{1}{N}\right) \qquad \text{if} \quad \lambda \neq [N]. \tag{A.8}$$

APPENDIX B. CLEBSCH–GORDAN SERIES FOR THE TENSOR PRODUCT OF IRREDUCIBLE REPRESENTATIONS OF S_N OF TYPES $[N-1, 1]$ AND $[\lambda_1, \lambda_2]$

Be α_l, $l = 1, 2,\ldots, N$ the number of cycles of order l for a permutation $s \in S_N$. Obviously we have $0 \leqslant \alpha_l \leqslant N$, $\forall l = 1,\ldots, N$ with

$$\sum_{l=1}^{N} l\alpha_l = N. \tag{B.1}$$

Actually, a sequence $\{\alpha_l\}$, $l = 1,\ldots, N$ characterizes a class of conjugated elements of S_N. Our first objective is to prove that the character $\chi_\lambda(s)$ of the irreducible representation of type $\lambda = [\lambda_1, \lambda_2]$ with $\lambda_1 + \lambda_2 = N$ is given by

$$\chi_\lambda(s) = \frac{1}{2\pi i}\int_{\Gamma_0} \frac{(1-z)\prod_{l=1}^{N}(1+z^l)^{\alpha_l}}{z^{\lambda_2}}\frac{dz}{z}, \tag{B.2}$$

where Γ_0 denotes a circular path of integration of radius smaller than 1 surrounding $z = 0$ in the trigonometric positive sense. The proof of the above relation based on the general expression (A.7) is technically rather difficult. In the present context it is more convenient to start from the properties mentioned at the beginning of Section 3.1. For our present purposes let us recall that the subspace of $\mathscr{H}_A \equiv (\mathbb{C}^2)^{\otimes N}$, generated by the basis vectors $|M, S, i\rangle$ for fixed S and M and $i = 1,\ldots, d_\lambda$, carries an irreducible

representation of S_N of type $[N/2+S, N/2-S]$. Consequently, defining the projectors

$$P_M = \sum_{S=M}^{N/2} \sum_{i=1}^{d_\lambda} |M, S, i\rangle\langle M, S, i|, \qquad 0 \leqslant M \leqslant N/2 \tag{B.3}$$

we can write

$$\sum_{S=M}^{N/2} \chi_{[N/2+S, N/2-S]}(s) = \sum_{\lambda_2=0}^{N/2-M} \chi_{[\lambda_1, \lambda_2]}(s) = \mathrm{Tr}(P_M U_A(s)) \equiv g_M(s), \tag{B.4}$$

where U_A denotes the unitary representation of S_N in the Hilbert space $\mathscr{H}_A$, which was defined in Eq. (3.1.6). Then, except for the trivial case $\chi_{[N]}(s) = 1$, we have

$$\chi_{[\lambda_1, \lambda_2]}(s) = g_{\frac{N}{2}-\lambda_2}(s) - g_{\frac{N}{2}-\lambda_2+1}(s), \qquad \lambda_2 > 0, \tag{B.5}$$

with

$$\begin{aligned} g_M(s) &= \sum_{\mathscr{A}_M} \langle m_1, \ldots, m_N | \, U_A(s) \, | m_1, \ldots, m_N \rangle \\ &= \sum_{\mathscr{A}_M} \langle m_1, \ldots, m_N \, | \, m_{s^{-1}(1)}, \ldots, m_{s^{-1}(N)} \rangle \\ &= \sum_{\mathscr{A}_M} \prod_{i=1}^{N} \delta^{m_i}_{m_{s^{-1}(i)}} = \sum_{\mathscr{A}_M} \prod_{i=1}^{N} \delta^{m_i}_{m_{s(i)}} \end{aligned} \tag{B.6}$$

and

$$\mathscr{A}_M = \left\{ (m_1, \ldots, m_N) \, | \, m_j = \pm 1/2, \forall j \text{ and } \sum_{j=1}^{N} m_j = M \right\}. \tag{B.7}$$

To evaluate $g_M(s)$ for s taken in the class of conjugated elements characterized by a sequence $\{\alpha_l, l = 1, \ldots, N\}$, we first recall that for given M, $N/2-M$ indices m_i have the values $-1/2$, the other $N/2+M$ indices have the values $+1/2$. The factor

$$\prod_{i=1}^{N} \delta^{m_i}_{m_{s(i)}}$$

is non-zero if and only if the group element s permutes only indices i of m_i's possessing the same value. This implies that there exist integers β_l, $l = 1,\ldots, N$ with $0 \leqslant \beta_l \leqslant \alpha_l$ such that

$$\sum_{l=1}^{N} l\beta_l = \frac{N}{2} - M.$$

Adopting the usual convention $0! = 1$, the number of sequences $\{m_1,\ldots, m_N\}$ satisfying the above condition becomes

$$\prod_{l=1}^{N} C_{\alpha_l}^{\beta_l} \equiv \prod_{l=1}^{N} \frac{\alpha_l!}{(\alpha_l - \beta_l)!\,\beta_l!},$$

and thus we get

$$g_M(s) = \sum_{\mathscr{B}_M(s)} \left(\prod_{l=1}^{N} C_{\alpha_l}^{\beta_l} \right) \tag{B.8}$$

with

$$\mathscr{B}_M(s) = \left\{ (\beta_1,\ldots, \beta_l) \;\middle|\; 0 \leqslant \beta_l \leqslant \alpha_l,\ l = 1,\ldots, N \text{ and } \sum_{l=1}^{N} l\beta_l = \frac{N}{2} - M \right\}. \tag{B.9}$$

Using the theorem of residues we can write

$$g_M(s) = \sum_{\mathscr{B}_M(s)} \frac{1}{2\pi i} \int_{\Gamma_0} \frac{\prod_{l=1}^{N} (C_{\alpha_l}^{\beta_l} z^{l\beta_l})}{z^{N/2-M}} \frac{dz}{z} = \frac{1}{2\pi i} \int_{\Gamma_0} \frac{\prod_{l=1}^{N} (1+z^l)^{\alpha_l}}{z^{N/2-M}} \frac{dz}{z}. \tag{B.10}$$

Inserting this expression on the right-hand side of Eq. (B.5), we obtain (B.2).

Now, to prove the properties (3.3.10), we have to evaluate

$$a_{\lambda'} = \frac{1}{N!} \sum_{s \in S_N} \chi_{\lambda'}(s)^{\star}\, \chi_{[N-1,1]}(s)\, \chi_{\lambda}(s) \tag{B.11}$$

with $\lambda = [\lambda_1, \lambda_2]$ and $\lambda' = [\lambda'_1, \lambda'_2]$. Clearly, we may assume $N > 1$. Then, in the particular case $\lambda = [N]$, which corresponds to $\lambda_2 = 0$, and where $\chi_\lambda(s) = 1$ for all $s \in S_N$, we have

$$a_{\lambda'} = \delta_{\lambda'}^{[N-1,1]}, \qquad \forall \lambda' \in \Lambda \qquad \text{for} \quad \lambda = [N], \tag{B.12}$$

which follows immediately from the orthogonality relation for the characters. Similarly, we get for $\lambda'_2 = 0$

$$a_{[N]} = \delta_{\lambda}^{[N-1,1]}, \qquad \forall \lambda \in \Lambda \qquad \text{for} \quad \lambda' = [N]. \tag{B.13}$$

The results (B.11) and (B.12) prove the validity of the relation (3.3.10) for $\lambda_2 = 0$ and/or $\lambda'_2 = 0$. Now we consider the case $\lambda_2 > 0$ and $\lambda'_2 > 0$. To evaluate $a_{\lambda'}$ given by Eq. (B.11), we first note that the number of conjugated elements in the class characterized by the sequence $\{\alpha_l, l = 1,\ldots, N\}$ satisfying the condition (B.1) is equal to

$$\frac{N!}{\prod_{l=1}^{N} l^{\alpha_l} \alpha_l!}.$$

Moreover, from Eq. (B.2) we obtain immediately

$$\chi_{[N-1,1]}(s) = \alpha_1 - 1, \qquad \forall s \in S_N. \tag{B.14}$$

Thus, using the relation (B.2) we can rewrite the right-hand side of Eq. (B.11), which becomes

$$a_{\lambda'} = \frac{1}{(2\pi i)^3} \sum_{\alpha_1,\ldots,\alpha_N = 0}^{N} \int_{\Gamma_0} \frac{dz}{z} \int_{\Gamma_0} \frac{dz'}{z'} \int_{\Gamma_0} \frac{du}{u} \frac{(1-z)(1-z')}{z^{\lambda_2} z'^{\lambda'_2}} \frac{\alpha_1 - 1}{u^N}$$

$$\times \prod_{l=1}^{N} \left\{ \frac{1}{\alpha_l!} \left(\frac{(1+z^l)(1+z'^l)\, u^l}{l} \right)^{\alpha_l} \right\}. \tag{B.15}$$

Condition (B.1) is satisfied, since the term

$$\frac{1}{2\pi i} \int_{\Gamma_0} \frac{du}{u} \frac{1}{u^N} \prod_{l=1}^{N} \{(u^l)^{\alpha_l}\}$$

becomes zero if it is not satisfied, otherwise it is equal to 1. For the same reason, we may extend the summations in Eq. (B.15) over $\alpha_1,\ldots, \alpha_N$ up to infinity. After Taylor expansion of the exponential and using

$$\sum_{\alpha_1 = 0}^{\infty} \frac{\alpha_1 - 1}{\alpha_1!} [(1+z)(1+z')\, u]^{\alpha_1}$$

$$= [(1+z)(1+z')\, u - 1] \exp[(1+z)(1+z')\, u]$$

we then get

$$a_{\lambda'} = \frac{1}{(2\pi i)^3}\int_{\Gamma_0}\frac{dz}{z}\int_{\Gamma_0}\frac{dz'}{z'}\int_{\Gamma_0}\frac{du}{u} \times \frac{(1-z)(1-z')[(1+z)(1+z')\,u-1]}{z^{\lambda_2}z'^{\lambda'_2}u^N}\exp\left\{\sum_{l=1}^{N}\left(\frac{(1+z^l)(1+z'^l)\,u^l}{l}\right)\right\}. \tag{B.16}$$

The summation over l in the exponential can be extended to infinity, since the extra terms $l > N$ do not contribute to the residue of the integrand at $u = 0$. With the identity

$$\sum_{l=1}^{\infty}\frac{(1+z^l)(1+z'^l)\,u^l}{l} = \ln\left\{\frac{1}{(1-u)(1-uz)(1-uz')(1-uzz')}\right\}$$

we get from Eq. (B.16)

$$a_{\lambda'} = \frac{1}{(2\pi i)^3}\int_{\Gamma_0}\frac{dz}{z}\int_{\Gamma_0}\frac{dz'}{z'}\int_{\Gamma_0}\frac{du}{u}\frac{(1-z)(1-z')[(1+z)(1+z')\,u-1]}{z^{\lambda_2}z'^{\lambda'_2}u^N(1-u)(1-uz)(1-uz')(1-uzz')}. \tag{B.17}$$

The integral is easily evaluated using Cauchy's theorem. The integrand is a meromorphic function of u with asymptotic behavior $O(u^{-N-4})$. Thus, the sum over the residues at $u = 0$, $u = 1$, $u = 1/z$, $u = 1/z'$, and $u = 1/(zz')$ is equal to zero, and the residue at $u = 0$ can be determined from the residues at $u = 1$, $u = 1/z$, $u = 1/z'$, and $u = 1/(zz')$. The latter have the values

$$\begin{aligned}
&-\frac{z+z'+zz'}{z^{\lambda_2+1}z'^{\lambda'_2+1}(1-zz')} && \text{at} \quad u=1\\
&\frac{z^{N+1-\lambda_2}(zz'+z'+1)}{(z-z')\,z'^{\lambda'_2+1}} && \text{at} \quad u=1/z\\
&\frac{z'^{N+1-\lambda'_2}(zz'+z+1)}{(z'-z)\,z^{\lambda_2+1}} && \text{at} \quad u=1/z'\\
&\frac{z^{N+1-\lambda_2}z'^{N+1-\lambda'_2}(z+z'+1)}{1-zz'} && \text{at} \quad u=1/(zz').
\end{aligned}$$

The residues at $u = 1/z$, $u = 1/z'$, and $u = 1/(zz')$ do not contribute to the integral in Eq. (B.17), since they possess no first-order poles at $z = 0$

or/and $z' = 0$. The only non-vanishing contribution is due to the residue at $u = 1$, which yields

$$a_{\lambda'} = -\frac{1}{(2\pi i)^2}\int_{\Gamma_0}\frac{dz}{z}\int_{\Gamma_0}\frac{dz'}{z'}\frac{z+z'+zz'}{z^{\lambda_2+1}z'^{\lambda_2'+1}(1-zz')}$$
$$= \frac{1}{(2\pi i)}\int_{\Gamma_0}\frac{dz}{z}\left(\frac{1}{z}+z+1\right)z^{\lambda_2'-\lambda_2}, \tag{B.18}$$

where we have again used Cauchy's theorem to evaluate the integral over z'. For $\lambda_2 > 0$ and $\lambda_2' > 0$ we obtain finally

$$a_{\lambda'} = \begin{cases} 1 & \text{if} \quad |\lambda_2' - \lambda_2| \leqslant 1 \\ 0 & \text{otherwise.} \end{cases} \tag{B.19}$$

This together with Eqs. (B.12) and (B.13), proves the result (3.3.10) for the multiplicities.

ACKNOWLEDGMENTS

We thank A. Robert for some very helpful hints concerning the theory of representations of the group of permutations. The continuous interest and encouragement of J. P. Ansermet has been essential to stay the course. One of us (V.C.) would like to express his gratitude to J. P. Ansermet, H. Brune, J. Buttet, and A. Châtelain for their financial support. This work was partly supported by the Swiss National Science Foundation under Grant Nos. 2000-53832.98, 2000-058972.99, and 2000-66681.01.

REFERENCES

1. E. Fick and G. Sauermann, *The Quantum Statistics of Dynamic Processes*, Springer Series in Solid State Sciences, Vol. 86, P. Fulde, ed. (Springer-Verlag, Heidelberg, 1990), p. 266.
2. J. von Neumann, *Die mathematischen Grundlagen der Quantenmechanik* (Springer, Berlin, 1932); *Mathematical Foundation of Quantum Mechanics* (Princeton University Press, Princeton, 1955).
3. P. A. M. Dirac, *Proc. Camb. Phil. Soc.* **25**:62 (1929); *ibid.* **26**:376 (1930); *ibid.* **27**:240 (1931).
4. R. P. Feynman, *Rev. Mod. Phys.* **20**:367 (1948).
5. R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw–Hill, London, 1955).
6. R. P. Feynman and F. L. Vernon, Jr., *Ann. Phys. (N.Y.)* **24**:118 (1963).
7. L. S. Schulman, *Techniques and Applications of Path Integration* (Wiley, 1981).
8. H. Kleinert, *Path Integrals in Quantum Mechanics, Statistics, and Polymer Physics* (World Scientific, Singapore, 1995).

9. F. Bloch, *Phys. Rev.* **102**:104 (1956).
10. R. K. Wangsness and F. Bloch, *Phys. Rev.* **89**:4 (1953).
11. A. G. Redfield, *Adv. Mag. Res.* **1**:1 (1965); *IBM J. Res. Dev.* **1**:19 (1957).
12. W. H. Louisell, *Quantum Statistical Properties of Radiation* (John Wiley & Sons, New York, 1990).
13. R. R. Puri, *Mathematical Methods of Quantum Optics*, Springer Series in Optical Sciences, Vol. 79 (Springer-Verlag, New York, 2001).
14. F. Haake, Statistical treatment of open systems by generalized master equations, *Springer Tracts in Modern Physics* **66**:98 (1973).
15. E. B. Davies, *Commun. Math. Phys.* **39**:91 (1974).
16. G. Lindblad, *Commun. Math. Phys.* **40**:147 (1975); *ibid.* **48**:119 (1976).
17. V. Gorini, A. Kossakowski, and E. C. G. Sudarshan, *J. Math. Phys.* **17**:821 (1976).
18. H. Spohn and J. L. Lebowitz, *Adv. Chem. Phys.* **38** (Wiley, New York, 1978).
19. R. Dümcke and H. Spohn, *Z. Physik B* **34**:419 (1979).
20. R. Alicki and K. Lendi, *Quantum Dynamical Semigroups and Applications*, Lecture Notes in Physics, Vol. 286 (Springer Verlag, Berlin, 1987).
21. G. L. Sewell, *Quantum Mechanics and Its Emergent Macrophysics* (Princeton University Press, Princeton, 2002).
22. R. Alicki and M. Fannes, *Quantum Dynamical Systems* (Oxford University Press, Oxford, 2001).
23. H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Oxford University Press, Oxford, 2002).
24. A. Vaterlaus, T. Beutler, and F. Meier, *Phys. Rev. Lett.* **67**:3314 (1991).
25. A. Vaterlaus, T. Beutler, D. Guarisco, M. Lutz, and F. Meier, *Phys. Rev. B* **46**:5280 (1992).
26. W. Hübner and K. H. Bennemann, *Phys. Rev. B* **53**:3422 (1996).
27. See, e.g., W. A. de Heer, P. Milani, and A. Châtelain, *Phys. Rev. Lett.* **65**:488 (1990); A. J. Cox, J. G. Louderback, and L. A. Bloomfield, *Phys. Rev. Lett.* **71**:923 (1993).
28. M. Ledermann, S. Schulz, and M. Ozaki, *Phys. Rev. Lett.* **73**:1986 (1994).
29. W. T. Coffey, D. S. F. Crothers, J. L. Dormann, Yu. P. Kalmykov, E. C. Kennedy, and W. Wernsdorfer, *Phys. Rev. Lett.* **80**:5655 (1998).
30. J. S. Lomont, *Application of Finite Groups* (Academic Press, New York, 1959).
31. H. Boerner, *Representations of Groups* (North-Holland Publishing Company, Amsterdam, 1963).
32. M. Hamermesh, *Group Theory and its Application to Physical Problems*, 2nd Ed. (Addison–Wesley, Reading, Massachussets, 1964).
33. D. S. Passman, *Permutation Groups* (W. A. Benjamin, Inc., Amsterdam, 1968).
34. C. W. Curtis and I. Reiner, *Representation Theory of Finite Groups and Associative Algebras* (Interscience, Wiley, New York, 1988).
35. L. Jansen and M. Boon, *Theory of Finite Groups, Applications in Physics* (North-Holland Publishing Company, Amsterdam, 1967).
36. G. James and A. Kerber, *The Representation Theory of the Symmetry Group* (Addison–Wesley, Reading, Massachussets, 1981).
37. Miller, Jr., *Symmetry Groups and their Applications* (Academic Press, New York, 1972).
38. A. Katak and B. Hasselblatt, *Introduction to the Modern Theory of Dynamical Systems* (Cambridge University Press, 1995), p. 142.
39. Ref. 34, p. 190.
40. Ref. 30, pp. 259–266; ref. 32, pp. 111–113; ref. 37, pp. 92–100.
41. Ref. 30, pp. 52–61; ref. 32, pp. 101–104.
42. Ref. 32, Chap. 10.

43. Ref. 31, p. 112.
44. Note that the Clebsch–Gordan coefficients $C^{1\ S\ S'}_{\alpha\ M\ M'}$ are basis dependent. At the present stage, the basis in $\mathscr{H}_A$ is not yet known, so that the Clebsch–Gordan coefficients cannot be specified. The reader should also be aware of the fact that the Clebsch–Gordan coefficients refer to the cartesian spatial components of the operators $\mathbf{\Sigma}^{\mu}$ rather than to the usually employed linear combinations.
45. Ref. 30, pp. 261–265.