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PHD THESIS

FROM THE HOLSTEIN-PRIMAKOFF TRANSFORMATION TO SEMICLASSICAL QUANTUM MARKOVIAN MASTER EQUATIONS – WITH APPLICATIONS IN MAGNETIC RESONANCE

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For my dear parents,

Jeorge and Regina.

Preface

The present dissertation concerns some theoretical and computational aspects of multispin dynamics, mainly, in relation to magnetic resonance.

From the theoretical side, a general approach to quantum dynamics is taken where we slightly revisit some concepts developed in the theory of open quantum systems [22] – which stem mainly from the seminal works of Gorini, Kossakowski, Sudarshan [58] and Lindlad [97]. Here, it was necessary to refine concepts like what it means, in general, for a quantum map to be *completely positive*. The papers of Tong *et al.* [155] and Salgado *et al.* [138] proved pivotal in this regard. In this very process, the distinction between *universal dynamical maps* (a concept borrowed from [132]) and *non-universal dynamical maps* (introduced here by the author) is paramount.

Furthermore, the quantization of both the system of interest and its environment has been the hallmark of the theory of open quantum systems (as developed from the ideas of Kraus, Gorini, Kossakowski, Lindblad, Davies, Spohn, and other pioneers). In this work, we propose a way to extend the application of the theory to those problems (for example, quantum dynamics of select systems in condensed phases) in which it suffices to treat the environment at the classical level.

A perturbation scheme, which we have termed *affine commutation perturbation* (ACP), is also introduced in this work. Unlike standard perturbation theory (where one has to go to at least the first-order of the approximation in order to find some effects of the perturbation), the ACP scheme makes it possible for some effects of the perturbation to be manifest even at the zeroth-order. Magnetic resonance of multispin systems (with isotropic Hamiltonians[1]) discussed in the work is used as proof of concept for all the above theoretical endeavors.

Regarding the computational side, we have been mainly concerned with – what one could call – 'counting problems' usually encountered in multispin dynamics. One simple example is the problem of determining the Clebsch-Gordan series (*i.e.* the distinct total spin quantum numbers and corresponding multiplicities) arising from the coupling of an arbitrary collection of spins. Limit cases of these sort of problems have been discussed in the literature [68, 108, 121, 169] from diverse perspectives. It is shown here that the Holstein-Primakoff (HP) transformation [13, 70] offers an easy way to treat such problems in the most general terms. In this dissertation, we give an introduction to the HP transformation which greatly differs from what is commonly offered in the literature. The connection between this transformation (on one side) and the quantum harmonic oscillator and discrete mathematics in general (on the other side), is greatly emphasized. We also show how the HP transformation may be easily used to generate simple stick-plot magnetic resonance spectra of certain multispin systems

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[1] In this work, we only consider isotropic multispin Hamiltonians.

under certain conditions.

The present dissertation is divided into five parts. Part I provides a quick overview of some fundamental concepts in quantum mechanics. The HP transformation is extensively discussed in Part II. Concepts from the theory of open quantum systems like completely positive maps, universal dynamical maps, quantum dynamical semigroups and quantum Markovian master equations are discussed in Part III. This is where we also refine, to some degree, many of these fundamental concepts. Part IV brings together concepts developed in Parts II and III. There, we introduce our proposal on how to still apply many of the ideas and concepts from open quantum system theory (the Gorini-Kossakowski-Sudarshan-Lindblad approach) even when the environment is treated at the classical level. In particular, we discuss semiclassical quantum Markovian master equations and apply it to describe continuous wave magnetic resonance of multispin spin systems. The ACP scheme is also introduced in Part IV. Conclusion and perspectives on the work are given in Part V.

The author hereby declares that this thesis was composed by himself and the work explicitly stated herein to be his are truly his own.

Verona, June 2020.

Jerryman A. Gyamfi.

We live in a world of refinement not in a
world of invention.
That's the way I see it.

A recipe is one thing but method is another.
It's about understanding and questioning
what you are trying to do.
I've always done that. I can't help it, it's in
my nature.

Marco Pierre White[a]

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[a] M. P. White *White Slave: the godfather of modern cooking*, Orion Publishing Group Ltd, London, **2006**.

Contents

V Conclusion 157

Part I

Overview of Quantum Mechanics

This part of the work briefly revises the fundamentals of quantum theory.

The material presented here is taken from the author's preprint:

[63] J.A. Gyamfi, *Fundamentals of Quantum Mechanics in Liouville Space*, arXiv:2003.11472, 2020.

Chapter 1

Postulate I: State space and state vector

The postulates of quantum mechanics are listed and formulated differently from author to author, even though the contents fundamentally do not disagree. The presentation offered here follows closely Ref. [114]. The first postulate defines the complex linear space in which one can describe *isolated* (or *closed*) quantum systems – *i.e.* systems not participating in any kind of interaction with other systems. (Some authors, for example [22], make a distinction between closed and isolated systems. We shall use the two terms interchangeably.)

> **Postulate I**: Let S be an arbitrary isolated physical system. Associated to S is a Hilbert space referred to as its *state space*. The state of S can be completely described by a unit vector $|\psi\rangle$ of its state space. $|\psi\rangle$ is called a *state vector*.

It is worth noting that, in the literature, the term 'Hilbert space' is often taken as synonymous with (or used as a shorthand for) 'state space'. This can sometimes be misleading because the notion of Hilbert space is a very broad one. In fact, any linear space which is complete and endowed with a norm is a Hilbert space [31, 39, 80, 110, 131, 152]. For the sake of clarity, we shall keep this distinction in our discussion.

Let us focus now on the state space. We shall be concerned with only finite-dimensional state spaces. So, let $\mathcal{H}_d$ be a finite-dimensional state space of dimension d. Let $|x\rangle$ be a vector in $\mathcal{H}_d$. $|x\rangle$ is, thus, a $(d \times 1)$ column vector. In linear algebra, we would have indicated such a $(d \times 1)$ vector with the bold symbol $\boldsymbol{x}$ or $\overrightarrow{x}$. But in quantum mechanics, we use what is called the Dirac bra-ket notation [42], and indicate such a column vector with the symbol '$|x\rangle$', called a *ket*. The advantage of Dirac's bra-ket notation is that it works fine even for infinite dimensional Hilbert spaces and allows us to do many interesting manipulations without much effort, as we shall soon see.

Associated with $\mathcal{H}_d$ is an *adjoint space* (or *dual space*), indicated as $\mathcal{H}_d^*$. There is a one-to-one correspondence between the elements of $\mathcal{H}_d$ and $\mathcal{H}_d^*$: if $|x\rangle \in \mathcal{H}_d$, then there exists its corresponding element, denoted as '$\langle x|$' (called *bra*) in $\mathcal{H}_d^*$. The relation between the two is

$$\langle x| = |x\rangle^\dagger \tag{1.1}$$

where, for any matrix (vector or operator) A, '$A^{\dagger}$' indicates the conjugate transpose of A. We therefore see that $\langle x|$ must be a row vector of dimension $(1 \times d)$. $\langle x|$ is also said to be the dual vector of $|x\rangle$.

For $\langle y| \in \mathcal{H}_d^*$ and $|x\rangle \in \mathcal{H}_d$, $\langle y|$ maps $|x\rangle$ to a scalar through the matrix product

$$\big(\,\langle y|\,\big)\big(\,|x\rangle\,\big) \equiv \langle y|\,x\rangle \ . \tag{1.2}$$

Equation (1.2) also defines an inner product (or scalar product) for $\mathcal{H}_d$ [31, 80, 131]. That is, given two vectors $|y\rangle\,, |x\rangle \in \mathcal{H}_d$, we can choose their inner product to be defined as

$$\big\langle\, |y\rangle\,, |x\rangle\,\big\rangle := \langle y|\,x\rangle \ . \tag{1.3}$$

For separable Hilbert spaces, (1.3) is the commonly used inner product, and so shall we in the following. Note that for $|x\rangle$ to be a state vector, according to Postulate I of quantum mechanics, $|x\rangle$ must be a unit vector – meaning $\langle x|\,x\rangle = 1$. The *null vector* of $\mathcal{H}_d$, which we may indicate as $|\emptyset\rangle$, is the vector whose inner product with any given element of $\mathcal{H}_d$ is zero, *i.e.* $\langle\emptyset|\,x\rangle = \langle x|\,\emptyset\rangle = 0\ , \forall\,|x\rangle \in \mathcal{H}_d$. $|\emptyset\rangle$ is simply the $(d \times 1)$ column vector whose entries are all zero.

The vector $|x\rangle$ can be expanded in any orthonormal basis $\{|\phi_n\rangle\}$ $(n = 1, \ldots, d)$ of the Hilbert space $\mathcal{H}_d$. That is,

$$|x\rangle = \sum_{n=1}^{d} c_n\,|\phi_n\rangle \ , \qquad \langle\phi_n|\,\phi_{n'}\rangle = \delta_{n,n'} \tag{1.4}$$

where the coefficients $\{c_n\}$ are complex scalars. Multiplying $|x\rangle$ in (1.4) from the left by $\langle\phi_m|$, we get

$$\langle\phi_m|\,x\rangle = \sum_{n=1}^{d} c_n\,\langle\phi_m|\,\phi_n\rangle = \sum_{n=1}^{d} c_n\ \delta_{n,m} = c_m \ . \tag{1.5}$$

Equation (1.5) therefore gives a prescription on how to determine the coefficients $\{c_n\}$ given the generic vector $|x\rangle$ and an orthonormal basis $\{|\phi_n\rangle\}$. For any given $\mathcal{H}_d$, there is an infinite number of possible orthornormal basis $\{|\phi_n\rangle\}$ – which means there is also an infinite number of ways of expressing the same vector $|x\rangle$ of $\mathcal{H}_d$.

If $|x\rangle$ is a unit vector, then (1.4) represents the state of an isolated system expressed as the linear combination of other state vectors $\{|\phi_n\rangle\}$ (remember each $|\phi_n\rangle$ is a unit vector, thus a potential state vector). In this case, $\sum_{n=1}^{d} |c_n|^2 = 1$ (*normalization condition*). Furthermore, it must be emphasized that for a state vector expressed by the sum in (1.4), the state of the system is *simultaneously* $|\phi_1\rangle\,, \ldots, |\phi_d\rangle$, each to some degree; for each $|\phi_n\rangle$, this degree is quantified by the respective coefficient c_n and we say there is *quantum coherence* between the components $\{|\phi_n\rangle\}$ [79, 140]. And $|x\rangle$ in (1.4) is said to be a *coherent superposition* of the state vectors $|\phi_1\rangle\,, \ldots, |\phi_d\rangle$. We observe that the phenomenon of quantum superposition is a basis-dependent one. This basis dependency plays an important role in ongoing research aimed at explaining how the classical world we are used to emerges from the quantum world [79, 139, 140].

1.1 The Hilbert space of linear operators $\mathcal{O}_d$ and the extended Hilbert-Schmidt inner product.

A vector $|x\rangle$ of $\mathcal{H}_d$ may be transformed into another vector $|x'\rangle$ of the same Hilbert space by means of what is called a *linear operator* A, *i.e.* $|x'\rangle = A\,|x\rangle$. A linear operator A on $\mathcal{H}_d$ is such that if

$|x\rangle, |y\rangle \in \mathcal{H}_d$, and c is a scalar, then

$$A(|x\rangle + |y\rangle) = A|x\rangle + A|y\rangle \tag{1.6a}$$

$$A\big(c|x\rangle\big) = cA|x\rangle \ . \tag{1.6b}$$

One important operator we shall often deal with is the identity operator on $\mathcal{H}_d$, denoted as $\mathbb{I}_d$. When applied to an arbitrary vector $|x\rangle \in \mathcal{H}_d$, $\mathbb{I}_d$ leaves the vector unchanged: *i.e.* $|x\rangle = \mathbb{I}_d|x\rangle, \ \forall |x\rangle \in \mathcal{H}_d$. If we go back to (1.4), use the result in (1.5) – and the fact that as a scalar, c_n commutes with the vector $|\phi_n\rangle$, *i.e.* $c_n|\phi_n\rangle = |\phi_n\rangle c_n$–, we see that

$$|x\rangle = \sum_{n=1}^{d} |\phi_n\rangle c_n = \sum_{n=1}^{d} |\phi_n\rangle \langle\phi_n| \, x\rangle \ . \tag{1.7}$$

Based on (1.2), we may rewrite (1.7) as

$$|x\rangle = \left(\sum_{n=1}^{d} |\phi_n\rangle\langle\phi_n|\right)|x\rangle \ . \tag{1.8}$$

Since $|x\rangle$ is an arbitrary vector of $\mathcal{H}_d$, it follows that

$$\mathbb{I}_d = \sum_{n=1}^{d} |\phi_n\rangle\langle\phi_n| \ . \tag{1.9}$$

This identity is commonly referred to as the *closure* (or *completeness*) *relation*. Equation (1.9) is valid for any arbitrary orthonormal basis of $\mathcal{H}_d$.

Certainly, for a given $\mathcal{H}_d$ there is an infinite number of linear operators one can define on it. These operators also form a finite-dimensional complex linear space. Let it be denoted as $\mathcal{O}_d$. In reality, there is a one-to-one correspondence between elements of $\mathcal{O}_d$ and $(d \times d)$ square matrices [80], so we shall speak of the elements of $\mathcal{O}_d$ as operators or square matrices, interchangeably.

Just as we could expand any vector $|x\rangle \in \mathcal{H}_d$ in any basis of of the same linear space, we can also expand any operator $X \in \mathcal{O}_d$ in any given basis of $\mathcal{H}_d$. What makes it easy to do so is the closure relation in (1.9) and the fact that for any $X \in \mathcal{O}_d$ and integers n, m, the relation: $\mathbb{I}_d^m X \mathbb{I}_d^n = X$ always holds. For example, say we want to expand the operator $X \in \mathcal{O}_d$ in the basis $\{|\phi_n\rangle\}$. Then, the following identities follows:

$$\begin{aligned} X = \mathbb{I}_d X \mathbb{I}_d &= \left(\sum_{n=1}^{d} |\phi_n\rangle\langle\phi_n|\right) X \left(\sum_{n'=1}^{d} |\phi_{n'}\rangle\langle\phi_{n'}|\right) \\ &= \sum_{n=1}^{d}\sum_{n'=1}^{d} |\phi_n\rangle\langle\phi_n| X |\phi_{n'}\rangle \langle\phi_{n'}| \end{aligned} \tag{1.10}$$

where $\langle\phi_n| X |\phi_{n'}\rangle$ is a shorthand for the matrix product $\big(\langle\phi_n|\big)\big(X\big)\big(|\phi_{n'}\rangle\big)$. Since $\langle\phi_n|$ is a $(1 \times d)$ matrix, X is a $(d \times d)$ matrix and $|\phi_{n'}\rangle$ is a $(d \times 1)$ matrix, we note that the product $\langle\phi_n| X |\phi_{n'}\rangle$ must therefore be a scalar, and hence, commutes with both $|\phi_n\rangle$ and $\langle\phi_{n'}|$. Thus,

$$X = \sum_{n=1}^{d}\sum_{n'=1}^{d} \langle\phi_n| X |\phi_{n'}\rangle \, |\phi_n\rangle\langle\phi_{n'}| = \sum_{n=1}^{d}\sum_{n'=1}^{d} X_{nn'} \, |\phi_n\rangle\langle\phi_{n'}| \tag{1.11}$$

where $X_{nn'} \equiv \langle \phi_n | X | \phi_{n'} \rangle$. The matrix product $|\phi_n\rangle\langle\phi_{n'}|$ is between a $(d \times 1)$ matrix (on the left) and a $(1 \times d)$ matrix (on the right), so $|\phi_n\rangle\langle\phi_{n'}|$ is actually a $(d \times d)$ matrix just like X. In fact, $|\phi_n\rangle\langle\phi_{n'}|$ is an element of $\mathcal{O}_d$. If we should write down X as a $(d \times d)$ matrix in the basis $\{|\phi_n\rangle\}$, we note that $X_{nn'}$ corresponds to the matrix element at the intersection between the $n-$th row and $n'-$th column. The sum of all the diagonal elements of X in the basis $\{|\phi_n\rangle\}$ is called its *trace* with respect to $\{|\phi_n\rangle\}$, denoted $\mathrm{Tr}_\phi[X]$:

$$\mathrm{Tr}_\phi[X] = \sum_{n=1}^{d} \langle \phi_n | X | \phi_n \rangle \ . \tag{1.12}$$

One important property of the trace is that it is independent of the basis. That is, if $\{|\phi_n\rangle\}$ and $\{|\vartheta_n\rangle\}$ are two independent basis of $\mathcal{H}_d$, the trace of $X \in \mathcal{O}_d$ remains the same with respect to both bases. In fact, from (1.12) we have

$$\begin{aligned}\mathrm{Tr}_\phi[X] &= \sum_{n=1}^{d} \langle \phi_n | X | \phi_n \rangle = \sum_{n=1}^{d} \langle \phi_n | \mathbb{I}_d X | \phi_n \rangle = \sum_{n=1}^{d} \langle \phi_n | \left(\sum_{n'=1}^{d} |\vartheta_{n'}\rangle\langle\vartheta_{n'}| \right) X | \phi_n \rangle \\ &= \sum_{n=1}^{d} \sum_{n'=1}^{d} \langle \phi_n | \vartheta_{n'} \rangle \langle \vartheta_{n'} | X | \phi_n \rangle = \sum_{n=1}^{d} \sum_{n'=1}^{d} \langle \vartheta_{n'} | X | \phi_n \rangle \langle \phi_n | \vartheta_{n'} \rangle\end{aligned} \tag{1.13}$$

where in the last step we have used that fact that $\langle \phi_n | \vartheta_{n'} \rangle$ and $\langle \vartheta_{n'} | X | \phi_n \rangle$ are scalars and therefore commute. Proceeding, we have

$$\begin{aligned}\mathrm{Tr}_\phi[X] &= \sum_{n'=1}^{d} \langle \vartheta_{n'} | X \left(\sum_{n=1}^{d} |\phi_n\rangle \langle\phi_n| \right) |\vartheta_{n'}\rangle = \sum_{n'=1}^{d} \langle \vartheta_{n'} | X \mathbb{I}_d | \vartheta_{n'} \rangle = \sum_{n'=1}^{d} \langle \vartheta_{n'} | X | \vartheta_{n'} \rangle \\ &= \mathrm{Tr}_\vartheta[X] \ .\end{aligned} \tag{1.14}$$

Given that the trace of X is independent of the basis, it is commonly indicated as $\mathrm{Tr}[X]$, without specifying the basis.

The linear space $\mathcal{O}_d$ also has its corresponding adjoint space, which we denote as $\mathcal{O}_d^*$. As usual, there is a one-to-one correspondence between the elements of $\mathcal{O}_d$ and $\mathcal{O}_d^*$: if $A \in \mathcal{O}_d$, then its dual is $A^\dagger$ $(\in \mathcal{O}_d^*)$. Also, since it is a linear space, we would expect to be able to define an inner product on $\mathcal{O}_d$. The commonly used one here is the Hilbert-Schmidt inner product. If A and B are two elements of $\mathcal{O}_d$, then their Hilbert-Schmidt inner product is

$$\big\langle A, B \big\rangle = \mathrm{Tr}\big[BA^\dagger\big] \ . \tag{1.15}$$

A and B are square matrices so $\big\langle A, B \big\rangle = \mathrm{Tr}\big[A^\dagger B\big]$, due to a property of the trace functional which can easily be proved. But on close examination, one observes that if we define an *ordered* inner product (meaning, the position of the elements A, B are to be strictly maintained) as given in (1.15) (which we may call '*extended* Hilbert-Schmidt' to differentiate it from the conventional one), then the inner product we defined for $\mathcal{H}_d$, (1.3), is also of the same kind. Indeed, from (1.3) and (1.9), and the fact that $|x\rangle = \mathbb{I}_d |x\rangle$, it follows that

$$\big\langle\, |y\rangle \,, |x\rangle \,\big\rangle = \langle y | x \rangle = \langle y | \mathbb{I}_d | x \rangle = \sum_{n=1}^{d} \langle y | \phi_n \rangle \langle \phi_n | x \rangle = \sum_{n=1}^{d} \langle \phi_n | x \rangle \langle y | \phi_n \rangle = \mathrm{Tr}\big[\, |x\rangle\langle y| \,\big] \ . \tag{1.16}$$

Thus, for both $\mathcal{H}_d$ and $\mathcal{O}_d$, we have the extended Hilbert-Schmidt inner product, (1.15), as the chosen inner product. Moreover, if $\{|\phi_n\rangle\}$ is an orthonormal basis for $\mathcal{H}_d$, then the set of operators $\{|\phi_n\rangle\langle\phi_{n'}|\}$

— where $n, n' = 1, 2, \ldots, d$ — constitute an orthonormal basis for $\mathcal{O}_d$: That is, any element of $\mathcal{O}_d$ can be expressed as linear combination of the elements of the set $\{|\phi_n\rangle\langle\phi_{n'}|\}$. This is what we achieved, for example, in (1.11). The orthonormality of the elements of $\{|\phi_n\rangle\langle\phi_{n'}|\}$ can be verified with the extended Hilbert-Schmidt inner product, (1.15). The linear space $\mathcal{O}_d$ is therefore complete and normed, which makes it a *(complex) Hilbert space*. The dimension of the set $\{|\phi_n\rangle\langle\phi_{n'}|\}$ — and, therefore, of $\mathcal{O}_d$ — is easily seen to be d^2.

An important class of elements of $\mathcal{O}_d$ are the so-called *Hermitian operators*. An operator $A \in \mathcal{O}_d$ is said to be Hermitian if it coincides with its conjugate transpose, *i.e.* $A = A^\dagger$. It turns out that physical dynamical variables of a system (like its total energy, magnetization vector, etc.) are represented by Hermitian operators. The *spectral decomposition theorem* [39, 80, 110, 114] of quantum mechanics asserts that given a Hermitian operator $A \in \mathcal{O}_d$ there exists an orthonormal basis $\{|a_n\rangle\langle a_{n'}|\}$ of $\mathcal{O}_d$ such that

$$A = \sum_{n=1}^{d} \lambda_n \, |a_n\rangle\langle a_n| \qquad \langle a_n|\, a_{n'}\rangle = \delta_{n,n'} \tag{1.17}$$

where the scalars $\{\lambda_n\}$ are real. The expansion in (1.17) is said to be the *diagonal representation* of the operator A. The vectors $\{|a_n\rangle\}$ are the eigenvectors of A and $\{\lambda_n\}$ are the corresponding eigenvalues; indeed, if we multiply (1.17) from the right by $|a_m\rangle$, we get $A\,|a_m\rangle = \lambda_m\,|a_m\rangle$ – which is a normal eigenvalue/eigenvector equation.

Chapter 2

Postulate II

The second postulate asserts how the state vector of a closed quantum system evolves in time.

> **Postulate II** The state vector $|\psi\rangle$ of a closed quantum system evolves in time according to the *Schrödinger equation*:
>
> $$\frac{d}{dt}|\psi\rangle = -\frac{i}{\hbar}H|\psi\rangle \tag{2.1}$$
>
> – where $\hbar$ is the reduced Planck constant; H is a linear operator called the *Hamiltonian* of the quantum system and it represents the total energy of the system.

Because $|\psi\rangle$ in (2.1) clearly depends on time, it is customary to indicate its time-dependence by writing $|\psi\rangle$ as $|\psi(t)\rangle$. Suppose $|\psi(t)\rangle$ is a vector of $\mathcal{H}_d$. If we choose to expand $|\psi(t)\rangle$ in the basis $\{|\phi_n\rangle\}$, then

$$|\psi(t)\rangle = \mathbb{I}_d|\psi(t)\rangle = \sum_{n=1}^{d}|\phi_n\rangle\langle\phi_n|\,\psi(t)\rangle = \sum_{n=1}^{d}c_n(t)|\phi_n\rangle \tag{2.2}$$

where the coefficients $c_n(t) \equiv \langle\phi_n|\,\psi(t)\rangle$ are now time-dependent.

At first glance, this postulate may seem very limiting because no system in the universe can be truly closed. In one way or the other, every system interacts with another system. Nonetheless, Postulate II is the basis on which *open* quantum systems (*i.e.* quantum systems engaged in some form of interaction with other systems) are effectively described. In fact, many approaches have been devised for describing how open quantum systems evolve in time and they all start with Postulate II by assuming the relevant system we wish to describe and the other systems with which it interacts (collectively called the *environment* or *reservoir*) form a closed system. These approaches collectively go under what is called theory of open quantum systems [162].

Chapter 3

Postulate III

To determine properties like energy or spin magnetic moment of a quantum system, we need to perform some measurements on the system. These actions ultimately constitute some form of interaction with the quantum system. In this sense, interaction and measurement are almost synonymous. It is thus no wonder this third postulate is important to the theory of open quantum systems. Postulate III of quantum mechanics is the quantum outlook on the process of measurements, and also introduces the concept of 'quantum measurement operators'.

> **Postulate III** Let the outcomes of a (quantum) measurement be a countable set indexed m, *i.e.* $\{r_m\}$. To each outcome r_m is associated an operator M_m called *measurement operator*. Let $|\psi\rangle$ be the state of the quantum system at the instant immediately prior to the measurement. Then, the probability $p(m)$ that the outcome is r_m is
>
> $$p(m) = \langle\psi|\, M_m^\dagger M_m \,|\psi\rangle \tag{3.1}$$
>
> and the new state $|\psi'\rangle$ of the system immediately after the measurement is
>
> $$|\psi'\rangle = \frac{M_m |\psi\rangle}{\sqrt{p(m)}} \; . \tag{3.2}$$
>
> If $|\psi\rangle \in \mathcal{H}_d$, then the measurement operators $\{M_m\}$ are such that
>
> $$\sum_m M_m^\dagger M_m = \mathbb{I}_d \; . \tag{3.3}$$

Equation (3.3) is the *completeness equation* for the measurement operators $\{M_m\}$. It is important because it indirectly instills the requirement that the probabilities $p(m)$ summed over all m adds up to the value 1. In fact, from (3.1), we have $\sum_m p(m) = \sum_m \langle\psi|\, M_m^\dagger M_m \,|\psi\rangle = \langle\psi| \sum_m M_m^\dagger M_m \,|\psi\rangle = \langle\psi|\,\psi\rangle = 1$. It should be quite clear that the observable being measured and the nature of the quantum system being probed determine the set $\{M_m\}$.

Another concept central to quantum mechanics is that of *expectation value* (or *mean value*) of a measurement. The expectation value of a measurement (related to an observable) is the average outcome of the measurements. If the outcomes of the observable represented by the operator B are

$\{\lambda_m\}$ with corresponding probabilities $\{p(m)\}$, it is clear that the expectation value of the observable, indicated as $\langle B \rangle$, is the weighted sum

$$\langle B \rangle = \sum_m \lambda_m \; p(m) = \sum_m \lambda_m \, \langle\psi| \, M_m^\dagger M_m \, |\psi\rangle = \langle\psi| \, B \, |\psi\rangle \tag{3.4}$$

where we have made use of (3.1), and have defined the operator B as

$$B = \sum_m \lambda_m M_m^\dagger M_m \;, \qquad \text{with} \; \sum_m M_m^\dagger M_m = \mathbb{I}_d \;. \tag{3.5}$$

Equation (3.5) is a more general operator representation of an observable in quantum mechanics (for finite-dimensional state space). It is evident from (3.4) that the value $\langle B \rangle$ is always real. Note that the measurement operators M_m may be Hermitian or not. As an example, consider the spin angular momentum operator S_z of an electron. We know the spin state space of the electron is a two-dimensional Hilbert space and

$$S_z = \hbar \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \;. \end{pmatrix} \tag{3.6}$$

which is a Hermitian operator. Note that we if we take $\{|0\rangle, |1\rangle\}$ as the basis of the electron's spin state space, where

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad |0\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad . \tag{3.7}$$

we may rewrite S_z as

$$S_z = \frac{\hbar}{2} \, |1\rangle\langle 1| - \frac{\hbar}{2} \, |0\rangle\langle 0| \;\; . \tag{3.8}$$

From (3.8), we can infer the outcomes $\{\lambda_m\}$ of the measurement of S_z, and their corresponding measurement operators $\{M_m\}$. Indeed, we notice that (3.8) may be rewritten as

$$S_z = \lambda_0 \; M_0^\dagger M_0 + \lambda_1 \; M_1^\dagger M_1 \tag{3.9}$$

where

$$\lambda_0 = -\frac{\hbar}{2} \;, \quad M_0 = |0\rangle\langle 0| \tag{3.10a}$$

$$\lambda_1 = +\frac{\hbar}{2} \;, \quad M_1 = |1\rangle\langle 1| \tag{3.10b}$$

and the completeness relation $M_0^\dagger M_0 + M_1^\dagger M_1 = \mathbb{I}_2$ is satisfied. For these particular measurement operators, it is observed that $M_m M_{m'} = \delta_{m,m'} M_m$. Such measurement operators give rise to what is called *projective measurements* [114]. Also, note that M_0 and M_1 may be expanded in any basis of our choice, but the fundamental structure of (3.9) remain unchanged. With the help of (3.10), one can determine, for example, through (3.2) the probability of the outcomes λ_0, λ_1 given any initial spin state $|\psi\rangle$ of the electron.

As another example, consider an observable F of the electron spin given by the outcomes $\{\lambda_\pm\}$ and their corresponding measurement operators $\{\sigma_\pm\}$, *i.e.*

$$F = \lambda_+ \sigma_+^\dagger \sigma_+ + \lambda_- \sigma_-^\dagger \sigma_- \tag{3.11}$$

– where $\sigma_+ = |1\rangle\langle 0|$ and $\sigma_- = |0\rangle\langle 1|$. We note that in this case the measurement operators are not Hermitian (*i.e.* $\sigma_\pm \neq \sigma_\pm^\dagger$) but, nonetheless, they satisfy the completeness relation for measurement operators, (3.3), *i.e.* $\sigma_+^\dagger \sigma_+ + \sigma_-^\dagger \sigma_- = \mathbb{I}_2$.

Chapter 4

Pure states, mixed states and density matrices

The state of a quantum system (closed or open) may be *pure* or *mixed*. It is *pure* when we have complete information on it [19, 98, 140]. 'Complete information' in the sense that there is no classical uncertainty as to what the quantum state is [98], so we can assign a single state vector $|\psi\rangle$ to the system. A classic way of illustrating this concept is through the Stern-Gerlach experiment, where a beam of silver atoms is passed through an inhomogeneous magnetic field. The spin quantum number of a normal silver atom is $\frac{1}{2}$, so in traversing the inhomogeneous magnetic field the beam is split into two: one in which each silver atom has a spin magnetic moment of $+\frac{1}{2}\hbar$ (let us call it Beam 1) and another in which each atom has a spin magnetic moment of $-\frac{1}{2}\hbar$ (Beam 2). Beam 1 can be collected. The spin state of all the silver atoms in Beam 1 is completely known so the beam is in a pure (spin) state. And we can assign a single spin state vector $|\psi\rangle$ to Beam 1. The same applies to Beam 2.

When we cannot assign a single state vector $|\psi\rangle$ to the system because there is classical uncertainty on the system's quantum state, we resort to (classical) statistics to describe the state. The result is what we call a *mixed state* [19, 98, 140]. This is a collection of positive real numbers $0 \leq P_k \leq 1$ and their corresponding vectors $|\psi_k\rangle \in \mathcal{H}_d$, where P_k is the probability that the state of the quantum system is given by the state vector $|\psi_k\rangle$. Mixed states are therefore typically expressed in the form of the collection $\{P_k, |\psi_k\rangle\}$ and they are symptom of the observer's lack of complete information on the quantum state of the system under study. Either P_k or $|\psi_k\rangle$ (or both) may depend on time. Nonetheless, the condition $\sum_k P_k = 1$ always holds.

Given the mixed state $\{P_k, |\psi_k\rangle\}$, where the state vectors $|\psi_k\rangle$ form an orthonormal basis of $\mathcal{H}_d$, we may introduce an operator $\rho \in \mathcal{O}_d$, the density matrix (or density operator), defined on $\mathcal{H}_d$ such that

$$\langle\psi_k| \rho |\psi_k\rangle = P_k \ , \ \forall k \ . \tag{4.1}$$

It is not difficult to realize that the operator ρ must be of the form

$$\rho = \sum_{k=1}^{d} P_k \, |\psi_k\rangle\langle\psi_k| \ . \tag{4.2}$$

Unlike the sum in (1.4), state of the quantum system as expressed in (4.2) is *not* one which is simultaneously the $\{|\psi_k\rangle\}$. Rather, (4.2) expresses a classical mixture of states. Equation (4.2) is also reminiscent of (1.17). Indeed, ρ is Hermitian and (4.2) is its diagonal representation. If we choose to represent ρ in a different orthonormal basis — say $\{|\phi_n\rangle\}$ — , then, from (4.2) and (1.9), we have

$$\begin{aligned}\rho = \sum_{k=1}^{d} P_k \, \mathbb{I}_d \, |\psi_k\rangle\langle\psi_k| \, \mathbb{I}_d &= \sum_{k=1}^{d} P_k \sum_{n=1}^{d} \sum_{n'=1}^{d} |\phi_n\rangle \langle\phi_n| \, \psi_k\rangle \langle\psi_k| \, \phi_{n'}\rangle \langle\phi_{n'}| \\ &= \sum_{n=1}^{d} \sum_{n'=1}^{d} \left(\sum_{k=1}^{d} P_k \langle\phi_n| \, \psi_k\rangle \langle\psi_k| \, \phi_{n'}\rangle \right) |\phi_n\rangle\langle\phi_{n'}| \\ &= \sum_{n=1}^{d} \sum_{n'=1}^{d} \rho_{nn'} \, |\phi_n\rangle\langle\phi_{n'}| \ .\end{aligned} \tag{4.3}$$

where we can see $\rho_{nn'} \equiv \langle\phi_n| \, \rho \, |\phi_{n'}\rangle$. Thus, in a different orthonormal basis, ρ ceases to be diagonal even though the statistics of measurement outcomes remain the same. Such different representations of the same density matrix ρ are related to each other through a unitary transformation. If the system is isolated, with Hamiltonian H, and we take the time derivative of $\rho(t)$, then, from (2.1) and (4.2), we obtain

$$\frac{d}{dt}\rho(t) = -\frac{i}{\hbar} [H, \rho(t)] \tag{4.4}$$

where ρ is now written as $\rho(t)$ to show its time-dependence and $|\psi_k\rangle\langle\psi_k| \to |\psi_k(t)\rangle\langle\psi_k(t)|$ in (4.2). (For any pair of operators $A, B \in \mathcal{O}_d$, their commutator $[A, B]$ is defined as $[A, B] \equiv AB - BA$. And their anti-commutator, $[A, B]_+$, is defined as $[A, B]_+ \equiv AB + BA$. We note that $[A, B] = -[B, A]$ and $[A, B]_+ = [B, A]_+$.) Equation (4.4) is referred to as the *Liouville-von Neumann equation.*

Note that a pure state may also be expressed in the form of a density matrix. If the quantum system is in the pure state $|\psi(t)\rangle$, then $\{P_k, |\psi_k\rangle\} \to \{1, |\psi(t)\rangle\}$, and so from (4.2), it follows that

$$\rho(t) = |\psi(t)\rangle\langle\psi(t)| \ . \tag{4.5}$$

If we express this pure state density matrix in the basis $\{|\phi_n\rangle\}$, for example, we get

$$\begin{aligned}\rho(t) = \mathbb{I}_d \, |\psi(t)\rangle \, \langle\psi(t)| \, \mathbb{I}_d &= \sum_{n=1}^{d} \sum_{n'=1}^{d} |\phi_n\rangle \langle\phi_n| \, \psi(t)\rangle \langle\psi(t)| \, \phi_{n'}\rangle \langle\phi_{n'}| \\ &= \sum_{n=1}^{d} \sum_{n'=1}^{d} c_{nn'}(t) \, |\phi_n\rangle\langle\phi_{n'}|\end{aligned} \tag{4.6}$$

with $c_{nn'}(t) \equiv \langle\phi_n| \, \psi(t)\rangle\langle\psi(t)| \, \phi_{n'}\rangle = \langle\phi_n| \, \rho(t) \, |\phi_{n'}\rangle$. We recognize the similarity between the final forms of ρ in (4.3) and (4.6). This tells us that the fact that a density matrix ρ has nonzero off-diagonal elements (*i.e.* coherence) in a basis, does not necessarily mean it represents a mixed state. To check whether a density matrix represents a mixed or pure state, one has to put it in its diagonal form, (4.2): if there are more than one nonzero P_k, then the state is mixed, otherwise it is pure. Put more elegantly, ρ represents a pure state if its rank (*i.e.* the number of nonzero eigenvalues) is 1; if the rank is greater than 1 then the state is mixed. Consider, for example, the following qubit density matrices:

$$\rho_1 = \begin{pmatrix} \frac{1}{2} & -\frac{e^{i\theta}}{2} \\ -\frac{e^{-i\theta}}{2} & \frac{1}{2} \end{pmatrix} \qquad \rho_2 = \begin{pmatrix} \frac{1}{2} & -i\frac{\sqrt{2}}{3}\sin\theta \\ i\frac{\sqrt{2}}{3}\sin\theta & \frac{1}{2} \end{pmatrix} \ . \tag{4.7}$$

where θ is some parameter of the system. Note that both density matrices have the same populations (*i.e.* diagonal elements), but ρ_1 is a pure state and ρ_2 is a mixed state.

The fact that the rank of a pure state's density matrix is 1 also leads to the assertion that $\mathrm{Tr}[\rho^2] = 1$ if ρ represents a pure state; while for a mixed state, $\mathrm{Tr}[\rho^2] < 1$. For ρ_1 and ρ_2 in (4.7), for example, one can easily verify that $\mathrm{Tr}[\rho_1^2] = 1$ and $\mathrm{Tr}[\rho_2^2] = \frac{1}{2} + \frac{4}{9}\sin^2\theta < 1$.

The final problem we wish to attend to before moving on to the Liouville space formalism is how Postulate III turns out when dealing with a mixed state $\{P_k, |\psi_k\rangle\}$ instead of a state vector $|\psi\rangle$. Suppose we have an observable B – described by a set of quantum measurement operators $\{M_m \mid \sum_m M_m^\dagger M_m = \mathbb{I}_d\}$ and their corresponding outcome values $\{\lambda_m\}$. We want to determine the probability $p(m)$ that the outcome of measuring B is λ_m, given that the state of the quantum system immediately prior to the measurement is given by the mixed state $\rho = \{P_k, |\psi_k\rangle\}$ – where the state vectors $\{|\psi_k\rangle\}$ are assumed orthogonal to each other. Naturally, we have to apply Postulate III. The only complication is that, contrary to what Postulate III originally describes, we are dealing here with a collection of states $\{P_k, |\psi_k\rangle\}$. But this is no complication because if immediately prior to the measurement, the state of the quantum system is $\{P_k, |\psi_k\rangle\}$, then the probability $p(m)$ that we get λ_m as the outcome is

$$p(m) = \sum_k p(m|k)\ P_k \tag{4.8}$$

where $p(m|k)$ is the probability that the outcome λ_m is a consequence of the quantum system being in the state $|\psi_k\rangle$ immediately prior to the measurement. That is, following (3.1),

$$p(m|k) = \left\langle \psi_k \right| M_m^\dagger M_m \left| \psi_k \right\rangle . \tag{4.9}$$

Note, however, that

$$\begin{aligned} \left\langle \psi_k \right| M_m^\dagger M_m \left| \psi_k \right\rangle &= \left\langle \psi_k \right| \mathbb{I}_d M_m^\dagger M_m \left| \psi_k \right\rangle = \sum_{n=1}^{d} \left\langle \psi_k \middle| \phi_n \right\rangle \left\langle \phi_n \right| M_m^\dagger M_m \left| \psi_k \right\rangle \\ &= \sum_{n=1}^{d} \left\langle \phi_n \right| M_m^\dagger M_m \left| \psi_k \right\rangle \left\langle \psi_k \middle| \phi_n \right\rangle = \mathrm{Tr}\Big[M_m^\dagger M_m \left|\psi_k\right\rangle\left\langle\psi_k\right| \Big] . \end{aligned} \tag{4.10}$$

Thus, $p(m|k) = \mathrm{Tr}\Big[M_m^\dagger M_m |\psi_k\rangle\langle\psi_k|\Big]$ and (4.8) may be written as

$$\begin{aligned} p(m) =& \sum_k \mathrm{Tr}\Big[M_m^\dagger M_m |\psi_k\rangle\langle\psi_k|\Big]\ P_k = \mathrm{Tr}\Big[M_m^\dagger M_m \Big(\sum_k |\psi_k\rangle\langle\psi_k|\, P_k\Big)\Big] \\ =& \mathrm{Tr}\Big[M_m^\dagger M_m\ \rho\Big] . \end{aligned} \tag{4.11}$$

The expectation value $\langle B \rangle$ is still given by the weighted sum $\langle B \rangle = \sum_m \lambda_m p(m)$, (3.4), as we saw above. But now, introducing the expression for $p(m)$, (4.11), we get

$$\begin{aligned} \langle B \rangle =& \sum_m \lambda_m\ p(m) = \sum_m \lambda_m \mathrm{Tr}\Big[M_m^\dagger M_m\ \rho\Big] = \mathrm{Tr}\Big[\Big(\sum_m \lambda_m M_m^\dagger M_m\Big)\ \rho\Big] \\ =& \mathrm{Tr}\big[B\ \rho\big] . \end{aligned} \tag{4.12}$$

Furthermore, we may be interested in what the mixed state $\rho = \{P_k, |\psi_k\rangle\}$ transforms into, immediately after the outcome of the measurement of B, if the outcome is recorded to be λ_m. Let us indicate this new mixed state as ρ_m. It can be shown that [114]

$$\rho_m = \frac{M_m \rho M_m^\dagger}{p(m)} \tag{4.13}$$

where $p(m)$ is given by (4.11). (This may be verified by taking ρ to be a pure state, $\rho = |\psi\rangle\langle\psi|$, and using (3.2).) Suppose we do not record the outcome, so that we are ignorant of what the state of the quantum system is immediately after the measurement. Then, it is easy to see that an effective way to describe the new mixed state ρ' is as a *mixture* of the states $\{\rho_m\}$ with probabilities $\{p(m)\}$. That is,

$$\rho' = \sum_m p(m)\ \rho_m = \sum_m M_m \rho M_m^\dagger\ . \tag{4.14}$$

This is called *non-selective measurement* [69, 96].

Part II

The Holstein-Primakoff Transformation

We introduce here the Holstein-Primakoff transformation and some of its applications in magnetic resonance. Most of the materials presented here are original contributions of the author, and are taken from the following publications/preprints of his:

[62] J.A. Gyamfi, *An Introduction to the Holstein-Primakoff Transformation, with Applications in Magnetic Resonance*, arXiv:1907.07122, 2019.

[65] J.A. Gyamfi, V. Barone, *Magnetic Resonance, Index Compression Maps and the Holstein - Primakoff Bosons: Towards a Polynomially Scaling Exact Diagonalization of Isotropic Multispin Hamiltonians*, arXiv:1803.10461, 2018.

[66] J.A. Gyamfi, V. Barone, *On the composition of an arbitrary collection of SU(2) spins: An Enumerative Combinatoric Approach*, `J. Phys. A: Mathematical and Theoretical` **51**(10):105205, 2018.

Notations and definitions

To make the concepts we will discuss later on more intelligible, it is important we get our terminologies and notations in order now. For example, we shall often speak of *multisets* [148]. Unlike ordinary sets where each distinct element must appear only once, in a multiset distinct elements can repeat any number of times. A set therefore can only tell us how many distinct elements we have and their identities. For instance, say P_4 the set of the first four prime numbers; then, $P_4 = \{2, 3, 5, 7\}$. Consider all the possible three digit (positive) integers we can create from the elements of P_4. The number "537" for example is a valid one. By representing the digits composing these numbers as elements of a collection, we may write "537" as "$\{5, 3, 7\}$", using the set notation. In the same spirit, $\{2, 2, 2\}, \{3, 7, 7\}$ and $\{5, 7, 5\}$ are all valid. While $\{5, 3, 7\}$ is a set, $\{2, 2, 2\}, \{3, 7, 7\}$ and $\{5, 7, 5\}$ are not, but are multisets. According to the criterion chosen to represent all possible three digit numbers from the set P_4, it is clear that the multiset $\{5, 3, 7\}$ is different from $\{3, 7, 5\}$. Order is therefore important here. Like a set, a multiset can also be ordered. If we are only interested in the number of times a number repeats as a digit, then order is no longer important and so we may indicate "377" and "737" as $\{3, 7, 7\}$ or $\{7, 3, 7\}$ or $\{7, 7, 3\}$, or – even more succinctly, using a customary notation in multiset theory – $\{3, 7^2\}$, the exponent (or *multiplicity*) here indicates the number of times an element repeats itself.

Consider now a multiset $\mathcal{A} = \{j_1, j_2, \ldots, j_i, \ldots, j_N\}$ of N spins, where j_i is the spin quantum number of the $i-$th spin. In the following, we shall reserve the Latin letter i to lower index $\mathcal{A}$'s elements when the latter is expressed in this laborious manner. A more efficient way to indicate the same multiset (if we are not interested in order as we are now) is to specify all the *distinct* elements and their multiplicities. We shall use the Greek letter α to index distinct elements of the multiset. Thus, if the spin multiset $\mathcal{A}$ has σ distinct elements, then we can express $\mathcal{A}$ also as $\mathcal{A} = \{j_\alpha^{N_\alpha}\}$, $\alpha = 1, 2, \ldots, \sigma$, where N_α is the multiplicity of the $\alpha-$th distinct spin quantum number. Naturally, $N = \sum_{\alpha=1}^{\sigma} N_\alpha$. It is crucial to point out that two elements j_i and $j_{i'}$ of $\mathcal{A}$ are distinct only if they correspond to different spin quantum numbers – other characteristics of the spins (like charge, magnetic moment etc.) are not of any merit whatsoever here. For example, the multiset $\mathcal{A} = \{\frac{1}{2}^9, 1^3\}$ indicates *any* aggregate of nine spin-1/2 and three spin-1; the actual composition could consist of, for instance, 1) nine electrons and three protons, or 2) five ${}^{15}_{7}\mathrm{N}_8$ plus four muons – both spin-1/2s – and three ${}^{14}_{7}\mathrm{N}_7$ nuclei (which are spin-1) [51], etc.

A very important distinction is due here. A system of N spins whereby $j_1 = j_2 = \ldots = j_N = j$ is termed as *univariate spin system* (USS) [66]. The multiset representation of the system is then $\mathcal{A} = \{j^N\}$. In a USS, the N spins could be mutually different in regards to mass, charge, magnetic moment, etc. On the other hand, a system of *identical spins* (IS) [66] is a univariate spin system whereby all the N spins share exactly the same intrinsic fundamental properties like mass and charge, and are indistinguishable from one another when placed under the same external conditions. Thus, an identical spin system is also necessarily USS, but a USS is in general not an IS.

In addition to the concept of univariate and identical spin systems, we also have *equivalent* spins (ES). Consider a given multiset $\mathcal{A} = \{j_1, j_2, \ldots, j_N\}$ of spins. Say $\mathcal{A}'$ a submultiset of $\mathcal{A}$, i.e. every element of $\mathcal{A}'$ is also an element of $\mathcal{A}$. $\mathcal{A}'$ is said to be a system of equivalent spins if every element of $\mathcal{A}'$ couples to all other elements of $\mathcal{A}$ and any external field in the same manner. Specifically, the elements of $\mathcal{A}'$ are said to be *equivalent* if one cannot distinguish between them on the basis of their coupling tensors with other spins and external fields. It mostly happens that equivalent spins are also identical, but in principle they do not need to be. The concept of equivalent nuclei in NMR, for example, is just a limit case of equivalent spins. If we take the methyl radical $^{\cdot}\mathrm{CH}_3$ for example (assuming all three hydrogen nuclei are ^{1}H and the carbon atom is ^{12}C), the spin system $\mathcal{A} = \{j_1, j_2, j_3, j_4\} = \{\frac{1}{2}^4\}$ is clearly univariate; the three hydrogen nuclei are identical spins. The same trio of spins also constitute a collection of equivalent spins when the system's Hamiltonian is invariant under the operation of the point group C_3.

Operators in Part II will be indicated with their usual hats while their matrix representations will bear none: for example, the matrix representation of the operator $\hat{\mathscr{A}}$ will be simply indicated as $\mathscr{A}$.

If j_i is the spin quantum number of the $i-$th spin, therefore a scalar ($j_i = \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \ldots$), then its corresponding spin vector operator will be indicated as $\hat{\boldsymbol{\mathcal{J}}}_i$, which, as we saw above, corresponds to the sum: $\hat{\boldsymbol{\mathcal{J}}}_i = \hat{\mathcal{J}}_i^x \boldsymbol{e}_x + \hat{\mathcal{J}}_i^y \boldsymbol{e}_y + \hat{\mathcal{J}}_i^z \boldsymbol{e}_z$, where $\hat{\mathcal{J}}_i^x$, $\hat{\mathcal{J}}_i^y$, $\hat{\mathcal{J}}_i^z$ are the spin angular operators along the respective axis and defined on the spin Hilbert space of spin i. In this article, we will not try to indicate spin vector operators of electrons and nuclei with different symbols: they will all be indicated simply as $\hat{\boldsymbol{\mathcal{J}}}_i$, and the index i will serve the purpose of recording the specific identity of the spins based on our chosen choice of integer-labelling of the latter.

Chapter 5

The quantum harmonic oscillator

The harmonic oscillator is perhaps the most important model in quantum mechanics. We are not going to belabor it here as it is extensively treated in almost every textbook on quantum mechanics. We only recall here that the Hamiltonian of a body of mass m tied to a spring able to move only in one direction (let us call it the x axis) is [11]:

$$\hat{\mathscr{H}} = \frac{\hat{\mathscr{P}}_x^2}{2m} + \frac{1}{2}k\hat{\mathscr{X}}^2 \tag{5.1}$$

where $\hat{\mathscr{P}}_x$ is the linear momentum operator along the $x-$axis, $\hat{\mathscr{X}}$ is the spatial displacement operator from the equilibrium position, and k is the force constant.

Since we shall be working in the position space, it is important to recall that the position eigenkets $\{|x\rangle\}$ are such that [137]:

$$\hat{\mathscr{X}}\,|x\rangle = x\,|x\rangle \tag{5.2}$$

and they obey the orthogonality condition:

$$\langle x'|\, x\rangle = \delta(x' - x) \tag{5.3}$$

where $\delta(\bullet)$ is the Dirac delta function. If we multiply (5.3) by $|x'\rangle$ and integrate over the entire range of x' we get:

$$\int dx'\,|x'\rangle\,\langle x'|\, x\rangle = \int dx'\,|x'\rangle\,\delta(x' - x) = |x\rangle \tag{5.4}$$

from which we deduce that:

$$\int dx'\,|x'\rangle\,\langle x'| = \hat{\mathbb{I}} \tag{5.5}$$

where $\hat{\mathbb{I}}$ is the identity operator. (5.5) is the completeness relation for the position eigenkets.

To study the behavior of the body quantum mechanically, what we can do is to solve the time-independent Schrödinger's equation for the body's energy eigenkets, $\{|E\rangle\}$:

$$\begin{gathered}\hat{\mathscr{H}}\,|E\rangle = E\,|E\rangle \\ \left(\frac{\hat{\mathscr{P}}_x^2}{2m} + \frac{1}{2}k\hat{\mathscr{X}}^2\right)|E\rangle = E\,|E\rangle\end{gathered} \tag{5.6}$$

where E is the energy of the body. Note that we may expand $|E\rangle$ in terms of the position eigenkets:

$$|E\rangle = \int dx\,|x\rangle\,\langle x|\, E\rangle \tag{5.7}$$

where ($\|\langle x|\, E\rangle\|^2\, dx$) can be interpreted as the probability to find the body in any of the points between x and $x + dx$ given that its energy is E. The coefficient $\langle x|\, E\rangle =: \psi_E(x)$ is therefore the probability amplitude, or wavefunction, in position space.

If we multiply both sides of (5.6) from the left by the identity operator $\int dx\, |x\rangle \langle x|$, we obtain:

$$\int dx\, |x\rangle \left(\frac{1}{2m} \left\langle x \middle| \hat{\mathscr{P}}_x^2 \middle| E \right\rangle + \frac{1}{2} k x^2 \langle x|\, E\rangle \right) = \int dx\, |x\rangle\, E\, \langle x|\, E\rangle \quad . \tag{5.8}$$

Making use of the fact that $\left\langle x \middle| \hat{\mathscr{P}}_x^2 \middle| E \right\rangle = -\hbar^2 \frac{d^2}{dx^2} \langle x|\, E\rangle$ [137], (5.8) becomes:

$$\int dx\, |x\rangle \left(\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} k x^2 \right) \psi_E(x) = \int dx\, |x\rangle\, E\, \psi_E(x) \tag{5.9}$$

that is,

$$\left(\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} k x^2 \right) \psi_E(x) = E\, \psi_E(x) \ . \tag{5.10}$$

The solution to this eigenspectrum problem is well known. The energy eigenvalues are found to be parameterized by n [11, 93]:

$$E_n = \left(n + \frac{1}{2} \right) \hbar\omega \ , \qquad n = 0, 1, 2, 3, \ldots \tag{5.11}$$

Thus, $\psi_E(x) = \psi_{\left(n+\frac{1}{2}\right)\hbar\omega}(x)$, which may be simply written as $\psi_n(x)$. Since there is a one-to-one correspondence between E and n (for fixed mass and force constant), we may henceforth simply indicate $|E\rangle$ as $|n\rangle$. Moreover, it is found that [11, 93]:

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} H_n\left(\zeta\right) e^{-\zeta^2/2} \tag{5.12}$$

where $\omega \equiv \sqrt{k/m}$, $\zeta \equiv x\sqrt{m\omega/\hbar}$ and $H_n(z)$ is the Hermite polynomial of order n in z.

At this point we may rewrite (5.7) as:

$$|n\rangle = \int dx\, |x\rangle\, \psi_n(x) \tag{5.13}$$

where we have effected the substitutions $|E\rangle \to |n\rangle$ and $\langle x|\, E\rangle \to \psi_n(x)$. It is evident from (5.13) that the wavefunction $\psi_n(x)$ is just the expansion coefficient when we expand $|n\rangle$ in terms of position eigenstates. Naturally, (5.13) is not the only possible expansion we could think of. We could have equally expanded $|n\rangle$ in terms of the momentum eigenstates (along the $x-$ axis), i.e. $\{|p_x\rangle\}$, where:

$$\hat{\mathscr{P}}_x\, |p_x\rangle = p_x\, |p_x\rangle \tag{5.14}$$

and,

$$\langle p'_x|\, p_x\rangle = \delta(p'_x - p_x) \tag{5.15}$$

from which follows the completeness relation:

$$\int dp'_x\, |p'_x\rangle \langle p'_x| = \hat{\mathbb{I}} \ . \tag{5.16}$$

In fact, introducing the momentum space completeness relation into (5.13) we get:

$$|n\rangle = \int dp_x\, |p_x\rangle \left(\int dx\, \langle p_x|\, x\rangle\, \psi_n(x) \right) = \int dp_x\, |p_x\rangle\, \phi_n(p_x) \tag{5.17}$$

where $\phi_n(p_x)$ is the wavefunction in momentum space. In complete analogy to $\psi_n(x)$, $\left(\|\phi_n(p_x)\|^2 dp_x\right)$ gives the probability of measuring the body's momentum to be between p_x and $p_x + dp_x$ if its energy is fixed at E_n. We briefly mention that because $\langle p_x | \, x\rangle = \frac{1}{\sqrt{2\pi\hbar}} \exp\left(-\frac{ip_x x}{\hbar}\right)$ [137], it follows that

$$\phi_n(p_x) = \frac{1}{\sqrt{2\pi\hbar}} \int dx \ \exp\left(-\frac{ip_x x}{\hbar}\right) \psi_n(x) \tag{5.18}$$

which means $\phi_n(p_x)$ and $\psi_n(x)$ are related through the Fourier transform, as one would expect.

The gist of the above arguments is that depending on the basis in which we expand $|n\rangle$, we get different wavefunctions. The appropriate wavefunction to talk about depends on how we intend to probe the quantum system: for example, if we intend to measure position given a fixed energy of the system, then $\{\psi_n(x)\}$ are the wavefunctions to go with; if, instead, we want to measure momentum then we need the $\{\phi_n(p_x)\}$. But in all these discussions, the nature of the ket $|n\rangle$ remains the same independent of whether we work in momentum or position space. As a matter of course, one might then ask why don't we just deal solely with the energy eigenkets $|n\rangle$ without resorting to wavefunctions – and that is precisely the quintessence of the so-called *second quantization* scheme (also known as the *occupation number representation*). When we expand $|n\rangle$ in some basis and then solve for the related coefficients, or wavefunctions, as we did above, (5.10), we speak then of *first quantization*. Thus, in first quantization, it is important to specify in which basis the expansion of the ket $|n\rangle$ is being done, normally in position or momentum space (but, in general, in the space of either one of a canonically conjugated pair of operators).

How then do we go about doing quantum mechanics without explicitly talking of wavefunctions? In other words, how does second quantization work? To see how it works, let us go back to (5.6), which at this point, we may conveniently write as:

$$\hat{\mathscr{H}} \, |n\rangle = E_n \, |n\rangle \ . \tag{5.19}$$

Instead of trying to find an expression for $|n\rangle$, we take it as it is – *viz.* $\{|n\rangle\}$ are eigenstates of $\hat{\mathscr{H}}$, period. What we rather do is to rewrite the Hamiltonian $\hat{\mathscr{H}}$ in terms of a set of mutually commuting operators which have $\{|n\rangle\}$ as their eigenstates. It is worth noting that the eigenenergy E_n, (5.11), depends only on n and not on neither the position (x) nor the momentum (p_x) of the body. Indeed, the mathematical expression for E_n in terms of n gives important clues on how we may rewrite $\hat{\mathscr{H}}$ in such a way that the new operators in the latter do really have $\{|n\rangle\}$ as their eigenkets. If we combine (5.19) and (5.11), we find that,

$$\hat{\mathscr{H}} \, |n\rangle = \left(n + \frac{1}{2}\right) \hbar\omega \, |n\rangle \tag{5.20}$$

which means that,

$$\hat{\mathscr{H}} = \left(\hat{\mathscr{A}} + \frac{1}{2}\right) \hbar\omega \tag{5.21}$$

where $\hat{\mathscr{A}}$ is, for now, an unknown operator with the following property:

$$\hat{\mathscr{A}} \, |n\rangle = n \, |n\rangle \ . \tag{5.22}$$

Comparing (5.6) with (5.21), we find that:

$$\hat{\mathscr{A}} = \frac{\omega m}{2\hbar} \left(\hat{\mathscr{X}}^2 + \frac{\hat{\mathscr{P}}^2}{\omega^2 m^2} - \frac{\hbar}{\omega m} \right) \ . \tag{5.23}$$

Traditionally, this form of $\hat{\mathscr{A}}$ is less preferred because it obscures some interesting insights. Rather, it is the factorized form:

$$\hat{\mathscr{A}} = \hat{a}^\dagger \hat{a} \tag{5.24}$$

where [11],

$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{\mathscr{X}} - \frac{i}{m\omega}\hat{\mathscr{P}}_x\right) \tag{5.25a}$$

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{\mathscr{X}} + \frac{i}{m\omega}\hat{\mathscr{P}}_x\right) \tag{5.25b}$$

that we prefer and use. The reason is that, despite the fact that the operators $\hat{a}^\dagger$ and $\hat{a}$ are not Hermitian, they allow for transition between the eigenstates – so they are extremely useful when discussing emission and absorption processes. As a matter of fact, one can derive that:

$$\hat{a}\left|n\right\rangle = \sqrt{n}\left|n-1\right\rangle \ , \qquad \hat{a}^\dagger\left|n\right\rangle = \sqrt{n+1}\left|n+1\right\rangle \ . \tag{5.26}$$

It is truly remarkable that the form $\hat{\mathscr{H}}$ assumes in light of the operators $\hat{a}$ and $\hat{a}^\dagger$, namely,

$$\hat{\mathscr{H}} = \left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)\hbar\omega \tag{5.27}$$

appears in many problems in quantum mechanics. Perhaps the most important is the quantization of the electromagnetic field, which was first done in the early years of quantum theory. There, one sees that the Hamiltonian of the field becomes a sum over an infinite number of harmonic oscillators, each representing a specific mode of the field. And the operators $\hat{a}^\dagger$ and $\hat{a}$ are tasked with increasing and decreasing by a quanta of energy their respective modes. Einstein had already discovered the photoelectric effect and the notion of the electromagnetic field as being composed of particles called photons was well established by then, so interpreting the operators $\hat{a}^\dagger$ and $\hat{a}$ as creating and annihilating photons of certain momentum was leapt at very easily – thus their eponymous current names. Soon after, the language introduced by the quantization of the electromagnetic field crept into all physical problems where the Hamiltonian could be recast into the likeness of (5.27). In every instance (with the exception of the harmonic oscillator), the particles which the creation and annihilation operators were meant to create or annihilate were given a specific name. In the case of lattice vibrations, for example, the particles are called phonons [93, 137]. In this narrative, the operator $\hat{a}^\dagger\hat{a}$ is interpreted as counting the number of particles occupying a certain state, hence its name *occupation number operator*, usually indicated as $\hat{n}$. In this view, the state $\left|n=0\right\rangle$ contains no particle, so we call it the *vacuum state*. The absence of particles in the vacuum state, though, does not necessarily imply a state of zero energy. As it mostly happens, it is characterized by a specific energy. For the harmonic oscillator, (5.11), this vacuum energy corresponds to $E_0 = \frac{1}{2}\hbar\omega$. And anytime a particle is added to the system, the energy of the latter increases by $\Delta E = \hbar\omega$ – which is commonly referred to as a *quanta of energy*. In addition, we can imagine creating any state $\left|n\right\rangle$ from the vacuum state $\left|0\right\rangle$. It is easy to prove from (5.26) that:

$$\left|n\right\rangle = \frac{\left(\hat{a}^\dagger\right)^n}{\sqrt{n!}}\left|0\right\rangle \ . \tag{5.28}$$

The vacuum state of the harmonic oscillator can thus accommodate any finite number of particles, hence the particles must be bosons. The normalization factor $\frac{1}{\sqrt{n!}}$ can be interpreted as accounting for the indistinguishability of these bosons. (It is interesting to note the analogy here with the solution to the Gibbs paradox.). The particle states $\{|n\rangle\}$ are the orthonormal basis elements of a vector space called the *Fock space* [82, 93, 137]. In this space, two basis states $|n\rangle$ and $|n'\rangle$ are orthogonal to each other if they differ in their occupation numbers. The Fock space for the harmonic oscillator is *bosonic* because, as stated above, we can fill the vacuum state with any number of bosons. There are Fock spaces where one cannot fill the vacuum state with more than one particle. These are called *fermionic* Fock spaces, and the particles in question are fermions. Finally, we mention that from the properties of the operators $\hat{a}^\dagger$ and $\hat{a}$, (5.26), one derives the commutation relation:

$$\left[\hat{a}, \hat{a}^\dagger\right] = \hat{\mathbb{I}} \tag{5.29}$$

which can also be easily derived applying the definition of $\hat{a}^\dagger$ and $\hat{a}$ given at (5.25).

In discussing the harmonic oscillator above, we made a very deep conceptual leap when we transitioned from first to second quantization. This has to do with the interpretation of the integer n. Under the first quantization scheme, n just indexed eigenfunctions like $\psi_n(x)$ and their respective energies ((5.12)). But according to the second quantization scheme, we came to see the same integer n as being an eigenvalue of the operator $\hat{a}^\dagger\hat{a}$ and also indicates the number of bosons occupying a Fock space ket. Both interpretations are correct and can be used interchangeably. However, some caution is needed in how far we drag the meaning of n together with the creation and annihilation operators in second quantization. In general, the particles created or annihilated according to second quantization represent excitations in the system under study. This is quite clear from the relation between n and the quantum harmonic oscillator's eigenenergy, (5.11): n indicates how energetically excited the state of the oscillator is. And the notion of $\hat{a}^\dagger$ and $\hat{a}$ creating and annihilating some bosons, respectively, according to the second quantization scheme, is just a mathematical construct which provide an alternative way of talking about these same harmonic excitations. The same applies to lattice vibrations: phonons, like the bosons for the harmonic oscillator, are just mathematically constructed particles which occupation numbers represent excitations in lattice vibrations.

However, there are also many instances whereby these particles one get from second quantizing a system are not just the fruits of some mathetmatical trickery, but are real particles to reckon with in Nature. For example, photons represent the excitations in the electromagnetic field according to second quantization, and are real. The Higgs boson represent excitations in the Higgs field, and it has recently been detected experimentally. The electromagnetic field and the Higgs field are examples of what we call *quantum fields*. In fact, all the elementary particles in physics (including the electron) are excitations of a particular quantum field. The study of quantum fields and their excitations is the subject of *quantum field theory* (QFT) [93]. We are not going to need QFT in the discussions that follow, but it is important we bear in mind the episteme related to these particles which transpire through second quantization.

To conclude this brief discussion on the harmonic oscillator and second quantization, we consider a collection of noninteracting harmonic oscillators, say N in total. If we work in the occupation number representation, the Hamiltonian here is a direct generalization of (5.21):

$$\mathscr{H} = \sum_{i=1}^{N} \left(\hat{a}_i^\dagger \hat{a}_i + \frac{1}{2}\right) \hbar\omega_i \tag{5.30}$$

It is then very easy to see that a generic state of the system can be expressed as $|n_1, n_2, \ldots, n_N\rangle$ where n_i indicates the number of bosons present in the $i-$th harmonic oscillator. The (overall) vacuum state of the system is the state in which $n_i = 0$ for any given oscillator i, i.e. $|0, 0, \ldots, 0\rangle$, which we shall simply indicate as $|\mathbb{0}\rangle$. The eigenenergies are also easily found to be:

$$E_{n_1,n_2,\ldots,n_N} = \sum_{i=1}^{N} \left(n_i + \frac{1}{2}\right) \hbar\omega_i \ . \tag{5.31}$$

The operators $\hat{a}_i^\dagger$ and $\hat{a}_i$ operate only on the Fock space of the $i-$th oscillator, therefore such operators with different indexes commute:

$$[\hat{a}_i, \hat{a}_{i'}] = \left[\hat{a}_i^\dagger, \hat{a}_{i'}^\dagger\right] = \hat{0} \ , \quad \left[\hat{a}_i, \hat{a}_{i'}^\dagger\right] = \delta_{i,i'}\hat{\mathbb{1}} \ . \tag{5.32}$$

As in the case of a single harmonic oscillator, the generic state $|n_1, n_2, \ldots, n_N\rangle$ can be generated from the vacuum state $|\mathbb{0}\rangle$:

$$|n_1, n_2, \ldots, n_N\rangle = \prod_{i=1}^{N} \frac{(\hat{a}_i^\dagger)^{n_i}}{\sqrt{n_i!}} |\mathbb{0}\rangle \ . \tag{5.33}$$

The generic multi-harmonic oscillator state $|n_1, n_2, \ldots, n_N\rangle$ is simply the direct product $|n_1\rangle \otimes |n_2\rangle \otimes \ldots \otimes |n_N\rangle$. The Fock space for this collection of oscillators is thus the vector space tensor product of the Fock spaces of the separated oscillators. The collection of integers $\{n_1, n_2, \ldots, n_N\}$ is an ordered multiset: the first element denotes the number of bosons in the first oscillator, the second element is the number of bosons in the second oscillator and so on. Each individual oscillator has its own vacuum state, and each of these has its own energy content. The energy ($E_{\mathbb{0}}$) of the overall vacuum state, $|\mathbb{0}\rangle$, is the sum of the energy of the various local vacuum states: $E_{\mathbb{0}} = \frac{1}{2}\sum_{i=1}^{N} \hbar\omega_i$.

Chapter 6

The Holstein-Primakoff transformation

Having discussed the harmonic oscillator, we are now ready to discuss the Holstein-Primakoff (HP) transformation.

Given an arbitrary particle of spin-j ($j = \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \ldots$), we commonly represent its spin quantum states through a set of orthonormal states $\{|j, m\rangle\}$ which are each a simultaneous eigenstate of the operators $\hat{\boldsymbol{\mathcal{J}}}^2$ and $\hat{\mathcal{J}}^z$:

$$\hat{\boldsymbol{\mathcal{J}}}^2 \, |j, m\rangle = j(j+1)\hbar^2 \, |j, m\rangle \tag{6.1a}$$

$$\hat{\mathcal{J}}^z \, |j, m\rangle = m\hbar \, |j, m\rangle \ . \tag{6.1b}$$

As we know, the possible values of the magnetic spin quantum number, m, depends on j and the *nature* of j. If j is an integral integer, then $m = \pm j, \pm(j-1), \ldots, 0$, while for half-integral j, $m = \pm j, \pm(j-1), \ldots, \pm 1/2$. The fact that the values of m can be either: 1) all integral or, 2) all half-integral integers, creates some discomfort when writing algorithms for doing computations on systems which may potentially involve spin quantum numbers of different types. The ideal way to go about this would be to have a simple way of representing the possible m values as function of some parameter which is independent of whether j is integral or half-integral. In fact, for a given j, it is easy to verify that the possible values of m can be simply expressed as:

$$m = j - n \ , \qquad \text{where } n = 0, 1, 2, \ldots, 2j \ . \tag{6.2}$$

Note that, alternatively, we could also have chosen the form:

$$m = j + n' \ , \qquad \text{where } n' = 0, -1, -2, \ldots, -2j \ . \tag{6.3}$$

However, the form given in (6.2) is preferred because the parameter n admits only nonnegative integers. But another reason why we choose n (6.2) over n' (6.3) is that the former allows a very natural transition to the second quantization scheme, and, as we shall see shortly, this is what leads to the Holstein-Primakoff transformation.

Indeed, the relation (6.2) implies that there is one-to-one correspondence between m and n for fixed j. So instead of the eigenstates $\{|j, m\rangle\}$, we can equally make use of the states $\{|j, n\rangle\}$ – which are also simultaneous eigenstates of $\hat{\boldsymbol{\mathcal{J}}}^2$ and $\hat{\mathcal{J}}^z$. Just as the states $\{|j,m\rangle\}$ are often simply indicated as $\{|m\rangle\}$, we will often indicate the states $\{|j,n\rangle\}$ as $\{|n\rangle\}$. For example, for a spin-1/2, the states $|m=+1/2\rangle$ and $|m=-1/2\rangle$ in the $|m\rangle$ representation become $|n=0\rangle$ and $|n=1\rangle$ in the $|n\rangle$ representation, respectively. If the new states $\{|n\rangle\}$ bring to mind the simple quantum harmonic oscillator, then you already get where this is going. In particular, if we combine (6.1) and (6.2), we get:

$$\hat{\mathcal{J}}^z\,|n\rangle = \hbar(j-n)\,|n\rangle \tag{6.4}$$

where we have effected the transformation $|j,m\rangle \to |n\rangle$. Repeating the reasoning which led to (5.21), we see that we may express $\hat{\mathcal{J}}^z$ as

$$\hat{\mathcal{J}}^z = \hbar\left(j-\hat{b}^\dagger\hat{b}\right) \tag{6.5}$$

where

$$\hat{b}^\dagger\hat{b}\,|n\rangle = n\,|n\rangle \ . \tag{6.6}$$

In the language of occupation number representation, the operator $\hat{b}^\dagger\hat{b}$ is the occupation number operator for some particles. The vacuum state of these particles, i.e. $|n=0\rangle$, is seen to correspond to the state $|j,j\rangle$; and as we increase n, m decreases by the same degree.

To delineate further the parallelism between this way of talking about spin states and the harmonic oscillator, let us consider a single spin$-j$ interacting with a static magnetic field $\mathbf{B}_o = B_o\boldsymbol{e}_z$. The spin Hamiltonian, as we know, is:

$$\hat{\mathscr{H}} = -\gamma B_o\hat{\mathcal{J}}^z \tag{6.7}$$

where γ is the spin's gyromagnetic ratio. According to (6.5), we can rewrite this Hamiltonian also as:

$$\hat{\mathscr{H}} = \left(j-\hat{b}^\dagger\hat{b}\right)\hbar\omega \tag{6.8}$$

where $\omega := -\gamma B_o$ is the Larmor frequency. And the eigenvalues of $\hat{\mathscr{H}}$ are easily seen to be:

$$E_n = (j-n)\hbar\omega \ . \tag{6.9}$$

The quanta of energy is still $\hbar\omega$ and the vacuum energy here is thus $E_0 = j\hbar\omega$. We also observe from (6.9) that the occupation number for the particles which $\hat{b}^\dagger\hat{b}$ counts indicates excitations in the spin, just as we saw for the quantum harmonic oscillator (5.11). It is worthwhile to point out that while the vacuum state of the harmonic oscillator is a true ground state (that is, the state with the lowest energy), in the present case, the vacuum state $|0\rangle$ is not always the ground state. Here, $|0\rangle$ is the ground state only when $\gamma > 0$, while for $\gamma < 0$ the $|0\rangle$ corresponds to the highest excited state.

Equations (6.9) and (6.8) rightly reminds us of (5.27) and (5.11) from the harmonic oscillator problem, respectively. In addition, the operators $\hat{b}^\dagger$ and $\hat{b}$ have the same properties as the $\hat{a}^\dagger$ and $\hat{a}$ encountered when we discussed the harmonic oscillator, respectively, (5.26); namely:

$$\hat{b}\,|n\rangle = \sqrt{n}\,|n-1\rangle \ , \qquad 1 \le n \le 2j \tag{6.10a}$$

$$\hat{b}^\dagger\,|n\rangle = \sqrt{n+1}\,|n+1\rangle \ , \qquad 0 \le n \le 2j-1 \tag{6.10b}$$

where the ranges on n have been set so as to remain consistent with (6.2). The above bounds imposed on n mark a very important difference between the new states $\{|n\rangle\}$ for the spin and those for the quantum harmonic oscillator. We shall come back to this point very soon.

Equation (6.5) gives a second quantization representation of the spin operator $\hat{\mathcal{J}}^z$, but this is not enough to allow us to fully do spin dynamics in second quantization. We also need to express the operators $\hat{\mathcal{J}}^x$ and $\hat{\mathcal{J}}^y$ in terms of the operators $\hat{b}^\dagger$ and $\hat{b}$. To achieve this, it is rather convenient to deal with their linear combinations $\hat{\mathcal{J}}^\pm = \hat{\mathcal{J}}^x \pm i\hat{\mathcal{J}}^y$. From the theory of angular momentum, we know that, for example [137, 170],

$$\hat{\mathcal{J}}^+ \left|m\right\rangle = \hbar\sqrt{(j-m)(j+m+1)}\left|m+1\right\rangle \ . \tag{6.11}$$

From (6.2), we have that if $\left|m\right\rangle \rightarrow \left|n\right\rangle$, then $\left|m+1\right\rangle \rightarrow \left|n-1\right\rangle$, therefore (6.11) in the occupation number representation becomes:

$$\hat{\mathcal{J}}^+ \left|n\right\rangle \equiv f^+(\hat{b}^\dagger,\hat{b})\left|n\right\rangle = \hbar\sqrt{2j-(n-1)}\sqrt{n}\left|n-1\right\rangle \tag{6.12}$$

where $f^+(\hat{b}^\dagger,\hat{b})$ is simply the operator $\hat{\mathcal{J}}^+$ written in terms of $\hat{b}^\dagger$ and $\hat{b}$. Our objective is to find $f^+(\hat{b}^\dagger,\hat{b})$. From the first equation of (6.10a), we note that:

$$f^+(\hat{b}^\dagger,\hat{b})\left|n\right\rangle = \hbar\sqrt{2j-(n-1)}\ \hat{b}\left|n\right\rangle \ . \tag{6.13}$$

Given that $\hat{b}\left|n\right\rangle \propto \left|n-1\right\rangle$, and the final state must remain $\left|n-1\right\rangle$, the operator which generates the coefficient $\sqrt{2j-(n-1)}$ must be in function of the occupation number operator, $\hat{b}^\dagger\hat{b}$, (6.6). We are then lead to the conclusion that:

$$\hat{\mathcal{J}}^+ = \hbar\sqrt{2j-\hat{b}^\dagger\hat{b}}\ \hat{b} \ . \tag{6.14}$$

Since $\hat{\mathcal{J}}^-$ and $\hat{\mathcal{J}}^+$ are Hermitian conjugate of each other, it follows immediately from (6.14) that:

$$\hat{\mathcal{J}}^- = \hbar\ \hat{b}^\dagger\ \sqrt{2j-\hat{b}^\dagger\hat{b}} \ . \tag{6.15}$$

Equations (6.5), (6.14) and (6.15) constitute the *Holstein-Primakoff transformation*. In the HP transformation the usual spin operators $\hat{\mathcal{J}}^x, \hat{\mathcal{J}}^y, \hat{\mathcal{J}}^z$ are all written in function of a single operator $\hat{b}^\dagger$ and its Hermitian conjugate, $\hat{b}$. The particles which $\hat{b}^\dagger$ ($\hat{b}$) creates (annihilates) are called the *Holstein-Primakoff bosons*. We emphasize that the HP bosons simply represent spin excitations, and we should not go beyond this interpretation. Interestingly, while $\hat{\mathcal{J}}^+\left|m\right\rangle \propto \left|m+1\right\rangle$ and $\hat{\mathcal{J}}^-\left|m\right\rangle \propto \left|m-1\right\rangle$, we observe from (6.14) and (6.15) that $\hat{\mathcal{J}}^+\left|n\right\rangle \propto \left|n-1\right\rangle$ and $\hat{\mathcal{J}}^-\left|n\right\rangle \propto \left|n+1\right\rangle$, which is consistent with the fact that an increase in m implies a decrease in n and vice versa (because the sum $m+n$ is conserved, (6.2)). Therefore, the operator $\hat{\mathcal{J}}^+$ (unlike $\hat{b}^\dagger$) annihilates HP bosons, but $\hat{\mathcal{J}}^-$ creates them. In complete analogy to the $m-$representation where we know $\hat{\mathcal{J}}^+$ cannot increase the magnetic spin quantum number m of the state $\left|m\right\rangle$ indefinitely, in the occupation number representation $\hat{\mathcal{J}}^+$ cannot annihilate the HP bosons indefinitely but ends when $n=0$, which corresponds to the HP vacuum state. Analogously, $\hat{\mathcal{J}}^-$ can fill the vacuum state with a maximum number of HP bosons, namely, $n=2j$. This limit is set by the operator $\sqrt{2j-\hat{b}^\dagger\hat{b}}$ in the definition of $\hat{\mathcal{J}}^-$, (6.15). This is all consistent with (6.2) where it was evident that n is a nonnegative integer, and whose range is bounded by the spin quantum number j: $0 \leq n \leq 2j$.

From (6.5), (6.14) and (6.15) we also derive the following:

$$\hat{\mathcal{J}}^x = \hbar \frac{\sqrt{2j - \hat{b}^\dagger \hat{b}}\ \hat{b} + \hat{b}^\dagger\ \sqrt{2j - \hat{b}^\dagger \hat{b}}}{2} \tag{6.16a}$$

$$\hat{\mathcal{J}}^y = \hbar \frac{\sqrt{2j - \hat{b}^\dagger \hat{b}}\ \hat{b} - \hat{b}^\dagger\ \sqrt{2j - \hat{b}^\dagger \hat{b}}}{2i} \tag{6.16b}$$

$$\hat{\boldsymbol{\mathcal{J}}}^2 = \hbar^2 j(j+1)\hat{\mathbb{1}}\ . \tag{6.16c}$$

Most importantly, one can verify that the Holstein-Primakoff transformation preserves the commutation relations:

$$\left[\hat{\mathcal{J}}^\alpha, \hat{\mathcal{J}}^\beta\right] = i\hbar\epsilon^{\alpha\beta\gamma}\hat{\mathcal{J}}^\gamma \tag{6.17}$$

or their equivalent:

$$\left[\hat{\mathcal{J}}^z, \hat{\mathcal{J}}^\pm\right] = \pm\hbar\hat{\mathcal{J}}^\pm \tag{6.18a}$$

$$\left[\hat{\mathcal{J}}^+, \hat{\mathcal{J}}^-\right] = 2\hbar\hat{\mathcal{J}}^z \tag{6.18b}$$

where α, β and γ represent any of the three directions x, y, z and $\epsilon^{\alpha\beta\gamma}$ is the three-dimensional Levi-Civita symbol. Hence, working in the HP representation is just the same as in the $m-$representation, in the sense that the physics does not change.

In analogy to the quantum harmonic oscillator, the HP spin states $\{|n\rangle\}$ can all be generated from the vacuum state $|0\rangle$:

$$|n\rangle = \frac{(\hat{b}^\dagger)^n}{\sqrt{n!}}\,|0\rangle\ , \qquad 0 \le n \le 2j\ . \tag{6.19}$$

We could also obtain $|n\rangle$ from $|0\rangle$ by applying repeatedly $\hat{\mathcal{J}}^-$. This has the advantage of incorporating inevitably the bound on n. Certainly,

$$|n\rangle \propto \left(\frac{\hat{\mathcal{J}}^-}{\hbar}\right)^n |0\rangle\ . \tag{6.20}$$

Indeed, the following identities can be easily proved:

$$|n\rangle = \frac{\left(\frac{\hat{\mathcal{J}}^-}{\hbar}\right)^n}{n!\sqrt{\binom{2j}{n}}}\,|0\rangle \tag{6.21}$$

$$|n\rangle = \frac{\prod_{k=1}^{n}(2j + k - \hat{b}^\dagger\hat{b})^{1/2}}{n!\sqrt{\binom{2j}{n}}}\ (\hat{b}^\dagger)^n\,|0\rangle \tag{6.22}$$

$$|n\rangle = \hat{\Lambda}(j,n)\ \frac{(\hat{b}^\dagger)^n}{\sqrt{n!}}\,|0\rangle \tag{6.23}$$

where, the operator $\hat{\Lambda}(j,n)$ is defined as:

$$\hat{\Lambda}(j,n) := \frac{\sqrt{\left(\!\binom{2j+1-\hat{b}^\dagger\hat{b}}{n}\!\right)}}{\sqrt{\binom{2j}{n}}} \tag{6.24}$$

and where $\left(\!\!\binom{x}{n}\!\!\right)$ is defined as:

$$\left(\!\!\binom{x}{n}\!\!\right) := \frac{x(x+1)(x+2)\dots(x+n-1)}{n!} \ . \tag{6.25}$$

x in (6.25) can be a number or an operator. For a nonnegatve integer x, $\left(\!\!\binom{x}{n}\!\!\right)$ is what we call the *multiset coefficient* (read as "*x multichoose n*") [148], and it gives the number of combinations of length n we can get from a set of x elements, if we allow repetition of elements and disregard order [148]. For example, the multisets of cardinality 2 we can get from a set of cardinality 3 like $\{i, j, k\}$ are: $\{i, i\}, \{i, j\}, \{i, k\}, \{j, j\}, \{j, k\}, \{k, k\}$; so $\left(\!\!\binom{3}{2}\!\!\right) = 6$, which can be checked from (6.25). By definition, $\left(\!\!\binom{x}{n}\!\!\right) = 1$ when $n = 0$ and x is a scalar; while $\left(\!\!\binom{x}{n}\!\!\right) = \hat{\mathbb{1}}$ when $n = 0$ and x is an operator. To prove (6.22) and (6.23) from (6.21) the following identity is very useful:

$$(\hat{b}^\dagger)^k \sqrt{2j - \hat{b}^\dagger \hat{b}} = \sqrt{2j + k - \hat{b}^\dagger \hat{b}}\ (\hat{b}^\dagger)^k \tag{6.26}$$

for nonnegative integer k. The identity can be easily proved using the properties of the operators $\hat{b}^\dagger$ and $\hat{b}$, (6.10a).

The operator $\hat{\Lambda}(j, n)$ defined in (6.24) is a very interesting one. It can be easily shown that:

$$\hat{\Lambda}(j, n)\,|n\rangle = \begin{cases} |n\rangle \ , & \text{if } 0 \le n \le 2j \\ \text{nonexistent} \ , & \text{otherwise} \end{cases} \ . \tag{6.27}$$

Equation (6.23) is very telling: $\frac{(\hat{b}^\dagger)^n}{\sqrt{n!}}\,|0\rangle$ certainly yields the quantum harmonic oscillator state $|n\rangle$ – (5.28). So, for now, n can be any nonnegative integer, just like with the quantum harmonic oscillator. But by multiplying $\frac{(\hat{b}^\dagger)^n}{\sqrt{n!}}\,|0\rangle$ from the left by the operator $\hat{\Lambda}(j, n)$, we restrict the range of values for n to $0 \le n \le 2j$. Evidently, $\hat{\Lambda}(j, n)$ plays the role of a "cut-off" operator: while it forbids n from being outside the range $0 \le n \le 2j$, it reduces to the identity operator when n is within the same range. Interestingly, this observation on the properties of $\hat{\Lambda}(j, n)$ entails a very peculiar implication. It begins with the observation that,

$$\lim_{j \to \infty} \hat{\Lambda}(j, n) = \hat{\mathbb{1}} \tag{6.28}$$

according to (6.24). But if $\hat{\Lambda}(j, n)$ becomes the identity operator for any occupation number n, then there is a one-to-one correspondence between the states $\{|n\rangle\}$ in (6.23) and the quantum harmonic oscillator states $\{|n\rangle\}$ we saw in (5.28). This means that the eigenvectors of the quantum harmonic oscillator are the same as those of a spin-∞ particle in Fock space [66]. Conversely, we can interpret the Fock space in which the spin states $\{|n\rangle\}$ are defined as a truncated version of the quantum harmonic's Fock space by means of the the operator $\hat{\Lambda}(j, n)$.

The next chapters of Part II dedicated to multispin systems notwithstanding, we briefly introduce the topic here. Given an arbitrary finite collection of spins, their spin quantum numbers form a multiset, which we shall indicate as $\mathscr{A}$, i.e. $\mathscr{A} = \{j_1, j_2, \dots, j_N\}$. Multispin states are normally indicated in the $m-$representation either using the coupled or uncoupled representations [170]. In the latter, the states, $\{|j_1 m_1, j_2 m_2, \dots, j_N m_N\rangle\}$, are simultaneous eigenstates of the individual $\hat{\boldsymbol{\mathcal{J}}}_i^2$ and $\hat{\mathcal{J}}_i^z$ operators. In the HP occupation number representation, $|j_1 m_1, j_2 m_2, \dots, j_N m_N\rangle \mapsto |n_1, n_2, \dots, n_N\rangle$, where n_i, $0 \le n_i \le 2j_i$, is the number of HP bosons introduced into the HP vacuum state of the $i-$th spin, and N is the total number of spins. Each possible combination of occupation numbers

$\{n_1, n_2, \ldots, n_N\}$ also forms an ordered multiset and corresponds to a specific multispin state. The overall HP vacuum state is obviously the $|n_1, n_2, \ldots, n_N\rangle$ state with $n_i = 0$ for every i. If we indicate such state as $|\mathbb{0}\rangle$, it trivially follows from (6.23) that:

$$|n_1, n_2, \ldots, n_N\rangle = \hat{\Lambda}(j_1, n_1; \ldots ; j_N, n_N) \prod_{i=1}^{N} \frac{(\hat{b}_i^\dagger)^{n_i}}{\sqrt{n_i!}} |\mathbb{0}\rangle \tag{6.29}$$

where,

$$\hat{\Lambda}(j_1, n_1; \ldots ; j_N, n_N) := \prod_{i=1}^{N} \frac{\sqrt{\left(\!\binom{2j_i+1-\hat{b}_i^\dagger \hat{b}_i}{n_i}\!\right)}}{\sqrt{\binom{2j_i}{n_i}}} \; . \tag{6.30}$$

If we consider a multiset of noninteracting spins $\mathscr{A} = \{j_1, j_2, \ldots, j_N\}$ placed in a region with static magnetic field $\mathbf{B}_o = B_o \boldsymbol{e}_z$, the multispin Hamiltonian of the system is a facile generalization of (6.8):

$$\hat{\mathscr{H}} = \sum_{i=1}^{N} \left(j_i - \hat{b}_i^\dagger \hat{b}_i \right) \hbar\omega_i \tag{6.31}$$

and the eigenenergies are simply:

$$E_{n_1, n_2, \ldots, n_N} = \sum_{i=1}^{N} (j_i - n_i)\, \hbar\omega_i \; . \tag{6.32}$$

and the total vacuum energy is $E_{\mathbb{0}} = \sum_i j_i \hbar\omega_i$. Like the single spin HP vacuum state, the multispin analogue is not necessarily the ground state. To get the ground state from $|\mathbb{0}\rangle$, one needs to fill all localized vacuum states characterized by nonnegative ω_i (i.e. negative γ_i) with HP bosons to their maximum capacity and leave those with negative ω_i empty.

Chapter 7

Index compression maps

7.1 Introduction

We have seen that the uncoupled representation of the multispin states associated with $\mathscr{A} = \{j_1, j_2, \ldots, j_N\}$ are $\{|n_1, n_2, \ldots, n_N\rangle\}$ in the HP occupation number representation, and the possible occupation numbers $(n_1, n_2, \ldots, n_N)$ are multisets of integers. To effectively discuss multispin dynamics, it is convenient to have a reasonable shorthand for indicating a generic state $|n_1, n_2, \ldots, n_N\rangle$. The so-called *index compression maps* are devised just for this purpose and they will be our first order of business in this section. In the second part, we will analyze the eigendecomposition problem for some general forms of isotropic multispin Hamiltonians using the HP representation.

7.2 Index compression maps

A detailed discussion on index compression maps is beyond the scope of this article, so we are going to keep the mathematical details to the minimum. We will concern ourselves here with only one special kind of index compression maps, denoted η_0. For more on index compression maps see [65]. Given a spin multiset $\mathscr{A} = \{j_1, j_2, \ldots, j_N\}$, the index compression map, η_0, maps each possible combination of occupation numbers $(n_1, n_2, \ldots, n_N)$ to a unique integer of the set $\{\mathbb{n}\}$. The mapping is one-to-one. η_0 is simply a function which has the HP occupation numbers $n_1, n_2, \ldots, n_N$ as variables. To be more specific:

$$\mathbb{n} = \eta_0(n_1, n_2, \ldots, n_N) = \sum_{i=1}^{N} \mathcal{W}_{R,i} \cdot n_i \ . \tag{7.1}$$

where,

$$\mathcal{W}_{R,i} := \delta_{N,i} + (1 - \delta_{N,i}) \prod_{k=1}^{N-i} d_{i+k} \tag{7.2}$$

where $\delta_{i,i'}$ is the Kronecker delta and d_i is the dimension of the spin-i's spin Hilbert space, i.e. $d_i = 2j_i + 1$. In more comprehensible terms, for $i \neq N$, $\mathcal{W}_{R,i}$ is the product of all the $d_{i'}$ with $i' > i$; while for $i = N$, $\mathcal{W}_{R,i} = 1$. For instance, $\mathcal{W}_{R,2} = d_3 \cdot d_4 \cdots d_N$. In the same spirit, $\mathcal{W}_{R,0}$ then corresponds to the dimension $D_{\mathcal{H}}$ of the entire spin Hilbert space of the multispin system. We thus infer from (7.1) that the possible values of $\mathbb{n}$ are: $0, 1, 2, \ldots, (D_{\mathcal{H}} - 1)$[65]. Note that since each of the states

$|n_1, n_2, \ldots, n_N\rangle$ constitute a basis for the multispin Hilbert space, the dimension of the latter must coincide with the number of all possible combinations of the HP occupation numbers $\{n_1, n_2, \ldots, n_N\}$, which is precisely $D_{\mathcal{H}}$. These combinations are ordered and restricted: restricted in the sense that for each n_i, $0 \leq n_i \leq 2j_i$, as we mentioned above. The range of $\mathbb{n}$ is thus consistent with the dimension of the multispin Hilbert space.

We adopt the following notation: if $\mathbb{n}$ is related to the multiset $\{n_1, n_2, \ldots, n_N\}$ through the index compression map η_0, (7.1), then we shall write the ket $|n_1, n_2, \ldots, n_N\rangle$ as $|\mathbb{n}\rangle$. The integers $\mathbb{n}$ will be indicated with the font $\mathbb{0}, \mathbb{1}, \mathbb{2}, \mathbb{3}, \ldots$ to differentiate them from the single spin states. The complete HP vacuum state of the system always has $\mathbb{n} = \mathbb{0}$, and so $|0, 0, \ldots, 0\rangle \mapsto |\mathbb{0}\rangle$, consistent with our previous notation for this particular state.

Consider the deuterated hydroxymethyl radical ($^{\cdot}CH_2OD$), for example. There are only four nonzero spins we need to take into consideration for the simulation of its ESR spectrum: 1) the radical electron, 2) the first hydrogen nuclear, 3) the second hydrogen nuclear, and 4) the deuterium nuclear. If we number the spins according to the same order, then the spin multiset in this case is $\mathcal{A} = \{j_1, j_2, j_3, j_4\} = \{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 1\}$. And from (7.1) we can write:

$$\mathbb{n} = 12n_1 + 6n_2 + 3n_3 + n_4 \ . \tag{7.3}$$

In table 7.1 the elements of $^{\cdot}CH_2OD$'s spin Hilbert space basis in the uncoupled representation ($|m_1, m_2, m_3, m_4\rangle$) are translated into the HP occupation number representation ($|n_1, n_2, n_3, n_4\rangle$), and their respective shorthand notation $|\mathbb{n}\rangle$ according to the index compression map η_0 is also given. As one can easily observe, the relationship between the integers $\mathbb{n}$ and the occupation numbers (n_1, n_2, n_3, n_4) according to the mapping η_0 strictly depends on how we label the spins.

It is interesting to note that once we know the labels on the spins from the multiset $\mathcal{A} = \{j_1, j_2, \ldots, j_N\}$, we can determine the corresponding HP occupation numbers $n_1, n_2, \ldots, n_N$ for any given $\mathbb{n}$. This is because the map η_0 is invertible and has a unique inverse: $\eta_0^{-1}(\mathbb{n}) = \{n_1, n_2, \ldots, n_N\}$. In this sense, (7.1) can be viewed as a linear multivariable Diophantine equation in the variables $n_1, n_2, \ldots, n_N$. The problem is somehow complicated by the fact that each variable n_i is restricted to a specific range. In any event, there is a simple algorithm one can follow to solve (7.1) for $n_1, n_2, \ldots, n_N$ when $\mathbb{n}$ is fixed. It goes as follows: Find the integer n_1, $0 \leq n_1 \leq 2j_1$, which maximizes the product $\mathcal{W}_{R,1} n_1$ but still keeps the latter less or equal to the given $\mathbb{n}$; find then n_2 in the range $0 \leq n_2 \leq 2j_2$ which maximizes the sum $\mathcal{W}_{R,1} \cdot n_1 + \mathcal{W}_{R,2} \cdot n_2$, still keeping the sum less or equal to $\mathbb{n}$. Continue with the procedure till you get to n_N. In the particular case where along the way you get to a certain occupation number n_k, where $n_1 \leq n_k < n_N$, such that $\mathbb{n} = \mathcal{W}_{R,1} \cdot n_1 + \mathcal{W}_{R,2} \cdot n_2 + \ldots + \mathcal{W}_{R,k} \cdot n_k$, then $n_{k+1} = n_{k+2} = \ldots = n_N = 0$.

For instance, say we want to find the HP occupation numbers n_1, n_2, n_3, n_4 corresponding to $\mathbb{n} = \mathbb{11}$ for the $^{\cdot}CH_2OD$ radical (assuming we maintain the same choice of spin labelling as done above). This amounts to solving the Diophantine equation:

$$\mathbb{11} = 12n_1 + 6n_2 + 3n_3 + n_4 \tag{7.4}$$

in accordance with (7.3), knowing that n_1, n_2, n_3 can be or 0 or 1, while n_4 can be any nonnegative integer not greater than 2. According to the algorithm discussed above, we see that n_1 must necessarily be 0, n_2 and n_3 must be 1 and, finally, $n_4 = 2$. Thus, $|\mathbb{11}\rangle = |0, 1, 1, 2\rangle$, which is in agreement with

$\lvert m_1, m_2, m_3, m_4\rangle$	$\lvert n_1, n_2, n_3, n_4\rangle$	$\lvert\mathbb{n}\rangle$
$\left\lvert +\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2}, +1\right\rangle$	$\lvert 0,0,0,0\rangle$	$\lvert\mathbb{0}\rangle$
$\left\lvert +\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2}, 0\right\rangle$	$\lvert 0,0,0,1\rangle$	$\lvert\mathbb{1}\rangle$
$\left\lvert +\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2}, -1\right\rangle$	$\lvert 0,0,0,2\rangle$	$\lvert\mathbb{2}\rangle$
$\left\lvert +\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2}, +1\right\rangle$	$\lvert 0,0,1,0\rangle$	$\lvert\mathbb{3}\rangle$
$\left\lvert +\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2}, 0\right\rangle$	$\lvert 0,0,1,1\rangle$	$\lvert\mathbb{4}\rangle$
$\left\lvert +\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2}, -1\right\rangle$	$\lvert 0,0,1,2\rangle$	$\lvert\mathbb{5}\rangle$
$\left\lvert +\frac{1}{2}, -\frac{1}{2}, +\frac{1}{2}, +1\right\rangle$	$\lvert 0,1,0,0\rangle$	$\lvert\mathbb{6}\rangle$
$\left\lvert +\frac{1}{2}, -\frac{1}{2}, +\frac{1}{2}, 0\right\rangle$	$\lvert 0,1,0,1\rangle$	$\lvert\mathbb{7}\rangle$
$\left\lvert +\frac{1}{2}, -\frac{1}{2}, +\frac{1}{2}, -1\right\rangle$	$\lvert 0,1,0,2\rangle$	$\lvert\mathbb{8}\rangle$
$\left\lvert +\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, +1\right\rangle$	$\lvert 0,1,1,0\rangle$	$\lvert\mathbb{9}\rangle$
$\left\lvert +\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, 0\right\rangle$	$\lvert 0,1,1,1\rangle$	$\lvert\mathbb{10}\rangle$
$\left\lvert +\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, -1\right\rangle$	$\lvert 0,1,1,2\rangle$	$\lvert\mathbb{11}\rangle$
$\left\lvert -\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2}, +1\right\rangle$	$\lvert 1,0,0,0\rangle$	$\lvert\mathbb{12}\rangle$
$\left\lvert -\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2}, 0\right\rangle$	$\lvert 1,0,0,1\rangle$	$\lvert\mathbb{13}\rangle$
$\left\lvert -\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2}, -1\right\rangle$	$\lvert 1,0,0,2\rangle$	$\lvert\mathbb{14}\rangle$
$\left\lvert -\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2}, +1\right\rangle$	$\lvert 1,0,1,0\rangle$	$\lvert\mathbb{15}\rangle$
$\left\lvert -\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2}, 0\right\rangle$	$\lvert 1,0,1,1\rangle$	$\lvert\mathbb{16}\rangle$
$\left\lvert -\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2}, -1\right\rangle$	$\lvert 1,0,1,2\rangle$	$\lvert\mathbb{17}\rangle$
$\left\lvert -\frac{1}{2}, -\frac{1}{2}, +\frac{1}{2}, +1\right\rangle$	$\lvert 1,1,0,0\rangle$	$\lvert\mathbb{18}\rangle$
$\left\lvert -\frac{1}{2}, -\frac{1}{2}, +\frac{1}{2}, 0\right\rangle$	$\lvert 1,1,0,1\rangle$	$\lvert\mathbb{19}\rangle$
$\left\lvert -\frac{1}{2}, -\frac{1}{2}, +\frac{1}{2}, -1\right\rangle$	$\lvert 1,1,0,2\rangle$	$\lvert\mathbb{20}\rangle$
$\left\lvert -\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, +1\right\rangle$	$\lvert 1,1,1,0\rangle$	$\lvert\mathbb{21}\rangle$
$\left\lvert -\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, 0\right\rangle$	$\lvert 1,1,1,1\rangle$	$\lvert\mathbb{22}\rangle$
$\left\lvert -\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, -1\right\rangle$	$\lvert 1,1,1,2\rangle$	$\lvert\mathbb{23}\rangle$

Table 7.1: Basis kets of $^{\cdot}CH_2OD$'s spin Hilbert space in the uncoupled representation ($\lvert m_1, m_2, m_3, m_4\rangle$), the HP representation ($\lvert n_1, n_2, n_3, n_4\rangle$) and their shorthand notation $\lvert\mathbb{n}\rangle$ according to the index compression map η_0.

Table (7.1). It therefore goes without saying that by means of the map η_0, we can easily encode multispin states in the form of integers, and the decoding process is as easy as that of encoding.

Before moving on, we point out that, unlike the multispin HP boson Fock states, the map η_0 cannot be applied to the boson Fock states for a finite collection of quantum harmonic oscillators (not even for a single oscillator). This is because the single spin HP boson Fock spaces we encounter in Nature are always finite in dimension (due to the action of the operator $\hat{\Lambda}(j, n)$, (6.27)) – this is in stark contrast to the boson Fock space related to a single quantum harmonic oscillator, which is of infinite dimension.

Chapter 8

Eigendecomposition of isotropic multispin Hamiltonians in the absence of an external magnetic field

8.1 Introduction

We discuss here how the HP transformation and the index compression map η_0 can be deployed to solve the eigendecomposition problem for isotropic multispin Hamiltonians. One of the advantages of the HP transformation is that it has the tendency of making it possible to find analytical solutions to seemingly intractable problems. This analytical element can be very useful when writing algorithms for multispin systems.

Symmetry arguments cannot be ignored in problems like the one we are about to discuss, and we will greatly make use of them. But it is important to note that symmetry arguments can get us to confidently reach certain conclusions without sharing light on *how* to effectively carry on the needed calculations. This is where the HP transformation and the index compression map η_0 come to our aid. To make the symmetry arguments more intelligible we are not going to consider the general isotropic multispin Hamiltonian in the presence of a static magnetic field straightaway; we will leave it till the next chapter. But along the way, we will discuss various symmetries and analyze the spin Hamiltonians we encounter with the help of the HP transformation and η_0.

Without loss of generality, we have set $\hbar = 1$ in the following.

8.2 The isotropic multispin Hamiltonian in the absence of an external magnetic field

The isotropic spin Hamiltonian $\hat{\mathscr{H}}_{spin-spin}$ of an arbitrary collection of spins $\mathscr{A} = \{j_1, j_2, \ldots, j_N\}$ in the absence of an external magnetic field takes the form [32, 61]:

$$\hat{\mathscr{H}}_{spin-spin} = \sum_{i>i'} T_{i,i'} \hat{\boldsymbol{\mathcal{J}}}_i \cdot \hat{\boldsymbol{\mathcal{J}}}_{i'} = \sum_{i>i'} T_{i,i'} \left[\hat{\mathcal{J}}_i^z \hat{\mathcal{J}}_{i'}^z + \frac{1}{2} \left(\hat{\mathcal{J}}_i^+ \hat{\mathcal{J}}_{i'}^- + \hat{\mathcal{J}}_i^- \hat{\mathcal{J}}_{i'}^+ \right) \right] . \tag{8.1}$$

$H_{spin-spin}$ manifestly remains the same in all directions (rotationally invariant). Not surprisingly, it is a zero rank spherical tensor operator. Another way of proving this is by recalling the definition of spherical tensor operators. A spherical tensor operator of rank k can be defined as an operator with $(2k+1)$ irreducible components which obey the following commutation relations [137]:

$$\left[\hat{\mathcal{J}}^z, \hat{T}_q^{(k)} \right] = \hbar q \hat{T}_q^{(k)} \tag{8.2a}$$

$$\left[\hat{\mathcal{J}}^\pm, \hat{T}_q^{(k)} \right] = \hbar \sqrt{(k \mp q)(k \pm q + 1)} \hat{T}_{q \pm 1}^{(k)} \tag{8.2b}$$

with $k = 0, 1, 2, \ldots$ and $-k \leq q \leq +k$. (Spherical tensor operators are often defined according to how they behave under rotation [170]. This involves the use of Wigner matrices and we would like to avoid them for now. We therefore stick to the definition above, which is much simpler to handle.) For example, if we compare the commutation relations in (6.18) with (8.2), we note that the trio $\hat{\mathcal{J}}^z, \hat{\mathcal{J}}^\pm$ must be proportional to the components of a rank $k = 1$ spherical tensor. Indeed, if we set:

$$\hat{T}_0^{(1)} = \hat{\mathcal{J}}^z \qquad \hat{T}_{\pm 1}^{(1)} = \mp \frac{1}{\sqrt{2}} \hat{\mathcal{J}}^\pm \tag{8.3}$$

we see that the relations in (8.2) are perfectly observed.

Going back to $\hat{\mathscr{H}}_{spin-spin}$, it can easily be verified that:

$$\left[\hat{\mathcal{J}}_{tot}^z, \hat{\mathscr{H}}_{spin-spin} \right] = \hat{0} \tag{8.4a}$$

$$\left[\hat{\mathcal{J}}_{tot}^\pm, \hat{\mathscr{H}}_{spin-spin} \right] = \hat{0} \tag{8.4b}$$

where, $\hat{\mathcal{J}}_{tot}^z = \sum_{i=1}^N \hat{\mathcal{J}}_i^z$ and $\hat{\mathcal{J}}_{tot}^\pm = \sum_{i=1}^N \hat{\mathcal{J}}_i^\pm$. In line with (8.2), we observe that since $\hat{\mathscr{H}}_{spin-spin}$ is not a null operator, (8.4) hold only if $\hat{\mathscr{H}}_{spin-spin}$ is proportional to a zero rank tensor ($k = 0$). From (8.4b), we also derive that:

$$\left[\hat{\mathcal{J}}_{tot}^x, \hat{\mathscr{H}}_{spin-spin} \right] = \hat{0} \tag{8.5a}$$

$$\left[\hat{\mathcal{J}}_{tot}^y, \hat{\mathscr{H}}_{spin-spin} \right] = \hat{0} \ . \tag{8.5b}$$

The conclusion we draw from the commutation relations stated in (8.4a), (8.5a) and (8.5b) is that the total spin angular momentum must be conserved along the three axes, just as one would expect from a rotationally invariant operator like $\hat{\mathscr{H}}_{spin-spin}$. The operators $\hat{\mathcal{J}}_{tot}^x, \hat{\mathcal{J}}_{tot}^y, \hat{\mathcal{J}}_{tot}^z$ are thus constants of motion for an isolated spin system whose spin Hamiltonian is given by $\hat{\mathscr{H}}_{spin-spin}$. Note that any linear combination of these three operators is also a constant of motion. Thus, the total spin angular momentum vector operator $\hat{\boldsymbol{\mathcal{J}}}_{tot}$, for example, is also a constant of motion. Not only that: any operator of the form $\hat{X}^r$, where $r = 1, 2, 3, \ldots$ and $\hat{X}$ is any of the operators $\hat{\boldsymbol{\mathcal{J}}}_{tot}$, $\hat{\mathcal{J}}_{tot}^x$, $\hat{\mathcal{J}}_{tot}^y$, $\hat{\mathcal{J}}_{tot}^z$, is also a constant of motion. The same applies to any linear combination of such powers of operators. However, not all pairs of operators of this vast family of constants of motions commute with each other. For example, $\hat{\mathcal{J}}^{x}_{tot}$ does not commute with $\hat{\mathcal{J}}^{y}_{tot}$. This is crucial because the easiest way to determine the energy spectrum of $\hat{\mathscr{H}}_{spin-spin}$, for example, is to express it as a function of a subset of mutually commuting operators which belong to this infinitely numerable family of constants of motion. Unfortunately, as far as we know at the moment, $\hat{\mathscr{H}}_{spin-spin}$ as given in (8.1) fails to succumb to this mathematical contrivance due to the arbitrary difference between the coupling constants $\{T_{i,i'}\}$. Numerical diagonalization of $\mathscr{H}_{spin-spin}$, therefore, seems the most reasonable route to the eigenvalues and eigenvectors of $\hat{\mathscr{H}}_{spin-spin}$, especially when dealing with multispin systems.

To find the eigenvalues and eigenvectors of $\mathscr{H}_{spin-spin}$, we can choose to simply take the whole $\mathscr{H}_{spin-spin}$ and diagonalize it using some standard software or algorithm (we may call this the 'tout court' approach). For very large $\mathscr{H}_{spin-spin}$, this route is hardly taken. The other approach is to first divide $\mathscr{H}_{spin-spin}$ into independent sub-units and then proceed with the diagonalization of each sub-unit. The HP transformation and the index compression map η_o discussed in Chap. 6 and Sec. 7.2, respectively, enables us to break $\mathscr{H}_{spin-spin}$ into sub-units in a computationally efficient manner.

First of all, consider two arbitrary multispin states $|\mathbb{n}\rangle\,(=|n_1,\ldots,n_N\rangle)$ and $|\mathbb{n}'\rangle\,(=|n'_1,\ldots,n'_N\rangle)$. From (8.4a), we have that:

$$\left\langle \mathbb{n}\right|\left[\hat{\mathcal{J}}^{z}_{tot},\hat{\mathscr{H}}_{spin-spin}\right]\left|\mathbb{n}'\right\rangle = 0\ . \tag{8.6}$$

Given that,

$$\hat{\mathcal{J}}^{z}_{tot} = \sum_{i=1}^{N}\left(j_i - \hat{b}^{\dagger}_{i}\hat{b}_{i}\right) = J_0 - \hat{\mathscr{N}} \tag{8.7}$$

(where $J_0 \equiv \sum_{i=1}^{N} j_i$ is the total spin of the system, and $\hat{\mathscr{N}} \equiv \sum_{i=1}^{N}\hat{b}^{\dagger}_{i}\hat{b}_{i}$ the total HP bosons occupation number operator), we note that – as one would expect – the kets $\{|\mathbb{n}\rangle\}$ are eigenvectors of $\hat{\mathcal{J}}^{z}_{tot}$:

$$\hat{\mathcal{J}}^{z}_{tot}\left|n_1,\ldots,n_N\right\rangle = \hat{\mathcal{J}}^{z}_{tot}\left|\mathbb{n}\right\rangle = \left(J_0 - n\right)\left|\mathbb{n}\right\rangle \tag{8.8}$$

where $n = \sum_{i=1}^{N} n_i$ is the total number of HP bosons contained in $|\mathbb{n}\rangle$. In light of (8.8), (8.6) reduces to the form:

$$\left(n - n'\right)\left\langle \mathbb{n}\right|\hat{\mathscr{H}}_{spin-spin}\left|\mathbb{n}'\right\rangle = 0 \tag{8.9}$$

where it becomes evident that $\left\langle \mathbb{n}\right|\hat{\mathscr{H}}_{spin-spin}\left|\mathbb{n}'\right\rangle = 0$ when $n \neq n'$. In other words, a necessary but not sufficient condition for the matrix element $\left\langle \mathbb{n}\right|\hat{\mathscr{H}}_{spin-spin}\left|\mathbb{n}'\right\rangle$ to be nonzero is that the two multispin states $|\mathbb{n}\rangle$ and $|\mathbb{n}'\rangle$ are represented by the same total number of HP bosons. The total number of HP bosons is thus conserved for a spin system with Hamiltonian $\hat{\mathscr{H}}_{spin-spin}$, (8.1); i.e. $\left[\hat{\mathscr{N}},\hat{\mathscr{H}}_{spin-spin}\right] = 0$ (this commutation relation easily follows from (8.4a) and (8.8)).

The importance of the relation in (8.9) even goes further than what we have concluded so far. Indeed, if $\left\langle \mathbb{n}\right|\hat{\mathscr{H}}_{spin-spin}\left|\mathbb{n}'\right\rangle$ is identically zero for any pair of states $|\mathbb{n}\rangle$ and $|\mathbb{n}'\rangle$ with different number of total HP bosons, it implies that in the matrix representation of $\hat{\mathscr{H}}_{spin-spin}$ according to the basis $\{|\mathbb{n}\rangle\}$, the matrix elements between states with the same total number n of HP bosons constitute a block which is orthogonal to all other possible blocks characterized by a different total number of HP bosons. In other words, if we decompose the Hamiltonian $\hat{\mathscr{H}}_{spin-spin}$ in the basis $\{|\mathbb{n}\rangle\}$, all the multispin states $|\mathbb{n}\rangle$ occupied by the same total number n of HP bosons compose a subspace $\mathcal{B}_n$ of the

HP bosons Fock space, and subspaces characterized by different n will be orthogonal to each other, i.e. $\mathcal{B}_n \perp \mathcal{B}_{n'}$ if $n \neq n'$. But since there is a one-to-one correspondence between the states $\{|\mathbb{n}\rangle\}$ and the normal multispin states $\{|j_1 m_1, \ldots, j_N m_N\rangle\}$, it means that the normal multispin Hilbert space of the system is also decomposed into orthogonal subspaces in similar fashion. In more concise mathematical terms, the subspace $\mathcal{B}_n$ is simply the set of kets defined as:

$$\mathcal{B}_n := \{|\mathbb{n}\rangle \;\mid \hat{\mathscr{N}}\,|\mathbb{n}\rangle = n\,|\mathbb{n}\rangle\,,\; \mathbb{0} \leq \mathbb{n} \leq (D_{\mathcal{H}} - 1)\} \tag{8.10}$$

(recall $D_{\mathcal{H}}$ is the dimension of the Hilbert space).

It is only natural at this point to ask ourselves to determine the range of n for a given multiset $\mathcal{A}$ of spins. Since $n = \sum_{i=1}^{N} n_i$, and $0 \leq n_i \leq 2j_i$, it is clear that $0 \leq n \leq 2J_0$. Consequently, for a given collection of spins whose Hamiltonian operator is the $q = 0$-th component of a rank k spherical tensor (see (8.2)) like $\hat{\mathscr{H}}_{spin-spin}$, the system's Hilbert space can always be decomposed into $(2J_0 + 1)$ orthogonal subspaces. This particular observation is far from new: as a matter of fact, it is well known that whenever an operator commutes with $\hat{\mathcal{J}}^z_{tot}$, the total spin magnetic quantum number M_z is conserved – which leads to the creation of orthogonal subspaces each characterized by a particular M_z. Since the total spin is J_0, the range of M_z is $-J_0 \leq M_z \leq J_0$, which means there are $(2J_0 + 1)$ distinct possible values of M_z, hence $(2J_0 + 1)$ orthogonal subspaces. Indeed, as it follows from (8.8), the connection between M_z and n is very simple: $M_z = J_0 - n$. Nonetheless, the use of n is far more convenient computationally than M_z because, unlike M_z whose values can be either all integers or all half-integers, the possible values of n are always nonnegative integers, independent of the collection of spins at hand. This is not the only advantage of using the HP transformation, and we shall discuss others shortly.

The realization of the orthogonal subspaces $\{\mathcal{B}_n\}$ also implies that the matrix representation of $\hat{\mathscr{H}}_{spin-spin}$, $\mathscr{H}_{spin-spin}$, is block-diagonalized in the basis $\{|\mathbb{n}\rangle\}$. In fact, the relation

$$\mathscr{H}_{spin-spin} = \bigoplus_{n=0}^{2J_0} \mathscr{B}_n = \operatorname{diag}\left(\mathscr{B}_0, \mathscr{B}_1, \ldots, \mathscr{B}_{2J_0}\right) = \begin{pmatrix} \boxed{\mathscr{B}_0} & & \\ & \boxed{\ddots} & \\ & & \boxed{\mathscr{B}_{2J_0}} \end{pmatrix} \tag{8.11}$$

holds true. The block matrix $\mathscr{B}_n$ collects the matrix elements of $\hat{\mathscr{H}}_{spin-spin}$ between kets belonging to the subspace $\mathcal{B}_n$, i.e.

$$\mathscr{B}_n := \left\{ \left\langle \mathbb{n} \middle| \hat{\mathscr{H}}_{spin-spin} \middle| \mathbb{n}' \right\rangle \;\middle|\; \forall \mathbb{n}, \mathbb{n}' \in \mathcal{B}_n \right\} \,. \tag{8.12}$$

Given a multiset $\mathcal{A}$ of spins, we shall indicate the dimension of the block matrix $\mathscr{B}_n$ as $\Omega_{\mathcal{A},n}$, which is also the dimension of the orthogonal subspace $\mathcal{B}_n$. Thus, for consistency,

$$D_{\mathcal{H}} = \sum_{n=0}^{2J_0} \Omega_{\mathcal{A},n} \,. \tag{8.13}$$

The very crucial implication of (8.11) is that the eigendecomposition of $\mathscr{H}_{spin-spin}$ can be equally achieved by eigendecomposing each $\mathscr{B}_n$ independently, with the benefit of reducing the computational cost (in both computing time and memory). If the computational cost of the eigendecomposition of a square matrix of dimension M is $\mathcal{O}(M^p)$ (in most cases $p \approx 3$), we see that the computational cost of eigendecomposing $\mathscr{H}_{spin-spin}$ tout court is $\mathcal{O}(D_{\mathcal{H}}^p)$. In contrast, if we choose to determine the eigenvalues and eigenvectors of $\mathscr{H}_{spin-spin}$ by eigendecomposing the block matrices $\mathscr{B}_n$, then the computational cost turns out to be: $\mathcal{O}(\Omega_{\mathcal{A},0}^p) + \mathcal{O}(\Omega_{\mathcal{A},1}^p) + \ldots + \mathcal{O}(\Omega_{\mathcal{A},2J_0}^p)$. Due to the relation in (8.13), it is patently obvious that for $p > 1$,

$$\mathcal{O}(D_{\mathcal{H}}^p) > \mathcal{O}(\Omega_{\mathcal{A},0}^p) + \mathcal{O}(\Omega_{\mathcal{A},1}^p) + \ldots + \mathcal{O}(\Omega_{\mathcal{A},2J_0}^p) \tag{8.14}$$

which confirms our assertion that eigendecomposing the block matrices $\mathscr{B}_n$ costs less than the tout court eigendecomposition of $\mathscr{H}_{spin-spin}$. (In this analysis, we have tacitly assumed that the computational cost of generating the $\mathscr{H}_{spin-spin}$ matrix is the same as the total cost of generating the block matrices $\{\mathscr{B}_n\}$.)

8.2.1 Integer partitions. Dimension of the submatrices $\mathscr{B}_n$. Density and sparseness of $\mathscr{H}_{spin-spin}$

Another significant feature of the HP transformation is that it allows us to easily determine the dimension $\Omega_{\mathcal{A},n}$ of the various submatrices $\mathscr{B}_n$, analytically. This is a feat hardly achievable using the normal spin representation.

The analytical determination of the value of $\Omega_{\mathcal{A},n}$ has been extensively covered in [66] so we shall just limit ourselves to some key points in the following. The interested Reader may see [66] for a more elaborate exposition of the problem.

Recall that $|\mathbb{n}\rangle = |n_1, n_2, \ldots, n_N\rangle$, and $\mathbb{n} = \eta_o(n_1, n_2, \ldots, n_N)$ (see (7.1)). As already seen above, if $\hat{\mathscr{N}}\,|\mathbb{n}\rangle = n\,|\mathbb{n}\rangle$, then $n = \sum_{i=1}^{N} n_i$ (see (8.7) and (8.8)). We also need to bear in mind that each n_i is restricted to the range $0 \leq n_i \leq 2j_i$. Since $\Omega_{\mathcal{A},n}$ is the number of kets $|\mathbb{n}\rangle$ which contain the same total number of HP bosons ((8.10) and (8.12)), the problem at hand is equivalent to asking: in how many distinct ways can we distribute n indistinguishable objects among N sites, knowing that the $i-$th site can contain at most $2j_i$ objects? The number of ways this can be done is exactly $\Omega_{\mathcal{A},n}$. Counting problems like this is the subject of a branch of discrete mathematics called Enumerative Combinatorics [148], which fundamentally deals with how to count the elements of a finite set. Several ways of computing $\Omega_{\mathcal{A},n}$ are illustrated in [66] but we shall focus here on just one of these, namely the generating function approach. Generating functions in Enumerative Combinatorics are *formal* power series (in one or multiple variables) whose coefficients are proportional to the solutions to a counting problem.

Consider for example the partition of integers. The partition of a positive integer n is a way one can obtain n through the sum of positive integers, order being irrelevant. For example, take the integer 4, since:

$$\begin{aligned} 4 &= 4 \\ &= 3+1 \\ &= 2+2 \\ &= 2+1+1 \\ &= 1+1+1+1 \end{aligned} \tag{8.15}$$

the sums on the RHS are all partitions of 4. Each summand in a given partition is referred to as a *part*. Thus, the partitions $3+1$ and $2+2$ have both two parts, while the partition $2+1+1$ has three parts. Say $p(n)$ the total number of partitions of the integer n. $p(n)$ is known as the *partition function*. We see that $p(n=4)=5$, for example, since the integer 4 can be partitioned in five different ways as illustrated above. We may then pose the following problem: given an arbitrary (positive) integer n, in how many ways can we partition it? Or, in other words, what is the value of its $p(n)$? Variant forms of this problem have been proposed throughout centuries. According to known records, it seems Gottfried Wilhelm von Leibniz (1646-1716) was the first to pose a variant of this problem in a letter to Johann Bernoulli (1667-1748) [40]. Leibniz was interested in how many ways an integer could be partitioned into two, three, etc., parts. In Leibniz's problem, we clearly see there is a constrain on the number of parts. This falls under what we call today *restricted partitions*. For example, there is only one way to partition 4 into three parts, and that is $2+1+1$. In a letter to the great Leonhard Euler, one Naudé wanted to know how many ways the integer 50 can be obtained from the sum of seven parts which are unequal to each other [1, 9, 47]. Here, the restriction is both on the nature of the parts (i.e. each part cannot appear more than once) and the total number of parts. It is not far fetched to assume that Naudé's letter is what led the great Euler to his memorable *Observationes analyticae variae de combinationibus* [*Various analytical observations about combinations*] presented to the St. Petersburg Academy in 1741 but published in 1751 [1]. This is where Euler introduced for the first time the concept of generating function (though he did not coin the name) in the theory of partitions (and by extension, number theory). For example, he showed that $p(n)$ is the coefficient of q^n when $\prod_{i=1}^{\infty}\frac{1}{1-q^i}$ is expanded in powers of q. Namely [9, 47],

$$\begin{aligned}\prod_{i=1}^{\infty}\frac{1}{1-q^i} &= \sum_{n=0}^{\infty}p(n)q^n \\ &= 1+q+2q^2+3q^3+5q^4+7q^5+11q^6+15q^7+22q^8+\dots\end{aligned} \tag{8.16}$$

The function $\prod_{i=1}^{\infty}\frac{1}{1-q^i}$ is thus said to be the *generating function* for $p(n)$. Recall at the beginning of this section we defined generating functions as being *formal* power series. This is so because their variables have no intrinsic meaning. In the case of (8.16), q is the variable but though its exponents and coefficients have definite interpretations in relation to our counting problem, q is devoid of any. Perhaps, the most famous generating function in Number theory and Combinatorics is the one reported in (8.16). In response to Naudé's problem, Euler showed that if we denote with $\tilde{p}_k(n)$ the number of ways n can be partitioned into k mutually unequal parts, then [1, 47]:

$$q^{k(k+1)/2}\prod_{i=1}^{k}\frac{1}{1-q^i}=\sum_{n=0}^{\infty}\tilde{p}_k(n)q^n\ . \tag{8.17}$$

Thus, $q^{k(k+1)/2}\prod_{i=1}^{k}\frac{1}{1-q^i}$ is the *generating function* for $\tilde{p}_k(n)$. To solve Naudé's original problem, we set $n=50$ and $k=7$; so from (8.17) it follows that $\tilde{p}_7(50)=522$, which is obtained by expanding $q^{28}\prod_{i=1}^{7}\frac{1}{1-q^i}$ and taking the coefficient of the term q^{50}. Hence, there are 522 ways one can write the integer 50 as the sum of exactly seven mutually unequal positive integers. Euler's original paper, now translated into English by Jordan Bell [47], is an excellent and easy-to-read introduction to generating functions and it is accessible to anyone with a high school knowledge of algebra. We strongly recommend it to Readers who are new to the concept.

Instead of determining the solution to counting problems by means of generating functions, we may seek explicit formulae for the desired quantities. For instance, we may ask ourselves if there is an explicit formula for $p(n)$. It is a problem which quite a number of generations of mathematicians had to wrestle with. The first significant breakthrough came in Godfrey H. Hardy (1877-1947) and Srinivasa Ramanujan's (1887-1920) celebrated 1918 paper entitled *Asymptotic formulae in combinatory analysis* [67]. In that paper, Hardy and Ramanujan presented an asymptotic series for $p(n)$ but whose main defect was that it failed to converge. A couple of decades had to pass before Hans Rademacher (1892-1969) derived an improved version of Hardy and Ramanujan's result which, finally, had no convergence problem [126].

The Reader might be wondering why we have dedicated so many lines to integer partitions. The reason is very simple: the determination of the value of $\Omega_{\mathscr{A},n}$ may be reinterpreted as an integer partition problem. This is how the close relation between multispin dynamics, on one hand, and Number theory and Enumerative Combinatorics (specifically in this case, the theory of partitions) elegantly emerges from the HP transformation. Indeed, if, as noted earlier, $\Omega_{\mathscr{A},n}$ is the number of ways the integer n can be obtained through the sum $n = \sum_{i=1}^{N} n_i$, where $0 \leq n_i \leq 2j_i$, it is clear that:

> $\Omega_{\mathscr{A},n}$ is the number of partitions of the integer n into N parts, with the $i-$th part restricted to the range $0 \leq n_i \leq 2j_i$.

Certainly, just like $\tilde{p}_k(n)$, $\Omega_{\mathscr{A},n}$ is restricted to a fixed number of parts. But unlike $p(n)$ and $\tilde{p}_k(n)$, $\Omega_{\mathscr{A},n}$ has the following properties:

1. the minimum value of a part in any of its partitions is 0, not 1;
2. the partitions of interest here are all *ordered* (so for example, $2+1+1$ must be considered different from $1+2+1$); this is because each part n_i refers to a distinct spin.

Consider for example the deuterated hydroxymethyl radical ($^{\cdot}\mathrm{CH_2OD}$), which corresponds to the multiset of spins $\mathscr{A} = \{j_1, j_2, j_3, j_4\} = \{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 1\}$ (see Chap. 7.2). Therefore, according to the conventions discussed in Sec. 7.2, we know that since $j_1 = j_2 = j_3 = \frac{1}{2}$ and $0 \leq n_i \leq 2j_i$, then $0 \leq n_1, n_2, n_3 \leq 1$, while $0 \leq n_4 \leq 2$. $\Omega_{\mathscr{A},n}$ is then the number of ordered partitions of n into exactly $N = 4$ parts, such that the first three parts are at most 1 and the fourth part is at most 2 (with 0 being an admissible value of a part). We also need to bear in mind that $\Omega_{\mathscr{A},n}$ is also equivalent to the number of states $|\mathbb{n}\rangle$ which contain exactly n HP bosons. For example, with $n = 2$, we find from table 7.1 that the states $|\mathbb{n}\rangle$ which contain in total two HP bosons are:

$$\begin{array}{ccc}
|\mathbb{2}\rangle = |0,0,0,2\rangle & |\mathbb{4}\rangle = |0,0,1,1\rangle & |\mathbb{7}\rangle = |0,1,0,1\rangle \\
|\mathbb{9}\rangle = |0,1,1,0\rangle & |\mathbb{13}\rangle = |1,0,0,1\rangle & |\mathbb{15}\rangle = |1,0,1,0\rangle \\
 & |\mathbb{18}\rangle = |1,1,0,0\rangle &
\end{array}$$

Thus, for the radical $^{\cdot}\mathrm{CH_2OD}$, $\Omega_{\mathscr{A},2} = 7$. That is, there are seven ways of partitioning the integer 2 into four parts, with the restriction that the first three parts cannot exceed the value of 1 and the fourth part cannot be greater than 2. Thus, the subspace $\mathcal{B}_{n=2}$ for $^{\cdot}\mathrm{CH_2OD}$ is of dimension $\Omega_{\mathscr{A},2} = 7$. In the particular case of $^{\cdot}\mathrm{CH_2OD}$, $n = 2$ corresponds to the total spin magnetic number $M_z = J_0 - n = \frac{5}{2} - 2 = +\frac{1}{2}$. Note that these results actually still hold for any multispin system with three spin-$\frac{1}{2}$ and one spin-1.

How can we determine the value of $\Omega_{\mathscr{A},n}$ without having to explicitly write down all the kets $|\mathbb{n}\rangle$ (and how the HP bosons are disposed in them)? This problem has been solved and discussed in [66]. We discuss here only the generating function for $\Omega_{\mathscr{A},n}$ without going into much details. The interested Reader may see [66] for further discussions, explicit formulae for $\Omega_{\mathscr{A},n}$ and proofs.

Before we present the generating function for $\Omega_{\mathscr{A},n}$ it is advisable we briefly see what is meant by the *q-analogue* of a nonnegative integer n. The $q-$analogue of the integer n, indicated as $[n]_q$, is defined as [66, 81]:

$$[n]_q := \frac{1-q^n}{1-q} = 1 + q + q^2 + \ldots + q^{n-1} \ . \tag{8.18}$$

Note that $\lim_{q\to 1}[n]_q = n$.

It can be shown that the generating function for $\Omega_{\mathscr{A},n}$, $G_{\mathscr{A},\Omega}(q)$, is [66]:

$$G_{\mathscr{A},\Omega}(q) = \prod_{\alpha} \left([2j_\alpha + 1]_q\right)^{N_\alpha} \tag{8.19}$$

where the index α runs over distinct values of the spin multiset $\mathscr{A}$ and N_α is the multiplicity of the $\alpha-$th distinct element in $\mathscr{A}$. Hence,

$$\prod_{\alpha} \left([2j_\alpha + 1]_q\right)^{N_\alpha} = \sum_{n=0}^{2J_0} \Omega_{\mathscr{A},n} q^n \ . \tag{8.20}$$

It is worth noting that if we take the limit $q \to 1$ of (8.20) we get (8.13). To illustrate the use of (8.20), let us consider once again $^{\cdot}\mathrm{CH_2OD}$. We know that for this radical, $\mathscr{A} = \{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 1\}$. $\mathscr{A}$ has thus only two distinct elements: $j_{\alpha=1} = \frac{1}{2}$ and $j_{\alpha=2} = 1$. The multiplicity of $j_{\alpha=1}$ is 3 while that of $j_{\alpha=2}$ is 1. Therefore, $N_{\alpha=1} = 3$ and $N_{\alpha=2} = 1$. Moreover, $[2j_{\alpha=1} + 1]_q = [2]_q = (1+q)$ and $[2j_{\alpha=2} + 1]_q = [3]_q = (1 + q + q^2)$. Thus, in the case of the radical $^{\cdot}\mathrm{CH_2OD}$, (8.20) becomes:

$$(1+q)^3(1+q+q^2) = \sum_{n=0}^{5} \Omega_{\mathscr{A},n} q^n \ . \tag{8.21}$$

Since,

$$(1+q)^3(1+q+q^2) = 1 + 4q + 7q^2 + 7q^3 + 4q^4 + q^5 \tag{8.22}$$

we conclude that:

$$\Omega_{\mathscr{A},0} = \Omega_{\mathscr{A},5} = 1 \qquad \Omega_{\mathscr{A},1} = \Omega_{\mathscr{A},4} = 4 \qquad \Omega_{\mathscr{A},2} = \Omega_{\mathscr{A},3} = 7 \tag{8.23}$$

which is in agreement with the previous value we found for $\Omega_{\mathscr{A},2}$. In regards to $^{\cdot}\mathrm{CH_2OD}$, its subspaces $\mathcal{B}_n$, their respective dimension and basis elements are reported in table 8.1. While the correspondence between the first two columns will always remain the same, the basis kets $|\mathbb{n}\rangle$ spanning each subspace depends on the order chosen when labelling the spins. The kets in table 8.1 are the same kets in table 7.1, therefore they correspond to the same ordered multiset of spins $\mathscr{A} = \{j_1, j_2, j_3, j_4\} = \{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 1\}$.

What immediately catches our attention looking at the RHS of (8.22) (or the second column of table 8.1) is the "palindromic" distribution of $\Omega_{\mathscr{A},n}$'s values. This is not an exception but the rule. Indeed, one can prove that the generating function $G_{\mathscr{A},\Omega}(q)$ is a *reciprocal* polynomial. Namely [66]:

$$\Omega_{\mathscr{A},n} = \Omega_{\mathscr{A},2J_0-n} \ . \tag{8.24}$$

Subspace $\mathcal{B}_n$	Dimension of subspace, $\Omega_{\mathscr{A},n}$	Basis elements, $\vert\mathbb{n}\rangle$
$\mathcal{B}_0$	1	$\vert\mathbb{0}\rangle$
$\mathcal{B}_1$	4	$\vert\mathbb{1}\rangle$, $\vert\mathbb{3}\rangle$, $\vert\mathbb{6}\rangle$, $\vert\mathbb{12}\rangle$
$\mathcal{B}_2$	7	$\vert\mathbb{2}\rangle$, $\vert\mathbb{4}\rangle$, $\vert\mathbb{7}\rangle$, $\vert\mathbb{9}\rangle$, $\vert\mathbb{13}\rangle$, $\vert\mathbb{15}\rangle$, $\vert\mathbb{18}\rangle$
$\mathcal{B}_3$	7	$\vert\mathbb{5}\rangle$, $\vert\mathbb{8}\rangle$, $\vert\mathbb{10}\rangle$, $\vert\mathbb{14}\rangle$, $\vert\mathbb{16}\rangle$, $\vert\mathbb{19}\rangle$, $\vert\mathbb{21}\rangle$
$\mathcal{B}_4$	4	$\vert\mathbb{11}\rangle$, $\vert\mathbb{17}\rangle$, $\vert\mathbb{20}\rangle$, $\vert\mathbb{22}\rangle$
$\mathcal{B}_5$	1	$\vert\mathbb{23}\rangle$

Table 8.1: Orthogonal subspaces $\mathcal{B}_n$, their respective dimension and basis kets for the radical $^{\cdot}\mathrm{CH_2OD}$ in the case whereby the system's spin Hamiltonian is proportional to the $q = 0-$th component of a spherical tensor of rank k – $\hat{\mathscr{H}}_{spin-spin}$, (8.1), being an example.

A polynomial $P(x) = a_0 + a_1x + a_2x^2 + \ldots + a_sx^s$ with real coefficients is said to be reciprocal (or *palindromic*) if its coefficients are such that $a_i = a_{s-i}$ for all $i = 0, 1, \ldots, s$ [10]. An equally equivalent definition is that $P(x)$ is reciprocal if $x^sP\left(\frac{1}{x}\right) = P(x)$ [10]. The implication of (8.24) is that the subspaces $\mathcal{B}_n$ and $\mathcal{B}_{2J_0-n}$ have the same dimension. We shall give a simple proof of (8.24) later when we discuss time-reversal symmetry. For now, we also point out that $G_{\mathscr{A},\Omega}(q)$ is also *unimodal* [10], namely, there exists an integer n' such that:

$$\Omega_{\mathscr{A},0} \leq \Omega_{\mathscr{A},1} \leq \Omega_{\mathscr{A},2} \leq \ldots \leq \Omega_{\mathscr{A},n'} \geq \Omega_{\mathscr{A},n'+1} \geq \Omega_{\mathscr{A},n'+2} \geq \ldots \geq \Omega_{\mathscr{A},2J_0} \; . \tag{8.25}$$

This n' is found to be $n' = \lfloor J_0 \rfloor$[66], where $\lfloor \bullet \rfloor$ is the floor function. Clearly, $\Omega_{\mathscr{A},\lfloor J_0 \rfloor}$ is the maximum value the $\{\Omega_{\mathscr{A},n}\}$ may assume. Note that $\Omega_{\mathscr{A},\lfloor J_0 \rfloor}$ may not be the only $\Omega_{\mathscr{A},n}$ with this maximum value (afterall, $G_{\mathscr{A},\Omega}(q)$ is reciprocal). For example, in the case of $^{\cdot}\mathrm{CH_2OD}$, whose $\mathscr{A} = \{\frac{1}{2}^3, 1\}$, $J_0 = 5/2$; hence, $\lfloor J_0 \rfloor = \lfloor \frac{5}{2} \rfloor = 2$. Therefore, we expect $\Omega_{\mathscr{A},2}$ to have the maximum value any $\Omega_{\mathscr{A},n}$ here can possibly have. In fact, that is the case but $\Omega_{\mathscr{A},2}$ is not the only $\Omega_{\mathscr{A},n}$ with this maximum value since $\Omega_{\mathscr{A},3}$ also has the same value as $\Omega_{\mathscr{A},2}$ ((8.23)). For more on the properties of $G_{\mathscr{A},\Omega}(q)$ see [66].

In the limit case whereby all the spins are spin-$\frac{1}{2}$, i.e. the spin system is univariate (see §II) with $j = \frac{1}{2}$, $\mathscr{A} = \left\{\frac{1}{2}^N\right\}$, the generating function $G_{\mathscr{A},\Omega}(q)$ takes the simple form:

$$\begin{aligned} G_{\mathscr{A},\Omega}(q) &= (1+q)^N \\ &= \sum_{n=0}^{N} \Omega_{\mathscr{A},n} q^n \end{aligned} \tag{8.26}$$

Consequently, the dimension of the subspace $\mathcal{B}_n$, $\Omega_{\mathscr{A},n} = \Omega_{\{\frac{1}{2}^N\},n}$, in this limit case is given by a binomial coefficient:

$$\Omega_{\{\frac{1}{2}^N\},n} = \binom{N}{n} \; . \tag{8.27}$$

Let us consider for instance a spin system which consists of $N = 10$ spin-$\frac{1}{2}$s, i.e. $\mathscr{A} = \left\{\frac{1}{2}^{10}\right\}$. We are dealing here with a univariate spin system. If the spin Hamiltonian of the system commutes with $\hat{\mathscr{J}}^z_{tot}$ (so the Hamiltonian is proportional to a spherical tensor of rank k but $q = 0$, see (8.2)), the tout court approach will have us diagonalize a matrix of dimension $2^{10} = 1024$. But with the creation of the subspaces $\mathcal{B}_n$, we know that

$$\begin{aligned} G_{\mathscr{A},\Omega}(q) &= (1+q)^{10} \\ &= 1 + 10q + 45q^2 + 120q^3 + 210q^4 + 252q^5 + 210q^6 + 120q^7 + 45q^8 + 10q^9 + q^{10} \ . \end{aligned} \tag{8.28}$$

Thus, instead of eigendecomposing a matrix of dimension 1024 to determine the eigenvectors and eigenvalues of the spin Hamiltonian, we can equally obtain the same results by eigendecomposing smaller matrices of dimension $1, 10, 45, 120, 210$ and 252.

The distribution of the values of $\Omega_{\mathscr{A},n}$ does not only inform us about the dimension of the subspaces $\mathcal{B}_n$, but they also help us to quantify how sparse the matrix $\mathscr{H}_{spin-spin}$ is. Let us define the density $\zeta(A)$ of an arbitrary matrix A as the ratio between the number of its nonzero elements and the dimension of A. Analogously, we define the sparseness $\chi(A)$ of the matrix A as the fraction of the elements of the latter which are identically zero. Naturally, for any given matrix A:

$$\zeta(A) + \chi(A) = 1 \ . \tag{8.29}$$

It is easy to prove that $\zeta(\mathscr{H}_{spin-spin})$ is subject to the tight upper bound:

$$\zeta(\mathscr{H}_{spin-spin}) \leq \frac{\sum_{n=0}^{2J_0} \Omega_{\mathscr{A},n}^2}{D_{\mathcal{H}}^2} \tag{8.30}$$

independent of the specific values of the coupling constants $T_{i,i'}$. If we go back to the radical $^{\cdot}CH_2OD$, for example, $\zeta(\mathscr{H}_{spin-spin}) \leq \frac{132}{24^2} \sim 0.23$. This means no matter what the values of the constants $T_{i,i'}$ are, the matrix representation of the Hamiltonian $\hat{\mathscr{H}}_{spin-spin}$ cannot have more than 23% of its elements being nonzero. This is not only true for $^{\cdot}CH_2OD$, but also for all multiset of spins $\mathscr{A} = \left\{\frac{1}{2}^3, 1\right\}$. Indeed, (8.30) holds for any arbitrary multiset of spins whose spin Hamiltonian is proportional to the zero-th component of a spherical tensor of rank k, where $k = 0, 1, 2, \ldots$

For a univariate spin system of N spin-$\frac{1}{2}$, i.e. $\mathscr{A} = \left\{\frac{1}{2}^N\right\}$, it follows from (8.27) and (8.30) that:

$$\zeta(\mathscr{H}_{spin-spin}) \leq \frac{\sum_{n=0}^{N} \binom{N}{n}^2}{2^{2N}} = \frac{\binom{2N}{N}}{4^N} \tag{8.31}$$

from which one derives that for very large N,

$$\zeta(\mathscr{H}_{spin-spin}) \lesssim \frac{1}{\sqrt{\pi N}} \ . \tag{8.32}$$

Equation (8.32) shows in unambiguous terms that for a system like $\mathscr{A} = \left\{\frac{1}{2}^N\right\}$, $\zeta(\mathscr{H}_{spin-spin})$ tends to zero as N becomes very large. For instance, if we consider the spin system $\mathscr{A} = \left\{\frac{1}{2}^{1000}\right\}$, i.e. a collection of 1000 spins, all of spin-$\frac{1}{2}$, then $\zeta(\mathscr{H}_{spin-spin}) \lesssim \frac{1}{\sqrt{\pi 1000}} \approx 0.018$; which means the elements of $\mathscr{H}_{spin-spin}$ which are identically zero will never drop below 98% of the total entries.

Interestingly, we note that if we begin with a spin system $\mathscr{A} = \left\{\frac{1}{2}^N\right\}$, and substitute one of the spins with a particle whose spin quantum number is greater than $1/2$, the new $\mathscr{H}_{spin-spin}$ is less denser than the original. We can thus imagine creating any collection of N spins from the multiset $\mathscr{A} = \left\{\frac{1}{2}^N\right\}$ by substitution. Given that anytime we substitute a spin-$1/2$ with a greater spin the density $\zeta(\mathscr{H}_{spin-spin})$ reduces, it implies that for any imaginable multiset $\mathscr{A} \neq \left\{\frac{1}{2}^N\right\}$ of spins,

$$\zeta(\mathscr{H}_{spin-spin}) < \frac{\binom{2N}{N}}{4^N} \tag{8.33}$$

and in the limit of a large number of spins,

$$\zeta(\mathscr{H}_{spin-spin}) < N^{-\delta} \ , \qquad \delta = \frac{1}{2}(1 + \log_N \pi) \ . \tag{8.34}$$

8.3 Eigenenergies of a system of equivalent spins in the absence of an external field.

We illustrate here another powerful application of the HP transformation. In the limit case whereby the multiset $\mathcal{A} = \{j_1, j_2, \ldots, j_N\}$ consists of solely N interacting *equivalent* spins (§II), $\hat{\mathscr{H}}_{spin-spin}$ ((8.1)) reduces to the form:

$$\hat{\mathscr{H}}_{spin-spin} = T \sum_{i>i'} \hat{\boldsymbol{\mathcal{J}}}_i \cdot \hat{\boldsymbol{\mathcal{J}}}_{i'} = T \sum_{i>i'} \left[\hat{\mathcal{J}}_i^z \hat{\mathcal{J}}_{i'}^z + \frac{1}{2} \left(\hat{\mathcal{J}}_i^+ \hat{\mathcal{J}}_{i'}^- + \hat{\mathcal{J}}_i^- \hat{\mathcal{J}}_{i'}^+ \right) \right] \ . \tag{8.35}$$

Since,

$$\hat{\boldsymbol{\mathcal{J}}}_{tot}^2 = \sum_i \hat{\boldsymbol{\mathcal{J}}}_i^2 + 2 \sum_{i>i'} \hat{\boldsymbol{\mathcal{J}}}_i \cdot \hat{\boldsymbol{\mathcal{J}}}_{i'} \ , \tag{8.36}$$

$\hat{\mathscr{H}}_{spin-spin}$ in (8.35) may be written as:

$$\hat{\mathscr{H}}_{spin-spin} = \frac{T}{2} \left(\hat{\boldsymbol{\mathcal{J}}}_{tot}^2 - \sum_i \hat{\boldsymbol{\mathcal{J}}}_i^2 \right) \ . \tag{8.37}$$

Given that $\hat{\boldsymbol{\mathcal{J}}}_{tot}$ commutes with $\hat{\boldsymbol{\mathcal{J}}}_i$, we can easily determine the eigenvalues of $\hat{\mathscr{H}}_{spin-spin}$ if we know those of $\hat{\boldsymbol{\mathcal{J}}}_{tot}^2$ and $\hat{\boldsymbol{\mathcal{J}}}_i^2$. Fortunately, the expression for the eigenvalues of this set of commuting operators is well known. From (6.16c), for example, we have that:

$$\hat{\mathscr{H}}_{spin-spin} = \frac{T}{2} \left[J_{tot} \left(J_{tot} + 1 \right) - \sum_i j_i (j_i + 1) \right] \hat{\mathbb{1}} \ . \tag{8.38}$$

As simple as (8.38) may seem, the actual computation of the eigenenergies is not an easy task for a generic $\mathcal{A}$ with $N > 2$. The difficulty here lies in computing the various total spin angular momentum J_{tot} and their multiplicities. But the J_{tot} and their respective multiplicities are the Clebsch-Gordan series, which is the multiset of all the possible total (spin) angular momenta one can get by coupling the N elements of $\mathcal{A}$. For example, if $N = 2$ (in which case (8.35) and (8.38) hold irrespective of whether the two spins are equivalent or not), we well know that $|j_1 - j_2| \leq J_{tot} \leq j_1 + j_2$. Certainly, when $N > 2$ one could determine the Clebsch-Gordan series by coupling j_1 and j_2, and then couple the resulting angular momenta with j_3, followed by the coupling of the new set of resulting angular momenta with j_4, and one repeats the scheme till one gets to j_N. Needless to say, this is truly cumbersome. It is understandable that if one has an easy and computationally efficient method of computing the Clebsch-Gordan series for a generic collection of spins, one also reduces dramatically the computational cost of determining the eigenvalues of $\hat{\mathscr{H}}_{spin-spin}$ in (8.35). Here again, the HP transformation is invaluable.

The problem of determining analytically the Clebsch-Gordan series for an arbitrary collection of spins $\mathcal{A}$ has been solved in [66]. We will therefore limit ourselves here to citing some salient results from [66] without providing any proof.

Consider an arbitrary collection of spins $\mathscr{A} = \{j_1, j_2, \dots, j_N\}$. The addition of the spin angular momentum of the elements of $\mathscr{A}$ will result in a collection (or multiset) of total spin angular momenta $\{J_{tot}\}$. Let us indicate the *distinct* elements of $\{J_{tot}\}$ as $J_0, J_1, J_2, \dots, J_m$, with J_0 being the maximum, J_1 the second highest and so forth. Consecutive distinct J_{tot} differ by 1, hence:

$$J_\kappa = J_0 - \kappa \ , \ \text{ where } \kappa = 0, 1, 2, \dots, m \ . \tag{8.39}$$

Clearly, $J_0 = j_1 + j_2 + \ldots + j_N$. The first big challenge we encounter here is computing the value of J_m. It has been proved that [66]:

$$J_m = \upsilon_{\mathscr{A}} \cdot H(\upsilon_{\mathscr{A}}) + (1 - H(\upsilon_{\mathscr{A}})) \cdot \frac{(2J_0 \bmod 2)}{2} \tag{8.40}$$

where,

$$\upsilon_{\mathscr{A}} := 2 \cdot \max \mathscr{A} - J_0 \tag{8.41}$$

and where $H(x)$ is the Heaviside step function, defined here to be

$$H(x) := \begin{cases} 0, & \text{if } x < 0 \\ 1, & \text{if } x \geq 0 \ . \end{cases} \tag{8.42}$$

Say N_J the total number of distinct elements in $\{J_{tot}\}$. Evidently, $N_J = J_0 - J_m + 1$. At this point, we may represent the multiset $\{J_{tot}\}$ as: $\{J_{tot}\} = \left\{J_0^{\lambda_0}, J_1^{\lambda_1}, \dots, J_m^{\lambda_m}\right\}$, where λ_κ is the multiplicity of J_κ.

Having determined all the distinct elements of $\{J_{tot}\}$ thanks to (8.39) and (8.40), we are half-way through in getting to the Clebsch-Gordan series. All we need to do now is to determine the multiplicities $\{\lambda_\kappa\}$. Once again, we can easily solve the problem by making use of the HP transformation. One can show that the generating function for λ_κ, $G_{\mathscr{A},\lambda}(q)$, is related to $G_{\mathscr{A},\Omega}(q)$ – (8.19) – through the relation [66]:

$$G_{\mathscr{A},\lambda}(q) = (1 - q) G_{\mathscr{A},\Omega}(q) = \sum_{\kappa=0}^{2J_0+1} \lambda_\kappa q^\kappa \ . \tag{8.43}$$

The polynomial $G_{\mathscr{A},\lambda}(q)$ is *antipalindromic* since,

$$\lambda_\kappa = -\lambda_{2J_0+1-\kappa} \ . \tag{8.44}$$

Moreover, it can be easily proved that:

$$\sum_{\kappa=0}^{m} \lambda_\kappa = \Omega_{\mathscr{A},m} \tag{8.45}$$

i.e. the cardinality of the Clebsch-Gordan series is exactly $\Omega_{\mathscr{A},m}$.

In our current quest to determine the eigenvalues of the Hamiltonian $\hat{\mathscr{H}}_{spin-spin}$ of (8.35), we see that since the multiset $\mathscr{A}$ is fixed, the eigenvalues of $\hat{\mathscr{H}}_{spin-spin}$ can be distinguished on the basis of J_{tot}. We may thus indicate these eigenenergies as $E_{J_{tot}}$, or E_κ on the basis of (8.39). We shall employ the latter in the following. It then follows from (8.38) and (8.39) that:

$$E_\kappa = E_0 - \frac{T}{2} \kappa \left(2J_0 + 1 - \kappa\right) \tag{8.46}$$

where $\kappa = 0, 1, 2, \ldots, m = (J_0 - J_m)$, and

$$E_0 := \frac{T}{2}\left(J_0^2 - \sum_i j_i^2\right) \ . \tag{8.47}$$

The following observations on the system readily follows from (8.46):

1. if $T > 0$, then E_m is the ground state ($J_{tot} = J_m$) energy and E_0 is the energy of the highest excited state;

2. if $T < 0$, then E_0 is the energy of the ground state ($J_{tot} = J_0$), and E_m is the energy of the highest excited state;

3. $E_{\kappa+1} - E_\kappa = -TJ_\kappa$. This means that the energy of multispin states with consecutive J_{tot} at the lower end of $\{J_{tot}\}$ (i.e. as J_κ approaches J_m) are relatively less spaced compared to their counterparts at the higher end.

Furthermore, given that the degeneracy of J_κ is $(2J_\kappa + 1)$, the total degeneracy of the energy level E_κ will thus be given by the product: $\lambda_\kappa(2J_\kappa + 1)$. The sum total of the degeneracy of the energy levels must return the dimension of the system's spin Hilbert space, $D_{\mathcal{H}}$. This leads us to the relation:

$$D_{\mathcal{H}} = \sum_{\kappa=0}^{m} \lambda_\kappa (2J_\kappa + 1) \tag{8.48}$$

which is a simple sum rule one can deploy to spot flaws in the calculations. Other sum rules can be derived from (8.48) by combining it with (8.39) and (8.45).

To illustrate the usefulness and potential of the relations and techniques discussed above, let us consider the multiset of spins $\mathscr{A} = \left\{\frac{1}{2}^7, 1^3\right\}$. Assuming $\mathscr{A}$ is a multiset of equivalent spins whose Hamiltonian is given by (8.38), we ask: what are the energy levels of the system and their respective degeneracy? As simple as this problem may appear, it is rather difficult – if not computationally time consuming – to solve using the conventional spin representation. The dimension of the spin Hilbert space alone is $D_{\mathcal{H}} = 3456$, though less than 0.96% of the matrix elements of the spin Hamiltonian is nonzero. It would be a waste of resources to construct such a matrix and then eigendecompose it to find the energy levels. It is even more computationally challenging to directly employ (8.38) to compute the energy levels because – to the best of my knowledge – there is not, hitherto, a generally valid efficient algorithm to compute the Clebsch-Gordan series for arbitrary multispin systems. In the framework of the HP transformation, such a problem can be effortlessly solved without the need to eigendecompose $\mathscr{H}_{spin-spin}$.

Naturally, the eigenenergies $\{E_\kappa\}$ of the system is given by (8.46). Concerning the distinct values of the multiset $\{J_{tot}\}$, we easily determine its maximum to be $J_0 = \frac{13}{2}$. From (8.40), the minimum J_{tot} is found to be $J_m = \frac{1}{2}$. Thus, there are $N_J = J_0 - J_m + 1 = 7$ distinct values of J_{tot}, and $m = J_0 - J_m = 6$. The distinct J_{tot} are: $\{J_0, J_1, J_2, J_3, J_4, J_5, J_6\} = \left\{\frac{13}{2}, \frac{11}{2}, \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}\right\}$. We now determine the multiplicity of each J_{tot} by employing the generating function $G_{\mathscr{A},\lambda}(q)$, (8.43). First of all, from (8.19), we have that $G_{\mathscr{A},\Omega}(q) = (1+q)^7(1+q+q^2)^3$. Therefore,

$$\begin{aligned} G_{\mathscr{A},\lambda}(q) &= (1-q)(1+q)^7(1+q+q^2)^3 \\ &= 1 + 9q + 38q^2 + 99q^3 + 174q^4 + 207q^5 + 145q^6 + \ldots - q^{14} \\ &= \sum_{\kappa=0}^{14} \lambda_\kappa q^\kappa \ . \end{aligned} \tag{8.49}$$

We therefore conclude that the Clebsch-Gordan series for $\mathscr{A} = \left\{\frac{1}{2}^7, 1^3\right\}$ is given by the multiset $\{J_{tot}\} = \left\{\frac{13}{2}, \frac{11}{2}^9, \frac{9}{2}^{38}, \frac{7}{2}^{99}, \frac{5}{2}^{174}, \frac{3}{2}^{207}, \frac{1}{2}^{145}\right\}$. With these values, we can now easily compute all the eigenenergies E_κ of the system from (8.46). The results are reported in table 8.2, where we have also calculated the degeneracy of each energy level. As expected on the basis of (8.48), the sum of these degeneracies gives exactly 3456 – which we recall is the dimension of the spin Hilbert space of the system.

κ	J_κ	λ_κ	$E_\kappa - E_0$	Degeneracy of E_κ
0	$\frac{13}{2}$	1	0	14
1	$\frac{11}{2}$	9	$-\frac{13}{2}T$	108
2	$\frac{9}{2}$	38	$-12T$	380
3	$\frac{7}{2}$	99	$-\frac{33}{2}T$	792
4	$\frac{5}{2}$	174	$-20T$	1044
5	$\frac{3}{2}$	207	$-\frac{45}{2}T$	828
6	$\frac{1}{2}$	145	$-24T$	290
				$\sum = 3456$

Table 8.2: Energy levels and their respective degeneracy for a system of equivalent spins composed of seven spin-1/2 and three spin-1, $\mathscr{A} = \left\{\frac{1}{2}^7, 1^3\right\}$, whose Hamiltonian is given by (8.35).

It is worth considering the same problem but this time with $\mathscr{A} = \left\{\frac{1}{2}^N\right\}$. Surely, $J_0 = N/2$, and from (8.40), we derive that,

$$J_m = \begin{cases} \frac{(2J_0 \mod 2)}{2} & \text{if } N > 2 \\ 0 & \text{if } N = 2 \ . \end{cases}$$

For $N > 2$, we observe that $J_m = 0$ if N is even, while $J_m = 1/2$ if N is odd. Thus, the number of distinct J_{tot} to expect is $N_J = \lceil \frac{N-1}{2} \rceil + 1$, and $m = \lceil \frac{N-1}{2} \rceil$, where $\lceil \bullet \rceil$ is the ceiling function. Therefore, the distinct J_{tot} we get from the Clebsch-Gordan series for $\mathscr{A} = \left\{\frac{1}{2}^N\right\}$ are: $\{J_0, J_1, \ldots, J_{\lceil \frac{N-1}{2} \rceil}\} = \{N/2, N/2-1, \ldots, N/2 - \lceil \frac{N-1}{2} \rceil\}$. Here, the multiplicity λ_κ of J_κ obeys the simple relation:

$$\lambda_\kappa = \binom{N}{\kappa} - \binom{N}{\kappa-1} = \frac{N+1-2\kappa}{N+1-\kappa}\binom{N}{\kappa} \ , \quad \kappa = 0, 1, 2, \ldots, m \ . \tag{8.50}$$

(8.50) readily follows from (8.26), (8.27) and (8.43).

8.4 Time-reversal symmetry. Creation of submatrices $\mathscr{B}_n$.

To the best of my knowledge, in the general context of (8.1), it is not in general possible to easily determine the eigenvalues of $\hat{\mathscr{H}}_{spin-spin}$ like we just did for an arbitrary collection of equivalent spins in the last section. In general, the eigendecomposition of $\hat{\mathscr{H}}_{spin-spin}$ requires, first of all, creating the submatrices $\{\mathscr{B}_n\}$ and then eigendecomposing each separately, (8.11). To create the submatrix $\mathscr{B}_n$ in the HP representation, we need a general formula for $\hat{\mathscr{H}}_{spin-spin}$'s matrix elements in terms of the HP bosons occupation numbers. Indeed, given any two basis kets $|\mathbb{n}'\rangle = |n'_1, n'_2, \ldots, n'_N\rangle$ and $|\mathbb{n}\rangle = |n_1, n_2, \ldots, n_N\rangle$, we derive from (8.1) that:

$$\begin{aligned}
\left\langle \mathbb{n}' \middle| \hat{\mathscr{H}}_{spin-spin} \middle| \mathbb{n} \right\rangle = \left\langle n'_1, n'_2, \ldots, n'_N \middle| \hat{\mathscr{H}}_{spin-spin} \middle| n_1, n_2, \ldots, n_N \right\rangle \\
= \delta_{\mathbb{n}',\mathbb{n}} \sum_{i>k} T_{i,k} (j_i - n_i)(j_k - n_k) \\
+ \frac{1}{2} \sum_{i>k} T_{i,k} \sqrt{\left(n_i + \frac{1 \pm 1}{2}\right)\left(2j_i - n_i + \frac{1 \mp 1}{2}\right)\left(2j_k - n_k + \frac{1 \pm 1}{2}\right)\left(n_k + \frac{1 \mp 1}{2}\right)} \\
\times\ \Delta_{i,k}\ \delta_{n'_i, n_i \pm 1}\ \delta_{n'_k, n_k \mp 1}
\end{aligned} \tag{8.51}$$

where,

$$\Delta_{i,k} := \prod_{l \neq i,k} \langle n'_l |\, n_l \rangle \ . \tag{8.52}$$

In deriving (8.51), we have made use of (6.14), (6.15) and (6.10a). (8.51) confirms once again that $\left\langle \mathbb{n}' \middle| \hat{\mathscr{H}}_{spin-spin} \middle| \mathbb{n} \right\rangle$ is identically zero when $|\mathbb{n}'\rangle$ and $|\mathbb{n}\rangle$ differ in the total number of HP bosons they contain.

It is worth noting that the creation of the submatrices $\mathscr{B}_n$ can be greatly simplified and done in an efficient manner if we make use of the time-reversal symmetry (or $T-$symmetry).

In the field of magnetic resonance (and in quantum chemistry, in general), we are accustomed to space symmetries like rotational and translational invariances, but we seldomly speak of time-reversal symmetry. One of the reasons for this, I suppose, can be attributed to the fact that unlike other symmetry operations like rotations and translations which are represented by unitary operators in quantum mechanics, $T-$ symmetry is represented by an *antiunitary* operator (see below) – whose properties depart considerably from the known unitary operators. In certain areas of quantum chemistry like vibrational spectroscopy, $T-$symmetry can be of no enlightening use, but in magnetic resonance it is often of vital importance as we shall shortly see. For more on $T-$symmetry, interested Readers may see (in this order): [136, 137, 171]. For an in-depth introduction embedded in some interesting philosophical discussions, see [133].

Let $\hat{\Theta}$ be the time-reversal operator. That is,

$$\hat{\Theta}\ t\ \hat{\Theta}^{-1} = -t \tag{8.53}$$

where t is the real parameter which indicates time. Like any operator representing a symmetry transformation, $\hat{\Theta}\hat{\Theta}^{-1} = \hat{\Theta}^{-1}\hat{\Theta} = \hat{\mathbb{1}}$. As already remarked above, unlike space rotation or translation operators which are unitary, the time-reversal operator $\hat{\Theta}$ is antiunitary. The major difference between these two types of symmetry operators is how they operate on complex scalars: unitary operators leave complex scalars intact, while antiunitary operators change complex scalars into their corresponding complex conjugate. For example, $\hat{\Theta} e^{i\alpha} \hat{\Theta}^{-1} = e^{-i\alpha^*}$, where α is a complex number whose complex conjugate is α^*.

There are many interesting properties of the time-reversal operator, but for our purposes, it suffices to know that all angular momentum operators (orbital and spin) are odd under the operation of time-reversal. Namely [133, 136, 137, 164],

$$\hat{\Theta}\hat{\boldsymbol{\mathcal{J}}}\hat{\Theta}^{-1} = -\hat{\boldsymbol{\mathcal{J}}} \ . \tag{8.54}$$

This simple relation has many profound consequences which will unfold before us shortly. To begin, it follows from (8.54) that $\hat{\Theta}\hat{\mathcal{J}}^z\hat{\Theta}^{-1} = -\hat{\mathcal{J}}^z$. Combining this with (6.5), we find that:

$$\hat{\Theta}\ \hat{b}^\dagger\hat{b}\ \hat{\Theta}^{-1} = 2j - \hat{b}^\dagger\hat{b} \ . \tag{8.55}$$

Till now, we have always seen spin kets of a spin-j as being represented by a number of HP bosons occupying a certain vacuum space which can accommodate at most $2j$ bosons. Another way of seeing it is to imagine this vacuum state as comprised of $2j$ holes (called HP holes), where each hole can be filled with no more than one HP boson at a time. In this picture, the sum of the number of HP bosons and holes is always $2j$. Therefore, if $\hat{b}^\dagger\hat{b}$ counts the number of HP bosons, then $(2j - \hat{b}^\dagger\hat{b})$ counts the number of holes. In other words, $(2j - \hat{b}^\dagger\hat{b})$ is the number operator for the holes. Going back to (8.55), the effect of the time-reversal operator now becomes perspicuous: it transforms the HP occupation number operator into a hole number operator. Put in another way, Θ instantly converts HP bosons into holes, and vice versa.

Before we proceed, let us see how $\hat{\Theta}$ transforms the single spin ket $|n\rangle$ and the multispin ket $|\mathbb{n}\rangle$. First of all, we note that (8.55) may be rewritten as:

$$\Big[\ \hat{\Theta},\ \hat{b}^\dagger\hat{b}\ \Big]_+ = 2j\hat{\Theta} \tag{8.56}$$

where $\Big[\hat{A},\hat{B}\Big]_+$ $(:= \hat{A}\hat{B} + \hat{B}\hat{A})$ denotes the anticommutation between $\hat{A}$ and $\hat{B}$. Say $|n\rangle$ a state ket of a particle of spin-j according to the HP representation, where, as usual, n represents the number of HP bosons. We define the state $\Theta\,|n\rangle \equiv |\overline{n}\rangle$ as the *time-reversed* or *hole complement of* $|n\rangle$. The state $|\overline{n}\rangle$ must necessarily be an admissible spin state, else the symmetry operation enacted by Θ would not be reversible. The reversibility of the time-reversal symmetry operation is guaranteed by the fact that $\hat{\Theta}\hat{\Theta}^{-1} = \hat{\Theta}^{-1}\hat{\Theta} = \hat{\mathbb{1}}$. After multiplying (8.56) from the right by $|n\rangle$, followed by an appropriate rearrangement of the terms, we get:

$$\hat{b}^\dagger\hat{b}\,|\overline{n}\rangle = (2j - n)\,|\overline{n}\rangle \tag{8.57}$$

where we have made use of (6.6). Comparing (8.57) with (6.6), it becomes immediately clear that:

$$\hat{\Theta}\,|n\rangle \equiv |\overline{n}\rangle = |2j - n\rangle \tag{8.58}$$

which is, once again, in line with the interpretation that $\hat{\Theta}$ converts HP bosons into holes, and holes into HP bosons. The dual ket relative to $\hat{\Theta}\,|n\rangle$ is $\langle n|\,\hat{\Theta}^{-1} \equiv \langle\overline{n}|$.

Let us now turn our attention to how $\hat{\Theta}$ operates on a multispin ket $|\mathbb{n}\rangle$. Consider the spin multiset $\mathcal{A} = \{j_1, j_2, \ldots, j_N\}$. From (8.7) and (8.55), it follows that:

$$\Big[\ \hat{\Theta},\ \hat{\mathscr{N}}\ \Big]_+ = 2J_0\hat{\Theta} \tag{8.59}$$

which is the analogous of (8.56) for multispin systems. Say $\hat{\Theta}\,|\mathbb{n}\rangle \equiv |\overline{\mathbb{n}}\rangle$ the hole complement of $|\mathbb{n}\rangle$ $(= |n_1, n_2, \ldots, n_N\rangle)$. We remind the Reader that the HP bosons occupation numbers n_i in $|n_1, n_2, \ldots, n_N\rangle$

are related to the integer $|\mathbb{n}\rangle$ through the index compression map η_0, (7.1). If we now multiply (8.59) from the right by $|\mathbb{n}\rangle$, we end up with the relation:

$$\hat{\mathscr{N}}\,|\overline{\mathbb{n}}\rangle = (2J_0 - n)\,|\overline{\mathbb{n}}\rangle \tag{8.60}$$

which implies that if $|\mathbb{n}\rangle$ belongs to the subspace $\mathcal{B}_n$, then its hole complement $|\overline{\mathbb{n}}\rangle$ is an element of the subspace $\mathcal{B}_{2J_0-n}$. Indeed, since there is a one-to-one correspondence between $|\mathbb{n}\rangle$ and $|\overline{\mathbb{n}}\rangle$, we also conclude that the hole complements of the basis kets in $\mathcal{B}_n$ constitute the basis kets of the subspace $\mathcal{B}_{2J_0-n}$. In other words, the two subspaces $\mathcal{B}_n$ and $\mathcal{B}_{2J_0-n}$ are related by time-reversal symmetry, and this holds independent of the nature of the spin Hamiltonian. The one-to-one correspondence we just mentioned, implies that the dimension of the subspaces $\mathcal{B}_n$ and $\mathcal{B}_{2J_0-n}$ must coincide, and indeed, that is something we already know from (8.24).

Note that,

$$\begin{aligned}\hat{\Theta}\,|\mathbb{n}\rangle = \hat{\Theta}\,|n_1, n_2, \ldots, n_N\rangle &= |\overline{n}_1, \overline{n}_2, \ldots, \overline{n}_N\rangle \\ &= |2j_1 - n_1, 2j_2 - n_2, \ldots, 2j_N - n_N\rangle \ .\end{aligned} \tag{8.61}$$

Thus,

$$|\overline{\mathbb{n}}\rangle = |2j_1 - n_1, 2j_2 - n_2, \ldots, 2j_N - n_N\rangle \ . \tag{8.62}$$

Hence, by virtue of the index compression map η_0, it follows from (7.1) that:

$$\overline{\mathbb{n}} = \sum_{i=1}^{N} \mathcal{W}_{R,i} \cdot (2j_i - n_i) = \sum_{i=1}^{N} \mathcal{W}_{R,i} \cdot (2j_i) - \mathbb{n} \ . \tag{8.63}$$

The term $\sum_{i=1}^{N} \mathcal{W}_{R,i} \cdot (2j_i)$ corresponds to the multispin state whereby all the single HP vacuum states are filled with the maximum number of HP bosons they can accommodate. But we know the index compression map η_0 always assigns to this state the integer $(D_{\mathcal{H}} - 1)$. Thus,

$$\overline{\mathbb{n}} = D_{\mathcal{H}} - 1 - \mathbb{n} \tag{8.64}$$

which leads us to conclude that:

$$\hat{\Theta}\,|\mathbb{n}\rangle \equiv |\overline{\mathbb{n}}\rangle = |D_{\mathcal{H}} - 1 - \mathbb{n}\rangle \tag{8.65}$$

where we recall once again that $D_{\mathcal{H}}$ is the dimension of the multispin Hilbert space. If we take the $^{\bullet}CH_2OD$ radical, for example, $D_{\mathcal{H}} = 24$, so $|\overline{\mathbb{n}}\rangle = |\mathbb{23} - \mathbb{n}\rangle$. This means that, for example, the multispin kets $|\mathbb{9}\rangle$ and $|\mathbb{14}\rangle$ $(= |\overline{\mathbb{9}}\rangle)$ are related by time-reversal symmetry. In fact, from table 7.1, one observes that if one converts all the HP bosons in $|\mathbb{9}\rangle$ into holes, and vice-versa, one obtains $|\mathbb{14}\rangle$. It is worth noting that for a given collection of spins $\mathscr{A}$, (8.65) is always valid, independent of how we choose to number-label the spins in $\mathscr{A}$. The corresponding dual ket of $\hat{\Theta}\,|\mathbb{n}\rangle$ is $\langle\mathbb{n}|\,\hat{\Theta}^{-1} \equiv \langle\overline{\mathbb{n}}| = \langle D_{\mathcal{H}} - 1 - \mathbb{n}|$.

We are now ready to see what the time-reversal symmetry reveals about the multispin system. To understand the importance of time-reversal symmetry here, it is worth considering how it transforms the multispin Hamiltonian $\hat{\mathscr{H}}_{spin-spin}$. From (8.1) and (8.54), it follows that:

$$\hat{\Theta}\hat{\mathscr{H}}_{spin-spin}\hat{\Theta}^{-1} = \hat{\mathscr{H}}_{spin-spin} \tag{8.66}$$

(note that the coupling constants $T_{i,i'}$ are all real) which means that $\hat{\mathscr{H}}_{spin-spin}$ is invariant under time-reversal. This is exactly what we should expect since $\hat{\mathscr{H}}_{spin-spin}$ describes the Hamiltonian of an isolated system, and we know that for such systems the homogeneity of time applies (i.e. the energy – or, in general, the physics – of the system remains the same under any time translation), so $\hat{\mathscr{H}}_{spin-spin}$ must certainly commute with $\hat{\Theta}$. Consider now the matrix element between the bra $\langle \mathbb{n}'|$ and ket $|\mathbb{n}\rangle$ according to (8.66):

$$\left\langle \mathbb{n}' \middle| \hat{\Theta}^{-1} \hat{\mathscr{H}}_{spin-spin} \hat{\Theta} \middle| \mathbb{n} \right\rangle = \left\langle \mathbb{n}' \middle| \hat{\mathscr{H}}_{spin-spin} \middle| \mathbb{n} \right\rangle \tag{8.67a}$$

$$\left\langle \overline{\mathbb{n}}' \middle| \hat{\mathscr{H}}_{spin-spin} \middle| \overline{\mathbb{n}} \right\rangle = \left\langle \mathbb{n}' \middle| \hat{\mathscr{H}}_{spin-spin} \middle| \mathbb{n} \right\rangle \ . \tag{8.67b}$$

Equation (8.67b) is of vital importance: it tells us that if we know the matrix element $\left\langle \mathbb{n}' \middle| \hat{\mathscr{H}}_{spin-spin} \middle| \mathbb{n} \right\rangle$ between the kets $|\mathbb{n}\rangle$ and $|\mathbb{n}'\rangle$ which are elements of the subspace $\mathcal{B}_n$, then we also know the corresponding matrix element between their hole complements in the subspace $\mathcal{B}_{2J_0-n}$. This observation reduces significantly the computational cost of creating the submatrices $\{\mathscr{B}_n\}$: once we know $\mathscr{B}_n$ we can easily create $\mathscr{B}_{2J_0-n}$. Another interpretation of (8.67b) is that if we convert all HP bosons into HP holes, and vice versa, the physics remain the same. This is a property we may call *particle-hole transformation invariance.*

Equation (8.66) has an even more profound implication. Since $\hat{\mathscr{H}}_{spin-spin}$ is decomposable into subspaces according to (8.11), each eigenvector of $\hat{\mathscr{H}}_{spin-spin}$ will also belong to only one of these subspaces. Say $\left|\mathscr{E}_\mu^{(n)}\right\rangle$ an eigenvector of $\hat{\mathscr{H}}_{spin-spin}$ but which belongs to the subspace $\mathcal{B}_n$:

$$\hat{\mathscr{H}}_{spin-spin} \left|\mathscr{E}_\mu^{(n)}\right\rangle = \mathscr{E}_\mu^{(n)} \left|\mathscr{E}_\mu^{(n)}\right\rangle \tag{8.68}$$

where $\mathscr{E}_\mu^{(n)}$ is the eigenvalue of $\hat{\mathscr{H}}_{spin-spin}$ relative to $\left|\mathscr{E}_\mu^{(n)}\right\rangle$. The index μ numbers the eigenvectors of $\hat{\mathscr{H}}_{spin-spin}$ in $\mathcal{B}_n$, so $\mu = 1, 2, \ldots, \Omega_{\mathcal{A},n}$ – where $\Omega_{\mathcal{A},n}$ is the dimension of $\mathcal{B}_n$, Sec. 8.2.1. As usual, the time-reversed state of $\left|\mathscr{E}_\mu^{(n)}\right\rangle$, $\left|\mathscr{E}_\mu^{(\overline{n})}\right\rangle$, is obtained by operating $\hat{\Theta}$ on $\left|\mathscr{E}_\mu^{(n)}\right\rangle$, i.e. $\left|\mathscr{E}_\mu^{(\overline{n})}\right\rangle = \hat{\Theta} \left|\mathscr{E}_\mu^{(n)}\right\rangle$. Given that $\left|\mathscr{E}_\mu^{(\overline{n})}\right\rangle = \left|\mathscr{E}_\mu^{(2J_0-n)}\right\rangle$, $\left|\mathscr{E}_\mu^{(\overline{n})}\right\rangle$ necessarily belongs to the subspace $\mathcal{B}_{2J_0-n}$. Since $\hat{\Theta}$ commutes with $\hat{\mathscr{H}}_{spin-spin}$ according to (8.66), it follows that:

$$\left[\hat{\mathscr{H}}_{spin-spin}, \hat{\Theta}\right] \left|\mathscr{E}_\mu^{(n)}\right\rangle = 0 \tag{8.69a}$$

$$\left(\mathscr{E}_\mu^{(\overline{n})} - \mathscr{E}_\mu^{(n)}\right) \left|\mathscr{E}_\mu^{(\overline{n})}\right\rangle = 0 \tag{8.69b}$$

from which we deduce that $\mathscr{E}_\mu^{(\overline{n})} = \mathscr{E}_\mu^{(n)}$. The implication of (8.69b) is this: two different eigenvectors of $\hat{\mathscr{H}}_{spin-spin}$ related by time-reversal symmetry also share the same eigenvalue. A far more reaching conclusion is that once we are able to create and eigendecompose the submatrice $\mathscr{B}_n$ of $\mathscr{H}_{spin-spin}$, (8.11), we do not need to create its hole complement $\mathscr{B}_{2J_0-n}$ and eigendecompose it de novo, because the eigenvalues of the two submatrices coincide and their eigenvectors are related through $\hat{\Theta}$. Finding the hole complement of an eigenvector can be easily done thanks to (8.65). For example, let the spin system whose Hamiltonian is given by $\hat{\mathscr{H}}_{spin-spin}$ in (8.1) be the $^{\cdot}CH_2OD$ radical. From table 7.1, we know that a generic normalized eigenvector $\left|\mathscr{E}_\mu^{(1)}\right\rangle$ of the subspace $\mathcal{B}_1$ is given by the linear combination:

$$\left|\mathscr{E}_\mu^{(n=1)}\right\rangle = c_{\mu,1} \left|\mathbb{1}\right\rangle + c_{\mu,2} \left|\mathbb{3}\right\rangle + c_{\mu,3} \left|\mathbb{6}\right\rangle + c_{\mu,4} \left|\mathbb{12}\right\rangle \tag{8.70}$$

where the $c_{\mu,i}$ are real coefficients, and $\sum_i c_{\mu,i}^2 = 1$. The corresponding hole complement of $\left|\mathscr{E}_\mu^{(n=1)}\right\rangle$,

$\left|\mathscr{E}_\mu^{(\overline{n}=4)}\right\rangle$, is an eigenvector which belongs to $\mathcal{B}_4$, and

$$\begin{aligned}\left|\mathscr{E}_\mu^{(\overline{n}=4)}\right\rangle &= \hat{\Theta}\left|\mathscr{E}_\mu^{(n=1)}\right\rangle \\ &= c_{\mu,1}\hat{\Theta}\left|\mathbb{1}\right\rangle + c_{\mu,2}\hat{\Theta}\left|\mathbb{3}\right\rangle + c_{\mu,3}\hat{\Theta}\left|\mathbb{6}\right\rangle + c_{\mu,4}\hat{\Theta}\left|\mathbb{12}\right\rangle \\ &= c_{\mu,1}\left|\mathbb{22}\right\rangle + c_{\mu,2}\left|\mathbb{20}\right\rangle + c_{\mu,3}\left|\mathbb{17}\right\rangle + c_{\mu,4}\left|\mathbb{11}\right\rangle\end{aligned} \tag{8.71}$$

where, in getting to the last step, we applied (8.65).

It is worth mentioning that there are instances whereby a subspace $\mathcal{B}_n$ coincides with its time-reversed counterpart. Recall that each subspace $\mathcal{B}_n$ is characterized by the total number n of HP bosons each of its basis kets contains. So, if each basis ket of the hole complement of $\mathcal{B}_n$, i.e. $\mathcal{B}_{2J_0-n}$, contains $(2J_0 - n)$ HP bosons, then $\mathcal{B}_n = \mathcal{B}_{2J_0-n}$ when both subspaces are characterized by the same number of HP bosons. That is, when $n = 2J_0 - n$ – which happens only when $n = J_0$. But n can assume the value of J_0 only when J_0 is an integer. This means that for multispin systems whose total spin quantum number J_0 is an integer, the subspace $\mathcal{B}_{n=J_0}$ is its own hole complement. While the eigenvalues of all the other subspaces are atleast double degenerate due to (8.69b), the same cannot be said of $\mathcal{B}_{n=J_0}$. Conversely, we also conclude that for multispin systems whose total spin quantum number J_0 is a half-integer, if the system's Hamiltonian is invariant under time-reversal symmetry, then the energy eigenvalues of the system are all atleast double degenerate. This conclusion is perfectly inline with Kramer's degeneracy theorem [137, 164].

Chapter 9

The isotropic multispin Hamiltonian in the presence of an external static magnetic field

The theoretical machinery developed in the previous chapters are still useful and relevant when we subject the previously isolated multispin system to a static magnetic field $\mathbf{B}_o$. If we take the direction of the external magnetic field $\mathbf{B}_o$ to be the axis of quantization $\boldsymbol{e}_z$, so that $\mathbf{B}_o = B_o \boldsymbol{e}_z$, then the new spin Hamiltonian of the system, $\hat{\mathscr{H}}_o$, is:

$$\hat{\mathscr{H}}_o = \hat{\mathscr{Z}} + \hat{\mathscr{H}}_{spin-spin} \tag{9.1}$$

where $\hat{\mathscr{H}}_{spin-spin}$ is still given by (8.1), and

$$\hat{\mathscr{Z}} := -B_o \sum_i \gamma_i \hat{\mathcal{J}}_i^z \ . \tag{9.2}$$

We know from (8.3) that $\hat{\mathcal{J}}^z$ is the zeroth component of a rank $k = 1$ spherical tensor, so $\hat{\mathscr{Z}}$ is also the zeroth component of a rank $k = 1$ tensor. We have also already seen that $\hat{\mathscr{H}}_{spin-spin}$ is a zero rank spherical tensor. Thus, $\hat{\mathscr{H}}_o$ is the sum of the zeroth components of spherical tensors of different ranks. But we know from (8.2a) that $\hat{\mathcal{J}}_{tot}^z$ commutes with the zeroth component ($q = 0$) of *any* spherical tensor operator. It therefore follows from these considerations that:

$$\left[\hat{\mathcal{J}}_{tot}^z, \hat{\mathscr{H}}_o\right] = \hat{0} \tag{9.3}$$

which is in complete analogy to (8.4a). This is significant because it means that all the results we derived above for the isolated multispin system on the basis of (8.4a) also apply here. For example, $\hat{\mathscr{H}}_o$, like $\hat{\mathscr{H}}_{spin-spin}$, conserves the total number of HP bosons. So, $\left\langle \mathbb{m}' \middle| \hat{\mathscr{H}}_o \middle| \mathbb{m} \right\rangle = 0$, if the multispin kets $|\mathbb{m}'\rangle$ and $|\mathbb{m}\rangle$ do not contain the same total number of HP bosons. The conservation of the total number of HP bosons also implies that, just like in the case of $\hat{\mathscr{H}}_{spin-spin}$, $\hat{\mathscr{H}}_o$ subdivides the system's Hilbert space into $(2J_0 + 1)$ subspaces: $\mathcal{B}_0, \mathcal{B}_1, \ldots, \mathcal{B}_{2J_0}$. Hence, the matrix representation of $\hat{\mathscr{H}}_o$, $\mathscr{H}_o$, can be written in the block diagonalized form:

$$\mathscr{H}_o = \bigoplus_{n=0}^{2J_0} \mathscr{B}_n = \operatorname{diag}\left(\mathscr{B}_0, \mathscr{B}_1, \ldots, \mathscr{B}_{2J_0}\right) = \begin{pmatrix} \boxed{\mathscr{B}_0} & & \\ & \ddots & \\ & & \boxed{\mathscr{B}_{2J_0}} \end{pmatrix} \tag{9.4}$$

just as we saw for $\mathscr{H}_{spin-spin}$ at (8.11), where the definition for $\mathcal{B}_n$ – (8.10) – still applies; and $\mathscr{B}_n$, in analogy to (8.12), is now defined as:

$$\mathscr{B}_n := \left\{ \left\langle \mathbb{n} \middle| \hat{\mathscr{H}}_o \middle| \mathbb{n}' \right\rangle \;\middle|\; \forall \mathbb{n}, \mathbb{n}' \in \mathcal{B}_n \right\} \; . \tag{9.5}$$

The generating function for the dimensions $\{\Omega_{\mathcal{A},n}\}$ of the subspaces $\{\mathcal{B}_n\}$ is, therefore, still given by $G_{\mathcal{A},\Omega}(q)$, (8.19).

The expression for the generic matrix element of $\hat{\mathscr{H}}_o$ between $|\mathbb{n}'\rangle = |n'_1, n'_2, \ldots, n'_N\rangle$ and $|\mathbb{n}\rangle = |n_1, n_2, \ldots, n_N\rangle$, follows directly from (8.51) and (9.2):

$$\begin{aligned} \left\langle \mathbb{n}' \middle| \hat{\mathscr{H}}_o \middle| \mathbb{n} \right\rangle &= \left\langle n'_1, n'_2, \ldots, n'_N \middle| \hat{\mathscr{H}}_o \middle| n_1, n_2, \ldots, n_N \right\rangle \\ &= \delta_{\mathbb{n}',\mathbb{n}} \left[-B_o \sum_i \gamma_i (j_i - n_i) + \sum_{i>k} T_{i,k} (j_i - n_i)(j_k - n_k) \right] \\ &+ \frac{1}{2} \sum_{i>k} T_{i,k} \sqrt{\left(n_i + \frac{1 \pm 1}{2}\right)\left(2j_i - n_i + \frac{1 \mp 1}{2}\right)\left(2j_k - n_k + \frac{1 \pm 1}{2}\right)\left(n_k + \frac{1 \mp 1}{2}\right)} \\ &\qquad \times \; \Delta_{i,k} \; \delta_{n'_i, n_i \pm 1} \; \delta_{n'_k, n_k \mp 1} \end{aligned} \tag{9.6}$$

where we can once again observe that $\hat{\mathscr{H}}_o$ conserves the total number of HP bosons. The submatrices $\mathscr{B}_n$ can be easily created by employing (9.6).

Here too, the subspaces $\mathcal{B}_n$ and $\mathcal{B}_{2J_0-n}$ are related by time-reversal symmetry. However, the striking difference between the isolated $\hat{\mathscr{H}}_{spin-spin}$ and $\hat{\mathscr{H}}_o$ is how they are transformed under the time-reversal operator $\hat{\Theta}$. Unlike $\hat{\mathscr{H}}_{spin-spin}$, $\hat{\mathscr{H}}_o$ is not time-reversal symmetric. In fact, from (8.54) and (8.66), we derive that:

$$\hat{\Theta} \hat{\mathscr{H}}_o \hat{\Theta}^{-1} = \hat{\mathscr{H}}_o - 2\hat{\mathscr{Z}} \; . \tag{9.7}$$

It must be emphasized that the time-reversal operator $\hat{\Theta}$ we have employed so many times above, including (9.7), is not a universal time-reversal operator but a local one restricted to the multispin system. Had $\hat{\Theta}$ been the time-reversal operator acting on the whole Universe, then $\hat{\mathscr{H}}_o$ would certainly commute with $\hat{\Theta}$ since the Universe is an isolated system. Similar results also follow if we consider the multispin system together with the external magnetic field $\mathbf{B}_o$ as one isolated system, and $\hat{\Theta}$ their combined time-reversal operator. By restricting $\hat{\Theta}$ only to the multispin system, we have inadvertently partitioned the system into two parts: a focus system (the spins) and its environment (the external magnetic field), which are both odd (i.e. they change sign) respect to time-reversal operation. This bipartite partitioning therefore leads to a broken T−symmetry in $\hat{\mathscr{H}}_o$.

Taking the matrix element of (9.7) between the two generic multispin states $|\mathbbm{n}'\rangle$ and $|\mathbbm{n}\rangle$, we obtain:

$$\left\langle \overline{\mathbbm{n}}' \middle| \hat{\mathscr{H}}_o \middle| \overline{\mathbbm{n}} \right\rangle = \left\langle \mathbbm{n}' \middle| \hat{\mathscr{H}}_o \middle| \mathbbm{n} \right\rangle - \delta_{\mathbbm{n}',\mathbbm{n}} \, 2\mathscr{Z}_{\mathbbm{n},\mathbbm{n}} \tag{9.8}$$

where, $\mathscr{Z}_{\mathbbm{n},\mathbbm{n}} := \left\langle \mathbbm{n} \middle| \hat{\mathscr{Z}} \middle| \mathbbm{n} \right\rangle$. If $|\mathbbm{n}'\rangle$ and $|\mathbbm{n}\rangle$ belong to the subspace $\mathcal{B}_n$, then $|\overline{\mathbbm{n}}'\rangle$ and $|\overline{\mathbbm{n}}\rangle$ are elements of $\mathcal{B}_{2J_0-n}$. Thus, (9.8) provides an easy way to generate the submatrix $\mathscr{B}_{2J_0-n}$ when $\mathscr{B}_n$ is known.

An even more important consequence of (9.7) is yet to be unveiled. It has to do with the relationship between the eigenvalues and eigenvectors of $\mathcal{B}_n$ and those of $\mathcal{B}_{2J_o-n}$. We assume $\mathcal{B}_n$ is not its own hole complement. Say $\left|E_\mu^{(n)}\right\rangle$ an eigenvector of $\hat{\mathscr{H}}_o$ in the subspace $\mathcal{B}_n$:

$$\hat{\mathscr{H}}_o \left|E_\mu^{(n)}\right\rangle = E_\mu^{(n)} \left|E_\mu^{(n)}\right\rangle \ , \qquad \mu = 1, 2, \ldots, \Omega_{\mathscr{A},n} \tag{9.9}$$

where $E_\mu^{(n)}$ is the eigenvalue of $\left|E_\mu^{(n)}\right\rangle$ according to $\hat{\mathscr{H}}_o$. Surely, the hole complement of $\left|E_\mu^{(n)}\right\rangle$, that is:

$$\hat{\Theta} \left|E_\mu^{(n)}\right\rangle \equiv \left|E_\mu^{(\overline{n})}\right\rangle = \left|E_\mu^{(2J_0-n)}\right\rangle \tag{9.10}$$

is also an eigenvector of $\hat{\mathscr{H}}_o$, but belongs to the subspace $\mathcal{B}_{2J_0-n}$:

$$\hat{\mathscr{H}}_o \left|E_\mu^{(\overline{n})}\right\rangle = E_\mu^{(\overline{n})} \left|E_\mu^{(\overline{n})}\right\rangle \ , \qquad \mu = 1, 2, \ldots, \Omega_{\mathscr{A},n} \tag{9.11}$$

where we recall that $\Omega_{\mathscr{A},n} = \Omega_{\mathscr{A},2J_0-n}$ according to (8.24). Now, from (9.7) we easily derive the commutation relation between $\hat{\mathscr{H}}_o$ and $\hat{\Theta}$:

$$\left[\ \hat{\mathscr{H}}_o\ ,\ \hat{\Theta}\ \right] = 2\hat{\mathscr{Z}}\hat{\Theta} \ . \tag{9.12}$$

If we now take the matrix element of (9.12) between the eigenvector $\left|E_\mu^{(n)}\right\rangle$ and its hole complement $\left|E_\mu^{(\overline{n})}\right\rangle$, we get:

$$\left\langle E_\mu^{(\overline{n})} \middle| \left[\ \hat{\mathscr{H}}_o\ ,\ \hat{\Theta}\ \right] \middle| E_\mu^{(n)} \right\rangle = 2 \left\langle E_\mu^{(\overline{n})} \middle| \hat{\mathscr{Z}}\hat{\Theta} \middle| E_\mu^{(n)} \right\rangle \tag{9.13a}$$

$$E_\mu^{(\overline{n})} - E_\mu^{(n)} = 2 \left\langle E_\mu^{(\overline{n})} \middle| \hat{\mathscr{Z}} \middle| E_\mu^{(\overline{n})} \right\rangle \tag{9.13b}$$

from which follows that:

$$E_\mu^{(\overline{n})} = E_\mu^{(n)} - 2 \left\langle E_\mu^{(n)} \middle| \hat{\mathscr{Z}} \middle| E_\mu^{(n)} \right\rangle \ . \tag{9.14}$$

Equation (9.14) asserts that we can easily compute the eigenvalue of the eigenvector $\left|E_\mu^{(\overline{n})}\right\rangle$ from its hole complement $\left|E_\mu^{(n)}\right\rangle$ if we already know the latter and its eigenvalue. The significance of (9.14) cannot be stressed enough. For example, suppose we have a univariate spin system of 10 spin-$\frac{1}{2}$, i.e. $\mathscr{A} = \left\{\frac{1}{2}^{10}\right\}$, whose Hamiltonian in the presence of a static magnetic field is given by $\hat{\mathscr{H}}_o$, (9.1). The total spin quantum number for the system is $J_0 = 5$, so, in principle, we can determine the eigenvectors and eigenvalues of $\hat{\mathscr{H}}_o$ by eigendecomposing the submatrices $\mathscr{B}_0, \mathscr{B}_1, \mathscr{B}_2, \ldots, \mathscr{B}_{10}$, (9.4). But by virtue of (9.10) and (9.14), there is no need to create and eigendecompose all the eleven submatrices: we only need $\mathscr{B}_0, \mathscr{B}_1, \mathscr{B}_2, \mathscr{B}_3, \mathscr{B}_4, \mathscr{B}_5$ to completely determine the eigenvalues and eigenvectors of $\hat{\mathscr{H}}_o$. This is an enormous simplification.

Most multispin systems of chemical interest present one or more groups of equivalent spins. We can further reduce the computational cost of diagonalizing $\hat{\mathscr{H}}_o$ if we exploit the presence of these groups in the system. The multiset $\mathscr{A}$ of spins can be viewed as the *sum* of multisets:

$$\mathscr{A} = \biguplus_{g}^{\phi(\mathscr{A})} \mathscr{A}_g \tag{9.15}$$

(for example, $\{1^2, 2, 5\} \uplus \{1^3, 2^2, 3, 5\} = \{1^5, 2^3, 3, 5^2\}$) where $\phi(\mathscr{A})$ is the number of groups of equivalent spins present in $\mathscr{A}$; the index g runs over the groups of equivalent spins, and $\mathscr{A}_g$ is the spin multiset for the $g-$th group of equivalent spins. Each $\mathscr{A}_g$ is then transformed into its Clebsch-Gordan series: $\mathscr{A}_g \mapsto \widetilde{\mathscr{A}}_g$ (see §8.3). Since the elements of the Clebsch-Gordan series $\widetilde{\mathscr{A}}_g$ are independent of each other (and irreducible), each element of the Cartesian product:

$$\bigtimes_{g}^{\phi(\mathscr{A})} \widetilde{\mathscr{A}}_g = \widetilde{\mathscr{A}}_1 \times \widetilde{\mathscr{A}}_2 \times \ldots \times \widetilde{\mathscr{A}}_{\phi(\mathscr{A})} \tag{9.16}$$

constitutes an independent multiset of spins subject to the same *form* of spin Hamiltonian and can be diagonalized independently. Take for example the $^{\cdot}CH_2OD$ radical. If the experimental conditions are such that the two hydrogen nuclei can be considered as equivalent spins, then the radical consists of three groups of equivalent spins: 1) the unpaired electron, $\mathscr{A}_1 = \left\{\frac{1}{2}\right\}$; 2) the two hydrogen nuclei, $\mathscr{A}_2 = \left\{\frac{1}{2}^2\right\}$; and 3) the deuterium nucleus, $\mathscr{A}_3 = \{1\}$. $\mathscr{A}_1$ and $\mathscr{A}_3$ have only one element each so they coincide with their Clebsch-Gordan multisets $\widetilde{\mathscr{A}}_g$. On the other hand, we immediately have that $\widetilde{\mathscr{A}}_2 = \{0, 1\}$. Hence,

$$\widetilde{\mathscr{A}}_1 \times \widetilde{\mathscr{A}}_2 \times \widetilde{\mathscr{A}}_3 = \left\{\frac{1}{2}\right\} \times \{0, 1\} \times \{1\} = \left\{\left\{\frac{1}{2}, 0, 1\right\}, \left\{\frac{1}{2}, 1^2\right\}\right\} \ . \tag{9.17}$$

What this means is that when the two hydrogen nuclei in $^{\cdot}CH_2OD$ are considered equivalent, the radical can be viewed as the sum of two smaller multispin systems, independent of each other: the first system consists of a spin-1/2 (the unpaired electron) and a spin-1 particle (the deuterium nucleus), while the second system consists of a spin-1/2 (the same electron) and two spin-1 particles (the deuterium nucleus and the triplet state of the two hydrogen nuclei). The Hamiltonian of both subsystems is still of the form given in (9.1). The Hilbert space of both subsystems can be block diagonalized as we saw above. For the first subsystem, the dimension of the block matrices are coefficients of the polynomial:

$$(1 + q)(1 + q + q^2) = 1 + 2q + 2q^2 + q^3 \ . \tag{9.18}$$

And the dimension of the block matrices for the second subsystem are the coefficients of the following polynomial:

$$(1 + q)(1 + q + q^2)^2 = 1 + 3q + 5q^2 + 5q^3 + 3q^4 + q^5 \ . \tag{9.19}$$

For each subsystem, all that has been discussed above in this section still applies. To recapitulate, we see that instead of diagonalizing a matrix of dimension 4 and one of dimension 7 to find the eigenvalues and eigenvectors of $\hat{\mathscr{H}}_o$ for the radical $^{\cdot}CH_2OD$ as we saw previously, we only need to diagonalize matrices of dimension $2, 3$ and 5 when the two hydrogen nuclei are equivalent. When applied to large spin systems with groups of equivalent spins, this approach reduces the computational cost of diagonalizing the multispin Hamiltonian significantly.

If we take the naphthalene anion for example, we are dealing with a univariate system of 9 spin-1/2 particles, i.e. $\mathscr{A} = \left\{\frac{1}{2}^9\right\}$. The dimension of the Hilbert space is, therefore, 512. Suppose we ignore the presence of equivalent spins in the system. Then, to engeindecompose the systems $\hat{\mathscr{H}_o}$, we will have to effectively diagonalize four matrices whose dimensions are $9, 36, 84$ and 126, according to the HP transformation scheme discussed above. If the experimental conditions are sufficiently favorable, the system can be thought of as consisting of three groups of equivalent spins: 1) the electron, $\mathscr{A}_1 = \left\{\frac{1}{2}\right\}$; 2) a collection four hydrogen nuclei, $\mathscr{A}_2 = \left\{\frac{1}{2}^4\right\}$; and 3) another collection of four hydrogen nuclei, $\mathscr{A}_3 = \left\{\frac{1}{2}^4\right\}$. Then, $\widetilde{\mathscr{A}}_2 = \{2, 1^3, 0^2\}$, and $\widetilde{\mathscr{A}}_3 = \{2, 1^3, 0^2\}$. Thus,

$$\begin{aligned}
\widetilde{\mathscr{A}}_1 \times \widetilde{\mathscr{A}}_2 \times \widetilde{\mathscr{A}}_3 &= \left\{\frac{1}{2}\right\} \times \{2, 1^3, 0^2\} \times \{2, 1^3, 0^2\} \\
&= \left\{ \left\{\frac{1}{2}, 2, 2\right\}, \left\{\frac{1}{2}, 2, 1\right\}^3, \left\{\frac{1}{2}, 2, 0\right\}^2, \left\{\frac{1}{2}, 1, 2\right\}^3, \left\{\frac{1}{2}, 1, 1\right\}^9, \right. \\
&\qquad \left. \left\{\frac{1}{2}, 1, 0\right\}^6, \left\{\frac{1}{2}, 0, 2\right\}^2, \left\{\frac{1}{2}, 0, 1\right\}^6, \left\{\frac{1}{2}, 0, 0\right\}^4 \right\} \; . \qquad (9.20)
\end{aligned}$$

So the eigendecomposition of the naphthalene anion's Hamiltonian $\hat{\mathscr{H}_o}$ can be done by considering a series of smaller but independent multisets: i) one multispin system comprised of a spin-1/2 and two spin-2 particles, i.e. $\{1/2, 2, 2\}$; ii) three multispin systems each of the type $\{1/2, 2, 1\}$, etc. For each of these subsystems, we can apply the HP transformation and create the block matrices. In the case of the naphthalene anion, the largest block matrix we shall encounter comes from the subsystem $\{1/2, 2, 2\}$. For this particular subsystem, the dimension of the block matrices follows from the generating function:

$$(1+q)(1+q+q^2+q^3+q^4)^2 = 1 + 3q + 5q^2 + 7q^3 + 9q^4 + 9q^5 + 7q^6 + 5q^7 + 3q^8 + q^9 \; . \qquad (9.21)$$

Hence, if we take into account the two groups of equivalent spins present in the naphthalene anion, the largest matrix we will ever have to diagonalize is of dimension 9, which is remarkable.

To fully exploit the presence of groups of equivalent spins in the multispin system, we need the Clebsch-Gordan coefficients. This constitutes the primary computational challenge in the method just illustrated. One can thus incorporate optimized subroutines for the calculation of Clebsch-Gordan coefficients into ones multispin algorithm. The somehow comforting observation we can make here is that, in most of the multispin systems of interest, groups of equivalent spins hardly exceed six in number – which means a subroutine which can handle the Clebsch-Gordan coefficients for the addition of up to six angular momenta suffices for most routine computations.

Chapter 10

Eigendecomposition of Liouvillians

In ordinary quantum mechanics in state space, the eigenvalues of observables — like the Hamiltonian or magnetization vector — , which are absolute quantities (at least, up to a constant), are the natural occurrences. Meanwhile, what we experimentally measure in spectroscopic experiments like nuclear magnetic resonance (NMR) are quantities related to the differences between these eigenvalues. This fact is nicely conveyed in the resonance conditions of said experiments. An alternative way of doing quantum mechanics whereby such energy differences naturally come up as the expectation values of some operator is thus more suitable to spectroscopy. Such an alternative is accomplished when we formulate quantum mechanics in the so-called Liouville space [63, 74]. In addition, the Liouville space formulation makes it relatively easier to treat relaxation processes, compared to the Hilbert space [74]. It is therefore understandable why the Liouville space formalism is popular in various fields of spectroscopy, including magnetic resonance. The catch, however, is that given a Hilbert space of finite dimension $D_{\mathcal{H}}$, the dimension of its corresponding Liouville space is $D_{\mathcal{H}}^2$ – which roughly translates into even higher computational costs when one works in Liouville space.

As it is well-known, operators in Hilbert space, including the density matrix, become vectors (*supervectors*) in Liouville space. Likewise, mappings which transformed one operator into another in Hilbert space become operators (*superoperators*) in Liouville space.

Recall that the Hamiltonian is known to be the generator of the dynamics of the density matrix in Hilbert space. When the density matrix becomes a supervector in Liouville space, its dynamics are generated by the superoperator called the *Liouvillian*. Just as we eigendecompose the Hamiltonian $\hat{\mathscr{H}}$ in the Hilbert space to get the eigenenergies of the system, the eigendecomposition of its corresponding Liouvillian $\hat{\hat{\mathfrak{L}}}$ returns all possible pairwise differences between the eigenenergies [63]. The relation between a given Hamiltonian $\hat{\mathscr{H}}$ and its Liouvillian $\hat{\hat{\mathfrak{L}}}$ is [63]:

$$\hat{\hat{\mathfrak{L}}} = \hat{\mathscr{H}} \otimes \hat{\mathbb{I}} - \hat{\mathbb{I}} \otimes \hat{\mathscr{H}}^* \tag{10.1}$$

where "⊗" denotes the operation of vector space tensor direct product; $\hat{\mathbb{I}}$ is the identity operator defined on the same Hilbert space as $\hat{\mathscr{H}}$, and $\hat{\mathscr{H}}^*$ is the complex conjugate of $\hat{\mathscr{H}}$. We once again observe from (10.1) that the dimension of the linear space where $\hat{\hat{\mathfrak{L}}}$ operates, i.e. the Liouville space, is of dimension $(D_{\mathcal{H}})^2$. For example, if we have a multispin system $\mathscr{A} = \left\{ \frac{1}{2}^{10} \right\}$, whose Hamiltonian is given by $\hat{\mathscr{H}}_o$ in (9.1), the simulation of the multispin system's magnetic spectra would require eigendecomposing a matrix of dimension $2^{10} = 1024$ according to the tout court approach if we work in the system's spin state space. If we choose to work in the Liouville space, the same tout court approach will have us eigendecompose the matrix representation of the Liouvillian, which is of dimension $2^{20} = 1,048,576$.

This apparent inconvenience in computational costs one has to grapple with when working in the Liouville space can be easily overcome. Indeed, if $\mathfrak{U}$ is the matrix (*supermatrix*) which diagonalizes $\mathfrak{L}$, i.e.

$$\mathfrak{U}\,\mathfrak{L}\,\mathfrak{U}^{-1} = \mathfrak{D} \tag{10.2}$$

where $\mathfrak{D}$ is the diagonal supermatrix of the eigenvalues of $\mathfrak{L}$, and $\mathscr{U}$ is the eigenvector matrix of $\mathscr{H}$:

$$\mathscr{U}\,\mathscr{H}\,\mathscr{U}^{-1} = \mathscr{D} \tag{10.3}$$

where $\mathscr{D}$ is the diagonal matrix containing the eigenvalues of $\mathscr{H}$, then it can be proved that:

$$\mathfrak{U} = \mathscr{U} \otimes \left(\mathscr{U}^{-1}\right)^{T} \tag{10.4}$$

and

$$\mathfrak{D} = \mathscr{D} \otimes \mathbb{I} - \mathbb{I} \otimes \mathscr{D} \tag{10.5}$$

where "$\otimes$" in (10.4) and (10.5) indicates the operation of Kronecker (or matrix direct) product, and $\mathbb{I}$ is the identity matrix of the same dimension as $\mathscr{D}$. Equation (10.4) is of great significance because it enables us to compute the eigenvector supermatrix $\mathfrak{U}$ directly from $\mathscr{U}$ by means of a simple matrix direct product, without having to diagonalize the Liouvillian $\mathfrak{L}$ de novo. Note that when the Hamiltonian is real, like in the case of the multispin Hamiltonian $\hat{\mathscr{H}}_o$ seen above, $\mathscr{U}$ is an orthogonal matrix, and so (10.4) reduces to the form:

$$\mathfrak{U} = \mathscr{U} \otimes \mathscr{U}\ . \tag{10.6}$$

Combining the relations given in (10.4) and (10.5) with the HP transformation and related techniques discussed in previous sections could be very useful in reducing the computational cost of simulating the magnetic resonance spectra of multispin systems described by isotropic Hamiltonians like $\hat{\mathscr{H}}_o$ in Liouville space. For example, going back to our previous example with the multiset $\mathscr{A} = \left\{\frac{1}{2}^{10}\right\}$, if we want to work in Liouville space, instead of eigendecomposing a square matrix of dimension 2^{20}, we can obtain the same eigen-supervectors and -supervalues through (10.6) and (10.5), respectively, by eigendecomposing only the submatrices $\mathscr{B}_0, \mathscr{B}_1, \mathscr{B}_2, \mathscr{B}_3, \mathscr{B}_4, \mathscr{B}_5$ which are of dimension $1, 10, 45, 120, 210$ and 252, respectively. The computational cost can be further drastically reduced if we take into consideration the presence of groups of equivalent spins as explained in Chap. 9.

Chapter 11

On Schwinger bosons

We conclude this part with a brief introduction to Schwinger bosons, which is another kind of spin representation commonly used in condensed matter physics. Schwinger bosons are closely related to the Holstein-Primakoff bosons, but the two representations are suitable for certain specific applications. The HP bosons are particularly useful in transforming quantum mechanical problems into counting problems. The Schwinger bosons are extremely powerful tools when we want to describe the behavior of spin states under unitary transformations like rotations. The literature provides a plethora of applications of the Schwinger bosons, mainly in quantum magnetic studies. This presentation of the HP transformation won't be complete without this brief introduction to Schwinger bosons. However, the introduction we provide below departs greatly from what one may find elsewhere. Besides the simplicity of our exposition below, we stress on the close link between Schwinger bosons and HP bosons – which is rarely done in such details in the literature. Readers may see [13, 143] for the mainstream exposition, interpretation and applications of Schwinger bosons.

We begin our introduction to Schwinger bosons by noting that the presence of the square root of operators in the HP transformation, (6.14) and (6.15), makes its use in the study of important problems like the rotation of spin states very inconvenient. The Schwinger transformation, from which derives the Schwinger bosons, provides an alternative way to represent the spin operators $\hat{\mathcal{J}}^{\pm}$ and $\hat{\mathcal{J}}^{z}$ in a very simple way without trace of any square roots. Interestingly, as we show below, the Schwinger representation follows directly from the HP transformation.

When we introduced the time-reversal operator in Sec. 8.4, (8.55), we saw that when it acts on a spin state represented by HP bosons, it transforms the HP bosons present into holes and the holes into HP bosons, contemporarily. We also saw that the sum of the number of holes and HP bosons in any given basis state $|n\rangle$ of a spin-j particle is always $2j$. And that, while $\hat{b}^{\dagger}\hat{b}$ counts the number of HP bosons, the operator $(2j - \hat{b}^{\dagger}\hat{b})$ counts the number of holes. The transition from HP transformation to the Schwinger transformation relies on one simple trick: treat the holes and HP bosons as two set of independent particles that can be created and annihilated separately (with the caveat that the sum of their occupation numbers remain constant). If we do so, then we need to assign an occupation number operator to the holes. Let us indicate this occupation number operator as $\hat{a}^{\dagger}\hat{a}$. Thus,

$$\hat{a}^{\dagger}\hat{a} = 2j - \hat{b}^{\dagger}\hat{b} \; . \tag{11.1}$$

Clearly, $\hat{a}^\dagger$ and $\hat{a}$ are the creation and annihilation operators for the holes, respectively; and they obey the same commutation rules as $\hat{b}^\dagger$ and $\hat{b}$. Equation (8.55) may, therefore, be rewritten as:

$$\hat{\Theta}\ \hat{b}^\dagger \hat{b}\ \hat{\Theta}^{-1} = \hat{a}^\dagger \hat{a}\ . \tag{11.2}$$

Since $\{\hat{b}, \hat{b}^\dagger\}$ effect only the HP bosons and $\{\hat{a}, \hat{a}^\dagger\}$ act on only the holes, the two set of operators commute with each other. For the sake of clarity, let $\hat{n}_b \equiv \hat{b}^\dagger \hat{b}$ and $\hat{n}_a \equiv \hat{a}^\dagger \hat{a}$; thus, the nonnegative integers n_b and n_a will indicate the number of HP bosons and holes, respectively. We are therefore representing spin states with two types of particles, i.e. HP bosons and (HP) holes:

$$\begin{array}{ccc} \text{HP representation} & \mapsto & \text{Schwinger representation} \\ |n\rangle & \mapsto & |n_b, n_a\rangle \end{array}$$

where, obviously, $n = n_b$. Hence, in the Schwinger representation we need two occupation numbers to indicate a single spin eigenvector of $\hat{\mathcal{J}}^z$. Moreover, given that the two sets of operators $\{\hat{b}, \hat{b}^\dagger\}$ and $\{\hat{a}, \hat{a}^\dagger\}$ operate on different particles, it follows that:

$$\hat{b}\,|n_b, n_a\rangle = \sqrt{n_b}\,|n_b - 1, n_a\rangle \qquad \hat{b}^\dagger\,|n_b, n_a\rangle = \sqrt{n_b + 1}\,|n_b + 1, n_a\rangle \tag{11.3}$$

$$\hat{a}\,|n_b, n_a\rangle = \sqrt{n_a}\,|n_b, n_a - 1\rangle \qquad \hat{a}^\dagger\,|n_b, n_a\rangle = \sqrt{n_a + 1}\,|n_b, n_a + 1\rangle \tag{11.4}$$

where the nonnegative integers n_a and n_b are subject to the contraint: $n_a + n_b = 2j$, (11.1).

In regards to the operator $\hat{\mathcal{J}}^z$, we note that if we combine (6.5) with (11.1), we obtain the following expression for $\hat{\mathcal{J}}^z$ in function of $\hat{n}_b$ and $\hat{n}_a$:

$$\hat{\mathcal{J}}^z = \frac{1}{2}\left(\hat{a}^\dagger \hat{a} - \hat{b}^\dagger \hat{b}\right) = \frac{1}{2}\left(\hat{n}_a - \hat{n}_b\right)\ . \tag{11.5}$$

(recall we have set $\hbar = 1$). It is clear from (11.5) that the usual spin magnetic number m in $|j, m\rangle$ relates to n_a and n_b through the expression:

$$m = \frac{1}{2}(n_a - n_b)\ . \tag{11.6}$$

Moreover, from (11.1), we also have the condition:

$$j = \frac{1}{2}(n_a + n_b)\ . \tag{11.7}$$

Equation (11.6) and (11.7), together, constitute the conditions the integers n_a and n_b must satisfy in order to represent the usual spin state $|j, m\rangle$.

What about the Schwinger representation for $\hat{\mathcal{J}}^\pm$? To begin, recall the operator $\hat{\mathcal{J}}^+ = \sqrt{2j - \hat{b}^\dagger \hat{b}}\,\hat{b}$ in the HP representation, (6.14). From this expression, we see that the operator $\hat{b}$ first reduces the number of HP bosons by 1 while the operator $\sqrt{2j - \hat{b}^\dagger \hat{b}}$ leaves the resulting state unchanged in the number of HP bosons. The net effect of $\hat{\mathcal{J}}^+$ is, therefore, to reduce n_b by 1. But, given that $n_a + n_b = 2j$, (11.7), it follows that if $\hat{\mathcal{J}}^+$ has the effect of reducing n_b by 1, then it must also have the effect of increasing the number of holes by the same quantity, i.e. $n_a \mapsto n_a + 1$. The operator which increases n_a by 1 is $\hat{a}^\dagger$. Therefore, $\hat{\mathcal{J}}^+$ must be proportional to $\hat{a}^\dagger \hat{b}$:

$$\hat{\mathcal{J}}^+ = c\ \hat{a}^\dagger\ \hat{b} = c\ \hat{b}\ \hat{a}^\dagger \tag{11.8}$$

where c is the proportionality constant. If we let $\hat{\mathcal{J}}^{+}$ operate on $|n_b, n_a\rangle$, we find that:

$$\begin{aligned}
\hat{\mathcal{J}}^{+}\,|n_b, n_a\rangle &= c\;\hat{a}^{\dagger}\;\hat{b}\,|n_b, n_a\rangle && (11.9a)\\
&= c\sqrt{(n_a+1)}\sqrt{n_b}\;\;|n_b-1, n_a+1\rangle && (11.9b)\\
&= c\sqrt{(2j-n_b+1)}\sqrt{n_b}\;\;|n_b-1, n_a+1\rangle && (11.9c)
\end{aligned}$$

where we have made use of (11.3) and (11.4). If we compare (11.9c) with (6.14), we immediately reach the conclusion that $c = 1$ (bear in mind that $n = n_b$, and as stated above, we have set $\hbar = 1$ throughout this section). Thus,

$$\hat{\mathcal{J}}^{+} = \hat{a}^{\dagger}\;\hat{b} = \hat{b}\;\hat{a}^{\dagger}\;. \tag{11.10}$$

Hence, it also follows that:

$$\begin{aligned}
\hat{\mathcal{J}}^{-} &= \left(\hat{\mathcal{J}}^{+}\right)^{\dagger}\\
&= \hat{a}\;\hat{b}^{\dagger} = \hat{b}^{\dagger}\;\hat{a}\;. && (11.11a)
\end{aligned}$$

Equations (11.5), (11.10) and (11.11a) constitute the Schwinger transformation. Unlike the HP transformation, we see that the Schwinger transformation is linear in the operators $\hat{a}^{\dagger}, \hat{a}, \hat{b}^{\dagger}, \hat{b}$.

In §6, we saw that the vacuum state $|n = 0\rangle$ in the HP representation of the $\hat{\mathcal{J}}^{z}$ eigenvectors of spin-j corresponds to the state $|j, j\rangle$ in the normal $|j, m\rangle$ −representation. The Schwinger representation also has its vacuum state, namely $|n_b = 0, n_a = 0\rangle = |0, 0\rangle$. This vacuum state, unlike the one we encountered in the HP representation, does not correspond to any specific spin state, and its energy is undefined. However, one interesting characteristic of the Schwinger vacuum is that it is the same for all spins. This is in net contrast to the HP vacuum.

Just as generic spin states in the HP representation can be created from the HP vacuum state by filling the latter with a number of HP bosons, generic spin states in the Schwinger representation can be easily created from the Schwinger vacuum $|0, 0\rangle$ by creating a number of holes and HP bosons. Thus,

$$|j, m\rangle \mapsto |n_b, n_a\rangle = \frac{\left(\hat{a}^{\dagger}\right)^{n_a}}{\sqrt{n_a!}}\frac{\left(\hat{b}^{\dagger}\right)^{n_b}}{\sqrt{n_b!}}\,|0, 0\rangle \tag{11.12}$$

where the factor $\frac{1}{\sqrt{n_a! n_b!}}$ is necessary to keep the state on the RHS normalized like $|n_b, n_a\rangle$. If we express n_a and n_b in (11.12) in terms of j and m, using (11.6) and (11.7), it turns out that:

$$|j, m\rangle \mapsto |j-m, j+m\rangle = \frac{\left(\hat{a}^{\dagger}\right)^{j+m}}{\sqrt{(j+m)!}}\frac{\left(\hat{b}^{\dagger}\right)^{j-m}}{\sqrt{(j-m)!}}\,|0, 0\rangle\;\;. \tag{11.13}$$

In the Schwinger representation, the HP bosons and HP holes are collectively called *Schwinger bosons.*

Among the many useful applications of the Schwinger bosons is the relatively straightforward ease with which they allow the derivation of the famous Majorana formula [144], which states the general expression for the transition probability between two generic spin states of an arbitrary spin in the presence of: 1) a static magnetic field along a specified direction in space (chosen as the quantization axis), and 2) a rf field perpendicular to the static field. Other applications of the Schwinger bosons include the derivation of analytical expressions for the matrix elements of the rotation operator. In particular, they can be used to easily derive a close expression for the elements of the Wigner $d-$matrix [137, 143]. Closed expressions for the Clebsch-Gordan coefficients for the addition of two, three and four angular momenta can also obtained using the Schwinger bosons [143].

Part III

Quantum Markovian master equations

Part III presents quantum Markovian master equations and the conditions which lead to them. The concept of universal dynamical maps (UDM) and completely positive (CP) maps are also presented.

The contents of this part are not original findings of the author. However, the presentations given here of these known results are mostly original presentations by the author. Some results are generalizations of those in the literature and others are unpublished results.

Chapter 12

Generalized Kraus operator sum representation on a convex set of finite-dimensional density matrices

12.1 Generalized Kraus operator sum representation

Say $\mathcal{H}_d$ a state space (Chap. 1) of dimension d, and $\mathcal{O}_d$ the Hilbert space of linear operators acting on $\mathcal{H}_d$ (Sec. 1.1). Let $\mathcal{O}_d^{+,1}$ denote the convex cone in the set of trace-class unit-trace positive semi-definite self-adjoint linear operators acting on $\mathcal{H}_d$ [138]. Naturally, $\mathcal{O}_d^{+,1} \subset \mathcal{O}_d$. Consider the mapping $\Lambda : \mathcal{O}_d^{+,1} \to \mathcal{O}_d^{+,1}$, where Λ is understood to be linear and conserves convexity (*i.e.* for scalars $\{c_1, c_2 | c_1, c_2 \geq 0 \wedge c_1 + c_2 = 1\}$ and operators $\rho_1, \rho_2 \in \mathcal{O}_d^{+,1}$, $\Lambda[c_1\rho_1 + c_2\rho_2] = c_1\Lambda[\rho_1] + c_2\Lambda[\rho_2] \in \mathcal{O}_d^{+,1}$). For arbitrary $\rho \in \mathcal{O}_d^{+,1}$, it can be shown that it is always possible to express $\rho' \equiv \Lambda\rho$ as [132, 138, 155]

$$\rho' = \Lambda\rho = \sum_\mu M_\mu \rho M_\mu^\dagger \tag{12.1}$$

where the operators $M_\mu \in \mathcal{O}_d$ satisfy the completeness relation

$$\sum_\mu M_\mu^\dagger M_\mu = \mathbb{I}_d \ . \tag{12.2}$$

Equation (12.2) is reminiscent of (3.3), and confirms the fact that the map Λ preserves trace. The map Λ also preserves Hermiticity and is obviously positive[1]. The sum in (12.1) may be referred to as a *generalized Kraus operator sum representation* of the map Λ, and the operators $\{M_\mu\}$ are the *generalized Kraus operators.*

In general, the operators M_μ depend on (the eigenvectors of) ρ [138, 155]. This assertion stems from the fact that given any pair of elements $\rho_A, \rho_B \in \mathcal{O}_d^{+,1}$, it is always possible to find a generalized Kraus operators $\{M_\mu\}$ such that

$$\rho_B = \sum_\mu M_\mu \rho_A M_\mu^\dagger \ . \tag{12.3}$$

---

[1] A map $\Phi : \mathfrak{M}_n \to \mathfrak{M}_m$ – where $\mathfrak{M}_n$ and $\mathfrak{M}_m$ are linear spaces of complex $n \times n$ and $m \times m$ matrices, respectively – is *positive* if for any positive semi-definite element A of $\mathfrak{M}_n$, $\Phi(A)$ is also positive semi-definite [28].

This can be easily proved, and we provide one below. The following proof follows closely that given in [155].

First of all, based on the spectral decomposition theorem (1.17), we may write

$$\rho_A = \sum_{k=1}^{d} \lambda_{A,k}\, |\alpha_k\rangle\langle\alpha_k| = U_A\ \rho_{A,\lambda}\ U_A^\dagger \tag{12.4}$$

where $\{|\alpha_k\rangle\}$, $\{\lambda_{A,k}\}$ are the eigenvectors and eigenvalues of ρ_A, respectively; U_A is the unitary transformation matrix whose $k-$th column is $|\alpha_k\rangle$ and $\rho_{A,\lambda}$ is the diagonal matrix whose $(k,k)-$th entry is $\lambda_{A,k}$. Analogously, for ρ_B we may write

$$\rho_B = \sum_{k=1}^{d} \lambda_{B,k}\, |\beta_k\rangle\langle\beta_k| = U_B\ \rho_{B,\lambda}\ U_B^\dagger\ . \tag{12.5}$$

Note also that for $\rho_{A,\lambda}$ and $\rho_{B,\lambda}$ we may write

$$\rho_{A,\lambda} = \sum_{k=1}^{d} \lambda_{A,k}\, |k\rangle\langle k| \qquad \rho_{B,\lambda} = \sum_{k=1}^{d} \lambda_{B,k}\, |k\rangle\langle k| \tag{12.6}$$

where $|k\rangle$ is the $k-$th canonical basis of dimension d, *i.e.*

$$|k\rangle = \Big(\underbrace{0\ \ \ldots\ \ 0}_{k-1}\ \ 1\ \ \underbrace{0\ \ \ldots\ \ 0}_{d-k}\Big)^T\ . \tag{12.7}$$

It can be shown that there exist operators $\{\Gamma_{B,\mu}\}$ $(\mu = 0, 1, 2, \ldots, d-1)$ such that

$$\rho_{B,\lambda} = \sum_{\mu} \Gamma_{B,\mu}\ \rho_{A,\lambda}\ \Gamma_{B,\mu}^\dagger \tag{12.8}$$

and who satisfy the completeness relation

$$\sum_{\mu} \Gamma_{B,\mu}^\dagger \Gamma_{B,\mu} = \mathbb{I}_d\ . \tag{12.9}$$

It can be verified that, up to a unitary transformation,

$$\Gamma_{B,\mu} = \sum_{k=1}^{d-\mu} \sqrt{\lambda_{B,k}}\ \ |k\rangle\langle k+\mu|\ + \sum_{k=d-\mu+1}^{d} \sqrt{\lambda_{B,k}}\ \ |k\rangle\langle k+\mu-d|\ . \tag{12.10}$$

Equations (12.8) and (12.9) can be easily verified. Indeed,

$$\begin{aligned}
\sum_{\mu=0}^{d-1} \Gamma_{B,\mu}^\dagger \Gamma_{B,\mu} &= \sum_{\mu=0}^{d-1}\sum_{k=1}^{d-\mu} \lambda_{B,k}\ \ |k+\mu\rangle\langle k+\mu|\ + \sum_{\mu=0}^{d-1}\sum_{k=d-\mu+1}^{d} \lambda_{B,k+\mu-d}\ \ |k+\mu-d\rangle\langle k+\mu-d| \\
&= \sum_{k=1}^{d}\sum_{\mu=0}^{d-1} \lambda_{B,k-\mu}\ \ |k\rangle\langle k|\ + \sum_{k=1}^{d}\sum_{\mu=0}^{d-1} \lambda_{B,d+k-\mu}\ \ |k\rangle\langle k| \\
&= \sum_{k=1}^{d}\left(\sum_{\mu=0}^{d-1} \lambda_{B,k-\mu}\ + \sum_{\mu=0}^{d-1} \lambda_{B,d+k-\mu}\right)|k\rangle\langle k| = \sum_{k=1}^{d}\left(\sum_{\mu=0}^{k-1} \lambda_{B,k-\mu}\ + \sum_{\mu=k}^{d-1} \lambda_{B,d+k-\mu}\right)|k\rangle\langle k| \\
&= \sum_{k=1}^{d} |k\rangle\langle k| = \mathbb{I}_d\ .
\end{aligned} \tag{12.11}$$

Also,

$$
\begin{aligned}
&\sum_{\mu=0}^{d-1} \Gamma_{B,\mu}\ \rho_{A,\lambda}\ \Gamma_{B,\mu}^{\dagger} \\
&\qquad = \sum_{\mu=0}^{d-1} \sum_{k=1}^{d} \Bigg[\sum_{k''=1}^{d-\mu} \sum_{k'=1}^{d-\mu} \sqrt{\lambda_{B,k'}} \sqrt{\lambda_{B,k''}}\ \ |k'\rangle\langle k'+\mu|\ k\rangle\langle k|\ k''+\mu\rangle\langle k''|\, \lambda_{A,k} \\
&\qquad + \sum_{k'=1}^{d-\mu} \sum_{k''=d-\mu+1}^{d} \sqrt{\lambda_{B,k'}} \sqrt{\lambda_{B,k''}}\ \ |k'\rangle\langle k'+\mu|\ k\rangle\langle k|\ k''+\mu-d\rangle\langle k''|\, \lambda_{A,k} \\
&\qquad + \sum_{k''=1}^{d-\mu} \sum_{k'=d-\mu+1}^{d} \sqrt{\lambda_{B,k'}} \sqrt{\lambda_{B,k''}}\ \ |k'\rangle\langle k'+\mu-d|\ k\rangle\langle k|\ k''+\mu\rangle\langle k''|\, \lambda_{A,k} \\
&\qquad + \sum_{k'=d-\mu+1}^{d} \sum_{k''=d-\mu+1}^{d} \sqrt{\lambda_{B,k'}} \sqrt{\lambda_{B,k''}}\ \ |k'\rangle\langle k'+\mu-d|\ k\rangle\langle k|\ k''+\mu-d\rangle\langle k''|\, \lambda_{A,k} \Bigg] \,.
\end{aligned}
\tag{12.12}
$$

Using the orthonormality property of the canonical basis, we find that

$$
\begin{aligned}
&\sum_{\mu=0}^{d-1} \Gamma_{B,\mu}\ \rho_{A,\lambda}\ \Gamma_{B,\mu}^{\dagger} \\
&\qquad = \sum_{\mu=0}^{d-1} \sum_{k=1}^{d} \Bigg[\sum_{k''=1}^{d-\mu} \sum_{k'=1}^{d-\mu} \sqrt{\lambda_{B,k'}} \sqrt{\lambda_{B,k''}} \lambda_{A,k}\ \ |k'\rangle\langle k''|\, \delta_{k'+\mu,k} \delta_{k',k''} \\
&\qquad + \sum_{k'=1}^{d-\mu} \sum_{k''=d-\mu+1}^{d} \sqrt{\lambda_{B,k'}} \sqrt{\lambda_{B,k''}} \lambda_{A,k}\ \ |k'\rangle\langle k''|\, \delta_{k'+\mu,k} \delta_{k'',k'+d} \\
&\qquad + \sum_{k''=1}^{d-\mu} \sum_{k'=d-\mu+1}^{d} \sqrt{\lambda_{B,k'}} \sqrt{\lambda_{B,k''}}\ \lambda_{A,k}\ \ |k'\rangle\langle k''|\, \delta_{k''+\mu,k} \delta_{k',k''+d} \\
&\qquad + \sum_{k'=d-\mu+1}^{d} \sum_{k''=d-\mu+1}^{d} \sqrt{\lambda_{B,k'}} \sqrt{\lambda_{B,k''}}\ \lambda_{A,k}\ \ |k'\rangle\langle k''|\, \delta_{k'+\mu-d,k} \delta_{k'',k'} \Bigg] \,.
\end{aligned}
\tag{12.13}
$$

The second and third terms vanish since $|k\rangle = 0$ for $k > d$. Hence

$$
\begin{aligned}
\sum_{\mu=0}^{d-1} \Gamma_{B,\mu}\ \rho_{A,\lambda}\ \Gamma_{B,\mu}^{\dagger} &= \sum_{\mu=0}^{d-1} \sum_{k'=1}^{d-\mu} \lambda_{B,k'} \lambda_{A,k'+\mu}\ \ |k'\rangle\langle k'| + \sum_{\mu=0}^{d-1} \sum_{k'=d-\mu+1}^{d} \lambda_{B,k'}\ \lambda_{A,k'+\mu-d}\ \ |k'\rangle\langle k'| \\
&= \sum_{k=1}^{d} \left(\sum_{w=k}^{d} \lambda_{A,w} \right) \lambda_{B,k}\, |k\rangle\langle k| + \sum_{k=1}^{d} \left(\sum_{w=1}^{k-1} \lambda_{A,w} \right) \lambda_{B,k}\, |k\rangle\langle k| \\
&= \sum_{k=1}^{d} \left(\sum_{w=k}^{d} \lambda_{A,w} + \sum_{w=1}^{k-1} \lambda_{A,w} \right) \lambda_{B,k}\, |k\rangle\langle k| = \sum_{k=1}^{d} \lambda_{B,k}\, |k\rangle\langle k| = \rho_{B,\lambda}\ .
\end{aligned}
\tag{12.14}
$$

Having verified that (12.8) and (12.9) hold, from (12.5) and (12.8), it follows that

$$
\rho_B = U_B\ \rho_{B,\lambda}\ U_B^{\dagger} = U_B \left(\sum_{\mu=0}^{d-1} \Gamma_{B,\mu}\ \rho_{A,\lambda}\ \Gamma_{B,\mu}^{\dagger} \right) U_B^{\dagger} = \sum_{\mu=0}^{d-1} U_B \Gamma_{B,\mu} \rho_{A,\lambda} \Gamma_{B,\mu}^{\dagger} U_B^{\dagger}\ . \tag{12.15}
$$

But from (12.4), we know

$$
U_A^{\dagger}\ \rho_A\ U_A = \rho_{A,\lambda} \tag{12.16}
$$

therefore,

$$\begin{aligned}\rho_B &= \sum_\mu U_B \Gamma_{B,\mu} U_A^\dagger \ \rho_A \ U_A \Gamma_{B,\mu}^\dagger U_B^\dagger \\ &= \sum_\mu M_{BA,\mu} \ \rho_A \ M_{BA,\mu}^\dagger\end{aligned} \tag{12.17}$$

where

$$M_{BA,\mu} \equiv U_B \Gamma_{B,\mu} U_A^\dagger \ . \tag{12.18}$$

And in addition, we also see that

$$\sum_\mu M_{BA,\mu}^\dagger M_{BA,\mu} = \mathbb{I}_d \ . \tag{12.19}$$

As mentioned above, we note that the operator $M_{BA,\mu}$ depends on ρ_A through U_A. And the operators U_B and $\Gamma_{B,\mu}$ determine the eigenvectors and eigenvalues of ρ_B. As pointed out in [155], since U_A collects only the eigenvectors of ρ_A, it is inferred that different elements of $\mathcal{O}_d^{+,1}$ with the same set of eigenvectors as ρ_A but with different eigenvalues share the same set of generalized Kraus operators $\{M_{BA,\mu}\}$ for fixed ρ_B.

12.2 Completely positive linear maps and Choi's theorem

Let $\mathfrak{M}_n$ and $\mathfrak{M}_m$ be linear spaces of complex $n \times n$ and $m \times m$ square matrices, respectively. A positive linear map $\Phi : \mathfrak{M}_n \to \mathfrak{M}_m$ is said to be *completely positive* (CP) if for any identity matrix $\mathbb{I}_p \in \mathfrak{M}_p$ ($p \in \{1, 2, 3, \ldots\}$), the map

$$\Phi \otimes \mathbb{I}_p : \mathfrak{M}_n \otimes \mathfrak{M}_p \to \mathfrak{M}_m \otimes \mathfrak{M}_p \tag{12.20}$$

is still positive.

According to Choi's theorem [28], a linear map $\Phi : \mathfrak{M}_n \to \mathfrak{M}_m$ is *completely positive* if and only if it admits the expression,

$$\Phi(A) = \sum_i V_i^\dagger A V_i \tag{12.21}$$

– where V_i is a $n \times m$ complex matrix. Based on this very important result and (12.1), we can say that ***any linear map*** $\Lambda : \mathcal{O}_d^{+,1} \to \mathcal{O}_d^{+,1}$***, is definitely CP – and not just positive***. Combining this with the trace-preserving property of Λ (sealed by the completeness relation in (12.2)), leads to Λ being *completely positive and trace-preserving* (CPT). The CPT property also becomes a criterion by which to ascertain whether or not a linear map is an endomorphism of the set $\mathcal{O}_d^{+,1}$ (*i.e.* if the map transforms elements of $\mathcal{O}_d^{+,1}$ into elements of the same set.). Namely, *a linear map* Λ *is an endomorphism of the set* $\mathcal{O}_d^{+,1}$ *if and only if it is CPT.*

The requirement that any linear map Λ which presupposes to be an endomorphism of $\mathcal{O}_d^{+,1}$ be CPT is not just an abstract mathematical preoccupation, but ensures a profound logical and empirical coherence in our understanding and description of how quantum states are transformed. We shall discuss this in more details in the next chapter but for the time being, consider a system S with state space $\mathcal{H}_d$ and the map $\Lambda : \mathcal{O}_d^{+,1} \to \mathcal{O}_d^{+,1}$. Consider now another system W with state space $\mathcal{H}_{d'}$. The state space of the bipartite system $S + W$ is $\mathcal{H}_d \otimes \mathcal{H}_{d'}$. Consider S and W to be noninteracting and no correlation between the two. If we want to describe the scenario where we apply the map Λ above in this very context of the $S + W$ system – where Λ continues to be an endomorphism of $\mathcal{O}_d^{+,1}$ while we leave W's state intact –, we will have to use the map

$$\Lambda \otimes \mathbb{I}_{d'} : \mathcal{O}_d^{+,1} \otimes \mathcal{O}_{d'}^{+,1} \to \mathcal{O}_d^{+,1} \otimes \mathcal{O}_{d'}^{+,1} \; . \tag{12.22}$$

It is reasonable that we require this map to be positive (besides preserving trace and Hermiticity). More than that, this positivity requirement must hold independent of d'; else, there could be values of d' whereby there is no interaction nor correlation between S and W (initially and beyond), but transforming the state of S suddenly creates some correlations between S and W. Obviously, such a transformation would be unphysical. But, as we have seen above, requiring $\Lambda \otimes \mathbb{I}_{d'}$ to be positive – independent of d' – tantamounts to requiring Λ to be CP (besides being trace-preserving), thus CPT. This is the physical justification for the importance of the CPT requirement.

However, the physical justification for the CPT requirement notwithstanding, (12.1) and (12.2) informs us that it is already an entrenched and inextricable property of all linear maps $\Lambda : \mathcal{O}_d^{+,1} \to \mathcal{O}_d^{+,1}$.

It is a simple exercise to generalize the above results and reach the conclusion that

Λ ***still remains CPT even if its domain and image are subsets of*** $\mathcal{O}_d^{+,1}$.

Chapter 13

Universal dynamical maps

In the study of quantum dynamics, we are usually interested in how the density matrix $\rho \in \mathcal{O}_d^{+,1}$ of a quantum system evolves in time. For a coherent account of this time evolution in the interval $t_o \leq t \leq t_f$ – where t_o and t_f are the initial and final instances of our observation we are interested in – it is easy to see that $\rho(t)$ must remain in the convex set $\mathcal{O}_d^{+,1}$. To this time evolution, we may associate the map

$$\Lambda_{t,t_o} : \mathsf{C}_d^{+,1} \rightarrow \mathsf{C}_d'^{+,1} \tag{13.1}$$

such that $\rho(t) = \Lambda_{t,t_o}\rho(t_o)$, where $\rho(t_o) \in \mathsf{C}_d^{+,1}$ and $\mathsf{C}_d^{+,1}, \mathsf{C}_d'^{+,1}$ are subsets of $\mathcal{O}_d^{+,1}$. We may refer to Λ_{t,t_o} as a *quantum dynamical map* (or simply *quantum map*). Using the results of the previous chapter, in particular (12.17), it follows readily that

$$\Lambda_{t,t_o}\rho(t_o) = \rho(t) = \sum_{\mu=0}^{d-1} M_\mu(t,t_o)\rho(t_o)M_\mu^\dagger(t,t_o) \tag{13.2}$$

where – from (12.18) and (12.10), respectively –

$$M_\mu(t,t_o) = U(t)\Gamma_\mu(t)U^\dagger(t_o) \tag{13.3}$$

$$\Gamma_\mu(t) = \sum_{k=1}^{d-\mu} \sqrt{\lambda_k(t)}\ \ |k\rangle\langle k+\mu|\ \ + \sum_{k=d-\mu+1}^{d} \sqrt{\lambda_k(t)}\ \ |k\rangle\langle k+\mu-d|\ \ . \tag{13.4}$$

We recall again here that $\{|k\rangle\}$ is the canonical basis of $\mathcal{H}_d$, (12.7). Moreover, $\{\lambda_k(t)\}$ are the eigenvectors of $\rho(t)$, while $U(t)$ and $U(t_o)$ are the unitary operators which diagonalize $\rho(t)$ and $\rho(t_o)$, respectively. Naturally, the generalized Kraus operators $\{M_\mu(t,t_o)\}$ satisfy the completeness relation in (12.2), namely,

$$\sum_{\mu=0}^{d-1} M_\mu^\dagger(t,t_o)M_\mu(t,t_o) = \mathbb{1}_d\ . \tag{13.5}$$

Again, we observe that the generalized Kraus operators $\{M_\mu(t,t_o)\}$ depend on the initial state $\rho(t_o)$, while $U(t)$ and $\{\Gamma_\mu(t)\}$ determine $\rho(t)$.

Interestingly, the operators $M_\mu(t,t_o)$ bear some important similarities to the quantum measurement operators we discussed in Chap. 3 and Chap. 4. In fact, comparing (13.2) with (4.14), we may view the former as some sort of generalized non-selective measurement, albeit a rather peculiar one. Contrary to the quantum measurement operators we saw in Chap. 3 and Chap. 4, which were independent of the initial state, the operators $M_\mu(t,t_o)$ here do actually depend on the initial state, as remarked earlier. From Chap. 12, it becomes conspicuously evident that this dependency on the initial state would confine the domain of Λ_{t,t_o} to the set $\mathsf{C}_d^{+,1}[\rho(0)] \subset \mathcal{O}_d^{+,1}$, where $\mathsf{C}_d^{+,1}[\rho(0)]$ is the set of all convex combinations of elements of $\mathcal{O}_d^{+,1}$ which commute with the initial state $\rho(0)$.

A simpler quantum map Λ_{t,t_o} will be one whose associated Kraus operators $\{M_\mu(t,t_o)\}$ are independent of the initial state – just like those encountered in Chap. 3 and Chap. 4. Such a map is commonly referred to as a *universal dynamical map* (UDM) [132]. The following definitions then follow:

Definition 13.0.1. Given the state space $\mathcal{H}_d$, a quantum map Λ is said to be a *universal dynamical map* (UDM) if

$$\Lambda : \mathcal{O}_d^{+,1} \to \mathsf{C}_d'^{+,1} \tag{13.6}$$

where $\mathsf{C}_d'^{+,1} \subseteq \mathcal{O}_d^{+,1}$.

Definition 13.0.2. Given the state space $\mathcal{H}_d$, a quantum map Λ is said to be a *non-universal dynamical map* (non-UDM) if

$$\Lambda : \mathsf{C}_d^{+,1}\big(\subset \mathcal{O}_d^{+,1}\big) \to \mathsf{C}_d'^{+,1}\ . \tag{13.7}$$

In other words, the domain of Λ is a proper subset of $\mathcal{O}_d^{+,1}$.

We also deduce from the results of the preceding chapter that *both UDMs and non-UDMs are CPT with respect to their respective domains.*

In the study of open quantum systems, we usually consider a bipartite system consisting of a system of interest S and its environment (or reservoir) R. The state space of the system-plus-reservoir, $S+R$, is $\mathcal{H}_S \otimes H_R$ – where $\mathcal{H}_X$ is the state space of free X $(X = S, R)$. An effective quantum map for the focused system S is obtained by tracing out R's degrees of freedom, reducing the state space therefore from $\mathcal{H}_S \otimes H_R$ to $\mathcal{H}_S$. The quantum dynamics stemming from this state space reduction is usually referred to as *reduced dynamics*. If the effective quantum map Λ_{t,t_o} obtained does not depend on the initial state of S, then we talk of an *induced* UDM. It can be shown [132] that the quantum map Λ_{t,t_o} for S is an induced UDM if and only if: i) the initial global system-plus-reservoir $(S+R)$ state $\rho(t_o)$ is a separable one, *i.e.* $\rho(t_o) = \rho_S(t_o) \otimes \rho_R(t_o)$ – where $\rho_S(t_o)$ and $\rho_R(t_o)$ are the initial density matrices of S and the reservoir/environment R, respectively –, and ii) $\rho_R(t_o)$ remains the same for any $\rho_S(t_o)$.

13.1 Induced universal dynamical maps – Schrödinger picture

To illustrate how a UDM may originate from reduced dynamics, consider a closed $S + R$ evolving according to the Hamiltonian H, where

$$H = H_S \otimes \mathbb{I}_R + \mathbb{I}_S \otimes H_R + H_I \tag{13.8}$$

– where H_S and H_R are the free Hamiltonians of S and R, respectively, and H_I is their interaction Hamiltonian. We consider the state spaces of S and R ($\mathcal{H}_S$ and $\mathcal{H}_R$, respectively) to be finite-dimensional, and $\mathbb{I}_S$ and $\mathbb{I}_R$ are the identity operators on $\mathcal{H}_S$ and $\mathcal{H}_R$, respectively. Since the $S + R$

is closed, it follows from Postulate II of quantum quantum mechanics, (2.1) and (4.4), that, in the Schrödinger picture,

$$\frac{d}{dt}\rho(t) = -i\left[H, \rho(t)\right] \tag{13.9}$$

from which follows that

$$\rho(t) = e^{-iHt}\rho(0)e^{iHt} \tag{13.10}$$

– where we have simply put $t_o = 0$. Then

$$\rho_S(t) = \mathrm{Tr}_R\left[\rho(t)\right] = \mathrm{Tr}_R\left[e^{-iHt}\rho(0)e^{iHt}\right] \tag{13.11}$$

where $\mathrm{Tr}_R[\bullet]$ denotes the operation of partial trace over R.

A few words on the partial trace are in order here. Given two linear operators A and B, defined on the finite-dimensional state spaces $\mathcal{H}$ and $\mathcal{H}'$, respectively, the partial trace $\mathrm{Tr}_B[A \otimes B]$ is defined as

$$\mathrm{Tr}_B[A \otimes B] \equiv \sum_b \left(\mathbb{I} \otimes \langle b|\,\right)\big(A \otimes B\big)\left(\mathbb{I} \otimes |b\rangle\,\right) \tag{13.12}$$

where $\mathbb{I}$ is the identity operator on $\mathcal{H}$, the set $\{|b\rangle\}$ is an orthonormal basis which spans $\mathcal{H}'$ and '$\otimes$' denotes the Kronecker product.

Going back to (13.11), and using (13.12), we may write

$$\begin{aligned} \rho_S(t) &= \mathrm{Tr}_R\left[e^{-iHt}\left(\rho_S(0) \otimes \rho_R(0)\right)e^{iHt}\right] \\ &= \sum_\beta \left(\mathbb{I}_S \otimes \langle\beta|\right)\left(e^{-iHt}\left(\rho_S(0) \otimes \rho_R(0)\right)e^{iHt}\right)\left(\mathbb{I}_S \otimes |\beta\rangle\right) \end{aligned} \tag{13.13}$$

where, without loss of generality, we choose the state vectors $\{|\beta\rangle\}$ to be the eigenvectors of $\rho_R(0)$. That is,

$$\rho_R(0) = \sum_\beta \lambda_\beta\, |\beta\rangle\langle\beta| \ \ . \tag{13.14}$$

With (13.14), we may also rewrite (13.13) as

$$\rho_S(t) = \sum_\beta \left(\mathbb{I}_S \otimes \langle\beta|\right)\left[e^{-iHt}\left(\rho_S(0) \otimes \sum_{\beta'} \lambda_{\beta'}\, |\beta'\rangle\,\langle\beta'|\right)e^{iHt}\right]\left(\mathbb{I}_S \otimes |\beta\rangle\right) \ . \tag{13.15}$$

Employing the properties of the Kronecker product, the following chain of algebraic rearrangements follows from (13.15):

$$\begin{aligned} \rho_S(t) &= \sum_\beta \sum_{\beta'} \left(\mathbb{I}_S \otimes \langle\beta|\right)e^{-iHt}\left[\left(\rho_S(0) \otimes 1\right)\left(\mathbb{I}_S \otimes \lambda_{\beta'}\, |\beta'\rangle\,\langle\beta'|\right)\right]e^{iHt}\left(\mathbb{I}_S \otimes |\beta\rangle\right) \\ &= \sum_\beta \sum_{\beta'} \lambda_{\beta'}\left(\mathbb{I}_S \otimes \langle\beta|\right)e^{-iHt}\left[\left(\rho_S(0) \otimes 1\right)\left(\mathbb{I}_S \otimes |\beta'\rangle\right)\left(\mathbb{I}_S \otimes \langle\beta'|\right)\right]e^{iHt}\left(\mathbb{I}_S \otimes |\beta\rangle\right) \\ &= \sum_\beta \sum_{\beta'} \lambda_{\beta'}\left(\mathbb{I}_S \otimes \langle\beta|\right)e^{-iHt}\left[\left(\mathbb{I}_S \otimes |\beta'\rangle\right)\left(\rho_S(0) \otimes 1\right)\left(\mathbb{I}_S \otimes \langle\beta'|\right)\right]e^{iHt}\left(\mathbb{I}_S \otimes |\beta\rangle\right) \\ &= \sum_\beta \sum_{\beta'} \left[\sqrt{\lambda_{\beta'}}\left(\mathbb{I}_S \otimes \langle\beta|\right)e^{-iHt}\left(\mathbb{I}_S \otimes |\beta'\rangle\right)\right]\rho_S(0)\left[\sqrt{\lambda_{\beta'}}\left(\mathbb{I}_S \otimes \langle\beta'|\right)\right]e^{iHt}\left(\mathbb{I}_S \otimes |\beta\rangle\right)\Big] \end{aligned} \tag{13.16}$$

which leads to the final result

$$\rho_S(t) = \sum_{\beta}\sum_{\beta'} K_{\beta\beta'}(t)\rho_S(0)K^{\dagger}_{\beta\beta'}(t) \tag{13.17}$$

where

$$K_{\beta\beta'}(t) \equiv \sqrt{\lambda_{\beta'}}\Big(\mathbb{I}_S \otimes \langle\beta|\Big)e^{-iHt}\Big(\mathbb{I}_S \otimes |\beta'\rangle\Big) \ . \tag{13.18}$$

We note that the operators $K_{\beta\beta'}(t)$ are independent of $\rho_S(t)$ as they depend solely on $\rho_R(0)$. We thus see that if $\rho_R(0)$ is fixed for an arbitrary $\rho_S(0)$, then the quantum map $\Lambda_{t,0} : \mathcal{O}_d^{+,1} \to \mathcal{O}_d^{+,1}$, where

$$\Lambda_{t,0}\rho_S(0) = \sum_{\beta}\sum_{\beta'} K_{\beta\beta'}(t)\rho_S(0)K^{\dagger}_{\beta\beta'}(t) \qquad (t \geq 0) \tag{13.19}$$

is a UDM in the Schrödinger picture. Note that the crucial step in the derivation of (13.17) is the separability of the initial state of the bipartite system. It can also be easily verified that

$$\sum_{\beta}\sum_{\beta'} K^{\dagger}_{\beta\beta'}(t)K_{\beta\beta'}(t) = \mathbb{I}_S \ . \tag{13.20}$$

It follows then from Choi's theorem (Sec. 12.2) and (13.20) that $\Lambda_{t,0}$ in (13.19) is CPT.

It must be emphasized that the operators $K_{\beta\beta'}(t)$ are linear operators acting on $\mathcal{H}_S$. Indeed, if we take an arbitrary orthonormal basis $\{|s\rangle\}$ of $\mathcal{H}_S$, then from (13.18), we may rewrite $K_{\beta\beta'}(t)$ as

$$\begin{aligned} K_{\beta\beta'}(t) &= \sum_{s,s'} \sqrt{\lambda_{\beta'}}\Big(|s\rangle\langle s| \otimes \langle\beta|\Big)e^{-iHt}\Big(|s'\rangle\langle s'| \otimes |\beta'\rangle\Big) \\ &= \sum_{s,s'} \sqrt{\lambda_{\beta'}}\ |s\rangle\left[\Big(\langle s| \otimes \langle\beta|\Big)e^{-iHt}\Big(|s'\rangle \otimes |\beta'\rangle\Big)\right]\langle s'| \\ &= \sum_{s,s'} \sqrt{\lambda_{\beta'}}\ c_{s\beta,s'\beta'}(t)\ \ |s\rangle\langle s'| \end{aligned} \tag{13.21}$$

where the coefficient $c_{s\beta,s'\beta'}(t)$ has the expression

$$c_{s\beta,s'\beta'}(t) \equiv \big\langle s,\beta\big|\, e^{-iHt}\,\big|s',\beta'\big\rangle \tag{13.22}$$

with $|s,\beta\rangle \equiv |s\rangle \otimes |\beta\rangle$. The final result in (13.21) clearly shows that $K_{\beta\beta'}(t) \in \mathcal{O}_S$[1] since it is a linear combination of the operators $\{|s\rangle\langle s'|\}$ which span the Hilbert space $\mathcal{O}_S$, Sec. 1.1.

Note that the operators $K_{\beta\beta'}(t)$ are indexed by states vectors of the environment. This may prove inconvenient when using (13.17) to describe the dynamics of S, especially when the dimension of $\mathcal{H}_R$ greatly exceeds that of $\mathcal{H}_S$. It is therefore advisable to rewrite (13.17) in a form where the Kraus operators are indexed by states directly related to $\mathcal{H}_R$. This can be easily achieved as follows: since, as we have seen, $K_{\beta\beta'}(t) \in \mathcal{O}_S$, we can express $K_{\beta\beta'}(t)$ as a linear combination of any orthonormal operator basis of $\mathcal{O}_S$, Sec. 1.1. Equation (13.21) is just an example of such an expansion. Let the dimension of $\mathcal{H}_S$ be d. For simplicity, let $\{\mathscr{A}_\mu\}$ $(\mu = 0, 1, 2, \ldots, d^2 - 1)$ be an orthonormal operator basis of $\mathcal{O}_S$. That is,

$$\mathrm{Tr}[\mathscr{A}_\mu \mathscr{A}^{\dagger}_{\mu'}] = \delta_{\mu,\mu'} \ . \tag{13.23}$$

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[1] $\mathcal{O}_S$ is the Hilbert space of linear operators acting on $\mathcal{H}_S$.

Then we may expand each $K_{\beta\beta'}(t)$ as a linear combination of $\{\mathscr{A}_\mu\}$:

$$K_{\beta\beta'}(t) = \sum_{\mu=0}^{d^2-1} c_{\mu,\beta\beta'}(t)\mathscr{A}_\mu \ , \qquad \text{where} \ \ c_{\mu,\beta\beta'}(t) \equiv \mathrm{Tr}[K_{\beta\beta'}(t)\mathscr{A}_\mu^\dagger] \ . \tag{13.24}$$

Introducing this expansion into (13.17) yields

$$\Lambda_{t,0}\rho_S(0) = \sum_{\mu=0}^{d^2-1}\sum_{\mu'=0}^{d^2-1} \zeta_{\mu\mu'}(t) \ \mathscr{A}_\mu \rho_S(0)\mathscr{A}_{\mu'}^\dagger \tag{13.25}$$

where

$$\zeta_{\mu\mu'}(t) \equiv \sum_{\beta}\sum_{\beta'} c_{\mu,\beta\beta'}(t) \ c^*_{\mu',\beta\beta'}(t) \ . \tag{13.26}$$

The significance of (13.25) is that the range of influences of the environment R on the time evolution of S is now succinctly encapsulated in the coefficients $\{\zeta_{\mu\mu'}(t)\}$. Interestingly, the matrix $\zeta(t)$ is positive semi-definite, *i.e.* given $x \in \mathbb{C}^{d^2}$, $x^\dagger \zeta x \geq 0$. Indeed

$$\begin{aligned} x^\dagger\zeta x &= \sum_{\mu,\mu'} x_\mu^\dagger \zeta_{\mu\mu'}(t) x_{\mu'} = \sum_{\beta}\sum_{\beta'}\sum_{\mu,\mu'} x_\mu^\dagger c_{\mu,\beta\beta'}(t) \ c^*_{\mu',\beta\beta'}(t) x_{\mu'} \\ &= \sum_{\beta}\sum_{\beta'}\left(\sum_{\mu} x_\mu^\dagger c_{\mu,\beta\beta'}(t)\right)\left(\sum_{\mu'} x_{\mu'}^\dagger c_{\mu',\beta\beta'}(t)\right)^\dagger = \sum_{\beta}\sum_{\beta'}\left|\sum_{\mu} x_\mu^\dagger c_{\mu,\beta\beta'}(t)\right|^2 \geq 0 \ . \end{aligned} \tag{13.27}$$

Since $\zeta(t)$ is positive semi-definite, we know its eigenvalues are nonnegative and there exits a unitary transformation $U(t)$ which diagonalizes $\zeta(t)$, *i.e.*

$$\zeta(t) = U(t)\gamma(t)U^\dagger(t) \tag{13.28}$$

where $\gamma(t)$ is the diagonal matrix which collects the eigenvalues of $\zeta(t)$. From (13.28), it follows that

$$\zeta_{\mu\mu'}(t) = \sum_{\mu''=0}^{d^2-1} U_{\mu\mu''}(t)\gamma_{\mu''\mu''}(t)U^\dagger_{\mu''\mu'}(t) \ . \tag{13.29}$$

Substituting (13.29) into (13.25), we get

$$\begin{aligned} \Lambda_{t,0}\rho_S(0) &= \sum_{\mu=0}^{d^2-1}\sum_{\mu'=0}^{d^2-1}\sum_{\mu''=0}^{d^2-1} U_{\mu\mu''}(t)\gamma_{\mu''\mu''}(t)U^\dagger_{\mu''\mu'}(t) \ \mathscr{A}_\mu\rho_S(0)\mathscr{A}^\dagger_{\mu'} \\ &= \sum_{\mu''=0}^{d^2-1}\left(\sqrt{\gamma_{\mu''\mu''}(t)} \ \sum_{\mu=0}^{d^2-1}\mathscr{A}_\mu U_{\mu\mu''}(t)\right)\rho_S(0)\left(\sqrt{\gamma_{\mu''\mu''}(t)} \ \sum_{\mu'=0}^{d^2-1} U^\dagger_{\mu''\mu'}(t)\mathscr{A}^\dagger_{\mu'}\right) \end{aligned} \tag{13.30}$$

which may be simply written as

$$\Lambda_{t,0}\rho_S(0) = \sum_{\mu=0}^{d^2-1} \mathscr{K}_\mu(t)\rho_S(0)\mathscr{K}_\mu^\dagger(t) \tag{13.31}$$

where

$$\mathscr{K}_\mu(t) \equiv \sqrt{\gamma_\mu(t)} \ \sum_{\mu'=0}^{d^2-1}\mathscr{A}_{\mu'}U_{\mu'\mu}(t) \ . \tag{13.32}$$

(we have simply written $\gamma_{\mu\mu}$ as γ_μ). Here too, it can be verified that the operators $\{\mathscr{K}_\mu(t)\}$ satisfy the completeness relation

$$\sum_{\mu=0}^{d^2-1} \mathscr{K}_\mu^\dagger(t)\mathscr{K}_\mu(t) = \mathbb{I}_S \ . \tag{13.33}$$

Naturally, the quantum map $\Lambda_{t,0}$ in (13.31) is still a UDM in the Schrödinger picture for a fixed initial state $\rho_R(0)$ of R. The fingerprints of R's influence on the time-evolution of S are to be found in the scalars $\{\gamma_\mu(t)\}$ and $\{U_{\mu\mu'}(t)\}$.

It is worth observing that while the generalized Kraus operators discussed in the previous chapter were at most d in total (see for example (12.17) and (12.18)), the Kraus operators $\mathscr{K}_\mu(t)$ in (13.31) are at most d^2 in total. The reason for this discrepancy lies in the fact that the map Λ_t in (13.31) is an induced UDM.

13.2 Induced universal dynamical maps – Heisenberg picture

As it is known, in the Heisenberg picture, we let elements of $\mathcal{O}_d$ other than the density matrix evolve in time. Given the Schrödinger picture quantum map $\Lambda_{t,0}$, its Heisenberg picture representation $(\Lambda^H_{t,0})$ can be easily derived from $\Lambda_{t,0}$ by imposing an invariance on the extended Hilbert-Schmidt inner product $\langle \Lambda_{t,0}\rho_S(0), A\rangle$ – where $A \in \mathcal{O}_d$ and $A \neq \rho_S$ – as one moves into the Heisenberg picture. That is,

$$\langle \Lambda_{t,0}\rho_S(0), A\rangle = \left\langle \rho_S(0), \Lambda^H_{t,0}A\right\rangle \tag{13.34}$$

– which, according to (1.15), translates into

$$\mathrm{Tr}\Big[A\ \Lambda_{t,0}\rho_S(0)\Big] = \mathrm{Tr}\Big[\Lambda^H_{t,0}A\ \rho_S(0)\Big] \tag{13.35}$$

where we have made use of Hermitian property of $\Lambda_{t,0}\rho_S(0)$ and $\rho_S(0)$. If we make use of (13.31), for example, then (13.35) may be written as

$$\begin{aligned} \mathrm{Tr}\left[A \sum_{\mu=0}^{d^2-1} \mathscr{K}_\mu(t)\rho_S(0)\mathscr{K}_\mu^\dagger(t)\right] &= \mathrm{Tr}\Big[\Lambda^H_{t,0}A\ \rho_S(0)\Big] \\ \mathrm{Tr}\left[\sum_{\mu=0}^{d^2-1} A\mathscr{K}_\mu(t)\rho_S(0)\mathscr{K}_\mu^\dagger(t)\right] &= \mathrm{Tr}\Big[\Lambda^H_{t,0}A\ \rho_S(0)\Big] \ . \end{aligned} \tag{13.36}$$

Making use of the cyclic property of the trace functional, we may conveniently rearrange the factors on the l.h.s., obtaining

$$\mathrm{Tr}\left[\left(\sum_{\mu=0}^{d^2-1} \mathscr{K}_\mu^\dagger(t)A\mathscr{K}_\mu(t)\right)\rho_S(0)\right] = \mathrm{Tr}\Big[\Lambda^H_{t,0}A\ \rho_S(0)\Big] \tag{13.37}$$

– from which follows that

$$\Lambda^H_{t,0}A = \sum_{\mu=0}^{d^2-1} \mathscr{K}_\mu^\dagger(t)A\mathscr{K}_\mu(t) \ . \tag{13.38}$$

The invariance in (13.35) is important because it allows the expectation value of an observable to remain unchanged with respect to either picture.

Chapter 14

Quantum dynamical semigroups

We saw in Sec. 13.1 how an induced UDM may originate from a reduced dynamics. If we revise our discussion in Sec. 13.1 attentively, we recognize that if we fix $t = t_f$, the quantum map $\Lambda_{t_f,0}$ as given in (13.31) takes as input $\rho_S(0)$ and maps it to a new state $\rho_S(t_f)$, parameterized by t_f. The caveat here is that at the initial time $t = 0$, the bipartite system $S + R$ must be in the separable state $\rho_S(0) \otimes \rho_R(0)$, where $\rho_R(0)$ is fixed. The map $\Lambda_{t_f,0}$ does not inform us, whatsoever, on how S evolves in the time interval $0 < t < t_f$, for example: it just tells us what the state of S is at the instant t_f. One might be inclined to assume that the map $\Lambda_{t_f,t'}$ – where $0 < t' < t_f$ –, must also be a UDM. It can be easily proved that that is not actually the case in general [132]. This problem is sometimes referred to as the 'time continuity problem' of UDMs [132].

However, there is a class of induced UDMs of particular interest in the theory of open quantum systems which are free from the time continuity problem. In particular, these UDMs are such that for $0 \leq t_1 \leq t_2 \leq t$,

$$\Phi_{t,t_2}\Phi_{t_2,t_1} = \Phi_{t,t_1} \ . \tag{14.1}$$

This composition property allows these maps to form a one-parameter (with respect to the initial time $t = 0$) semigroup $\{\Phi_{t,0}|t \in \mathbb{R}^+\}$[1] on $\mathcal{O}_d^{+,1}$ – technically referred to as a *quantum dynamical semigroup* [5, 22, 37]. Equation (14.1) is usually referred to as the *semigroup condition* or *Markov property* [5]. It is not difficult to also realize that for quantum dynamical semigroups, the extended Hilbert-Schmidt inner product (1.15) $\langle \Phi_{t,0}\rho_S(0), A\rangle = \mathrm{Tr}\big[A\ \Phi_{t,0}\rho_S(0)\big]$, for $A \in \mathcal{O}_d$, is a continuous function of t [5][2].

14.1 Generators of quantum dynamical semigroups

If $\{\Phi_{t,0}|t \in \mathbb{R}^+\}$ is a quantum dynamical semigroup, then it can be shown that [5, 22, 37, 58, 97, 132]

$$\frac{d}{dt}\rho_S(t) = \mathcal{L}\rho_S(t) \tag{14.2}$$

where $\rho_S(t) \equiv \Phi_{t,0}\rho_S(0)$. The map $\mathcal{L} : \mathcal{O}_d^{+,1} \to \mathcal{O}_d$ is said to be the *generator* of the quantum dynamical semigroup $\{\Phi_{t,0}|t \in \mathbb{R}^+\}$. And (14.2) is referred to as a *quantum Markovian master equation*[3]/ *Lindblad*

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[1] $\mathbb{R}^+$ is the set of nonnegative real numbers.

[2] This is actually true for all induced UDMs.

[3] Or *Markovian quantum master equation* [22].

master equation/ the *Gorini-Kossakowski-Sudarshan-Lindblad (GKSL) equation*. An important result in the theory of open quantum systems states that all generators of quantum dynamical semigroups may be cast into a specific standard form. This important result is due to Gorini, Kossakowski, Sudarshan [58] and Lindblad [97]. Using the fact that $\rho_S(t) \equiv \Phi_{t,0}\rho_S(0)$, it is easily realized that (14.2) leads to the following formal master equation for the map $\Phi_{t,0}$:

$$\frac{d}{dt}\Phi_{t,0} = \mathcal{L}\Phi_{t,0} \tag{14.3}$$

which has the formal solution

$$\Phi_{t,0} = e^{t\mathcal{L}} \ . \tag{14.4}$$

Given the Markov property of the semigroup (14.1), we know $\Phi_{t,t'}\Phi_{t',0} = \Phi_{t,0}$, with $0 \leq t' \leq t$. Using (14.4), it is deduced that

$$\Phi_{t,t'} = e^{(t-t')\mathcal{L}} \ . \tag{14.5}$$

We need to also recall that the elements of the quantum dynamical semigroup $\{\Phi_{t,0}|t \in \mathbb{R}^+\}$ are also induced UDMs, and as such, it follows from (13.31) that

$$\Phi_{t,0}\rho_S(0) = \sum_{\mu=0}^{d^2-1} \mathscr{K}_\mu(t)\rho_S(0)\mathscr{K}_\mu^\dagger(t) = \rho_S(t) \tag{14.6}$$

where the Kraus operators are independent of arbitrary $\rho_S(0) \in \mathcal{O}_d^{+,1}$. Putting together (14.4) and (14.6), the formal relation

$$e^{t\mathcal{L}}\rho_S(0) \equiv \sum_{\mu=0}^{d^2-1} \mathscr{K}_\mu(t)\rho_S(0)\mathscr{K}_\mu^\dagger(t) = \rho_S(t) \tag{14.7}$$

then holds. This also implies that

$$\Phi_{t,0}\rho_S(0) = \Phi_{t,t'}\Phi_{t',0}\rho_S(0) = \Phi_{t,t'}\rho_S(t') \equiv e^{(t-t')\mathcal{L}}\rho_S(t') \tag{14.8}$$

where we have made use of (14.5). From (14.6), it follows that

$$e^{(t-t')\mathcal{L}}\rho_S(t') \equiv \sum_{\mu=0}^{d^2-1} \mathscr{K}_\mu(t-t')\rho_S(t')\mathscr{K}_\mu^\dagger(t-t') \ . \tag{14.9}$$

With these results we can determine the general form of the generator $\mathcal{L}$ of a quantum dynamical semigroup. In other words, we can determine the general features a reduced quantum master equation for $\rho_S(t)$ must possess in order to guarantee that the associated induced UDMs form a quantum dynamical semigroup.

14.2 Derivation of the Lindblad master equation

Consider the quantum dynamical semigroup $\{\Phi_{t,0}|t \in \mathbb{R}^+\}$ on the state space $\mathcal{H}_d$ of the focus system S. Naturally, (14.6) holds. As elements of $\mathcal{O}_d$, we may expand the Kraus operators $\{\mathscr{K}_\mu(t)\}$ in any orthonormal basis of $\mathcal{O}_d$. In the literature, the basis always chosen is one in which one of the elements is proportional to the identity operator $\mathbb{I}_d$, without specifying the nature of the other $(d^2 - 1)$ elements.

To fill this gap, we draw the Reader's attention to the fact that any finite dimensional state space $\mathcal{H}_d$ can be mapped to the spin state space of a spin-$(d-1)/2$ particle. For example, any two-dimensional state space can be mapped to the spin state space of a spin-$1/2$ particle. From this observation, it is easy to conclude that any finite dimensional Hilbert space of linear operators $\mathcal{O}_d$ can be mapped to the Hilbert space of linear operators acting on the spin state space of a spin-$(d-1)/2$ particle. Allard and Härd in [6] have provided a complete operator basis set for any spin quantum number. The advantage of their proposed spin operator basis is that it always includes an operator which is proportional to the identity operator. This makes their basis appropriate for our purpose. Using the results in [6], we choose as basis of $\mathcal{O}_d$ the set of operators $\{F^S_{k,q,\varpi}\}$, where $S \equiv (d-1)/2$, $\varpi \in \{x, y, z\}$ and

$$\begin{aligned} F^S_{k,qx} &= \frac{1}{\sqrt{2(2S+1)}} \left(T^S_{k,-q} + (-1)^q \; T^S_{k,q}\right) \qquad (q \neq 0) \\ F^S_{k,qy} &= \frac{i}{\sqrt{2(2S+1)}} \left(T^S_{k,-q} - (-1)^q \; T^S_{k,q}\right) \qquad (q \neq 0) \\ F^S_{k,qz} &= \frac{1}{\sqrt{2S+1}} T^S_{k,q} \qquad (q = 0) \end{aligned} \tag{14.10}$$

– where for fixed S, $0 \leq k \leq 2S$, and $-k \leq q \leq k$ (k is a non-negative integer and q is an integer). With respect to [6], we have changed the normalization constant of the operators $\{F^S_{k,q,\varpi}\}$. The operators $T^S_{k,q}$ are irreducible spherical tensors defined as [6]:

$$T^S_{k,q} = \sqrt{2S+1}\sqrt{2k+1} \sum_{m=-S}^{S} \sum_{m'=-S}^{S} (-1)^{S-m} \begin{pmatrix} S & k & S \\ -m & q & m' \end{pmatrix} |S, m\rangle\langle S, m'| \tag{14.11}$$

where $\begin{pmatrix} S & k & S \\ -m & q & m' \end{pmatrix}$ denotes a Wigner-$3j$ symbol (see Appendix A) and the $|S, m\rangle$ denotes the spin ket of a spin-$S[= (d-1)/2]$ particle with spin quantum magnetic number $-S \leq m \leq S$[4]. Using the symmetric and orthogonality properties of the Wigner-$3j$ symbols outlined in Appendix A, it can be verified that

$$\mathrm{Tr}\left[T^S_{k,q} T^{S\dagger}_{k',q'}\right] = (2S+1) \; \delta_{k,k'} \; \delta_{q,q'} \; . \tag{14.12}$$

Employing this orthogonality relation, it can be easily proved that

$$\mathrm{Tr}\left[F^S_{k,q\varpi} F^{S\dagger}_{k',q'\varpi'}\right] = \delta_{k,k'} \; \delta_{q,q'} \; \delta_{\varpi,\varpi'} \; . \tag{14.13}$$

Since the set $\{F^S_{k,q,\varpi}\}$ is countable, it is possible to enumerate its elements. We may choose an enumeration ranging from 1 to d^2 (that is, the cardinality of the set). This is equivalent to performing a mapping of the sort $\{k, q, \varpi\} \rightarrow \{\nu\}$, where $\nu = 1, 2, \ldots, d^2$. Consequently, $\{F^S_{k,q,\varpi}\} \rightarrow \{F^S_\nu\}$, and (14.14) becomes simply

$$\mathrm{Tr}\left[F^S_\nu F^{S\dagger}_{\nu'}\right] = \delta_{\nu,\nu'} \; . \tag{14.14}$$

In light of these results, we may express each Kraus operator $\mathscr{K}_\mu(t)$ in (14.6) as a linear combination of the set $\{F^S_\nu\}$, obtaining:

$$\mathscr{K}_\mu(t) = \sum_{\nu=1}^{d^2} c_{\mu\nu}(t) \; F^S_\nu \; , \qquad c_{\mu\nu}(t) \equiv \mathrm{Tr}\big[\mathscr{K}_\mu(t) \; F^{S\dagger}_\nu\big] \; . \tag{14.15}$$

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[4] It is also possible to express the operators $T^S_{k,q}$ (14.11) in terms of the HP bosons, Chap. 6.

Substituting (14.15) into (14.6) yields

$$\rho_S(t) = \sum_{\nu=1}^{d^2} \sum_{\nu'=1}^{d^2} \zeta_{\nu\nu'}(t)\ F^S_\nu \rho_S(0) F^{S\dagger}_{\nu'} \tag{14.16}$$

where the coefficient $\zeta_{\nu\nu'}(t)$ is defined as

$$\zeta_{\nu\nu'}(t) \equiv \sum_{\mu=0}^{d^2-1} c_{\mu\nu}(t) c^*_{\mu\nu'}(t)\ . \tag{14.17}$$

Just as we did in (13.27), one can show that the matrix $\zeta(t)$ in (14.17) is positive semi-definite.

Let $F^S_{0,0z}$ be $F^S_{\nu=d^2}$. Then, it follows from the properties of the Wigner-3j symbols (Appendix A) that $F^S_{d^2} = \frac{1}{\sqrt{d}} \mathbb{I}_d$. With this choice, it readily follows that $\mathrm{Tr}\big[F^S_\nu\big] = 0$ for $\nu = 1, 2, \ldots, (d^2 - 1)$.

Furthermore, from the limit definition of derivate, we know

$$\frac{d}{dt}\rho_S(t) = \lim_{\epsilon \to 0} \frac{1}{\epsilon} \Big[\rho_S(t+\epsilon) - \rho_S(t) \Big]\ . \tag{14.18}$$

Recall according to (14.6), $\rho_S(t+\epsilon) = \Phi_{t+\epsilon,0}\rho_S(0)$ and $\rho_S(t) = \Phi_{t,0}\rho_S(0)$. Using the Markov property of the dynamical semigroup $\{\Phi_{t,0} | t \in \mathbb{R}^+\}$, *i.e.* (14.1), it follows that

$$\rho_S(t+\epsilon) = \Phi_{t+\epsilon,0}\rho_S(0) = \Phi_{t+\epsilon,t}\Phi_{t,0}\rho_S(0) = \Phi_{t+\epsilon,t}\rho_S(t) \tag{14.19a}$$

$$= \sum_{\mu=0}^{d^2-1} \mathscr{K}_\mu(\epsilon) \rho_S(t) \mathscr{K}^\dagger_\mu(\epsilon) \tag{14.19b}$$

$$= \sum_{\nu=1}^{d^2} \sum_{\nu'=1}^{d^2} \zeta_{\nu\nu'}(\epsilon)\ F^S_\nu \rho_S(t) F^{S\dagger}_{\nu'} \tag{14.19c}$$

where in obtaining (14.19b) we have made use of (14.8), and (14.19c) follows from (14.15) and (14.17).

With (14.19c), (14.18) becomes

$$\frac{d}{dt}\rho_S(t) = \lim_{\epsilon \to 0} \frac{1}{\epsilon} \left[\sum_{\nu=1}^{d^2} \sum_{\nu'=1}^{d^2} \zeta_{\nu\nu'}(\epsilon)\ F^S_\nu \rho_S(t) F^{S\dagger}_{\nu'} - \rho_S(t) \right]\ . \tag{14.20}$$

From (14.20), it follows that

$$\begin{aligned}
\frac{d}{dt}\rho_S(t) &= \lim_{\epsilon \to 0} \frac{1}{\epsilon} \Bigg[\zeta_{d^2 d^2}(\epsilon) F^S_{d^2} \rho_S(t) F^{S\dagger}_{d^2} + \sum_{\nu'=1}^{d^2-1} \zeta_{d^2\nu'}(\epsilon) F^S_{d^2} \rho_S(t) F^{S\dagger}_{\nu'} + \sum_{\nu=1}^{d^2-1} \zeta_{\nu d^2}(\epsilon) F^S_\nu \rho_S(t) F^{S\dagger}_{d^2} \\
&\quad + \sum_{\nu=1}^{d^2-1} \sum_{\nu'=1}^{d^2-1} \zeta_{\nu\nu'}(\epsilon) F^S_\nu \rho_S(t) F^{S\dagger}_{\nu'} - \rho_S(t) \Bigg] \\
&= \lim_{\epsilon \to 0} \frac{1}{\epsilon} \Bigg[\frac{\zeta_{d^2 d^2}(\epsilon) - d}{d} \rho_S(t) + \sum_{\nu'=1}^{d^2-1} \frac{\zeta_{d^2\nu'}(\epsilon)}{\sqrt{d}} \rho_S(t) F^{S\dagger}_{\nu'} + \sum_{\nu=1}^{d^2-1} \frac{\zeta_{\nu d^2}(\epsilon)}{\sqrt{d}} F^S_\nu \rho_S(t) \\
&\quad + \sum_{\nu=1}^{d^2-1} \sum_{\nu'=1}^{d^2-1} \zeta_{\nu\nu'}(\epsilon) F^S_\nu \rho_S(t) F^{S\dagger}_{\nu'} \Bigg] \\
&= \kappa_{d^2 d^2} \rho_S(t) + \rho_S(t) \mathscr{F}^\dagger + \mathscr{F} \rho_S(t) + \sum_{\nu=1}^{d^2-1} \sum_{\nu'=1}^{d^2-1} \kappa_{\nu\nu'} F^S_\nu \rho_S(t) F^{S\dagger}_{\nu'}\ .
\end{aligned} \tag{14.21}$$

where we have set

$$\mathscr{F} \equiv \sum_{\nu=1}^{d^2-1} \kappa_{\nu,d^2} F_\nu^S \tag{14.22}$$

with

$$\kappa_{\nu\nu'} \equiv \begin{cases} \lim_{\epsilon\to 0} \ \frac{1}{\epsilon}\frac{\zeta_{d^2d^2}(\epsilon)-d}{d} & (\text{for } \nu=\nu'=d^2) \\ \lim_{\epsilon\to 0} \ \frac{1}{\epsilon}\frac{\zeta_{\nu d^2}(\epsilon)}{\sqrt{d}} & (\text{for } \nu'=d^2 \text{ and } \nu\neq d^2) \\ \lim_{\epsilon\to 0} \ \frac{1}{\epsilon}\zeta_{\nu\nu'}(\epsilon) & (\text{for } \nu'\neq d^2 \text{ and } \nu\neq d^2) \end{cases} . \tag{14.23}$$

Since the trace is conserved (due to the completeness relation satisfied by the Kraus operators, (13.33)), it follows from the last equation in (14.21) that

$$\kappa_{d^2d^2}\mathbb{I}_d + \mathscr{F}^\dagger + \mathscr{F} + \sum_{\nu=1}^{d^2-1}\sum_{\nu'=1}^{d^2-1} \kappa_{\nu\nu'} F_{\nu'}^{S\dagger} F_\nu^S = 0 \tag{14.24}$$

from which we derive that

$$\kappa_{d^2d^2}\mathbb{I}_d = -\mathscr{F}^\dagger - \mathscr{F} - \sum_{\nu=1}^{d^2-1}\sum_{\nu'=1}^{d^2-1} \kappa_{\nu\nu'} F_{\nu'}^{S\dagger} F_\nu^S \ . \tag{14.25}$$

Writing the product between $\left(\kappa_{d^2d^2}\mathbb{I}_d\right)$ and $\rho_S(t)$ in the symmetric form and using (14.25) yields[5]

$$\begin{aligned} \kappa_{d^2d^2}\rho_S(t) &= \frac{1}{2}\Big[\kappa_{d^2d^2}\rho_S(t) + \rho_S(t)\kappa_{d^2d^2}\Big] \\ &= -\frac{1}{2}\left\{\rho_S(t), \mathscr{F}^\dagger + \mathscr{F}\right\} - \frac{1}{2}\sum_{\nu=1}^{d^2-1}\sum_{\nu'=1}^{d^2-1} \kappa_{\nu\nu'} \left\{F_{\nu'}^{S\dagger} F_\nu^S, \rho_S(t)\right\} \ . \end{aligned} \tag{14.26}$$

Inserting (14.26) into (14.21), we get

$$\frac{d}{dt}\rho_S(t) = -\frac{1}{2}\left\{\rho_S(t), \mathscr{F}^\dagger + \mathscr{F}\right\} + \rho_S(t)\mathscr{F}^\dagger + \mathscr{F}\rho_S(t) + \sum_{\nu=1}^{d^2-1}\sum_{\nu'=1}^{d^2-1} \kappa_{\nu\nu'} \left[F_\nu^S \rho_S(t) F_{\nu'}^{S\dagger} - \frac{1}{2}\left\{F_{\nu'}^{S\dagger} F_\nu^S, \rho_S(t)\right\}\right] . \tag{14.27}$$

But note that

$$-\frac{1}{2}\left\{\rho_S(t), \mathscr{F}^\dagger + \mathscr{F}\right\} + \rho_S(t)\mathscr{F}^\dagger + \mathscr{F}\rho_S(t) = \frac{1}{2}\rho_S(t)\Big(\mathscr{F}^\dagger - \mathscr{F}\Big) - \frac{1}{2}\Big(\mathscr{F}^\dagger - \mathscr{F}\Big)\rho_S(t) \ . \tag{14.28}$$

Since $\mathscr{F}^\dagger - \mathscr{F}$ is skew-Hermitian, we may write

$$\frac{1}{2}\Big(\mathscr{F}^\dagger - \mathscr{F}\Big) = iH \tag{14.29}$$

where $H \in \mathcal{O}_d$ is Hermitian. Thus,

$$-\frac{1}{2}\left\{\rho_S(t), \mathscr{F}^\dagger + \mathscr{F}\right\} + \rho_S(t)\mathscr{F}^\dagger + \mathscr{F}\rho_S(t) = -i\big[H, \rho_S(t)\big] \ . \tag{14.30}$$

Inserting this into (14.27) finally yields

$$\frac{d}{dt}\rho_S(t) = -i\big[H, \rho_S(t)\big] + \sum_{\nu=1}^{d^2-1}\sum_{\nu'=1}^{d^2-1} \kappa_{\nu\nu'} \left[F_\nu^S \rho_S(t) F_{\nu'}^{S\dagger} - \frac{1}{2}\left\{F_{\nu'}^{S\dagger} F_\nu^S, \rho_S(t)\right\}\right] . \tag{14.31}$$

---

[5] For $X, Y \in \mathcal{O}_d$, $\{X, Y\}$ denotes the anti-commutator. That is, $\{X, Y\} = XY + YX$.

In other words – according to (14.2) –, the generator $\mathcal{L}$ of the quantum dynamical semigroup $\{\Phi_{t,0}|t \in \mathbb{R}^+\}$ is such that

$$\mathcal{L}\rho_S(t) = -i\big[H, \rho_S(t)\big] + \sum_{\nu=1}^{d^2-1}\sum_{\nu'=1}^{d^2-1} \kappa_{\nu\nu'} \left[F_\nu^S \rho_S(t) F_{\nu'}^{S\dagger} - \frac{1}{2}\left\{ F_{\nu'}^{S\dagger} F_\nu^S, \rho_S(t) \right\} \right] . \tag{14.32}$$

The first term of (14.32) describes a unitary evolution. The second term is called the *dissipator* term and describes non-unitary transformations of the density matrix. It is important to note that the matrix κ appearing in the dissipator term is a (d^2-1) square matrix. But more importantly, it follows from (14.23) that it is also positive semi-definite, just like $\zeta(t)$. This observation allows two more alternative ways of expressing the result in (14.32). Indeed, in analogy to (13.28) and (13.29), we have that

$$\kappa_{\nu\nu'} = \sum_{\nu''=1}^{d^2-1} U_{\nu\nu''}\gamma_{\nu''\nu''}U^\dagger_{\nu''\nu'} \tag{14.33}$$

where U is the unitary transformation which diagonalizes κ and γ is the diagonal matrix containing the eigenvalues of κ. Introducing (14.33) into (14.32) yields

$$\mathcal{L}\rho_S(t) = -i\big[H, \rho_S(t)\big] + \sum_{\nu=1}^{d^2-1} \gamma_\nu \left[A_\nu \rho_S(t) A_\nu^\dagger - \frac{1}{2}\left\{ A_\nu^\dagger A_\nu, \rho_S(t) \right\} \right] \tag{14.34}$$

where $\gamma_\nu \equiv \gamma_{\nu\nu}$ and

$$A_\nu \equiv \sum_{\nu'=1}^{d^2-1} F_{\nu'}^S U_{\nu'\nu} \ . \tag{14.35}$$

But since the eigenvalues $\{\gamma_\nu\}$ are all nonnegative reals due to the fact that κ is positive semi-definite, we may also rewrite (14.34) as

$$\mathcal{L}\rho_S(t) = -i\big[H, \rho_S(t)\big] + \sum_{\nu=1}^{d^2-1} \left[V_\nu \rho_S(t) V_\nu^\dagger - \frac{1}{2}\left\{ V_\nu^\dagger V_\nu, \rho_S(t) \right\} \right] \tag{14.36}$$

with $V_\nu \equiv \sqrt{\gamma_\nu} A_\nu$. Moreover, (14.34) and (14.36) are said to be the *diagonal forms* of the generator $\mathcal{L}$ [22]. And the operators $\{A_\nu\}$ (or even $\{V_\nu\}$) are usually referred to as *Lindblad operators*.

Chapter 15

Microscopic derivation of quantum Markovian master equations

In the previous chapter, we derived the Lindblad master equation, (14.32)/(14.34)/(14.36), starting from the Kraus operator sum representation of the quantum dynamical semigroup, (14.6). The derivation therefore rests on knowing the Kraus operators $\{K_\mu(t)\}$ related to the semigroup. In practical scenarios, one do not know the Kraus operators beforehand, for they also constitute the unknowns of the quantum dynamics. For open quantum systems, what one usually has is the total Hamiltonian H of the $S+R$ system, assumed to be a closed quantum system. This then begs the question: under what conditions/approximations/assumptions can the induced UDMs of such a system form a quantum dynamical semigroup? Put slightly differently, we are asking what are the necessary conditions/approximations/assumptions which ensure that the generator $\mathcal{L}$ of the reduced dynamics of the focused system S is a generator of quantum dynamical semigroup, if we start from the unitary dynamics of the $S+R$ closed system. The derivation of such a generator from the equation of motion for the unitary dynamics of the $S+R$ is what goes under the name of *microscopic derivation* of quantum Markovian master equations.

In the microscopic derivation we are going to undertake below, we will resort to the so-called *weak-coupling* assumption. This assumption will be a central theme in subsequent discussions, especially in the Part IV. With the total Hamiltonian H of the closed bipartite quantum system given in (13.8), the assumption entails that

$$\|H_S \otimes \mathbb{1}_R + \mathbb{1}_S \otimes H_R\| \gg \|H_I\| \ . \tag{15.1}$$

That is, the interaction Hamiltonian H_I is a perturbation term with respect to the sum of the free Hamiltonians of S and R. In this work, we shall assign a stricter interpretation to (15.1): for Hermitian $X, Y \in \mathcal{O}_d$, where $X\left|x_k\right\rangle = E_k \left|x_k\right\rangle,\ k = 1, 2, \ldots, d,\ E_k \in \mathbb{R}$, – we shall adopt the following meaning:

$$\|X\| \gg \|Y\| \quad \Rightarrow \quad \left|\frac{\left\langle x_k\right| Y \left|x_{k'}\right\rangle}{E_k - E_{k'}}\right| \ll 1 \qquad \forall\ E_k \neq E_{k'} \ . \tag{15.2}$$

15.1 Unitary evolution of the closed quantum system

As mentioned above, we start with the Schrödinger equation for the closed bipartite quantum system, (13.9):

$$\frac{d}{dt}\rho(t) = -i\,[H, \rho(t)] \tag{15.3}$$

where $H = H_S \otimes \mathbb{I}_R + \mathbb{I}_S \otimes H_R + H_I$, (13.8). It is clear that the initial state must still be a separable one as we discussed in Chap. 13, *i.e.*

$$\rho(0) = \rho_S(0) \otimes \rho_R(0) \tag{15.4}$$

– else, the quantum map we get after tracing out the environment R will fail to be an induced UDM [132] – to begin with.

In light of the weak-coupling assumption, we may transit into the interaction picture. By doing so, we transform (15.3) into

$$\frac{d}{dt}\varrho(t) = -i\,[V(t), \varrho(t)] \tag{15.5}$$

where

$$\begin{aligned} \varrho(t) &\equiv e^{it[H_S\otimes\mathbb{I}_R + \mathbb{I}_S\otimes H_R]}\rho(t)e^{-it[H_S\otimes\mathbb{I}_R+\mathbb{I}_S\otimes H_R]} \\ &= \left(e^{itH_S}\otimes e^{itH_R}\right)\rho(t)\left(e^{-itH_S}\otimes e^{-itH_R}\right) \end{aligned} \tag{15.6}$$

and

$$V(t) \equiv \left(e^{itH_S}\otimes e^{itH_R}\right)H_I\left(e^{-itH_S}\otimes e^{-itH_R}\right)\ . \tag{15.7}$$

The formal integration of (15.5) results in

$$\varrho(t) = \varrho(0) - i\int_0^t dt'\,[V(t'), \varrho(t')]\ . \tag{15.8}$$

With this formal solution, (15.5) becomes

$$\begin{aligned} \frac{d}{dt}\varrho(t) &= -i\,[V(t), \varrho(0)] - \int_0^t dt'\,[V(t), [V(t'), \varrho(t')]] \\ &= -i\,[V(t), \varrho(0)] - \int_0^t d\tau\,[V(t), [V(t-\tau), \varrho(t-\tau)]]\ . \end{aligned} \tag{15.9}$$

Tracing out the environment R, we obtain

$$\begin{aligned} \frac{d}{dt}\widetilde{\varrho}_S(t) &= -i\mathrm{Tr}_R\,[V(t), \varrho(0)] - \int_0^t d\tau\ \mathrm{Tr}_R\,[V(t), [V(t-\tau), \varrho(t-\tau)]] \\ &= -i\mathrm{Tr}_R\,[V(t), \varrho(0)] - \int_0^t d\tau\ \mathrm{Tr}_R\Big(\,[V^\dagger(t), V(t-\tau)\varrho(t-\tau)] + h.c.\Big) \end{aligned} \tag{15.10}$$

where $\widetilde{\varrho}_S(t) \in \mathcal{O}_d^{+,1}$ is the reduced density matrix of S in the interaction picture:

$$\widetilde{\varrho}_S(t) = \mathrm{Tr}_R[\varrho(t)]\ . \tag{15.11}$$

The operation $\mathrm{Tr}_R[\bullet]$ denotes partial trace over R and is defined in (13.12).

15.2 Defining $\rho(t)$ and H_I

To proceed with the derivation, we need to consider explicit expressions for $\rho(t)$ and H_I.

First of all, we note that given the initial condition in (15.4) – imposed by induced UDMs –, we may express $\rho(t)$ as

$$\rho(t) = \rho_S(t) \otimes \rho_R(0) + \rho_{corr}(t) \tag{15.12}$$

where the operator $\rho_{corr}(t) \in \mathcal{O}_{S+R}$ is traceless and satisfies the initial condition

$$\rho_{corr}(0) = 0 \ . \tag{15.13}$$

The operator $\rho_{corr}(t)$ accounts for the correlations between S and R which may come into effect in the time interval $t > 0$. Substituting (15.12) into (15.6), we obtain

$$\varrho(t) = \varrho_S(t) \otimes \varrho_R^o(t) + \varrho_{corr}(t) \tag{15.14}$$

where

$$\varrho_S(t) \equiv e^{itH_S}\rho_S(t)e^{-itH_S} \tag{15.15a}$$

$$\varrho_R^o(t) \equiv e^{itH_R}\rho_R(0)e^{-itH_R} \tag{15.15b}$$

$$\varrho_{corr}(t) \equiv \left(e^{itH_S} \otimes e^{itH_R}\right)\rho_{corr}(t)\left(e^{-itH_S} \otimes e^{-itH_R}\right) \ . \tag{15.15c}$$

Regarding H_I, we may express it as

$$H_I = \sum_{i,j} c_{ij} \ A_i \otimes B_j \tag{15.16}$$

where $A_i \in \mathcal{O}_S$ and $B_j \in \mathcal{O}_R$ and c_{ij} is a scalar[1]. The Hermiticity of H_I naturally requires that

$$\sum_{i,j} c_{ij}^* \ A_i^\dagger \otimes B_j^\dagger = \sum_{i,j} c_{ij} \ A_i \otimes B_j \ . \tag{15.19}$$

Note that even if H_I is not in the form as given in (15.16), we can still put it in a similar form by simply expanding it in any operator basis of $\mathcal{O}_{S+R}$. Indeed, if $\{|s\rangle\langle s'|\}$ and $\{|\alpha\rangle\langle\alpha'|\}$ are operator basis of $\mathcal{O}_S$ and $\mathcal{O}_R$, respectively, then $\{|s\rangle\langle s'| \otimes |\alpha\rangle\langle\alpha'|\}$ is an operator basis for $\mathcal{O}_{S+R}$. Thus, we may expand $H_I \in \mathcal{O}_{S+R}$ in the basis $\{|s\rangle\langle s'| \otimes |\alpha\rangle\langle\alpha'|\}$, no matter the form of H_I. That is,

$$H_I = \sum_{s,s'}\sum_{\alpha,\alpha'} h_{s\alpha,s'\alpha'} \ \ |s\alpha\rangle \ \langle s'\alpha'| = \sum_{s,s'}\sum_{\alpha,\alpha'} h_{s\alpha,s'\alpha'} \ \ |s\rangle\langle s'| \otimes |\alpha\rangle\langle\alpha'| \tag{15.20}$$

---

[1] In the literature, H_I is usually assumed to be of the form

$$H_I = \sum_i A_i \otimes B_i \tag{15.17}$$

where $A_i \in \mathcal{O}_S$, $B_i \in \mathcal{O}_R$ and $A_i^\dagger = A_i$ and $B_i^\dagger = B_i$. Certainly, (15.16) is more general than (15.17). But in [22], for example, it is claimed that (15.17) is the most general form of the interaction Hamiltonian H_I. That is obviously not accurate. To give a simple example, if S and R are both two-level systems, then a possible interaction Hamiltonian H_I is

$$H_I = c_{+-}\sigma_+ \otimes \sigma_- + c_{+-}^*\sigma_- \otimes \sigma_+ + c_{33}\sigma_3 \otimes \sigma_3 \tag{15.18}$$

where c_{33} is real, c_{+-} is a complex scalar and the $\{\sigma_\mu\}$ are related to the Pauli matrices. See also [71].

where $|s\alpha\rangle \equiv |s\rangle \otimes |\alpha\rangle$ and

$$h_{s\alpha,s'\alpha'} \equiv \langle s\alpha| H_I |s'\alpha'\rangle \ . \tag{15.21}$$

With (15.16), it follows from (15.7) that

$$V(t) = \sum_{i,j} c_{ij} \ A_i(t) \otimes B_j(t) \tag{15.22}$$

where

$$A_i(t) \equiv e^{itH_S} A_i e^{-itH_S} \tag{15.23a}$$

$$B_j(t) \equiv e^{itH_R} B_j e^{-itH_R} \ . \tag{15.23b}$$

Employing these new expressions for $\varrho(t)$ and $V(t)$ – *i.e.* (15.14) and (15.22) – in (15.10), it turns out that

$$\begin{aligned}
\frac{d}{dt}\widetilde{\varrho}_S(t) = & -i\sum_i \Bigg(\sum_j c_{ij}\big\langle B_j(t)\big\rangle_R\Bigg)\big[A_i(t), \varrho_S(0)\big] \\
& - \Bigg\{\int_0^t d\tau \ \sum_{i,i'}\Bigg(\sum_{j,j'} c^*_{ij}c_{i'j'}\big\langle B_j^\dagger(\tau)B_{j'}(0)\big\rangle_R\Bigg) \ \big[A_i^\dagger(t), A_{i'}(t-\tau)\varrho_S(t-\tau)\big] + h.c. \\
& + \int_0^t d\tau \ \mathrm{Tr}_R\Bigg[\Bigg(\sum_{i,j}\sum_{i',j'} c^*_{ij}c_{i'j'} \ A_i^\dagger(t)A_{i'}(t-\tau)\otimes B_j^\dagger(t)B_{j'}(t-\tau)\Bigg)\varrho_{corr}(t-\tau)\Bigg] + h.c. \\
& - \int_0^t d\tau \mathrm{Tr}_R\Bigg[\Bigg(\sum_{i',j'} c_{i'j'} \ A_{i'}(t-\tau)\otimes B_{j'}(t-\tau)\Bigg)\varrho_{corr}(t-\tau)\Bigg(\sum_{i,j} c^*_{ij} \ A_i^\dagger(t)\otimes B_j^\dagger(t)\Bigg)\Bigg] + h.c.\Bigg\}
\end{aligned} \tag{15.24}$$

where

$$\big\langle B_j(t)\big\rangle_R \equiv \mathrm{Tr}_R\big[B_j(t)\rho_R(0)\big] \tag{15.25a}$$

$$\big\langle B_j^\dagger(\tau)B_{j'}(0)\big\rangle_R \equiv \mathrm{Tr}_R\big[B_j^\dagger(\tau)B_{j'}(0)\rho_R(0)\big] \ . \tag{15.25b}$$

The functions $\big\langle B_j^\dagger(\tau)B_{j'}(0)\big\rangle_R$ are the so-called *environment/reservoir correlation functions*. Note that this particular form of these correlation functions as given in (15.25b) is usually obtained in the literature [22] by assuming that the reservoir is in a stationary state with respect to its free Hamiltonian, so that $[H_R, \rho_R(0)] = 0$. In obtaining (15.25b), however, we made use of no such assumption, for the result simply follows from the fact that

$$\begin{aligned}
\mathrm{Tr}_R\Big[B_j^\dagger(t)B_{j'}(t-\tau)\varrho^o_R(t-\tau)\Big] &= \mathrm{Tr}_R\Big[e^{itH_R}B_j^\dagger e^{-itH_R}e^{i(t-\tau)H_R}B_{j'}e^{-i(t-\tau)H_R}e^{i(t-\tau)H_R}\rho_R(0)e^{-i(t-\tau)H_R}\Big] \\
&= \mathrm{Tr}_R\Big[e^{i\tau H_R}B_j^\dagger e^{-i\tau H_R}B_{j'}\rho_R(0)\Big] = \mathrm{Tr}_R\Big[B_j^\dagger(\tau)B_{j'}\rho_R(0)\Big] \\
&= \big\langle B_j^\dagger(\tau)B_{j'}(0)\big\rangle \ .
\end{aligned} \tag{15.26}$$

15.3 The Born approximation and the stability condition of environment

So far, the only approximation or assumption we have made is the weak-coupling assumption. Thus, in this limit, (15.24) is exact. We now introduce the first of a series of approximations which will ultimately turn the generator of the dynamics into a generator of a quantum dynamical semigroup. This is the *Born approximation*. With this approximation, we are assuming the correlations between S and R which may come into play in the course of the bipartite system's time evolution is negligible. In other words, $\|\rho_S(t) \otimes \rho_R(0)\| \gg \|\rho_{corr}(t)\| \sim 0$ for $t \geq 0$[2]. With this approximation, (15.24) becomes

$$\begin{aligned} \frac{d}{dt}\varrho_S(t) = &-i \sum_i \left(\sum_j c_{ij} \big\langle B_j(t) \big\rangle_R \right) \left[A_i(t), \varrho_S(0) \right] \\ &- \left\{ \int_0^t d\tau \sum_{i,i'} \left(\sum_{j,j'} c^*_{ij} c_{i'j'} \big\langle B^\dagger_j(\tau) B_{j'}(0) \big\rangle_R \right) \left[A^\dagger_i(t), A_{i'}(t-\tau)\varrho_S(t-\tau) \right] + h.c. \right\} . \end{aligned} \tag{15.27}$$

(Note that with the Born approximation, $\widetilde{\varrho}_S(t) \to \varrho_S(t)$.)

The second approximation we are going to introduce is what is sometimes referred to as the *stability condition of environment*. Here, one assumes the first term in (15.10) (or (15.27)) is identically zero. That is,

$$\mathrm{Tr}_R \left[V(t), \varrho(0) \right] = \sum_i \left(\sum_j c_{ij} \big\langle B_j(t) \big\rangle_R \right) \left[A_i(t), \varrho_S(0) \right] = 0 \, . \tag{15.28}$$

In the literature [22], the more stringent assumption that $\big\langle B_j(t) \big\rangle = 0 \, , \forall B_j(t)$ is often adopted. Also in the literature [22, 100], it is argued that even if (15.28) is not satisfied, one can redefine H_S and H_I as follows

$$H_S \to H_S + \sum_{i,j} c_{ij} \big\langle B_j(t) \big\rangle_R A_i \tag{15.29a}$$

$$H_I \to \sum_{i,j} c_{ij} \; A_i \otimes \left(B_j - \big\langle B_j(t) \big\rangle_R \mathbb{1}_R \right) \tag{15.29b}$$

so that the first term in (15.27) still remains identically zero. Despite the fact that this strategy allows one to get rid of the first term in (15.27), great caution must be exercised when applying it because it could have unanticipated dramatic effects on the results[3]. This strategy may thus be said to be airbrushed in the literature. We are, therefore, simply going to assume (15.28) holds. In light of this assumption, (15.27) further simplifies to

$$\frac{d}{dt}\varrho_S(t) = - \left\{ \int_0^t d\tau \sum_{i,i'} \left(\sum_{j,j'} c^*_{ij} c_{i'j'} \big\langle B^\dagger_j(\tau) B_{j'}(0) \big\rangle_R \right) \left[A^\dagger_i(t), A_{i'}(t-\tau)\varrho_S(t-\tau) \right] + h.c. \right\} . \tag{15.30}$$

15.4 The Markov approximations

The presence of $\rho_S(t-\tau)$ in (15.30) implies that the master equation is not local in time [103], and that ρ_S evolves with some memory effects. To make the master equation local in time – so that if

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[2] Here, with $\|X\|$, we intend any linear operator norm, but not necessarily the stricter specification given in (15.2).

[3] This is the subject of a paper the author is currently working on.

we take a snapshot of ρ_S at any chosen instant $t \geq 0$, its time evolution will depend on the state at that very instant, *i.e.* $\rho_S(t)$, and not on states of previous instances –, we introduce the first Markov approximation, where we substitute $\varrho_S(t-\tau)$ in (15.30) with $\varrho_S(t)$:

$$\frac{d}{dt}\varrho_S(t) = -\left\{ \int_0^t d\tau \sum_{i,i'} \left(\sum_{j,j'} c_{ij}^* c_{i'j'} \left\langle B_j^\dagger(\tau) B_{j'}(0) \right\rangle_R \right) \left[A_i^\dagger(t), A_{i'}(t-\tau)\varrho_S(t) \right] + h.c. \right\} \ . \tag{15.31}$$

The master equation hereby obtained is essentially the *Redfield equation* [129]. This approximation can be justified in real applications whereby the timescale τ_B over which the reservoir correlation functions decay is very short compared to the timescale τ_S of S' evolution, [22], and the timescale τ_B is not accessible to experimental observations [15]. If τ_B is very short compared to the timescale of observation of S, then we may go further by extending the upper limit of the integration in (15.32) to infinity (second Markov approximation), obtaining:

$$\frac{d}{dt}\varrho_S(t) = -\left\{ \int_0^\infty d\tau \sum_{i,i'} \left(\sum_{j,j'} c_{ij}^* c_{i'j'} \left\langle B_j^\dagger(\tau) B_{j'}(0) \right\rangle_R \right) \left[A_i^\dagger(t), A_{i'}(t-\tau)\varrho_S(t) \right] + h.c. \right\} \ . \tag{15.32}$$

The Born approximation and Markov approximations are sometimes collectively referred to as the *Born-Markov approximation* [22].

15.5 The secular approximation

Let $\{|\varepsilon_n\rangle\}$ $(n = 1, 2, \ldots, d)$ be the eigenvectors of H_S. Naturally,

$$H_S\,|\varepsilon_n\rangle = \varepsilon_n\,|\varepsilon_n\rangle \tag{15.33}$$

where the real scalar ε_n is the eigenvalue corresponding to the eigenvector $|\varepsilon_n\rangle$. With the set $\{|\varepsilon_n\rangle\}$, we can decompose the operators $\{A_i\}$ as follows:

$$A_i = \sum_{\omega_o} A_i(\omega_o) \tag{15.34}$$

where

$$A_i(\omega_o) \equiv \sum_{n,n'} |\varepsilon_n\rangle\langle\varepsilon_n|\,A_i\,|\varepsilon_{n'}\rangle\langle\varepsilon_{n'}|\,\delta_{\omega_o,\varepsilon_{n'}-\varepsilon_n} \ . \tag{15.35}$$

The frequencies $\{\omega_o\}$ are thus seen to range over all possible pairwise differences between the eigenvalues of H_S. Note that because the $\{A_i\}$ are not assumed to be Hermitian (as it is usually the case in the literature [22]) , we have from (15.35), that

$$\left[A_i(\omega_o)\right]^\dagger = \sum_{n,n'} |\varepsilon_n\rangle\langle\varepsilon_n|\,A_i^\dagger\,|\varepsilon_{n'}\rangle\langle\varepsilon_{n'}|\,\delta_{-\omega_o,\varepsilon_{n'}-\varepsilon_n} = A_i^\dagger(-\omega_o) \ . \tag{15.36}$$

Had A_i been Hermitian, then $\left[A_i(\omega_o)\right]^\dagger = A_i(-\omega_o)$, as given in the literature [22]. The distinction between $\left[A_i(\omega_o)\right]^\dagger$ and $A_i^\dagger(\omega_o)$ is therefore paramount, and should be kept in mind. In the following, we shall simply write $\left[A_i(\omega_o)\right]^\dagger$ as $A_i(\omega_o)^\dagger$.

Using (15.34) and (15.35), it readily follows from (15.23a) that

$$A_i(t) = \sum_{\omega_o} e^{-it\omega_o} A_i(\omega_o) \tag{15.37}$$

– from which follows that

$$A_i^\dagger(t) = \sum_{\omega_o} e^{it\omega_o} A_i(\omega_o)^\dagger \ . \tag{15.38}$$

Equations (15.37) and (15.38) allow us to rewrite (15.32) as

$$\frac{d}{dt}\varrho_S(t) = -\left\{ \int_0^\infty d\tau \sum_{i,i'} \sum_{\omega_o,\omega_o'} \left(\sum_{j,j'} c_{ij}^* c_{i'j'} \big\langle B_j^\dagger(\tau) B_{j'}(0) \big\rangle_R \right) e^{it(\omega_o-\omega_o')} e^{i\tau\omega_o'} \big[A_i(\omega_o)^\dagger, A_{i'}(\omega_o')\varrho_S(t) \big] + h.c. \right\} \tag{15.39}$$

or, more succinctly,

$$\frac{d}{dt}\varrho_S(t) = -\left\{ \sum_{i,i'} \sum_{\omega_o,\omega_o'} e^{it(\omega_o-\omega_o')} \Gamma_{ii'}(\omega_o') \big[A_i(\omega_o)^\dagger, A_{i'}(\omega_o')\varrho_S(t) \big] + h.c. \right\} \ . \tag{15.40}$$

where

$$\Gamma_{ii'}(\omega_o) \equiv \sum_{j,j'} c_{ij}^* c_{i'j'} \int_0^\infty d\tau \ e^{i\tau\omega_o} \big\langle B_j^\dagger(\tau) B_{j'}(0) \big\rangle_R \ . \tag{15.41}$$

It is clear from (15.40) that the timescale τ_S of S' evolution in the interaction picture is in the order of $\tau_S^{-1} \sim \min\{|\omega_o - \omega_o'| \mid \omega_o \neq \omega_o'\}$. If the timescale of S' relaxation τ_{rel} (which, for nondimensional $\{A_i\}$, depends on the matrix $\Gamma_{ii'}(\omega_o')$) is very long compared to τ_S, then the factors $e^{it(\omega_o-\omega_o')}$ will be rapidly oscillating for $\omega_o - \omega_o' \neq 0$. Superimposing these rapid oscillations with the relaxation of S, we see that we will barely resolve the oscillations as they are fast compared to the relaxation. This means that we can simply set $\omega_o = \omega_o'$ in (15.40), and the latter becomes

$$\begin{aligned}
\frac{d}{dt}\varrho_S(t) &= -\left\{ \sum_{i,i'} \sum_{\omega_o} \Gamma_{ii'}(\omega_o) \big[A_i(\omega_o)^\dagger, A_{i'}(\omega_o)\varrho_S(t) \big] + h.c. \right\} \\
&= \sum_{i,i'} \sum_{\omega_o} \Big[\Gamma_{ii'}(\omega_o) A_{i'}(\omega_o)\varrho_S(t) A_i(\omega_o)^\dagger - \Gamma_{ii'}(\omega_o) A_i(\omega_o)^\dagger A_{i'}(\omega_o)\varrho_S(t) \\
&\quad + \Gamma_{i'i}^*(\omega_o) A_{i'}(\omega_o)\varrho_S(t) A_i(\omega_o)^\dagger - \Gamma_{i'i}^*(\omega_o)\varrho_S(t) A_i(\omega_o)^\dagger A_{i'}(\omega_o) \Big] \ .
\end{aligned} \tag{15.42}$$

Note that we may decompose $\Gamma_{ii'}(\omega_o)$ as follows:

$$\begin{aligned}
\Gamma_{ii'}(\omega_o) &= \frac{1}{2}\big[\Gamma_{ii'}(\omega_o) + \Gamma_{i'i}^*(\omega_o)\big] + i\frac{1}{2i}\big[\Gamma_{ii'}(\omega_o) - \Gamma_{i'i}^*(\omega_o)\big] \\
&= \frac{1}{2}\gamma_{ii'}(\omega_o) + iS_{ii'}(\omega_o)
\end{aligned} \tag{15.43}$$

where

$$\gamma_{ii'}(\omega_o) \equiv \Gamma_{ii'}(\omega_o) + \Gamma_{i'i}^*(\omega_o) \tag{15.44a}$$

$$S_{ii'}(\omega_o) \equiv \frac{1}{2i}\big[\Gamma_{ii'}(\omega_o) - \Gamma_{i'i}^*(\omega_o)\big] \ . \tag{15.44b}$$

With this decomposition of $\Gamma_{ii'}(\omega_o)$, (15.42) becomes

$$\frac{d}{dt}\varrho_S(t) = -i\big[H_{LS}, \varrho_S(t)\big] + \sum_{\omega_o} \sum_{i,i'} \gamma_{ii'}(\omega_o) \left[A_{i'}(\omega_o)\varrho_S(t) A_i(\omega_o)^\dagger - \frac{1}{2}\left\{ A_i(\omega_o)^\dagger A_{i'}(\omega_o), \varrho_S(t) \right\} \right] \tag{15.45}$$

where the Hermitian operator H_{LS}, called the *Lamb shift Hamiltonian* [22], has the expression

$$H_{LS} \equiv \sum_{\omega_o} \sum_{i,i'} S_{ii'}(\omega_o) A_i(\omega_o)^\dagger A_{i'}(\omega_o) \ . \tag{15.46}$$

And one can easily verify that the Lamb shift Hamiltonian H_{LS} commutes with H_S:

$$\big[H_{LS}, H_S\big] = 0 \ . \tag{15.47}$$

We also note that the master equation in (15.45) is quite reminiscent of (14.31), which we saw gives the general structure of a quantum Markovian master equation. For the quantum map related to the master equation in (15.45) to be CPT, the matrix $\big[\gamma_{ii'}(\omega_o)\big]$ needs to be positive semi-definite. But from its definition in (15.44a), there is no indication that $\big[\gamma_{ii'}(\omega_o)\big]$ is positive semi-definite. Let us take a closer look at this matrix.

15.6 Approximating $\rho_R(0)$ as a H_R stationary state

From (15.44a) and (15.44a), it follows that

$$\begin{aligned}\gamma_{ii'}(\omega_o) &= \Gamma_{ii'}(\omega_o) + \Gamma^*_{i'i}(\omega_o) \\ &= \sum_{j,j'} c^*_{ij} c_{i'j'} \int_0^\infty d\tau \ e^{i\tau\omega_o} \big\langle B_j^\dagger(\tau) B_{j'}(0)\big\rangle_R + \left(\sum_{j,j'} c^*_{i'j} c_{ij'} \int_0^\infty d\tau \ e^{i\tau\omega_o} \big\langle B_j^\dagger(\tau) B_{j'}(0)\big\rangle_R\right)^* \\ &= \sum_{j,j'} c^*_{ij} c_{i'j'} \left(\int_0^\infty d\tau \ e^{i\tau\omega_o} \big\langle B_j^\dagger(\tau) B_{j'}(0)\big\rangle_R + \int_{-\infty}^0 d\tau \ e^{i\tau\omega_o} \big\langle B_{j'}^\dagger(-\tau) B_j(0)\big\rangle_R^*\right) \ . \end{aligned} \tag{15.48}$$

We observe that the matrix $\Big[\sum_{j,j'} c^*_{ij} c_{i'j'}\Big]$ is positive semi-definite, so for $\big[\gamma_{ii'}(\omega_o)\big]$ to be positive semi-definite, it must be required that

$$\left(\int_0^\infty d\tau \ e^{i\tau\omega_o} \big\langle B_j^\dagger(\tau) B_{j'}(0)\big\rangle_R + \int_{-\infty}^0 d\tau \ e^{i\tau\omega_o} \big\langle B_{j'}^\dagger(-\tau) B_j(0)\big\rangle_R^*\right) \geq 0 \ . \tag{15.49}$$

It is worth noting at this point that

$$\big\langle B_{j'}^\dagger(-\tau) B_j(0)\big\rangle_R^* = \mathrm{Tr}_R\big[B_j^\dagger(\tau) B_{j'}(0) \varrho_R^o(\tau)\big] \tag{15.50}$$

where, from (15.15b), we know $\varrho_R^o(t) = e^{itH_R}\rho_R(0)e^{-itH_R}$ – which is the initial density matrix of the reservoir in the interaction picture. One easily realizes that if $\rho_R(0)$ is a stationary state with respect to H_R, so that $\big[H_R, \rho_R(0)\big] = 0$, then $\varrho_R^o(t) = \rho_R(0)$ and (15.50) becomes

$$\big\langle B_{j'}^\dagger(-\tau) B_j(0)\big\rangle_R^* = \mathrm{Tr}_R\big[B_j^\dagger(\tau) B_{j'}(0) \rho_R(0)\big] = \big\langle B_{j'}^\dagger(\tau) B_j(0)\big\rangle_R \ . \tag{15.51}$$

With (15.51), (15.48) simply becomes

$$\gamma_{ii'}(\omega_o) = \sum_{j,j'} c^*_{ij} c_{i'j'} \int_{-\infty}^\infty d\tau \ e^{i\tau\omega_o} \big\langle B_j^\dagger(\tau) B_{j'}(0)\big\rangle_R \geq 0 \ . \tag{15.52}$$

The matrix $\big[\gamma_{ii'}(\omega_o)\big]$ is now positive semi-definite because according to Bochner's theorem [130], the Fourier transform

$$\int_{-\infty}^\infty d\tau \ e^{i\tau\omega_o} \big\langle B_j^\dagger(\tau) B_{j'}(0)\big\rangle_R \geq 0 \tag{15.53}$$

given that the reservoir correlation functions $\langle B_j^\dagger(\tau)B_{j'}(0)\rangle_R$ are positive definite. We therefore realize that the assumption that $\rho_R(0)$ is a stationary state with respect to H_R is sufficient to make the matrix $\big[\gamma_{ii'}(\omega_o)\big]$ positive semi-definite, turning the master equation in (15.45) into a quantum Markovian master equation.

15.7 Summary

Recapitulating, we have seen that starting from the master equation in (15.3) for the unitary dynamics of the bipartite quantum system $S+R$, we have been able to derive a reduced dynamics for the subsystem S which is a UDM after applying a series of approximations and assumptions. We found that the equation of motion for S' density matrix is

$$\frac{d}{dt}\varrho_S(t) = \mathcal{L}\varrho_S(t) \tag{15.54}$$

where

$$\mathcal{L}\varrho_S(t) = -i\big[H_{LS},\varrho_S(t)\big] + \sum_{\omega_o}\sum_{i,i'}\gamma_{ii'}(\omega_o)\left[A_{i'}(\omega_o)\varrho_S(t)A_i(\omega_o)^\dagger - \frac{1}{2}\left\{A_i(\omega_o)^\dagger A_{i'}(\omega_o),\varrho_S(t)\right\}\right] \tag{15.55}$$

and $\gamma_{ii'}(\omega_o)$ has the expression

$$\gamma_{ii'}(\omega_o) = \sum_{j,j'} c_{ij}^* c_{i'j'} \int_{-\infty}^{\infty} d\tau\ e^{i\tau\omega_o}\langle B_j^\dagger(\tau)B_{j'}(0)\rangle_R\ . \tag{15.56}$$

Since the matrix $\big[\gamma_{ii'}(\omega_o)\big]$ is positive semi-definite, $\mathcal{L}$ must be the generator of a quantum dynamical semigroup. Another way to express the generator $\mathcal{L}$ is:

$$\mathcal{L}\varrho_S(t) = -i\big[H_{LS},\varrho_S(t)\big] + \mathcal{D}\big[\varrho_S(t)\big] \tag{15.57}$$

where, $\mathcal{D}\big[\varrho_S(t)\big]$, the dissipator term has the expression:

$$\mathcal{D}\big[\varrho_S(t)\big] \equiv \sum_{\omega_o}\sum_{i,i'}\gamma_{ii'}(\omega_o)\left[A_{i'}(\omega_o)\varrho_S(t)A_i(\omega_o)^\dagger - \frac{1}{2}\left\{A_i(\omega_o)^\dagger A_{i'}(\omega_o),\varrho_S(t)\right\}\right]\ . \tag{15.58}$$

Naturally, one can put the dissipator term $\mathcal{D}\big[\varrho_S(t)\big]$ into its diagonal form, as we saw in (14.34) and (14.36).

Part IV

Semiclassical quantum Markovian master equations

In this Part, we try to devise a methodology which allows one to use the ideas and mathematical tools discussed in Part III even when the environment is not fully quantized. We use continuous wave (CW) magnetic resonance as proof of concept. We also introduce an approximation scheme we have termed *affine commutation perturbation* (ACP) and show that the ACP scheme entails non-trivial results even at the zeroth-order approximation. And indeed, we shall focus mainly on the zeroth-order approximation of the ACP scheme.

We shall undertake a microscopic derivation of quantum Markovian master equation for CW magnetic resonance in the weak-coupling limit when the environment (the external magnetic fields) is treated classically. In this derivation, the microscopic derivation discussed in Chapter 15 will prove very helpful. One major departure from what we discussed in Chapter 15 is that we shall not enforce the environment stability condition, (15.28). This means we shall keep the term linear in the system-environment interaction in the master equation. Concentrating on the zeroth-order of the ACP scheme, we show that this choice leads to a non-UDM (non-universal dynamical map, Chap. 13). However, by enforcing the environment stability condition, the map becomes UDM. And it is interesting to observe that while most of the non-UDMs hitherto studied in the literature (with a quantized environment) are a result of initial system-environment correlations [21, 26, 72, 104, 106, 134, 145], in our case, such a map stems from the presence of the term linear in the system-environment interaction in the master equation. As we shall show, this term is also crucial for the correct theoretical description of CW magnetic resonance experiments.

The contents in this Part are primarily the original contributions of the author and are based on his preprints:

> [62] J.A. Gyamfi, *An Introduction to the Holstein-Primakoff Transformation, with Applications in Magnetic Resonance*, arXiv:1907.07122, 2019.
>
> [64] J.A. Gyamfi, *Semiclassical Quantum Markovian Master Equations. Case Study: Continuous Wave Magnetic Resonance of Multispin Systems.*, arXiv:2004.10872, 2020.

Unlike [64], we make full use of the distinction between UDMs and non-UDMs here.

Chapter 16

Why semiclassical quantum Markovian master equations

In Part III of this work, we discussed bipartite systems whereby both the focused system and its environment are treated as quantum entities. This approach to open quantum system theory outlined in Part III is one of many alternative approaches one can find in the literature [162], and it is sometimes referred to as the Gorini-Kossakowski-Sudarshan-Lindblad (GKSL) approach. The requirement that both the focused system S and its environment R be quantized, naturally impedes its application in those areas where, for all practical purposes, it suffices to treat the environment (or part of it) at the classical level. Cogent examples here include the description of processes like vibronic dynamics, molecular vibrations and electronically nonadiabatic molecular dynamics – in condensed-phase systems [83, 135, 166]. This has motivated the development of diverse open quantum system models and techniques where the focused system is treated quantum mechanically while the whole environment (or part of it) is described classically. In some of these approaches, the quantum bath correlation functions in the equation of motion for the quantum focused subsystem are substituted with appropriately symmetrized classical correlation functions [111]. One other approach which has gained traction goes as follows: one begins with the Liouville-von Neumann equation for the fully quantized $S+R$ system, and then performs a partial Wigner transformation over the relevant external degrees of freedom of the environment [83]. This has the advantage of imparting a classical character to the environment's degrees of freedom while maintaining their operator character. One may go further and define an appropriate projection operator for the quantum system's degrees of freedom and then derive a Nakajima-Zwanzig equation from the equation of motion resulting from the partial Wigner transformation described earlier [156]; this yields an equation of motion for the reduced density matrix $\rho_S(t)$ of the focused system S. What seems to be missing in the literature, however, is a similar development within the GKSL approach.

We show here in Part IV that it is possible to derive a quantum master equation for the quantum subsystem S along the lines of the GKSL approach, even when part of the environment (if not the whole) is not explicitly treated quantum mechanically. We illustrate this by developing a quantum theory for continuous wave (CW) magnetic resonance within the GKSL approach. We shall not take into account any of the molecular non-spin degrees of freedom – for example, molecular tumbling or rotations [71, 173], to name a few.

Magnetic resonance experiments, both ESR (electron spin resonance) and NMR (nuclear magnetic resonance), provide a very simple and reliable test ground to study and understand open quantum systems and its quantum technological applications [12, 16, 34, 55, 76–78, 92, 123, 141, 150, 161]. This is one of the reasons why it is only fitting that we bridge the gap between the theory of quantum magnetic resonance as formulated by pioneers like Bloch, Wangsness, Purcell, Pound, Bloembergen, Anderson, Kubo etc during the early decades of research in magnetic resonance [2, 8, 17, 32, 33, 35, 46, 61, 89, 116, 127, 142, 159, 160, 163] and the theory of open quantum systems (within the GKSL framework) [22, 29, 57, 58, 87, 97, 114, 132, 165]. We focus here on CW magnetic resonance – instead of the pulsed technique – for historical reasons. In addition, there has been a renewed interest in the CW technique because of advancements made in electronic engineering, which could improve the sensitivity and reduce the cost of its application in research laboratories [113].

Chapter 17

Wavefunction vs density matrix formalism in magnetic resonance

17.1 Wavefunction formalism

Like in many other areas, the history of magnetic resonance shows that the theoretical investigation of the dynamics of the focused quantum system has been developed along the lines of two main formalisms. These are: the wavefunction and the density matrix formalism [18].

In the wavefunction formalism, the primary object of interest is the transition probability per unit time (or transition rate) between various pairs of spin states. These transition rates are then employed to derive an expression for the spectrum [147]. The derivation of expressions for the transition rate are based on a first-order time-dependent perturbation approximation of the probability amplitudes [147]. This is normally accompanied by the assumption that the system is initially in a given specific normalized pure state. The time-dependent perturbation theory used is that due to Dirac [41], where one obtains the probability amplitudes by solving a system of differential equations.

To appreciate better the density matrix approach to spin dynamics to be discussed in the latter part of this chapter and the next chapters, we briefly discuss here the limitations of the wavefunction formalism, especially in relation to magnetic resonance. We also point out the assumptions on which the often used transition rate equations [147] derived from the formalism and used in magnetic resonance rest. (In this chapter, the constant $\hbar$ is not set equal to 1.)

Consider a spin system with its spin Hilbert space $\mathcal{H}_S$, and whose spin Hamiltonian $\mathscr{H}(t)$ is given by the sum

$$\mathscr{H}(t) = \mathscr{H}_o + \mathscr{H}'(t) \ . \tag{17.1}$$

$\mathscr{H}_o$ in (17.1) is the time-independent component of $\mathscr{H}(t)$. We denote the eigenvectors of $\mathscr{H}_o$ as $\{|k\rangle\}$, where

$$\mathscr{H}_o |k\rangle = E_k |k\rangle \ , \quad \text{and} \quad \langle k| \, k'\rangle = \delta_{k,k'} \ . \tag{17.2}$$

$\mathscr{H}'(t)$ in (17.1), on the other hand, is the time-dependent part of $\mathscr{H}(t)$.

According to the time-dependent Schrödinger equation (2.1), the equation of motion for a generic normalized spin ket $|\psi(t)\rangle \in \mathcal{H}_S$ satisfies the first-order linear differential equation

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \mathscr{H}(t) |\psi(t)\rangle \ . \tag{17.3}$$

Let us assume that at the initial time t_o, the corresponding normalized spin ket is $|\psi(t_o)\rangle$ (which is supposed to be known).

If $\mathscr{H}'(t)$ can be considered as a perturbation term with respect to $\mathscr{H}_o$ (in the sense of (15.2)), then, we may solve (17.3) for $|\psi(t)\rangle$ through a perturbation expansion. To ensure convergence of this expansion, we may transit to the interaction picture by introducing the following transformation:

$$|\psi(t)\rangle = \mathscr{U}_o(t, t_o) |\phi(t)\rangle \tag{17.4}$$

with

$$\mathscr{U}_o(t, t_o) := e^{-i(t-t_o)\mathscr{H}_o/\hbar} \tag{17.5}$$

where $|\phi(t)\rangle$ is the spin ket in the interaction picture. Then, in light of this transformation, it follows from (17.1) and (17.3) that

$$i\hbar \frac{d}{dt} |\phi(t)\rangle = \mathscr{V}_{t_o}(t) |\phi(t)\rangle \qquad \mathscr{V}_{t_o}(t) := \mathscr{U}_o^{\dagger}(t, t_o)\mathscr{H}'(t)\mathscr{U}_o(t, t_o) \tag{17.6}$$

from which we derive that

$$|\phi(t)\rangle = \mathscr{U}_I(t, t_o) |\phi(t_o)\rangle \tag{17.7}$$

where,

$$\begin{aligned}\mathscr{U}_I(t, t_o) := \mathbb{I} + \frac{1}{i\hbar}\int_{t_o}^{t} dt' \ \mathscr{V}_{t_o}(t') + \left(\frac{1}{i\hbar}\right)^2 \int_{t_o}^{t} dt' \int_{t_o}^{t'} dt'' \ \mathscr{V}_{t_o}(t')\mathscr{V}_{t_o}(t'') \\ + \left(\frac{1}{i\hbar}\right)^3 \int_{t_o}^{t} dt' \int_{t_o}^{t'} dt'' \int_{t_o}^{t''} dt''' \ \mathscr{V}_{t_o}(t')\mathscr{V}_{t_o}(t'')\mathscr{V}_{t_o}(t''') + \ldots\end{aligned} \tag{17.8}$$

where $\mathbb{I}$ is the identity operator on $\mathcal{H}_S$. Since the normalized eigenkets $\{|k\rangle\}$ constitute an orthonormal basis for the Hilbert space $\mathcal{H}_S$, we may expand $|\phi(t)\rangle$ in this basis,

$$|\phi(t)\rangle = \sum_k |k\rangle \langle k| \ \phi(t)\rangle = \sum_k a_k(t) |k\rangle \tag{17.9}$$

where,

$$a_k(t) := \langle k| \ \phi(t)\rangle \ . \tag{17.10}$$

It then definitely follows from (17.7) and (17.10) that

$$a_k(t) = \langle k| \mathscr{U}_I(t, t_o) |\phi(t_o)\rangle \ . \tag{17.11}$$

Naturally,

$$|\phi(t_o)\rangle = |\psi(t_o)\rangle = \sum_k a_k(t_o) |k\rangle \ . \tag{17.12}$$

Since the initial ket $|\psi(t_o)\rangle$ is normalized, it follows that

$$\sum_k |a_k(t)|^2 = 1 \qquad (t \geq t_o) \ . \tag{17.13}$$

Given that the initial ket $|\psi(t_o)\rangle$ is supposed to be known, the coefficients $\{a_k(t_o)\}$ are also known. If we make use of (17.12), (17.11) becomes

$$a_k(t) = \sum_{k'} \langle k| \mathscr{U}_I(t,t_o) |k'\rangle \, a_{k'}(t_o) \ . \tag{17.14}$$

From (17.11) and (17.14), we see that we have succeeded in expressing the coefficients $\{a_k(t)\}$ in function of only known quantities. More importantly, these expressions for a_k are also exact. According to (17.11), we may interpret $a_k(t)$ as the transition amplitude from the initial state $|\phi(t_o)\rangle$ to the eigenstate $|k\rangle$, by means of the evolution operator $\mathscr{U}_I(t,t_o)$. In particular, we note from (17.14) that $a_k(t)$ is a weighted sum of all the initial probability amplitudes $\{a_{k'}(t_o)\}$; the weighting factor here is the transition amplitude from the generic eigenstate $|k'\rangle$ to $|k\rangle$ by means of $\mathscr{U}_I(t,t_o)$.

Going back to the Schrödinger picture, it follows from (17.4) and (17.9) that

$$|\psi(t)\rangle = \sum_k a_k(t) e^{-i(t-t_o)E_k/\hbar} \, |k\rangle \ . \tag{17.15}$$

17.1.1 The first-order approximation and the zero-temperature limit

The derivation carried out above is exact. In general, however, it is hardly possible to exactly evaluate (17.14) for the coefficient $a_k(t)$ without any approximations. In practical computations, the approximations are introduced at the level of the evolution operator $\mathscr{U}_I(t,t_o)$, (17.8). We consider in this subsection and the next expressions for the probabilities $|a_k(t)|^2$, since these are most often of practical interest.

If we choose to approximate $a_k(t)a_l^*(t)$ up to first-order in $\mathscr{H}'(t)$, then from (17.14) and (17.8) we have

$$\begin{aligned} a_k(t)a_l^*(t) = a_k(t_o)a_l^*(t_o) &- \frac{1}{i\hbar}\sum_{k'}\int_{t_o}^{t} dt_1 \ e^{-i(t_1-t_o)\omega_{l,k'}} \, \langle k'| \mathscr{H}'(t_1) |l\rangle \, a_k(t_o)a_{k'}^*(t_o) \\ &+ \frac{1}{i\hbar}\sum_{k'}\int_{t_o}^{t} dt_1 \ e^{-i(t_1-t_o)\omega_{k',k}} \, \langle k| \mathscr{H}'(t_1) |k'\rangle \, a_{k'}(t_o)a_l^*(t_o) \end{aligned} \tag{17.16}$$

($\omega_{m,m'} \equiv (E_m - E_{m'})/\hbar$), from which we derive that

$$|a_k(t)|^2 = |a_k(t_o)|^2 + \frac{2}{\hbar}\Im\left[\sum_{k'}\int_{t_o}^{t} dt_1 \ e^{-i(t_1-t_o)\omega_{k',k}} \, \langle k| \mathscr{H}'(t_1) |k'\rangle \, a_{k'}(t_o)a_k^*(t_o)\right] \ . \tag{17.17}$$

Note that these first-order approximation expressions are generally valid for any initial ket $|\psi(t_o)\rangle$. However, it is common practice in the literature to assume $|\psi(t_o)\rangle$ is precisely one of the eigenkets $\{|k\rangle\}$ of $\mathscr{H}_o$, say $|k_o\rangle$ [11, 33, 116]. Accordingly, the coefficients $\{a_k(t_o)\}$ are such that

$$a_k(t_o) = \delta_{k,k_o} \ , \qquad \forall \ k. \tag{17.18}$$

Without loss of generality, we may refer to this assumption as the "zero-temperature limit" [56]. The zero-temperature limit assumption, (17.18), is obviously a great simplification even within the wavefunction formalism. In standard magnetic resonance experiments conducted at $T > 0K$, the initial state of the probed spin system is hardly a pure state [18], let alone one whose expansion coefficients in $\{|k_o\rangle\}$ satisfy (17.18).

At any rate, in the zero-temperature limit, (17.17) simplifies to:

$$|a_k(t)|^2 = \delta_{k,k_o} + \frac{2}{\hbar}\Im\left[\int_{t_o}^{t} dt_1\; e^{-i(t_1-t_o)\omega_{k_o,k}}\,\langle k|\,\mathscr{H}'(t_1)\,|k_o\rangle\,\delta_{k_o,k}\right] = \delta_{k,k_o}\ . \tag{17.19}$$

Thus, nothing interesting happens at the first-order approximation in the zero-temperature limit. Nevertheless, the normalization condition, (17.13), is satisfied.

17.1.2 The second-order approximation and the zero-temperature limit

From (17.14) and (17.8), we see that the expression for $|a_k(t)|^2$ approximated to second-order in $\mathscr{H}'(t)$ yields

$$\begin{aligned}|a_k(t)|^2 = |a_k(t_o)|^2 &+ \frac{2}{\hbar}\Im\left[\sum_{k'}\int_{t_o}^{t} dt_1\,\langle k|\,\mathscr{V}_{t_o}(t_1)\,|k'\rangle\,a_{k'}(t_o)a_k^*(t_o)\right]\\ &- 2\left(\frac{1}{\hbar}\right)^2\Re\left[\sum_{k'}\int_{t_o}^{t} dt_1\int_{t_o}^{t_1} dt_2\,\langle k|\,\mathscr{V}_{t_o}(t_1)\mathscr{V}_{t_o}(t_2)\,|k'\rangle\,a_{k'}(t_o)a_k^*(t_o)\right]\\ &+\left(\frac{1}{\hbar}\right)^2\left|\sum_{k'}\int_{t_o}^{t} dt_1\,\langle k|\,\mathscr{V}_{t_o}(t_1)\,|k'\rangle\,a_{k'}(t_o)\right|^2\ .\end{aligned} \tag{17.20}$$

In the zero-temperature limit, (17.20) simplifies to:

$$\begin{aligned}|a_k(t)|^2 = \delta_{k_o,k} &- 2\left(\frac{1}{\hbar}\right)^2\Re\left[\int_{t_o}^{t} dt_1\int_{t_o}^{t_1} dt_2\,\langle k_o|\,\mathscr{V}_{t_o}(t_1)\mathscr{V}_{t_o}(t_2)\,|k_o\rangle\right]\delta_{k,k_o}\\ &+\left(\frac{1}{\hbar}\right)^2\left|\int_{t_o}^{t} dt_1\; e^{-i(t_1-t_o)\omega_{k_o,k}}\,\langle k|\,\mathscr{H}'(t_1)\,|k_o\rangle\right|^2\end{aligned} \tag{17.21}$$

– from which follows that $\sum_k |a_k(t)|^2 = 1$. Thus, the normalization condition stated in (17.13) is also satisfied at this order of approximation. This is actually the case for all orders of approximation.

It is easily derived from (17.21) that for $k \neq k_o$,

$$|a_k(t)|^2 = \left(\frac{1}{\hbar}\right)^2\left|\int_{t_o}^{t} dt_1\; e^{-i(t_1-t_o)\omega_{k_o,k}}\,\langle k|\,\mathscr{H}'(t_1)\,|k_o\rangle\right|^2\ . \tag{17.22}$$

This is the ubiquitous transition probability equation in the wavefunction formalism [11], which is applied in many problems – including magnetic resonance [33, 116]. In fact, theoretical derivations in quantum magnetic resonance studies based on the wavefunction formalism are usually carried out: 1) with the product $a_k(t)a_l^*(t)$ approximated to second-order in $\mathscr{H}'(t)$, and 2) assuming the zero-temperature limit condition. Together, these two have been extensively applied both in the theory of electron spin resonance (ESR) [116] and nuclear magnetic resonance (NMR) [33]. As limiting as the zero-temperature assumption is, its employment has played an invaluable role in our understanding of the magnetic resonance phenomenon in the framework of quantum mechanics. Certainly, the reduction in mathematical complexity one achieves with it has been a decisive factor in its widespread applications. For example, the starting point of Solomon's derivation of expressions for the transition rates between the states in a system of two spins in his 1955 seminal paper [147] – which has had an enormous impact on the field – is actually the expression in (17.22). Consequently, the expressions for the relaxation times T_1 and T_2 in [147] should be used bearing in mind the limitations of the zero-temperature limit and the wavefunction formalism [2, 18].

17.2 Density matrix formalism

The wavefunction formalism has long been known to be inadequate for the full quantum mechanical description of spin dynamics because it fails to account for the evolution of the coherences (which, we know, play a crucial role in the quantum mechanical description of the magnetic resonance phenomenon) [2, 129]. In the study of magnetic resonance, the density matrix formalism [18, 117] has been widely used to treat relaxation processes in the presence of a random perturbation. The Wangsness-Bloch-Redfield [129, 160] theory is the archetypal example. In all such theories, the goal is to find a reasonably approximated expression for the density matrix $\rho_S(t)$ (or $\frac{d}{dt}\rho_S$) of the focused spin system, neglecting, however, key questions regarding the nature of $\rho_S(t)$'s evolution in time. The GKSL approach, on the other hand, pays particular attention to these aspects and tries to provide general requisites on the properties of the map under which $\rho_S(t)$ evolves. The completely positive trace-preserving (CPT) [5, 22, 28, 57, 58, 96, 97, 114, 132, 165] property is arguably the most celebrated of these. Even more, it has been the common view that the CPT property is a fundamental requisite of any reputable quantum map [4]. This view, however, has been challenged by some authors [119, 146]. According to the opposing view, the fundamental requisite to be required of a quantum map is that it preserves Hermiticity, trace and positivity [146, 149]. The unclenching of the view of the CPT requirement as an inescapable one has been met with an increase in research on non-CP maps [26, 72, 106, 145, 168]. After all, studies [21, 104, 134] have shown a close connection between non-CP maps and non-Markovian [23, 30, 103, 122, 128] dynamics – the latter being a hot topic.

On a close examination, one realizes that the debate on how fundamental the CPT requirement is could be a problem of definition. The reason is that, viewed along the lines of UDMs and non-UDMs, it is clear – as explained in Sec. 12.2 and the beginning of Chap. 13 – that the CPT property and the very concept of quantum dynamical maps are two inextricable notions, for a map cannot be a quantum dynamical map, in the first place, without being CPT. And that the CPT property is inarguably fundamental. It is an accident of history that what we have termed UDMs here are what are commonly referred to in the literature as CPT maps. The consequence of this misnomer is that non-UDMs (or what some may call positive but non-CP maps [26, 168]) became something of an anathema – even though they are CPT with respect to their domain and admit Kraus operator sum representations (Chap. 13). We shall give a concrete practical example of a Kraus operator sum for a non-UDM in Sec. 20.5.

All in all, applying the GKSL approach to some problems of considerable interest like multispin magnetic resonance is not an easy sell because the environment (*i.e.* the applied magnetic fields, in the case of magnetic resonance) needs to be fully quantized. In the theory of magnetic resonance, as formulated by the above-mentioned pioneers and others, the so-called Maxwell-Bloch scheme [75] is used. In this scheme, the spin system is quantized while the external magnetic fields are consigned to a classical description (Maxwell equations). Naturally, we could quantize the applied electromagnetic fields and carry out our derivations without any significant conceptual hurdle. Using quantized applied electromagnetic fields in magnetic resonance theory has been done, for example, by Jeener and Henin [75], and also by Engelke [45]. The results one obtains are in good agreement with those obtained under the Maxwell-Bloch scheme [45, 75]. A fully quantized electromagnetic field, though, may be necessary under more sophisticated experiments, but for what concerns standard NMR and ESR experiments, it suffices to treat the external fields classically. And this will be our strategy in the next chapters.

Chapter 18

Proposal on how to handle classical environments

In Chap. 15, we saw how the generator for a quantum dynamical semigroup can be obtained from the unitary dynamics of a closed bipartite quantum system, following a number of approximations and assumptions. The steps involved – under the assumptions of weak-coupling limit – may be summarized as follows:

1. start with a Liouville-von Neumann equation for $\rho_{R+S}(t)$ (the density matrix for the closed $S+R$ bipartite system) – Sec. 15.1, (15.3);
2. transition to the interaction picture – Sec. 15.1, (15.5);
3. trace out the environment degrees of freedom to obtain an equation of motion for S' density matrix in the interaction picture – Sec. 15.1, (15.10);
4. introduce the Born approximation and the environment stability condition – Sec. 15.3;
5. introduce the Markov approximations – Sec. 15.4;
6. introduce the secular approximation – Sec. 15.5; and
7. assume the initial density matrix $\rho_R(0)$ of the environment is stationary with respect to its free Hamiltonian H_S – Sec. 15.6.

When R is considered classical, a GKSL-like equation may be obtained in the weak-coupling limit as follows:

1. start with a Liouville-von Neumann equation for the reduced density matrix $\rho_S(t)$, where S' Hamiltonian is an effective one. Here, the (time-dependent) factors and parameters in the effective Hamiltonian will originate from the environment's degrees of freedom and would have been determined by some other means;
2. transform the equation of motion into the interaction picture;
3. introduce the Markov approximations; and then

4. perform the secular approximation.

It is implicitly assumed in step (1) (in the case of classical R) that the initial state of $S+R$ is 'separable' (*i.e.* no initial correlations between the quantum system and the classical environment). Somewhere between steps (2) and (4), one has to define an appropriate set of Lindblad operators; this may prove difficult to accomplish for some problems or may require some very ingenious choices, but, nonetheless, there is, somehow – looking at Chap. 15, for example – a general understanding on how to proceed [22]. This is more so when the resonance condition consists of a set of independent conditions which must occur concurrently. CW magnetic resonance is a good example in this regard.

Chapter 19

Semiclassical Quantum Markovian Master Equation Approach to CW Magnetic Resonance

19.1 Preamble

In standard CW magnetic resonance experiments, the sample is subjected to an oscillating field $\mathbf{B}_1(t)$ of constant frequency ω while, simultaneously, a steady magnetic field $\mathbf{B}_o$ (perpendicular to $\mathbf{B}_1(t)$, with $\|\mathbf{B}_1(t)\| \ll \|\mathbf{B}_o\|$) is sweepingly applied so as to tune the focus system to resonance.[1] Keeping strict adherence to this faithful description will land us into what we may call generalized Landau-Zener [94, 99, 172] transition problems, obscuring the central effort of this part – which is, to derive a GKSL-like equation for CW magnetic resonance experiments whereby we treat the applied fields ($\mathbf{B}_o$ and $\mathbf{B}_1$) as classical entities. For the sake of argument, we shall not explicitly take into account the sweeping of $\mathbf{B}_o$. Rather, we take the view that for any instance of $\mathbf{B}_o$, the spin system settles very fast to an equilibrium state (solely dependent on $\mathbf{B}_o$) upon its interaction with the latter field, before it begins to adjust to the presence of $\mathbf{B}_1(t)$. Put in other terms, we may view the experiment as a two step process, whereby we first apply $\mathbf{B}_o$ and then $\mathbf{B}_1(t)$. If any justification at all is to be allowed for this simplified view of the CW experiment under discussion, we may invoke the fact that: 1) except at very low temperatures, the scale of resonance energy in magnetic resonance experiments is quite small compared to thermal energy (*high-temperature approximation*) [53], and 2) $\|\mathbf{B}_1(t)\| \ll \|\mathbf{B}_o\|$. Naturally, the function of the steady field $\mathbf{B}_o$ is to create the Zeeman effect, while $\mathbf{B}_1(t)$ stimulates transitions between the energy levels resulting from the Zeeman effect.

Bearing in mind the above reinterpretation of the experiment, consider an ensemble of noninteracting molecules in some condensed phase environment. Each member of the ensemble is a multispin

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[1] Another alternative is to hold the frequency $\mathbf{B}_o$ constant and vary ω, but this scheme is not the experimentally preferred way of doing business.

system $\mathscr{A}$ with the isotropic Hamiltonian $H_{spin-spin}$, where:

$$H_{spin-spin} := \sum_{i>j} T_{ij} \boldsymbol{S}_i \cdot \boldsymbol{S}_j \tag{19.1}$$

where $\boldsymbol{S}_i \, (\equiv S_i^x \boldsymbol{e}_x + S_i^y \boldsymbol{e}_y + S_i^z \boldsymbol{e}_z)$ is the $i-$th element's spin vector operator, and T_{ij} is the coupling constant between spins i and j. S_i^α is the spin operator along the axis $\alpha \in \{x, y, z\}$ for spin i. Note that all the other degrees of freedom with the exception of the spin degrees in question constitute the environment, so in a fully quantum treatment, the coupling constants will result from the tracing out of the environment's degrees of freedom. A fully quantized condensed phase like the liquid phase – in which many of these experiments are carried out – is all but easy to manage. The coupling constants T_{ij} here are, therefore, assumed to have been determined by some other means [43, 50, 84, 95, 112]. Surely, these constants incorporate the influence of the environment. And in the liquid phase, one usually speaks of 'solvent effects' [43, 95, 112].

If we take $\mathbf{B}_o$ as lying along the $z-$axis (i.e. $\mathbf{B}_o = B_o \boldsymbol{e}_z$), and consider the latter as the axis of quantization, then the Hamiltonian of the multispin system acquires a new term (i.e. the Zeeman term):

$$H_o = H_{spin-spin} + \xi^z B_o \tag{19.2}$$

where,

$$\xi^\alpha := -\mu^\alpha = -\sum_i \gamma_i S_i^\alpha \qquad \alpha \in \{x, y, z\} \tag{19.3}$$

where μ^α indicates the total magnetic moment operator of the multispin system along the axis α, and γ_i is the effective gyromagnetic ratio of the $i-$th spin. Suppose we apply the oscillating field $\mathbf{B}_1(t)$ at the instant t_o, and assume the spin system had reached its thermal equilibrium state under $\mathbf{B}_o$ prior to t_o. Then, the density matrix of the multispin system immediately before the instant t_o, $\rho_S(t_o)$, is:

$$\rho_S(t_o) = \frac{e^{-\beta H_o}}{\mathcal{Z}} \ , \qquad \mathcal{Z} := \mathrm{Tr}\left[e^{-\beta H_o}\right] \ , \tag{19.4}$$

where $\beta \equiv \frac{1}{k_B T}$ (k_B is the Boltzmann constant and T is the absolute temperature), and H_o is defined in (19.2). Equation (19.4) can be justified on the basis of statistical mechanics, and we give a detailed account of it in Appendix B. The operator ρ_S (which we now, henceforth, simply indicate as ρ) – after the application of $\mathbf{B}_1(t)$ – must then satisfy the Cauchy initial value problem:

$$\begin{cases} \frac{d}{dt}\rho(t) = -i\left[H_o + V(t), \rho(t)\right] \ , & (t > t_o) \\ \rho(t) = \frac{e^{-\beta H_o}}{\mathcal{Z}} \ , & (t = t_o) \end{cases} \tag{19.5}$$

where,

$$V(t) := \boldsymbol{\xi} \cdot \mathbf{B}_1(t) \tag{19.6}$$

with the components of $\boldsymbol{\xi}$ defined in (19.3). Two observations are due here: First of all, it is implicit in the initial condition on ρ, (19.5), that there is no correlation (quantum or classical) between the spin system and the oscillating field. This is tantamount to the Born approximation (Sec. 15.3). Secondly, the same equation will have us think $\rho(t)$ may evolve by means of a unitary evolution superoperator, but that would contradict the fact that $\rho(t)$ represents the density matrix of an open quantum system. Nevertheless, although the experimental conditions largely justify the series of approximations (like the Markovian) we shall introduce in the course of our discussion, they also have the advantage of leading to a non-unitary evolution of $\rho(t)$.

Taking into account the fact that the oscillating magnetic fields actually used in experiments are not perfectly monochromatic, it is only reasonable that we take $\mathbf{B}_1(t)$ to be a superposition of various independent oscillating fields (for simplicity, all of zero phase and with the same maximum):

$$\mathbf{B}_1(t) = \sum_r 2B_1 \cos(\omega_r t)\mathbf{e}_x \tag{19.7}$$

where $2B_1$ and ω_r are the maximum amplitude and frequency of the $r-$th oscillating field, respectively. The frequencies ω_r are distributed around a central frequency ω, and we assume $\omega \gg |\delta\omega_r|$, where $\delta\omega_r \equiv \omega - \omega_r$. $\mathbf{B}_1(t)$ in (19.7) is a generalization of the usual $\mathbf{B}_1(t) = 2B_1\cos(\omega t)\mathbf{e}_x$ used in the literature [8, 17, 33]. For the sake of clarity, we choose to decompose $\mathbf{B}_1(t)$ into two cluster of rotating fields in the $x - y$ plane, both with the same intensity but each having a sense of rotation opposite to the other:

$$\mathbf{B}_1(t) = \mathbf{B}_{1,+}(t) + \mathbf{B}_{1,-}(t) \tag{19.8}$$

where,

$$\mathbf{B}_{1,\pm}(t) := \sum_r B_1 \left[\cos(\omega_r t)\mathbf{e}_x \pm \sin(\omega_r t)\mathbf{e}_y\right] \ . \tag{19.9}$$

$\mathbf{B}_{1,\pm}(t)$ rotate in the anticlockwise and clockwise directions, respectively, when observed from the top of the direction parallel to that of $\mathbf{B}_o$. As it is well-known, for a given spin, only one of these may give rise to the resonance phenomenon depending on the sign of its Larmor frequency [2]. On similar footing, we may decompose the interaction term $V(t)$ as follows:

$$V(t) = V_+(t) + V_-(t) \tag{19.10}$$

with

$$V_\pm(t) = B_1 \sum_r \left[\xi^x \cos(\omega_r t) \pm \xi^y \sin(\omega_r t)\right] \tag{19.11a}$$

$$= B_1 \sum_r \ e^{\mp i\omega_r t S^z} \xi^x e^{\pm i\omega_r t S^z} \tag{19.11b}$$

where $S^z := \sum_i S^z_i$, i.e. the total spin operator along the $z-$axis. According to the sign of the Larmor frequency of the spin, only one of $V_\pm(t)$ contributes significantly to the observed resonance spectra; for example, if the Larmor frequency is positive (thus, negative gyromagnetic ratio), then the observed spectra is primarily due to the interaction term $V_+(t)$, with negligible contributions from $V_-(t)$.

As noted earlier, in the usual experimental setup, $B_1 \ll B_o$, so we can consider $V(t)$ as a perturbation with respect to H_o. We may then take (19.5) into the interaction picture. The result is:

$$\begin{cases} \frac{d}{dt}\varrho(t) = -i\left[\mathscr{V}(t), \varrho(t)\right] \ , & (t > t_o) \\ \varrho(t_o) = \frac{e^{-\beta H_o}}{\mathscr{Z}} \ , & (t = t_o) \end{cases} \tag{19.12}$$

where,

$$\varrho(t) := e^{itH_o}\rho(t)e^{-itH_o} \tag{19.13a}$$

$$\mathscr{V}(t) := e^{itH_o}V(t)e^{-itH_o} = \mathscr{V}_+(t) + \mathscr{V}_-(t) \ . \tag{19.13b}$$

From (19.12), it follows that:

$$\frac{d}{dt}\varrho(t) = -i\,[\mathscr{V}(t), \varrho(t_o)] - \int_0^{t-t_o} d\tau\,[\mathscr{V}(t), [\mathscr{V}(t-\tau), \varrho(t-\tau)]] \tag{19.14}$$

– which is analogous to (15.27). Obviously, the difference between (19.14) and (15.27) lies in the fact that the latter was derived after tracing out a quantum mechanically described environment and imposing the Born approximation, while (19.14) simply results from a dynamics described by an effective Hamiltonian in which the effects of the environment are manifest through some given (time-dependent) parameters. Like in (15.27), we also observe from (19.14) that the evolution of $\varrho(t)$ depends on its history due to the presence of $\varrho(t-\tau)$ on the l.h.s. Let us assume the evolution of ϱ does effectively depend on its history only in the time-frame $0 \leq \tau \leq \tau_B$, where τ_B is some characteristic time which depends on the interaction between the spin system and the external fields. Supposing the resolution of our experiment does make the time-frame $0 \leq \tau \leq \tau_B$ practically inaccessible to our investigation [15], so that measurements on the spin system effectively refer to $t \gg \tau_B$, instances during which the evolution of ϱ does not depend on its history, but only on its present state, then we may substitute $\varrho(t-\tau)$ in (19.14) with $\varrho(t)$ (Markov approximation). (When the experimental technique being employed is capable of appropriately resolving certain system-environment correlations [15], it may be necessary to account for the non-Markovian [23, 30, 103, 122, 128] property in $\varrho(t)$'s evolution). If, in addition, we set $t_o = 0$ and extend the upper limit of the integral over τ to infinity (this is just an approximation on the integral over τ; and it is particularly justified for steady-state experiments like the one under discussion), the final result is:

$$\frac{d}{dt}\varrho(t) = -i\,[\mathscr{V}(t), \varrho(0)] - \int_0^{+\infty} d\tau\,[\mathscr{V}(t), [\mathscr{V}(t-\tau), \varrho(t)]]\ . \tag{19.15}$$

Note that by taking the limit $t_o \to -\infty$ (i.e. adiabatic approximation[56]) in (19.14), we also get (19.15) since $\varrho(0) = \varrho(-\infty) = \frac{e^{-\beta H_o}}{\mathcal{Z}}$. Though the adiabatic approximation – which assumes the system, prior to the application of $\mathbf{B}_1(t)$, had been in the equilibrium state for a very, very long time – leads essentially to the same equation of motion as (19.15) for $\varrho(t)$, it requires that the lower limit of the integral over t be $t = -\infty$ instead of $t = 0$. This is a subtle but important difference as there could be instances whereby this lower limit of t according to the adiabatic approximation leads to infinite expectation values of some observables. In the following, we stick to (19.15) bearing in mind that the lower limit of t is $t = 0$.

One other important thing to note is that (19.15) is analogous to (15.32) if we suppress the first-order term in $\mathscr{V}(t)$. Recall that this first-order term in the system-reservoir interaction Hamiltonian was suppressed in (15.32) by applying the environment stability condition, (15.28). Contrary to what we did in Sec. 15.3, we choose to keep this linear term simply because – unlike in the usual microscopic derivations in the literature whereby this term usually becomes zero (or is assumed to be) upon a trace operation over the environment's quantum degrees of freedom [22] – here, only the spin system is treated at the quantum level from the beginning and there are no quantum degrees of freedom of the environment (the magnetic fields) to trace over. We have thus no reason to neglect the term. As it will turn out later in our discussion, this term is crucial to the quantum theory of magnetic resonance and allows us to derive a number of important results already known in the literature. Most importantly, we shall show that it is the springboard to the development of a linear response theory from the perspective of quantum Markovian master equations.

19.2 Affine commutation perturbation

Following the microscopic derivation we did in Chap. 15, the very next step[2] from (19.15) will be a decomposition – analogous to the decomposition in (15.37) – of the operator $\mathscr{V}(t)$. And that would be followed by the secular approximation. We choose, however, to detour a little bit by introducing at this very stage a second level of perturbation. This will help us further breakdown the dynamics of the multispin system into the key contributing factors, while at the same time help us obtain quite accurate results even at lower orders of perturbation.

Let us now go back to (19.2) and analyze H_o. Under usual experimental conditions, it is often the case that $\|\xi^z B_o\| \gg \left\|\sum_{i>j} T_{ij} \boldsymbol{S}_i \cdot \boldsymbol{S}_j\right\|$ (in the sense of (15.2)). The spin-spin interaction term, $H_{spin-spin}$, may therefore be treated as a perturbation with respect to the Zeeman term, $\xi^z B_o$. Instead of simply treating $H_{spin-spin}$ as a perturbation term with respect to $\xi^z B_o$, we are going to do what we call *affine commutation perturbation* (ACP). In this scheme, the perturbation term is rewritten as a sum of two operators: $A' + B'$, where the operator A' commutes with the leading term, while B' does not. A' is then added to the leading term and their sum is treated as the new leading term, while B' becomes the new perturbation term and the normal perturbation expansion is then carried out. If A' exists and one performs the ACP expansion, the results one obtains – compared to those from the standard perturbation expansion – are more accurate even at low orders.

As we intend to perform an ACP, we rewrite H_o as:

$$H_o = \mathscr{Z}_o + \mathscr{X} \tag{19.16}$$

where,

$$\mathscr{Z}_o := B_o \xi^z + \sum_{i>j} T_{ij} S_i^z S_j^z \tag{19.17a}$$

$$\mathscr{X} := \frac{1}{2} \sum_{i>j} T_{ij} \left(S_i^+ S_j^- + S_i^- S_j^+ \right) \tag{19.17b}$$

($S_j^{\pm} \equiv S_j^x \pm i S_j^y$). Note that $\|\mathscr{Z}_o\| \gg \|\mathscr{X}\|$. Moreover, $\mathscr{Z}_o$ commutes with the total spin operator along the $z-$axis, S^z. And more importantly, the eigenvectors of $\mathscr{Z}_o$ are simply the multispin kets in the uncoupled representation.

Using Feynman's operator calculus [48], we now expand all operators in (19.15) dependent on $\mathscr{X}$ in powers of the latter. Namely, the rotated operators: 1) $\varrho(t) = e^{it(\mathscr{Z}_o + \lambda\mathscr{X})} \rho(t) e^{-it(\mathscr{Z}_o + \lambda\mathscr{X})}$, 2) $\mathscr{V}(t) = e^{it(\mathscr{Z}_o + \lambda\mathscr{X})} V(t) e^{-it(\mathscr{Z}_o + \lambda\mathscr{X})}$ and 3) $\varrho(0) = \frac{e^{-\beta(\mathscr{Z}_o + \lambda\mathscr{X})}}{\mathrm{Tr}[e^{-\beta(\mathscr{Z}_o + \lambda\mathscr{X})}]}$ (where the constant λ, introduced here for book-keeping purposes, will be set equal to 1 at the end). For the first two, we get:

$$\varrho(t) = \sum_{n=0}^{\infty} \lambda^n \ \varrho^{(n)}(t) \tag{19.18a}$$

$$\mathscr{V}(t) = \sum_{n=0}^{\infty} \lambda^n \ \mathscr{V}^{(n)}(t) \tag{19.18b}$$

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[2] One could also redefine H_o and $V(t)$, following (15.29) so that the first term on the r.h.s. of (19.14) becomes identically zero. Though it is formally doable, on a closer examination, one realizes that it is more pragmatic not to go down that path.

where,

$$\varrho^{(n)}(t) = e^{it\mathscr{Z}_o} \left[\sum_{k=0}^{n} \sum_{k'=0}^{k} \mathscr{Y}^{(n-k)}(t)\; \rho^{(k-k')}(t)\; \mathscr{Y}^{(k')\dagger}(t) \right] e^{-it\mathscr{Z}_o} \tag{19.19}$$

$$\mathscr{V}^{(n)}(t) = e^{it\mathscr{Z}_o} \left[\sum_{k=0}^{n} \mathscr{Y}^{(n-k)}(t)\; V(t)\; \mathscr{Y}^{(k)\dagger}(t) \right] e^{-it\mathscr{Z}_o} \tag{19.20}$$

where, for $n \geq 1$,

$$\mathscr{Y}^{(n)}(t) \equiv i^n \int_0^t ds_1 \int_0^{s_1} ds_2 \cdots \int_0^{s_{n-1}} ds_n\;\, \mathscr{X}(s_1)\mathscr{X}(s_2)\cdots\mathscr{X}(s_n) \tag{19.21}$$

while $\mathscr{Y}^{(n)}(t) \equiv \mathbb{I}$ for $n = 0$ – with

$$\mathscr{X}(x) := e^{-ix\mathscr{Z}_o}\mathscr{X}e^{ix\mathscr{Z}_o}\ . \tag{19.22}$$

Naturally, $\rho(t)$ depends on $\mathscr{X}$. This dependence slightly complicates the expansion of $\varrho(t)$ in powers of $\mathscr{X}$, compared to $\mathscr{V}(t)$. The operator $\rho^{(m)}(t)$ in (19.19) denotes the $m-$th term coming from the formal expansion of $\rho(t)$ in powers of $\mathscr{X}$. Put differently, $\rho^{(m)}(t)$ is the equivalent of $\varrho^{(m)}(t)$ in the Schrödinger picture. In general, the relation between the two is not a simple unitary transformation. As a matter of fact, only $\varrho^{(0)}(t)$ and $\rho^{(0)}(t)$ are related through a unitary transformation. To illustrate this very important point, consider, for example, the cases $n = 0$ and $n = 1$ from (19.19); these yield the following expressions:

$$\varrho^{(0)}(t) = \ e^{it\mathscr{Z}_o}\rho^{(0)}(t)e^{-it\mathscr{Z}_o} \tag{19.23a}$$

$$\varrho^{(1)}(t) = e^{it\mathscr{Z}_o}\rho^{(1)}(t)e^{-it\mathscr{Z}_o} + i\int_0^t ds\ \left[\varrho^{(0)}(t), \mathscr{X}(s-t)\right]. \tag{19.23b}$$

from which we derive that:

$$\rho^{(0)}(t) = \ e^{-it\mathscr{Z}_o}\varrho^{(0)}(t)e^{it\mathscr{Z}_o} \tag{19.24a}$$

$$\rho^{(1)}(t) = e^{-it\mathscr{Z}_o}\varrho^{(1)}(t)e^{it\mathscr{Z}_o} - i\int_0^t ds\ \left[\rho^{(0)}(t), \mathscr{X}(s)\right]. \tag{19.24b}$$

Moving on, to fully expand (19.15) in powers of $\mathscr{X}$, we are only left with the expansion of $\varrho(0)$. Resorting once more to Feynman's operator calculus [48], one can show that, for a fixed $\beta = \frac{1}{k_B T}$:

$$\varrho(0) = \sum_{n=0}^{\infty} \lambda^n \varrho^{(n)}(0) \tag{19.25}$$

where,

$$\varrho^{(n)}(0) \equiv \varrho^{(0)}(0) \sum_{n'=0}^{n} \zeta_{n'}(i\beta)\; \mathscr{Y}^{(n-n')}(i\beta) \tag{19.26}$$

and

$$\varrho^{(0)}(0) \equiv \frac{e^{-\beta\mathscr{Z}_o}}{\mathrm{Tr}\left[e^{-\beta\mathscr{Z}_o}\right]}\ . \tag{19.27}$$

The coefficients $\{\zeta_n(i\beta)\}$ are the solution to a system of linear equations (of infinite dimension), characterized by a coefficient matrix which is a lower triangular Toeplitz matrix. It can be verified that every $\zeta_n(i\beta)$ is proportional to the determinant of an upper Hessenberg matrix. Indeed, for $n \geq 1$,

$$\zeta_n(x) = (-1)^n \ \det \begin{vmatrix} \langle \mathscr{Y}^{(1)}(x) \rangle_o & \langle \mathscr{Y}^{(2)}(x) \rangle_o & \langle \mathscr{Y}^{(3)}(x) \rangle_o & \langle \mathscr{Y}^{(4)}(x) \rangle_o & \dots & \langle \mathscr{Y}^{(n-1)}(x) \rangle_o & \langle \mathscr{Y}^{(n)}(x) \rangle_o \\ 1 & \langle \mathscr{Y}^{(1)}(x) \rangle_o & \langle \mathscr{Y}^{(2)}(x) \rangle_o & \langle \mathscr{Y}^{(3)}(x) \rangle_o & \dots & \langle \mathscr{Y}^{(n-2)}(x) \rangle_o & \langle \mathscr{Y}^{(n-1)}(x) \rangle_o \\ 0 & 1 & \langle \mathscr{Y}^{(1)}(x) \rangle_o & \langle \mathscr{Y}^{(2)}(x) \rangle_o & \dots & \langle \mathscr{Y}^{(n-3)}(x) \rangle_o & \langle \mathscr{Y}^{(n-2)}(x) \rangle_o \\ 0 & 0 & 1 & \langle \mathscr{Y}^{(1)}(x) \rangle_o & \dots & \langle \mathscr{Y}^{(n-4)}(x) \rangle_o & \langle \mathscr{Y}^{(n-3)}(x) \rangle_o \\ \vdots & \vdots & \vdots & \vdots & \dots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \dots & 1 & \langle \mathscr{Y}^{(1)}(x) \rangle_o \end{vmatrix} \tag{19.28}$$

while for $n = 0$, $\zeta_n(x) = 1$. Moreover,

$$\left\langle \mathscr{Y}^{(n)}(x) \right\rangle_o \equiv \mathrm{Tr}\left[\varrho^{(0)}(0)\ \mathscr{Y}^{(n)}(x) \right] \ . \tag{19.29}$$

(On passing, we would like to draw the Reader's attention to an evident connection between the expression for the coefficient $\zeta_n(x)$ as given in (19.28) and the determinant expression for the $n-$th complete Bell polynomial [115].) The recursive relation for the coefficients $\{\zeta_n(x)\}$, for $n \geq 1$, is as follows:

$$\zeta_n(x) = -\sum_{n'=0}^{n-1} \zeta_{n'}(x) \left\langle \mathscr{Y}^{(n-n')}(x) \right\rangle_o \ . \tag{19.30}$$

(Compare (19.28) and (19.30) with Theorem I of [73].)

With these expansions of the operators $\varrho(t), \mathscr{V}(t)$ and $\varrho(0)$ in $\mathscr{X}$, (19.15) turns out to be:

$$\begin{aligned} \sum_{n=0}^{\infty} \lambda^n \frac{d}{dt} \varrho^{(n)}(t) = & -i \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} \lambda^{n+n'} \left[\mathscr{V}^{(n)}(t), \varrho^{(n')}(0) \right] \\ & - \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} \sum_{n''=0}^{\infty} \int_0^{+\infty} d\tau\ \lambda^{n+n'+n''} \left[\mathscr{V}^{(n)}(t), \left[\mathscr{V}^{(n')}(t-\tau), \varrho^{(n'')}(t) \right] \right] \ . \end{aligned} \tag{19.31}$$

Equating terms of the same order in λ on both sides of (19.31) yields a non-homogeneous system of triangular differential equations for $\{\varrho^{(n)}(t)\}$, which can be solved step-by-step beginning with the line $n = 0$. Indeed, one can easily derive from (19.31) that the generic $\varrho^{(n)}(t)$ satisfies the differential equation:

$$\frac{d}{dt} \varrho^{(n)}(t) = -i \sum_{k=0}^{n} \left[\mathscr{V}^{(n)}(t), \varrho^{(n-k)}(0) \right] - \sum_{k=0}^{n} \sum_{k'=0}^{k} \int_0^{+\infty} d\tau \left[\mathscr{V}^{(n-k)}(t), \left[\mathscr{V}^{(k-k')}(t-\tau), \varrho^{(k')}(t) \right] \right] \ . \tag{19.32}$$

19.3 The zeroth-order approximation

In standard perturbation theory, one has to necessarily go to first-order or beyond in order to see the effects of the perturbation term. This is not the case with ACP, where some effects of the perturbation are already manifest at zeroth-order. We demonstrate this point by showing below that if we simply take $\varrho(t) = \varrho^{(0)}(t) + O(\mathscr{X})$, i.e. the zeroth-order approximation, the results we obtain are in excellent agreement with experiments.

In the discussions below, we are going to make use of the Holstein-Primakoff transformation and the index compression map η_o we discussed in Part II (see Chap. 6 and Chap. 7). In particular, if each member of the ensemble of noninteracting molecules is represented by the multiset of spins $\mathscr{A} = \{j_1, j_2, \ldots, j_N\}$, then, a generic multispin state of a member of the ensemble in the uncoupled representation is span by the basis $\{|j_1, m_1\rangle\, |j_2, m_2\rangle \cdots |j_N, m_N\rangle\}$, where $-j_i \leq m_i \leq j_i$ is the spin magnetic quantum number of the $i-$th spin. In conjunction with the index compression map η_o, we saw – in Chap. 7, (7.1) – that the HP transformation makes it possible to map each of these basis elements to a unique nonnegative integer $\mathbb{n}$, whose range is $\mathbb{0} \leq \mathbb{n} \leq (D_{\mathcal{H}} - 1)$ – where $D_{\mathcal{H}}$ is the dimension of the multispin Hilbert space: $D_{\mathcal{H}} = \prod_{i=1}^{N} d_i$, $d_i \equiv 2j_i + 1$. Thus, we can simply indicate a multispin basis element in the uncoupled representation as $|\mathbb{n}\rangle$. Naturally, $\langle \mathbb{n}'|\, \mathbb{n}\rangle = \delta_{\mathbb{n}',\mathbb{n}}$.

As remarked earlier, the eigenstates of $\mathscr{H}_o$ are simply the uncoupled multispin states

$$\{|j_1, m_1\rangle\, |j_2, m_2\rangle \cdots |j_N, m_N\rangle\}$$

– which we have just seen can be simply represented as $\{|\mathbb{n}\rangle\}$. Thus, by virtue of the HP representation and the index compression map η_o, we have that:

$$\mathscr{H}_o\, |\mathbb{n}\rangle = \epsilon_{\mathbb{n}}\, |\mathbb{n}\rangle \tag{19.33a}$$

$$S^z\, |\mathbb{n}\rangle = M_{\mathbb{n}}\, |\mathbb{n}\rangle \tag{19.33b}$$

where,

$$\epsilon_{\mathbb{n}} := \langle \mathbb{n}|\, \mathscr{H}_o\, |\mathbb{n}\rangle \tag{19.34a}$$

$$M_{\mathbb{n}} := \langle \mathbb{n}|\, S^z\, |\mathbb{n}\rangle \ . \tag{19.34b}$$

$M_{\mathbb{n}}$ is the multispin state $|\mathbb{n}\rangle$'s total spin magnetic quantum number along the axis of quantization.

In the following, we are going to assume that *if* $\epsilon_{\mathbb{n}'} - \epsilon_{\mathbb{n}} = \epsilon_{\mathbb{n}''} - \epsilon_{\mathbb{n}}$, *then* $\mathbb{n}' = \mathbb{n}''$. That is, we are assuming there are no accidental degeneracies of the multispin states in relation to the Hamiltonian $\mathscr{H}_o$.

19.3.1 Derivation of zeroth-order approximation to the semiclassical quantum Markovian master equation

As remarked earlier, with the zeroth-order approximation, we are taking $\varrho(t) = \varrho^{(0)}(t) + O(\mathscr{X})$, and – according to (19.32) – $\varrho^{(0)}(t)$ satisfies the differential equation

$$\frac{d}{dt}\varrho^{(0)}(t) = -i\left[\mathscr{V}^{(0)}(t), \varrho^{(0)}(0)\right] - \int_0^{+\infty} d\tau \left[\mathscr{V}^{(0)}(t), \left[\mathscr{V}^{(0)}(t-\tau), \varrho^{(0)}(t)\right]\right] \ . \tag{19.35}$$

We now present a microscopic derivation of a GKSL-like equation for $\varrho^{(0)}(t)$ starting from (19.35).

We begin our derivation by noting that (19.35) may be rewritten in the following form:

$$\frac{d}{dt}\varrho^{(0)}(t) = -i\left[\mathscr{V}^{(0)}(t), \varrho^{(0)}(0)\right] - \int_0^{+\infty} d\tau \left(\left[\mathscr{V}^{(0)\dagger}(t), \mathscr{V}^{(0)}(t-\tau)\varrho^{(0)}(t)\right] + h.c.\right) \tag{19.36}$$

where $h.c.$ denotes the presence of the Hermitian conjugate term. By virtue of (19.13b) and (19.20),

$$\mathscr{V}^{(0)}(t) = \mathscr{V}_{+}^{(0)}(t) + \mathscr{V}_{-}^{(0)}(t) \tag{19.37a}$$

$$\mathscr{V}_{\pm}^{(0)}(t) = B_1 \sum_{r} e^{it(\mathscr{H}_o \mp \omega_r S^z)}\, \xi^x\, e^{-it(\mathscr{H}_o \mp \omega_r S^z)} \ . \tag{19.37b}$$

(19.37a) allows us to divide the r.h.s. of (19.36) into contributions from $\mathscr{V}_{\pm}^{(0)}(t)$, with cross-terms (*i.e.* terms involving the factors $\mathscr{V}_{+}^{(0)}$, $\mathscr{V}_{-}^{(0)}$ – simultaneously) coming from the second term. Assuming these cross-terms do not contribute, we may reduce (19.36) to the form:

$$\begin{aligned}\frac{d}{dt}\varrho^{(0)}(t) = -i\left[\mathscr{V}_{+}^{(0)}(t) + \mathscr{V}_{-}^{(0)}(t), \varrho^{(0)}(0)\right] \\ - \int_{0}^{+\infty} d\tau \left(\left[\mathscr{V}_{+}^{(0)\dagger}(t), \mathscr{V}_{+}^{(0)}(t-\tau)\varrho^{(0)}(t)\right] + h.c.\right) \\ - \int_{0}^{+\infty} d\tau \left(\left[\mathscr{V}_{-}^{(0)\dagger}(t), \mathscr{V}_{-}^{(0)}(t-\tau)\varrho^{(0)}(t)\right] + h.c.\right) \ . \qquad (19.38)\end{aligned}$$

It is most convenient, at this point, to proceed with our derivation by expanding the operator ξ^{x} in the eigenbasis of $\mathscr{Z}_o$ in the following manner[3]:

$$\xi^{x} = \sum_{n,\omega_o} \xi^{x}(n,\omega_o) \qquad (19.39)$$

where[4],

$$\xi^{x}(n,\omega_o) := \sum_{\mathbb{n},\mathbb{n}'} |\mathbb{n}\rangle \langle\mathbb{n}|\, \xi^{x}\, |\mathbb{n}'\rangle \langle\mathbb{n}'|\, \delta_{\omega_o,\epsilon_{\mathbb{n}'}-\epsilon_{\mathbb{n}}} \delta_{n,M_{\mathbb{n}'}-M_{\mathbb{n}}} \qquad (19.40)$$

where $\{|\mathbb{n}\rangle\}$ are the eigenvectors of $\mathscr{Z}_o$, (19.33). Note that the $\{n\}$ in (19.39) and (19.40) are necessarily integers, and the $\{\omega_o\}$ are the pairwise frequency separation between the eigenvalues of $\mathscr{Z}_o$. Interestingly, one also observes that:

$$[\mathscr{Z}_o, \xi^{x}(n,\omega_o)] = -\omega_o\, \xi^{x}(n,\omega_o) \qquad (19.41a)$$

$$[S^{z}, \xi^{x}(n,\omega_o)] = -n\, \xi^{x}(n,\omega_o) \qquad (19.41b)$$

while,

$$\left[\mathscr{Z}_o, \xi^{x\dagger}(n,\omega_o)\right] = \omega_o\, \xi^{x\dagger}(n,\omega_o) \qquad (19.42a)$$

$$\left[S^{z}, \xi^{x\dagger}(n,\omega_o)\right] = n\, \xi^{x\dagger}(n,\omega_o) \ . \qquad (19.42b)$$

Thus, from (19.41) and (19.42), the identity:

$$\xi^{x\dagger}(n,\omega_o) = \xi^{x}(-n,-\omega_o) \qquad (19.43)$$

readily follows. The same identity could have been proved directly from (19.40). The commutation relations in (19.41) and (19.43) indicate that the operator $\xi^{x}(n,\omega_o)$ is a generalized ladder operator which, when applied to a generic eigenket $|\mathbb{n}\rangle$ of $\mathscr{Z}_o$, transforms $|\mathbb{n}\rangle$ into a weighted sum of other eigenkets of $\mathscr{Z}_o$, who all share the same eigenvalue $\equiv (\epsilon_{\mathbb{n}} - \omega_o)$, as well as the same total spin magnetic quantum number $\equiv (M_{\mathbb{n}} - n)$. Likewise, $\xi^{x\dagger}(n,\omega_o)$ transforms $|\mathbb{n}\rangle$ into a sum of other eigenkets of $\mathscr{Z}_o$, each of which is characterized by the same eigenvalue and total spin magnetic quantum numbers; namely, $(\epsilon_{\mathbb{n}} + \omega_o)$ and $(M_{\mathbb{n}} + n)$, respectively. Indeed, it follows from (19.39) that:

$$\xi^{x}(n,\omega_o)\,|\mathbb{n}\rangle = \sum_{\mathbb{n}'} C_{\mathbb{n}',\mathbb{n}}(n,\omega_o)\,|\mathbb{n}'\rangle \qquad (19.44a)$$

$$\xi^{x\dagger}(n,\omega_o)\,|\mathbb{n}\rangle = \sum_{\mathbb{n}'} C_{\mathbb{n}',\mathbb{n}}(-n,-\omega_o)\,|\mathbb{n}'\rangle \qquad (19.44b)$$

---

[3] This is analogous to the decomposition in (15.34).

[4] Compare this with (15.35).

where,

$$C_{\mathbb{m}',\mathbb{m}}(n,\omega_o) := \langle \mathbb{m}' |\, \xi^x \,| \mathbb{m} \rangle \, \delta_{\omega_o,\epsilon_{\mathbb{m}}-\epsilon_{\mathbb{m}'}} \delta_{n,M_{\mathbb{m}}-M_{\mathbb{m}'}} \ . \tag{19.45}$$

Going back to (19.37b), we note that with the introduction of the decomposition of ξ^x according to (19.39), $\mathscr{V}_{\pm}^{(0)}(t)$ simplifies to[5]:

$$\mathscr{V}_{\pm}^{(0)}(t) = B_1 \sum_r \sum_{n,\omega_o} e^{-it(\omega_o \mp \omega_r n)} \xi^x(n,\omega_o) \ . \tag{19.46}$$

With this new expression for $\mathscr{V}_{\pm}^{(0)}(t)$, (19.38) becomes, – in analogy to (15.40) –:

$$\begin{aligned}\frac{d}{dt}\varrho^{(0)}(t) = -iB_1 \sum_r \sum_{n,\omega_o} &\left(e^{-it(\omega_o-\omega_r n)} + e^{-it(\omega_o+\omega_r n)}\right) \left[\xi^x(n,\omega_o), \varrho^{(0)}(0)\right] \\ -&\left(\sum_{r,r'} \sum_{n,\omega_o} \sum_{n',\omega_o'} e^{it\left[(\omega_o-\omega_o')-(\omega_r n-\omega_{r'} n')\right]}\, \Gamma(\omega_o'-n'\omega_{r'}) \left[\xi^{x\dagger}(n,\omega_o), \xi^x(n',\omega_o')\varrho^{(0)}(t)\right] + h.c.\right) \\ -&\left(\sum_{r,r'} \sum_{n,\omega_o} \sum_{n',\omega_o'} e^{it\left[(\omega_o-\omega_o')+(\omega_r n-\omega_{r'} n')\right]}\, \Gamma(\omega_o'+n'\omega_{r'}) \left[\xi^{x\dagger}(n,\omega_o), \xi^x(n',\omega_o')\varrho^{(0)}(t)\right] + h.c.\right)\end{aligned} \tag{19.47}$$

where,

$$\begin{aligned}\Gamma(\omega_o' \pm \omega_{r'} n') &:= B_1^2 \int_0^{+\infty} d\tau \ e^{i\tau(\omega_o' \pm \omega_{r'} n')} \\ &= B_1^2 \left[\pi\delta(\omega_o' \pm n'\omega_{r'}) + i\ \mathcal{P}\left(\frac{1}{\omega_o' \pm n'\omega_{r'}}\right)\right]\end{aligned} \tag{19.48}$$

and the operation $\mathcal{P}(\bullet)$ indicates Cauchy's Principal Value.

The time-dependent factors in (19.47) are all complex exponential functions. For the first term in (19.47), these factors lead to what we have termed the *linear response Hamiltonian*, $H_{LR}(t)$ (see below). Unlike the time-dependent factors in the first term, those in the second and third terms of (19.47) are functions of the differences between the eigenvalues $\{\omega_o\}$, as well as weighted differences between the field frequencies ω_r. These factors can be rapidly oscillating when the frequency function multiplying t is far from zero. The contribution of those rapidly oscillating factors to the evolution of $\varrho^{(0)}(t)$ is negligible compared to those terms where the frequency function multiplying t is in the neighborhood of zero. We may therefore discard those rapidly oscillating terms in the second and third terms of (19.47) (*secular approximation*). This leads to the condition: $(\omega_o - \omega_o') \pm (\omega_r n - \omega_{r'} n') = 0$, which is easily satisfied if

$$\omega_o = \omega_o' \ , \quad n = n' \ , \quad \omega_r = \omega_{r'} \ . \tag{19.49}$$

We emphasize that this is also the only solution compatible with our assumption (see (19.38)) that the cross-terms involving $\mathscr{V}_{+}^{(0)}(t)$ and $\mathscr{V}_{-}^{(0)}(t)$ do not contribute at second-order in B_1^2 to the equation of motion.

With (19.49), the sum of the last two terms of (19.47) reduces to:

$$-\sum_r \sum_{n,\omega_o} \left(\Gamma(\omega_o - n\omega_r) + \Gamma(\omega_o + n\omega_r)\right) \left[\xi^{x\dagger}(n,\omega_o), \xi^x(n,\omega_o)\varrho^{(0)}(t)\right] + h.c. \ . \tag{19.50}$$

---

[5] This is the equivalent of (15.37).

It is convenient at this point to decompose $\Gamma(\omega_o \pm \omega_r n)$ into the sum:

$$\Gamma(\omega_o \pm \omega_r n) = \frac{1}{2}\eta^{xx}(\omega_o \pm \omega_r n) + i\zeta^{xx}(\omega_o \pm \omega_r n) \tag{19.51}$$

where,

$$\eta^{xx}(\omega_o \pm \omega_r n) := 2\pi B_1^2 \; \delta(\omega_o \pm n\omega_r) \tag{19.52a}$$

$$\zeta^{xx}(\omega_o \pm \omega_r n) := B_1^2 \; \mathcal{P}\left(\frac{1}{\omega_o \pm n\omega_r}\right) . \tag{19.52b}$$

If we now assume a continuous distribution of the frequencies in the applied radiation field, then $\sum_r \mapsto \int d\omega' \rho_f(\omega')$ and $\omega_r \mapsto \omega'$ – where $\rho_f(\omega')$ is the probability density function for the radiation field's frequencies (still centered on ω, as discussed earlier). And it can be verified, after some algebraic manipulations, that:

$$\begin{aligned} -\int d\omega' \rho_f(\omega') \sum_{n,\omega_o} \Big(\Gamma(\omega_o - n\omega') + \Gamma(\omega_o + n\omega')\Big) \Big[\xi^{x\dagger}(n,\omega_o), \xi^x(n,\omega_o)\varrho^{(0)}(t)\Big] + h.c. \\ = -i\left[H_{LS+} + H_{LS-}, \varrho^{(0)}(t)\right] + \mathcal{D}_+\left[\varrho^{(0)}(t)\right] + \mathcal{D}_-\left[\varrho^{(0)}(t)\right] \end{aligned} \tag{19.53}$$

where,

$$H_{LS\pm} \equiv \sum_{n,\omega_o} \int_{-\infty}^{+\infty} d\omega' \rho_f(\omega') \zeta^{xx}(\omega_o \mp \omega' n) \xi^{x\dagger}(n,\omega_o)\xi^x(n,\omega_o) \tag{19.54}$$

and

$$\begin{aligned} \mathcal{D}_\pm\left[\varrho^{(0)}(t)\right] \equiv \sum_{n,\omega_o} \int_{-\infty}^{+\infty} d\omega' \; \rho_f(\omega')\eta^{xx}(\omega_o \mp \omega' n) \Big[\xi^x(n,\omega_o)\varrho^{(0)}(t)\xi^{x\dagger}(n,\omega_o) \\ - \frac{1}{2}\left\{\xi^{x\dagger}(n,\omega_o)\xi^x(n,\omega_o), \varrho^{(0)}(t)\right\}\Big] . \end{aligned} \tag{19.55}$$

It is quite clear that the sum $\left(H_{LS+} + H_{LS-}\right)$ constitute a Lamb shift Hamiltonian (see (15.46)), while the sum $\left(\mathcal{D}_+\left[\varrho^{(0)}(t)\right] + \mathcal{D}_-\left[\varrho^{(0)}(t)\right]\right)$ is the dissipator term (see (15.58)). The sign subscripts for H_{LS} and $\mathcal{D}$ indicate their origins: the subscript '+' means the object originates from the second term of (19.38), while '−' indicates its origin is the third term of (19.38). Furthermore, in (19.73) and (19.55), we have extended the lower limit of the integral over ω' from zero to $(-\infty)$. This causes no appreciable error in subsequent calculations since the frequency ω at which $\rho_f(\omega')$ is centered on is in the order of MHz, and is usually quite sharply peaked. Naturally, the normalization condition $\int_{-\infty}^{+\infty} d\omega' \; \rho_f(\omega') = 1$ holds.

A closer look at the integrals in (19.73) and (19.55) shows that:

$$\int_{-\infty}^{+\infty} d\omega' \rho_f(\omega') \zeta^{xx}(\omega_o \mp \omega' n) = \begin{cases} \pm\frac{\pi B_1^2}{n} \; \rho_f^{\succ}(\pm\omega_o/n), & (n \neq 0) \\ B_1^2 \; \mathcal{P}\left(\frac{1}{\omega_o}\right), & (n = 0) \end{cases} \tag{19.56}$$

$$\int_{-\infty}^{+\infty} d\omega' \; \rho_f(\omega')\eta^{xx}(\omega_o \mp \omega' n) = \begin{cases} \frac{2\pi B_1^2}{|n|}\rho_f(\pm\omega_o/n), & (n \neq 0) \\ 2\pi B_1^2 \; \delta(\omega_o), & (n = 0) \end{cases} \tag{19.57}$$

where $\rho_f^{\succ}(\pm\omega_o/n)$ is the Hilbert transform [86] of ρ_f centered on $\pm\omega_o/n$:

$$\rho_f^{\succ}(\pm\omega_o/n) := \frac{1}{\pi}\int_{-\infty}^{+\infty} d\omega' \; \mathcal{P}\left(\frac{\rho_f(\omega')}{\pm\omega_o/n - \omega'}\right) . \tag{19.58}$$

Note that given a specific $\xi^x(n,\omega_o)$, it follows from (19.43) that if we make the transformation $n \mapsto -n$, then $\omega_o \mapsto -\omega_o$ must also follow. Making use of this property and the fact that $\xi^x(0,0)=0$, we may conveniently rewrite the dissipator terms $\mathcal{D}_\pm$, (19.55), as:

$$\begin{aligned}\mathcal{D}_\pm\left[\varrho^{(0)}(t)\right] &= \sum_{n>0,\omega_o} \frac{2\pi B_1^2}{n}\rho_f(\pm\omega_o/n)\left[\xi^x(n,\omega_o)\varrho^{(0)}(t)\xi^{x\dagger}(n,\omega_o) - \frac{1}{2}\left\{\xi^{x\dagger}(n,\omega_o)\xi^x(n,\omega_o),\varrho^{(0)}(t)\right\}\right]\\ &+ \sum_{n>0,\omega_o} \frac{2\pi B_1^2}{n}\rho_f(\pm\omega_o/n)\left[\xi^{x\dagger}(n,\omega_o)\varrho^{(0)}(t)\xi^x(n,\omega_o) - \frac{1}{2}\left\{\xi^x(n,\omega_o)\xi^{x\dagger}(n,\omega_o),\varrho^{(0)}(t)\right\}\right] \qquad (19.59)\end{aligned}$$

and for the Lamb shift Hamiltonians, $H_{LS\pm}$, (19.73), we may write:

$$H_{LS\pm} = \pm\sum_{n>0,\omega_o}\frac{\pi B_1^2}{n}\rho_f^{\succ}(\pm\omega_o/n)\left[\xi^{x\dagger}(n,\omega_o),\xi^x(n,\omega_o)\right] \ . \qquad (19.60)$$

Drawing on the fact that the operator ξ^x is the $q=\pm1$ component of a rank $k=1$ spherical tensor (see (8.3)), we see that $n=+1$ in (19.59) and (19.60).

Let us now turn to the first term on the r.h.s. of (19.47) and split it into two:

$$-\ iB_1\sum_r\sum_{n,\omega_o} e^{-it(\omega_o-\omega_r n)}\left[\xi^x(n,\omega_o),\varrho^{(0)}(0)\right] \ -\ iB_1\sum_r\sum_{n,\omega_o} e^{-it(\omega_o+\omega_r n)}\left[\xi^x(n,\omega_o),\varrho^{(0)}(0)\right] \quad . \qquad (19.61)$$

We focus now on the first term of (19.61). Assuming here a continuous distribution of the frequencies of the applied radiation field, we get:

$$\begin{aligned}&-iB_1\sum_r\sum_{n,\omega_o} e^{-it(\omega_o-\omega_r n)}\left[\xi^x(n,\omega_o),\varrho^{(0)}(0)\right]\\ &\qquad\mapsto -iB_1\sum_{n,\omega_o}\int_{-\infty}^{+\infty}d\omega'\ \rho_f(\omega')\ e^{it(\omega' n-\omega_o)}\left[\xi^x(n,\omega_o),\varrho^{(0)}(0)\right] \ . \qquad (19.62)\end{aligned}$$

But,

$$\begin{aligned}-iB_1\sum_{n,\omega_o}&\int_{-\infty}^{+\infty}d\omega'\ \rho_f(\omega')\ e^{it(\omega' n-\omega_o)}\left[\xi^x(n,\omega_o),\varrho^{(0)}(0)\right]\\ &= -iB_1\sum_{\omega_o}e^{-it\omega_o}\int_{-\infty}^{+\infty}d\omega'\ \rho_f(\omega')\ e^{it\omega'}\left[\xi^x(+1,\omega_o),\varrho^{(0)}(0)\right] + h.c.\\ &= -iB_1\sum_{\omega_o}e^{-it\omega_o}\varphi_f(t)\left[\xi^x(+1,\omega_o),\varrho^{(0)}(0)\right] + h.c.\\ &= -i\left[H_{LR+}(t),\varrho^{(0)}(0)\right]\end{aligned} \qquad (19.63)$$

where we can easily recognize $\varphi_f(t)$ in the above expression as the characteristic function of $\rho_f(\omega')$:

$$\varphi_f(t) \equiv \int_{-\infty}^{+\infty}d\omega'\ \rho_f(\omega')\ e^{it\omega'} \qquad (19.64)$$

and

$$H_{LR+}(t) \equiv B_1\varphi_f(t)\sum_{\omega_o}e^{-it\omega_o}\xi^x(+1,\omega_o) + h.c. \ . \qquad (19.65)$$

Analogously, for the second term of (19.61), we have

$$-iB_1 \sum_r \sum_{n,\omega_o} e^{-it(\omega_o+\omega_r n)} \left[\xi^x(n,\omega_o), \varrho^{(0)}(0)\right] = -i\left[H_{LR-}(t), \varrho^{(0)}(0)\right] \tag{19.66}$$

where

$$H_{LR-}(t) \equiv B_1 \varphi_f^*(t) \sum_{\omega_o} e^{-it\omega_o} \xi^x(+1,\omega_o) + h.c. \tag{19.67}$$

($\varphi_f^*(t)$ is the complex conjugate of $\varphi_f(t)$).

19.3.2 Summary

Putting these results together, it follows that (19.47) – after secular approximation – becomes

$$\boxed{\frac{d}{dt}\varrho^{(0)}(t) = \mathcal{A}(t)\varrho^{(0)}(0) + \mathcal{L}\varrho^{(0)}(t)} \tag{19.68}$$

where:

$$\mathcal{A}(t)\varrho^{(0)}(0) := -i\left[H_{LR}(t), \varrho^{(0)}(0)\right] \tag{19.69}$$

with $H_{LR}(t)$, the linear response Hamiltonian, defined as:

$$H_{LR}(t) := 2B_1 \Re[\varphi_f(t)] \sum_{\omega_o} e^{-it\omega_o} \xi^x(+1,\omega_o) + h.c. \tag{19.70}$$

Moreover, the superoperator $\mathcal{L}$ in (19.68) is the generator of a quantum dynamical semigroup, and is given as follows:

$$\mathcal{L}\varrho^{(0)}(t) := -i\left[H_{LS}, \varrho^{(0)}(t)\right] + \mathcal{D}\left[\varrho^{(0)}(t)\right] \tag{19.71}$$

where the first and second terms in (19.71) are the unitary evolution and dissipator terms at zeroth-order (in $\mathscr{X}$), respectively. H_{LS} is the Lamb shift Hamiltonian at zeroth-order, and is given by the expression:

$$H_{LS} = H_{LS+} + H_{LS-} \tag{19.72}$$

with

$$H_{LS\pm} = \pm\pi B_1^2 \sum_{\omega_o} \rho_f^{\succ}(\pm\omega_o)\left[\xi^{x\dagger}(+1,\omega_o), \xi^x(+1,\omega_o)\right] \tag{19.73}$$

where $\rho_f^{\succ}(\pm\omega_o)$ is defined in (19.58).

Similarly, the dissipator term, $\mathcal{D}\left[\varrho^{(0)}(t)\right]$, in (19.71) is given by the sum:

$$\mathcal{D}\left[\varrho^{(0)}(t)\right] = \mathcal{D}_+\left[\varrho^{(0)}(t)\right] + \mathcal{D}_-\left[\varrho^{(0)}(t)\right] \tag{19.74}$$

where

$$\begin{aligned}
&\mathcal{D}_\pm\left[\varrho^{(0)}(t)\right] \\
&\quad = \sum_{\omega_o} 2\pi B_1^2 \rho_f(\pm\omega_o)\left[\xi^x(+1,\omega_o)\varrho^{(0)}(t)\xi^{x\dagger}(+1,\omega_o) - \frac{1}{2}\left\{\xi^{x\dagger}(+1,\omega_o)\xi^x(+1,\omega_o), \varrho^{(0)}(t)\right\}\right] \\
&\quad + \sum_{\omega_o} 2\pi B_1^2 \rho_f(\pm\omega_o)\left[\xi^{x\dagger}(+1,\omega_o)\varrho^{(0)}(t)\xi^x(+1,\omega_o) - \frac{1}{2}\left\{\xi^x(+1,\omega_o)\xi^{x\dagger}(+1,\omega_o), \varrho^{(0)}(t)\right\}\right] .
\end{aligned} \tag{19.75}$$

For $\omega_o > 0$, the operator $\xi^x(+1, \omega_o)$ may be described as responsible for emission of a photon at the frequency ω_o; while in the case $\omega_o < 0$, the equivalent absorption process may be attributed to the same operator. It is also important to recognize that for a radiation field with a sharply peaked frequency distribution $\rho_f(\omega')$, either $\mathcal{D}_+$ or $\mathcal{D}_-$ will contribute significantly, at resonance, to the dissipator term – depending on the sign of ω_o; for example, if $\omega_o > 0$, $\mathcal{D}_+$ will dominate. In any case, it is quite clear from (19.75) that the rate of emission and absorption coincide. This comes at no surprise since we treated the oscillating field classically. Had we treated the field quantum mechanically, we would have found a contribution to the dissipator term due to spontaneous emission [22], which would have made the rates of total emission of photons differ from that of absorption.

Perhaps, a number of other noteworthy observations are also due here. First of all, we note that despite the fact that the master equation in (19.68) is local in time, the presence of the term $\mathcal{A}(t)\varrho^{(0)}(0)$ deprives the quantum map of the semigroup property. However, we may deduce a very important feature of the superoperator $\mathcal{A}(t)$ due to the presence of the characteristic function $\varphi_f(t)$ in the expression for the linear response Hamiltonian $H_{LR+}(t)$, (19.70). Indeed, for all practical reasons, ρ_f is a real-valued continuous symmetric function in the shift frequency $\delta\omega \equiv \omega - \omega'$ (ω' is a random frequency), and whose range coincides with $\mathbb{R}$. (Infact, the most common distributions for ρ_f are Lorentzian, Gaussian and Voight – which are symmetric in $\delta\omega$.) According to Pòlya's theorem [120], we must expect the characteristic function of $\rho_f(\delta\omega)$, $\varphi_f(t)$, to satisfy the following properties: i) be a real-valued, symmetric and continuous function defined for all real values of t; ii) with maximum at $t = 0$ – specifically, $\varphi_f(0) = 1$; iii) with $\lim_{t\to\infty} \varphi_f(t) = 0$ and iv) be convex for $t > 0$. The most important property to notice here, for the purpose of our discussion, is property iii). Its implication is that when $t \gg \tau_f$ (where τ_f is the time scale of relaxation of $\varphi_f(t)$), $H_{LR}(t)$ approaches zero, leading therefore the $\mathcal{A}(t)$ term in (19.68) to effectively become negligible and the equation becomes a true quantum Markovian master equation, thus restoring the semigroup property. Hence, the generator in (19.68) approaches asymptotically that of a quantum dynamic semigroup. For example, suppose the distribution $\rho_f(\omega')$ is taken to be a Lorentzian, such that:

$$\rho_f(\omega') = \frac{1}{\pi}\frac{\left(\frac{\Delta\nu}{2}\right)^2}{\left(\frac{\Delta\nu}{2}\right)^2 + (\omega - \omega')^2} \tag{19.76}$$

where $\Delta\nu$ is the distribution's full-width at half maximum (FWHM). Then, the corresponding characteristic function, $\varphi_f(t)$, is:

$$\varphi_f(t) = \int_{-\infty}^{+\infty} d\omega'\ e^{i\omega' t}\rho_f(\omega') = e^{i\omega t}e^{-\left(\frac{\Delta\nu}{2}\right)|t|} \tag{19.77}$$

hence, with $\tau_f^{-1} = \frac{\Delta\nu}{2}$.

Moreover, we note that the superoperator $\mathcal{A}(t)$ does not operate on $\varrho^{(0)}(t)$, for $t > 0$. This means the master equation in (19.68) may therefore be regarded as a time-dependent Markovian [36, 103] one, whereby the time-dependence is not to be found in the rate constants present in the quantum dynamical semigroup's generator $\mathcal{L}$, but in the inhomogeneous term present in the master equation which is independent of $\varrho^{(0)}(t > 0)$.

Formally solving Eq (19.68) for $\varrho^{(0)}(t)$, we find that (see Appendix C.1 for derivation):

$$\varrho^{(0)}(t) = \Lambda(t)\varrho^{(0)}(0) \tag{19.78}$$

with

$$\Lambda(t) := e^{\mathcal{L}t} + \int_0^t dt' \; e^{\mathcal{L}(t-t')}\mathcal{A}(t') \; . \tag{19.79}$$

Surely, with $\mathcal{A}(t) = 0$, the map $\Lambda(t)$ is clearly a UDM[6], and therefore CPT. However, $\Lambda(t)$ – as given in (19.79) – is in general non-UDM[7][8] (see Appendix C.2). It is interesting to note that $\Lambda(t)$ replicates the same structure of linear non-UDMs present in the literature [26, 72] (where both the focus system and the environment are quantized). Namely, it is the sum of two terms: the first term is a UDM, while the second (or inhomogeneous) term is a more complicated map which is traceless [21, 26, 72]. Furthermore, $\Lambda(t)$ may also be written as the difference between two CP maps (see Appendix C.2) – which again proves $\Lambda(t)$ to be a non-UDM [145, 168]. It is important to observe that, here in the zeroth-order, the theory restricts the domain of the map $\Lambda(t)$, $\{\varrho^{(0)}(0)\}$, to $\varrho^{(0)}(0) = \frac{e^{-\beta \mathscr{Z}_o}}{\mathrm{Tr}[e^{-\beta \mathscr{Z}_o}]}$, (19.27) – which is a Boltzmann state. Failing to do so may lead to unphysical results (see Appendix C.4). Moreover, there are strong indications that $\Lambda(t)$ is positive on its domain. We provide a heuristic argument in favor of this proposition in Appendix C.3. A more careful, and perhaps elegant, analysis of the positivity of $\Lambda(t)$ needs to be done. Nevertheless, the positivity of $\Lambda(t)$ on its domain would imply that

$$\Lambda(t) : \mathsf{C}_d^{+,1}[\varrho^{(0)}(0)]\big(\subset \mathcal{O}_d^{+,1}\big) \to \mathcal{O}_d^{+,1} \tag{19.80}$$

where $\mathsf{C}_d^{+,1}[\varrho^{(0)}(0)]$ denotes the set of all convex combinations of elements of $\mathcal{O}_d^{+,1}$ which commute with $\varrho^{(0)}(0)$. But what is more revealing, (19.80) – in light of Chap. 12 – would also imply that $\Lambda(t)$ is CPT on $\mathsf{C}_d^{+,1}[\varrho^{(0)}(0)]$.

As we shall see below (Chap.s 20-22), despite the fact that it breaks the UDM property of $\Lambda(t)$ in (19.79), the presence of $\mathcal{A}(t)$ puts the predictions of the theory impressively in line with experimental results; on the other hand, the predictions become quite incompatible with experimental results if we choose to neglect the inhomegeneous term.

19.4 On higher-order terms

We have concerned ourselves so far with the zeroth-order term of the ACP scheme, (19.32). If, in deriving the master equation for the higher order terms (i.e. $n \geq 1$) of $\varrho(t)$, we apply the same techniques and reasoning which led to (19.68), then, one can see that, in general:

$$\frac{d}{dt}\varrho^{(n)}(t) = \mathcal{L}\varrho^{(n)}(t) + \mathcal{A}(t)\varrho^{(n)}(0) + \mathcal{G}^{(n)}(t) \tag{19.81}$$

where the initial condition, $\varrho^{(n)}(0)$, is given by (19.26), and where

$$\mathcal{G}^{(n)}(t) := \begin{cases} 0 & (\text{for } n = 0) \\ \sum_{l=1}^{n} \mathcal{A}^{(l)}(t)\varrho^{(n-l)}(0) + \sum_{l=1}^{n} \mathcal{L}^{(l)}\varrho^{(n-l)}(t) & (\text{for } n \geq 1) \end{cases} . \tag{19.82}$$

The superoperators $\mathcal{A}(t)$ and $\mathcal{L}$ in (19.81) are still given by (19.69) and (19.71), respectively. We note that the master equation for the higher order term $\varrho^{(n\geq 1)}(t)$, (19.81), is just the same as that for

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[6] See Definition 13.0.1.

[7] See Definition 13.0.2.

[8] What we refer to here as 'non-UDM' is what is commonly referred to in the literature as '(positive but) non-CP' maps [26].

$\varrho^{(0)}(t)$, (19.68), except for the presence of the time-dependent operator $\mathcal{G}^{(n)}(t)$ in the former. Evidently, $\mathcal{G}^{(n)}(t)$ depends on the lower order corrections to $\varrho(0)$ and $\varrho(t)$, i.e. $\varrho^{(n')}(0)$ and $\varrho^{(n')}(t)$ with $n' < n$. We also remark that the superoperators $\mathcal{A}^{(l)}(t)$ and $\mathcal{L}^{(l)}$ in (19.82) differ from $\mathcal{A}(t)$ and $\mathcal{L}$ in (19.81), and may be seen as some form of higher-order corrections to the latter two, respectively. (More on this shortly.)

The formal solution to (19.81) is:

$$\varrho^{(n)}(t) = \left(e^{\mathcal{L}t} + \int_0^t dt'\ e^{\mathcal{L}(t-t')}\mathcal{A}(t') \right) \varrho^{(n)}(0) + \int_0^t dt'\ e^{\mathcal{L}(t-t')}\mathcal{G}^{(n)}(t')\ . \tag{19.83}$$

We have reasons to believe that the quantum map involved here is also non-UDM. In fact, we see again in (19.83) the same structure observed for non-UDMs maps [21, 26, 72]: the first term, $e^{\mathcal{L}t}\varrho^{(n)}(0)$, involves a UDM, while $\int_0^t dt'\ e^{\mathcal{L}(t-t')}\mathcal{A}(t')\varrho^{(n)}(0) + \int_0^t dt'\ e^{\mathcal{L}(t-t')}\mathcal{G}^{(n)}(t')$ constitute the traceless inhomogeneous term. It must be mentioned, however, that $e^{\mathcal{L}t}\varrho^{(n)}(0)$ for $n \geq 1$ is also traceless.

For any given order n in (19.32), the approximations and arguments (see Sec. 19.3.1 for details) we laid out for the zeroth-order must be replicated. This leads to an equation of motion of the form given in (19.81). Specifically, the secular approximation must be applied to the second term in (19.32). But before that, if one had assumed at the zeroth-order that the cross-terms involving $\mathscr{V}_{\pm}^{(n)}(t)$ may be neglected (as we did), then the same assumption must be applied to the second term in (19.32). Finally, one must also assume a continuous distribution of the frequencies in the oscillating field for both terms in (19.32).

If we consider the first-order correction to $\varrho(t)$, $\varrho^{(1)}(t)$, for example, it follows from (19.32) that

$$\begin{aligned}\frac{d}{dt}\varrho^{(1)}(t) = -i\left[\mathscr{V}^{(0)}(t), \varrho^{(1)}(0)\right] - i\left[\mathscr{V}^{(1)}(t), \varrho^{(0)}(0)\right] \\ - \int_0^{+\infty} d\tau \left[\mathscr{V}^{(1)}(t), \left[\mathscr{V}^{(0)}(t-\tau), \varrho^{(0)}(t)\right]\right] \\ - \int_0^{+\infty} d\tau \left[\mathscr{V}^{(0)}(t), \left[\mathscr{V}^{(1)}(t-\tau), \varrho^{(0)}(t)\right]\right] \\ - \int_0^{+\infty} d\tau \left[\mathscr{V}^{(0)}(t), \left[\mathscr{V}^{(0)}(t-\tau), \varrho^{(1)}(t)\right]\right]\ .\end{aligned} \tag{19.84}$$

We note that the first and last terms in (19.84) are actually copies of the r.h.s. of (19.35), except that $\varrho^{(0)}(0)$ and $\varrho^{(0)}(t)$ are now substituted with $\varrho^{(1)}(0)$ and $\varrho^{(1)}(t)$, respectively. So, after applying the above mentioned approximations and assumptions, these two terms transform as follows:

$$-i\left[\mathscr{V}^{(0)}(t), \varrho^{(1)}(0)\right] \mapsto \mathcal{A}(t)\varrho^{(1)}(0) \tag{19.85a}$$

$$-\int_0^{+\infty} d\tau \left[\mathscr{V}^{(0)}(t), \left[\mathscr{V}^{(0)}(t-\tau), \varrho^{(1)}(t)\right]\right] \mapsto \mathcal{L}\varrho^{(1)}(t) \tag{19.85b}$$

where $\mathcal{A}(t)$ and $\mathcal{L}$ are still given by (19.69) and (19.71), respectively. And the expression for $\varrho^{(1)}(0)$ is derived from (19.26).

Similarly, for the second term of (19.84), we may write

$$-i\left[\mathscr{V}^{(1)}(t), \varrho^{(0)}(0)\right] \mapsto \mathcal{A}^{(1)}(t)\varrho^{(0)}(0) \tag{19.86}$$

where $\mathcal{A}^{(1)}(t)$ will be linear in $\mathscr{X}$ and bear some similarities with $\mathcal{A}(t)$. The third and fourth terms of (19.84) may be put together after applying the said approximations and assumptions, and we may write

$$
\begin{aligned}
-\int_0^{+\infty} d\tau \left[\mathscr{V}^{(1)}(t), \left[\mathscr{V}^{(0)}(t-\tau), \varrho^{(0)}(t)\right]\right] \\
-\int_0^{+\infty} d\tau \left[\mathscr{V}^{(0)}(t), \left[\mathscr{V}^{(1)}(t-\tau), \varrho^{(0)}(t)\right]\right] \\
\mapsto \mathcal{L}^{(1)}\varrho^{(0)}(t) \ . \qquad (19.87)
\end{aligned}
$$

Here too, the superoperator $\mathcal{L}^{(1)}$ will linearly depend on $\mathscr{X}$.

Thus, after implementing the said approximations and assumptions, (19.84) simply becomes

$$
\frac{d}{dt}\varrho^{(1)}(t) = \mathcal{A}(t)\varrho^{(1)}(0) + \mathcal{L}\varrho^{(1)}(t) + \mathcal{G}^{(1)}(t) \qquad (19.88)
$$

where

$$
\mathcal{G}^{(1)}(t) = \mathcal{A}^{(1)}(t)\varrho^{(0)}(0) + \mathcal{L}^{(1)}\varrho^{(0)}(t) \ . \qquad (19.89)
$$

Note that (19.88) and (19.89) are in agreement with (19.81) and (19.82), respectively. In fact, following the same line of reasoning as we just did for the first-order correction, one can show by induction that (19.81) and (19.82) hold for any given order n. Furthermore, in solving (19.88) for $\varrho^{(1)}(t)$, we must impose the condition $\mathrm{Tr}[\varrho^{(1)}(t)] = 0$ (this also applies to all $\varrho^{(n)}(t)$ with $n \geq 1$).

Chapter 20

Application I: CW experiment with an ensemble of spin-$1/2$ particles.

20.1 The master equation

To illustrate the application of the equations and concepts derived and discussed in the preceding chapter, it may help to consider an ensemble of particles of spin-1/2. In this case, there won't be any need of ACP, given that we do not have the spin-spin coupling term, $H_{spin-spin}$, (19.1), to begin with. Indeed, almost all equations in Chap. 19, from (19.2) to (19.79), apply here – only that we just need to set $H_{spin-spin} \to 0$, which also translates into setting $\mathscr{X} \to 0$ and $\mathscr{Z}_o \to B_o \xi^z$, (19.17). With these transformations, we note that the non-homogeneous system of triangular differential equations in (19.32) reduces to a single differential equation, namely (19.35). Actually, the overall result of putting $H_{spin-spin} \to 0$ is that $\varrho(t)$ coincides now exactly with $\varrho^{(0)}(t)$, and (19.68) becomes:

$$\frac{d}{dt}\varrho(t) = \mathcal{A}(t)\varrho(0) + \mathcal{L}\varrho(t) \tag{20.1}$$

which is now, by default, the relative exact equation of motion for $\varrho(t)$ – *i.e.* within the very limitations of the approximations and assumptions which led to (19.68).

20.2 Determining the Lindblad operators

All that is left now is to determine the operators $\{\xi^x(+1, \omega_o)\}$ and substitute them into (19.69), (19.73) and (19.75). To make the connection with some known results in the literature more intelligible, we shall make use of the Pauli matrices:

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{20.2}$$

In this regard, $\mathscr{Z}_o$, as stated in the previous paragraph, becomes:

$$\mathscr{Z}_o = -\frac{\gamma B_o}{2}\sigma_3 \tag{20.3}$$

with γ being the gyromagnetic ratio of the spin-1/2, and B_o the magnitude of the steady magnetic field. The eigenkets of $\mathscr{H}_o$ are: $\left|+\frac{1}{2}\right\rangle$ and $\left|-\frac{1}{2}\right\rangle$, which according to the HP representation and the index compression map η_o, may also be denoted as $|\mathbb{0}\rangle$ and $|\mathbb{1}\rangle$, respectively. With just two eigenkets, it is easily observed that the possible frequency difference ω_o between these eigenkets are: $\omega_o \in \{0, \pm\gamma B_o\}$.

Furthermore, it is clear from the definition given in (19.40) that:

$$\xi^x(+1, \omega_o) = -\frac{\gamma}{2}\sigma_-, \quad \xi^x(-1, -\omega_o) = -\frac{\gamma}{2}\sigma_+ \tag{20.4}$$

when $\omega_o = -\gamma B_o$, i.e. the Larmor frequency – with

$$\sigma_\pm = \frac{1}{2}\left(\sigma_1 \pm i\sigma_2\right) \ . \tag{20.5}$$

However, when $\omega_o = 0$, $\xi^x(n, \omega_o) = 0$ for all possible values of n. We may, therefore, in the following, intend ω_o as the Larmor frequency without loss of generality. Interestingly, given (20.4), it readily follows from (19.41) and (19.42) that:

$$[\mathscr{H}_o, \sigma_\pm] = \pm\omega_o \ \sigma_\pm \tag{20.6}$$

and the initial density matrix $\varrho(0)$ is

$$\varrho(0) = \frac{e^{-\beta\mathscr{H}_o}}{\mathrm{Tr}[e^{-\beta\mathscr{H}_o}]} \ . \tag{20.7}$$

20.3 Explicit expression for the master equation

With the identity of the operators $\{\xi^x(n, \omega_o)\}$ in our possession, thanks to (20.4), we now determine $H_{LR}(t)$, H_{LS} and $\mathcal{D}_\pm[\bullet]$ through (19.70), (19.73) and (19.75), respectively. Namely:

$$H_{LR}(t) = \Re[\varphi_f(t)]\omega_1 e^{-it\omega_o}\sigma_- + h.c. \tag{20.8}$$

$$\begin{aligned} H_{LS} &= \pi\left(\frac{\omega_1}{2}\right)^2 \left[\rho_f^{\succ}(\omega_o) - \rho_f^{\succ}(-\omega_o)\right][\sigma_-, \sigma_+] \\ &= -\pi\left(\frac{\omega_1}{2}\right)^2 \left[\rho_f^{\succ}(\omega_o) - \rho_f^{\succ}(-\omega_o)\right] \ \sigma_3 \end{aligned} \tag{20.9}$$

with $\omega_1 := -\gamma B_1$. Regarding the dissipator term, it easily follows from (19.75) and (20.4) that:

$$\begin{aligned} \mathcal{D}_\pm[\varrho(t)] = 2\pi\left(\frac{\omega_1}{2}\right)^2 \rho_f(\pm\omega_o)\left[\sigma_-\varrho(t)\sigma_+ - \frac{1}{2}\{\sigma_+\sigma_-, \varrho(t)\}\right] \\ + 2\pi\left(\frac{\omega_1}{2}\right)^2 \rho_f(\pm\omega_o)\left[\sigma_+\varrho(t)\sigma_- - \frac{1}{2}\{\sigma_-\sigma_+, \varrho(t)\}\right] \ . \end{aligned} \tag{20.10}$$

This dissipator component is reminiscent of its analogue in the quantum optical master equation (see (3.219) of [22]). The only difference between the two are the rate constants. In the quantum optical master equation [22], the radiation field is treated quantum mechanically, thus allowing to account for the rate of spontaneous emission, besides the usual stimulated rates of emission and absorption. In (19.75) and (20.10), there is no trace of rate of spontaneous emission simply because the oscillating field is treated classically.

Regarding the rates of stimulated emission and absorption, it is worth observing that when $\omega_o > 0$ (i.e. $\gamma < 0$), the first term in (20.10) describes the stimulated emission process $\left|-\tfrac{1}{2}\right\rangle \leftarrow \left|+\tfrac{1}{2}\right\rangle$ at the rate $\Gamma_{-\frac{1}{2},+\frac{1}{2}}$, while the second term of the same equation describes the stimulated absorption process $\left|+\tfrac{1}{2}\right\rangle \leftarrow \left|-\tfrac{1}{2}\right\rangle$ at the rate $\Gamma_{+\frac{1}{2},-\frac{1}{2}}$. The rate of both processes coincides:

$$\begin{aligned}\Gamma_{-\frac{1}{2},+\frac{1}{2}} = \Gamma_{+\frac{1}{2},-\frac{1}{2}} &= 2\pi \left(\frac{\omega_1}{2}\right)^2 \left[\rho_f(\omega_o) + \rho_f(-\omega_o)\right] \\ &\equiv \Gamma(\omega_o) \ . \end{aligned} \tag{20.11a}$$

If we write

$$\varrho(t) = \frac{1}{2}\left[\mathbb{1} + 2\left\langle\sigma_-(t)\right\rangle'\sigma_+ + 2\left\langle\sigma_+(t)\right\rangle'\sigma_- + \left\langle\sigma_3(t)\right\rangle'\sigma_3\right] \tag{20.12}$$

where $\left\langle\sigma_\pm(t)\right\rangle' \equiv \mathrm{Tr}[\varrho(t)\sigma_\pm]$ and $\left\langle\sigma_3(t)\right\rangle' \equiv \mathrm{Tr}[\varrho(t)\sigma_3]$, (with $\langle x\rangle'$ we mean the expectation value of x in the interaction picture; the unprimed $\langle x\rangle$, until otherwise stated, will be the analogous expectation value in the Schrödinger picture) then (20.12) and (20.1) lead to the differential equations

$$\begin{aligned}&\frac{d}{dt}\left\langle\sigma_3(t)\right\rangle' = -2\Gamma(\omega_o)\left\langle\sigma_3(t)\right\rangle' \qquad (20.13a)\\ &\frac{d}{dt}\left\langle\sigma_+(t)\right\rangle' = i\omega_1\tanh(\beta\omega_o/2)\Re[\varphi_f(t)]e^{-it\omega_o} - \left[\Gamma(\omega_o) + i\varpi(\omega_o)\right]\left\langle\sigma_+(t)\right\rangle'\end{aligned}$$

with $\varpi(\omega_o)$ given by the expression:

$$\frac{\varpi(\omega_o)}{2} \equiv \pi\left(\frac{\omega_1}{2}\right)^2\left[\rho_f^{\succ}(\omega_o) - \rho_f^{\succ}(-\omega_o)\right] \equiv \omega_{LS}(\omega_o) \tag{20.14}$$

where ω_{LS} is the ‘Lamb shift rate’ and originates from H_{LS}, (20.9). In the following we shall simply write Γ and ϖ, but their dependence on ω_o must be kept in mind. Naturally, $\left\langle\sigma_-(t)\right\rangle' = \left\langle\sigma_+(t)\right\rangle'^*$.

Bearing in mind that in the Schrödinger picture $\left\langle\sigma_\pm(t)\right\rangle' \mapsto \left\langle\sigma_\pm(t)\right\rangle e^{\mp i\omega_o t}$, we deduce that the stationary solutions for $\left\langle\sigma_3(t)\right\rangle$ and $\left\langle\sigma_+(t)\right\rangle$ – namely, $\left\langle\sigma_3(t)\right\rangle_s$ and $\left\langle\sigma_+(t)\right\rangle_s$ – in the Schrödinger picture are:

$$\left\langle\sigma_3(t)\right\rangle_s = 0 \tag{20.15a}$$

$$\left\langle\sigma_\pm(t)\right\rangle_s = -\frac{\omega_1\tanh(\beta\omega_o/2)}{[\omega_o - \varpi] \pm i\Gamma}\Re[\varphi(t)] \ . \tag{20.15b}$$

Since $\Re[\varphi(t)]$ tends to zero as $t \to +\infty$ according to Pòlya’s theorem, it follows that $\left\langle\sigma_\pm(t)\right\rangle$ also tend to zero as $t \to +\infty$. Putting this observation together with (20.12), we readily come to the conclusion that the equilibrium state, $\varrho_{eq} = \rho_{eq}$, of the qubit ensemble in our CW experiment is the corresponding maximally mixed state, i.e. $\rho_{eq} = \frac{1}{2}\mathbb{1}$. This also means that the associated quantum map contracts the Bloch sphere to a point, namely the center. Indeed, solving the differential equations in (20.13) in the Schrödinger picture, we find:

$$\left\langle\sigma_3(t)\right\rangle = -\tanh(\beta\omega_o/2)\ e^{-2\Gamma t} \tag{20.16}$$

$$\left\langle\sigma_\pm(t)\right\rangle = \Re\left\langle\sigma_+(t)\right\rangle \pm i\Im\left\langle\sigma_+(t)\right\rangle \tag{20.17}$$

where

$$\Re\left\langle\sigma_+(t)\right\rangle = e^{-\Gamma t}\omega_1\tanh(\beta\omega_o/2)\int_0^t dt'\ e^{\Gamma t'}\sin[(\varpi - \omega_o)(t - t')]\ \Re[\varphi_f(t')] \tag{20.18}$$

$$\Im\left\langle\sigma_+(t)\right\rangle = e^{-\Gamma t}\omega_1\tanh(\beta\omega_o/2)\int_0^t dt'\ e^{\Gamma t'}\cos[(\varpi - \omega_o)(t - t')]\ \Re[\varphi_f(t')] \ . \tag{20.19}$$

It is thus evident that $\left\langle\sigma_\pm(t)\right\rangle$ inexorably approaches zero as $t \to +\infty$. From (20.5), we also find that

$$\left\langle\sigma_1(t)\right\rangle = 2\Re\left\langle\sigma_+(t)\right\rangle \qquad \text{and} \qquad \left\langle\sigma_2(t)\right\rangle = 2\Im\left\langle\sigma_+(t)\right\rangle \ . \tag{20.20}$$

20.4 Some applications in linear response theory

To illustrate how the present model of semiclassical quantum Markovian master equation, (20.1), also entails known results in LRT (linear response theory), we determine the dynamical structure factor [56] of $\xi^x(+1,\omega_o)$. Since $\xi^x(+1,\omega_o)$ is proportional to σ_-, (20.4), we can equally concentrate below on the dynamic structure factor of σ_-, $S_{\sigma_-\sigma_+}(\omega')$:

$$S_{\sigma_-\sigma_+}(\omega') = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\ e^{i\omega' t}\left\langle \sigma_-(t)\sigma_+\right\rangle \tag{20.21}$$

where the correlation $\langle\sigma_-(t)\sigma_+\rangle \equiv \mathrm{Tr}[\sigma_-(t)\sigma_+\rho(0)]$ is evaluated in the Heisenberg picture. We therefore need to determine how our quantum map evolves σ_- in the Heisenberg picture.

Given that any qubit operator X can be written as

$$X = \frac{1}{2}\left[c_0(0)\mathbb{1} + c_1(0)\sigma_1 + c_2(0)\sigma_2 + c_3(0)\sigma_3\right] \tag{20.22}$$

with

$$c_i(0) = \mathrm{Tr}[X\sigma_i] \qquad i = \{0,1,2,3\} \tag{20.23}$$

(where $\sigma_0 \equiv \mathbb{1}$), it naturally follows that the Heisenberg picture evolution of X, $X(t)$, must be of the form

$$X(t) = \frac{1}{2}\left[c_0(t)\mathbb{1} + c_1(t)\sigma_1 + c_2(t)\sigma_2 + c_3(t)\sigma_3\right] \tag{20.24}$$

where the coefficients $c_i(t)$ are to be determined through the condition we saw in (13.34) – namely,

$$\mathrm{Tr}[\rho(t)X] = \mathrm{Tr}[\rho(0)X(t)]\ . \tag{20.25}$$

After some algebra, one finds that with $\rho(0) = \frac{e^{-\beta\mathscr{H}_o}}{\mathrm{Tr}[e^{-\beta\mathscr{H}_o}]} = \frac{1}{2}[\mathbb{1} + \langle\sigma_3(0)\rangle\,\sigma_3]$, where $\langle\sigma_3(0)\rangle = -\tanh(\beta\omega_o/2)$,

$$\begin{pmatrix} c_0(t)\\ c_1(t)\\ c_2(t)\\ c_3(t)\end{pmatrix} = \begin{pmatrix} \kappa_0(t) & \kappa_1(t) & \kappa_2(t) & \kappa_3(t)\\ \kappa_1(t) & \kappa_0(t) & -i\kappa_3(t) & i\kappa_2(t)\\ \kappa_2(t) & i\kappa_3(t) & \kappa_0(t) & -i\kappa_1(t)\\ \kappa_3(t) & -i\kappa_2(t) & i\kappa_1(t) & \kappa_0(t)\end{pmatrix}\begin{pmatrix} c'_0(t)\\ c'_1(t)\\ c'_2(t)\\ c'_3(t)\end{pmatrix} \tag{20.26}$$

where

$$\begin{pmatrix} c'_0(t)\\ c'_1(t)\\ c'_2(t)\\ c'_3(t)\end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0\\ 0 & \cos(\omega_o t) & \sin(\omega_o t) & 0\\ 0 & -\sin(\omega_o t) & \cos(\omega_o t) & 0\\ 0 & 0 & 0 & 1\end{pmatrix}\begin{pmatrix} c_0(0)\\ c_1(0)\\ c_2(0)\\ c_3(0)\end{pmatrix} \tag{20.27}$$

and

$$\kappa_0(t) \equiv \frac{1-\langle\sigma_3(0)\rangle'\langle\sigma_3(t)\rangle'}{1-\langle\sigma_3(0)\rangle'^2} \tag{20.28a}$$

$$\kappa_1(t) \equiv i\left[\frac{\langle\sigma_2(t)\rangle'\langle\sigma_3(0)\rangle' - i\langle\sigma_1(t)\rangle'}{1-\langle\sigma_3(0)\rangle'^2}\right] \tag{20.28b}$$

$$\kappa_2(t) \equiv -i\left[\frac{\langle\sigma_1(t)\rangle'\langle\sigma_3(0)\rangle' + i\langle\sigma_2(t)\rangle'}{1-\langle\sigma_3(0)\rangle'^2}\right] \tag{20.28c}$$

$$\kappa_3(t) \equiv \frac{\langle\sigma_3(t)\rangle' - \langle\sigma_3(0)\rangle'}{1-\langle\sigma_3(0)\rangle'^2} \tag{20.28d}$$

and where, as remarked earlier – (20.12) – $\langle\sigma_i(t)\rangle'$ is the equivalent of $\langle\sigma_i(t)\rangle$ in the interaction picture. Namely,

$$\begin{pmatrix}\langle\sigma_1(t)\rangle'\\ \langle\sigma_2(t)\rangle'\\ \langle\sigma_3(t)\rangle'\end{pmatrix}=\begin{pmatrix}\cos(\omega_o t) & \sin(\omega_o t) & 0\\ -\sin(\omega_o t) & \cos(\omega_o t) & 0\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}\langle\sigma_1(t)\rangle\\ \langle\sigma_2(t)\rangle\\ \langle\sigma_3(t)\rangle\end{pmatrix} \tag{20.29}$$

where $\langle\sigma_3(t)\rangle$ is given by (20.16) and, $\langle\sigma_1(t)\rangle$ and $\langle\sigma_2(t)\rangle$ are defined in (20.20).

It follows then that with the initial density matrix $\rho(0)=\frac{e^{-\beta\mathscr{Z}_o}}{\mathrm{Tr}[e^{-\beta\mathscr{Z}_o}]}$, given a qubit operator X, its corresponding dynamical structure factor $S_{XX^\dagger}(\omega')=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\ e^{i\omega' t}\left\langle X(t)X^\dagger\right\rangle$ in terms of the coefficients $c_i(0), c_i(t)$ is:

$$\begin{aligned}S_{XX^\dagger}(\omega')=\frac{1}{4}\Bigg[\Big(\mathscr{C}_{3,0}(\omega')+\mathscr{C}_{0,3}(\omega')\Big)\langle\sigma_3(0)\rangle+\mathscr{C}_{0,0}(\omega')\\ +\mathscr{C}_{3,3}(\omega')+4\frac{e^{\beta\omega_o/2}}{\mathrm{Tr}[e^{-\beta\mathscr{Z}_o}]}\mathscr{C}_{+,+}(\omega')+4\frac{e^{-\beta\omega_o/2}}{\mathrm{Tr}[e^{-\beta\mathscr{Z}_o}]}\mathscr{C}_{-,-}(\omega')\Bigg]\end{aligned} \tag{20.30}$$

where

$$\mathscr{C}_{\nu,\mu}(\omega')=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\ e^{i\omega' t}c_\nu(t)c_\mu^*(0) \tag{20.31}$$

with

$$c_\pm(t)=\frac{1}{2}\left[c_1(t)\pm ic_2(t)\right]\qquad (t\geq 0)\ . \tag{20.32}$$

Going back to $S_{\sigma_-\sigma_+}(t)$, (20.21), we may apply (20.30) by setting $X=\sigma_-$. This reduces (20.30) to

$$\begin{aligned}S_{\sigma_-\sigma_+}(\omega')&=\frac{e^{\beta\omega_o/2}}{\mathrm{Tr}[e^{-\beta\mathscr{Z}_o}]}\mathscr{C}_{+,+}(\omega')\\ &=\frac{e^{\beta\omega_o/2}}{\mathrm{Tr}[e^{-\beta\mathscr{Z}_o}]}\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\ e^{i(\omega'-\omega_o)t}\frac{1-\langle\sigma_3(t)\rangle}{1-\langle\sigma_3(0)\rangle}\\ &=\frac{1}{2}\left[\delta(\omega'-\omega_o)+\tanh(\beta\omega_o/2)\cdot\frac{1}{\pi}\frac{2\Gamma}{(2\Gamma)^2+(\omega'-\omega_o)^2}\right]\ .\end{aligned} \tag{20.33}$$

This tells us that the spectrum of the time-dependent fluctuations of σ_- has a Lorentzian profile centered on the Larmor frequency ω_o and its HWHM (half width at half maximum) is twice the transition rate between the two level system. The temperature dependence of the profile is embodied in the factor $\tanh(\beta\omega_o/2)$.

Conversely, if we put $X=\sigma_+$, it turns out from (20.30) that

$$\begin{aligned}S_{\sigma_+\sigma_-}(\omega')&=\frac{e^{-\beta\omega_o/2}}{\mathrm{Tr}[e^{-\beta\mathscr{Z}_o}]}\mathscr{C}_{-,-}(\omega')\\ &=\frac{e^{-\beta\omega_o/2}}{\mathrm{Tr}[e^{-\beta\mathscr{Z}_o}]}\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\ e^{i(\omega'+\omega_o)t}\frac{1+\langle\sigma_3(t)\rangle}{1+\langle\sigma_3(0)\rangle}\\ &=\frac{1}{2}\left[\delta(\omega'+\omega_o)-\tanh(\beta\omega_o/2)\cdot\frac{1}{\pi}\frac{2\Gamma}{(2\Gamma)^2+(\omega'+\omega_o)^2}\right]\ .\end{aligned} \tag{20.34}$$

It is evident that for $\omega_o>0$, $S_{\sigma_-\sigma_+}(\omega')$ is the stimulated absorption spectrum and $S_{\sigma_+\sigma_-}(\omega')$ is the stimulated emission spectrum [56]. At any rate, the two spectra are related through the relation

$$S_{\sigma_-\sigma_+}(\omega')-S_{\sigma_+\sigma_-}(-\omega')=\tanh(\beta\omega_o/2)\cdot\frac{1}{\pi}\frac{2\Gamma}{(2\Gamma)^2+(\omega'-\omega_o)^2}\ . \tag{20.35}$$

This relation differs from the one given in LRT (see, for example, (3.73) of [56]). To recover the LRT limit from (20.35), we need to remember that the whole edifice of LRT rests on the adiabatic process assumption, where it is assumed the interaction between the system and the bath is weak enough so as not to change appreciably the occupation probabilities of the initial state of the system, and that the system has remained in its equilibrium state in the far past prior to its encounter with the bath. This is equivalent to taking the limit $\mathcal{L} \to 0$ in our master equation, (20.1), and having t_o(the initial time) $\to -\infty$. In other terms, we can get the adiabatic process limit of a given dynamic structure factor obtained from the full solution of the quantum Markovian master equation by taking the limits $\Gamma \to 0$ and $\omega_{LS} \to 0$. Now, if we introduce

$$S^{ad}_{\sigma_-\sigma_+}(\omega') \equiv \lim_{\omega_{LS},\Gamma\to 0} S_{\sigma_-\sigma_+}(\omega') \tag{20.36a}$$

$$S^{ad}_{\sigma_+\sigma_-}(\omega') \equiv \lim_{\omega_{LS},\Gamma\to 0} S_{\sigma_+\sigma_-}(\omega') \tag{20.36b}$$

– where $S^{ad}_{\sigma_-\sigma_+}(\omega')$ and $S^{ad}_{\sigma_+\sigma_-}(\omega')$ indicate the adiabatic process limits of $S_{\sigma_-\sigma_+}(\omega')$ and $S_{\sigma_+\sigma_-}(\omega')$, respectively – then we readily derive from (20.33) and (20.34) that

$$S^{ad}_{\sigma_+\sigma_-}(-\omega') = e^{-\beta\omega_o} S^{ad}_{\sigma_-\sigma_+}(\omega') \tag{20.37}$$

which is the relation between the two spectra according to LRT [56].

It is certainly worth noting that without the linear response Hamiltonian $H_{LR}(t)$, (20.8), we would have had $\langle\sigma_\pm(t)\rangle = 0 \ \forall t \geq 0$ since $\langle\sigma_\pm(0)\rangle = 0$ (see (20.13)). As a consequence, the dynamic structure factors $S_{\sigma_\mp\sigma_\pm}(\omega')$, for example, would result to be always zero, meaning we do not observe any absorption or emission spectrum – but that would have been contrary to experimental observations. Given that $H_{LR}(t)$ stems from the superoperator $\mathcal{A}(t)$, (19.69), the observation just made reinforces the assertion that $\mathcal{A}(t)$ is central to the theory and cannot be simply – generally speaking – put to zero (or ignored) in (20.1) in order to make the quantum map $\Lambda(t)$, (19.79), a UDM.

20.5 Generalized Kraus operator sum representation

As indicated in Appendix C.2, the quantum map $\Lambda(t)$ related to the master equation in (20.1) cannot be a UDM. It is interesting to note that in this particular simple example where we are dealing with an ensemble of spin-1/2 particles, it can be fairly easily shown – using the results discussed in Chap. 12 – that the density matrix $\varrho(t)$ in (20.12) may nevertheless – in spite of $\Lambda(t)$ not being UDM – be written according to a (generalized) Kraus operator sum as follows:

$$\varrho(t) = \Lambda(t)\varrho(0) = \sum_{\mu=0}^{1} M_\mu(t)\varrho(0)M^\dagger_\mu(t) \tag{20.38}$$

where $\varrho(0)$ is given by (20.7), and

$$M_\mu(t) \equiv U(t)\Gamma_\mu(t)\ . \tag{20.39}$$

The matrix $U(t)$ is unitary:

$$U(t) = \begin{pmatrix} a_+(t) & a_-(t) \\ b_+(t) & b_-(t) \end{pmatrix} \tag{20.40}$$

where

$$a_\pm(t) = \cos\left[\beta_\pm(t)/2\right] e^{-i\vartheta(t)/2} \tag{20.41a}$$

$$b_\pm(t) = \sin\left[\beta_\pm(t)/2\right] e^{i\vartheta(t)/2} \tag{20.41b}$$

$$\frac{\beta_+(t)}{2} = \arctan\left[-\frac{1-\sqrt{1+|\eta(t)|^2}}{|\eta(t)|}\right] = \arctan\left[\frac{|\eta(t)|}{1+\sqrt{1+|\eta(t)|^2}}\right] \tag{20.42}$$

$$\frac{\beta_-(t)}{2} = -\arctan\left[\frac{1+\sqrt{1+|\eta(t)|^2}}{|\eta(t)|}\right] \tag{20.43}$$

and finally,

$$\eta(t) \equiv 2\frac{\langle\sigma_+(t)\rangle'}{\langle\sigma_3(t)\rangle'} \qquad e^{i\vartheta(t)} \equiv \frac{\langle\sigma_+(t)\rangle'}{\left|\langle\sigma_+(t)\rangle'\right|} \tag{20.44}$$

– where expressions for $\langle\sigma_+(t)\rangle'$ and $\langle\sigma_3(t)\rangle'$ follow from (20.13) (or, alternatively, can be derived from (20.15))[1].

Regarding the matrix $\Gamma_\mu(t)$, we have:

$$\Gamma_0(t) = \begin{pmatrix} \sqrt{\lambda_+(t)} & 0 \\ 0 & \sqrt{\lambda_-(t)} \end{pmatrix} \qquad \Gamma_1(t) = \begin{pmatrix} 0 & \sqrt{\lambda_+(t)} \\ \sqrt{\lambda_-(t)} & 0 \end{pmatrix} \tag{20.45}$$

where

$$\lambda_\pm(t) \equiv \frac{1}{2}\left[1 \pm \langle\sigma_3(t)\rangle' \sqrt{1+|\eta(t)|^2}\right] . \tag{20.46}$$

The functions $\lambda_\pm(t)$ are positive-definite. One way to see this is by observing that since $\varrho(t)$ is always a mixed state, we have that (Chap. 4):

$$\begin{gathered} \mathrm{Tr}\left[\varrho(t)\varrho^\dagger(t)\right] < 1 \\ \frac{1}{2} + \frac{\left|\langle\sigma_3(t)\rangle'\right|^2}{2} + 2\left|\langle\sigma_+(t)\rangle'\right|^2 < 1 \\ \frac{\left|\langle\sigma_3(t)\rangle'\right|^2}{4} + \left|\langle\sigma_+(t)\rangle'\right|^2 < \frac{1}{4} \end{gathered} \tag{20.47}$$

– from which it readily follows that

$$\frac{1}{2}\left|\langle\sigma_3(t)\rangle'\right|\sqrt{1+|\eta(t)|^2} = \sqrt{\frac{1}{4}\left|\langle\sigma_3(t)\rangle'\right|^2 + \left|\langle\sigma_+(t)\rangle'\right|^2} < \frac{1}{2} . \tag{20.48}$$

It can also be easily verified that the generalized Kraus operators $\{M_\mu(t)\}$, (20.39), satisfy the completeness relation

$$\sum_{\mu=0}^{1} M_\mu^\dagger(t) M_\mu(t) = \mathbb{I}_2 . \tag{20.49}$$

If one should compare (20.39) with (12.18), one might think a unitary matrix is missing in (20.39). That unitary matrix is one which diagonalizes $\varrho(0)$. But $\varrho(0)$ is already diagonal in the basis $\{|\mathbb{0}\rangle, |\mathbb{1}\rangle\}$, so one may say the unitary matrix which diagonalizes $\varrho(0)$ in this very basis is the identity matrix

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[1] Note that $\langle\sigma_3(t)\rangle' = \langle\sigma_3(t)\rangle$, as remarked earlier on in this chapter. We have chosen to keep $\langle\sigma_3(t)\rangle'$ for consistency since we are clearly working in the interaction picture.

$\mathbb{I}_2$. Note, however, that one exquisite implication of this observation is that the (positivity) domain of $\Lambda(t)$ comprises all qubit density matrices which are diagonal in the basis $\{|\mathbb{0}\rangle, |\mathbb{1}\rangle\}$, as pointed out in Sec. 19.3.2.

We conclude this chapter by noting that – from (20.38), (20.39) and appropriate subsequent equations –,

$$\varrho(t) = \lambda_+(t)\,|\psi_+(t)\rangle\langle\psi_+(t)| + \lambda_-(t)\,|\psi_-(t)\rangle\langle\psi_-(t)| \tag{20.50}$$

where

$$|\psi_\pm(t)\rangle = a_\pm(t)\,|\mathbb{0}\rangle + b_\pm(t)\,|\mathbb{1}\rangle\ \ . \tag{20.51}$$

We thus conclude (or, perhaps, confirm) that $\lambda_\pm(t)$ are the eigenvalues of $\varrho(t)$. In other words, $\lambda_\pm(t)$ express the populations of the qubit system in the course of the dynamics (obviously, in the basis $\{|\psi_\pm(t)\rangle\}$).

Chapter 21

Application II: The Linear Response Theory connection.

Since the seminal work of Davies and Spohn [38], there have been a number of works [3, 27, 107] aimed at revisiting at least some aspects of Kubo's LRT [56, 59, 101, 154, 158] from the perspective of quantum (non-)Markovian master equations. Much of these efforts have been concentrated on deriving fluctuation-dissipation theorems. We showed in the preceding chapter how the theory and formalism we are developing entail some of the key results in LRT. In this chapter, we shall try to extend some of the results obtained in Sec. 20.4 to the general case of an arbitrary multispin system. We also show how the celebrated LRT fluctuation-dissipation theorem [56] is easily derived as a limit case.

We begin with the following formal solution to (19.68):

$$\varrho^{(0)}(t) - \varrho^{(0)}(0) = \int_0^t dt' \ \mathcal{A}(t')\varrho^{(0)}(0) + \int_0^t dt' \ \mathcal{L}\varrho^{(0)}(t') \tag{21.1}$$

which in the Schrödinger picture (see (19.23a)) becomes:

$$\rho^{(0)}(t) - \rho^{(0)}(0) = -i\int_0^t dt' \ \left[e^{-it\mathscr{X}_o} H_{LR}(t') e^{it\mathscr{X}_o}, \rho^{(0)}(0)\right] + \int_0^t dt' \ \mathcal{L}\left[e^{-i(t-t')\mathscr{X}_o}\rho^{(0)}(t')e^{i(t-t')\mathscr{X}_o}\right] \ . \tag{21.2}$$

Thus, for any given operator X of the multispin system, we derive from (21.2) that:

$$\left\langle X^{(0)}(t)\right\rangle - \left\langle X^{(0)}(0)\right\rangle = -i\int_0^t dt' \ \left\langle \left[X, e^{-it\mathscr{X}_o} H_{LR}(t') e^{it\mathscr{X}_o}\right]\right\rangle_o + \int_0^t dt' \ \mathrm{Tr}\left(X\mathcal{L}\left[e^{-i(t-t')\mathscr{X}_o}\rho^{(0)}(t')e^{i(t-t')\mathscr{X}_o}\right]\right) \tag{21.3}$$

where $\left\langle X^{(0)}(t)\right\rangle \equiv \mathrm{Tr}\left[X\rho^{(0)}(t)\right]$ and $\left\langle F\right\rangle_o \equiv \mathrm{Tr}\left[F\rho^{(0)}(0)\right]$. Naturally, $\left\langle X^{(0)}(t)\right\rangle$ is the expectation value of the observable X at zeroth-order in $\mathscr{X}$. We now show that if we take the limit $\mathcal{L} \to 0$ (or if the quantum dynamic semigroup generator term is negligible with respect to the linear response term), we get a richer version of linear response theory [56, 59, 101, 154, 158] from (21.3). We may term this the 'LRT limit' of (21.3). Indeed, with $\mathcal{L} \to 0$, (21.3) reduces to:

$$\left\langle X^{(0)}(t)\right\rangle - \left\langle X^{(0)}(0)\right\rangle = -i\int_0^t dt' \ \left\langle \left[X, e^{-it\mathscr{X}_o} H_{LR}(t') e^{it\mathscr{X}_o}\right]\right\rangle_o \ . \tag{21.4}$$

In any case, after some simple rearrangements, it can be shown that:

$$-i\int_0^t dt' \, \left\langle \left[X, e^{-it\mathscr{L}_o} H_{LR}(t') e^{it\mathscr{L}_o}\right]\right\rangle_o = 2B_1 \int_{-\infty}^{+\infty} d\omega' \rho_f(\omega') \sum_{\omega_o} \frac{e^{it\omega_o}}{2} \left[\chi_{\omega_o,\infty}(\omega') + \chi_{\omega_o,t}(\omega')\right] + c.c. \tag{21.5}$$

with

$$\chi_{\omega_o,\infty}(\omega') \equiv \chi_{+,\omega_o,\infty}(\omega') + \chi_{-,\omega_o,\infty}(\omega') \tag{21.6a}$$

$$\chi_{\omega_o,t}(\omega') \equiv \chi_{+,\omega_o,t}(\omega') + \chi_{-,\omega_o,t}(\omega') \tag{21.6b}$$

where $\chi_{\pm,\omega_o,\infty}(\omega')$ and $\chi_{\pm,\omega_o,t}(\omega')$ together define the *linear* frequency-dependent response function of the spin system's observable X to the perturbation defined by the coupling between the rotating fields, $\mathbf{B}_{1,\pm}(t)$, and $\boldsymbol{\xi}^x$. In particular, $\chi_{\pm,\omega_o,\infty}(\omega')$, which define the steady-state limit of the linear response, are given by the expressions:

$$\chi_{\pm,\omega_o,\infty}(\omega') := \lim_{\eta\to 0^+} \frac{\langle [X, \xi^x(+1,\omega_o)]\rangle_o}{(\pm\omega' - \omega_o) + i\eta} \tag{21.7}$$

while for $\chi_{\pm,\omega_o,t}(\omega')$, the transient elements of the response function, we have:

$$\chi_{\pm,\omega_o,t}(\omega') := -\lim_{\eta\to 0^+} \frac{\langle [X, \xi^x(+1,\omega_o)]\rangle_o}{(\pm\omega' - \omega_o) + i\eta} e^{[i(\pm\omega'-\omega_o)-\eta]t} \tag{21.8}$$

where,

$$\langle [X, \xi^x(+1,\omega_o)]\rangle_o := \mathrm{Tr}\left([X, \xi^x(+1,\omega_o)]\, \rho^{(0)}(0)\right) . \tag{21.9}$$

It is interesting to observe that $\chi_{\pm,\omega_o,\infty}(\omega')$, (21.7), are precisely the usual frequency response functions one would define for the pair of operators X and $\xi^x(+1,\omega_o)$ in LRT under the so-called Lehmann representation [56]. In LRT, one obtains $\chi_{\pm,\omega_o,\infty}(\omega')$ under the assumption of an adiabatic process [56, 59, 101, 154, 158], where, as remarked earlier, can be seen as taking the limits $\mathcal{L} \to 0$, $t_o \to -\infty$. It is crucial to note here that while the first limit alone retains the transient components of the response functions, the introduction of the second limit dumps these. For steady-state experiments like CW magnetic resonance, taking the limit $t_o \to -\infty$ is acceptable since it practically translates into the limit $t \to +\infty$, i.e. the steady-state limit; but for transient experiments like pulsed NMR and ESR, these transient response functions play a crucial role in the theory. Interestingly, the integral $\int_{-\infty}^{+\infty} d\omega' \rho_f(\omega') \chi_{\omega_o,t}(\omega')$ is an exponentially decaying oscillatory function, with decay rate τ_f. So, for $t \gg \tau_f$, the transient component of the response function becomes negligible and (21.5) reduces to the form:

$$\begin{aligned} -i\int_0^t dt' \, \left\langle \left[X, e^{-it\mathscr{L}_o} H_{LR}(t') e^{it\mathscr{L}_o}\right]\right\rangle_o &= 2B_1 \int_{-\infty}^{+\infty} d\omega' \rho_f(\omega') \sum_{\omega_o} \left[\frac{e^{it\omega_o}}{2} \chi_{\omega_o,\infty}(\omega') + c.c.\right] \\ &= 2B_1 \int_{-\infty}^{+\infty} d\omega' \rho_f(\omega') \sum_{\omega_o} \left[\cos(\omega_o t) \chi^{'}_{\omega_o,\infty}(\omega') + \sin(\omega_o t) \chi^{''}_{\omega_o,\infty}(\omega')\right] \end{aligned} \tag{21.10}$$

where:

$$\chi^{'}_{\omega_o,\infty}(\omega') := \Re\chi_{\omega_o,\infty}(\omega') = \Re\chi_{+,\omega_o,\infty}(\omega') + \Re\chi_{-,\omega_o,\infty}(\omega') \tag{21.11a}$$

$$-\chi^{''}_{\omega_o,\infty}(\omega') := \Im\chi_{\omega_o,\infty}(\omega') = \Im\chi_{+,\omega_o,\infty}(\omega') + \Im\chi_{-,\omega_o,\infty}(\omega') \tag{21.11b}$$

and

$$\Re\chi_{\pm,\omega_o,\infty}(\omega') = \Bigg[\mathcal{P}\left(\frac{\Re\left\langle\left[X^\dagger(+1,\omega_o),\xi^x(+1,\omega_o)\right]\right\rangle_o}{\pm\omega'-\omega_o}\right) \\ + \pi\delta(\pm\omega'-\omega_o)\Im\left\langle\left[X^\dagger(+1,\omega_o),\xi^x(+1,\omega_o)\right]\right\rangle_o\Bigg] \tag{21.12}$$

$$\Im\chi_{\pm,\omega_o,\infty}(\omega') = \Bigg[\mathcal{P}\left(\frac{\Im\left\langle\left[X^\dagger(+1,\omega_o),\xi^x(+1,\omega_o)\right]\right\rangle_o}{\pm\omega'-\omega_o}\right) \\ - \pi\delta(\pm\omega'-\omega_o)\Re\left\langle\left[X^\dagger(+1,\omega_o),\xi^x(+1,\omega_o)\right]\right\rangle_o\Bigg] . \tag{21.13}$$

In these last two equations, we have made use of the fact that

$$\langle[X,\xi^x(+1,\omega_o)]\rangle_o = \left\langle\left[X^\dagger(+1,\omega_o),\xi^x(+1,\omega_o)\right]\right\rangle_o . \tag{21.14}$$

(The expression for $X(+1,\omega_o)$ follows from (19.40).) This identity clearly indicates that the linear response functions $\chi_{\pm,\omega_o,\infty}(\omega')$ and $\chi_{\pm,\omega_o,t}(\omega')$ become identically zero if X is not proportional to the $q=\pm1$ component of a spherical tensor of rank $k\geq1$ like $\xi^x(+1,\omega_o)$. For, example, if $X=\xi^z$, which is the zeroth-component of a rank $k=1$ tensor, $\xi^z(+1,\omega_o)=0$, therefore, $\langle[\xi^z,\xi^x(+1,\omega_o)]\rangle_o=0$ as a consequence.

Moreover, one can easily show that $\Re\chi_{\omega_o,\infty}(\omega')$ is the Hilbert transform of $\Im\chi_{\omega_o,\infty}(\omega')$ (which also means the latter is the Hilbert transform of the former multiplied by (-1)), as one would expect from the Kramers-Krönig dispersion relation [56, 59].

It is worth noting that the LRT limit of (21.3) is always real, independent of whether X is real Hermitian or not. This is clear from (21.5). In the limit case whereby X is real Hermitian, $\left\langle\left[X^\dagger(+1,\omega_o),\xi^x(+1,\omega_o)\right]\right\rangle_o$ is also real and we get:

$$\Re\chi_{\pm,\omega_o,\infty}(\omega') = \mathcal{P}\frac{\left\langle\left[X^\dagger(+1,\omega_o),\xi^x(+1,\omega_o)\right]\right\rangle_o}{\pm\omega'-\omega_o} \tag{21.15}$$

and

$$\Im\chi_{\pm,\omega_o,\infty}(\omega') = -\pi\delta(\pm\omega'-\omega_o)\left\langle\left[X^\dagger(+1,\omega_o),\xi^x(+1,\omega_o)\right]\right\rangle_o . \tag{21.16}$$

These expressions coincide with those from LRT [56]. Many of the results known in LRT can also be derived from the above relations but care must be taken when comparing these relations. Most importantly, one must note that the spin operators here, i.e. $\xi^x(+1,\omega_o)$, which get coupled to the relevant part of the external field are not Hermitian.

For example, in the qubit problem discussed in the previous chapter, we saw that $\xi^x(+1,\omega_o)$ is given by (20.4). Then, for the response of μ^x (the magnetic moment operator of the qubit system along the direction x) to the coupling of $\xi^x(+1,\omega_o)$ to $\mathbf{B}_1(t)$, we simply put $X=\mu^x=-\xi^x$ (see (19.3)) . And since in this case $\left\langle\left[X^\dagger(+1,\omega_o),\xi^x(+1,\omega_o)\right]\right\rangle_o = -(\gamma/2)^2\left\langle[\sigma_+,\sigma_-]\right\rangle_o$ is real, (21.15) and (21.16) also hold. Now, if – in order to keep tradition with the notations in use in LRT [56] – we write $\chi_{\omega_o,\infty}(\omega')\equiv(\gamma/2)^2\chi_{\sigma_-\sigma_+}(\omega')$, we see that for positive ω_o, it follows from (21.16) that

$$\Im\chi_{\sigma_-\sigma_+}(\omega') = \pi\delta(\omega'-\omega_o)\left\langle[\sigma_+,\sigma_-]\right\rangle_o = -\pi\delta(\omega'-\omega_o)\tanh(\beta\omega_o/2) . \tag{21.17}$$

It is interesting to observe that if we now take the adiabatic process limit of (20.35), and then make use of (20.37) and (21.17), we end up with

$$\Im\chi_{\sigma_-\sigma_+}(\omega') = -\pi\left(1 - e^{-\beta\omega_o}\right) S^{ad}_{\sigma_-\sigma_+}(\omega') \tag{21.18}$$

which is the celebrated LRT fluctuation-dissipation theorem [56].

Chapter 22

Application III: Theoretical zeroth-order spectrum in the adiabatic process limit.

22.1 Theoretical considerations

At this stage, it should be evident to the Reader that, when it comes to theoretical spectra, the Lindblad superoperator $\mathcal{L}$ in our master equation, (19.68), has the role of primarily allowing for a finite width of the resonance lines. This is quite evident, for example, from the qubit dynamic structure factors we derived in (20.33) and (20.34). On the other hand, by taking the adiabatic process limit, we shrink the finite-width resonance lines to Dirac-delta-like ones. This tells us that if we are only interested in determining the position and intensity of the resonance lines, then we just have to consider the adiabatic process limit of our master equation in (19.68). In the following, our object of concern will be the position and intensity of the resonance lines so we consider the adiabatic process limit of (19.68).

In CW experiments, the signal detected is the induced voltage $\mathscr{E}$ in the receiver coil caused by the time variation of the magnetic flux therein due to the relaxation of the sample's spin polarization vector. It is known that [33, 44]:

$$\mathscr{E} \propto \frac{\mathscr{P}}{B_1} \tag{22.1}$$

where $\mathscr{P}$ is the power absorbed per unit volume of the sample. In the steady-state limit,

$$\mathscr{P} = \lim_{t \to +\infty} \frac{1}{t} \int_0^t dt' \; \frac{dE(t')}{dt'} \tag{22.2}$$

– where $\frac{dE(t)}{dt}$ is the rate at which the spin system absorbs energy from the oscillating field, per unit volume of sample. With $\mathbf{B}_1(t)$ given by (19.7), we have that,

$$\frac{dE(t)}{dt} = \mathbf{B}_1(t) \cdot \frac{d \langle \mathbf{M}(t) \rangle}{dt} = 2 \sum_{\omega_r} B_1 \cos(\omega_r t) \frac{d \left\langle M_x^{(0)}(t) \right\rangle}{dt} + O(\mathscr{X}) \tag{22.3}$$

where $\left\langle M_x^{(0)}(t) \right\rangle$ is the zeroth-order approximation of the expectation value of the operator M_x ($\equiv (N/V)\mu^x = -(N/V)\xi^x$; (N/V) is the number of particles per unit volume), i.e. the magnetization operator along the $x-$ axis. Hence, it follows from (22.2) that:

$$\mathscr{P} = \lim_{t\to+\infty}\frac{1}{t}\int_0^t dt'\ 2\sum_{\omega_r} B_1\cos(\omega_r t')\frac{d\left\langle M_x^{(0)}(t')\right\rangle}{dt'} \tag{22.4}$$

or alternatively,

$$\begin{aligned}\mathscr{P} = 4B_1^2\sum_{\omega_{r'}}\sum_{\omega_r}\sum_{\omega_o}\omega_o\lim_{t\to+\infty}\frac{1}{t}\int_o^t dt'\Big[&-\cos(\omega_{r'}t')\sin(\omega_o t')\chi'_{\omega_o,\infty}(\omega_r)\\ &+\cos(\omega_{r'}t')\cos(\omega_o t')\chi''_{\omega_o,\infty}(\omega_r)\Big]\ .\end{aligned} \tag{22.5}$$

Here, we have used the steady-state limit of $\left\langle M_x^{(0)}(t)\right\rangle$, derived directly from (21.4) and (21.10):

$$\left\langle M_x^{(0)}(t)\right\rangle = 2B_1\int_{-\infty}^{+\infty}d\omega'\rho_f(\omega')\sum_{\omega_o}\left[\cos(\omega_o t)\chi^{'}_{\omega_o,\infty}(\omega')+\sin(\omega_o t)\chi^{''}_{\omega_o,\infty}(\omega')\right] \tag{22.6}$$

– where, as usual, the relations in (21.11) hold, with

$$\chi'_{\pm,\omega_o,\infty}(\omega') = \mathcal{P}\frac{\left\langle\left[M_x^\dagger(+1,\omega_o),\xi^x(+1,\omega_o)\right]\right\rangle_o}{\pm\omega'-\omega_o} \tag{22.7}$$

$$\chi''_{\pm,\omega_o,\infty}(\omega') = \pi\delta(\pm\omega'-\omega_o)\left\langle\left[M_x^\dagger(+1,\omega_o),\xi^x(+1,\omega_o)\right]\right\rangle_o \tag{22.8}$$

and

$$\left\langle\left[M_x^\dagger(+1,\omega_o),\xi^x(+1,\omega_o)\right]\right\rangle_o = \left(\frac{N}{V}\right)\sum_{\mathbb{n},\mathbb{n}'}\left|\langle\mathbb{n}|\,\xi^x(+1,\omega_o)\,|\mathbb{n}'\rangle\right|^2\left(P_{\mathbb{n}}^{(0)}-P_{\mathbb{n}'}^{(0)}\right) \tag{22.9}$$

– where

$$P_{\mathbb{n}}^{(0)} \equiv \left\langle\mathbb{n}\right|\rho^{(0)}(0)\left|\mathbb{n}\right\rangle = \frac{e^{-\beta\epsilon_{\mathbb{n}}}}{\mathrm{Tr}\left[e^{-\beta\mathscr{H}_o}\right]}\ . \tag{22.10}$$

The fact that we are working in the steady-state limit is confirmed by the absence of the transient magnetic susceptibilities $\chi'_{\omega_o,t},\chi''_{\omega_o,t}$ in (22.5). In obtaining (22.5), we have made use of (22.6) and the transformation $\int_{-\infty}^{+\infty}d\omega'\rho_f(\omega')\mapsto\sum_{\omega_r}$. Upon going through with the integration in (22.5), we see that the terms proportional to $\chi'_{\omega_o,\infty}$ either vanish or may be neglected altogether for all practical purposes. Thus,

$$\mathscr{P} = 2B_1^2\sum_{\omega_{r'}}\sum_{\omega_r}\sum_{\omega_o}\omega_o\lim_{t\to+\infty}\Big(\mathrm{sinc}\left[(\omega_o+\omega_{r'})t\right]+\mathrm{sinc}\left[(\omega_o-\omega_{r'})t\right]\Big)\chi''_{\omega_o,\infty}(\omega_r)\ . \tag{22.11}$$

But the fact that $\omega_{r'}$ is always positive, together with the presence of the Dirac delta function in the definition of $\chi''_{\pm,\omega_o,\infty}$, (22.8), also makes the term proportional to $\mathrm{sinc}\left[(\omega_o\pm\omega_{r'})t\right]$ negligible with respect to the $\mathrm{sinc}\left[(\omega_o\mp\omega_{r'})t\right]$ term for positive and negative ω_o, respectively, reducing, therefore, (22.11) to:

$$\begin{aligned}\mathscr{P} &= 2B_1^2\sum_{\omega_r}\sum_{\omega_o}\omega_o\lim_{t\to+\infty}\Big(\mathrm{sinc}\left[(\omega_o-\omega_r)t\right]\chi''_{+,\omega_o,\infty}(\omega_r)+\mathrm{sinc}\left[(\omega_o+\omega_r)t\right]\chi''_{-,\omega_o,\infty}(\omega_r)\Big)\\ &= 2B_1^2\sum_{\omega_o}\omega_o\int d\omega'\rho_f(\omega')\lim_{t\to+\infty}\Big(\mathrm{sinc}\left[(\omega_o-\omega')t\right]\chi''_{+,\omega_o,\infty}(\omega')+\mathrm{sinc}\left[(\omega_o+\omega')t\right]\chi''_{-,\omega_o,\infty}(\omega')\Big)\\ &= \mathscr{P}_+ + \mathscr{P}_-\end{aligned} \tag{22.12}$$

where

$$\mathscr{P}_{\pm} = 2\pi B_1^2 \sum_{\omega_o} \omega_o \; \rho_f(\pm\omega_o) \left\langle \left[M_x^{\dagger}(+1,\omega_o), \xi^x(+1,\omega_o) \right] \right\rangle_o \; . \tag{22.13}$$

Making use of the relation in (22.9), we may rewrite (22.12) as:

$$\mathscr{P} = \left(\frac{N}{V}\right) \sum_{\omega_o} \omega_o \sum_{\mathbb{n},\mathbb{n}'} \left(P_{\mathbb{n}}^{(0)} - P_{\mathbb{n}'}^{(0)} \right) \Gamma_{\mathbb{n},\mathbb{n}'}(\omega_o) \tag{22.14}$$

where

$$\Gamma_{\mathbb{n},\mathbb{n}'}(\omega_o) = \Gamma^{+}_{\mathbb{n},\mathbb{n}'}(\omega_o) + \Gamma^{-}_{\mathbb{n},\mathbb{n}'}(\omega_o) \tag{22.15a}$$

$$\Gamma^{\pm}_{\mathbb{n},\mathbb{n}'}(\omega_o) := 2\pi B_1^2 \rho_f(\pm\omega_o) \left| \langle \mathbb{n} | \, \xi^x(+1,\omega_o) \, | \mathbb{n}' \rangle \right|^2 \; . \tag{22.15b}$$

$\Gamma^{\pm}_{\mathbb{n},\mathbb{n}'}(\omega_o)$ is the transition rate between the states $|\mathbb{n}\rangle$ and $|\mathbb{n}'\rangle$ at the frequency $\pm\omega_o$, respectively – with $\omega_o = \epsilon_{\mathbb{n}'} - \epsilon_{\mathbb{n}}$. The expression for $\Gamma_{\mathbb{n},\mathbb{n}'}(\omega_o)$ in (22.15a) can be easily derived from (19.68) if one expands $\dot{\varrho}^{(0)}_{\mathbb{n},\mathbb{n}}(t) \equiv \left\langle \mathbb{n} \right| d\varrho^{(0)}(t)/dt \left| \mathbb{n} \right\rangle$, and compares the result with the general expression for the Pauli master equation [5, 22].

If the applied oscillating field has a frequency distribution $\rho_f(\omega')$ sharply peaked at ω, and $\omega = \pm\omega_o'$, where ω_o' is one of the allowed transition frequencies of the spin system, we see that only the frequency ω_o' in the summation $\sum_{\omega_o}$, (22.14), survives. In this case, one of $\Gamma^{\pm}_{\mathbb{n},\mathbb{n}'}(\omega_o')$ dominates the other in the sum in (22.15a). For example, $\Gamma^{+}_{\mathbb{n},\mathbb{n}'}(\omega_o') \gg \Gamma^{-}_{\mathbb{n},\mathbb{n}'}(\omega_o')$ if ω_o' is positive.

If we apply the high temperature approximation [53], i.e. $\rho^{(0)}(0) \approx D_S^{-1}\left(\mathbb{I} - \beta\mathscr{Z}_o\right)$, with $\beta = \frac{1}{k_B T}$ (D_S is the dimension of the multispin Hilbert space) in (22.14), and introduce the obtained zeroth-order approximation for $\mathscr{P}$ (i.e. (22.14)) into (22.1), we get:

$$\mathscr{E} \propto \sum_{\omega_o} \Omega(\omega_o) \cdot \frac{1}{D_S} \sum_{\mathbb{n},\mathbb{n}'} \left| \langle \mathbb{n} | \, \xi^x(+1,\omega_o) \, | \mathbb{n}' \rangle \right|^2 \tag{22.16}$$

$$\Omega(\omega_o) := \left(\frac{N}{V}\right) 2\pi B_1 \omega_o^2 \beta \left[\rho_f(\omega_o) + \rho_f(-\omega_o) \right] \; . \tag{22.17}$$

For fixed $\Omega(\omega_o)$, we note from (22.16) that the intensity of the resonance signal at $\omega = \pm\omega_o$, $\texttt{Int}(\omega_o)$, is:

$$\texttt{Int}(\omega_o) \propto \frac{1}{D_S} \sum_{\mathbb{n},\mathbb{n}'} \left| \langle \mathbb{n} | \, \xi^x(+1,\omega_o) \, | \mathbb{n}' \rangle \right|^2 \; . \tag{22.18}$$

This means at zeroth-order, all pair of states $\{|\mathbb{n}\rangle, |\mathbb{n}'\rangle\}$ such that $\epsilon_{\mathbb{n}'} - \epsilon_{\mathbb{n}} = \omega_o$ and $M_{\mathbb{n}'} - M_{\mathbb{n}} = +1$, contribute to $\texttt{Int}(\omega_o)$. The operator ξ^x being the sum of single spin operators, (19.3), we also note that another implication of the observation just made is the following: for a specific choice of $|\mathbb{n}\rangle, |\mathbb{n}'\rangle$, the nonzero value of $\langle \mathbb{n} | \, \xi^x(+1,\omega_o) \, | \mathbb{n}' \rangle$ can only be interpreted as a transition involving a single spin of the multiset $\mathscr{A} = \{j_1, j_2, \ldots, j_N\}$ – at a given time. Let's call this spin the "resonance spin". We therefore find from (19.33) and (19.17) that:

$$\epsilon_{\mathbb{n}'} - \epsilon_{\mathbb{n}} = -\gamma_i B_o + \sum_{k \neq i} T_{ik} m_{z,k} \tag{22.19}$$

where the resonance spin is assumed to be the $i-$th element of the multiset $\mathscr{A} = \{j_1, j_2, \ldots, j_N\}$, and $m_{z,k} = \langle \mathbb{n} | \, S_k^z \, | \mathbb{n} \rangle = \langle \mathbb{n}' | \, S_k^z \, | \mathbb{n}' \rangle$ is the magnetic quantum number of the $k-$th spin according to the multispin states $|\mathbb{n}\rangle$ and $|\mathbb{n}'\rangle$.

To proceed with our discussion, it is much helpful to reconsider the multiset of spins $\mathcal{A} = \{j_1, j_2, \ldots, j_N\}$ in terms of equivalent spins. By "equivalent" spins we mean a submultiset $\mathcal{A}'$ of $\mathcal{A}$ whose elements cannot be distinguished from each other on the basis of their coupling tensors with other spins and external fields [62] (see Part II). Say the resonance spin i belongs to the group of equivalent spins labeled α. In terms of equivalent spins, we may rewrite (22.19) as:

$$\epsilon_{\mathbb{m}'} - \epsilon_{\mathbb{m}} = -\gamma_\alpha B_o + \sum_{\alpha' \neq \alpha} T_{\alpha\alpha'} M_{z,\alpha'} \ . \tag{22.20}$$

$M_{z,\alpha'}$ is the total spin magnetic quantum number of the $\alpha'-$th group of equivalent spins according to the multispin states $|\mathbb{m}\rangle$ and $|\mathbb{m}'\rangle$. In the HP representation, we may express $M_{z,\alpha'}$ as [62, 66]:

$$M_{z,\alpha'} = J_{\alpha'} - n_{\alpha'} \tag{22.21}$$

where $J_{\alpha'} = j_{\alpha'} N_{\alpha'}$ is the total spin of the $\alpha'-$th group of equivalent spins ($N_{\alpha'}$ is the cardinality of the group and $j_{\alpha'}$ is the spin quantum number of each member of the group, assumed to be identical for all). The integer $n_{\alpha'}$ is the total number of HP bosons distributed among the $N_{\alpha'}$ spins of the $\alpha'-$th group [66].

Suppose in our CW experiment, the frequency ω and the amplitude B_1 of the rotating field are fixed, with $\omega = \omega_o$, while the steady magnetic field B_o is slowly tuned to resonance. If the frequency gap $\epsilon_{\mathbb{m}'} - \epsilon_{\mathbb{m}}$ in (22.20) coincides with ω_o, then we derive from the latter that the resonance condition in terms of the amplitude of the steady field is (see also [163]):

$$B_o = B_\alpha(\omega_o) + \sum_{\alpha' \neq \alpha} \lambda_{\alpha\alpha'} n_{\alpha'} \tag{22.22}$$

where,

$$B_\alpha(\omega_o) := -\frac{\omega_o}{\gamma_\alpha} - \sum_{\alpha' \neq \alpha} \lambda_{\alpha\alpha'} J_{\alpha'} \tag{22.23a}$$

$$\lambda_{\alpha\alpha'} := -\frac{T_{\alpha\alpha'}}{\gamma_\alpha} \ . \tag{22.23b}$$

The absolute values $|\lambda_{\alpha,\alpha'}|$ are the so-called *splitting constants* in magnetic resonance. $B_\alpha(\omega_o)$ is the position of the resonance line originating from the transition event (involving obviously the resonance spin) whereby all the spins of the other groups are with their maximum spin projection along the quantization axis (i.e. $n_{\alpha'} = 0 \ \forall \alpha'$). As we can see from (22.23a), for a fixed frequency ω_o, $B_\alpha(\omega_o)$ is constant. Below, we shall use $B_\alpha(\omega_o)$ as the reference for the other resonance lines, i.e. we shall be considering $\Delta B \equiv [B_o - B_\alpha(\omega_o)]$.

We readily infer from (22.22) that, in this weak coupling limit under consideration, the resonance position B_o depends on the total HP bosons' occupation numbers $\{n_{\alpha'}\}$. The intensity of the detected magnetic resonance signal – in reference to the resonance spin group α – is proportional to the degeneracy $C_{\alpha,\{n_{\alpha'}\}}$ of the collection $\{n_{\alpha'}\}$. Indeed, if $c_{n_{\alpha'}}$ is the degeneracy of HP boson's total occupation number $n_{\alpha'}$ for the $\alpha'-$th group of equivalent spins (i.e. $c_{n_{\alpha'}}$ is the number of different distinct ways of distributing a total of $n_{\alpha'}$ HP bosons between the $N_{\alpha'}$ spins of the $\alpha'-$th group; or, in other words, $c_{n_{\alpha'}}$ is the number of distinct ways of configuring the spins of the $\alpha'-$th group so as to obtain a total spin magnetic quantum number of $M_{z,\alpha'} = (J_{\alpha'} - n_{\alpha'})$), then it readily follows that:

$$C_{\alpha,\{n_{\alpha'}\}} = \prod_{\alpha'} c_{n_{\alpha'}} \tag{22.24}$$

since distinct groups of equivalent spins are independent of each other. It is easy to prove that the generating function for the integers $C_{\alpha,\{n_{\alpha'}\}}$ is the polynomial $P_\alpha(\boldsymbol{x})$ [62, 66]:

$$\begin{aligned} P_\alpha(\boldsymbol{x}) &:= \prod_{\alpha'\neq\alpha}\left(1+x_{\alpha'}+\ldots+x_{\alpha'}^{2j_{\alpha'}}\right)^{N_{\alpha'}} \\ &= \sum_{\{n_{\alpha'}\}} C_{\alpha,\{n_{\alpha'}\}}\prod_{\alpha'} x_{\alpha'}^{n_{\alpha'}} \ . \end{aligned} \tag{22.25}$$

Having determined $C_{\alpha,\{n_{\alpha'}\}}$, we may now go back to (22.16). It is now clear that for fixed $\omega=\pm\omega_o$, if the transition frequency for the $\alpha-$th group of equivalent spins happen to coincide with ω_o, then the induced voltage in the receiver coil is:

$$\mathscr{E}\propto\Omega(\omega_o)\frac{\gamma_\alpha^2 N_\alpha}{D_{\alpha,S}}\binom{2j_\alpha+2}{3}C_{\alpha,\{n_{\alpha'}\}} \ . \tag{22.26}$$

Consequently,

$$\mathtt{Int}(B_o)\propto\frac{\gamma_\alpha^2 N_\alpha}{D_{\alpha,S}}\binom{2j_\alpha+2}{3}C_{\alpha,\{n_{\alpha'}\}} \tag{22.27}$$

where $D_{\alpha,S}$ is the dimension of the spin Hilbert subspace comprising the resonance group α and all the other equivalent groups with which it effectively interacts with (i.e. those with $T_{\alpha\alpha'}\neq 0$). In this case, the index α' in (22.25) (and in (22.20)-(22.24)) may then be re-interpreted as running over only those groups with $T_{\alpha\alpha'}\neq 0$. From the last two equations above, we note the dependence of the signal intensity on the quantum spin number j_α of the resonance group through the $2j_\alpha-$th tetrahedral number, i.e. $\binom{2j_\alpha+2}{3}$. With all other parameters and conditions held constant, these equations inform us that the higher the spin quantum number of the resonance group, the higher the intensity of the signal. We also note that for a fixed resonance group α, the integers $\{C_{\alpha,\{n_{\alpha'}\}}\}$ are effectively the relative intensities of the resonance signals.

In our derivation of (22.26), we have assumed the resonance spin group α is present in all the initial N chemical species of the ensemble. This is not always the case. (22.26) and (22.27) may therefore be multiplied by the fraction f_α of the initial N which contains the resonance group α. In NMR, for example, if the resonance group in the sample has not undergone any alteration of its isotopic concentration f_α becomes the natural abundance of the group.

Moreover, if there are more than one resonance spin groups who satisfy the resonance conditions, it is clear that (22.26) and (22.27) must be summed over such groups since the operator $\xi^x(n,\omega_o)$ is the sum of single spin operators, (19.3) and (19.39).

(22.22) and (22.27), together determine the resonance spectrum of the spin system at zeroth-order in $\mathscr{X}$ according to ACP, in the adiabatic process limit. While the former gives the resonance steady field B_o for a given configuration of the spins in terms of $\{n_{\alpha'}\}$, the latter equation gives the intensity of the resonance signal. And the properties of the spectrum – which one can easily conclude from these two equations – are in agreement with those reported by Gutowsky, McCall and Slichter [60, 61]. But more importantly, we must remark that the polynomial $P_\alpha(\boldsymbol{x})$, (22.25), is the *generating function* for the resonance spectrum. Once we construct $P_\alpha(\boldsymbol{x})$ and are in possession of the value of parameters like the constants $\lambda_{\alpha,\alpha'}$, γ_α and ω_o, we can easily generate the stick-plot spectrum. Each term of $P_\alpha(\boldsymbol{x})$ represents a resonance line: for a given term, the coefficient indicates the relative intensity of the corresponding resonance line, while the exponents of the variables determine – by means of (22.22)

– the position of the resonance line. The advancement in computer algebra makes the computational implementation of this protocol easy to achieve. We illustrate these points by considering specific examples from ESR, namely the absorption spectrum of naphthalene, anthracene and biphenyl anions. The parameters are taken from [163] and the plots were generated from a simple Python code which implemented (22.22) and (22.25) (and an extensive use of the SymPy [109] library was made).

22.2 Naphthalene anion

The naphthalene anion, Fig. 22.1, has two groups of equivalent nuclei: the first group comprises the hydrogen nuclei in the positions $1, 4, 5, 8$, and those in the positions $2, 3, 6, 7$ form the second group. The splitting constants for the two groups are $\lambda_{e,1} = 4.90$ G and $\lambda_{e,2} = 1.83$ G (counterion is K^+)[163]. From (22.25), we conclude that the generating function for this anion's ESR spectra at zeroth-order

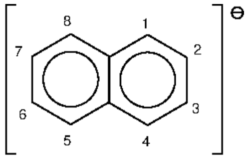

Figure 22.1: Naphthalene anion

is:

$$\begin{aligned} P_e(\boldsymbol{x}) &= (1+x_1)^4(1+x_2)^4 \\ &= x_2^4x_1^4 + 4x_2^3x_1^4 + 6x_2^2x_1^4 + 4x_2x_1^4 + x_1^4 + 4x_2^4x_1^3 + 16x_2^3x_1^3 + 24x_2^2x_1^3 + 16x_2x_1^3 \\ &\quad + 4x_1^3 + 6x_2^4x_1^2 + 24x_2^3x_1^2 + 36x_2^2x_1^2 + 24x_2x_1^2 + 6x_1^2 + 4x_2^4x_1 + 16x_2^3x_1 \\ &\quad + 24x_2^2x_1 + 16x_2x_1 + 4x_1 + x_2^4 + 4x_2^3 + 6x_2^2 + 4x_2 + 1 \ . \end{aligned} \tag{22.28}$$

Let the exponents of x_1 and x_2 count the total number of HP bosons held by the first and second group of equivalent nuclei, respectively. As remarked above, every term in the polynomial $P_e(\boldsymbol{x})$ represents a resonance line: The coefficient of a given term indicates the relative intensity of the corresponding resonance line and the exponents of the variables of the term determine the position of the resonance line by means of (22.22). If we take the term $(24x_2^2x_1^3)$, for example, the relative intensity of the resonance line it represents is 24, the number of HP bosons specifying the configuration of group 1 (x_1), and group 2 (x_2) are 3 and 2, respectively. So, from (22.22), we determine that the corresponding resonance line falls at $\Delta B = 3\lambda_{e,1} + 2\lambda_{e,2} = 18.36$ G from the reference position $B_\alpha(\omega_o)$ (which may be set equal to zero for convenience). We show the stick-plot ESR spectrum of the naphthalene anion computed this way in Fig. 22.2. The experimental [163] positions and relative intensities of the spectral lines are in very good agreement with the simple theoretical spectrum in Fig. 22.2.

22.3 Biphenyl anion

The biphenyl anion, Fig. 22.3, has three groups of equivalent protons: two of which are of cardinality 4, and the last of cardinality 2. Let $\lambda_{e,1}, \lambda_{e,2}$ be the splitting constants of the first and second groups of equivalent protons (of size 4), and $\lambda_{e,3}$ the splitting constant of the set of equivalent protons of size

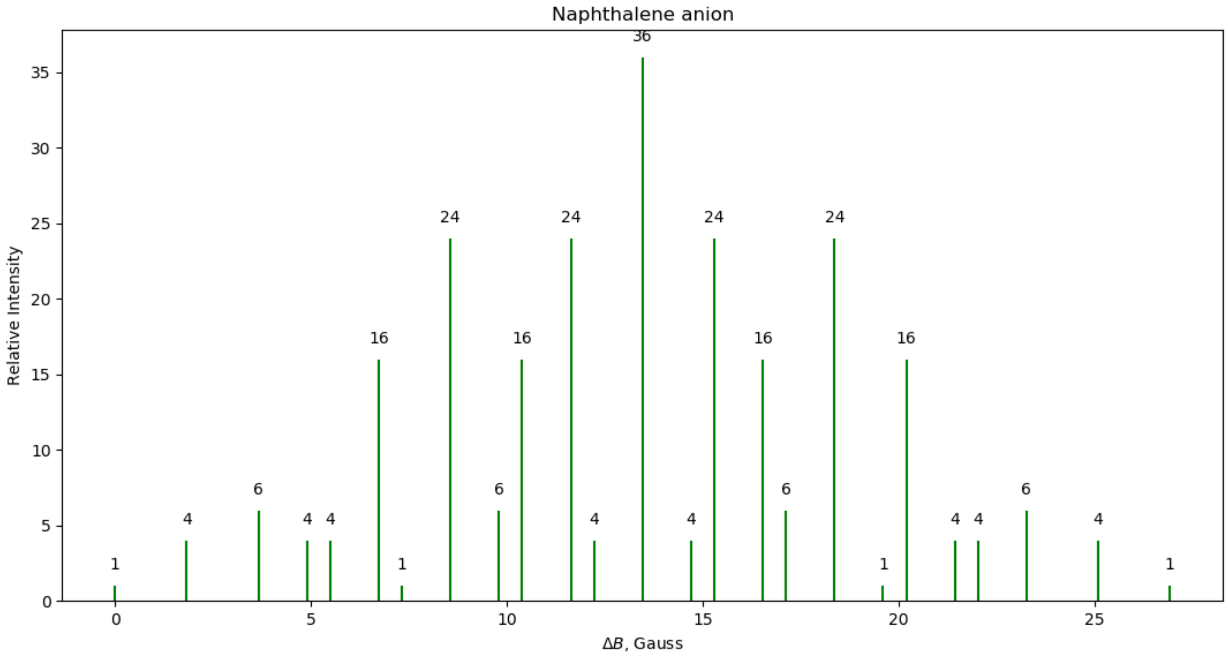

Figure 22.2: Theoretical ESR stick-plot spectrum of naphthalene anion (counterion: K^+). Parameters used were taken from [163]. Each spectral line is labeled by its relative intensity.

2. From the literature [163], we have: $\lambda_{e,1} = 2.675$ G, $\lambda_{e,2} = 0.394$ G and $\lambda_{e,3} = 5.387$ G. Once again,

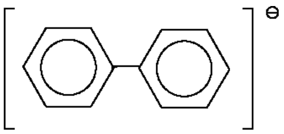

Figure 22.3: Biphenyl anion

we see from (22.25) that the generating function for biphenyl anion's ESR spectrum is:

$$
\begin{aligned}
P_e(\boldsymbol{x}) &= (1+x_1)^4(1+x_2)^4(1+x_3)^2 \\
&= x_2^4x_1^4 + 4x_2^3x_1^4 + 6x_2^2x_1^4 + x_2^4x_3^2x_1^4 + 4x_2^3x_3^2x_1^4 + 6x_2^2x_3^2x_1^4 + 4x_2x_3^2x_1^4 + x_3^2x_1^4 + 4x_2x_1^4 + 2x_2^4x_3x_1^4 \\
&+8x_2^3x_3x_1^4+12x_2^2x_3x_1^4+8x_2x_3x_1^4+2x_3x_1^4+x_1^4+4x_2^4x_1^3+16x_2^3x_1^3+24x_2^2x_1^3+4x_2^4x_3^2x_1^3+16x_2^3x_3^2x_1^3+24x_2^2x_3^2x_1^3 \\
&+16x_2x_3^2x_1^3+4x_3^2x_1^3+16x_2x_1^3+8x_2^4x_3x_1^3+32x_2^3x_3x_1^3+48x_2^2x_3x_1^3+32x_2x_3x_1^3+8x_3x_1^3+4x_1^3+[\ldots]+1
\end{aligned}
\tag{22.29}
$$

For each term, the exponent of x_i corresponds to the number of HP bosons held by the $i-$th group of equivalent protons. The ESR spectrum can be generated from this polynomial as explained above. For example, if we take the term $(4x_2^3x_1^4)$, the relative intensity of the corresponding spectral line is 4, and it falls at a distance of $\Delta B = 4\lambda_{e,1} + 3\lambda_{e,2} = 11.882$ G from $B_\alpha(\omega_o)$, the reference position. The generating function in (22.29) has 75 terms, which is also the number of spectral lines to expect

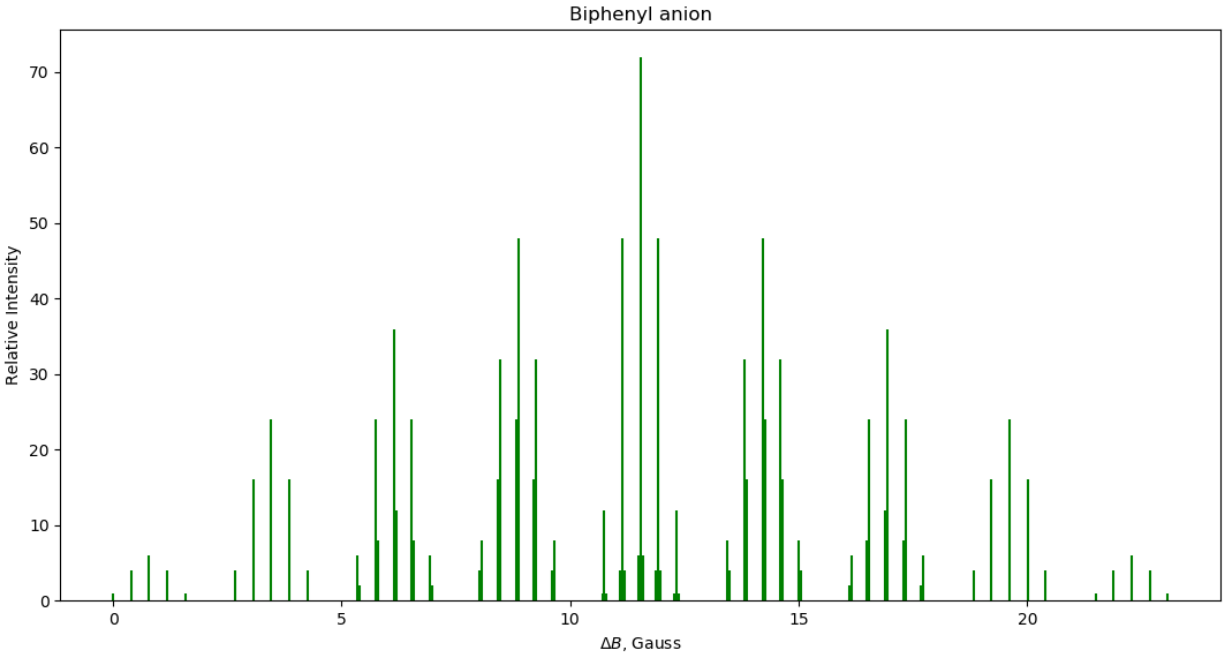

Figure 22.4: High-field theoretical ESR stick-plot absorption spectrum of biphenyl anion (counterion: K^+). Parameters were taken from [163].

experimentally. We show in Fig. 22.4 the stick-plot ESR spectrum for the biphenyl anion generated from $P_e(\boldsymbol{x})$, (22.29).

22.4 Anthracene anion

Like the biphenyl anion, the anthracene anion – Fig. 22.5 – has three groups of equivalent protons and of the same dimension as those of the biphenyl anion. Let $\lambda_{e,1}$ and $\lambda_{e,2}$ be the splitting constants

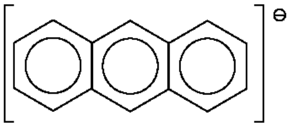

Figure 22.5: Anthracene anion

of the first and second groups of equivalent spins of dimension 4, and $\lambda_{e,3}$ the splitting constant of the group of dimension 2. Their values are taken from the literature [163] to be: $\lambda_{e,1} = 2.73$ G, $\lambda_{e,2} = 1.51$ G and $\lambda_{e,3} = 5.34$ G. Given that the biphenyl and anthracene anions present the same groups of equivalent spins (cardinality-wise), their high-field spectra also share the same generating function. As a matter of fact, using the generating function in (22.29), we can determine the stick-plot spectrum of the anthracene anion. The result is reported in Fig. 22.6. Both spectra in Figs. 22.2 and 22.6 have the same number of resonance lines, and the distribution of the relative intensities of

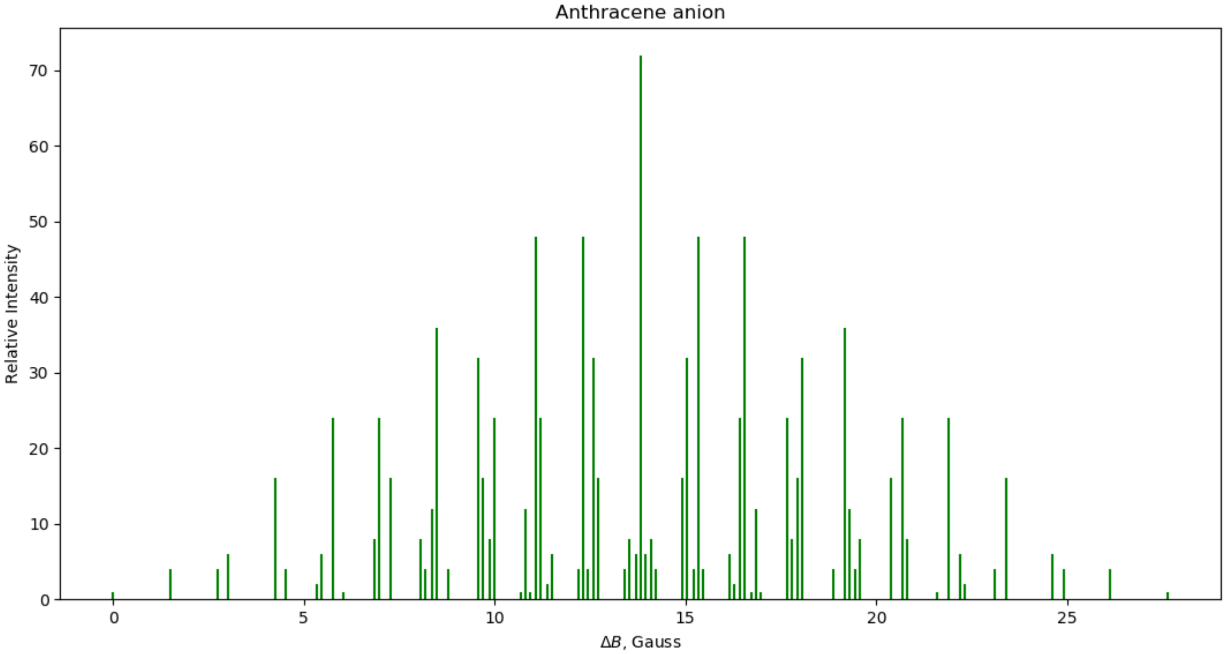

Figure 22.6: High-field theoretical ESR stick-plot absorption spectrum of anthracene anion (counterion: K^+). Parameters were taken from [163].

these lines is the same in both spectra. The only difference between the two are the *positions* of the resonance lines.

Part V

Conclusion

Chapter 23

Conclusion and perspectives

23.1 On the distinction between UDMs and non-UDMs

In this work, we have tried to refine certain concepts in relation to the theory of open quantum systems taking inspiration from results in [138, 155]. We have seen that quantum dynamical maps may be classified into two categories: *universal dynamical maps* (UDMs) [132] and *non-universal dynamical maps* (non-UDMs) based on the nature of their domain. For a finite-dimensional state space $\mathcal{H}_d$, UDMs have as domain the entire set $\mathcal{O}_d^{+,1}$ (*i.e.* the convex cone in the set of trace-class unit-trace positive semi-definite self-adjoint linear operators acting on $\mathcal{H}_d$). On the other hand, the domain of a non-UDM is restricted to a proper subset of $\mathcal{O}_d^{+,1}$. We have shown that it is an entrenched and inextricable property of both UDMs and non-UDMs to be completely positive and trace-preserving (CPT) with respect to their respective domains. This marks a stark contrast to the notion of CPT maps in the literature – where a quantum map is understood to be CPT if its domain coincides with $\mathcal{O}_d^{+,1}$. We thus see that what we have termed here UDMs (non-UDMs) is what is normally called CPT (positive but non-CP) maps in the literature [26, 72, 106, 145, 168].

It is important we view the domains of quantum maps as significant as the maps themselves[1]. In this sense, the distinction between UDMs and non-UDMs becomes crucial. This distinction, we believe, could also help settle the debate [4, 119, 146] on how fundamental CPT maps are. We believe the debate is, in ultimate analysis, a problem of definition. This is because, viewed along the lines of UDMs and non-UDMs, it is clear – as explained in Sec. 12.2 and the beginning of Chap. 13 – that the CPT property and the very concept of quantum dynamical maps are two indivisible notions, for a map cannot be a quantum dynamical map, in the first place, without being CPT. By referring to UDMs as CPT maps in the literature, the community came under the impression that a map is CPT if and only if it is UDM. So when Pechukas [119] or Shaji and Sudarshan [146] assert that, for example, a reduced dynamics need not be CP, what they actually meant is that the map needs not be UDM. In fact, these authors stress on the map having its (positivity) domain – which again reminds us of non-UDMs.

The arguments put forward in [138, 155] and in this thesis exhort us to be more circumspect

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[1] Just as it is good practice – if not imperative – to specify the domain of an analytic function in complex analysis, so should we make it a habit of specificying the domain of a quantum map, especially when it is a non-UDM.

about the notion of CPT maps. With the distinction between UDMs and non-UDMs now clear, some interesting problems also come to mind. For example, we saw in Chap. 13 the conditions under which a quantum dynamical semigroup may emerge from an induced UDM (*i.e.* a UDM resulting from reduced dynamics) [132]. Analogously, we may ask:

1. what are the general conditions which lead to an induced non-UDM (from a unitary $S + R$ dynamics)?;
2. Is it possible for induced non-UDMs to form a one-parameter quantum dynamical semigroup?;
3. If the answer to the last question is affirmative, what is the general form of the generator for such a quantum dynamical semigroup?

23.2 On semiclassical quantum Markovian master equations

We have shown that it is possible to extend the GKSL approach to open quantum system theory to those problems where one wants to treat the environment at a classical level. A quantum theory for CW magnetic resonance was developed in this work as proof of concept. And in the development of the theory, we introduced the affine commutation perturbation (ACP) scheme, which makes it possible to account for some effects of the perturbation even at the zeroth-order approximation. Indeed, we were able to derive the CW magnetic spectra of multispin systems at the zeroth-order of the ACP scheme and computed the ESR spectra for a number of radicals – which are in good agreement with the experimental spectra. It must, however, be emphasized that the generating function method for computing theoretical spectra expounded in Sec. 22 predicates on the weak-coupling assumption, and on the condition that $\|\mathscr{H}_o\| \gg \|\mathscr{H}\|$ (in the sense of (15.2)). We also mention that quadrupolar effects may also be accounted for by adding the corresponding isotropic term to H_o in (19.2).

We have focused here on quantum Markovian master equations, but the approach can easily be extended to non-Markovian ones as well. More importantly, in discussing the dynamics at the zeroth-order, we have argued and illustrated the importance of the term linear in the system-environment interaction, $\mathcal{A}(t)\varrho^{(0)}(0)$, (19.68). We have shown that this term – which is usually discarded (even when not identically zero) on the basis of the environment stability condition (Sec. 15.3) in standard microscopic derivations of quantum Markovian master equations – actually leads to a linear response theory (LRT) within the GKSL formalism (Sec. 21). With it, we were able to derive some known results in standard LRT [56] as limit cases. Despite its vital importance, we also observed that the presence of this linear term prohibits the zeroth-order quantum map $\Lambda(t)$, (19.79), from: i) becoming a UDM and ii) forming a (one-parameter) quantum dynamical semigroup. Nonetheless, we have also shown that there are strong indications suggesting that the map $\Lambda(t)$ is a positive on its assigned domain, namely $\varrho^{(0)}(0) = \frac{e^{-\beta\mathscr{H}_o}}{\mathrm{Tr}[e^{-\beta\mathscr{H}_o}]}$, (19.27). This simply means $\Lambda(t)$ is a non-UDM with domain $\{\varrho^{(0)}(0)\}$, according to the theory. In the broader context, the domain of $\Lambda(t)$ is the set $\mathsf{C}_d^{+,1}[\varrho^0(0)]$ (*i.e.* the set of all convex combinations of elements of $\mathcal{O}_d^{+,1}$ which commute with $\varrho^{(0)}(0)$) – for a multispin system whose (spin) state space is of dimension d. Despite being a non-UDM, we know from Sec. 12.2 that $\Lambda(t)$ is CPT and has a Kraus operator sum representation on its domain. We illustrated this point by considering a CW experiment with an ensemble of spin-1/2 particles in Sec.

20.5. There, we observed that in spite of the presence of the term $\mathcal{A}(t)\varrho(0)$ in the master equation (20.1) which impeded the generator from becoming that of a quantum dynamical semigroup, we were still able to find a Kraus operator sum representation for $\Lambda(t)$, *i.e.* (20.38). We also showed that the Kraus operators also satisfied the usual completeness relation, (20.49) – guaranteeing that the map $\Lambda(t)$ preserves trace on its domain.

We have considered only the quantum map associated with the zeroth-order ACP quantum master equation, (19.68). Concerning the maps associated with the higher-order terms[2] of the ACP scheme (Sec. 19.4), similar detailed studies need to be carried out but we have reason to believe that by restricting these maps to their respective specified domains (*i.e.* $\{\varrho^{(n)}(0)\}$, (19.26)), the resulting $n-$th-order approximated map which evolves $\varrho(0)$ approximated to the $n-$th order in $\mathscr{X}$ (*i.e.* $\sum_{m=0}^{n}\varrho^{(m)}(0)$), will also be a non-UDM. The ideas and guiding principles necessary to study these higher-order corrections are quite clear but the mathematical manipulations involved could be lengthy and quite demanding.

Imagine applying the techniques developed in Chap. 19 to a certain problem (where one treats the focused system quantum mechanically but the environment is treated classically). Naturally, if for some reasons the term linear in the system-environment interaction, $\mathcal{A}(t)\varrho^{(0)}(0)$, (19.68), is identically zero, then (19.68) reduces to a truly semiclassical quantum Markovian master equation, and the map $\Lambda(t)$ becomes a UDM.

In this semiclassical approach to open quantum system theory, it may be necessary (or more appropriate) to explicitly treat certain classical environment degrees of freedom as stochastic variables. For example, if we want to account for the influence of non-spin degrees of freedom like molecular rotations and vibrations on the dynamics of the multispin degrees of freedom, we will have to treat the former as part of the environment (with respect to the spin degrees). These non-spin degrees of freedom may also be adequately described as stochastic variables whose probability distributions evolve according to some master equation – which could be, for example, a Fokker-Planck or Smoluchowski equation [54, 118, 157]. In these cases, the semiclassical quantum master equation (Markovian or non-Markovian), will depend explicitly on the stochastic variables, and to obtain the effective (or 'reduced') semiclassical dynamics, one will have to integrate the master equation over the said probability distribution functions for the stochastic variables[3]. This approach may be seen as an alternative to the so-called 'stochastic Liouville equation' [14, 53, 88, 151].

23.3 On the Holstein-Primakoff transformation

We have also shown how with the Holstein-Primakoff (HP) transformation, we may easily translate certain problems in multispin magnetic resonance into counting problems. This connection may be an indication of a profound and no less consequential relationship between magnetic resonance and discrete mathematics; a relationship, which, if ultimately fully understood, might help free – to a significant degree – multispin magnetic resonance from the spell of the curse that is of dimensionality [90, 91]. On this note, it is only reasonable that we envisage a future where the full power and glory

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[2] Surely, as explained in Sec. 19.4, one will have to apply to the corresponding higher-order correction master equations the same approximations and assumptions invoked for the zeroth-order term.

[3] The author has extensively explored this approach together with Prof. V. Giovannetti and Prof. D. Rossini, and hope to publish their findings soon.

of discrete mathematics are unequivocally brought to bear in the study of magnetic resonance. Here, computer algebra – now almost ubiquitous in modern computing languages and which is finding its way also into magnetic resonance [7, 49] – is going to play a central role in the simulation of multispin magnetic resonance spectra. And the recurrent use of generating functions like $G_{\mathcal{A},\Omega}(q)$ (8.19), $G_{\mathcal{A},\lambda}(q)$ (8.43) and $P_\alpha(\boldsymbol{x})$ (22.25) in this work strongly suggests the pivotal role polynomial algebra is also going to play in magnetic resonance simulations.

Furthermore, the usefulness of the HP transformation is not only limited to counting problems. For example, it can be used to calculate Clebsch-Gordan coefficients (thus, Wigner-$3nj$ symbols) – $(n = 1, 2, 3, \ldots)$. Schwinger [143] has used his eponymous transformation to derive analytic expressions for Clebsch-Gordan coefficients arising from the addition of up to four angular momenta. Early research conducted by the author suggests that the HP transformation probably offers an elegant way to go beyond that. This is an important and interesting problem which we believe should command the attention of many in the community as the calculation of Wigner-$12j$, -$15j$ symbols and beyond [20, 85, 167] is becoming an important problem in several areas of physics, including quantum computing [24, 25].

We would also like to mention the connection between the HP transformation and Quantum Calculus [81]. This connection was moderately discussed in one of the author's publications [66]. We believe more research elucidating this connection is needed and worth the effort. In studying the HP transformation and its relation to discrete mathematics and Quantum Calculus, one cannot help but see the many territories which await explorations.

Appendices

Appendix A

Wigner-$3j$ symbols

The Wigner-$3j$ symbol offers a compact way to express and distill the properties of the Clebsch-Gordan coefficients arising from the coupling of two angular momenta j_1 and j_2. The Wigner-$3j$ symbol is defined as [164, 170]

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \equiv \frac{(-1)^{j_1-j_2-m_3}}{\sqrt{2j_3+1}} \langle j_1 m_1, j_2 m_2 | \, j_3 \; -m_3 \rangle \tag{A.1}$$

where $-j_i \leq m_i \leq j_i$ with $i \in \{1,2,3\}$. The general formular for the Clebsch-Gordan coefficient $\langle j_1 m_1, j_2 m_2 | \, j_3 m_3 \rangle$ is given by Racah's formula [124, 125, 170]

$$\begin{aligned} \langle j_1 m_1, j_2 m_2 | \, j_3 m_3 \rangle = \delta_{m_1+m_2,m_3} \Bigg[(2j_3+1) \frac{(s-2j_3)!(s-2j_2)!(s-2j_1)!}{(s+1)!} \\ \times (j_1+m_1)!(j_1-m_1)!(j_2+m_2)!(j_2-m_2)!(j_3+m_3)!(j_3-m_3)! \Bigg]^{1/2} \\ \times \sum_\nu (-1)^\nu \Big[\nu!(j_1+j_2-j_3-\nu)!(j_1-m_1-\nu)!(j_2+m_2-\nu)! \\ \times (j_3-j_2+m_1+\nu)!(j_3-j_1-m_2+\nu)! \Big]^{-1} \end{aligned} \tag{A.2}$$

where the index ν ranges over all integral values which do not make any of the arguments of the factorials in the denominator negative, and $s = j_1 + j_2 + j_3$.

The Wigner-$3j$ symbols have the following symmetric properties [164, 170]:

1. Odd permutation of columns:

$$(-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} = \begin{pmatrix} j_1 & j_3 & j_2 \\ m_1 & m_3 & m_2 \end{pmatrix} = \begin{pmatrix} j_3 & j_2 & j_1 \\ m_3 & m_2 & m_1 \end{pmatrix} \tag{A.3}$$

2. Even permutation of columns:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix} \tag{A.4}$$

3. Negating the $\{m_i\}$:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \,. \tag{A.5}$$

The orthogonality properties of Wigner-3j symbols are [164, 170]:

1. Summation over m_1, m_2:

$$\sum_{m_1,m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix} = \frac{1}{\sqrt{2j_3+1}} \delta_{j_3,j_3'} \delta_{m_3,m_3'} \tag{A.6}$$

2. Summation over j_3, m_3 with weight $(2j_3+1)$:

$$\sum_{j_3,m_3} (2j_3+1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3 \end{pmatrix} = \delta_{m_1,m_1'} \delta_{m_2,m_2'} \,. \tag{A.7}$$

Appendix B

Microcanonical and Canonical Ensembles in Magnetic Resonance

We cannot apply the concepts of statistical mechanics to one isolated molecule or spin of interest. Statistical mechanics requires the thermodynamic limit, *i.e.* $N \to \infty, V \to \infty$, but $N/V =$ finite quantity. We therefore need to consider a huge collection of identical molecules. In line with the assumption made in Sec. 19.1 concerning the ensemble, we shall assume that the interaction between the molecules is very weak, so as to approximate the system as consisting of essentially free molecules. In practical terms, this may be realized when the concentration of the molecules to be probed is very low[1]. Thus, we have an *ensemble* of 'free' solvated molecules. These free solvated molecules are essentially quasi particles. The effect of the solvent cloud is made manifest in change of the bare molecules properties like "effective mass", "effective charge" etc. We shall assume that the spin properties of the bare molecule are the same as those of the quasi particle. Our aim here is to describe this collection of quasi particles on sound statistical and mathematical principles. The derivation given here follows closely a similar derivation given in [105] for the Ising model.

Say $\nu^{(n)}$, a specific set of parameters specifying the state of the $n-$th quasi particle. We shall indicate the energy corresponding to $\nu^{(n)}$ as $\mathscr{E}^{(n)}(\nu^{(n)})$. By *configuration*, we mean a possible state of the ensemble. Each configuration C_a will be represented by a set of states $\{\nu_a^{(1)}, \nu_a^{(2)}, \ldots, \nu_a^{(N)}\}$, where $\nu_a^{(n)}$ indicates the state of the $n-$th quasi particle according to the configuration C_a.

Say $\mathscr{C}(N)$ the set of all possible configurations of the N quasi particles. We may now partition $\mathscr{C}(N)$ into subsets characterized by the same total energy $\mathscr{E}_{tot}$. Thus, $\mathscr{C}(N, \mathscr{E}_{tot})$ indicates a collection of configurations each with a total energy of $\mathscr{E}_{tot}$.

If we fix the total energy of the N quasi particles as E_{tot}, we may assume that all possible configurations of states $\{C_a, C_b, \ldots\}$ whose total energy $\mathscr{E}_{tot}$ amounts to E_{tot} are equally probable. That is all the elements of the subset $\mathscr{C}(N, \mathscr{E}_{tot} = E_{tot})$ are equally probable. This is the *microcanonical ensemble* ($N, \mathscr{E}_{tot}, V$ fixed). Since we have fixed the total energy, the ensemble can only assume the

---

[1] Looking back on the CW experiment, we can say that prior to the 'application' (i.e. the system adjusting to the presence) of $\mathbf{B}_1(t)$, we are dealing with an isolated collection of solvated molecules in which the only relevant external interactions these have are those with the solvent molecules and the external field $\mathbf{B}_o$, and the Hamiltonian of each member of the ensemble is H_o, (19.2).

configurations of the set $\mathscr{C}(N, \mathscr{E}_{tot} = E_{tot})$, and none other. It follows then that, in the microcanonical ensemble, the probability that the configurations of the N quasi particles are $\nu^{(1)}, \nu^{(2)}, \ldots, \nu^{(N)}$ is simply

$$P\left(\nu^{(1)}, \nu^{(2)}, \ldots, \nu^{(N)}; E_{tot}\right) = \frac{1}{\Omega(E_{tot})} \delta_{E_{tot}, \mathscr{E}_{tot}} \tag{B.1}$$

where

$$\begin{aligned} \Omega(E_{tot}) &= \dim \mathscr{C}(N, \mathscr{E}'_{tot} = E_{tot}) \\ &= \sum_{\nu'^{(1)}} \cdots \sum_{\nu'^{(N)}} \delta_{E_{tot}, \mathscr{E}'_{tot}} \end{aligned} \tag{B.2}$$

$$\mathscr{E}_{tot} = \sum_{n=1}^{N} \mathscr{E}^{(n)}(\nu^{(n)}) \qquad \mathscr{E}'_{tot} = \sum_{n=1}^{N} \mathscr{E}^{(n)}({\nu'}^{(n)}) \ . \tag{B.3}$$

We may choose a better way to study the statistical mechanical properties of the collection of quasi particles by moving from the microcanonical to the *canonical* ensemble (where instead of keeping $N, V, \mathscr{E}_{tot}$ fixed, we rather keep N, V, T fixed). The latter seems suitable because it is practically an arduous task to keep the energy of a macroscopic system fixed, but not the temperature T. Here, we imagine selecting one of the N quasi particles, say the $n-$th, and asking ourselves what is the probability that it has the configuration $\nu^{(n)}$ given that the total energy of the system is E_{tot}. What we have done is to partition the whole system into a focus system (*i.e.* the $n-$th quasi particle) and the environment (*i.e.* the remaining quasi particles). The thermodynamic temperature is determined by the environment. At equilibrium, it is natural to expect that each arbitrarily chosen quasi particle as the focus system should see the same environment. This amounts to saying that at equilibrium, the temperature is fixed.

Now, it is obvious that the probability $P(\nu^{(n)}; \mathscr{E}_{tot} = E_{tot})$ that the configuration of the $n-$th quasi particle is $\nu^{(n)}$ given that $\mathscr{E}_{tot} = E_{tot}$, is

$$\begin{aligned} P(\nu^{(1)}; \mathscr{E}_{tot} = E_{tot}) &= \sum_{\nu^{(2)}} \cdots \sum_{\nu^{(N)}} P\left(\nu^{(1)}, \nu^{(2)}, \ldots, \nu^{(N)}; E_{tot}\right) \\ &= \sum_{\nu^{(2)}} \cdots \sum_{\nu^{(N)}} \frac{1}{\Omega(E_{tot})} \delta_{E_{tot}, \mathscr{E}_{tot}} \\ &= \frac{\sum_{\nu^{(2)}} \cdots \sum_{\nu^{(N)}} \delta_{E_{tot}, \mathscr{E}_{tot}}}{\Omega(E_{tot})} \end{aligned} \tag{B.4}$$

where for simplicity we have chosen n to be 1.

At this point, it is convenient to express the Kronecker delta function $\delta_{x,y}$ as

$$\delta_{x,y} = \frac{1}{2\pi} \lim_{\alpha \to \infty} \frac{1}{\alpha} \int_{-\pi\alpha}^{\pi\alpha} d\theta \ e^{i(x-y)\theta} \ . \tag{B.5}$$

Making use of the identity in (B.5), we have

$$\delta_{E_{tot}, \mathscr{E}_{tot}} = \frac{1}{2\pi} \lim_{\alpha \to \infty} \frac{1}{\alpha} \int_{-\pi\alpha}^{\pi\alpha} d\theta \ e^{i(E_{tot} - \mathscr{E}_{tot})\theta} \ . \tag{B.6}$$

Thus $\Omega(E_{tot})$ becomes

$$\begin{aligned} \Omega(E_{tot}) &= \sum_{\nu^{(1)}} \cdots \sum_{\nu^{(N)}} \delta_{E_{tot},\mathscr{E}_{tot}} \\ &= \sum_{\nu^{(1)}} \cdots \sum_{\nu^{(N)}} \frac{1}{2\pi} \lim_{\alpha\to\infty} \frac{1}{\alpha} \int_{-\pi\alpha}^{\pi\alpha} d\theta \; e^{i(E_{tot}-\mathscr{E}_{tot})\theta} \\ &= \sum_{\nu^{(1)}} \cdots \sum_{\nu^{(N)}} \frac{1}{2\pi} \lim_{\alpha\to\infty} \frac{1}{\alpha} \int_{-\pi\alpha}^{\pi\alpha} d\theta \; e^{i\left[E_{tot}-\sum_{n=1}^{N} \mathscr{E}^{(n)}(\nu^{(n)})\right]\theta} \\ &= \frac{1}{2\pi} \lim_{\alpha\to\infty} \frac{1}{\alpha} \int_{-\pi\alpha}^{\pi\alpha} d\theta \; e^{iE_{tot}\theta} \left(\sum_{\nu^{(1)}} \cdots \sum_{\nu^{(N)}} e^{-i\left[\sum_{n=1}^{N} \mathscr{E}^{(n)}(\nu^{(n)})\right]\theta} \right) \\ &= \frac{1}{2\pi} \lim_{\alpha\to\infty} \frac{1}{\alpha} \int_{-\pi\alpha}^{\pi\alpha} d\theta \; e^{i\theta E_{tot}} \mathcal{Z}(i\theta) \; , \end{aligned} \tag{B.7}$$

where

$$\mathcal{Z}(x) := \sum_{\nu^{(1)}} \cdots \sum_{\nu^{(N)}} e^{-x\mathscr{E}_{tot}} = \sum_{\nu^{(1)}} \cdots \sum_{\nu^{(N)}} e^{-x\left[\sum_{n=1}^{N} \mathscr{E}^{(n)}(\nu^{(n)})\right]} \; . \tag{B.8}$$

Note that because the particles are identical, we may also rewrite the expression for $\mathcal{Z}(i\theta)$ as follows:

$$\begin{aligned} \mathcal{Z}(i\theta) &= \sum_{\nu^{(1)}} \cdots \sum_{\nu^{(N)}} e^{-i\theta\left[\sum_{n=1}^{N} \mathscr{E}^{(n)}(\nu^{(n)})\right]} \\ &= \left(\sum_{\nu^{(1)}} e^{-i\theta \mathscr{E}^{(1)}(\nu^{(1)})} \right) \left(\sum_{\nu^{(2)}} e^{-i\theta \mathscr{E}^{(2)}(\nu^{(2)})} \right) \cdots \left(\sum_{\nu^{(N)}} e^{-i\theta \mathscr{E}^{(N)}(\nu^{(N)})} \right) \\ &= \left(\sum_{\nu^{(1)}} e^{-i\theta \mathscr{E}^{(1)}(\nu^{(1)})} \right)^{N} \\ &= \mathcal{Z}_s^N(i\theta) \end{aligned} \tag{B.9}$$

with

$$\mathcal{Z}_s(x) := \sum_{\nu} e^{-x\mathscr{E}_s(\nu)} \tag{B.10}$$

where $\mathscr{E}_s$ is the energy of a single quasi particle. But note also that

$$\mathcal{Z}(i\theta) = e^{\ln \mathcal{Z}(i\theta)} = e^{\ln \mathcal{Z}_s^N(i\theta)} = e^{N \ln \mathcal{Z}_s(i\theta)} \; . \tag{B.11}$$

Hence,

$$\begin{aligned} \Omega(E_{tot}) &= \frac{1}{2\pi} \lim_{\alpha\to\infty} \frac{1}{\alpha} \int_{-\pi\alpha}^{\pi\alpha} d\theta \; e^{i\theta E_{tot}} \mathcal{Z}(i\theta) \\ &= \frac{1}{2\pi} \lim_{\alpha\to\infty} \frac{1}{\alpha} \int_{-\pi\alpha}^{\pi\alpha} d\theta \; e^{i\theta E_{tot}} e^{N \ln \mathcal{Z}_s(i\theta)} \\ &= \frac{1}{2\pi i} \lim_{\alpha\to\infty} \frac{1}{\alpha} \int_{-i\pi\alpha}^{i\pi\alpha} d\eta \; e^{\eta E_{tot}} e^{N \ln \mathcal{Z}_s(\eta)} \end{aligned} \tag{B.12}$$

where in the last line, we now have a complex variable of integration. We now evaluate this integral in the limit $N \to \infty$. One way of doing so is the so-called *method of steepest descent* (or the Darwin-Fowler method) [102].

To begin with, it is clear that since η is complex, the integrand in the last line of (B.12) is oscillatory. Since $\Omega(E_{tot})$ is finite, it implies that the integrand goes to zero as $|\eta| \to \infty$, thus the integrand has a peak. This means that the integrand is a succession of decreasing crests which vanishes $|\eta| \to \infty$. We may imagine that in the limit $N \to \infty$, only the peak of the integrand contributes significantly to the integral. Hence, we may approximate the integrand as its peak plus the immediate contour. We therefore need to find the absolute maximum of the integrand. We may express η as

$$\eta = \beta + iy \ . \tag{B.13}$$

Then,

$$\begin{aligned} \left| e^{\eta E_{tot}} e^{N \ln \mathscr{Z}_s(\eta)} \right| &= \left| e^{\eta E_{tot}} \mathscr{Z}_s^N(\eta) \right| \\ &= \left| e^{(\beta+iy)E_{tot}} \right| \left| \mathscr{Z}_s^N(\eta) \right| \\ &= e^{\beta E_{tot}} \left| \mathscr{Z}_s(\eta) \right|^N \end{aligned} \tag{B.14}$$

But,

$$\begin{aligned} |\mathscr{Z}_s(\eta)| &= \left| \left(\sum_\nu e^{-\eta \mathscr{E}_s(\nu)} \right) \right| \\ &= \left(\sum_\nu e^{-(\beta+iy)\mathscr{E}_s(\nu)} \right) \left(\sum_\nu e^{-(\beta-iy)\mathscr{E}_s(\nu)} \right) \\ &= \sum_{\nu,\nu'} e^{-\beta\left[\mathscr{E}_s(\nu)+\mathscr{E}_s(\nu')\right]} e^{-iy\left[\mathscr{E}_s(\nu)-\mathscr{E}_s(\nu')\right]} \\ &= \sum_{\nu,\nu'} e^{-\beta\left[\mathscr{E}_s(\nu)+\mathscr{E}_s(\nu')\right]} \cos\left(y\left[\mathscr{E}_s(\nu)-\mathscr{E}_s(\nu')\right]\right) + i \sum_{\nu,\nu'} e^{-\beta\left[\mathscr{E}_s(\nu)+\mathscr{E}_s(\nu')\right]} \sin\left(y\left[\mathscr{E}_s(\nu)-\mathscr{E}_s(\nu')\right]\right) \\ &= \sum_{\nu,\nu'} e^{-\beta\left[\mathscr{E}_s(\nu)+\mathscr{E}_s(\nu')\right]} \cos\left(y\left[\mathscr{E}_s(\nu)-\mathscr{E}_s(\nu')\right]\right) \ . \end{aligned} \tag{B.15}$$

Thus,

$$\begin{aligned} \max \left| e^{\eta E_{tot}} e^{N \ln \mathscr{Z}_s(\eta)} \right| &= \max \ e^{\beta E_{tot}} \left(\sum_{\nu,\nu'} e^{-\beta\left[\mathscr{E}_s(\nu)+\mathscr{E}_s(\nu')\right]} \cos\left(y\left[\mathscr{E}_s(\nu)-\mathscr{E}_s(\nu')\right]\right) \right)^N \\ &= e^{\beta E_{tot}} \left(\sum_{\nu,\nu'} e^{-\beta\left[\mathscr{E}_s(\nu)+\mathscr{E}_s(\nu')\right]} \ \max \ \cos\left(y\left[\mathscr{E}_s(\nu)-\mathscr{E}_s(\nu')\right]\right) \right)^N \end{aligned} \tag{B.16}$$

which implies that we obtain the absolute maximum of the integrand when $y = 0$. Since the integration is only along the imaginary line and the integrand is analytic, we may deform the integration contour, branching into the real part, without changing the value of the integral since the contribution of the real part cancels out. We may therefore choose wisely β in such a way that when $N \to \infty$, the only significant contributions to the integral originate from values of y around the peak, that is points in the neighborhood of $y = 0$. This is the *steepest descent method.* We are therefore going to evaluate both the denominator and the numerator on the RHS of (B.4) by the steepest descent method.

To begin with,

$$\begin{aligned} \Omega(E_{tot}) &= \frac{1}{2\pi i} \lim_{\alpha\to\infty} \frac{1}{\alpha} \int_{-i\pi\alpha}^{i\pi\alpha} d\eta \ e^{\eta E_{tot}} e^{N \ln \mathscr{Z}_s(\eta)} \\ &= \frac{1}{2\pi i} \lim_{\alpha\to\infty} \frac{1}{\alpha} \int_{-i\pi\alpha}^{i\pi\alpha} d\eta \ e^{N\left[\eta \overline{E} + \ln \mathscr{Z}_s(\eta)\right]} \end{aligned} \tag{B.17}$$

where

$$\overline{E} := \frac{E_{tot}}{N} \ . \tag{B.18}$$

Let us now expand the $\eta \overline{E} + \ln \mathcal{Z}_s(\eta)$ around some arbitrary η_o. We get

$$\begin{aligned} \eta \overline{E} + \ln \mathcal{Z}_s(\eta) = \eta_o \overline{E} + \ln \mathcal{Z}_s(\eta_o) + (\eta - \eta_o) \left[\overline{E} + \frac{\partial}{\partial \eta} \ln \mathcal{Z}_s(\eta) \Big|_{\eta=\eta_o} \right] \\ + \frac{(\eta-\eta_o)^2}{2} \left[\frac{\partial^2}{\partial \eta^2} \ln \mathcal{Z}_s(\eta) \Big|_{\eta=\eta_o} \right] + \mathcal{O}((\eta-\eta_o)^3) \ . \end{aligned} \tag{B.19}$$

Hence,

$$\begin{aligned} \Omega(E_{tot}) = \frac{1}{2\pi i} \lim_{\alpha\to\infty} \frac{1}{\alpha} \int_{-i\pi\alpha}^{i\pi\alpha} d\eta \ e^{N\left[\eta_o \overline{E} + \ln \mathcal{Z}_s(\eta_o)\right]} \times e^{N(\eta-\eta_o)\left[\overline{E} + \frac{\partial}{\partial \eta} \ln \mathcal{Z}_s(\eta)\big|_{\eta=\eta_o}\right]} \\ \times e^{\frac{N(\eta-\eta_o)^2}{2}\left[\frac{\partial^2}{\partial \eta^2} \ln \mathcal{Z}_s(\eta)\big|_{\eta=\eta_o}\right]} \times \mathcal{O}\left(e^{N(\eta-\eta_o)^3}\right) \ . \end{aligned} \tag{B.20}$$

The integration, having only complex extrema, implies a contour integration along the real value of η (*i.e.* the real value of η is kept contant). Now, assuming $\Re[\eta] = \eta_o = \beta$, it follows then that $(\eta - \eta_o)$ is purely complex. Indeed, if $\eta = \beta + iy$, then $\eta - \eta_o = iy$. Therefore, $d\eta = idy$ and the integral becomes

$$\begin{aligned} \Omega(E_{tot}) = \frac{1}{2\pi} \lim_{\alpha\to\infty} \frac{1}{\alpha} \int_{-\pi\alpha}^{\pi\alpha} dy \ e^{N\left[\beta \overline{E} + \ln \mathcal{Z}_s(\beta)\right]} \times e^{iNy\left[\overline{E} + \frac{\partial}{\partial \eta} \ln \mathcal{Z}_s(\eta)\big|_{\eta=\beta}\right]} \\ \times e^{-\frac{Ny^2}{2}\left[\frac{\partial^2}{\partial \eta^2} \ln \mathcal{Z}_s(\eta)\big|_{\eta=\beta}\right]} \times \mathcal{O}\left(e^{-iNy^3}\right) \ . \end{aligned} \tag{B.21}$$

We note that the integrand factor whose exponent is linear in y oscillates. In particular, these oscillations become very rapid as $N \to \infty$. We may eliminate these rapid oscillations by imposing the condition that the exponent vanishes all together, *i.e.*

$$Ny \left[\overline{E} + \frac{\partial}{\partial \eta} \ln \mathcal{Z}_s(\eta) \Big|_{\eta=\beta} \right] = 0 \tag{B.22}$$

whose non trivial solution requires that

$$\overline{E} = - \frac{\partial}{\partial \eta} \ln \mathcal{Z}_s(\eta) \Big|_{\eta=\beta} = \frac{\sum_\nu \mathscr{E}(\nu) e^{-\beta \mathscr{E}(\nu)}}{\mathcal{Z}(\beta)} \ . \tag{B.23}$$

What we have done is a sort of coarse graining. The integral at this point becomes

$$\Omega(E_{tot}) = \frac{1}{2\pi} e^{N\left[\beta \overline{E} + \ln \mathcal{Z}_s(\beta)\right]} \times \lim_{\alpha\to\infty} \frac{1}{\alpha} \int_{-\pi\alpha}^{\pi\alpha} dy \ e^{-\frac{Ny^2}{2}\left[\frac{\partial^2}{\partial \eta^2} \ln \mathcal{Z}_s(\eta)\big|_{\eta=\beta}\right]} \times \mathcal{O}\left(e^{-iNy^3}\right) \ . \tag{B.24}$$

For the integral to converge in the limit $\alpha \to \infty$, we see that

$$\frac{\partial^2}{\partial \eta^2} \ln \mathcal{Z}_s(\eta) \Big|_{\eta=\beta} \geq 0 \tag{B.25}$$

which means that the function $\frac{\partial}{\partial \eta} \ln \mathcal{Z}_s(\eta)$ must be monotonic. We now show that (B.25) is always satisfied for real β. Indeed,

$$
\begin{aligned}
\frac{\partial}{\partial\eta}\left(\frac{\partial}{\partial\eta}\ln\mathcal{Z}_s(\eta)\right) &= \frac{\partial}{\partial\eta}\left(\frac{1}{\mathcal{Z}_s(\eta)}\ \frac{\partial}{\partial\eta}\sum_\nu e^{-\eta\mathscr{E}_s(\nu)}\right)\\
&= \frac{\partial}{\partial\eta}\left(-\frac{1}{\mathcal{Z}_s(\eta)}\ \sum_\nu \mathscr{E}_s(\nu)e^{-\eta\mathscr{E}_s(\nu)}\right)\\
&= -\frac{-\mathcal{Z}_s(\eta)\sum_\nu\mathscr{E}_s^2(\nu)e^{-\eta\mathscr{E}_s(\nu)}+\left(\sum_\nu\mathscr{E}_s(\nu)e^{-\eta\mathscr{E}_s(\nu)}\right)^2}{\mathcal{Z}_s^2(\eta)}\\
&= \frac{\sum_\nu\mathscr{E}_s^2(\nu)e^{-\eta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\eta)}-\left(\frac{\sum_\nu\mathscr{E}_s(\nu)e^{-\eta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\eta)}\right)^2\\
&= \frac{\sum_\nu\mathscr{E}_s^2(\nu)e^{-\eta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\eta)}-\left(-\frac{\partial}{\partial\eta}\ln\mathcal{Z}_s(\eta)\right)^2\ .
\end{aligned}
\tag{B.26}
$$

And so,

$$
\begin{aligned}
\frac{\partial}{\partial\eta}\left(\frac{\partial}{\partial\eta}\ln\mathcal{Z}_s(\eta)\right)\bigg|_{\eta=\beta} &= \frac{\sum_\nu\mathscr{E}_s^2(\nu)e^{-\beta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\beta)}-\overline{E}^2\\
&= \frac{\sum_\nu\mathscr{E}_s^2(\nu)e^{-\beta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\beta)}-\overline{E}^2\frac{\sum_\nu e^{-\beta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\beta)}\\
&= \frac{\sum_\nu\left(\mathscr{E}_s^2(\nu)-\overline{E}^2\right)e^{-\beta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\beta)}\\
&= \frac{\sum_\nu\left(\mathscr{E}_s^2(\nu)+\overline{E}^2-2\overline{E}\cdot\overline{E}\right)e^{-\beta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\beta)}\ .
\end{aligned}
\tag{B.27}
$$

Thus,

$$
\begin{aligned}
\frac{\partial}{\partial\eta}\left(\frac{\partial}{\partial\eta}\ln\mathcal{Z}_s(\eta)\right)\bigg|_{\eta=\beta} &= \frac{\sum_\nu\mathscr{E}_s^2(\nu)e^{-\beta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\beta)}+\overline{E}^2+-2\overline{E}\cdot\overline{E}\\
&= \frac{\sum_\nu\mathscr{E}_s^2(\nu)e^{-\beta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\beta)}+\overline{E}^2+-2\overline{E}\frac{\sum_\nu\mathscr{E}_s(\nu)e^{-\beta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\beta)}\\
&= \frac{\sum_\nu\mathscr{E}_s^2(\nu)e^{-\beta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\beta)}+\overline{E}^2\frac{\sum_\nu e^{-\beta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\beta)}+-2\overline{E}\frac{\sum_\nu\mathscr{E}_s(\nu)e^{-\beta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\beta)}\\
&= \frac{\sum_\nu\left(\mathscr{E}_s^2(\nu)+\overline{E}^2-2\mathscr{E}_s(\nu)\overline{E}\right)e^{-\beta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\beta)}\\
&= \frac{\sum_\nu\left(\mathscr{E}_s(\nu)-\overline{E}\right)^2e^{-\beta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\beta)}\geq 0\ .
\end{aligned}
\tag{B.28}
$$

Note that

$$
\frac{\sum_\nu\mathscr{E}_s^2(\nu)e^{-\beta\mathscr{E}_s(\nu)}}{\mathcal{Z}_s(\beta)}=\overline{\mathscr{E}^2}\ \text{(mean square energy per particle)}
\tag{B.29}
$$

and so $\frac{\partial^2}{\partial^2\eta}\ln\mathcal{Z}_s(\eta)\Big|_{\eta=\beta}$ is the variance of the energy per particle, which is always positive.

Now, returning to the integral in (B.24), i.e.

$$
\Omega(E_{tot})=\frac{1}{2\pi}e^{N\left[\beta\overline{E}+\ln\mathcal{Z}_s(\beta)\right]}\times\lim_{\alpha\to\infty}\frac{1}{\alpha}\int_{-\pi\alpha}^{\pi\alpha}dy\ e^{-\frac{Ny^2}{2}\left[\frac{\partial^2}{\partial\eta^2}\ln\mathcal{Z}_s(\eta)\big|_{\eta=\beta}\right]}\times\mathcal{O}\left(e^{-iNy^3}\right)
$$

we recall that

$$
\operatorname{erf}(A)=\frac{1}{\sqrt{\pi}}\int_{-A}^{A}dx\ e^{-x^2}\ .
\tag{B.30}
$$

Now, if we introduce the variable x, where

$$x^2 := \frac{Ny^2}{2}\left[\frac{\partial^2}{\partial\eta^2}\ln \mathcal{Z}_s(\eta)\Big|_{\eta=\beta}\right] \equiv \frac{Ny^2}{2}\sigma^2_{\mathscr{E}}(\beta) \tag{B.31}$$

where

$$\sigma^2_{\mathscr{E}}(\beta) := \frac{\partial^2}{\partial\eta^2}\ln \mathcal{Z}_s(\eta)\Big|_{\eta=\beta} \tag{B.32}$$

we see that

$$dy = \sqrt{\frac{2}{N\sigma^2_{\mathscr{E}}(\beta)}}\, dx \tag{B.33}$$

and so,

$$\begin{aligned}
\int_{-\pi\alpha}^{\pi\alpha} dy\; e^{-\frac{Ny^2}{2}\sigma^2_{\mathscr{E}}(\beta)} &= \sqrt{\frac{2}{N\sigma^2_{\mathscr{E}}(\beta)}} \int_{-\pi\alpha\sqrt{\frac{N\sigma^2_{\mathscr{E}}(\beta)}{2}}}^{\pi\alpha\sqrt{\frac{N\sigma^2_{\mathscr{E}}(\beta)}{2}}} dx\; e^{-x^2} \\
&= \sqrt{\frac{2\pi}{N\sigma^2_{\mathscr{E}}(\beta)}}\frac{1}{\sqrt{\pi}} \int_{-\pi\alpha\sqrt{\frac{N\sigma^2_{\mathscr{E}}(\beta)}{2}}}^{\pi\alpha\sqrt{\frac{N\sigma^2_{\mathscr{E}}(\beta)}{2}}} dx\; e^{-x^2} \\
&= \sqrt{\frac{2\pi}{N\sigma^2_{\mathscr{E}}(\beta)}}\; \mathrm{erf}\left[\pi\alpha\sqrt{\frac{N\sigma^2_{\mathscr{E}}(\beta)}{2}}\right]
\end{aligned} \tag{B.34}$$

from which follows that

$$\begin{aligned}
\Omega(E_{tot}) &\sim \frac{1}{2\pi}e^{N\left[\beta\overline{E}+\ln \mathcal{Z}_s(\beta)\right]} \times \lim_{\alpha\to\infty}\frac{1}{\alpha}\sqrt{\frac{2\pi}{N\sigma^2_{\mathscr{E}}(\beta)}}\; \mathrm{erf}\left[\pi\alpha\sqrt{\frac{N\sigma^2_{\mathscr{E}}(\beta)}{2}}\right] \\
&\sim \frac{1}{\sqrt{2\pi N\sigma^2_{\mathscr{E}}(\beta)}}e^{N\left[\beta\overline{E}+\ln \mathcal{Z}_s(\beta)\right]} \times \lim_{\alpha\to\infty}\frac{1}{\alpha}\; \mathrm{erf}\left[\pi\alpha\sqrt{\frac{N\sigma^2_{\mathscr{E}}(\beta)}{2}}\right] .
\end{aligned} \tag{B.35}$$

We now evaluate the numerator of (B.4) using the same procedure. First of all, we find that

$$\begin{aligned}
\sum_{\nu^{(2)}}\cdots\sum_{\nu^{(N)}}\delta_{E_{tot},\mathscr{E}_{tot}} &= \sum_{\nu^{(2)}}\cdots\sum_{\nu^{(N)}}\frac{1}{2\pi}\lim_{\alpha\to\infty}\frac{1}{\alpha}\int_{-\pi\alpha}^{\pi\alpha} d\theta\; e^{i(E_{tot}-\mathscr{E}_{tot})\theta} \\
&= \sum_{\nu^{(2)}}\cdots\sum_{\nu^{(N)}}\frac{1}{2\pi}\lim_{\alpha\to\infty}\frac{1}{\alpha}\int_{-\pi\alpha}^{\pi\alpha} d\theta\; e^{i\left[E_{tot}-\mathscr{E}^{(1)}(\nu^{(1)})-\sum_{n=2}^{N}\mathscr{E}^{(n)}(\nu^{(n)})\right]\theta} \\
&= \frac{1}{2\pi}\lim_{\alpha\to\infty}\frac{1}{\alpha}\int_{-\pi\alpha}^{\pi\alpha} d\theta\; e^{i\left[E_{tot}-\mathscr{E}^{(1)}(\nu^{(1)})\right]\theta}\left(\sum_{\nu^{(2)}}\cdots\sum_{\nu^{(N)}} e^{-i\left[\sum_{n=2}^{N}\mathscr{E}^{(n)}(\nu^{(n)})\right]\theta}\right) \\
&= \frac{1}{2\pi}\lim_{\alpha\to\infty}\frac{1}{\alpha}\int_{-\pi\alpha}^{\pi\alpha} d\theta\; e^{i\theta\left[E_{tot}-\mathscr{E}^{(1)}(\nu^{(1)})\right]}\mathcal{Z}'(i\theta) ,
\end{aligned} \tag{B.36}$$

where it is obvious that

$$\mathcal{Z}'(i\theta) = \mathcal{Z}_s^{N-1}(i\theta) = e^{(N-1)\ln \mathcal{Z}_s(i\theta)} . \tag{B.37}$$

Hence,

$$\begin{aligned}
\sum_{\nu^{(2)}}\cdots\sum_{\nu^{(N)}}\delta_{E_{tot},\mathscr{E}_{tot}} &= \frac{1}{2\pi}\lim_{\alpha\to\infty}\frac{1}{\alpha}\int_{-\pi\alpha}^{\pi\alpha} d\theta\; e^{i\theta\left[E_{tot}-\mathscr{E}^{(1)}(\nu^{(1)})\right]+(N-1)\ln \mathcal{Z}_s(i\theta)} \\
&= \frac{1}{2\pi i}\lim_{\alpha\to\infty}\frac{1}{\alpha}\int_{-i\pi\alpha}^{i\pi\alpha} d\eta\; e^{\eta\left[E_{tot}-\mathscr{E}^{(1)}(\nu^{(1)})\right]+(N-1)\ln \mathcal{Z}_s(\eta)} .
\end{aligned} \tag{B.38}$$

From (B.12), we see immediately that the solution of the above is formally the same as (B.35) provided we make the following transformations in the latter:

$$\begin{aligned} E_{tot} \mapsto E_{tot} - \mathscr{E}^{(1)}(\nu^{(1)}) &= N\overline{E} - \mathscr{E}^{(1)}(\nu^{(1)}) \\ N \ln \mathcal{Z}_s(\eta) &\mapsto (N-1)\ln \mathcal{Z}_s(\eta) \ . \end{aligned} \tag{B.39}$$

Thus,

$$\begin{aligned} \sum_{\nu^{(2)}} \cdots \sum_{\nu^{(N)}} \delta_{E_{tot},\mathscr{E}_{tot}} &\sim \frac{1}{\sqrt{2\pi(N-1)\sigma^2_{\mathscr{E}}(\beta)}} e^{\left[N\beta\overline{E} - \beta\mathscr{E}^{(1)}(\nu^{(1)}) + (N-1)\ln \mathcal{Z}_s(\beta)\right]} \times \lim_{\alpha\to\infty} \frac{1}{\alpha} \operatorname{erf}\left[\pi\alpha\sqrt{\frac{(N-1)\sigma^2_{\mathscr{E}}(\beta)}{2}}\right] \\ &= \frac{1}{\sqrt{2\pi(N-1)\sigma^2_{\mathscr{E}}(\beta)}} e^{\left[N\beta\overline{E} + N\ln \mathcal{Z}_s(\beta)\right]} e^{\left[-\beta\mathscr{E}^{(1)}(\nu^{(1)}) - \ln \mathcal{Z}_s(\beta)\right]} \\ &\quad \times \lim_{\alpha\to\infty} \frac{1}{\alpha} \operatorname{erf}\left[\pi\alpha\sqrt{\frac{(N-1)\sigma^2_{\mathscr{E}}(\beta)}{2}}\right] \ . \end{aligned} \tag{B.40}$$

And so finally, we may substitute (B.35) and (B.40) into (B.4) and take the thermodynamic limit, *i.e.* $N \to \infty$,

$$\begin{aligned} P(\nu^{(1)};\mathscr{E}_{tot} = E_{tot}) &= \lim_{N\to\infty} \frac{\sum_{\nu^{(2)}} \cdots \sum_{\nu^{(N)}} \delta_{E_{tot},\mathscr{E}_{tot}}}{\Omega(E_{tot})} \\ &= \lim_{N\to\infty} \left[\frac{\frac{1}{\sqrt{2\pi(N-1)\sigma^2_{\mathscr{E}}(\beta)}} e^{\left[N\beta\overline{E} + N\ln \mathcal{Z}_s(\beta)\right]} e^{\left[-\beta\mathscr{E}^{(1)}(\nu^{(1)}) - \ln \mathcal{Z}_s(\beta)\right]}}{\frac{1}{\sqrt{2\pi N\sigma^2_{\mathscr{E}}(\beta)}} e^{N\left[\beta\overline{E} + \ln \mathcal{Z}_s(\beta)\right]}} \right. \\ &\qquad \left. \times \frac{\lim_{\alpha\to\infty} \frac{1}{\alpha} \operatorname{erf}\left[\pi\alpha\sqrt{\frac{(N-1)\sigma^2_{\mathscr{E}}(\beta)}{2}}\right]}{\lim_{\alpha\to\infty} \frac{1}{\alpha} \operatorname{erf}\left[\pi\alpha\sqrt{\frac{N\sigma^2_{\mathscr{E}}(\beta)}{2}}\right]} \right] \\ &\sim \frac{e^{-\beta\mathscr{E}^{(1)}(\nu^{(1)})}}{\mathcal{Z}_s(\beta)} \ . \end{aligned} \tag{B.41}$$

From (B.23), the constant β is known from statistical mechanics to be $\beta = \frac{1}{k_B T}$ – where k_B is Boltzmann's constant and T is the absolute temperature of the system [117]. In the case of an ensemble of identical molecules subjected to a static magnetic field $\mathbf{B}_o = B_o\mathbf{e}_z$, whereby each member of the ensemble has Hamiltonian H_o, (19.2), we see that $\mathscr{E}^{(1)}(\nu^{(1)}) \mapsto H_o$ (if we transition to quantum statistics). And $P(\nu^{(1)};\mathscr{E}_{tot} = E_{tot})$ in (B.41) becomes $\rho_S(t_o)$ (i.e. $\rho_S(0)$) in (19.4). Upon transitioning to quantum statistics, we need to view members of the ensemble as quantum particles. This means we need to also take into account their *indistinguishability*. This normally brings about profound implications leading to Bose-Einstein statistics or Fermi-Dirac statistics (or even something in between). It is however known that for high-temperatures and low densities (which is our case), the importance of implementing quantum indistinguishability into the derivation fades out since in this limit, the behavior of the system approaches asymptotically that of a classical system [117]. This justifies the density matrix in (19.4) as the initial state of the multispin system prior to the 'application' of $\mathbf{B}_1(t)$.

Appendix C

Some analyses on the quantum map $\Lambda(t)$

C.1 Derivation of the equation for $\Lambda(t)$

We want to find the map $\Lambda(t)$ associated with the zeroth-order master equation in (19.79), which reads

$$\frac{d}{dt}\varrho^{(0)}(t) = \mathcal{A}(t)\varrho^{(0)}(0) + \mathcal{L}\varrho^{(0)}(t) \ . \tag{C.1}$$

Following [30], let

$$\varrho^{(0)}(t) = \Lambda(t)\varrho^{(0)}(0) \ . \tag{C.2}$$

Then, from (C.1) we have

$$\frac{d}{dt}\Lambda(t) = \mathcal{A}(t) + \mathcal{L}\ \Lambda(t) \tag{C.3}$$

which after performing the Laplace transform (indicated by the operational symbol L) becomes

$$s\widetilde{\Lambda}(s) - \mathbb{I} = \widetilde{\mathcal{A}}(s) + \mathcal{L}\ \widetilde{\Lambda}(s) \tag{C.4}$$

where $\mathsf{L}\left[\Lambda(t)\right] = \widetilde{\Lambda}(s)$ and $\mathsf{L}\left[\mathcal{A}(t)\right] = \widetilde{\mathcal{A}}(s)$. Upon a rearrangement of the terms in (C.4), we end up with

$$\left(s\mathbb{I} - \mathcal{L}\right)\widetilde{\Lambda}(s) = \widetilde{\mathcal{A}}(s) + \mathbb{I} \ . \tag{C.5}$$

That is,

$$\widetilde{\Lambda}(s) = \left(s\mathbb{I} - \mathcal{L}\right)^{-1}\left(\widetilde{\mathcal{A}}(s) + \mathbb{I}\right) \ . \tag{C.6}$$

If we now expand the resolvent $\left(s\mathbb{I} - \mathcal{L}\right)^{-1}$ in powers of the generator $\mathcal{L}$, we get

$$\left(s\mathbb{I} - \mathcal{L}\right)^{-1} = \sum_{n=0}^{\infty}\frac{\mathcal{L}^n}{s^{n+1}} \tag{C.7}$$

with $\mathcal{L}^n = \mathbb{I}$ for $n = 0$. Thus, (C.6) becomes

$$\widetilde{\Lambda}(s) = \sum_{n=0}^{\infty}\mathcal{L}^n\left(\widetilde{\mathcal{A}}(s)\frac{1}{s^{n+1}} + \mathbb{I}\frac{1}{s^{n+1}}\right) \ . \tag{C.8}$$

The inverse Laplace transform of this last equation is

$$\begin{aligned}\Lambda(t) &= \sum_{n=0}^{\infty} \mathcal{L}^n \left(\mathsf{L}^{-1}\left[\widetilde{\mathcal{A}}(s) \frac{1}{s^{n+1}} \right] + \mathbb{I} \cdot \mathsf{L}^{-1}\left[\frac{1}{s^{n+1}} \right] \right) \\ &= \int_0^t d\tau \left(\sum_{n=0}^{\infty} \mathcal{L}^n \frac{\tau^n}{n!} \right) \mathcal{A}(t-\tau) + \mathbb{I} \cdot \left(\sum_{n=0}^{\infty} \mathcal{L}^n \frac{t^n}{n!} \right) \\ &= \int_0^t d\tau \; e^{\mathcal{L}\tau} \mathcal{A}(t-\tau) + e^{\mathcal{L}t} \; = \int_0^t d\tau \; e^{\mathcal{L}(t-\tau)} \mathcal{A}(\tau) + e^{\mathcal{L}t} \; .\end{aligned} \tag{C.9}$$

C.2 $\Lambda(t)$ is a not a UDM

Certainly, $\Lambda(t)$ preserves trace for any input state $\varrho^{(0)}(0)$. For $\Lambda(t)$ to qualify as a UDM (universal dynamical map[1]), its output state must always be positive semi-definite (with unit trace), irrespective of the input state $\varrho^{(0)}(0) \neq 0$. It can be easily shown that this is not the case for $\Lambda(t)$. Again, it has to do with the presence of the superoperator $\mathcal{A}(t)$ in the expression for $\Lambda(t)$ (19.79). If we take a look at (19.78),

$$\varrho^{(0)}(t) = e^{\mathcal{L}t} \varrho^{(0)}(0) + \int_0^t dt' \; e^{\mathcal{L}(t-t')} \mathcal{A}(t') \varrho^{(0)}(0) \tag{C.10}$$

we see that while the first term on the right is certainly UDM, the second term involves the composition of two superoperators acting on $\varrho^{(0)}(0)$. In the Kraus operator sum representation, (C.10) may be rewritten as

$$\varrho^{(0)}(t) = \sum_\alpha \mathscr{K}_\alpha(t) \varrho^{(0)}(0) \mathscr{K}_\alpha^\dagger(t) + \sum_\alpha \int_0^t d\tau \; \mathscr{K}_\alpha(t-\tau) \left[\mathcal{A}(\tau) \varrho^{(0)}(0) \right] \mathscr{K}_\alpha^\dagger(t-\tau) \tag{C.11}$$

where the Kraus operators $\{\mathscr{K}_\alpha(t)\}$ obey the usual completeness relation $\sum_\alpha \mathscr{K}_\alpha^\dagger(t) \mathscr{K}_\alpha(t) = \mathbb{I}$. Or, more explicitly,

$$\begin{aligned}\varrho^{(0)}(t) = \sum_\alpha \mathscr{K}_\alpha(t) \varrho^{(0)}(0) \mathscr{K}_\alpha^\dagger(t) &+ \sum_\alpha \int_0^t d\tau \; \mathscr{K}_\alpha(t-\tau) \mathscr{M}(\tau) \varrho^{(0)}(0) \mathscr{M}^\dagger(\tau) \mathscr{K}_\alpha^\dagger(t-\tau) \\ &- \sum_\alpha \int_0^t d\tau \; \mathscr{K}_\alpha(t-\tau) \mathscr{M}^\dagger(\tau) \varrho^{(0)}(0) \mathscr{M}(\tau) \mathscr{K}_\alpha^\dagger(t-\tau)\end{aligned} \tag{C.12}$$

with [52, 153]

$$\mathscr{M}(t) \equiv \frac{1}{\sqrt{2}} \left[\mathbb{I} - i H_{LR}(t) \right] \tag{C.13}$$

where $H_{LR}(t)$ is the linear response Hamiltonian, (19.70). Furthermore, we note that

$$\begin{aligned}\mathbb{I} = \sum_\alpha \mathscr{K}_\alpha^\dagger(t) \mathscr{K}_\alpha(t) &+ \sum_\alpha \int_0^t d\tau \; \mathscr{M}^\dagger(\tau) \mathscr{K}_\alpha^\dagger(t-\tau) \mathscr{K}_\alpha(t-\tau) \mathscr{M}(\tau) \\ &- \sum_\alpha \int_0^t d\tau \; \mathscr{M}(\tau) \mathscr{K}_\alpha^\dagger(t-\tau) \mathscr{K}_\alpha(t-\tau) \mathscr{M}^\dagger(\tau)\end{aligned} \tag{C.14}$$

– which confirms again that $\Lambda(t)$ is trace-preserving. However, from (C.12), we see that $\varrho^{(0)}(t)$ cannot be guaranteed to be always positive for an arbitrary $\varrho^{(0)}(0)$ – given that it is the difference between two positive operators. In fact, $\Lambda(t)$ can be seen as the difference between two CP maps:

$$\Lambda(t) = \Phi_{1,t} - \Phi_{2,t} \tag{C.15}$$

---

[1] See Definition 13.0.1.

$$\Phi_{1,t}[\varrho^{(0)}(0)] \equiv \sum_{\alpha} \mathscr{K}_{\alpha}(t)\varrho^{(0)}(0)\mathscr{K}_{\alpha}^{\dagger}(t) + \sum_{\alpha}\int_0^t d\tau\ \mathscr{K}_{\alpha}(t-\tau)\mathscr{M}(\tau)\varrho^{(0)}(0)\mathscr{M}^{\dagger}(\tau)\mathscr{K}_{\alpha}^{\dagger}(t-\tau) \tag{C.16a}$$

$$\Phi_{2,t}[\varrho^{(0)}(0)] \equiv \sum_{\alpha}\int_0^t d\tau\ \mathscr{K}_{\alpha}(t-\tau)\mathscr{M}^{\dagger}(\tau)\varrho^{(0)}(0)\mathscr{M}(\tau)\mathscr{K}_{\alpha}^{\dagger}(t-\tau)\ . \tag{C.16b}$$

Thus, the map $\Lambda(t)$ is not a UDM[2] [26, 145, 168].

C.3 Positivity of $\Lambda(t)$ on its specified domain, some indications

Even though $\Lambda(t)$ is not a UDM, this, however, does not imply that it is a non-UDM. To prove it is a non-UDM, we need to prove that it is positive on its domain. There are strong indications this is exactly the case. These indications stem from the parameters involved in the theory and assumptions like $\frac{B_1}{B_o} \ll 1$. The positivity of $\Lambda(t)$ on its domain, if that be the case, may therefore be attributed to these parameters and the assumptions of the theory (which are to some extent, experimental constraints in many cases), rather than an elegant theorem like Choi's [28]. We present these arguments in the following. A better analysis may, perhaps, be necessary in the future.

Let $|\nu\rangle$ be a generic vector of the spin system's Hilbert space $\mathcal{H}_S$. We show below that there are indications that

$$\sum_{\alpha}\left\langle \nu \middle| \mathscr{K}_{\alpha}(t)\varrho^{(0)}(0)\mathscr{K}_{\alpha}^{\dagger}(t) \middle| \nu \right\rangle > \left| \sum_{\alpha}\int_0^t d\tau\ \left\langle \nu \middle| \mathscr{K}_{\alpha}(t-\tau)\left[\mathcal{A}(\tau)\varrho^{(0)}(0)\right]\mathscr{K}_{\alpha}^{\dagger}(t-\tau) \middle| \nu \right\rangle \right| \tag{C.17}$$

for the Boltzmann input state $\varrho^{(0)}(0) = \frac{e^{-\beta\mathscr{Z}_o}}{\mathrm{Tr}[e^{-\beta\mathscr{Z}_o}]}$ – making, therefore, the map $\Lambda(t)$ positive for this particular input state.

To begin with, from the expressions for $\mathcal{A}(t)$ and $\varrho^{(0)}(0)$, we have that

$$\mathcal{A}(t)\varrho^{(0)}(0) = i2B_1\Re[\varphi_f(t)]\sum_{\omega_o}\sum_{\mathbb{m},\mathbb{m}'}\delta_{\omega_o,\epsilon_{\mathbb{m}'}-\epsilon_{\mathbb{m}}}\delta_{+1,M_{\mathbb{m}'}-M_{\mathbb{m}}}\left(P_{\mathbb{m}'}^{(0)} - P_{\mathbb{m}}^{(0)}\right)$$
$$\times\left(e^{i\omega_o t}\,|\mathbb{m}'\rangle\langle\mathbb{m}'|\,\xi^x\,|\mathbb{m}\rangle\,\langle\mathbb{m}| - h.c.\right) \tag{C.18}$$

---

[2] Recall what we call 'non-UDM' is commonly referred to the literature as 'non-CP' map.

– where $P_{\mathbb{n}}^{(0)} = \frac{e^{-\beta\epsilon_{\mathbb{n}}}}{\mathrm{Tr}[e^{-\beta\mathscr{H}_o}]}$, (22.10) –, which means

$$\begin{aligned}
&\left|\sum_\alpha\int_0^t d\tau\ \left\langle\nu\middle|\mathscr{K}_\alpha(t-\tau)\left[\mathcal{A}(\tau)\varrho^{(0)}(0)\right]\mathscr{K}_\alpha^\dagger(t-\tau)\middle|\nu\right\rangle\right|\\
&\quad= \Bigg|4B_1\sum_{\omega_o}\sum_{\mathbb{n},\mathbb{n}'}\delta_{\omega_o,\epsilon_{\mathbb{n}'}-\epsilon_{\mathbb{n}}}\delta_{+1,M_{\mathbb{n}'}-M_{\mathbb{n}}}\left(P^{(0)}_{\mathbb{n}'}-P^{(0)}_{\mathbb{n}}\right)\langle\mathbb{n}'|\,\xi^x\,|\mathbb{n}\rangle\\
&\qquad\times\Im\left(\int_0^t d\tau\ e^{i\omega_o\tau}\Re[\varphi_f(\tau)]\sum_\alpha\langle\nu|\,\mathscr{K}_\alpha(t-\tau)\,|\mathbb{n}'\rangle\,\langle\mathbb{n}|\,\mathscr{K}^\dagger_\alpha(t-\tau)\,|\nu\rangle\right)\Bigg|\\
&\quad\leq 4B_1\sum_{\omega_o}\sum_{\mathbb{n},\mathbb{n}'}\delta_{\omega_o,\epsilon_{\mathbb{n}'}-\epsilon_{\mathbb{n}}}\delta_{+1,M_{\mathbb{n}'}-M_{\mathbb{n}}}\left|P^{(0)}_{\mathbb{n}'}-P^{(0)}_{\mathbb{n}}\right|\ \left|\langle\mathbb{n}'|\,\xi^x\,|\mathbb{n}\rangle\right|\\
&\qquad\times\left|\Im\left(\int_0^t d\tau\ e^{i\omega_o\tau}\Re[\varphi_f(\tau)]\sum_\alpha\langle\nu|\,\mathscr{K}_\alpha(t-\tau)\,|\mathbb{n}'\rangle\,\langle\mathbb{n}|\,\mathscr{K}^\dagger_\alpha(t-\tau)\,|\nu\rangle\right)\right|\\
&\quad\leq 4B_1\sum_{\omega_o}\sum_{\mathbb{n},\mathbb{n}'}\delta_{\omega_o,\epsilon_{\mathbb{n}'}-\epsilon_{\mathbb{n}}}\delta_{+1,M_{\mathbb{n}'}-M_{\mathbb{n}}}\left|P^{(0)}_{\mathbb{n}'}-P^{(0)}_{\mathbb{n}}\right|\ \left|\langle\mathbb{n}'|\,\xi^x\,|\mathbb{n}\rangle\right|\\
&\qquad\times\left|\Im\left(\int_0^t d\tau\ e^{i\omega_o\tau}\Re[\varphi_f(\tau)]\right)\right|\times\max_{|\mathbb{n}''\rangle,t}\left(\sum_\alpha\left|\langle\nu|\,\mathscr{K}_\alpha(t)\,|\mathbb{n}''\rangle\right|^2\right)\ . \qquad (C.19)
\end{aligned}$$

Furthermore, since $\varphi_f(t)$ is the characteristic function of a symmetric distribution function, we know from Pòlya's theorem [120] that $|\Re[\varphi_f(\tau)]|\leq 1$, so

$$\begin{aligned}
&\left|\sum_\alpha\int_0^t d\tau\ \left\langle\nu\middle|\mathscr{K}_\alpha(t-\tau)\left[\mathcal{A}(\tau)\varrho^{(0)}(0)\right]\mathscr{K}_\alpha^\dagger(t-\tau)\middle|\nu\right\rangle\right|\\
&\quad\leq 4B_1\sum_{\omega_o}\sum_{\mathbb{n},\mathbb{n}'}\delta_{\omega_o,\epsilon_{\mathbb{n}'}-\epsilon_{\mathbb{n}}}\delta_{+1,M_{\mathbb{n}'}-M_{\mathbb{n}}}\left|P^{(0)}_{\mathbb{n}'}-P^{(0)}_{\mathbb{n}}\right|\ \left|\langle\mathbb{n}'|\,\xi^x\,|\mathbb{n}\rangle\right|\\
&\qquad\times\left|\Im\left(\int_0^t d\tau\ e^{i\omega_o\tau}\right)\right|\times\max_{|\mathbb{n}''\rangle,t}\left(\sum_\alpha\left|\langle\nu|\,\mathscr{K}_\alpha(t)\,|\mathbb{n}''\rangle\right|^2\right)\\
&\quad= 4B_1\sum_{\omega_o}\sum_{\mathbb{n},\mathbb{n}'}\delta_{\omega_o,\epsilon_{\mathbb{n}'}-\epsilon_{\mathbb{n}}}\delta_{+1,M_{\mathbb{n}'}-M_{\mathbb{n}}}\left|P^{(0)}_{\mathbb{n}'}-P^{(0)}_{\mathbb{n}}\right|\ \left|\langle\mathbb{n}'|\,\xi^x\,|\mathbb{n}\rangle\right|\\
&\qquad\times\left|\frac{\cos(\omega_o t)-1}{\omega_o}\right|\times\max_{|\mathbb{n}''\rangle,t}\left(\sum_\alpha\left|\langle\nu|\,\mathscr{K}_\alpha(t)\,|\mathbb{n}''\rangle\right|^2\right)\ . \qquad (C.20)
\end{aligned}$$

Given that $\xi^x = -\sum_i\gamma_i S_i^x$, (19.3), we thus have

$$\begin{aligned}
&\left|\sum_\alpha\int_0^t d\tau\ \left\langle\nu\middle|\mathscr{K}_\alpha(t-\tau)\left[\mathcal{A}(\tau)\varrho^{(0)}(0)\right]\mathscr{K}_\alpha^\dagger(t-\tau)\middle|\nu\right\rangle\right|\\
&\quad\leq 4\sum_{\omega_o}\sum_{\mathbb{n},\mathbb{n}'}\delta_{\omega_o,\epsilon_{\mathbb{n}'}-\epsilon_{\mathbb{n}}}\delta_{+1,M_{\mathbb{n}'}-M_{\mathbb{n}}}\left|P^{(0)}_{\mathbb{n}'}-P^{(0)}_{\mathbb{n}}\right|\ \left(\sum_i\frac{|\omega_1(i)|}{|\omega_o|}\left|\langle\mathbb{n}'|\,S_i^x\,|\mathbb{n}\rangle\right|\right)\\
&\qquad\times\left|\cos(\omega_o t)-1\right|\times\max_{|\mathbb{n}''\rangle,t}\left(\sum_\alpha\left|\langle\nu|\,\mathscr{K}_\alpha(t)\,|\mathbb{n}''\rangle\right|^2\right) \qquad (C.21)
\end{aligned}$$

where $|\omega_1(i)|\equiv|\gamma_i|\,B_1$. If the spin configurations in the states $|\mathbb{n}\rangle$ and $|\mathbb{n}'\rangle$ are such the $i-$th spin is the only spin which alters its spin state so that: 1) $\langle\mathbb{n}'|\,S_i^x\,|\mathbb{n}\rangle\neq 0$, 2) $\omega_o=\epsilon_{\mathbb{n}'}-\epsilon_{\mathbb{n}}$ and 3) $1=M_{\mathbb{n}'}-M_{\mathbb{n}}$, then it follows from (22.20) that $|\omega_o|\approx|\gamma_i|\,B_o$. This implies that for all the nonzero terms on the r.h.s.

of (C.21), $\left|\frac{\omega_1(i)}{\omega_o}\right| \approx \frac{B_1}{B_o} \ll 1$. In high-resolution NMR [33], for example, the ratio $\frac{B_1}{B_o}$ is in the order of 10^{-6}. Note also that all the factors multiplying the sum $\left(4\sum_i \frac{|\omega_1(i)|}{|\omega_o|} |\langle\mathbb{n}'| S_i^x |\mathbb{n}\rangle|\right)$ are all positive numbers which are at most equal to unity, and almost all of them can be compared to a counterpart on the l.h.s. of (C.17). Indeed, it may be argued that the validity of the inequality in (C.17) pivots on the ratio $\frac{B_1}{B_o}$. In fact,

$$\sum_\alpha \left\langle \nu \middle| \mathscr{K}_\alpha(t)\varrho^{(0)}(0)\mathscr{K}_\alpha^\dagger(t) \middle| \nu \right\rangle = \sum_{\mathbb{n}} P_{\mathbb{n}}^{(0)} \left(\sum_\alpha |\langle\nu| \mathscr{K}_\alpha(t) |\mathbb{n}\rangle|^2\right) \tag{C.22}$$

so,

$$\begin{aligned} \sum_{\mathbb{n}} P_{\mathbb{n}}^{(0)} \left(\sum_\alpha |\langle\nu| \mathscr{K}_\alpha(t) |\mathbb{n}\rangle|^2\right) \gg 4 \sum_{\mathbb{n},\mathbb{n}'} \sum_{\omega_o} \delta_{\omega_o,\epsilon_{\mathbb{n}'}-\epsilon_{\mathbb{n}}} \delta_{+1,M_{\mathbb{n}'}-M_{\mathbb{n}}} \left|P_{\mathbb{n}'}^{(0)} - P_{\mathbb{n}}^{(0)}\right| \left(\sum_i \frac{|\omega_1(i)|}{|\omega_o|} |\langle\mathbb{n}'| S_i^x |\mathbb{n}\rangle|\right) \\ \times |\cos(\omega_o t) - 1| \times \max_{|\mathbb{n}''\rangle,t} \left(\sum_\alpha |\langle\nu| \mathscr{K}_\alpha(t) |\mathbb{n}''\rangle|^2\right) \end{aligned} \tag{C.23}$$

for the non-null Boltzmann state $\varrho^{(0)}(0)$, due to the fact that $\frac{|\omega_1(i)|}{|\omega_o|} \ll 1$ (recall $\omega_o \neq 0$). This confirms the inequality stated in (C.17). Therefore, $\Lambda(t)$ is a non-UDM with domain $\mathsf{C}_d^{+,1}[\varrho^{(0)}(0)]$ (19.80).

C.4 On restricting $\Lambda(t)$ to its specified domain

As discussed in Sec. 19.3.2, without the term $\mathcal{A}(t)\varrho^{(0)}(0)$ in (19.68) (or (C.1)), $\Lambda(t)$ is obviously a UDM, and therefore also CP. We have seen in the last subsection an argument indicating why $\Lambda(t)$ is positive for input states

$$\varrho^{(0)}(0) = \frac{e^{-\beta\mathscr{Z}_o}}{\mathrm{Tr}[e^{-\beta\mathscr{Z}_o}]} \tag{C.24}$$

with $\mathscr{Z}_o$ given by (19.17), i.e.

$$\mathscr{Z}_o \equiv -\sum_i \gamma_i B_o S_i^z + \sum_{i>j} T_{ij} S_i^z S_j^z \ . \tag{C.25}$$

It is vital the input states are restricted to (C.24), else one risks obtaining unphysical results. We can see this by studying, for example, $\Lambda(t)$ in the limit $\mathcal{L} \to 0$ (this is close to taking the adiabatic process limit). Then, $\Lambda(t)$ reduces to

$$\Lambda(t) = \mathbb{I} + \int_0^t d\tau\ \mathcal{A}(\tau) = \mathbb{I} + \mathcal{F}(t) \tag{C.26}$$

where, for an operator X,

$$\mathcal{F}(t)X = -i\,[K(t), X] \ , \qquad K(t) \equiv \int_0^t d\tau\ H_{LR}(\tau) \tag{C.27}$$

where $H_{LR}(t)$ is the linear response Hamiltonian, (19.70). Consequently, with $\mathcal{L} = 0$,

$$\varrho^{(0)}(t) = \Lambda(t)\varrho^{(0)}(0) \tag{C.28a}$$

$$= \varrho^{(0)}(0) - i\left[K(t), \varrho^{(0)}(0)\right] \tag{C.28b}$$

$$= [\mathbb{I} - iK(t)]\,\varrho^{(0)}(0)\,[\mathbb{I} + iK(t)] - K(t)\varrho^{(0)}(0)K(t) \ . \tag{C.28c}$$

(This equation can also be derived from (C.12) by noting that $\sum_\alpha \mathscr{K}_\alpha(t) X \mathscr{K}_\alpha^\dagger(t) \to X$ as $\mathcal{L} \to 0$.) The resulting $\varrho^{(0)}(t)$ in (C.28c) is still the difference between two positive operators, so it cannot be positive for an arbitrary input state – unless extra information or assumptions are provided. Nonetheless, it has the Kraus operator sum representation for Hermitian non-CP maps [145], and satisfies the related trace preserving condition [145] – namely,

$$[\mathbb{I} - iK(t)]^\dagger \, [\mathbb{I} - iK(t)] - K^\dagger(t) K(t) = \mathbb{I} \; . \tag{C.29}$$

These last two observations notwithstanding, the action of the map $\Lambda(t)$ needs to be restricted to its specified domain, i.e. (C.24). As mentioned above, failing to do so may lead to unphysical results. To illustrate this very important point, we shall analyze (C.28c) under two scenarios: 1) without considering (C.24)[3] , and 2) taking into account (C.24). These arguments reinforce the notion that $\Lambda(t)$ is non-UDM.

C.4.1 Analyzing (C.28c) without taking into account (C.24)

For example, if $\varrho^{(0)}(0)$ is taken to be a pure state, *i.e.* $\varrho^{(0)}(0) = |0\rangle\langle 0|$, and we do not take into account (C.24), it can be shown that $\varrho^{(0)}(t)$ in (C.28c) would appear in this case to be nonpositive for $K(t) \neq 0$. Thus, $\Lambda(t)$ would describe an unphysical process.

To prove the proposition, we first observe that with $\varrho^{(0)}(0) = |0\rangle\langle 0|$, (C.28c) may be rewritten as

$$\varrho^{(0)}(t) = |v_1\rangle\langle v_1| - |v_o\rangle\langle v_o| \tag{C.30}$$

where

$$|v_o\rangle \equiv K(t)\,|0\rangle \;\; , \qquad |v_1\rangle \equiv [\mathbb{I} - iK(t)]\,|0\rangle = |0\rangle - i\,|v_o\rangle \tag{C.31}$$

whose norms are

$$\| |v_o\rangle \| = \sqrt{\langle 0|\, K(t)^2 \,|0\rangle} \; , \qquad \| |v_1\rangle \| = \sqrt{1 + \langle 0|\, K(t)^2 \,|0\rangle} \tag{C.32}$$

– where we have exploited the fact that $K(t)$, (C.27), is Hermitian. For non-null $K(t)$ (which is the case if $H_{LR}(t)$ is nonzero), $\| |v_o\rangle \|$ is strictly positive, *i.e.* $\| |v_o\rangle \| > 0$.

Let $x = \sqrt{\langle 0|\, K(t)^2 \,|0\rangle}$ and $K(t) \neq 0$. Furthermore, let $|\widetilde{v_o}\rangle$ and $|\widetilde{v_1}\rangle$ be the normalized kets corresponding to $|v_o\rangle$ and $|v_1\rangle$, respectively – that is, $|\widetilde{v_o}\rangle \equiv \frac{|v_o\rangle}{\||v_o\rangle\|}$ and $|\widetilde{v_1}\rangle \equiv \frac{|v_1\rangle}{\||v_1\rangle\|}$. Then, (C.30) may be rewritten as

$$\varrho^{(0)}(t) = (1 + x^2) \left[|\widetilde{v_1}\rangle \, \langle \widetilde{v_1}| - \frac{x^2}{1 + x^2} \, |\widetilde{v_o}\rangle \, \langle \widetilde{v_o}| \right] \; . \tag{C.33}$$

We may expand $|\widetilde{v_1}\rangle$ as

$$|\widetilde{v_1}\rangle = \alpha \, |\widetilde{v_o}\rangle + \beta \, |\widetilde{v_{o\perp}}\rangle \tag{C.34}$$

where $|\widetilde{v_{o\perp}}\rangle$ is the normalized ket perpendicular to $|\widetilde{v_o}\rangle$, while α and β are complex scalars which also satisfy the condition $|\alpha|^2 + |\beta|^2 = 1$. Substituting (C.34) into (C.33) yields

$$\varrho^{(0)}(t) = (1 + x^2) \left[\left(|\alpha|^2 - \frac{x^2}{1 + x^2} \right) |\widetilde{v_o}\rangle \, \langle \widetilde{v_o}| + \alpha\beta^* \, |\widetilde{v_o}\rangle \, \langle \widetilde{v_{o\perp}}| + \alpha^*\beta \, |\widetilde{v_{o\perp}}\rangle \, \langle \widetilde{v_o}| + |\beta|^2 \, |\widetilde{v_{o\perp}}\rangle \, \langle \widetilde{v_{o\perp}}| \right] \tag{C.35}$$

---

[3] The argument to be laid out in the next subsection to illustrate this point is a paraphrase of an argument originally put forward by Prof. Vittorio Giovannetti in the course of private discussions with the author. All errors are that of the author alone.

– which in matrix form simply becomes

$$\varrho^{(0)}(t) = (1+x^2)\begin{bmatrix} \left(|\alpha|^2 - \frac{x^2}{1+x^2}\right) & \alpha\beta^* \\ \alpha^*\beta & |\beta|^2 \end{bmatrix} . \tag{C.36}$$

From this last equation, it follows that the determinant of $\varrho^{(0)}(t)$ is

$$\det[\varrho^{(0)}(t)] = -x^2(1+x^2)\,|\beta|^2 \ . \tag{C.37}$$

Thus, $\det[\varrho^{(0)}(t)] < 0$ since $x > 0$ for non-null $K(t)$. So, for $\mathcal{L} = 0$ and $\mathcal{A}(t) \neq 0$, the map $\Lambda(t)$ would blatantly describe an unphysical process for a pure input state.

Note, however, that – according to (C.26) – for $K(t) = 0$, while $\mathcal{L} = 0$, $\Lambda(t)$ simply becomes the identity operator $\mathbb{I}$. As we shall see in the next subsection, it turns out that this is actually the case if $\varrho^{(0)}(0)$ is pure and we take into account (C.24).

C.4.2 Analyzing (C.28c) taking into account (C.24)

On a closer examination, if we restrict the input states to $\Lambda(t)$'s domain, i.e. (C.24), we realize that $\varrho^{(0)}(0)$ cannot be a pure state unless *all* the particles composing the chemical species have zero spin quantum number (examples are ^{16}O and ^{12}C nuclei). For such a system, it can be shown that $K(t)$ becomes identically zero, therefore, making $\mathcal{A}(t) = 0$ and $\Lambda(t) = \mathbb{I}$.

To prove the last proposition, let us recall that $H_{LR}(t)$, (19.70), is defined as

$$H_{LR}(t) = 2B_1\Re[\varphi_f(t)]\sum_{\omega_o} e^{-i\omega_o t}\xi^x(+1,\omega_o) + h.c. \tag{C.38}$$

where, according to (19.40),

$$\xi^x(+1,\omega_o) = \sum_{\mathbb{m},\mathbb{m}'} |\mathbb{m}\rangle\,\langle\mathbb{m}|\,\xi^x\,|\mathbb{m}'\rangle\,\langle\mathbb{m}'|\,\delta_{\omega_o,\epsilon_{\mathbb{m}'}-\epsilon_{\mathbb{m}}}\delta_{+1,M_{\mathbb{m}'}-M_{\mathbb{m}}} \ . \tag{C.39}$$

In addition, we know from (19.3) that

$$\xi^x = -\sum_i \gamma_i S_i^x \ . \tag{C.40}$$

The operator ξ^x is therefore a zero-trace operator.

Now, if we set $\varrho(0) = |0\rangle\langle 0|$, then we are somehow admitting that the spin system in question is a collection of spin zero particles, and $|0\rangle$ is the (spin) state vector of the collection (up to a phase-factor). In this case, we easily deduce from (C.39) that

$$\xi^x(+1,\omega_o) = \delta_{\omega_o,0}\delta_{+1,0}\mathrm{Tr}[\xi^x]\,|0\rangle\langle 0| \tag{C.41}$$

which is identically zero. Consequently, $H_{LR}(t)$ and $K(t)$ also become identically zero. And as a result, $\Lambda(t) \to \mathbb{I}$.

We may also note that for a non-entirely-spin-zero system, $\varrho^{(0)}(0)$ *approaches* a pure spin state when T(temperature) $\to 0$ and/or $B_o \to \infty$. In any case, even under these extreme conditions, it is mathematically impossible for $\varrho^{(0)}(0)$ of a non-entirely-zero-spin system – as defined in (C.24) – to be of rank 1 (thus, a pure state).

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