Molecular Quantum Electrodynamics at Finite Temperatures: Applications to Nuclear Magnetic Resonance.

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In this document it is shown that the chemical shift, spin-spin couplings and return to equilibrium observed in Nuclear Magnetic Resonance (NMR) are naturally contained in the realtime nuclear spin dynamics, if the dynamics is calculated directly from molecular Quantum Electrodynamics at finite temperatures. Thus, no effective NMR parameters or relaxation superoperators are used for the calculation of continuous NMR spectra. This provides a basis for the repeal of Ramsey’s theory from the 1950s, NMR relaxation theory and later developments which form the current basis for NMR theory. The presented approach replaces the discrete spectrum of the effective spin model by a continuous spectrum, whose numerical calculation is enabled by the usage of the mathematical structure of algebraic Quantum Field Theory. While the findings are demonstrated for the hydrogen atom, it is outlined that the approach can be applied to any molecular system for which the electronic structure can be calculated by using a common quantum chemical method. Thus, the presented approach has potential for an improved NMR data analysis and more accurate predictions for hyperpolarized Magnetic Resonance Imaging.

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I. INTRODUCTION

Nuclear Magnetic Resonance (NMR) spectroscopy is one of the most used and most advanced methods for molecular structure determination and has many applications in pharmacy, chemistry and nano science [1], [2]. Hyperpolarized Magnetic Resonance Imaging (hMRI) is a related technique which aims at the introduction of new diagnostic and therapeutic methods in biomedical imaging and medicine [3], [4]. Prominent applications of hMRI include the early stage detection of cancer [5]. The quantum mechanical calculation of the nuclear spin dynamics and of effective NMR parameter provided helpful predictions and interpretations of experimental NMR spectra [6], [7] [8] and crucially assists the development of potential pharmaceuticals [9]. The very large number of publications (2,020,000 for searching ”NMR theory” in google scholar) using or improving NMR-theory indicates the importance for the development of advanced theoretical frameworks for NMR.
Actual theoretical approaches to investigate NMR spectra involve effective NMR-parameters, e. g. the magnetic shielding tensor \( \sigma \) and spin-spin coupling constants \( J_{ij} \). In common spin-dynamics simulations these parameters are used in the effective spin Hamiltonian:\[10], [11].

\[
H_{\text{eff}} = -\sum \gamma_i \vec{I}_i (1 - \sigma_i) \vec{B}_{\text{ext}} + 2\pi \sum_{i<j} J_{ij} \vec{I}_i \cdot \vec{I}_j + \sum_{i<j} \vec{I}_i D_{ij} \vec{I}_j. \tag{1}
\]

\( D_{ij} \) is a tensor describing the magnetic dipole-dipole interaction between the nuclear spins \( \vec{I}_i \) and \( \vec{I}_j \). \( \vec{B}_{\text{ext}} \) is a classical, external magnetic field and \( \gamma \) is the gyromagnetic ratio. In the most widely used approach the effective parameters are calculated according to second order derivatives of the ground state energy (Taylor-expansion) [10]:

\[
\langle a_{\alpha\beta} \rangle \equiv \frac{\partial^2 E_0}{\partial \mu_i^\alpha \partial B^\beta} \quad \text{and} \quad \langle J_{ij} \rangle = \hbar \gamma_i \gamma_j \frac{\partial^2 E_0}{\partial \mu_i^\alpha \partial \mu_j^\beta}. \tag{2}
\]

Many applications of eq. (2) can be found in chemistry, pharmacy and nano science [6], [7], [8], [9]. During the last decades there were done many works on the optimization of eq. (2) by including relativistic [14], [15], [16] and QED effects [17], [18], [19], [20] to the effective NMR parameters. Also numerically more efficient alternatives were introduced [21], [22]. At this point it should be noticed that all of the mentioned investigations were worked out within the effective NMR description and calculated effective NMR parameters \( \sigma \) and \( J_{ij} \). This is in contrast to the presented method which replaces the effective description by a non-effective description.

Thermalization (return to equilibrium) plays a further central role in NMR. The unitary dynamics generated by [1] has bad thermalization properties. Small systems consisting of a few spins does not thermalize at all and larger systems thermalize only approximately in very specific cases [23]. In order to include return to equilibrium anyway the von Neumann equation was modified phenomenologically by introducing relaxation superoperators \( \Gamma \) [24], [25]:

\[
\frac{d\rho(t)}{dt} = -\frac{i}{\hbar} [H_{\text{eff}}, \rho(t)] - \Gamma(\rho(t) - \rho_0). \tag{3}
\]

The final state \( \rho_0 \) to which the system shall evolve must be chosen "by hand". Certainly, it is preferable when the correct final state is an outcome and not an input of a theory. Thus, the effective spin system eq. (1), (2) and (3) were successfully applied in various research fields. However, there are also several weak points of the effective description:

(I) While NMR-experiments provide continuous spectra, the effective model in eq. (1) possesses a discrete spectrum. The analysis of an NMR-spectrum using a discrete spectrum may be a suitable approximation if the experimental NMR-spectrum contains only very sharp peaks. However, in many experiments certain lineshapes and linewidths occur which cannot adequately be described by a discrete set of numbers. Up-to-date methods for NMR lineshape analysis (e. g. Bloch-McConnell equations) are strongly phenomenological and neglect completely the causal connection between the microscopic structure and the lineshape [26].

(II) A basic reason for the occurrence of line broadening in NMR spectra are delocalized nuclei due to rotational and vibrational degrees of freedom as well as proton exchange. Since the effective model describes nuclei as fixed point particles a detailed investigation of these effects is not possible within the effective description [27].

(III) There is no unique procedure for the construction of relaxation superoperators \( \Gamma \) and at least some constructions are unable to reproduce the for hMRI very important lifetimes of "long-lived singluett spin states" (LLSSs) exceeding \( T_1 \) [28]. Additionally, the construction of \( \Gamma \) often requires experimentally estimated parameters which limits the predictive power [29].

(IV) The Fourier transformation of the unitary dynamics from the effective model provides "\( \delta \)-peaks" with infinite amplitudes. On the contrary the values of the finite amplitudes in NMR-spectra contain important information.

(V) The thermal equilibrium state associated with eq. (1) is at room temperature nearly independent from the temperature. Although small changes in the temperature close to room temperature can cause significant and important changes in experimental NMR spectra [30].

(VI) Indeed, effects from the quantized nature of the electromagnetic field are expected if a small number of photons is involved in a process. Since an exited nuclear spin in NMR has absorbed the energy of one photon from the pulse sequence one may expected that quantum radiative corrections occur in NMR. In the effective model eq. (1) quantum radiative corrections can only be considered as corrections to effective NMR-parameters. However, the variety of effects from quantized fields can only be fully included in the unitary QED dynamics.
The usage of a continuous spectrum from mQED to analyze and predict NMR or hMRI experiments may have striking advantages compared to the effective description:

(I) In mQED there would be a direct and causal connection between NMR lineshapes and molecular structures.

(II) Rotations and vibrations of molecular groups can be included in the (approximated) nuclear wave function. Hence, the simplification that nuclei are fixed point particles can be repealed.

(III) Thermal equilibration is a consequence of the continuous spectrum, naturally contained in the unitary QED spin-dynamics \([31], [32]\), and based on the molecular structure instead on phenomenological parameters. Hence, life-times of LLSSs and thermalization in general may be analyzed and predicted more accurately.

(IV) Finite amplitudes and line widths would occur naturally based on physical interactions instead of phenomenological parameters.

(V) The drawback of a nearly temperature-independent initial state could be repealed and a nuclear wave function with sound temperature-dependence can be used instead.

(VI) The unitary, realtime nuclear spin-dynamics calculated directly from mQED at finite temperatures provides a much better handling of quantum radiative corrections than possible with the effective model.

The occurrence of divergences in perturbation series involving quantized fields and the infinite number of field quanta involved in finite temperature QED processes are two basic challenges for numerical calculations. Recent works investigated and avoided the occurrence of divergences by introducing IR- and UV-cutoffs \([33], [34], [32]\). It remained to show which effect these cutoffs have on expectation values. Recently, a perturbation series for interacting, massive quantum fields was constructed by Fredenhagen and Lindner \([35]\). This approach solved a fundamental and longstanding problem in Mathematical Physics and its extension to the Dirac field is of interest for relativistic effects from heavy nuclei in NMR. Further important structural developments were achieved in \([36]\).

In certain cases one may avoid the numerical and mathematical problems related to quantized fields at finite temperatures by using the ground state instead \([37], [38]\). However, in NMR at room temperature the nuclear spins are far away from their ground state and the temperature of the quantized electromagnetic field determines the temperature of the final state of the nuclear spins after equilibration \([32]\). Hence, the approach of using a ground state for the quantized electromagnetic field is obviously unsuitable for NMR and hMRI at room temperature. There are several works on a method called Thermo Field Dynamics (TFD) \([39], [40], [41]\) which is about quantized fields at finite temperatures. While this approach is widely used it also involves a large number of field quanta in the construction of the thermal state \(| O(\beta) \rangle \):\n
\[
| O(\beta) \rangle = Z(\beta)^{-1/2} \sum_n e^{-\beta E_n/2} | n, \tilde{n} \rangle
= Z(\beta)^{-1/2} \sum_n \frac{e^{-\beta E_n/2}}{n!} (a^\dagger)^n (\tilde{a}^\dagger)^n | 0, \tilde{0} \rangle.
\]

| n, \tilde{n} \rangle is an Eigenstate of the Hamiltonian, \(a^\dagger \) and \(\tilde{a}^\dagger \) are creation operators and | 0, \tilde{0} \rangle is a vacuum state. Hence, the calculation of an expectation value in this state involves a relatively large number of photons in the numerical calculations. Furthermore, the state \(| O(\beta) \rangle \) in eq. (4) is constructed using a discrete set of energy values \(E_n \) while the free quantized electromagnetic field posses a continuous energy spectrum \(E(\vec{k}) = \hbar c | \vec{k} | \) with \(\vec{k} \in \mathbb{R}^3\). An extension of eq. (4) to the continuous case is not possible. As it turns out later in the document a continuous spectrum is of paramount importance for the NMR application. Hence, TFD is not suitable for the calculation of NMR-spectra. Furthermore, in TFD also the field operators posses a temperature dependence,\n
\[
a(\beta) = U(\beta) a U^\dagger(\beta), \text{ where } U(\beta) = e^{-\theta(\beta)(\tilde{a}a - \tilde{a}^\dagger a^\dagger)} \text{ and } \theta(\beta) = \cos^{-1} \left( \frac{1}{\sqrt{1 + e^{-\beta \pi}}} \right), \tag{5}
\]

which further complicates numerical calculations. In this document we do not follow the TFD approach at all and use a different approach originating from the mathematical structure of algebraic Quantum Field Theory (aQFT). It is shown that a purified form of the Araki-Woods representation \([42]\), denoted by \((\Omega_{\text{AW}}, \pi_{\text{AW}}^\beta)\), enables the numerical calculations involving bosonic fields at finite temperatures with striking advantages: In each order of the perturbation series at most one "Araki-Woods boson" is produced while small coupling constants, connecting spins and the quantized electromagnetic field, reduce higher order contributions. This is due to the structure of the vector representative \(\Omega_{\text{AW}}\) and the action of the field operators \(\pi_{\text{AW}}^\beta(a_1(f))\) and \(\pi_{\text{AW}}^\beta(a_2(f))\) on \(\Omega_{\text{AW}}\). The representation \((\Omega_{\text{AW}}, \pi_{\text{AW}}^\beta)\) rigorously respects the continuous energy spectrum of the quantized electromagnetic field at finite temperatures and reduces the required computational resources for numerical calculations strongly.
II. MOLECULAR QUANTUM ELECTRODYNAMICS

In order to use the perturbation theory developed by Araki, Bratelli, Robinson and Kishimoto the Hamiltonian will be separated into \( H = H_0 + H_{\text{Int.}} \). The physical system will be described by a combination of a Pauli-Fierz and a generalized Spin-Bose model in Coulomb gauge \([31], [53]\). The resulting molecular QED Hamiltonian is given by

\[
H_0 = -\left( \sum_{j=1}^{K} \gamma_j \hat{I}_j + \sum_{i=1}^{E} \mu_{ij} \right) \cdot \vec{B}_{\text{ext}} + \hbar \sum_{\lambda=1,2} \int_{\mathbb{R}^3} d^3k \omega(k) a_{\lambda}(k, \lambda) a(k, \lambda) + \sum_{i=1}^{E} \frac{\vec{p}_i^2}{2m_e} + \sum_{j=1}^{K} \frac{\vec{p}_j^2}{2M_j} + V(X^e, X) \tag{6}
\]

and

\[
H_{\text{Int}} = -\sum_{j=1}^{K} \gamma_j \hat{I}_j \cdot \vec{B}_\varphi(\vec{x}_j^0) + \sum_{i=1}^{E} \left( \frac{e^2}{m_e} \vec{A}_\varphi(\vec{x}_i^0) \cdot \nabla \psi_i + \frac{e^2}{2m_e} (\vec{A}_\varphi(\vec{x}_i^0))^2 - \mu_{ij} \cdot \vec{B}_\varphi(\vec{x}_i^0) \right). \tag{7}
\]

The first term in \( H_0 \) couples the \( K \) nuclear spins \( \hat{I}_j \) and the \( E \) total magnetic moments \( \mu_{ij} = -\mu_B / (g_e \delta_i + \vec{l}_i) \) of the electrons to the classical, external magnetic field \( \vec{B}_{\text{ext}} \). For high field strengths of the external magnetic field, i.e., \( B_{\text{ext}}^2 > 3T \), spin-orbit couplings can be neglected due to the Paschen-Back effect. The second term describes the energy of the quantized, electromagnetic field. \( a^\ast(k, \lambda) \) and \( a(k, \lambda) \) are the common creation and annihilation operators with commutation relations

\[
[a(k, \lambda), a^\ast(k', \lambda')] = \delta(k - k') \delta_{\lambda, \lambda'}, \quad [a(k, \lambda), a(k', \lambda')] = 0, \quad \text{and} \quad [a^\ast(k, \lambda), a^\ast(k', \lambda')] = 0 \tag{8}
\]

and with momentum \( \vec{k} \in \mathbb{R}^3 \) and polarization \( \lambda = 1,2 \). The last three terms provide the non-relativistic Schrödinger-Operator. Thus, \( \vec{p}_i \) is the momentum operator of electron \( i \), \( \vec{P}_j \) is the momentum operator of nucleus \( j \) and the potential \( V(X^e, X) \) depending on coordinates \( X^e \) of \( E \) electrons and \( X \) of \( K \) nuclei is given by

\[
V(X^e, X) = \sum_{i<j}^{E} \frac{e^2}{4\pi \varepsilon_0 \varepsilon_{ij}} - \sum_{i=1}^{E} \sum_{j=1}^{K} \frac{Z_j e^2}{4\pi \varepsilon_0 \| \vec{x}_i^0 - \vec{x}_j^0 \|} + \sum_{i<j}^{K} Z_i Z_j e^2. \tag{9}
\]

\( Z_j \) is the number of protons in nucleus \( j \), \( \vec{x}_i^0 \) is the coordinate of electron \( i \) and \( \vec{x}_j^0 \) of nucleus \( j \). \( x_{ij}^e \) and \( x_{ij}^a \) are the distances between electrons or nuclei and the other constants can be found in the literature \([43]\). \( H_{\text{Int}} \) couples the independent terms and enables energy exchange between the nuclear spins and the rest of the system. We use the definition \( \vec{A}_\varphi(\vec{x}_j^0) = \vec{A}_{\varphi}(\vec{x}_j^0, 0) \) and for the quantized vector potential the free time evolution provides

\[
\vec{A}_{\varphi}(\vec{x}, t) = \sqrt{\frac{\hbar}{2e\varepsilon_0(2\pi)^3}} \sum_{\lambda=1,2} \int_{\mathbb{R}^3} d^3k \hat{e}_\lambda(\vec{k}) \frac{\varphi(\vec{k})}{\sqrt{\omega(\vec{k})}} \left( e^{-i\vec{k}\hat{e}_\lambda(\vec{k})t} a^\ast_{\lambda}(\vec{k}) + e^{i\vec{k}\hat{e}_\lambda(\vec{k})t} a_{\lambda}(\vec{k}) \right). \tag{10}
\]

The quantized magnetic field is given by \( \vec{B}_\varphi = \vec{\nabla} \times \vec{A}_\varphi \) and we have

\[
\vec{B}_{\varphi}(\vec{x}, t) = i\sqrt{\frac{\hbar}{2e\varepsilon_0(2\pi)^3}} \sum_{\lambda=1,2} \int_{\mathbb{R}^3} d^3k \hat{e}_\lambda(\vec{k}) \times \hat{e}_\lambda(\vec{k}) \frac{\varphi(\vec{k})}{\sqrt{\omega(\vec{k})}} \left( e^{-i\vec{k}\hat{e}_\lambda(\vec{k})t} a^\ast_{\lambda}(\vec{k}) - e^{i\vec{k}\hat{e}_\lambda(\vec{k})t} a_{\lambda}(\vec{k}) \right), \tag{11}
\]

where \( \varphi \in L^2(\mathbb{R}^3) \) is the coupling function with suitable IR and UV behavior \([31], [43], [44]\) to prevent divergences in the individual terms of the perturbation series. The presented model is independent of a specific choice of the polarization vectors. Using the notation \( x = (\vec{x}, t), k = (\vec{k}, \omega(\vec{k})) \) and Einstein’s sum convention \( k^\mu x_\mu = \vec{k} \cdot \vec{x} - \omega(\vec{k}) t \) we have

\[
[B_{\varphi}^\alpha(x), B_{\varphi}^\gamma(y)] = -\sum_{\lambda=1,2} \int d^3k \varphi^\alpha(\vec{k}) \varphi^\gamma(\vec{k}) \Delta_k (x - y) \tag{12}
\]

with \( \varphi^\alpha(\vec{k}) = (\sqrt{\hbar/\varepsilon_0}) \varphi(\vec{k}) (\vec{k} \times \hat{e}_\lambda(\vec{k}))^\alpha, \alpha, \gamma = x, y, z \) and

\[
i\Delta_k (x - y) = \frac{e^{-ik(\mu_\mu - y_\mu)} - e^{ik(\mu_\mu - y_\mu)}}{(2\pi)^3 2\omega(\vec{k})}. \tag{13}
\]

Since the commutator function is linked to the Feynman propagator we will have the interpretation for the probability for the propagation of field quanta between the nuclear spins located at \( x \) and \( y \).
III. ALGEBRAIC QUANTUM FIELD THEORY

Operator algebras are central objects in the algebraic reformulation of Quantum Statistical Mechanics and Quantum Field Theory. Several structural elements of operator algebras are required for the numerical calculations in the application of mQED at finite temperatures to NMR. Therefore, some mathematical basics of operator algebras are briefly reviewed in [15] and [16] before the Field Theory is described.

**Basics of Operator Algebras.** The commutant of an algebra $\mathfrak{A}$ is denoted by $\mathfrak{A}'$ and we have $(\mathfrak{A}')' = \mathfrak{A}''$. The set of bounded operators on a Hilbert space $\mathfrak{H}$ is denoted by $\mathfrak{B}(\mathfrak{H})$.

**Definition 1:** A von Neumann algebra on a Hilbert space $\mathfrak{H}$ is a $^*$-subalgebra $\mathfrak{M}$ of $\mathfrak{B}(\mathfrak{H})$ such that
\[
\mathfrak{M} = \mathfrak{M}''.
\] (14)

The terminology $W^*$-algebra is often used for the abstractly defined algebra and then the name von Neumann algebra is reserved for the operator algebras. Note that a $C^*$-algebra is a closed set in the norm topology and a $W^*$-algebra is weakly closed. A bounded observable $A$ is a selfadjoint element of a $C^*$- or a $W^*$-algebra $\mathfrak{A}$. A $^*$-morphism $\pi$ between two $^*$-algebras $\mathfrak{C}$ and $\mathfrak{B}$ is defined as a mapping $\pi: A \in \mathfrak{C} \rightarrow \pi(A) \in \mathfrak{B}$ for all $A \in \mathfrak{C}$ such that $\pi(\alpha A + \gamma C) = \alpha \pi(A) + \gamma \pi(C)$, $\pi(AC) = \pi(A) \pi(C)$, and $\pi(A^*) = \pi(A)^*$ for all $A, C \in \mathfrak{C}$ and $\alpha, \gamma \in \mathbb{C}$. The kernel of a $^*$-morphism is given by the set $\text{ker}(\pi) = \{ A \in \mathfrak{A} \mid \pi(A) = 0 \}$. A state $\omega$ is a positive, normalized, and linear functional on $\mathfrak{A}$, i.e., $\omega \in \mathfrak{A}^*$, where $\mathfrak{A}^*$ is the dual of $\mathfrak{A}$. An expectation value is given by $\omega(A) = \langle \psi_\omega, \pi(A) \psi_\omega \rangle$, where $\psi_\omega: \mathfrak{H} \rightarrow \mathfrak{B}(\mathfrak{H})$ and $\psi_\omega \in \mathfrak{H}_\omega$, where the index $\omega$ denotes the association of the representation $(\mathfrak{H}_\omega, \pi_\omega)$ with the state $\omega$. The space $\mathfrak{H}_\omega$ is called the representation space and the operator examples $\pi(A)$ are called the representatives of $\mathfrak{A}$. The representation is said to be faithful if and only if, $\pi_\omega$ is a $^*$-isomorphism between $\mathfrak{A}$ and $\pi(\mathfrak{A})$, i.e., if, and only if, $\text{ker}(\pi_\omega) = \{0\}$. A faithful representation satisfies $\| \pi_\omega(A) \| = \| A \|$, for all $A \in \mathfrak{A}$. If $(\mathfrak{H}, \pi)$ is a representation of the $C^*$-algebra $\mathfrak{A}$ and if $\mathfrak{H}_0$ is a subspace of $\mathfrak{H}$, then $\mathfrak{H}_0$ is said to be invariant under $\pi$ if $\pi(A)\mathfrak{H}_0 \subseteq \mathfrak{H}_0$ for all $A \in \mathfrak{A}$. Hence, if $\mathfrak{H}_0$ is invariant under $\pi$ and $\mathfrak{H}_0^\perp$ is the orthogonal complement of $\mathfrak{H}_0$, i.e., $\mathfrak{H}_0^\perp = \{ \xi \in \mathfrak{H} \mid \langle \xi, \psi \rangle = 0, \forall \psi \in \mathfrak{H}_0 \}$, then we have $\langle \xi, \pi(A) \psi \rangle = 0$ for all $A \in \mathfrak{A}$ and all $\xi \in \mathfrak{H}_0^\perp$, $\psi \in \mathfrak{H}_0$. A $^*$-isomorphism of an algebra $\mathfrak{A}$ into itself is called a $^*$-automorphism $\tau$. The time evolution of a physical system is given by a one-parametric group of $^*$-automorphisms $\tau_t$, which is generated by a derivation $\delta$. Thus, the derivation $\delta$ contains the information of the Hamiltonian $H$ and one formally has $A \mapsto \tau_t(A) = e^{\delta t}(A)$.

**Definition 2:** A $W^*$-dynamical system is a pair $(\mathfrak{M}, \tau)$, where $\mathfrak{M}$ is a $W^*$-algebra and $\tau: G \rightarrow \text{Aut}(\mathfrak{M})$, $G \ni g \rightarrow \tau_g$ is a weakly continuous representation of a locally compact group $G$ as $^*$-automorphisms acting on $\mathfrak{M}$.

Note that a $C^*$-dynamical system $(\mathfrak{A}, \tau)$ is defined in a similar fashion. In this case $\mathfrak{A}$ is a $C^*$-algebra and $\tau$ is a strongly continuous representation of a locally compact group as $^*$-automorphisms acting on $\mathfrak{A}$. In order to proceed with equilibrium states we define the strip $S_\beta = \{ z \in \mathbb{C} \mid 0 < \Im(z) < \beta \}$ and have

**Definition 3:** Let $(\mathfrak{A}, \tau)$ be a $C^*$- or a $W^*$-dynamical system. A state $\omega^\beta$ on $\mathfrak{A}$, supposed to be normal in the $W^*$-case, is a $(\tau, \beta)$-KMS state for some $\beta \in \mathbb{R}^+$ if the following holds. For any $A, B \in \mathfrak{A}$ there exist a function $F_\beta(A, B; z)$ which is analytic on the strip $S_\beta$, continuous on its closure and satisfies the Kubo-Martín-Schwinger condition
\[
F_\beta(A, B; t) = \omega^\beta(A \tau_t(B)) \quad \text{and} \quad F_\beta(A, B; t + i\beta) = \omega^\beta(\tau_t(B)A)
\] (15)
on the boundary of $S_\beta$.

**Description of the field theory.** A single boson is described as a square integrable function $f \in \mathfrak{H} = L^2(\mathbb{R}^3)$ in position or momentum space $\mathbb{R}^3$. The Hilbert space $\mathfrak{H}$ is called the 1-particle Hilbert space. The n-particle Hilbert space $\mathfrak{H}^n$ is given by the n-fold tensor product of $\mathfrak{H}$ with itself, i.e., $\mathfrak{H}^n = \mathfrak{H} \otimes \mathfrak{H} \cdots \otimes \mathfrak{H}$. The projection $P_+ = \mathfrak{H}^n_+ = \bigoplus_{n=0}^{\infty} \mathfrak{H}^n_+$ onto totally symmetric n-particle wave functions reflects that the particles obey the Bose-Einstein statistics. The bosonic Fock-space is then defined by
\[
\mathfrak{F}^0_+ = \bigoplus_{n=0}^{\infty} \mathfrak{H}^n_+.
\] (16)

We have $\mathfrak{H}^0 = \mathbb{C}$ and the vacuum is described by $\Omega_0 = (1, 0, 0, ...) \in \mathfrak{F}^0_+$. The smeared creation and annihilation operators are defined by
\[
a^*_\lambda(f) = \int d^3k \, f(\vec{k}) a^*_\lambda(\vec{k}) \quad \text{and} \quad a_\lambda(f) = \int d^3k \, \vec{f}(\vec{k}) a_\lambda(\vec{k})
\] (17)
for \( f \in \mathcal{H} \). \( a^*_\lambda(\vec{k}) \) and \( a_\lambda(\vec{k}) \) satisfy the commutation relations in eq. (8), which translates to
\[
[a_\lambda(f), a^*_\lambda(g)] = \delta_{\lambda,\lambda'} \langle f | g \rangle_H \quad \text{and} \quad [a_\lambda(f), a_\lambda(g)] = [a^*_\lambda(f), a^*_\lambda(g)] = 0
\]
with scalar product \( \langle \cdot | \cdot \rangle \) on \( \mathcal{H} \) given by
\[
\langle f | g \rangle_H = \int_{\mathbb{R}^3} d^3k \, \bar{f}(k) g(k).
\]

The notation for the quantized magnetic field in section II is recovered by
\[
B^\alpha(x) = \Phi(b^\alpha(x)) \equiv \frac{1}{\sqrt{2}} \sum_{\lambda = 1, 2} (a^*_\lambda(b^\alpha_{\phi\lambda}) + a_\lambda(b^\alpha_{\phi\lambda})).
\]

According to eq. (11) the functions \( b^\alpha_{\phi\lambda} : \mathbb{R}^3 \to \mathbb{C} \) are given by
\[
b^\alpha_{\phi\lambda}(\vec{k}) = i \sqrt{\frac{\hbar}{\varepsilon_0(2\pi)^3}} (\vec{k} \times \vec{\epsilon}_\lambda(\vec{k}))^\alpha \frac{\varphi(\vec{k})}{\sqrt{\omega(\vec{k})}} e^{-i k^\mu x_\mu} \quad \text{and} \quad \alpha = x, y, z.
\]

Since the field operators are unbounded one introduces the bounded Weyl operators
\[
W(f) = \exp(i\Phi(f)), \quad \text{satisfying} \quad W(f)W(g) = e^{-i\Omega(\langle f | g \rangle_H)}W(f + g).
\]

In order to rigorously define equilibrium states the one-particle Hilbert space has to be restricted by \( \mathcal{H}_r = \{ f \in \mathcal{H}; \omega^{-1/2} f \in \mathcal{H} \} \), which ensures a suitable infrared behavior. This basically means to ”reduce or neglect” extremely low energetic photons. However, in this document no infrared divergences were found in the numerical calculations and the restriction of \( b^\alpha_{\phi\lambda} \) to \( \mathcal{H}_r \) can be chosen such that the influence of the restriction on the expectation value is arbitrarily small. We define a \( C^* \)-algebra \( \mathfrak{A}_{EM} \) for the quantized electromagnetic field by
\[
\mathfrak{A}_{EM} = \overline{\text{span}\{W(f); f \in \mathcal{H}_r\}},
\]
where the closure is taken in the uniform norm \( \| \cdot \| \) for bounded operators on the bosonic Fock space \( \mathfrak{F}_+ \). The dispersion relation is given by \( \omega(\vec{k}) = c \, | \vec{k} | \) where \( c \) is the speed of light and the free field Hamiltonian is given by
\[
H_{EM} = d\Gamma(\omega) \equiv \hbar \int_{\mathbb{R}^3} d^3k \omega(\vec{k}) a^*\vec{k})a(\vec{k}).
\]

\( d\Gamma(\omega) \) provides an infinitesimal generator \( \delta_{EM} \), formally given by \( \delta_{EM} = [H_{EM}, \cdot] \), that generates the one-parameter group \( \{\tau^EM_t\}_{t \in \mathbb{R}} \) for the quantized electromagnetic field. This group provides the free field dynamics and the action is given by
\[
W(f) \mapsto \tau^EM_t(W(f)) = W(e^{i\omega t}f) \quad \text{which implies} \quad \Phi(f) \mapsto \tau^EM_t(\Phi(f)) = \Phi(e^{i\omega t}f).
\]

This is also known as Bogoliubov transformation. Note that the group \( \{\tau^EM_t \mid t \in \mathbb{R}\} \) is not strongly continuous because \( \| W(f) - W(g) \| = 2 \forall g \neq f \) and hence \( \langle W(\mathfrak{F}_r), \tau^EM \rangle \) is not a \( C^* \)-dynamical system.

The GNS-representation \( \{\mathfrak{H}_{AW}, \sigma^\beta_{AW}\} \) which is induced by the \( (\tau^EM, \beta) \)-KMS state \( \omega^\beta_{EM} \) on \( \mathfrak{A}_{EM} \) was found by Araki and Woods [12] and is therefore referred as Araki-Woods representation. The representation space is given by
\[
\mathfrak{H}_{AW} = \mathfrak{F}_+(\mathfrak{F}_r) \otimes \mathfrak{F}_+(\mathfrak{F}_r) \otimes \mathfrak{F}_+(\mathfrak{F}_r) \otimes \mathfrak{F}_+(\mathfrak{F}_r),
\]
and the annihilation operators are given by
\[
\pi^\beta_{AW}(a_1(f)) = (a^*\sqrt{1 + \rho^\beta f}) \otimes \hat{1} \otimes \hat{1} + c(\sqrt{\rho^\beta f}) \otimes \hat{1} \otimes \hat{1}
\]
and
\[
\pi^\beta_{AW}(a_2(f)) = \hat{1} \otimes \hat{1} \otimes (a^*\sqrt{1 + \rho^\beta f}) \otimes \hat{1} + \hat{1} \otimes \hat{1} \otimes \hat{1} \otimes c(\sqrt{\rho^\beta f}).
\]
The function $\rho_\beta$ is a physical input which ensures that Planck’s law for the thermal radiation density and Bose-Einstein statistics is satisfied and we have

$$\rho_\beta = \frac{1}{e^{\beta\omega(k)} - 1}. \quad (29)$$

The vector representative $\Omega_{AW} = \Omega_0 \otimes \Omega_0 \otimes \Omega_0 \otimes \Omega_0$ of $\omega_\text{EM}$ is cyclic and separating for the weak closure $\pi_\text{AW}^\beta(\mathfrak{A}_{\text{EM}})''$ of $\mathfrak{A}_{\text{EM}}$ and it turns out that $(\pi_\text{AW}^\beta(\mathfrak{A}_{\text{EM}})'' \cdot \pi_\text{AW}^\beta \circ \gamma_\text{EM})_{t \in \mathbb{R}}$ is a $W^*$-dynamical system $\mathfrak{H}_\text{AW}$, Using $(\mathfrak{H}_\text{AW}, \pi_\text{AW}^\beta)$ it can be derived that

$$\omega_\text{EM}^{\beta}(\pi_\text{AW}^\beta(\mathfrak{H}(b^\alpha_{\varphi}(\vec{x}))))_{\pi_\text{AW}^\beta(\mathfrak{H}(b^\beta_{\varphi}(\vec{y})))} = \sum_{\lambda = 1, 2} \int_{\mathbb{R}^3} d^3 \vec{k} \left( \frac{b^\alpha_{\varphi}(\vec{x}, \vec{y})}{\rho_\beta} \frac{b^\beta_{\varphi}(\vec{y}, \vec{z})}{\rho_\beta} \right)(1 + \rho_\beta) + b^\alpha_{\varphi}(\vec{x}, \vec{y}) b^\beta_{\varphi}(\vec{y}, \vec{z}) \rho_\beta. \quad (30)$$

For later purpose we define the magnetic quantum exchange $m_{\rho, \beta}^\gamma : \mathbb{R}^3 \times \mathbb{R}^3 \times \mathbb{R}^3 \rightarrow \mathbb{C}$ with the strip $Z = [0, \infty) \times [0, i\beta)$ in the complex plane $\mathbb{C}$ by

$$(\vec{x}, \vec{z}, \vec{y}, \vec{z}, \vec{k}) \mapsto m_{\rho, \beta}^\gamma(\vec{x}, \vec{z}, \vec{y}, \vec{z}, \vec{k}) = \sum_{\lambda = 1, 2} \int_{\mathbb{R}^3} d^3 \vec{k} \left( \frac{b^\alpha_{\varphi}(\vec{x}, \vec{y})}{\rho_\beta} \frac{b^\beta_{\varphi}(\vec{y}, \vec{z})}{\rho_\beta} \right)(1 + \rho_\beta) + b^\alpha_{\varphi}(\vec{x}, \vec{y}) b^\beta_{\varphi}(\vec{y}, \vec{z}) \rho_\beta. \quad (31)$$

The following useful symmetry is valid: $m_{\rho, \beta}^\gamma(\vec{x}, \vec{z}, \vec{y}, \vec{z}, \vec{k}) = m_{\rho, \beta}^\gamma(\vec{z}, \vec{x}, \vec{y}, \vec{z}, \vec{k})$. In applications to NMR it turns out that the family $\{m_{\rho, \beta}^\gamma\}_{\gamma = x, y, z}$ takes a central role for the strength and occurrence of the magnetic shielding (chemical shift) and determines return to equilibrium properties.

### IV. QUANTUM SPIN SYSTEMS AND SPIN BOSON SYSTEMS

In the perturbation series used in this document Quantum Spin Systems (QSS) occur as subsystems of Spin Boson Systems (SBS) while SBS occur as subsystems of the mQED systems.

**Quantum Spin Systems.** The mathematical framework for QSS is taken from [40, 47]. A quantum spin system consists of particles on a lattice $\mathbb{Z}^d$. We associate with each point $x \in \mathbb{Z}^d$ a Hilbert space $\mathfrak{H}_x$ of dimension $2s(x) + 1$ and with a finite subset $\Lambda = \{x_1, ..., x_v\} \subset \mathbb{Z}^d$ we associate the tensor product space $\mathfrak{H}_\Lambda = \bigotimes_{x \in \Lambda} \mathfrak{H}_x$. The lattice can be equipped with a metric $d(\cdot, \cdot)$. The local physical observables are contained in the algebra of all bounded operators acting on $\mathfrak{H}_\Lambda$, that is the local $C^*$-algebra $\mathfrak{A}_\Lambda \cong \bigotimes_{x \in \Lambda} M_{2s(x) + 1}$ in which $M_n$ denote the algebra of $n \times n$ complex matrices. If $\Lambda_1 \cap \Lambda_2 = \emptyset$, then $\mathfrak{A}_{\Lambda_1 \cup \Lambda_2} = \mathfrak{A}_{\Lambda_1} \otimes \mathfrak{A}_{\Lambda_2}$ and $\mathfrak{A}_{\Lambda_1}$ is isomorphic to the $C^*$-subalgebra $\mathfrak{A}_{\Lambda_1} \otimes \mathfrak{I}_{\Lambda_2}$ of $\mathfrak{A}_{\Lambda_1 \cup \Lambda_2}$, where $\mathfrak{I}_{\Lambda_2}$ denotes the identity operator on $\mathfrak{H}_{\Lambda_2}$. If $\Lambda_1 \subset \Lambda_2$ then $\mathfrak{A}_{\Lambda_1} \subset \mathfrak{A}_{\Lambda_2}$ and operators with disjoint support commute, i.e. $[\mathfrak{A}_{\Lambda_1}, \mathfrak{A}_{\Lambda_2}] = 0$ whenever $\Lambda_1 \cap \Lambda_2 = \emptyset$. We may define the algebra of ”all local observables” as $\mathfrak{A}_{\text{loc}} = \bigcup_{\Lambda \subset \mathbb{Z}^d} \mathfrak{A}_{\Lambda}$. The operator norm of an element $A \in \mathfrak{A}_\Lambda$ is given by $\|A\| = \sup\{\|A\Phi\| : \Phi \in \mathfrak{H}_{\Lambda}, \|\Phi\| = 1\}$. An $\epsilon$-neighborhood of an operator $A$ is the set of operators $B$ with $\|A - B\| \leq \epsilon$. The local convex topology which is induced by the operator norm is called the uniform topology and the quantum spin algebra $\mathfrak{A}$ is then obtained by taking the closure of the algebra $\mathfrak{A}_{\text{loc}}$ in this topology, i.e. $\mathfrak{A} = \mathfrak{A}_{\text{loc}} \|\|$. An interaction $\Phi$ is defined to be a function from a finite subset $X \subset \mathbb{Z}^d$ into the hermitian elements of $\mathfrak{A}$ such that $\Phi(X) \in \mathfrak{A}_X$. The Hamiltonian associated with the region $\Lambda$ is then given by

$$H_\Phi(\Lambda) = \sum_{X \subset \Lambda} \Phi(X). \quad (32)$$

An interaction of a spin with a classical, external magnetic field [23, 49, 50] is given by

$$\Phi_{x} = \gamma_0 \vec{I}_x \cdot \vec{B}_{\text{ext}} \quad \text{for nuclear spins} \quad \Phi_{e} = g_s \frac{B}{h} \vec{S}_x \cdot \vec{B}_{\text{ext}} \quad \text{for spins of electrons}. \quad (33)$$

An NMR pulse induces a time-dependent interaction $P_t$ involving spins and oscillating, external magnetic fields [51, 52]

$$P_t = \sum_{j=1}^{K} \Phi^\gamma_t(\{j\}), \quad \text{where} \quad \Phi^\gamma_t(\{j\}) = \gamma_0 \vec{I}_j \cdot \vec{B}_{\text{ext}}(t). \quad (34)$$
For example, a single pulse in x-direction, which is switched on from time \( t = 0 \) to \( t = t_0 \), is described by a magnetic field of the form

\[
B^y_{\text{ext}}(t) = B_P \int d\omega_P f(\omega_P) \theta(t, 0, t_0) \cos(\omega_P t + \phi),
\]

(35)

\( \theta \) is the step function, \( B_P \) provides the amplitude of the pulse (some milli Tesla), \( \phi \) is the phase of the magnetic field at \( t = 0 \) and \( f \) provides the frequency distribution of the pulse. Often, the frequency distribution provided by \( f \) is of rectangular form and of course it has to cover the excitation frequencies of the nuclei which shall be excited. The dynamical evolution of an observable \( A \in \mathfrak{A}_A \) for a system with time-independent Hamiltonian \( H(\Lambda) \in \mathfrak{A}_A \) can be described by the Heisenberg relations

\[
\tau^A_t : \mathfrak{A}_A \to \mathfrak{A}_A, \quad A \mapsto \tau^A_t(A) = e^{\frac{iH(\Lambda)}{\hbar}} A e^{-\frac{iH(\Lambda)}{\hbar}}.
\]

(36)

Thus the map \( t \mapsto \tau^A_t \) is a one-parameter group of \(^*\)-automorphisms of the matrix algebra \( \mathfrak{A}_A \) and \( S \) denotes that this automorphism group acts only on the quantum spin algebra. The corresponding derivation is denoted by \( \delta_A \) and \( (\mathfrak{A}_A, \tau^A_t) \) is a \( C^* \)-dynamical system because \( \tau^A_t \) is strongly continuous for finite external fields. Since effective spin-spin couplings are absent in the mQED Hamiltonian eq. (6) and (7) a spin system consisting of \( K \) nuclei and \( E \) electrons forms a subsystem of (6) whose equilibrium state is given by

\[
\omega^\beta = \bigotimes_{j=1}^{K+E} \omega^\beta_{S_j}.
\]

(37)

\( \omega^\beta_{S_j} \) is the \((\tau^S, \beta)\)-KMS state of the single nucleus or electron enumerated by \( j \). The representation which is induced by \( \omega^\beta_{S_j} \) is denoted by \( (\mathfrak{D}_S, \pi_S) \).

**Perturbative description of Spin Boson Systems.** A \( C^* \)-algebra \( \mathfrak{A}_{SB} \) for spins located in \( \Lambda \) interacting with bosons from the quantized electromagnetic field is given by

\[
\mathfrak{A}_{SB} = \text{span}\{A \otimes W(f) \mid A \in \mathfrak{A}_A, f \in \mathfrak{F}_\Lambda\} = \mathfrak{A}_A \otimes \mathfrak{A}_{\text{EM}}.
\]

(38)

where \( \mathfrak{D}_{SB} = \mathfrak{D}_A \otimes \mathfrak{D}_{\text{AW}} \) is a representation space. The index \( \Lambda \) is neglected for simplicity. The free time evolution \( \tau^A_t = \tau^A_t \otimes \tau^\text{EM}_t \), with derivation \( \delta_{SB} = \delta_A + \delta_{\text{EM}} \), acts on \( \mathfrak{A}_{SB} \) and we have \( \tau^A_t (A \otimes W(f)) \in \mathfrak{A}_{SB} \) [32]. Interactions of the form

\[
H^\text{SB}_{\text{int}} = \sum_{\alpha=x,y,z} \left( \sum_{j=1}^K \gamma_j I^\alpha_j \otimes \Phi(b^\alpha_j(x_j^\tau)) + \sum_{i=1}^E g_s \frac{\mu_B}{\hbar} S^\alpha_i \otimes (\Phi(b^\alpha_i(x_i^\tau))) \right)
\]

(39)

enable energy exchange between spins and bosons. Interactions given by (39) are unbounded and if the derivation induced by \( H^\text{SB}_{\text{int}} \) is denoted by \( \delta^\text{SB}_{\text{int}} \) then the evolution group \( \{\tau^{ISB}_t\}_{t \in \mathbb{R}} \) generated by \( \delta^\text{SB}_{\text{int}} = \delta^A_{SB} + \delta^\text{int}_{SB} \) does not necessarily leaves \( \mathfrak{A}_{SB} \) invariant. However, if some general conditions are satisfied [32] \( \tau^{ISB}_t(A) \) lies in the weak closure \( \mathfrak{A}^\text{SB} \), i.e. \( \tau^{ISB}_t(\mathfrak{A}_{SB}) \subseteq \mathfrak{A}^\text{SB} \). Furthermore, if the conditions from [32] are satisfied the convergence of the right hand side of

\[
\tau^{ISB}_t(A) = \tau^A_t(A) + \sum_{n \geq 1} t^n \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \left[ \tau^A_t(H^\text{SB}_{\text{int}}), \cdots, \tau^A_t(H^\text{SB}_{\text{int}}), \tau^A_t(A) \right]
\]

(40)

towards \( \tau^{ISB}_t(A) \) holds strongly on vectors of the form \( |\Omega\rangle = |\Omega_A\rangle \otimes |\Omega_0\rangle \) and observables of the form \( A = I \otimes W(f) \), where \( I \in \mathfrak{A}_A \) and \( |\Omega_0\rangle \in \mathfrak{D}_A \). For a large class of coupling functions \( \varphi \) [32] the pair

\[
(\pi^\beta_{SB}(\mathfrak{A}_{SB})'', \pi^\beta_{SB} \circ \tau^{ISB})
\]

(41)

is a \( W^* \)-dynamical system and \( \pi^\beta_{SB} = \pi_S \otimes \pi^\beta_{\text{AW}} \). An important state \( \hat{\omega}^{ISB}_{SB} \) on the von Neumann algebra \( \pi^\beta_{SB}(\mathfrak{A}_{SB})'' \) is given by [36]

\[
\hat{\omega}^{ISB}_{SB}(A) = \hat{\omega}^\beta_{SB}(A) + \sum_{n \geq 1} (-1)^n \int_0^\beta ds_1 \int_0^{s_1} ds_2 \cdots \int_0^{s_{n-1}} ds_n \hat{\omega}^\beta_{SB}(A, \hat{\tau}^\beta_{SB}(H^\text{SB}_{\text{int}}), \cdots, \hat{\tau}^\beta_{SB}(H^\text{SB}_{\text{int}})),
\]

(42)
where $\omega_{SB}^\beta$ is the extension of $\omega_{SB} = \omega_{S} \otimes \omega_{EM}$ on $\mathfrak{A}_{SB}$ to $\pi_{SB}^\beta(\mathfrak{A}_{SB})''$, $\tau_{SB}^\beta = \pi_{SB}^\beta \circ \tau_{SB}$, $A \in \pi_{SB}^\beta(\mathfrak{A}_{SB})''$ and $T$ denotes that truncated functions are used [46]. If the conditions from [32] are satisfied one finds for a large class of states $\eta$ and observables $A$ return to equilibrium for the interacting system, formally given by

$$\lim_{t \to \infty} \eta \circ \tau_{SB}^\beta(A) = \omega_{SB}^\beta(A).$$

In this case $\omega_{SB}^\beta$ is a $(\tau_{SB}^\beta, \beta)$-KMS state. For applications to NMR we define the evolution group $\{\tau_{P_t}^\beta\}_{t \in \mathbb{R}}$ which is generated by $\delta_{SB}^\beta + \delta_{P_t}$. For $A \in \mathfrak{A}_\Lambda$ we have $\delta_{P_t}(A) = i[\Pi_t, A]$ and $t \in \mathbb{R} \mapsto \Pi_t = P_t^\prime \in \mathfrak{A}_\Lambda$ is a one-parameter family of selfadjoint elements which contains the information of the pulse sequence given by eq. (34). From now on we make the identification $\mathfrak{M} = \mathfrak{A}_{SB}^\prime$. Although there exist not yet a rigorous proof it seems to be obvious [53] that if $(\pi_{SB}^\beta(\mathfrak{A}_{SB})'')$, $\omega_{SB}^\beta \circ \tau_{SB}^\beta$) is a $W^*$-dynamical system then $(\tau_{SB}^\beta(\mathfrak{M}), \omega_{SB}^\beta \circ \tau_{P_t}^\beta)$ is a $W^*$-dynamical system for a suitable class of pulse sequences $P$.

V. APPLICATION TO NMR

A typical NMR experiment consists basically of molecules interacting with external magnetic fields. In most experiments the interacting system is in thermal equilibrium at the beginning of the experiment. The molecular structures are then investigated by the application of a pulse sequence which consists of oscillating, external magnetic fields. Pulse sequences provide an out of equilibrium nuclear spin dynamics and they act only for a short time at the beginning of the experiment. When the pulse sequence is finished the system is again governed by the equilibrium dynamics which is then responsible for a return to thermal equilibrium. This equilibration process is experimentally detected in NMR and referred as free induction decay (FID). In most experiments the $x$- and $y$-components of the nuclear spins are recorded, while the $z$-component is not recorded. The detected FID is called NMR-signal, $\langle M^+ \rangle(t)$, and its Fourier transform provides the NMR-spectrum $S(\nu)$. An NMR spectrometer detects the radiation from the nuclear spins in the xy-plane which is identical to the time-evolution of the $x$- and $y$-components of the nuclear spins. Therefore, the NMR spectrometer records the NMR signal $\langle M^+ \rangle(t) = \sum_j I_j^+(t)$ which consists of expectation values with observables $I_j^+(t) = I_j^+(t) + iI_j^j(t)$. The real and imaginary parts of the NMR-signal are given by $\Re(\langle M^+ \rangle(t)) = \sum_j I_j^j(t)$ and $\Im(\langle M^+ \rangle(t)) = \sum_j I_j^j(t)$ respectively. In certain cases, the NMR-spectrum contains only very sharp peaks of "Lorentzian shape". NMR spectra which show any other distribution may be obtained by superpositions of Lorentz functions. It is always seen that the positions of the peaks are shifted towards lower frequencies compared to the Lamor frequency $v_0 = \gamma | B^e_\text{ext} |$. This chemical shift is a consequence of the magnetic shielding which is caused by the electrons: In the presence of an external magnetic field the magnetic moments of electrons show into the opposite direction compared to the magnetic moments of the nuclei. Hence, the external magnetic field at the position of a nucleus is reduced (shielded) by electrons.

Figure 1: Example of an experimental 1H NMR signal $\langle M^+ \rangle(t)$ (left side) and the corresponding NMR spectrum $S(\nu)$ (right side). There is an exponentially fast return to equilibrium of $\langle M^+ \rangle(t)$ (a). The peaks in the spectrum (b) possess different line widths and originate from protons with different electronic environment. A discrete spectrum is unable to give an accurate description of the domain around 1 ppm. The presence of several peaks provides oscillations in the NMR-signal decay. A smooth exponential decay is obtained if only identical protons contribute to the signal, e. g. the protons from water.
Fig. 1 shows exemplary 1H NMR-data of 12µl benzyl azide with impurities in dimethyl sulfoxide-D6. The NMR signal $\langle M^+ \rangle(t)$ is shown in (a) and the spectrum $S(\nu)$ in (b). An exponentially fast thermalization for $\langle M^+ \rangle(t)$ can be seen on the left image. It’s Fourier transform (right image) provides the frequencies involved in the nuclear spin dynamics during thermalization. It can be seen that the peaks possess different widths and positions. The domain around 1 and 3 ppm is generated only by a few protons but the description of this domain by a discrete spectrum is not accurate. Hence, model-calculations involving a continuous spectrum are desirable for a detailed analysis of this spectrum.

According to the description of an experimental NMR setup the mQED system in the algebraic framework is applied as follows. At times before pulse sequences, $t \leq 0$, the description of the molecular system interacting with the classical and quantized electromagnetic field will be described by the Hamiltonian $H = H_0 + H_{\text{int}}^{\text{SB}}$ from eq. (6) and (39). $H_{\text{int}}$ contains the same interactions as $H_{\text{int}}$ from eq. (7) except the interactions which does not involve spins. Hence, it may be referred as Spin Boson approximation of mQED. This approximation is based on the assumption that the energy of a pulse sequence is too low to change the momentum and geometry of the investigated electronic structure. This approximation is also made by the effective spin model and there seems to be no obvious reason why this approximation should be unsuitable. For $t = 0$ the system is in thermal equilibrium and the equilibrium state $| \Omega^\beta \rangle$ is determined by $H$. Pulse sequences are initiated at $t = 0$, such that for $t > 0$ the system is described by $H + P_t$. The time-dependent operator $P_t$ from eq. (40) contains the information of the pulse sequence. Hence, the time-dependence of a nuclear spin operator, e.g., $I^x(t)$ or $I^+(t)$, during a pulse sequence is determined by $H + P_t$.

Let $\mathcal{B}(\mathcal{H}_M)$ denote the set of bounded operators on the Hilbert space $\mathcal{H}_M$ of the molecular system. The spatial structure of the molecular system is contained in the state $\omega^\beta_M : \mathcal{B}(\mathcal{H}_M) \to \mathbb{C}$. In the application to NMR the Born-Oppenheimer approximation will be used and the wave function $\psi$ of the electrons will be approximated by the ground state. Ideally the KMS state is used for the nuclear wave function $\Psi$. However, in most cases it is practically not possible to estimate this KMS state explicitly. Therefore, a suitable procedure may be used which approximates the square $| \Psi^\beta(X) |^2$ of the KMS state. A good choice may be given by inserting the potential energy surface (PSE) into the classical Gibbs state at inverse temperature $\beta$. For a function $f \in \mathcal{B}(\mathcal{H}_M)$ the expectation value is given by

$$\omega^\beta_M(f) = \int d^3K x \int d^3E x^c | \Psi^\beta(X) |^2 | \psi(X, X^c) |^2 f(X, X^c).$$

(44)

Remember that the dependence of $\tau^{\text{PSB}}_t$ and $\tilde{\omega}^\beta_{\text{SB}}$ on the coordinates $(X, X^c)$ was so far neglected in the notation for simplicity. For the main result this dependence is now written explicitly for clarity. Usually the temperature dependence is not explicitly indicated for the NMR-signal but we will do this in the following.

Main Result (NMR-signal from mQED): Assume that $(\mathcal{M}, \tau^{\text{PSB}}_t)$ is a $\text{W}^*$-dynamical system and let

$$\tau^{\text{PSB}}_t : \mathcal{M} \to \mathcal{M}, \quad \pi^{\beta}_{\text{SB}} : \mathcal{M} \to \mathcal{B}(\mathcal{H}_\text{SB})\quad \text{and} \quad \tilde{\omega}^\beta_{\text{SB}} : \mathcal{B}(\mathcal{H}_\text{SB}) \to \mathbb{C}$$

be constructed as in section IV. Furthermore, let $\mathcal{L}^\beta_t : \mathcal{A}_A \to \mathcal{B}(\mathcal{H}_\text{SB})$, $\mathcal{A}_A \ni A \to \mathcal{L}^\beta_t(A) \in \mathcal{B}(\mathcal{H}_\text{SB})$ be given by

$$\mathcal{L}^\beta_t(A) : \mathbb{R}^3K \times \mathbb{R}^3E \to \mathbb{C} \quad \text{with} \quad \mathbb{R}^3K \times \mathbb{R}^3E \ni (X, X^c) \to \mathcal{L}^\beta_t(A)(X, X^c) \equiv \tilde{\omega}^\beta_{\text{SB}}(\pi^{\beta}_{\text{SB}} \circ \tau^{\text{PSB}}_t(A))(X, X^c),$$

(46)

where $\tilde{\omega}^\beta_{\text{SB}}$ is calculated according to eq. (42) and $\tau^{\text{PSB}}_t(A)$ is calculating according to eq. (40) by using $H_{\text{int}} + P_t$ instead of $H_{\text{int}}^{\text{SB}}$. For a molecular system described by $\omega^\beta_M$ according to eq. (44) the NMR signal $\langle M^+ \rangle_\beta(t)$ is defined by

$$\langle M^+ \rangle_\beta(t) = \sum_{j=1}^{K} \omega^\beta_M(\mathcal{L}^\beta_t(I^+_j)).$$

(47)

Note that $\mathcal{L}^\beta_t(A)(X, X^c)$ gives thermal equilibrium at the beginning of the experiment and $\mathcal{L}^\beta_{t=0}$ describes the time-evolution during the experiment. As usual the (1-dimensional) NMR spectrum, $S_\beta(\nu)$, is calculated as the Fourier transform

$$S_\beta(\nu) = \int_0^\infty dt \langle M^+ \rangle_\beta(t)e^{-i\nu t}.$$

(48)

The notation $\mathcal{L}^\beta_t(A)(X, X^c)$ is unconventional but easier to read in later applications. A conventional notation is given by $\mathcal{L}^\beta_0(A)(X, X^c)$ but this is more difficult to read when dealing with $\omega^\beta_M(\mathcal{L}^\beta_t)$. The structural validity of the main result will now be checked in the next two sections.
VI. BREAKUP OF THE EFFECTIVE SPIN MODEL

The breakup of the effective spin model is shown for the time-independent expectation value in thermal equilibrium as well as for the out of equilibrium spin dynamics. In thermal equilibrium the expectation value of the z-component of a nuclear spin of a molecule is reduced, if compared to the case where the spin is isolated. This is due to the action of the external magnetic field on the magnetic moments of the surrounding electrons, which then reduce the external magnetic field at the positions of the nuclei. For diagonal $\sigma_j$ the effective model from eq. (1) provides

$$\langle J_z \rangle_{\text{eff}} = \text{Tr}(\rho_{\text{eff}}^b J_z) \approx \frac{\hbar^2}{4} \beta \gamma_j B_z^{\text{ext}} (1 - \sigma_z^{\text{eff}}) \quad \text{where} \quad \rho_{\text{eff}}^b = \frac{\exp(-\beta H_{\text{eff}})}{\text{Tr}(\exp(-\beta H_{\text{eff}}))}. \quad (49)$$

Higher order terms can be neglected in the high temperature approximation. The effective magnetic shielding (chemical shift) constant is always small and positive, i.e., $1 > \sigma_z^{\text{eff}} > 0$. Hence, the expectation value of an isolated nuclear spin is reduced in the molecular system by $\sigma_z^{\text{eff}}$.

In this document the hydrogen atom is used as basic example for mQED calculations. One finds similar results for a Helium atom. Remember that $I^z$ denotes the z-component of the spin operator of the proton while $S^z$ denotes the operator from the electron. While the first order of eq. (42) is zero for $A = I^z$ one derives in the second order that

$$\omega_M^\beta(Q_0^\beta(I^z)) = \omega_S^\beta(I^z) - \omega_S^\beta(S^z) r^\beta + \ldots \quad (50)$$

The dots (…) denote higher order terms from the perturbation series. $r^\beta$ and $a_z^\beta$ differ by a constant and the high temperature approximation is made for $\omega_S^\beta(I^z)$ and $\omega_S^\beta(S^z)$. It can be seen that $a_z^\beta$, derived non-effectively from mQED, replaces the effective parameter $\sigma_z^{\text{eff}}$ which is commonly derived according to eq. (2). It can be checked that $a_z^\beta$ is dimensionless and therefore $a_z^\beta$ can be given in “parts per million” (ppm) in analogy to $\sigma_z^{\text{eff}}$. One finds

$$a_z^\beta = \frac{g_z^2 \mu_B^2}{4} \int_0^{\beta} ds_1 \int_0^{s_1} ds_2 \int_{\mathbb{R}^3} d^3 x \int_{\mathbb{R}^3} d^3 x' \int_{\mathbb{R}^3} d^3 k \ | \Psi^\beta(\vec{x}) \rangle^2 | \psi_{100}(\vec{x}, \vec{x'}) \rangle^2 m_z^{\text{eff}}(\vec{x}, i s_2, \vec{x'}, i s_1, \vec{k}). \quad (52)$$

In case of a hydrogen atom $a_z^\beta$ is indeed independent from a particular choice of the nuclear wave function $\Psi^\beta$. This reflects the fact that the magnetic shielding is independent from the position of the atom in the homogeneous external field. The distribution of the electron is chosen to be the 1-s orbital of the hydrogen atom, i.e.

$$\psi_{100}(\vec{x}) = \frac{1}{\sqrt{\pi a_B}} \exp \left( -\frac{\| \vec{x} \|}{a_B} \right), \quad (53)$$

where $a_B$ is the Bohr radius.

Observation 1

A comparison provides a further advantage for the non-effective model. For $B_z^{\text{ext}} \rightarrow \infty$ we have $\sigma_z^{\text{eff}} B_z^{\text{ext}} \rightarrow \infty$. Hence, the effective model predicts that the magnetic field which originates from the electron and reduces the magnetic field at the position of the proton tends to infinity. This is certainly wrong because there is a maximum magnetic field strength which can be produced by the electron and the maximum is achieved when the spin of the electrons is completely in the | +1/2⟩ or | −1/2⟩ state. In contrast the mQED model contains this effect and the limit is given by $\text{Tr}(\rho_{\text{eff}}^b S^z) \leq \hbar/2$ in eq. (50). In this case the high temperature approximation made in $a_z^\beta$ is unsuitable and eq. (50) provides more accurate predictions than eq. (51). Thus, for low temperatures and high external magnetic fields the mQED model is much more realistic. The deviation from the non-linear regime for $\sigma_z^{\text{eff}} B_z^{\text{ext}} \rightarrow \infty$ may be measured experimentally and validates the more realistic description of the mQED model. This is of potential relevance for NMR at low temperatures, e.g. Dynamic Nuclear Polarization (DNP).

Observation 2

We have $a_z^\beta > 0$ for all $\varphi \in L^2(\mathbb{R}^3)$ which follows from the fact that $\varphi$ enters $a_z^\beta$ with $| \varphi(\vec{k}) |^2$ and

$$a_z^\beta = \frac{g_z^2 \mu_B^2 \mu_0}{6\pi^2 \hbar c} \int_0^\infty dk | \varphi(k) |^2 \left( e^{-2\beta \hbar c k} e^{-2\beta \hbar c k} + 0.5 \right) \left( 1 + 2\rho^\beta(k) \right) \frac{k}{(1 + k^2 a_B^2/4)^2}. \quad (54)$$
In eq. (54) spherical coordinates were introduced for \( \vec{k} \) and all integrals except the one for \( k \) were evaluated. Furthermore, we have assumed that \( \varphi \) depends only on \( |\vec{k}| \) which is a natural and common choice. This is a nice result, because the non-effective magnetic shielding \( a^\beta_\varphi \) needs to be positive in any case and \( \varphi \) is a free parameter in mQED.

**Numerical investigation of \( a^\beta_\varphi \).**

It is important to know that for any given molecular structure the coupling function \( \varphi \) from eq. (11) is the only free parameters and - of course - \( \varphi \) is independent of \( \Psi \) and \( \psi \). Thus, a particular choice for \( \varphi \) which accurately reproduces a well-understood experiment can be used to predict or analyze NMR data of proposed or unknown molecular structures. We have \( g_s^2\mu_B^2/6\pi^2\hbar c \approx 7.271326950237399 \cdot 10^{-8}\text{Å}^2 \), where \( \text{Å} \) is the unit Angström. For the numerical calculations we choose

\[
\varphi(k) = \begin{cases} 
  g & \text{for } \delta_{IR} \leq k \leq \delta_{UV}, \\
  0 & \text{for } k < \delta_{IR} \lor k > \delta_{UV}, 
\end{cases} 
\quad g, \delta_{UV} \in \mathbb{R}^+ \quad \text{and} \quad \delta_{UV} > \delta_{IR} \in \mathbb{R}^+_0. \tag{55}
\]

\( \delta_{IR} \) and \( \delta_{UV} \) are the infrared and ultraviolet cutoff respectively and normalization of \( \varphi \) implies \( g = 1/(\delta_{UV} - \delta_{IR}) \).

For the numerical calculations in this document the infrared cutoff \( \delta_{IR} \) can be chosen arbitrarily small (and also zero) such that it has a negligible influence on \( a^\beta_\varphi \).

Figure (2) shows the dependence of \( a^\beta_\varphi \) on \( \delta_{UV} \) for a hydrogen atom. The unit of \( \delta_{UV} \) is millimeter\(^{-1} \) (1 mm\(^{-1} \) \approx 0.00124 eV). The temperature is chosen to be \( T=293 \text{ K} \) (room temperature) and the infrared cutoff is chosen to be zero, \( \delta_{IR} = 0 \). There is a linear increase of \( a^\beta_\varphi \) for increasing \( \delta_{UV} \), which is in agreement with the dynamical calculations shown below. The ppm (parts per million) scale is chosen such that the Lamor frequency \( \nu_0 \) is located at zero. Higher order contributions should increase the magnetic shielding.

![Graph showing the magnetic shielding \( a^\beta_\varphi \) as a function of \( \delta_{UV} \).](image)

**The dynamic case**

Analytically the breakup of the effective model can, for example, be seen by the occurrence of direct spin-spin interactions (dipole-dipole interactions) in the second order of eq. (40). One finds,

\[
[r^{SB}_t(H^SB_{int}), [r^{SB}_t(H^SB_{int}), \gamma^{SB}_t(I^{+})]] = \sum_{i<j} J^{\alpha \beta}_{ji}(t, t_1, t_2) I^{+}_i \otimes I^{+}_j + ...
\]

(56)

with

\[
J^{\alpha \beta}_{ji}(t, t_1, t_2) = -\gamma_j \gamma_i u_j(t) u_i(t_1) \langle [B^\alpha_\varphi(x, t_2), B^\beta_\varphi(x', t_1)] + i[B^\alpha_\varphi(x, t_2), B^\beta_\varphi(x', t_1)] \rangle.
\]

(57)

and similar terms for the x- and y-components. Following the calculations from [51] the direct coupling \( \vec{I}_i D_{ij} \vec{I}_j \) from the effective model eq. (1) is obtained with quantum radiative corrections. Indirect spin-spin couplings occur in the fourth order of eq. (40) in a similar fashion. For the magnetic shielding in the dynamic case the numerical investigation of the breakup of the effective spin model is detailed shown in the next section.
VII. NMR SPECTRA AND REAL-TIME SPIN DYNAMICS.

The real-time nuclear spin dynamics as well as the spectra according to eq. (40) and the second order of eq. (42) according to eq. (47) and eq. (48). After long-lasting calculations NMR-spectra are obtained from terms of the form

\[ S_\beta (v) = \theta_1 \int_0^\infty dt e^{-iwt} \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^t dt_1 \int_0^t dt_2 \int \int \int \int d^3 x \int \int d^3 x' \int \int d^3 k \int \int d^3 k' \times \]

\[ \times | \Psi (\vec{x}) |^2 \psi_{100}(\vec{x}, \vec{x'})^2 \times \]

\[ \times (m_{\beta\beta}(\vec{x}, is_2, x', is_1, \vec{k}) \omega_0^0 (F' \tau_{is_2}(F')) + m_{\beta\beta}(\vec{x}, is_2, x', is_1, \vec{k}) \omega_0^0 (F' \tau_{is_2}(F'))) \times \]

\[ \times \sum_{\lambda=1,2} \varphi_\lambda (\vec{k}) (\varphi_\lambda (\vec{k}) + i\varphi_\lambda (\vec{k}) ) \Delta_\lambda (\vec{x}, t_2) - (\vec{x}, t_1))u(t)\bar{u}(t_1) + ... \]

where \( u(t) = e^{-it\nu_0} \) and \( \theta_1 \in \mathbb{C} \). In case of the hydrogen atom one finds again that \( S_\beta (v) \) is independent of \( \Psi^\beta \) which means that the chemical shift does not depend on the position of the hydrogen atom in the homogenous external field. For molecules with two or more nuclei \( S_{\beta}(v) \) depends on \( \Psi^\beta \).

Figure 3 shows the NMR spectra \( S_\beta (v) \) from eq. (47) with eq. (48) for a hydrogen atom. The ppm scale is chosen such that the Lamor frequency \( \nu_0 \) is located at zero ppm. The spectra is calculated for the values \( \delta_{UV} = 4, 5, 6, 7, 8, 9, 10, 11 \) (a) and \( \delta_{IR} = 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.01, 0.011 \) with unit megameter\(^{-1} \) (Mm\(^{-1} \)). The temperature is chosen to be \( T = 293 \) K (room temperature), \( B_{0\beta} = 20 \) T (Tesla) and the infrared cutoff is chosen to be zero, \( \delta_{IR} = 0 \). In every case it can be seen that a Lorentz distribution is obtained as observed in NMR experiments. Small variations of \( \delta_{IR} \) only had a negligible impact on the magnetic shielding. As in the case for \( g^\beta \) the strength of the magnetic shielding increases linear with \( \delta_{UV} \). Furthermore, the "Full Width at Half Maximum" (FWHM) \( \Delta \nu \) increases linearly with increasing \( \delta_{UV} \). Remember that \( \Delta \nu \) is directly related with the life-time of an excited nucleus which will be checked later. Comparing the left figure (a) and the right figure (b) one finds that if \( \delta_{UV} \) is reduced by a factor of 100 then \( \Delta \nu \) as well as strength of the magnetic shielding (distance of the peak to 0 ppm) is also reduced by a factor of 100. The maximum value (height) of each peak is nearly the same. This a result of the normalization of \( \varphi \) and it makes sense because these small changes of the magnetic field strength should not have a significant impact on the amplitude of the NMR signal. This is also in agreement with experimental data.

![Figure 3: NMR-spectra \( S_\beta (v) \) of a hydrogen atom calculated from eq. (47) with eq. (48) for different values of \( \delta_{UV} \). All peaks have a Lorentz shape which is in agreement with experimental data. The chemical shift and \( \Delta \nu \) increase linear with \( \delta_{UV} \).](image_url)

Figure 4 (a) shows the long-time dynamics \( \langle F' \rangle (t) \) (real part of NMR-signal) for \( \delta_{UV} = 0.1 \) Mm (orange line) and \( \delta_{UV} = 0.05 \) Mm (blue line). All other parameters are the same for the calculations for fig. 3. In both cases there is an exponentially fast return to equilibrium as observed in NMR experiments. The starting point at \( t = 0 \) is chosen to be directly after the 90°-pulse has finished. The amplitudes are normalized to the value 0.5 at \( t = 0 \) corresponding to the excitation of a single nucleus. The thermalization which is associated with the orange line happens twice as fast as the thermalization which is associated with the blue line. Hence, doubling the value \( \delta_{UV} \) halves the life-time (T2 in NMR language) of the excited spin. The nuclear spin can release energy in a frequency range with double length.

Figure 4 (b) shows the short-time dynamics \( \langle F' \rangle (t) = \Re (\langle M^+ \rangle (t)) \) and \( \langle F' \rangle (t) = \Im (\langle M^+ \rangle (t)) \) for the same parameters which were used for the orange line from fig. 4 (a). The cross shows that there is an exact 90° phase
shift between $\langle F(t) \rangle$ and $\langle F^2(t) \rangle$ as it should be. The frequency is slightly reduced compared to the Lamor frequency which can also be seen from fig. 3(b).

Figure 4: (a) Long-time spin dynamics from the real part of the NMR-signal, $\Re (\langle M^+ \rangle (t)) = \langle F(t) \rangle$, for $\delta_{UV} = 0.1$ Mm (orange line) and $\delta_{UV} = 0.05$ Mm (blue line). Doubling the value $\delta_{UV}$ halves the life-time of the NMR-signal. (b) Short time spin dynamics $\langle F'(t) \rangle$ (orange line) and $\langle F''(t) \rangle$ (blue line) for the same parameters as used for the orange line from fig. 4(a). There is an exact $90^\circ$ phase shift between $\langle F'(t) \rangle$ and $\langle F''(t) \rangle$ as it should be. The very smooth exponential decay is due to the fact that the NMR signal contains only one peak. Several peaks provide oscillations as in fig. 1.

VIII. CONCLUSION AND OUTLOOK

The main result of this work (page 10) presents the structural application of molecular Quantum Electrodynamics with the algebraic reformulation of Quantum Field Theory and Quantum Statistical Mechanics to NMR. Analytical and numerical calculations as well as comparisons with experimental NMR data showed the validity of this approach. Several striking advantages against well-established NMR theory were shown. In particular, the very important process of return to equilibrium is included in a natural and microscopic way instead phenomenologically. This provides a basis for a detailed research towards stable spin structures which are of paramount importance for hyperpolarized MRI.

While the effective model describes nuclei as fixed point particles the presented method uses the nuclear wave function, whose square can be approximated by a suitable method. This provides a basis for a more detailed investigation of molecular structures which is in most cases the main goal of NMR. Chemical shifts (magnetic shieldings) as well as spin-spin couplings occur naturally and must not be described effectively. Hence, quantum radiative corrections are included naturally in the calculated NMR spectrum. On the example of a hydrogen atom it was shown that the presented approach has potential to breakup the current NMR theory, which is based on eq. 1, 2 and 3, also for more complex molecular systems. By choosing a $\varphi$ which reproduces the NMR spectrum of a known molecular structure its transfer to unknown molecular structures may be used for more accurate NMR data analysis and predictions for hMRI.

The presented method makes use of the physical approximation that the energy of an NMR pulse is too weak to change the molecular geometry which is obviously realistic for NMR. The numerical calculations involving continuous excitations of the quantized electromagnetic field at finite temperatures were enabled by a purification of the Araki-Woods representation which served as a key element. The involvement of only a few Araki-Woods bosons in the numerical calculations and the continuous excitation spectrum of the quantized electromagnetic field provide striking advantages against the method called Thermo Field Dynamics (TFD). TFD uses a discrete spectrum for the quantized electromagnetic field while the presented method emphasizes the importance of the continuous spectrum to calculate the correct NMR signal decay in the real-time spin dynamics (T2 and T1 in NMR). Due to the Boltzmann distribution of the nuclear spins in thermal equilibrium the usage of the ground state for the quantized electromagnetic field should lead to a wrong long-time spin-dynamics. This emphasizes the importance of treating the quantized field at finite temperatures.

In summary, the mathematical structure of a new method was developed which enables the numerical calculation of the real-time spin dynamics, where the interactions involving spins are provided by the quantized electromagnetic field at finite temperatures with continuous energy spectrum. Furthermore, the full molecular structure is directly
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