Spin decoherence in inhomogeneous media

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Abstract

A Green’s function formalism for describing the decoherence of a ‘central spin’ in inhomogeneous media is developed. By embedding the ‘central spin’ in a background medium and performing real-cavity, local-field corrections on the macroscopic fields at the location of the ‘central spin’ one can show that the Green’s function splits up into two main contributions, a contribution that is related to the bulk properties of the background medium and a contribution that is related inhomogeneities within the background medium. As an example, the coherence time of a shallow NV center in diamond close to a planar interface, both in the absence and presence of surface spins, is computed. It is found that the coherence time of the NV center increases as it moves away from the interface and, at distances greater than \( \approx 1 \) nm, the interaction with the interface is negligible with the main source of decoherence coming from the interaction with the surface spins. Above \( \approx 50 \) nm the interaction with the surface spins is also negligible and one recovers the bulk coherence time.

1. Introduction

Owing to their ability to generate and maintain coherent superpositions, single spin qubits show much promise as a platform for realizing quantum computing and quantum information processing [1, 2]. However, as these spins are unavoidably coupled to the environment, the coherence times of these superposition states is finite and, if left to freely evolve, the spin will ‘decohere’ to a mixed state of the two eigenstates [3, 4]. This finite coherence time is a major limiting factor in the realization of many quantum information protocols.

For many spin systems the main source of decoherence is the interaction with nuclear spins in the surrounding material. For example, the main source of decoherence for phosphorus donors in silicon are the \(^{29}\)Si isotopes that are present at a concentration of about 4.7% in natural silicon [5] and, likewise, \(^{13}\)C, at a concentration of about 1.1%, are the primary source of decoherence for NV centers in diamond [6]. The main technique for modeling decoherence is to use a microscopic spin-bath model [4] where one couples the ‘central spin’ individually to a bath nuclear spins. Further interactions couple the nuclear spins within the bath inducing intrabath correlations which also affect the coherence properties of the ‘central spin’ [7]. The coherence time can then be computed by applying one of the usual cluster-expansion techniques by which one can obtain a numerically tractable expression. Despite this, for large systems, these methods can be computationally intensive. Furthermore, although one can specify the exact position of the bath spins within the spin bath, this technique proves awkward when one needs to consider inhomogeneities in the medium in which the ‘central spin’ is embedded. An example of this can be seen when one considers a ‘central spin’ located close to an interface (shallow NV centers, which can be located within several nanometers of the diamond surface, would be an example of such a system). Naïvely, one may think that as the ‘central spin’ approaches the surface the coherence time will increase as the number of nearby nuclear spins decreases. However, experimental work has shown that this is not the case and, in fact, the coherence time decreases dramatically close to the surface [8, 9].

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number of phenomenological models have been constructed to account for this effect \cite{10,11} but a general framework for studying such systems is absent.

Previously, it was shown that, by considering a spin–boson model and expanding the bosonic modes of the environment using the macroscopic quantum electrodynamics formalism \cite{12,13}, one can obtain an expression for the decoherence of a ‘central spin’ in terms of the electromagnetic Green’s function of the surrounding material \cite{14}. By substituting the homogeneous Green’s function into the general expression, the coherence time for a spin in an infinitely extended medium can be found. However, the Green’s function formalism applies to any general material geometry and by replacing the homogeneous Green’s function with the appropriate inhomogeneous Green’s function the coherence time within an inhomogeneous medium can also be computed.

Here, we extend the Green’s function formalism of spin decoherence from homogeneous media to inhomogeneous media and compute analytical expressions for the coherence time for a ‘central spin’ close to a surface and in the presence of surface spins. Although we only consider planar layered geometries here, the Green’s function formalism is general and, hence, applicable to any material configuration. Analytical expressions for the coherence time can be obtained for regular geometries (planes, cylinders, spheres, etc) where a closed form expression for the Green’s function are known. For non–regular geometries, numerical methods for computing the Green’s function for arbitrary media are well developed. For example, similar computation techniques are required to compute Casimir and Casimir–Polder interactions, which have been implemented in the computational package SCUFF-EM \cite{15}. Hence, numerical methods are already available to implement the following theory, which would allow one to calculate spin coherence under any material geometry.

2. Theory

2.1. The spin–boson model

Consider a spin–boson model where a two-level, ‘central spin’, described by the spin operator, \( \hat{S} \), is placed in a magnetic field, oriented in the z-direction, and coupled to an ‘environment’ consisting of magnetic fluctuations described by a bath of bosonic operators, \( \hat{b}(r, t) \). The dynamics of a ‘central spin’ subject to a magnetic field are governed by the Zeeman Hamiltonian

\[
H_0 = \omega_0 \hat{S}_z,
\]

with the two energy levels, corresponding to the ‘spin up’ and ‘spin down’ eigenstates, separated by an energy \( \Delta E = 2\omega_0 \). The interaction with the magnetic fluctuations can be described by an interaction term of the form \( \hat{H}_I = \gamma \vec{S} \cdot \vec{b}(r, t) \),

\[
H_I = \gamma \vec{S} \cdot \vec{b}(r, t),
\]

where we assume the energy of the fluctuations described by the operator \( \hat{b}(r, t) \) are much smaller than the energy splitting of the spin eigenstates, \( \Delta E \), and hence the interaction with the environment can be treated as a small perturbation. Here, the coupling strength between the ‘central spin’ and the magnetic fluctuations is given by the gyromagnetic ratio \( \gamma = g\mu_B/\hbar \), where \( g \) is the landé g-factor and \( \mu_B \) is the bohr magneton.

The transverse part of the interaction Hamiltonian induces spin flips which relaxes the higher energy spin state to the lower energy spin state, or equivalently leads to the decay of the certain diagonal elements of the spin’s density matrix. This class of Hamiltonian has been extensively studied (notably in \cite{3}) and, from the dynamics of the ‘central spin’ subject to such an interaction, a characteristic time for this relaxation process, usually designated \( T_1 \), can be computed.

The longitudinal part of the interaction Hamiltonian induces pure dephasing which leads to loss of coherence of the two spin states, i.e. the decay of the off–diagonal elements of the spin’s density matrix. The characteristic time for this process is usually designated \( T_2 \), and is usually less than \( T_1 \) (\( T_2 < T_1 \)). Here, we will consider the longitudinal problem as this is the main limiting process for quantum technology. The longitudinal problem also has the advantage that the interaction Hamiltonian commutes with the Zeeman Hamiltonian and hence the eigenstates of the \( \hat{S} \) are unchanged by the interaction.

To simplify the analysis one can remove the free evolution of the spin by moving to the interaction picture. It also proves to be convenient to write the magnetic fluctuations as a sum of their modes. In this new frame the ‘central spin’ evolves under the Hamiltonian

\[
\hat{H}(t) = \gamma \hat{S}_z \int_0^\infty \text{d}\omega [\hat{b}_2(r, \omega, t) + \hat{b}_2^\dagger(r, \omega, t)].
\]

The coherence, \( I(t) \), of a ‘central spin’ can be found by taking the expectation value of the coherence operator \( \hat{S}_+ = \hat{S}_x + i\hat{S}_y \),
\[ L(t) = \langle \hat{S}_z \rangle = L(0) e^{-\phi(t)}, \]  

with the function, \( \phi(t) \), giving the decoherence rate as a function of time, \( t \).

### 2.2. Magnetic fluctuations

We wish to find a bosonic operator that correctly describes the magnetic fluctuations of the environment. In any dissipative system, the act of dissipation results in the generation of noise. This is formally described by the fluctuation-dissipation theorem which relates the power spectrum of the noise to the imaginary part of the response function. An example of this would be Johnson noise in a resistor. The energy dissipated by the resistor when a current flows leads to heating and the resulting thermal fluctuations, in turn, drive noise currents. Thus, noise is generated in the resistor by the dissipation process. Similar processes generate noise in all absorbing media. As absorption is a necessary consequence of the Kramers–Kronig relations, which themselves are a consequence of causality [16], then one would expect absorption, and hence noise, in any responding system.

It is possible to derive a quantum field theory description of such noise by considering a three part coupled system where an external electromagnetic field interacts with a matter field which, in turn, is coupled to a bath of oscillators that models absorption. This system can be quantized from first principles to give a set of bosonic operators that describe collective excitations of the oscillators that models absorption. This system can be quantized from first principles to give a set of bosonic operators that describe collective excitations of the oscillators that models absorption. This system can be quantized from first principles to give a set of bosonic operators that describe collective excitations of the oscillators that models absorption.

To compute how the fluctuations in the material affect the ‘central spin’ one needs to find the macroscopic fields that the Langevin noise generates. To do this one can return to Maxwell’s equations and, by using the new ‘noise’ fields as source terms, the electromagnetic fields generated by the fluctuations can be found. The resulting equations read

\[ \nabla \cdot \hat{B}(r, \omega) = 0, \]  \[ \nabla \times \hat{E}(r, \omega) - i\omega \hat{B}(r, \omega) = 0, \]  \[ \nabla \cdot \hat{D}(r, \omega) = \hat{\rho}_N(r, \omega), \]  \[ \nabla \times \hat{H}(r, \omega) + i\omega \hat{D}(r, \omega) = \hat{J}_N(r, \omega), \]

with the noise charge density and noise current density defined by \( \hat{\rho}_N(r, \omega) = \nabla \cdot \hat{\Pi}_N \) and \( \hat{J}_N(r, \omega) = -i\omega \hat{\Pi}_N(r, \omega) + \nabla \times \hat{M}_N(r, \omega) \), respectively. Resubstituting equations (5) and (6) into Maxwell’s equations, one can show that the magnetic field operator, which describes longitudinal magnetic fluctuations within the medium, is given by [12, 13]

\[ \hat{B}_z(r, \omega, t) = \frac{e^{i\omega t}}{i\omega} \sum_{\lambda=e,m} \int d^3r' \hat{G}_\lambda(r, r', \omega) \cdot \hat{J}_\lambda(r', \omega). \]

Here, the coefficients \( G_\lambda (r, r', \omega) \) are defined as

\[ G_\lambda (r, r', \omega) = \frac{\omega^2}{c^2} \sqrt{\frac{\hbar}{\pi \mu_0}} \text{Im} [\hat{\varepsilon}(r', \omega)] \hat{G}(r, r', \omega), \]
\[ G_m(\mathbf{r}, \mathbf{r}', \omega) = -\frac{i}{\hbar} \frac{1}{\mu(\mathbf{r}, \omega)} \left( \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) \times \nabla' \right), \]

with the backward arrow referring to the fact that the operator acts on the right-hand variable (here \( \mathbf{r}' \)). The function, \( \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) \), is the electromagnetic Green’s function, which is the solution to the Helmholtz equation for a point source

\[ \nabla \times \left( \frac{1}{\mu(\mathbf{r}, \omega)} \nabla \times \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) \right) - \frac{\omega^2}{c^2} \varepsilon(\mathbf{r}, \omega) \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}'). \]

### 2.3. Spin decoherence

Substituting the operator for the magnetic field corrections and using it to evaluate the expression for the spin coherence in equation (4) leads to [14] (see supplementary information, which is available online at stacks.iop.org/NJP/22/033017/mmedia)

\[ \phi(t) = \hbar \mu_0 \gamma^2 \int_0^\infty \frac{d\omega}{2\pi} \text{sinc}^2(\omega t/2) \coth(\hbar \omega/2k_B T) \hat{\mathbf{z}} \cdot \nabla \times \text{Im} \mathbf{G}(\mathbf{r}, \mathbf{r}, \omega) \times \mathbf{\nabla} \cdot \hat{\mathbf{z}}. \]

Here, the ‘sinc’ function is the usual free-induction decay noise filter function and the ‘coth’ function is the thermal boson occupation number. The imaginary part of the double curl of the Green’s function gives the local density of states and, hence, the decoherence rate is proportional to the density of magnetic fluctuations at \( \mathbf{r}_0 \), the location of the ‘central spin’.

For systems whose coherence evolves exponentially as \( L = e^{-\Gamma t} \), the coherence time is easily defined as \( T_\nu = 1/\Gamma \) i.e. the time when the coherence has dropped to \( L = e^{-1} = 36.8\% \). From equation (16) it is easy to see that the coherence dynamics of a ‘central spin’ is a complicated function of time, \( t \), and, hence it is not possible to simply define the coherence time in terms of a simple exponential decay parameter. However, in the long time limit the ‘sinc’ function becomes nascent \( \delta \)-function

\[ \lim_{t \to \infty} \frac{t \text{sinc}(\omega t/2)}{\pi} = \delta(\omega/2). \]

Thus, in the long time limit the coherence reduces to a simple exponential decay with the decay rate, \( \Gamma \), given by

\[ \Gamma = \hbar \mu_0 \gamma^2 \lim_{\omega \to 0} \left[ \coth(\hbar \omega/2k_B T) \hat{\mathbf{z}} \cdot \nabla \times \text{Im} \mathbf{G}(\mathbf{r}, \mathbf{r}, \omega) \times \mathbf{\nabla} \cdot \hat{\mathbf{z}} \right]. \]

However, as \( \coth(\omega) \sim 1/\omega \) as \( \omega \to 0 \), this limit only converges if the imaginary part of the double curl of the Green’s function scales as \( \hat{\mathbf{z}} \cdot \nabla \times \text{Im} \mathbf{G}(\mathbf{r}, \mathbf{r}, \omega) \times \mathbf{\nabla} \cdot \hat{\mathbf{z}} \sim \omega^s \) with \( s \geq 1 \) as \( \omega \to 0 \). Although this result can give an reasonable estimate of the coherence time in some cases, it neglects the short time dynamics and hence will be a poor approximation in situations where the behavior of the ‘central spin’ around the initial time is important. In light of this, the results presented here will not use this approximation and for practical purposes the coherence time will be taken to be the time in which the coherence drops to \( L = e^{-1} = 36.8\% \).

### 2.4. Regularization via local-field corrections

There is one last issue that needs to be addressed, namely that the double curl of the Green’s function for a homogeneous medium in the coincident limit diverges if the absorption in the medium is non-zero. As previously mentioned, vanishing absorption over the full frequency range is forbidden by the Kramers–Krönig relations which, themselves, are a result of causality [16]. Hence, to properly model the coherence properties of a ‘central spin’ embedded in a realistic medium, a further step is required.

The divergences of the Green’s function can be regularized by performing local-field corrections on the electromagnetic field at the location of the ‘central spin’ [14]. To perform these corrections one assumes that the spin is located at the center of a spherical cavity whose radius, \( R_c \), is much smaller than the characteristic wavelength of the system [19, 20]. This procedure is the quantum mechanical equivalent of the Onsager model [21, 22], which is often used in physical chemistry to compute the effects of a dielectric medium on a polarizable molecule [23, 24]. The cavity is considered to be vacuum and hence free of noise sources and the interface with the surrounding material to be a simple ‘step function’ interface devoid of gradients, roughness or impurities. It is important to stress that the cavity used in this procedure is merely mathematical technique for computing the field corrections and does not represent anything physical. Essentially, the presence of a cavity introduces an ‘ultraviolet’ cutoff on the wavevector at \( k \approx 2\pi/R_c \) and, hence, regularizes the Green’s function.

With this construction, the Green’s function can be split up into three parts [25, 26]

\[ \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) = \mathbf{G}^{(1)}(\mathbf{r}, \mathbf{r}', \omega) + \mathbf{G}^{(2)}(\mathbf{r}, \mathbf{r}', \omega) + \mathbf{G}^{(3)}(\mathbf{r}, \mathbf{r}', \omega). \]

The first term is proportional to the reflective part of the cavity Green’s function and gives the bulk decoherence rate that was studied in [14]. The second term is proportional to the transmissive part of the cavity Green’s
function and gives the decoherence rate owing to the scattering from inhomogeneities external to the cavity. The final term gives the contribution from multiple scattering between the external side of the cavity and other inhomogeneities. As this last contribution scales as $\approx \frac{\omega R_c}{c}$ and the cavity radius, $R_c$, is assumed to be much smaller than the characteristic wavelength of the interaction, this term is negligible compared to the bulk and scattering contributions and, hence, will be neglected in the following. These contributions are shown schematically in figure 1(a).

2.5. The Green’s function

Consider a ‘central spin’ located at the center ($r = 0$) of a spherical cavity embedded in an inhomogeneous medium. The Green’s function for the whole medium, including the spherical cavity, reads

$$G^{(i)}(r, r', \omega) = \frac{ik}{4\pi} \sum_{\mu_1, \mu_2} \sum_{l=1}^{\infty} \sum_{m=0}^{l} (2 - \delta_{0l}) \frac{2l + 1}{l(l + 1)} \frac{(l - m)!}{(l + m)!} \left[ \tilde{R}_{\mu_1}(\omega)M_{\mu_1}(k, r') \otimes M_{\mu_2}(k, r) + \tilde{R}_{\mu_2}(\omega)N_{\mu_1}(k, r') \otimes N_{\mu_2}(k, r) \right],$$

where $\tilde{R}_{\mu_1}$ and $\tilde{R}_{\mu_2}$ are the generalized reflection coefficients for the TE and TM polarized waves respectively and the $M_{\mu_1}(k, r)$ and $N_{\mu_1}(k, r)$ dyads are given by

$$M_{\mu_1}(\omega, k, r) = \pm \frac{m}{\sin \theta} \frac{P^n_{l(m)}(\cos \theta)}{\cos m \phi} \xi_0 - j_1(kr) \frac{dP^n_{l(m)}(\cos \theta)}{d\theta} \left[ \frac{\cos m \phi}{\sin m \phi} \right] \xi_0,$$

$$N_{\mu_1}(\omega, k, r) = \frac{l(l + 1)}{kr} j_1(kr) P^n_{l(m)}(\cos \theta) \left[ \frac{\cos m \phi}{\sin m \phi} \right] \xi_0 + \frac{1}{kr} [j_1(kr)] \left[ \frac{dP^n_{l(m)}(\cos \theta)}{d\theta} \right] \left[ \frac{\cos m \phi}{\sin m \phi} \right] \xi_0,$$

where $j_1(x)$ are spherical Bessel functions of the first kind and $P^n_{l(m)}(x)$ are the associated Legendre polynomials.

Taking $r, r' \to 0$ one finds that the only contribution is from $l = 1$ and $m = 0$. Hence, the TM mode vanishes and the only contribution is from the TE mode. Thus, the Green’s function reduces to
\[ \mathbf{\hat{z}} \cdot \nabla \times \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) \times \nabla \cdot \mathbf{\hat{z}}|_{\mathbf{r}' \to -\mathbf{r}} = \frac{3\mathbf{i}k}{8\pi} \tilde{R}_{\text{TE}}(\omega) \sum_{n \in \mathcal{E}, \mathcal{O}} \nabla \times \mathbf{M}_{01n}(k, \mathbf{r}) \otimes \mathbf{M}_{01n}(k, \mathbf{r}') \times \nabla|_{\mathbf{r}' \to -\mathbf{r}} = \frac{\mathbf{i}\alpha^3}{6\pi c^3} \tilde{R}_{\text{TE}}(\omega). \] (23)

2.6. The bulk contribution

The bulk contribution is given by \( G^{(1)}(\mathbf{r}, \mathbf{r}', \omega) \) which describes reflection from the walls of the spherical cavity (see figure 1(a)). In this case the generalized reflection coefficient is just the reflection coefficient for the spherical cavity \( R_{\text{TE}}(\omega) = R_{\text{TE}}(\omega) \) which is given by the Mie scattering coefficient

\[ R_{\text{TE}}(\omega) = \frac{h_{l}^{(1)}(z_0)[zh_{l}^{(1)}(z)]'}{\mu(\omega)h_{l}^{(1)}(z)[z_0h_{l}^{(1)}(z_0)]'} - \frac{j_{l}(z_0)[zh_{l}^{(1)}(z)]'}{\mu(\omega)h_{l}^{(1)}(z)[z_0h_{l}^{(1)}(z_0)]'}, \] (24)

where \( z_0 = \omega R_c/c \) and \( z = n(\omega) R_c/c \), with \( R_c \) the radius of the cavity, and \( j_{l}(z) \) and \( h_{l}(z) \), respectively, the spherical Bessel and Hankel functions of the first kind for \( l = 1 \)

\[ j_{1}(z) = \frac{\sin(z)}{z^2} - \frac{\cos(z)}{z}, \] (25)

\[ h_{1}(z) = \left( \frac{1}{z} + \frac{i}{z^2} \right) e^z. \] (26)

Following [14], we will assume that \( R_c \) is small compared to the main wavelengths associated with the decoherence process (in fact the free induction decay filter is the square of the ‘sinc’ function and, hence, is strongly peaked around \( \omega = 0 \) so the main wavelength \( \rightarrow \infty \) and we expand \( R_{\text{TE}}(\omega) \) in powers of \( \omega R_c/c \)

\[ R_{\text{TE}}(\omega) = \frac{3\mu(\omega)}{2|\mu(\omega) + 1| |\omega R_c|^2} + \frac{9}{5} \left( \frac{\mu(\omega)^2 |5e(\omega) - 11 - 3\mu(\omega) - 1|}{|\mu(\omega) + 1|^2} \right) \int \frac{\mathbf{i}c}{\omega c} \] (27)

By taking the reflection coefficient to leading order and substituting the result into equation (23), one finds

\[ \mathbf{\hat{z}} \cdot \nabla \times \mathbf{G}^{(1)}(\mathbf{r}, \mathbf{r}', \omega) \times \nabla \cdot \mathbf{\hat{z}} = \frac{1 - \mu(\omega)}{2\pi R_c^2} \frac{1 + 2\mu(\omega)}{1 + 2\mu(\omega)}. \] (28)

Substituting the result into equation (16) leads to

\[ \phi(t) = \frac{\mathbf{i}\mu(\omega)}{2\pi R_c^2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} 2\pi \sin^2(\omega t/2) \coth (\omega t/2k_0 T) \text{Im} \left[ \frac{1 - \mu(\omega)}{1 + 2\mu(\omega)} \right]. \] (29)

2.7. The scattering contribution

In inhomogeneous media, one obtains a further contribution to the decoherence rate which is caused by scattering off surfaces external to the spherical cavity (see figure 1(a)). This contribution is given by \( G^{(2)}(\mathbf{r}, \mathbf{r}', \omega) \) which describes waves that are transmitted through the surface of the spherical cavity, scatter off an external inhomogeneity and are then transmitted back into the cavity. In this case the generalized reflection coefficient is given by \( \tilde{R}_{\text{TE}} = \frac{T_{\text{out}}}{T_{\text{in}}} \tilde{R}_{\text{TE}} T_{\text{in}}^* \) where \( T_{\text{out}} \) is the transmission coefficient for outgoing waves through the wall of the spherical cavity, \( T_{\text{in}}^* \) is the transmission coefficient for incoming waves through the wall of the spherical cavity and \( \tilde{R}_{\text{TE}} \) is the generalized reflection coefficient for all other interfaces external to the cavity. The appropriate Mie scattering coefficients read

\[ T_{\text{TE}}^{\text{out}}(\omega) = \frac{-i\mu(\omega)}{z_0(j_{l}^{(3)}(z_0)[zh_{l}^{(1)}(z)]') - \mu(\omega)h_{l}^{(1)}(z)[z_0h_{l}^{(1)}(z_0)]'}, \] (30)

and

\[ T_{\text{TE}}^{\text{in}}(\omega) = \frac{-i}{z(j_{l}^{(3)}(z_0)[zh_{l}^{(1)}(z)]' - \mu(\omega)h_{l}^{(1)}(z)[z_0h_{l}^{(1)}(z_0)]')}. \] (31)

As before we expand these coefficients for small values of \( \omega R_c/c \) to give

\[ T_{\text{TE}}^{\text{out}}(\omega) = \frac{3}{1 + 2\mu(\omega)} \frac{\mu(\omega)n(\omega)^2}{1 + 2\mu(\omega)} + \mathcal{O} \left( \frac{\omega R_c}{c} \right). \] (32)
and
\[ T_{\text{in}}^{\text{TE}}(\omega) = \frac{3}{1 + 2\mu(\omega)} n(\omega) + \mathcal{O}\left(\frac{\omega R_s}{c}\right), \tag{33} \]
where \( n(\omega) = \sqrt{\varepsilon(\omega)\mu(\omega)} \) is the refractive index. Thus, this part of the Green’s function to zeroth order in \( \omega R_s/c \) becomes
\[
\hat{\mathbf{z}} \cdot \mathbf{\nabla} \times \mathbf{G}^{(2)}(\mathbf{r}, \mathbf{r}', \omega) \times \mathbf{\hat{z}} \big|_{\mathbf{r} \to 0} = \left( \frac{3}{1 + 2\mu(\omega)} \right)^2 \mathbf{\nabla} \times \mathbf{G}^{(5)}(\mathbf{r}, \mathbf{r}, \omega) \times \mathbf{\hat{z}}. \tag{34} \]
The term in square brackets is just the scattering Green’s function in the coincident limit for a medium without the spherical cavity, hence we can write
\[
\hat{\mathbf{z}} \cdot \mathbf{\nabla} \times \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) \times \mathbf{\hat{z}} \big|_{\mathbf{r} \to 0} = \left( \frac{3}{1 + 2\mu(\omega)} \right)^2 \mathbf{\nabla} \times \mathbf{G}(\mathbf{r}, \mathbf{r}, \omega) \times \mathbf{\hat{z}}, \tag{35} \]
where \( \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) \) is the scattering Green’s function for the medium without the spherical cavity. Thus, the decoherence owing to inhomogeneities in the background medium is given by
\[
\phi(t) = 9\hbar \mu_0^2 t^2 \int_0^\infty \frac{d\omega}{2\pi} \sin^2(\omega t/2) \coth(\hbar\omega/2k_B T) \text{Im} \left[ \frac{1}{1 + 2\mu(\omega)} \right] \hat{\mathbf{z}} \cdot \mathbf{\nabla} \times \mathbf{G}(\mathbf{r}, \mathbf{r}, \omega) \times \mathbf{\hat{z}}. \tag{36} \]
The expression in equation (36) is valid for any geometry—one just needs to substitute in the appropriate Green’s function. As an example, we will now compute the coherence time of a ‘central spin’ for a specific inhomogeneous medium, namely a planar half-space.

3. Decoherence close to a surface

3.1. Decoherence from the interface

A ‘central spin’ inside a medium close to a surface can be modeled by considering a planar half-space with a single interface at \( z = 0 \). Here, the upper half plane, labeled 1, consists of a medium within which the spin is located and the lower half plane, labeled 2, corresponding to an external environment (see figure 1(b)). Taking the coincident limit of the double curl of the single half-space Green’s function \([13, 27]\), converting to polar coordinates and computing the angular part of the integral leads to (see supplementary information)
\[
\hat{\mathbf{z}} \cdot \mathbf{\nabla} \times \mathbf{G}(\mathbf{r}, \mathbf{r}, \omega) \times \mathbf{\hat{z}} = \frac{i\mu_1(\omega)}{4\pi} \int_{0}^{\infty} dk_p \frac{k_p^2}{k_{z,1}} e^{2ik_{z,1}|z|/R_{\text{TE}}}, \tag{37} \]
with \( k_{z,1} = \sqrt{k^2 - k_p^2}, k_i = n_i(\omega)c/\epsilon \) and the reflection coefficient for the TE mode given by
\[
R_{\text{TE}} = \frac{\mu_2(\omega)k_{z,1} - \mu_1(\omega)k_{z,2}}{\mu_2(\omega)k_{z,1} + \mu_1(\omega)k_{z,2}}. \tag{38} \]
Once again we see that only the TE component of the wave contributes. Owing to the highly oscillatory nature of the Greens’ function as a function of frequency, computing both the integral over \( k_p \) in equation (37) and \( \omega \) in equation (36) numerically is computationally highly intensive. Furthermore, as the ‘sinc’ function diverges at \( \omega \to +\infty \) it is not possible to convert the frequency integral to the usual Matsubara summation. However, the free induction decay filter is strongly peaked about \( \omega = 0 \) (\( \lambda \to \infty \)) and the distance from the ‘central spin’ to the surface is typically on the order of tens of nanometers. This means that the ‘central spin’ is within a wavelength of the surface and, hence, one can use a near field expansion to obtain an analytical approximation for the Green’s function. In this limit \( z_r \ll \lambda = 2\pi n(\omega)/k \). Thus, \( k \ll k_p \) and we can expand \( k_z \) as
\[
k_z = \sqrt{k^2 - k_p^2} = ik_p \sqrt{1 - k_p^2/k^2} \approx ik_p. \tag{39} \]
Hence, the reflection coefficient simplifies to
\[
R_{\text{TE}} \approx \frac{\mu_2(\omega) - \mu_1(\omega)}{\mu_2(\omega) + \mu_1(\omega)}, \tag{40} \]
and the integral to
\[
\hat{\mathbf{z}} \cdot \mathbf{\nabla} \times \mathbf{G}(\mathbf{r}, \mathbf{r}, \omega) \times \mathbf{\hat{z}} = \frac{\mu_1(\omega) \mu_2(\omega) - \mu_1(\omega)}{4\pi \mu_2(\omega) + \mu_1(\omega)} \int_{0}^{\infty} dk_p k_p^2 e^{-2k_{z,1}|z|}. \tag{41} \]
which can be integrated analytically to give

\[ \hat{z} \cdot \nabla \times G(r, r', \omega) \times \hat{z} = \frac{\mu_1(\omega) \mu_2(\omega) - \mu_1(\omega) \mu_2(\omega)}{16\pi |z|^3} \]  

Equation (42)

Essentially, the Green’s function comprises of two contributions, a propagating contribution and an evanescent (decaying) contribution. The near-field expansion negates the propagating contribution in favor of the dominant evanescent contribution.

Substituting equation (42) into (36) one finds that the surface contribution to the spin coherence reads

\[ \phi(t) = \frac{9 \mu_1(\omega) \gamma^2}{16\pi |z|^3} \int_0^\infty \frac{d\omega}{2\pi} \frac{sinc^2(\omega t/2)}{\coth(\omega t/2k_B T)} \text{Im}\left[ \frac{\mu_1(\omega) \mu_2(\omega) - \mu_1(\omega) \mu_2(\omega)}{[1 + 2\mu_1(\omega)]^2 \mu_2(\omega) + \mu_1(\omega)} \right] \]  

Equation (43)

The result exhibits the same \( z^{-3} \) scaling that was found in previous phenomenological models [11]. However, here we find the decoherence rate is also a function of the frequency dependent permeabilities \( \mu_1 \) and \( \mu_2 \) of the upper and lower layers. Hence, not only are the magnetic properties of the layer in which the spin is embedded important when determining the coherence time of the spin but the magnetic properties of the neighboring layer also play a role.

3.2. Decoherence from surface spins

Another effect that has been discussed [10] is the effect of spins that lie on the surface of the medium in which the ‘central spin’ is embedded. One can model the effect of spins located on the surface of the medium by assuming that they induce a surface magnetization (see figure 1(c)). This surface magnetization can then, in turn, be modeled as being generated by an ‘effective’ bound current. Here, we assume that the surface spins are, primarily, a source of static magnetization rather than an additional noise source but are able respond to perturbations in the magnetic field owing to the surface spins.

The presence of this extra magnetization field at the surface becomes (see supplementary information)

\[ R_{FE} = \frac{k_{g2} \mu_2(\omega) - k_{g1} \mu_1(\omega)}{k_{g1} \mu_2(\omega) + k_{g2} \mu_1(\omega)} \frac{2ik_{g2}^2 k_{g1} \chi_s(\omega) \mu_1(\omega) \mu_2(\omega)}{[k_{g1} \mu_2(\omega) + k_{g2} \mu_1(\omega)]^2}. \]  

Equation (44)

The first term in equation (44) is the usual reflection coefficient for a surface without surface spins and the second term gives the reflection owing to the magnetization field of the surface spins. In this case the Green’s function has the same form as before (equation (37)) except with the reflection coefficient of the surface (including the surface spin layer) now given by the (44). Applying the same near field approximation and analytically integrating the result leads to

\[ \hat{z} \cdot \nabla \times G(r, r', \omega) \times \hat{z} = \frac{\mu_1(\omega) \mu_2(\omega) - \mu_1(\omega) \mu_2(\omega)}{16\pi |z|^3} \frac{3 \mu_1(\omega) \chi_s(\omega) \mu_2(\omega) \mu_2(\omega)}{[1 + 2\mu_1(\omega)]^2 \mu_2(\omega) + \mu_1(\omega)} \]  

Equation (45)

The first term is the same as for the case of a single interface with no surface spins. The second term gives the contribution from the surface spins alone. Thus, the surface spin contribution to the spin coherence reads
\[ \phi(t) = -\frac{279\mu_0^2\gamma^2T^2}{16\pi|z_i|^2} \int_0^\infty \frac{d\omega}{2\pi} \sin^2(\omega t/2) \coth(\hbar\omega/2k_B T) \text{Im} \left[ \frac{\mu_1(\omega)}{1 + 2\mu_1(\omega)} \chi_i(\omega) \mu_1(\omega) \mu_2(\omega) \right] \left[ \frac{\mu_1(\omega) + \mu_2(\omega)}{\mu_1(\omega) + \mu_2(\omega)} \right]^2. \]  

(46)

Again, we see that the expression displays both the \( z_i^{-4} \) scaling and the linear dependence in the surface spin susceptibility that has been found in previous phenomenological models [10]. Note that, in this case the imaginary term is, in general, negative so the coherence still exponentially decays.

### 4. Results

#### 4.1. Permeability models

In order to validate the theoretical results we will compute the depth dependence of the decoherence of a shallow NV center in diamond, which was measured experimentally in [8, 9].

First, consider the case of a single interface without the presence of surface spins such as depicted in figure 1(b). Here, the material with permeability \( \mu_1 \) in which the spin is located is diamond. The interface at \( z = 0 \) depicts an interface with another material with permeability, \( \mu_2 \). For the experiments documented in [8, 9] this other medium is just the vacuum (\( \mu_2 = 1 \)).

In this system the main source of decoherence comes from the \(^{13}\text{C} \) nuclear spins, which are present at a concentration of \( \approx 1.1\% \) in the electronic-grade diamond used in the experiments. In this formalism, the effect of the nuclear spins is described by the magnetic permeability, \( \mu_i \). We can use the common frequency dependent paramagnetic permeability model [28]

\[ \mu_i(\omega) = \frac{\chi_i}{1 + i\omega\tau_i} + 1, \]  

(47)

to model the magnetic response in \( i \)th layer. Here, \( \chi \) is the magnetic susceptibility of the nuclear spins and \( \tau \) is the magnetization relaxation time (i.e. the time it takes the background spins to de-align when the magnetic field is switched off). In this model the static permeability (\( \omega \to 0 \)) is given by \( \chi_i + 1 \) and at high frequencies (\( \omega \to \infty \)) \( \mu(\omega) \to 1 \) and, hence, the medium becomes transparent. The vacuum (\( \mu(\omega) \to 1 \)) occurs when \( \chi = 0 \).

Although, we do not know the susceptibility of the \(^{13}\text{C} \) nuclear spins in layer \( i = 1 \) precisely, we can make an order of magnitude estimate by noting that the susceptibility of unpaired electrons in paramagnetic atoms is on the order of \( \chi \approx 1 \times 10^{-5} \). However, the coupling of electron spins to magnetic fields is much stronger than that of nuclear spins. The difference is quantified by the square of the gyromagnetic ratio. The gyromagnetic ratio for an electron is \( \gamma = 1.76 \times 10^{13} \text{ rads s}^{-1} \text{ T}^{-1} \) whereas the gyromagnetic ratio for \(^{13}\text{C} \) nuclear spins is over three orders of magnitude smaller, \( \gamma_i = 6.73 \times 10^7 \text{ rads s}^{-1} \text{ T}^{-1} \). Scaling the paramagnetic susceptibility with regard to the weaker coupling and lower concentration of nuclear spins leads to an estimate of the nuclear susceptibility on the order of \( \chi_i \approx 1.6 \times 10^{-14} \). The relaxation time is estimated to be \( \tau_i \approx 3 \text{ ms} \) from NMR linewidth measurements [29]. For the \( i = 2 \) layer we take \( \chi_2 \) and \( \tau_2 \) to be variables of a similar order of magnitude to represent materials with different magnetic responses.

In the second case, consider a single interface with the presence of surface spins such as depicted in figure 1(c). The material parameters of the diamond can be estimated in the same way as before. In addition, we can estimate the susceptibility of the surface spins in a similar way by assuming that they respond in the same manner as the nuclear spins and hence they obey the same frequency dependent model

\[ \chi_i(\omega) = \frac{\chi_i^0}{1 + i\omega\tau_i}. \]  

(48)

Reference [10] found the density of surface spins to be \( \rho_{\text{spins}} = 0.04 \text{ nm}^{-2} \), which is about two orders of magnitude smaller than the density of the bulk \(^{13}\text{C} \) nuclear spins, hence we take \( \chi_i^0 \approx 10^{-16} \). Reference [10] also gives the surface spin relaxation rate to be \( \tau_i = 5 \mu\text{s} \).

Finally, when computing the bulk coherence time, a value of \( R = 0.8 \text{ nm} \) was used, which is the average distance from the ‘central spin’ to the nearest nuclear spin and the temperature in all cases was taken to be 40 K.

#### 4.2. Decoherence from the interface

Figure 2 shows the coherence time for an NV center as a function of distance for interfaces between diamond and various magnetically responding materials. In figures 2(a) and (b) \( \tau_1 = \tau_2 = 3 \text{ ms} \) and \( \chi_2 \) is varied. \( \chi_2 = 0 \) models the interface of diamond with the vacuum, where as \( \chi_2 > 0 \) models the interface of diamond materials with ever increasing magnetic responses. Figure 2(a) shows that for \( \chi_2 \leq \chi_1 \) the coherence time decreases as the NV center moves closer to the interface. Conversely, as the NV center moves away from the interface the coherence time approaches the homogeneous medium coherence time and, at distance greater of over 1 nm the effect of the interface is negligible. Furthermore, as the value of \( \chi_2 \) approaches the value of \( \chi_1 \) the coherence time increases. This is because, as the magnetic responses of the two materials becomes closer, the reflection
the coherence time is equal to the homogeneous medium value. Magnetic responses are equal then the material in the two layers is the same and there is no interface at all, and coefficient at the interface is smaller and, hence, fewer magnetic fluctuations are reflected. Note that, if the two magnetic responses are equal then the material in the two layers is the same and there is no interface at all, and the coherence time is equal to the homogeneous medium value.

Figure 2(b) shows that for \( \chi_2 \geq \chi_1 \) the coherence time increases as the NV center moves closer to the interface. This is because the phase shift that occurs on reflection from a strongly magnetically responding material leads to destructive interference of the magnetic fluctuations close to the interface. This effect might contribute to the suppression of decoherence at very short distances from the interface that was observed in [9]. Similarly, the larger \( \chi_2 \), the longer the coherence time because the phase shift is greater and, hence, the incident and reflected magnetic fluctuations are further out of phase and, thus, the destructive interference is stronger.

In figures 2(c) and (d) \( \chi_2 = 1.6 \times 10^{-14} \) in both layers and \( \tau_2 \) is varied. Again, we see that the coherence time decreases as the NV center moves closer to the interface when \( \tau_2 \leq \tau_1 \) and increases for \( \tau_2 \geq \tau_1 \). This is, again, owing to the phase shift of the reflected fluctuations. For \( \tau_2 \leq \tau_1 \) the longer the relaxation time the shorter the coherence time. This is because the magnetic fluctuations persist for longer and, hence, have more of an effect on the NV center.

4.3. Decoherence from surface spins

Figures 3(a) and (b) show the coherence time for an NV center as a function of distance from an interface between diamond and the vacuum (\( \chi_2 = 0 \)) in the presence of surface spins. In figure 3(a) \( \tau_1 = 5 \mu s \) and \( \chi_s \) is varied. The susceptibility of the surface spins is taken to be between 1% and 4% of the bulk nuclear spin susceptibility. As ever, the coherence time decreases as the NV center moves closer to the interface and the larger the surface spin susceptibility the shorter the coherence time.

Here, as before, the coherence time decreases as the NV center moves closer to the interface and the longer the relaxation time the shorter the coherence time. An important feature to note is that the distance over which the surface spins effect the NV center; the coherence time approaches the homogeneous medium coherence time at a depth of 50 nm, which is between 1 and 2 orders of magnitude larger than the distance range over which the interface alone interacts. Hence for shallow NV centers with depths greater than 1 nm the dominant decoherence method is the interaction with the surface spins. The interaction with the interface itself is negligible. These distances are the same order of magnitude as those found experimentally in [8, 9].
5. Summary

Here, we have extended the Green’s function formalism for spin decoherence in a bulk material that was developed in [14] to inhomogeneous media. To validate the theory we have computed the decoherence rate of a shallow NV center in diamond placed within 50 nm from the surface. In the presence of surface spins, the coherence time decreases as one approaches the surface from a value of ≈240 μs at 50 nm to a value on the order of 10 μs for distances less than 10 nm. These coherence times are a similar order of magnitude to those found experimentally in [8, 9]. For a more precise estimate of the coherence times one would need more sophisticated permeability models and more accurate values for the magnetic properties of the 13C spins in diamond and of any adjoining materials. However, these results show that the Green’s function formalism is able to model decoherence in inhomogeneous spins systems. The formalism also shows that at distances greater than 1 nm it is the interaction with the surface spins that is dominant as opposed to the interaction with the interface itself.

Experimental work in [9] showed that the influence of the interface falls off for distances >8 nm and hence the Green’s function formalism also gives the correct order of magnitude result for this feature as well.

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