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Quantum theory of spectral-diffusion-induced electron spin decoherence

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A quantum cluster expansion method is developed for the problem of localized electron spin decoherence due to dipolar fluctuations of lattice nuclear spins. At the lowest order it provides a microscopic explanation for the Lorentzian diffusion of Hahn echoes without resorting to any phenomenological Markovian assumption. Our numerical results show remarkable agreement with recent electron spin echo experiments in phosphorus doped silicon.

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It was realized a long time ago that spectral diffusion due to the dipolar fluctuations of nuclear spins often dominates the coherence decay in electron spin echo experiments.[1,2] The recent advent of spin-based quantum computation in semiconductor nanostructures revived the interest in spectral diffusion, which is expected to be the dominant channel for low-temperature spin decoherence in several spin-based quantum computer architectures.[3] In spectral diffusion, the electron spin Zeeman frequency diffuses in time due to the noise produced by the nuclear spin bath. Dipolar fluctuations in the nuclear spins give rise to a temporally random effective magnetic field at the localized electron spin, leading to irreversible decoherence (i.e., a T_2 process). All available theories to date are based on classical stochastic modeling of the nuclear field, a Markovian theoretical framework which is inevitably phenomenological since it requires an arbitrary choice for the spectrum of nuclear fluctuations. Such a classical Markovian modeling is arguably incompatible with the strict requirements of spin coherence and control in a quantum information device. In addition, recent rapid experimental progress in single spin measurements,[4] which in the near future promise sensitive measurements of quantum effects in spin resonance, also warrant a quantum theory of spectral diffusion. Here we propose a quantum theoretical framework for spectral diffusion which is nonstochastic and fully microscopic. In addition, our theory produces an accurate quantitative prediction for the initial decoherence, which is the most important regime for quantum computation.

Spectral diffusion is not a limiting decoherence process for silicon or germanium based quantum computer proposals because these can, in principle, be fabricated free of nuclear spins using isotopic purification. Unfortunately this is not true for the important class of materials based on III–V compounds, where spectral diffusion has been shown to play a major role.[3,5] There is as yet no experimental measurement of localized spin decoherence (echo decay) in III–V materials, but such experimental results are anticipated in the near future.

Our theory reveals that the inclusion of quantum corrections to nuclear spin fluctuation increases the degree of decoherence, as is best evidenced from our explanation of the existing factor of three discrepancy between the Markovian stochastic theory[5] and experimental data[6–8] of spin echo decay in phosphorus doped silicon. Our method allows a fully microscopic explanation for the observed time dependence of Hahn echo decay due to a nuclear spin environment. It was pointed out a long time ago[2,7] that the observed time dependence of these echoes are well fitted to the expression $\exp(-\tau^2)$ (here τ is half of the time lag between the initial signal and an echo), a behavior which can be derived phenomenologically by assuming Lorentzian Brownian motion for the electron spin Zeeman frequency.[2,9] In our method this behavior arises naturally from the collective quantum evolution of the dipolar coupled nuclei, without any phenomenological assumption on the dynamics of the environment responsible for decoherence. A proper description of coupled spin dynamics is rather difficult due to the absence of Wick's theorem for spin degrees of freedom. In that regard, variations of our method may prove rather useful, since environmental spin baths are ubiquitous in any device exploiting the coherent properties of quantum spin systems.

The free evolution Hamiltonian for the spectral diffusion problem is given by[5]

$$\mathcal{H} = \mathcal{H}_{Ze} + \mathcal{H}_{Zn} + \mathcal{H}_A + \mathcal{H}_B, \tag{1}$$

where

$$\mathcal{H}_{Ze} = \gamma_S B S_z, \tag{2}$$

$$\mathcal{H}_{Zn} = -\gamma_I B \sum_n I_{nz}, \tag{3}$$

$$\mathcal{H}_A = \sum_n A_n I_{nz} S_z, \tag{4}$$

$$\mathcal{H}_B = \sum_{n \neq m} b_{nm} (I_{n+} I_{m-} - 2 I_{nz} I_{mz}). \tag{5}$$

Here S denotes the electron spin operator which couples to the nuclear spin I_n located at the lattice site R_n. The nuclear spins are coupled to the electron through the hyperfine constant A_n. We have truncated Eq. (4) since the nonsecular hyperfine coupling can be neglected at moderate magnetic fields ($B > 0.1$ T for the Si:P case). This interaction leads to interesting effects at $B=0$,[10] but at the moderate magnetic fields required for spin resonance measurements it only contributes a small visibility decay.[11] Each nuclear spin is

coupled to all others via the dipolar interaction Eq. (5), which is again truncated in the range of moderate B fields (for further details we refer to Ref. 5). The Hahn echo experiment consists in preparing the electron spin in the initial state $|y_e\rangle=(|\uparrow\rangle+i|\downarrow\rangle)/\sqrt{2}$, and then allowing free evolution for time τ. A π- pulse (here described by the Pauli operator $\sigma_{x,e}$) is then applied to the electron spin, and after free evolution for one more interval τ an echo is observed, which provides a direct measurement of single spin coherence (i.e., T_2 or T_M in the usual notation).

We will now derive an exact expression for the Hahn echo decay due to Eq. (1). The density matrix (for electron and nuclear spins) describing Hahn echo is given by

$$\rho(\tau) = U(\tau)\rho_0 U^{\dagger}(\tau), \tag{6}$$

with the evolution operator

$$U(\tau) = \mathrm{e}^{-i\mathcal{H}\tau}\sigma_{x,e}\mathrm{e}^{-i\mathcal{H}\tau}. \tag{7}$$

Here ρ_0 is taken to be a thermal state for the nuclear spins

$$\rho_0 = \frac{1}{2M}|y_e\rangle\langle y_e| \otimes \mathrm{e}^{-\mathcal{H}_n/k_BT}, \tag{8}$$

where $\mathcal{H}_n=\mathcal{H}_{Zn}+\mathcal{H}_B$ and M is its partition function ($M \approx 2^N$ for $T \gg$ nK,[5] where N is the number of nuclear spins). The spin echo envelope is then given by

$$v_E(\tau) = 2|\mathrm{Tr}\{(S_x + iS_y)\rho(\tau)\}|. \tag{9}$$

An explicit expression for Eq. (9) can be obtained by noting that the electron and nuclear spin Zeeman energies commute with the total Hamiltonian, and $\sigma_{x,e}$ anticommutes with S_z. After a few manipulations we get

$$v_E(\tau) = \frac{1}{M}|\mathrm{Tr}\{U_+U_-\mathrm{e}^{-\mathcal{H}_n/k_BT}U_+^{\dagger}U_-^{\dagger}\}|, \tag{10}$$

where

$$U_{\pm}(\tau) = \mathrm{e}^{-i\mathcal{H}_{\pm}\tau} \tag{11}$$

are evolution operators under the effective Hamiltonians

$$\mathcal{H}_{\pm} = \mathcal{H}_B \pm \frac{1}{2}\sum_n A_n I_{nz}, \tag{12}$$

which describe dipolar evolution under the effect of an electron spin up ($\mathcal{H}_+$) or down ($\mathcal{H}_-$). The trace in Eq. (10) is taken over nuclear spin states only.

In the high temperature limit ($k_BT \gg \gamma_I B$) we can expand Eq. (10) in powers of τ to get

$$v_E(\tau) = 1 - \sum_{l=1}^{\infty} D_{2l}\tau^{2l}. \tag{13}$$

Defining the parameter

$$c_{nm} = \frac{A_n - A_m}{4b_{nm}}, \tag{14}$$

we obtain the first five coefficients D_{2l} as a power series of c_{nm} and b_{nm}. For example, the first two coefficients become explicitly $D_2=0$, $D_4=4\Sigma_{n<m}c_{nm}^2 b_{nm}^4$. Truncating Eq. (13) gives physical results only for extremely short τ unless most nuclear pairs satisfy the condition $c_{nm} \ll 1$. Nevertheless most physical problems are characterized by several $c_{nm} \gg 1$, making evident the need for an alternative expansion. Thus the τ expansion, while being formally exact, is not practical for coherence calculation except for extremely short τ.

In the $c_{nm} \gg 1$ regime, nondegenerate perturbation theory is applicable to Eq. (12). We introduce a bookkeeping parameter λ such that $\pm\mathcal{H}_{\pm}=\mathcal{H}_0 \pm \lambda\mathcal{H}'$. Here the unperturbed Hamiltonian $\mathcal{H}_0=\frac{1}{2}\Sigma_n A_n I_{nz}$ is diagonal in the nuclear spin z-basis, while $\mathcal{H}'=(1/\lambda)\mathcal{H}_B$ is the dipolar interaction rescaled to have the same magnitude as $\mathcal{H}_0$. A convenient choice for an order of magnitude estimate of $\lambda \sim 1/|c_{nm}|$ is to use the minimum possible value of $b_{nm}/|A_n - A_m|$ between nearest neighbors: $\lambda \sim \mathrm{Max}(b_{nm})/\mathrm{Max}(A_n) \sim 10^{-3}$ for Si:P. Below we introduce a cluster expansion that can be related to powers of λ in this perturbation approach when $c_{nm} \gg 1$.

Let $\mathcal{D}$ be a subset of the nuclei in the problem. Let $v_{\mathcal{D}}(\tau)$ be the solution of $v_E(\tau)$ [Eq. (10)] when only including the nuclei in $\mathcal{D}$. We recursively define the contribution from subset $\mathcal{D}$ as $v_{\mathcal{D}}(\tau)$ minus contributions from any proper subset of $\mathcal{D}$,

$$v'_{\mathcal{D}}(\tau) = v_{\mathcal{D}}(\tau) - \sum_{\mathcal{S}\subset\mathcal{D}} v'_{\mathcal{S}}(\tau). \tag{15}$$

For the empty set, we define $v'_{\varnothing}(\tau)=v_{\varnothing}(\tau)=1$. Consider a subset contribution written in the form of the nondegenerate perturbation expansion. Assuming $\mathrm{Max}(b_{nm})\tau \ll 1$, we can show by the specific properties of $\mathcal{H}'$ that a cluster of size k is composed of terms that are $O(\lambda^k)$ or higher. In other words, we can write the following expansion:

$$v_E(\tau) = 1 + \sum_{k=2}^{k_0}\sum_{|\mathcal{D}|=k} v'_{\mathcal{D}}(\tau) + O(\lambda^{k_0+1}), \tag{16}$$

where the second summation is over all possible nuclear subsets of size k (containing k distinct nuclear sites). We note that a subset of size 1 gives no contribution.

The $O(\lambda^{k_0+1})$ error in Eq. (16) is misleading because the number of terms of a given order of λ may be large compared to λ. The nature of this problem, as well as a solution, becomes apparent when we use a nearest neighbor approximation. With this approximation, we ignore the interaction between distant nuclei (i.e., pairs of nuclei for which b_{nm} is below some threshold) and divide our nuclear subsets into connected "clusters." A subset contribution is then the product of its cluster contributions.

Consider all possible contributing subsets of size k. We can categorize these subsets by the number of clusters they contain. To estimate the number of subsets of size k with l clusters, consider building the subset randomly. First select l nuclei at random for each of the l clusters. The remaining $k-l$ nuclei are chosen randomly from the neighbors of any previously chosen nuclei. Let L be the average number of "nearest neighbors" for each nucleus. The probability that a nucleus will bridge two clusters that were meant to be separate is at most $O(kL/N)$. So the probability that any of the k

nuclei will bridge two clusters is at most $O[1-(1-kL/N)^k] \rightarrow O(k^2L/N)$. Therefore, as long as $k^2 \ll N/L$, we can accurately estimate the number of subsets in this manner of choosing nuclei at random. Under this condition, the number of subsets of size k with l clusters will scale roughly (without dividing out permutations) as $O(N^l L^{k-l})$, growing exponentially with N as we increase the number of clusters. Clusters of size one give no contribution; therefore, assuming $k \ll \sqrt{N/L}$ and $N \gg L$, the possible contributing subsets of size k are dominated by those containing all pairs (and a single triplet if k is odd) which maximizes the number of contained clusters. If $k=2l$ is even, then the number of contributing subsets of size $k \ll \sqrt{N/L}$, largely composed of l pairs, is $O[(NL)^l/2^l l!]$. Therefore, our subset expansion [Eq. (16)] error grows with $k_0=2l_0 \ll \sqrt{N/L}$ as $O[(\lambda^2 NL/2)^{l_0}/l_0!]$. This is problematic because $\lambda^2 NL$ is not necessarily small. Noting, however, that most contributing subsets are composed entirely of pairs (except the one triplet of odd-sized subsets), we can approximate the solution up to order $k_0 \sim \sqrt{N/L}$ by adding all possible products of pair contributions as obtained by distributing the product in the following:

$$v_E(\tau) = \prod_{n<m} \{1 + v'_{nm}(\tau)[1 + O(\lambda L)]\} + O\left[\frac{(\lambda^2 NL)^{l_0}}{2^{l_0} l_0!}\right], \tag{17}$$

which gives the lowest order of our cluster expansion. The correction $O[(\lambda^2 NL/2)^{l_0}/l_0!]$ is infinitesimal provided $l_0 = k_0/2 \sim \sqrt{N/L} \gg \lambda^2 NL$, or $\lambda \ll 1/(NL^3)^{1/4}$. For $N \sim 10^4$ and $L \sim 10$, we get $\lambda \ll 0.02$ as the condition for disconnected pairs to dominate spectral diffusion decay. The $O(\lambda L)$ in Eq. (17) represents the error incurred by not considering clusters larger than pairs (including what is required for odd subsets) and can be thought of as the contribution you get by adding a neighbor to one of the distributed pairs. Not all of the terms obtained by distributing Eq. (17) will contain pairs that are disconnected from each other. However, using the same argument we used to estimate numbers of contributing subsets, $l < k_0/2$ random pairs will most likely be disconnected when $k_0 \sim \sqrt{N/L}$. These extraneous terms are therefore negligible at each order below k_0.

For a cluster of two nuclear spins ($\mathcal{D}=\{n,m\}$) exact evaluation of $v_{\mathcal{D}}(\tau)$ using Eq. (10) in the high temperature limit leads to

$$v_{nm}(\tau) = 1 + v'_{nm}(\tau) = 1 - \frac{c_{nm}^2}{(1+c_{nm}^2)^2}[\cos(\omega_{nm}\tau) - 1]^2, \tag{18}$$

$$\omega_{nm} = 2b_{nm}\sqrt{1+c_{nm}^2}, \tag{19}$$

with c_{nm} defined in Eq. (14). Using Eq. (17) and the condition $\mathrm{Max}(b_{nm})\tau \ll 1$ we write the final expression for the lowest order cluster expansion as

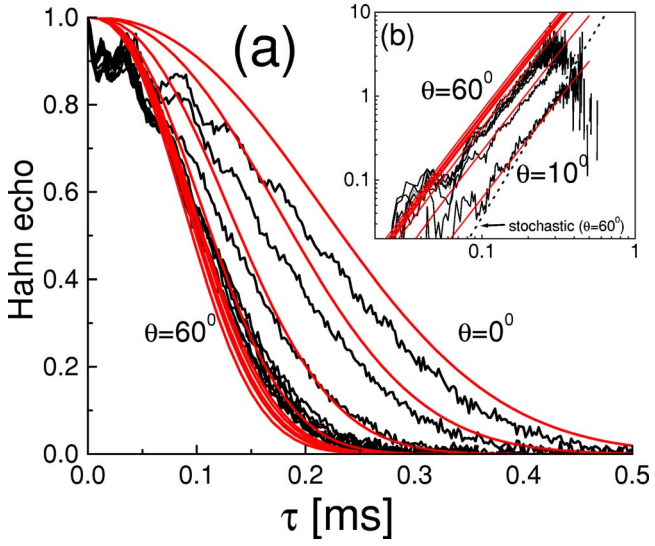

FIG. 1. (Color online) Hahn echo decay $v_E(\tau,\theta)$ of a phosphorus donor electron spin in silicon. (a) Theory (solid lines) and experiment is shown for several orientation angles of the magnetic field with respect to the crystal lattice, ranging from the [100] to the [110] direction ($\theta=0,10,20,\ldots,90$). (b) Here we plot $-\ln v_E(\tau,\theta) + \ln v_E(\tau,\theta=0)$, allowing for the removal of any decoherence mechanism which is independent of θ. The qualitative and quantitative agreement between theory and experiment is remarkable, in contrast to the stochastic approach (dashed).

$$v_E(\tau) \approx \exp\left\{\sum_{n<m} v'_{nm}(\tau)[1 + O(\lambda L)]\right\}. \tag{20}$$

Note that including clusters of three adds a correction $O(\lambda L)$ to the decay.

We have presented two theories. Both require $\tau \ll \mathrm{Max}(b_{nm})^{-1}$; however, in problems we have considered, the decay time is well within this limit. We argued the τ expansion [Eq. (13)] converges for $c_{nm} \ll 1$ while the cluster expansion [Eq. (17)] for $c_{nm} \gg 1$. The cluster expansion becomes nonperturbative through the use of the exact solution Eq. (18). In fact, in the same way that cluster size was related to minimum orders of λ in the perturbation expansion, we can also relate cluster size to minimum orders of τ in the τ expansion. For example, by taking $c_{nm} \ll 1$ in Eq. (18) we recover Eq. (13) to lowest order, showing that this exact solution interpolates between the two regimes at lowest order. For physical problems where a wide range of parameters c_{nm} coexist, exact evaluation of larger clusters provides a systematic approximation to the problem of spectral diffusion.

We use Eqs. (18) and (20) to perform explicit calculations of electron spin echo decay of phosphorus impurities in silicon.[5–7] In this case the parameter A_n is given by the hyperfine shift of a nuclear spin positioned a vector $\boldsymbol{R}_n$ from the donor center

$$A_n = \frac{8\pi}{3}\gamma_S\gamma_I\hbar|\Psi(\boldsymbol{R}_n)|^2. \tag{21}$$

We used $\gamma_S = 1.76\times10^7 (\mathrm{s\,G})^{-1}$ and $\gamma_I = 5.31\times10^3 (\mathrm{s\,G})^{-1}$. Here $\Psi(\boldsymbol{R}_n)$ is the Kohn-Luttinger wave function of a phos-

phorus donor impurity in silicon, as described in Ref. 5. The central ^{31}P nuclear spin does not contribute to spectral diffusion because its hyperfine energy is significantly larger than any of its neighbors, suppressing the spin flips by energy conservation. Dipolar coupling is given by

$$b_{nm} = -\frac{1}{4}\gamma_I^2\hbar\frac{1-3\cos^2\theta_{nm}}{R_{nm}^3}. \tag{22}$$

It contains an important anisotropy with respect to the angle θ_{nm} formed between the applied magnetic field and the bond vector linking the two spins ($\boldsymbol{R}_{nm}$). This property leads to a strong dependence of spin echo decay when the sample is rotated with respect to the applied B field direction. Figure 1 shows experimental data when the sample is rotated from the [100] to the [110] direction. Here the cluster approximation is expected to be appropriate for $\tau \ll 1-5$ ms. Finally, in a natural sample of silicon only a small fraction $f=4.67\%$ of lattice sites have nonzero nuclear spin (these are the spin-1/2 ^{29}Si isotopes). Averaging Eq. (17) we get

$$v_E(\tau) = \prod_{n<m}[(1-f^2)+f^2 v_{nm}(\tau)]. \tag{23}$$

Our numerical calculations of Hahn echo decay for several magnetic field orientation angles are shown in Fig. 1(a). We also show experimental data taken for bulk natural silicon with phosphorus doping concentration equal to 2×10^{15} cm^3[8]. The high concentration of phosphorus donors leads to an additional decoherence channel arising from the direct spin-spin coupling between the electron spins that contribute to the echo. This contribution can be shown to add a multiplicative factor $\exp(-\tau/1\ \text{ms})$ to Eq. (23).[12] Because this contribution is independent of the orientation angle, we can factor it out by subtracting the $\theta=0$ contribution from the logarithm of the experimental data taken at angle θ. The result is shown in Fig. 1(b) (log-log scale). Our theory seems to explain the time dependence of the echo quite well. To check convergence of our cluster expansion we have gone to the next order. Including clusters of three amounts to a contribution of 0.1%, in agreement with our estimate of $\lambda fL \sim 10^{-3}$. We have also verified that our cluster expansion results agree quantitatively with Eq. (13) for small τ when excluding nuclei close to the center of the electron wave function where $c_{nm} \gg 1$. This result is to be compared with the recent stochastic theory developed by two of us[5] [dashed line in Fig. 1(b) shows the stochastic calculation for $\theta=60°$]. Although the stochastic theory yields correct order of magnitude for the coherence times, it fails qualitatively in explaining the time dependence. The present method is able to incorporate all these features within a fully microscopic framework.

An important issue in the context of quantum information is the behavior of spin coherence at the shortest time scales. The experimental data in Fig. 1 reveal several oscillating features which are not explained by our current method. These are echo modulations arising from the anisotropic hyperfine coupling omitted in Eq. (1).[7] This effect can be substantially reduced by going to higher magnetic fields (In a quantum computer $B\sim9$ T will probably be required in order to avoid loss of fidelity due to echo modulation.[13]) On the other hand, spectral diffusion is essentially independent of magnetic field even to extremely high values ($B\sim10$ T). Nevertheless this effect is expected to be absent in III–V materials,[14] hence, our theory allows the study of spin coherence at time scales of great importance for quantum information purposes but currently inaccessible experimentally.

In conclusion, we describe a quantum approach for the problem of localized electron spin decoherence due to the fluctuation of dipolar coupled nuclear spins. In contrast to former theories, our method requires no *ad hoc* stochastic assumption on the complex dynamics of the environment responsible for decoherence. Hence, it provides an important example where direct integration of the environmental equations of motion provides a systematic understanding of the loss of coherence which needs to be controlled for quantum information applications.

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