Incoherent Landau-Zener-Stückelberg transitions in single-molecule magnets

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It is shown that in experiments on single molecule magnets in which transitions between two lowest spins states are induced by sweeping the applied magnetic field along the easy axis; the transitions are fully incoherent. Nuclear spins and the dipolar coupling of molecular spins are identified as the main sources of decoherence, and the form of the decoherence is calculated. The Landau-Zener-Stückelberg (LZS) process is examined in light of this decoherence, and it is shown that the correct formula for the spin-flip probability is better given by a more recent formula of Kayanuma than that of LZS. The two formulas are shown to be identical in the limit of rapid sweeps. An approximate way of incorporating the molecular spin dipole field into the rate equations for this process is developed.

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I. INTRODUCTION

A large number of molecular solids made from organic molecules containing magnetic ions have come to be known as single-molecule magnets (SMMs) and their magnetization dynamics has been studied intensively for over a decade now.[1] The designation SMM comes about because the intermolecular magnetic interactions are much weaker than the intramolecular ones, yet one sees hysteresis,[2] a phenomenon generally associated with ferromagnets in which the spins are strongly interacting. Of special interest, and the subject of this paper, is the study of low-temperature quantum tunneling between the two lowest Zeeman sublevels of one molecular spin (MS) since, then, processes such as phonon induced excitation or relaxation do not come into play[3] and the dynamics is, *a priori*, purely quantum mechanical.

The above conclusion is strongly reinforced by experiments in which the magnetization relaxes in the presence of a time-dependent magnetic field which is swept through the value where the two Zeeman levels are degenerate.[4–8] At first sight, this constitutes a classic Landau-Zener-Stückelberg (LZS) process[9] and the data appear to confirm this idea, especially in Fe_8. The strongest check comes from the fact that the transition probability depends on the sweep rate over 2.5 orders of magnitude in agreement with the LZS formula.[5] Further, the tunneling amplitude extracted by fitting to this formula agrees with direct numerical diagonalization of the single MS Hamiltonian. Most importantly, the matrix element so deduced varies with a static *transverse* magnetic field in oscillatory fashion,[4] as required by the model Hamiltonian.[10]

It is, however, surprising that the LZS formula should be so well obeyed, since it is derived for isolated noninteracting spins. The MSs in SMMs interact with many other degrees of freedom, and anything in the environment that can distinguish between the two tunneling states of the system will tend to suppress quantum tunneling and act as a source of decoherence. Phonons are an obvious such environment, but can be excluded by working at low enough temperatures. The remaining environment is that of the nuclear spins. These have been previously studied in connection with magnetization tunneling in small magnetic particles[11] and in SMMs.[12–14] In addition, one must also consider the other MSs. The general picture that emerges from Refs. 12–14 is that nuclear spins give rise to incoherent transitions and the other MSs give rise to an additional magnetic field that must be added to the applied field in determining whether a given MS is at degeneracy or not. Other authors have adopted this point of view and studied these systems via Monte Carlo simulations.[15,16] Chapter 9 of Ref. 1 contains a good discussion of these and related points.

Our purpose in this paper is to re-examine the decoherence from nuclear and molecular spins, especially the latter. In Fe_8, the dipole field from other MSs is about ten times larger than that due to the nuclear spins, so *a priori*, they should be a significant source of decoherence. It may at first sight be puzzling that the MSs which form the "system," can also behave as an "environment." The situation is analogous to how the electron-electron interaction in metals contributes to the electrical resistivity. In a model in which the MSs are coupled to each other, but not to any other degrees of freedom, the *many-body* (or many-spin) wave function of the MSs evolves coherently, yet the off-diagonal elements of the *one-body* (one-spin) density matrix can still decohere, i.e., decay with time. Since the magnetization is a sum of one-spin operators, such decay is relevant to its dynamics. Whether the model is adequate is a quantitative question depending on whether the omitted degrees of freedom are stronger or weaker decoherers than the ones considered. Thus, in metals at room temperature, phonon and impurity scattering are greater contributors to the resistivity than electron-electron scattering and should not be omitted in a good model. The converse is true at very low temperatures in very pure samples (less than ~1 K in potassium, for example).

The model we study is the following. Each magnetic molecule is taken to have a total spin S in its ground manifold and to have two easy directions, $\pm\hat{\mathbf{z}}$, separated by a barrier V_B. It is assumed that other spin multiplets can be ignored at low temperatures, so that each molecule can be treated as a single spin of magnitude S. In zero external field, an isolated MS can tunnel between the $m=\pm S$ states. The corresponding energy splitting is denoted Δ.

Next, the MSs are coupled to the nuclear spins (NS). Two broadly different types of couplings may be distinguished. If the magnetic ions have nuclei with nonzero magnetic moments, the contact hyperfine interaction between an ion and its own nucleus must be considered. The corresponding energy scale is 1–10 mK. The second is the dipolar coupling between the MSs and other nuclear spins, with an energy scale $E_{dn} \sim 1$ mK for close by nuclei. (The suffixes "d" and "n" stand for "dipole" and "nuclear," respectively.) We shall assume that $E_{dn} \gg \Delta$, as is the case in Fe_8.

In addition, different MSs are coupled via the dipole-dipole interaction, which is taken to have a scale $\sim E_{dm}$ for nearest neighbors. (The suffixes "d" and "m" stand for "dipole" and "molecular," respectively.) There is clear separation of energy scales: $V_B \gg E_{dm} \gg \Delta$. This is a good description of many SMMs. In Fe_8, e.g., $V_B \sim 20$ K, $E_{dm} \sim 0.1$ K, and $\Delta \sim 10^{-7}–10^{-8}$ K. Stray and dipolar magnetic fields along $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ are unimportant since they are not large enough to give any significant mixing of the $m = \pm S$ states with the higher Zeeman states and they affect Δ only weakly. Along $\hat{\mathbf{z}}$ on the other hand, such fields are very important, since they move MSs off resonance. Under these conditions, each MS may be replaced by a pseudospin with spin-1/2 with the $|\uparrow,\downarrow\rangle$ states representing the $m = \pm S$ states of the true spin.

The plan of the paper is as follows. We calculate the decoherence from nuclear and molecular spins in Secs. II and III, respectively, pushing various details of the calculations to the Appendixes. In Sec. IV, we consider the two environments together. In Sec. V we consider the implications of the decoherence for the LZS process. We find that although the tunneling is indeed incoherent, the net spin-flip probability in a single LZS sweep is remarkably insensitive to the details of the decoherence mechanism. In a simple model where the dipole field due to the other MSs is omitted, the probability turns out to be given exactly by Kayanuma's formula for a spin coupled to an oscillator bath in the strong damping limit.[17] In the limit of high-field sweep rate this formula agrees precisely with the LZS formula. This explains why the experiments appear to be in accord with the LZS scenario. We also consider a better approximation where the dipole field is included in a macroscopically averaged way. This approximation improves the agreement with the experiments by Wernsdorfer and co-workers.[5,6]

II. MODEL FOR NUCLEAR-SPIN ENVIRONMENT

As our first model, we consider a single molecular spin interacting with the nuclear spins via the dipolar coupling. Hyperfine and transferred hyperfine interactions are not explicitly included, although in the end they are unlikely to have qualitatively different effects and only to lead to a modification of the parameter W introduced below. We assume that all nuclear spins have spin 1/2 and neglect the local magnetic field H_{loc} at the nuclear site. This is a good assumption if $H_{loc} \ll k_B T/\mu_n$, where μ_n is the nuclear magnetic moment. This is indeed so since $k_B T/\mu_n \sim 10$ T at 10 mK. The dipolar coupling between nuclear spins can be neglected for the same reason. With these assumptions, our Hamiltonian is

$$\mathcal{H}_{mn} = \frac{1}{2}(\Delta\sigma_{0x} + \epsilon\sigma_{0z}) + \sum_i \frac{E_{dn}a^3}{r_{0i}^3} \times [\sigma_{0z}\sigma_{iz} - 3\sigma_{0z} \cos\theta_{0i}\vec{\sigma}_i \cdot \hat{\mathbf{r}}_{0i}]. \tag{2.1}$$

Here, i labels the different nuclear spins, $\vec{\sigma}_0$ and $\vec{\sigma}_i$ denote the Pauli-spin matrices for the MS and the ith nuclear spin, $\mathbf{r}_{0i}$ is the position of the ith NS relative to the MS, $r_{0i} = |\mathbf{r}_{0i}|$, and $\cos\theta_{0i} = \hat{\mathbf{z}} \cdot \mathbf{r}_{0i}/r_{0i}$. Further, a is the characteristic distance from the MS to the nearest NS. We expect $a \sim 1–2$ Å for any SMM. Finally, we have included an energy bias ϵ between the $|\uparrow\rangle$ and $|\downarrow\rangle$ states of the MS, which could arise from an external magnetic field. The suffixes in $\mathcal{H}_{mn}$ stand for "molecular" and "nuclear."

We now suppose that at time $t=0$ the MS is in the state $|\uparrow\rangle$ and that every NS is in a completely disordered state described by the density matrix 1/2. Again, this assumption is well justified at the temperatures at which experiments have been carried out so far. The quantity of interest is the probability, $P(t)$, that the MS will be in the state $|\downarrow\rangle$ irrespective of the NS state.

Even for this simple model, an exact calculation of $P(t)$ is not possible (but see below). We therefore turn to the approximate methods described in Secs. IIIA–IIID of Ref. 18. We cannot assume that the damping is weak or that the NSs are fast compared to the MSs. A "golden rule" approach is still fruitful, however, as Δ is the smallest energy scale in the problem. Moreover, the validity of this approach can be self-consistently checked. Second-order perturbation theory yields

$$P(t) = \frac{\Delta^2}{4}\int_0^t dt_1 \int_0^t dt_2 e^{i\epsilon(t_1-t_2)} \prod_i F_i(t_1,t_2), \tag{2.2}$$

where

$$F_i(t_1,t_2) = \frac{1}{2}\mathrm{Tr}_i[e^{i\mathcal{H}_{i+}t_1} e^{i\mathcal{H}_{i-}(t_1-t_2)} e^{-i\mathcal{H}_{i+}t_2}], \tag{2.3}$$

with

$$\mathcal{H}_{i\pm} = \pm \frac{E_{dn}a^3}{r_{0i}^3}[\sigma_{iz} - 3\cos\theta_{0i}\vec{\sigma}_i \cdot \hat{\mathbf{r}}_{0i}]. \tag{2.4}$$

The quantity F_i is the contribution of the ith environmental spin to Feynman's influence functional evaluated for a particular pair of forward and backward paths of the "system" spin, namely, that in which this spin flips from up to down at time t_1 on the forward path and time t_2 on the backward path. We therefore refer to F_i as the (environmental) influence factor or function.

The trace in Eq. (2.3) is easy to evaluate. Defining

$$t_{12} = t_1 - t_2, \tag{2.5}$$

$x_{0i} = \mathbf{r}_{0i} \cdot \hat{\mathbf{x}}$, etc. and the vector

$$\mathbf{h}_i = \frac{E_{dn}a^3}{r_{0i}^5}(-3z_{0i}x_{0i}, -3z_{0i}y_{0i}, r_{0i}^2 - 3z_{0i}^2), \tag{2.6}$$

we have

$$F_i(t_1,t_2) = \cos 2h_i t_{12}. \tag{2.7}$$

Now,

$$h_i = \frac{E_{dn}a^3}{r_{0i}^3}(1 + 3\cos^2\theta_{0i})^{1/2}, \tag{2.8}$$

so $h_i \sim E_{dn}$ for the nearest NS and drops as $1/r^3$ for more distant ones. Thus, for $t_{12} \gtrsim E_{dn}^{-1}$ the different F_i's have random signs, and since they cannot exceed 1 in magnitude, they essentially multiply out to zero. We conclude that phase coherence is lost on the time scale $t_c \sim E_{dn}^{-1}$, and for $t \gg t_c$, we get incoherent tunneling. For such times, we can approximate

$$\prod_i F_i(t_1,t_2) \simeq \exp\left(-2\sum_i h_i^2 t_{12}^2\right). \tag{2.9}$$

Further, in the double integral in Eq. (2.2), we may introduce sum and difference variables $\bar{t}=(t_1+t_2)/2$ and $\tau = t_{12}$. The integral over τ is essentially independent of $\bar{t}$ and its limits may be extended to $\pm\infty$. The $\bar{t}$ integral then gives an overall factor of t, yielding

$$P(t) \simeq \Gamma_n t, \tag{2.10}$$

where, with

$$W^2 = 4\sum_i h_i^2, \tag{2.11}$$

$$\Gamma_n = \frac{1}{4}\Delta^2\int_{-\infty}^{\infty} d\tau e^{i\epsilon\tau}e^{-1/2W^2\tau^2} = \frac{\sqrt{2\pi}}{4}\frac{\Delta^2}{W}e^{-\epsilon^2/2W^2}. \tag{2.12}$$

We may estimate W by replacing the sum in Eq. (2.11) by an integral, taking a uniform density of nuclear spins equal to $1/a^3$ outside a sphere of radius a. Since

$$h_i^2 = \frac{E_{dn}^2 a^6}{r_{0i}^6}(1 + 3\cos^2\theta_{0i}), \tag{2.13}$$

$$W^2 \simeq 4E_{dn}^2 a^6 \int_{r>a}\frac{d^3r}{a^3}(1 + 3\cos^2\theta)\frac{1}{r^6} \tag{2.14}$$

$$= \frac{32\pi}{3}E_{dn}^2. \tag{2.15}$$

In fact, the integral estimates the contribution of the nearest neighbors rather poorly, and for the simple, body-centered, and face-centered cubic lattices, the numbers multiplying E_{dn}^2 are 67.2, 98.0, and 116, respectively.[19] Thus, in order of magnitude, we may take $W \simeq 10E_{dn}$ for any magnetic molecular solid. It should be noted that for a fixed bias ϵ, the rate Γ_n goes up with increasing E_{dn} as long as $\epsilon > W$. The converse is true for the very small number of MSs on which the bias is small, $\epsilon < W$.

The result (2.10) is essentially a Fermi golden rule rate and is limited to $t \ll \Gamma_n^{-1}$. For longer times, a formal answer can be obtained as follows.[20] We can write

$$\mathcal{H}_{mn} = \frac{1}{2}\vec{\Lambda}\cdot\vec{\sigma}_0, \tag{2.16}$$

where

$$\vec{\Lambda} = \Delta\hat{\mathbf{x}} + \left(\epsilon + 2\sum_i \mathbf{h}_i\cdot\vec{\sigma}_i\right)\hat{\mathbf{z}}. \tag{2.17}$$

Thus, $\vec{\Lambda}$ is an operator with respect to the bath spins. With the understanding that these must be traced over, we get

$$\langle\downarrow|e^{-i\mathcal{H}_{mn}t}|\uparrow\rangle = -\frac{i\Delta}{\Lambda}\sin\frac{1}{2}\Lambda t. \tag{2.18}$$

Thus,

$$P(t) = \Delta^2\prod_i \frac{1}{2}\mathrm{tr}_i\left(\frac{1}{\Lambda^2}\sin^2\frac{\Lambda t}{2}\right), \tag{2.19}$$

where tr_i indicates a trace over the ith NS. To perform this trace we take the quantization axis for it to be parallel to $\mathbf{h}_i$. This means that the variable

$$B_n = 2\sum_i h_i s_i \tag{2.20}$$

takes on all possible values obtained by letting each s_i be +1 or −1 independently.[21] That is to say, B_n is a stochastic variable with some probability distribution, $P(B_n)$, and the spin-flip probability is obtained by averaging over this distribution:

$$P(t) = \int_{-\infty}^{\infty}\frac{\Delta^2}{\Lambda^2}\sin^2\left(\frac{1}{2}\Lambda t\right)P(B_n)dB_n, \tag{2.21}$$

with

$$\Lambda = [\Delta^2 + (\epsilon + B_n)^2]^{1/2}. \tag{2.22}$$

To proceed further, we need the form of $P(B_n)$. We find this approximately by arguing that because of the law of large numbers B_n is a Gaussian with a variance W^2, i.e.,

$$P(B_n) = \left(\frac{1}{2\pi W^2}\right)^{1/2} e^{-B_n^2/2W^2}. \tag{2.23}$$

We can do somewhat better by looking at the moments of B_n. We clearly have $\langle B_n^2\rangle = W^2$, but

$$\langle B_n^4\rangle = 3\langle B_n^2\rangle^2 - 32\sum_i h_i^4. \tag{2.24}$$

Thus the fourth moment is less than what it is for a Gaussian (negative kurtosis) and the distribution has less weight in the wings than a Gaussian. We shall see that the detailed form of $P(B_n)$ is not too important and for our purposes, Eq. (2.23) is good enough.

For $W^{-1} \ll t \ll \Delta^{-1}$, we may evaluate $P(t)$ by replacing Λ by $(B_n + \epsilon)$. [This replacement is no longer valid when $\Delta t \gtrsim 1$, for then the phase of $\sin^2(\Lambda t/2)$ is significantly altered by throwing away Δ.] Then by the usual textbook argument for Fermi's golden rule,

$$\frac{\sin^2[(B_n+\epsilon)t/2]}{(B_n+\epsilon)^2} = \frac{2\pi t}{4}\delta(B_n+\epsilon). \tag{2.25}$$

The integral for $P(t)$ is then trivial and yields

$$P(t) = \frac{\sqrt{2\pi}}{4}\frac{\Delta^2}{W}e^{-\epsilon^2/2W^2}t, \tag{2.26}$$

which is the same as before.

For $\Delta t \gtrsim 1$, the integral is dominated by $B_n \approx -\epsilon$ and we may put $B_n = -\epsilon$ in the Gaussian factor, yielding

$$P(t) = \frac{\Delta^2}{\sqrt{8\pi}W}e^{-\epsilon^2/2W^2}\int_{-\infty}^{\infty}\frac{1-\cos(\sqrt{\Delta^2+b^2}t)}{\Delta^2+b^2}db$$
$$= \sqrt{\frac{\pi}{8}}\frac{\Delta}{W}e^{-\epsilon^2/2W^2}\left[1-\int_{\Delta t}^{\infty}J_0(z)dz\right], \tag{2.27}$$

where $b = B_n + \epsilon$ and we used Ref. 22 in the last step. Using the asymptotic behavior of the Bessel function, we find that for $\Delta t \gg 1$,

$$P(t) \approx \sqrt{\frac{\pi}{8}}\frac{\Delta}{W}e^{-\epsilon^2/2W^2}\left[1-\sqrt{\frac{2}{\pi\Delta t}}\sin\left(\Delta t - \frac{\pi}{4}\right)\right]. \tag{2.28}$$

The important point is that even for $\epsilon=0$, the nuclear-spin environment impedes the spin from flipping appreciably and the net flip probability is only of order Δ/W.

III. MODEL FOR MOLECULAR SPIN ENVIRONMENT

For our second model, we consider only the dipolar coupling between MSs and ignore the nuclear spins altogether. Let us denote the energy scale of the mutual dipole-dipole interaction between MSs by E_{dm} [see Eq. (3.3) below for the exact definition]. Since $E_{dm} \gg E_{dn}$, we may *a priori* expect decoherence by the mutual interaction to be much greater than that by the interaction with NSs. This model is studied in an attempt to investigate this point.

In terms of the Pauli matrices, the Hamiltonian for interacting MSs can be written as

$$\mathcal{H}_C = \frac{1}{2}\sum_i (\Delta\sigma_{ix} + \epsilon_i\sigma_{iz}) + \frac{1}{2}\sum_{i<j} K_{ij}\sigma_{iz}\sigma_{jz}. \tag{3.1}$$

Here i and j label the different spins, x and z denote the axes, ϵ_i is the bias field on spin i that moves it off resonance, and K_{ij} is the dipolar coupling.

Let us now focus on one MS, which we shall call the system, and label it with a suffix 0. This is prepared in the $|\uparrow\rangle$ state at time $t=0$, and the other spins, which we call the bath, are prepared in a density matrix ρ_B. Let $P(t)$ denote the probability that the system spin is in the state $|\downarrow\rangle$ at a later time t irrespective of the state of the bath. For an isolated spin, $P(t) = \sin^2(\Delta t/2)$. If decoherence is weak, we expect the oscillations to be weakly damped and if it is strong, we expect a decay without any oscillation. Indeed, these qualitative behaviors define what we mean by weak and strong decoherence. Since the dipole interaction is long ranged, we anticipate that the decoherence might depend on the spatial position of spin 0 in the sample, especially if ρ_B corresponds to a fully or nearly fully polarized bath, but otherwise there is nothing special about its choice.

The calculation of $P(t)$ for the model (3.1) appears daunting because of the couplings between the bath spins. We therefore consider a simpler model

$$\mathcal{H}_{mm} = \frac{1}{2}(\Delta\sigma_{0x} + \epsilon\sigma_{0z}) + \frac{1}{2}\sum_{i\neq 0} (\Delta\sigma_{ix} + \epsilon_i\sigma_{iz}) + \frac{1}{2}\sum_{i\neq 0} K_i\sigma_{0z}\sigma_{iz}. \tag{3.2}$$

(Both suffixes in $\mathcal{H}_{mm}$ stand for "molecular.") The dipolar couplings between the bath spins are now replaced by a distribution of dipole fields by treating the bias energies ϵ_i as independent random variables, distributed on the scale E_{dm}. The calculation of $P(t)$ should include an ensemble average over this distribution. The coupling K_i between spin 0 and spin i of the bath is, however, retained as is and is, explicitly,

$$K_i = \frac{2E_{dm}a^3}{r_{0i}^3}(1 - 3\cos\theta_{0i}^2). \tag{3.3}$$

Here, a is the nearest-neighbor distance, r_{0i} is the distance from spin 0 to spin i, and θ_{0i} is the angle the line joining them makes with the z axis. Finally, ϵ is an additional bias on spin 0, due to an external field, for example.

For purposes of explicit calculation, we shall take the probability density of the biases ϵ_i to be Gaussian

$$f(\epsilon) = \frac{1}{\sqrt{2\pi E_b^2}}e^{-\epsilon^2/2E_b^2}, \tag{3.4}$$

where $E_b \sim E_{dm}$. Dipolar field distributions in Fe_8 have been measured by Ohm *et al.*[23] and by Wernsdorfer *et al.*[24] They have also been inferred from linewidth measurements in optical spectroscopy by Mukhin *et al.*[25] The assumption of a Gaussian form is consistent with these measurements. Berkov[26] has given theoretical and Monte Carlo arguments for a Gaussian distribution in a system of dense interacting dipoles. We shall see, nevertheless, that the detailed form of this distribution is not physically important for us.

Even the model (3.2) cannot be treated exactly. It is again seen that the weak-coupling approximation is totally invalid and adiabatic renormalization is inapplicable since the bath and system spins move on the same time scale. The golden rule is still good, however. Second-order perturbation theory in Δ yields

$$P(t) = \frac{\Delta^2}{4}\int_0^t dt_1\int_0^t dt_2 e^{i\epsilon(t_1-t_2)}F, \tag{3.5}$$

where

$$F = \mathrm{Tr}_B\left[\rho_B\prod_i e^{i\mathcal{H}_{i+}t_1}e^{-i\mathcal{H}_{i-}(t_1-t_2)}e^{-i\mathcal{H}_{i+}t_2}\right], \tag{3.6}$$

with

$$\mathcal{H}_{i\pm} = \frac{1}{2}[\Delta\sigma_{ix} + (\epsilon_i \pm K_i)\sigma_{iz}]. \tag{3.7}$$

The choice of ρ_B demands some care. It would now be incorrect to take $\rho_B=2^{-N_m}$, where N_m is the number of MSs since these spins do not equilibrate between the $|\uparrow\rangle$ and $|\downarrow\rangle$ states on a time scale short compared to Δ^{-1}. Instead we choose each spin to be in a definite state, either $|\uparrow\rangle$ or $|\downarrow\rangle$. (In the language of statistical mechanics, the bath is in a state of quenched disorder.) This then means that in principle we have to calculate the second-order influence function for every configuration of MSs separately. In practice, this is not so and we shall see that the functions for up and down spins differ only by phases. When these phases are added together for all the MSs in the bath, they will reproduce exactly the effect of the local dipole field at spin 0. This field is dependent on the MS configuration, but except for special configurations such as all or nearly all MSs polarized in the same direction, we can treat it statistically as a field with a rms value of order E_{dm}.

In equations, the above means that if we specify the spin configuration by giving $s_i=\langle\sigma_{iz}\rangle=\pm 1$, then

$$\rho_B=\prod_i \rho_i;\quad \rho_i=\frac{1}{2}(1+s_i\sigma_{iz}). \tag{3.8}$$

Accordingly, F factorizes into a product of factors, one for each bath MS. If the ith spin is "up," this factor is

$$F_i=\langle\uparrow|e^{i\mathcal{H}_{i+}t_1}e^{-i\mathcal{H}_{i-}(t_1-t_2)}e^{-i\mathcal{H}_{i+}t_2}|\uparrow\rangle. \tag{3.9}$$

If the spin is "down," F_i is given by the expectation value of the same operator in the $|\downarrow\rangle$ state. The calculation of these influence factors is lengthy and is presented in Appendix A. We find that

$$F_i\simeq e^{is_iK_it_{12}}(1-\eta_i), \tag{3.10}$$

with η_i given by Eq. (A46) with the addition of a suffix i to K and $\Omega_\pm$, $\bar{t}=(t_1+t_2)/2$, and $t_{12}=t_1-t_2$.

We call the quantity η_i the *mismatch* since it arises from a difference in the time evolution of the ith environmental spin in response to different paths taken by the system spin. The derivation in Appendix A shows that $0\le\eta_i\ll 1$, vanishing only when $t_{12}=0$.[27] Hence we may put $1-\eta_i\approx e^{-\eta_i}$, leading to

$$P(t)=\frac{\Delta^2}{4}\int_0^t dt_1\int_0^t dt_2 e^{i\epsilon_T t_{12}}e^{-\sum_i\eta_i}, \tag{3.11}$$

where

$$\epsilon_T=\epsilon+\sum_i K_i s_i. \tag{3.12}$$

This is the total bias that the spin at 0 sees including the dipole field of other MSs. Its value is of order E_{dm} except for special spin configurations.

We show in Appendix B that for $|t_{12}|\gg E_{dm}^{-1}$ and $\Delta^{-1}\ll\bar{t}\ll E_{dn}^2/\Delta$,

$$\sum_i \eta_i\simeq\gamma_m\Delta|t_{12}|, \tag{3.13}$$

where γ_m is a constant of order unity. We have also evaluated this sum numerically, as described in Appendix B 2. This work shows that the form (3.13) is good even for $\Delta|t_{12}|\sim 1$. Employing it in Eq. (3.11), we get

$$P(t)=\frac{\Delta^2}{2}\mathrm{Re}\left[\frac{t}{(\gamma_m\Delta-i\epsilon_T)}-\frac{1-e^{-(\gamma_m\Delta-i\epsilon_T)t}}{(\gamma_m\Delta-i\epsilon_T)^2}\right]. \tag{3.14}$$

Thus, $P(t)$ displays damped oscillations about a slowly rising mean. The time scale of the decoherence is Δ^{-1}, which is comparable to the time scale of the oscillations when the total bias, ϵ_T, is zero. The amplitude of the oscillations is $\sim\Delta^2/\epsilon_T^2$ if the bias is large. For $t\gg\Delta^{-1}$, we obtain

$$P(t)\simeq\Gamma_m t, \tag{3.15}$$

with

$$\Gamma_m=\frac{1}{2}\frac{\gamma_m\Delta^3}{\gamma_m^2\Delta^2+\epsilon_T^2}. \tag{3.16}$$

This quantity may be interpreted as an average *rate* at which the spin flips. If the net bias is large ($\gg\Delta$), this rate is $\gamma_m\Delta^3/2\epsilon_T^2$, while if the bias is zero, it is much larger, $\Delta/2\gamma_m$. (The amplitude of the oscillations is also very small when the bias is large.) It is interesting that the zero-bias rate is proportional to Δ and not to Δ^2 as might be expected from a naive application of the golden rule; this is because the decoherence time scale is also set by Δ.

IV. COMBINED NUCLEAR AND MOLECULAR SPIN ENVIRONMENTS

Let us now consider both environments together. The combined influence factor is the product of the influence factors for each separate environment, leading to

$$P(t)=\frac{\Delta^2}{4}\int_0^t dt_1\int_0^t dt_2 e^{i\epsilon_T t_{12}}e^{-\gamma_m\Delta|t_{12}|}e^{-W^2t_{12}^2/2}. \tag{4.1}$$

If, as is generally the case, $W\sim E_{dn}\gg\Delta$, the integrals may be evaluated as in Sec. II. We once again get $P(t)\simeq\Gamma t$, with

$$\Gamma=\frac{\Delta^2}{4}\int_{-\infty}^{\infty}dt e^{i\epsilon_T t}e^{-\gamma\Delta|t|}e^{-W^2t^2/2}. \tag{4.2}$$

In general this integral leads to an error function, but if $E_{dn}\gg\Delta$, it simplifies and we get

$$\Gamma=\frac{\sqrt{2\pi}}{4}\frac{\Delta^2}{W}e^{-\epsilon_T^2/2W^2}. \tag{4.3}$$

This is of the same form as Γ_n and the main effect of the molecular spins is to change the bias field.

V. QUASISTATIC MODEL OF FIELD SWEEPS

We have seen in the previous sections that the molecular spin relaxes incoherently from $|\uparrow\rangle$ to $|\downarrow\rangle$. There may in addition be some vestige of the coherent oscillations, but these decay because of the coupling to nuclear spins and to other molecular spins. The decay time scales due to these two couplings are E_{dn}^{-1} and Δ^{-1}, respectively, and the former is the relevant one since it is so much shorter. If the externally applied field is swept slowly enough that the bias on any one spin changes by much less than E_{dn} in a time E_{dn}^{-1}, that is, if $\dot{\epsilon}_T \ll E_{dn}^2$, then it is a good approximation to neglect the off-diagonal elements of the density matrix and to write simple rate equations for the diagonal elements. If we denote the probability for a particular molecular spin to be in the $|\uparrow\rangle$ or $|\downarrow\rangle$ states by $p_\uparrow$ and $p_\downarrow$, we have

$$\frac{dp_\uparrow}{dt} = \Gamma[\epsilon_T(t)](p_\downarrow - p_\uparrow) = \Gamma[\epsilon_T(t)](1-2p_\uparrow), \tag{5.1}$$

where the rate Γ has been allowed to vary with time through its dependence on the bias. Let the spin state be $|\downarrow\rangle$ at $t=-\infty$. Then, Eq. (5.1) is easily integrated to yield

$$p_\uparrow(t) = \frac{1}{2}\left[1 - \exp\left\{-2\int_{-\infty}^{t} \Gamma[\epsilon_T(t')]dt'\right\}\right]. \tag{5.2}$$

In particular, the probability for the spin to flip is given by

$$p_f \equiv p_\uparrow(\infty) = \frac{1}{2}\left[1 - \exp\left\{-2\int_{-\infty}^{\infty} \Gamma[\epsilon_T(t')]dt'\right\}\right]. \tag{5.3}$$

It is interesting to analyze the spin-flip probability neglecting the contribution of the other molecular spins to the bias. That is, we take $\epsilon_T(t)$ to be $\epsilon_a(t)$, the applied bias field. Further, as in the standard LZS protocol, we take $\dot{\epsilon}_a$ to be a constant. Such an analysis would be directly applicable to a situation in which the molecular spins were very dilute and E_{dm} was smaller than E_{dn}. Since we chose $p_\uparrow(-\infty)=0$, we must take the bias field to be swept from large positive to large negative values and the integral in Eq. (5.3) becomes

$$\int_{-\infty}^{\infty} \Gamma[\epsilon_a(t)]dt = \frac{1}{|\dot{\epsilon}_a|}\int_{-\infty}^{\infty} \Gamma(\epsilon_a)d\epsilon_a. \tag{5.4}$$

Equation (4.2) now yields (writing ϵ_a for ϵ_T)

$$\int_{-\infty}^{\infty} \Gamma(\epsilon_a)d\epsilon_a = \frac{\Delta^2}{4}\int_{-\infty}^{\infty} d\epsilon_a \int_{-\infty}^{\infty} dt e^{i\epsilon_a t} e^{-\gamma\Delta|t|} e^{-W^2t^2/2}$$
$$= \frac{\Delta^2}{4}\int_{-\infty}^{\infty} dt e^{-\gamma\Delta|t|} e^{-W^2t^2/2} 2\pi\delta(t) = \frac{\pi\Delta^2}{2}. \tag{5.5}$$

Hence,

$$p_f = \frac{1}{2}(1 - e^{-\pi\Delta^2/|\dot{\epsilon}_a|}). \tag{5.6}$$

This is the same as the Kayanuma[17] result for a spin coupled to an oscillator bath in the strong damping limit. Our derivation shows that this result is valid more generally whenever the transitions are so incoherent as to allow for rate equations. The striking fact that the details of the decoherence mechanism drop out of the final result can also be understood. If the decoherence is large, the rate Γ is small, but the spin can flip over a larger energy interval around the crossing, i.e., over a larger range of bias energy. For pure nuclear-spin decoherence, $\Gamma \sim \Delta^2/W$, but the crossing region is broadened to a width $\sim W$. For pure molecular spin decoherence, $\Gamma \sim \Delta$, and the crossing region is also of width $\sim\Delta$.

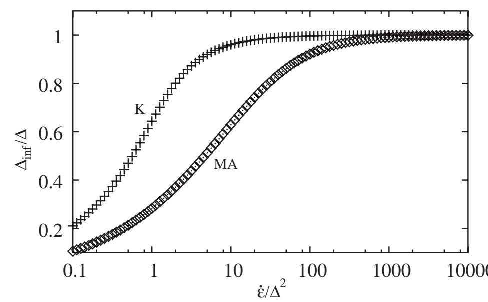

FIG. 1. Inferred values of tunnel splitting as a function of the rate at which the applied field is swept, assuming that the spin-flip probability is given by the Landau-Zener-Stuckelberg formula, Eq. (5.7). The curves marked K and MA are obtained when the true flip probability is taken to obey Kayanuma's formula, Eq. (5.6), and the macroscopically averaged formula obtained by integrating Eq. (5.17). For the latter, we took $4\alpha E_{dm}/W=40$. This figure should be compared to Fig. 7 of Ref. 5.

The quasistatic result (5.6) should be compared to the LZS spin-flip probability

$$p_{f,\mathrm{LZS}} = (1 - e^{-\pi\Delta^2/2|\dot{\epsilon}_a|}). \tag{5.7}$$

In the fast-sweep limit, i.e., with $|\dot{\epsilon}_a| \gg \Delta^2$, $p_f \ll 1$ and the two results are identical

$$p_f = p_{f,\mathrm{LZS}} \simeq \frac{\pi\Delta^2}{2|\dot{\epsilon}_a|}. \tag{5.8}$$

This remarkable result has very interesting implications for the experiments by Wernsdorfer and co-workers.[4–6] It has always been a surprise that the data in these experiments agree with the LZS formula, even in the fast-sweep limit. After all, the LZS formula is derived for a single noninteracting spin and the spins in Fe_8 are not noninteracting and are subject to strong and rapidly fluctuating fields from the NSs and possibly the MSs. Indeed, it is the systematics of the agreement with the LZS formula that has been used to argue that one can extract the underlying tunneling matrix element from the incoherent relaxation of the net magnetization in a swept external field. Equation (5.8) provides an explanation of this fact. It also means, in a stroke of luck, that the analysis of Ref. 28 continues to be valid.

In the slow-sweep limit, on the other hand, $p_{f,\mathrm{LZS}} \simeq 1$, while $p_f \simeq 1/2$. This means that if we continue to infer a tunneling matrix element, Δ_{inf}, by fitting the flip probability to an LZS form, we have

$$\Delta^2_{\mathrm{inf}}(\dot{\epsilon}) = -\frac{2\dot{\epsilon}}{\pi}\ln\left(\frac{1+e^{-\pi\Delta^2/|\dot{\epsilon}|}}{2}\right). \tag{5.9}$$

We plot this in Fig. 1, which should be compared to Fig. 7 of Ref. 5. Although our plot is qualitatively similar, it does not agree in detail. In particular, the experimentally inferred splitting drops more rapidly with $\dot{\epsilon}$ once $\dot{\epsilon} \lesssim 50\Delta^2$ than our model shows. Nevertheless, the general trend indicates that we have captured some of the essential physics. On the other hand, this simple formula does not contain the experimentally seen dependence of the splitting as inferred from the fast-sweep data on the nuclear-spin coupling.[6]

To prevent misunderstanding, we note here that we have described the sweep as fast or slow depending on the ratio $|\dot{\epsilon}_a|/\Delta^2$. However, because $\Delta \ll E_{dn}$, even if $|\dot{\epsilon}_a| \gg \Delta^2$, it is possible to satisfy $|\dot{\epsilon}_a| \ll E_{dn}^2$, the condition for the quasistatic treatment to apply.

Let us now ask how to include the effect of the mutual dipole field as the external magnetic field is swept. The picture that emerges is that each MS flips at a rate that depends on the bias field seen by it. If at time t, the MS configuration is set of Ising spin variables $\{s_i\}$ and the net bias on the ith spin is ϵ_{iT}, then at a short time Δt later,

$$s_i \to -s_i \text{ with probability } \Gamma[\epsilon_{iT}(t)]\Delta t. \tag{5.10}$$

The spins and the dipole fields then become a complicated coupled stochastic process. As noted in Ref. 1, this is a Glauber process with the difference that the flipping rate depends on the long-ranged dipole field. Monte Carlo studies of such processes have been performed by Cuccoli *et al.*[15] and by Fernandez and Alonso.[16] It would be interesting to conduct similar studies in a swept field with the rates found by us.

Here, we consider a simpler way to incorporate the dipole field in the rate equation [Eq. (5.1)] in an average way that ignores its site to site variation, through the macroscopic demagnetization field. To forestall confusion, it pays to recall the distinction between **B**, **H**, and the contribution of the demagnetization field to the latter. We work in the Gaussian system of units. Let $\mathbf{H}_a$ be the applied magnetic field, i.e., the field that a solenoid wound around the sample would produce if the sample were not there. Let **M** be the magnetization, i.e., the magnetic-dipole moment density, and let $\mathbf{H}_{\text{demag}}$ be the demagnetization field, i.e., the field produced by a volume charge density $\nabla \cdot \mathbf{M}$ and a surface charge density $\mathbf{M} \cdot \hat{\mathbf{n}}$, where $\hat{\mathbf{n}}$ is the outward normal at the surface of the sample. The field to which an individual MS responds is the induction

$$\mathbf{B} = \mathbf{H}_a + 4\pi\mathbf{M} + \mathbf{H}_{\text{demag}}, \tag{5.11}$$

through a term in the Hamiltonian

$$\mathcal{H}_{\text{bias}} = -g\mu_B \mathbf{S}^{\text{op}} \cdot \mathbf{B}. \tag{5.12}$$

Here, $\mathbf{S}^{\text{op}}$ is the operator for the total spin of the molecule in question. Since, as we have argued, the MSs behave as essentially classical variables with only a z component, the total bias on this MS is

$$\epsilon_T = -2g\mu_B S B_z. \tag{5.13}$$

Henceforth we will write just H_a and M for $H_{a,z}$ and M_z. For simplicity we will ignore the spatial inhomogeneity of **M** and $\mathbf{H}_{\text{demag}}$, as well as the tensorial character of their proportionality, and write

$$4\pi\mathbf{M} + \mathbf{H}_{\text{demag}} = \alpha\mathbf{M}. \tag{5.14}$$

The constant α is shape dependent: it would be $8\pi/3$ for a perfectly uniformly magnetized sphere, 4π for a thin long rod parallel to $\mathbf{H}_a$, and 0 for a thin flat disk normal to $\mathbf{H}_a$.

With the above definitions, the bias is given by

$$\epsilon_T = -2g\mu_B S[H_a - \alpha n g\mu_B S(1-2p_\uparrow)], \tag{5.15}$$

where n is the number density of MSs. Hence, $n(g\mu_B S)^2 \sim E_{dm}$. Let us again take $p_\uparrow(-\infty)=0$ and $H_a<0$ at $t\to-\infty$, so $\dot{\epsilon}_a<0$. Adjusting the zero of time and absorbing another constant of order unity in α, we get

$$\epsilon_T(t) = \dot{\epsilon}_a t - 4\alpha E_{dm} p_\uparrow(t) \tag{5.16}$$

and feed this into the rate equation (5.1). The resulting differential equation for $p_\uparrow$ is

$$\frac{dp_\uparrow}{du} = \frac{\sqrt{2\pi}}{4}\frac{\Delta^2}{|\dot{\epsilon}_a|}(1-2p_\uparrow)\exp\left[-\frac{1}{2}\left(u + \frac{4\alpha E_{dm}}{W}p_\uparrow\right)^2\right], \tag{5.17}$$

where $u=|\dot{\epsilon}_a|t/W$. This equation can also be formally solved as before by treating $\Gamma[\epsilon_T(t)]$ as a known function of time. The solution is then again given by Eq. (5.2), but since $\epsilon_T(t)$ depends on $p_\uparrow(t)$, it is now in the form of an integral equation. We have found it simpler to integrate the differential equation numerically for different values of $\dot{\epsilon}$. The results are shown in Fig. 1. The qualitative agreement with Ref. 5 is improved, although we cannot make a direct comparison because of uncertainty in the ratio $\alpha E_{dm}/W$.

Finally, let us return to the point that for slow sweeps, $p_\uparrow(\infty) \simeq 1$ for coherent LZS sweeps, while $p_\uparrow(\infty) \simeq \frac{1}{2}$ for incoherent sweeps, both from Kayanuma's formula (5.6) or formula (5.17) which includes MS dipolar fields.[29] This means that starting from a sample with a saturated magnetization $-M_0$, we are arguing that the final magnetization will be 0 and not M_0 if the field is swept slowly. And indeed, studies of the Mn_4 (Ref. 30) and Mn_{12} wheel SMMs (Ref. 31) show just such behavior. In Ref. 30, it is found that the final magnetization is zero for slow sweeps [see Figs. 8(a)–8(c) in Ref. 30] and is fully reversed only for ultraslow sweeps [Figs. 8(d) and 8(h)]. For sweep rates in between, and for inverse LZS sweeps [Figs. 8(c), 8(f), and 8(g)], the final magnetization is not zero, but is not completely reversed either. (See also Fig. 1(a) of Ref. 31. This supports the conclusion that the transitions are incoherent. It also means that to fully explain the ultraslow sweep and the inverse LZS sweep data, one must have a mechanism for the spin to relax from the higher energy state to the lower energy one even (but not vice versa) when the bias is much larger than E_{dn}. One possibility is to have a second-order Fermi golden rule process in which (assuming the spin is 10) the spin tunnels from the $m=-10$ to an $m=9$ or $m=8$ virtual state followed by a transition to the $m=10$ state with the emission of a phonon. We shall address this issue further in a separate publication.

VI. DISCUSSION

We have considered the transitions in a swept field in the presence of nuclear and molecular spin decoherences. Our qualitative conclusions regarding the former are in accord with those of Refs. 12–14, but the quantitative form of the decoherence is different. Similarly, with regard to the molecular spins, we agree with them and other authors[15,16] that their main effect is to add an essentially c-number contribution to the bias field on any given MS. However, we believe that this conclusion was not foregone and that our treatment gives a proper justification for neglecting the additional decoherent effect of these degrees of freedom.

The quasistatic approximation enables us to answer the question posed at the start, *viz.*, why the LZS formula appears to describe the swept field experiments so well. We find that this is not because the transitions are coherent, but because the effective width of the crossing and the incoherent spin-flip rate vary inversely, leading to a fortuitous cancellation. It remains an open question to study the stochastic variation of the bias field and thus understand this process even better.

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APPENDIX A: CALCULATION OF SINGLE-SPIN INFLUENCE FACTORS FOR MOLECULAR SPINS

In this appendix, we calculate the factor F_i in Eq. (3.9). To save writing, we omit the index i henceforth. Let us denote the influence factor by $F_\uparrow$ or $F_\downarrow$ when the environmental spin is up or down, respectively. We further abbreviate

$$\epsilon_\pm = \epsilon \pm K, \tag{A1}$$

$$\Omega_\pm^2 = \Delta^2 + \epsilon_\pm^2, \tag{A2}$$

and $t_{12}=t_1-t_2$ as before.

Let us find $F_\uparrow$ first. As a first approximation, we argue that because Δ is much smaller than the typical value of ϵ or K, we may neglect it altogether. This yields

$$F_\uparrow \approx e^{iKt_{12}}. \tag{A3}$$

This approximation is too crude. It implies $|F_\uparrow|=1$, which is the maximum possible value it can have. Decoherence arises precisely from the fact that $|F_\uparrow|<1$ because $[\mathcal{H}_+,\mathcal{H}_-]\neq 0$. It is important to find the departure from unity. With this in mind, let us write

$$F_\uparrow = e^{i\phi}(1-\eta), \tag{A4}$$

where ϕ is a real phase and η is another real quantity that we have referred to as the *mismatch*. Our crude calculation shows that η is small and $\phi \approx Kt_{12}$.

Before calculating η more carefully, let us relate $F_\downarrow$ to $F_\uparrow$. Since $|\downarrow\rangle = -i\sigma_y|\uparrow\rangle$, we can write

$$F_\downarrow = \langle\uparrow|\sigma_y e^{i\mathcal{H}_+t_1}\sigma_y\sigma_y e^{-i\mathcal{H}_-(t_1-t_2)}\sigma_y\sigma_y e^{-i\mathcal{H}_+t_2}\sigma_y|\uparrow\rangle, \tag{A5}$$

and since σ_y anticommutes with $\mathcal{H}_\pm$, this can be transformed to

$$F_\downarrow = \langle\uparrow|e^{-i\mathcal{H}_+t_1}e^{i\mathcal{H}_-(t_1-t_2)}e^{i\mathcal{H}_+t_2}|\uparrow\rangle, \tag{A6}$$

which is the same expression as $F_\uparrow$ with the signs of t_1 and t_2 reversed. That is,

$$F_\downarrow(t_1,t_2) = F_\uparrow(-t_1,-t_2). \tag{A7}$$

In particular, we shall see that the mismatch for $F_\downarrow$ is the same as that for $F_\uparrow$, so that

$$F_\downarrow(t_1,t_2) \approx e^{-iKt_{12}}(1-\eta). \tag{A8}$$

To find the mismatch more accurately, we write

$$F_\uparrow = \langle\hat{\mathbf{n}}_1|\hat{\mathbf{n}}_2\rangle, \tag{A9}$$

where

$$|\hat{\mathbf{n}}_a\rangle = e^{i\mathcal{H}_-t_a}e^{-i\mathcal{H}_+t_a}|\uparrow\rangle, \quad a=1,2. \tag{A10}$$

The notation in this equation exploits the fact that every pure state of a spin-1/2 system can be written as a spin-coherent state, i.e., a state with maximal spin projection along *some* direction in space. Thus, the states defined in Eq. (A10) have maximal spin projections along directions $\hat{\mathbf{n}}_1$ and $\hat{\mathbf{n}}_2$. These directions remain to be found. Of course, the states also have phases which also need to be found.

Let us now view Eq. (A10) in terms of two rotations applied to the state $|\uparrow\rangle$. Since $\Delta \ll \epsilon$, these rotations are both about directions very close to $\hat{\mathbf{z}}$. Accordingly, $\hat{\mathbf{n}}_1$ and $\hat{\mathbf{n}}_2$ are also very close to $\hat{\mathbf{z}}$ and we may write

$$n_{az} \approx 1 - \frac{1}{2}n_{a\perp}^2, \tag{A11}$$

where $\mathbf{n}_{a\perp}$ is the component of $\hat{\mathbf{n}}_a$ perpendicular to $\hat{\mathbf{z}}$. Now, since

$$|\langle\hat{\mathbf{n}}_1|\hat{\mathbf{n}}_2\rangle|^2 = \frac{1}{2}(1+\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2) \tag{A12}$$

for spin-1/2 coherent states, we may write

$$|F_\uparrow|^2 \approx \frac{1}{2}\left(2 - \frac{1}{2}n_{1\perp}^2 - \frac{1}{2}n_{2\perp}^2 + \mathbf{n}_{1\perp}\cdot\mathbf{n}_{2\perp}\right) \tag{A13}$$

$$= 1 - \frac{1}{4}(\mathbf{n}_{1\perp}-\mathbf{n}_{2\perp})^2. \tag{A14}$$

Taking the square root, and recalling the definition of the mismatch, we get

$$\eta \approx \frac{1}{8}(\mathbf{n}_{1\perp}-\mathbf{n}_{2\perp})^2. \tag{A15}$$

The problem is thus to find $\mathbf{n}_{a\perp}$. We have not been able to find any simple way to do this except by explicit expansion and multiplication of the exponentiated operators in Eq. (A10). The resulting trigonometric expressions can be made somewhat easier to handle if we introduce the abbreviations

$$\theta_{1\pm} = \Omega_\pm t_1/2, \quad \theta_{2\pm} = \Omega_\pm t_2/2. \tag{A16}$$

With these, we may write

$$e^{-i\mathcal{H}_+t_2} = c_0 + \mathbf{c}\cdot\vec{\sigma}, \tag{A17}$$

where

$$c_0 = \cos\,\theta_{2+}, \quad \mathbf{c} = -\frac{i}{\Omega_+}\sin\,\theta_{2+}(\Delta,0,\epsilon_+). \tag{A18}$$

Similarly,

$$e^{i\mathcal{H}_- t_2} = b_0 + \mathbf{b}\cdot\vec{\sigma}, \tag{A19}$$

with

$$b_0 = \cos\,\theta_{2-}, \quad \mathbf{b} = \frac{i}{\Omega_-}\sin\,\theta_{2-}(\Delta,0,\epsilon_-). \tag{A20}$$

Then,

$$|\hat{\mathbf{n}}_2\rangle = (b_0 + \mathbf{b}\cdot\vec{\sigma})(c_0 + \mathbf{c}\cdot\vec{\sigma})|\uparrow\rangle = A_{2\uparrow}|\uparrow\rangle + A_{2\downarrow}|\downarrow\rangle, \tag{A21}$$

with

$$A_{2\uparrow} = (b_0 + b_z)(c_0 + c_z) + b_x c_x, \tag{A22}$$

$$A_{2\downarrow} = (b_0 - b_z)c_x + b_x(c_0 + c_z). \tag{A23}$$

In terms of these quantities, we have

$$n_{2+} = n_{2x} + i n_{2y} = \langle\hat{\mathbf{n}}_2|\sigma_+|\hat{\mathbf{n}}_2\rangle = 2A^*_{2\uparrow}A_{1\downarrow}. \tag{A24}$$

By comparing real and imaginary parts of both sides, we obtain n_{2x} and n_{2y}. We now note that the quantities $A_{2\uparrow}$ and $A_{2\downarrow}$ consist of various terms oscillating at the sums and differences of the frequencies $\Omega_\pm/2$. Since $\Delta \ll \Omega_\pm$ for all but very distant (and therefore very weakly coupled) MSs, we may expand the amplitudes of these oscillatory factors in powers of Δ. Using the results

$$\frac{\epsilon_+}{\Omega_+} \simeq 1 - \frac{\Delta^2}{2\Omega_+^2}, \tag{A25}$$

etc., we obtain

$$c_0 + c_z = e^{-i\theta_{2+}} + O(\Delta)^2, \tag{A26}$$

$$b_0 \pm b_z = e^{\pm i\theta_{2-}} + O(\Delta)^2. \tag{A27}$$

Therefore,

$$A_{2\uparrow} = e^{i(\theta_{2-}-\theta_{2+})} + O(\Delta)^2, \tag{A28}$$

$$A_{2\downarrow} = -i\frac{\Delta}{\Omega_+}\sin\,\theta_{2+}e^{-i\theta_{2-}} + i\frac{\Delta}{\Omega_-}\sin\,\theta_{2-}e^{-i\theta_{2+}}, \tag{A29}$$

and

$$A^*_{2\uparrow}A_{2\downarrow} = -i\left[\frac{\Delta}{\Omega_+}\sin\,\theta_{2+}e^{-i(2\theta_{2-}-\theta_{2+})} - \frac{\Delta}{\Omega_-}\sin\,\theta_{2-}e^{-i\theta_{2-}}\right]. \tag{A30}$$

From this expression, we can get n_{2x} and n_{2y} by taking real and imaginary parts:

$$n_{2x} = -2\frac{\Delta}{\Omega_+}\sin\,\theta_{2+}\sin(2\theta_{2-}-\theta_{2+}) + 2\frac{\Delta}{\Omega_-}\sin^2\theta_{2-} \tag{A31}$$

$$= -\frac{\Delta}{\Omega_+}[\cos 2(\theta_{2+}-\theta_{2-}) - \cos 2\theta_{2-}] + \frac{\Delta}{\Omega_-}[1 - \cos 2\theta_{2-}] \tag{A32}$$

$$= \frac{\Delta}{\Omega_-} - \frac{2\Delta K}{\Omega_+\Omega_-}\cos 2\theta_{2-} - \frac{\Delta}{\Omega_+}\cos 2(\theta_{2+}-\theta_{2-}), \tag{A33}$$

where in the last line we have used the result

$$\frac{1}{\Omega_+} - \frac{1}{\Omega_-} \simeq -\frac{2K}{\Omega_+\Omega_-}. \tag{A34}$$

In the same way, we have

$$n_{2y} = -2\frac{\Delta}{\Omega_+}\sin\,\theta_{2+}\cos(2\theta_{2-}-\theta_{2+}) + 2\frac{\Delta}{\Omega_-}\sin\,\theta_{2-}\cos\,\theta_{2-} \tag{A35}$$

$$= -\frac{\Delta}{\Omega_+}[\sin 2(\theta_{2+}-\theta_{2-}) + \sin 2\theta_{2-}] + \frac{\Delta}{\Omega_-}\sin 2\theta_{2-} \tag{A36}$$

$$= \frac{2\Delta K}{\Omega_+\Omega_-}\sin 2\theta_{2-} - \frac{\Delta}{\Omega_+}\sin 2(\theta_{2+}-\theta_{2-}). \tag{A37}$$

For n_{1x} and n_{1y}, we simply change the suffix 2 in $\theta_{2\pm}$ from 2 to 1. We then have

$$n_{1x} - n_{2x} = \frac{2\Delta K}{\Omega_+\Omega_-}[\cos 2\theta_{2-} - \cos 2\theta_{1-}] + \frac{\Delta}{\Omega_+}[\cos 2(\theta_{2+}-\theta_{2-}) - \cos 2(\theta_{1+}-\theta_{1-})], \tag{A38}$$

$$n_{1y} - n_{2y} = -\frac{2\Delta K}{\Omega_+\Omega_-}[\sin 2\theta_{2-} - \sin 2\theta_{1-}] + \frac{\Delta}{\Omega_+}[\sin 2(\theta_{2+}-\theta_{2-}) - \sin 2(\theta_{1+}-\theta_{1-})]. \tag{A39}$$

We can simplify these expressions by first noting that

$$\theta_{a+} - \theta_{a-} \simeq K t_a[1 + O(\Delta/\epsilon_\pm)^2], \quad (a = 1,2) \tag{A40}$$

and then defining sum and difference variables

$$\bar{t} = \frac{1}{2}(t_1 + t_2), \quad t_{12} = t_1 - t_2 \tag{A41}$$

in terms of which we have identities such as

$$\cos 2\theta_{2-} - \cos 2\theta_{1-} = 2\sin\,\Omega_-\bar{t}\,\sin\tfrac{1}{2}\Omega_- t_{12}, \tag{A42}$$

$$\sin 2\theta_{2-} - \sin 2\theta_{1-} = -2\cos\,\Omega_-\bar{t}\,\sin\tfrac{1}{2}\Omega_- t_{12}, \tag{A43}$$

etc. Putting all these together, we obtain

$$n_{1x}-n_{2x}=\frac{4\Delta K}{\Omega_+\Omega_-}\sin\Omega_-\bar{t}\sin\frac{1}{2}\Omega_-t_{12}+\frac{2\Delta}{\Omega_+}\sin 2K\bar{t}\sin Kt_{12}, \tag{A44}$$

$$n_{1y}-n_{2y}=\frac{4\Delta K}{\Omega_+\Omega_-}\cos\Omega_-\bar{t}\sin\frac{1}{2}\Omega_-t_{12}-\frac{2\Delta}{\Omega_+}\cos 2K\bar{t}\sin Kt_{12}. \tag{A45}$$

Squaring and adding these two expressions, we obtain the mismatch as

$$\eta=2\left(\frac{\Delta K}{\Omega_+\Omega_-}\right)^2\sin^2\frac{1}{2}\Omega_-t_{12}+\frac{1}{2}\left(\frac{\Delta}{\Omega_+}\right)^2\sin^2 Kt_{12} -2\frac{\Delta^2K}{\Omega_+^2\Omega_-}\cos\Omega_+\bar{t}\sin\frac{1}{2}\Omega_-t_{12}\sin Kt_{12}. \tag{A46}$$

We can also write this in a manifestly positive form

$$\eta=\frac{\Delta^2}{2\Omega_+^2}\left[2\frac{K}{\Omega_-}\sin\frac{\Omega_-t_{12}}{2}-\sin Kt_{12}\right]^2 +4\frac{\Delta^2K}{\Omega_+^2\Omega_-}\sin^2\frac{1}{2}\Omega_+\bar{t}\sin\frac{1}{2}\Omega_-t_{12}\sin Kt_{12}. \tag{A47}$$

Since this expression is unchanged when the signs of both t_1 and t_2 are reversed, we have now proven our claim that it is also the mismatch for $F_\downarrow$. Equations (A46) and (A47) are valid for $t_{1,2}\ll E_{dm}/\Delta^2$ on account of Eq. (A40).

To find the phase ϕ in Eq. (A4), we note that from Eqs. (A29) and (A40) that

$$A_{2\uparrow}=e^{-iKt_2+O(\Delta)^2}+O(\Delta)^2, \tag{A48}$$

and likewise for $A_{1\uparrow}$. Now, since $A_{a\downarrow}=O(\Delta)$,

$$\langle\hat{\mathbf{n}}_1|\hat{\mathbf{n}}_2\rangle=A_{1\uparrow}^*A_{2\uparrow}+A_{1\downarrow}^*A_{2\downarrow} \tag{A49}$$

$$=A_{1\uparrow}^*A_{2\uparrow}+O(\Delta)^2 \tag{A50}$$

$$=e^{iKt_{12}}+O(\Delta)^2. \tag{A51}$$

Thus, the dominant term in ϕ is just the zeroth order one, i.e., $\phi\approx Kt_{12}$, and we have

$$F_\uparrow(t_1,t_2)\approx e^{iKt_{12}}(1-\eta), \tag{A52}$$

with η given by Eq. (A46). As a check, note that $F_\uparrow$ correctly equals unity when $t_{12}=0$.

The calculation above assumes that $K\sim\epsilon\gg\Delta$. We shall see in Appendix B that distant spins for which $K\sim\Delta$ play an important role in determining the net influence factor. It is therefore desirable to find η when K is small. This can be done by evaluating Eq. (3.9) for $F_\uparrow$ by a standard perturbation expansion in K. The result is

$$\eta=\frac{K^2\epsilon^2\Delta^2}{2\Omega^4}t_{12}^2-\frac{K^2\epsilon^2\Delta^2}{\Omega^5}t_{12}\sin\Omega t_{12}+2\frac{K^2\Delta^2}{\Omega^4}\sin^2\frac{1}{2}\Omega t_{12} -\frac{K^2\Delta^4}{2\Omega^6}\sin^2\Omega t_{12}. \tag{A53}$$

Here, $\Omega=(\epsilon^2+\Delta^2)^{1/2}$. The last term is smaller than the first three by order $(\Delta/E_{dm})^2$. The remaining three terms are qualitatively very similar to what we get from Eq. (A46) when $K\to 0$.

APPENDIX B: ESTIMATE OF MULTISPIN INFLUENCE FACTOR FOR MOLECULAR SPIN ENVIRONMENT

In this appendix, we will estimate the total influence factor $F=\Pi_iF_i$ for $|t_{12}|\gg E_{dm}^{-1}$ using a mix of analytic and numerical approaches.

1. Preliminary analytic estimate

Since $\eta_i\ll 1$, the total influence factor is given by

$$F\simeq e^{i\Sigma_iK_is_i}e^{-\Sigma_i\eta_i}, \tag{B1}$$

so $|F|\simeq\exp(-\Sigma_i\eta_i)$. We therefore focus on the sum $\Sigma_i\eta_i$. Let us divide it into three parts, S_1, S_2, and S_3, corresponding to the three terms in η_i in Eq. (A46).

The first sum is

$$S_1=2\sum_i\Delta^2\left(\frac{K_i}{\Omega_{i+}}\right)^2\left(\frac{\sin(\Omega_{i-}t_{12}/2)}{\Omega_{i-}}\right)^2. \tag{B2}$$

For large $|t_{12}|$ (but with $|t_{12}|\ll\Delta^{-1}$), we may replace the factor $\Omega_{i-}^{-2}\sin^2(\Omega_{i-}t_{12}/2)$ by a term proportional to $\delta(\Omega_{i-})|t_{12}|$ as in textbook derivations of Fermi's golden rule. The replacement must be done with care, however. The physical point is that for large $|t_{12}|$, the only sites that contribute significantly to S_1 are those for which Ω_{i-} is very small. By taking the distribution as $\delta(\Omega_{i-})$, we get a vanishing answer for S_1 since $\Omega_{i-}\geq\Delta$, and so the argument of the δ function is never satisfied. The correct result which preserves the integral with respect to Ω_{i-} is

$$\left[\frac{\sin(\Omega_{i-}t_{12}/2)}{\Omega_{i-}}\right]^2\approx\frac{\pi}{4}\delta(\Omega_{i-}-\Delta)|t_{12}|. \tag{B3}$$

In this equation, the weight of the delta function is $\pi/4$ instead of $\pi/2$ since on the left we only integrate over positive values of Ω_{i-}, but on the right we wish to interpret the delta function in the standard way, that is, as a distribution to be integrated over all Ω_{i-}. Using Eq. (B3) in Eq. (B2) yields

$$S_1=\frac{\pi}{2}\sum_i\Delta^2\frac{K_i^2}{\Omega_{i+}^2}\delta(\Omega_{i-}-\Delta)|t_{12}|. \tag{B4}$$

To further simplify this result, we note that $\Omega_{i-}=\Delta$ implies $\epsilon_{i-}=0$, $\epsilon_{i+}=2K_i$, and $\Omega_{i+}^2=\Delta^2+4K_i^2$. Therefore,

$$\delta(\Omega_{i-}-\Delta)=\frac{\Omega_{i-}}{|\epsilon_i|}\delta(\epsilon_i-K_i)=\frac{\Delta}{|K_i|}\delta(\epsilon_i-K_i) \tag{B5}$$

and

$$S_1=\frac{1}{2}\pi\Delta^3|t_{12}|\sum_i\frac{|K_i|}{4K_i^2+\Delta^2}\delta(\epsilon_i-K_i). \tag{B6}$$

We now average over the bias distribution (3.4). This turns $\delta(\epsilon_i-K_i)$ into $f(K_i)$. It then remains to do the sum over the sites. Because the summand is slowly varying, we may replace the sum by an integral. This integral may in turn be performed by introducing the density of couplings $g(K)$, defined so that $g(K)dK$ is the number of sites for which K_i lies between K and $K+dK$. In this way we get

$$S_1 = \frac{1}{2}\pi\Delta^3|t_{12}|\int_{|K|>c\Delta} dK\frac{|K|}{4K^2+\Delta^2}f(K)g(K). \quad \text{(B7)}$$

We have cut off the K integration so as to exclude very distant spins for which the coupling is weaker than $c\Delta$, where c is some constant of order unity. The reason is that for such spins the mismatch will be essentially zero, since they are insensitive to the orientation of the central spin.

We show in Appendix C that

$$g(K) = \frac{16\pi}{9\sqrt{3}}\frac{E_{dm}}{K^2}. \quad \text{(B8)}$$

Note that couplings $+K$ and $-K$ are equally likely. Using this result, we obtain

$$S_1 = \frac{8\pi}{9}\sqrt{\frac{2\pi}{3}}\frac{\Delta^3 E_{dm}}{E_b}|t_{12}|\int_{c\Delta}^{\infty} dK\frac{1}{K(4K^2+\Delta^2)}e^{-K^2/2E_b^2}. \quad \text{(B9)}$$

The integral is dominated by small values of K close to Δ, so it may be evaluated by parts. Doing so, and setting $e^{-\Delta^2/2E_b^2} \simeq 1$, we obtain

$$S_1 = \frac{4\pi}{9}\sqrt{\frac{2\pi}{3}}\ln\left(1+\frac{1}{4c^2}\right)\frac{\Delta E_{dm}}{E_b}|t_{12}|. \quad \text{(B10)}$$

Note that the Gaussian form of $f(\epsilon)$ is not essential to the form of the answer.

The second term in Eq. (A46) leads to the sum

$$S_2 = \frac{1}{2}\sum_i \frac{\Delta^2}{\Omega_{i+}^2}\sin^2(K_i t_{12}). \quad \text{(B11)}$$

Since $\sin^2(K_i t_{12})$ is bounded by 1 the dominant contribution will come from sites on which $\Omega_{i+}^2 \approx O(\Delta^2)$. Averaging over the bias field distribution gives

$$S_2 = \frac{1}{2}\sum_i \int_{-\infty}^{\infty} \frac{\Delta^2}{\Delta^2+(\epsilon+K_i)^2}f(\epsilon)\sin^2(K_i t_{12})d\epsilon. \quad \text{(B12)}$$

Because $\Delta \ll E_{dm}$, the integral is very sharply peaked at $\epsilon = -K_i$. We may therefore replace $f(\epsilon)$ by the constant $f(-K_i)$. The integral is then elementary and we obtain

$$S_2 = \frac{1}{2}\pi\Delta\sum_i f(-K_i)\sin^2(K_i t_{12}). \quad \text{(B13)}$$

The sum is now evaluated as before by converting to an integral over K. Using the result (B8) for $g(K)$, we obtain

$$S_2 = \frac{8\pi^2}{9\sqrt{3}}\Delta E_{dm}\int_{|K|>c\Delta} dK f(-K)\frac{\sin^2(Kt_{12})}{K^2}. \quad \text{(B14)}$$

This time the integrand is sufficiently convergent near $K=0$, so the limit $c\Delta$ can be replaced by 0. The factor $K^{-2}\sin^2(Kt_{12})$ behaves like $\pi|t_{12}|\delta(K)$ for large $|t_{12}|$. We may therefore replace $f(-K)$ by $f(0)=(2\pi E_b^2)^{-1/2}$, after which the integral is trivial and yields

$$S_2 = \frac{4\pi^2}{9}\sqrt{\frac{2\pi}{3}}\frac{\Delta E_{dm}}{E_b}|t_{12}|. \quad \text{(B15)}$$

This result is also valid only for $|t_{12}| \ll \Delta^{-1}$.

The last sum, S_3, from the third term in Eq. (A46), is given by

$$S_3 = 2\sum_i \frac{\Delta^2}{\Omega_{i+}^2}\frac{K_i}{\Omega_{i-}}\sin(\Omega_{i-}t_{12}/2)\sin(K_i t_{12})\cos(\Omega_{i+}\bar{t}). \quad \text{(B16)}$$

As $|t_{12}|$ increases, the term $\Omega_{i-}^{-1}\sin(\Omega_{i-}t_{12}/2)$ behaves like a δ function of Ω_{i-}. By the same reasoning as for S_1, we find that the correct replacement is

$$\frac{\sin(\Omega_{i-}t_{12}/2)}{\Omega_{i-}} = \frac{\pi}{2}\delta(\Omega_{i-}-\Delta)\mathrm{sgn}(t_{12}). \quad \text{(B17)}$$

Further writing $\Omega_{i\pm}$ in terms of Δ, ϵ_i, and K_i, we obtain

$$S_3 = \pi\sum_i \frac{\Delta^3}{4K_i^2+\Delta^2}\sin(|K_i t_{12}|)\cos(\sqrt{4K_i^2+\Delta^2}\bar{t})\delta(\epsilon_i - K_i), \quad \text{(B18)}$$

where we have incorporated the $\mathrm{sgn}(t_{12})$ and $\mathrm{sgn}\, K_i$ factors by taking an absolute value of the argument in $\sin(|K_i t_{12}|)$. The next step is to average over the bias distribution and integrate over the sites. As in the case of S_1, we exclude distant spins and obtain

$$S_3 = \frac{16}{9}\sqrt{\frac{2\pi^3}{3}}\frac{\Delta^3 E_{dm}}{E_b}\int_{c\Delta}^{\infty} dK\frac{1}{K^2(4K^2+\Delta^2)}\sin(K|t_{12}|) \times\cos(\sqrt{4K^2+\Delta^2}\bar{t})e^{-K^2/2E_b^2}. \quad \text{(B19)}$$

This integral is also dominated by the lower limit, but the answer is different depending on $\bar{t}$. If $\bar{t} \ll \Delta^{-1}$, we may argue that for $K \sim \Delta$ and for $E_{dm}^{-1} \ll |t_{12}| \ll \Delta^{-1}$, $\sin(K|t_{12}|) \approx K|t_{12}|$, and $\cos(\sqrt{4K^2+\Delta^2}\bar{t}) \approx 1$. The resulting integral is identical to that which appeared in S_1. Hence, we have

$$S_3 = \frac{8\pi}{9}\sqrt{\frac{2\pi}{3}}\ln\left(1+\frac{1}{4c^2}\right)\frac{\Delta E_{dm}}{E_b}|t_{12}|, \quad (\bar{t} \ll \Delta^{-1}). \quad \text{(B20)}$$

If on the other hand $\bar{t} \gtrsim \Delta^{-1}$, the oscillations in the $\cos(\sqrt{4K^2+\Delta^2}\bar{t})$ factor reduce S_3 significantly. The precise form is unimportant and it suffices to put

$$S_3 \simeq 0, \quad (\bar{t} \gtrsim \Delta^{-1}). \quad \text{(B21)}$$

For short times $\bar{t} \ll \Delta^{-1}$ (which automatically implies $|t_{12}| \ll \Delta^{-1}$), all three sums S_i, have the same behavior. Adding them together, we obtain

$$\sum_i \eta_i = S_1 + S_2 - S_3$$
$$= \frac{4\pi}{9}\sqrt{\frac{2\pi}{3}}\left[\pi - \ln\left(1+\frac{1}{4c^2}\right)\right]\frac{\Delta E_{dm}}{E_b}|t_{12}|. \tag{B22}$$

On the other hand, for longer $\bar{t}$, but still obeying $\Delta|t_{12}| \ll 1$, S_3 may be neglected and

$$\sum_i \eta_i = \frac{4\pi}{9}\sqrt{\frac{2\pi}{3}}\left[\pi + \ln\left(1+\frac{1}{4c^2}\right)\right]\frac{\Delta E_{dm}}{E_b}|t_{12}|. \tag{B23}$$

2. Improved estimate incorporating numerics

Since the analytical estimate given above entails several approximations, we have also evaluated $|F|$ numerically. We take the contribution F_i from the ith MS to be given by $e^{is_iKt_{12}}(1-\eta_i)$, with η_i given by Eq. (A46). The different factors η_i are found and the factors $(1-\eta_i)$ multiplied to obtain $|F|$. This calculation is valid for a much larger range of times, $t_{1,2} \sim E_{dm}/\Delta^2$, since expression (A46) then holds.

In more detail, our algorithm is as follows. We first create a set of sites on a nearly cubic lattice. That is, each site is offset from a perfect cubic lattice by a small random amount equal to 0.01 times the lattice constant in each of the three cartesian directions. (The reason for adding the offsets was to avoid exact cancellations of the dipole field from an aligned shell of nearest-neighbor spins. We do not believe that this step is essential, but it does not invalidate the calculation either.) We next place a spin on each site with the orientation s_i randomly chosen to be ± 1 with equal probability and choose a particular value of t_{12}. Next, at each site we select an energy bias ϵ_i by sampling a normal distribution with mean zero and standard deviation $E_b = 1000$ in units such that $\Delta = 1$. [In Fe_8 the ratio E_b/Δ is $\sim 10^6$. Taking such a large ratio in the numerics makes each individual mismatch prohibitively small, making it very hard to see departures from unity in $\Pi(1-\eta_i)$. The physically important point is to ensure $E_b/\Delta \gg 1$, which we do.] The dipole field K_i at each site due to the central spin is computed using Eq. (3.3) with E_{dm} also equal to 1000Δ. That is, we do not take E_b and E_{dm} to be different. With these values of K_i and ϵ_i, we can then find (all energies are computed in units of Δ)

$$\epsilon_{i\pm} = \epsilon_i \pm K_i, \quad \Omega_{i\pm}^2 = \epsilon_{i\pm}^2 + \Delta^2. \tag{B24}$$

It is now possible to calculate the expression (A46) for η_i for any $\bar{t}$ and t_{12}. The dependence on two time variables is inconvenient, however, so instead we calculate the lower and upper bounds with respect to $\bar{t}$, which are given by

$$\eta_{i\,\min} = 2\left(\frac{\Delta}{\Omega_+}\right)^2\left[\left(\frac{K_i}{\Omega_{i-}}\right)\sin\left(\frac{\Omega_{i-}t_{12}}{2}\right) - \frac{1}{2}\sin(K_it_{12})\right]^2, \tag{B25}$$

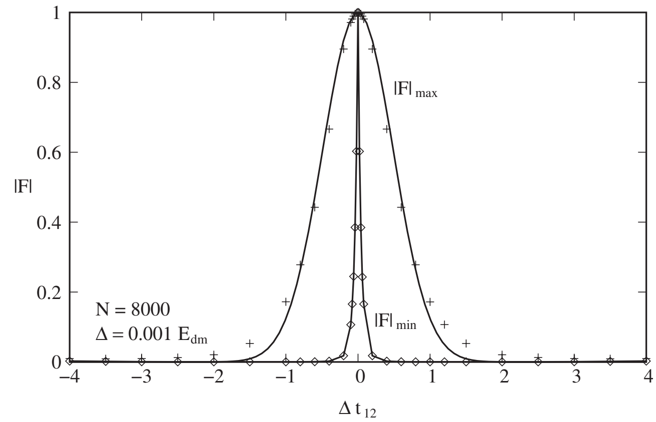

FIG. 2. Numerically computed lower and upper bounds $|F|_{\min}$ and $|F|_{\max}$, plotted vs Δt_{12}, for a central spin in a lattice of 8000 spins. We have chosen $\Delta = 0.001E_{dm}$. Curves are best fits to $e^{-a|\Delta t_{12}|}$ for $|F|_{\min}$ and $e^{-b|\Delta t_{12}|^2}$ for $|F|_{\max}$.

$$\eta_{i\,\max} = 2\left(\frac{\Delta}{\Omega_+}\right)^2\left[\left(\frac{K_i}{\Omega_{i-}}\right)\sin\left(\frac{\Omega_{i-}t_{12}}{2}\right) + \frac{1}{2}\sin(K_it_{12})\right]^2. \tag{B26}$$

Since $|F| = \Pi_i|1-\eta_i|$, we have

$$\prod_i (1-\eta_{i\,\max}) \le |F| \le \prod_i (1-\eta_{i\,\min}). \tag{B27}$$

These bounds, $|F|_{\min}$ and $|F|_{\max}$, are now found using the computed maxima and minima for η_i. At the same time, we also compute the sums S_1, S_2, and

$$S_3' = 2\sum_i \frac{\Delta^2}{\Omega_{i+}^2}\frac{K_i}{\Omega_{i-}}\sin(\Omega_{i-}t_{12}/2)\sin(K_it_{12}), \tag{B28}$$

which differs from S_3 in that the factor $\cos(\Omega_{i+}\bar{t})$ is lacking in the summand. As argued above, $S_3' \simeq S_3$ when $\Delta\bar{t} \ll 1$. In this time range, therefore, we expect $|F| \simeq |F|_{\max}$. For longer $\bar{t}$ on the other hand, $|F| \simeq \exp[-(S_1+S_2)]$. We nevertheless shall find it useful to continue to calculate S_3'.

We then recompute the S's and the bounds for $|F|$ using a different set of biases, ϵ_i. All told, we do this for about 10^5 bias configurations in order to generate averages for the S's,

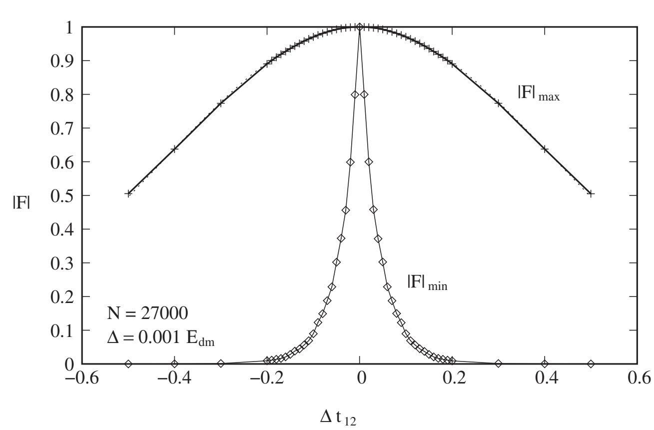

FIG. 3. Same as Fig. 2 for a lattice of 27 000 spins.

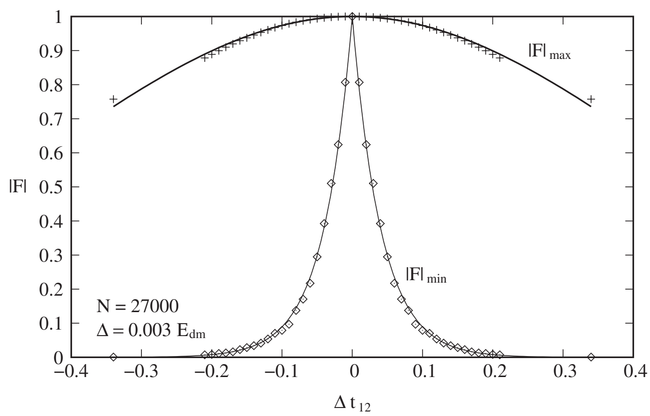

FIG. 4. Same as Fig. 3 but with $\Delta=0.003E_{dm}$.

$|F|_{\min}$, and $|F|_{\max}$. We also calculate the variances in these quantities at this stage. The entire calculation is then repeated for different t_{12}.

The lower and upper bounds of $|F|$, $|F|_{\min}$, and $|F|_{\max}$ are plotted as a function of t_{12} in Figs. 2–5. (We do not show the data for $N=8000$ and Δ/E_{dm} values of 0.003 or 0.005.)

We see that $|F|_{\min}$ does die as an exponential, i.e., we can fit it to a form $e^{-a|\Delta t_{12}|}$ very well. On the other hand, $|F|_{\max}$ dies like $e^{-b|\Delta t_{12}|^2}$, which is rather different. We show the best fit values of a and b for three different Δ/E_{dm} in Table I. As can be seen, a and b are reasonably independent of this ratio.

The result $|F|_{\max}\sim e^{-b(\Delta t_{12})^2}$ is rather surprising, since

$$|F|_{\min} \simeq e^{-(S_1+S_2+S_3')}, \tag{B29}$$

$$|F|_{\max} \simeq e^{-(S_1+S_2-S_3')}, \tag{B30}$$

and we showed that all three sums vary linearly with $|t_{12}|$. We can understand the t_{12}^2 behavior from our numerics. We first note that we do indeed find an excellent linear $|t_{12}|$ variation for the individual S's. We therefore write $S_i=\zeta_i\Delta|t_{12}$ and determine ζ_i from our data. These values are shown in Table II. Examining the table, we see that (a) $\zeta_1\simeq\zeta_2$ and (b) there is a nearly total cancellation in $\zeta_1+\zeta_2-\zeta_3'$, i.e., $\zeta_3'\simeq\zeta_1+\zeta_2$.

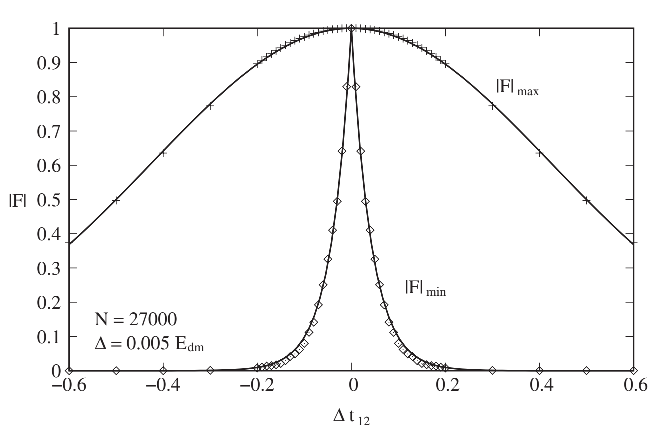

FIG. 5. Same as Fig. 3 but with $\Delta=0.005E_{dm}$.

TABLE I. Best fit values of the parameters a and b.

Δ/E_{dm}	a		b	
	$N=8000$	$N=27\,000$	$N=8000$	$N=27\,000$
0.001	23.7	24.4	2.09	2.80
0.003	24.0	24.2	2.52	2.65
0.005	23.1	23.3	2.64	2.77

We can use the numerical results to improve our analytical estimate as follows. We assume that the above-mentioned cancellation is perfect. In other words, the unknown parameter c in Eq. (B22) is such that

$$\ln\left(1+\frac{1}{4c^2}\right)=\pi. \tag{B31}$$

This implies that

$$\sum_i \eta_{i\,\max} = S_1+S_2+S_3' = \frac{4\pi}{9}\sqrt{\frac{2\pi}{3}}\left[\pi+3\ln\left(1+\frac{1}{4c^2}\right)\right]\frac{\Delta E_{dm}}{E_b}|t_{12}| \tag{B32}$$

$$=\frac{16\pi^2}{9}\sqrt{\frac{2\pi}{3}}\frac{\Delta E_{dm}}{E_b}|t_{12}|. \tag{B33}$$

With $E_{dm}=E_b$, this equals $25.4\Delta t_{12}$. Our numerical fits to $|F|_{\min}$ yield $a\simeq24$, which is quite close. This gives us confidence in fixing c as per Eq. (B31).[32]

We can now estimate $\Sigma_i\eta_i$ for long $\bar{t}$ (but $\ll E_{dm}^2/\Delta$). Using Eq. (B31), we have

$$\sum_i \eta_i \simeq S_1+S_2=\frac{8\pi^2}{9}\sqrt{\frac{2\pi}{3}}\frac{\Delta E_{dm}}{E_b}|t_{12}|. \tag{B34}$$

Since we do not know E_{dm}/E_b precisely, however, we limit ourselves to stating that

$$\sum_i \eta_i \simeq \gamma_m\Delta|t_{12}|, \tag{B35}$$

where γ_m is a constant of order unity.

TABLE II. Numerically calculated values of the coefficients ζ_1, ζ_2, and ζ_3' in the sums S_1, S_2, and S_3'.

Δ/E_{dm}	$N=8000$			$N=27\,000$		
	ζ_1	ζ_2	ζ_3'	ζ_1	ζ_2	ζ_3'
0.001	5.44	5.41	10.42	6.06	6.06	11.82
0.003	6.08	6.08	11.90	6.12	6.11	11.77
0.005	5.98	5.99	11.78	6.03	6.11	11.01

APPENDIX C: DENSITY OF DIPOLE COUPLING STRENGTHS

The density of dipole couplings, $g(K)$, introduced in Eq. (B8), is given by

$$g(K) = \sum_i \delta(K - K_i), \tag{C1}$$

with

$$K_i = \frac{2E_{dm}a^3}{r_i^3}(1 - 3\cos^2\theta_i). \tag{C2}$$

We evaluate the sum over lattice sites assuming that the spins are uniformly distributed with a density a^{-3}. Except when $K \simeq E_{dm}$, corresponding to nearest or next-nearest-neighbor sites, we may replace the sum by an integral, obtaining

$$g(K) = \frac{2\pi}{a^3}\int_0^\infty dr r^2 \int_{-1}^1 du\, \delta\left[K - \frac{2E_{dm}a^3}{r^3}(1 - 3u^2)\right], \tag{C3}$$

where $u = \cos\theta$. Performing the r integral, we get

$$g(K) = \frac{4\pi E_{dm}}{3K^2}\int_{-1}^1 du |1 - 3u^2| \Theta\left(\frac{1 - 3u^2}{K}\right), \tag{C4}$$

where $\Theta(\cdot)$ is the Heaviside step function; equal to 1 when its argument is positive, and zero otherwise. The integral on u is best done separately for positive and negative K. When $K > 0$, we have

$$g(K) = \frac{8\pi E_{dm}}{3K^2}\int_0^{3^{-1/2}} du(1 - 3u^2) = \frac{16\pi}{9\sqrt{3}}\frac{E_{dm}}{K^2}. \tag{C5}$$

Likewise, when $K < 0$, we have

$$g(K) = \frac{8\pi E_{dm}}{3K^2}\int_{3^{-1/2}}^1 du(3u^2 - 1) = \frac{16\pi}{9\sqrt{3}}\frac{E_{dm}}{K^2}, \tag{C6}$$

the same expression as for $K > 0$. This is Eq. (B8).

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[27] More precisely, it is conceivable that η_i could vanish for isolated unequal values of t_1 and t_2, but this would require a coincidence of the directions $\hat{\mathbf{n}}_1$ and $\hat{\mathbf{n}}_2$ defined in Eq. (A10). Such a coinci-

dence can only happen for a measure-zero set of K_i, ϵ_i, t_1, and t_2. It can therefore be regarded as accidental and for all practical purposes we can say that $\eta_i > 0$ if $t_{12} \neq 0$.

[28] E. Keçecioğlu and A. Garg, Phys. Rev. B **76**, 134405 (2007).

[29] We were led to think about the points in this paragraph in a correspondence with Jacques Villain and Wolfgang Wernsdorfer.

[30] W. Wernsdorfer, S. Bhaduri, A. Vinslava, and G. Christou, Phys. Rev. B **72**, 214429 (2005).

[31] W. Wernsdorfer, arXiv:0804.1246 (unpublished).

[32] Even though we do not need it to find $\Sigma_i \eta_i$, the argument that follows provides still more support for our approach. The $\exp(-bt_{12}^2)$ behavior of $|F|_{\max}$ can be understood if we note that the weight of the delta functions in the replacements (B3) and (B17) should be multiplied by another factor $(1-\Delta|t_{12}|/\pi)$ because the integrals over Ω_{i-} begin from Δ, not 0. (This is readily seen by performing the integrals from 0 to ∞, and from 0 to Δ, and subtracting.) When we make these changes, and fix c according to Eq. (B31), we find $S_1+S_2-S_3=b|\Delta t_{12}|^2$, with $b=2.02E_{dm}/E_b$, or just 2.02 if $E_{dm}=E_b$. Our numerical fits yield $b\sim 2.1-2.8$, which is close enough given the crudeness of our estimates.