Decoherence of spin qubits in the “Frozen Core”: Equivalent Pairs model

R. Guichard, S. J. Balian, G. Wollowicz, P. A. Mortemousque, and T. S. Monteiro

1Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom
2London Centre for Nanotechnology, University College London, London WC1H 0AH, UK
3School of Fundamental Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

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Hybrid qubit systems combining electronic and surrounding proximate nuclear spins registers offer a promising avenue towards quantum information processing, with even multi-spin error correction protocols recently demonstrated in diamond. For the alternative platform offered by spin donors in natural silicon at cryogenic temperatures, however, the mechanism limiting coherence of proximate nuclear-spin registers is not yet understood. We argue here that the dominant mechanism, yielding $T_2^\ast$ values of order 1 second, arises from the dynamics of a comparatively small number of symmetrically sited nuclear impurities, which have been neglected in previous spin decoherence studies as they are too widely separated. In that case, measurements of nuclear coherence decays provide highly sensitive probes of the symmetries of the donor electronic wavefunction.

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The coherent manipulation of individual quantum spins in either silicon or diamond represent two promising alternative approaches to the development of a raft of quantum technologies including not only quantum information but also sensing, metrology and magnetometry. In the case of diamond, the remarkable properties of nitrogen vacancy (NV) colour centres for spin-dependent optical read-out and polarisation are the cornerstones of a large number of proposed applications at the single spin level [1–5]. In silicon, shallow donors (mainly group V atoms including phosphorus) provide coupled electron-nuclear spin systems which form the basis for the seminal proposal of Kane [6] for scalable silicon-based quantum computing. While there has been good progress in single-spin detection and read-out [7], most studies are on ensembles [8,9]. For donors such as bismuth and arsenic, strong mixing between the host electronic and nuclear spins allows greatly enhanced coherence and manipulation times even in natural silicon [10,15].

Natural silicon comprises of (mostly) spin-free $^{28}\text{Si}$ isotopes, but 4.67\% of atomic sites hold $^{29}\text{Si}$ impurities which represent $I = 1/2$ nuclear spins. Similarly, natural diamond is mostly spin-free $^{12}\text{C}$, but the central NV system interacts with the $I = 1/2$ nuclear spins of the 1.1\% of diamond atomic sites occupied by $^{13}\text{C}$ nuclei. In these samples, if otherwise free of paramagnetic impurities, $^{29}\text{Si}$ or $^{13}\text{C}$ nuclei represent a major source of decoherence [16,20]. However, interest in these impurities has now moved far beyond their role as a destructive source of decoherence; in particular in their use as a testbed for the detection and read-out of proximate nuclear spins. For instance, applications to single-molecule nuclear magnetic resonance [3]; and to quantum information [21] via quantum registers combining the central electronic qubit with proximate spins [22,23].

Proximate nuclear qubits can interact not only via direct dipolar coupling, but also via much longer-ranged interactions mediated by the central electronic spin. However, in the case of strong coupling to the central spin, the detuning induced by the hyperfine coupling on each partner of the pairs overwhelms the intrinsic dipolar coupling, suppressing their flip-flopping and greatly ameliorating decoherence within a so-called “frozen core” region.

The frozen core is a well-established concept [24,25] in electron spin resonance (ESR) studies but is now attracting new interest as a reservoir of protected qubits [27]. The frozen core is commonly estimated to lie within a boundary radius $R$ where the ratio of the typical hyperfine coupling between central electron and the $n$-th nuclear impurity is comparable with the intrabath interaction between two neighbouring nuclei, which may be approximately inferred from the linewidth. For example, the $\sim 127$ Hz measured natural linewidth of $^{29}\text{Si}$ [28] is consistent with an estimated $R \approx 80$ Å for Si:P donors.

Although single-nuclear spin experimental studies remain a challenge, hyperfine couplings of proximate $^{29}\text{Si}$ sites in an ensemble were already resolved spectroscopically in 1969 [29] by continuous wave ESR and their coherence can also be investigated with current techniques. For a nuclear bath far outside the frozen core, $T_2^\ast$ is of order of milliseconds [28]. However, here we show that the residual effect of these far bath spins on the decoherence of proximate spin qubits (which lie within $\sim 20 \sim 30$ Å of the center) yields $T_2^\ast$ orders of magnitude longer than even the seconds timescale.

We argue instead that the dominant decoherence mechanism arises from a few dozen $^{29}\text{Si}$ spin pairs, well within the frozen core, for which: (i) the members of the pair are symmetrically sited relative to the central spin and thus have equivalent detuning values (ii) at
FIG. 1: Decoherence of (a) electronic and (b) proximate nuclear spin qubits by a flip-flopping nuclear spin bath. The background plots the electronic wavefunction; blue denotes approximately the strong-detuning region, where the energy cost of a bath spin flip $\Delta_n^e \propto \pm (J_1 - J_2)$ exceeds the strongest intrabath coupling $C_{12}$. (a) **Electronic spin decoherence** is dominated by an active zone of pairs of neighbouring nuclear spins which are strongly detuned with $\Delta_n^e/C_{12} = \pm (J_1 - J_2)/C_{12} \sim 5 - 50$ for Si:P, so are within the blue region. The reason is that for large $|\Delta_n^e|$ flip-flop amplitudes are damped, qubit state-dependence of the quantum bath evolution, essential for decoherence is also $\propto |\Delta_n^e|$. (b) **Nuclear qubit decoherence by our Equivalent Pairs model**. The detuning is $\Delta_n^e + \Delta_n^n n_0$; the $\Delta_n^n \propto \pm (C_1^A - C_2^A)$ component is state dependent and leads to qubit-bath entanglement, while now $\Delta_n^e$ simply damps flip-flopping. $|\Delta_n^e| \gtrsim |\Delta_n^n|$ implies $J_1 - J_2 \simeq 0$, selecting equivalent sites (determined by the symmetry of the electronic wavefunction). Additionally, $\Delta_n^n \gtrsim 1$ implies that one member of the pair must be close enough to the qubit to allow appreciable direct dipolar coupling (as opposed to long-range coupling between nuclear spins mediated by the electron). Pairs which satisfy this requirement (exemplified by the upper, but not the lower, equivalent pair) are rare but can account for the observed nuclear decoherence times.

There are interesting differences between the well-studied decoherence of electronic qubits [10, 19, 50, 31] and the proximate nuclear qubits which are the subject of the present study; the key processes are summarised in Fig. 1. In both cases, a dephasing process arising from entanglement with a quantum bath is assumed. The qubit (nuclear or electronic with upper and lower states $|\pm\rangle_{n,e}$ and $|\mp\rangle_{n,e}$) is prepared in a superposition state by an applied (radio frequency (RF) for the nuclear or microwave (MW) for the electron) $\pi/2$ pulse at $t = 0$

$$|\Psi(0)\rangle = \frac{1}{\sqrt{2}} (|+\rangle + |-\rangle)_{n,e} \otimes |\mathcal{B}(0)\rangle \otimes |\phi(0)\rangle_{e,n}$$

(1)

where $|\phi(0)\rangle_{e,n}$ denotes the initial spin state (electronic or nuclear) which is not resonant with the external control pulses, while $|\mathcal{B}(0)\rangle$ denotes an initial state of the bath. We consider first the effect of a single nuclear impurity pair (both $I = 1/2$ spins); then, $|\mathcal{B}(0)\rangle$ is one of the four thermal states: $\{|\downarrow\downarrow\rangle, |\downarrow\uparrow\rangle\}$ or $\{|\uparrow\downarrow\rangle, |\uparrow\uparrow\rangle\}$. The joint dynamics of the qubit spins and bath are given by:

$$\hat{H} = \hat{H}_q + \hat{H}_{\text{int}} + \hat{H}_\text{bath}.$$  

(2)

where the qubit Hamiltonian $\hat{H}_q = \gamma_e \omega_0 \hat{S}_z + \gamma_n \omega_0 \hat{I}^A_z$ represents the Zeeman terms for the electron and nuclear qubit (labelled $A$), either one of which is resonant with any applied control field. Here we limit ourselves to the unmixed cases where any coupling between the qubit and the host nuclear spin is neglected. The interaction...
Hamiltonian:
\[ \hat{H}_{int} = \sum_{i=1,2} \left( \hat{S} \cdot \hat{J} + \hat{I}^{A} \cdot \mathbf{C}_{i}^{A} \right) \cdot \hat{I}_{i} \]  
(3)
represents the hyperfine coupling \( \hat{J} \) between the central spin and bath spins and the dipolar interaction \( \mathbf{C}_{i}^{A} \) between the resonant nuclear qubit and the remainder of the 2-spin bath. For simplicity, we do not include explicitly the term \( \hat{S} \cdot \hat{J} \cdot \hat{I}^{A} \) coupling the electron to the resonant nucleus, which is only significant in the specific (but minor) contribution from direct flip-flopping processes. Finally, the intrabath coupling \( \hat{H}_{bath} = \hat{I}_{1} \cdot \mathbf{C}_{12} \cdot \hat{I}_{2} = C_{12} \hat{I}_{1}^{z} \hat{I}_{2}^{z} - \frac{C_{12}}{4} (\hat{I}_{1}^{+} \hat{I}_{2}^{-} + \hat{I}_{1}^{-} \hat{I}_{2}^{+}) \), represents the dipolar coupling between the bath nuclei.

Under the action of the full Hamiltonian Eq. (3) the product state in Eq. (2) evolves into an entangled state:
\[ |\Psi(t)\rangle = \left[ |\uparrow\rangle_{n,e} |\mathcal{O}_{+}(t)\rangle + |\downarrow\rangle_{n,e} |\mathcal{O}_{-}(t)\rangle \right] \frac{\text{e}^{i\alpha(t)}}{\sqrt{\rho_{n}}} \]  
(4)
The coherence decay is calculated from either \( \mathcal{L}_{n}(t) = \langle \Psi(t)| \hat{S}^{z} |\Psi(t)\rangle \) or \( \mathcal{L}_{n}(t) = \langle \Psi(t)| \hat{I}^{\pm} |\Psi(t)\rangle \). For both cases,
\[ |\mathcal{L}_{n}(t)| \propto \left| \langle \mathcal{O}_{+}(t)|\mathcal{O}_{-}(t)\rangle \right| \]  
(5)
disregarding a constant prefactor \( \langle |\uparrow\rangle_{\mathcal{O}_{+}} |\downarrow\rangle_{\mathcal{O}_{-}} \) or \( \langle |\uparrow\rangle_{\mathcal{O}_{+}} |\uparrow\rangle_{\mathcal{O}_{-}} \), the coherence has a (real) decaying envelope for the normalized \( \ell \)-th bath spin pair contribution:
\[ \mathcal{L}(t) = \left| \langle \mathcal{O}_{+}(t)|\mathcal{O}_{-}(t)\rangle \right| \leq 1, \]  
(6)
the measured decays, whether Hahn echos or more complex dynamical decoupling sequences, are obtained from the combined contributions from all spin pairs:
\[ \langle \mathcal{L}(t) \rangle = \langle \prod_{\ell} \mathcal{L}(t) \rangle \]  
(7)
where the average denotes an average over all bath states, and if required, an ensemble average over different realisations of the impurity bath. The above procedure is a simplification of the successful CCE (cluster correlation expansion) method which, in general, combines clusters of all sizes, not just pairs. In our case, donor electronic spin decoherence can be well simulated with restricted spin pairs dynamics in practically all regimes [15]. Nevertheless, the nuclear qubit decoherence represents an example of a central spin decoherence problem where the central and bath spins are the same species and higher correlations arising from clusters of three, four, up to six spins cannot be neglected [30]. However, for proximate nuclei, suitable clusters of more than two spins are too sparse to contribute appreciably but could be included in a more refined model.

An accurate and insightful simplification arises if \( \gamma_{c}\omega_{0} \gg |J| \) or if \( \gamma_{n}\omega_{0} \gg |C| \) where \( |J|, |C| \) denote typical values of the qubit-bath interaction. In that case, the interaction Hamiltonian in Eq. (3) reduces to the Ising form \( \hat{H}_{int} = J_{1} \hat{S}^{z}_{1} \hat{I}_{1}^{z} + J_{2} \hat{S}^{z}_{2} \hat{I}_{2}^{z} + C_{1} \hat{I}_{1}^{z} \hat{I}_{2}^{z} + C_{2} \hat{I}_{1}^{z} \hat{I}_{2}^{z} \), a simple diagonal energy shift in \( \hat{I}_{2}^{z} \) terms relative to \( \hat{I}_{2}^{z} \) or a detuning of bath spin 1 relative to bath spin 2. Referred to as the pseudospin model [31] in this case, \( \{|\uparrow\rangle, |\downarrow\rangle\} \) bath states do not contribute while the dynamics of the \( \{|\uparrow\rangle, |\downarrow\rangle\} \) states is given by an effective state-dependent Hamiltonian:
\[ \hat{H} = \frac{1}{4}(\Delta_{z}^{+} \hat{\sigma}_{+} + C_{12} \hat{\sigma}_{x}) \]  
(8)
with the detuning \( \Delta_{z}^{+} \approx \Delta_{z}^{\pm} = 2(J_{1} - J_{2})(\pm|\hat{S}^{z}|\pm) \) for an electronic qubit and \( \Delta_{z}^{\pm} = \Delta_{e} \pm (C_{1}^{A} - C_{2}^{A}) \) for a nuclear qubit. In the latter case, the electronic detuning \( \Delta_{e} \) represents a potentially large contribution which is not sensitive to the qubit state. From Eq. (8) decays (indirect and direct flip-flops) are deduced analytically and for the Hahn echo case we obtain:
\[ \mathcal{L}(t) \simeq \left| 1 - 2 \alpha(t) (\alpha(t) + i\beta(t)) \right| \]  
(9)
where \( \alpha = \sin(\omega t) \sin(\theta^+) \sin(\theta^-) \), \( \beta = \sin(\omega t) \cos(\theta^+) \sin(\theta^-) + \sin(\omega t) \cos(\omega t) \sin(\theta^-) \) while \( \theta^+ = \tan^{-1}(C_{12}/\Delta_{z}^{+}) \) and the eigenvalues \( \omega_{\pm} = \frac{1}{4} \sqrt{\Delta_{z}^{+}^{2} + (C_{12})^{2}} \), where we have dropped the \( \ell \) indices for convenience.

We obtained excellent agreement with full numerical CCE solutions provided that a perturbative correction for the non-Ising (anisotropic) hyperfine terms [31] is added to the dipolar coupling when using Eq. (9):
\[ C_{12}(t) \rightarrow C_{12}(t) + \frac{J_{1}^{(t)} J_{2}^{(t)}}{\omega_{0}} \]  
(10)
allowing remote bath spins a long ranged interaction mediated by the central electronic spin. This correction, negligible for electron qubit decoherence, is absolutely essential to allow remote, but symmetrically placed equivalent nuclear pairs members to interact. Distinguishability of qubit state enters in Eq. (9) principally through the sin \( (\theta^+ - \theta^-) \) prefactor but is suppressed by the electronic component. This imposes the requirement \( |\Delta_{n}^{\pm}| = |(C_{1}^{A} - C_{2}^{A})| \geq \Delta_{e} \) for decoherence.

Central to our model is the identification of spin pairs which can contribute non-negligibly to the decoherence of a proximate spin (i.e. well within the frozen core radius of \( R_{FC} \approx 80 \) Å). By means of numerical investigation and by a simple argument (see Appendix A) we can exclude the contribution of remote spin pairs outside the frozen core. We now proceed to introduce our model.

Equivalent Pairs model. The isotropic part of the hyperfine interaction is modeled using the Kohn-Luttinger (KL) wavefunction (see Appendix B) which is an approximation of the ground state wavefunction of the
The density of equivalent pairs $D(n, R)$ is given by the estimated average number of significant EP in each shell. For instance, the ranges were adjusted to ensure summation over complete shells (see Appendix B) and we obtain estimates for $\mathcal{M}_{n_s}(N)$:

\begin{align}
\mathcal{M}_{12}(N) &= 4N^2 \\
\mathcal{M}_{24}(N) &= \frac{4}{3}N(N^2 - 1) + N^2 \\
\mathcal{M}_{48}(N) &= \frac{2}{3}N^3 - N^2 + \frac{N}{3},
\end{align}

while $\mathcal{M}_6(N) = \mathcal{M}_6(N) = N, \mathcal{M}_4(N) = 2N$. Then assuming a binomial distribution, taking an abundance of $p = 0.0467$ for nuclear spin impurities in natural silicon, the estimated average number of significant EP in each shell is:

$$\zeta_{n_s} \approx \sum_k \binom{n_s}{k} \frac{1}{p^k(1-p)^{n_s-k}} \frac{k(k-1)}{2},$$

where $\binom{n}{k} = \frac{n^k}{k!(n-k)!}$ is the binomial coefficient. For the two dominant shells $\zeta_{48} \approx 2.3$ and $\zeta_{24} \approx 0.6$ at large $N$.

In these cases, it is quite likely that any impurity spin has an equivalent partner somewhere, albeit remotely located. Nevertheless, due to the long-range electron-mediated coupling, a $C_{12}$ of about tens of Hz is present. Within a sphere of radius $N$ cubic cells, we expect the total number of EP to be simply:

$$\mathcal{M}_{EP} \approx \sum_s \zeta_{n_s} \mathcal{M}_{n_s}(N).$$

For instance, within a radius of $R = 100 \, \text{Å}$, we find $\mathcal{M}_{EP} \approx 19,000$. For a proximate nucleus however, one member of the pair must be dipolar-coupled to the resonant spin, i.e., within about $m \approx 3$ cubic cells. Each nuclear qubit thus interacts with other nuclei in the neighbouring $(2m)^3 \approx 200$ cells. We can define a local density of spin pairs:

$$D(n_s, R = N a_0) = \zeta_{n_s} \frac{\mathcal{M}_{n_s}(N)}{(2N)^3},$$

which gives the mean number of EP in each cubic cell as a function of distance, $R = N a_0$ from the electron. We see in Fig. 2 that the mean number for large $R$ is about $0.2 - 0.3$ pairs per cubic cell (cf. solid blue line), thus each nuclear qubit interacts with about 50 equivalent spin pairs and averaging over 100 realizations. The above neglects anisotropic components of the hyperfine interaction and predicts decay rates yielding $T_{2n} \sim 0.2 - 0.3 \, \text{s}$ (see Appendix B).

To account for the anisotropy, which is less easy to calculate reliably, we assume that any degree of anisotropy detunes spin pairs so much that their contribution becomes negligible. Thus to remain an equivalent pair we require that spins have the same $\hat{\mathbf{B}} \cdot \mathbf{n}$, where $\hat{\mathbf{B}}$ is the direction of the magnetic field. The effect is to reduce the symmetry but to increase the number of shells, i.e., for $\mathbf{n}_B = (1 \, 0 \, 0)$ and the main shells with $n_s = 48, 24, 12$ partners, we have $n_s \rightarrow n_s/3$ and therefore $\mathcal{M}_{n_s} \rightarrow 3\mathcal{M}_{n_s}$ (cf. Fig. 2 dash dot blue line). The corresponding $T_{2n}$ for isotropic case and with lowered symmetry due to anisotropy, are shown in Fig. 3. As not all shells are affected by anisotropy, this model is intended to provide an upper bound to the expected $T_{2n}$ rather than a quantitative simulation. The lowered symmetry results are of the same order of magnitude (about 1 second) as measured $T_{2n}$ values for the host spin.

In conclusion, we propose here a new model which provides a likely dominant mechanism for the decoherence of proximate nuclear spins surrounding donor spins in silicon. The results are purely indicative and a more refined version would consider improved wavefunctions, more accurate than the KL wavefunction.
FIG. 3: Calculated $T_{2n}$ times for phosphorus donors Si:P including anisotropy correction. There is a weak trend for $T_{2n}$ to increase as the hyperfine coupling increases (blue line least square fitting), possibly indicative of the decreasing density to increase as the hyperfine coupling increases (blue line least square fitting), possibly indicative of the decreasing density in Equivalent Pairs (EP) as $R \rightarrow 0$. Calculated $T_{2n}$ are in the seconds timescale; for a cooled sample not limited by electronic $T_{1}$ and reasonable donor density $\sim 10^{17}$ cm$^{-3}$ or less, EPs are the dominant mechanism.

Intrumental investigation of the dependence on symmetry-breaking mechanisms (such as crystal strain or orientation) will be necessary to conclusively establish this as the – to date not established – dominant decoherence mechanism for proximate spins.

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A: Bath spins outside the frozen core

From numerical simulations with a very large spin bath, we conclude that distant spin pairs outside the frozen core radius $R_{FC}$ make a negligible contribution to decoherence. One can also use a simple argument to exclude the large numbers of non-equivalent, but distant spin pairs beyond $R_{FC}$; this is important since for such spins, one can have $C_{12}^{(f)} \sim \Delta_e$, so the flip-flop amplitude is appreciable. At internuclear separations of $R \approx 80$ Å, mutual dipolar coupling is negligible. Nevertheless, since hyperfine coupling to a proximate spin, $J_A$, is large, the electron mediated interaction $C_{12}^{A} \approx \frac{J_{12}^{A}}{\omega_0}$ is enhanced. However, then, the decoherence criterion becomes:

$$\left( C_{1}^{A} - C_{2}^{A} \right) \approx \frac{J_{12}^{A}(J_1 - J_2)}{\omega_0} \gtrsim \Delta_e = (J_1 - J_2)$$  \quad (15)

imposing the requirement that:

$$\left| \frac{J_A}{\omega_0} \right| \gtrsim 1.$$  \quad (16)

But for X-band, $\omega_0 \approx 2\pi \times 10$ GHz, while the largest $J_A \sim 10$ MHz.

A more careful argument examines the $\sin(\theta^+ - \theta^-)$ prefactor as we can show [15] that the approximate weight of the $l$-th pair assuming approximately Gaussian temporal decays is:

$$\left( \frac{1}{T_2^{(l)}} \right)^2 \propto \sin^2(\theta^+_l - \theta^-_l).$$  \quad (17)

For a non-negligible contribution $|\sin(\theta^+ - \theta^-)| \sim 1 - 1/100$. From our pseudospin model (leaving out the $l$ labels),

$$\sin(\theta^+ - \theta^-) = \frac{C_{12} \Delta^-}{\omega^+ \omega^-} - \frac{C_{12} \Delta^+}{\omega^+ \omega^-} = \frac{2C_{12}(C_{1}^{A} - C_{2}^{A})}{\omega^+ \omega^-};$$  \quad (18)

if the interaction is mediated by the electron,

$$|\sin(\theta^+ - \theta^-)| \approx \left| \frac{2C_{12}J_{12}^{A} \Delta_e}{\omega^+ \omega^- \omega_0} \right|$$  \quad (19)

We consider two cases: (i) if the distant spin pair is strongly interacting (two $^{29}$Si quite close to each other), then $\Delta_e < C_{12} \sim \omega^+ \sim \omega^-$, hence $|\sin(\theta^+ - \theta^-)| \sim \left[ \frac{2J_{12}^{A} \Delta_e}{\omega_0 C_{12}} \right] \ll 10^{-4}$ as both factors in the product are very small. (ii) If the distant spins are weakly interacting such that $\Delta_e \gg C_{12}$, then $C_{12} \ll \Delta_e \sim \omega^+ \sim \omega^-$, $|\sin(\theta^+ - \theta^-)| \sim \left[ \frac{2J_{12}^{A} \Delta_e}{\omega_0 C_{12}} \right] \ll 10^{-4}$ so once again there is a negligible contribution. A numerical simulation using a very large bath (which yields, in the complete absence of a central spin, the asymptotic measured value $T_{2\alpha} \sim 4$ ms confirms that the impurity spins pairs outside the frozen core make no contribution to the decoherence of proximate spins, despite the long-ranged electron-mediated interaction.

B: Counting equivalent sites

Equivalent sites are those with the same hyperfine interaction and we obtain this from the Kohn-Luttinger (KL) wavefunction as follows. Consider an electron $\hat{\mathbf{S}}$ interacting with a nucleus $\hat{I}$ via the hyperfine interaction by

$$\hat{H}_{\text{int}} = J \hat{\mathbf{S}} \cdot \hat{\mathbf{I}},$$  \quad (20)

where $J$ is the isotropic hyperfine strength (“Fermi contact”). For a donor electron interacting with a nucleus, $J$ is given by see e.g [17]:

$$J = P \left[ F_1(\mathbf{r}) \cos(k_0 x) + F_2(\mathbf{r}) \cos(k_0 y) + F_3(\mathbf{r}) \cos(k_0 z) \right]^2.$$  \quad (21)

Here, $\mathbf{r} = (x, y, z)$ denotes the relative position vector between the electron and nucleus and $k_0 = (0.85)2\pi/a_0$ with lattice constant $a_0$. The prefactor $P$ contains the electronic and nuclear gyromagnetic ratios ($\gamma_S$ and $\gamma_I$), the charge density on each atomic site $\eta$, and vacuum permeability $\mu_0 = 4\pi \times 10^{-7}$ N A$^{-2}$:

$$P = \frac{4}{9} \gamma_S \gamma_I \hbar \mu_0.$$  \quad (22)

The relevant envelope functions of the KL wavefunction are:

$$F_1(\mathbf{r}) = \exp \left[ -\sqrt{\frac{x^2}{(nb)^2} + \frac{y^2 + z^2}{(na)^2}} \right],$$  \quad (23)

$$F_2(\mathbf{r}) = F_1(\mathbf{r}) \text{ with } \{x \rightarrow y, y \rightarrow z, z \rightarrow x\},$$  \quad (24)

$$F_3(\mathbf{r}) = F_1(\mathbf{r}) \text{ with } \{x \rightarrow z, y \rightarrow x, z \rightarrow y\},$$  \quad (25)

where $a$ and $b$ are lengths characteristic to the donor and $n = \sqrt{0.029 \text{ eV}}/E_i$ with the electron ionization energy $E_i$ in eV.

Now we consider the allowed coordinates of the impurities in the crystal. The Si crystal structure can be described by a simple cubic structure with lattice parameter $a_0 = 5.43$ Å and an 8-site basis. All atomic sites are represented by an integer vector $\mathbf{n} = (n_1, n_2, n_3)$ which are

| $n_3$ | 48 | 24 | 12 |
|-------|----|----|----|
| Class 1 | $24N^2(N-1)$ | $12N(3N-1)$ | $12N$ |
| Class 2 | $8N(N-1)(N-2)$ | $36N(N-1)$ | $12N$ |
| Class 3 | $16N(N-1)(2N-1)$ | $24N(2N-1)$ | |

TABLE I: Class contribution to the equivalent sites group as a function of $N$. 
obtained from translations (modulo 4) in all directions of
the 8 basis vectors $(0,0,0)$, $(0,2,2)$, $(2,0,2)$, $(2,2,0)$, $(3,3,3)$,
$(3,1,1)$, $(1,3,1)$, $(1,1,3)$. For simplicity, we can sort these
vectors into three classes: class 1 contains $(0,2,2)$, $(2,0,2)$,
$(2,2,0)$, class 2 contains $(0,0,0)$ and class 3 $(3,3,3)$, $(3,1,1)$,
$(1,3,1)$, $(1,1,3)$. To ensure counting over complete shells
described by the basis vectors, summations must range between
$[-N,N]$ for the $2$ coordinates and $[-N,N-1]$ for the $0$ coordinate of class 1 giving $4N^2(2N+1)$ number of sites; between $[-N,N]$ for class 2 giving $(2N+1)^3$ number of sites and between $[-N,N-1]$ for class 3 giving $8N^3$ number of sites. Owing to the symmetry of the
system, each site possesses several equivalent partners with positions which can be deduced by permutations of $(n_1,n_2,n_3)$ and which lie on the surface of shells of radius
$R = \frac{a_0}{4} \sqrt{n_1^2 + n_2^2 + n_3^2}$.[29] By consideration of
the symmetries of the KL wavefunction we can assign each
vector $n$ to a group of $n_s = 48, 24, 12, 8, 6$ or 4 partners.

For each class, the contribution to a shell comprising $n_s$
partners within a radius of $R = Na_0$ of the center as
a function of $N$ is summarized in Table I. Additionally,
class 2 contributes as $8N$ to $n_s = 8$ and as $6N$ to $n_s = 6$
and class 3 contributes as $8N$ to $n_s = 4$. Finally, in Fig. 4
we compare the effect of the further desymmetrisation if
we constrain EP to have in addition the same anisotropy
correction, i.e. same $(\hat{n}_B \cdot n)^2$. 

FIG. 4: Simulations of decays the coherence decays of a set
of proximate spins corresponding to $J = 0.1$ a), $J = 0.3$ b),
$J = 0.5$ c), $J = 0.7$ d), $J = 1$ e), $J = 3.8$ f) MHz. The blue
lines correspond to isotropic coupling only and yield $T_{2n} \approx
0.2 - 0.3$ s; red lines show the effect of symmetry reduction
due to the anisotropy of couplings: we compare the effect of
the further desymmetrisation if we constrain EP to have in
addition the same orientation condition (same $(\hat{n}_B \cdot n)^2$ as
discussed in main text). The effect is to produce $T_{2n}$ in the
seconds timescale.