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$^{13}$C hyperfine interactions in the nitrogen-vacancy centre in diamond

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Abstract. The electronic spin associated with the nitrogen-vacancy (NV) centre in diamond interacts with an environment formed by isotopic impurities and paramagnetic defects; the strength of these interactions depends on the location of each impurity relative to the NV centre. From the electron spin resonance spectra of individual NV centres we infer the possible values and signs of hyperfine splittings from nearby $^{13}$C nuclear spins at different lattice sites. Moreover, single-defect-centre nuclear magnetic resonance allows the examination of some of the inhomogeneities associated with the mesoscopic environment of NV–$^{13}$C systems. These measurements provide a check on ab initio calculations of electron spin density and have relevance for potential applications in nuclear spin quantum registers.

Interactions between the nitrogen-vacancy (NV) centre in diamond and proximal spins offer a fertile ground for studying the coherent dynamics of multi-spin systems [1]–[4] and suggest potential implementations for quantum information processing schemes [4]–[7]. Moreover, the discrete lattice sites available to substitutional spin impurities such as $^{13}$C can be exploited to obtain information about the electronic spin density of the NV centre [8, 9]. While conventional ensemble electron paramagnetic resonance (EPR), electron–nuclear double resonance (ENDOR) and nuclear magnetic resonance (NMR) techniques can measure electron–nuclear spin interactions for the native $^{14}$N or $^{15}$N and a few strongly coupled $^{13}$C

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Figure 1. (a) The spin levels of the electronic ground state and optically excited state of the NV centre at room temperature [15, 16]. The excited state level anticrossing (ESLAC) near 510 G is indicated by a dashed oval. At the ESLAC, electron spin resonance (ESR) transitions are observed in the ground state with a resonance frequency of approximately 1.45 GHz. (b) The hyperfine levels within the ground state $m_s = 0, m_s = -1$ manifold. Levels are shown for an NV centre coupled to a $^{14}$N and $^{13}$C spin in the situation where the hyperfine splitting parameter for $^{13}$C is positive. At low magnetic fields, our measurements sample all possible configurations of the nuclear spins, leading to the hyperfine transitions (1)–(6). At the ESLAC, only the $m_I = +1$ $^{14}$N state is occupied, so only two hyperfine transitions (3) and (6) are visible.

lattice sites [10, 11], the sensitivity of such ensemble methods depends largely on defect concentrations; even under optimal measurement conditions they cannot resolve weakly coupled rare impurities. By contrast, single-defect measurements can detect weak hyperfine interactions with a resolution well below 1 MHz [3, 12, 13]. We therefore undertake a systematic study of the possible hyperfine interactions between single NV centres in diamond and individual $^{13}$C nuclear spins. These results may inform selection of $^{13}$C lattice sites for applications, provide a check on ab initio theory and guide the interpretation of data suggesting interactions between the NV centre and other paramagnetic impurities.

The NV centre in diamond is a spin triplet, its ground state (see figure 1(a)) showing optical spin polarization and spin-dependent fluorescence [14]. For high-purity type Ia diamond, the NV electronic spin interacts with the native nitrogen nuclear spin and a bath of $^{13}$C isotopic impurities that are distributed randomly in the diamond lattice with 1.1% probability. Each NV centre thus couples with a different mesoscopic environment, leading to distinct hyperfine structure and coherence properties. In particular, there is a discrete set of proximal lattice sites that will be probabilistically occupied by a $^{13}$C nuclear spin, leading to a discrete set of possible hyperfine splittings.

To study these hyperfine interactions, we isolate individual NV centres using a scanning confocal microscope (figure 2(c), inset). We record optically detected ESR spectra at two static magnetic field settings. Data shown in figure 2 include both pulsed spectra, taken by applying a microwave $\pi$ pulse before optical illumination, and continuous-wave (CW) spectra, taken by simultaneous weak optical and weak microwave excitation. In both cases, we record fluorescence as a function of microwave frequency. For a $^{14}$NV centre and a proximal $^{13}$C, the...
Figure 2. (a) A sample ESR spectrum showing coupling to both $^{14}$N and $^{13}$C nuclear spins. Transitions are labelled as in figure 1(b). Data are taken using a 1.0 $\mu$s pulse of microwaves with a Rabi frequency of approximately 0.5 MHz, and detuning is given around a central frequency of 2.83 GHz. The inset shows the same centre at the ESLAC, where 1.15 $\mu$s pulses of $\approx$0.4 MHz Rabi frequency near 1.455 GHz are used. (b) As for (a), but for a different proximal $^{13}$C site. Low-field data are taken using 1.75 $\mu$s pulses of roughly 0.3 MHz Rabi frequency around a central frequency of 2.74 GHz, while the inset is taken under continuous optical and microwave excitation around 1.45 GHz. (c) Hyperfine splittings observed from a sample of roughly 300 NV centres at both low and high magnetic fields for 20 MHz $>$ $A_{\text{hfs}}$ $>$ 2 MHz. Of the surveyed centres, we show the subset exhibiting clear coupling to a single $^{13}$C. Error bars are 95% confidence statistical error in the fits. Letters indicate possible lattice sites (see figure 4). The inset represents a scanning confocal image of the type IIa CVD diamond sample (Sumitomo) showing individual NV centres. (d) Observed polarization at the ESLAC (x-axis) versus hyperfine splitting (y-axis). Polarization is calculated as the difference in fitted depth of two resonances divided by their sum; positive polarization corresponds to a positive hyperfine splitting in the ground state. Lorentzian fits are used for CW spectra, whereas Gaussian fits are used for pulsed spectra, but the two curves yield the same polarization within error.
resulting transitions are given by the Hamiltonian

\[ H = \Delta S_z^2 + P (I_\text{N}^z)^2 + B \cdot (g_\mu_B S - \gamma N I_\text{N}^z) + S \cdot (A_N \cdot I_\text{N} + A \cdot I), \]

where \( \Delta = 2.87 \text{GHz} \) is the electronic zero-field splitting, \( P = -5 \text{MHz} \) is the \(^{14}\text{N} \) quadrupole splitting and \( A_N \) (\( A \)) is the hyperfine tensor and \( \gamma_N(\gamma) \) is the gyromagnetic ratio for the \(^{14}\text{N} \) (\(^{13}\text{C} \)) nuclear spin \( I_\text{N} \) (\( I \)). The nitrogen hyperfine tensor \( A_N \) has been extracted from both ensemble \([11]\) and single-NV \([12, 13]\) measurements, and causes a splitting of \(-2.16 \text{MHz} \) between ESR transition frequencies for different \( I_\text{N}^z \) projections. Although most NV centres will show only three hyperfine lines corresponding to the three \(^{14}\text{N} \) nuclear spin projections, those coupling strongly to a single \(^{13}\text{C} \) nuclear spin will have six possible transitions. The optically detected ESR spectrum at low magnetic field can thus show six lines (see figures 1(b), 2(a) and (b)) corresponding to all of the possible combined nuclear spin orientations that occur during the measurement.

The ESR hyperfine spectrum is sensitive to the change in \(^{13}\text{C} \) nuclear spin splitting caused by flipping the electronic spin from \( m_s = 0 \) to \( m_s = -1 \). Because the axis connecting the N and V in the crystal lattice (NV axis \( \parallel \hat{z} \) in equation (1)) provides a definite quantization axis for the electronic spin, we measure a specific combination of hyperfine tensor components. In the secular approximation, the \(^{13}\text{C} \) hyperfine splitting is \( A_{\text{hfs}} = \pm \sqrt{A_{xz}^2 + A_{yz}^2 + A_{zz}^2} \) with a sign determined by the sign of \( A_{zz} \).

To determine low-field (<50 G \( \parallel \hat{z} \)) hyperfine splittings, we fit the data to six Gaussians constrained to have equal splitting between the \(^{14}\text{N} \) lines, and extract the frequency difference between the two \(^{13}\text{C} \) manifolds (see figures 2(a) and (b)). The Gaussian profile is chosen because of rapid (~a few \( \mu s \)) dephasing of the electronic spin by its spin-bath environment, but no significant difference in extracted hyperfine splitting is observed by fitting to a square pulsed excitation or Lorentzian profiles. In an examination of roughly 300 NV centres, only certain discrete values for the hyperfine splitting were observed, corresponding to the possible discrete lattice sites for a nearby \(^{13}\text{C} \). Most NV centres show only \(^{14}\text{N} \) hyperfine structure; the data plotted in figure 2(c) are a representative subset of the surveyed centres observed to interact strongly with a single \(^{13}\text{C} \). We do not show the 130 MHz splitting of the nearest neighbour \(^{13}\text{C} \) lattice sites, as they have been well documented in the literature \([1, 11]\). In addition to NV centres strongly coupled to a single \(^{13}\text{C} \) nuclear spin, NV centres with multiple proximal \(^{13}\text{C} \) nuclear spins (not included in figure 2(c)) are observed with some regularity, and show the same discrete values of the hyperfine splittings.

We note that previous single-site \(^{13}\text{C} \) measurements have attempted to use electron spin echo envelope modulation (ESEEM) to extract a full hyperfine tensor for two NV centres; however, fits did not yield unique results \([3]\). Furthermore, inhomogeneity in hyperfine splittings observed for nominally identical NV–\(^{13}\text{C} \) configurations (see figure 3) undermines the value of the greater precision of ESEEM for establishing discrete values of \( A_{\text{hfs}} \). The hyperfine splittings we extract from ESR (a technique chosen to facilitate faster data acquisition) agree within error both with published ESEEM data \([3]\) and with ESEEM data taken for a subset of the NV centres we study (data not shown).

Further information about the hyperfine interaction can be obtained by examining ESR spectra at the ESLAC (figure 1(a)). At a magnetic field near 510 G (oriented along the NV axis), hyperfine flip-flops and electronic spin polarization processes drive both \(^{14}\text{N} \) and \(^{13}\text{C} \) nuclear spins into the maximal spin projection along the excited state quantization axis \([12, 15, 17]\).
Because the $^{14}\text{N}$ hyperfine interaction is negative in the ground state [11], it polarizes into the highest frequency ESR line; the nearly full polarization of the $^{14}\text{N}$ indicates that its quantization axis is parallel to the NV axis in both the ground and excited states (as expected by symmetry).

Different $^{13}\text{C}$ lattice sites will show different (and generally anisotropic) interactions with the NV spin, leading to different $^{13}\text{C}$ polarization properties at the ESLAC. In figure 2(a), polarization into the lowest frequency line allows us to deduce that the hyperfine splitting for this $^{13}\text{C}$ lattice site must be positive, and a relatively high polarization suggests that the quantization axis for the $^{13}\text{C}$ is nearly commensurate with the NV axis in both the ground state and excited state $m_s = -1$ manifolds (as would be expected for e.g. a predominantly contact interaction). In figure 2(b), the opposite situation occurs: while nearly full polarization is observed, the sign is reversed, indicating that the lattice site for this $^{13}\text{C}$ nuclear spin likely coincides with a region of negative NV spin density [9]. While the hyperfine splittings observed at low and high fields mostly agree, some lattice sites (e.g. $\sim 4$ MHz) show a slightly different splitting at the ESLAC. This may arise from a finite angle between the NV axis and the nuclear spin quantization axis in the $m_s = -1$ electronic spin manifold. Polarization at the ESLAC for different $^{13}\text{C}$ hyperfine splittings is shown in figure 2(d).

The imprecision in ESR data—limited by electronic spin dephasing—makes it difficult to deduce the level of inhomogeneity among NV centres coupled to nominally the same $^{13}\text{C}$ lattice site. While ESEEM provides a more precise tool (limited by electronic spin $T_2$), direct nuclear magnetic resonance (NMR, limited by nuclear spin dephasing) is even less sensitive to environmental noise. Moreover, it provides an additional check that the splittings we observe do arise from $^{13}\text{C}$ interactions. To investigate the degree of homogeneity among hyperfine splittings, we perform NMR within the $m_s = -1$ manifold on $^{13}\text{C}$–NV pairs all with a nominal hyperfine splitting of 13.7 MHz. NMR measurements begin by polarizing the electronic and nuclear spins using optical excitation at the ESLAC; after driving NMR transitions within the $m_s = -1$ manifold, we map the nuclear spin state onto the electronic spin state with a
pulse, enabling optical detection of nuclear spin transitions \[12\]. The NMR frequency \( f_{\text{NMR}} \) is found by fitting to a square pulse profile; because it includes both the hyperfine and Zeeman terms in the nuclear spin Hamiltonian, \( f_{\text{NMR}} \) is \( \sim 500 \text{kHz} \) larger than \( A_{\text{hfs}} \) at the ESLAC (see figure 3(a)), consistent with the positive \( A_{zz} \) deduced from polarization data for the 13.7 MHz \( ^{13}\text{C} \) spins. Because \( f_{\text{NMR}} \) includes Zeeman terms, we constrain systematic error from drift in \( B_z \) by measuring the ESR frequency for a reference NV before and after each data set. The inhomogeneity observed in \( f_{\text{NMR}} \) is outside the statistical and systematic magnetic field drift error, indicating that local paramagnetic defects or other local effects may shift the nuclear spin levels for different NV centres.

The coherence properties of nominally identical NV–\( ^{13}\text{C} \) systems also show inhomogeneity. Focusing on the 13.7 MHz \( ^{13}\text{C} \) lattice sites, we study the \( ^{13}\text{C} \) nuclear spin dephasing times (Ramsey fringe decay) within the \( m_s = -1 \) manifold and compare them to the electronic spin dephasing times for the same NV centre (see figure 3(b)). Data taken for two other lattice sites are included, as noted in the legend, and all data are taken at the ESLAC. Magnetic field drift is an important factor in accurate coherence measurements, which can require days of averaging for a single data point. We monitor the ESR frequency at 15 min intervals during experiments and shift the ESR and/or NMR detuning to compensate for any observed drift in \( B_z \). Assuming slow magnetic field drift, the uncertainty in our ESR (NMR) resonant frequency is thus reduced to \( \sim 0.15 \text{MHz} \) (0.06 kHz), so the electronic and nuclear spin dephasing times we measure are primarily limited by intrinsic fluctuations. To further guard against systematic error, we take electronic and nuclear spin data for a given centre on different days. Overall, the trend in figure 3(b) indicates that the same inhomogeneities affect both the electronic and nuclear spin dephasing rates. The outlier in our data set may indicate that electronic and nuclear spins couple differently to the mesoscopic bath, but could also be accounted for by unmeasured rapid external magnetic field fluctuations. Quantitative examination of the degree to which electronic and nuclear spins couple to the same mesoscopic environment is an intriguing avenue for future research.

Beyond documenting the strength of hyperfine interactions between different \( ^{13}\text{C} \) lattice sites and individual NV centres, these measurements have implications for other areas of research in NV diamond. In particular, the observed discrete hyperfine splittings provide data against which calculations of the NV ground state spin density \[8, 9\] can be compared. Using a recent \textit{ab initio} model \[18\], we carried out all-electron plane wave supercell density functional calculations on a 512-atom defective supercell with PBE functional \[19\] to calculate the hyperfine tensors of the NV centre. Predicted and measured hyperfine splittings (and signs) are shown in table 1, along with the distance from the vacancy to the lattice site used to obtain the theoretical prediction. Close agreement allows identification of the lattice site associated with each \( ^{13}\text{C} \) impurity (see table 1, figure 4).

The agreement between theory and experiment motivates using the calculated electronic spin density to predict useful properties of \( ^{13}\text{C} \) nuclear spins. For example, none of the \( ^{13}\text{C} \) nuclear spins we observe sit on a lattice site along the NV axis. Such axial sites would share the symmetry of the NV defect, and yield hyperfine interactions that preserve the quantization axis of the nuclear spin (provided \( \mathbf{B} \parallel \hat{z} \)) regardless of the orbital or spin configuration of the NV defect. The symmetry of the nitrogen nuclear spin has already been exploited to enable single-shot spin readout at room temperature \[20\], and a second axial spin could expand this capability. \textit{Ab initio} calculations indicate that the most strongly coupled axial \( ^{13}\text{C} \) lattice site has a very small hyperfine splitting (\( \sim 0.15 \text{MHz} \)), weaker than nearly 200 lattice sites in the vicinity of
Table 1. Observed hyperfine splittings ($A_{\text{hfs}}$) at low magnetic field and 510 G, NMR resonance frequencies ($f_{\text{NMR}}$), and polarization ($P$), compared to results from \textit{ab initio} theory. All frequencies are given in MHz. Numbers in parentheses give error in the last digit: one standard deviation in the fit (single experimental data points), scatter (multiple data points), or maximal deviation among nominally identical $^{13}$C lattice sites (theory); numbers in square brackets indicate the number of NV centres for which experimental data were included. For $\sim$4 and $\sim$2 MHz data, two lattice sites are possible; calculated splittings for both are provided.

<table>
<thead>
<tr>
<th>Lattice site</th>
<th>Distance to site (Å)</th>
<th>$A_{\text{hfs}}$ theory</th>
<th>Sites</th>
<th>$A_{\text{hfs}}$ &lt; 50 G</th>
<th>$A_{\text{hfs}}$ ESLAC</th>
<th>Polarization (ESLAC)</th>
<th>$f_{\text{NMR}}$ (ESLAC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.52</td>
<td>$-7.5(1)$</td>
<td>3</td>
<td>$-8.92(3)$ [3]</td>
<td>$-8.6(3)$ [2]</td>
<td>$-0.7(2)$ [2]</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>2.50</td>
<td>$-5.7(2)$</td>
<td>6</td>
<td>$-6.52(4)$ [5]</td>
<td>$-6.46(3)$ [4]</td>
<td>$-0.80(7)$ [4]</td>
<td>5.997(2) [1]</td>
</tr>
<tr>
<td>E, F</td>
<td>2.93, 2.96</td>
<td>4.6(1), 4.67(4)</td>
<td>6, 3</td>
<td>4.2(1) [5]</td>
<td>4.15(3) [4]</td>
<td>0.2(2) [4]</td>
<td>4.719(2) [1]</td>
</tr>
<tr>
<td>G, H</td>
<td>5.05, 5.05</td>
<td>2.63(7), 2.27(4)</td>
<td>6, 3</td>
<td>2.4(3) [5]</td>
<td>2.60(4) [3]</td>
<td>0.29(6) [3]</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4. Two views of the geometry of the NV defect, with lattice sites for proximal $^{13}$C nuclear spins labelled as in table 1. The nitrogen is labelled ‘N’, whereas sites labelled ‘0’ are the nearest neighbours to the vacancy ($A_{\text{hfs}} = 130$ MHz).

the NV. Nevertheless, for natural isotopic abundance diamond, where a fraction $\epsilon = 0.011$ of lattice sites are occupied by $^{13}$C, roughly $\epsilon(1 - \epsilon)^{200}$ or 1 in $10^3$ NV centres would be most strongly coupled to an axial $^{13}$C; finding one may thus be possible with automated search routines.

In addition to verifying \textit{ab initio} spin density calculations, knowledge of the set of hyperfine splittings and polarization behaviours also provides critical information for interpreting ESR spectra for NV centres coupled to other systems. In particular, experiments examining NV interactions with other systems must be careful to distinguish the coupling of interest from
effects of $^{13}$C nuclei. For example, some of the data illustrated in figure 2 closely resemble observations interpreted as evidence of coupling between an NV and an electronic spin associated with a substitutional nitrogen impurity [2, 21]; $^{13}$C interactions may provide an alternative explanation. A lookup table of known $^{13}$C splittings and polarization behaviour thus provides an important check for discerning novel interactions.

Finally, we note that some of the methods we use may also prove applicable to other defect centres. Defects such as vacancy-related centres in silicon carbide (SiC) can show optically detected magnetic resonance (ODMR) and optical electronic spin polarization [22, 23] that should enable single-defect hyperfine measurements. Theoretical studies indicate (with partial support of photo-EPR studies) that the divacancy (two adjacent vacancies) in SiC is a very promising alternative for realizing solid state qubits [24]–[26]. For the Si-vacancy, it has already been demonstrated that polarization could be transferred to isotopic impurity nuclei by tuning to the appropriate magnetic field strength for the $S = 3/2$ electronic spin state [22, 23, 27].

In summary, we provide a systematic survey of NV hyperfine splittings associated with $^{13}$C isotopic impurity nuclear spins in diamond. Our results offer confirmation of ab initio theory for the ground state electronic spin density, and highlight inhomogeneities even between nominally identical configurations. Ultimately, greater understanding of NV–$^{13}$C interactions may have relevance for applications in quantum information technology [5] and inform our understanding of the mesoscopic spin-bath environment in diamond [28].

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