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<td>As Published</td>
<td><a href="http://dx.doi.org/10.1103/PhysRevA.94.021401">http://dx.doi.org/10.1103/PhysRevA.94.021401</a></td>
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<tr>
<td>Publisher</td>
<td>American Physical Society</td>
</tr>
<tr>
<td>Version</td>
<td>Final published version</td>
</tr>
<tr>
<td>Accessed</td>
<td>Fri Dec 28 07:43:28 EST 2018</td>
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<tr>
<td>Citable Link</td>
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Diamond-nitrogen-vacancy electronic and nuclear spin-state anticrossings under weak transverse magnetic fields

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(Received 22 February 2016; published 2 August 2016)

We report on detailed studies of electronic and nuclear spin states in the diamond-nitrogen-vacancy (NV) center under weak transverse magnetic fields. We numerically predict and experimentally verify a previously unobserved NV hyperfine level anticrossing (LAC) occurring at bias fields of tens of gauss—two orders of magnitude lower than previously reported LACs at ~500 and ~1000 G axial magnetic fields. We then discuss how the NV ground-state Hamiltonian can be manipulated in this regime to tailor the NV’s sensitivity to environmental factors and to map into the nuclear spin state.

DOI: 10.1103/PhysRevA.94.021401

Nitrogen-vacancy (NV) defect centers in diamond are optically polarizable quantum systems with spin-dependent fluorescence. Using electron spin resonance (ESR) under ambient conditions, sensitivity to electric fields [1–4], transverse and axial magnetic fields [5–10], temperature [11–14], strain [15], and pressure [16] have been observed via resonance frequency shifts of the NV ground-state manifold. Nonseparable sensitivity to multiple environmental factors is problematic when it comes to using the NV as a sensor. However, the Hamiltonian governing the measurable frequency shifts can be tailored to enhance (or to suppress) sensitivity to different physical phenomena. A magnetic bias field applied parallel or perpendicular [B∥ or B⊥ as shown in Fig. 1(a)] to the NV’s axis in the diamond crystal lattice energetically separates the spin states and increases sensitivity to magnetic or electric fields, respectively.

In this Rapid Communication, we investigate an unexplored weak-field regime in which electronic spin ground-state energy level splittings are on par with the Zeeman shift induced by an applied magnetic field. Here we account for both the electron and the nuclear spin of the NV, which reveals complex dynamics of nuclear spin state degeneracy and previously unobserved hyperfine level anticrossings. These features occur at a low magnetic field (B⊥ ≤ 40 G) as compared to the B∥ ~ 500 and B∥ ~ 1000 G excited- and ground-state crossings [17–20], which have been used for nuclear spin polarization, providing increased sensitivity to resonance shifts through narrow effective linewidth and increased contrast [21–24]. We find excellent agreement between experiment and theory and discuss the utility of the nuclear spin degeneracy regime toward NV sensing applications and solid-state atomic memories based on nuclear spin polarization. While the results described here are specific to the NV, similar anticrossings are expected in any spin-1 (or higher) defect center that shows hyperfine level splitting on the same order of magnitude as double-electron spin flip anticrossings.

The NV is a two-site defect with a spin-1 electronic ground state, which is magnetically coupled to nearby nuclear spins. For a single NV orientation, energy level shifts are described by the following spin Hamiltonian of the ground triplet state in the presence of magnetic, electric, and strain fields [25], taking into account the zero-field splitting, nuclear and electronic Zeeman shifts, Stark shifts, hyperfine splitting, and nuclear quadrupole fields:

\[
\mathcal{H}_{gs} = (h D_{gs} + d_0 \Pi_z) \left[ S_z^2 - \frac{1}{3} S(S+1) \right] - d_\perp \left[ \Pi_x (S_x^2 - S_y^2) + \Pi_y (S_x S_y + S_y S_z) \right] + \mu_B g_e (\vec{S} \cdot \vec{B}) - \mu_n g_n (\vec{B} \cdot \vec{l}) + A_\perp S_z I_z + A_\perp (S_x I_x + S_y I_y) + P_{gs} \left( I_z^2 - I_x^2 - I_y^2 \right),
\]

(1)

where \( h D_{gs} \) is the NV ground-state crystal field splitting energy (which is temperature-dependent [14]), \( d_0 \) and \( d_\perp \) are the components of the ground-state electronic dipole moment, the total effective electric field \( \vec{E} = \vec{E} + \vec{\sigma} \) encompasses both static electric fields \( \vec{E} \) and strain \( \vec{\sigma} \), \( g_e \) and \( g_n \) are the electric and nuclear Landé \( g \) factors, \( \mu_B \) and \( \mu_n \) are the Bohr and nuclear magneton constants, \( \vec{B} \) is the applied magnetic field, \( A_\perp \) and \( A_\parallel \) describe the axial and transverse magnetic hyperfine interactions with the \(^{14}\text{N}\) nucleus, \( P_{gs} \) is the nuclear electric quadrupole parameter, \( \vec{S} \) is the electron spin operator, and \( \vec{l} \) is the spin operator of the \(^{14}\text{N}\) nucleus.

Figure 1 shows the numerically calculated electronic ground-state triplet and \(^{14}\text{N}\) hyperfine energy levels \( |m_x,m_I| \), where \( m_x \) is the electronic spin state and \( m_I \) is the nuclear spin state, as a function of the axial magnetic field for a fixed transverse magnetic field. State-mixing-induced anticrossings are seen when the dressed states (black lines) do not follow high-axial field eigenstates (solid and dashed colored lines). With the addition of a weak (<3 G) axial magnetic field, we see mixing and crossing of the energy levels, resulting from off-diagonal terms in \( \mathcal{H}_{gs} \) in the \( |m_x,m_I| \) basis. The double-electron spin flip anticrossings occur as the nondressed \( m_x = 1 \) states cross \( m_x = -1 \) states with identical nuclear spin, for example, as \( |1,0| \) crosses \( |-1,0| \). The transverse magnetic field leads to second-order mixing of the \( m_x = \pm 1 \) states; therefore the coupling strength \( E_g \) of these electronic Zeeman

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interaction driven level anticrossings scales quadratically with respect to the applied transverse magnetic field as described in [25].

For transverse magnetic fields under \( \sim 40 \) G, as shown in Fig. 1(b), an additional level anticrossing arises. As this phenomena has not been previously described, to our knowledge, we investigate it here in greater detail. The dressed states are indicated with colored lines and dressed states are indicated with black lines.

\[
\begin{align*}
|m_s, m_I\rangle & \\
|+1, 0\rangle & \\
|+1, -1\rangle & \\
|+1, +1\rangle & \\
|-1, 0\rangle & \\
|-1, -1\rangle & \\
|-1, +1\rangle & \\
|0, 0\rangle & \\
|0, -1\rangle & \\
|0, +1\rangle & \\
\end{align*}
\]

FIG. 1. (a) Axial and transverse magnetic field directions with respect to the NV axis. As \( B_\perp \) is increased from (b) 35 to (c) 45 G, the \( m_I = 0 \) energy levels are separated from the \( m_I = \pm 1 \) energy levels, removing the degeneracy which results in an electron-nuclear spin flip anticrossing, which is detailed in the inset of (b). Nondressed states are indicated with colored lines and dressed states are indicated with black lines.

as the coupling strength of the double-electron spin flip anticrossing is proportional to the applied transverse magnetic field squared.

\[
\begin{align*}
E_{\perp} & \propto B_\perp^2
\end{align*}
\]

\[
\begin{align*}
E_{\perp} & \propto (\mu_B g_s B_\perp)^2 / (D_{gs} + d_{1s} \Pi_1) \quad \text{in the weak electric field, weak axial magnetic field regime.}
\end{align*}
\]

We experimentally validate this anticrossing by performing ESR measurements on an NV ensemble. The epitaxially grown diamond is polished to trap the green pump light and guide the red spin-dependent fluorescence to a photodetector in a light-trapping diamond waveguide geometry [26]. We estimate the intrinsic strain in this sample to be \( \sim 3 \times 10^{-5} \) from the ~600 kHz strain splitting of the central hyperfine resonance at zero applied field, given values of \( d_{1s} \) from the literature [27]. We expect this to be the average strain experienced across the sample. The NV has four orientations in the diamond lattice, labeled as \( k = 1, 2, 3, 4 \) as seen in Fig. 3(b). We lift the \( m_s = \pm 1 \) degeneracy and the orientation degeneracy by applying a static magnetic field at an angle resulting in nonequivalent
projections onto each orientation. A 60 G Halbach array (magnitude uniformity > 99% over a 2 cm³ volume at the center) is positioned around the sample [Fig. 3(a)] to provide this static magnetic field. In addition, up to ±30 G can be applied in $\hat{X}$, $\hat{Y}$, or $\hat{Z}$ (lab frame) using Helmholtz coils. The total magnetic field is aligned to be perpendicular to the $k = 1$ orientation. A weak axial magnetic field sweep ($B_{1,||}$) in addition to this transverse field confirms the anticrossings in the ESR spectra [Fig. 3(c)]. Each NV orientation produces two Zeeman-split triplets, corresponding to the hyperfine coupling of the $^{14}$N nuclear spins. These pairs are located symmetrically around $\omega_c = D_p + \frac{3\mu_B^2}{2m_e\beta_0^2}B_{1,\perp}^2$. In levels 1 and 1′, for which the magnetic field is perpendicular, we observe both predicted anticrossings around $B_{1,||} = N_p$. This is highlighted in the inset to Fig. 3(c).

While Fig. 1 gives insight into the origin of the level anticrossings in the energy level diagram, Fig. 4 shows the corresponding energy level transitions at $B_{1,\perp} = 35$ and 45 G. Numerical solutions to $\mathcal{H}_{13}$ accounting for $S_1$ and $S_3$ operators in the selection rules are plotted in conjunction with the experimental data. For both values of the transverse field, we clearly see double-electron spin flip anticrossings centered at $B_{1,||} = 0, \pm A_1\hbar/g_e\mu_B$ [Fig. 2(b)] with anticrossing coupling strengths corresponding to those expected from Fig. 2(a). As expected, we also see the center frequency between the split resonances increase with increased applied transverse magnetic field.

Figure 5 concentrates on the region of interest at $B_{1,\perp} = 30$ G around which the electron-nuclear spin flip anticrossings is maximized. We observe the electron-nuclear spin flip anticrossings at $\sim \pm 0.35$ G applied axial magnetic field as predicted by analytically solving $\mathcal{H}_{13}$ (see Appendix A). Double-electron spin flip anticrossings are centered at $E_p = 0, \pm A_1\hbar/g_e\mu_B$ [Fig. 2(b)] with anticrossing coupling strengths corresponding to those predicted by simulation and plotted.
Next, we propose a transverse magnetic field regime method to remove temperature sensitivity from diamond-based magnetometry measurements. Taking the derivative of $\alpha_{G}$ with respect to temperature ($T$), the temperature-dependent $D_{G}$ term in the denominator of the second order term leads to a decrease in $d\omega_{c}/dT$ with increased transverse magnetic field [14]. We expect a 1% decrease in $d\omega_{c}/dT$ with an 80 G applied transverse magnetic field. Combining this advantage with the aforementioned increase in contrast and insensitivity to changes in $B_{z}$ in a high signal-to-noise ratio light-trapping diamond waveguide results in a regime that is well suited for temperature-stabilized measurements, relying on the ability to probe multiple subensembles with different crystallographic projections of the applied transverse magnetic field. Synchronizing the ratio of the resonance frequencies of subensembles with known, varying dependences on temperature allows the temperature dependence to be stabilized, similar to the method proposed by Hodges et al. using strain engineering [28]. This method further decouples the diamond from its thermal environment, addressing an ongoing challenge in diamond-based electric and magnetic field sensing.

Finally, using these low-transverse-field anticrossings, we introduce an alternate route to polarize the nuclear spin host of the nitrogen-vacancy center [21,29–32]. This method articulates successive shifting of the magnetic field and radiofrequency pulses iteratively to transfer the spin polarization into a single nuclear state, similar to methods explored for optical quantum dots [33–35]. Unlike existing schemes at $\sim$500 and $\sim$1000 G axial magnetic fields for the excited state and ground-state level anticrossings (LACs), this approach relies on the control of weak magnetic fields and state-selective rf pulses. It requires fewer pulses and a smaller range of rf excitation than other low-magnetic field recursively repeated protocols [36]. The heart of the scheme relies on adiabatic passage, which results in a change in the nuclear spin state. Following Landau-Zener-Stueckelberg theory [37–39], the probability $P$ of adiabatic passage through an anticrossing with coupling strength $\Delta$ is $P = 1 - e^{-\pi \Delta^2/(4 \Delta^2)}$ where $\Delta^2$ is the rate of change of the energy difference as the gap is approached. Under these conditions, sweeping a bias field through the $\pm B_\parallel = N_\ell$ electron-nuclear spin flip anticrossing results in spin exchange from $|m_z = \mp 1, m_I = \pm 1\rangle$ to $|m_z = \pm 1, m_I = 0\rangle$. For a 99.99% probability of adiabatic passage, a rate of magnetic field change of 1 G/225 $\mu$s is required.

While many nuclear spin exchange sequences are possible, here we note a two-step example to polarize into $|m_I = 0\rangle$. Assuming an initial ensemble of NVs in a mixture of eigenstates $|0, -1\rangle$, $|1, 1\rangle$, and $|1, 0\rangle$, which can be prepared through state-selective excitations, a single application of the protocol results in a mixture of eigenstates $|0, -1\rangle$, $|1, 0\rangle$, and $|1, 0\rangle$. The population transferred through the electron-nuclear spin flip anticrossing is then shelved in $m_z = 0$ and the remaining population in $|0, -1\rangle$ is transferred to $|1, -1\rangle$ with a resonant rf pulse. The second application of the protocol then results in eigenstates $|1, 0\rangle$, $|0, 0\rangle$, and $|1, 0\rangle$. Exploiting the robustness of the nuclear spin state against the optical excitation of the NV, all $m_z$ levels can be pumped into the $m_\ell = 0$ with green laser excitation [40]. This type of protocol would be useful both for sensing applications, due to the increased contrast, but also for applications like diamond-based...
gyroscopes \cite{41,42} and atomic memories \cite{32,43,44}, which utilize the longer-lived nuclear spin state.

Additionally, the transverse magnetic fields may help overcome the influence of inhomogeneous strain present from diamond growth processes, a challenge in working with very large ensembles of NV centers. Combining this with insensitivity to small axial magnetic fields and potential insensitivity to temperature, the resultant system also presents itself as a strong candidate for a quantum memory. Transverse and axial magnetic fields could be used to read and write to the system, which is otherwise isolated from its environment.

In conclusion, in this Rapid Communication we present a careful study of the effect of weak transverse magnetic fields on the NV system. We predict and experimentally verify an electron-nuclear spin anticrossing, with close agreement between theory and experiment. We also experimentally measure the predicted double-electron spin anticrossing under transverse magnetic fields. These anticrossings show potential for a variety of sensing applications because of (i) increased signal contrast, (ii) axial magnetic fields near the anticrossing points, (iii) potential for nuclear spin polarization schemes, and (iv) selective decoupling of the NV from its environment through the synchronization of different orientations with varying transverse fields. With applied transverse magnetic fields on the order of tens of gauss, we can achieve increases in contrast on the order of those seen previously only at the much higher, axially applied ~500 and ~1000 G LACs.

The authors would like to thank L. Pham, M. E. Trusheim, C. McNally, and T. Schröder for helpful discussions. The Lincoln Laboratory portion of this work is sponsored by the Assistant Secretary of Defense for Research & Engineering under Air Force Contract No. FA8721-05-C-0002. Opinions, interpretations, conclusions, and recommendations are those of the authors and are not necessarily endorsed by the United States Government. D.E. acknowledges support from ONR (N00014-13-1-0316). H.C. and E.H.C. are supported by the NASA Office of the Chief Technologist’s Space Technology Research Fellowship.

APPENDIX A: ANALYTICAL EXPRESSION FOR THE LOCATION OF AN ELECTRON-NUCLEAR SPIN FLIP ANTICROSSING

Using second order degenerate perturbation theory, we calculate the change in energy as a function of applied magnetic and electric and/or strain fields. By solving for the axial magnetic field \( B_1 \) at which the intersection of the \( |m_I = 0 \rangle \) and the \( |m_I = 1 \rangle \) energy levels occurs, we show a closed-form solution for the location of the electron-nuclear spin flip level anticrossing. This is in good agreement with our numerical and experimental observations as seen in Fig. 2.

\[
N_p = \frac{-A_I D_{gs} \xi + |P_{gs}| \sqrt{\xi (D_{gs}^2 \xi + B_1^2)}}{2D_{gs} \xi} \tag{A1}
\]

where \( \xi = A_1^2 - P_{gs}^2 \), \( A_1 \) is the axial hyperfine interaction, \( D_{gs} \) the crystal field splitting, \( P_{gs} \) the quadrupole energy, and \( B_1 \) the transverse component of the magnetic field in the NV frame of reference. Figure 5 depicts this transverse field regime. Numerical solutions to \( H_{\text{ESR}} \), accounting for selection rules are shown in conjunction with experimental data. For questions or comments on this calculation and the numerical simulations, please contact E.H.C. at echen@alum.mit.edu.

APPENDIX B: IMPLEMENTATION WITH \( ^{15}N \)

Unlike \( ^{14}N \), which is a spin-1 system, \( ^{15}N \) is a spin-1/2 system. The hyperfine splitting of the NV center would therefore result in two resonances (±1/2) instead of three (0, ±1). This gives a 50% increase in contrast, which is linearly proportional to sensor sensitivity. Furthermore, at zero applied axial magnetic field \( (B_1 = 0) \) full contrast is achieved, even at low applied transverse magnetic fields. The electron-nuclear spin anticrossing is not present in the \( ^{15}N \) case. Under a transverse magnetic field, the two nuclear spin states become mixed. Therefore the application of a linearly polarized microwave field induces transitions between all \((2 \times 2)\) possible mixed states, giving rise to the doublet of the ESR spectrum in Fig. 6(a).

\[\text{FIG. 6. Comparison of (a) } ^{15}\text{N and (b) } ^{14}\text{N samples at } B_1 = 30 \text{ G.}\]