Hyperfine tensors of nitrogen-vacancy center in diamond from \textit{ab initio} calculations

Adam Gali$^{1,2}$

\textit{1Department of Atomic Physics, Budapest University of Technology and Economics, Budafoki út 8., H-1111, Budapest, Hungary}
\textit{2Department of Physics and School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA}

We determine and analyze the charge and spin density distributions of nitrogen-vacancy (N-V) center in diamond for both the ground and excited states by \textit{ab initio} supercell calculations. We show that the hyperfine tensor of $^{15}\text{N}$ nuclear spin is negative and strongly anisotropic in the excited state, in contrast to previous models used extensively to explain electron spin resonance measurements. In addition, we detect a significant redistribution of the spin density due to excitation that has serious implications for the quantum register applications of N-V center.

Nitrogen-vacancy (N-V) centers in diamond have numerous peculiar properties that make them a very attractive solid state system for fundamental investigations of spin based phenomena. Recently, this defect has been proposed for several applications, like quantum information processing [1-4], ultrasensitive magnetometer [5, 6], and measurement of zero-point fluctuations or preparing quantum-correlated spin-states [7] over macroscopic distance [8]. In these measurements, a room temperature read-out of single nuclear spins in diamond has been achieved by coherently mapping nuclear spin states onto the electron spin of a single N-V center [3, 8] which can be optically polarized and read out with long coherence time [3, 10]. Particularly, this has been the basis in realization of a nuclear-spin-based quantum register [11] and multipartite entanglement among single spins at room temperature [12]. The polarization of a single nuclear spin has been achieved by using either a combination of selective microwave excitation and controlled Larmor precession of the nuclear-spin state [11] or a level anticrossing in the excited state [13]. Understanding the spin states and levels is of critical importance for optical control of N-V centers in both the ground and excited states. Especially, the hyperfine interaction couples the electron spin and nuclear spin, thus determination of hyperfine tensors of the nuclei with non-zero nuclear spin plays a key role both in creation of entanglement states and in the decoherence process [3, 14].

Recently, the hyperfine signals in the ground [13, 15] and excited [16] states have been detected in N-V centers but with contradicting interpretations. In a conventional electron paramagnetic resonance (EPR) spectrum on the ensemble of N-V centers, the $^{15}\text{N}$ signal was assumed to be positive with slight anisotropy in the ground state while Fuchs et al. and Jacques et al. assumed an isotropic negative hyperfine constant for $^{15}\text{N}$ in the ground state [13, 16] based on previous EPR and optically detected magnetic resonance (ODMR) measurements [17, 18]. Recently, Fuchs et al. have reported that the hyperfine splitting of $^{15}\text{N}$ should be $\sim 20 \times$ larger in the excited state than in the ground state [16]. The excited-state $^{15}\text{N}$ hyperfine signal was assumed to be isotropic in their model [16]. While we already addressed the hyperfine tensor of $^{14}\text{N}$ in the ground state [19], the lack of the detailed study on $^{15}\text{N}$ hyperfine signal and the proximate $^{13}\text{C}$ isotopes both in the ground and excited states prohibits the understanding of the intriguing physical properties of this defect. In this Letter, we thoroughly investigate the hyperfine tensors of proximate $^{15}\text{N}$ and $^{13}\text{C}$ isotopes of the N-V center both in the ground and excited states by means of high level \textit{ab initio} supercell all-electron plane wave calculations. In addition, we analyse the overall charge and spin density distributions before and after the optical excitation. We show that the hyperfine constants of $^{15}\text{N}$ is positive and possibly slightly anisotropic in the ground state while negative and strongly anisotropic in the excited state. In addition, the hyperfine splittings of the proximate $^{13}\text{C}$ isotopes change also significantly that has serious implications both in the interpretation of the excited-state spectroscopy signals and in the quantum-information applications.

The negatively charged NV-center in diamond [20] consists of a substitutional nitrogen atom associated with a vacancy at an adjacent lattice site (Fig. 1a). The ground state has $^3A_2$ symmetry where one $a_1$ defect level in the gap is fully occupied by electrons while the double degenerate $e$-level above that is occupied by only two electrons with parallel alignment of spins (Fig. 1b). Thus, this defect has $S=1$ high spin ground state [21]. By promotion one electron from the $a_1$-level to the $e$-level will result in the excited $^3E$ state. Both states can be described by conventional density functional methods. The ground state can be readily described by spin density functional theory while the excited state can be obtained by constrained occupation of states [19]. We optimized the geometry for both the ground and excited states, and calculated the charge and spin densities at the optimized geometries.

We applied the PBE functional [24] to calculate the spin density of the defect. First, the diamond primitive lattice was optimized, then a simple cubic 512-atom supercell was constructed from that. Finally, we placed the negatively charged NV-defect into the supercell, and optimized under the given electronic configuration. We utilized the VASP code for geometry optimization [25]. We applied plane wave basis set (cut-off: 420 eV) with PAW-method [26]. During the optimization of the lattice constant we applied twice as high plane wave cut-off and $12^3$ Monkhorst–Pack K-point set [27]. For the 512-atom supercell we used the $\Gamma$-point that provided convergent charge density. We plugged the optimized geometry into the CPPAW supercell plane wave code with PAW-method that provides the hyperfine tensors [28]. We applied...
FIG. 1: (Color online) a) The structure of nitrogen-vacancy (N-V) defect in our particular working frame. The place of vacancy is denoted by an empty circle. b) The schematic single particle picture of the $m_s = 1$ high spin states in ground state ($^2A_2,gs$) and excited state ($^3E,es$). c) The fine structure of the $^3A_2$ and $^3E$ states at room temperature due to spin-spin interaction. Zero-field splittings are $D_{gs}=2.88$ GHz [22], $D_{es}=1.42$ GHz [23]. During optical excitations the fluorescence is predominantly active for the cited state ($\mid 1 \rangle$) due to a non-radiative intersystem crossing of the $\mid \pm 1 \rangle$ es states with the many-body singlet states (not shown here). d) Splittings of the es substates in the presence of the magnetic field (B). LAC is expected between $\mid 0 \rangle$ and $\mid 1 \rangle$ states. e) Simplified energy-level diagram with including the hyperfine structure associated with $^{15}$N nuclear spin states $\mid 1 \rangle$ and $\mid 0 \rangle$ in the case of LAC regime of the applied B-field. At LAC, precession frequency $\Omega$ between excited-state sublevels $\mid 0 \rangle \mid 1 \rangle$ can lead to nuclear-spin flip, which can be transferred to the ground state through nonradiative intersystem crossing (curved arrow).

the same basis set and projectors in both codes yielding virtually equivalent spin density of the defects. Other technical details are given in Ref. [19]. The charge density distribution was analyzed by the Bader-method [29]. We briefly mention here that we provide the principal values of the hyperfine structure associated with $^{14}$N nuclear spin states $\mid 1 \rangle$ and $\mid 0 \rangle$ in the case of LAC regime of the applied B-field. At LAC, precession frequency $\Omega$ between excited-state sublevels $\mid 0 \rangle \mid 1 \rangle$ can lead to nuclear-spin flip, which can be transferred to the ground state through nonradiative intersystem crossing (curved arrow).

In the excited state we found a significant re-arrangement of atoms compared to the ground state. The $C_a$ atoms now farther from the vacant site (1.70 Å) than the N-atom (1.63 Å) in contrast to the case of the ground state. The N-atom attracts less electrons from its neighbor C-atoms: the Bader-charge of C$_a$ atoms increases by 0.03 e. Thus, the excitation induces a change in the dipole moment of the defect. Next, we discuss the change in the spin density distribution upon excitation. Fig. 2 shows...
The calculated spin density difference between the excited $^3E$ and the ground $^3A_2$ states of the NV center. We chose two representative isosurface values indicated in the colored rectangles. The blue(cyan) ball(s) represent the nitrogen(carbon) atoms. The vacant site is below the nitrogen atom.

Consequently, the spin polarization of the C $\alpha_a$-atoms will be enhanced a lot around N-atom (indicating with red lobes). Indeed, it has been very recently found by using excited state spectroscopy in $^{15}$N enriched diamond samples that the $^{15}$N hyperfine signal is $\approx20$ times larger ($\approx60$ MHz) in the excited state than in the ground state [16]. Our calculations can explain this feature. However, the applied model Hamiltonian for describing the EPR of $^{15}$N hyperfine signal ($A^{(N)}$) was incomplete in Refs. [13] [16]. Fuchs et al. and Jacques et al. studied individual NV centers by confocal photoluminescence microscopy where the actual defect was aligned to the [111] axis and the applied magnetic field was parallel to this axis, thus the angular dependence of $A^{(N)}$ was not measured. They assumed isotropic $A^{(N)}$ for the excited state while our study shows that it is strongly anisotropic. Fuchs et al. also noticed that $A^{(N)}$ should have the opposite sign in the ground and excited states [16]. Our study shows that $A^{(N)}$ is positive(negative) in the ground(excited) states in contrast to the previous assumptions [13] [16].

Now, we discuss the consequence of our findings in the light of recent experiments on the dynamic polarization of single nuclear spins of the NV center [13] [16]. It has been demonstrated that the effective nuclear-spin temperature corresponds to a $\mu$K in this process [13] decoupled from the ambient temperature that can be the basic physical process in the measurement of zero-point fluctuations [7]. In these measurements the de-polarization of the nuclear spins of $^{15}$N [13] [16] and $^{13}$C, 13 have been demonstrated. This has been achieved by the level anticrossing (LAC) of the electron spin $m_s$ sublevels in the excited state. The LAC effect may appear if the $m_s$ sublevels cross at a given external magnetic field (see Fig. 1c,d). We show a refined and corrected model of Ref. [13] accounted for LAC. We study the de-polarization of $^{15}$N isotope but it can be generalized for the $^{13}$C isotopes straightforwardly. The Hamiltonian of the system (with neglecting the nuclear-Zeeman splitting) can be written as [13],

$$H = D_{es}\hat{S}_z^2 + g_e\mu_B B\hat{S}_z + A_{es}\hat{S}\hat{L},$$

(1)

where $\hat{S}$ and $\hat{L}$ are the electron and nuclear-spin operators, $D_{es}$ the excited-state zero-field splitting, $g_e$ the electron $g$ factor, $\mu_B$ the Bohr-magneton, and $A_{es}$ the excited hyperfine coupling. We assume positive $B$-field. Because $A_{es}$ is anisotropic, the $A_{es}\hat{S}\hat{L}$ term can be written with the $a_{es}$ and $b_{es}$ hyperfine splittings and the spin-shift operators as,

$$\frac{\hat{S}_z \hat{L}_z + \hat{S}_- \hat{L}_-}{2} = (a_{es} - b_{es}) + \frac{\hat{S}_z \hat{L}_z}{2}(a_{es} + 2b_{es})$$

(2)

The hyperfine field of $^{15}$N is parallel to the symmetry axis, and $(a_{es} - b_{es})= A_1 \approx -39$ MHz while $(a_{es} + 2b_{es})= A_1 \approx 58$ MHz.

According to a recent study [23] $D_{es} = +1.42$ GHz ($m_s = 0$ sublevel is below $m_s = \pm1$ sublevels), so we can restrict our study to the excited state $m_s = 0$ and $m_s = -1$ sublevels (see Fig. 1b). In the basis $|\downarrow\downarrow\rangle; |\downarrow\uparrow\rangle; |\uparrow\downarrow\rangle; |\uparrow\uparrow\rangle$ and by choosing the origin of energy level at level $|\downarrow\rangle$, the Hamiltonian described by Eqs. [12] can be written as

$$H = \begin{pmatrix}
\xi_1^\downarrow - c & 0 & 0 & 0 \\
0 & \xi_1^\uparrow - c & d & 0 \\
0 & d & 0 & 0 \\
0 & 0 & 0 & -d \end{pmatrix} \frac{\xi_1^\downarrow}{2} = D_{es} \pm \frac{A_1}{2},$$

$$c = g_e\mu_B B, \quad d = A_1 / \sqrt{2}.$$ 

The eigenstates of this Hamiltonian are $|0, \uparrow\rangle$, $|\downarrow, \downarrow\rangle$, $|\downarrow, \uparrow\rangle = \alpha |0, \downarrow\rangle + |0, \uparrow\rangle$ and $|\downarrow, \downarrow\rangle = \beta |0, \downarrow\rangle - |0, \uparrow\rangle$. By following the arguments in Ref. [13] the transition from the ground state $|0, \downarrow\rangle$ to the excited state remains nuclear spin conserving, whereas the transition from $|0, \uparrow\rangle$ results in $(\alpha |\downarrow\rangle + \beta |\uparrow\rangle)$ in the excited state (see Fig. 1b). This superposition state then starts to precess between the appropriate states at frequency $\Omega = 1/(2\hbar) \times [(\xi_1^\downarrow - c)^2 + 4d^2]^{1/2}$.
where $h$ is Planck’s constant. The precession frequency depends on $B$ via electron Zeeman-effect ($c$ in our notation) that is minimal at LAC resonance, and will be equal to $|d|/h = |A_{\perp}|/\sqrt{2}h$. Jacques et al. assumed isotropic hyperfine splitting for $^{15}$N, therefore, they applied $\approx$60 MHz in this formula [13]. Our analysis shows that rather the $|A_{\perp}| \approx 39$ MHz should be substituted here. Nevertheless, this precession frequency is still at the same order of magnitude as the excited state decay rate, 12 ns [16]. Thus, the spin-flip process is very efficient between $|0, \downarrow\rangle$ and $|−1, \uparrow\rangle$ states, and we can explain the depolarization of $^{15}$N found in the experiments [10, 13, 16]. It has been found that the probability of the depolarization effect significantly depends on the misalignment of the magnetic field from the symmetry axis [13]. This may be partially explained by the anisotropy of the $^{15}$N hyperfine splitting beside the mixing of the spin states.

We found other intriguing properties of the spin density in the excited state. As apparent in Fig. 2 the spin density and the corresponding hyperfine tensors change considerably also for the proximate $^{13}$C isotopes. We show the hyperfine tensors only for the most significant change, for C$_a$ atoms in Table I. Beside that new $^{13}$C isotope becomes active above N-atom that has negligible spin density in the ground state. In addition, the spin density of the sets of 6(3) C-atoms at $R=3.9$ Å decreases/increases due to excitation where $R$ is the distance from the vacant site. According to our previous study [19], one of these $^{13}$C isotopes was manipulated in the qubit and quantum register applications [3, 11]. Our study shows that during the optical set and read-out processes the spin-density of the addressed proximate $^{13}$C isotopes changes indicating an effective oscillating magnetic field with the inverse lifetime of the excited state. This may also influence the decoherence of the entangled electron-nuclear spin state that has not yet been considered [14].

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[1] A. Gruber et al., Science 276, 2012 (1997).