PHYSICAL REVIEW B **80**, 241204(R) (2009)

Identification of individual ^{13}C isotopes of nitrogen-vacancy center in diamond by combining the polarization studies of nuclear spins and first-principles calculations

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(Received 29 October 2009; published 29 December 2009)

We determine the charge- and spin-density distributions of nitrogen-vacancy center in diamond for both the ground and excited states by *ab initio* supercell calculations yielding very good agreement with the experiment. We correctly determine the polarization of ^{15}N nuclear spin in the level anticrossing (LAC) mechanism. We show that LAC together with the accurate *ab initio* data can be used to identify the individual ^{13}C nuclei around the defect that can also reveal the dominant component of the precession vector responsible for the decoherence of the addressed nuclear-spin qubit.

DOI: 10.1103/PhysRevB.80.241204 PACS number(s): 71.55.Cn, 42.50.Ex, 42.50.Md, 61.72.Bb

Nitrogen-vacancy (NV) 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 over macroscopic distance.[7] In these measurements, a room-temperature readout of *single nuclear spins* in diamond has been achieved by coherently mapping nuclear-spin states onto the electron spin of a single NV center[3,8] which can be *optically* polarized and read out with long coherence time.[9,10] 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 (LAC) *in the excited state*.[13] Understanding the spin states and levels is of critical importance for optical control of NV 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 nonzero nuclear spin plays a key role both in creation of entanglement states and in the decoherence process.[3,14,15] While we already addressed the hyperfine tensor of ^{14}N and ^{13}C isotopes in the ground state,[16] the lack of the detailed study on ^{15}N hyperfine signal and the proximate ^{13}C isotopes *in the excited state* prohibits the understanding of the intriguing physical properties of this defect. Particularly, the sign of the ^{15}N hyperfine constant[17–20] is controversially used to model the LAC effect.

In this Rapid Communication, we thoroughly investigate the hyperfine tensors of ^{15}N and proximate ^{13}C isotopes of the NV center *both* in the ground and excited states by means of high level *ab initio* supercell all-electron plane-wave calculations. Based on the accurate first-principles results we can correctly determine the polarization of ^{15}N nucleus spin. We show that LAC may polarize the spins of the ^{13}C isotopes together with N nucleus but the probability of polarization depends on the change of the hyperfine tensor due to optical excitation. We show that the combination of *ab initio* data and LAC can identify individual ^{13}C nuclei. We particularly show that stochastic phase accumulation is responsible for the decoherence of 14 MHz ^{13}C nuclei that has been applied as quantum logic recently.[21]

The negatively charged NV center in diamond[22] consists of a substitutional nitrogen atom associated with a vacancy at an adjacent lattice site [Fig. 1(a)]. 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. 1(b)]. Thus, this defect has $S=1$ high spin ground state.[23] By promotion one electron from the a_1 level to the e level will result in the excited ^3E state. 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[26] to calculate the spin density of the defect. We utilized the VASP code for geometry optimization.[27] We applied plane-wave basis set (cutoff: 420 eV) with projector augmented wave (PAW) method.[28] We used a 512-atom supercell with Γ-point to model the defect that provided convergent spin density. We plugged the optimized geometry into the CPPAW supercell plane-wave code with PAW method that provides the hyperfine tensors.[29] We applied the same basis set and projectors in both codes yielding virtually equivalent spin density of the defects. Other technical details are given in Ref. 16. The charge-density distribution was analyzed by the Bader method.[30] We briefly mention here that we provide the principal values of the hyperfine tensors, called, A_{11}, A_{22}, and A_{33} that can be found by diagonalization of the hyperfine tensors. If the hyperfine field has C_{3v} symmetry then $A_{11}=A_{22}=A_\perp$ and $A_{33}=A_\parallel$. θ and ϕ azimuth and polar angles give the orientation of the A_{33} component as defined in Ref. 17. The Fermi-contact term (a) is defined as $a=(A_\parallel+2A_\perp)/3$ while the dipole-dipole term (b) as $b=(A_\parallel-A_\perp)/3$. The hyperfine field is isotropic when $b=0$; i.e., $A_\perp=A_\parallel$.

In the nitrogen-vacancy defect there are three carbon atoms (C_a) and one nitrogen atom (N) closest to the vacant site each possessing a dangling bond [Fig. 1(a)]. We found by DFT-PBE calculations that N atom is closer(farther) to the

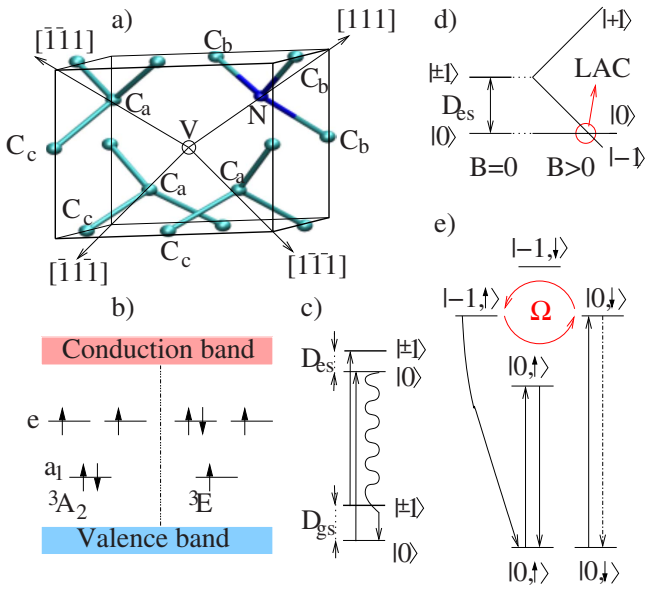

FIG. 1. (Color online) (a) The structure of NV defect in our particular working frame. The place of vacancy is denoted by an empty circle. C_d atom in the text (not shown) is a nearest neighbor of C_c atom. (b) The schematic single-particle picture of the $m_s=1$ high spin states in ground state ($^3A_2$,gs) 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 (Ref. 24), $D_{es}=1.42$ GHz (Refs. 18 and 25). During optical excitations the fluorescence is predominantly active for the $m_s=0$ ground state ($|0\rangle$) due to a nonradiative intersystem crossing of the $|\pm 1\rangle$ 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 $|0\rangle$ and $|-1\rangle$ states. (e) Simplified energy-level diagram with including the hyperfine structure associated with ^{15}N nuclear-spin states $|\uparrow\rangle$ and $|\downarrow\rangle$ in the case of LAC regime of the applied B field. At LAC, precession frequency Ω between excited-state sublevels $|0,\downarrow\rangle$ and $|-1,\uparrow\rangle$ can lead to nuclear-spin flip, which can be transferred to the ground state through nonradiative intersystem crossing (curved arrow).

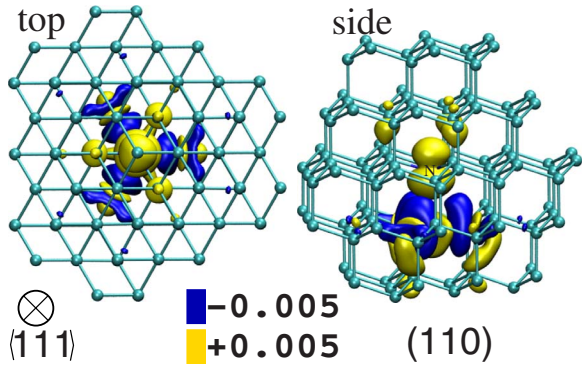

FIG. 2. (Color online) The calculated spin-density difference between the excited ^3E and the ground $^3A_2$ states of the NV center in the respective views. We chose two representative isosurface values indicated by the colored rectangles. The balls represent the carbon atoms. The nitrogen atom is labeled in the side view. The vacant site is below the nitrogen atom.

vacant site than the C_a atoms in the ground(excited) state. Thus, the excitation induces a change in the geometry. Our Bader analysis revealed a large charge transfer from the C_b atoms toward the N-atom, that is $0.97e(0.93e)$ in the ground(excited) state. The C_a atoms are positively(negatively) polarized in the ground(excited) state by an amount of $\sim 0.03e$. This indicates a considerable change in the dipole moment upon excitation. The spin density also changes due to optical excitation. Figure 2 shows the calculated difference of the spin densities in the excited and ground states. Apparently the spin density enhanced a lot around N atom (indicating with yellow lobes) while it dropped around the C_a atoms (indicating with blue lobes). This can be explained by the hole left on the a_1 defect level in the gap after excitation. The a_1 defect level is significantly localized on the N atom.[16] Thus, the spin polarization of the a_1 defect level will spin polarize the N atom considerably. Consequently, the spin polarization of the C_a atoms will be smaller. According to the calculations the hyperfine constants of ^{13}C isotopes are dropped by around 50% (see Table I). However, the overall magnetization density of the N and C_a atoms is about 95% the same *both* in the ground and excited states. In other words, the spin density mostly redistributed between the N atom and the three C_a atoms upon excitation. We further note that (i) the hyperfine constants of ^{15}N are *positive* in the ground state and *negative* in the excited state, (ii) the sign and the orientation of the C_a hyperfine tensors are the same in both the ground and excited state, and (iii) the spin density changes significantly for other proximate ^{13}C nuclei that have been used as nuclear qubits.[3,16]

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[13,18] and the nature of the decoherence of the nuclear qubits.[15] It has been demonstrated that the effective nuclear-spin temperature corresponds to a μK in this process[13] *decoupled* from the ambient (room) temperature that can be the basic physical process in the measurement of zero-point fluctuations.[7] In these measurements the depolarization of the nuclear spins of ^{15}N (Refs. 13 and 18) and $^{13}C_a$ (Ref. 13) have been reported. This has been achieved by the 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 Figs. 1(c) and 1(d)). We show a refined model of Ref. 13 accounted for LAC. First, we discuss the polarization of a single ^{15}N isotope. The Hamiltonian of the system (with neglecting the nuclear-Zeeman splitting) can be written as[13]

$$H = D_{\rm es}\hat{S}_z^2 + g_e\mu_B B\hat{S}_z + A_{\rm es}\hat{\underline{S}}\hat{\underline{I}}, \tag{1}$$

where $\hat{\underline{S}}$ and $\hat{\underline{I}}$ are the electron and nuclear-spin operators, $D_{\rm es}$ the excited-state zero-field splitting, g_e the electron g factor, μ_B the Bohr magneton, and $A_{\rm es}$ the hyperfine coupling in the excited state. We assume positive B-field. We found that the $A_{\rm es}$ of ^{15}N is anisotropic, so we refine the spin Hamiltonian of Ref. 13. The $A_{\rm es}\hat{\underline{S}}\hat{\underline{I}}$ term can be written with the $a_{\rm es}$ and $b_{\rm es}$ hyperfine splittings and the spin-shift operators as

TABLE I. $^3A_2$ ground state (rows 2,5) versus ^3E excited state (rows 6,8). The calculated principal values of the hyperfine tensor (columns 2 to 6) compared to the known experimental data (columns 7–11) in MHz. The experimental data on ^{15}N is taken from Refs. 17 and 18. See text for the meaning of the question mark.

Atom	A_{11}	A_{22}	A_{33}	θ	ϕ	A_{11}^{exp}	A_{22}^{exp}	A_{33}^{exp}	θ^{exp}	ϕ^{exp}
^{15}N	2.7	2.7	2.3	55	45	3.65(3)	3.65(3)	3.03(3)	55	45
$^{13}C_a(3\times)$	119.7	120.4	201.1	126	45	121.1(1)	121.1(1)	199.21(1)	125	45
$^{13}C_b(3\times)$	−9.0	−8.7	−7.3	135	98					
$^{13}C_c(3\times)$	13.0	13.1	18.3	125	45	13.26(5)	13.26(5)	18.49(5)	125	45
^{15}N	−39.2	−39.2	−57.8					61 ± 6		
$^{13}C_a(3\times)$	56.7	56.7	126.0	125	45					
$^{13}C_b(3\times)$	−6.0	−5.3	−2.5	131	119					
$^{13}C_c(3\times)$	10.7	10.9	16.2	127	49					

$$\frac{\hat{S}_+\hat{I}_- + \hat{S}_-\hat{I}_+}{2}(a_{\mathrm{es}} - b_{\mathrm{es}}) + \hat{S}_z\hat{I}_z(a_{\mathrm{es}} + 2b_{\mathrm{es}}). \qquad (2)$$

The hyperfine field of ^{15}N is parallel to the symmetry axis, and $(a_{\mathrm{es}}-b_{\mathrm{es}})=A_\perp\approx-39$ MHz while $(a_{\mathrm{es}}+2b_{\mathrm{es}})=A_\parallel\approx-58$ MHz. According to a recent study[25] $D_{\mathrm{es}}=+1.42$ 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. 1(d)]. In the basis $[|-1,\downarrow\rangle;|-1,\uparrow\rangle;|0,\downarrow\rangle;|0,\uparrow\rangle]$ and by choosing the origin of energy level at level $|0,\uparrow\rangle$, the Hamiltonian described by Eqs. (1) and (2) can be written as

$$H=\begin{pmatrix} \mathcal{E}_{-1}^{\downarrow}-c & 0 & 0 & 0 \\ 0 & \mathcal{E}_{-1}^{\uparrow}-c & d & 0 \\ 0 & d & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}; \quad \begin{matrix} \mathcal{E}_{-1}^{\downarrow\uparrow}=D_{\mathrm{es}}\pm A_\parallel/2 \\ c=g_e\mu_B B \\ d=A_\perp/\sqrt{2} \end{matrix}.$$

The eigenstates of this Hamiltonian are $|0,\uparrow\rangle$, $|-1,\downarrow\rangle$, $|+\rangle=\alpha|0,\downarrow\rangle+\beta|-1,\uparrow\rangle$, and $|-\rangle=\beta|0,\downarrow\rangle-\alpha|-1,\uparrow\rangle$. The transition from the ground state $|0,\uparrow\rangle$ to the excited state remains nuclear spin conserving. This corrects the previous model that assumed the $|0,\downarrow\rangle$ to be the nuclear-spin conserving state[13] because of the false assumption of the *positive* ^{15}N hyperfine splitting in the excited state. Our finding also resolves a contradiction in Ref. 18 where they found that the sign of A_{es} and A_{gs} should be different and they used positive sign for A_{es}.

The transition from $|0,\downarrow\rangle$ results in $(\alpha|+\rangle+\beta|-\rangle)$ in the excited state [see Fig. 1(e)]. This superposition state then starts to precess between $\alpha|+\rangle+\beta|-\rangle=|0,\downarrow\rangle$ and $\alpha|+\rangle-\beta|-\rangle=(\alpha^2-\beta^2)|0,\downarrow\rangle+2\alpha\beta|-1,\uparrow\rangle$ states at frequency $\Omega=1/(2\hbar)\times[(\mathcal{E}_{-1}^{\uparrow}-c)^2+4d^2]^{1/2}$, where $\hbar$ is Planck's constant. The precession frequency depends on B via electron Zeeman effect (c in our notation) that is minimal at LAC resonance, i.e., at $D_{\mathrm{es}}-A_\parallel/2\approx506+10=516$ G which is close to the experimental values. The precession frequency will be equal $|d|/\hbar=|A_\perp|/\sqrt{2}\hbar$ in this case. Jacques *et al.* assumed isotropic hyperfine splitting for ^{15}N; therefore, they applied ≈60 MHz in this formula.[13] Our analysis shows that rather the $|A_\perp|\approx39$ 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.[18] Thus, the spin-flip process is very efficient between $|0,\downarrow\rangle$ and $|-1,\uparrow\rangle$ states.[13]

Now, we discuss the polarization of ^{13}C spins. We emphasize that the measurements are carried out with B field along the NV-axis ($\langle111\rangle$ direction in our case). The calculated A_{gs} of C_a atoms projected onto NV axis is 131.2 MHz, while for C_c and C_d atoms are −8.74 and 13.74 MHz, respectively (see Fig. 1 and Table I). The polarization of C_a spin has been demonstrated in Ref. 13 with ~130 MHz while we here identify the C_c (~9 MHz in Ref. 3) and C_d (~14 MHz in Ref. 21) nuclear spins that have been used as nuclear qubits. The polarization of ^{13}C nuclear spins can only happen together with the ^{14}N or ^{15}N nuclear spin in NV center. Equation (1) should be modified by the sum of the hyperfine interaction associated with ^{13}C and N nuclei. The nuclear spin nuclear spin interaction may be neglected as it has about 2–3 orders of magnitude less energy than the other terms. Assuming a single ^{13}C spin together with ^{15}N spin with the aforementioned assumptions one finds an eight-dimensional Hamiltonian with the following basis: $[|-1,\downarrow\downarrow\rangle;|-1,\downarrow\uparrow\rangle;|-1,\uparrow\downarrow\rangle;|-1,\uparrow\uparrow\rangle;|0,\downarrow\downarrow\rangle;|0,\downarrow\uparrow\rangle;|0,\uparrow\downarrow\rangle;|0,\uparrow\uparrow\rangle]$, where the first (second) arrow represents the nuclear spin of ^{15}N(^{13}C). The $|0,\uparrow\uparrow\rangle$ will be nuclear-spin conserving state while the $A_\perp$ hyperfine term of ^{13}C or ^{15}N in the *excited* state will polarize the $\downarrow$ spins of either ^{13}C or ^{15}N with some probability, and the minimal precession frequency will depend on $A_\parallel$ of both nuclei. *We emphasize here that the nuclear spin gets polarized into the positive projection along the es quantization axis while the nuclear-spin projections along the gs quantization axis are measured. If the es and gs quantization axes are not aligned then one polarizes into a superposition of gs projections, and measures no polarization along that axis.* Our calculations show that C_a atom has the same gs and es quantization axes, so the polarization at the appropriate B-field should occur with high probability as has been detected in the experiment.[13] We found that the hyperfine tensor of C_d nuclei (~14 MHz) has very similar gs and es quantization axes, so we predict an efficient nuclear-spin polarization. However, C_c atom (~9 MHz) changes their gs and es quantization axes considerably, so the measured polarization of C_c spin should be very weak. We found that many symmetrically inequivalent proximate ^{13}C

nuclei can have very similar hyperfine tensors in gs but they selectively change or keep the quantization axis in es with respect to that of gs. By combining the accurate *ab initio* data with the measured polarization property of the ^{13}C spin, it is feasible to identify the individual ^{13}C isotopes with possessing accidentally degenerate hyperfine values that is barely doable with conventional EPR studies. Beside the identification of the proximate ^{13}C nuclei the polarization property may reveal the dominant process of the decoherence of the electron-nuclear-spin entanglement. For instance, we found that the C_d nuclei of $\sim$14 MHz in gs decreases its hyperfine constants by $\sim$2 MHz in es but the quantization axes are very similar. This indicates that the $\sim$14 MHz qubit decoheres dominantly due to the stochastic phase accumulation,[15] whereas both the spin flip and the stochastic phase accumulation processes may be responsible for the decoherence of $\sim$9 MHz nuclear-spin qubit according to our calculations since both the magnitude and the axis of its hyperfine tensor changed upon excitation.

In summary, we showed that the spin density and the hyperfine splitting change significantly due to optical excitation in the negatively charged nitrogen-vacancy defect in diamond. Our analysis showed that the previous models applied for this system should be refined and we could resolve some controversies regarding the excited-state spectroscopy of this defect. We present a method to identify the individual C-atoms around the defect.

A.G. acknowledges support from Hungarian OTKA Grant No. K-67886 and the János Bolyai program of the Hungarian Academy of Sciences. The fruitful discussion with Jeronimo Maze and Lilian Childress is appreciated.

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