Theory of neutral nitrogen-vacancy center in diamond and its qubit application

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The negatively charged nitrogen-vacancy defect (NV\textsuperscript{−}) in diamond has attracted much attention in recent years in qubit and biological applications. The negative charge is donated from nearby nitrogen donors that could limit or stem the successful application of (NV\textsuperscript{−}). In this Letter, we unambiguously identify the neutral nitrogen-vacancy defect (NV\textsuperscript{0}) by \textit{ab initio} supercell calculations. Our analysis shows that i) the spin state can be selectively occupied optically, ii) the electron spin state can be manipulated by time-varying magnetic field, and iii) the spin state may be read out optically. Based on this NV\textsuperscript{0} is a new hope for realizing qubit in diamond without the need of nitrogen donors.

Realization of qubits is of extremely high importance because that can be used in quantum cryptography, quantum optics and quantum computing. One of the most promising candidate is the \textit{negatively charged} nitrogen-vacancy defect (NV\textsuperscript{−} \cite{1, 2}) that can operate at \textit{room temperature} \cite{3, 4, 5, 6, 7, 8, 9, 10, 11}. The negative charge is donated from nitrogen substitutional (N\textsubscript{3}) \cite{12, 13}. It has been very recently shown that the major source of the decoherence of the electron spin of the negatively charged NV center is the electron spin bath of nitrogen substitutionals in type-Ib diamond, that can be eliminated only at low temperature using a giant magnetic field \cite{14}. This is a serious limiting factor towards the development for \textit{practical} applications. In addition, it has been recently demonstrated that nanometer-sized diamond particles containing NV\textsuperscript{−} are useful as fluorescent biomarkers for \textit{in vitro} imaging applications \cite{15, 16}. However, the requirement of the extra charge on NV defect from N\textsubscript{3} could be critical in biomarker applications, where the size of the nanodiamond is reduced to some nanometers in diameter \cite{17}. One solution of this problem would be to apply the paramagnetic neutral NV defect (NV\textsuperscript{0}) which produces strong photoluminescence at 2.156 eV (similar to NV\textsuperscript{−}) and it \textit{does not require an extra electron}. The NV\textsuperscript{−} center is well identified \cite{12} while its strong connection to its neutral counterpart is well established experimentally \cite{18, 19, 20}. However, the overall knowledge about NV\textsuperscript{0} is scarce. Very recently, an $S = \frac{1}{2}$ electron paramagnetic resonance (EPR) center has been found in photo-excited diamond doped by $^{15}$N \cite{21}. A sizeable $^{15}$N hyperfine constants have been detected in the EPR measurements and it was proposed that the signal was originated from one of the excited states of NV\textsuperscript{0} \cite{21}. We emphasize that the identification of the EPR signal of NV\textsuperscript{0} is a \textit{key step} in order to apply it for qubit, and to trace it magnetically in biomarker applications.

In this Letter we i) unambiguously \textit{identify} the EPR signal of NV\textsuperscript{0} ii) provide a detailed spin density distribution around the defect; the results indicate that the defect states are well-localized and the electron spin can be decoupled from the spin bath of $^{13}$C nuclei iii) analyze the electronic structure by group theory explaining the photo-excitation of NV\textsuperscript{0}; this shows that the $M_S = \pm 1/2$ sublevels are selectively occupied in the photo-ionization process and appropriate microwave magnetic field can be applied to choose also selectively either $M_S = +3/2$ or $M_S = -3/2$ which finally can be used as qubit iv) we propose that the $M_S = +3/2$ or $M_S = -3/2$ states may be read out optically during the emission process from the excited state to the ground state. This gives a hope for realization of qubit by NV\textsuperscript{0} defect.

We employed density functional theory calculations with local density approximation (LDA) using a large, 512-atom simple cubic diamond supercell. We used two different codes: the geometry of the defect was optimized with the VASP code \cite{22} while the hyperfine tensors of NV\textsuperscript{0} were calculated by the CPPAW code \cite{23}. Both VASP and CPPAW codes apply the all-electron PAW method and plane wave basis set. We used a cut-off of 30 Ry and $\Gamma$-point for k-point sampling. Other details and references can be found in our previous publication \cite{24} where we could successfully describe the negatively charged NV center and can reproduce well the experimental hyperfine data.

The NV defect has $C_{3v}$ symmetry, if no reconstruction occurs. We use defect-molecule and group theory analysis below as for NV\textsuperscript{−} (c.f. \cite{24} and references therein). Four dangling bonds point to the vacant site resulting in $a_1(1)^2a_1(2)^2e^1$ configuration for the neutral defect, where $a_1(2)^2$ and the double degenerate $e^1$ appear in the fundamental band gap. In this configuration, the system is basically Jahn-Teller unstable because the degenerate state is only partially filled by electrons. The static Jahn-Teller effect would result in $C_{1h}$ symmetry of the defect. PL studies indicate that the system has $C_{3v}$ symmetry ($2E$ state) with possibly exhibiting dynamic Jahn-Teller effect that inhibits the EPR detection of the $2E$ ground state \cite{25}. The $C_{1h}$ symmetry configuration and the $2E$ ground state of $C_{3v}$ symmetry can be described by single Slater-determinants, so we could address this issue directly at LDA level. The lowest excitation can be obtained by promoting one electron from $a_1(2)$ level to $e$ level resulting in $a_1(1)^2a_1(2)^1e^2$ configuration. The possible excited states of $a_1(1)^2a_1(2)^1e^2$ configuration have $2A_1$, $4A_2$ and $2E$ multiplets. The $M_S = \pm 3/2$ state of $4A_2$ multiplet can be described by a single Slater-determinant by simply aligning all the electrons spin-up on the $a_1(2)$ and $e$ levels, thus the spin density can be determined by usual LDA calculation. We note that no Jahn-Teller effect occurs for $4A_2$ state, so we considered only $C_{3v}$ symmetry for this state in the calculations. We focused our research on the ground state of $C_{1h}$ and $C_{3v}$ symmetries,
and the $^4A_2$ excited state that are relevant in the recent EPR study [21]. We note here that the nitrogen dangling bond is hybridized into $a_1(2)$ but not into the $e$ defect states, therefore, negligible spin density is expected for the $^2E$ ground state but considerable spin polarization may be expected for the $^4A_2$ excited state.

First, we investigated the ground state of NV$^0$. Since Jahn-Teller effect can occur, we distorted the symmetry to $C_{1h}$, and allowed the atoms to relax to find the energy minimum within LDA. We found that the system conserves its $C_{1h}$ symmetry and it does not form the $C_{3v}$ configuration. The single occupied $e$-level in the gap is split by 0.3 $eV$ resulting in an occupied $a'$ state and an unoccupied $a''$ state of the spin-up electrons. The neighbor N and C atoms relaxed outward from the vacant site. The nitrogen atom remained very close to the vacant site. The neighbor N and C atoms relaxed outward from the vacant site. The nitrogen atom remained very close to the vacant site. The neighbor N and C atoms relaxed outward from the vacant site. The nitrogen atom remained very close to the vacant site. The neighbor N and C atoms relaxed outward from the vacant site. The nitrogen atom remained very close to the vacant site.

Next, we constrained the system to preserve the $C_{3v}$ symmetry during the geometry optimization in order to calculate the total energy of $^2E$ state. We found that it is about 0.09 $eV$ higher in energy than the Jahn-Teller distorted one. Then, we allowed the system to relax without symmetry constraints starting from the optimum $C_{3v}$ geometry. The atoms automatically relaxed to the $C_{1h}$ symmetry. This result indicates that $C_{3v}$ symmetry is a local maximum. This finding seems to contradict the PL spectrum which shows $^2E$ ground state within $C_{3v}$ symmetry. However, we carried out quasi-static calculations at 0 K, and we did not take the vibronic states and temperature effects into account. This result shows clearly a multi-valley potential surface for the ground state of this defect as was already hinted by Davies [25]. Our calculated Jahn-Teller energy (0.09 $eV$) is very close to the estimation of Davies (0.14±0.07 $eV$) based on the luminescence measurements [25]. There are three equivalent $C_{1h}$ configurations around the vacant site rotated by 120 degrees about the $C_{3v}$-axis with each possessing the global minimum. At LDA-level, we can estimate the upper limit of the energy barrier between the three global minima, that is \( \approx 0.09 \) $eV$. There may exist more favorable path between these global minima than through the $C_{3v}$ configuration, so the actual barrier energy may be even lower than that. Due to the strong C-C bonds in diamond \( \leq 0.09 \) $eV$ energy difference can be gained even at very low temperature because this is about the zero point energy of the phonons with the highest energy (\( \leq 0.083 \) $eV$). This results in a motional average of the single electron between the three equivalent $C_{1h}$ configurations, showing an effective $C_{3v}$ symmetry. It was speculated [21,25] that the dynamic Jahn-Teller effect is responsible for the missing EPR signal of the $^2E$ ground state. Our calculations support this assumption.

We also investigated the $^4A_2$ excited state. This state has indeed much higher energy by about 0.86 $eV$ compared to that of the low-symmetry ground state. We note that the LDA total energy differences should not be directly compared to the measured transition energies as previously discussed in Ref. [24]. In this state the $a_1(2)$ defect level is polarized, thus the nitrogen atom is polarized in contrast to $^2E$ state. This results in considerable rearrangement of the atoms around the vacancy, namely, the nitrogen moves closer to the vacant site. We calculated the hyperfine tensors of atoms for the optimum geometry and compared to a recently found EPR center as explained in the introduction [21] (see Table I). The agreement between the calculated and measured hyperfine signal is excellent. In addition, the calculated binding energy of the NV$^0$ complex (=3.0 $eV$) shows a high thermal stability, and its (0/-) occupation level is at about 2.0 $eV$ above valence band edge, in line with the experimental observations [18]. Thus, we identify the EPR signal of NV$^0$. We provide the hyperfine data of the three nearest carbon atom near the vacant site that has the largest hyperfine interaction. These carbon atoms may be measured by future EPR experiments when the signal to noise ratio can be reduced there.

After identification of NV$^0$ defect we discuss its possible role in spin physics. NV$^-$ was successfully used to realize qubits [9,10]. Second order correlation and EPR measurements were employed to detect individual NV$^-$.

| Atom   | $A_{11}$ | $A_{22}$ | $A_{33}$ | $A_{11}^{exp}$ | $A_{22}^{exp}$ | $A_{33}^{exp}$ |
|--------|----------|----------|----------|----------------|----------------|----------------|
| $^{14}N$ | -23.4    | -23.4    | -39.0    | -23.8(3)       | -23.8(3)       | -35.7(3)       |
| $^{13}C(3\times)$ | 60.6 | 61.0 | 126.2 | | | |

The $^{13}C$ hyperfine signal could not be resolved in that experiment.
which has much smaller hyperfine interaction with the proximal $^{13}$C nucleus than the $M_S = 1$ state [9]. This effect was responsible for the collapse and revival of the electron spin coherent state. The $M_S$ states could be read-out also optically after the measurements by using the fact that they have different fluorescence rates [9].

In NV$^0$ defect the optical pump can change the $S = \frac{1}{2}$ state to $S = \frac{3}{2}$ excited state, and by switching off the light excitation this can be transformed back to the $S = \frac{1}{2}$ state. The nature of the spin-flip process will be discussed shortly. The group theory analysis tells us that no spin-orbit coupling arises for the $4A_2$ excited state. However, the spin-spin interaction is active, which can be given by the following effective spin-Hamiltonian for this particular system: $H_S = D' (S_z^2 - 5/4)$, where $D'$ is the zero-field constant and $S_2$ has the $M_S$ eigenvalue. So, the $4 \times 4$ degenerate $4A_2$ state will split to two double degenerate states due to spin-spin interaction resulting in the lower lying $M_S = 1/2; -1/2$ and the upper lying $M_S = 3/2; -3/2$ levels (see Fig. 1). These levels are separated by $2 \times D' = D, D \approx 1685$ MHz was experimentally measured by EPR [21]. According to Davies PL analysis $\sim 2.2$ eV excitation occurs between $^2E$ ground state to the $^2A_1$ excited state. We propose that the $M_S = 1/2; -1/2$ electron states of the $^2A_1$ excited state can relax to the $M_S = 1/2; -1/2$ sublevels of $4A_2$ state with a finite probability instead of relaxing back to the ground state. While the spin-orbit interaction is not active for $^2A_1$ state itself the axial spin-orbit interaction couples the $^2A_1$ states selectively with the $M_S = 1/2; -1/2 4A_2$ states. That is the source of the spin-flip process which may be further mediated by phonons in order to satisfy the energy conservation of this transition. Indeed, the threshold excitation energy of the EPR signal, $2.2(1)$ eV [21], is larger than the ZPL energy of $2.156$ eV, and it has the highest intensity using excitation energy of about $2.5$ eV. The probability of the relaxation process between the original $^2E$ and $^1A_1 (S = \frac{1}{2})$ states should be higher than for the original $^1A_2 (S = \frac{3}{2})$ state. One may estimate from the known data of the NV$^-$ center [26] that the duration of the direct transition process is about $10$ ns, while for the spin flip process it could be about $30$ ns. Therefore, the duration of the optical pumping can be relatively long in order to arrive at $M_S = 1/2; -1/2$ sublevels of $^4A_2$ state from the $^2E$ ground state. The typical EPR condition for $^4A_2$ state is shown in Fig. 1. The small external constant magnetic field (B) will split the $M_S = 1/2; -1/2$ sublevels lowering the energy of $M_S = -1/2$ state. Finally, we predict that during the optical pumping the $M_S = 1/2; -1/2$ sublevels of $^4A_2$ state will be selectively populated with somewhat higher probability for $M_S = -1/2$ because it is lower in energy. Then, the varying microwave magnetic field induce the transitions $M_S = \pm 1/2 \leftrightarrow \mp 3/2$ in the EPR measurements. This scenario can explain all the photo-EPR findings in Ref. [21].

The question arises what kind of entity can be used as a qubit from NV$^0$ defect. The first choice it to use simply the $S$-state. By optical pumping the $S$-state of NV$^0$ defect can be transformed from $1/2$ to $3/2$, and by switching off the light it can be transformed back from $3/2$ to $1/2$ with $t \ll 1$ s [21]. However, it is not probable that coherent state can be achieved for the ground state as we showed that it exhibits a dynamic Jahn-Teller effect causing a rapidly varying effective magnetic field for the $^{13}$C nuclei around the NV$^0$ defect. Furthermore, the time-averaged effective hyperfine interaction of both states are very similar. This is also disadvantageous.

Another possibility is to use the $M_S$ sublevels of the $^4A_2$ state as qubit. As explained above by optical pumping one can select the $M_S = 1/2; -1/2$ sublevels of $^4A_2$ state of the NV$^0$ defect with almost equal probability. That is not applicable for qubits. However, one can selectively set either $M_S = +3/2$ (with energy of $h\nu_2$) or $M_S = -3/2$ ($h\nu_2$) states by applying a $\pi$ pulse [9] to induce the EPR transition ($\Delta M_S = \pm 1$) (see Fig. 1). The $M_S = \pm 3/2$ states may be used as qubit. It is clear in the above mentioned scenario that $\nu_1$ can only be associated with $M_S = +3/2$ while $\nu_2$ only with $M_S = -3/2$. We would like to emphasize that these metastable $M_S = \pm 3/2$ states are extremely long living (>1 µs) because i) the $^4A_2$ state is the only $S = 3/2$ state, so there is no way for radiative recombination for this state ii) the $M_S = \pm 3/2$ states are not coupled to the $^2A_1$ excited state at all that hinders the recombination of these states to the $^2E$ ground state via $^2A_1$ excited state. This is unique compared to the NV$^-$ center [26] and suggests a longer lifetime of these metastable states than for the measured lifetime of the singlet metastable state in NV$^-$ center (300 ns) [26]. We note that the $M_S = \pm 3/2$ states are very weakly coupled to the $^2E$ ground state by non-axial spin-orbit interaction. However, the non-axial spin-orbit interaction is very small (as assumed for NV$^-$ center [26]) and is too far in energy in order to mediate this process by phonons. So, the probability of this decay is very small ensuring the very long lifetime of these states. The coherent state between these $M_S = \pm 3/2$ states and the proximate $^{13}$C nuclei can certainly be maintained similar to NV$^-$ [9]. The readout process could be very simple: by applying a $\pi$ pulse again the $M_S = \pm 3/2$ states scatter to $^4A_2 M_S = \pm 1/2$ states that through the spin-orbit coupling can go back to the $^2A_1$ excited state, finally by radiative recombination to the $^2E$ ground state. Therefore, the spin qubit state can be readout optically. This process can be tuned by applying the appropriate constant magnetic field to split the levels and the microwave magnetic field ($\pi$ pulse) to induce transitions between the levels.

In this work we investigated the neutral nitrogen-vacancy defect in diamond in detail by ab initio LDA supercell calculations. We showed that the defect indeed shows the dynamic Jahn-Teller effect for the ground state. We identified the recently found EPR center [21], as the $^4A_2$ excited state of the neutral nitrogen-vacancy defect. That EPR center can be used to trace the NV$^0$-contained nanodiamonds magnetically. We found that NV$^0$ is a promising candidate for realizing qubits in diamond without the need of nitrogen donors.

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FIG. 1: (Color online) The process of the manipulation of a qubit in NV$^0$ defect. Straight red arrow: radiative recombination. Curved green arrow: spin-orbit coupling ($\hat{H}_{SO}$) possibly mediated by phonons. Grey dotted arrows represent very weak interaction. Blue straight line: microwave alternating magnetic field pulse. Filled(empty) circle: initial(final) state of the electron. Setting the qubit state: i) excitation from the $^2E$ ground state to the $^4A_1$ excited state ii) spin-flip to the appropriate $^4A_2$ states iii) setting either $M_S = 3/2$ or $M_S = -3/2$ state by $\pi$ pulse. Readout the qubit state: i) $\pi$ pulse to go back to $M_S = \pm 1/2$ states ii) spin-flip to the $^1A_1$ state iii) radiative recombination to the $^2E$ ground state. We show the fine structure of $^4A_2$ states in the absence of external magnetic field ($B=0$) (2nd column) and at $B > 0$ with typical EPR conditions in the next columns. $D \approx 1685$ MHz fine structure constant was determined by EPR [21]. The figure does not show the true scale for the sake of clarity.

[1] L. du Preez, PhD. dissertation, University of Witwatersrand, 1965.
[2] G. Davies and M. F. Hamer, Proc. R. Soc. London Ser. A 348, 285 (1976).
[3] J. Wrachtrup, S. Y. Kilin, and A. P. Nizotsev, Opt. Spectrosc. 91, 429 (2001).
[4] F. Jelezko, I. Popa, A. Gruber, C. Tietz, J. Wrachtrup, A. Nizotsev, and S. Kilin, Appl. Phys. Lett. 81, 2160 (2002).
[5] F. Jelezko, T. Gaebel, I. Popa, A. Gruber, and J. Wrachtrup, Phys. Rev. Lett. 92, 076401 (2004).
[6] F. Jelezko, T. Gaebel, I. Popa, M. Domhan, A. Gruber, and J. Wrachtrup, Phys. Rev. Lett. 93, 130501 (2004).
[7] R. J. Epstein, F. Mendoza, Y. K. Kato, and D. D. Awschalom, Nat. Phys. 1, 94 (2005).
[8] R. Hanson, F. M. Mendoza, R. J. Epstein, and D. D. Awschalom, Phys. Rev. Lett. 97, 087601 (2006).
[9] L. Childress, M. V. Gurudev Dutt, J. M. Taylor, A. S. Zibrov, F. Jelezko, J. Wrachtrup, P. R. Hemmer, and M. D. Lukin, Science 314, 281 (2006).
[10] M. V. Gurudev Dutt, L. Childress, L. Jiang, E. Togan, J. Maze, F. Jelezko, A. S. Zibrov, P. R. Hemmer, and M. D. Lukin, Science 316, 312 (2007).
[11] R. Hanson, V. V. Dobrovitski, A. E. Feiguin, O. Gywat, and D. D. Awschalom, Science 320, 352 (2008).
[12] J. H. N. Loubser and J. P. van Wyk, in Diamond Research (London) (Industrial Diamond information Bureau, London, 1977), pp. 11–15.
[13] R. Hanson, O. Gywat, and D. D. Awschalom, Phys. Rev. B 74, 161203(R) (2006).
[14] S. Takahashi, R. Hanson, J. van Tol, M. S. Sherwin, and D. D. Awschalom, Physical Review Letters 101, 047601 (2008).
[15] S.-J. Yu, M.-W. Kang, H.-C. Chang, K.-M. Chen, and Y.-C. Yu, J. Am. Chem. Soc. 127, 17604 (2005).
[16] Y.-R. Chang, H.-Y. Lee, K. Chen, C.-C. Chang, D.-S. Tsai, C.-C. Fu, T.-S. Lim, Y.-K. Tseng, C.-Y. Fang, C.-C. Han, H.-C. Chang, and W. Fann, Nature Nanotechnology 3, 284 (2008).
[17] J. Rabeau, A. Stacey, A. Rabeau, S. Prawer, F. Jelezko, I. Mirza, and J. Wrachtrup, Nano Letters 7, 3433 (2007).
[18] Y. Mita, Phys. Rev. B 53, 11360 (1996).
[19] G. Davies, S. C. Lawson, A. T. Collins, A. Mainwood, and S. J. Sharp, Phys. Rev. B 46, 11360 (1992).
[20] T. A. Kennedy, J. S. Colton, J. E. Butler, R. C. Linares, and P. J. Doering, Applied Physics Letters 83, 4190 (2003).
[21] S. Felton, A. M. Edmonds, M. E. Newton, P. M. Martineau, D. Fisher, and D. J. Twitchen, Physical Review B 77, 081201(R) (2008).
[22] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
[23] P. E. Blöchl, C. J. Först, and J. Schimpihl, Bull. Mater. Sci. 26, s33 (2001).
[24] A. Gali, M. Fyta, and E. Kaxiras, Physical Review B 77, 155206 (2008).
[25] G. Davies, J. Phys. C 12, 2551 (1979).
[26] N. B. Manson, J. P. Harrison, and M. J. Sellars, Physical Review B 74, 104303 (2006).