An ab initio study of local vibration modes of the nitrogen-vacancy center in diamond

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Abstract. The negatively charged nitrogen-vacancy (NV) defect (NV center) in diamond is a leading candidate to realize solid-state qubits and ultrasensitive magnetometers in ambient conditions. A new interpretation of some of the properties of the center is presented. We show that the double peak in the absorption phonon sidebands may correspond to the local \( a_1 \) and \( e \) vibration modes of the defect that have very similar energies, and that tunneling of nitrogen atoms in the vacancy does not occur as had been previously suggested.

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Contents

1. Introduction
2. Atomistic structure of the nitrogen-vacancy (NV) center and its electronic properties
3. Computational methodology for calculating local vibration modes (LVMs)
4. Results and discussion
5. Summary
Acknowledgments
References

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1. Introduction

The nitrogen-vacancy (NV) defect centers in diamond have become potential candidates for a number of applications. These range from magnetometry [1]–[4] to high spatial resolution imaging [5] to quantum computation [6]. At low temperatures, optical transitions at the NV center become very narrow and can be coherently manipulated. This can be used to explore further interesting applications such as spin–photon entanglement generation [7] and optical control [8]. A detailed understanding of the electronic and vibronic properties of the defect is necessary to reliably control and manipulate the spin state of the defect.

Several studies have addressed the electronic properties both experimentally [9, 10] and theoretically [11, 12], and recent ab initio calculations revealed the electronic properties of the ground and excited electronic states [13]–[20]. The role of vibrations in excitation and deexcitation processes and the effect of temperature on the magnetic and optical properties of the NV center only recently began to be studied experimentally [21]–[23]. An advanced density functional theory study has shown [24] that high-energy vibronic states are occupied when a focused laser beam is applied in single NV center measurements. In addition, it has been claimed [12, 20] that vibrations should mediate the spin-flip de-excitation in the NV center, which is a key issue in its applications. Therefore, it is of immediate importance to explore the vibronic properties of the NV center in diamond using a similar ab initio approach. More recently, the role of vibrations at the vacancy in diamond has been studied using an ab initio approach [25], and this has revealed good correspondence to the early Jahn–Teller interpretation of the optical features associated with this defect. We apply this approach to studying the vibration modes of the NV center in diamond.

2. Atomistic structure of the nitrogen-vacancy (NV) center and its electronic properties

Before turning to the calculation of the vibration modes of the defect, we briefly summarize basic knowledge about the atomistic and electronic structures of the NV center. The NV center was observed many years ago in diamond [26]. It is established that the concentration of NV centers can be enhanced in N-contaminated diamond by irradiation and annealing [26, 27] and thus a model for the NV center consisting of a substitutional nitrogen atom near a vacancy in diamond [26]–[29] has been identified. Associated with the center is a strong optical transition with a zero phonon line (ZPL) at 1.945 eV (637 nm) that is accompanied by a vibronic band at higher energy in absorption and lower energy in emission. Detailed analysis of the ZPL revealed that the center has trigonal, \( C_{3v} \) symmetry [27]. It is important to note here that absorption and emission did not show the same vibronic feature [27] and that this point will be discussed later in this paper.

Early electron paramagnetic resonance studies revealed that the NV center has \( S = 1 \) ground state [30, 31], which led to a model that the NV center is the negatively charged NV defect in diamond (see figure 1). According to first principles calculations [13, 14] the nitrogen and carbon atoms around the vacancy relax outward conserving the \( C_{3v} \) symmetry. Two fundamental levels appear in the band gap: a fully occupied \( a_1 \) level and two electrons occupying a double degenerate \( e \) level. These two electrons follow the Hund rule stabilizing the high-spin \( S = 1 \) ground state. The symmetry of the many-body wave function is then \( 3A_2 \). The excited state of the defect may be described by promoting one electron from the \( a_1 \) level to the \( e \) level in the independent particle approximation forming the \( 3E \)-multiplet state. While
this independent particle picture of excitation is generally oversimplified, calculations beyond standard approximations of density functional theory (DFT) have shown [18, 32] that this simplified picture works very well for this particular defect. Since the $M_S = 1$ state of the $^3A_2$ and $^3E$ multiplets can be described by a single Slater determinant [11], the ground state can be calculated by the standard DFT method in a straightforward manner, while the excited state can be addressed by the constrained DFT method with fixed occupation of defect states corresponding to the excited $^3E$ state [13, 14, 17, 24, 32].

3. Computational methodology for calculating local vibration modes (LVMs)

We calculated the numerical derivative of the quantum mechanical forces acting on the atoms upon distortion from the equilibrium positions in order to calculate the Hessian matrix of vibrations of the NV center in diamond. As a first step, we assume quasi-harmonic vibrations, so we do not consider here the anharmonicity of the vibration modes but focus our study on the identification of local vibration modes (LVMs) of the NV center. We applied a 64-atom supercell method to model the defect with the projector augmentation wave (PAW) method, pseudopotentials to treat the effect of the nuclei with the core electrons [33, 34]. The VASP5.2 code [35, 36] was used to carry out these calculations with an energy cut-off of 420 eV. In this study, we choose the local density approximation (LDA) [37, 38] because previous calculations showed that it produced superior results regarding both elastic moduli and the phonon states of bulk diamond over the generalized gradient approximations [25]. First, we optimized the geometry of the defect in the supercell applying very stringent convergence criteria for the forces ($1 \mu eV \AA^{-1}$) and preserving $C_{3v}$ symmetry. Then we allowed all the atoms to vibrate in the supercell taking the symmetry of the system into account. In a previous study [14], it was shown that the wave function of the NV center was quite localized in the 64-atom unit cell, so we applied this procedure both for the ground and excited states where the excited state could be treated by the constraint DFT method. An overall estimate of the accuracy of
Figure 2. Motion of the atoms associated with the mostly localized vibration modes of the NV center. We show the motion only in the ground state because the motions are very similar in the excited state. We have cut the NV center from the 64-atom supercell for clarity. The carbon atoms close to the vacancy or nitrogen atom are depicted as yellow balls, the nitrogen atom as a blue ball, its immediate C neighbor atoms as red balls and the other carbon atoms as cyan balls. The direction of the arrows shows the direction of motion of the atoms along the positive amplitude, while the length of the arrow represents the relative values of the amplitudes. (a) 59.1 meV mode, (b) 59.7 meV mode, (c) 63.3 meV mode and (d) 77.0 meV mode. See movie files about these vibrations in the supplementary material (available from stacks.iop.org/NJP/13/025016/mmedia).

calculations as suggested by earlier calculations on the diamond vacancy [25] is about 5 meV for the vibration energies. We note that this estimate is relatively crude because we use quasi-harmonic approximation in the calculation of vibrations, and the anharmonic effects may mix the vibration levels to different extents in different single defects.

After obtaining the Hessian matrix in this procedure, the eigenvalues and eigenvectors of this matrix gave us the relative intensity of the vibration modes together with the normalized coordinates of the atoms. If the relative intensity of the vibration was larger for the selected atoms near the vacancy than for the other atoms in the supercell, then we identified this vibration as local mode coupled to the defect. This identification is a bit arbitrary: we chose the criterion that the sum of the amplitude of motion of the selected vibrating atoms should be < 1.6× larger than the sum of the amplitude of motion of the other vibrating atoms in the supercell. The selected atoms in this procedure were as follows: carbon atoms nearest to the vacancy (yellow balls in figure 2), the nitrogen atom (blue ball in figure 2) and its first neighbor carbon atoms (red balls in figure 2). We emphasize here that the highest occupied orbitals are very localized...
Table 1. Calculated LVMs in meV units. The symmetry of the vibration is indicated in parentheses.

| State | LVM       |
|-------|-----------|
| $^3A_2$ | 59.1 ($e$) 59.7 ($a_1$) 63.3 ($e$) 77.0 ($a_1$) |
| $^3E$   | 47.2 ($e$) 59.0 ($a_1$) 63.9 ($e$) 76.9 ($a_1$) |

on the three yellow-colored C-atoms in the $^3A_2$ ground state, while the unpaired electrons are localized significantly on both these yellow-colored C-atoms and the nitrogen atom in the $^3E$ excited state. The reason for selecting the red C-atoms is the fact that charge transfer between the nitrogen atom and these C-atoms is significant, which differentiates the red C-atoms from the other C-atoms in diamond lattice.

4. Results and discussion

By taking the very simple model of the NV center as the yellow-colored C-atoms and the nitrogen atom one can find in group theory analysis of the possible vibration modes of this defect that two fully symmetric $a_1$ modes and two degenerate $e$ modes should appear under $C_{3v}$ symmetry with excluding the translational and rotational modes. Indeed, we found these four modes as the most prominent LVMs of the NV center in table 1. Basically, the ground state $^3A_2$ and the excited state $^3E$ exhibit similar modes but with some differences. In particular, the lowest degenerate $e$ mode is about 10 meV lower than the next fully symmetric $a_1$ mode in the excited $^3E$ state whereas they have very similar energies in the ground state within 1 meV. We observed that the LVM at around 77 meV has the largest intensity both in the ground and excited states and belongs to the symmetric breathing mode of the yellow-colored C-atoms, while the movement of the nitrogen atom is not so significant. The lowest double degenerate LVM is associated with the non-symmetric motion of the yellow-colored C-atoms, while the next two LVMs ($a_1$ and $e$ modes) are associated with a translational-like motion of N-C$_3$ unit in the diamond lattice where the C$_3$ atoms are shown as red balls in figure 2. In the case of $a_1$ mode, the nitrogen moves along the symmetry axis, while it moves in a plane perpendicular to the symmetry axis in the double degenerate $e$ mode.

Now, we turn to a discussion of our results and their relevance to the interpretation of the absorption and emission spectra of the NV center. The optical transition of the NV center is accompanied by a vibronic band to high energy in absorption and low energy in emission. The vibronic sidebands show small peaks superimposed on a smooth band due to a coupling of phonon-like modes. The small peaks are presumably the fingerprints of LVMs coupled more strongly with the defect than the (de-localized) phonon-like modes. In the vibration bands of luminescence and emission, three small peaks follow each other by about 65 meV steps. These numbers are estimates from the spectra taken by Davies and Hamer [27] at liquid nitrogen temperature on the ensemble of NV centers in diamond. The read out of these peaks is not ambiguous due to the obscurity of phonon bands and presence of other luminescence centers in the detected spectra, and these small peaks are themselves relatively broad. Nevertheless, the almost equidistant position of these peaks strongly implies that they are the LVMs of the NV.
An unusual aspect of this vibronic sideband is that the first feature in absorption gives a double peak (with a distance of a few meV), whereas the first feature in emission is a single peak. A difference in the vibronic structure between absorption and emission is frequently related to a Jahn–Teller effect. However, in uniaxial stress measurements, Davies and Hamer [27] obtained the same polarization for the sideband and the ZPL and interpreted the results so that the sidebands were associated with coupling of symmetric modes. They concluded that the variation in the sideband structure is not related to a Jahn–Teller effect. They attributed the difference to nitrogen being able to interchange positions with the vacancy and, hence, was energetically placed in a double potential well. In the excited state, the depth of the potential well suggested for this tunneling coincides with the energy of the axial mode frequency of $\sim 70$ meV and tunneling between the two wells was considered to give rise to the double peak in absorption.

We calculated the depth of the potential well using a 512-atom supercell (see [14] for more technical details), by moving the N-atom step-by-step from one site of the vacancy to the opposite site while letting the other atoms relax (a sketch of the movement of a nitrogen atom can be seen in figure 3). The calculated barrier energy for this movement was greater than 4 eV, which is about two orders of magnitude larger than proposed from the interpretation of absorption measurements based on the tunneling model. The nitrogen atom strongly binds to its three neighboring C-atoms, and breaking these bonds needs too much energy. Hence, another explanation for the occurrence of the double peak has to be found as these results very strongly suggest that any model involving motion of the N is unlikely. In addition, a more recent measurement on a single NV center has shown that the Jahn–Teller effect may occur in the excited state [21] in contrast to the earlier work [27].

In the interpretation of the absorption and emission sidebands the Franck–Condon approximation is often used, which has been discussed for the NV center in our recent paper [17]. In this picture the total wave function is decomposed into the electronic wave function and the vibration function, which is based on the adiabatic or more strictly on Born–Oppenheimer approximation. In the harmonic approximation of vibrations, the single vibration modes are Hermite polynomials multiplied by an exponential function of $R^2$, where $R$ is the distance of the nuclei from its equilibrium position. Since the quasi-particles associated with the vibrations are bosons, the many-body wave function of the vibrations is a simple product of single vibration modes, and the Hermite polynomial for the ground state will follow the full symmetry of the system, which transforms as $A_1$ under $C_{3v}$ symmetry. The ground state vibration wave function in the occupation representation may be written as $|000\cdots000\rangle$ where the number of zeros represents the number of possible single vibration modes in the system. If a single vibration mode is excited to its first excitation energy (one quantum), say, the first one, then the vibration wave function $|100\cdots000\rangle$ will transform as the first vibration mode itself.

At this point, we have to note that the full decoupling of electronic and vibration functions is not always a good approximation. The ab initio calculation of the electron–vibration coupling is beyond the scope of this study but one can claim that the local vibration modes can couple to the electronic wave function stronger than other modes (phonon-like states) because the electron–vibration coupling depends on the derivative of the wave function as a function of change in the coordinates following the normal coordinates of the vibration when perturbation theory of electron–vibration coupling is considered. Since local vibration modes will change

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5 It would be worthwhile to repeat these measurements in pure diamond samples with improved detectors.
Figure 3. (a) The proposed mechanism for the occurrence of a double peak in the vibration sideband of the absorption spectrum in [27]: tunneling of the nitrogen atom in the NV defect. This mechanism does not take place according to our calculations. (b) Our proposed mechanism in a simplified configuration coordinate diagram: due to the Jahn–Teller effect, both \( a_1 \) and \( e \) local modes will couple in the vibration band of absorption, whereas only \( a_1 \) local mode will couple in the vibration band of emission. ZPL transition will occur between the vibronic ground states of \( n = 0 \) and \( m = 0 \). In DFT calculations, the electronic wave functions are calculated with energies \( E_g \) in the ground state and \( E_e \) in the excited state. We show the possible transitions to the first vibration quanta of \( m = 1 \) in the absorption and \( n = 1 \) in emission. \( q_g \) and \( q_e \) represent the coordinates of atoms in the electronic ground and excited states. The figure does not show the true scale for the sake of clarity.

The coordinates of those atoms where the defect wave functions are strongly localized, the above-mentioned derivative will be stronger for the local modes than for phonon-like modes. We use the following protocol in our analysis: (i) we monitor the localization of the single-particle electronic wave functions both in the \( ^3A_2 \) ground and \( ^3E \)-excited states and (ii) we monitor the localization of the vibrations at both electronic configurations. We argue that the coupling of a vibration in the absorption/emission process is most likely when both the electronic and vibration wave functions are localized the strongest to the defect in the final state of the absorption/emission process. The unpaired electrons are localized on the three yellow-colored C-atoms in the \( ^3A_2 \) ground state, while they are localized on these C-atoms and the nitrogen atom in the \( ^3E \) excited state; thus different local vibration modes may couple in absorption and luminescence by following our arguments.

There is another important issue that may significantly influence the absorption spectrum of the NV center. The final state is \( ^3E \) in the absorption process where one electron occupies a double degenerate \( e \) state (see figure 1). This system is principally a subject of the Jahn–Teller effect where the electron–phonon coupling is dramatically different from the case of the orbitally non-degenerate electronic states [39]. The decoupling of electronic and vibronic
functions is not valid any more (strong coupling limit), and the full wave function including both the electronic and vibration parts with equal footing has to be considered in the analysis of the excitation. Briefly, this full wave function is called vibronic function too.

We now discuss the experimental results using the aforementioned arguments. Davies and Hamer [27] carried out the absorption measurements at liquid nitrogen temperature (77 K), which corresponds to only a few meV in energy. Thus, one can assume that the optical transition started at the vibration ground state that transforms as $A_1^{\text{vib}}$, where ‘(vib)’ refers to the irreducible representation of the full vibration wave function in order to distinguish it from the irreducible representation of the electronic wave function. Electronic dipole transitions ($e\vec{r}$) will couple the electronic wave functions and do not act directly on the vibration functions. Thus, if the optical transition starts from the vibration ground state that always transforms as $A_1^{\text{vib}}$, then only $a_1$ vibration modes in the electronic excited state are allowed to couple in the first order because the full vibration function of this excited state will transform as $A_1^{\text{vib}}$ and all the other modes will give zero probability.

In our calculations, we identified the local vibration modes both in the ground and excited states as listed in table 1. In the excited state the 59.0 meV mode and the 76.9 meV mode transform as $a_1$. These modes may couple more strongly in the optical transitions than others that may cause peaky features in the absorption spectrum. Both modes are close to the experimental value of about 65 meV. Since the defect wave function is strongly localized both on nitrogen and carbon atoms nearest to the vacancy in $^3E$ state [11, 14], the nitrogen-related 59.0 meV mode can be a good candidate for the observed feature (first quantum of the local vibration mode) in the absorption spectrum. There is another nitrogen-related vibration mode at 63.9 meV that transforms as $e$ irreducible representation. Since the final state is orbitally degenerate in the absorption process this $E^{\text{vib}}$ vibration may couple in the transition. The vibronic function will transform as the direct product $E \otimes E^{\text{vib}} = A_1 \oplus A_2 \oplus E$ in the electronic excited state, but as $A_2 \otimes A_1^{\text{vib}} = A_2$ in the electronic ground state. By taking the $E$ vibronic state in the electronic excited state, the optical transition by light polarized perpendicular to the symmetry axis of the defect (transforms as $E$ under $C_{3v}$) will be allowed, because this transition can be described as $A_2 \otimes E \otimes E$ in group theory, which contains $A_1$; however, the light polarized parallel to the symmetry axis of the defect (transforms as $A_1$ under $C_{3v}$) is not allowed because this transition can be described as $A_2 \otimes A_1 \otimes E$ in group theory, which does not contain $A_1$. Coupling to the $a_1 \rightarrow A_1^{\text{vib}}$ vibration mode shows the same polarization properties as the vibronic $E$ state. Thus, the double peak in the absorption may be explained by the nitrogen-related $a_1$ and $e$ local vibration modes that are coupled strongly to the double degenerate $E$ electronic state. The energy difference between these vibration modes is close to the measured one. This finding is in line with a recent measurement showing the Jahn–Teller effect in the $^3E$ excited state [21].

In the luminescence process, the electron cools down to the vibration ground state (transforms as $A_1^{\text{vib}}$) of the $^3E$ electronic excited state. The final state is orbitally non-degenerate in the emission process; thus no coupling to the $e$ vibration mode is to be expected. There are two $a_1$ local modes that may contribute to the transition. We speculate that the 77.0 meV mode couples more strongly to this transition because the intensity of vibration is strongest on the three yellow carbon atoms where the unpaired electrons are mostly localized in the ground state [11, 14]. This will result in a single feature associated with this local vibration mode in the emission spectrum. This scenario may explain the asymmetry between the absorption and emission spectra of the NV center in diamond, which we summarize in figure 3.
5. Summary

We calculated the vibrations of the NV center in diamond under quasi-harmonic approximations by means of \textit{ab initio} supercell calculations. We found that the double peak in absorption may be explained by the double degenerate $e$ local vibration mode in the electronic excited state. This finding concurs with a recent measurement claiming the Jahn–Teller effect for the double degenerate electronic excited state.

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References

[1] Taylor J M, Cappellaro P, Childress L, Jiang L, Budker D, Hemmer P R, Yacoby A, Walsworth R and Lukin M D 2008 High-sensitivity diamond magnetometer with nanoscale resolution Nat. Phys. 4 810–6
[2] Degen C L 2008 Scanning magnetic field microscope with a diamond single-spin sensor Appl. Phys. Lett. 92 243111
[3] Maze J R et al 2008 Nanoscale magnetic sensing with an individual electronic spin in diamond Nature 455 644–7
[4] Balasubramanian G et al 2008 Nanoscale imaging magnetometry with diamond spins under ambient conditions Nature 455 648–51
[5] Rittweger E, Han K Y, Irvine S E, Eggeling C and Hell S E 2009 STED microscopy reveals crystal colour centres with nanometric resolution Nat. Photonics 3 144–7
[6] Wrachtrup J and Jelezko F 2006 Processing quantum information in diamond J. Phys.: Condens. Matter 18 S807–24
[7] Togan E et al 2010 Quantum entanglement between an optical photon and a solid-state spin qubit Nature 466 730–4
[8] Santori C et al 2006 Coherent population trapping of single spins in diamond under optical excitation Phys. Rev. Lett. 97 247401
[9] Manson N B, Harrison J P and Sellars M J 2006 Nitrogen-vacancy center in diamond: model of the electronic structure and associated dynamics Phys. Rev. B 74 104303
[10] Batalov A, Jacques V, Kaiser F, Siyushev P, Neumann P, Rogers L J, McMurtrie R L, Manson N B, Jelezko F and Wrachtrup J 2009 Low temperature studies of the excited-state structure of negatively charged nitrogen-vacancy color centers in diamond Phys. Rev. Lett. 102 195506
[11] Lenef A and Rand S 1996 Electronic structure of the NV center in diamond: theory Phys. Rev. B 53 13441–5
[12] Rogers L J, McMurtrie R, Sellars M and Manson N B 2009 Time-averaging within the excited state of the nitrogen-vacancy centre in diamond New J. Phys. 11 063007
[13] Goss J P, Jones R, Breuer S, Briddon P and Oberg S 1996 The twelve-line 1.682 eV luminescence center in diamond and the vacancy–silicon complex Phys. Rev. Lett. 77 3041
[14] Gali A, Fyta M and Kaxiras E 2008 \textit{Ab initio} supercell calculations on nitrogen-vacancy center in diamond: electronic structure and hyperfine tensors Phys. Rev. B 77 155206
[15] Larsson J A and Delaney P 2008 Electronic structure of the nitrogen-vacancy center in diamond from first-principles theory Phys. Rev. B 77 165201
[16] Hossain F M, Doherty M W, Wilson H F and Hollenberg L C L 2008 *Ab initio* electronic and optical properties of the N-V− center in diamond *Phys. Rev. Lett.* **101** 26403

[17] Gali A 2009 Identification of individual 13C isotopes of nitrogen-vacancy center in diamond by combining the polarization studies of nuclear spins and first-principles calculations *Phys. Rev.* B **80** 241204

[18] Ma Y, Rohlfling M and Gali A 2010 Excited states of the negatively charged nitrogen-vacancy color center in diamond *Phys. Rev.* B **81** 041204

[19] Delaney P, Greer J C and Larsson J A 2010 Spin-polarization mechanisms of the nitrogen-vacancy center in diamond *Nano Lett.* **10** 610–4

[20] Maze J R, Gali A, Togan E, Chu Y, Trifonov A, Kaxiras E and Lukin M D 2010 Group theory of defects: nitrogen-vacancy center in diamond arXiv:quant-ph/1010.1338

[21] Fu K-M C, Santori C, Barclay P E, Rogers L J, Manson N B and Beausoleil R G 2009 Observation of the dynamic Jahn–Teller effect in the excited states of nitrogen-vacancy centers in diamond *Phys. Rev. Lett.* **103** 256404

[22] Acosta V M, Bauch E, Ledbetter M P, Waxman A, Bouchard L-S and Budker D 2010 Temperature dependence of the nitrogen-vacancy magnetic resonance in diamond *Phys. Rev. Lett.* **104** 070801

[23] Acosta V M, Jarmola A, Bauch E and Budker D 2010 Optical properties of the nitrogen-vacancy singlet levels in diamond *Phys. Rev.* B **82** 201202

[24] Gali A, Janzén E, Deák P, Kresse G and Kaxiras E 2009 Theory of spin-conserving excitation of the N-V− center in diamond *Phys. Rev. Lett.* **103** 186404

[25] Lowther J E 2009 Local modes of vibration at the vacancy and vacancy models of defects in diamond *Comput. Mater. Sci.* **46** 520

[26] du Preez L 1965 PhD Dissertation University of Witwatersrand, Johannesburg

[27] Davies G and Hamer M F 1976 Optical studies of the 1.945 eV vibronic band in diamond *Proc. R. Soc. A* **348** 285

[28] Collins A T 1983 Luminescence decay time of the 1.945 eV centre in type Ib diamond *J. Phys. C: Solid State Phys.* **16** 2177

[29] Lowther J E 1984 The form of different charge states of the vacancy in diamond *J. Phys. Chem. Solids* **45** 127

[30] Loubser J H N and van Wyk J A 1977 *Diamond Res. (London)* **11** 4

[31] Redman D A, Brown S, Sands R H and Rand S C 1991 Spin dynamics and electronic states of N-V centers in diamond by EPR and four-wave-mixing spectroscopy *Phys. Rev. Lett.* **67** 3420

[32] Gali A 2010 Time-dependent density functional study on the excitation spectrum of point defects in semiconductors *Phys. Status Solidi b* doi:10.1002/pssb.201046254

[33] Blöchl P E 1994 Projector augmented-wave method *Phys. Rev.* B **50** 17953

[34] Kresse G and Joubert D 1999 From ultrasoft pseudopotentials to the projector augmented-wave method *Phys. Rev.* B **59** 1758

[35] Kresse G and Furthmüller J 1996 Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set *Phys. Rev.* B **54** 11169

[36] Paier J, Marsman M, Hummer K, Kresse G, Gerber I C and Ángyán J G 2006 Screened hybrid density functionals applied to solids *J. Chem. Phys.* **124** 154709

[37] Ceperley D M and Alder B J 1980 Ground state of the electron gas by a stochastic method *Phys. Rev. Lett.* **45** 566

[38] Perdew J P and Zunger A 1981 Self-interaction correction to density-functional approximations for many-electron systems *Phys. Rev.* B **23** 5048

[39] Watts R K 1977 *Point Defects in Crystals* (New York: Wiley-Interscience)