Towards \textit{ab initio} identification of paramagnetic substitutional carbon defects in hexagonal boron nitride acting as quantum bits

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Paramagnetic substitutional carbon (C$_B$, C$_N$) defects in hexagonal boron nitride (hBN) are discussed as candidates for quantum bits. Their identification and suitability are approached by means of photoluminescence (PL), charge transitions, electron paramagnetic resonance, and optically detected magnetic resonance (ODMR) spectra. Several clear trends in these are revealed by means of an efficient plane wave periodic supercell \textit{ab initio} density functional theory approach. In particular, this yields insight into the role of the separation between C$_B$ and C$_N$. In most of the cases the charge transition between the neutral and a singly charged ground state of a defect is predicted to be experimentally accessible, since the charge transition level (CTL) position lies within the band gap. \textit{A posteriori} charge corrections are also discussed. A near-identification of an experimentally isolated single spin center as the neutral C$_B$ point defect was found via comparison of results to recently observed PL and ODMR spectra.

I. INTRODUCTION

Single-photon emitters (SPEs) in semiconductors are the most attractive fundamental building blocks for novel quantum technologies such as quantum computing [1-6], quantum information distribution [1,5,7], quantum sensing [1,5,6], quantum photonics [7,9], quantum cryptography [2-4], hybrid spin-photon interfaces [8] and spin-mechanics interfaces [8].

To create more versatile structures an embedding material with a large band gap, such as diamond [10], is desirable, because atomic like defect states and levels isolated from the environment can be controlled. In particular, this control over the electronic configuration also concerns charge and spin. Another issue is to engineer the suitable atomic like defects for scalable quantum architecture where twodimensional (2D) materials offer a natural platform to this end.

Hence hexagonal boron nitride (hBN), an sp$^2$-bonded strongly covalent [8] layered van-der-Waals solid with indirect band gap at 5.955 eV [11] and excellent chemical and thermal stability [2,3] retaining the wide band gap in its exfoliated form [8], has recently emerged as a promising alternative [11,3,5,9,12]. It hosts a plethora of stable optically active defects with a broad emission range (1.2-5.3 eV [8]) and very high brightness, also at room temperature [5]. Moreover they exhibit additional favorable quantum-optical properties including narrow linewidth, high emission into the zero-phonon line (ZPL) and addressability via spin-selective optical transitions [7].

Recently, a breakthrough has been achieved by observing single spin resonance in hBN as spin-dependent fluorescence intensity, i.e., continuous-wave (cw) optically detected magnetic resonance (ODMR) measurements, where the electron spin resonance (ESR) spectrum was broadened by the interaction with the electron spin and the proximate nuclear spins of the host [12]. The origin of the single spin centers is unknown, in stark contrast to the other ODMR center in hBN [13] which is the negatively charged boron-vacancy defect [14,15]. The negatively charged boron-vacancy was proposed earlier as a quantum bit candidate by theory [16] which implies a strong predictive power of first principles calculations. With using the same theoretical approach, this study now focuses on the recently observed single spin centers with using the advantage that the observed ESR signals provide direct information about the spin density distribution of the defect in the paramagnetic ground state [12].

Generally the atomic structure of isolated optical emitters in hBN cannot be determined directly in experiments. This is due to the vast number of candidates, e.g. different complexes of substitutional carbon or oxygen atoms possibly with adjacent vacancies or antisites. However, simple models can be developed to capture the fundamental motifs before the identification of specific defects. Substitutional carbon defects are popular candidates, since they exhibit low formation energies [2] as well as high migration barriers [8] and carbon interstitials are highly mobile [1]. Indeed Mendelson et al. [7] recently found a direct correlation between the photoluminescence of visible SPEs ($E_{ZPL}=2.08-2.16$ eV upon 532-nm illumination) and implanted carbon surveying various samples grown via metalorganic vapor-phase epitaxy (MOVPE), molecular beam epitaxy (MBE) and highly oriented pyrolytic graphite (HOPG) conversion. Additionally they also associated the spin readout of room-temperature ODMR performed on MOVPE samples with the density of carbon-related quantum emitters which was varied from singles to ensembles. Their X-ray photospectroscopy (XPS) experiments yielded even more evidence for the presence of carbon point defects and complexes thereof. The neutral C$_B$C$_N$ dimer has been proposed to explain the ubiquitous 4.1-eV photoluminescence [9]. Since a stepwise change of ZPL energies has been reported for the single spin centers [12], not only isolated...
or adjacent point defects, but also structures with increased separation between C_B and C_N are analyzed. At a later stage the results might also be helpful for target-oriented engineering of charge transition level (CTL) positions in quantum technologies. We note that, parallel to our work, the optical signatures of neutral C_B and C_N pair and trimer configurations have been considered by first principles studies [11,12]. In our study, beside the optical signals, we systematically investigate CTLs associated with the photostability upon illumination and the ESR signals associated with ODMR spectra too, including charged C_B and C_N pair configurations that are paramagnetic in their ground state.

This paper is organized as follows. Section II elucidates the theoretical model. Section III discusses the results for substitutional carbon (C_B, C_N) defects focusing on paramagnetic structures. It successively elaborates on photoluminescence (Sec. IIIA), charge transition levels (Sec. IIIB) and cw EPR/ODMR spectra (Sec. IIIC). The results are summarized in Sec. III D. Finally, Sect. IV consolidates the implications for defect identification and quantum bit engineering, and it provides an outlook. The Supplemental Material [17] is a collection of data regarding hyperfine coupling and electronic electric field gradients (EFGs) at the atomic nuclei.

II. METHODOLOGY

The investigation is conducted within the framework of plane wave periodic supercell ab initio density functional theory (DFT) using the VASP package https://www.vasp.at/ [18,19]. The systems are intralayer defects and respective defect complexes consisting of one to three substitutional carbon atoms embedded in bulk hexagonal boron nitride (hBN). The bulk cells are hexagonal (8×8×1) cells. All calculations are performed for the Γ point.

Screened hybrid DFT, the modified Heyd-Scuseria-Ernzerhof (HSE) [20,21] with dispersion corrections, 32% exact exchange (instead of the original HSE06 at 25%), screening parameter ω = 0.2/Å is used to describe electronic structures and to calculate total energies. For the given supercell size it yields an indirect (direct) band gap of 5.950 eV (6.439 eV), which is almost identical to the experimental value of 5.955 eV [11] (6.42 eV [22]). Ions are relaxed only in the defective molecular layer as other deviations from the ideal bulk crystal geometry turned out to be negligible. It was found that it is more efficient to optimize the geometry of the systems with semilocal generalized gradient approximation DFT (PBE) [23,24] including dispersion corrections. Only the hybrid DFT lattice constants a = 2.487 Å and c = 6.459 Å have to be adjusted afterwards. They are ≤ 2% smaller than the experimental values [25]. Dispersions corrections (Grimme-D3 [26,27] with Becke-Johnson (BJ) damping [28]) are indispensable for an adequate treatment of the interlayer interaction and hence the determination of the distance (c/2) between adjacent layers.

The photoluminescence (PL) spectra are determined after the additionally required data have been obtained from two separate calculations [29]. The total energy and geometry of the excited state are obtained from a ΔSCF calculation [30]. We note that the ΔSCF method inherently contains the electron-hole interaction which is strong in hBN [31]. For singlets the ZPL energy is corrected as given in Ref. [11]. The ground state phonon modes are calculated on the aforementioned semilocal gradient DFT level, which is considered a reliable approximation drastically reducing the computational effort [11,18,13]. Again only the ions in the defective molecular layer are allowed to move. Furthermore the cw ODMR defect line broadening can also be accessed, since the hyperfine coupling for the most abundant nuclear spin active isotopes (11B, 14N, 13C) is analyzed with the aforementioned screened hybrid DFT [32,33]. The cw ODMR spectra are calculated based on this data employing the MATLAB toolbox EasySpin [34-36]. EasySpin can also take the nuclear Zeeman and quadrupole interaction into account. The electronic electric field gradients (EFGs) at the positions of the (quadrupolar) atomic nuclei (I ≥ 1) required for the latter are calculated with VASP [37]. The EFG matrix V is converted into the quadrupole matrix Q according to

\[ Q = \frac{e q_n}{2I(2I-1)} h V, \]

where q_n and I are the nuclear quadrupole moment and nuclear spin quantum number, respectively [38], and h is the Planck constant. This leads to \( Q(\text{MHz}) = 0.01636 V(\text{V}/\text{Å}^2) \) for 11B and \( Q(\text{MHz}) = 0.02471 V(\text{V}/\text{Å}^2) \) for 14N. Carbon atom has only non-quadrupolar isotopes.

The plane wave energy cutoff is 500 eV throughout. The energies are considered converged for differences of less than 0.01 meV. In the semilocal generalized gradient approximation DFT calculations the Hellmann-Feynman force components within the defective molecular layer are reduced to less than 5 meV/Å. The PL spectra were calculated with a Gaussian smearing of 5 meV.

The total energy of the charged systems, and hence the position of the charge transition levels (CTLs), is affected by a spurious contribution due to the interaction between the charge and its periodic images. Hence a posteriori charge corrections according to Freysoldt et al. [39,40] are applied for the charged bulk defects.

III. RESULTS

Chejanovsky et al. [12] recorded the PL spectrum of an isolated optical emitter (cf. Fig. 10) with \( E_{ZPL} = 1.71 \text{ eV} \) (cf. Tab. II) upon illumination by 633-nm (1.96-eV) laser. Its ground state has to be paramagnetic with non-integer spin as concluded based on ODMR (cf. Fig. 12) and photokinetics. Furthermore, the electronic spin density is es-
sentially out-of-plane and π-like as indicated by angular-
dependence and magnitude of the hyperfine coupling. We
concluded that paramagnetic substitutional carbon de-
fects with $S = 1/2$ spin states can satisfy these criteria
(see Fig. 5 for electronic structure). Since the abundance
of $I = 1/2$ $^{13}$C is low no hyperfine splitting due to the
carbon impurity is expected for the vast majority of the
spin centers.

With up to three adjacent carbon atoms there are six
basic ways to construct a paramagnetic defect (complex)
exhibiting paramagnetic $S = 1/2$ states: two neutral iso-
olated point defects ($C_B$, $C_N$), two singly charged dimers
($C_B C_N (+)$, $C_B C_N (-)$) and two neutral trimers ($C_2 C_B$, $C_2 C_N$) (cf. Figs. 1, 2 and 4 respectively). Starting
from the $C_B C_N$ dimer structures with larger separation
between the point defects are also investigated. These
are called “donor-acceptor pairs” (DAPs), because for
the neutral case an electron transfer resulting in a non-
paramagnetic structure ($C_B^+$ and $C_N^-$) is energetically fa-
vorable (see the text below as well as Secs. III A and
III B). The DAPs are labeled according to their separa-
tion in the ideal lattice with “1” being the dimer. The
five smallest separations are 1, 2, $\sqrt{7}$, $\sqrt{13}$, 4 (cf. Figs. 2
3).

We plot the in-gap Kohn-Sham levels of the neutral
defects in Fig. 5 The isolated neutral $C_B$ and $C_N$ de-
fects introduce a single defect level into the fundamental
band gap occupied by a single electron. The occupied
level of $C_B$ lies at higher energy than the empty level
of $C_N$, thus the electron transfer occurs from $C_B$ to-
wards $C_N$ when the defects are relatively close to each
forming DAP complexes as noted above. This reflects in
the calculated defect levels of DAP defects which show a
completely filled low-energy level (localized around $C_N$)
and an empty high-energy level (localized around $C_B$).
By combining three carbon defects, i.e., the considered
tramer complexes in our study, the electronic structure
shows the characteristic of the constituent defects. In
$C_2 C_B$-trimer, two low-energy defect levels appear local-
ized around $C_N$ atoms and a high-energy defect localized
around $C_B$ atom where the two low-energy defect levels
are occupied by three electrons. In $C_2 C_N$-trimer, rather
one low-energy defect level and two high-energy defect
levels appear in the gap occupied by three electrons.

The calculated binding energies are listed in Ta-
ble I. The donor-acceptor pairs are stabilized through
charge transfer from $C_B$ donor to $C_N$ acceptor which in-

![Figure 1](image1.png)
**Figure 1.** Substitutional carbon defects in hBN (part 1, neutral paramagnetic, from left to right): $C_B$, $C_N$; (B in ochre, N in cyan, C in purple)

![Figure 2](image2.png)
**Figure 2.** Substitutional carbon defects in hBN (part 2, singly charged paramagnetic, from left to right): $C_B C_N$-DAP-1 (dimer), $C_B C_N$-DAP-2, $C_B C_N$-DAP-$\sqrt{7}$; (B in ochre, N in cyan, C in purple, cf. text for DAPs)

![Figure 3](image3.png)
**Figure 3.** Substitutional carbon defects in hBN (part 3, singly charged paramagnetic, from left to right): $C_B C_N$-DAP-$\sqrt{13}$, $C_B C_N$-DAP-4; (B in ochre, N in cyan, C in purple, cf. text for DAPs)

![Figure 4](image4.png)
**Figure 4.** Substitutional carbon defects in hBN (part 4, neutral paramagnetic, from left to right): $C_2 C_B$-trimer, $C_2 C_N$-trimer; (B in ochre, N in cyan, C in purple)
volves Coulomb-interaction. As the attractive Coulomb-interaction increases with shorter distances the binding between C\textsubscript{B} and C\textsubscript{N} is stronger for pairs with shorter distances. The calculated binding energies clearly show this trend. We note that this looks to hold for the immediate C-C dimer defect but a C-C bond is created in that defect, and it cannot be described by the simple donor-acceptor pair model. Since the isolated carbon impurities introduce defect wavefunctions localized inside the host sheet and interlayer diffusion of carriers is hindered in hBN, complexes of carbon substitutional defects within a single sheet of hBN layer are considered in which we expect direct electron transfer between the constituting carbon defects. Certainly, different configurations of DAP and trimer complexes may occur in each hBN layer in multilayered hBN but we do not expect direct interaction between carbon defects residing in different layers of hBN.

### A. Photoluminescence

The ZPL energy \( E_{ZPL} \) is the first criterion for potentially identifying an experimentally isolated emitter. It has been calculated for all neutral systems and additionally also for the singly charged DAPs (cf. Tab. I). The theoretical values range from 0.44 eV to 4.13 eV. \( E_{ZPL} \) depends on the electronic structure of the defect (complex), in particular its states inside the band gap, and its ionic relaxation triggered via deexcitation resp. emission.

The first optical excitation of a neutral point defect either transfers the unpaired electron from the band gap to the conduction band minimum (C\textsubscript{B}, \( E_{ZPL} \)=1.695 eV, cf. Fig. I) or instead transfers another electron from the valence band maximum into its orbital (C\textsubscript{N}, \( E_{ZPL} \)=2.468 eV, cf. Fig. I). The former electron transfer is within the majority spin channel, while it is the minority spin channel for the latter. This behavior was obtained earlier by Jara et al. [I], but they gave no values for \( E_{ZPL} \).

Although the neutral point defects (C\textsubscript{B}, C\textsubscript{N}) are paramagnetic, their interaction leads to non-paramagnetic structures (C\textsubscript{B}C\textsubscript{N}-DAPs with “charge structure” C\textsuperscript{+}\textsubscript{B}-C\textsubscript{N}\textsuperscript{-}), because transferring the unpaired electron from C\textsubscript{B} to C\textsubscript{N} is energetically favorable. The CTLs C\textsubscript{B}(+1)0) and C\textsubscript{N}(0)-1 (cf. Tab. II) explain this for the limiting case of large separations. All numerical calculations at finite separations yielded the same behavior. Each C\textsubscript{B}C\textsubscript{N}-DAP exhibits two orbitals inside the band gap. The lower one is fully occupied and localized at C\textsubscript{N}, while the higher one is empty and localized at C\textsubscript{B}. The energy difference between them diminishes with increasing separation corroborating the results of Linderälv et al. [8].

\( E_{ZPL} \) of the neutral C\textsubscript{B}C\textsubscript{N}-DAPs diminishes with separation (cf. Tab. I) as expected in view of the previous findings. The neutral C\textsubscript{B}C\textsubscript{N} dimer has been proposed to explain the ubiquitous 4.1-eV photoluminescence [9]. The calculated \( E_{ZPL} \)=4.13 eV is consistent with that and agrees well with the hybrid DFT (HSE) results of Mackoit-Sinkevičien˙e et al. (4.31 eV in Ref. 9), who also employed a bulk model, and Jara et al. (4.12 eV in Ref. I), who employed a single layer model instead. On the contrary the underlying gradient DFT (PBE) is not sufficient to reproduce this result as found by Linderälv et al. (3.34 eV in Ref. [8]).

\( E_{ZPL} \) of both singly charged C\textsubscript{B}C\textsubscript{N}-DAPs increases with separation (cf. Tab. II). It seems to approach a value equal, or at least similar, to that of the respective isolated neutral (paramagnetic) point defect. This convergence behavior had to be expected, because it turned out that the lowest optical excitation is linked to the same electronic transition as for the isolated neutral point defect. Hence the influence of the charged (non-paramagnetic) point defect vanishes with separation. The aforementioned Jara et al. [I] also found that \( E_{ZPL} \) of the singly

| Defect       | Binding energy (eV) |
|--------------|---------------------|
| C\textsubscript{B}C\textsubscript{N}-DAPs |                     |
| 1            | -3.93               |
| 2            | -2.04               |
| \( \sqrt{7} \) | -1.90               |
| \( \sqrt{13} \) | -1.52               |
| 4            | -1.49               |
| trimers      |                     |
| C\textsubscript{2}C\textsubscript{B} | -5.31               |
| C\textsubscript{2}C\textsubscript{N} | -5.28               |

Figure 5. Calculated Kohn-Sham defect levels for neutral carbon defects in the fundamental band gap of hBN. DAP refers to the C\textsubscript{B}C\textsubscript{N}-DAP donor acceptor pair defects. The spinpolarized calculation introduces a gap between the occupied (filled triangle) and unoccupied (empty triangle) defect levels.

Table I. The calculated binding energy of neutral carbon complexes within a layer of hBN. The negative binding energy refers to the favor of complex formation.
charged dimers is too low for the visible range.

Placing a point defect (C_B or C_N) adjacent to the dimer (C_BCN, abbreviated as C_2) creates a basic trimer (C_2C_B or C_2C_N with the desired S = 1/2 paramagnetic ground state, cf. Fig. 4). E_{ZPL} of the neutral basic trimers (1.36 eV for C_2C_B, 1.62 eV for C_2C_N) is lower than that of their neutral “building blocks” point defect and dimer (cf. Tab. I). This is essentially due to the (overlap of) additional states inside the band. Jara et al. [11] obtained a similar value for C_2C_N (1.62 eV), but a clearly higher one for C_2C_B (1.65 eV). The origin of the discrepancy in the latter is unclear.

Beside the characteristic ZPL emission line (cf. Figs. 6, 7, 8, and 9), the most intense feature in the phonon sideband (PSB) always exhibited an energy detuning of 0.15-0.17 eV with respect to ZPL peak, except for the neutral dimer (0.20 eV). The intensity of its replica decreases with the number of quanta. Linderälv et al. [8] obtained similar results including a mostly somewhat larger PSB energy detuning of 0.18-0.20 eV for the neutral points defects and DAPs. According to them, these phonons are slightly distorted high-frequency in-plane modes of the ideal lattice, which would be at 0.15 eV, with the only exception (local mode) being the dimer (C-C bond). The present results are corroborated by Jara et al. [11], who report 0.20 eV resp. 0.16 eV for neutral C_BCN resp. C_2C_N and ascribe both to a local vibration mode. They also mention values in the same range for other substitutional carbon defects. Experimental PL spectra with similar features have been recorded by various groups [6, 7, 12, 11]. E.g. Mendelson et al. [7] recently observed several emitters with E_{ZPL}=2.08-2.16 eV and 0.16-0.20 eV PSB energy detuning upon illumination by 532-nm (2.33-eV) laser. The characteristics of the ODMR spin readout are in line with those found in a previous report [12] giving evidences for their connection to carbon-related defects although using a longer excitation wavelength (at least 594 nm or 2.09 eV) insufficient for exciting all of these emitters. Hence the singly positive C_BCN-DAPs at larger separations (at least √7, cf. Tab. I) may explain the observations if the defect ground state spin is S = 1/2.

Fig. 10 compares the PSBs of optical emitter D_1, which was experimentally isolated by Chejanovsky et al. [12], to those of the candidates for its identification. D_1 has E_{ZPL}=1.71 eV with a very similar PSB to the calculated ones and is paramagnetic with half-integer spin. We note that the other reported single photon emitters with longer wavelength ZPLs than that of 1.71-eV D_1 center in Ref. [12] have different PL lineshape, so the characteristic PSBs are distinct from that of D_1. On the other hand, all the considered carbon substitutional defects have very similar PSB features. Thus our paper now focuses on the identification of D_1 center and it is beyond the scope to identify the other single photon emitters.

An error of 0.2 eV was allowed to take any kind of inaccuracy into account when the D_1 ZPL energy is compared to the calculated ZPL energies. Hence the present study provides four candidates: C_B(0), C_BCN-DAP-2(+), C_BCN-DAP-4(-), C_2C_B(0) (cf. Tab. I). We note that we often anticipate an accuracy of about 0.1 eV for the calculated ZPLs. Here we expect a larger error for some of the considered defects as excitation to band edges is involved in the excited state which is a subject of finite size error for the neutral defects. Tests on C_B defect shows that the calculated E_{ZPL} increases by about 0.12 eV going from 8 × 8 × 1 to 11 × 11 × 1 supercell. Nevertheless, we provide the calculated ZPL energies within meV throughout the paper which is technically convergent in terms of the given supercell size (8 × 8 × 1) and DFT functional.

| Defect          | E_{ZPL} (eV) |
|-----------------|-------------|
| C_B(0)          | 1.695       |
| C_N(0)          | 2.468       |
| C_BCN-DAPs (+)  | 2.229       |
| C_BCN-DAPs (0)  | 1.547       |
| C_BCN-DAPs (−)  | 1.525       |
| √3              | 2.194       |
| √7              | 2.018       |
| 2               | 1.814       |
| 1 (dimer)       | 1.055       |
| 4               | 4.131       |
| Trimmers        |             |
| C_2C_B(0)       | 1.360       |
| C_2C_N(0)       | 1.623       |
| Emitter D_1     | 1.71        |

Figure 6. Calculated photoluminescence (PL) spectrum for the neutral point defects (C_B and C_N, cf. Fig. 1) and basic trimers (C_2C_B and C_2C_N, cf. Fig. 4) in bulk hBN.
Figure 7. Calculated photoluminescence (PL) spectrum for the five closest neutral DAPs (cf. Figs. 2 and 3) in bulk hBN

Figure 8. Calculated photoluminescence (PL) spectrum for the five closest singly positive DAPs (cf. Figs. 2 and 3) in bulk hBN

Figure 9. Calculated photoluminescence (PL) spectrum for the five closest singly negative DAPs (cf. Figs. 2 and 3) in bulk hBN

Figure 10. Comparing calculated phonon sidebands (PSBs) of candidates (cf. Figs. 1-4) for identification of optical emitter D$_1$ experimentally isolated by Chejanovsky et al. [12] in hBN

### B. Charge transition levels

To modify the charge state of a specific defect $X$ it has to be understood how it depends on the Fermi level $E_F$. The transition between two charge states happens at the CTL position $E_{F^{CT}}$ where they are equally favorable. The defect charge $q$ can be modified accordingly if this transition is between the two most stable states and $E_{F^{CT}}$ lies within the band gap.

The CTLs between neutral and singly charged ground states with respect to valence band maximum ($\epsilon_{VBM}$) are calculated as

$$E_{F(X)}^{CT(+1|0)} + \epsilon_{VBM} = E_{0(X)}^0 - E_{0(X)}^{+1} - \Delta_{+1}(X)$$

$$E_{F(X)}^{CT(0|-1)} + \epsilon_{VBM} = E_{0(X)}^{-1} - E_{0(X)}^{0} + \Delta_{-1}(X)$$

(2)

where $E_{0(X)}^q$ is the total energy of the defect $X$ with charge $q$ and $\Delta_q(X)$ is the charge correction. We note that we believe that the threedimensional model corresponds to the experimental conditions where the defects were found in multilayer hBN on a substrate which introduce a charge screening.

Tab. III summarizes the CTL positions. All uncorrected CTLs lie within the band gap as displayed in Fig. 11. C$_N^{(+1|0)}$ resp. C$_B^{(0|-1)}$ is closest to the VBM.
resp. CBM. Since the charge structure of the neutral DAPs is \(C_{\text{B}}^{2}\) it is possible to either add an electron to \(C_{\text{B}}^{2}\) or to remove an electron from \(C_{\text{N}}\) in the presence of the other charged point defect. Hence \(C_{\text{B}}C_{\text{N}}^{(+1|0)}\) resp. \(C_{\text{B}}C_{\text{N}}^{(0|-1)}\) converges to \(C_{\text{N}}^{(0|-1)}\) resp. \(C_{\text{B}}^{(+1|0)}\) with increasing separation. Meanwhile \(C_{\text{B}}C_{\text{N}}^{(+1|0)}\) is raised whereas \(C_{\text{B}}C_{\text{N}}^{(0|-1)}\) is lowered. This is not only due to the diminishing, and finally vanishing, stabilizing effect of the Coulomb interaction between the charged point defects on the neutral ground state (cf. Eq. (2)). It is also due to the decreasing energy difference between the orbitals involved in the charge transitions (highest occupied at \(C_{\text{N}}\) and lowest empty at \(C_{\text{B}}\)). As a consequence of this a “forbidden region” in which the Fermi level \(E_{\text{F}}\) can be modified without affecting the charge of the point defects and DAPs exists between \(C_{\text{N}}^{(0|-1)}\) and \(C_{\text{B}}^{(+1|0)}\). The CTLs have also been calculated for the basic trimers \(C_{2}\text{C}_{\text{B}}\) and \(C_{2}C_{\text{N}}\). \(C_{2}C_{\text{B}}^{(+1|0)}\) and \(C_{2}C_{\text{N}}^{(0|-1)}\) are similar to those of the isolated point defects without the “additional dimer” \(C_{2}\), whereas \(C_{2}C_{\text{B}}^{(0|-1)}\) and \(C_{2}C_{\text{N}}^{(+1|0)}\) resemble those of \(C_{2}\).

The charge corrections stabilize the charged systems by several hundreds of meV (cf. Tab. III) but the expected trend of convergence is not obvious for the corrected CTLs (cf. Fig. 11).

Note that similar values for the corrected CTL positions of point defects and dimer were found by Mackoiti-Sinkevičienė et al. 4, while Weston et al. 2 3 also give a similar value for \(C_{\text{B}}^{(+1|0)}\) but a somewhat lower one for \(C_{\text{N}}^{(0|-1)}\). Just like in this work both employed a bulk model, hybrid DFT and charge corrections according to Freysoldt et al. 39 40.

### Table III. Charge transition levels (CTLs) of substitutional carbon defects in bulk hBN relative to the valence band maximum (VBM) obtained from screened hybrid DFT with (and without) a posteriori charge corrections 39 40 (cf. text and Fig. 11)

| Defect        | CTL(+1|0) (eV) | CTL(0|-1) (eV) |
|---------------|--------------|---------------|
| \(C_{\text{B}}\) | 3.81 (4.11)  | 6.39 (5.79)   |
| \(C_{\text{N}}\) | 0.21 (0.47)  | 3.27 (2.72)   |
| \(C_{\text{B}}C_{\text{N}}\)-DAPs |           |               |
| 1             | 0.85 (1.13)  | 5.99 (5.42)   |
| 2             | 1.73 (2.01)  | 5.25 (4.68)   |
| \(\sqrt{3}\)  | 2.02 (2.31)  | 5.10 (4.53)   |
| \(\sqrt{13}\)| 2.29 (2.57)  | 4.81 (4.23)   |
| 4             | 2.37 (2.65)  | 4.77 (4.20)   |
| Trimmers     |              |               |
| \(C_{2}\text{C}_{\text{B}}\) | 3.66 (3.94)  | unclear (5.40) |
| \(C_{2}\text{C}_{\text{N}}\) | 0.71 (0.98)  | 3.29 (2.72)   |

*green*: outside the indirect band gap (above the conduction band minimum (CBM)), *blue*: close to the CBM, *orange*: most likely above the CBM (too large oscillations in potential alignment)

Figure 11. Charge transition levels (CTLs) of substitutional carbon defects in bulk hBN relative to the valence band maximum (VBM) obtained directly from screened hybrid DFT (light green (point defects) and dark green (complexes)) and with a posteriori charge corrections (light blue (point defects) and dark blue (complexes)) 39 40 (cf. text and Tab. III).

### C. cw ODMR spectra

The cw ODMR spectrum, in particular the line shape resp. broadening, serves as a further criterion for identifying experimentally isolated emitters. It has been analyzed for all ground state \(S = 1/2\) systems (doublets), i.e. the neutral point defects and basic trimers as well as the singly charged DAPs (see also 17).

The theoretical ODMR spectra are mostly obtained based on a simplified spin Hamiltonian \(H = H_{\text{EZI}} + \sum_{k} H_{\text{HFI}}(k)\) taking into account the interaction of the unpaired electron with the external magnetic field \(B\) (electron Zeeman interaction \(H_{\text{EZI}}\) and the spins of the nuclei \(k\) (hyperfine interaction \(\sum_{k} H_{\text{HFI}}(k)\)). In the chosen approximation they are determined by the external magnetic field \(B\) (assuming a gyromagnetic tensor \(g = 2 \times 1_{3}\) for the electron), the isotopic composition and the associated hyperfine matrices \(A(k)\) from hybrid DFT. The hyperfine parameters are calculated for the most abundant nuclear spin active isotopes \((^{11}\text{B},^{14}\text{N},^{13}\text{C})\). Since nuclear spin active carbon is rare \((^{13}\text{C} of 1.1\%)\), it is assumed that only boron \((^{11}\text{B} of 80.1\%)\) and nitrogen \((^{14}\text{N}\ of 99.6\%)\) contribute to the hyperfine splitting. For the neutral point defects and singly charged DAPs up to second neighbors \((d=\sqrt{3})\) of the paramagnetic carbon atom carrying the unpaired electron are taken into account. For the neutral basic trimers those of each carbon atom were chosen instead. The results and the justification of the underlying assumptions are discussed in the following.

We also considered a full spin Hamiltonian for test cases, e.g., \(C_{\text{B}}\) defect, which reads as

\[
H = H_{\text{EZI}} + \sum_{k} (H_{\text{HFI}} + H_{\text{NZI}} + H_{\text{NQI}})(k), \tag{3}
\]

which includes \(H_{\text{NZI}}\) nuclear Zeeman-term and \(H_{\text{NQI}}\) nuclear quadrupole term too. The terms can be in Eq. 3.
expressed as
\[
\hat{H}_{\text{EZI}} = \mu_B \mathbf{B}^T \mathbf{g} \hat{\mathbf{S}}
\]
\[
= \mu_B \begin{pmatrix} B_x & B_y & B_z \end{pmatrix} \begin{pmatrix} 2 & 2 & 2 \\ 2 & 2 & 2 \end{pmatrix} \begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix}
\]
\[
= 2\mu_B (\mathbf{B} \cdot \mathbf{S})
\]
\[
\hat{H}_{\text{HF1}}(k) = \hbar \mathbf{S}^T A(k) \hat{\mathbf{I}}_k
\]
\[
\hat{H}_{\text{NQI}}(k) = \hbar \hat{\mathbf{I}}_k^T Q(k) \hat{\mathbf{I}}_k,
\]
where \( \mu_B \) and \( \mu_k \) are the Bohr-magneton of the electron and nuclei \( k \), \( g_k \) and \( Q(k) \) are the gyromagnetic factor and quadrupole moment of nuclei \( k \). In terms of broadening of the ESR signal, the most important parameter is the hyperfine tensor \( A(k) \) for nuclei \( k \). We will show that \( \hat{H}_{\text{NQI}} \) and \( \hat{H}_{\text{NQI}} \) can be typically neglected at zero magnetic fields, although, \( \hat{H}_{\text{NQI}} \) can contribute to the final shape of the ESR or ODMR spectrum coming from the \( ^{14}\text{N} \) nuclei spins.

Table IV summarizes the calculated line broadening and peak positions at an external magnetic field of 42 Gauss as used for the ODMR measurement of D1 spin center (cf. Fig. 12 and Ref. 12). The line broadening FWHM\(_{\text{(Gauss)}} = 2\sqrt{2\ln(2)}\sigma_\nu \) is defined as the FWHM of a Gaussian normal distribution with the same standard deviation \( \sigma_\nu \). The original peak position due to the electron Zeeman interaction is at 118 MHz (cf. Tab. IX). The asymmetric influence of the hyperfine interaction induces a defect-dependent blueshift of up to 15 MHz. Neutral C\(_{N}(0)\) exhibits a much larger line broadening (74 MHz) than neutral C\(_{B}(43 \text{ MHz})\) as expected in view of the hyperfine constants (cf. Tabs. V and VI and 17). The underlying reason is that the gyromagnetic ratio of the boron isotope \((\gamma_B/2\pi = 1366 \text{ Hz/Gauss for } ^{11}\text{B})\), which is a first neighbor of the paramagnetic carbon for C\(_{B}\) but only a second neighbor for C\(_{N}\), is more than four times larger than that of the nitrogen isotope \((\gamma_N/2\pi = 308 \text{ Hz/Gauss for } ^{14}\text{N})\). In view of the charge structure the line broadening of the singly positive resp. negative DAP has to converge to that of neutral C\(_{N}\) resp. C\(_{B}\) with increasing separation. While no unambiguous trend is found for the former, the presence of the charged point defect increases it for the latter. The line broadening of the basic trimers is smaller than that of the corresponding point defect without the adjacent dimer. We note that the C\(_2\)C\(_N\) defect create a dense eigenvalue spectrum of the spin Hamiltonian with contribution of 14 nuclear spins which will result in a relatively smooth ODMR spectrum in the simulation.

The experimental ODMR spectrum of D1 is compared to those calculated for the defect identification candidates C\(_B(0)\), C\(_B\)C\(_N\)-DAP-2(+-), C\(_B\)C\(_N\)-DAP-4(--), C\(_2\)C\(_N\)(0) (cf. Fig. 12). It is concluded that D1 has to be either C\(_B(0)\) or at least a very similar structure where the spin density is localized around C\(_B\). As previously discussed the theoretical model fulfills the conditions found by Che-
The hyperfine parameters include the contribution of the spin polarization of the core electrons to the Fermi contact interaction. Tab. VII takes neutral C\textsubscript{N} as an example to show that this contribution can be significant, in particular if the carbon is nuclear spin active. Without it Sajid et al. \cite{14} found hyperfine constants in reasonable agreement employing a 2D model and the regular HSE06 functional. Our calculations imply that the core polarization should be included in the calculations of accurate hyperfine tensors.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
 & \(A_{xx}\) & \(A_{yy}\) & \(A_{zz}\) \\
\hline
total & \(d(C_B)\) & MHz & MHz & MHz \\
\hline
C & 1 & 0 & 12.1 & 12.1 & 231.3 \\
N & 3 & 1 & -9.0 & -5.1 & -9.0 \\
B & 6 & \(\sqrt{3}\) & 1.4 & -0.9 & 6.1 \\
\hline
\end{tabular}
\caption{Hyperfine constants \((A_{xx}, A_{yy}, A_{zz})\) of the neutral \(C_B\) point defect in bulk hBN up to second neighbors obtained from screened hybrid DFT \(# := \text{numbers of atoms}, d := \text{distance within ideal lattice}\).}\label{tab:V}
\end{table}

The influence of the isotopic composition on the ODMR spectra of the point defects (see Tabs. VII and VIII) was analyzed, because \(^{10}\text{B}\) is also significantly abundant (19.9\%). Replacing \(^{11}\text{B}\) with \(^{10}\text{B}\) gradually reduces the line broadening, because the hyperfine matrices scale linearly with the nuclear gyromagnetic factor \((g_n = 0.600 \text{ instead of 1.792})\) although the nuclear spin is increased \((I = 3 \text{ instead of 3/2})\). \cite{14} This effect is more pronounced for neutral \(C_N\), since the boron isotopes are first neighbors of the paramagnetic carbon. In this case it also affects the peak center which is slightly redshifted. Considering only \(^{11}\text{B}\) is usually a good approximation, since large changes of the ODMR spectra (dominant contribution of \(^{10}\text{B}\)) are unlikely to be observed at the natural distribution of isotopes.

The peak broadening is essentially determined by the hyperfine interaction and the simplified spin Hamiltonian (evaluated with second-order perturbation theory) yields already a good approximation of the ODMR spectra. This is demonstrated using the most basic example of the neutral point defects \(C_B\) and \(C_N\). However it has to be kept in mind that a comprehensive discussion of the full spin Hamiltonian is beyond the scope of the present study. Tab. IX summarizes the results for line broadening and peak center position obtained from different approaches. Further simplifying the spin Hamiltonian via using only the hyperfine constants, instead of the full hyperfine tensor \(A\) is not justified. It leads to a significant overestimation of the line broadening, in particular for \(C_N\) (38 MHz) whose peak center is additionally redshifted (5 MHz). Since second-order perturbation theory cannot be combined with exact diagonalization for specific nuclei in the code, first-order perturbation theory is also considered. Since the \(C_N\) peak center is redshifted by 14 MHz, this seems to be a non-accurate approach. Exact diagonalization allows to include the nuclear Zeeman interaction and additionally the nuclear quadrupole interaction, which have an indirect effect on the electronic transitions as the HFI couples the electronic spin to the nuclear spins. Due to computational expense which scales exponentially with the number of spins in the Hilbert space it was performed only for the first (1st) neighbors of the respective point defect. Including the NZI reverses the 14 MHz redshift of the \(C_N\) peak center. However this might also be related to the underlying change of the algorithm to solve the spin Hamiltonian. Note that the NZI leads to core transition peaks in a low frequency range (<30 MHz) that was not included in the calculation of peak center and line broadening. Judging from Fig. 13 the NZI can still have a non-negligible effect on the spectral shape although peak center and line broadening are hardly affected (cf. Tab. IX). Indeed the entries of the Q matrices (cf. Eqs. 1 and 3 and 17) are \(\leq\)1MHz. Hence the line splittings induced by the NZI can only be correspondingly small. However it can also induce significant intensity redistribution explaining its importance in the given context. The results for \(C_B\) are further evidence for its near-identification as experimentally isolated optical emitter \(D_1\).

\section{Summary}

Paramagnetic substitutional carbon defects in hexagonal boron nitride have been characterized via modeling their photoluminescence spectra, charge transition levels and cw ODMR spectra. Clear trends in all of these were found by analyzing the separation between \(C_B\) and \(C_N\). Furthermore a near-identification of an experimentally isolated optical emitter \(D_1\) as neutral \(C_{13}\) is given.

\[ E_{ZPL} = 1.695 \text{ eV (2.468 eV)} \] was obtained for neutral \(C_{13}\).
Table VI. Hyperfine constants \( (A_{xx}, A_{yy}, A_{zz}) \) of the neutral C\(_N\) point defect in bulk hBN up to second neighbors obtained from screened hybrid DFT \((A_{1c} := \text{core contribution}, () := \text{value without} A_{1c}, \# := \text{numbers of atoms}, d := \text{distance within ideal lattice}, \text{cf. text and Fig. } 1)\)

|   | \# | \(d(\text{C}_N)\) | \(A_{xx}\) (MHz) | \(A_{yy}\) (MHz) | \(A_{zz}\) (MHz) | \(A_{1c}\) (MHz) |
|---|---|---|---|---|---|---|
| C | 1 | 0 | -19.2 (44.8) | -19.2 (44.8) | 156.5 (220.5) | -64.0 |
| B | 3 | 1 | -17.9 (-16.7) | -16.0 (-14.8) | -24.5 (-23.3) | -1.2 |
| N | 6 | \(\sqrt{3}\) | -0.2 (0.8) | -0.8 (0.1) | 2.4 (3.4) | -1.0 |

Table VII. Calculated effect of the isotopic composition on ODMR line broadening FWHM (and peak center \(\nu\)) for the neutral C\(_B\) point defect in bulk hBN at an external magnetic field of 42 Gauss (boron isotopes are 2nd neighbors \(d = \sqrt{3}\) of \(\text{C}_B\), \(p := \text{abundance of isotopic composition}\))

| \((^{11}\text{B})\) | \((^{10}\text{B})\) | \(p(\%)\) | \(\nu\) (MHz) | FWHM (MHz) |
|---|---|---|---|---|
| 6 | 0 | 26.41 | 119 | 43 |
| 5 | 1 | 39.37 | 119 | 41 |
| 4 | 2 | 24.45 | 119 | 39 |
| 3 | 3 | 8.10 | 119 | 37 |
| 2 | 4 | 1.51 | 119 | 34 |
| 1 | 5 | 0.15 | 119 | 32 |
| 0 | 6 | 0.01 | 119 | 29 |

Table VIII. Calculated effect of the isotopic composition on ODMR line broadening FWHM (and peak center \(\nu\)) for the neutral \(\text{C}_N\) point defect in bulk hBN at an external magnetic field of 42 Gauss (boron isotopes are 1st neighbours \((d = 1)\) of \(\text{C}_N\), \(p := \text{abundance of isotopic composition}\))

| \((^{11}\text{B})\) | \((^{10}\text{B})\) | \(p(\%)\) | \(\nu\) (MHz) | FWHM (MHz) |
|---|---|---|---|---|
| 3 | 0 | 51.39 | 132 | 74 |
| 2 | 1 | 38.30 | 129 | 66 |
| 1 | 2 | 9.52 | 126 | 57 |
| 0 | 3 | 0.79 | 123 | 45 |

\((\text{C}_N)\) which are approximate values due to the finite size effects and the accuracy in the applied DFT functional. \(E_{\text{ZPL}}\) of the singly negative (positive) \(\text{C}_B\text{C}_N\)-DAP converges to this, or at least a similar, value from below with increasing separation. This behavior is explained based on the relevant electronic transition and the charge structure. The result for the neutral dimer \((\text{C}_B\text{C}_N\), \(E_{\text{ZPL}}=4.131\text{ eV}\)\), which allegedly causes the ubiquitous 4.1-eV photoluminescence [9], is consistent with previous hybrid DFT results [1, 9]. \(E_{\text{ZPL}}\) of the neutral \(\text{C}_B\text{C}_N\)-DAPs has to decrease with separation due to the position of the states inside the band gap (see also [8]). Each basic trimer has a lower \(E_{\text{ZPL}}\) than its “building blocks” point defect and dimer as expected in view of the overlap of their states inside the band gap. An intense feature in PSB next to ZPL at 0.15-0.17 eV (except for the neutral dimer at 0.20 eV) was found for all defects. Similar results were obtained in theoretical [1, 8] as well as experimental [6, 7, 12, 41] studies. In particular ODMR experiments yielded evidences for the connection of these features to carbon-related defects [7, 12]. Four candidates for the identification of \(D_1\) spin center were provided based on the agreement with the ZPL energies within 0.2 eV accuracy.

The cw ODMR spectra for all ground state \(S = 1/2\) systems have been calculated at 42 Gauss external magnetic field based on a simplified spin Hamiltonian. The
asymmetric influence of the hyperfine interaction induces a defect-dependent blueshift of the peak positions from 118 MHz up to 133 MHz. C\textsubscript{N} exhibits a much larger line broadening than C\textsubscript{B} due to the hyperfine parameters. Replacing \textsuperscript{11}B with the less abundant \textsuperscript{10}B reduces the peak width and can also shift the peak center. However, large changes are unlikely to be observed at the natural distribution of isotopes. The charge structure explains the convergence of the line broadening of the singly charged C\textsubscript{B}C\textsubscript{N}-DAPs.

The calculated ZPL energy and PSB as well as the ESR spectrum strongly implies that C\textsubscript{B} is involved as spin-active part of the D\textsubscript{1} spin center, and it could be the isolated neutral C\textsubscript{B} defect. Measuring the ODMR splitting due to \textsuperscript{13}C isotope would provide further insight about the chemical composition of D\textsubscript{1} or other emitters.

An exemplary analysis of the point defects demonstrates that the ODMR line broadening is essentially due to hyperfine interaction. The simplified spin Hamiltonian together with second-order perturbation theory results in a good approximation of the spectra. Using only the hyperfine constants, i.e. neglecting the Euler angles, is not appropriate as it leads to a large overestimation of the line broadening. A hybrid approach allowed to include the nuclear Zeeman and additionally the quadrupole interaction for the first neighbors. The line broadening remained essentially unaffected. Nuclear quadrupole interaction is important for an exact description of the spectral shape as it can lead to non-negligible modifications of the intensities but it does not effect the overall broadening of the ESR signal.

**IV. CONCLUSIONS AND OUTLOOK**

The modeling of PL and ODMR spectra has yielded helpful criteria for the identification of paramagnetic substitutional carbon defects in hBN. An example for a near-identification as neutral C\textsubscript{B} has been given. The separation between C\textsubscript{B} and C\textsubscript{N} emerged as key to control the ZPL wavelength and charge compensation of defects. All findings are further steps towards the identification of these structures and later their target-oriented engineering as quantum bits.

It is demonstrated that first principles theory is able to predict the complex electron spin resonance spectrum of defects in hBN. It has been found that the full hyperfine tensor of the nuclei is required to accurately determine the linewidth and the central position of the ODMR signal at a given external magnetic fields. As direct measurement of the full hyperfine tensors is challenging our results demonstrate that the accurate interpretation of ESR and ODMR signals in hBN requires a tight cooperation between experimental and \textit{ab initio} theoretical spectroscopy.

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