

Towards an accurate electronic structure of single photon emitters in hexagonal boron nitride

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Understanding single photon emission from defects in hexagonal boron nitride (h-BN) is an essential yet challenging step towards further utilizing the material as a room-temperature quantum device. Here, we systematically examine potential luminescence candidates in h-BN using the full configuration interaction quantum Monte Carlo approach. With such a high-level treatment of electron correlation, we can finally determine the electronic states of all the defects studied, revealing high-spin ground states for quantum manipulation and correcting previous misunderstandings. Furthermore, by computing the low-lying electronic states and analyzing the corresponding many-body wave functions, we identify two potential sources for the mysterious luminescence band in the visible region, including a doublet-doublet transition. Our calculations shed light on the intricate correlated electronic states of single photon emitters in h-BN, and establish a reliable theoretical foundation for addressing other challenges beyond the electronic structure.

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Hexagonal boron nitride (h-BN) is a van der Waals material with a wide band gap of 6 eV [1], making it a promising platform in quantum technologies [2–5]. Point defects in h-BN with addressable spin states are the most promising for quantum computing and sensing [6–9]. Over the past decade, many experimental measurements have observed emission signals in h-BN, especially a band in the visible region, ranging from 1.5 to 2.5 eV [10–16] and a band in the ultraviolet region, around 4 eV [17–20]. Proposals have been made to assign experimental signals to various point defects, including intrinsic defects such as vacancies and atomic substitutions [10,13,21], as well as impurity elements such as carbon [15,16,20,22]. However, a significant challenge lies in the lack of direct measurements of isolated defects in h-BN. Consequently, current proposals depend heavily on theoretical calculations and analyses, leading to a lack of consensus in the field, as Fig. 1 shows [23–30]. The difficulty of the identification of spin states is a major obstacle for designing h-BN based quantum technologies.

Unfortunately, theoretical calculations and analyses have their limitations, especially when dealing with complex systems that encompass various theoretical aspects, such as electronic correlation, electron-phonon coupling, and spin-orbital coupling [9]. In particular, strong electron correlation is considered to be a major obstacle to approaching the exact theoretical description of quantum emitters in h-BN [8,23,30,31]. These emitters often possess multiple energy levels within the band gap, facilitating the formation of multiple spin states. Currently, most theoretical studies have relied on the mean-field treatment of the electronic structure such as the density functional theory (DFT), which approximates the many-body wave function of spin states with a single Slater determinant. In DFT, electron correlation effects are approximated through the selected exchange-correlation functional. Therefore, their accuracy is functional dependent and different functionals can yield entirely different ground states [23,24,26–30]. More accurate theoretical treatments beyond DFT are much desired but so far such attempts have been rather limited, either focusing on a particular defect, or studying small cluster model systems, or have treated correlation with low-level many-body methods [23,30,31]. The uncertainty in electronic structures would also affect the modeling of other effects such as electron-phonon coupling and optical dynamics [9,32,33]. Therefore, clarifying the correlated electronic structure of quantum emitters in h-BN with a high-level many-body method is a crucial step.

In this Letter, we aim to clarify the complex in-gap spin states of various defects in h-BN, particularly those that

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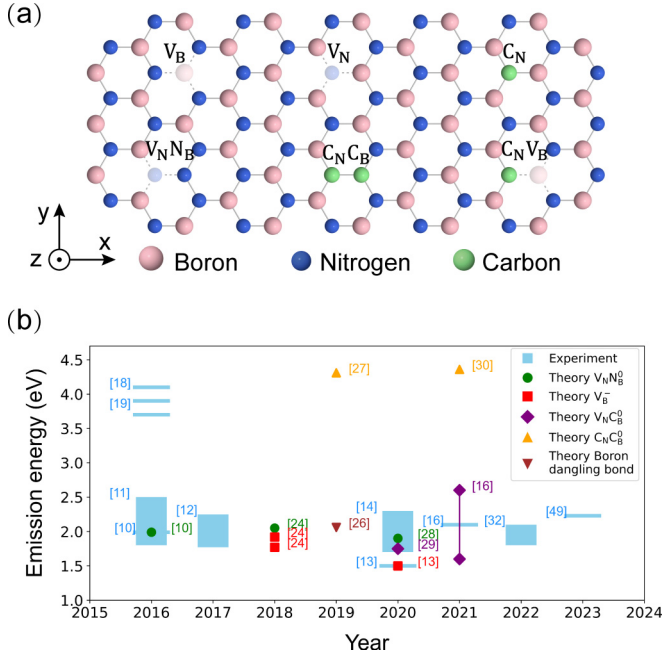


FIG. 1. (a) Atomic configurations of point defects on h-BN studied in this Letter. V_X represents a vacancy at the site of atom X, and X_Y denotes the substitution of atom Y atom by atom X. The figure includes three single-site defects with D_{3h} point symmetry: V_B , V_N , C_N (with a C_3 axis along the z axis); and three double-site defects with C_{2v} point symmetry: $V_N N_B$, $C_N V_B$, $C_N C_B$ (with a C_2 axis along the x axis). The notation of defects with superscripts $+$, 0 , and $-$, representing charge states of one positive charge, electrically neutral, and one negative charge, respectively. (b) A summary of recent measurements and calculations of the emission energy for luminescence of h-BN. Subscripts denote the corresponding references.

are still under dispute and have garnered extensive experimental attention. To achieve this, we employ the recently developed FCIQMC-in-DFT method [34], which combines the full configuration interaction quantum Monte Carlo (FCIQMC) [35,36] with an embedded quantum environment described by density functional theory [37,38]. FCIQMC is a stochastic sampling method that solves the full configuration interaction problem, yielding accurate solutions in a large space of configurations within a given basis set [35,36]. Such a treatment avoids dependence on the choice of exchange-correlation functionals in DFT. The quantum embedding part employs density matrix functional embedding theory (DMFET) [37] and orbital projection techniques [38] to capture the medium- to long-range interactions with the surrounding atoms at the DFT level. Overall, FCIQMC-in-DFT explicitly accounts for the electron correlation effect in the defect region, and the accuracy of this method has been validated in earlier research on the NV center in diamond [34], yielding results consistent with both experimental data and other highly accurate theoretical methods [39–45]. Here, the calculations allow us to fully determine the spin states of defects in h-BN, reveal the explicit roles of electron excitation, and analyze the transition pathways. These calculations fill the vacancy of accurate theoretical data for emitters in h-BN and provide a fresh perspective on the experimentally observed emissions.

Figure 1 shows all the atomic structures of defects in h-BN considered in this Letter, including six different structures with different charge states, which covers the most likely candidates discussed in the literature. For each defect, we construct a large H-terminated BN cluster with the defect at the center of the total system. The defect center and the nearest-neighbor atoms in the first shell are defined as the “embedded region” to be treated at the FCIQMC level, while the remaining atoms in the model are treated as the DFT “environment.” Details on model construction, optimization of the embedding potential, and FCIQMC calculations are given in Supplemental Material (SM) Sec. I [46].

To lay the foundation for further discussions, we first investigate the ground states of various defects, which are summarized in Table I. According to the results of FCIQMC-in-DFT, the defects V_B^- and $V_N N_B^+$ possess spin triplet ground states. Optically addressable spin triplet states, such as those found in the negatively charged nitrogen-vacancy center in diamond [48], are considered for potential applications in quantum technologies as spin qubits [6,9]. We confirm that V_B^- and $V_N N_B^+$ can be alternative choices. The ground states of V_B^0 , C_N^0 , V_N^0 , and $C_N V_B^-$ are spin doublets, which also allow for coherent spin operations via magnetic fields [49]. The remaining defects studied, C_N^- , C_N^+ , $C_N C_B^0$, and $V_N N_B^-$, exhibit spin singlet ground states.

In Table I, we also list the results from the relevant literature, where the ground states of these defects were reported. Despite the fact that DFT calculations can qualitatively predict the correct ground states for most of the defects, their predictions for $V_N N_B^+$ and $C_N V_B^-$ are questionable. $V_N N_B$ defects are studied due to their good thermodynamic stability. DFT calculations with the semilocal Perdew-Burke-Ernzerhof (PBE) functional and hybrid Heyd-Scuseria-Ernzerhof (HSE) functional both incorrectly predict the spin singlet as the ground state of $V_N N_B^+$ [23,24], while our results reestablish that the true ground state is a triplet. For $C_N V_B^-$, DFT calculations suggested a quartet as the ground state, but we now reveal that the doublet has the lowest energy. In the SM [46], we present a series of tests to demonstrate that our conclusions are not determined by other factors such as atomic structure and embedding environment. The discrepancies shown in Table I are solely due to the insufficient description of correlation effects by DFT.

We now provide deeper insights into the multiconfigurational correlation effects that result in the significant discrepancies. FCIQMC is based on the configuration interaction expansion of the many-body wave function Ψ , where a configuration is a determinant D_i formed by single-particle orbitals ($\Psi = \sum_i C_i D_i$). In FCIQMC the weights C_i reflecting the contribution of all configurations within the Hilbert space are sampled unbiasedly. In contrast, mean-field approaches such as DFT assume the wave function with only one determinant, although the correlation effects are approximately described by the orbital relaxation under a selected exchange-correlation potential. As an example, Fig. 2(b) plots the C_i of the four most populated configurations of the triplet state (ground state, GS) and the singlet state (excited state, ES) of V_B^- . One obvious observation is that in the triplet state, the C_i coefficients of the other three configurations are relatively small compared to the leading one, $^3A_2'$. These subdominant

TABLE I. Ground states obtained from FCIQMC-in-DFT calculations and the corresponding irreducible representations (Table S15 [46]) based on the dominant configuration of the many-body wave functions, categorized by spin triplet, doublet, and singlet states. Results from related references are also included, with spin states differing from FCIQMC-in-DFT results highlighted in bold.

Method	V_B^-	$V_N N_B^+$	V_B^0	C_N^0	V_N^0	$C_N V_B^-$	C_N^-	C_N^+	$C_N C_B^0$	$V_N N_B^-$
FCIQMC-in-DFT	$^3A_2'$	$^3B_2$	$^2E''$	$^2A_2''$	$^2A_2''$	$^2B_1$	$^1A_1'$	$^1A_1'$	$^1A_1$	$^1A_1$
DFT/PBE and DFT/HSE [23] ^a		S			D					S
DFT/HSE and group theory analysis [24]	$^3A_2'$	$^1A_1$								$^1A_1$
DFT/HSE [27]									$^1A_1$	
DFT/CAM-B3LYP and DFT/HSE [16]				$^2A_2''$		$^4A_2$	$^1A_1'$	$^1A_1'$		
DFT/PBE [47] ^b			D	D	D				S	

^aReference [23] only uses S and D to represent the singlet and doublet spin states, respectively.

^bReference [47] only uses S and D to represent the singlet and doublet spin states, respectively.

configurations mainly involve rare single excitations from the inner orbitals to the e' orbital, with respect to the $^3A_2'$. Such behavior is a typical case where the mean-field approximation is reasonable, and DFT is usually capable of capturing the correlation effects well. On the contrary, the singlet state is an open-shell singlet that involves much stronger multiconfigurational correlation effects, as indicated by the relatively large weights of the nonleading configurations. Therefore, although DFT can predict a qualitatively consistent conclusion of the ground state, the prediction on the singlet-triplet spin gap is likely to be unreliable, as we will discuss below. However, the situation can be opposite when the ground state exhibits strong

correlation effects, as shown for $C_N V_B^-$ in Fig. 2(d). In this case, the ground state is a doublet, and it is quite obvious that the second to fourth configurations contribute much more than those in the quartet state. A further examination reveals that the electron correlations involve single and double excitations between the frontier orbitals, including $a_1 \rightarrow a_1^*$ and $b_2 \rightarrow a_1^*$. Therefore, DFT methods are likely to struggle in describing such states and tend to overestimate the stability of the doublet, which ultimately leads to the incorrect prediction of the quartet as the ground state. In SM Sec. III D [46], we show the DFT results depend sensitively on the exchange-correlation functional used, but with FCIQMC-in-DFT the

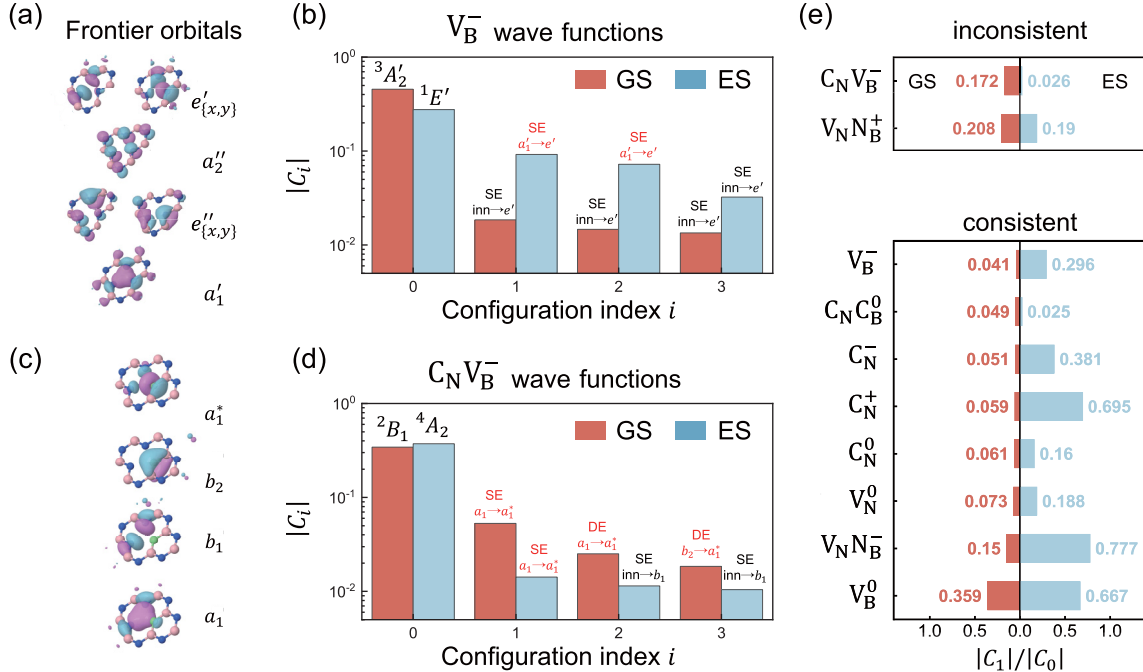


FIG. 2. Electron correlation effects. (a) and (b) show the key frontier orbitals and the C_i coefficients of the four highest populated configurations obtained from FCIQMC for V_B^- . The images of the key frontier orbitals for all ten point defects studied are shown in SM Sec. II [46]. (c) and (d) show the case for $C_N V_B^-$. Ground state (GS) and excited state (ES) indicate the spin state with lower and higher energy, respectively, based on FCIQMC-in-DFT calculations. SE and DE represent single electron and double electron excitations with respect to the dominant configuration ($i = 0$), where the electron hopping pathways are also indicated. Here, “inn” presents other inner occupied orbitals. The excitations involving frontier orbitals are highlighted in red. (e) is a measure of electronic correlation effects for all defects. The defects are categorized based on whether or not the ground state obtained from the mean-field approach is consistent with the FCIQMC-in-DFT, as shown in Table I.

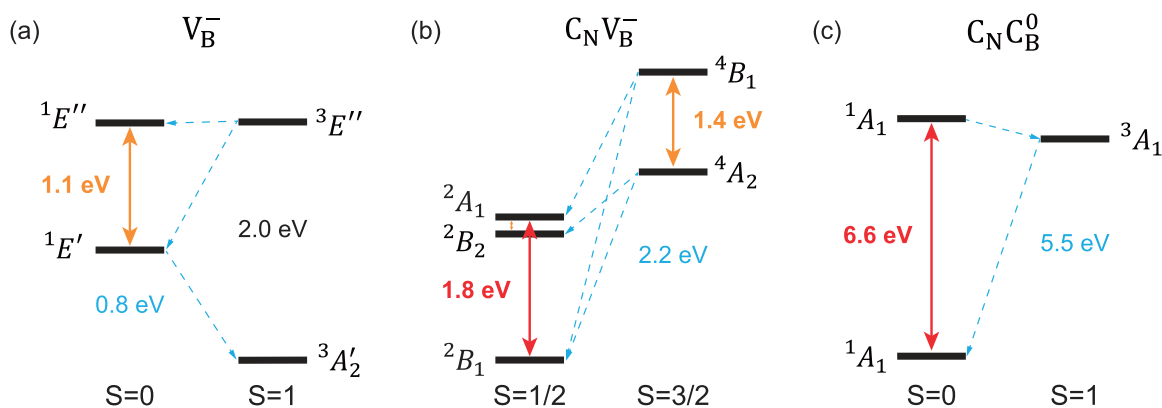


FIG. 3. Excited state level and optical transition. The diagram displays the energy levels and transition gaps. The radiative transitions are marked by arrows for in-plane (red arrow) and out-of-plane (orange arrow) modes. The spin-orbit coupling (SOC) induced nonradiative transitions (e.g., intersystem crossing ISC) are shown by blue dashed lines. Energy gaps are not to the scale.

conclusion of a singlet ground state remains insensitive to the functional employed for the environment. Similar situations can be observed in the ground state of $V_N N_B^+$ (see SM Sec. III B [46]), where the wave functions contain significant contributions from excitations between the frontier orbitals. Consequently, the incomplete description of these excitations leads to wrong ground spin states in the single-particle picture.

To provide a broader picture of the strength of electron correlation effects, Fig. 2(e) shows the ratio of the C_1 coefficient (subdominant configuration) to C_0 (dominant configuration). The higher the ratio, the more important is the subdominant configuration and the stronger are the electron correlation effects. We find that DFT always tends to favor the relatively weakly correlated state. For example, for $C_N V_B^-$ and $V_N N_B^+$ the excited states (ES, blue bars) are less correlated than the true ground states (GS, red bars), so DFT may incorrectly predict the order. For other defects, the GS states are less correlated than the ES states, so DFT calculations have made correct predictions. $C_N C_B^0$ looks like an exception, but it is also not a surprise that DFT can make good predictions because both the GS and ES states are weakly correlated. Extended analyses of each state are presented in SM Sec. III [46]. We note that the above discussions are based on excitation configurations from canonical Hartree-Fock orbitals, and to further verify the discussed insights on correlation effects from a different perspective we analyze the natural orbitals from FCIQMC (SM Sec. III C [46]). The visualization and occupancy of natural orbitals both support the conclusions shown in Fig. 2(e).

Now, let us move on to discussing the excited states of the defects and examining their potential roles in single photon emission. First, as we already discussed, excited states generally exhibit stronger electron correlation effects than ground states. In Fig. 3, we present the low-lying levels and excitation transitions of three specific defects, namely V_B^- , $C_N V_B^-$, and $C_N C_B^0$. These three defects are the most likely candidates to have important contributions to quantum emission in h-BN [13,16,23,27]. Higher-energy levels are calculated using the multireplica technique in FCIQMC, and optical transition properties between states were determined through a group theory analysis based on the FCIQMC many-body wave function (see details in SM Sec. II [46]).

The first defect we investigate is V_B^- [Fig. 3(a)], which has been proposed as a candidate for the 2.0 eV luminescence band [13,33,50]. The computed first excited state in the triplet channel is the $3E''$ state, which is 2.0 eV above the ground state $3A'_2$. However, although this energy gap fits the experimental regime, our analysis (SM Sec. II [46]) shows that direct radiative transitions between the $3E''$ and $3A'_2$ states are forbidden, supporting earlier findings that other excited states should be involved in the emission of V_B^- within this energy range [13]. In the singlet channel, the lowest excited state is $1E''$, which is at nearly the same energy level as the $3E''$ state and is 1.1 eV above the $1E'$ state. In addition, for V_B^- , we developed a self-consistency validation method for the FCIQMC-in-DFT energy level accuracy, based on the FCIQMC natural orbitals (see details in SM Sec. III D [46]). Specifically, FCIQMC calculations should yield fully converged exact solutions regardless of the chosen orbitals. We performed FCIQMC calculations using a different set of improved orbitals, namely the FCIQMC natural orbitals, obtaining a $1E'$ to $3A'_2$ gap of 0.85 eV, consistent with the original orbitals' 0.82 eV gap, with a maximum error of less than 0.03 eV. This further verifies the reliability of our calculations.

A more interesting case is $C_N V_B^-$, depicted in Fig. 3(b). This defect was proposed as the main contributor to the 2.0 eV luminescence by Mendelson *et al.* through a systematic study combining experimental and theoretical analyses [16]. Their DFT calculations, based on the Coulomb-attenuating method with the Becke 3-parameter Lee-Yang-Parr (CAM-B3LYP) functional, suggested that the ground state of $C_N V_B^-$ is a quartet state $4A_2$, and there exists a 1.6 eV optical transition in the quartet channel. However, we find that $4A_2$ is not the true ground state. A doublet state $2B_1$ resides 2.2 eV lower in energy. Even the excited states in the doublet channel are lower than those in the quartet channel. This discrepancy arises from the strong electron correlation effects in the ground state of $C_N V_B^-$, which is reflected in its strong dependence on the choice of functional in DFT calculations. Specifically, using the same atomic structure, DFT calculations with HSE06 and CAM-B3LYP functionals yield two different ground states, $2B_1$ and $4A_2$, respectively. However, with FCIQMC-in-DFT, the ground state is consistently $2B_1$ regardless of whether

HSE06 or CAM-B3LYP is used, demonstrating FCIQMC's ability to overcome the inherent functional dependence of DFT (see details in SM Sec. III E [46]). Based on the newly computed electronic structure, we observe an out-of-plane optical transition (${}^4A_2 \leftrightarrow {}^4B_1$, y axis in Fig. 1) in the quartet channel, with a similar transition energy of 1.4 eV. The corresponding optical transition should start from the ${}^2B_1$ state and proceed through an in-plane optical transition to the excited state ${}^2A_1$ (perpendicular to the C_2 axis) with an energy of 1.8 eV, while the transition between another excited state ${}^2B_1$ and ${}^2B_2$ is forbidden. This provides an alternative explanation for the experimental observation of the 2.0 eV luminescence reported in Ref. [16]. Intersystem crossing pathways involving the quartet channel are also possible, but the probability would be low due to the high energies of the quartets.

Finally, regarding the 4.1 eV luminescence, previous theoretical calculations pointed to the $C_N C_B^0$ defect, also referred to as the carbon dimer defect, as the most likely candidate [27,30]. The associated transition is between the ${}^1A_1$ and ${}^1A_1^*$ states, primarily driven by the electron being promoted to the b_2^* from b_2 orbital. However, our FCIQMC calculations reveal that the transition energy between these two states is 6.6 eV, which is too large to explain the experimental luminescence [Fig. 3(c)]. Further analysis of the natural orbitals obtained through FCIQMC shows the b_2 's occupancy is reduced to 1.83, and the b_2^* 's occupancy slightly increases to 0.02. It is also observed that there are notable contributions from orbitals within the surrounding environment, leading to a more delocalized wave function for the b_2^* orbital than DFT predictions (details in SM Sec. II C [46]). The effects then elevate the energy level and the transition energy. The transition between ${}^1A_1$ and ${}^3A_1$ is slightly smaller, but it is optically

forbidden. Our calculations suggest there is a more complex mechanism beyond the current theoretical model behind the 4.1 eV luminescence.

In summary, we have investigated the electronic structure of quantum emitters in h-BN, focusing on clarifying the disputed electronic states of various defects and analyzing the impact of electronic correlation effects. By explicitly considering the electron correlation effects using the FCIQMC-in-DFT method, we significantly improved the accuracy in determining the spin states of ten relevant defects, which are crucial for clarifying the roles of these defects in photoemission. We also uncover a doublet-doublet transition in the $C_N V_B^-$ defect, which is very likely to play an important role in the mysterious single photon emission in the visible region. Quantum emission in h-BN is a complex phenomenon, which might involve multiple emitters simultaneously and other effects such as phonon renormalization. In this Letter, we do not aim to provide a final answer to all the experimental observations, but our results offer a solid foundation for an electronic structure to approach the accurate modeling of defects in h-BN. The theoretical insights can effectively assist experiments in detecting and controlling the spin states in h-BN.

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