

First-principles calculations of quantum defects in bulk WS₂: Effect of carbon doping in spin-photon interfaces

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Point defects in two-dimensional and layered materials have attracted considerable interest as promising qubit candidates for quantum information processing due to their highly localized electronic states and spin-dependent optical properties. In this work, we use r^2 SCAN density functional calculations combined with complete active space self-consistent field theory to investigate bulk carbon-doped tungsten disulfide (WS₂) as a potential platform for scalable quantum technologies. The meta-generalized gradient approximation exchange-correlation functional r^2 SCAN is found to offer a balance between accuracy and computational efficiency for specific properties, while its performance has not been tested in bulk WS₂ before. By substituting sulphur atoms with carbon impurities, we achieve stable paramagnetic excited states characterized by well-defined defect levels deep within the band gap. Moreover, we investigate the zero-phonon line, radiative lifetime, and zero-field splitting due to the carbon impurities. The presence of tungsten introduces relativistic effects which are desired for some quantum applications, facilitating efficient initialization, coherent manipulation, and readout of defect spin states. We elucidate the role of carbon in lowering the emission energies into technologically relevant wavelengths for quantum information science, while we compare the present results with the extensively investigated monolayer structure. Our results highlight carbon-doped WS₂ as an attractive solid-state quantum platform due to its zero-phonon line, zero-field splitting, and radiative lifetime values, enabling robust optical control and manipulation of spin states for quantum applications.

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I. INTRODUCTION

Quantum technologies are based upon precise control, manipulation, and storage of quantum bits (qubits), which have shown potential in computing, secure communication, and sensing applications. Among various platforms, paramagnetic point defects in wide-band-gap semiconductors have shown great promise due to their potential as single-photon emitters and efficient spin-photon interfaces, essential for integrated quantum circuits and quantum communication networks [1–3]. For practical applications, solid-state qubits should exhibit optical emissions at technologically compatible wavelengths, minimal zero-field splitting (ZFS) value for effective microwave manipulation, and robust optical initialization and readout mechanisms enabled by intersystem crossing (ISC) and negligible phonon sideband losses [4].

The negatively charged nitrogen-vacancy (NV[−]) center in diamond has been the most studied system for quantum communications and sensors, due to the coherent spin control, optical initialization, and readout, primarily covered

through ISC pathways arising from electron-phonon coupling [5,6]. Nevertheless, despite its success, the NV[−] center faces significant limitations, such as difficulties in precise defect placement, scalability, and integration into existing photonic and electronic devices [7,8]. Consequently, the exploration of alternative host materials and defect centers has become an active area of research to overcome these limitations.

Two-dimensional (2D) and layered van der Waals (vdW) materials have recently attracted attention as promising alternatives due to the absence of dangling bonds at the surface, easy defect engineering, and compatibility with advanced fabrication techniques for large-scale production [9]. Defect engineering in these materials can be performed with atomic precision using methods such as scanning tunneling microscopy (STM) and focused ion beam techniques, enhancing the prospects of scalable and deterministic defect placement critical for quantum device integration [10]. Transition metal dichalcogenides (TMDs), particularly WS₂, have attracted considerable attention as platforms for hosting quantum defects due to their unique electronic and optical properties [11,12]. For example, WS₂ and WSe₂ exhibit sizable direct band gaps in their monolayer forms, strong spin-orbit coupling, and pronounced zero-phonon line values which are in the telecom bandwidth, making it especially suitable for applications requiring precise optical and spin control at the quantum level [12,13]. Experimental observations have already confirmed single-photon emission in monolayer WS₂

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arising from intrinsic defects or artificially introduced defect states [14]. Nevertheless, the precise origin of many of these defect-related emissions remains unexplored and further systematic studies are required [15]. In the case of a layered materials, when the defect is created within the bulk, the outer layers help reduce environmental interactions, which is an important consideration for practical quantum information processing [11]. In the case of the defect symmetry, the bulk structure can also help achieve better coherence times compared to the monolayer. For example, Gao *et al.* [16] have shown that when the geometry of $V_N N_B$ defect in hBN is kept planar, the radiation lifetime is significantly reduced to 19 ns but, due to the interlayer interactions occurring in the bulk, the displacement of the N atom is reduced and the radiative lifetime is increased to 147 ns. Finally, creating a bulk material compared to a monolayer material is sometimes easier as it can be done with low-cost experimental techniques such as sol-gel and spin coating.

Recent theoretical studies have demonstrated significant progress in the controlled generation and characterization of specific defects in WS_2 [12]. Notably, carbon atoms substituting sulfur atoms (C^- defects) have been investigated at atomic precision providing insights into their electronic structure and spin-dependent optical properties. On the other hand, the literature on bulk WS_2 is very limited compared to the monolayer. The bulk structure provides additional degrees of freedom for defect engineering due to its structural robustness, enhanced thermal and mechanical stability, and greater ease of integration with conventional semiconductor fabrication processes.

Recent studies by Li *et al.* [12] employing density functional theory (DFT) calculations have revealed that carbon impurities substituting sulfur atoms in monolayer WS_2 give rise to stable paramagnetic centers capable of encoding quantum information. As they describe in their work, C doping is stable in two charge states, neutral and negative, with the neutral being in a singlet ground state. Their reported ZPL was 0.923 eV and an intersystem crossing to a triplet 3E state was possible, which was 0.847 eV higher in energy than the ground state [12]. As a result, the effect of C doping in bulk is an interesting route for investigation.

Experimental studies on carbon-doped WS_2 demonstrate that carbon substitutional impurities C_S exhibit spin-dependent optical transitions, essential for coherent spin initialization, manipulation, and optical readout—critical components for quantum technological applications [17]. Comparative studies of similar quantum defects in other layered materials, such as hexagonal boron nitride (hBN) [18] and molybdenum disulfide (MoS_2) [19], have shown interesting characteristics which could also be applied to bulk WS_2 , for example, paramagnetic defects like V_B^{-1} [20] which have room-temperature coherent spin control, establishing fundamental principles that could also be applied to WS_2 .

Defect emitters in monolayer WS_2 are bright and tuneable but remain sensitive to substrate- and adsorbate-induced charge noise (spectral diffusion). In bulk (multilayer) WS_2 the reduced surface exposure and stronger, more homogeneous dielectric screening favor charge-state stability and diminished spectral wandering; stable room-temperature defect emission has indeed been reported in WS_2 multilayers. In gen-

eral, monolayer TMDs offer bright, strain-, and field-tunable single-photon emission, but the proximity to substrates and adsorbates makes them susceptible to charge-noise-driven spectral diffusion and blinking [21]. Our focus on bulk WS_2 is motivated by the reduced coupling to surfaces and the more homogeneous 3D dielectric screening, which are expected to stabilize charge states and lessen spectral wandering; thickness-dependent screening and the much larger exciton binding energies in monolayers underscore how strongly the dielectric environment shifts optical energies [22]. Although stable defect emission has been observed in WS_2 multilayers [23], the role of carbon, which is expected to exist within the structure during synthesis, is not yet fully understood. Moreover, WS_2 has the usual quiet nuclear-spin bath because, among the naturally abundant isotopes, only ^{183}W and ^{33}S are spin active. By contrast, hBN and MoS_2 have many more isotopes that are spin active. Consequently, once T1 is prolonged, T2 tends to be limited by hyperfine coupling to the residual nuclear bath, making WS_2 a mix of low spin isotopes, a clear materials advantage [9].

Recently developed functionals such as meta-generalized gradient approximations (meta-GGA) have shown great promise for accurately predicting defect-related properties in semiconductors [24]. Specifically, the r^2SCAN functional [25], includes the kinetic energy density, significantly enhancing its ability to describe both localized and delocalized electronic states compared to traditional local density approximations (LDA) and generalized gradient approximations (GGA). Beyond the favorable scaling relative to hybrid functionals, r^2SCAN brings three practical advantages for defect studies. First, it is numerically robust yet nonempirical, restoring SCAN's exact constraints while avoiding the original grid/regularization instabilities; this makes geometry relaxations and energy differences reproducible without special integration settings. Secondly, it delivers reliable structures and energetics for solids (cell volumes, cohesive/bulk properties, and noncovalent/layered interactions) at near-GGA cost, which is ideal for exploring many charge states, supercell sizes, and symmetry-broken configurations prior to any expensive spot checks. Thirdly, as a meta-GGA that uses the kinetic-energy density, it captures bonding-environment changes (e.g., near defects) better than GGAs, often preserving the correct level ordering and spin densities; by contrast, HSE06 is preferred when accurate band edges and band-gap opening are essential. Consequently, readers should expect our r^2SCAN and HSE06 results to agree on level hierarchy and spin multiplicities, while HSE06 opens the gap (primarily via band-edge shifts) so unoccupied in-gap levels appear higher above the valence-band maximum (VBM) and occupied ones slightly farther from the band edges than at the semilocal level; we therefore report all level positions relative to the VBM for clarity.

Given these promising experimental and theoretical results, this work intends to explore the carbon-doped bulk WS_2 which has not yet been investigated and, as we show, represents a compelling platform for scalable and integrable quantum technologies. The enhanced spin-photon interface capabilities provided by carbon impurities, combined with deterministic defect placement and the technological maturity of bulk WS_2 processing techniques, suggest

significant potential for practical quantum applications. From a fabrication standpoint, site-controlled emitters are readily engineered in *monolayer* WS₂/WSe₂ using He-ion/e-beam, plasma/laser methods, or strain-templated nanocavities, whereas creating and activating *bulk* (multilayer) WS₂ defects with true 3D control remains markedly more challenging, with only limited demonstrations [26–28]. This gap motivates our theory-led approach to preselect stable bulk defect configurations and charge states to guide forthcoming experiments. Furthermore, this work proposes a workflow for detailed theoretical investigations aimed at further investigating the quantum characteristics of carbon-doped WS₂, paving the way toward integrated quantum devices operating efficiently within the critical telecom wavelength regime.

II. METHODOLOGY

For the DFT calculations we used the Vienna *ab initio* simulation package (VASP) version 6.5, a plane-wave-based code employing projector augmented wave (PAW) pseudopotentials [29,30]. To simulate the electronic exchange and correlation effects, the r²SCAN meta-GGA exchange-correlation functional was used in combination with HSE06 to validate its accuracy, including also the DFT-D3 dispersion corrections to accurately describe van der Waals interactions of the layered bulk WS₂ [25,31]. The accuracy of reported findings for the SCAN functional is transferable to r²SCAN as the latter preserves all exact constraints of SCAN while improving its numerical stability. A plane-wave cutoff energy of 500 eV was found to converge the total energy of the system to 1 meV per formula unit (f.u.) while structural optimizations proceeded until the residual atomic forces fell below 0.01 eV/Å. Electronic self-consistency was achieved to within a convergence criterion of 10^{−6} eV. The convergence of the primitive cell was achieved using a set of 6 × 6 × 2. For the supercell, the Brillouin zone was sampled with a Gamma-centered 2 × 2 × 2 Monkhorst-Pack *k*-point mesh to ensure accurate representation of the electronic states of bulk WS₂. The spin-orbit coupling is calculated within the noncollinear approach implemented in VASP, evaluated at the relaxed geometry obtained from spin-polarized calculations. We note that the standard HSE06 (25% exact exchange) parameters may not be fully optimized for WS₂ [32]. In fact, prior work on WS₂ found that a higher fraction of exact exchange was needed to reproduce the experimental band gap, underlining a system-specific tuning aspect [32]. In contrast, the meta-GGA r²SCAN functional involves no adjustable Hartree–Fock fraction, which is a practical advantage as it avoids any system-dependent parameter fitting.

For our DFT calculations, we examined different supercell sizes to converge all the key quantities that are presented in this paper. Specifically, we used a supercell of 10 Å in each direction consisting of 72 atoms, up to a supercell of 20 Å in each direction consisting of 588 atoms. The electronic structure for both supercells is similar. Accurate identification of the defect ground-state structures was achieved by the ShakeNBreak approach [33], systematically evaluating possible symmetry-breaking configurations to successfully capture the true ground state of each system. Defect formation energies and charge transition levels (CTLs)

were calculated according to standard methods for charged supercells, considering finite-size image charge corrections using the Freysoldt–Neugebauer–Van de Walle scheme [34]. For a defect *D* with charge *q*, the formation energy is calculated as

$$E_{\text{form}}[D^q] = E_{\text{tot}}[D^q] - E_{\text{tot}}[\text{bulk}] - \sum_i n_i \mu_i + qE_F + E_{\text{corr}}, \quad (1)$$

where $E_{\text{tot}}[D^q]$ is the total energy of the supercell containing the defect *D* at charge *q* and $E_{\text{tot}}[\text{bulk}]$ is the energy of the pristine supercell of WS₂. n_i is the number of atoms of type *i* that are added ($n_i > 0$) or removed ($n_i < 0$) with chemical potentials μ_i and E_F is the Fermi level relative to the valence band maximum (VBM) eigenvalue energy, which serves as a free parameter. The chemical potentials for C, W, and S are calculated from diamond, W (bcc), and S₂ molecule in a box, respectively. The term E_{corr} includes image charge correction and potential alignment corrections.

The defect charge transition levels (CTLs) between two charges *q* and *q'* are computed using the formation energies as follows:

$$\varepsilon(q/q') = \frac{E^f(D, q; E_F = 0) - E^f(D, q'; E_F = 0)}{q' - q}, \quad (2)$$

where $E^f(D, q; E_F = 0)$ and $E^f(D, q'; E_F = 0)$ represent the formation energies of the defect in charge states *q* and *q'*, respectively, evaluated at the VBM (i.e., for $E_F = 0$). To determine these levels, formation energies of the defects at different charge states were calculated and the CTLs were identified as the values of the Fermi level at which two different charged defect states have equal formation energies.

For electronic excitations and optical properties, the constrained DFT (cDFT) method was used, allowing the manipulation of the electron occupation of defect-localized states to simulate excited-state configurations and determine zero-phonon line (ZPL) energies [35]. Within the constrained density functional theory (cDFT) method, the excited-state energy of a point defect is calculated by considering a Kohn–Sham system where an energetically higher energy level orbital, previously unoccupied, is filled. During this procedure, the excited state energy of a point defect is obtained by promoting an electron from the last occupied level to the first unoccupied, within the band gap. The new occupation of the selected orbitals is kept fixed during the self-consistent Kohn–Sham calculations, while allowing the atomic structure to relax. The energy difference between the relaxed ground and excited states represents the ZPL energy. This methodology has been successfully applied in studies involving electronic excitations between defect-centered states, showing excellent agreement with experimental data for the NV center in diamond [36]. For the simulation of the excitation process we disabled the use of symmetry, to avoid any mixing of constrained excited states. Furthermore, in this work, we constrained the spin-up channel for the excitation and in total we used 376 and 3072 bands for the small and large supercells, respectively.

Radiative lifetimes were calculated using the Wigner–Weisskopf theory, with wave function data extracted via a

modified PYVASPWF code to compute transition dipole moments accurately. The excitation lifetime is approximated using [37,38]

$$\frac{1}{\tau} = \frac{n_r (2\pi)^3 v^3 |\mu|^2}{3\epsilon_0 \hbar c^3}, \quad (3)$$

where τ is the excitation lifetime, n_r is the refractive index, v is the transition frequency between the ground and excited states, μ is the k -point integrated transition dipole moment, and ϵ_0 is the vacuum permittivity. $\hbar$ and c represent the Planck constant and the speed of light in a vacuum.

The transition dipole moment at k -point k is defined as

$$\mu_k = \frac{i\hbar}{(\epsilon_{f,k} - \epsilon_{i,k})m} \langle \psi_{f,k} | p | \psi_{i,k} \rangle, \quad (4)$$

where $\epsilon_{i,k}$ and $\epsilon_{f,k}$ represent the eigenvalues of the initial and final states, m is the electron mass, $\psi_{i,k}$ and $\psi_{f,k}$ are the initial and final wave functions, and p is the momentum operator.

The zero-field splitting (ZFS) is a physical phenomenon which breaks the degeneracy of sublevels in a spin multiplet in the absence of an external magnetic field. For a single effective spin system, the ZFS Hamiltonian is given by

$$\hat{H}_{\text{ZFS}} = \hat{\mathbf{S}} \cdot \mathbf{D} \cdot \hat{\mathbf{S}}, \quad (5)$$

where $\hat{\mathbf{S}}$ is the effective spin operator and $\mathbf{D}$ is the ZFS tensor. Due to the anisotropic nature of the ZFS, $\mathbf{D}$ is traceless and, on rotation to a coordinate system in which it is diagonal, can be reduced to two parameters: the axial ZFS D and rhombic ZFS E [39]. The ZFS Hamiltonian thus becomes

$$\hat{H}_{\text{ZFS}} = D(\hat{S}_z^2 - \frac{1}{3}S(S+1)) + E(\hat{S}_x^2 - \hat{S}_y^2), \quad (6)$$

with D and E defined as

$$D = D_{zz} - \frac{1}{2}(D_{xx} + D_{yy}), \quad E = \frac{1}{2}(D_{xx} - D_{yy}),$$

$$0 \leq \frac{E}{D} \leq \frac{1}{3}. \quad (7)$$

The ZFS tensor may be calculated directly from a multiconfigurational wave function describing the defect system through quasidegenerate perturbation theory and the construction of an effective Hamiltonian [40].

For the nonrelativistic Hamiltonian $\hat{H}_0$, all components with spin projection M_S of a spin S multiplet are degenerate and the zeroth-order wave function may be written as a linear combination of spin-adapted configuration state functions $|\Phi_K^{SM_S}\rangle$ as

$$|\Psi_I^{SS}\rangle = \sum_K c_{KI} |\Phi_K^{SS}\rangle \quad (8)$$

in which only the components with $M_S = S$ need to be considered since all other M_S components may be generated from this using the Wigner-Eckart theorem [41]. The eigenstates of the nonrelativistic Hamiltonian form a basis in which the relativistic eigenstates may be expanded; relativistic SOC and spin-spin coupling (SSC) effects may be included through quasidegenerate perturbation theory (QDPT) [42,43]. An approximation to the relativistic Hamiltonian matrix is

constructed by evaluating a sum of nonrelativistic, spin-orbit, and spin-spin Hamiltonians in the basis of nonrelativistic eigenstates as

$$\begin{aligned} & \langle \Psi_I^{SM_S} | \hat{H}_0 + \hat{H}_{\text{SOC}} + \hat{H}_{\text{SSC}} | \Psi_J^{S'M'_S} \rangle \\ &= \delta_{IJ} \delta_{SS'} \delta_{M_S M'_S} E_I^S + \langle \Psi_I^{SM_S} | \hat{H}_{\text{SOC}} + \hat{H}_{\text{SSC}} | \Psi_J^{S'M'_S} \rangle. \end{aligned} \quad (9)$$

The eigenstates of this Hamiltonian matrix are the spin-orbit and spin-spin coupled states, represented as a linear combination of the nonrelativistic eigenstates, with eigenvalues which approximate the relativistic energy levels.

Effective Hamiltonian theory provides a convenient approach for the evaluation of the ZFS tensor from QDPT states. This relies on a one-to-one correspondence between a model space, spanning the effective Hamiltonian, and a target space comprising a subspace of solutions to the exact electronic Hamiltonian. For a spin S multiplet, the model space is comprised of the manifold of $|SM_S\rangle$ states, while the target space is spanned by the corresponding eigenstates of Eq. (9). The effective Hamiltonian then has the form

$$\hat{H}_{\text{eff}} = \sum_K |S^{-\frac{1}{2}} \tilde{\Psi}_K\rangle E_K \langle S^{-\frac{1}{2}} \tilde{\Psi}_K| \quad (10)$$

in which $|S^{-\frac{1}{2}} \tilde{\Psi}_K\rangle$ are projections of the eigenstates of Eq. (9) onto the model space, orthogonalized accordingly using the overlap matrix $\mathbf{S}$ following the des Cloizeaux formalism, and E_K are the eigenvalues of Eq. (9) [44]. Given the model Hamiltonian Eq. (5), its matrix elements in the model space $|SM_S\rangle$ are given by $\langle SM_S | \hat{H}_{\text{ZFS}} | S'M'_S \rangle$ and can each be expressed in terms of elements D_{ij} . Comparison of the resulting matrix elements with those of $\langle SM_S | \hat{H}_{\text{eff}} | S'M'_S \rangle$ yields a set of simultaneous equations which uniquely determine $\mathbf{D}$. The parameters D and E are then obtained according to Eq. (7) [45].

The molecular cluster calculations in this work were undertaken using the ORCA (version 6.0.1) computational chemistry package [46]. The excited state structure was relaxed under periodic boundary conditions, using the VASP code, and a small molecular cluster constructed by extracting the carbon substituent and its neighboring atoms from the supercell. Cleaved bonds were terminated with hydrogen atoms, the positions of which were subsequently optimized using the r²SCAN exchange-correlation model [47] with Grimme's D3 dispersion correction [31]. The strategy of constructing a molecular cluster passivated with hydrogen atoms is justified for this system since the electronegativities of W, S, and H are similar; hence the effect of hydrogen atom termination of the cluster will be minimal on the charge density of the carbon defect. Unless otherwise specified, all molecular cluster calculations were carried out in the exact two-component (X2C) formalism [48,49] to account for scalar relativistic effects and employing the x2c-TZVPall orbital basis.

The ZFS were calculated using the state-specific complete active space self-consistent field (CASSCF) method [50]. For this spin defect, the minimal active space would comprise four electrons in three orbitals, the degenerate e orbital in the valence band, and the a_1 orbital in the band gap. Since the e orbitals are not necessarily at the valence level, a larger active space is required to ensure these are included. To define the

active space, the natural orbitals from second order Møller-Plesset perturbation theory were calculated and used as the starting orbitals for the CASSCF calculation, with an active space spanning all natural orbitals with significant fractional occupation, between 0.2 and 1.8, selected. This yielded an active space of eight electrons in eight orbitals to represent the near-degenerate electronic structure, with dynamical correlation captured by using second-order n -electron valence state perturbation theory (NEVPT2) [51]. QDPT as described previously was employed to incorporate the effects of SOC and SSC, with the ZFS tensor subsequently computed with effective Hamiltonian theory.

Hyperfine interaction tensors, crucial for understanding spin coherence times and interactions with nuclear spins, were calculated to evaluate defect suitability for quantum memory applications [52]. The hyperfine interaction tensor describes the coupling between an electron spin S and a nuclear spin J and is given by

$$A_{ij} = \frac{1}{2S} \gamma_J \gamma_e \hbar^2 \left[\frac{8\pi}{3} \int \delta(r - R_J) \sigma(r) dr + W_{ij}(R_J) \right], \quad (11)$$

where the first term in the square brackets is the Fermi-contact isotropic term. The dipole-dipole anisotropic contribution is defined as

$$W_{ij}(R) = \int \left(\frac{3(r - R)_i(r - R)_j}{|r - R|^5} - \frac{\delta_{ij}}{|r - R|^3} \right) \sigma(r) dr, \quad (12)$$

where γ_J , γ_e represent the nuclear magneton of nucleus J and the electron Bohr magneton, respectively, while $\sigma(r)$ represents the electron spin density. The hyperfine tensor can be diagonalized and the three principal values which represent the hyperfine constants are labeled as A_{xx} , A_{yy} , and A_{zz} . The calculation of hyperfine tensors is implemented in VASP.

III. RESULTS AND DISCUSSION

A. Bulk properties

Bulk 2H-WS₂ crystallizes in the hexagonal $P6_3/mmc$ (no. 194) space group and has experimental lattice parameters of $a \approx 3.15$ Å and $c \approx 12.36$ Å [53,54]. Structural relaxation with SCAN and r²SCAN functional including the D3 dispersion correction resulted in lattice parameters $a = 3.152$ (3.169) Å and $c = 12.327$ (12.404) Å, in excellent agreement (within 1%) with the experimental values. These results confirm that both the SCAN+D3 and r²SCAN + D3 approach predicts accurate structural parameters for layered transition metal dichalcogenides (TMDs), serving as a robust alternative to more computationally intensive hybrid functionals.

We calculated an indirect band gap for pristine WS₂ equal to 1.23 eV using r²SCAN, slightly underestimated compared to the experimentally reported band gap, which ranges between 1.3 [55] and 1.4 eV [56]. Similarly, using SCAN we calculated a band gap of 1.19 eV. This difference is common among meta-GGA functionals and it does not significantly impact studies involving defect states within the material, as shown in previous works [57]. Prior works have found that HSE06 typically overestimates the experimental band gap, yielding a value of 1.58–1.60 eV [58], while the PBE0 hybrid functional further overestimated it to a value of 2.51 eV [59].

Semilocal density functional approximations, such as PBE, also underestimate the band gap, as we show in Table I. This demonstrates that meta-GGAs are a good choice for describing the electronic properties of the system. Furthermore, as shown in the work of Abbas *et al.* [57], meta-GGAs have been used to calculate zero-phonon lines (ZPLs) and charge transition levels in various quantum hosts, including SiC and diamond. Their results agreed with great accuracy with experimental and HSE-based values. From their work, we can conclude that the slight underestimation in the band gap is not critical for assessing these properties for systems such as carbon-doped WS₂, further establishing the reliability of the SCAN and r²SCAN functional in defect thermodynamics and quantum technology properties prediction.

According to the quantum computing guidelines provided by Weber *et al.* [60], a host with a wide band gap is typically required to avoid thermal excitations which could manipulate the quantum information and lead to decoherence. Nevertheless, for other quantum applications such as communication and sensing, we have seen various hosts being proposed, even though their band gap is significantly smaller than diamond, for example, silicon [61]. The results are summarized in Table I, where interestingly the HSE shows an overestimation of the band gap, while the r²SCAN value is underestimated.

B. Defect energetics

The calculated formation energies and charge transition levels (CTLs) for the carbon substitutional defect, C[−], in bulk WS₂, computed with the r²SCAN functional, are presented in Fig. 1. We chose r²SCAN as it is a better parametrized functional which makes the calculations run faster and also is found to predict formation energies more accurately than SCAN and PBESol in a wide range of materials [62]. Under W-rich conditions, the defect formation energy is significantly lower compared to S-rich conditions, indicating that carbon incorporation into WS₂ is energetically favored when the sulfur chemical potential is low. The S-rich conditions are closer to the realistic experimental synthesis conditions. Specifically, the neutral-to-negatively charged (0/−1) transition occurs at about 0.4 eV above the valence band maximum (VBM), identifying the defect as a stable deep acceptor in bulk WS₂. Such behavior is consistent with previous theoretical studies on related chalcogen-substitutional defects in TMDs, emphasizing how local chemical potentials critically influence defect energetics [63,64]. The incorporation and concentration of C_S defects in bulk WS₂ are highly dependent on the synthesis route and, for that reason, we calculated the Brouwer diagrams which are shown in Figs. 1(c) and 1(d). The diagrams indicate a substantial increase in the concentration of C_S defects under W-rich conditions, where the low sulfur chemical potential energetically favors carbon incorporation at sulfur sites. On the other hand, for the S-rich environment, which closely represents the experimental environment, the lattice strongly retains sulfur atoms, dramatically increasing the formation energy for C_S defects and thus suppressing their incorporation. As a result, from the high concentration of these defects in WS₂, it can be deduced that these defects may impact the application of WS₂ to quantum technologies, though these defect complexes are not investigated in this manuscript. It

TABLE I. Lattice constants and electronic band gap of pristine WS₂ calculated using r²SCAN and compared with experimental values.

	r ² SCAN	SCAN	HSE06 [56]	PBE0 [59]	PBE [55]	Experiment [56]
Lattice constant a (Å)	3.17	3.15	3.14	3.13	3.16	3.15
Lattice constant c (Å)	12.41	12.32	12.33	12.31	12.37	12.36
Band gap (eV)	1.23	1.19	1.60	2.51	0.97	1.30–1.40

is worth mentioning that C in monolayer and C in bulk have some slightly different geometries, although the symmetry is C_{3v} in both cases. Specifically, the distances from the nearest W atoms are 2.026 Å and 2.002 Å.

C. Electronic structure

The electronic structure of the defected system at neutral and negative charge states are presented in Fig. 2. For our defects, we found that they maintain a local point group symmetry of C_{3v} . In the next figures, we use the group theory notation for the C_{3v} group to label electronic states and orbitals. Our results are in qualitative agreement for the neutral carbon substitution defect with prior theoretical studies conducted on monolayer WS₂. To be more specific, HSE06 calculations for the C_S^0 defect in the monolayer introduce a nondegenerate unoccupied defect level about 2.11 eV above the VBM. Furthermore, C_S^{-1} was characterized by an

occupied defect level positioned around 1.09 eV above the VBM. These theoretical predictions have been verified experimentally through scanning tunneling spectroscopy (STS) measurements [17]. The neutral defect in the bulk host has an a_1 level in both spin channels at approximately 0.40 eV. In addition, the SOC has minimal contribution to the electronic structure of the C_S^0 defect. For the C_S^{-1} :WS₂ system, there are two gap states present at ≈ 0.40 eV and ≈ 1.10 eV. In the monolayer, only one gap state is created at 1.09 eV, while the second state lies deep in the conduction band. These deep localized states thus facilitate spin-dependent optical transitions and spin-orbit coupling effects, enhancing their potential as quantum emitters and qubit candidates due to the resulting long-lived excited spin states [41]. To further validate our results, we performed HSE06 calculations on both defects and we found that the energy level positions agree well between meta-GGAs and HSE06. Moreover, as we show in Fig. 2, it

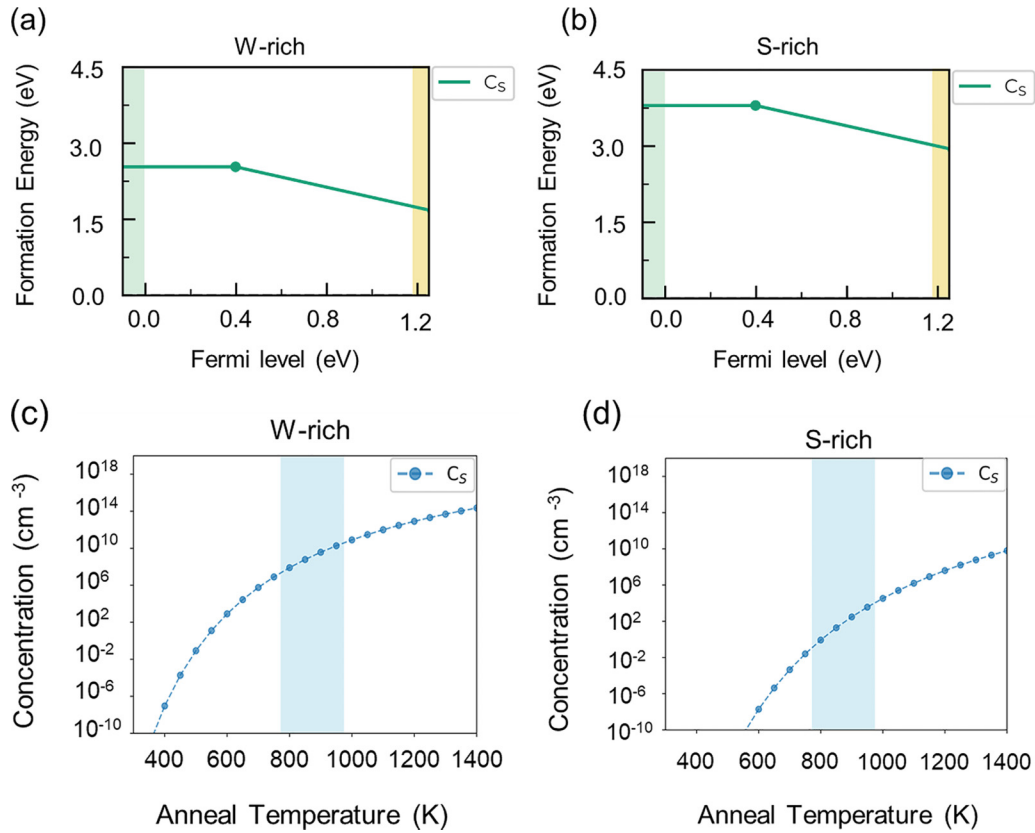


FIG. 1. Thermal stability of the C_S in WS₂. Formation energy as a function of Fermi level for the C_S defect in the (a) W-rich and (b) S-rich environment. We describe the W-rich environment using the WC competing phase while for the S-rich we used the elemental chemical potentials as predicted using *Doped* [65]. The total defect concentration is shown in the (c) W-rich and (d) S-rich environment. We define the total defect concentration as $c = N_{\text{sites}} \exp(\frac{D^0}{kT})$.

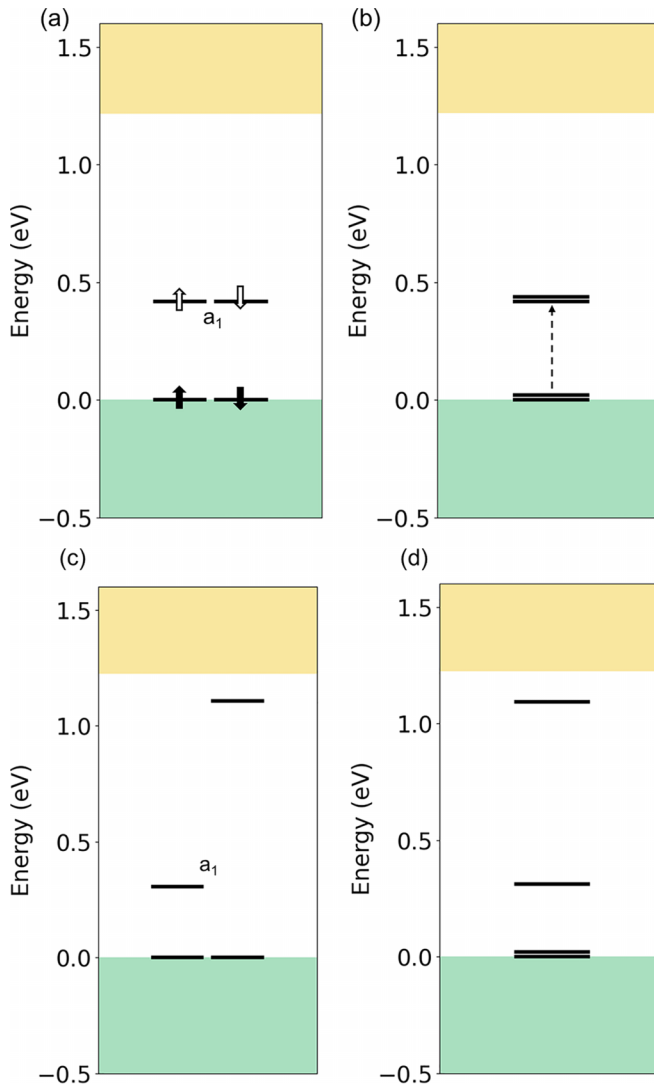


FIG. 2. (a) Electronic structure of the C_S^0 without and (b) with SOC. The energy levels diagram of C_S^{-1} at ground state without (c) and with (d) the SOC effect. The green and orange colors denote the VBM and CBM. The CTL energy is aligned to VBM. The arrows indicate spin-up and spin-down channels. The Kohn-Sham energy levels were constructed at a supercell converged at the Gamma point.

is evident that both charged states of the carbon substitution defect provide available gap states for intragap transitions, similar to the case for the monolayer material.

DFT has been crucial in uncovering how carbon impurities behave in bulk TMDs, although the literature is very limited compared to other defect complexes. Substitutional carbon at a chalcogen site, for example, has been shown to support spin-active states analogous to the NV center in diamond. According to our literature review, the majority of defects studied in TMDs are intrinsic defects (namely vacancies and antisites). High-throughput hybrid DFT screenings have revealed that anion antisites in group-VI TMDs can stabilize a spin-triplet ground state with multiple gap state levels [11]. Such defects fulfill key criteria for quantum bits, such as a paramagnetic triplet ground state, spin-conserving optical transitions, and accessible spin sublevels. To our knowledge,

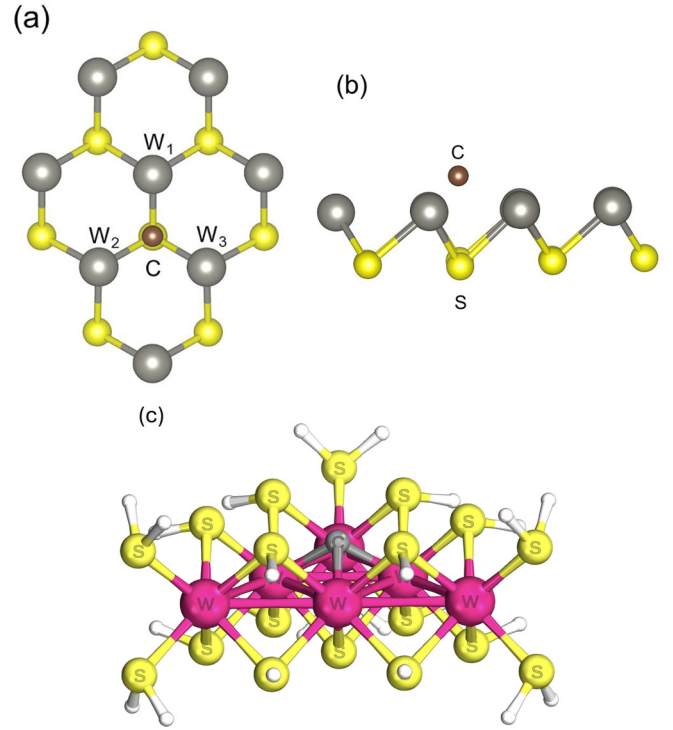


FIG. 3. (a), (b) Structure of the C_S^0 in WS_2 used in the calculated hyperfine tensors presented in Table II. (c) The molecular cluster used for CASSCF and NEVPT2 simulations.

no study has investigated the effect of carbon or its potential role in quantum defects. As discussed earlier, its concentration at room temperature ensures the presence of these defects in the sample. As we show below, it may also enable access to a paramagnetic triplet excited state. Such triplet states enable spin-dependent phenomena and optical transitions useful to quantum technologies. These observations further support the viability of carbon-doped bulk WS_2 for similar quantum defect engineering, aligning with broader strategies for defect-based quantum information systems across the family of layered TMDs.

D. Hyperfine tensors and ZFS

In Table II the calculated hyperfine constants for the C_S^0 in the triplet excited state are presented. These values were obtained using the r^2 SCAN, SCAN, HSE06, and HSE06* functionals. Our results reveal a highly localized defect spin primarily on the C dopant and the nearby W atoms. The values of the hyperfine tensor ($A_{xx} = 110.248$, $A_{yy} = 110.221$, and $A_{zz} = 182.063$ MHz for r^2 SCAN) show a large coupling to the ^{13}C nucleus at the defect site [Figs. 3(a) and 3(b)]. The interactions with the three nearest neighbor ^{183}W nuclei have much more moderate values ranging from 6 to 9 MHz. In contrast, the hyperfine coupling to the nearby ^{33}S nucleus is much smaller, suggesting a low unpaired electron density localized on this atom.

The majority of these results are in good agreement with the reported theoretical predictions for the C impurity in the monolayer. In their work, Li *et al.* [12] found that the neutral carbon substitutional has an unpaired electron, which

TABLE II. Calculated hyperfine constant (MHz) with r^2 SCAN, HSE06, and HSE06 with exchange 40% (HSE06*) with the contributions of the spin polarization of the core states (A_{1c}) in the Fermi-contact term. The first neighboring W atoms and the S atom below the C_s defect are considered.

	A_{xx}				A_{yy}				A_{zz}			
	r^2 SCAN	SCAN	HSE06	HSE06*	r^2 SCAN	SCAN	HSE06	HSE06*	r^2 SCAN	SCAN	HSE06	HSE06*
$^{183}\text{W}_1$	8.452	10.564	8.454	10.784	6.338	8.235	5.140	8.414	8.944	11.718	10.859	11.997
$^{183}\text{W}_2$	8.460	10.486	8.450	10.807	6.342	8.143	5.134	8.428	8.939	11.650	10.846	11.999
$^{183}\text{W}_3$	8.489	10.626	6.903	10.827	6.383	8.275	3.352	8.464	8.991	11.762	9.548	12.051
^{33}S	4.579	5.240	3.055	2.134	4.576	5.217	3.015	2.134	15.631	20.016	13.017	13.570
^{13}C	110.248	81.154	95.557	109.901	110.221	81.096	94.775	109.871	182.063	152.466	165.922	186.376

is mostly localized on the carbon atom, thus resulting in a very large hyperfine interaction with the ^{13}C nucleus. Our hyperfine tensor values agree well with the reported values for the monolayer, with small discrepancies.

Relative to the hybrid functionals, r^2 SCAN yields comparable hyperfine accuracy at far lower cost and without needing system-specific tuning of the fraction of Fock exchange, while preserving the same tensor structure and level ordering. As shown in Table II, r^2 SCAN reproduces the large ^{13}C tensors essentially at the HSE06* (40% Fock exchange) level and clearly above that of standard HSE06 (166 MHz), consistent with the general trend that increasing exact exchange localizes spin density and increases the Fermi contact terms. For heavy-nuclei couplings, r^2 SCAN yields modestly lower ^{183}W HFC values than hybrids (e.g., $A_{zz} \approx 9$ MHz vs ~ 11 – 12 MHz for HSE06/HSE06*) and the HFC values for ^{33}S remain within ~ 15 – 20% of hybrid functional predictions (e.g., 15.6 MHz vs 13.0–13.6 MHz), indicating small, interpretable shifts in spin-density partitioning rather than qualitative changes.

Hyperfine interactions of the C_s^0 center are very important for its performance as a qubit in quantum applications. Specifically, coupling to nuclear spins is highly related to the spin decoherence fluctuations and its coherence time [66]. Moreover, the presence of nuclear spins and the hyperfine interactions with them can be a useful resource for quantum information processing, enabling the entanglement of electron-nuclear spins in these defects to be used for applications in quantum memory registers and quantum error correction.

To accurately calculate the ZFS and include the effects of SOC and SSC in the neutral C_s^0 defect in bulk WS_2 , we employed a multiconfigurational wave function approach combining both CASSCF and NEVPT2 methodologies. This strategy allows for a reliable treatment of near-degenerate states, which are essential for describing open-shell systems such as the triplet state of C_s^0 . The molecular cluster used for these simulations is shown in Fig. 3(c); the highly localized nature of the defect orbitals and the rapid attenuation of the SOC and SSC operators with interelectronic distance, this molecular cluster was of adequate size to evaluate the ZFS reliably for this defect. While this model system reduces the problem to that of a monolayer rather than the bulk material considered in this work, the highly localized nature of SSC means that contributions between layers would be expected to be negligible, particularly since the pristine layers are non-magnetic. The primary difference in ZFS exhibited by the

defect in bulk WS_2 compared with that in monolayer WS_2 would be expected to arise from differences in the relaxed geometry of the defect, which are fully accounted for in the structural relaxations undertaken in this work. Since the WS_2 layers are only weakly bound by van der Waals interactions, the difference in defect structure between bulk and monolayer WS_2 would be expected to be minimal; indeed, the similarity in the values of ZFS for the defect in bulk and monolayer WS_2 supports this argument. We calculated the ZFS using the effective Hamiltonian approach reported in the methodology section. The ZFS parameters obtained are $|D| = 2.12$ GHz and $|E| = 0.28$ GHz. The $|D|$ is close to the reported value in the monolayer, which was 2.5 GHz. Interestingly, the similarity in ZFS parameters is also seen for the vacancy of boron (V_B) hBN monolayer and its bulk form [67]. The axial zero-field splitting D is predominantly determined by the short-range spin-spin dipolar interaction of the triplet state and therefore depends on the local anisotropy of the spin density around the defect. Because the defect wave function in WS_2 is strongly confined to a single S-W-S trilayer and the immediate W-S bonding geometry is essentially unchanged from monolayer to multilayer, the near-field spin density and thus D remains nearly the same in both WS_2 and hBN monolayer and bulk structures.

E. ZPL and qubit operation

In Fig. 4 the C_s^0 defect qubit operation protocol is presented. We have identified two possible excitations—one spin allowed from spin singlet to spin singlet and one spin forbidden from spin singlet to spin triplet with ZPL values 0.71 eV and 0.63, respectively. At this point it is worth mentioning that the excited state has a multiconfigurational character and can be approximated using the methodology described in [68]. In this multireference case, the ZPL value is calculated at 0.79 eV. We repeated these calculations with SCAN / HSE06 and we found a ZPL of 0.73 eV / 0.82 eV for the spin allowed transition. This proves that essentially meta-GGAs and HSE06 provide a similar ZPL. As we increase the supercell size to 20 Å in each direction, the value of the ZPL is reduced and converged to 0.35 eV for the singlet-to-singlet transition. In general, it should be noted that the singlet-to-singlet transitions could involve charge transfer and thus it is very common to apply charge corrections even to the ZPL value and in this case the ZPL value of the larger cells is equal to 0.35 eV (0.52 eV) using the r^2 SCAN (HSE06) density functional

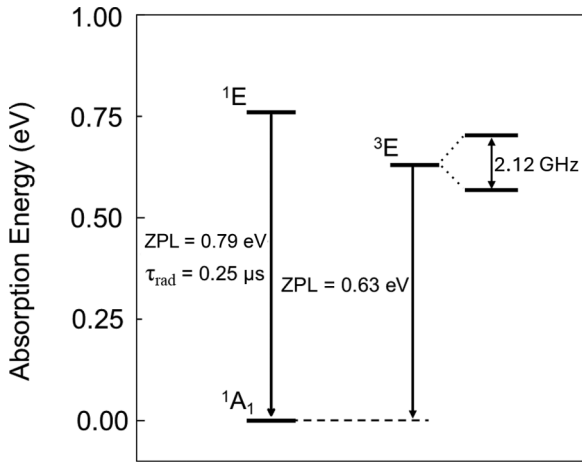


FIG. 4. Energy level diagrams showing the ZPL and ZFS parameters, which are the key to qubit operation for the $C_s^0:WS_2$ qubit using r^2SCAN .

approximations, respectively. However, as discussed previously, the spin allowed excitation arises from the creation of a bound exciton, which comes from an electron at the VBM occupying the intragap states. Furthermore, the spin forbidden transition is enabled by the spin-orbit coupling of tungsten, which mixes the spin states and creates a nonradiative decay pathway. The calculated radiative lifetime of the spin allowed transition is $0.25 \mu s$, which is in the acceptable ranges for quantum applications; for example, the T-center in silicon exhibits a lifetime of $1.39 \mu s$. We should note here that the transition dipole moments in our radiation lifetime calculations were sampled at the gamma point for the converged supercell and we used a refractive index of 4.1. The transition dipole moment intensity is calculated as 12.07. In monolayer WS_2 , the same excitation was predicted to emit at 0.92 and 0.85 eV for the spin allowed and spin forbidden transitions. Compared to the monolayer, it is obvious that the phosphorescence transition is redshifted and the ZPL is much lower. This infrared ZPL is of interest as a potential spin-photon interface, but as we discuss later its suitability must be weighed for applications involving quantum communication and telecom compatibility.

Normally the spin forbidden transitions do not emit; however, due to the presence of SOC it is possible that even the energy level of the triplet could participate in emission. The spin-forbidden ZPL is again calculated using both r^2SCAN and HSE06 and we found them to be equal to 0.63 eV and 0.74 eV, respectively. If used as a single photon source, these would not be directly compatible with the existing telecom networks without incurring higher losses or needing specialized optical fibers. For long-distance quantum communication, one might require frequency conversion to the desirable bandwidths to take advantage of this defect. For that reason, defects such as C_s^0 in monolayer WS_2 can have more practical applications

as they can operate with standard telecom fiber technology. At this point, we should point out though that shifts to the optical transition and spin levels can occur as a result of lattice strain or changes in temperature, so this low ZPL may be increased under real-world conditions. Moreover, in a related study by Tsai *et al.* [11] the authors examined triplet defects in TMDs and they reported low-energy ZPL from W_S^0 falling below the telecom window. In their work, they propose that these low-ZPL defects can be particularly promising for midinfrared quantum applications as they allow integration with some photonic platforms used for quantum information science which require long-wavelength photons [11]. Here we propose that the C_s defect in WS_2 can have similar applications.

IV. CONCLUSIONS

In summary, we have comprehensively investigated the electronic structure and magneto-optical properties of C_s in bulk WS_2 using a multilevel theoretical approach, combining r^2SCAN meta-GGA density functional theory calculations with advanced multiconfigurational wave function methods (CASSCF and NEVPT2). The present results show that carbon doping introduces metastable paramagnetic triplet excited states and well-defined intragap energy levels, enabling robust spin-photon interactions. We calculated the zero-phonon lines at 0.71 eV (singlet-to-singlet) and 0.63 eV (triplet-to-singlet). These transitions also have spin-orbit coupling due to the tungsten atom, making them promising candidates for quantum devices. With our multilevel approach, we found the ZFS at a value of 2.12 GHz, which is relatively close to the value of the monolayer defected WS_2 , making this defect a promising candidate for quantum sensing. Further investigations are required to advance this system towards implementation, such as investigating intersystem crossing rates to assess spin fidelity and coherence times as well as the lifetime of the metastable triplet excited state.

ACKNOWLEDGMENT

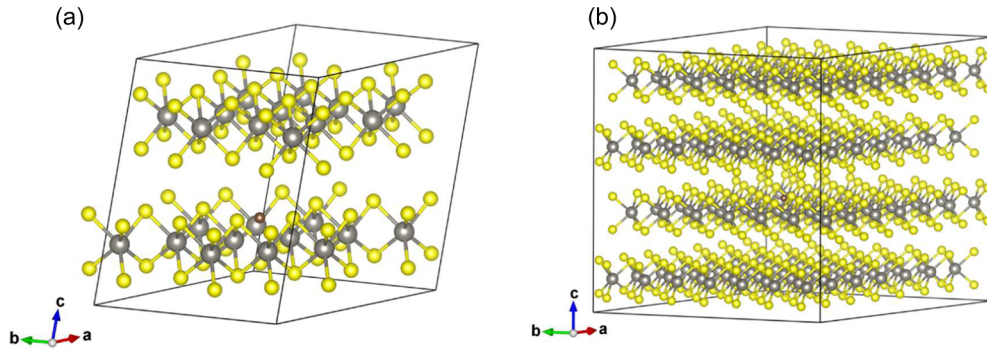
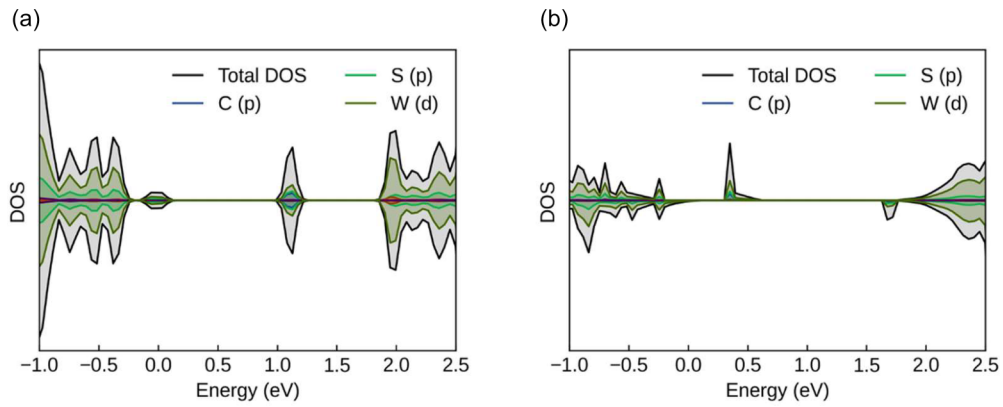
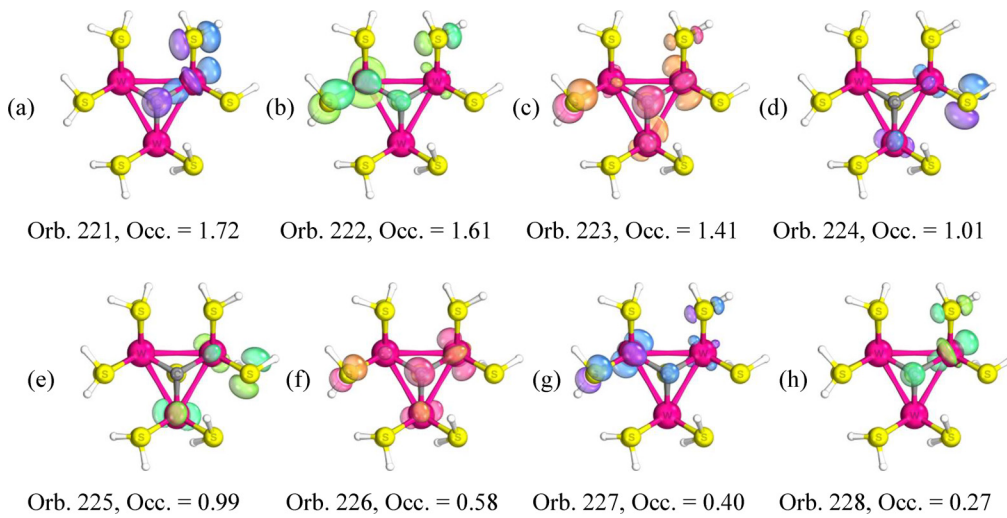
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DATA AVAILABILITY

All the data are available from the authors upon reasonable request.

APPENDIX

Our defected supercells for the neutral C_s^0 are shown in Fig. 5. In Fig. 6 the density of states are shown using the HSE06 functionals both for neutral and negatively charged defects. Figure 7 shows the active space of the C_s^0 using the Complete Active Space Self-Consistent Field. In Fig. 8 we present the relaxed structure of C_s^0 in bulk and monolayer WS_2 .


 FIG. 5. (a) the 72-atom supercell and (b) the 588 atom supercell for C_S^0 spin defects.

 FIG. 6. The density of states for C_S^0 and C_S^{-1} defects using HSE06 functional.

 FIG. 7. The active space orbitals of the C_S^0 defect computed using CASSCF.

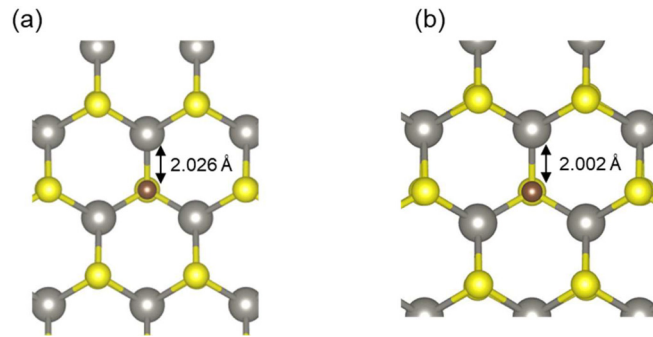


FIG. 8. The position of the carbon defect in C_{3v} symmetry in the (a) bulk and (b) monolayer.

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