Charged defects in 2D materials have emerging applications in quantum technologies such as quantum emitters and quantum computation. Advancement of these technologies requires rational design of ideal defect centers, demanding reliable computation methods for quantitatively accurate prediction of defect properties. We present an accurate, parameter-free and efficient procedure to evaluate quasiparticle defect states and thermodynamic charge transition levels of defects in 2D materials. Importantly, we solve critical issues that stem from the strongly anisotropic screening in 2D materials, that have so far precluded accurate prediction of charge transition levels in these materials. Using this procedure, we investigate various defects in monolayer hexagonal boron nitride (h-BN) for their charge transition levels, stable spin states and optical excitations. We identify C_{VB}N (nitrogen vacancy adjacent to carbon substitution of boron) to be the most promising defect candidate for scalable quantum bit and emitter applications.

Two-dimensional (2D) materials such as graphene, hexagonal Boron Nitride (h-BN) and transition metal dichalcogenides exhibit a wide range of remarkable properties at atomic-scale layer thicknesses, holds promise for both conventional and new optoelectronic functionality at drastically reduced dimensions [1–5]. It is well established that point defects play a central role in the properties of bulk 3D semiconductors but their corresponding role in 2D materials is not yet well understood. In particular, the weak screening environment surrounding the defect charge distribution and the strong confinement of wavefunctions due to the atomic-scale thickness could lead to vastly different behavior compared to conventional semiconductors.

Defects in 2D materials such as h-BN show promise as polarized and ultra-bright single-photon emitters at room temperature, with potentially better scalability than the long-studied nitrogen-vacancy center (NV) in diamond [6–8] for emerging applications in nanophotonics and quantum information [9]. Progress beyond initial experimental demonstration of promising properties requires rational design and development of quantum defects in 2D materials that exhibit high emission rate, long coherence time, single photon purity and stability. Specifically, the promising defects should have the following properties: defect levels should be deep (far from band edges) to avoid resonance with the bulk band edges and thereby exhibit long coherence time; [10] optically-addressable spin conserving excitations facilitate exploiting spin-selective decays in high-spin defect states, similar to the NV center in diamond. [11] Anisotropic polarization of the defect states in combination with quantum bits could provide a pathway to quantum optical computation.

In this work, we use first-principles methods to theoretically investigate the suitability of several complex defects in monolayer h-BN for quantum bit and emitter applications. We choose n-type defects which are closely related to common intrinsic and extrinsic defects in BN and can potentially create several occupied defect levels in the band gap and high spin states. For each candidate defect, we examine the charge transition level (CTL) which determines the stability ranges of various charge states of each defect. For each stable charge state, we evaluate spin states and optical excitations along different polarization directions. With these calculations, we will show C_{VB}N (a nitrogen vacancy adjacent to boron...
substituted by carbon as shown in Fig. 1 to be the most promising defect in 2D h-BN, analogous to the NV center in 3D diamond, which has a stable triplet ground state and a bright anisotropic optical transition between defect levels.

However, calculating properties such as CTLs and optical excitations of charged defects in 2D materials present serious challenges for state-of-the-art first-principles methods, which have so far limited the accuracy of previous calculations. We start this Letter by outlining these challenges and then discuss our methodology to address them.

The formation energy of a defect in charge state \( q \), ionic coordinates \( \mathbf{R} \) and electron chemical potential \( \varepsilon_F \) (often set to the valence band maximum for insulators or semiconductors) is given by \[1\]

\[
E_q^f(\mathbf{R})|\varepsilon_F = E_q(\mathbf{R}) - E_{\text{pot}} + \sum_i \mu_i \Delta N_i + q\varepsilon_F. \tag{1}
\]

Here \( E_q(\mathbf{R}) \) is the total energy of the system with the charged defect, and \( E_{\text{pot}} \) is the total energy of the pristine system. The third term on the right side accounts for the change \( \Delta N_i \) in number of atoms of element \( i \) between these two configurations, with \( \mu_i \) being the atomic chemical potential of that element in its stable form. The charge transition level (CTL) is the value of the electron chemical potential at which the stable charge state of the defect changes from \( q \) to \( q + 1 \), which corresponds to equal formation energies of the \( q \) and \( q + 1 \) states, and is therefore given by

\[
\varepsilon^{q+1}\vert_q = E_q^f(\mathbf{R}_q) - E_{q+1}^f(\mathbf{R}_{q+1}). \tag{2}
\]

where \( \mathbf{R}_q \) are the ionic coordinates of the charge state \( q \).

Within density-functional theory (DFT), CTLs can be determined by calculating formation energies in Eq. 2 in their respective equilibrium geometries, but this introduces two problems. First, DFT calculations of defects employ periodic boundary conditions on a supercell; formation energies of charged defects converge very slowly with supercell size due to periodic charge interactions and this is even more problematic for 2D materials. Second, the well-known band gap problem and self-interaction errors within standard DFT methods introduce significant errors in calculated CTLs, even if the supercell convergence issue could be dealt with.

The second issue above can be effectively solved by combining DFT with the many-body perturbation theory GW method \[16 \[19\]. This involves rewriting the CTL calculation as \[19 \ \[21\]

\[
\varepsilon^{q+1}\vert_q = E_q^f(\mathbf{R}_q) - E_{q+1}^f(\mathbf{R}_{q+1}) + E_q^f(\mathbf{R}_{q+1}) - E_{q+1}^f(\mathbf{R}_{q+1}), \tag{3}
\]

by adding and subtracting \( E_q^f(\mathbf{R}_{q+1}) \) (we note that the results are insensitive to the choice of path for defects in monolayer BN as discussed in SI). The second pair of terms on the right-hand side of Eq. 3 is the structural relaxation energy \( E_{\text{relx}} \) at the charge state \( q \), which can be calculated with reasonable accuracy at the DFT level (provided we solve the periodic charge interaction issue). The first pair of terms in Eq. 3 is the quasiparticle (QP) excitation energy \( E_{\text{QP}} \) at the fixed geometry \( \mathbf{R}_q \), which can be calculated accurately using the GW method \[16 \ \[22 \ \[23\]. However, GW calculations of quasiparticle energies in 2D materials exhibit serious convergence difficulties \[24 \ \[26\] that make the calculations of charged defects that require large supercells extremely challenging.

At this stage, Eq. 3 provides accurate CTLs in principle, provided we can address the periodic charge interaction issue in formation energies of charged defects at the DFT level, and resolve convergence issues for GW calculations of 2D materials. Below, we discuss each of these two issues and our methodology to overcome them.

First, the basic problem in charged defect formation energy calculations in DFT is the spurious interaction of the charged defect with its periodic images and with the uniform compensating background charge (necessary to make the total energy finite). For 3D systems, correction schemes \[27 \ \[30\] by removing the spurious periodic interaction from the DFT results using a model charge distribution for the defect and a model dielectric response for the bulk material work reliably well, because the self-energies of a model charge distribution both with periodic boundary conditions and without i.e. the isolated case can be computed easily \[27\].

However, for 2D materials, the dielectric screening is strongly anisotropic and localized to one atomic layer; correction schemes now require a spatially-dependent anisotropic dielectric function, whose spatial profile is not unambiguously defined. Most importantly, calculation of the isolated charge self-energy for the correction has so far relied on extrapolating periodic calculations in various supercell sizes, \[31\] an approach we find here to be problematic due to its strong nonlinear dependence on the supercell sizes (as shown in Fig. 2(a)). This nonlinearity comes both from the highly anisotropic screening in monolayer 2D materials and the spatial distribution of bound charge in the dielectric surrounding the model charge, which has also been found in defects of MoS\(_2\) \[22\].

We recently developed a robust scheme for calculating formation energies of charged defects in bulk and interfaces, \[33\] that (a) redefines DFT electrostatic potentials to avoid strong oscillations near atom centers improving supercell convergence with geometry optimization, (b) unambiguously defines a spatial dielectric profile \( \varepsilon^{-1}(z) = \frac{-\partial \Delta V(z)}{\partial z} \) as the change in the now-smooth total potential \( \Delta V(z) \) upon applying a normal electric field \( E_0 \), and importantly, (c) it also completely avoids the problematic extrapolation between supercell sizes \[31\] (or convergence issues in image charge methods \[25\]) by us-
produced large discrepancies in literature even for properties of pristine 2D materials. As an example, converging GW calculations of pristine monolayer MoS₂ requires at least 6000 bands, 25 Å vacuum spacing, and a \( 24 \times 24 \times 1 \) \( k \)-point grid for Brillouin zone integration. Adopting such parameters for large supercell calculations containing defects would make them impractical.

The slow convergence with respect to the number of bands can be overcome by using a recent implementation of the GW method that does not explicitly require any empty states as implemented in the WEST code, \([16, 17, 23, 35-37]\) based on density functional perturbation theory \([38]\) and the projective dielectric eigen-potential (PDEP) algorithm, \([39, 40]\).

For 2D materials, the remaining convergence issues arise from the long-range nature of the dielectric matrix and GW self-energy (in contrast to DFT), which have not been solved by current implementations. Here the polarization of repeated images in the direction perpendicular to the plane spuriously screens the Coulomb interaction and lowers the QP gap. These image interactions can be avoided in the correlation part of the self-energies by using a truncated Coulomb potential,

\[
\tilde{\varepsilon}(\mathbf{k}) = \frac{4\pi}{k^2} \left(1 - e^{-k_S L_z/2} \cos \frac{k_x L_x}{2}ight),
\]

expressed here in reciprocal space \([41]\). In Eq. (4) we have \( \mathbf{k} = \mathbf{q} + \mathbf{G} \), where \( \mathbf{q} \) is a wave vector in the first Brillouin zone and \( \mathbf{G} \) denotes the reciprocal lattice vectors. Fig. 3(a) shows that this truncation results in excellent convergence with vacuum spacing for the GW QP gap of monolayer BN. Specifically, we performed \( G_0 W_0 \) calculations in which the self-energy is approximated from DFT states with the PBE exchange correlation functional \([42]\). At 30 Bohr (16 Å), the QP gap is converged within 10 meV, while the conventional treatment results in a smaller gap as discussed above, which does not converge even at 100 Bohr.

When \( \mathbf{G} = 0 \) and \( q_z = 0 \), the potential in Eq. (4) diverges as \( 2\pi L_z/q_{xy} \) for \( q_{xy} \to 0 \) and the inverse dielectric matrix has a ‘dip’ feature in this limit. Accordingly, around the \( \Gamma \) point a fine \( q \) mesh is required to compute absolute QP energies. Explicit \( q \)-mesh convergence is not practical for large supercell calculations with defects. Instead, since discarding the \( q_{xy} = 0 \) component introduces an error proportional to \( L^{-2} \), we extrapolate quasi-particle corrections to the \( L \to \infty \) limit from three supercell sizes \((L^2 = 6 \times 6, 9 \times 9, 12 \times 12 \, \text{a}^2)\). Fig. 3(b) shows that this extrapolation works very well, with a deviation within 0.03 eV with respect to more sophisticated models for the \( \mathbf{q} \to 0 \) contribution \([43]\). The QP correction for the \( 12 \times 12 \, \text{a}^2 \) is converged within 0.1 eV compared to the extrapolated value.

We implemented the DFT charge correction scheme discussed above in JDFTx \([44]\) and the method to treat...
FIG. 3. (a) Coulomb truncation substantially improves convergence of GW band gap of h-BN with respect to vacuum spacing (with a 3 × 3 a^2 lateral supercell size). (b) GW correction to the VBM (valence band maximum) extrapolates reliably with lateral supercell size. Black dots are the computed values with Coulomb truncation and dot blue and dashed green lines are extrapolated values with two different formula.

2D materials in GW calculations in WEST.[37] Optimized geometry and DFT eigenvalues and wavefunctions are obtained using Quantum ESPRESSO.[45] (See SI for further computational details.)

Having eliminated all the roadblocks in calculating CTLS of 2D materials, we now predict properties of the simple (CB (carbon substitution of boron), VN (nitrogen vacancy)) and complex (CBVN, NBNVN (nitrogen substitution of boron adjacent to a nitrogen vacancy)) charged defects (CBVN see Fig. 1). As discussed earlier, promising candidate defects should have stable high-spin states, localized and deep defect levels, spin conserved excitations and anisotropic optical response.[6, 9] Fig.4 shows their optical (without geometry relaxation, dashed lines) and thermodynamic CTLS (solid lines) at both the DFT (left panel) and GW (right panel) levels of theory (see note 46).

Table I. Physical properties of defects in monolayer h-BN relevant for quantum technologies. Below, “S”, “D” and “T” denote singlet, doublet and triplet spin states respectively.

| Defects   | CB  | VN | NBN | CBVN |
|-----------|-----|----|-----|------|
| Deep level | Yes | Yes| Yes | Yes  |
| Spin at \( q = 0 \) | D   | D  | D   | D    |
| Spin at \( q = \pm 1 \) | S   | S  | S   | D    |
| Bright transition between defect states | No | No | Yes | Yes |
| Optical anisotropy | No | No | Yes | Yes |

All four defects have deep CTLS with the neutral state being stable for a wide range of \( \varepsilon_F \), but their spin and optical properties are rather different as Table I shows. CBVN center has a spin triplet ground state as shown in Fig. 1 left panel, which is advantageous for quantum applications, while the doublet states are rather different. Furthermore, we computed the optical transitions and absorption spectra for all defect cases and found both CBVN and NBNVN have bright defect-to-defect state transition well separated by over 1 eV from any defect-bulk and bulk-bulk transitions. A strong in-plane polarization anisotropy was also found in their absorption spectra (see Fig. 4 and SI for details of absorption spectra
and selection rules).

In summary, we developed a methodology to reliably calculate thermodynamic CTLs in 2D materials by solving several critical issues in charged defect formation energies and GW QP energies for 2D systems in general. The source of difficulties originate from the highly anisotropic and localized screening of 2D systems, which necessitates proper treatment of electrostatic potentials of charges near a 2D plane and of the screened Coulomb interaction in the GW approximation. Using this methodology, we examined several possible defects in h-BN and identified C$_3$V$_N$ center to be promising for quantum technologies, which has multiple deep defect levels, a triplet ground state and bright defect-to-defect transitions.

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