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Perspective

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Quantum defects by design

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Abstract: Optically active point defects in wide-bandgap crystals are leading building blocks for quantum information technologies including quantum processors, repeaters, simulators, and sensors. Although defects and impurities are ubiquitous in all materials, select defect configurations in certain materials harbor coherent electronic and nuclear quantum states that can be optically and electronically addressed in solid-state devices, in some cases even at room temperature. Historically, the study of quantum point defects has been limited to a relatively small set of host materials and defect systems. In this article, we consider the potential for identifying defects in new materials, either to advance known applications in quantum science or to enable entirely new capabilities. We propose that, in principle, it should be possible to reverse the historical approach, which is partially based on accidental discovery, in order to *design* quantum defects with desired properties suitable for specific applications. We discuss the biggest obstacles on the road towards this goal, in particular those related to theoretical prediction, materials growth and processing, and experimental characterization.

Keywords: point defects; quantum information processing; semiconductors; photonics; NV center; materials discovery; inverse engineering; quantum sensing; quantum emitters.

1 Introduction

Miniaturization of electronic and opto-electronic semiconductor devices has been happening ever since the first such devices appeared. Eventually, one can envision a device that is composed of just a few atoms. As these atoms ideally should not float in free space, but should be embedded in a solid-state matrix, this naturally brings one to the concept of a point defect (an impurity atom or complex of atoms) as the ultimate electronic or opto-electronic device. At such tiny length scales the behavior of physical systems is governed by the laws of quantum mechanics. Therefore, it is no surprise that an increasing number of point defects are being considered as building blocks for various applications in the field of quantum information science; more specifically, in quantum sensing, quantum communication, and quantum computing [1–4]. We refer to these desirable defects as *quantum point defects* (QPDs). Prominent examples include the nitrogen-vacancy (NV) center in diamond, the silicon-vacancy (SiV) center in diamond, the divacancy in silicon carbide, and rare-earth impurities in complex oxides; see Figure 1.

The number of possible QPDs is extremely large, and each defect system has its own unique set of properties. Some properties arise directly from the defect's chemical structure, whereas others stem from characteristics of its host material; together, these properties determine a defect's quantum functionality. Despite continued advances in theoretical understanding, accurate first-principles calculations, and experimental capabilities, an exhaustive search remains impractical. Therefore, a deep understanding of these property-function relationships is essential to developing efficient, heuristic screening criteria that guide exploration through a large materials parameter space.

The purpose of this article is to contemplate this challenge in the context of current experimental and theoretical capabilities. It is organized as follows. After reviewing the current role of defects in quantum science and technology in Section 2, we highlight the potential for identifying QPDs in new materials systems and present a vision for application-driven discovery in Section 3. As a counterpoint to this vision, Section 4 features a brief

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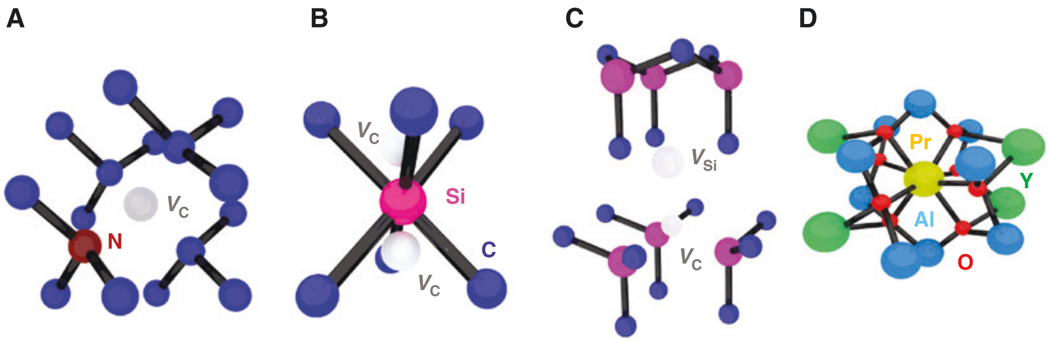

Figure 1: Prominent quantum point defects.
(A) Nitrogen-vacancy center in diamond; (B) silicon-vacancy center in diamond; (C) divacancy in 4*H*-SiC; and (D) substitutional Pr ion in yttrium aluminum garnett (YAG).

historical overview of a prototypical QPD – the diamond NV center – highlighting how new applications continue to emerge from investigations of the defect's fundamental properties. This historical perspective acknowledges the role of serendipity in scientific discovery. Ultimately, we hope that a design-driven approach can supplement the traditional modes of investigation. Towards that end, we reflect on the opportunities for exploration of new materials systems in Section 5, and review the main criteria one must consider in designing quantum defects. Finally, Section 6 discusses several key challenges in theoretical prediction, materials synthesis, and experimental characterization. We highlight promising new directions in these domains and consider what is needed to achieve the goal of *quantum defects by design*.

2 Why defects?

Defects are ubiquitous in all materials. They can dramatically modify a material's electrical, optical, and mechanical properties, enabling widely tunable responses and new functionality (e.g. for transistors and lasers). At concentrations where defects do not interact with one another, they are analogous to trapped atoms or molecules, with individual electronic states isolated within the host material's band gap – the semiconductor vacuum [5] – with orbital and spin degrees of freedom that can be controlled using electromagnetic fields.

Especially in wide-bandgap materials, where deep defect levels are characterized by tightly bound electronic wavefunctions, a defect's electronic structure is determined by its symmetry and chemical composition in direct analogy to individual molecules. Indeed, molecular orbital theory is the prevailing tool to achieve qualitative – and sometimes quantitative – understanding of a defect's electronic structure and optical dynamics [6, 7].

In certain configurations, the orbital or spin degrees of freedom of electrons and nuclei associated with a defect are sufficiently isolated from environmental perturbations (including thermal phonons, electromagnetic noise, free carriers, and other defects in the material) that quantum-mechanical superpositions of these states can be prepared and maintained for periods of time that enable their practical use for quantum information science. The prototypical and most well-studied QPD is the diamond NV center (Figure 1A), whose electronic spin state can be initialized, controlled, and read out at room temperature using optical pumping, microwave spin resonance, and photoluminescence, respectively [8]. The sensitivity of these spins to local fields (e.g. electric, magnetic, thermal, and strain) and the ability to embed the defects in nanostructures facilitate revolutionary modalities of nanoscale sensing for physics [9–12], chemistry [13–15], and biology [16, 17]. Each NV center also constitutes a quantum register of electron and nuclear spins that can be individually controlled [18–20], entangled [21, 22], stored coherently for several seconds [23, 24], and used to perform quantum operations including teleportation [25] and error correction [26–28]. At liquid helium temperatures, NV-center electronic spins couple coherently to light [29–32], and they can be remotely entangled through photonic channels [33–35], forming the basis for distributed quantum networks [36, 37].

However, the diamond NV center is by no means unique nor the optimal QPD for many situations. Spurred by the potential to identify other spin qubits with improved properties and new functionalities, exploration of semiconductor defects has grown rapidly in recent years to include additional systems in diamond [38–44] (see Figure 1B) and SiC [45–47] (see Figure 1C), rare-earth ions in oxide crystals [48–51] (see Figure 1D), as well as wide-bandgap group II–VI and III–V materials such as ZnO [52–54] and GaN [55–57], and low-dimensional van der Waals materials such as the transition metal dichalcogenide (TMD) WSe_2 [58–62] and hexagonal boron nitride (hBN) [63–67]. A theoretical understanding of many of these systems is still lacking, and in some cases even the defect's chemical structure remains unknown. Nonetheless, they offer potential advantages over NV centers including optical indistinguishability [68, 69], high brightness [56, 63], improved performance in nanophotonic devices [70, 71], and incorporation in a more technologically mature semiconductor host [72].

3 Defects by design

Historically, the discovery and development of semiconductor defects – either as spin qubits or for other purposes – has been a sequential process focused on the specific properties of individual materials. Experimental observation of a new phenomenon, such as a prominent spectral line or a strong magneto-optical response, motivated the construction of theoretical models and numerical calculations to establish the electronic structure. This, in turn, motivated the identification and development of potential applications. The throughput of this sequential approach is fundamentally limited, because it is impractical to experimentally measure or computationally model all possible defects in one material host, let alone in all possible hosts.

Ultimately, it would be desirable to complement this historical approach with an inverted discovery paradigm, as shown in Figure 2. Beginning with scientific or application goals, one would assess the relevant requirements and figures of merit, demarcate a range of crystal hosts and defects that should exhibit the required properties, screen the candidates, and only then initiate targeted research to engineer the materials and refine experimental techniques. Lessons can be drawn from past research that concentrated on the properties of individual defects, but addressing this challenge requires considerations of broader questions including: What is the ideal QPD electronic structure for a particular application? What defects within which crystal hosts would exhibit the required properties? Which systems from the selected hosts are most feasible from the experimental and engineering standpoint? In addition to electronic structure, how precisely can we predict complex QPD properties such as optical lineshapes, quantum efficiency, spin coherence, and fidelities for initialization and readout?

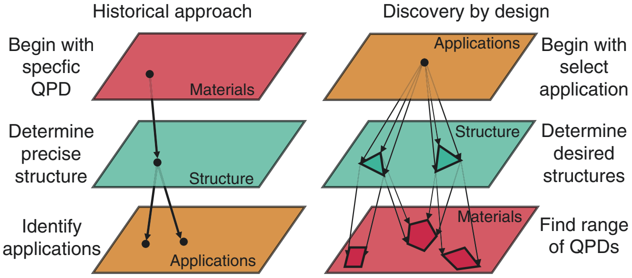

Figure 2: An efficient approach to QPD discovery would invert the existing paradigm (left) to identify materials and defects optimized for specific applications in quantum science (right).

Given the complex interdependence of host material characteristics, defect properties, and quantum functionality (see Section 5), it is unlikely that we will converge on a single "best" QPD; more likely, development of new QPDs will yield varied systems that are optimized for particular applications. The rich history of the diamond NV center's development as a platform for quantum science (see Section 4) provides abundant examples of unanticipated applications that emerged from fundamental investigations, so one can reasonably anticipate that many new applications will similarly sprout from research on QPD systems with different properties. In this way, as with any research endeavor, the actual progression of QPD knowledge will always be a combination of the serendipitous historical approach and the systematic design paradigm illustrated in Figure 2. Nonetheless, with continued progress in computational models that enable quantitative theoretical prediction of QPD properties, as well as efficient experimental techniques for synthesis and screening of QPD candidates, it should be possible to significantly accelerate the discovery process.

4 A brief history of the NV center, a prototypical QPD

Here, we take a short historical tour to illustrate the interplay between our physical understanding of a quantum defect, the drive toward a given quantum technology, and materials advancements in the field of QPDs. We utilize the negatively-charged NV center in diamond, already introduced, but note that parallel histories could be constructed for other quantum defects. For example, the QPD timeline for phosphorous donors in silicon [73] could start from the Kane proposal for a silicon quantum computer [74], while a timeline for rare-earth doped crystals [75, 76] could start from the first demonstration of electromagnetically-induced transparency [77]. Fantastic in-depth reviews on the fundamental properties [8, 78] and applications [9, 17, 79, 80] of NV centers already exist in the literature. Here we focus on a few key, enabling discoveries.

The turning point, which eventually led to the realization of the NV center as a QPD, was the optical detection of single centers *via* confocal microscopy of a bulk diamond sample by Gruber et al. in 1997 [81]. In contrast to various reports today of QPDs of as yet unknown origin [53, 56, 58–61, 63], Gruber et al. purposefully synthesized a previously identified defect at concentrations low enough for single center isolation. NV-center formation was reported as early as 1965 [82], with the atomic structure of the defect confirmed by the 1970s [83]. Optical spin polarization (or optical pumping) was reported in electron-spin-resonance measurements in 1977 [84] and optically-detected magnetic resonance (ODMR), a key spectroscopic technique to access spin dynamics, had been reported at low temperature for NV-center ensembles in 1990 [85]. Thus, in some sense, the stage was set for rapid development with respect to quantum technologies once single-center isolation was achieved. In fact, in the first demonstration of single-NV-center isolation, Gruber et al. also demonstrated single-center ODMR at room temperature. The application of NV centers in quantum technology was not yet on the radar. The main motivation for Gruber et al. was to allow “detailed material characterization at a local level that is otherwise masked by ensemble averaging” [81].

Within several years of Gruber et al.’s seminal work, the utilization of the NV center as a single-photon source had been demonstrated [86, 87], again with synthesized centers. The next major developments were single electron spin control [88], single nuclear spin control, and spin-spin quantum gates [89], all enabled by optical pumping and ODMR techniques developed a decade earlier. Yet quantum coherence times were short, limited by the high nitrogen content of the type Ib synthetic diamond. The use of NV centers unintentionally incorporated in type IIa natural diamond enabled long room-temperature coherence times, elucidating the rich dynamics between the NV electronic spin and the nuclear spin bath [18], which further enabled multi-qubit registers [19, 21]. The combination of spin control and long room-temperature spin coherence led to theoretical proposals to utilize the NV center as a nanoscale magnetic sensor in 2008 [90, 91], followed almost immediately by experimental demonstrations [92, 93].

A proliferation of NV-center-based research over the next decade in both quantum information and quantum sensing can be attributed to the combination of these seminal demonstrations and the commercial availability of “electronic grade” diamond [94, 95], with nitrogen concentration of less than 1 part per billion (ppb), from the company Element Six around 2007. These high-purity diamond substrates host unintentionally-incorporated NV centers with quantum properties on par with the best natural diamond samples [96] and at concentrations suitable for single NV-center isolation using basic confocal microscopy. Additionally, electronic-grade substrates facilitated experiments to improve the quantum properties of single, near-surface NV centers formed via N^+ ion implantation [97–99].

As key technologies, such as single-shot single-spin readout [100], remote spin-spin entanglement [33, 35], and single protein magnetic resonance spectroscopy [13, 14] were demonstrated, the limitations of the NV center for each particular application became more apparent. These limitations motivated further research and discovery in the fundamental understanding of the specific physics that limits the NV center’s performance in order to engineer methods to overcome the limitation. We next use the specific example of the NV center’s inter-system crossing (ISC) and its role in spin readout to illustrate this process.

High-performance spin readout [101] is essential for spin-based quantum information protocols and for high-sensitivity sensing. The NV center’s spin-dependent ISC enables room-temperature single-spin detection via photoluminescence intensity. However, whereas high-fidelity readout can be achieved at cryogenic temperatures using resonant optical pumping [100], the transience and low contrast of the ISC-mediated spin-dependent photoluminescence has prevented single-shot spin measurement at room temperature. This limitation, as well as the need to understand the fundamentals of NV centers, motivated the development of the theory (including *ab initio* theory) for the radiative and non-radiative transition rates [102–104]. It also motivated the development of an alternative method for spin read-out: high-fidelity charge state readout [105] and spin-to-charge conversion [106, 107]. This second approach can improve the experimental signal-to-noise ratio for single-shot spin readout by over an order of magnitude [101]. The development of spin-to-charge conversion further motivated theoretical work on the photoionization properties of the NV center [108]. Finally, the relatively low speed and high complexity of optical readout, requiring optics and detectors to collect single photons, combined with advances in photoionization theory, has led to the demonstration of photoelectrically-detected magnetic resonance (PDMR) [109, 110], including recently of single spins [111].

The connection between a physical property of a QPD (in this case the ISC), the physics behind the property, the

Table 1: Connections between the physical properties of a defect, in this case the NV center, and potential applications.

Property	Physics	Challenges	Mitigations	Applications
Inter-system crossing (ISC) [8, 78]	Spin-orbit coupling, phonon interactions, excited state structure	Spin-readout SNR	Alternative readout strategies	Optical readout [101]
Ground-state response to local fields [8, 78]	Ground-state electronic structure	Inhomogeneous broadening, sensor stability	Double quantum magnetometry, active control	Sensors [9]
Phonon-assisted/ phonon-broadened transitions [8, 78]	Excited-state structure, Jahn-Teller interactions	Photon indistinguishability, ZPL efficiency	Photonic cavities	Off-resonant spin readout [101], thermometry [112]
^{13}C nuclear bath [113]	Central spin model, non-Markohvian dynamics	Spin decoherence	Isotope purification dynamic decoupling	Qubit registers [19, 27]
Multiple charge states [105]	Charge capture, nonlinear and non-equilibrium effects	Stabilization of desired charge state	Optical charge control Fermi-level control	Enhanced readout schemes [101], free carrier spin bus [114]

The first row follows the discussion in the main text linking the ISC to optical readout. References are either review articles or illustrative references and are not intended to be exhaustive.

challenges it presents, and the opportunities it enables (e.g. with respect to mitigating the challenges and enabling new applications), can be made again and again for different properties. Several examples of this rich interplay for the NV center are given in Table 1. While performance in NV-center-based applications continues to increase, performance is alternatively limited or facilitated by the defect's basic properties. Starting with defects with different properties will drastically increase the quantum-enabled application space. We thus need an efficient way to find these defects.

5 Opportunities in a complex parameter space

In expanding the QPD parameter space beyond traditional hosts, such as group IV materials, it is crucial to realize that each potential application poses a unique set of requirements on QPD functionality, which are in turn related in complex ways to the structural and functional properties of the defect and its host. The interconnected network of property-function relationships is qualitatively depicted in Figure 3, where lines indicate connections that are important for determining particular properties or functionality of QPDs, and the size of each circle is proportional to the number of connections it involves. The diagram is far from exhaustive and does not capture information regarding the relative importance of different properties; rather, it shows how myriad features collectively give rise to specific quantum functionality. For example, an application for single-photon sources might require bright, high-purity emission in a specific, narrow spectral band with a well-defined optical polarization axis, whereas the main criteria for a quantum sensor is the signal-to-noise ratio for spin readout. In the latter case, the key property is a strong spin-dependent optical signal, and a wider emission bandwidth might actually be preferable in order to simplify isolation of the signal from the excitation background.

Identifying novel QPDs is a combinatorial problem. Even if one considers just three QPD classes – substitutional dopants, native vacancies, and dopant-vacancy complexes – in commercially available wide-bandgap hosts, there are millions of potential host-defect combinations. Clearly, this massive parameter space precludes an exhaustive search by detailed calculations or experimentation.

Systematic discovery of new QPDs thus requires the development of heuristics to efficiently screen this parameter space. Weber et al. [115] took a key step in this direction, showing how independent consideration of host properties (e.g. band gap, nuclear spin isotopes, and spin-orbit coupling) can guide the identification of QPDs analogous to the diamond NV center. In particular, this analysis elevated the profile of SiC as a QPD host, spurring efforts to identify and control single spins in that material – especially the divacancy and silicon vacancy [45–47]. As in the case of the diamond NV center, key features of the divacancy and silicon-vacancy defects in SiC were already established [116, 117], and high-quality substrates were commercially available. For these reasons, and leveraging experience gained from the diamond NV center, SiC QPDs have seen rapid development [37]. Ultimately, it should be possible to extend Weber et al.'s methodology to a higher

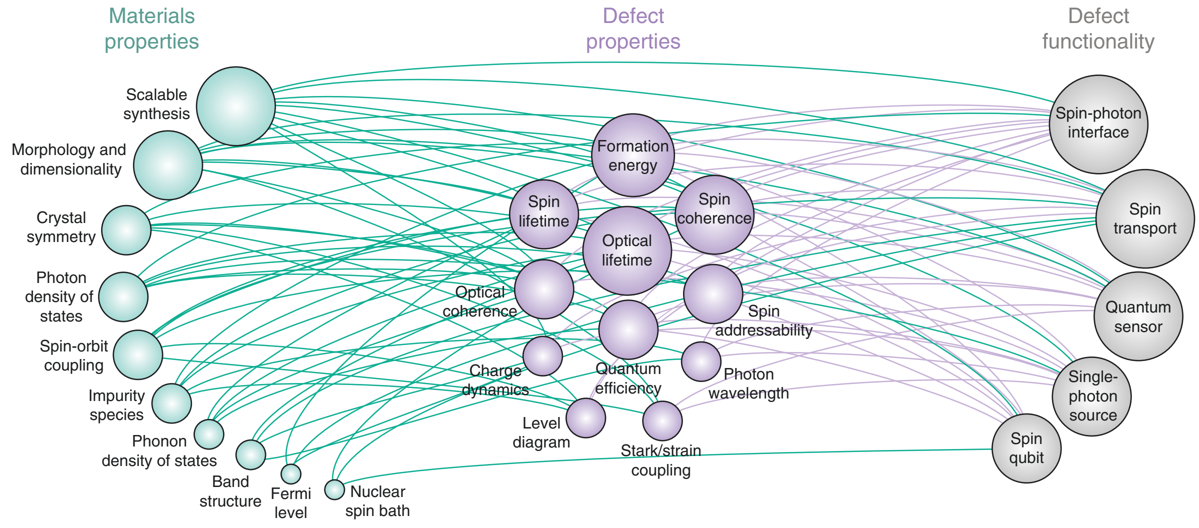

Figure 3: The functionality of a defect for quantum science applications depends in complex ways on the defect's propeties, which are in turn related to the fundamental properties of the host material and the defect's composition. Each application requires a different set of properties.

level of abstraction, combining analytical and computational theory to predict how host symmetry, defect configuration, and chemical composition couple to produce the desired electronic structure for a given application. In the sections that follow, we discuss some general considerations to guide investigations of new materials, especially considering the role of the host material's dimensionality and symmetry in constraining defect properties.

5.1 Guiding criteria for exploration

Excellent rationale underlies the field's current emphasis on group IV hosts, and these materials will surely remain prominent as the field expands. Nonetheless, many other materials have properties conducive to hosting QPDs, but are largely unexplored. Whereas group IV materials are mainly available as bulk crystals, many other compound semiconductors are amenable to sophisticated synthesis via molecular beam epitaxy (MBE) or synthetic chemistry and are available in various morphologies such as epitaxial thin films, nanocrystals, and nanowires. Such materials offer potential advantages for applications through their tailored electronic, optical, or chemical properties. Given the large parameter space, however, it is best to proceed beyond group IV systematically with clear goals in mind.

We can lay out several guiding criteria based on basic material properties. The criteria are reminiscent of those articulated by Weber et al. [115], albeit informed by recent developments in the field and with a somewhat more general context, as we are not only interested in analogs to the diamond NV center. We also emphasize that these are guidelines, not rules; often there are competing effects, and application-specific considerations may lead to choices that violate the criteria.

5.1.1 Band gap

Generally, QPDs feature highly isolated states deep within the semiconductor's band gap, such that they are spatially confined and energetically isolated from direct interactions with delocalized charge carriers. If a localized optical excited state is also desired within the band gap, e.g. for optical spin initialization or coherent interactions with photons in the visible-to-near-infrared range, then the host material's band gap should be at least 2 eV. Larger band gaps provide additional room to accommodate multiple charge states or even different defect configurations in order to achieve the desired spin structure. For example, diamond's large band gap has facilitated exploration of the entire QPD family of group IV-vacancy complexes (SiV, GeV, SnV, PbV), all of which have the structure shown in Figure 1B; these defects have similar electronic structures but differ in their optical transition energies and spin-orbit coupling [118]. Similarly, wide-bandgap hosts of transition-metal and rare-earth ions exhibit defect families associated with impurity atoms from same row of the periodic table, whose spin and optical properties are determined by the electrons in the ion's *d*- or *f*-shell orbitals, respectively.

The choice is not always simple, however. It is difficult to control the Fermi level of wide bandgap materials, and challenging to realize electronically active devices. Indeed, a large band gap is less important for paradigms where optical excitations are not required, e.g. for electrically controlled phosphorus-donor qubits in silicon. Even for optical QPDs, it is not always essential for states to be completely isolated from the band edges. Donor-bound excitons feature optical transitions that are close to the bandgap energy [54, 119], and the resulting hybridization with delocalized electron-hole pairs increases the donors' optical cross section and determines their selection rules.

5.1.2 Nuclear spin bath

Nuclear spins generally remain unpolarized at experimentally accessible temperatures and magnetic fields, and random fluctuations in this bath induce decoherence for QPDs. Nuclear spins are not always detrimental, and in the proper configuration they offer additional quantum degrees of freedom for applications. Nonetheless, it is usually desirable to choose materials with a dilute nuclear bath. Elements in groups II, IV, and VI possess spinless nuclear isotopes, whereas all elements in odd groups exhibit nonzero nuclear spin.

One can assess the natural abundance of spinless isotopes for a quick evaluation of a material's nuclear spin bath in the absence of isotopic purification, however, the actual effect of this bath on QPD spin coherence is somewhat more difficult to estimate. For example, the isotopic abundance of spinful isotopes in SiC (2.9%) is more than twice that of diamond (1.1%). Nevertheless, divacancies in naturally isotopic SiC exhibit spin coherence times that are comparable to or even longer than those for diamond NV centers [46]. One needs to account for the details of the hyperfine coupling and spin-bath dynamics that cause decoherence; in the case of SiC, a larger lattice spacing and weak coupling between nuclear species with different gyromagnetic ratios in SiC mitigates the effect of a higher spin density compared to diamond [120, 121]. Furthermore, the application of dynamical decoupling techniques for cancelling low-frequency noise and dynamical nuclear polarization for cooling the spin bath mitigates many of the detrimental effects of nuclear spins [122]; this can make materials like group III–V semiconductors a viable option, especially to leverage the advanced synthesis and nanofabrication capabilities associated with these materials to realize integrated electronic and photonic devices.

5.1.3 Spin-orbit coupling

The fundamental attraction of spins as qubit degrees of freedom is that they respond mainly to magnetic fields and are relatively immune to environmental noise from fluctuating charges and phonons. Orbital degrees of freedom, by contrast, respond directly to these pervasive sources of noise. Therefore, low spin-orbit coupling is usually desirable in order to achieve long spin coherence times. As spin-orbit coupling generally scales with atomic number Z, this can be accomplished by choosing materials composed of light elements.

Again, however, the choice is not always straightforward. Spin-orbit coupling is the fundamental mechanism responsible for coherent spin-light interactions – it limits the rate at which spins can be controlled using light [29, 31, 32], sets the selection rules for generation of spin-photon entanglement [30], and underlies the ISC transitions that mediate spin initialization and readout for the diamond NV center [102, 104] and other defects [123]. Spin-orbit coupling further enables control of spins using mechanical waves [124, 125], and potentially the use of phonons as a quantum bus between spatially separated spins [126–128]. Moreover, depending on the system and experimental parameters, spin decoherence can be dominated by different effects, including hyperfine coupling to the nuclear spin bath or various spin-lattice relaxation processes [119, 129, 130]. Therefore, one should not assume that spin-orbit coupling should always be minimized; rather, it is a crucial tuning parameter that should be carefully considered in the context of a given application. One attractive way to achieve such tuning is to study families of defects with similar electronic structures, composed from impurity atoms drawn from the same group, as for the group IV-vacancy defects in diamond, where the spin-orbit coupling increases for elements of increasing atomic number [118].

5.1.4 Crystal symmetry

In a first approximation, a defect's orbital and spin structure derives directly from its spatial symmetry. The point group determines the multiplicity of each level according to molecular orbital theory [6, 7]. Generally, higher symmetry allows for degenerate orbitals. Degenerate orbital levels are important, since, as per Hund's rule, they will give rise to high spin states ($S>1/2$) in the electronic ground state. High spin states are often desirable for QPDs, as they exhibit zero-field splitting parameters in the spin Hamiltonian; this decouples the QPD from background electronic impurities in the material with $S=1/2$

and allows for coherent spin control even at zero magnetic field. Orbital degeneracies also give rise to various spin-orbit combinations with definite symmetry in the electronic ground or excited state that can produce spin-photon entanglement [30].

As prototypical defect models, let us consider two types of lattice imperfections. One type is a simple vacancy or a substitutional impurity, whereby only one lattice site is affected (e.g. the Pr defect in YAG, Figure 1D). The other type is a complex between a vacancy and an impurity, two impurities, or a divacancy (Figure 1A–C). In a given material, the point group with the highest symmetry belongs to the first type of defect, whereas the second type transforms according to subgroups with lower symmetry. In some cases, a defect's symmetry is different than one might naïvely predict due to lattice distortions; for example, the static Jahn-Teller effect generally lowers the symmetry whereas the split-vacancy configuration – where the impurity sits between two vacancies – can have higher symmetry than the traditional vacancy-impurity complex.

Table 2 shows point groups of the two basic types of defects in five different crystal lattices: diamond, zinc-blende, rock-salt (cubic crystal system), hBN, and TMD (hexagonal crystal system). In the case of cubic crystals, the first type of defect has either the T_d or O_h symmetry, both of which allow the existence of doubly and triply degenerate single-particle levels. In these materials, defects of the second type have symmetries C_{3v}, D_{3d}, or C_{4v}, all of which similarly allow the existence of doubly degenerate single-particle levels.

The situation is different in the case of layered hexagonal materials. Defects of the first type have symmetry D_{3h} (hBN or cation-site defects in TMDs) or C_{3v} (anion-site defects in TMDs), both of which allow for the existence of doubly-degenerate states. However, defects of the second type possess symmetry C_{2v}, which does not have degenerate levels. This makes the occurrence of high spin states in the electronic ground state less likely. When there are no degenerate levels, the condition for the occurrence of high-spin states (e.g. a triplet state) is that the exchange coupling between electrons in different defect states is larger than the single-particle energy splitting between those states. This condition is fulfilled, for example, in the case of a complex between the boron vacancy and substitutional oxygen, V_B–O_N, in hBN [131]. While this example shows that high spin states are possible, generally they are expected to be less frequent in layered materials like hBN or TMDs.

Overall, this analysis suggests it is preferable to start with a host material with high symmetry, in order to have design flexibility in the defects' electronic structure. In practice, it is challenging to initialize spin systems with $S>1$ using optical pumping, as multiple pumping pathways need to be considered. Moreover, for odd-electron systems the spin levels form Kramers doublets characterized by the same irreducible representation, such that one level cannot be selectively populated on the basis of symmetry through ISC dynamics. This implies that orbital doublets with $S=1$ are generally desirable, as occur for most axially-symmetric systems such as divacancies or vacancy-impurity complexes in cubic binary crystals. However, even if a defect does not have a high spin state in the electronic ground state, it can still have a high spin state in the electronically excited state, as was demonstrated for defects in hBN [67]. This is in complete analogy with closed-shell molecular systems which possess a metastable triplet manifold besides the singlet manifold. Such a configuration can actually be an advantage for quantum sensing applications, as the QPD system can be pumped to the triplet state when sensing of the target is desired, while the nonmagnetic singlet ground-state configuration eliminates back-action at other times.

Depending on the application, inversion symmetry can also be desirable, for both the host crystal and the

Table 2: Selected properties of two types of defects in various crystals.

Crystal (space group)	**Vacancy/substitutional impurity**		**Impurity-vacancy complex/divacancy/double substitutional impurity/impurity-split-vacancy complex**	
	Point group	**Degenerate levels**	**Point group**	**Degenerate levels**
Diamond ($Fd\overline{3}m$, No. 227)	T_d	Yes	C_{3v} D_{3d} (split vacancy)	Yes
Zinc-blende ($F\overline{4}3m$, No. 216)	T_d	Yes	C_{3v}	Yes
Rock-salt ($Fm\overline{3}m$, No. 225)	O_h	Yes	C_{4v}	Yes
hBN ($P6_3/mmc$, No. 194)	D_{3h}	Yes	C_{2v}	No
TMDs ($P6_3/mmc$, No. 194)	D_{3h} (cation site) C_{3v} (anion site)	Yes	C_{2v}	No

Apart from the impurity-split-vacancy defect, all atoms are assumed to be in ideal crystal positions.

defect itself. Inversion-symmetric defects cannot feature a permanent electric dipole, which makes them insensitive to external electric fields to leading order, reducing inhomogeneous broadening and spectral diffusion of optical transitions. Similarly, crystals without inversion symmetry are generally piezoelectric, and this introduces additional vibronic couplings between photons and phonons that can broaden the emission lines. Of the crystals listed in Table 2, the diamond and rock-salt structures are inversion symmetric, whereas zinc-blende is not. HBN and TMDs also exhibit inversion symmetry in the bulk limit of many layers, but not as a monolayers. Layered materials derive many of their characteristics from the properties of single sheets, and although this means they have lower symmetry than their three-dimensional counterparts, it also makes them extremely interesting for defect engineering for other reasons, as we discuss next.

5.1.5 Dimensionality and morphology

Low-dimensional materials offer interesting opportunities as well as challenges as hosts of QPDs. By low-dimensional materials, we mean both nanoscale morphologies of three-dimensional crystals, such as nanocrystals (zero-dimensional) or nanowires (one-dimensional), as well as layered van der Waals crystals, such as hBN or TMDs, as mono-to-few-layer systems (two-dimensional).

For deep defects in wide-bandgap materials, the material's morphology has little effect on the defect's electronic structure, as even nanostructures with dimensions below 10 nm are generally much larger than the size of the defect's wavefunction which extends over only a few angstroms. However, semiconductor nanostructures have profound effects on electromagnetic interactions, and they can be integrated with other optical or electronic structures in order to tailor the QPD's properties or enable new control protocols. One-dimensional nanowires act as natural optical waveguides, directing emission into a well-defined spatial mode. Both nanowires and nanocrystals can be combined with plasmonic or dielectric elements that modify the QPD's optical absorption or emission properties. Whereas diamond and SiC nanoparticles are typically produced by etching or milling bulk crystals, nanowires and nanocrystals of many group II–VI and III–V semiconductors can be directly synthesized using MBE or colloidal chemistry, which offer improved control over size, shape, and composition. Some materials can also be synthesized as core-shell heterostructures, which offers additional design flexibility in controlling the electronic and optical functionality.

For QPDs in low-dimensional materials, the presence of nearby surfaces or interfaces affects the defect's spin and charge dynamics. This is often a problem that leads to decoherence if the surface is uncontrolled, as is the case for diamond and SiC. The influence of surfaces is a crucial consideration for nanoscale sensing applications, where the goal is to locate the QPD as near as possible to a target outside the material. It is therefore crucial to understand the surface chemistry and to pursue strategies for effective surface termination or passivation. In contrast to three-dimensional crystals, surfaces of van der Waals-bonded crystals do not have unsaturated dangling bonds. Therefore, at least in principle, their surfaces should contain fewer unpaired spins and charge traps compared to materials with covalent (or partially covalent) bonding. This potentially makes layered materials more suitable as QPD hosts for quantum sensing applications.

Along with their atomic thinness, the unique mechanical, electronic, and optical properties of layered materials offer the potential for dramatic physical effects. In particular, the ability to stack van der Waals materials into heterostructures allows the mixing of dissimilar materials irrespective of lattice matching or other typical requirements of epitaxially-grown heterostructures [132]. QPDs confined to monolayers should be considerably more tunable than in bulk crystals, through the intrinsic tunability of the host two-dimensional crystal and the proximity to other materials. For example, the Fermi level and carrier concentration of two-dimensional materials can be tuned with electrostatic gates to control a QPD's charge and spin state [133], and strain tuning can modify the optical emission properties or enable optomechanical coupling [134, 135]. With a growing library of layered materials that includes conductors, semiconductors, superconductors, topological materials, and magnetic solids, the paradigm of van der Waals heterostructures is a rich landscape for QPD engineering. QPD-based sensors in layered materials will be a powerful tool for studying fundamental physical phenomena. Moreover, proximity-induced quantum mechanical interactions such as exchange and orbital hybridization between adjacent layers could allow for dramatic modification of spin-photon selection rules and the realization of hybrid quantum systems that link localized QPD degrees of freedom using collective quantum states.

5.2 Practical considerations and promising materials

Alongside all these idealized material properties, equally important criteria for choosing a QPD host are the most practical ones: the availability of pure starting material and knowledge of the defect chemistry. The starting material can take different forms, including bulk single crystals, thin films, or nanocrystals, however there should be a pathway towards producing material in the required morphology and purity for relevant applications. A material's defect chemistry gets more complicated as the number of elements and inequivalent sites increases; for this reason it makes sense to begin with elemental or binary compounds with simple unit cells.

The binary oxide materials MgO and SrO exhibit inversion symmetry and can be synthesized via MBE. ZnO is an attractive material with a moderate band gap and low spin-orbit coupling. Other group II–VI materials like ZnS, ZnSe, CdS, and CdSe are well-known optically active semiconductors and can be chemically synthesized as nanowires or nanocrystals with precisely tailored size, shape, and composition. Despite the lower symmetry of layered van der Waals materials, the potential for cleaner surfaces and novel functionality motivates efforts to identify QPDs in these systems. Certain complex oxides such as YAG and yttrium orthosilicate (YSO) are also attractive hosts, especially to accommodate larger impurities like rare-earth ions. These materials are available as relatively pure bulk crystals through their development for laser crystals, and some (YSO especially) exhibit long spin coherence times due to a dilute nuclear spin environment [136]. Despite an unavoidable nuclear spin bath, wide-bandgap group III–V materials such as GaN and AlN are attractive for their technological sophistication, especially in optoelectronics and electromechanics. Ultimately, more complex materials such as perovskites can also be of interest, since they feature widely tunable electronic, optical, and magnetic properties. Some of these materials can be synthesized with sufficient purity to explore quantum effects [137]. Nevertheless, it remains a major challenge to engineer QPDs in such complex materials, and success likely requires advances in both theory and experiment, as we consider in Section 6.

6 State of the field and challenges

Efficiently predicting, creating, and characterizing new quantum defects will require simultaneous advancements in defect theory, materials and QPD synthesis, and experimental characterization. In this section we summarize the state of the field, highlighting the outstanding challenges in each of the three areas.

6.1 Theory

We will focus here on *ab initio* theory, as its predictive power is especially important in the discovery of novel QPDs. This theory is no substitute for the classic theoretical machinery of solid-state physics [6, 7, 138]; rather, it complements analytical theory and allows for the quantitative calculation of parameters that can be used in modeling various phenomena. While in certain situations qualitative understanding of defects is sufficient, a quantitative description is key for applications in quantum technologies. There is substantial difference if a QPD's quantum efficiency is, e.g. 95% or 5%, or whether the energy of the zero phonon line (ZPL) falls within one of the telecommunications bands or outside them.

The past few decades have seen tremendous progress in the quantitative description of the electronic structure of solids in general, mainly due to developments in the field of density functional theory (DFT) [139]. While DFT is in principle an exact reformulation of the many-body quantum mechanical problem, it relies on the so-called exchange-correlation functional, the explicit form of which is unknown. A huge research effort, continuing to this day, has produced different generations of functionals of increasing sophistication (the so-called "Jacobs's ladder"). Simultaneously, tremendous advances in computational algorithms and computer hardware has driven the boom of electronic structure calculations of materials [139].

For the application of DFT to the calculation of point defects in solids, we refer to excellent reviews by Freysoldt et al. and Dreyer et al. [140, 141]. The latter specifically focuses on QPDs. Here, our goal is to assess the level of accuracy and computational ease with which different properties of QPDs can be modeled. To this avail, we divide properties of point defects into three major categories, as summarized in Table 3 and described in detail:

(i) **Basic ground-state properties.** When initially considering the defect chemistry in any material or analyzing a new class of defects, several key parameters need to be established: defect formation energies, charge-state transition, and ionization levels, defect geometries in different charge states, ground-state spin configurations, and vibrational properties in the ground state. Most of the major developments in the electronic structure calculations of point defects in the past decades addressed one of these properties in one way or another. The existing methodology to calculate these properties is sound and nearly universally accepted [140]. The most important aspect of theory needed to reliably describe these properties

Table 3: Categories of point-defect properties organized according to the development of theoretical methodology for quantitative calculations.

Brief description of properties	Defect properties	Status of development
(i) Basic ground-state properties	Geometries, defect formation energies, charge-state transition levels, ionization levels, ground-state spin multiplicity, vibrational modes and frequencies	Methodology well-developed and accepted, widely implemented and tested, ready for high-throughput calculations
(ii) Specific ground-state properties	Magnetic interactions (zero-field splitting, spin-orbit, hyperfine), electron-phonon coupling, spin-phonon coupling	No principle difficulties, may be practical difficulties, not widely implemented yet, developments and testing taking place
(iii) Excited-state properties	Excited-state energies and geometries, multiplet structure, transition dipole moments, radiative rates, optical lineshapes, nonraditative transitions	Principle difficulties persist, rigorous approaches computationally very expensive, need for approximate methods that have to be tested more systematically

is the correct description of the host's atomic and electronic structure (including the band gap), as well as the correct description of charge localization. So-called hybrid density functionals [140] that incorporate a fraction of exact (Fock) exchange perform well on both fronts. Calculations of the basic properties using these functionals have become routine, and they can be even done in a high-throughput manner [142, 143]. Continued progress in developing new functionals with improved accuracy is also expected.

(ii) Specific ground-state properties. This category comprises properties that are not yet routinely calculated, but of which the calculation in principle poses no fundamental problems. They mainly involve the spin structure and magnetic interactions of the ground state, as well as electron-phonon and spin-phonon interaction in the ground state. Many of these properties are crucial for QPDs, but not necessarily for other areas of defect physics (e.g. they are not needed for understanding doping, defect compensation, Fermi-level pinning, or material growth). As such, methodological developments to calculate these properties have been relatively more recent.

Spin properties and magnetic interactions are paramount for many QPD applications. One such property is the spin-spin interaction that leads to the zero-field splitting (ZFS) between spin sub-levels [144]. The calculation of the ZFS is currently implemented in several major electronic structure codes [145], and recent developments focused on improvements in accuracy [146]. Similarly, the calculation of spin-orbit interactions are also currently possible for point defects in solids [147]. Spin-orbit interactions contribute to the ZFS in certain defects (e.g. the SiV center) and are very important for various other processes, for example, the ISC. Hyperfine interactions between the QPD's electron spin and the surrounding nuclear spins also play a crucial role for qubits and quantum memory applications. First-principles calculations of hyperfine couplings have been possible for some time [148], and the accuracy of such calculations continues to improve through the use of hybrid functionals [149].

A few recent studies have used hyperfine coupling calculations to study the behavior of entire systems of coupled spins, demonstrating the power of first-principles methods. Ivady et al. [150] introduced a method to model dynamic nuclear polarization, i.e. polarization transfer from the electron to nuclear spins. Seo et al. [121] showed how the knowledge of hyperfine parameters can be used to calculate spin decoherence times of qubits in SiC. These examples represent first steps towards addressing properties of an entire interacting many-body spin system using first-principles methods.

First-principles methods have been also useful in calculating various manifestations of electron-phonon coupling at defects, for example, the temperature shift of defect levels [151]. The interaction of spins with phonons, for example, the calculation of the intrinsic longitudinal spin relaxation time, can be also addressed [152] with first-principles methods.

(iii) Excited state properties. Finally, some defect properties still pose considerable fundamental and practical hurdles. Most importantly, these are properties related to excited states. DFT is, at its core, a ground-state theory. To access electronically excited states, one needs to go beyond DFT in one way or another. The problems of excited states are not restricted to point defects, but are a general problem of many-body quantum mechanics. The peculiarity of point defects is that they are intrinsically non-periodic systems involving a very large number of coupled ions and electrons.

On the one hand, approaches developed for periodic solids, such as many-body perturbation theory, i.e. the *GW* approximation for the quasiparticle band structure and the subsequent solution of the Bethe-Salpeter equation for optical excitations [153], could be also applied to point defects [154, 155]. However, these approaches are computationally expensive, especially for large systems, and therefore they are too demanding for a systematic study of many defects. Furthermore, the *GW* approach itself suffers from core deficiencies even for periodic solids [156], and the practical application of the improved method (the so-called $GW\Gamma$ approximation [153]) will not be computationally feasible in the near future [156].

On the other hand, there have been significant advances in methods that split the electronic system into a local sub-system that describes active electrons at or near the defect, and the bulk sub-system which provides electronic screening. One example is an approach based on parameterizing the Hubbard-type electronic Hamiltonian [157], and another example is the constrained-RPA method [158]. These approaches are promising. However, it is not clear whether they always converge to the correct result, and in our opinion their predictive power is yet to be demonstrated. Serious work on these many-body methods is still needed.

Given the state of affairs regarding these many-body approaches, approximate methods to calculate excited states are very important. One such approach is the constrained DFT method [159]. An example of this method is the ΔSCF (delta-self consistent field) scheme, whereby electronic excitation is modeled within DFT by constraining orbital occupations [160]. When optical excitations occur between single-Slater-determinant states of different spatial symmetry, the ΔSCF approach yields good results [161]. However, defect states are often made of a few Slater determinants (multi-determinant states). Proposals for how to address these states within the ΔSCF approach exist [162], but work in this area targeting point defects has been sporadic and inconclusive. More research is needed on this front.

Once the excited state wavefunction is obtained within a certain approach, then one can calculate important properties related to optical transitions, in particular the polarization of emitted light, transition dipole moments, and thus also radiative lifetimes. In addition, by studying lattice relaxation due to optical excitation, one can calculate Huang-Rhys factors that quantify electron-phonon coupling during optical transitions [163, 164]. With additional effort, one can explicitly compute photoluminescence lineshapes [165]. Absorption and photo-ionization cross sections can also be calculated rather straightforwardly [108]. Studies of nonradiative transitions, including carrier capture rates that are important for understanding QPD charge dynamics, are now feasible as well [166]. Apart from difficulties in describing the excited state itself, the subsequent calculation of properties described in the current paragraph poses practical rather than fundamental problems. These calculations could therefore be also ascribed to category (ii).

Success in the calculation of magnetic interactions as well as of optical and vibrational properties has recently enabled the *ab initio* study of the whole spin initialization cycle for NV centers in diamond [104]. These are still early days for such calculations, but it is clear that they will become more wide-spread in the near future, as the methodolgy continues to improve.

Computation of excited-state properties for point defects will benefit from ongoing efforts within the entire field of electronic structure calculations. Nonetheless, accurate and systematic methods will likely remain computationally demanding, and further work on various approximate methods is currently of high priority.

The discussion above is our subjective view on the status of theory regarding the three categories of properties of isolated point defects. In particular, categories (ii) and especially (iii) require further development. Not discussed in our brief overview are theoretical approaches to deal with finite-temperature effects. Neither did we touch on a huge area related to the *kinetics* of defect creation under non-equilibrium conditions. Another, closely related topic for the theory is the effect of a defect's environment, by which we mean the variation of defect properties in the vicinity of surfaces, the effects of strain and external fields, interactions of point defects with other point and line defects, etc. (see, e.g. [167]) Many of these effects can be studied explicitly using a combination of analytical approaches, electronic structure calculations, and atomistic modeling. Understanding these aspects is essential for many QPD applications, so this represents fertile ground for theoretical work.

6.2 Synthesis

With respect to synthesis, advancements are needed regarding the availability of suitable host materials, the purity of those materials, and methods for defect creation.

6.2.1 Host materials

As discussed in Section 4, early efforts to identify, isolate, and reproducibly create NV centers in diamond were propelled by commercially available high-purity material. The semiconductor industry similarly provides the infrastructure for pure Si and SiC crystals on which QPD development has piggy-backed. The past decade has seen an explosion of commercial offerings of potential QPD host materials and morphologies, driven by new technologies in energy, solid-state lighting, and nanotechnology. For example, colloidal semiconductor quantum dots are now widely used in display technologies [168, 169], and the emergence of graphene-based technologies has elevated the profile of many complementary layered materials such as TMDs and hBN [132]. Some of these materials are attractive QPD hosts, as discussed in Section 5.2. However, the level of materials purity required for QPD research often exceeds the demands of these other applications.

Study of new QPDs requires a sample containing either individual defects that can be studied in isolation, or a homogeneous ensemble that can be isolated from other defect signals. Single QPD isolation *via* confocal microscopy typically requires defect densities less than 10^{11} cm^{-3}. This concentration is exceedingly small by typical synthesis standards; in Si, an impurity density of 10^{11} cm^{-3} corresponds to two parts per trillion. Additionally, unwanted photoluminescence from the host material due to other unintentional defects or surface states must be low enough to enable detection of the single QPD of interest. This is one reason for the field's focus on defect complexes (e.g. NV and SiV centers in diamond, divacancies in SiC) over single-site defects. Complexes typically have larger formation energies, and therefore smaller concentrations, than single-site defects. This extreme purity requirement can be relaxed somewhat in the case where inhomogeneous broadening of the optical transitions allows one to spectrally filter the signal from a single defect [44, 48] or in cases where nanoparticles or nanoscale devices are utilized for defect isolation [48, 170, 171]. Ensemble studies can also be useful for characterizing the basic properties of new QPDs [40, 45, 54]. Nevertheless, there should be an eventual pathway towards isolation of individual defects in high-purity, single-crystal substrates.

The most ubiquitous synthesis technique is chemical vapor deposition (CVD); it is the preferred technique for growing high-quality diamond and is widely employed for the investigation of semiconductor materials in non-QPD research. However, CVD usually leads to larger defect concentrations than the part-per-trillion levels discussed above. Alternative methods for synthesis and sample preparation that offer potential advantages for QPD studies should be further developed. These methods include melt-based bulk crystalization methods such as the Czochralski, Bridgeman, and float-zone processes; epitaxial growth techniques such as MBE and atomic layer deposition (ALD); direct exfoliation of bulk layered crystals; and wet chemical synthesis. Each of these approaches is only suitable for a subset of possible materials. Epitaxial techniques such as MBE and ALD are advantageous with regards to achieving high purity and precise control over layer thickness, however they are exceedingly slow.

In two-dimensional systems, the purity requirement for accessing individual defects via confocal microscopy (in terms of the bulk defect density), can be significantly relaxed as the materials are thin. For example, achieving a lateral defect density below 10^8 cm^{-2} in a monolayer of hBN requires a concentration below 20 parts per billion. However, the synthesis of many two-dimensional materials remains underdeveloped, and challenges remain, especially with respect to generating large-scale single-crystal samples [172]. Further obstacles exist in reducing contamination and damage during post-growth transfer processes onto other substrates, as the predominant CVD techniques use metal foils as growth substrates. A variety of transfer and post-transfer healing methods have been reported, and work is ongoing to address these challenges [173, 174]. Nonetheless, alternatives to CVD methods are still of significant interest in these lower-dimensional systems.

Developing ultrapure, single-crystal growth for a new QPD host will require significant investment. Promise for the defect must already be assured. We should thus seriously consider how to facilitate QPD discovery in materials with lower purity. Nanoscale materials platforms, in the form of nanoparticles, wires, and films, are a potential solution. Due to their restricted size, nanocrystal morphologies can facilitate isolation of single QPDs to enable rapid and efficient exploration of basic properties such as energy-level structure and quantum efficiency, facilitate structural characterization, and explore the effect of various synthesis and sample treatment techniques. Whereas the purity, size uniformity, and surface chemistry of diamond nanostructures are notoriously uncontrolled, many other semiconductors can be colloidally synthesized at the nanoscale with precise control over size, shape, and surface termination [169]. In addition to their utility for exploratory studies, nanomaterials are also ideally suited to quantum sensing and nanophotonics applications.

6.2.2 Defect creation

Historically, *in situ* incorporation during growth [94, 175] and ion implantation/irradiation [47, 97–99, 176–178] have proven to be effective means of synthesizing QPDs. *In situ* growth incorporation typically has the advantage of higher crystal quality, but it severely limits the types of defects that can be incorporated and offers no control over lateral defect placement. Ion implantation provides some degree of spatial localization, though at the cost of material damage. Additionally, there still remains statistical uncertainty in defect formation [176] as well as uncertainty in defect placement (typically tens of nanometers) [178].

Research to broaden and increase the control of defect incorporation through *in situ* growth and implantation should continue. Improved understanding of defect energetics (e.g. formation energies) and kinetics is critical to designing precise synthesis strategies. Experimental results can inform theoretical calculations, and *vice versa*, with recent examples including the preferential orientation of NV centers during CVD growth [179–181] and the reorientation of NV centers at elevated temperatures [182].

It is also important to develop more precise techniques. MBE allows for impurities to be introduced at precise depths, however, it is does not immediately provide control over lateral positioning. Defect fabrication by scanning tunneling microscopy (STM), followed by material overgrowth, has been used to create single-site dopants in Si [183]. Not only can this technology enable near atomic-scale placement, it might also provide a route toward controlled fabrication of multi-qubit registers [27, 184]. However, STM placement has not been successfully demonstrated in QPD systems apart from Si. Scanning transmission electron microscopy (STEM) offers a precise way to create and visualize single vacancies [185–188], and it could potentially be adapted for creating two-site defects in combination with dopant incorporation. Two-dimensional host materials provide an ideal platform for exploring the potential of STEM-based techniques.

6.3 Characterization and identification

The identification of QPDs requires the correlation of many complementary measurements, as depicted in Figure 4. Individually, different techniques reveal information about a defect's electronic or chemical structure, and crucially for QPDs, about its spin and optical dynamics. Only together, supported by understanding and control over the material synthesis, the role of treatments such as irradiation and annealing, and through comparisons with theory, do such measurements yield a comprehensive picture.

This approach is supported by a long history in the identification of optically active defects in solids [6, 7]. Traditionally, experiments were performed on defect ensembles, typically using a combination of optical spectroscopy, elemental analysis, and magnetic resonance. In contrast, recent investigations of QPDs in new and emerging materials have predominantly focused on optical spectroscopy [3]. The reason for this focus is the need to detect extremely low impurity concentrations – eventually the signal from a single defect – which exceeds the limits of many traditional techniques.

For example, consider studies on the recently (2016) discovered single-photon emitters in hBN, emitting in the ~2 eV range. Initial reports provided significant data characterizing the electronic structure and optical dynamics [63–66]. Subsequent studies explored the role of strain [135], electric [189], and magnetic [67, 190] fields on the optical emission properties, along with various methods for creating defects [65, 191, 192]. As of July 2019, over 70 papers have appeared on the subject, and yet the defects'

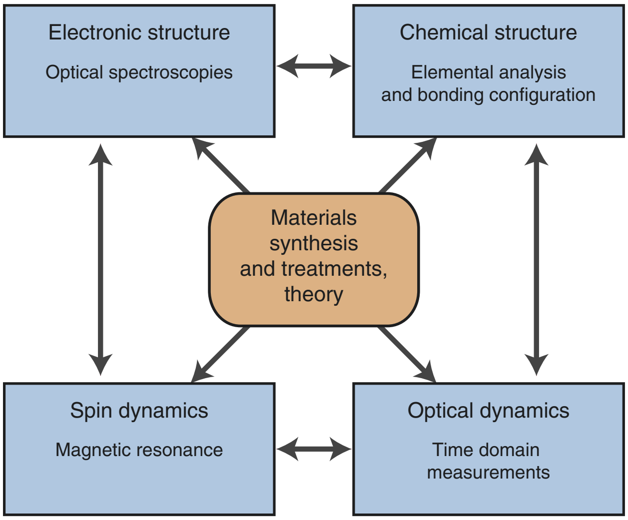

Figure 4: Identification and characterization of new QPDs requires the cross correlation of multiple experimental techniques, together with control over materials synthesis, treatments that alter the defect chemistry, and interpretation from theory. New or improved techniques are required to study QPDs in low concentrations and to bridge gaps between different measurement modalities.

chemical structure remains unresolved. Progress has been limited by a lack of high-purity host material and limited understanding of hBN's defect chemistry, as well as an absence of correlative measurements such as optically detected magnetic resonance. A similar situation exists for QPDs in WSe_2 and other two-dimensional materials [193]. These examples highlight the need for new experimental approaches to characterize and identify QPDs more efficiently.

6.3.1 Existing approaches

Optical measurements yield a wealth of information. A defect's photoluminescence signal, especially in the presence of applied magnetic, electric, and strain fields, contains information about its electronic Hamiltonian and environmental interactions [67, 194]. Spectral decomposition of the emission identifies the ZPL and phonon contributions [66, 165]. Measurements of the optical polarization dependence for excitation and emission yield information regarding the defect's symmetry and optical dipole configurations [40, 195]. Time-resolved photoluminescence measurements reveal excited state lifetimes and dynamics [196, 197]. Under steady-state illumination, measurements of the photon emission statistics provide valuable information about optical dynamics; photon antibunching at zero delay confirms single-photon emission, whereas photon bunching over longer delays implies the existence of metastable states and ionization dynamics [198, 199]. Even for inhomogeneously broadened defect ensembles, variations in the spectral lineshape or polarization in response to applied electric, magnetic, or strain fields reveals information about the ground and excited-state electronic structure, including clues about the spin Hamiltonian [6, 7].

While these optical techniques are powerful, they are typically not enough to positively identify an unknown defect as they provide limited ground-state, structural, and chemical information. Some well-established defect characterization techniques that could provide this information are rarely utilized by the QPD community. These include secondary ion mass spectrometry (SIMS), X-ray absorption spectrocopy (XAS), and X-ray photoelectron spectroscopy (XPS) to quantify impurity concentrations and – in the case of XAS and XPS – chemical bonding information. Vibrational probes such as Raman and Fourier-transform infrared (FTIR) spectroscopy also reveal structural and chemical information. Optoelectronic techniques such as photoconductivity measurements and deep level transient spectroscopy (DLTS) probe electronically active defects and charge transfer mechanisms. Finally, electron paramagnetic resonance (EPR), nuclear magnetic resonance (NMR), and their variants including double electron-electron resonance (DEER) and electron nuclear double resonance (ENDOR) are essential tools for studying spin properties, and they can also yield clues about a defect's structure (e.g. through its hyperfine spectrum) as well as interactions between different defect species.

The primary reason the QPD community has not adopted these techniques is that they are all ensemble characterization methods with a limit of detection (LOD) significantly higher than the level targeted for single defects, $\lesssim 10^{11}$ cm^{-3}. In some cases, the LOD can potentially be improved. In other cases, new techniques are required, and we consider some possibilities below. Nevertheless, the characterization techniques listed above should not be ignored as they characterize a material's purity and – even when they cannot resolve a population of QPDs – they provide valuable information about other coexisting defect populations that might be optically inactive and yet present at far greater concentrations than the QPD of interest.

6.3.2 Advances in measurement to facilitate discovery

As experimental capabilities improve, new approaches that could circumvent the QPD characterization bottleneck are becoming viable. Keeping in mind the need to access and correlate the four quadrants depicted in Figure 4, we highlight in particular the need for (i) further emphasis on defect ensemble measurements, (ii) lowering the LOD for traditional characterization techniques, and (iii) innovating new cross-correlative measurements.

(i) **Ensemble measurements.** While it is necessary for most QPD applications to isolate single defects, any scalable technology also requires the ability to create many homogeneous defects. Advances in our ability to synthesize high-quality hosts and homogeneous defect ensembles, discussed in Section 6.2, will facilitate the adoption of non-optical techniques by the QPD community. Ensemble measurements also enable higher-throughput defect characterization in the optical domain.

The ensemble approach is complementary to the prevalent modern approach based on observations of single defects. While single defect spectroscopy will still be required when synthesis of homogenous QPD ensembles is not possible, non-optical characterization of host materials can elucidate the properties of optically inactive defect species [200] that can influence a QPD's charge or spin dynamics. Moreover, optically dark defects can have desirable quantum properties. For example, the record 39 min quantum memory time of the phosphorous donor nucleus in silicon was measured using ensemble techniques [201]. These non-optical QPDs, optimized for memory or coupling [202], could be coupled to optically active defects in hybrid qubit platforms.

(ii) **Improving the LOD.** Many of the non-optical defect characterization techniques were developed for applications that did not require ppb- or ppt-level detection. The need for lower LODs to address emerging applications in quantum science can spur further investment in these techniques. In some cases, advances have already been made. For example, ODMR, a type of EPR, can be realized at the single-defect limit; however determining whether or not a defect can exhibit ODMR is currently a challenge for theory (see Section 6.1), and brute-force experiments on single defects require time-consuming experimental parameter sweeps.

(iii) **New techniques.** Advances in atomic-resolution imaging techniques provide new opportunities to directly characterize the chemical structure of individual QPDs. These techniques are ideally suited to low-dimensional materials and nanomaterials, which are often more difficult to study using traditional approaches. Atom probe tomography provides sub-nanometer spatial information of the chemical composition, although sample preparation can be prohibitive, and the measurement technique is destructive. Improvements in the resolution and detection efficiency for STEM imaging and spectroscopy at low beam energy has enabled the characterization of individual defects in hBN [203–207], although beam-induced damage remains a challenge. Atomic electron tomography (AET), based on STEM, can determine the precise location of every atom in a material, however it is currently limited to very small particles (<10 nm) [208] or very thin samples [209] consisting of heavy elements.

Ideally, these structural imaging techniques can be directly correlated with measurements of the orbital and spin structure. Recent efforts attempt to bridge the gap between atomic-resolution imaging and optical spectroscopy [210–213], although sample preparation and measurements remain extremely challenging. Another intriguing possibility is to use QPDs themselves as probes for materials exploration. Shallow NV centers in diamond are extremely sensitive probes of nanoscale materials [13–15], and they can be employed to study surface states, interfaces, and even other individual defects [214]. While much of this correlative work is still in its nascent stage, it moves the field in a direction towards a common set of characterization tools that can be leveraged, along with theory, to identify, manipulate, and control QPDs for quantum technologies.

We hope that these new and emerging characterization techniques can expand from their current status as specialized tools scattered in individual research labs to become more pervasive in the overall QPD research community. In some cases, where experimental hardware is the main obstacle, opportunities exist for companies to develop upgrades or add-ons for existing equipment. One example would be specialized STEM sample probes that facilitate correlated optical and structural measurements. In other cases, techniques can be disseminated by sharing experimental acquisition routines and technical know-how between labs.

One cannot measure everything, and it is essential to consider the application criteria when designing a measurement scheme, following the guidelines laid out in Section 5. High-throughput schemes can be considered for some techniques (e.g. optical spectroscopy), whereas others are inherently limited in terms of sample throughput (e.g. STM or STEM imaging). For this reason, it will be especially valuable to combine several complementary techniques in a system that facilitates rapid iterations between materials synthesis, treatment under various conditions, and comprehensive characterization of QPD-relevant quantities, in order to direct and optimize the search and development of new QPD systems within a large parameter space.

7 Outlook

In a letter to Rudolph Peierls from 1931, Wolfgang Pauli pronounced: "One shouldn't work on semiconductors; that is a filthy mess.[1] Who knows if they really exist?" Pauli was responding to the difficulty at the time in making sense of various conflicting measurements on semiconductor materials, including strange changes in Hall voltages – and their signs – as a function of temperature, along with apparently random variations between samples. Today we know that the source of that "filthy mess" was in fact defects. Just as it must have been nearly impossible in 1931 to anticipate how early experiments on semiconductors would lead to the age

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[1] Actually, the original German quotation was even more colorful. Pauli called semiconductors a "Schweinerei" – a pigsty.

of integrated circuits, it is foolish to assume in the present day that we understand the full scope of future quantum technologies. What seems clear is that Pauli's filthy mess will continue to drive scientific discovery and technological innovation, as semiconductor devices finally reach the ultimate scale of individual atoms.

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