ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de



# Quantum Materials with Atomic Precision: Artificial Atoms in Solids: Ab Initio Design, Control, and Integration of Single Photon Emitters in Artificial Quantum Materials

*Prineha Narang,* Christopher J. Ciccarino, Johannes Flick, and Dirk Englund*

**This Progress Report explores advances and opportunities in the atomic-scale design, fabrication, and imaging of quantum materials toward creating artificial atoms in solids with tailored optoelectronic and quantum properties. The authors outline an "ab initio" approach to quantitatively linking first-principles calculations and atomic imaging with atomic patterning, setting the stage for new designer quantum nanomaterials.**

## 1. Introduction

As early as the 5th Century B.C., the Greek philosophers Democritus and Leucippus made the first contribution to modern quantum theory: they proposed the notion that all matter is composed of tiny, indivisible "atoms" (from the Greek a- "not" + temnein "to cut") in an infinite void. Two and a half millennia later, we find ourselves at the beginning of the next atomic revolution: it is now becoming possible to design, fabricate, image, and measure general quantum materials and their properties at the single atom level. There now exists an opportunity for major advances by developing tools to predict—from first-principles quantum theory—the properties of general quantum materials, and then to fabricate, image, and measure them at the atomic scale. In this perspective, we will outline that this "ab initio" approach provides a new level of scientific understanding of materials and the quantum effects they exhibit, combining computational and experimental tools to design and use them.

Understanding many complex phenomena associated with the quantum nature of materials requires an improved understanding of atomic defects and disorder. These effects not only have drastic consequences on bulk physical properties, but also serve as isolated quantum systems and sources of single-photon emission at the atomic scale. Most notably, these systems have been shown to display quantum phenomena under ambient conditions, in contrary to conventional realizations of few-level state dynamics, such as cryogenic temperatures needed for qubit arrays or single atom measurements. Atom-like quantum emitters in solids[1,2] have seen exceptional progress and now set the state of the art in several key quantum technologies, from quantum computation and communications,[3] to nanoscale quantum sensing.[4] However, there are many open questions: What is the microscopic origin of the inhomogeneous distribution of optical transitions and spin properties? How can we create designer "artificial atoms" that have all the properties desired for a given application? How can we produce arrays of emitters for applications such as entanglement-assisted sensing or quantum error corrected logical qubits? Combining recent methods in atomic-resolution structural imaging with quantum spectroscopy and first-principles electronic structure simulations now promises to approach quantum materials theory and experiment in a fundamentally new way: atom by atom, with small error or uncertainty.

**Figure 1**a shows our standard concept of a crystal made of a perfect lattice. But this idealized view does not capture many of the properties of the real material, which has a complex atomic structure, including disorder, defects, strain, and environmental effects. All of these can contribute to altered physical behavior, including electronic, optical, vibrational, and magnetic properties, as illustrated in Figure 1a. As illustrated in Figure 1b, atomic defect emitter systems can take on many configurations (see **Scheme 1**). They serve as excellent model systems to exhibit the essential quantum physics probed by optical and microwave spectroscopy. These material systems can be described by applying methods that have been previously used to capture complex physical phenomena in solid-state systems, for example, the strongly-interacting materials shown in Figure 1c.

As indicated in Figure 1d, there is now the possibility of an "ab initio" feedback loop consisting of an integrated approach to calculating, fabricating, and measuring emitter-host systems at atomic resolution. With both computation and fully atomically resolved imaging becoming possible on the scale of hundreds to thousands of atoms—larger than the electronic wavefunction

Prof. P. Narang, C. J. Ciccarino, Dr. J. Flick
John A. Paulson School of Engineering and Applied Sciences
Harvard University
Cambridge, MA 02138, USA
E-mail: prineha@seas.harvard.edu
C. J. Ciccarino
Department of Chemistry and Chemical Biology
Harvard University
Cambridge, MA 02138, USA
Prof. D. Englund
Department of Electrical Engineering and Computer Science
Massachusetts Institute of Technology
Cambridge, MA 02139, USA
The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.201904557.

**DOI: 10.1002/adfm.201904557**

of the atomic defects extend into the lattice—it is now becoming possible to capture nearly all of the relevant material behavior. Although these systems are nanoscale, the techniques to be developed will likely provide important insights into the properties of the bulk system as a whole, including the magnitude and role of disorder, strain, and inhomogeneity. As such, these capabilities may also lead to disruptive advances in established industries, such as semiconductor manufacturing and optoelectronic device technologies.

## 2. A Unified Framework

The ability for theory and experiment to consider materials with full atomic resolution leads to a truly atomic framework for materials with minimal approximations. It is this framework that we want to consider in this perspective, which is organized as 1) the need for atomic-scale prediction and experiment for artificial atoms; 2) theory for first-principles many-body predictions, simulation, and screening of quantum materials; and 3) tools to pattern, image, and control quantum materials at the atomic scale. As we discuss in this perspective, closing the loop between design, fabrication, and characterization promises breakthrough advances in solid-state quantum systems for quantum information processing and sensing.

### 2.1. The Need for Atomic-Scale Prediction and Experiment for Artificial Atoms

The idea of solid-state artificial atoms can be traced back to the seminal work of Kane,[10] with related ideas presented within the context of quantum dots.[11,12] Today, the nitrogen-vacancy (NV) center in diamond illustrates both the promise and challenges for current solid-state quantum systems. Progress for NV centers in many areas of quantum information science has been astonishing. After more than a decade of advances,[3,13–15] NV centers can be arranged in ensembles to act as multiqubit systems with coherence times exceeding 1 s even at room temperature.[16] These defect systems have also been demonstrated for quantum nondemolition readout, high-fidelity multiqubit gates enabling multiple rounds of error correction, and efficient electron–photon coupling that enabled the first links of quantum networks.[16,17] In the area of quantum sensing, advanced NV quantum control has brought the "holy grail" of single-molecule magnetic resonance imaging[18] within reach.

Despite these advances, the NV center also has its limitations. The NV center is a nonideal emitter, as only 3% of its photon emission originates from the zero phonon line (corresponding to a small Debye–Waller factor). Additionally, the inability to pattern NV centers with well-defined atomic spacing presents a challenge for multi-NV registers, which are needed for scalable networks, fault-tolerant computing, and advanced quantum sensor arrays. Additionally the coherence properties of the NV center are limited by its susceptibility to charge fluctuations, due to its permanent electronic dipole moment.

In this sense the NV is not unique: all of today's advanced solid-state quantum systems face similar challenges. But some recently discovered solid-state defect systems[3,19–26] show what might be possible in an "ideal quantum system." The SiV, GeV, SnV, and PbV color centers (all group IV elements) in diamond all possess inversion symmetry and can be found in different charge states. While nitrogen vacancy centers have a long spin lifetime, but relatively poor optical properties, the negatively charged group IV vacancy centers have the opposite characteristics. So far only the SiV has been measured in the neutral charge state, with recent experiments[27] indicating that isolated SiV emitters could combine long coherence times with stable optical properties. Atomic emitters in other wide bandgap 3D materials also have seen tremendous progress, as have rare earth atoms in solids.

2D materials have emerged as another promising host material–one in which surface imaging techniques can soon reveal every atom's position around an atomic defect emitter. For instance, quantum emission in 2D and multilayered hexagonal boron nitride is attributed to atom-like fluorescent defects of the crystal structure that confine electronic levels within the wide bandgap (≈6 eV), yielding robust emitters.[28,29] Although these color centers have shown remarkable properties, such as photostability at ambient conditions,[19] high brightness, and strain tunability,[20] the real atomic and spin structure of these defects is still under debate. They have been tentatively assigned to nitrogen vacancy ($N_BV_N$) and substitutional carbon defects ($C_BV_N$).[30] A significant hurdle in these systems is the lack of clear signatures which identify the source of emission.[29] Combined with fluorescence imaging, atomic-resolution imaging

**Prineha Narang** is an Assistant Professor at the John A. Paulson School of Engineering and Applied Sciences at Harvard University. Prior to joining the faculty in 2017, Prineha came to Harvard as a Ziff Fellow; she was also a Research Scholar in Condended Matter Theory at the MIT Department of Physics, working on new theoretical methods to describe quantum interactions.

**Dirk Englund** received his BS in Physics from Caltech in 2002, and an MS in E.E. and a Ph.D. in Applied Physics from Stanford University in 2008. He was a postdoctoral fellow at Harvard University until 2010, when he became Assistant Professor of E.E. and Applied Physics at Columbia University. He joined the MIT EECS faculty in 2013.

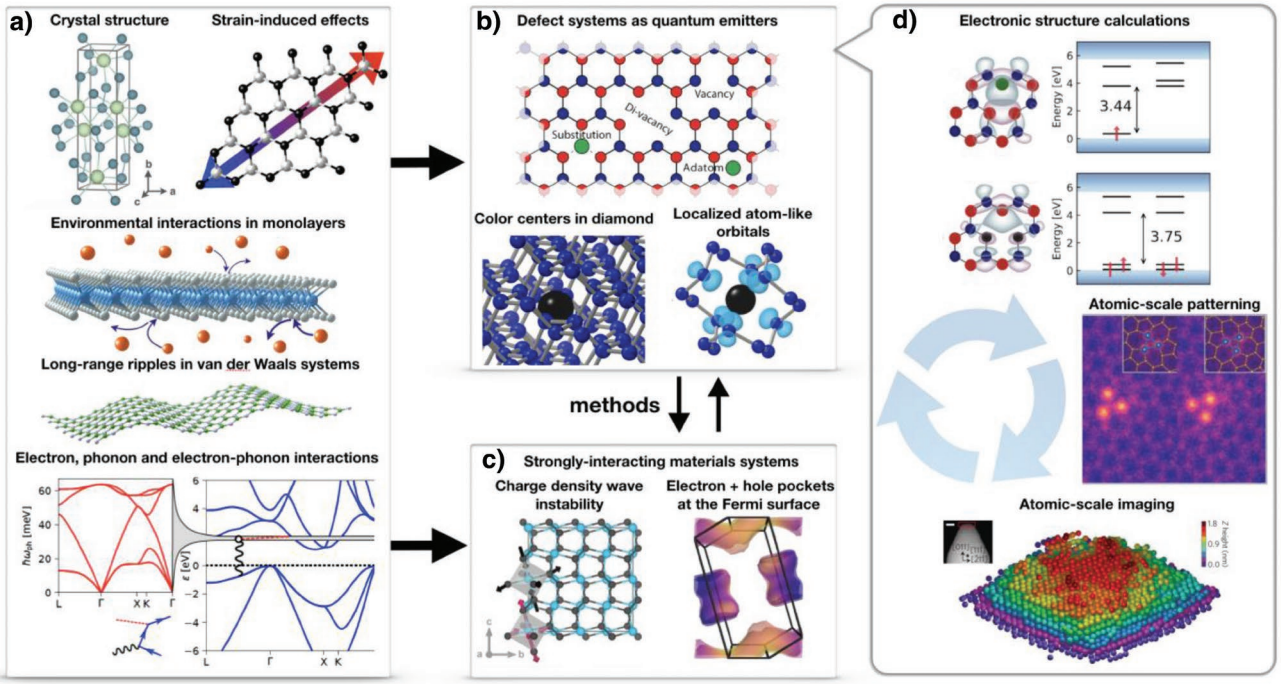
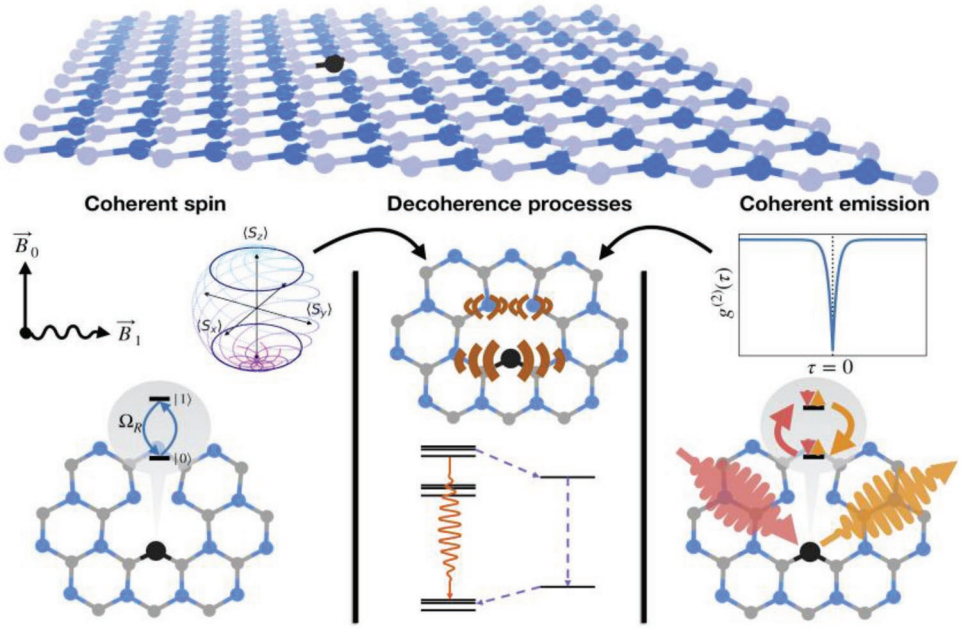



**Figure 1.** a) A variety of different solid-state systems, such as bulk and 2D materials, are altered by long-range ripple effects, environmental and electron–phonon interactions. Different defect emitter systems are shown in (b); these can be described with methods also used in other fields of physics, such as strongly-interacting materials c), examples of which include phenomena such as charge-density wave instability in TMDC $CuS_2$ or complex Fermi surface behavior in Type-II Weyl semimetal $WP_2$. In (d), we show how an experimental and theoretical ("ab initio") feedback loop could be structured, where electronic structure calculations complement both atomic patterning and imaging techniques, which provides important insights into these light-emitting materials. Third panel in d) reproduced with permission.[5] Copyright 2019, Wiley-VCH. Fourth panel in d) reproduced with permission.[6] Copyright 2015, Nature Publishing Group. Second panel in b) reproduced with permission.[7] Copyright 2019, American Physical Society. First panel in a) and right panel in c) reproduced with permission.[8] Copyright 2018, American Physical Society. Left panel in c) reproduced under the terms of the arXiv.org perpetual, non-exclusive license.[9] Copyright 2019.




**Scheme 1.** Quantum emitters: a testbed for nanoscopic artificial quantum materials. Solid-state defect systems, as depicted on top for a carbon substitution and nitrogen vacancy in a layer of hexagonal boron nitride, allow for the study of coherent quantum phenomena in a system small enough to be imaged and modeled with every relevant atom included. These phenomena include coherent spin dynamics (left) originating from defect electrons. The right panel depicts single photon emission, characterized by $g^{(2)}$ measurements (inset), as a result of electronic transitions between well-localized orbitals within the bandgap of the bulk host. Processes such as coupling to vibrational modes of the system and spin-forbidden intersystem crossing (center) contribute to spin decoherence.

such as scanning transmission electron microscopy[5,31] or scanning tunneling microscopy[32,33] will likely soon lift these ambiguities by providing atomic details of quantum emitters.[34–36]

### 2.2. Theory for First-Principles Many-Body Predictions, Simulation, and Screening of General Quantum Materials

So far, however, because of a lack of experimental and theoretical tools, the search for new emitters which overcome these obstacles is largely based on intuition-guided "trial and error." Looking forward, the field would strongly benefit from first-principles prediction[7,22,23,37] and design of emitters with desired quantum properties, including a large Debye–Waller factor, long coherence time, high emission efficiency, single-photon purity, as well as spectral stability. Rational materials design using first-principles methods has already revolutionized fields, such as catalysis and photovoltaics, where systematic search of composition space,[38,39] narrowed by theory and refined by experiment, has accelerated material discovery. It appears likely that the field for quantum materials will similarly be transformed by first-principles-driven design to develop atom-like emitters.[40]

In this context, a suite of theoretical and computational tools is necessary. The standard method in the field of computational material science, density-functional theory (DFT),[41] has been highly successful in studying the electronic structure of quantum defects. The underlying accuracy of these theoretical predictions is limited by the computational cost associated with the size of the supercell as well as the quality of the exchange-correlation functional. Through more efficient algorithms[42] and the evolution of computing power, supercells up to thousands of atoms are now feasible. Meanwhile hybrid functionals, which are useful in describing long-range and exchange effects with greater accuracy, are now the state-of-the-art.[43,44] In addition to conventional DFT, recent years have seen dramatic improvements in method development, for example, the extension to strong light-matter interactions.[45–49] While in its original formulation, DFT is restricted to ground-state properties, excited-state properties can be accessed with constrained ΔSCF, which uses the energy different of different self-consistent calculations, or time-dependent DFT.[50] These ΔSCF methods have been successful, for example, in describing excited state energetics[7,23] and luminescence lineshapes[51] of defects in diamond with excellent experimental agreement. However ΔSCF methods are only useful in describing low-lying excited states and cannot capture effects such as exciton formation. Meanwhile time-dependent DFT methods for capturing the full excited state spectrum suffer from the lack of sufficient nonadiabatic functionals.[52] More accurate but computationally expensive methods such as many-body perturbation theory (e.g., *GW*[53]) and the use of the Bethe–Salpeter equation (BSE)[54] should be considered in capturing a more complete description of the excited state manifolds for such defect emitter systems.

The first step in any such calculation is to identify possible defect configurations in the host material,[44,55] and for each, identifying stable charge and spin states.[56] To further test the accuracy of the theoretical methods used these predictions can be tested against atomic structure and quantum spectroscopy measurements. While predicted formation energies and transition levels using DFT allows for screening suitable defect states, calculating spin properties requires higher level modeling of the electronic structure, necessitating novel quantitative models. Current theory can identify the optical activity of the defects[57] at both the single particle and at the many-body perturbation theory level (*GW*+BSE), however dynamics that involve nonradiative decay of the state are much more challenging.[58–60] Due to high computational cost, many-body perturbation methods have been mainly been applied to smaller systems, e.g., to describe the electron–vibration coupling induced renormalization for diamondoids.[61] Possible nonradiative decay mechanisms include electron–phonon interactions, which are impractical in conventional electronic structure methods.[62] The difficulty results from a mismatch in the energy-scales of phonons and electrons, which requires fine-grained sampling of the momentum of electron and phonon states. In defect systems, typically the nonradiative decay of the states are estimated by evaluating special phonon modes that are most likely to contribute to the decay.[63] However, this approach does not generalize easily and cannot be adapted for a "high-throughput" evaluation of defect states. This gap highlights a unique opportunity for the computational condensed matter community to develop accelerated electron–phonon and spin–phonon methods with design of quantum emitters as the focus.

Besides ab initio methods, the field of quantum materials also largely benefits from calculations using effective Hamiltonians. These methods have been recently successful in describing novel excitations, such as Moiré excitons.[64–66] Model systems have been very useful to calculate observables that are not easily accessible in a first principle framework, such as decoherence and spin relaxation times.[67–73] For such effective systems, first-principle methods are usually used to provide single-particle wave functions and parameters that build the models of the system of interest. Due to the reduced dimensionality of these models, they can often be solved even by exact diagonalization or similar methods leading to a very accurate description. Future work will include a closer coupling to first-principle methods and effective models that could then allow to access decoherence and spin relaxation times in a self-consistent manner. These effective Hamiltonian methods would also be of great use when describing possible arrays of defects.

Data-driven approaches could be particularly useful to identify new quantum emitters with desired properties. These techniques are especially relevant given that the range of possibilities for different combinations of atomic defect atoms, charge/spin states and host materials is far too large for brute-force searches. Statistical learning of materials properties or functions typically start with a choice of descriptive parameters such as elemental composition.[74,75] To describe optical and excited-state properties of artificial quantum materials using methods of machine learning, however, either novel descriptors have to be developed or the currently available ones have to be adapted. One promising possibility is to develop first-principles calculated descriptors, such as excited-state configuration coordinates, as opposed to traditionally used atomic descriptors, such as crystal structure. For example, Bayesian optimization models could identify the most likely candidate to test next in order to optimize the optoelectronic property of interest.

This approach has been effective in accelerating materials discovery,[75–78] but it has not been reported on for single photon emitters including color centers in diamond, rare-earths in new 3D wide-gap material hosts or low-dimensional materials.

### 2.3. Patterning, Imaging, and Controlling Quantum Materials at the Atomic Scale

For this materials-by-design approach, development of methods for atomic-resolution fabrication or synthesis is critical. 2D materials systems offer a good test case as all atoms are "presented" to the observer. Scanning probe microscopy, in particular scanning tunneling microscopy (STM) has been demonstrated to manipulate atoms, such as quantum corrals[79] and bits,[80] but it is limited to weakly-bounded surface atoms and vacancies. On the other hand, aberration-corrected electron beam methods nowadays provide atomic resolution[81] that are promising for imaging and even patterning at the atomic scale on suspended materials. The next step toward atomic-scale manipulation of defects in 2D materials is the control of kinetic structural evolution. Promisingly approaches include to control kinetics includes in situ heating inside of a scanning transmission electron microscope.[82] Another promising approach is to pattern the surface of a high-bandgap material by STM lithography, already highly successful for P doping on silicon.[83] These and related techniques have also been explored in the context of other quantum phenomena.[84–86]

## 3. Conclusions

Atomic defect quantum emitter systems are on the cusp of a revolution: the possibility to predict, produce, and evaluate materials from the position of all of its constituent atoms is within our grasp. This possibility has come about thanks to rapid progress in advanced computing tools (many from the rapidly evolving intersection of quantum simulations and materials machine learning), atomic-resolution imaging and fabrication, and measurements that capture highly coherent quantum mechanical effects. The field is now positioned to quantitatively link first-principles calculations and atomic imaging with atomic patterning and quantum spectroscopy. This approach could lead to a positive feedback loop to systematically improve scientific understanding and research tools, setting the stage for new designer quantum nanomaterials.

## Acknowledgements

P.N., C.C., and D.E. acknowledge support from the Army Research Office MURI (Ab-Initio Solid-State Quantum Materials) Grant No. W911NF-18-1-0431. J.F. acknowledges fellowship support from the Deutsche Forschungsgemeinschaft (DFG) under Contract No. FL 997/1-1. P.N. is a Moore Inventor Fellow and a CIFAR Azrieli Global Scholar.

## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

artificial atoms in solids, atomic-scale design, quantum emitters, quantum materials

Received: June 7, 2019
Revised: August 8, 2019
Published online: September 30, 2019

[1] M. Atatüre, D. Englund, N. Vamivakas, S.-Y. Lee, J. Wrachtrup, *Nat. Rev. Mater.* **2018**, *3*, 38.
[2] L. Childress, R. Walsworth, M. Lukin, *Phys. Today* **2014**, *67*, 38.
[3] I. Aharonovich, D. Englund, M. Toth, *Nat. Photonics* **2016**, *10*, 631.
[4] C. L. Degen, F. Reinhard, P. Cappellaro, *Rev. Mod. Phys.* **2017**, *89*, 035002.
[5] O. Dyck, S. Kim, E. Jimenez-Izal, A. N. Alexandrova, S. V. Kalinin, S. Jesse, *Small* **2019**, *15*, 1805310.
[6] R. Xu, C.-C. Chen, L. Wu, M. C. Scott, W. Theis, C. Ophus, M. Bartels, Y. Yang, H. Ramezani-Dakhel, M. R. Sawaya, H. Heinz, L. D. Marks, P. Ercius, J. Miao, *Nat. Mater.* **2015**, *14*, 1099.
[7] M. E. Trusheim, N. H. Wan, K. C. Chen, C. J. Ciccarino, J. Flick, R. Sundararaman, G. Malladi, E. Bersin, M. Walsh, B. Lienhard, H. Bakhru, P. Narang, D. Englund, *Phys. Rev. B* **2019**, *99*, 075430.
[8] J. Coulter, R. Sundararaman, P. Narang, *Phys. Rev. B* **2018**, *98*, 115130.
[9] Y. Yin, J. Coulter, C. J. Ciccarino, P. Narang, *arXiv:1903.09142* [cond-mat.mes-hall] **2019**.
[10] B. E. Kane, *Nature* **1998**, *393*, 133.
[11] L. P. Kouwenhoven, D. G. Austing, S. Tarucha, *Rep. Prog. Phys.* **2001**, *64*, 701.
[12] R. Hanson, L. P. Kouwenhoven, J. R. Petta, S. Tarucha, L. M. K. Vandersypen, *Rev. Mod. Phys.* **2007**, *79*, 1217.
[13] L. Li, T. Schröder, E. H. Chen, M. Walsh, I. Bayn, J. Goldstein, O. Gaathon, M. E. Trusheim, M. Lu, J. Mower, M. Cotlet, M. L. Markham, D. J. Twitchen, D. Englund, *Nat. Commun.* **2015**, *6*, 6173.
[14] D. Englund, B. Shields, K. Rivoire, F. Hatami, J. Vučković, H. Park, M. D. Lukin, *Nano Lett.* **2010**, *10*, 3922.
[15] H. Clevenson, M. E. Trusheim, C. Teale, T. Schröder, D. Braje, D. Englund, *Nat. Phys.* **2015**, *11*, 393.
[16] T. Schröder, S. L. Mouradian, J. Zheng, M. E. Trusheim, M. Walsh, E. H. Chen, L. Li, I. Bayn, D. Englund, *J. Opt. Soc. Am. B* **2016**, *33*, B65.
[17] W. B. Gao, A. Imamoglu, H. Bernien, R. Hanson, *Nat. Photonics* **2015**, *9*, 363.
[18] I. Lovchinsky, A. O. Sushkov, E. Urbach, N. P. de Leon, S. Choi, K. De Greve, R. Evans, R. Gertner, E. Bersin, C. Müller, L. McGuinness, F. Jelezko, R. L. Walsworth, H. Park, M. D. Lukin, *Science* **2016**, *351*, 836.
[19] T. T. Tran, C. Elbadawi, D. Totonjian, C. J. Lobo, G. Grosso, H. Moon, D. R. Englund, M. J. Ford, I. Aharonovich, M. Toth, *ACS Nano* **2016**, *10*, 7331.
[20] G. Grosso, H. Moon, B. Lienhard, S. Ali, D. K. Efetov, M. M. Furchi, P. Jarillo-Herrero, M. J. Ford, I. Aharonovich, D. Englund, *Nat. Commun.* **2017**, *8*, 705.
[21] A. M. Berhane, K.-Y. Jeong, Z. Bodrog, S. Fiedler, T. Schröder, N. V. Triviño, T. Palacios, A. Gali, M. Toth, D. Englund, I. Aharonovich, *Adv. Mater.* **2017**, *29*, 1605092.
[22] G. Thiering, A. Gali, *npj Comput. Mater.* **2019**, *5*, 18.
[23] G. Thiering, A. Gali, *Phys. Rev. X* **2018**, *8*, 021063.
[24] S. Ditalia Tchernij, T. Lühmann, T. Herzig, J. Küpper, A. Damin, S. Santonocito, M. Signorile, P. Traina, E. Moreva, F. Celegato,

S. Pezzagna, I. P. Degiovanni, P. Olivero, M. Jakšić, J. Meijer, P. M. Genovese, J. Forneris, *ACS Photonics* **2018**, *5*, 4864.
[25] S. Sun, J. L. Zhang, K. A. Fischer, M. J. Burek, C. Dory, K. G. Lagoudakis, Y.-K. Tzeng, M. Radulaski, Y. Kelaita, A. Safavi-Naeini, Z.-X. Shen, N. A. Melosh, S. Chu, M. Lončar, J. Vučković, *Phys. Rev. Lett.* **2018**, *121*, 083601.
[26] R. E. Evans, M. K. Bhaskar, D. D. Sukachev, C. T. Nguyen, A. Sipahigil, M. J. Burek, B. Machielse, G. H. Zhang, A. S. Zibrov, E. Bielejec, H. Park, M. Lončar, M. D. Lukin, *Science* **2018**, *362*, 662.
[27] B. C. Rose, D. Huang, Z.-H. Zhang, P. Stevenson, A. M. Tyryshkin, S. Sangtawesin, S. Srinivasan, L. Loudin, M. L. Markham, A. M. Edmonds, D. J. Twitchen, S. A. Lyon, N. P. de Leon, *Science* **2018**, *361*, 60.
[28] T. T. Tran, K. Bray, M. J. Ford, M. Toth, I. Aharonovich, *Nat. Nanotechnol.* **2016**, *11*, 37.
[29] F. Hayee, L. Yu, J. L. Zhang, C. J. Ciccarino, M. Nguyen, A. F. Marshall, I. Aharonovich, J. Vučković, P. Narang, T. F. Heinz, J. A. Dionne, arXiv:1901.05952[cond-mat.mtrl-sci] **2019**.
[30] S. A. Tawfik, S. Ali, M. Fronzi, M. Kianinia, T. T. Tran, C. Stampfl, I. Aharonovich, M. Toth, M. J. Ford, *Nanoscale* **2017**, *9*, 13575.
[31] J. Miao, P. Ercius, S. J. L. Billinge, *Science* **2016**, *353*, 464.
[32] G. Binnig, H. Rohrer, *Rev. Mod. Phys.* **1987**, *59*, 615.
[33] C. V. Parker, A. Pushp, A. N. Pasupathy, K. K. Gomes, J. Wen, Z. Xu, S. Ono, G. Gu, A. Yazdani, *Phys. Rev. Lett.* **2010**, *104*.
[34] X. Tian, D. S. Kim, S. Yang, C. J. Ciccarino, Y. Gong, Y. Yang, Y. Yang, B. Duschatko, Y. Yuan, P. M. Ajayan, J.-C. Idrobo, P. Narang, J. Miao, preprint arXiv:1901.00633, **2019**.
[35] D. Rhodes, S. H. Chae, R. Ribeiro-Palau, J. Hone, *Nat. Mater.* **2019**, *18*, 541.
[36] S. Dai, W. Fang, N. Rivera, Y. Stehle, B.-Y. Jiang, J. Shen, R. Y. Tay, C. J. Ciccarino, Q. Ma, D. Rodan-Legrain, P. Jarillo-Herrero, E. H. T. Teo, M. M. Fogler, P. Narang, J. Kong, D. N. Basov, *Adv. Mater.* **2019**, *31*, 1806603.
[37] I. Harris, C. J. Ciccarino, J. Flick, D. R. Englund, P. Narang, arXiv:1907.12548 [quant-ph], **2019**.
[38] A. Jain, G. Hautier, C. J. Moore, S. Ping Ong, C. C. Fischer, T. Mueller, K. A. Persson, G. Ceder, *Comput. Mater. Sci.* **2011**, *50*, 2295.
[39] A. Franceschetti, A. Zunger, *Nature* **1999**, *402*, 60.
[40] L. Gordon, J. R. Weber, J. B. Varley, A. Janotti, D. D. Awschalom, C. G. Van de Walle, *MRS Bull.* **2013**, *38*, 802.
[41] W. Kohn, *Rev. Mod. Phys.* **1999**, *71*, 1253.
[42] L. Lin, *J. Chem. Theory Comput.* **2016**, *12*, 2242.
[43] J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.* **2003**, *118*, 8207.
[44] C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti, C. G. Van de Walle, *Rev. Mod. Phys.* **2014**, *86*, 253.
[45] M. Ruggenthaler, J. Flick, C. Pellegrini, H. Appel, I. V. Tokatly, A. Rubio, *Phys. Rev. A* **2014**, *90*, 012508.
[46] J. Flick, N. Rivera, P. Narang, *Nanophotonics* **2018**, *7*, 1479.
[47] J. Flick, P. Narang, *Phys. Rev. Lett.* **2018**, *121*, 113002.
[48] M. Ruggenthaler, N. Tancogne-Dejean, J. Flick, H. Appel, A. Rubio, *Nat. Rev. Chem.* **2018**, *2*, 0118.
[49] N. Rivera, J. Flick, P. Narang, *Phys. Rev. Lett.* **2019**, *122*, 193603.
[50] M. A. L. Marques, C. A. Ullrich, F. Nogueira, A. Rubio, K. Burke, E. K. U. Gross, *Time-Dependent Density Functional Theory*, Springer Science & Business Media, Berlin, **2006**.
[51] A. Alkauskas, B. B. Buckley, D. D. Awschalom, C. G. Van de Walle, *New J. Phys.* **2014**, *16*, 073026.
[52] N. T. Maitra, K. Burke, C. Woodward, *Phys. Rev. Lett.* **2002**, *89*, 023002.
[53] M. Govoni, G. Galli, *J. Chem. Theory Comput.* **2015**, *11*, 2680.
[54] E. E. Salpeter, H. A. Bethe, *Phys. Rev.* **1951**, *84*, 1232.
[55] S. Chen, P. Narang, H. A. Atwater, L.-W. Wang, *Adv. Mater.* **2014**, *26*, 311.
[56] P. Rinke, A. Janotti, M. Scheffler, C. G. Van de Walle, *Phys. Rev. Lett.* **2009**, *102*, 026402.
[57] A. L. Exarhos, D. A. Hopper, R. R. Grote, A. Alkauskas, L. C. Bassett, *ACS Nano* **2017**, *11*, 3328.
[58] J. Noffsinger, E. Kioupakis, C. G. Van de Walle, S. G. Louie, M. L. Cohen, *Phys. Rev. Lett.* **2012**, *108*, 167402.
[59] J. Jung, A. Raoux, Z. Qiao, A. H. MacDonald, *Phys. Rev. B* **2014**, *89*, 205414.
[60] A. M. Brown, R. Sundararaman, P. Narang, W. A. Goddard, H. A. Atwater, *Phys. Rev. B* **2016**, *94*, 075120.
[61] A. Gali, T. Demján, M. Vörös, G. Thiering, E. Cannuccia, A. Marini, *Nat. Commun.* **2016**, *7*, 11327.
[62] F. Giustino, M. L. Cohen, S. G. Louie, *Phys. Rev. B* **2007**, *76*, 165108.
[63] A. Alkauskas, Q. Yan, C. G. Van de Walle, *Phys. Rev. B* **2014**, *90*, 075202.
[64] K. Tran, G. Moody, F. Wu, X. Lu, J. Choi, K. Kim, A. Rai, D. A. Sanchez, J. Quan, A. Singh, J. Embley, A. Zepeda, M. Campbell, T. Autry, T. Taniguchi, K. Watanabe, N. Lu, S. K. Banerjee, K. L. Silverman, S. Kim, E. Tutuc, L. Yang, A. H. MacDonald, X. Li, *Nature* **2019**, *567*, 71.
[65] C. Jin, E. C. Regan, A. Yan, M. Iqbal Bakti Utama, D. Wang, S. Zhao, Y. Qin, S. Yang, Z. Zheng, S. Shi, K. Watanabe, T. Taniguchi, S. Tongay, A. Zettl, F. Wang, *Nature* **2019**, *567*, 76.
[66] E. M. Alexeev, D. A. Ruiz-Tijerina, M. Danovich, M. J. Hamer, D. J. Terry, P. K. Nayak, S. Ahn, S. Pak, J. Lee, J. I. Sohn, M. R. Molas, M. Koperski, K. Watanabe, T. Taniguchi, K. S. Novoselov, R. V. Gorbachev, H. S. Shin, V. I. Fal'ko, A. I. Tartakovskii, *Nature* **2019**, *567*, 81.
[67] C. E. Dreyer, A. Alkauskas, J. L. Lyons, A. Janotti, C. G. Van de Walle, *Annu. Rev. Mater. Res.* **2018**, *48*, 1.
[68] M. Ye, H. Seo, G. Galli, *npj Comput. Mater.* **2019**, *5*, 44.
[69] L.-P. Yang, C. Burk, M. Widmann, S.-Y. Lee, J. Wrachtrup, N. Zhao, *Phys. Rev. B* **2014**, *90*, 241203.
[70] H. Seo, A. L. Falk, P. V. Klimov, K. C. Miao, G. Galli, D. D. Awschalom, *Nat. Commun.* **2016**, *7*, 12935.
[71] N. Zhao, S.-W. Ho, R.-B. Liu, *Phys. Rev. B* **2012**, *85*, 115303.
[72] W. Yang, R.-B. Liu, *Phys. Rev. B* **2008**, *78*, 085315.
[73] S. J. Whiteley, G. Wolfowicz, C. P. Anderson, A. Bourassa, H. Ma, M. Ye, G. Koolstra, K. J. Satzinger, M. V. Holt, F. J. Heremans, A. N. Cleland, D. I. Schuster, G. Galli, D. D. Awschalom, *Nat. Phys.* **2019**, *15*, 490.
[74] D. Jha, L. Ward, A. Paul, W.-K. Liao, A. Choudhary, C. Wolverton, A. Agrawal, *Sci. Rep.* **2018**, *8*, 17593.
[75] B. Sanchez-Lengeling, A. Aspuru-Guzik, *Science* **2018**, *361*, 360.
[76] K. Alberi, M. B. Nardelli, A. Zakutayev, L. Mitas, S. Curtarolo, A. Jain, M. Fornari, N. Marzari, I. Takeuchi, M. L. Green, M. Kanatzidis, M. F. Toney, S. Butenko, B. Meredig, S. Lany, U. Kattner, A. Davydov, E. S. Toberer, V. Stevanovic, A. Walsh, N.-G. Park, A. Aspuru-Guzik, D. P. Tabor, J. Nelson, J. Murphy, A. Setlur, J. Gregoire, H. Li, R. Xiao, A. Ludwig, L. W. Martin, A. M. Rappe, S.-H. Wei, J. Perkins, *J. Phys. D: Appl. Phys.* **2019**, *52*, 013001.
[77] T. Dimitrov, C. Kreisbeck, J. S. Becker, A. Aspuru-Guzik, S. K. Saikin, *ACS Appl. Mater. Interfaces* **2019**, *11*, 24825.
[78] R. Gómez-Bombarelli, J. Aguilera-Iparraguirre, T. D. Hirzel, D. Duvenaud, D. Maclaurin, M. A. Blood-Forsythe, H. S. Chae, M. Einzinger, D.-G. Ha, T. Wu, G. Markopoulos, S. Jeon, H. Kang, H. Miyazaki, M. Numata, S. Kim, W. Huang, S. I. Hong, M. Baldo, R. P. Adams, A. Aspuru-Guzik, *Nat. Mater.* **2016**, *15*, 1120.
[79] M. F. Crommie, C. P. Lutz, D. M. Eigler, *Science* **1993**, *262*, 218.

[80] F. E. Kalff, M. P. Rebergen, E. Fahrenfort, J. Girovsky, R. Toskovic, J. L. Lado, J. Fernández-Rossier, A. F. Otte, *Nat. Nanotechnol.* **2016**, *11*, 926.
[81] S. Jesse, A. Y. Borisevich, J. D. Fowlkes, A. R. Lupini, P. D. Rack, R. R. Unocic, B. G. Sumpter, S. V. Kalinin, A. Belianinov, O. S. Ovchinnikova, *ACS Nano* **2016**, *10*, 5600.
[82] C. Gong, A. W. Robertson, K. He, G.-D. Lee, E. Yoon, C. S. Allen, A. I. Kirkland, J. H. Warner, *ACS Nano* **2015**, *9*, 10066.
[83] T. F. Watson, B. Weber, Y.-L. Hsueh, L. L. C. Hollenberg, R. Rahman, M. Y. Simmons, *Sci. Adv.* **2017**, *3*, e1602811.
[84] A. A. Khajetoorians, D. Wegner, A. F. Otte, I. Swart, arXiv:1904.11680 [cond-mat.mes-hall] **2019**.
[85] L. Yan, P. Liljeroth, arXiv:1905.03328 [cond-mat.mtrl-sci] **2019**.
[86] N. A. García-Martínez, J. Fernández-Rossier, arXiv:1906.11343 [cond-mat.mes-hall] **2019**.