

# First-principles calculations of defects and electron-phonon interactions: Seminal contributions of Audrius Alkauskas to the understanding of recombination processes

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## ABSTRACT

First-principles calculations of defects and electron-phonon interactions play a critical role in the design and optimization of materials for electronic and optoelectronic devices. The late Audrius Alkauskas made seminal contributions to developing rigorous first-principles methodologies for the computation of defects and electron-phonon interactions, especially in the context of understanding the fundamental mechanisms of carrier recombination in semiconductors. Alkauskas was also a pioneer in the field of quantum defects, helping to build a first-principles understanding of the prototype nitrogen-vacancy center in diamond, as well as identifying novel defects. Here, we describe the important contributions made by Alkauskas and his collaborators and outline fruitful research directions that Alkauskas would have been keen to pursue. Audrius Alkauskas' scientific achievements and insights highlighted in this article will inspire and guide future developments and advances in the field.

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## I. INTRODUCTION

Point defects (by which we mean both intrinsic native defects as well as impurities) have a profound impact on the properties of materials. Doping of semiconductors with acceptors and donors is essential for electronic and optoelectronic applications. Native defects often counteract the intended electrical activity, and, therefore, they are typically considered detrimental. However, point defects can also be functional and are currently vigorously pursued as qubits, single-photon emitters, or quantum memories in the burgeoning field of quantum information.<sup>1</sup> **Control of point defects is clearly essential, and first-principles calculations have been instrumental in building the understanding that enables such control.**

The basic formalism of first-principles calculations for point defects has been well established.<sup>2</sup> One may employ a reasonably sized supercell of the material of interest and intentionally create a point defect by inserting or removing related atoms. First-principles calculations then allow evaluating defect-induced structural relaxations, total energies of the pristine and defect-containing supercells, as well as chemical potentials of related atomic species and electrons. Based on these quantities, the formation energies and charge-state transition levels of a defect can be determined.

While the basic methodology is clear, there were two critical challenges associated with accurately evaluating the defect properties and their impact on material and device performance. First, early first-principles calculations using density functional theory (DFT) were often based on local or semilocal functionals. While computationally tractable, the predicted electronic structure with such functionals is not sufficiently accurate; for instance, the bandgap is underestimated<sup>3</sup> and the positions of the band edges (relative to, e.g., vacuum) are problematic. As a result, the formation energies and charge-state transition levels of defects can be inaccurate. Second, charge-state transition levels of defects deep in the bandgap can mediate capture of carriers enabled by, e.g., electron-phonon interactions. Such processes lead to carrier recombination and energy dissipation. Even if charge-state transition levels are correctly computed, a quantitative methodology to evaluate carrier capture rates from first principles was lacking.

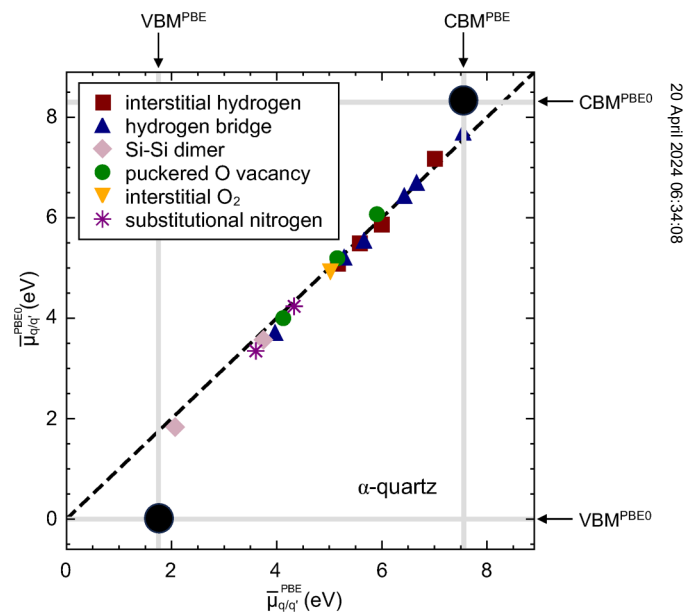
Audrius Alkauskas tackled these challenges by increasing the accuracy of defect calculations, particularly through the use of hybrid functionals, and by developing rigorous methodologies to quantitatively calculate recombination rates. In this Perspective, we highlight the key contributions of the late Alkauskas to the development of computational methodologies for defects and their induced carrier recombination and to applications of these computational approaches to the investigations of defects in technologically important semiconductors and to defects relevant for quantum information technology. We will also outline fruitful directions for future research that Alkauskas himself was keenly pursuing. Alkauskas' scientific achievements and his perceptive ways of addressing scientific challenges have already greatly benefited the field and will continue to shine light on forthcoming conceptual and technical advances.

## II. DEFECT LEVELS THROUGH HYBRID DENSITY FUNCTIONALS

In 2006, Alkauskas took the lead of a project on the alignment of defect levels as obtained with hybrid functionals.<sup>4,5</sup> Through the

incorporation of a fraction of Fock exchange, these functionals offer the possibility of overcoming the severe bandgap problem found with semilocal density functionals but also require special attention due to the occurrence of a singularity when using plane wave basis sets.<sup>6</sup> The main purpose of the project was to understand the benefits of aligning defect levels with respect to the band edge levels as the bandgap was progressively tuned closer to its experimental value.<sup>4</sup> A comparative study was carried out between charge-state transition levels calculated with semilocal and hybrid functionals for a series of atomically localized defects in various materials.<sup>4</sup> In Fig. 1, such a comparison is illustrated in the case of  $\alpha$ -quartz  $\text{SiO}_2$ .<sup>4,7,8</sup> The result indicates that the defect levels calculated with the semilocal functional stay nearly put when calculated with the hybrid functional, provided that an alignment with respect to the average electrostatic potential is adopted in the two calculations. The invariant defect levels strikingly contrast with the levels pertaining to the delocalized conduction- and valence-band states, which instead move significantly in order to encompass the larger bandgap obtained with the hybrid functional (see Fig. 1).

The observed alignment of the defect levels was found to result from the atomically localized nature of the defect states.<sup>4</sup> Indeed, deviations from the ideal alignment were identified to correlate with the extent of delocalization of the defect wave



**FIG. 1.** Charge-state transition levels of various defects in  $\alpha$ -quartz calculated with the hybrid functional by Perdew, Ernzerhof, and Burke (commonly referred to as PBE0)<sup>9</sup> ( $\epsilon_F^{\text{PBE0}}$ ) vs corresponding levels calculated with the semilocal Perdew–Burke–Ernzerhof (PBE) functional<sup>10</sup> ( $\epsilon_F^{\text{PBE}}$ ) upon alignment of the average electrostatic potential. The energy levels corresponding to the valence-band maximum (VBM) and the conduction-band minimum (CBM) as calculated with the two functionals are also shown (black disks). Reproduced with permission from Broqvist *et al.*, Phys. Status Solidi A **207**, 270 (2010). Copyright 2010 John Wiley and Sons.

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functions.<sup>4</sup> Furthermore, in the extreme case of shallow defects, the defect wave function is primarily composed of states lying close to the concerned band edge and, consequently, the defect level remains tied to the band when the bandgap is increased.<sup>4,5,11</sup> In other particular cases, the defect states are atomically localized but, nevertheless, closely resemble the character of the band edge states. For instance, in the case of the substitutional Li defect in ZnO, both the defect wave function and the valence-band wave functions are mostly composed of O 2*p* states, leading to noticeable deviations from the ideal alignment.<sup>12</sup>

The use of the average electrostatic potential as a common reference is conceptually meaningful because this energy level directly stems from the charge density, which is known to be well described with both semilocal and hybrid functionals.<sup>5,11</sup> Consequently, the ideal alignment observed with respect to the average electrostatic potential also implies a good alignment on the absolute scale, i.e., with respect to the external vacuum level.<sup>5,11</sup>

The understanding provided by this rationale proved very useful in reconciling conflicting results obtained in the literature for the (+2/0) transition level of the oxygen vacancy in ZnO.<sup>11</sup> The defect levels calculated with different bandgap correction schemes were all found to agree when aligned to a suitable common reference. This result indicates that the origin of the inconsistencies among different calculations resides in the determination of the energy levels of the delocalized band edge states rather than in the defect-level calculations.

An important implication of the picture emerging from this analysis is that there is an effective decoupling between the delocalized band edge states and the atomically localized defect states (see also Fig. 1). Hence, in practical terms, the application of correction schemes that attempt to overcome the bandgap underestimation of semilocal functionals leave the defect states invariant as long as they have been properly aligned with respect to a suitable reference.<sup>5,8</sup> This consideration underlies the formulation of the “band edge problem” and brings to the foreground the issue of the accuracy by which electronic-structure schemes describe the energy levels of the delocalized band states on the absolute scale.<sup>11</sup> This has direct relevance for defect levels as they are measured with respect to the band edges in typical experimental setups.

To address this issue, Alkauskas and collaborators used hybrid functionals to calculate the band offsets at semiconductor–oxide interfaces, finding excellent agreement with experiment.<sup>13</sup> The fraction of Fock exchange in hybrid functionals was adjusted to reproduce the experimental bandgaps of the interface components.<sup>5,13</sup> Despite the empirical nature of this approach, the good agreement with experiment shows that hybrid functionals reproducing the experimental bandgaps yield accurate energy corrections of valence- and conduction-band levels.<sup>13</sup> To provide a deeper understanding associated with the bandgap adjustment practice, an analogy with the static GW approximation was highlighted and exploited to establish a relationship between the adjusted fraction of Fock exchange ( $\alpha^{\text{gap}}$ ) and the high-frequency dielectric constant ( $\epsilon_\infty$ ):  $\alpha^{\text{gap}} = 1/\epsilon_\infty$ .<sup>5</sup> This contributed *de facto* to the foundation of dielectric-dependent hybrid functionals.

Through the insightful contributions of Alkauskas, it was clearly understood that the defect levels and band edge levels could be separately referred to the local electrostatic potential, i.e., by

combining results obtained with different functionals. This resulted in a highly successful scheme to determine numerous defect levels with respect to the overall band alignment at various semiconductor–oxide interfaces.<sup>14–19</sup>

### III. ELECTRON-PHONON INTERACTIONS

#### A. Luminescence line shapes and photoionization

Since the early days of color center research, the study of photoluminescence (PL) and absorption processes has been pivotal in identifying and characterizing defects. Theoretical efforts have been directed at understanding the broadening effects of optical transitions at defect sites, particularly those caused by electron–phonon interactions. These efforts enabled the evaluation of the lineshape function, which describes the degree of light absorbed or emitted at a particular frequency. The seminal works by Huang and Rhys,<sup>20</sup> Pekar,<sup>21</sup> Lax,<sup>22</sup> Kubo and Toyozawa,<sup>23</sup> and Markham<sup>24</sup> were crucial in deciphering the profiles of experimental optical spectra. However, these early approaches relied on empirically fitted parameters, and despite their importance for the theoretical foundations, faced challenges in identifying the microscopic nature of defects and making quantitative predictions. Alkauskas significantly advanced this field by developing first-principles theoretical approaches to profiling the optical spectra.<sup>25–27</sup> His contributions have notably enhanced our ability to predict and interpret electron–phonon coupling at defects in various materials.

Broad optical spectra emerging from strong electron–phonon interactions of point defects are typically analyzed using one-dimensional (1D) configuration coordinate diagrams.<sup>28</sup> These diagrams effectively distill the complex, multidimensional vibrational structure that influences lineshapes into a single, effective vibrational mode. Alkauskas<sup>25,29</sup> developed an innovative and accessible first-principles methodology to accurately determine the PL line shapes. This method works well for defects with strong electron–phonon interactions, i.e., with Huang–Rhys factor<sup>20</sup> (average number of phonons emitted during a single optical transition)  $S \gg 1$ . Very good agreement with experiment was found for deep acceptors and donors in GaN and ZnO.<sup>25</sup> For the first time, precise computation of optical lineshapes for defects in materials became possible, and this approach has been adopted by many research groups. The methodology also facilitates identification of the microscopic mechanisms underlying the broad PL bands.

First-principles calculations of the vibrational structure of a defect usually rely on supercells with only a few hundred atoms, resulting in an unconverged representation of the vibrational structure. Recognizing this challenge, Alkauskas proposed an innovative embedding methodology that enables simulation of the defect vibrational structure with supercells encompassing tens of thousands of atoms.<sup>26,30</sup> This approach allowed performing first-principles calculations of the PL lineshape of the nitrogen-vacancy (NV) center in diamond.<sup>26</sup> Alkauskas further recognized the significance of the non-adiabatic Jahn–Teller effect<sup>31,32</sup> in describing optical signatures of defects for transitions involving degenerate states. He established a theoretical framework and a practical methodology to account for this effect, enabling accurate description of the absorption spectrum of the NV center.<sup>27</sup>

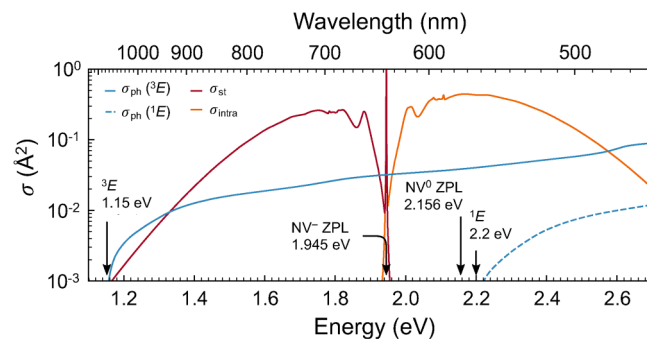
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Photoionization is another process that demands precise treatment of the electron–phonon interactions. Modeling photoionization presents additional challenges not encountered in the analysis of intra-defect processes as it involves interactions not with a single defect level but with the bulk bands. The methodological difficulties that needed to be addressed were (i) the emergence of mini-gaps in the conduction band due to perturbation of band states by the periodically repeated defect supercell and (ii) the slow convergence of photoionization cross sections in terms of Brillouin zone sampling.

Alkauskas and collaborators successfully addressed these issues and presented a computationally accessible recipe for obtaining smooth spectral dependences of absolute photoionization cross sections.<sup>30</sup> This methodology was used to investigate the photoionization of the negatively charged NV center. Absolute cross sections were computed for photoionization from the  ${}^3E$ ,  ${}^3A_2$ , and  ${}^1E$  states, as well as for stimulated emission and intra-defect absorption. The results depicted in Fig. 2 provided valuable insights to guide optical experiments involving negatively charged NV centers. Analyzing the cross sections allowed for an estimation of the spectral dependence of the ratio of probabilities for photoionization and stimulated emission. These results are in very good agreement with the experimental findings,<sup>33–35</sup> validating the reliability of the methodology.

## B. Carrier capture at defects

One of the key detrimental effects of defects in semiconductor devices is the capture of charge carriers, which leads to energy dissipation and limits the efficiency of energy conversion. Defect-assisted nonradiative capture, commonly referred to as the Shockley–Read–Hall (SRH) process,<sup>36,37</sup> is a dominant channel for this loss. In the SRH process, a defect undergoes charge-state transitions by capturing a carrier, facilitated by electron–phonon interactions. The subsequent dissipation of energy to the lattice occurs through multiphonon emission. While nonradiative capture

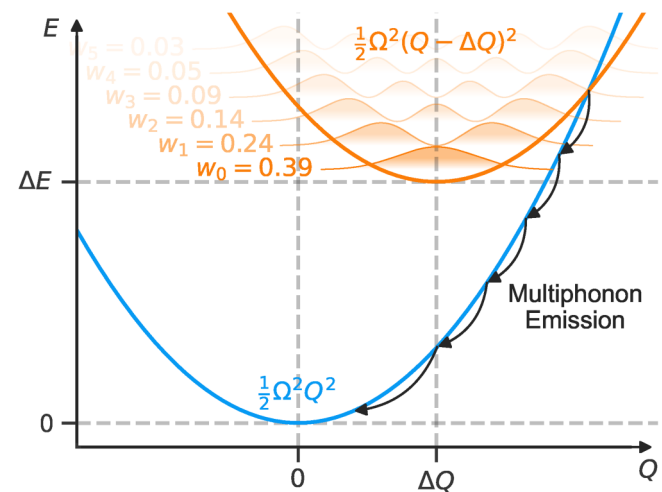


**FIG. 2.** Calculated cross section as a function of photon energy for the negatively charged NV center in diamond. Solid blue: photoionization from the excited state  ${}^3E$ ,  $\sigma_{ph}({}^3E)$ ; dark red: stimulated emission,  $\sigma_{st}$ ; orange: intra-defect absorption,  $\sigma_{intra}$ ; dashed blue: photoionization from the singlet state  ${}^1E$ . Photoionization thresholds from  ${}^3E$  and  ${}^1E$  are indicated (estimated error bar 0.1 eV), together with the experimental values of the zero-phonon line (ZPL) energy for  $NV^-$  and  $NV^0$ . Reproduced with permission from Razinkovas *et al.*, Phys. Rev. B **104**, 235 301 (2021). Copyright 2021 American Physical Society.

coefficients can be experimentally measured, pinpointing the chemical nature of the involved defect presents a formidable challenge. Rigorous computation of nonradiative capture coefficients from first-principles greatly assists in identifying relevant defects, and provides valuable insights into the underlying mechanisms that experimental methods may struggle to discern.

A number of efforts have been devoted to developing computational methodologies for explicit calculation of nonradiative capture.<sup>20,23,38–42</sup> An intuitive understanding of the multiphonon process can be derived from the configuration coordinate diagram—the same one used in the case of broad optical spectra discussed in Sec. III A—schematically illustrated in Fig. 3. The defect in its initial charge state (orange curve) may capture a carrier by transitioning to another charge state (blue curve).  $\Delta E$  is the transition energy with respect to the conduction-band minimum (CBM) or valence-band maximum (VBM), depending on the nature of the carrier. In a semiclassical picture, the rate-limiting step involves surmounting the energy barrier defined by the crossing point of the potential energy surfaces. The actual nonradiative capture process is quantum-mechanical and the rate can be evaluated by using Fermi's golden rule.<sup>28</sup> First-principles calculations enable computing the charge-state transition energy and the potential energy surfaces of the defect in the two charge states as a function of lattice distortion. However, evaluating the rate is extremely demanding due to the need to handle high-dimensional phonon integrals.

Alkauskas tackled this challenging problem by developing a 1D approximation,<sup>42,43</sup> motivated by the effectiveness of this approximation in describing luminescence (Sec. III A). While all



**FIG. 3.** A schematic configuration coordinate diagram. Orange corresponds to the initial state with phonon frequency  $\Omega$  and equilibrium geometry at  $Q = \Delta Q$ . Blue corresponds to the final state with equilibrium geometry at  $Q = 0$ . The phonon probability densities in the excited state are schematically depicted; the opacity of the phonon states is intended to depict the probability of occupation at a given temperature. The black arrows show the multiphonon emission process.

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phonon modes in principle contribute to the electron–phonon interactions, the dominant contribution stems from the one that couples most strongly to the distortion associated with defect relaxation. This mode is known as the accepting mode<sup>44</sup> and corresponds to the 1D mode in the configuration coordinate diagram. Alkauskas demonstrated that this approach yields very reliable results,<sup>42</sup> especially for defects with strong electron–phonon interactions ( $S \gg 1$ ). As a benchmark, the theory was applied to several hole-capturing centers in GaN and ZnO. The calculated capture coefficients align well with experimental data, affirming the validity of the theoretical framework. The approach has become widely used and been successfully applied to various technologically important materials,<sup>45–55</sup> showing a substantial impact on the field.

In addition to nonradiative processes (mediated by phonons), defects may also capture carriers radiatively in a photon-mediated transition. The general theory of such processes had been laid down,<sup>56</sup> but a rigorous first-principles approach was lacking until Alkauskas' contributions connected the formal theory to explicit quantum-mechanical calculations.<sup>57</sup> The work also tested the universally applied Condon approximation, which posits that the dipole coupling does not change significantly with atomic displacements. The methodology, quantitative calculations, and analysis also pointed to an important conclusion; that radiative capture rates are typically too slow to be relevant for SRH recombination in semiconductors.<sup>57</sup>

The above approaches for nonradiative and radiative carrier capture can address most of the defect-assisted capture processes in conventional semiconductors. However, in semiconductors with bandgaps exceeding 2.5 eV SRH recombination based on the standard multiphonon emission formalism yields rates that are significantly lower than experimental results.<sup>58–61</sup> Alkauskas made seminal contributions to unraveling this puzzle by elucidating the critical role of excited states of defects<sup>62,63</sup> and the importance of the trap-assisted Auger–Meitner (TAAM) process.<sup>64,65</sup>

The conventional theory of nonradiative recombination dictates that capture rates decrease exponentially as the transition energy increases.<sup>39</sup> Hence, for a defect level close to the CBM one expects fast electron capture and slow hole capture. However, experiments have yielded results that are at odds with this conventional wisdom. For example, for substitutional Fe on the Ga site in GaN (defect level located at 0.6 eV below the CBM), measurements showed that both electron capture and hole capture are fast.<sup>66,67</sup> Alkauskas' insight on the role of excited states in recombination processes helped resolve this seeming contradiction. His work used the  $\Delta$ -SCF approach<sup>68</sup> to determine the energies of excited states and accounted for these excited states within the nonradiative recombination cycle,<sup>62,63</sup> yielding results for capture coefficients in good agreement with experiment. This general approach was crucial in highlighting and elucidating the important role of excited states in recombination processes in semiconductors and insulators.

Excited states cannot account for all discrepancies between calculated rates based on multiphonon emission and experimentally observed rates. Alkauskas was instrumental in pushing for exploration of alternative mechanisms. The TAAM process enables the capture of carriers by defects, with the excess energy being given to a second carrier that is excited to higher energies through

the Coulomb interaction. While this process had been described in the literature,<sup>69</sup> rigorous evaluations were totally lacking. Alkauskas played a key role in the development of a tractable first-principles formalism to evaluate the TAAM coefficient.<sup>65</sup> Since two carriers are involved in the process (one that is captured and one that is excited), the TAAM process scales quadratically with the carrier density. Using a new methodology, Alkauskas *et al.* were able to demonstrate the importance of the TAAM mechanism by studying the example of Ca in InGaN alloys. When the bandgap exceeds 2.5 eV, the nonradiative recombination rate enabled by TAAM exceeds the rate including only multiphonon emission by many orders of magnitude.<sup>65,70</sup> Thanks to Alkauskas' work, the importance of the TAAM process has been established and can now be investigated for other defects and materials.

#### IV. APPLICATIONS TO QUANTUM DEFECTS IN DIAMOND AND BN

It has become established that point defects in insulators and semiconductors are robust and manipulable quantum systems that are promising for components in next-generation quantum devices. They can be prepared in coherent quantum states similar to single atoms or molecules, and the host crystal lattice provides both isolation from the environment and avenues for addressing the state electronically or optically. Indeed, defects have been demonstrated as qubits for quantum computation, single-photon emitters for quantum communication, and nanoprobe for quantum metrology.<sup>1</sup> Here, the defect is important not because it degrades the properties of an electronic or optoelectronic device, but rather because “the defect is the device” (a phrase coined by Alkauskas as an homage to the Nobel lecture of Herbert Kroemer<sup>71</sup>).

In order for “quantum defects” to fulfill this promise, it is crucial to understand and characterize the properties of known defects to unprecedented precision, and to accurately predict new defects with desired properties. First-principles calculations play a significant role in this context, and many of the methods developed by Alkauskas described in the previous sections are key, as reviewed by Alkauskas and co-workers in Ref. 1. In this section, we summarize the contributions of Alkauskas to the field of quantum defects.

Given the importance of the NV center as the prototype quantum defect, robust spectroscopic data at the single defect level is available, making it a testbed for theoretical methods.<sup>72</sup> One of the most important inherent features is its spin-selective fluorescence, which is associated with the spin-selective intersystem crossing (ISC) between the bright triplet excited state ( $^3E$ ) and a lower-energy dark singlet state ( $^1A_1$ ). However, it was found that the spin selectivity is only stable up to about 400 K, making optical readout of the spin infeasible at higher temperatures.<sup>73</sup> The temperature dependence of the ISC can be understood with a configuration coordinate diagram (Fig. 3) and can be described by the phenomenological Mott–Seitz formula for nonradiative relaxation via multiphonon emission.<sup>73</sup> In experiments, a semiclassical barrier energy of  $\approx 0.48 \pm 0.14$  eV was found.

Alkauskas developed an approach to calculate the adiabatic potential energy surface (APES) for the  $^3E$  and  $^1A_1$  excited states that are involved in the ISC by constrained DFT. While the calculated energy gap between  $^3E$  and  $^1A_1$  was not as accurate as that

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obtained in later experimental<sup>74</sup> and theoretical studies beyond DFT<sup>75</sup> due to strong electron–phonon coupling between the higher- and lower-energy singlet states,<sup>76</sup> the key contribution of Alkauskas’ first-principles calculations<sup>73</sup> was to provide the physical picture behind the observed phenomenon. These results have inspired other studies; for instance, the theory has been demonstrated to work for the temperature dependence of the spin-readout contrast of divacancy-related quantum defects in SiC<sup>77</sup> and can be applied to other quantum defects as well.

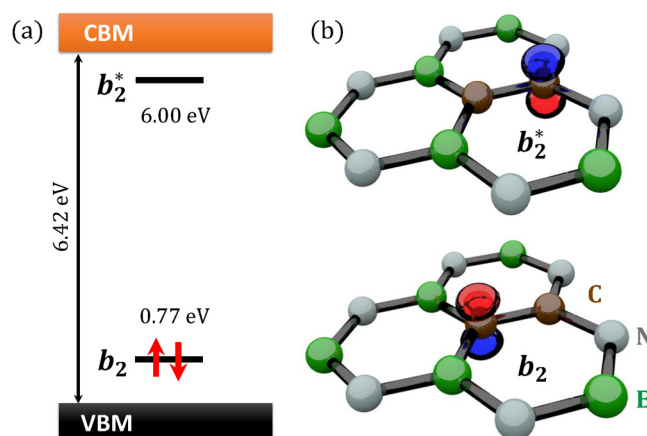
The so-called silicon-vacancy (SiV) center and related group-IV-vacancy defects (e.g., GeV, SnV, and PbV) are prime alternatives to the NV center in diamond. These defects are insensitive to charge noise due to higher symmetry ( $D_{3d}$ )<sup>78,79</sup> and have stronger emission into the zero-phonon line (ZPL) in their negative charge state with doublet ground-state spin.<sup>80,81</sup> Despite their promise, the microscopic details of their luminescence spectra were not fully understood; for instance, since the dopant atom vibrates in the void of divacancies in the lattice, the respective vibrational modes fall to lower frequencies.<sup>79</sup>

Alkauskas and collaborators calculated the vibrational spectrum of the SiV center with very large supercells (see Sec. III A).<sup>82</sup> They found that the quasilocal vibrational modes are not single modes but broaden into a band, showing significant supercell-size dependence. This has important consequences for the interpretation of the isotope shift in the luminescence spectrum:<sup>83</sup> Alkauskas demonstrated that the central position of the broadened peak should be used to calculate the isotope shift, as opposed to individual modes that lead to false results.<sup>82</sup> This conclusion is general and should also apply to other defect systems with quasilocal vibrational modes. For the SiV center, the quasilocal modes scale perfectly with the inverse square root of the mass, resulting from motion of the isolated Si atom.

Alkauskas and collaborators also examined the isotope shift of the ZPL, which can be used for pressure sensing. They demonstrated that phonons other than the quasilocal modes dominate the shift.<sup>82</sup> In addition to the SiV center, they also examined the ZPL shift for the GeV and SnV centers as a function of pressure and found good agreement with experiment.<sup>84</sup>

While defects in diamond have enabled the realization of many facets of quantum information science, there is still much room for improvement. The drive to realize the “ideal” quantum defect has motivated a large field of work; Alkauskas has contributed by developing guidelines to realize “quantum defects by design.”<sup>85</sup> A key aspect is identifying novel quantum defects in different materials. Hexagonal boron nitride (h-BN) is one such material;<sup>81,86</sup> Alkauskas played a pivotal role in developing h-BN as a platform for quantum defects. By investigating native defects and common impurities, he contributed to the understanding of defect chemistry in h-BN<sup>87</sup> and was able to elucidate the formation energetics, electrical activity, mobility, and optical properties of such centers. This work was foundational in building an understanding of h-BN.

Several classes of single-photon emitters had been observed<sup>88–90</sup> in h-BN. While they were attributed to point defects in the lattice, the precise microscopic origin eluded researchers for several years. One class of single-photon emitter was found to emit light in the visible spectrum near 2 eV.<sup>88,89,91</sup> These emitters are



**FIG. 4.** (a) Energies of Kohn–Sham states and (b) wave functions of the defect states of the carbon dimer in h-BN. Reproduced with permission from Mackoitis-Sinkevičienė *et al.*, Appl. Phys. Lett. **115**, 212 101 (2019). Copyright 2019 AIP Publishing LLC.

exceptionally bright with minimal coupling to phonons and exhibit spin-dependent transitions,<sup>91,92</sup> making them excellent candidates for quantum information applications. However, they are also notoriously heterogeneous,<sup>88</sup> making identification of their microscopic origin particularly challenging. Among other models for the emission,<sup>93,94</sup> Alkauskas helped to propose boron dangling bonds as a compelling explanation for the origin of the emission.<sup>95,96</sup> Boron dangling bonds have optical transitions around 2.0 eV that are sensitive to the local environment, explaining the observed heterogeneity. Their coupling to phonons is characterized by a Huang–Rhys factor of 2.3, in agreement with experiment.

Another class of single-photon emitters had been observed in the ultraviolet spectrum at 4.1 eV. Alkauskas helped to dispel an early misattribution to a  $C_N$  defect<sup>97</sup> by clearly demonstrating that  $C_N$  could not explain the emission.<sup>87</sup> Instead he demonstrated that a pair of substitutional carbon atoms (the “carbon dimer,”  $C_N-C_B$ , shown in Fig. 4) was a better match.<sup>98</sup> Indeed the transition energy, coupling to phonons, and radiative lifetime are all in good agreement with the experimental values. More generally, carbon has been implicated as a key impurity in h-BN.<sup>87,99</sup> Alkauskas elucidated the thermodynamics of carbon incorporation in h-BN<sup>100</sup> by considering the variety of potential complexes that may form and the competition with entropy. Overall, Alkauskas’ work has had a major impact on the study of h-BN and, more generally, on the understanding of quantum defects.

## V. CONCLUSIONS AND FUTURE DIRECTIONS

The pioneering contributions of Alkauskas in the field of non-radiative recombination have laid the foundation for a variety of future works. Regarding methodological developments, a number of advances relating to configuration coordinate diagrams can be envisioned; here, we highlight three of them that Alkauskas himself was keenly pursuing.

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First, assessing the accuracy and limitations of the 1D approximation for carrier capture is a major outstanding challenge.<sup>46,101,102</sup> This entails the development of a multidimensional formalism that includes coupling to all phonon modes.<sup>103</sup>

Second, a correction scheme for vertical excitation energies has been developed,<sup>104,105</sup> and it was suggested that this should be included when constructing configuration coordinate diagrams.<sup>106</sup> However, the effect of this correction in the context of lineshape functions or nonradiative capture—or whether it is even consistent to apply such a correction in this formalism—has not yet been assessed.

Third, anharmonicity has been incorporated in the configuration coordinate diagrams,<sup>49,107,108</sup> expanding the range of defects and materials that can be addressed. Alkauskas was very interested in this development, but he also pointed out that accurate treatment of the anharmonicity might require going beyond the 1D approximation. Systematic investigations of anharmonicity within the multidimensional formalism would be highly interesting and important.

Alkauskas remained very interested in exploring the capabilities and limitations of various functionals within DFT, as evidenced by Ref. 109, and considered this an important area for future progress.

In his very last days, Alkauskas was actively involved in discussions about the possibility of nonradiative capture of more than one charge carrier at once. He thought that while such processes are, in principle, possible, a rigorous computational methodology is required to accurately calculate the capture rates. The rates of capturing two electrons or holes at once scale quadratically with the carrier density and would, thus, be negligibly small at typical carrier densities in solar cells or light-emitting diodes. For such processes to become relevant the capture barriers would have to be significantly reduced. Whether this happens, e.g., in negative-*U* centers, can only be assessed by quantitative calculations.

These considerations fit into Alkauskas' broader interest in the physics of interactions between charge carriers and the defects at which they may eventually be captured. Coulomb interactions play an important role and can be described by a so-called Sommerfeld factor,<sup>42,43,110</sup> but giant cross sections have sometimes been observed<sup>111</sup> that have eluded quantitative descriptions. Alkauskas envisioned developing a rigorous methodology to address such cascade capture processes.

Overall, there is huge potential for applying the methodologies developed by Alkauskas to new defect and material combinations. Such work generates benefits ranging from improving the efficiency of optoelectronic devices to characterizing novel quantum defects. Alkauskas' memory will live on through the impact of his contributions.

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## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

### Author Contributions

**Xie Zhang:** Conceptualization (lead); Writing – original draft (lead); Writing – review & editing (lead). **Mark E. Turiansky:** Conceptualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Lukas Razinkovas:** Writing – original draft (equal); Writing – review & editing (equal). **Marek Maciaszek:** Writing – original draft (equal); Writing – review & editing (equal). **Peter Broqvist:** Writing – original draft (equal); Writing – review & editing (equal). **Qimin Yan:** Writing – original draft (equal); Writing – review & editing (equal). **John L. Lyons:** Writing – original draft (equal); Writing – review & editing (equal). **Cyrus E. Dreyer:** Writing – original draft (equal); Writing – review & editing (equal). **Darshana Wickramaratne:** Writing – original draft (equal); Writing – review & editing (equal). **Ádám Gali:** Writing – original draft (equal); Writing – review & editing (equal). **Alfredo Pasquarello:** Writing – original draft (equal); Writing – review & editing (equal). **Chris G. Van de Walle:** Conceptualization (equal); Funding acquisition (equal); Writing – original draft (equal); Writing – review & editing (equal).

## DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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