

# Theory of inelastic multiphonon scattering and carrier capture by defects in semiconductors: Application to capture cross sections

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Inelastic scattering and carrier capture by defects in semiconductors are the primary causes of hot-electron-mediated degradation of power devices, which holds up their commercial development. At the same time, carrier capture is a major issue in the performance of solar cells and light-emitting diodes. A theory of nonradiative (multiphonon) inelastic scattering by defects, however, is nonexistent, while the theory for carrier capture by defects has had a long and arduous history. Here we report the construction of a comprehensive theory of inelastic scattering by defects, with carrier capture being a special case. We distinguish between capture under thermal equilibrium conditions and capture under nonequilibrium conditions, e.g., in the presence of an electrical current or hot carriers where carriers undergo scattering by defects and are described by a mean free path. In the thermal-equilibrium case, capture is mediated by a nonadiabatic perturbation Hamiltonian, originally identified by Huang and Rhys and by Kubo, which is equal to linear electron-phonon coupling to first order. In the nonequilibrium case, we demonstrate that the primary capture mechanism is within the Born-Oppenheimer approximation (adiabatic transitions), with coupling to the defect potential inducing Franck-Condon electronic transitions, followed by multiphonon dissipation of the transition energy, while the nonadiabatic terms are of secondary importance (they scale with the inverse of the mass of typical atoms in the defect complex). We report first-principles density-functional-theory calculations of the capture cross section for a prototype defect using the projector-augmented wave, which allows us to employ all-electron wave functions. We adopt a Monte Carlo scheme to sample multiphonon configurations and obtain converged results. The theory and the results represent a foundation upon which to build engineering-level models for hot-electron degradation of power devices and the performance of solar cells and light-emitting diodes.

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## I. INTRODUCTION

Elastic scattering of electrons by phonons, impurities, and other defects limits the conductivity in metals and the carrier mobility in semiconductors. The fundamental theory is well established, parameter-free mobility calculations have become possible [1,2], and engineering-level modeling methods are widely available. Inelastic scattering of hot electrons by defects has long been known to cause device degradation. For example, hot electrons in Si-SiO<sub>2</sub> structures can transfer energy and release hydrogen from passivated interfacial Si dangling bonds [3,4]. More recently, it was found that hot electrons cause degradation of power devices based on wide-band-gap semiconductors [5]. It has been shown that the degradation is caused by hot-electron-mediated release of hydrogen from hydrogenated defects such as Ga vacancies or impurities [6]. In other cases, carrier capture transforms benign defects to metastable configurations that cause recoverable degradation [7]. Similarly, nonradiative carrier capture by defects, which is a special case of inelastic scattering, limits the performance of photovoltaic cells, light-emitting diodes, and other devices [8,9].

A theory of inelastic scattering by defects by multiphonon processes (MPPs) does not exist while the theory of non-

radiative carrier capture or emission by defects by MPPs has a long and controversial history. In 1950, Huang and Rhys [10] reported a theory of how the energy of lattice relaxation that accompanies the photoionization of a defect is dissipated by MPPs. The process was described within the Born-Oppenheimer or adiabatic approximation (BOA) and the Franck-Condon approximation (FCA). The former says that electronic and nuclear (vibrational) wave functions obey decoupled equations. The latter states that an electronic excitation occurs instantaneously and relaxation processes follow at a relatively slow pace, allowing one to write the excitation rate (Fermi's golden rule) as the product  $P = AF$ , where  $A$  describes the instantaneous electronic excitation in the initial lattice configuration and  $F$ , the so-called line-shape function, describes the MPPs that occur during lattice relaxation. In the Huang-Rhys theory, the operator that causes the excitation is strictly the photon field and MPPs dissipate only the energy of the ensuing lattice relaxation.

In the same paper, Huang and Rhys [10] also proposed a theory for nonradiative multiphonon transitions between defect levels. Such transitions are caused by the terms that are dropped when the BOA is made, namely, derivatives of the electronic wave functions with respect to nuclear positions (nonadiabatic terms). In 1952, Kubo [11] independently invoked the same nonadiabatic terms as being responsible for the thermal ionization of a defect. In subsequent years, Kubo and Toyozawa [12] and later Gummel and Lax [13] adopted

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Kubo's formalism to explore carrier capture and emission using analytical approximations. Kovarskii and Sinyavskii [14–16] published several papers expanding on Kubo's formalism. In 1977, in search of a practical scheme to model electron capture in experiments, Henry and Lang [17] adopted a Huang-Rhys analog: the electronic transition is caused instantaneously by the perturbation potential  $\Delta V$  generated by atomic vibrations—the linear electron-phonon coupling potential that is normally thought to cause elastic scattering and is used for mobility calculations [18]. The following year, Ridley [19] showed that the Henry-Lang model exhibits the correct temperature dependence at high temperatures (the semiclassical limit) but pointed out that the correct way to calculate nonradiative capture cross sections is through the nonadiabatic perturbation terms identified by Huang and Rhys [10] and by Kubo [11]. In 1981, however, Huang showed that the nonadiabatic perturbation Hamiltonian and the linear electron-phonon coupling perturbation Hamiltonian are equivalent to first order [20]. The issue whether such a first-order calculation is adequate remained open as, throughout the years of all these developments, only model calculations were pursued, largely analytical, employing model defect wave functions. Furthermore, calculations of the line-shape function were typically restricted by the assumption that a single vibrational mode contributes to the MPPs. In the chemical literature, nonradiative transitions between molecular orbitals have been studied [21,22]. It was recognized that the inclusion of all vibrational modes in the MPP calculation leads to exploding computational requirements as the size of the molecule increases [21]. The so-called parallel-mode approximation or simply a single vibrational mode is typically used [22].

The first application of modern density-functional-theory (DFT) calculations to MPPs in the case of luminescence, i.e., the classic Huang-Rhys problem, where an electronic transition is caused by the photon field and MPPs dissipate the ensuing lattice relaxation, was reported by Alkauskas *et al.* [23]. Those authors studied the luminescence spectra of defects in GaN employing DFT pseudowave functions for the electronic matrix elements and the single-phonon-mode approximation to the Huang-Rhys line-shape function. In a more recent paper, Alkauskas *et al.* [24] reported calculations of nonradiative capture of electrons by defects using the linear electron-phonon coupling perturbation Hamiltonian, pseudowave functions, and a single-phonon mode to calculate the MPPs that dissipate the transition energy. They pointed out that the electronic transition is a slow process because capture is mediated by the phonons that are localized around the defect.

In this paper we first revisit the theory of carrier capture by defects. We identify two distinct regimes that are governed by different processes. One is carrier capture under thermal-equilibrium conditions; i.e., capture occurs in tandem with emission with electrons in the conduction band (or holes in the valence band) are not being accelerated. Under these conditions, capture and emission are inverse processes; i.e., the role of the initial and final states is reversed. For an electron bound at a defect, emission amounts to a transition to a band state that is an eigenstate of the same Hamiltonian (perfect crystal plus defect potential). Band states are occupied according to

the Fermi-Dirac distribution function. Any of these carriers can be captured into the defect's ground state. Under such conditions, band carriers are effectively undergoing diffusive Brownian motion. In this case, the Huang-Rhys-Kubo (HRK) nonadiabatic Hamiltonian perturbation is the only possible cause of these thermal transitions.

Under nonequilibrium conditions, however, e.g., in the presence of an electrical current, carriers are accelerated in a specific direction and a mean free path is defined by scattering events. It is then standard procedure to treat the band electrons as being in eigenstates of the perfect crystal Hamiltonian and consider scattering by the defects. In particular, one considers elastic scattering by defects as a mechanism that limits the carrier mobility. In this case, the initial and final states are eigenstates of the perfect crystal Hamiltonian and the defect potential acts as the perturbation that causes the transitions, i.e., the defect potential is “turned on” in order to use time-dependent perturbation theory and arrive at Fermi's golden rule. Clearly, hot carriers can undergo inelastic scattering as well, dropping to a Bloch state of lower energy, with the energy dissipated by MPPs. For such calculations, one must again turn on the defect potential, though the HRK nonadiabatic perturbation must also be included. Transitions caused by the defect potential are within the BOA, whereas those caused by the HRK perturbation Hamiltonian are nonadiabatic. Finally, under such nonequilibrium conditions, carrier capture can be viewed as a special case of inelastic scattering: if the defect potential can cause elastic scattering and inelastic scattering with energy dissipation via MPPs, then it certainly should also be included as a cause of capture.

In the capture case, however, there is a subtle difficulty. In order to derive a transition rate using Fermi's golden rule, initial and final states must be eigenstates of the same Hamiltonian. In the carrier capture case, however, the final state is an eigenstate of the crystal Hamiltonian plus the defect potential, whereas the initial state is an eigenstate of the perfect-crystal Hamiltonian. The difficulty can be overcome if we prepare a propagating state for the incoming electron that is not aware of the bound state's existence, with capture being triggered by the sudden turning-on of a suitable coupling (initial and final states must belong to the same Hamiltonian for the concept of a transition to be meaningful). Such adiabatic transitions have not been considered so far in the context of multiphonon transitions at defects in semiconductors, but they are commonly invoked in chemistry for electron transitions in molecules [25–27].

We develop a comprehensive theory of inelastic scattering and capture for transitions caused both by the defect potential (adiabatic transitions) and by the nonadiabatic HRK perturbation Hamiltonian. We show that, for carrier capture, adiabatic transitions are the zeroth-order term in an expansion in the defect-atom displacements that following capture (lattice relaxation) and are, therefore, dominant under nonequilibrium conditions. The electronic transition is caused instantaneously by the defect potential (it is effectively a Franck-Condon transition) and the energy is dissipated by MPPs. The next order in the series, which is linear in the atomic displacements, comprises two terms, only one of which has been captured by prior theories [20,24,28]. We estimate that these “linear terms” make smaller contributions to the capture rate as they scale

with  $1/m$ , where  $m$  is a typical nuclear mass in the defect complex. The adiabatic perturbation Hamiltonian that couples the incoming electron to the defect is constructed in terms of Hamiltonian matrices as in the Förster theory of electron and exciton transfer in molecules [25], which allows the derivation of Fermi's golden rule for these transitions.

In addition to presenting the basic elements of the fundamental theory, we report explicit calculations for capture cross sections as functions of energy transfer for a prototype defect using DFT for the electronic matrix elements. We employ the projector-augmented wave (PAW) scheme [29], which allows the use of the all-electron defect potential and wave functions as opposed to pseudopotentials and pseudo-wave functions. For calculation of the line-shape function, we introduce a Monte Carlo scheme to sample the space of phonon combinations that contribute to the MPP energy dissipation and find that random configurations containing up to *twelve different phonon modes* and *trillions of configurations* are needed to obtain converged results.

A few more observations are in order before we describe the present theory in detail. In a perfect crystal without defects, the HRK perturbation Hamiltonian is responsible for electron-phonon scattering (only linear coupling is usually included) and for the formation of polarons, which are electrons or holes dressed by phonons. Under strong-coupling conditions, the HRK Hamiltonian can be responsible for polaron self-trapping. When a defect is present, the HRK Hamiltonian can cause carrier capture. As Alkauskas *et al.* [24] pointed out, such capture is very slow. Indeed it is caused by the derivatives of the electronic wave functions with respect to nuclear displacements, which amounts to a “frozen electron approximation” (recall that the BOA is effectively a “frozen nuclei approximation”). As we noted, this kind of capture occurs under thermal equilibrium conditions, which corresponds to constant emission and capture by inverse processes; i.e., the band electrons are definitely “aware” of the defects, i.e., they should not be treated as “free” carriers with a mean free path, undergoing scattering by defects and phonons. In this regard, the linear coupling approximation [24] should be viewed as the zero mean-free-path limit, whereas the theory put forward in this paper represents the limit in which the mean free path is bounded only by  $L_{\text{capture}}$ , the mean distance an electron travels before being captured by a defect.

The conditions under which capture cross sections are measured by junction capacitance methods [17] are close to equilibrium; i.e., they are slow. Similarly, in light-emitting diodes, carriers by design have minimal acceleration through the pn junction. However, even in such deliberate setups, there must still be some nonequilibrium driving forces, e.g., a current must flow through the system, in order to carry out the measurement or for the device to operate. The carrier mean free path is always finite, never exactly zero. Therefore, a realistic model of the measured capture cross sections can be obtained by scaling the difference between the two limits according to the factor  $L/L_{\text{capture}}$ , where  $L$  is the elastic scattering mean free path,

$$\sigma = \frac{L}{L_{\text{capture}}} \sigma_{\text{adiabatic}} + \sigma_{\text{nonadiabatic}}, \quad (1)$$

where  $\sigma_{\text{nonadiabatic}}$  is the capture cross section due to the HRK Hamiltonian and  $\sigma_{\text{adiabatic}}$  is the adiabatic capture cross section calculated in this paper.

For scattering of a carrier into another propagating state at a lower energy, the defect is left in the same charge state, which requires that scattering by the defect potential is elastic (no energy can be dissipated in the FCA in such a case). We find that inelastic scattering can still occur within the BOA by the first-order correction to the FCA, which are the linear terms discussed above.

## II. FERMI GOLDEN RULE FOR ADIABATIC AND NONADIABATIC TRANSITIONS

As discussed in the previous section, in order to describe transitions, it is always necessary to identify the piece of the total Hamiltonian that causes the transition between eigenstates of an approximate Hamiltonian. Let us be more specific. In the hydrogen atom, one usually includes only the Coulombic attraction between the proton and the electron, leaving out the electromagnetic field at large. The calculated energy levels are only eigenstates of this approximate Hamiltonian. The electromagnetic field, treated as a perturbation, then causes a transition from, say, a  $2p$  state to the  $1s$  state. In Auger transitions, one must leave out specific electron-electron interactions, which are then introduced to cause transitions [30]. Our task here is to identify the approximate Hamiltonian whose eigenstates are the propagating state of the incoming electron, which is not aware of the bound state of the defect potential, and the final state, which can be either another propagating state that is not aware of the existence of a bound state at a lower energy or the bound state itself, and determine the perturbation Hamiltonian that causes the transition.

In the BOA, the many-electron Hamiltonian depends parametrically on the nuclear positions and the total wave functions are products of many-electron wave functions and phonon wave functions. Within DFT, the many-electron wave functions are Slater determinants of Kohn-Sham wave functions. We start by defining the many-electron Hamiltonian  $H^0$  for the perfect crystal and the corresponding eigenvalue problem:

$$H^0 |\Psi_n^0\rangle = E_n^0 |\Psi_n^0\rangle. \quad (2)$$

For the crystal containing a single defect, we have

$$H |\Phi_m\rangle = E_m |\Phi_m\rangle. \quad (3)$$

One normally writes

$$H = H^0 + \Delta H. \quad (4)$$

The partitioning of the total Hamiltonian  $H$  according to Eq. (4) is not useful for our purposes. Instead, we write

$$H = \tilde{H}^0 + H_1^{\text{BO}}, \quad (5)$$

where

$$\tilde{H}^0 |\Psi_n\rangle = \epsilon_n |\Psi_n\rangle. \quad (6)$$

In order to obtain an explicit description of  $H_1^{\text{BO}}$ , which then defines  $\tilde{H}^0$  through Eq. (5), we express  $\Delta H$  in terms of the

complete set of functions  $\Psi_n$ :

$$\begin{aligned}\Delta H &= \sum_m |\Psi_m\rangle\langle\Psi_m| \Delta H \sum_n |\Psi_n\rangle\langle\Psi_n| \\ &= \sum_{mn} |\Psi_m\rangle \Delta H_{mn} \langle\Psi_n|. \end{aligned} \quad (7)$$

We then define  $H_1^{\text{BO}}$  by

$$H_1^{\text{BO}} = |\Psi_i\rangle \Delta H_{if} \langle\Psi_f| + |\Psi_f\rangle \Delta H_{fi} \langle\Psi_i|, \quad (8)$$

where the subscripts  $i$  and  $f$  denote the eigenstates of  $\tilde{H}^0$  that are the initial and final states of our problem. This definition of  $H_1^{\text{BO}}$  is analogous to the so-called Förster transition often used in energy transfer in molecules [25]. In effect,  $H_1^{\text{BO}}$  eliminates the coupling of the incoming electron via the defect potential to the final state, whether propagating or bound. The defect potential  $\Delta H$ , which can be arbitrarily strong, is still present. It is the perturbation Hamiltonian  $H_1^{\text{BO}}$  that is weak and can cause transitions whose rate is describable by Fermi's gold rule, i.e., to first order in  $H_1^{\text{BO}}$ . Note also that the state  $|\Psi_i\rangle$  contains an incoming electron that "sees" the defect potential but does not couple to the bound state. Also, for all practical purposes, for carrier capture we have  $|\Psi_f\rangle = |\Phi_f\rangle$  (i.e., the bound state is not affected by the presence of an incoming electron that does not couple to the defect).

The adiabatic transition rate is given by the usual Fermi's golden rule,

$$w_{if}^{\text{BO}} = \frac{2\pi}{\hbar} \sum_f |\langle X_f | \langle\Psi_f| H_1^{\text{BO}} | \Psi_i \rangle | X_i \rangle|^2 \delta(\Theta_f - \Theta_i + \epsilon_{if}), \quad (9)$$

where  $\Theta_{i,f}$  are the total phonon energies of states  $|X_{i,f}\rangle$  and  $\epsilon_{if} = \epsilon_f - \epsilon_i$  is the energy difference between the electronic states  $|\Psi_i\rangle$  and  $|\Psi_f\rangle$ . For capture, it is usually assumed that there is one final electronic state with a given energy difference  $\epsilon_{if}$ , but there are many phonon configurations that can make up this difference. If there are multiple electronic states at the same energy, we need to sum Eq. (9) over all such states.

In addition to  $H_1^{\text{BO}}$ , there are terms beyond the BOA, usually referred to as nonadiabatic terms [10,11], which cause multiphonon transitions. These terms contain derivatives of the electron wave functions with respect to nuclear coordinates  $\{\mathbf{R}_k\}$  and are the terms neglected when one invokes the BOA. They contribute to the total transition rate  $w_{if}$  via the matrix element,

$$\begin{aligned} & - \sum_k \frac{\hbar^2}{2m_k} [\langle X_f | \langle\Psi_f| \nabla_{\mathbf{R}_k}^2 (|\Psi_i\rangle | X_i \rangle) \\ & - \langle X_f | \langle\Psi_f| \Psi_i \rangle \nabla_{\mathbf{R}_k}^2 | X_i \rangle], \end{aligned} \quad (10)$$

where  $m_k$  is the mass of atom  $k$ . This contribution is discussed in detail later.

One can define a cross section for inelastic scattering or carrier capture by

$$\sigma_{if} = \frac{w_{if} \Omega}{v_g}, \quad (11)$$

where  $v_g$  is the group velocity of the incident electron and  $\Omega$  is the volume over which state  $|i\rangle$  is normalized, so that  $v_g/\Omega$  represents the flux of the incoming electrons.

We work within DFT so that the many-electron wave functions are Slater determinants of Kohn-Sham one-electron wave functions and the many-electron Hamiltonians are those of noninteracting Kohn-Sham quasiparticles in the presence of an effective single-particle external potential. From now on we view the Hamiltonians and wave functions in Eqs. (9) and (10) as one-electron Kohn-Sham Hamiltonians and electron wave functions without change of notation.

### A. Adiabatic series

We now examine the electronic part of the transition matrix element in the BOA by showing explicitly its dependence on the atomic coordinates:

$$M_e^{\text{BO}}(\{\mathbf{R}_j\}) = |\langle\Psi_f(\{\mathbf{R}_j\})| H_1^{\text{BO}}(\{\mathbf{R}_j\}) |\Psi_i(\{\mathbf{R}_j\})\rangle|^2. \quad (12)$$

The BOA by itself does not separate electron and phonon matrix elements. A further approximation is needed. We expand

$$\begin{aligned} M_e^{\text{BO}}(\{\mathbf{R}_j\}) &= M_e^{\text{BO}}(\{\mathbf{R}_j^{(0)}\}) \\ &+ \sum_k (\mathbf{R}_k - \mathbf{R}_k^{(0)}) \cdot \nabla_{\mathbf{R}_k} M_e^{\text{BO}}(\{\mathbf{R}_j\}) + \dots \end{aligned} \quad (13)$$

in terms of the atomic displacements  $\mathbf{R}_k - \mathbf{R}_k^{(0)}$ , where  $\mathbf{R}_k^{(0)}$  are the atomic positions in a reference state, which is determined later. The transition rate is then

$$\begin{aligned} w_{if}^{\text{BO}} &= \frac{2\pi}{\hbar} |M_e^{\text{BO}}(\{\mathbf{R}_j^{(0)}\})|^2 \sum_f |\langle X_f | X_i \rangle|^2 \delta(\Theta_f - \Theta_i + \epsilon_{if}) \\ &+ \frac{2\pi}{\hbar} \sum_f \left| \sum_k \nabla_{\mathbf{R}_k} M_e^{\text{BO}}(\{\mathbf{R}_j^{(0)}\}) \cdot \langle X_f | (\mathbf{R}_k - \mathbf{R}_k^{(0)}) | X_i \rangle \right|^2 \\ &\times \delta(\Theta_f - \Theta_i + \epsilon_{if}) + \dots \end{aligned} \quad (14)$$

Here the cross terms are dropped because the zeroth-order and first-order terms cannot have the same final phonon wave functions: the number of phonons needed to ensure a nonzero overlap matrix element are different for the two cases. The first term in this expansion represents a complete separation of the electron and phonon wave functions as if they are independent of each other and corresponds to the FCA. The second term is the first-order correction to the FCA arising from the BOA perturbation Hamiltonian  $H_1^{\text{BO}}$ .

### B. Nonadiabatic series

According to Huang [20], the nonadiabatic matrix element defined in Eq. (10) can be evaluated for linear phonon coupling,

$$\begin{aligned} & \sum_k \langle\Psi_f(\{\mathbf{R}_j^{(0)}\}) | \nabla_{\mathbf{R}_k} H_e(\{\mathbf{R}_j^{(0)}\}) | \Psi_i(\{\mathbf{R}_j^{(0)}\}) \rangle \\ & \cdot \langle X_f | (\mathbf{R}_k - \mathbf{R}_k^{(0)}) | X_i \rangle, \end{aligned} \quad (15)$$

where  $H_e$  is the electron part of the Hamiltonian. When electron-phonon coupling  $H_{ep} = H_e(\{\mathbf{R}_j\}) - H_e(\{\mathbf{R}_j^{(0)}\})$  is introduced, the electron wave functions are changed by a



perturbation,

$$|\delta\Psi_i(\{\mathbf{R}_j\})\rangle = \sum_{i' \neq i} \frac{\langle \Psi_{i'} | H_{ep} | \Psi_i \rangle}{\epsilon_{i'} - \epsilon_i} |\Psi_{i'}(\{\mathbf{R}_j^{(0)}\})\rangle \quad (16)$$

$$\begin{aligned} & - \sum_k \frac{\hbar^2}{2M_k} [\langle X_f | \nabla_{\mathbf{R}_k}^2 (\langle \Psi_f(\{\mathbf{R}_j^{(0)}\}) | \delta\Psi_i | X_i \rangle) - \langle X_f | \langle \Psi_f(\{\mathbf{R}_j^{(0)}\}) | \delta\Psi_i \rangle \nabla_{\mathbf{R}_k}^2 | X_i \rangle] \\ & = (\Theta_i - \Theta_f) \langle X_f | \langle \Psi_f(\{\mathbf{R}_j^{(0)}\}) | \delta\Psi_i | X_i \rangle \\ & = \sum_k \sum_{i' \neq i} \frac{\epsilon_{i'}}{\epsilon_{i'} - \epsilon_i} \langle \Psi_{i'} | \nabla_{\mathbf{R}_k} H | \Psi_i \rangle \langle \Psi_f(\{\mathbf{R}_j^{(0)}\}) | \Psi_{i'}(\{\mathbf{R}_j^{(0)}\}) \rangle \cdot \langle X_f | (\mathbf{R}_k - \mathbf{R}_k^{(0)}) | X_i \rangle \\ & = \sum_k \langle \Psi_f | \nabla_{\mathbf{R}_k} H_e | \Psi_i \rangle \cdot \langle X_f | (\mathbf{R}_k - \mathbf{R}_k^{(0)}) | X_i \rangle. \end{aligned} \quad (18)$$

Here the first equality results from the Schrödinger equations for the phonon wave functions, and for the second equality we used  $\Theta_i - \Theta_f = \epsilon_{if}$ .

We note that the above linear-order term in the nonadiabatic series has the same phonon matrix element as the linear-order term in the BOA series in the previous section. This indicates that the leading nonadiabatic term is a smaller contribution to the electron capture rate compared to the zeroth-order BOA term. The electronic matrix element in the nonadiabatic series is different from that in the BOA series. We show later that both these terms scale as  $1/m$ , where  $m$  is the mass of a typical atom in the defect complex.

The linear term in Eq. (15) is usually referred to as the linear electron-phonon coupling term. A similar term has been calculated by Alkauskas *et al.* [24], with the exception that in that work the wave functions are  $|\Phi_{i(f)}\rangle$ , which are the eigenstates of the full Hamiltonian  $H_e$ , whereas in our case the wave functions are  $\Psi_{i(f)}$ , which are the eigenstates of the Hamiltonian  $\hat{H}^0$ . We recover the term calculated by Alkauskas *et al.* if we combine the BOA and the nonadiabatic series. We make use of the result in Eq. (24) and get, for our final result,

$$\begin{aligned} w_{if} &= \frac{2\pi}{\hbar} |M_e^{\text{BO}}(\{\mathbf{R}_j^{(0)}\})|^2 \sum_f |\langle X_f | X_i \rangle|^2 \delta(\Theta_f - \Theta_i + \epsilon_{if}) \\ &+ \frac{2\pi}{\hbar} \sum_f \left| \sum_k [\langle \Phi_f | \nabla_{\mathbf{R}_k} H_e | \Phi_i \rangle - \langle \Phi_f | \Psi_i^0 \rangle \right. \\ &\quad \times \langle \Phi_f | \nabla_{\mathbf{R}_k} H_e | \Phi_f \rangle] \cdot \langle X_f | (\mathbf{R}_k - \mathbf{R}_k^{(0)}) | X_i \rangle \left. \right|^2 \\ &\quad \times \delta(\Theta_f - \Theta_i + \epsilon_{if}) + \dots \end{aligned} \quad (19)$$

Here the first term is the zeroth-order term that corresponds to the FCA and the second term is the totality of contributions from the linear terms in the two series. The first term in brackets is precisely the term that Alkauskas *et al.* [24] calculated. We note that there exists a second term, which has the appearance of a force term. These two terms can either add or subtract. We show shortly that these linear-order terms are proportional to  $1/m$ , where  $m$  is a typical atomic mass in the defect complex,

(and a similar equation applies for the final states). We write both the initial and the final states in the form

$$|\Psi_{i(f)}(\{\mathbf{R}_j\})\rangle = |\Psi_{i(f)}(\{\mathbf{R}_j^{(0)}\})\rangle + |\delta\Psi_{i(f)}\rangle. \quad (17)$$

Substituting this into Eq. (10) and keeping only the linear terms,

and are, therefore, significantly smaller than the zeroth-order Franck-Condon term, which is dominant.

### III. ELECTRON MATRIX ELEMENTS

We first consider the zeroth-order term in the BOA series, which yields a capture cross section that can be written in the familiar factorized form,

$$\sigma_{if} = A_{if} F_{if}, \quad (20)$$

where  $A_{if}$  contains the electronic part of the matrix element,

$$A_{if} = \frac{2\pi\Omega}{\hbar v_g} |\langle \Psi_f(\{\mathbf{R}_j^{(0)}\}) | H_1^{\text{BO}}(\{\mathbf{R}_j^{(0)}\}) | \Psi_i(\{\mathbf{R}_j^{(0)}\}) \rangle|^2, \quad (21)$$

and  $F$  is called the line-shape factor due to vibrations,

$$F_{if} = \sum_f |\langle X_f | X_i \rangle|^2 \delta(\Theta_f - \Theta_i + \epsilon_{if}). \quad (22)$$

Next we consider these two factors separately.

Detailed derivations given in Appendixes A and B give the final results:

$$M_e^{\text{BO}} = -\langle \Phi_f | \Psi_i^0 \rangle \epsilon_{if} \quad (23)$$

and

$$\begin{aligned} & \nabla_{\mathbf{R}_k} M_e^{\text{BO}} + \langle \Psi_f | \nabla_{\mathbf{R}_k} H | \Psi_i \rangle \\ & = \langle \Phi_f | \nabla_{\mathbf{R}_k} H | \Phi_i \rangle - \langle \Phi_f | \Psi_i^0 \rangle \langle \Phi_f | \nabla_{\mathbf{R}_k} H | \Phi_f \rangle. \end{aligned} \quad (24)$$

For evaluation of the above matrix elements, we employ the PAW scheme, which allows us to use all-electron wave functions instead of pseudo-wave functions. Details are given in Appendix C.

### IV. PHONON MATRIX ELEMENTS

First, we consider the effect of displacements for a classical Hamiltonian. We derive this Hamiltonian for the ion motion, from which the phonon wave functions and matrix elements can be calculated. For this purpose we start with a supercell containing a number of atoms  $n_a$ , with the defect site at

its center. This supercell is repeated  $N$  times using the Born–von Karman periodic boundary condition. For the initial state, the equilibrium positions of the atoms are  $R_k$ , where the subscript  $k$  runs through both the atomic index within the supercell and the Cartesian components. Each atom oscillates around its equilibrium position with displacement  $u_{kl}$ , where the subscript  $l$  labels different copies of the supercell under the Born–von Karman periodicity. Using the harmonic approximation for the potential energy, under which only terms that are second order in displacements make a contribution, and introducing force constants  $\Phi_{kl,k'l'}$ , we can write [25]

$$H'_i = \frac{1}{N} \sum_{kl} \left[ \frac{1}{2} m_k \left( \frac{du_{kl}}{dt} \right)^2 + \frac{1}{2N} \sum_{k'l'} u_{kl} \Phi_{kl,k'l'} u_{k'l'} \right], \quad (25)$$

for the initial state, where the atomic mass  $m_k$  also carries the subscript  $k$  for convenience even though it depends only on the atomic index, and not the coordinate component index.

When an electron is absorbed or emitted from the lattice, the equilibrium positions of the atoms change. The new equilibrium positions are  $R_k + \Delta_k$ . The new Hamiltonian has the same form after the initial displacement vectors  $u_{kl}$  are replaced by  $u'_{kl} = u_{kl} - \Delta_k$ . The final-state Hamiltonian is then written as

$$H'_f = \frac{1}{N} \sum_{kl} \left\{ \frac{1}{2} m_k \left[ \frac{d(u_{kl} - \Delta_k)}{dt} \right]^2 + \frac{1}{2N} \sum_{k'l'} (u_{kl} - \Delta_k) \Phi_{kl,k'l'} (u_{k'l'} - \Delta_{k'}) \right\}, \quad (26)$$

where we make the assumption that force constants do not change due to the electron capture or absorption. Since displacements  $\Delta_k$  do not depend on time, the kinetic energy term remains unchanged. Expanding the potential energy to first order in displacements reproduces the same term in the original Hamiltonian plus a term that includes  $u_{k'l'} \Delta_k$ :

$$H'_f = H'_i - \frac{1}{N} \sum_{kl,k'l'} \Phi_{kl,k'l'} \Delta_k u_{k'l'}. \quad (27)$$

Transforming to the normal-mode representation in terms of the generalized coordinates,

$$q_j = \frac{1}{\sqrt{N}} \sum_{kl} \sqrt{m_k} u_{kl} w_{j,kl}, \quad (28)$$

where  $w_{j,kl}$  is the  $kl$ th element of the eigenvector for mode  $j$ . Note that in this definition of the generalized coordinate  $q_j$ , it has absorbed the mass factor  $\sqrt{m_k}$ . The Hamiltonian is expressed as

$$H'_f = \frac{1}{2} \sum_j \dot{q}_j^2 + \frac{1}{2} \sum_j \omega_j^2 q_j^2 - \frac{1}{\sqrt{N}} \sum_j q_j \sum_{kk'} D_{kk'}(\mathbf{k}_j) w_{jk'} \sqrt{m_k} \Delta_k, \quad (29)$$

where  $\omega_j$  are the eigenfrequencies. A phase factor of the form  $\exp(i\mathbf{k}_j \cdot \mathbf{r}_{l'})$ , where  $\mathbf{k}_j$  is the wave vector of mode  $j$ , from

$w_{j,k'l'}$  is absorbed into the force constant matrix  $\Phi$ , yielding the dynamical matrix  $D$  and reducing  $w_{j,k'l'}$  to  $w_{jk'}$  (independent of  $l'$ ). Since we assume that force constants remain the same after electron capture,

$$\sum_{k'} D_{kk'}(\mathbf{k}_j) w_{jk'} = \omega_j^2 w_{jk}. \quad (30)$$

The linear term causes a general coordinate displacement,

$$\delta q_j = -\frac{1}{\sqrt{N}} \sum_k \sqrt{m_k} \Delta_k w_{jk}. \quad (31)$$

We can express the normal coordinates of the lattice for the final ( $f$ ) state,  $q_{j,f}$ , in terms of those for the initial ( $i$ ) state,  $q_j$ ,

$$q_{f,j} = q_j + \delta q_j, \quad (32)$$

so that the final Hamiltonian is

$$H'_f = \frac{1}{2} \sum_j \dot{q}_{f,j}^2 + \frac{1}{2} \sum_j \omega_j^2 q_{f,j}^2. \quad (33)$$

#### A. Zeroth-order phonon matrix elements

We have derived the expression for the generalized coordinates resulting from the lattice displacements. These generalized displacements enter the phonon wave functions  $|X_{n_j^i}(q_j)\rangle$  and  $|X_{n_j^f}(q_j + \delta q_j)\rangle$ , respectively, in the quantized versions of the harmonic oscillator Hamiltonians  $H'_i$  and  $H'_f$ . Now we turn to the evaluation of phonon matrix elements  $\langle X_{n_j^f}(q_j + \delta q_j) | X_{n_j^i}(q_j) \rangle$ . When the displacements  $\delta q_j$  are small, we can show that the dominant contribution comes from single-phonon emission or absorption for each normal mode. Suppose the initial state of mode  $j$  has  $n$  phonons and its final state has  $n + p$  phonons (we dropped the index for the mode, since it is present in the notation of generalized coordinate). Using the integrals provided in Appendix D, the matrix elements for the phonon part are

$$\langle X_{n+1}(q_j + \delta q_j) | X_n(q_j) \rangle = -\sqrt{\frac{(n+1)\omega_j}{2\hbar}} \delta q_j, \quad (34)$$

$$\langle X_{n-1}(q_j + \delta q_j) | X_n(q_j) \rangle = \sqrt{\frac{n\omega_j}{2\hbar}} \delta q_j. \quad (35)$$

The integrals for phonon modes that maintain the same occupation numbers are calculated to second order in  $q_j$ :

$$\langle X_n(q_j + \delta q_j) | X_n(q_j) \rangle = 1 - \frac{(2n+1)\omega_j}{4\hbar} \delta q_j^2. \quad (36)$$

Now we consider how to evaluate Eq. (22). The total number of phonon modes in the supercell is  $M = 3(n_a - 1)$  excluding the translational motion, and the total number of phonon modes in the entire system is  $MN$ , since the supercell is repeated  $N$  times. We assume that there is a one-to-one correspondence between phonon bands before and those after capture. The

wave function of the initial phonon state is

$$|X_i\rangle = \prod_{j=1}^{MN} |X_{n_j^i}\rangle, \quad (37)$$

and that of any one of the final phonon states is

$$|X_f\rangle = \prod_{j=1}^{MN} |X_{n_j^f}\rangle, \quad (38)$$

where  $n_j^i$  and  $n_j^f$  are the occupation numbers of phonon mode  $j$  before and after the capture and are also used to label the wave functions. The total phonon energies for initial and final configurations are

$$\Theta_i = \frac{1}{N} \sum_{j=1}^{MN} n_j^i \hbar \omega_j^i \quad (39)$$

and

$$\Theta_f = \frac{1}{N} \sum_{j=1}^{MN} n_j^f \hbar \omega_j^f, \quad (40)$$

respectively, where  $\omega_j^i$  and  $\omega_j^f$  are the phonon frequency of mode  $j$  in the initial and final configurations of the defect, respectively. With the overlap matrix for each individual mode expressed as Eq. (D1) and using Eqs. (37)–(40), Eq. (22) now

takes the form

$$F_{if} = \sum_{\{n_j^f\}} \left\{ \prod_{j=1}^{MN} \left| \int X_{n_j^f}(q_j + \delta q_j) X_{n_j^i}(q_j) dq_j \right|^2 \right\} \times \delta \left( \frac{1}{N} \sum_{j=1}^{MN} (n_j^f \hbar \omega_j^f - n_j^i \hbar \omega_j^i) + \epsilon_{if} \right), \quad (41)$$

where  $n_j^f = n_j^i - 1, n_j^i, n_j^i + 1$ . We see below that as the limit of  $N \rightarrow \infty$  is taken, the discrete modes in  $N$  will become continuous spectra in  $\mathbf{k}$  over the Brillouin zone of the reciprocal space.

Now we are ready to put all the phonon matrix elements together and perform the configurational sum. To do this we follow the steps of Huang and Rhys [10] but generalize them for a system with multiple phonon frequencies. For multiple phonon bands, we assume that the frequency variation within each band is much smaller than the frequency difference between the bands. This is the flat band approximation, which is complemented with the requirement of finite spacing between the bands. We finally find

$$F_j = \exp \left[ \frac{p_j \hbar \omega_j}{2kT} - S_j \coth \left( \frac{\hbar \omega_j}{2kT} \right) \right] I_{p_j} \left[ \frac{S_j}{\sinh(\hbar \omega_j / 2kT)} \right] \quad (42)$$

and

$$F = \frac{1}{\Omega_{\mathbf{k}}} \sum_{\{p_j\}} \left\{ \left( \prod_{j=1}^M F_j \right) \sum_{j=1}^M \left\{ p_j + \frac{S_j}{\sinh(\hbar \omega_j / 2kT)} \frac{I_{p_j+1} \left[ \frac{S_j}{\sinh(\hbar \omega_j / 2kT)} \right]}{I_{p_j} \left[ \frac{S_j}{\sinh(\hbar \omega_j / 2kT)} \right]} \right\} D(\omega_j) \right\} \Bigg|_{\sum_{j=1}^M p_j \hbar \omega_j + \epsilon_{if} = 0}, \quad (43)$$

where  $D(\omega_j)$  is the phonon density of states

$$S_j = \frac{\omega_j}{2\hbar} N \delta q_j^2 \quad (44)$$

and  $I_p$  is the modified Bessel function of order  $p$ .

### B. Linear phonon matrix elements

To evaluate the phonon matrix elements for the linear term, we rewrite it in terms of the normal mode coordinates  $q_j$ ,

$$\begin{aligned} & \sum_f \left| \sum_j M_j \langle X_f | q_j | X_i \rangle \right|^2 \\ &= \sum_f \sum_j |M_j \langle X_f | q_j | X_i \rangle|^2 \\ &= \frac{1}{2} \sum_f \frac{\partial^2}{\partial \lambda^2} \left| \langle X_f | \prod_j [1 + \lambda M_j q_j \exp(i\phi_j)] | X_i \rangle \right|_{\lambda=0}^2, \quad (45) \end{aligned}$$

where  $\phi_j$  is a random phase introduced to cancel out the cross terms, and

$$M_j = \langle \Phi_f | \partial_{q_j} H_e | \Phi_i \rangle - \langle \Phi_f | \Psi_i \rangle \langle \Psi_f | \partial_{q_j} H_e | \Psi_f \rangle. \quad (46)$$

The rest of the steps are exactly the same as for the zeroth-order matrix elements. Using the integrals provided in Appendix D, the matrix elements for the phonon part are

$$\begin{aligned} & \langle X_{n+1}(q_j + \delta q_j) | [1 + \lambda M_j q_j \exp(i\phi_j)] | X_n(q_j) \rangle \\ &= -\sqrt{\frac{(n+1)\omega_j}{2\hbar}} \left[ \delta q_j - \frac{\lambda \hbar M_j}{\omega_j} \exp(i\phi_j) \right], \quad (47) \\ & \langle X_{n-1}(q_j + \delta q_j) | [1 + \lambda M_j q_j \exp(i\phi_j)] | X_n(q_j) \rangle \\ &= \sqrt{\frac{n\omega_j}{2\hbar}} \left[ \delta q_j + \frac{\lambda \hbar M_j}{\omega_j} \exp(i\phi_j) \right], \quad (48) \end{aligned}$$

and

$$\begin{aligned} & \langle X_n(q_j + \delta q_j) | [1 + \lambda M_j q_j \exp(i\phi_j)] | X_n(q_j) \rangle \\ &= 1 - \frac{(2n+1)\omega_j}{4\hbar} \delta q_j^2 - \frac{1}{2} \lambda M_j \delta q_j \exp(i\phi_j) \\ &= 1 - \frac{S_j}{2N} - \frac{1}{2} \lambda M_j \delta q_j \exp(i\phi_j). \end{aligned} \quad (49)$$

Define

$$\begin{aligned} S_{\pm}(\lambda) &= \left( \binom{n+1}{n} \frac{\omega_j}{2\hbar} N \left| \delta q_j \mp \frac{\lambda \hbar M_j}{\omega_j} \exp(i\phi_j) \right|^2 \right. \\ &\approx \left. \binom{n+1}{n} \frac{\omega_j}{2\hbar} N \delta q_j^2 \left| \exp \left[ \mp 2 \frac{\lambda \hbar M_j}{\omega_j \delta q_j} \exp(i\phi_j) \right] \right|. \end{aligned} \quad (50)$$

The approximation in the second step is accurate to  $\lambda^2$ , with the consideration that terms such as  $\lambda^2 \sin 2\phi_j$  and  $\lambda^2 \cos 2\phi_j$  drop out after the configurational average. Then

$$\sqrt{S_+ S_-} \approx \sqrt{n(n+1)} S_j, \quad (51)$$

$$\frac{S_+(\lambda)}{S_-(\lambda)} \approx \frac{n+1}{n} \left| \exp \left[ -4 \frac{\lambda \hbar M_j}{\omega_j \delta q_j} \exp(i\phi_j) \right] \right|. \quad (52)$$

$$F_1 = \frac{1}{2\Omega_{\mathbf{k}}} \sum_{\{p_j\}} \left\{ \frac{\partial^2}{\partial \lambda^2} \left[ \prod_{j=1}^M F_j(\lambda) \right] \right\}_{\lambda=0} \left\{ \sum_{j=1}^M \left\{ p_j + \frac{S_j}{\sinh(\hbar\omega_j/2kT)} \frac{I_{p_j+1} \left[ \frac{S_j}{\sinh(\hbar\omega_j/2kT)} \right]}{I_{p_j} \left[ \frac{S_j}{\sinh(\hbar\omega_j/2kT)} \right]} \right\} D(\omega_j) \right\}_{\sum_{j=1}^M p_j \hbar\omega_j + \epsilon_{if} = 0}. \quad (56)$$

### C. Ratio of zeroth-order and linear terms

From the different expressions for the zeroth-order and the linear phonon matrix elements, we can estimate the ratio between the linear term and the zeroth-order term in the transition rate. This is of the order of

$$2 \left| \frac{M_j \hbar p_j}{M_e^{\text{BO}} \omega_j \delta q_j} \right|. \quad (57)$$

To estimate  $M_j/M_e^{\text{BO}}$ , we note that the leading term in  $M_j$  is [see Eq. (B4)]

$$M_j \approx -\epsilon_{if} \left\langle \frac{\partial \Phi_f}{\partial q_j} \middle| \Psi_i \right\rangle. \quad (58)$$

To estimate  $\partial \Phi_f / \partial q_j$ , we assume rigid atomic orbitals, where the atomic wave functions move rigidly in space with each atom. The derivative of such a wave function with respect to atomic displacements simply reflects the change in the relative spatial phase, which is dictated by the phonon wave vector,

$$\frac{\partial \Phi_f}{\partial q_j} \approx i \sqrt{\frac{N}{m}} \frac{2\pi}{\lambda_j} \Phi_f \exp(i\phi), \quad (59)$$

where  $\lambda_j$  is the acoustic wavelength for mode  $j$ ,  $m$  is the mass of an atom, and  $\phi$  is the phase factor due to the movement of the atoms, which is different in each Born–von Karman supercell. Integrating over all  $N$  Born–von Karman supercells, the sum

The  $\lambda$ -dependent line-shape factor for a single phonon band is

$$\begin{aligned} F_j(\lambda) &= \exp \left[ \frac{p_j \hbar \omega_j}{2kT} - S_j \coth \left( \frac{\hbar \omega_j}{2kT} \right) - \lambda N \delta q_j |M_j \exp(i\phi_j)| \right] \\ &\times I_{p_j} \left[ \frac{S_j}{\sinh(\hbar\omega_j/2kT)} \right] \exp \left[ -2\lambda p_j \frac{\hbar M_j}{\omega_j \delta q_j} \exp(i\phi_j) \right]. \end{aligned} \quad (53)$$

Let us now compare the two  $\lambda$  factors by evaluating the ratio

$$\frac{N \omega_j \delta q_j^2}{2\hbar} = \frac{m \omega_j \delta R^2}{\hbar}. \quad (54)$$

For a hydrogenated vacancy defect our calculation shows that  $\delta R \approx 0.2 \text{ \AA}$  for the nearest Si atom. Using  $m \approx 4.66 \times 10^{-26} \text{ kg}$  for the Si atom and  $\omega_j \approx 10^{12} \text{ s}^{-1}$ , we have

$$\frac{N \omega_j \delta q_j^2}{2\hbar} \approx 0.09. \quad (55)$$

Thus the first  $\lambda$  factor has a much smaller contribution than the second one. The final linear phonon squared matrix element is

of the  $\exp(i\phi)$  factors scales as  $1/N$  for large  $N$ . Thus,

$$M_j \approx i \frac{2\pi}{\sqrt{Nm} \lambda_j} M_e^{\text{BO}}. \quad (60)$$

Finally,  $p_j$  is mostly 0, occasionally taking the values  $\pm 1$ , and  $\delta q_j \approx \sqrt{(m/N)} \delta R$ , where  $\delta R$  is the largest atomic displacement and  $m$  is the mass of the corresponding atom. The ratio between the linear and the zeroth-order terms simplifies to

$$2 \left( \frac{\hbar}{cm \delta R} \right)^2, \quad (61)$$

where  $c$  is the sound velocity in the material. For a hydrogenated vacancy defect our calculation shows that  $\delta R \approx 0.2 \text{ \AA}$  for the nearest Si atom. Using this number and  $c \approx 8 \times 10^3 \text{ m/s}$  for bulk silicon and  $m \approx 4.66 \times 10^{-26} \text{ kg}$  for the Si atom, we find

$$2 \left( \frac{\hbar}{cm \delta R} \right)^2 \approx 3.6 \times 10^{-4}. \quad (62)$$

Thus the linear phonon term (nonadiabatic term) is several orders of magnitude smaller than the leading BOA term.

### D. Monte Carlo method for the configurational sum

The summation over all configurations  $\{p_j\}$  involves a large number of terms when  $P = \sum_j |p_j|$  is greater than a few. We use a Monte Carlo approach to calculate this sum. For a given number of phonon modes,  $P$ , and a given



number of bands,  $B$ , we use Monte Carlo to construct a fixed number of configurations,  $K$ . We rewrite the sum over the configurations as a sum over the number of phonons  $P$  of a configuration, a sum over the number of bands  $B$  used to

construct a configuration with  $P$  phonons, and a sum over the configurations sampled (Monte Carlo steps). In each Monte Carlo step, we randomly pick  $B$  bands and then we construct all the possible configurations with  $P$  phonons constructed by these bands.

In order to generate and count the configurations correctly, we first rewrite Eq. (43) as

$$F = \frac{1}{\Omega_{\mathbf{k}}} \sum_P \sum_{B=1}^P w_B \sum_{\{p_j\}'}^K \left\{ \prod_{j=1}^M F_j \sum_{j=1}^M \left\{ p_j + \frac{S_j}{\sinh(\hbar\omega_j/2kT)} \frac{I_{p_j+1} \left[ \frac{S_j}{\sinh(\hbar\omega_j/2kT)} \right]}{I_{p_j} \left[ \frac{S_j}{\sinh(\hbar\omega_j/2kT)} \right]} \right\} D(\omega_j) \right\} \Bigg|_{\sum_{j=1}^M p_j \hbar\omega_j + \epsilon_{if} = 0}. \quad (63)$$

Then we normalize the sum so that the total weight,  $w_B$ , in each subgroup of configurations (configurations with the same number of bands) is equal to the total number of possible configurations for this number of bands:

$$w_B = \frac{1}{K} \frac{M!}{B!(M-B)!}. \quad (64)$$

All configurations with up to four phonon modes are constructed and calculated explicitly. For configurations with more than four phonons, all the configurations constructed with up to three bands are calculated explicitly and the above equations are used to calculate the line-shape function for configurations with more than three bands.

The last step in the Monte Carlo scheme is to collect the line-shape function into different energy bins for a distribution. To do this, we note that with an incomplete sampling of the phase space via Monte Carlo, we may not be able to resolve

the energy distribution to arbitrary accuracy. Specifically, when we sample one configuration and weigh it according to Eq. (64), we are effectively using it to approximate several configurations with different energies. Thus, the energy resolution must be consistent with the number of configuration samples: fewer configurations should correspond to a coarser energy resolution. For this reason, we define the energy bin width separately for each value of  $P$  based on the requirement that there is at least one configuration inside each energy bin. To ensure the correct normalization, we rewrite the phonon density of states for band  $j$  as

$$D(\omega_j) = \frac{1}{\Delta E} \int D(E) dE = \frac{\Omega_{\mathbf{k}}}{\Delta E}, \quad (65)$$

where  $\Delta E$  is the energy bin width and we assume that the phonon band is sufficiently flat so that it falls entirely within one energy bin. Then Eq. (63) becomes

$$F = \frac{1}{\Delta E} \sum_P \sum_{B=1}^P w_B \sum_{\{p_j\}'}^K \left\{ \left( \prod_{j=1}^M F_j \right) \sum_{j=1}^M \left\{ p_j + \frac{S_j}{\sinh(\hbar\omega_j/2kT)} \frac{I_{p_j+1} \left[ \frac{S_j}{\sinh(\hbar\omega_j/2kT)} \right]}{I_{p_j} \left[ \frac{S_j}{\sinh(\hbar\omega_j/2kT)} \right]} \right\} \right\} \Bigg|_{\sum_{j=1}^M p_j \hbar\omega_j + \epsilon_{if} = 0}. \quad (66)$$

The evaluation of the linear phonon terms is similar.

## V. APPLICATION TO A DEFECT IN SILICON

In this paper, we present only one application of the theory and computer codes for the capture cross section of a prototype defect in Si, namely, a triply hydrogenated vacancy with a bare dangling bond. Our purpose here is to demonstrate the feasibility of calculations, especially the first-ever calculation of the line-shape function that is converged with respect to the number of phonon modes that are used to construct random configurations whose energy is equal to the amount of energy that needs to be dissipated following the instantaneous electronic transition. We defer calculations for defects for which experimental data are available to a future paper where we anticipate using hybrid functionals in the DFT calculations of the electronic matrix elements. Such calculations are computationally demanding but would provide more accurate transition energies and electronic matrix elements. In addition, we plan to code the additional contributions from the linear terms which we estimated to be significantly smaller because

they scale with the inverse of the mass of a typical atom in the defect cluster. It will be interesting to see how the two terms in brackets in Eq. (19) add or subtract for different defects.

In Fig. 1, we show the values of calculated electronic matrix elements as a function of the energy. At each energy value, there are a number of  $k$  points that contribute. Their contributions are indicated by (red) squares. The size of the energy bin is determined by the number of  $k$  points. For the example shown in Fig. 1 the average matrix element as a function of energy is shown by the (blue) line. The size of the energy bin fixes the resolution. A smooth curve can only be obtained with very small energy bins, which requires a very large number of  $k$  points. It is clear from the figure that the capture electronic matrix element is relatively constant as a function of the energy, whereby it seems best at this point to take it to be a constant, either an average value or the value at the threshold for capture, which introduces an error bar of a factor of  $\sim 1.7$  (clearly, to validate the theory against accurate experimental data, we need a very accurate calculation in the near-threshold region).

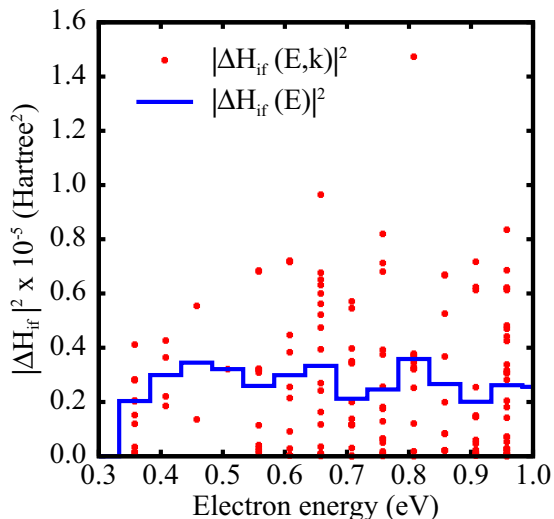


FIG. 1. (Color online) Calculated electronic matrix elements as a function of the initial-state electron energy for a triply hydrogenated vacancy in Si with a bare dangling bond: (red) squares, matrix element values at each energy for different  $k$  points; (blue) curve, averaged matrix element over all  $k$  points for each energy.

In Fig. 2, we show the calculated capture cross section using a constant matrix element to show clearly the convergence of the line-shape function as we increase the number of phonon modes that are used to construct configurations (the electronic matrix element is just a multiplier that sets the absolute value). The dominant contribution to the line-shape function comes from the balance between the modes with the largest general coordinate displacement and the growth of the number of allowed combinations with smaller general coordinate displacement. Note that the curves are smooth because we employ millions of configurations at each energy and therefore we have very tiny energy bins. It is clear that a single-phonon-mode approximation would be very poor

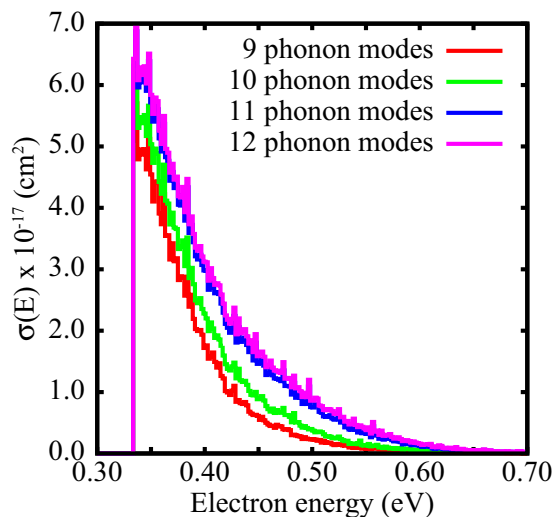


FIG. 2. (Color online) Calculated electron capture cross section using a constant electron matrix element and different numbers of phonon modes.

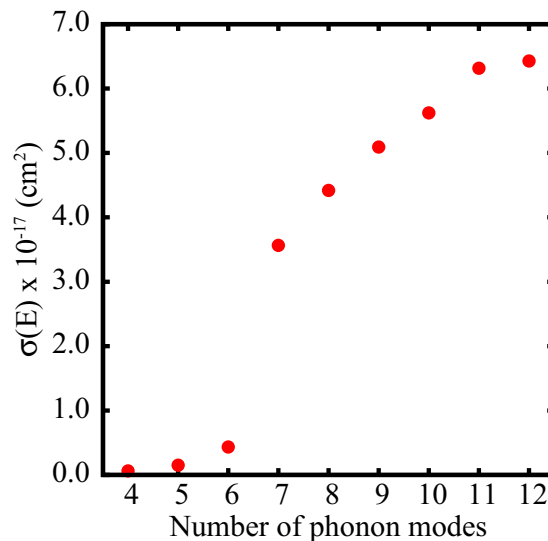


FIG. 3. (Color online) Convergence of the calculated electron capture cross section at the threshold as a function of the number of phonon modes.

indeed. In Fig. 3 we show the convergence of the capture cross section at threshold (for electrons at the bottom of the conduction band), which is what is usually measured. Once more, it is clear that the single-phonon-mode approximation would be inadequate.

For a calculation of the cross section using electronic matrix elements that depend on the energy, the resolution is limited by the energy bin size. We show the result in Fig. 4. Clearly, the size of the energy bin is important. For capture cross sections, one is often interested only in the threshold value. The calculations presented here are a prelude to calculations of hot-electron inelastic multiphonon scattering, for which the energy dependence is important. The energy dependence is also important in luminescence curves, i.e., the classic Huang-Rhys problem that was treated in the single-phonon approximation

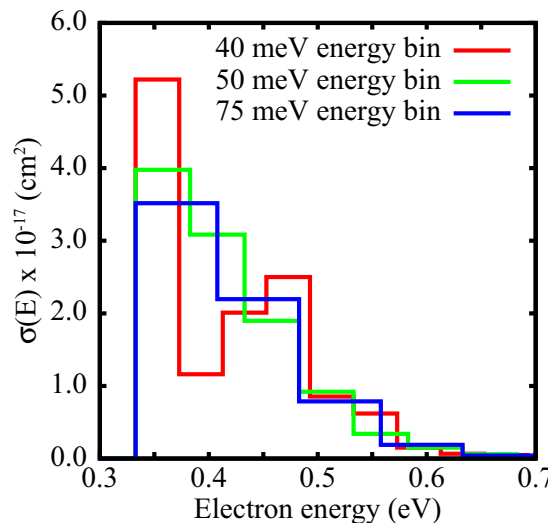


FIG. 4. (Color online) Calculated full capture cross section using the electron matrix element from Fig. 1 and 12 phonon modes in the line-shape function.

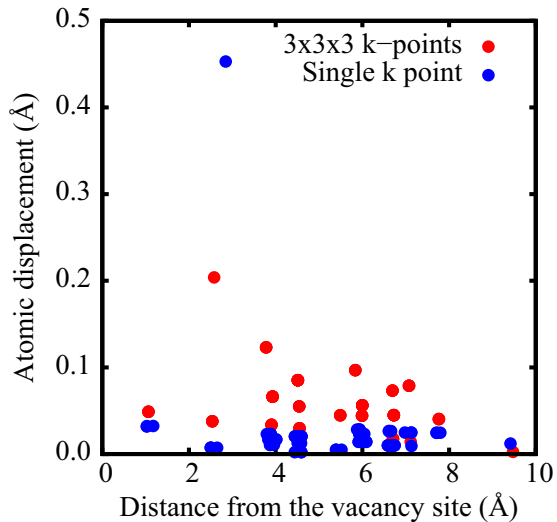


FIG. 5. (Color online) Atomic displacements of the triply hydrogenated Si vacancy as a function of the distance from the vacancy site for a 64-atom supercell.

in Ref. [23] (in the case of luminescence, MPPs dissipate only the relaxation energy of the defect, when one expects the phonon mode corresponding to the actual relaxation to dominate; nevertheless, a fully convergent calculation would be needed to establish the degree of accuracy one obtains with the single-mode approximation). The accuracy of the calculation of the line-shape function is controlled by the accuracy of the calculation of the generalized displacements. The latter depends on the accuracy of the calculation of the atomic displacements. We found that the accuracy is enhanced significantly if we allow the entire supercell to relax, which allows the defect's neighbors to relax more freely. At the same time, a dense  $k$ -point mesh is necessary. In Fig. 5, we present the atomic displacements of the triply hydrogenated Si vacancy as a function of the distance from the vacancy site for a 64-atom supercell. Using only one  $k$  point and not allowing the supercell to relax we get only the Si atom near the defect to move significantly, while the rest of the crystal remains essentially frozen (blue circles). This kind of relaxation leads to only a few phonon modes being significant, and thus the system is artificially able to dissipate energy efficiently at certain frequencies. On the other hand, the well-relaxed crystal of the  $(3 \times 3 \times 3)$   $k$ -point grid (red circles) has more atoms contributing to the generalized displacements, and thus almost all the phonon modes contribute in the dissipation to the energy of the incoming electron. The use of supercells with more than 64 atoms would be prohibitively expensive for the line-shape-function calculation.

The above MPP calculations leave out the effect of the phonons that are emitted during the process, i. e. only equilibrium phonons are assumed to be available for absorption. This effect will be explored in future work.

## VI. SUMMARY

We have presented a comprehensive theory of inelastic multiphonon carrier capture and scattering processes. We showed that, under nonequilibrium conditions, i.e., in the presence

of currents or hot electrons, the defect potential is primarily responsible for capture through a zeroth-order term in an expansion in terms of the atomic displacements (relaxation) that accompanies capture. These terms have not been included in any prior theory. Instead, the focus has always been on the linear terms, which we showed here to be much smaller because they depend on the inverse of the mass of typical atoms in the defect complex. The linear terms are dominant only in the limit of thermal equilibrium. For the first time, we used accurate all-electron wave functions obtained by the PAW method for the electronic matrix elements and an accurate Monte Carlo scheme to sample random configurations of up to 12 distinct phonon modes for the line-shape functions to achieve convergence (a single-phonon-mode approximation has been standard in prior calculations). We have presented results for a prototype defect. More accurate hybrid exchange-correlation functionals are needed to produce results that are accurate enough for comparison with experimental data. In addition, a reliable comparison with data can only be made with experimental measurements of capture cross sections simultaneously with determination of the elastic mean free path and the capture mean free path, as they appear in Eq. (1).

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## APPENDIX A: EVALUATION OF THE ELECTRONIC MATRIX ELEMENT FOR THE BOA TRANSITION

In the basis of  $|\Psi_n\rangle$ , the unperturbed Hamiltonian  $\tilde{H}^0$  is diagonal with eigenenergies  $\epsilon_n$ . The total electron Hamiltonian

$H = \tilde{H}^0 + H_1^{\text{BO}}$  has coupling terms only between state  $|\Psi_i\rangle$  and state  $|\Psi_f\rangle$ . We can, therefore, construct solutions of

$$(\tilde{H}^0 + H_1^{\text{BO}})|\Phi\rangle = E|\Phi\rangle \quad (\text{A1})$$

in the form  $|\Phi\rangle = a|\Psi_i\rangle + b|\Psi_f\rangle$ , so that

$$\begin{pmatrix} \epsilon_i & \Delta H_{if} \\ \Delta H_{fi} & \epsilon_f \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = E \begin{pmatrix} a \\ b \end{pmatrix}. \quad (\text{A2})$$

There are two sets of solutions,

$$E_{i(f)} = \frac{1}{2}[\epsilon_i + \epsilon_f \pm \sqrt{(\epsilon_i - \epsilon_f)^2 + 4|\Delta H_{if}|^2}], \quad (\text{A3})$$

where state  $i$  takes the positive sign and state  $f$  takes the minus sign, since  $E_i > E_f$ . The coefficients satisfy

$$\epsilon_i a_i + \Delta H_{if} b_i = E_i a_i \quad (\text{A4})$$

and

$$|a_i|^2 + |b_i|^2 = 1. \quad (\text{A5})$$

There is an arbitrary phase factor within  $a_i$ . We can define a set of solutions as

$$a_i = b_f^* = \sqrt{\frac{1}{2} + \sqrt{\frac{1}{4} - \left| \frac{\Delta H_{if}}{E_i - E_f} \right|^2}} \quad (\text{A6})$$

and

$$b_i = -a_f^* = \frac{\Delta H_{if}}{E_i - E_f} \frac{1}{\sqrt{\frac{1}{2} + \sqrt{\frac{1}{4} - \left| \frac{\Delta H_{if}}{E_i - E_f} \right|^2}}}. \quad (\text{A7})$$

If we can compute the overlap integral  $\langle \Phi_f | \Psi_i \rangle = a_f$ , then we can solve for  $|\Delta H_{if}|^2$  from  $|a_f|^2$  and find

$$|\Delta H_{if}|^2 = \frac{|\langle \Phi_f | \Psi_i \rangle|^2 - |\langle \Phi_f | \Psi_i \rangle|^4}{(1 - 2|\langle \Phi_f | \Psi_i \rangle|^2)^2} \epsilon_{if}^2. \quad (\text{A8})$$

To be consistent with the phase of Eq. (A7), we have

$$\begin{aligned} M_e^{\text{BO}} &= \langle \Psi_f | H_1^{\text{BO}} | \Psi_i \rangle = \Delta H_{if} \\ &= -\frac{\sqrt{1 - |\langle \Phi_f | \Psi_i \rangle|^2}}{1 - 2|\langle \Phi_f | \Psi_i \rangle|^2} \langle \Phi_f | \Psi_i \rangle \epsilon_{if}. \end{aligned} \quad (\text{A9})$$

The wave function  $|\Psi_i\rangle$  is related to that of a perfect crystal  $|\Psi_i^{(0)}\rangle$  through a perturbation expansion,

$$|\Psi_i^{(0)}\rangle = |\Psi_i\rangle - \sum_{i' \neq i, f} \frac{\langle \Psi_{i'} | \Delta H | \Psi_i \rangle}{\epsilon_{i'} - \epsilon_i} |\Psi_{i'}\rangle. \quad (\text{A10})$$

Because  $H_1$  has only nonzero elements between state  $|\Psi_i\rangle$  and state  $|\Psi_f\rangle$ , for  $j \neq i, f$ , the wave functions  $|\Psi_j\rangle = |\Phi_j\rangle$  so that  $\langle \Phi_f | \Psi_j \rangle = 0$ . Thus, to first order in the defect potential,

$$\langle \Phi_f | \Psi_i \rangle = \langle \Phi_f | \Psi_i^0 \rangle, \quad (\text{A11})$$

and assuming that  $|\langle \Phi_f | \Psi_i^0 \rangle| \ll 1$ , we arrive at Eq. (23), which simplifies the evaluation of the overlap integral.

## APPENDIX B: EVALUATION OF THE GRADIENT TERMS

Using the result in the previous section for the matrix element  $M_e^{\text{BO}}$ , we now calculate the gradient terms in Eq. (19),  $\nabla_{\mathbf{R}_k} M_e^{\text{BO}} + \langle \Psi_f | \nabla_{\mathbf{R}_k} H_e | \Psi_i \rangle$ . Neglecting higher order  $|\langle \Phi_f | \Psi_i \rangle|^2$  terms, the first gradient term is

$$\begin{aligned} \nabla_{\mathbf{R}_k} M_e^{\text{BO}} &= -(\langle \nabla_{\mathbf{R}_k} \Phi_f | \Psi_i \rangle + \langle \Phi_f | \nabla_{\mathbf{R}_k} \Psi_i \rangle) \epsilon_{if} - \langle \Phi_f | \Psi_i \rangle \nabla_{\mathbf{R}_k} \epsilon_{if} \\ &= -(\langle \nabla_{\mathbf{R}_k} \Phi_f | \Psi_i \rangle + \langle \Phi_f | \nabla_{\mathbf{R}_k} \Psi_i \rangle) \epsilon_{if} \\ &\quad - \langle \Phi_f | \Psi_i \rangle \langle \Psi_f | \nabla_{\mathbf{R}_k} H_0 | \Psi_f \rangle, \end{aligned} \quad (\text{B1})$$

where in the last step we have used the fact that  $\nabla_{\mathbf{R}_k} \epsilon_i = 0$  (the initial state is at equilibrium) and the Hellmann-Feynman theorem for  $\nabla_{\mathbf{R}_k} \epsilon_f$ . From Eq. (16) we have

$$|\nabla_{\mathbf{R}_k} \Psi_i\rangle = \sum_{i' \neq i} \frac{\langle \Psi_{i'} | \nabla_{\mathbf{R}_k} H_e | \Psi_i \rangle}{\epsilon_{i'} - \epsilon_i} |\Psi_{i'}\rangle, \quad (\text{B2})$$

where we have used  $\nabla_{\mathbf{R}_k} H_{el} = \nabla_{\mathbf{R}_k} H_e$ . Because  $|\Psi_{i'}\rangle = |\Phi_{i'}\rangle$  for  $i' \neq i, f$  and  $\langle \Phi_f | \Psi_f \rangle = 1 + O(|\langle \Phi_f | \Psi_i \rangle|^2)$ , we have

$$\langle \Phi_f | \nabla_{\mathbf{R}_k} \Psi_i \rangle = \frac{\langle \Psi_f | \nabla_{\mathbf{R}_k} H_e | \Psi_i \rangle}{\epsilon_{if}} \langle \Phi_f | \Psi_f \rangle = \frac{\langle \Psi_f | \nabla_{\mathbf{R}_k} H_e | \Psi_i \rangle}{\epsilon_{if}}. \quad (\text{B3})$$

Similarly,

$$\begin{aligned} \langle \nabla_{\mathbf{R}_k} \Phi_f | \Psi_i \rangle &= -\frac{\langle \Phi_f | \nabla_{\mathbf{R}_k} H_e | \Phi_i \rangle}{\epsilon_{if}} \langle \Phi_i | \Psi_i \rangle \\ &= -\frac{\langle \Phi_f | \nabla_{\mathbf{R}_k} H_e | \Phi_i \rangle}{\epsilon_{if}}. \end{aligned} \quad (\text{B4})$$

Combining these results and noting that  $H_1^{\text{BO}}$  does not have diagonal components, we arrive at

$$\begin{aligned} \nabla_{\mathbf{R}_k} M_e^{\text{BO}} + \langle \Psi_f | \nabla_{\mathbf{R}_k} H | \Psi_i \rangle &= \langle \Phi_f | \nabla_{\mathbf{R}_k} H | \Phi_i \rangle - \langle \Phi_f | \Psi_i \rangle \langle \Psi_f | \nabla_{\mathbf{R}_k} H | \Psi_f \rangle. \end{aligned} \quad (\text{B5})$$

We can use Eq. (A11) and approximate  $|\Psi_f\rangle \approx |\Phi_f\rangle$  to get Eq. (24).

## APPENDIX C: EVALUATION OF THE OVERLAP INTEGRAL WITHIN THE PAW

Consider the problem of evaluating the overlap integral  $\langle \Psi | \Phi \rangle$  between two wave functions from two different solids (e.g., one is a perfect crystal and the other contains a defect). Using the PAW expansion of the full wave functions,

$$|\Psi\rangle = |\tilde{\Psi}\rangle + |\Psi^{\text{AE}}\rangle_a - |\Psi^{\text{PS}}\rangle_a, \quad (\text{C1})$$

where  $|\tilde{\Psi}\rangle$  is the pseudo-wave function and  $|\Psi^{\text{AE}}\rangle_a$  and  $|\Psi^{\text{PS}}\rangle_a$  are the atomic wave functions inside the augmentation sphere of each atom  $a$ , and similarly,

$$|\Phi\rangle = |\tilde{\Phi}\rangle + |\Phi^{\text{AE}}\rangle_b - |\Phi^{\text{PS}}\rangle_b. \quad (\text{C2})$$

Now  $\langle \Psi | \Phi \rangle$  is given as

$$\begin{aligned} \langle \Psi | \Phi \rangle &= (\langle \tilde{\Psi} | + \langle \Psi^{\text{AE}} | - \langle \Psi^{\text{PS}} |) (\langle \tilde{\Phi} | + \langle \Phi^{\text{AE}} | - \langle \Phi^{\text{PS}} |) \\ &= \langle \tilde{\Psi} | \tilde{\Phi} \rangle + \langle \tilde{\Psi} | \Phi^{\text{AE}} \rangle_b - \langle \tilde{\Psi} | \Phi^{\text{PS}} \rangle_b + \langle \Psi^{\text{AE}} | \tilde{\Phi} \rangle \\ &\quad - \langle \Psi^{\text{PS}} | \tilde{\Phi} \rangle + (\langle \Psi^{\text{AE}} | - \langle \Psi^{\text{PS}} |) (\langle \Phi^{\text{AE}} | - \langle \Phi^{\text{PS}} |). \end{aligned} \quad (\text{C3})$$

The first term,  $\langle \tilde{\Psi} | \tilde{\Phi} \rangle$ , is the overlap of the pseudo-wave functions and can be easily calculated since the pseudo-wave functions are expanded in the same base set of plane waves.

In order to evaluate the terms  $\langle \tilde{\Psi} | \Phi^{\text{AE}} \rangle_b - \langle \tilde{\Psi} | \Phi^{\text{PS}} \rangle_b$  and  ${}_a \langle \Psi^{\text{AE}} | \tilde{\Phi} \rangle - {}_a \langle \Psi^{\text{PS}} | \tilde{\Phi} \rangle$ , we make use of the unitary operators constructed by the projectors  $|\tilde{p}\rangle$  and the pseudo-atomic wave functions  $|\tilde{\phi}\rangle$ ,

$$\sum_{b,i_b} |\tilde{p}_{i_b}^b\rangle \langle \tilde{\phi}_{i_b}^b| = 1 \quad (\text{C4})$$

and

$$\sum_{a,i_a} |\tilde{\phi}_{i_a}^a\rangle \langle \tilde{p}_{i_a}^a| = 1, \quad (\text{C5})$$

inside the augmentation sphere of each atom  $b$  of the perfect crystal and each atom  $a$  of the solid with the defect, respectively. Thus,

$$\begin{aligned} & \langle \tilde{\Psi} | \Phi^{\text{AE}} \rangle_b - \langle \tilde{\Psi} | \Phi^{\text{PS}} \rangle_b \\ &= \sum_{b,i_b} (\langle \tilde{\Psi} | \tilde{p}_{i_b}^b \rangle \langle \tilde{\phi}_{i_b}^b | \Phi^{\text{AE}} \rangle_b - \langle \tilde{\Psi} | \tilde{p}_{i_b}^b \rangle \langle \tilde{\phi}_{i_b}^b | \Phi^{\text{PS}} \rangle_b) \end{aligned} \quad (\text{C6})$$

and

$$\begin{aligned} & {}_a \langle \Psi^{\text{AE}} | \tilde{\Phi} \rangle - {}_a \langle \Psi^{\text{PS}} | \tilde{\Phi} \rangle \\ &= \sum_{a,i_a} ({}_a \langle \Psi^{\text{AE}} | \tilde{\phi}_{i_a}^a \rangle \langle \tilde{p}_{i_a}^a | \tilde{\Phi} \rangle - {}_a \langle \Psi^{\text{PS}} | \tilde{\phi}_{i_a}^a \rangle \langle \tilde{p}_{i_a}^a | \tilde{\Phi} \rangle). \end{aligned} \quad (\text{C7})$$

Equations (C6) and (C7) ensure that in the case where the two solids are identical, i.e.,  $|\tilde{\Psi}\rangle$  and  $|\tilde{\Phi}\rangle$  are eigenstates of the same Hamiltonian and the augmentation spheres are identical, the one center expansion  $\sum_i |\tilde{\phi}\rangle \langle \tilde{p} | \tilde{\Psi}\rangle$  of the pseudo-wave function is identical to the pseudo-wave function  $|\tilde{\Psi}\rangle$  inside the augmentation sphere and

$$\langle \tilde{\Psi}_f | \Phi^{\text{AE}} \rangle - \langle \tilde{\Psi} | \Phi^{\text{PS}} \rangle = \langle \tilde{\Psi}^{\text{PS}} | \Phi^{\text{AE}} \rangle - \langle \tilde{\Psi}^{\text{PS}} | \Phi^{\text{PS}} \rangle. \quad (\text{C8})$$

To evaluate Eqs. (C6) and (C7), we need the projections of the pseudo-wave functions of the first solid to the projectors of the atomic wave functions of the second solid,  $\langle \tilde{\Psi} | \tilde{p}_{i_b}^b \rangle$ , and vice versa for the projections  $\langle \tilde{p}_{i_a}^a | \tilde{\Phi} \rangle$ . This can be easily calculated since both the pseudo-wave functions and the projectors are expanded in the same base set of plane waves.

The difficulty in evaluating the last term in Eq. (C3) ( ${}_a \langle \Psi^{\text{AE}} | - {}_a \langle \Psi^{\text{PS}} | \rangle (|\Phi^{\text{AE}}\rangle_b - |\Phi^{\text{PS}}\rangle_b)$ ) is that the cutoff spheres for the two wave functions are usually not identical. We can bypass this difficulty by evaluating the integral with the assistance of a complete set of plane waves  $|\mathbf{k}\rangle$ :

$$\begin{aligned} & ({}_a \langle \Psi^{\text{AE}} | - {}_a \langle \Psi^{\text{PS}} | \rangle) (|\Phi^{\text{AE}}\rangle_b - |\Phi^{\text{PS}}\rangle_b) \\ &= \sum_{\mathbf{k}} ({}_a \langle \Psi^{\text{AE}} | - {}_a \langle \Psi^{\text{PS}} | \rangle) |\mathbf{k}\rangle \langle \mathbf{k} | (|\Phi^{\text{AE}}\rangle_b - |\Phi^{\text{PS}}\rangle_b) \\ &= \sum_{\mathbf{k}} ({}_a \langle \Psi^{\text{AE}} | \mathbf{k}\rangle - {}_a \langle \Psi^{\text{PS}} | \mathbf{k}\rangle) (\langle \mathbf{k} | \Phi^{\text{AE}} \rangle_b - \langle \mathbf{k} | \Phi^{\text{PS}} \rangle_b). \end{aligned}$$

The plane waves can be expanded in either sphere as

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{lm} i^l j_l(kr) Y_{lm}^*(\hat{\mathbf{k}}) Y_{lm}(\hat{\mathbf{r}}), \quad (\text{C9})$$

and using

$$|\mathbf{k}\rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (\text{C10})$$

the all-electron and the pseudoatomic wave functions are written as

$$|\Phi^{\text{AE}}\rangle_b = \sum_{b,i_b} R_{b,i_b}^{\text{AE}} Y_{l_b,m_b}(\tilde{p}_{b,i_b}) |\tilde{\Phi}_i\rangle, \quad (\text{C11})$$

$$|\Phi^{\text{PS}}\rangle_b = \sum_{b,i_b} R_{b,i_b}^{\text{PS}} Y_{l_b,m_b}(\tilde{p}_{b,i_b}) |\tilde{\Phi}_i\rangle, \quad (\text{C12})$$

$$\begin{aligned} {}_a \langle \Psi^{\text{AE}} | \mathbf{k}\rangle - {}_a \langle \Psi^{\text{PS}} | \mathbf{k}\rangle &= \frac{4\pi}{\sqrt{V}} \sum_{a,i_a} \langle \tilde{\Psi} | \tilde{p}_{a,i_a} \rangle e^{i\mathbf{k}\cdot\mathbf{R}_a} i^{l_a} Y_{l_a,m_a}^*(\hat{\mathbf{k}}) \\ &\times \int_0^{r_a} j_{l_a}(kr) (R_{a,i_a}^{\text{AE}} - R_{a,i_a}^{\text{PS}}) r^2 dr, \end{aligned} \quad (\text{C13})$$

and

$$\begin{aligned} \langle \mathbf{k} | \Phi^{\text{AE}} \rangle_b - \langle \mathbf{k} | \Phi^{\text{PS}} \rangle_b &= \frac{4\pi}{\sqrt{V}} \sum_{b,i_b} \langle \tilde{p}_{b,i_b} | \tilde{\Phi} \rangle e^{-i\mathbf{k}\cdot\mathbf{R}_b} (-i)^{l_b} Y_{l_b,m_b}(\hat{\mathbf{k}}) \\ &\times \int_0^{r_b} j_{l_b}(kr) (R_{b,i_b}^{\text{AE}} - R_{b,i_b}^{\text{PS}}) r^2 dr. \end{aligned} \quad (\text{C14})$$

#### APPENDIX D: PHONON INTEGRALS

The overlap matrix between the initial and the final states for mode  $j$  is

$$\langle X_{n_j^f}(q_j + \delta q_j) | X_{n_j^i}(q_j) \rangle = \int X_{n_j+p_j}(q_j + \delta q_j) X_{n_j}(q_j) dq_j, \quad (\text{D1})$$

where  $n_j^i = n_j$  and  $n_j^f = n_j + p_j$ . For convenience, we drop the subscript  $j$  for  $n_j$  and  $p_j$ . Expanding  $X_n(q_j + \delta q_j)$  in terms of  $\delta q_j$ ,

$$X_n(q_j + \delta q_j) = \sum_l \frac{1}{l!} \frac{d^l X_n(q_j)}{dq_j^l} \delta q_j^l. \quad (\text{D2})$$

Defining the raising and lowering operators

$$\hat{a}_{\pm} = \mp \sqrt{\frac{\hbar}{2\omega_j}} \frac{d}{dq_j} + \sqrt{\frac{\omega_j}{2\hbar}} q_j, \quad (\text{D3})$$

we have

$$\hat{a}_+ X_n(q_j) = \sqrt{n+1} X_{n+1}(q_j) \quad (\text{D4})$$

and

$$\hat{a}_- X_n(q_j) = \sqrt{n} X_{n-1}(q_j). \quad (\text{D5})$$

Subtracting the two, we find

$$\begin{aligned} \frac{d}{dq_j} X_n(q_j) &= \sqrt{\frac{\omega_j}{2\hbar}} (\hat{a}_- - \hat{a}_+) X_n(q_j) \\ &= \sqrt{\frac{n\omega_j}{2\hbar}} X_{n-1}(q_j) - \sqrt{\frac{(n+1)\omega_j}{2\hbar}} X_{n+1}(q_j). \end{aligned} \quad (\text{D6})$$



Using this recursive relation, we find that the lowest order term for  $\int X_n(q_j + \delta q_j) X_{n+k}(q_j) dq_j$  is  $\delta q_j^{|k|}$ . Therefore, for small  $\delta q_j$ , only  $k = \pm 1$  terms dominate. This means that each mode would emit or absorb at most a single phonon.

The results for the integrals are

$$\int \frac{dX_n(q)}{dq} X_{n+1}(q) dq = -\sqrt{\frac{(n+1)\omega_j}{2\hbar}} \quad (\text{D7})$$

(note that this was incorrectly given as  $-(\sqrt{\hbar m \omega / 2})\sqrt{n+1}$  in Ref. [10]) and

$$\int \frac{dX_n(q)}{dq} X_{n-1}(q) dq = \sqrt{\frac{n\omega_j}{2\hbar}}. \quad (\text{D8})$$

For linear phonon matrix elements, we have

$$\begin{aligned} q_j X_n(q_j) &= \sqrt{\frac{\hbar}{2\omega_j}} (\hat{a}_- + \hat{a}_+) X_n(q_j) \\ &= \sqrt{\frac{n\hbar}{2\omega_j}} X_{n-1}(q_j) + \sqrt{\frac{(n+1)\hbar}{2\omega_j}} X_{n+1}(q_j). \end{aligned} \quad (\text{D9})$$

The integrals needed are

$$\int X_n(q) X_{n+1}(q) q dq = \sqrt{\frac{(n+1)\hbar}{2\omega_j}}, \quad (\text{D10})$$

$$\int X_n(q) X_{n-1}(q) q dq = \sqrt{\frac{n\hbar}{2\omega_j}}, \quad (\text{D11})$$

and

$$\int \frac{dX_n(q)}{dq} X_n(q) q dq = -\frac{1}{2}. \quad (\text{D12})$$

## APPENDIX E: LINE-SHAPE FUNCTION

We first consider a single phonon band; i.e., all of the phonon modes  $\omega_j = \omega(\mathbf{k}_j)$  form a single continuous band described by wave vectors  $\mathbf{k}_j$ . Because of the Born-von Karman periodic boundary condition, the phonon band is discretized into  $N$  modes. Suppose that  $s$  modes go down by one quantum and  $s + p$  modes go up by one quantum. Then the line-shape factor, Eq. (41) with  $M = 1$ , contains contributions formed from the products

$$\begin{aligned} &\left\{ \prod_{j=1}^N t_j \right\} \left\{ \prod_{k \in s} f_{k,-} \right\} \left\{ \prod_{l \in s+p} f_{l,+} \right\} \delta \left( \sum_{l \in s+p} [n_l^i \hbar (\omega_l^f - \omega_l^i) + \hbar \omega_l^f] + \sum_{k \in s} [n_k^i \hbar (\omega_k^f - \omega_k^i) - \hbar \omega_k^f] + \sum_{m \ni \{s, s+p\}} n_m^i \hbar (\omega_m^f - \omega_m^i) + \epsilon_{if} \right), \\ &\times \left\{ \prod_{j=1}^N t_j \right\} \left\{ \prod_{k \in s} f_{k,-} \right\} \left\{ \prod_{l \in s+p} f_{l,+} \right\} \delta \left( \sum_{l \in s+p} \hbar \omega_l^f - \sum_{k \in s} \hbar \omega_k^f + \sum_{j=1}^N n_j^i \hbar (\omega_j^f - \omega_j^i) + \epsilon_{if} \right), \end{aligned} \quad (\text{E1})$$

where  $\sum_{j=1}^N n_j^i \hbar (\omega_j^f - \omega_j^i)$  is the energy difference because of the different phonon frequencies of the initial and final configurations of the defect, and  $t_j$ ,  $f_-$ , and  $f_+$  are defined as

$$\begin{aligned} t_j &= \left| \int X_{n_j}(q_j) X_{n_j}(q_j + \delta q_j) dq_j \right|^2, \quad f_{k,-} = \frac{\left| \int X_{n_k}(q_k) X_{n_k-1}(q_k + \delta q_k) dq_k \right|^2}{\left| \int X_{n_k}(q_k) X_{n_k}(q_k + \delta q_k) dq_k \right|^2}, \\ f_{l,+} &= \frac{\left| \int X_{n_l}(q_l) X_{n_l+1}(q_l + \delta q_l) dq_l \right|^2}{\left| \int X_{n_l}(q_l) X_{n_l}(q_l + \delta q_l) dq_l \right|^2}. \end{aligned} \quad (\text{E2})$$

A naive way to sum over all possible configurations is to neglect the difference in the frequencies and apply the same counting method as Huang and Rhys [10] to write the configurational sum for all such combinations of phonons as

$$\frac{1}{s!(s+p)!} \left\{ \prod_{j=1}^N t_j \right\} \left\{ \sum_{k=1}^N f_{k,-} \right\}^s \left\{ \sum_{l=1}^N f_{l,+} \right\}^{s+p} \delta \left( \sum_{l \in s+p} \hbar \omega_l^f - \sum_{k \in s} \hbar \omega_k^f + \sum_{j=1}^N n_j^i \hbar (\omega_j^f - \omega_j^i) + \epsilon_{if} \right). \quad (\text{E3})$$

This would not be correct if the frequencies are different for each mode. Furthermore, the summation over configurations for large  $N$  is needed to integrate out the  $\delta$  function. Therefore the  $\delta$  function cannot be left outside the summations. Let us consider one term in the  $\delta$  function at a time. Consider one the plus terms  $\hbar\omega_m^f$  and insert the  $\delta$  function into one of the summations:

$$\frac{1}{s!(s+p)!} \left\{ \prod_{j=1}^N t_j \right\} \left\{ \sum_{k=1}^N f_{k,-} \right\}^s \left\{ \sum_{l=1}^N f_{l,+} \right\}^{s+p-1} \sum_{m=1}^N \left\{ f_{m,+} \delta \left( \hbar\omega_m^f + \sum_{l \in s+p-1} \hbar\omega_l^f - \sum_{k \in s} \hbar\omega_k^f + \sum_{j=1}^N n_j^i \hbar(\omega_j^f - \omega_j^i) + \epsilon_{if} \right) \right\}. \quad (\text{E4})$$

For large  $N$ , each of the summations inside the curly braces can be converted into integrals and evaluated,

$$S_{\pm} = \sum_{k=1}^N f_{k,\pm} = \frac{N}{\Omega_{\mathbf{k}}} \int f_{\mathbf{k},\pm} d\mathbf{k} = \binom{n+1}{n} \frac{\omega}{2\hbar} N \delta q^2, \quad (\text{E5})$$

where  $\Omega_{\mathbf{k}}$  is the volume of the reciprocal-space Brillouin zone. In the last step we have assumed that the frequency and displacement do not change with  $\mathbf{k}$ .

In order to evaluate the last factor, which includes the  $\delta$  function, we note that each term in the summation over  $m$  has a different  $\omega_m^f$ , which spans the entire phonon band when  $m$  scans from 1 to  $N$ . Thus as we convert the sum over  $m$  to the integral over  $\mathbf{k}$ , the argument  $\omega_m^f$  is also converted to  $\omega_{\mathbf{k}}$ ,

$$\begin{aligned} & \sum_{m=1}^N \left\{ f_{m,+} \delta \left( \hbar\omega_m^f + \sum_{l \in s+p-1} \hbar\omega_l^f - \sum_{k \in s} \hbar\omega_k^f + \sum_{j=1}^N n_j^i \hbar(\omega_j^f - \omega_j^i) + \epsilon_{if} \right) \right\} \\ & \approx \frac{N}{\Omega_{\mathbf{k}}} \int f_{\mathbf{k},+} \delta \left( \hbar\omega_{\mathbf{k}}^f + \sum_{l \in s+p-1} \hbar\omega_l^f - \sum_{k \in s} \hbar\omega_k^f + \sum_{j=1}^N n_j^i \hbar(\omega_j^f - \omega_j^i) + \epsilon_{if} \right) d\mathbf{k} \\ & = S_+ \frac{D(\omega)}{\Omega_{\mathbf{k}}} \Big|_{\hbar\omega^f + \sum_{l \in s+p-1} \hbar\omega_l^f - \sum_{k \in s} \hbar\omega_k^f + \sum_{j=1}^N n_j^i \hbar(\omega_j^f - \omega_j^i) + \epsilon_{if} = 0}, \end{aligned} \quad (\text{E6})$$

where  $D(\omega)$  is the phonon density of states. Combining the above equations and then setting all frequencies to  $\omega$ , Eq. (E4) becomes

$$\frac{1}{s!(s+p)!} \left\{ \prod_{j=1}^N t_j \right\} S_-^s S_+^{s+p} \frac{D(\omega)}{\Omega_{\mathbf{k}}} \Big|_{p\hbar\omega + \sum_{j=1}^N n_j^i \hbar(\omega_j^f - \omega_j^i) + \epsilon_{if} = 0}. \quad (\text{E7})$$

But there is one such contribution for each  $\omega_k$  or  $\omega_l$  in the  $\delta$  function, regardless of the sign of the frequency. For  $s$  modes subtracting a phonon and  $s+p$  modes adding a phonon there is a total of  $2s+p$  such contributions. We thus sum over all the terms and obtain

$$\frac{2s+p}{s!(s+p)!} \left\{ \prod_{j=1}^N t_j \right\} S_-^s S_+^{s+p} \frac{D(\omega)}{\Omega_{\mathbf{k}}} \Big|_{p\hbar\omega + \sum_{j=1}^N n_j^i \hbar(\omega_j^f - \omega_j^i) + \epsilon_{if} = 0}. \quad (\text{E8})$$

Finally, the factor  $\prod_{j=1}^N t_j$  is

$$\prod_{j=1}^N \left| \int X_{n_j}(q_j) X_{n_j}(q_j + \delta q_j) dq_j \right|^2 = \left[ 1 - \frac{(2n+1)\omega}{4\hbar} \delta q^2 \right]^{2N} = \exp[-(S_+ + S_-)]. \quad (\text{E9})$$

The line-shape factor for a single phonon band is

$$\begin{aligned} & \frac{D(\omega)}{\Omega_{\mathbf{k}}} \Big|_{p\hbar\omega + \epsilon_{if} = 0} \exp[-(S_+ + S_-)] \sum_{s=0}^{\infty} \frac{2s+p}{s!(s+p)!} S_+^{s+p} S_-^s = \frac{D(\omega)}{\Omega_{\mathbf{k}}} \Big|_{p\hbar\omega + \epsilon_{if} = 0} \exp[-(S_+ + S_-)] \left( \frac{S_+}{S_-} \right)^{p/2} \\ & \quad \times [p I_p(2\sqrt{S_+ S_-}) + 2\sqrt{S_+ S_-} I_{p+1}(2\sqrt{S_+ S_-})]. \end{aligned} \quad (\text{E10})$$

To generalize the above expression to multiple phonon bands, the normalization factor must be evaluated with a summation over both the band index and the  $\mathbf{k}$  points within each band. If we use  $F_j$  to denote the factor for a band that adds net  $p_j$  phonons, i.e.,

$$F_j = \sum_{s_j=0}^{\infty} \frac{1}{s_j!(s_j+p_j)!} \left\{ \prod_{m=1}^N t_{jm} \right\} \left\{ \sum_{k=1}^N f_{jk,-} \right\}^{s_j} \left\{ \sum_{l=1}^N f_{jl,+} \right\}^{s_j+p_j}, \quad (\text{E11})$$

then, in a similar manner as for the case of a single phonon band,  $F_j$  is evaluated to be

$$F_j = \left( \frac{n_j + 1}{n_j} \right)^{p_j/2} \exp[-S_j(2n_j + 1)] I_{p_j} [2S_j \sqrt{n_j(n_j + 1)}]. \quad (\text{E12})$$

Now we insert the  $\delta$  function into the product of  $F_j$  in the same manner as in the case of a single band to form the full line-shape factor, one phonon band at a time. For now let us consider the case where all  $p_j$ 's are positive. We have

$$\begin{aligned} & \frac{\prod_{j=1}^M F_j}{F_{j''}} \sum_{s_{j''}=0}^{\infty} \frac{2S_{j''} + p_{j''}}{s_{j''}!(s_{j''} + p_{j''})!} \left\{ \prod_{m=1}^N t_{j''m} \right\} \left\{ \sum_{k=1}^N f_{j''k,-} \right\}^{s_{j''}} \left\{ \sum_{l=1}^N f_{j''l,+} \right\}^{s_{j''} + p_{j''} - 1} \\ & \times \sum_{m=1}^N f_{j''m,+} \delta \left( \hbar\omega_{j''m}^f + \sum_{l \in s_{j''} + p_{j''} - 1} \hbar\omega_{j''l}^f - \sum_{k \in s_{j''}} \hbar\omega_{j''k}^f + \sum_{l'=1}^N n_{j''l'}^i \hbar(\omega_{j''l'}^f - \omega_{j''l'}^i) \right. \\ & \left. + \sum_{j' \neq j'', l \in s_{j'} + p_{j'}} \hbar\omega_{j'l}^f - \sum_{j' \neq j'', l \in s_{j'}} \hbar\omega_{j'l}^f + \sum_{j' \neq j'', k'=1}^N n_{j'k'}^i \hbar(\omega_{j'k'}^f - \omega_{j'k'}^i) + \epsilon_{if} \right) \\ & = \left( \prod_{j=1}^M F_j \right) \frac{D(\omega_{j''})}{\Omega_{\mathbf{k}}} \Big|_{\sum_{j'} p_{j'} \hbar\omega_{j'} + \sum_{j=1}^M \sum_{l=1}^N n_{jl}^i \hbar(\omega_{jl}^f - \omega_{jl}^i) + \epsilon_{if} = 0} \\ & \times \left\{ p_{j''} + 2S_{j''} \sqrt{n_{j''}(n_{j''} + 1)} \frac{I_{p_{j''}+1} [2S_{j''} \sqrt{n_{j''}(n_{j''} + 1)}]}{I_{p_{j''}} [2S_{j''} \sqrt{n_{j''}(n_{j''} + 1)}]} \right\}, \end{aligned} \quad (\text{E13})$$

where  $j''$  is one of the phonon bands and we have used Eqs. (E5) and (E6). Summing over all possible  $j''$  terms and with an additional summation over all configurations  $\{p_j\}$ , we find

$$F = \frac{1}{\Omega_{\mathbf{k}}} \sum_{\{p_j\}} \left\{ \left( \prod_{j=1}^M F_j \right) \sum_{j=1}^M \left\{ p_j + 2S_j \sqrt{n_j(n_j + 1)} \frac{I_{p_j+1} [2S_j \sqrt{n_j(n_j + 1)}]}{I_{p_j} [2S_j \sqrt{n_j(n_j + 1)}]} \right\} D(\omega_j) \right\} \Big|_{\sum_{j=1}^M p_j \hbar\omega_j + \epsilon_{if} = 0}. \quad (\text{E14})$$

If some of the  $p_j$ 's are negative, we need to switch the roles of  $S_+$  and  $S_-$  following Ref. [10]. Redefining  $s_j + p_j \rightarrow s_j$  and  $s_j \rightarrow s_j - p_j$  in Eq. (E13), the factor corresponding to  $p_j$  becomes

$$\begin{aligned} & -p_j + 2S_j \sqrt{n_j(n_j + 1)} \frac{I_{-p_j+1} [2S_j \sqrt{n_j(n_j + 1)}]}{I_{-p_j} [2S_j \sqrt{n_j(n_j + 1)}]} \\ & = p_j + 2S_j \sqrt{n_j(n_j + 1)} \frac{I_{p_j+1} [2S_j \sqrt{n_j(n_j + 1)}]}{I_{p_j} [2S_j \sqrt{n_j(n_j + 1)}]}, \end{aligned} \quad (\text{E15})$$

using the recurrence relation for the Bessel functions. Therefore Eq. (E14) is valid for both positive and negative  $p_j$ 's. Applying the thermodynamic average to the occupation numbers,  $n_j$  is replaced by the Bose-Einstein distribution function,

$$n_j \rightarrow \frac{1}{\exp(\hbar\omega_j/kT) - 1}, \quad (\text{E16})$$

$$\frac{n_j + 1}{n_j} \rightarrow \exp\left(\frac{\hbar\omega}{kT}\right), \quad (\text{E17})$$

$$2n_j + 1 \rightarrow \coth\left(\frac{\hbar\omega}{2kT}\right), \quad (\text{E18})$$

and

$$2\sqrt{n_j(n_j + 1)} \rightarrow \frac{1}{\sinh(\hbar\omega/2kT)}; \quad (\text{E19})$$

we obtain Eqs. (42) and (43).

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