

# Absorption coefficients of silicon: A theoretical treatment

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A theoretical model with explicit formulas for calculating the optical absorption and gain coefficients of silicon is presented. It incorporates direct and indirect interband transitions and considers the effects of occupied/unoccupied carrier states. The indirect interband transition is calculated from the second-order time-independent perturbation theory of quantum mechanics by incorporating all eight possible routes of absorption or emission of photons and phonons. Absorption coefficients of silicon are calculated from these formulas. The agreements and discrepancies among the calculated results, the Rajkanan-Singh-Shewchun (RSS) formula, and Green's data are investigated and discussed. For example, the RSS formula tends to overestimate the contributions of indirect transitions for cases with high photon energy. The results show that the state occupied/unoccupied effect is almost negligible for silicon absorption coefficients up to the onset of the optical gain condition where the energy separation of Quasi-Fermi levels between electrons and holes is larger than the band-gap energy. The usefulness of using the physics-based formulas, rather than semi-empirical fitting ones, for absorption coefficients in theoretical studies of photovoltaic devices is also discussed. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5028053>

## I. INTRODUCTION

Optical absorption coefficient  $\alpha$  is one of the most important material parameters associated with photovoltaic devices. Its paramount importance in the research and development of semiconductor photovoltaic devices therefore deserves a proper theoretical study. Since the absorption coefficient is a function of photon energy  $\alpha(E_\lambda)$ , it is a common practice to express it as

$$\alpha_{\text{dir}}(E_\lambda) = A_{\text{dir}} \sqrt{E_\lambda - E_g}, \quad (1)$$

for processes involving the direct interband carrier transition, and

$$\alpha_{\text{ind}}(E_\lambda) = A_{\text{ind}} \begin{cases} \frac{(E_\lambda - E_g + E_{\text{phonon}})^2}{\exp(E_{\text{phonon}}/k_B T) - 1}, & \text{phonon absorption} \\ \frac{(E_\lambda - E_g - E_{\text{phonon}})^2}{1 - \exp(-E_{\text{phonon}}/k_B T)}, & \text{phonon emission,} \end{cases} \quad (2)$$

for processes involving the indirect interband carrier transition. Here,  $E_\lambda$  and  $E_{\text{phonon}}$  denote the photon and phonon energies, respectively.  $E_g$  is the band gap energy.  $A_{\text{dir}}$  and  $A_{\text{ind}}$  are the coefficients related to direct and indirect transitions, respectively. They are usually given as constant values to represent material parameters. Due to their simplicity, Eqs. (1) and (2) are commonly used for showing the essential features regarding the relations between absorption coefficients and photon energy near the band gap: square-root-dependent for direct-band-gap semiconductors and square-dependent for indirect ones.

Although Eqs. (1) and (2) are widely used in the literature, their validity and applicability are seldom questioned and investigated. For example, it will be shown in the following that they are different from Ridley's theoretical results<sup>1</sup> and also the theoretical results presented in this work. Nevertheless, Eqs. (1) and (2) have been used by Rajkanan *et al.*<sup>2</sup> to fit experimental data of silicon absorption coefficients. Their formula will be named the Rajkanan-Singh-Shewchun (RSS) formula in the following discussion. The RSS formula is widely cited and employed in many theoretical works regarding silicon photovoltaic devices. Similarly, the validity and applicability of the RSS formula are rarely questioned and investigated.

There are many experimental measurements for Si absorption coefficients either directly<sup>3–10</sup> or indirectly interpreted from the photoluminescence spectrum.<sup>11–13</sup> Theoretical works on the absorption coefficients of direct and indirect interband carrier transitions have been elaborately discussed and documented by Ridley.<sup>1</sup> However, the Ridley's formula for calculating absorption coefficients of indirect interband carrier transitions has a singular feature if the photon energy is close to the gap energy between the initial and intermediate states. As a result, the Ridley's formula is seldom employed or cited to explain the results of experimental data despite it providing a fundamental theoretical framework in treating this subject. In addition, several approximations assumed in the Ridley's formula could also limit its applicability. For example, the state occupied/unoccupied effect has been neglected and only two routes (instead of eight routes) of photon/phonon absorption/emission processes have been considered.

In this work, a theoretical model for calculating the optical absorption coefficients will be described and presented in detail. Photon absorption from direct and indirect interband transitions will be calculated by the first- and second-order time-dependent perturbation theory of quantum mechanics, respectively, and also by considering the effects

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of occupied/unoccupied carrier states. The indirect interband transition will incorporate all eight possible routes of absorption or emission of photons and phonons. The similarity and difference between this theoretical work and Ridley's work will be examined and illustrated. Explicit formulas derived from this theoretical model will be used to calculate silicon absorption coefficients. The agreements and discrepancies among the calculated results, the RSS formula, and Green's data<sup>3,4</sup> will be investigated and discussed.

## II. THEORETICAL MODEL

The calculation of the optical absorption coefficient for an indirect-band-gap semiconductor is based on the time-dependent perturbation theory of quantum mechanics, in which the transition rate  $W_{i \rightarrow f}$  from an initial state  $|i\rangle$  via an intermediate state  $|n\rangle$  to a final state  $|f\rangle$  due to the perturbation of the interaction Hamiltonian  $H_{\text{int}}$  can be calculated by

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| \langle f | H_{\text{int}} | i \rangle + \sum_{n \neq i} \frac{\langle f | H_{\text{int}} | n \rangle \langle n | H_{\text{int}} | i \rangle}{E_i - E_n + i\Gamma_n} \right|^2 \delta(E_f - E_i). \quad (3)$$

Here, only the first- and second-order terms are explicitly expressed. The higher order terms are assumed to negligible in the problem discussed here.  $\delta(E_f - E_i)$  is the Dirac delta function denoting the conservation of energy between the system's total initial energy  $E_i$  and final energy  $E_f$ . The summation includes all the possible intermediate states but excludes the initial state. Because of the denominator factor  $1/(E_i - E_n + i\Gamma_n)$ , the intermediate states with energy  $E_n$  far away from the initial state will not contribute significantly to the transition rate and thus normally only states located near the gap of conduction and valence band edges will be considered. The damping factor  $\Gamma_n = \hbar/\tau_{\text{dp}}$  accounts for the carrier dephasing processes at intermediate states from other scattering processes that can be characterized by a dephasing time  $\tau_{\text{dp}}$ . If this dephasing factor is taken into account in the first-order perturbation, it will be responsible for the Lorentzian-like spectral broadening for the optical gain/absorption coefficient of direct transitions.<sup>14</sup> The necessity of including the damping factor in the theoretical model for Raman scattering has also been demonstrated.<sup>15</sup> The details of these dephasing processes are too complicated to be discussed here.<sup>16</sup> For simplicity, they will be deliberately ignored for the first-order perturbation, while they will be included in the second-order perturbation to eliminate the singular features resulting from the bare denominator factor  $1/(E_i - E_n)$  when  $E_i \approx E_n$ .

The interaction Hamiltonian is composed of

$$H_{\text{int}} = H_{\lambda}^e + H_{\lambda}^a + H_q^e + H_q^a, \quad (4)$$

where only the emission and absorption of the electron-photon interaction Hamiltonians,  $H_{\lambda}^e$  and  $H_{\lambda}^a$ , and the emission and absorption of the electron-phonon interaction Hamiltonians,  $H_q^e$  and  $H_q^a$ , will be considered in this problem. It should be noted that the system's states in this problem are in fact comprised of electrons, photons, and phonons. Since coupled states among different particles are not considered here, only the

carrier states will be presented explicitly in the following discussion in order to simplify the notations.

### A. Direct interband transition

If the cross interference between the first- and second-order transitions is assumed to be negligible in Eq. (3), then the first-order transition rate for an electron with wave vector  $\mathbf{k}$  at an initial state in the valence band  $|\mathbf{vk}\rangle$  absorbing a photon to a final state in the conduction band  $|\mathbf{ck}'\rangle$  with wave vector  $\mathbf{k}'$  will become

$$W_{\mathbf{vk} \rightarrow \mathbf{ck}'}^{(1)} = \frac{2\pi}{\hbar} |\langle \mathbf{ck}' | H_{\lambda}^a | \mathbf{vk} \rangle|^2 \delta(E_f - E_i). \quad (5)$$

Similarity, the reverse process of Eq. (5), for an electron with wave vector  $\mathbf{k}'$  at an initial state in the valence band  $|\mathbf{ck}'\rangle$  to a final state in the conduction band  $|\mathbf{vk}\rangle$  with wave vector  $\mathbf{k}$ , is

$$W_{\mathbf{ck}' \rightarrow \mathbf{vk}}^{(1)} = \frac{2\pi}{\hbar} |\langle \mathbf{vk} | H_{\lambda}^e | \mathbf{ck}' \rangle|^2 \delta(E_f - E_i). \quad (6)$$

In order to calculate the optical absorption coefficient, the carrier occupation probability of quantum states should be taken into account. We can usually assume that carriers are in a quasi-equilibrium condition and their statistically average number in states energy can be described by the Fermi-Dirac distribution function. As a result, if  $f_{\mathbf{ck}'}$  and  $f_{\mathbf{vk}}$  denote the statistically average numbers of electrons in the states  $|\mathbf{ck}'\rangle$  and  $|\mathbf{vk}\rangle$ , respectively, its rate of change due to the first-order direction transition will be

$$\frac{df_{\mathbf{ck}'}}{dt} = \sum_{\mathbf{k}} \left[ W_{\mathbf{vk} \rightarrow \mathbf{ck}'}^{(1)} f_{\mathbf{vk}} (1 - f_{\mathbf{ck}'}) - W_{\mathbf{ck}' \rightarrow \mathbf{vk}}^{(1)} f_{\mathbf{ck}'} (1 - f_{\mathbf{vk}}) \right]. \quad (7)$$

It can be shown in the Appendix that the electron-photon interaction matrices are given by

$$\begin{aligned} |\langle \mathbf{ck}' | H_{\lambda}^a | \mathbf{vk} \rangle|^2 V_t &= |M_{\lambda}|^2 N_{\lambda} \delta_{\mathbf{k}, \mathbf{k}'}, & \text{photon absorption} \\ |\langle \mathbf{vk} | H_{\lambda}^e | \mathbf{ck}' \rangle|^2 V_t &= |M_{\lambda}|^2 (N_{\lambda} + 1) \delta_{\mathbf{k}, \mathbf{k}'}, & \text{photon emission.} \end{aligned} \quad (8)$$

Here,  $V_t$  is the volume of photons. For unguided electromagnetic waves,  $V_t = V_c = V$  is generally assumed where  $V_c$  is the volume of carriers.  $N_{\lambda}$  is the statistically average photon number.  $\delta_{\mathbf{k}, \mathbf{k}'}$  represents the Kronecker delta symbol, where  $\delta_{\mathbf{k}, \mathbf{k}'} = 1$  for  $\mathbf{k} = \mathbf{k}'$  and zero otherwise. The form of  $\delta_{\mathbf{k}, \mathbf{k}'}$  implies the conservation of momentum assuming that the photon's momentum is insignificant and negligible compared with the carrier's momentum.  $|M_{\lambda}|$  is the volume-independent electron-photon interaction matrices (see the Appendix)

$$|M_{\lambda}|^2 = \frac{\hbar^2 e^2}{2\epsilon m_0^2 E_{\lambda}} |\hat{\mathbf{e}}_{\lambda} \cdot \langle \mathbf{vk} | \mathbf{p} | \mathbf{ck} \rangle|^2, \quad (9)$$

where  $\epsilon$  is the material permittivity and  $E_{\lambda}$  and  $\hat{\mathbf{e}}_{\lambda}$  denote the photon energy and the unit vector along the direction of photon's polarization, respectively. For bulk semiconductors incident with unpolarized light, the momentum matrix element

$|\hat{\mathbf{e}}_\lambda \cdot \langle \mathbf{v} \mathbf{k} | \mathbf{p} | \mathbf{c} \mathbf{k} \rangle|$  is usually assumed to be anisotropic and  $\mathbf{k}$ -independent at the zone center of the  $\mathbf{k}$ -space. It can be represented by an energy parameter  $E_p$  as

$$|\hat{\mathbf{e}}_\lambda \cdot \langle \mathbf{v} \mathbf{k} | \mathbf{p} | \mathbf{c} \mathbf{k} \rangle|^2 = p_{cv}^2 = \frac{m_0}{6} E_p. \quad (10)$$

After the above denotations, Eq. (7) can be expressed as

$$\frac{df_{\mathbf{c} \mathbf{k}}}{dt} = \frac{2\pi}{\hbar V_t} |M_\lambda|^2 [N_\lambda (f_{\mathbf{v} \mathbf{k}} - f_{\mathbf{c} \mathbf{k}}) - f_{\mathbf{c} \mathbf{k}} (1 - f_{\mathbf{v} \mathbf{k}})] \times \delta(E_{\mathbf{c} \mathbf{k}} - E_{\mathbf{v} \mathbf{k}} - E_\lambda). \quad (11)$$

Since  $f_{\mathbf{c} \mathbf{k}}$  represents the electrons' statistical average numbers in the state  $|\mathbf{c} \mathbf{k}\rangle$  the conduction bands, the electron number density (also called concentration) of the conduction band can therefore be calculated by summarizing these average numbers associated with all the  $\mathbf{k}$ -states as

$$n = \frac{2}{V_c} \sum_{\mathbf{k}} f_{\mathbf{c} \mathbf{k}}. \quad (12)$$

Here,  $V_c$  is the volume of carriers and the degeneracy factor of two accounts for two possible spins associated with each  $\mathbf{k}$  state. Combining Eqs. (11) and (12) yields

$$\frac{dn}{dt} = \frac{2}{V_c} \sum_{\mathbf{k}} \frac{2\pi}{\hbar V_t} |M_\lambda|^2 [N_\lambda (f_{\mathbf{v} \mathbf{k}} - f_{\mathbf{c} \mathbf{k}}) - f_{\mathbf{c} \mathbf{k}} (1 - f_{\mathbf{v} \mathbf{k}})] \times \delta(E_{\mathbf{c} \mathbf{k}} - E_{\mathbf{v} \mathbf{k}} - E_\lambda). \quad (13)$$

Equation (13) can be separated into two parts: one is proportional with  $N_\lambda$  (i.e., the stimulation emission and absorption part) and the other has no relation with  $N_\lambda$  (i.e., the spontaneous emission part) as

$$\frac{dn}{dt} = v_g \alpha_{\text{dir}} s - r_{\text{rad}}, \quad (14)$$

where  $s \equiv N_\lambda / V_t$  is defined as the photon density.  $v_g$  is the group velocity of photons. If the photon dispersion relation is linear, then  $v_g = c / n_r$  where  $n_r$  is the refractive index and  $c$  is the speed of light in vacuum. Equation (14) in fact gives the definitions of the absorption coefficient  $\alpha_{\text{dir}}$  and the carrier radiative recombination rate  $r_{\text{rad}}$  due to the spontaneous emission of photons as

$$\alpha_{\text{dir}} = \frac{2}{v_g V_c} \sum_{\mathbf{k}} \frac{2\pi}{\hbar} |M_\lambda|^2 (f_{\mathbf{v} \mathbf{k}} - f_{\mathbf{c} \mathbf{k}}) \delta(E_{\mathbf{c} \mathbf{k}} - E_{\mathbf{v} \mathbf{k}} - E_\lambda), \quad (15)$$

and

$$r_{\text{rad}} = \frac{2}{V_t} \sum_{\lambda} \frac{2}{V_c} \sum_{\mathbf{k}} \frac{2\pi}{\hbar} |M_\lambda|^2 f_{\mathbf{c} \mathbf{k}} (1 - f_{\mathbf{v} \mathbf{k}}) \delta(E_{\mathbf{c} \mathbf{k}} - E_{\mathbf{v} \mathbf{k}} - E_\lambda). \quad (16)$$

Equations (15) and (16) are the general expressions for calculating the absorption coefficient  $\alpha_{\text{dir}}$  and the carrier radiative recombination rate  $r_{\text{rad}}$  for direct-band-gap semiconductors. Note that  $\alpha_{\text{dir}}$  is defined for photons with a specific wavelength  $\lambda$  or energy  $E_\lambda$ . On the other hand,  $r_{\text{rad}}$  is defined from the contribution of all photons with different wavelengths.

The summation of all wavelengths  $\sum_\lambda$  in Eq. (16) simply implies this fact.

Further simplifications for calculating Eq. (15) can be achieved if  $E_{\mathbf{c} \mathbf{k}}$  and  $E_{\mathbf{v} \mathbf{k}}$  are assumed to be isotropic and parabolic. Consequently, the conservation of energy requires

$$E_\lambda = E_g + \frac{\hbar^2 k^2}{2m_c} + \frac{\hbar^2 k^2}{2m_v} = E_g + \frac{\hbar^2 k^2}{2m_{cv}}, \quad (17)$$

where the joint density-of-states effective mass  $m_{cv}$  is defined as  $1/m_{cv} = 1/m_c + 1/m_v$ . Let  $E = \hbar^2 k^2 / 2m_{cv}$ , then, the summation of all the  $\mathbf{k}$ -states can be transformed into an  $E$ -integral as

$$\frac{2}{V_c} \sum_{\mathbf{k}} \dots = \int_0^\infty dE \frac{m_{cv} \sqrt{2m_{cv} E}}{\hbar^3 \pi^2} \dots = \int_0^\infty dE \rho_{cv}(E) \dots, \quad (18)$$

where  $\rho_{cv}(E)$  denotes the joint density of states between the conduction and valence bands. As a result, Eq. (15) can be explicitly calculated as

$$\alpha_{\text{dir}} = \alpha_{\text{dir}0} \sqrt{\frac{E_g}{E_\lambda}} \sqrt{1 - \left(\frac{E_g}{E_\lambda}\right)} [f_v(E_\lambda - E_g) - f_c(E_\lambda - E_g)] \times H(E_\lambda - E_g), \quad (19)$$

with the following definitions:

$$\alpha_{\text{dir}0} = \frac{\sqrt{2} e^2 m_{cv}^{3/2} p_{cv}^2}{\pi \hbar^2 m_0^2 c \epsilon_0 n_r E_g^{1/2}}, \quad (20)$$

$$f_c(E) = \left\{ \exp \left[ \frac{Em_{cv}/m_c - (E_{Fc} - E_c)}{k_B T} \right] + 1 \right\}^{-1}, \quad (21)$$

$$f_v(E) = 1 - \left\{ \exp \left[ \frac{Em_{cv}/m_v - (E_v - E_{Fv})}{k_B T} \right] + 1 \right\}^{-1}. \quad (22)$$

Here,  $H(x)$  denotes the Heaviside unit step function.  $E_{Fc}$  and  $E_{Fv}$  are the energies of the quasi-Fermi levels (also known as the electrochemical potential) associated with electrons in the conduction and valence bands where  $E_c$  and  $E_v$  are the band-edge energies, respectively. Note that  $\alpha_{\text{dir}0}$  in Eq. (20) is deliberately defined to become  $E_\lambda$ -independent.

If the state occupied/unoccupied effect is not considered, that is, the initial states are assumed to be fully occupied, while the final state completely unoccupied, i.e.,  $f_c(E) = 0$  and  $f_v(E) = 1$  is assumed, then, the optical absorption coefficient will become

$$\alpha_{\text{dir}}(E_\lambda) = \alpha_{\text{dir}0} \sqrt{\frac{E_g}{E_\lambda}} \sqrt{1 - \left(\frac{E_g}{E_\lambda}\right)} H(E_\lambda - E_g). \quad (23)$$

Equation (23) is identical to the result given by Ridley<sup>1</sup> with different denotations. Compared with Eq. (23), the conventional expression of Eq. (1) is oversimplified by ignoring the fact of  $|M_\lambda|^2 \propto 1/E_\lambda$  in Eq. (9). According to Eq. (23), the absorption coefficient of direct interband transition  $\alpha_{\text{dir}}$  reaches its maximum value at  $E_\lambda = 2E_g$ . On the other hand, in the conventional formula of Eq. (1),  $\alpha_{\text{dir}}$  reaches its maximum value

as  $E_\lambda \rightarrow \infty$ , as shown in Fig. 1. In fact, Eqs. (1) and (23) agree with each other rather well in the range  $1 < E_\lambda/E_g < 1.2$ , i.e., near the band gap. As  $E_\lambda > 2E_g$ , Eq. (23) indicates that  $\alpha_{\text{dir}}$  will decrease by increasing  $E_\lambda$ , while Eq. (1) denotes that  $\alpha_{\text{dir}}$  will increase by increasing  $E_\lambda$ . This certainly implies that Eq. (1) will lose its credibility for cases of  $E_\lambda > 2E_g$ .

## B. Indirect interband transition

For indirect interband absorption processes, an electron transits from an initial state in the valence band  $|v\mathbf{k}\rangle$  via an intermediate state  $|n\mathbf{k}''\rangle$  to a final state in the conduction band  $|c\mathbf{k}'\rangle$ . The transition rate of this process can be calculated by the second-order perturbation term in Eq. (3) as

$$W_{v\mathbf{k} \rightarrow c\mathbf{k}'}^{(2)} = \frac{2\pi}{\hbar} \sum_{n,\mathbf{k}''} \left| \frac{\langle c\mathbf{k}' | H_{\text{int}} | n\mathbf{k}'' \rangle \langle n\mathbf{k}'' | H_{\text{int}} | v\mathbf{k} \rangle}{E_i - E_n + i\Gamma_n} \right|^2 \delta(E_f - E_i). \quad (24)$$

Similarly, as a reverse process of the above transition, an electron transits from an initial state in the conduction band  $|c\mathbf{k}'\rangle$  via an intermediate state  $|n\mathbf{k}''\rangle$  to a final state in the valence band  $|v\mathbf{k}\rangle$ , the transition rate can be calculated by using

$$W_{c\mathbf{k}' \rightarrow v\mathbf{k}}^{(2)} = \frac{2\pi}{\hbar} \sum_{n,\mathbf{k}''} \left| \frac{\langle v\mathbf{k} | H_{\text{int}} | n\mathbf{k}'' \rangle \langle n\mathbf{k}'' | H_{\text{int}} | c\mathbf{k}' \rangle}{E_i - E_n + i\Gamma_n} \right|^2 \delta(E_f - E_i). \quad (25)$$

As a result, taking the effects of occupied/unoccupied states into consideration, the rate of change of  $f_{c\mathbf{k}'}$  due to  $W_{v\mathbf{k} \rightarrow c\mathbf{k}'}^{(2)}$  and  $W_{c\mathbf{k}' \rightarrow v\mathbf{k}}^{(2)}$  can be calculated by

$$\frac{df_{c\mathbf{k}'}}{dt} = \sum_{\mathbf{k}} \left[ W_{v\mathbf{k} \rightarrow c\mathbf{k}'}^{(2)} f_{v\mathbf{k}} (1 - f_{c\mathbf{k}'}) - W_{c\mathbf{k}' \rightarrow v\mathbf{k}}^{(2)} f_{c\mathbf{k}'} (1 - f_{v\mathbf{k}}) \right]. \quad (26)$$

Consequently, the rate of change of the electron number density of the conduction band due to the second-order transition processes can be calculated by

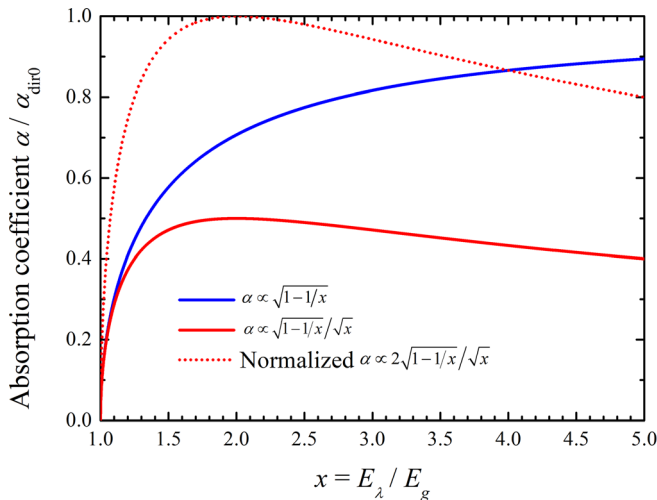


FIG. 1. Dimensionless absorption coefficient of the direct interband transition as a function of the photon energy over band-gap energy,  $E_\lambda/E_g$ .

$$\begin{aligned} \frac{dn}{dt} &= \frac{2}{V_c} \sum_{\mathbf{k}'} \left( \frac{df_{c\mathbf{k}'}}{dt} \right) \\ &= \frac{2}{V_c} \sum_{\mathbf{k}'} \sum_{\mathbf{k}} \left[ W_{v\mathbf{k} \rightarrow c\mathbf{k}'}^{(2)} f_{v\mathbf{k}} (1 - f_{c\mathbf{k}'}) - W_{c\mathbf{k}' \rightarrow v\mathbf{k}}^{(2)} f_{c\mathbf{k}'} (1 - f_{v\mathbf{k}}) \right]. \end{aligned} \quad (27)$$

As suggested by Ridley,<sup>1</sup> there are eight possible processes for the transition between  $|v\mathbf{k}\rangle$  and  $|c\mathbf{k}'\rangle$ , as shown in Fig. 2. However, only two processes are considered by Ridley: the processes 1 and 2 in Fig. 2. As it will be demonstrated in the following, all these eight processes should be considered for silicon. These eight processes combine the sequential order of the emission and absorption of a photon and a phonon, as indicated by the corresponding labels in Fig. 2. For example, in process 1, an electron in the valence band absorbs a photon via an intermediate state of the conduction band, then absorbs a phonon, and transits to an empty state of the conduction band. While process 8 is the reverse of process 1, an electron in the conduction band emits a phonon via this intermediate state, then emits a photon, and transits to an empty state of the valence band. All eight processes in Fig. 2 should be incorporated into Eq. (27). As a result, the

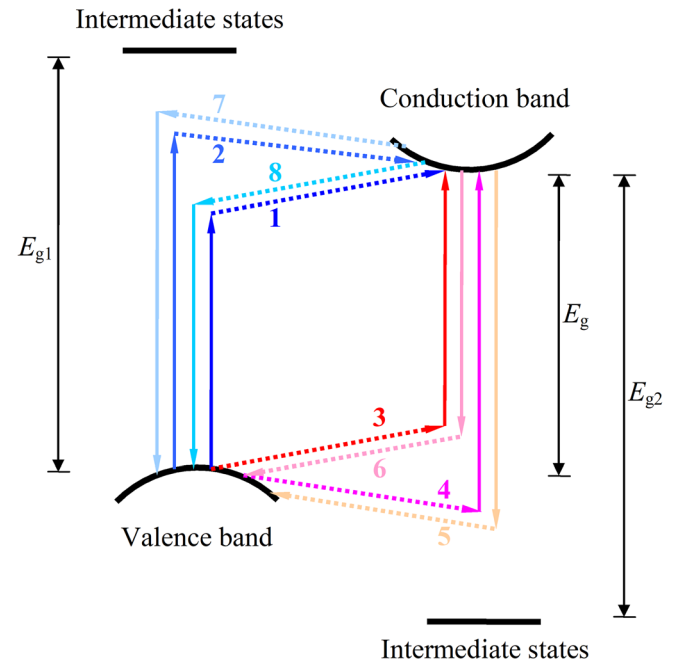


FIG. 2. Schematic diagram of the eight routes of the second-order transition in an indirect band-gap semiconductor between a state in the conduction band and a state in the valence band via an intermediate state. Each process involves different sequences of the absorption/emission of photons and phonons. For example, in process 1, an electron in the valence band absorbs a photon (represented by a solid line) via an intermediate state, then absorbs a phonon (represented by a dotted line), and transits to an empty state in the conduction band. While process 8 is the reverse of process 1, an electron in the conduction band emits a phonon via this intermediate state, then emits a photon, and transits to an empty state of the valence band.  $E_g$  denotes the indirect band gap energy between the band edges of conduction and valence bands.  $E_{g1}$  and  $E_{g2}$  are the direct gap energies providing intermediate states. For Si,  $E_g$  is the energy difference between the valence band edge (at the  $\Gamma$ -point) and the conduction band edge (near the X-point along the  $\Delta$ -direction).  $E_{g1}$  is the direct gap energy between the conduction and valence band at the  $\Gamma$ -point, and  $E_{g2}$  is the direct gap energy near the X-point along the  $\Delta$ -direction at the conduction band edge.



transition rates of Eqs. (24) and (25) can be calculated by incorporating the corresponding processes as

$$W_{\mathbf{v}\mathbf{k} \rightarrow \mathbf{c}\mathbf{k}'}^{(2)} = \frac{2\pi}{\hbar} \sum_{n, \mathbf{k}''} |S_1 + S_2 + S_3 + S_4|^2 \delta(E_f - E_i), \quad (28)$$

and

$$W_{\mathbf{c}\mathbf{k}' \rightarrow \mathbf{v}\mathbf{k}}^{(2)} = \frac{2\pi}{\hbar} \sum_{n, \mathbf{k}''} |S_5 + S_6 + S_7 + S_8|^2 \delta(E_f - E_i), \quad (29)$$

respectively.  $S_i$  is the interaction element of each process where the index  $i$  indicates the  $i$ th process in Fig. 2, and their explicit expression are listed in the following:

$$S_1 = -\frac{\langle \mathbf{c}\mathbf{k} + \mathbf{q} | H_q^a | \mathbf{c}\mathbf{k} \rangle \langle \mathbf{c}\mathbf{k} | H_\lambda^a | \mathbf{v}\mathbf{k} \rangle}{E_{\mathbf{g}\mathbf{k}} - E_\lambda - i\Gamma_{\mathbf{c}\mathbf{k}}}, \quad (30)$$

$$S_2 = -\frac{\langle \mathbf{c}\mathbf{k} - \mathbf{q} | H_q^c | \mathbf{c}\mathbf{k} \rangle \langle \mathbf{c}\mathbf{k} | H_\lambda^a | \mathbf{v}\mathbf{k} \rangle}{E_{\mathbf{g}\mathbf{k}} - E_\lambda - i\Gamma_{\mathbf{c}\mathbf{k}}}, \quad (31)$$

$$S_3 = \frac{\langle \mathbf{c}\mathbf{k} + \mathbf{q} | H_\lambda^a | \mathbf{v}\mathbf{k} + \mathbf{q} \rangle \langle \mathbf{v}\mathbf{k} + \mathbf{q} | H_q^a | \mathbf{v}\mathbf{k} \rangle}{E_{\mathbf{g}\mathbf{k}+\mathbf{q}} - E_\lambda + i\Gamma_{\mathbf{v}\mathbf{k}+\mathbf{q}}}, \quad (32)$$

$$S_4 = \frac{\langle \mathbf{c}\mathbf{k} - \mathbf{q} | H_\lambda^a | \mathbf{v}\mathbf{k} - \mathbf{q} \rangle \langle \mathbf{v}\mathbf{k} - \mathbf{q} | H_q^c | \mathbf{v}\mathbf{k} \rangle}{E_{\mathbf{g}\mathbf{k}-\mathbf{q}} - E_\lambda + i\Gamma_{\mathbf{v}\mathbf{k}-\mathbf{q}}}, \quad (33)$$

$$S_5 = \frac{\langle \mathbf{v}\mathbf{k}' + \mathbf{q} | H_q^a | \mathbf{v}\mathbf{k}' \rangle \langle \mathbf{v}\mathbf{k}' | H_\lambda^c | \mathbf{c}\mathbf{k}' \rangle}{E_{\mathbf{g}\mathbf{k}'} - E_\lambda + i\Gamma_{\mathbf{v}\mathbf{k}'}}, \quad (34)$$

$$S_6 = \frac{\langle \mathbf{c}\mathbf{k}' - \mathbf{q} | H_q^c | \mathbf{v}\mathbf{k}' \rangle \langle \mathbf{v}\mathbf{k}' | H_\lambda^c | \mathbf{c}\mathbf{k}' \rangle}{E_{\mathbf{g}\mathbf{k}'} - E_\lambda + i\Gamma_{\mathbf{v}\mathbf{k}'}}, \quad (35)$$

$$S_7 = -\frac{\langle \mathbf{v}\mathbf{k}' + \mathbf{q} | H_\lambda^a | \mathbf{c}\mathbf{k}' + \mathbf{q} \rangle \langle \mathbf{c}\mathbf{k}' + \mathbf{q} | H_q^a | \mathbf{c}\mathbf{k}' \rangle}{E_{\mathbf{g}\mathbf{k}'+\mathbf{q}} - E_\lambda - i\Gamma_{\mathbf{c}\mathbf{k}'+\mathbf{q}}}, \quad (36)$$

$$S_8 = -\frac{\langle \mathbf{v}\mathbf{k}' - \mathbf{q} | H_\lambda^c | \mathbf{c}\mathbf{k}' - \mathbf{q} \rangle \langle \mathbf{c}\mathbf{k}' - \mathbf{q} | H_q^c | \mathbf{c}\mathbf{k}' \rangle}{E_{\mathbf{g}\mathbf{k}'-\mathbf{q}} - E_\lambda - i\Gamma_{\mathbf{c}\mathbf{k}'-\mathbf{q}}}. \quad (37)$$

Here,  $E_{\mathbf{g}\mathbf{k}} = E_{\mathbf{c}\mathbf{k}} - E_{\mathbf{v}\mathbf{k}}$  represents the energy difference between an electron and a hole at the zone center with wave vector  $\mathbf{k}$ .  $E_{\mathbf{g}\mathbf{k}} \approx E_{\mathbf{g}1}$  is assumed in this work in which its  $\mathbf{k}$ -dependent feature is neglected. Similarly,  $E_{\mathbf{g}\mathbf{k}\pm\mathbf{q}} = E_{\mathbf{c}\mathbf{k}\pm\mathbf{q}} - E_{\mathbf{v}\mathbf{k}\pm\mathbf{q}}$  represents the energy difference between an electron and a hole near the zone edge with wave vector  $\mathbf{k}' = \mathbf{k} \pm \mathbf{q}$ .  $E_{\mathbf{g}\mathbf{k}\pm\mathbf{q}} \approx E_{\mathbf{g}2}$  is also assumed to be  $\mathbf{k}$ -independent. Note that the expressions of Eqs. (30) and (31) are identical to Ridley's results except for the extra damping term. However, the  $S_1$  and  $S_2$  here are denoted as  $S_{2+}$  and  $S_{2-}$  by Ridley, respectively.

It should be noted that the carriers momentum is conserved when a single photon absorption or emission process is involved due to the negligible photons momentum, as implied by Eq. (8). As a result, the triple summation in Eq. (27) can be transformed into a double summation as

$$\sum_{\mathbf{k}'} \sum_{\mathbf{k}} \sum_{n, \mathbf{k}''} \cdots = \sum_{\mathbf{k}'} \sum_{\mathbf{k}} \cdots = \sum_{\mathbf{k}} \sum_{\mathbf{q}} \cdots. \quad (38)$$

The summation of all the possible final states over all the  $\mathbf{k}'$  state of electron in the conduction band can be changed to the summation of all the possible phonon emission or absorption with momentum  $\mathbf{q}$  when a phonon absorption or emission process is involved and if the electron-phonon interaction matrix is  $\mathbf{q}$ -dependent. However, since the intervalley phonon processes are usually  $\mathbf{q}$ -independent, the double summation of  $\mathbf{k}$  and  $\mathbf{k}'$  will be used in the following. In addition, the cross terms from different interaction elements  $S_i$  in Eqs. (28) and (29) are assumed to be negligible; that is,

$$|S_1 + S_2 + S_3 + S_4|^2 \approx |S_1|^2 + |S_2|^2 + |S_3|^2 + |S_4|^2, \quad (39)$$

$$|S_5 + S_6 + S_7 + S_8|^2 \approx |S_5|^2 + |S_6|^2 + |S_7|^2 + |S_8|^2. \quad (40)$$

As a result, the rate of change of the electron concentration of the conduction band in Eq. (27) can be explicitly calculated by using

$$\begin{aligned} \frac{dn}{dt} = & \frac{2}{V_c} \sum_{\mathbf{k}'} \sum_{\mathbf{k}} \frac{2\pi}{\hbar V_t V_n} \left[ |M_1|^2 f_{\mathbf{v}\mathbf{k}} (1 - f_{\mathbf{c}\mathbf{k}'}) N_{\mathbf{q}} N_\lambda \delta(E_{\mathbf{v}\mathbf{k}} - E_{\mathbf{c}\mathbf{k}'} + \hbar\omega_{\mathbf{q}} + E_\lambda) \right. \\ & + |M_2|^2 f_{\mathbf{v}\mathbf{k}} (1 - f_{\mathbf{c}\mathbf{k}'}) (N_{\mathbf{q}} + 1) N_\lambda \delta(E_{\mathbf{v}\mathbf{k}} - E_{\mathbf{c}\mathbf{k}'} - \hbar\omega_{\mathbf{q}} + E_\lambda) \\ & + |M_3|^2 f_{\mathbf{v}\mathbf{k}} (1 - f_{\mathbf{c}\mathbf{k}'}) N_{\mathbf{q}} N_\lambda \delta(E_{\mathbf{v}\mathbf{k}} - E_{\mathbf{c}\mathbf{k}'} + \hbar\omega_{\mathbf{q}} + E_\lambda) \\ & + |M_4|^2 f_{\mathbf{v}\mathbf{k}} (1 - f_{\mathbf{c}\mathbf{k}'}) (N_{\mathbf{q}} + 1) N_\lambda \delta(E_{\mathbf{v}\mathbf{k}} - E_{\mathbf{c}\mathbf{k}'} - \hbar\omega_{\mathbf{q}} + E_\lambda) \\ & - |M_5|^2 f_{\mathbf{c}\mathbf{k}'} (1 - f_{\mathbf{v}\mathbf{k}}) N_{\mathbf{q}} (N_\lambda + 1) \delta(E_{\mathbf{c}\mathbf{k}'} - E_{\mathbf{v}\mathbf{k}} + \hbar\omega_{\mathbf{q}} - E_\lambda) \\ & - |M_6|^2 f_{\mathbf{c}\mathbf{k}'} (1 - f_{\mathbf{v}\mathbf{k}}) (N_{\mathbf{q}} + 1) (N_\lambda + 1) \delta(E_{\mathbf{c}\mathbf{k}'} - E_{\mathbf{v}\mathbf{k}} - \hbar\omega_{\mathbf{q}} - E_\lambda) \\ & - |M_7|^2 f_{\mathbf{c}\mathbf{k}'} (1 - f_{\mathbf{v}\mathbf{k}}) N_{\mathbf{q}} (N_\lambda + 1) \delta(E_{\mathbf{c}\mathbf{k}'} - E_{\mathbf{v}\mathbf{k}} + \hbar\omega_{\mathbf{q}} - E_\lambda) \\ & \left. - |M_8|^2 f_{\mathbf{c}\mathbf{k}'} (1 - f_{\mathbf{v}\mathbf{k}}) (N_{\mathbf{q}} + 1) (N_\lambda + 1) \delta(E_{\mathbf{c}\mathbf{k}'} - E_{\mathbf{v}\mathbf{k}} - \hbar\omega_{\mathbf{q}} - E_\lambda) \right], \quad (41) \end{aligned}$$

where  $M_i$  is defined from  $S_i$  and it represents a combined interaction matrix of the electron-photon and electron-phonon interactions in which

$$|M_1|^2 = |M_8|^2 = \frac{|M_{ij}|^2 |M_{\lambda 1}|^2}{|E_{\mathbf{g}\mathbf{k}} - E_\lambda + i\Gamma_{\mathbf{c}\mathbf{k}}|^2} \simeq \frac{|M_{ij}|^2 |M_{\lambda 1}|^2}{|E_{\mathbf{g}1} - E_\lambda - i\Gamma_1|^2}, \quad (42)$$

$$|M_2|^2 = |M_7|^2 = \frac{|M_{ij}|^2 |M_{\lambda 1}|^2}{|E_{gk} - E_\lambda + i\Gamma_{ck}|^2} \simeq \frac{|M_{ij}|^2 |M_{\lambda 1}|^2}{|E_{g1} - E_\lambda - i\Gamma_1|^2}, \quad (43)$$

$$|M_3|^2 = |M_6|^2 = \frac{|M_{ij}|^2 |M_{\lambda 2}|^2}{|E_{gk+q} - E_\lambda + i\Gamma_{vk+q}|^2} \simeq \frac{|M_{ij}|^2 |M_{\lambda 2}|^2}{|E_{g2} - E_\lambda + i\Gamma_2|^2}, \quad (44)$$

$$|M_4|^2 = |M_5|^2 = \frac{|M_{ij}|^2 |M_{\lambda 2}|^2}{|E_{gk-q} - E_\lambda + i\Gamma_{k-q}|^2} \simeq \frac{|M_{ij}|^2 |M_{\lambda 2}|^2}{|E_{g2} - E_\lambda + i\Gamma_2|^2}. \quad (45)$$

Here,

$$|M_{\lambda 1}|^2 = \frac{\hbar^2 e^2}{2\varepsilon E_\lambda m_0^2} |\hat{\mathbf{e}}_\lambda \cdot \langle \mathbf{vk} | \mathbf{p} | \mathbf{ck} \rangle|^2, \quad (46)$$

and

$$|M_{\lambda 2}|^2 = \frac{\hbar^2 e^2}{2\varepsilon E_\lambda m_0^2} |\hat{\mathbf{e}}_\lambda \cdot \langle \mathbf{vk}' | \mathbf{p} | \mathbf{ck}' \rangle|^2, \quad (47)$$

are the electron-photon interaction matrices near the  $E_{g1}$  and  $E_{g2}$  positions in the  $\mathbf{k}$ -space, respectively. The approximation signs in Eqs. (42)–(47) represent the assumptions of  $E_{gk} = E_{g1}$ ,  $E_{gk\pm q} = E_{g2}$ ,  $\Gamma_{ck} = \Gamma_1$ , and  $\Gamma_{vk\pm q} = \Gamma_2$ , i.e., their  $\mathbf{k}$ -independent details are omitted for simplicity.

In the case of indirect interband transition, the electron-phonon scatterings are mostly intervalley ones. These intervalley scatterings mainly result from the deformation potential of the zone edge optical or acoustic phonons with almost

$\mathbf{q}$ -independent nature. Therefore, their interaction matrix is usually expressed similar to the case of deformation potential optical phonons

$$|M_{ij}|^2 = \frac{D_{ij}^2 \hbar^2}{2\rho_L \hbar \omega_{ij}}. \quad (48)$$

Here,  $|M_{ij}|^2$  is the electron-phonon interaction matrix.  $D_{ij}$  is the deformation potential of phonons with energy  $\hbar \omega_{ij}$ .  $\rho_L$  is the material mass density.  $V_c$ ,  $V_\lambda$ , and  $V_n$  are the volumes of carriers, photons, and phonons, respectively. Usually, for bulk semiconductors without any confinement structure for photons or phonons, carriers, photons, and phonons are assumed to have the same volume, i.e.,  $V_c = V_t = V_n = V$  will be assumed in the following. Note that  $|M_\lambda|^2$  and  $|M_{ij}|^2$  are deliberately defined to be volume-independent in this work.

Equation (41) is by far the most general expression for any category of problems without specifically referring to any type of phonons or photons. Similarly with the case of direct interband transition, Eq. (41) can be separated into two parts: one is proportional with the mean photon number  $N_\lambda$  (i.e., the stimulation emission and absorption part) and the other has no relation with  $N_\lambda$  (i.e., the spontaneous emission part). As a result, Eq. (41) can be expressed into the following expression:

$$\frac{dn}{dt} = v_g \alpha_{\text{ind}} S - r_{\text{rad}}. \quad (49)$$

Here,  $r_{\text{rad}}$  is the term corresponding to the carrier radiative recombination rate due to the spontaneous emission of photons.  $v_g$  is the group velocity of photons.  $s = N_\lambda/V_\lambda$  is defined as the photon density. The optical absorption coefficient of indirect interband transition  $\alpha_{\text{ind}}$  defined from Eqs. (41) and (49) is then given by

$$\begin{aligned} \alpha_{\text{ind}} = & \frac{2}{v_g V^2} \sum_{\mathbf{k}'} \sum_{\mathbf{k}} \frac{2\pi}{\hbar} \left\{ |M_1|^2 [f_{v\mathbf{k}}(1 - f_{c\mathbf{k}'})N_{\mathbf{q}} - f_{c\mathbf{k}'}(1 - f_{v\mathbf{k}})(N_{\mathbf{q}} + 1)] \delta(E_{v\mathbf{k}} - E_{c\mathbf{k}'} + \hbar \omega_{\mathbf{q}} + E_\lambda) \right. \\ & + |M_2|^2 [f_{v\mathbf{k}}(1 - f_{c\mathbf{k}'})N_{\mathbf{q}} + 1 - f_{c\mathbf{k}'}(1 - f_{v\mathbf{k}})N_{\mathbf{q}}] \delta(E_{v\mathbf{k}} - E_{c\mathbf{k}'} - \hbar \omega_{\mathbf{q}} + E_\lambda) \\ & + |M_3|^2 [f_{v\mathbf{k}}(1 - f_{c\mathbf{k}'})N_{\mathbf{q}} - f_{c\mathbf{k}'}(1 - f_{v\mathbf{k}})(N_{\mathbf{q}} + 1)] \delta(E_{v\mathbf{k}} - E_{c\mathbf{k}'} + \hbar \omega_{\mathbf{q}} + E_\lambda) \\ & \left. + |M_4|^2 [f_{v\mathbf{k}}(1 - f_{c\mathbf{k}'})N_{\mathbf{q}} + 1 - f_{c\mathbf{k}'}(1 - f_{v\mathbf{k}})N_{\mathbf{q}}] \delta(E_{v\mathbf{k}} - E_{c\mathbf{k}'} - \hbar \omega_{\mathbf{q}} + E_\lambda) \right\}. \end{aligned} \quad (50)$$

Note that Eq. (50) can also be used to calculate optical gain coefficient  $g$  which is simply the minus of the optical absorption coefficient, i.e.,  $g = -\alpha$ . The group velocity of photons is usually assumed to be  $v_g \approx c/n_r$  and  $\varepsilon = \varepsilon_0 n_r^2$ .  $n_r$  is the refractive index. The approximation of  $v_g \approx c/n_r$  simply assumes the completely linear dispersion relation of photons; in other words, all photons travel with the same speed inside the medium.

Equation (50) is a general expression for calculating  $\alpha_{\text{ind}}$ . It can be further simplified by assuming that the density of states at the conduction and valence band edges is parabolic and isotropic. If this is the case, Eq. (50) can be numerically calculated by changing the summations of the discrete

$\mathbf{k}$ -states into the integrations in the continuous  $\mathbf{k}$ -space momentum which can be further changed into the integrations of carrier energies above the band edges as

$$\begin{aligned} & \frac{2}{V^2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \cdots \delta(E_{v\mathbf{k}} - E_{c\mathbf{k}'} \pm \hbar \omega_{\mathbf{q}} + E_\lambda) \\ & = \frac{2N_{\text{val}}}{(2\pi)^6} \int d^3 \mathbf{k} \int d^3 \mathbf{k}' \cdots \delta \left( -\frac{\hbar^2 k^2}{2m_c} - \frac{\hbar^2 k'^2}{2m_v} \pm \hbar \omega_{ij} + E_\lambda - E_g \right) \\ & = N_{\text{val}} \frac{m_v \sqrt{2m_v}}{\hbar^3 \pi^2} \frac{m_c \sqrt{2m_c}}{2\hbar^3 \pi^2} \int_0^{E_{\text{max} \pm}} dE \sqrt{E(E_{\text{max} \pm} - E)} \cdots, \end{aligned} \quad (51)$$

where

$$E_{\max\pm} \equiv E_\lambda \pm \hbar\omega_{ij} - E_g, \quad (52)$$

and  $E = \hbar^2 k^2 / 2m_v$  in Eq. (51).  $m_c$  and  $m_v$  denote the density-of-state effective masses of conduction and valence bands, respectively,  $N_{\text{val}}$  represents the number of equivalent valleys at the conduction band edge. For example,  $N_{\text{val}} = 6$  for Si with the conduction band bottom along the  $\Delta$ -direction and locating near the X-point of the  $\mathbf{k}$ -space, while  $N_{\text{val}} = 4$  for Ge at the L-point.  $\hbar\omega_{ij}$  denotes the phonon energy involving the transition between the different valleys.  $E_g$  is the band gap energy between the band edges of conduction and valence bands which is shown distinguished from the gap energies  $E_{g1}$  and  $E_{g2}$  between the band edges and the intermediate states, as shown in Fig. 2.

In the following, the band structure near the band edges is assumed to be parabolic and isotropic, in which  $m_c$  and  $m_v$  are the effective masses of the density of states of conduction and valence bands, respectively. The constant energy surface for the conduction-band valleys at L and X points is basically an ellipsoid which can be characterized by a longitudinal effective mass  $m_l$  along the principle direction and a transverse effective mass  $m_t$  transverse the principle direction towards the conduction band edge. Hence, the effective masses of the density of states of conduction bands is  $m_c = (m_l m_t^2)^{1/3}$ . Silicon has six lowest equivalent valleys at points along the  $\Delta$  direction distance from the X-points by  $0.15(2\pi/a)$ . Germanium has four lowest equivalent valleys are at the L-points. On the other hand, the effective mass of the density states of the valence band can be obtained from the heavy- and light-hole effective masses as  $m_v = (m_{\text{hh}}^{3/2} + m_{\text{lh}}^{3/2})^{2/3}$  by assuming that only the heavy- and light-hole valence bands with isotropic and parabolic energy-momentum relations are considered in the theoretical model with effective masses of  $m_{\text{hh}}$  and  $m_{\text{lh}}$ , respectively.

In this work, the calculations use parabolic band approximations around the minimum of conduction bands. The conduction band edges at the valleys near the X-points along the  $\Delta$ -direction and the valleys at the L-points are fairly parabolic. Nonetheless, the direct gap at the  $\Gamma$ -point is less so. If this is the case, another non-parabolic factor  $\alpha$  can be introduced to account for the non-parabolic effects.<sup>1</sup> However, this only complicates the calculation results. Alternatively, the real band structures from pseudo potential or density-function-theory (DFT) calculations can be employed to resolve this issue, but these calculations will resort to a fully numerical procedure in Eq. (50), rather than employing the explicit formula provided in the following.

With some further elaborate derivations, Eq. (50) can be transformed into explicit formulas for calculating the absorption coefficient of indirect interband transition as

$$\alpha_{\text{ind}} = \frac{2(m_c m_v)^{3/2} N_{\text{val}}}{v_g \pi^3 \hbar^7} |M_{ij}|^2 \cdot \left[ \frac{|M_{\lambda 1}|^2 I_+}{|E_{g1} - E_\lambda - i\Gamma_1|^2} + \frac{|M_{\lambda 1}|^2 I_-}{|E_{g1} - E_\lambda - i\Gamma_1|^2} + \frac{|M_{\lambda 2}|^2 I_+}{|E_{g2} - E_\lambda + i\Gamma_2|^2} + \frac{|M_{\lambda 2}|^2 I_-}{|E_{g2} - E_\lambda + i\Gamma_2|^2} \right], \quad (53)$$

$$I_+ = \int_0^{E_{\max+}} dE \sqrt{E(E_{\max+} - E)} \{f_v(E)[1 - f_{c+}(E)]N_q - f_{c+}(E)[1 - f_v(E)](N_q + 1)\}, \quad (54)$$

$$I_- = \int_0^{E_{\max-}} dE \sqrt{E(E_{\max-} - E)} \{f_v(E)[1 - f_{c-}(E)](N_q + 1) - f_{c-}(E)[1 - f_v(E)]N_q\}, \quad (55)$$

$$f_v(E) = 1 - \left\{ \exp \left[ \frac{E - (E_v - E_{\text{Fv}})}{k_B T} \right] + 1 \right\}^{-1}, \quad (56)$$

$$f_{c\pm}(E) = \left\{ \exp \left[ \frac{-E + E_\lambda \pm \hbar\omega_{ij} - E_g - (E_{\text{Fc}} - E_c)}{k_B T} \right] + 1 \right\}^{-1}, \quad (57)$$

$$N_q = \left[ \exp \left( \frac{\hbar\omega_{ij}}{k_B T} \right) - 1 \right]^{-1}. \quad (58)$$

Usually, the effects of occupied/unoccupied states resulting from the electrons distribution function are not considered in the calculation of the optical absorption coefficient, that is, the initial states are assumed to be fully occupied, while the final state completely unoccupied, i.e.,  $f_v(E) = 1$  and  $f_{c\pm}(E) = 0$  in Eqs. (56) and (57), respectively. If this is the case, the processes 5, 6, 7, and 8 in Fig. 2 can be neglected in the calculation of the optical absorption coefficient. Hence, the integration can be explicitly calculated as

$$\int_0^{E_{\max\pm}} dE \sqrt{E(E_{\max\pm} - E)} = \frac{\pi E_{\max\pm}^2}{8}. \quad (59)$$

It has been argued that the interaction matrix elements,  $|M_{\lambda 1}|$  and  $|M_{\lambda 2}|$  in Eqs. (46) and (47) which represent the electron-photon interaction matrices at  $E_{g1}$  and  $E_{g2}$ , respectively, can be approximately assumed to be the same in the vicinity of the indirect band gap.<sup>15</sup> Furthermore,  $\Gamma_1 = \Gamma_2 = \Gamma$  is also assumed for simplicity. In short, if  $|M_{\lambda 1}| = |M_{\lambda 2}| = |M_\lambda|$  and  $\Gamma_1 = \Gamma_2 = \Gamma$  are assumed, for a specific type of intervalley-phonon interaction, the optical absorption coefficient can be calculated as

$$\alpha_{\text{ind}} = \alpha_{\text{ind0}} \frac{E_g}{E_\lambda} \left[ \frac{(E_\lambda - E_g + \hbar\omega_{ij})^2 N_q}{|E_{g1} - E_\lambda - i\Gamma|^2} \text{H}(E_\lambda - E_g + \hbar\omega_{ij}) + \frac{(E_\lambda - E_g - \hbar\omega_{ij})^2 (N_q + 1)}{|E_{g1} - E_\lambda - i\Gamma|^2} \text{H}(E_\lambda - E_g - \hbar\omega_{ij}) + \frac{(E_\lambda - E_g + \hbar\omega_{ij})^2 N_q}{|E_{g2} - E_\lambda + i\Gamma|^2} \text{H}(E_\lambda - E_g + \hbar\omega_{ij}) + \frac{(E_\lambda - E_g - \hbar\omega_{ij})^2 (N_q + 1)}{|E_{g2} - E_\lambda + i\Gamma|^2} \text{H}(E_\lambda - E_g - \hbar\omega_{ij}) \right], \quad (60)$$

with  $\alpha_{\text{ind0}}$  defined free from  $E_\lambda$ -dependent by

$$\alpha_{\text{ind0}} = \frac{e^2 m_c^{3/2} m_v^{3/2} N_{\text{val}} p_{\text{cv}}^2 D_{ij}^2}{16\pi^2 \hbar^3 m_0^2 \epsilon_0 n_r \rho_L E_g \hbar\omega_{ij}}, \quad (61)$$

where  $H(x)$  denotes the Heaviside unit step function. Equation (60) is exactly identical to the expression given by Ridley<sup>1</sup> but with different notations except the damping factor  $\Gamma$  and the last two terms involved with the energy gap  $E_{g2}$  are omitted by the assumption that  $E_{g1} \ll E_{g2}$ . This omission has also been discussed by Ridley. Since  $E_{g\Gamma} = 3.4$  eV for Si and  $E_{g\Gamma} = 0.81$  eV for Ge,  $E_{g\Delta} \approx 4$  eV for Si and  $E_{gL} \approx 4$  eV Ge (as suggested by Ridley), the omission of  $E_{g2}$  terms in Eq. (60) is indeed a rather reasonable approximation for Ge, but not for the case of Si. Therefore, all these 4 terms in Eq. (60) will be retained for calculating the Si absorption coefficient in the following. The reason for keeping all 4 terms in Eq. (60) (i.e., all 8 processes in Fig. 2) will be verified in the following results.

Apparently, comparing the formulas of Eq. (60) with the conventional formula of Eq. (2), the conventional formula neglects two factors in calculating the relation between the absorption coefficient and photon energy  $\alpha_{\text{ind}}(E_\lambda)$ . One is the electron-photon interaction matrix that is proportional to the inverse of photon energy, i.e.,  $|M_\lambda|^2 \propto 1/E_\lambda$ . The other is the denominators of  $1/|E_{g1} - E_\lambda - i\Gamma|^2$  and  $1/|E_{g2} - \hbar\omega_\lambda + i\Gamma|^2$  in Eq. (60). It will be demonstrated in the following discussion, neglecting the fact these two factors tend to overestimate the contribution of indirect transition in absorption coefficients if  $E_\lambda - E_g$  becomes large.

### III. RESULTS AND DISCUSSION

After introducing the theoretical framework, the absorption coefficient of bulk crystalline intrinsic silicon will be calculated in the following. It should be particularly mentioned that although the theoretical framework provided by this work could be extended to discuss the case of doped Si, there are several complicated issues which need to be taken into consideration. The eigenstates determined by the dopants are no longer simple Bloch functions; hence, the interaction matrices presented in the Appendix will be different. Likewise, the density of states (e.g., the bandtailed states in a heavily doped Si) provided by the dopants will be different from that of Bloch electrons. In addition, dopants, like phonons, can provide extra momentum in impurity scattering for carriers to participate in and contribute to the light absorption/emission processes in indirect band-gap semiconductors. Furthermore, some subtle issues (e.g., the core effect<sup>1</sup>) associated with different types of impurities will further complicate the problems for heavily doped Si. As a result, this study will only focus on the case of intrinsic Si.

The physical parameters incurred from this theoretical model are listed in Table I. It should be reminded here that these parameters neither represent the exact and precise values, nor can be asserted as the only set of reasonable choice. These parameters are chosen to fit experimental data, such as Green's data and the data fitted with the RSS formula. It should be reminded here that the main purpose of this work is to provide a detailed theoretical framework for the calculation of optical absorption (and gain) coefficients for Si considering all processes involving electron-photon-phonon interactions. Since Green's data seem to be the only published and tabulated experimental data openly available,<sup>3,4</sup> they will be used as an

TABLE I. Physical parameters for calculating the absorption coefficient of bulk crystalline intrinsic silicon.

Physical parameters	Si
Indirect gap between $\Gamma$ and near X along $\Delta$ , $E_{\Gamma\Delta} = E_g$	1.1557 eV (at 0 K)
Indirect gap between $\Gamma$ and L, $E_{\Gamma L}$	2.5 eV
Direct gap at $\Gamma$ , $E_{g\Gamma}$	3.2 eV
Direct gap near X along $\Delta$ , $E_{g\Delta}$	4 eV
Direct gap at L, $E_{gL}$	4 eV
Number of valleys near X along $\Delta$ , $N_{\text{val}}$	6
Number of valleys at L, $N_{\text{val}}$	4
Longitudinal effective mass of the conduction band, $m_l$	0.98 $m_0$
Transverse effective mass of the conduction band, $m_t$	0.19 $m_0$
Effective mass of heavy holes, $m_{hh}$	0.49 $m_0$
Effective mass of light holes, $m_{lh}$	0.16 $m_0$
Energy parameter of the electron-photon interaction, $E_p$	25 eV
Reflective index, $n_r$	3.42
Material density, $\rho_L$	2.328 g/cm <sup>3</sup>
Energy of TA phonons, $\hbar\omega_{TA}$	18.27 meV
Deformation potential of TA phonons, $D_{TA}$	$8.8 \times 10^8$ eV/cm
Energy of TO phonons, $\hbar\omega_{TO}$	57.73 meV
Deformation potential of TA phonons, $D_{TO}$	$1.3 \times 10^9$ eV/cm
Damping factor, $\Gamma$	1.35 eV
Effective-mass factor for $E_{\Gamma L}$ indirect transition, $C_{\Gamma L}$	7
Effective-mass factor for $E_{g\Gamma}$ direct transition, $C_{g\Gamma}$	30
Temperature (carrier and lattice)	300 K

example to verify this theoretical framework. For other experimental results, this framework can also be applicable if the data are openly accessible.

Apparently, the explicit formulas derived from this theoretical model, i.e., Eqs. (23) and (60), are different from the conventional expressions of Eqs. (1) and (2). The discrepancy in the calculated results from these two different sets of formulas will be examined in the following. However, before embarking on any calculations, the conflicts and confusion regarding gap energies in the literature need to be clarified first. In this work, there are five gap energies which are relevant for silicon: indirect gap between the valence band  $\Gamma$ -point and near the conduction band X-point along the  $\Delta$ -direction  $E_{\Gamma\Delta}$  (i.e., the fundamental band gap  $E_g$ ), indirect gap between the conduction and  $\Gamma$ -point and the valence band L-point  $E_{\Gamma L}$ , direct gap at the  $\Gamma$ -point  $E_{g\Gamma}$ , direct gap near the X-point along the  $\Delta$ -direction  $E_{g\Delta}$ , and direct gap at the L-point  $E_{gL}$ . The RSS formula considers only three transitions for silicon: indirect transitions of two indirect gaps  $E_{\Gamma\Delta}$  and  $E_{\Gamma L}$ , and one direct transition of one direct gap  $E_{g\Gamma}$ . The direct transition of the two other direct gaps  $E_{g\Delta}$  and  $E_{gL}$  (about 4 eV both) is not included in the RSS formula, although their associated features are speculated to appear in Green's data. This discrepancy will be further illustrated and discussed in the following. As a result, in the RSS formula, energy states around these two direct gaps  $E_{g\Delta}$  and  $E_{gL}$  only act as intermediate states. Therefore,  $E_{g2} = E_{g\Delta}$  for indirect transition of  $E_{\Gamma\Delta}$  or  $E_{g2} = E_{gL}$  for indirect transition of  $E_{\Gamma L}$ . In both cases,  $E_{g1} = E_{g\Gamma}$ . The density of states associated with these three transitions for silicon (indirect transitions of two indirect gaps  $E_{\Gamma\Delta} = E_g$  and  $E_{\Gamma L}$ , and one direct transition of one direct gap  $E_{g\Gamma}$ ) is shown in Fig. 3.



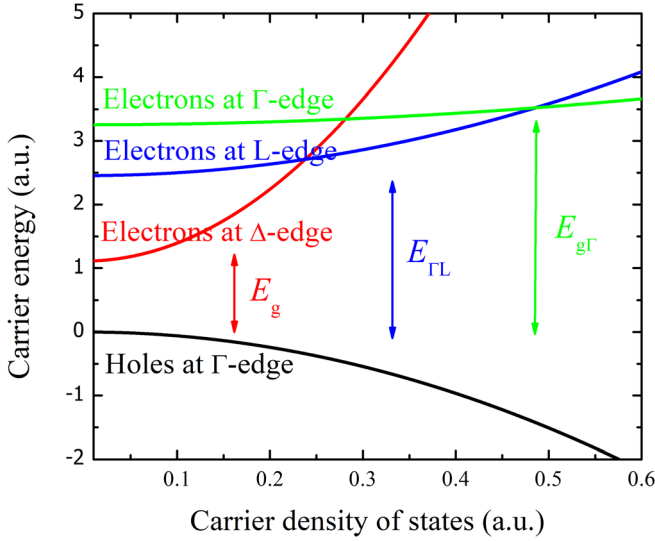


FIG. 3. Schematic diagram showing the density of states associated with the three transitions for silicon: indirect transitions of two indirect gaps  $E_{\Gamma\Delta} = E_g$  and  $E_{\Gamma L}$ , and one direct transition of one direct gap  $E_{g\Gamma}$ .

In addition, since some of the physical parameters, as far as the author knows, cannot be found in the published literature, for example, the effective masses for the conduction band of  $E_{\Gamma L}$  and  $E_{g\Gamma}$ , as a result, there is no choice but to introduce two factors to account for these yet-to-disclosed physical parameters: the effective-mass factor  $C_{\Gamma L}$  for  $E_{\Gamma L}$  indirect transition and the effective-mass factor  $C_{g\Gamma}$  for  $E_{g\Gamma}$  direct transition. In other words,  $C_{\Gamma L} \cdot m_c^{3/2}$  is used for  $E_{\Gamma L}$  indirect transition and  $C_{g\Gamma} \cdot m_c^{3/2}$  for  $E_{g\Gamma}$  direct transition.

Another issue regarding the exact nature of  $D_{ij}$  and  $\hbar\omega_{ij}$ , subjugated to the constraints of symmetry, is rather complicated by itself.<sup>1</sup> In order to compare the calculated results with the RSS formula, there is no choice but to expediently assume the TA and TO phonons to be the same as the RSS formula. However, it should be reminded again that these phonon modes neither can be claimed as the exact ones, nor can be asserted as the only set of reasonable choice.

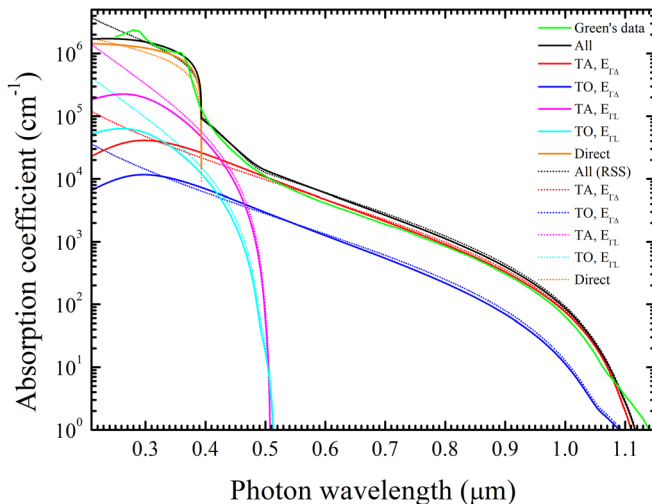


FIG. 4. Si absorption coefficients as a function of photon wavelength. The solid lines are the results from this work. The corresponding dotted lines are the results of the RSS fitting formula.

The silicon absorption coefficient calculated from Eqs. (23) and (60) as a function of photon wavelength and energy at 300 K is shown in Figs. 4 and 5, respectively. Several interesting features can be observed from the comparison among the calculated results, the RSS formula, and Green's data. Since the TA and TO phonon energies and the energy gaps are chosen to be the same with the RSS formula, the calculated results almost completely agree with the RSS formula except when photon energy is larger than 4 eV where the RSS fitting formula tends to overestimate the roles of indirect transition involving TA phonons. In other words, calculation from Eq. (2) tends to overestimate the absorption coefficients when the photon energy becomes larger. In addition, there is also a small discrepancy between the calculated results and the RSS formula around 3.2 eV (the onset of the direct transition) which simply illustrates the difference between the use of Eq. (1) in the RSS formula and Eq. (19) in this work.

It can be observed from the results in Figs. 4 and 5 that several features in Green's data cannot be well described from the RSS formula: (1) absorption with wavelengths larger than 1.1 μm; (2) the energy of the onset of the direct transition at 3.2 eV; (3) the linear exponential absorption feature around 3.2 eV; (4) the small absorption peak at 3.5 eV; and (5) the distinct absorption peak around 4 eV.

The obvious difference for the absorption near the fundamental band gap between the Green's data and the RSS formula can be further illustrated in Fig. 6. It can be conjectured that this discrepancy results from the parameters of phonon energy  $\hbar\omega_{ij}$  and the associated the interaction strength of the deformation potential  $D_{ij}$ . Therefore, the silicon absorption coefficient is re-calculated with the modifications of parameters as:  $\hbar\omega_{TA} = 17$  meV,  $\hbar\omega_{TO} = 65$  meV,  $D_{TA} = 6.8 \times 10^8$  eV/cm, and  $D_{TO} = 2.2 \times 10^9$  eV/cm. The results are shown in Fig. 7 in which Green's data can be fitted more accurately by this set of parameters. Nevertheless, a small discrepancy still persists between 1.0 to 1.1 eV. This might be due to some contributions from the intervalley or intravalley free carrier absorption.<sup>17</sup>

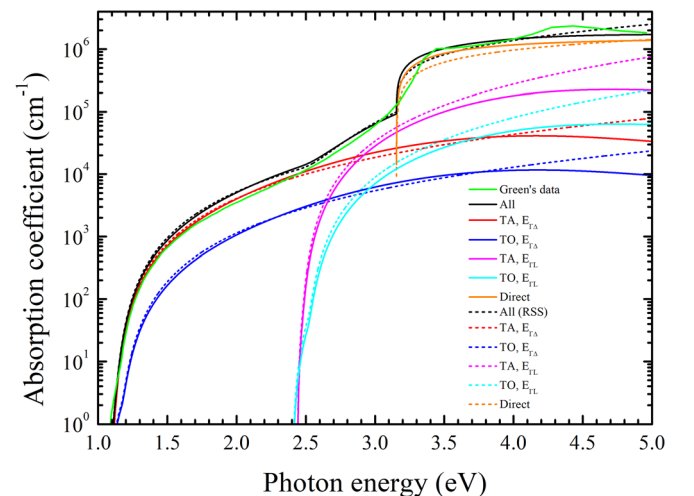


FIG. 5. Si Absorption coefficients as a function of photon energy. The solid lines are the results from this work. The corresponding dotted lines are the results of the RSS fitting formula. The green line is Green's data.

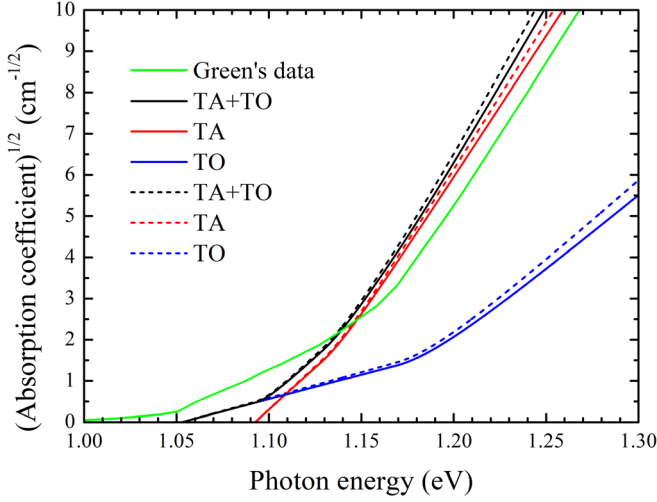


FIG. 6. Square root of the Si absorption coefficient as a function of photon energy. The solid lines are the results from this work. The corresponding dotted lines are the results of the RSS fitting formula. The green line is Green's data.

Since the formulas of Eqs. (23) and (60) are based on the physical model, it would be more sensible to adjust physical parameters according to different physical conditions. With these modified parameters and an additional  $E_{g\Gamma} = 3.3$  eV, Si absorption coefficients are re-calculated. The calculated results are shown in Figs. 8 and 9. The overall agreement between the calculated results and Green's data is rather well, except for the linear exponential absorption feature around 3.2 eV, the absorption peak at 3.5 eV, and the absorption peak around 4 eV. The absorption peak that appears above 4 eV in Green's data is speculated to be from the results of the direct transition of the two direct gaps  $E_{g\Delta}$  and  $E_{gL}$  (about 4 eV both).

The necessity to include the damping factor  $\Gamma$  which is neglected by Ridley<sup>1</sup> can be seen from the results in Fig. 10. Even all the eight processes are incorporated into the Ridley formula, the singular feature around  $E_{g\Gamma} = 3.3$  eV

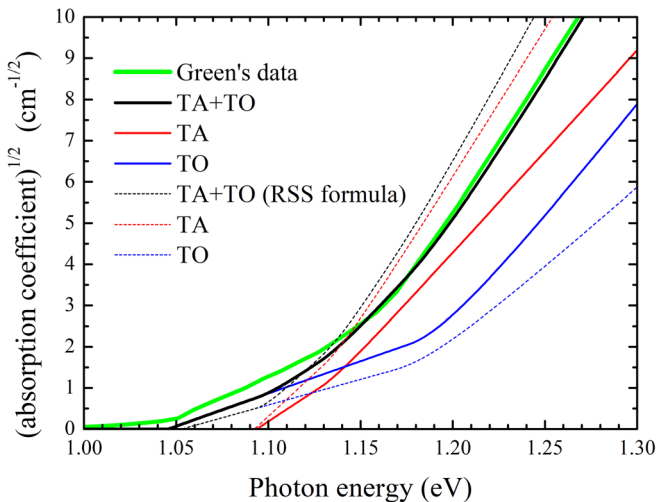


FIG. 7. Square root of the Si absorption coefficients as a function of photon energy with the modifications of parameters as:  $\hbar\omega_{TA} = 17$  meV,  $\hbar\omega_{TO} = 65$  meV,  $D_{TA} = 6.8 \times 10^8$  eV/cm, and  $D_{TO} = 2.2 \times 10^9$  eV/cm. The solid lines are the results from this work. The corresponding dotted lines are the results of the RSS fitting formula. The green line is Green's data.

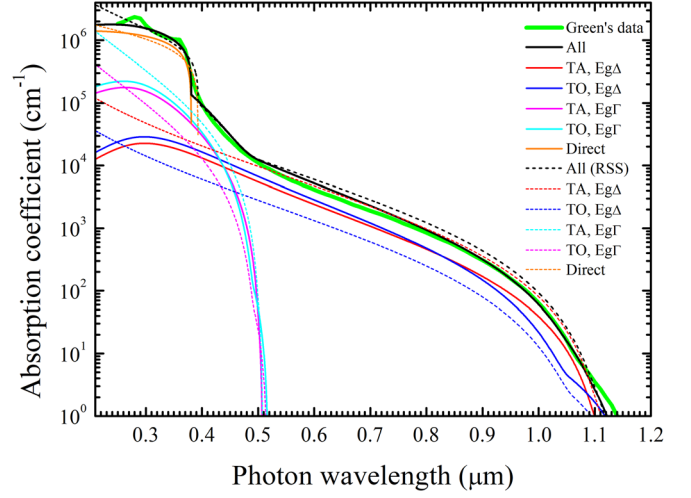


FIG. 8. Si absorption coefficients as a function of photon wavelength with the modifications of parameters as:  $\hbar\omega_{TA} = 17$  meV,  $\hbar\omega_{TO} = 65$  meV,  $D_{TA} = 6.8 \times 10^8$  eV/cm,  $D_{TO} = 2.2 \times 10^9$  eV/cm,  $E_{g\Gamma} = 3.3$  eV, and  $C_{TL} = 10$ . The solid lines are the results from this work. The corresponding dotted lines are the results of the RSS fitting formula. The green line is Green's data.

and  $E_{g\Delta} = E_{gL} = 4$  eV will appear to be erroneous and therefore, the Ridley formula will not be useful in this case.

The essential difference between this theoretical model and the RSS formula is that this model can be used to examine the different contributions from 8 individual processes described in Fig. 2. The results are shown in Fig. 11. Obviously, all 8 processes contribute to the overall silicon absorption coefficient but with different magnitudes. This just concludes the necessity of including all 8 possible routes of absorption or emission of photons and phonons into the calculation of Si absorption coefficients.

The unique feature in the theoretical model presented here is the inclusion of the state occupied/unoccupied effect in Eqs. (53)–(58) which is free from the conventional assumption with fully occupied states in the valence band and completely unoccupied states in the conduction band. If these effects are

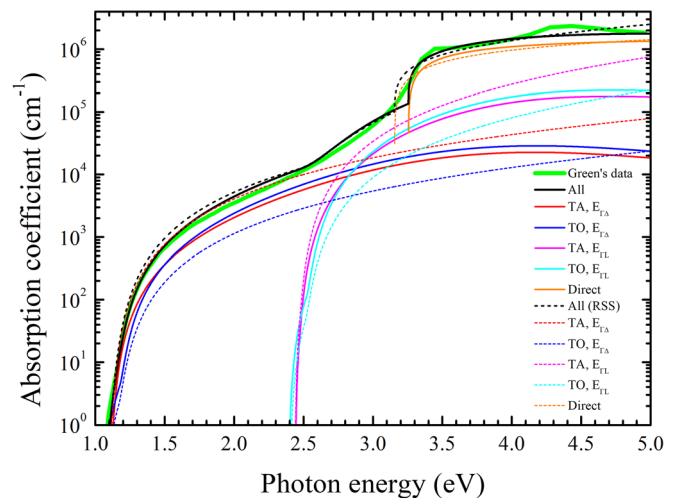


FIG. 9. Si absorption coefficients as a function of photon energy with the modifications of parameters as:  $\hbar\omega_{TA} = 17$  meV,  $\hbar\omega_{TO} = 65$  meV,  $D_{TA} = 6.8 \times 10^8$  eV/cm,  $D_{TO} = 2.2 \times 10^9$  eV/cm,  $E_{g\Gamma} = 3.3$  eV, and  $C_{TL} = 10$ . The solid lines are the results from this work. The corresponding dotted lines are the results of the RSS fitting formula. The green line is Green's data.

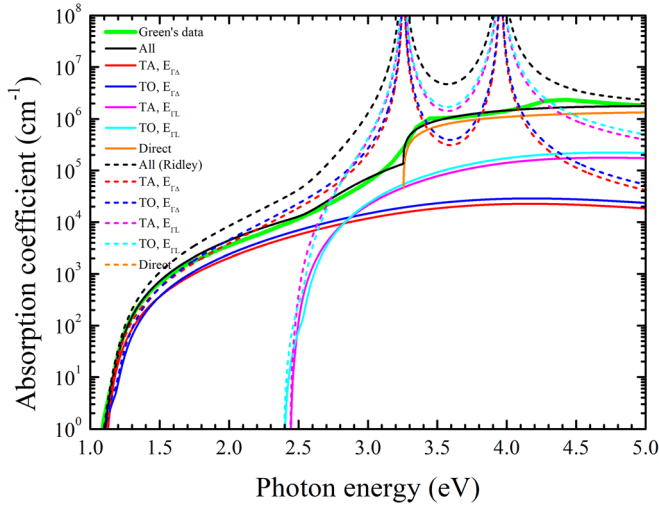


FIG. 10. Si absorption coefficients as a function of photon energy with the modifications of parameters as in Fig. 8. The solid lines are the results from this work. The corresponding dotted lines are the results of the Ridley formula. The green line is Green's data.

taken into account, absorption coefficients as a function of carrier number density and temperature can therefore be investigated. In an operating photovoltaic device, its carrier number density and temperature will certainly vary with different operating conditions. As a result, it is questionable to treat any physical quantity as a constant value if it is strongly dependent on carrier number density and temperature.

The effects of occupied/unoccupied states on absorption coefficients are calculated from our theoretical model of Eqs. (53)–(58). The results are shown in Fig. 12. The results for the energy separation of quasi-Fermi levels between conduction-band electrons and valence-band holes (i.e.,  $E_{Fc} - E_{Fv}$ ) between 0 to 1 eV are almost indistinguishable. In other words, the state occupied/unoccupied effect is almost negligible in Si absorption coefficients for  $E_{Fc} - E_{Fv}$  below 1 eV. The results also show that if  $E_{Fc} - E_{Fv}$  is larger than 1.15 eV, Si absorption coefficients in a certain spectral range become negative, i.e., they become optical gains. Outside these gain regions, absorption coefficients are also reduced

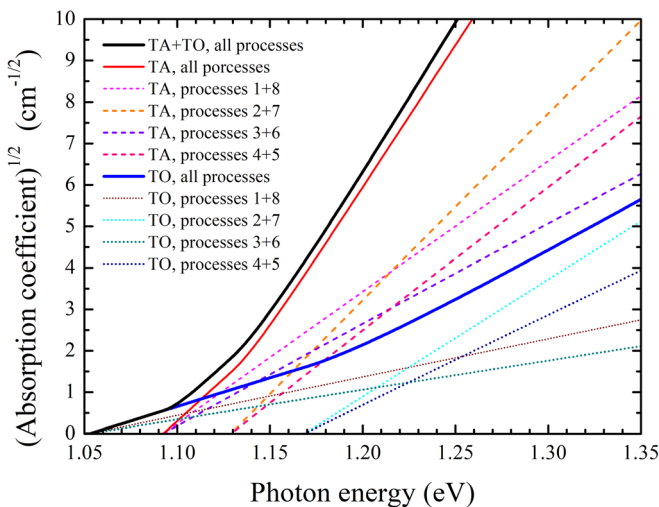


FIG. 11. Square root of Si absorption coefficients as a function of photon energy from the contribution of each individual process defined in Fig. 2.

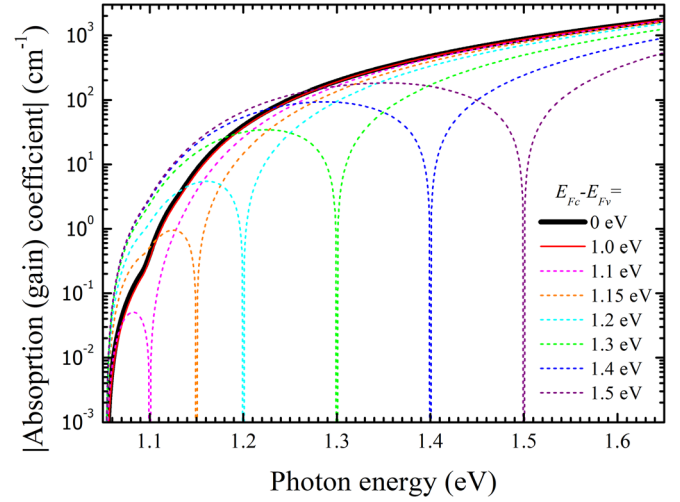


FIG. 12. Absolute value of Si absorption (or gain) coefficients as a function of photon energy at different separation energy of quasi-Fermi levels between electrons in the conduction band and holes in the valence band. The results for  $E_{Fc} - E_{Fv}$  between 0 to 1 eV are almost indistinguishable. In other words, the state occupied/unoccupied effect is almost negligible in Si absorption coefficients for  $E_{Fc} - E_{Fv}$  below 1 eV.

due to the state occupied/unoccupied effect in which the occupied state blocks the accessible route for optical absorption. The results show that an optical gain can be achieved if  $E_{Fc} - E_{Fv}$  is larger than 1.15 eV. However, the magnitude of this calculated Si optical gain coefficient is two or three orders of magnitude smaller than that of direct-band-gap semiconductors, such as GaAs (as shown in the results in Fig. 13). In short, this theoretical model and the associated formulas presented in this work can be used to calculate optical gain coefficients of indirect-band-gap semiconductors;<sup>18</sup> nevertheless, such an issue is certainly outside the scope of this work and will not be discussed here for simplicity.

#### IV. CONCLUSION

In this work, a theoretical model for calculating the optical absorption coefficients is described and presented in detail. Photon absorption from direct and indirect interband transitions

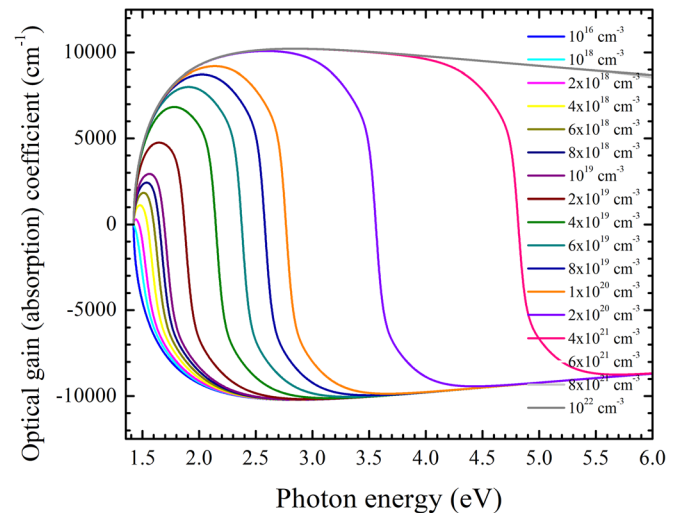


FIG. 13. GaAs gain (or absorption) coefficients as a function of photon energy at different carrier densities.

is calculated by the first- and second-order time-dependent perturbation theory of quantum mechanics, respectively, and also by considering the effects of occupied/unoccupied carrier states. The indirect interband transition incorporates all eight possible routes of absorption or emission of photons and phonons. The similarity and difference between this theoretical work and Ridley's work are examined and illustrated. Explicit formulas derived from this theoretical model are used to calculate the Si absorption coefficient. The agreements and discrepancies among the calculated results, the RSS formula, and Green's data are investigated and discussed.

Compared with the theoretical model and the associated formulas presented in this work, several results can be concluded and listed as follows:

- (1) The conventional formula for direct interband transition of Eq. (1) loses its credibility for cases of  $E_\lambda > 2E_g$ .
- (2) The conventional formula for indirect interband transition of Eq. (2) tends to overestimate the contribution of indirect transition in absorption coefficients if  $E_\lambda - E_g$  becomes large.
- (3) Conventional formulas of Eqs. (1) and (2), and thus the RSS formula cannot be used to investigate each individual process of absorption/emission of photons and phonons. This work demonstrates that all 8 possible routes of absorption or emission of photons and phonons should be considered for calculating Si absorption coefficients.
- (4) Conventional formulas of Eqs. (1) and (2) and thus the RSS formula do not consider the state occupied/unoccupied effect, they cannot be used to study the variations of the absorption coefficients at different carrier number densities or carrier temperatures. Nor can they be used to study the conditions for achieving optical gain.
- (5) For materials with absorption coefficients strongly dependent on carrier number density or carrier temperature, it is certainly questionable to use conventional formulas of Eqs. (1) and (2) to study the effects of light absorption on the performance of photovoltaic devices.

## APPENDIX: THE INTERACTION MATRICES OF ELECTRON-PHONON AND ELECTRON-PHOTON INTERACTIONS

The interaction matrices of electron-phonon and electron-photon interactions will be briefly outlined in this Appendix to serve the purposes of the definitions of related physical quantities and their associated notations used in this work.

The Hamiltonian of a Bloch electron in a crystal is given as

$$H = -\frac{\hbar^2}{2m_0} \nabla^2 + U(\mathbf{r}). \quad (\text{A1})$$

Here,  $m_0$  is the electron mass. The potential energy is spatially periodic as  $U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r})$ ,  $\mathbf{R}$  is a vector in the Bravais lattice of the real space ( $\mathbf{r}$ -space). The eigenstates  $|n\mathbf{k}\rangle$  and eigenenergy  $E_{n\mathbf{k}}$  that resulted from this Hamiltonian can be expressed in the Dirac notation as

$$H|n\mathbf{k}\rangle = E_{n\mathbf{k}}|n\mathbf{k}\rangle, \quad (\text{A2})$$

where  $n$  denotes the indices of energy bands and  $\mathbf{k}$  is the crystal momentum. The eigenstate  $|n\mathbf{k}\rangle$  can be represented by a normalized wave function (i.e., Bloch function) as

$$\langle \mathbf{r} | n\mathbf{k} \rangle = \psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \quad (\text{A3})$$

where  $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$ .  $V$  is the normalization volume of electrons. The normalization of the wave function in Eq. (A3) requires

$$\int_{\text{unit cell}} d^3\mathbf{r} u_{n\mathbf{k}}^*(\mathbf{r}) u_{n\mathbf{k}}(\mathbf{r}) = v_{\text{cell}}, \quad (\text{A4})$$

where  $v_{\text{cell}}$  is the volume of a unit cell in the Bravais lattice. It is interesting to know that the periodicity of a crystal (i.e., the Bravais lattice) is not present in the wave function  $\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) \neq \psi_{n\mathbf{k}}(\mathbf{r})$  but in its probability as  $|\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R})|^2 = |\psi_{n\mathbf{k}}(\mathbf{r})|^2$  which manifests the delocalized nature of a Bloch electron. In fact, the periodicity of a crystal is present in the eigenstates  $|n, \mathbf{k} + \mathbf{K}\rangle = |n, \mathbf{k}\rangle$  and eigenenergy  $E_{n, \mathbf{k} + \mathbf{K}} = E_{n, \mathbf{k}}$  of its Bloch electrons. They have the periodicity of the reciprocal lattice in the momentum space ( $\mathbf{k}$ -space). As a result, all the notions of the band structure  $E_{n\mathbf{k}}$  are normally discussed within the first Brillouin zone of the  $\mathbf{k}$ -space (generally the Wigner-Seitz cell). The band edges are normally located at three highly symmetric points in the  $\mathbf{k}$ -space: the  $\Gamma$ -point at  $2\pi/a(0, 0, 0)$ , the L-point at  $2\pi/a(1/2, 1/2, 1/2)$  along the  $(1, 1, 1)$   $\Delta$ -axis, and the X-point at  $2\pi/a(1, 0, 0)$  along the  $(1, 0, 0)$   $\Delta$ -axis for diamond and zincblende crystal structures.

The quantization of the displacement field of phonons  $\mathbf{u}(\mathbf{r}, t)$  which describes the lattice vibration (i.e., phonons) can be expressed as

$$\mathbf{u}(\mathbf{r}, t) = \sum_{\mathbf{q}} \hat{\mathbf{e}}_{\mathbf{q}} \sqrt{\frac{\hbar}{2NM\omega_{\mathbf{q}}}} \left[ \hat{a}_{\mathbf{q}} e^{i(\mathbf{q} \cdot \mathbf{r} - \omega_{\mathbf{q}} t)} + \hat{a}_{\mathbf{q}}^\dagger e^{-i(\mathbf{q} \cdot \mathbf{r} - \omega_{\mathbf{q}} t)} \right]. \quad (\text{A5})$$

Here,  $\hat{\mathbf{e}}_{\mathbf{q}} = \mathbf{u}/|\mathbf{u}|$  denotes the unit vector of displacement direction.  $N$  is the number of unit cell in a crystal.  $M$  is the total mass in the case of acoustic modes (or the reduced mass in the case of long-wavelength optical modes) of the atoms in a unit cell. Usually,  $NM = \rho V$  where  $\rho$  is material mass density and  $V$  is the material volume.  $\omega_{\mathbf{q}}$  is the vibration frequency which is a function of the vibration wave vector  $\mathbf{q}$  (i.e., the dispersion relation).  $\hat{a}_{\mathbf{q}}$  and  $\hat{a}_{\mathbf{q}}^\dagger$  denote the annihilation and creation operators that resulted from field quantization. The quantum states of phonons are usually represented by the Fock states (i.e., number states) as

$$|N_{\mathbf{q}_1}\rangle |N_{\mathbf{q}_2}\rangle \cdots |N_{\mathbf{q}_i}\rangle \cdots = |N_{\mathbf{q}_1}, N_{\mathbf{q}_2}, \dots, N_{\mathbf{q}_i}, \dots\rangle = |\cdots N_{\mathbf{q}} \cdots\rangle, \quad (\text{A6})$$

where  $N_{\mathbf{q}}$  and  $|N_{\mathbf{q}}\rangle$  is the eigenvalue (also the expectation value) and eigenstate of the number operator  $\hat{N}_{\mathbf{q}} = \hat{a}_{\mathbf{q}}^\dagger \hat{a}_{\mathbf{q}}$ . If the electrons are not treated with the method of second quantization, the quantum states of the system of Bloch electrons and phonons can be represented as

$$|\text{system}\rangle = |n\mathbf{k}\rangle |\cdots, N_{\mathbf{q}}, \dots\rangle. \quad (\text{A7})$$



The absorption and emission of a phonon result from the annihilation operator  $\hat{a}_{\mathbf{q}}$  and the creation operator  $\hat{a}_{\mathbf{q}}^\dagger$  in the interaction matrix of  $H_{\text{int}}$  will be

$$\langle \cdots | H_{\text{int}} | \cdots \rangle = \begin{cases} \langle \cdots, N_{\mathbf{q}} - 1, \dots | \hat{a}_{\mathbf{q}} | \cdots, N_{\mathbf{q}}, \dots \rangle \propto \sqrt{N_{\mathbf{q}}}, & \text{absorption} \\ \langle \cdots, N_{\mathbf{q}} + 1, \dots | \hat{a}_{\mathbf{q}}^\dagger | \cdots, N_{\mathbf{q}}, \dots \rangle \propto \sqrt{N_{\mathbf{q}} + 1}, & \text{emission.} \end{cases} \quad (\text{A8})$$

Since the electron-phonon interaction  $H_{\text{int}}$  contains no operators on the eigenstates of electrons, the interaction matrix can therefore be expressed as

$$|\langle n' \mathbf{k}' | H_{\text{int}} | n \mathbf{k} \rangle|^2 = \begin{cases} |M_{n'n\mathbf{q}}|^2 N_{\mathbf{q}} I_{nn'}^2(\mathbf{k}, \mathbf{k}', \mathbf{K}) \delta_{\mathbf{k}, \mathbf{k}' - \mathbf{q} + \mathbf{K}}, & \text{absorption} \\ |M_{n'n\mathbf{q}}|^2 (N_{\mathbf{q}} + 1) I_{nn'}^2(\mathbf{k}, \mathbf{k}', \mathbf{K}) \delta_{\mathbf{k}, \mathbf{k}' + \mathbf{q} + \mathbf{K}}, & \text{emission,} \end{cases} \quad (\text{A9})$$

where  $\mathbf{K}$  is a vector of the reciprocal lattice. It will be a normal process if  $\mathbf{K} = 0$ ; otherwise, an Umklapp process if  $\mathbf{K} \neq 0$ . The notations associated with the Umklapp processes will be deliberately suppressed for simplicity. However, it should be reminded that the intervalley scatterings can be Umklapp processes.  $\delta_{\mathbf{k}, \mathbf{k}'}$  represents the Kronecker delta symbol, where  $\delta_{\mathbf{k}, \mathbf{k}'} = 1$  for  $\mathbf{k} = \mathbf{k}'$  and zero otherwise.  $I_{nn'}(\mathbf{k}, \mathbf{k}', \mathbf{K})$  is the overlap integral defined by

$$I_{nn'}(\mathbf{k}, \mathbf{k}', \mathbf{K}) = \int_{\text{unit cell}} d^3 \mathbf{r} u_{n'\mathbf{k}'}^*(\mathbf{r}) u_{n\mathbf{k}}(\mathbf{r}) e^{i\mathbf{K} \cdot \mathbf{r}}. \quad (\text{A10})$$

An interaction element is further defined as  $|M_{n'n}|^2 = |M_{n'n\mathbf{q}}|^2 V_n$  which will be benefited from its volume-independent expression.

Unlike photons, phonons provide substantial amounts of momentum for electrons in electron-phonon interactions. The requirement of  $\delta_{\mathbf{k}, \mathbf{k}' + \mathbf{q} \pm \mathbf{K}}$  certainly becomes enormously complicated where both electrons band structure  $E_{n\mathbf{k}}$  and phonons dispersion relation  $\omega_{\mathbf{q}}$  need to be known precisely. As a result, it is a common practice to keep the band structure  $E_{n\mathbf{k}}$  intact but to simplify the dispersion relation  $\omega_{\mathbf{q}}$  in electron-phonon interactions. For electron-phonon interactions which involve zone center phonons (such as polar optical phonons, deformation potential optical phonons, deformation potential acoustic phonons, and piezoelectric acoustic phonons), it is generally assumed that the Einstein approximation for optical phonons is  $\omega_{\mathbf{q}} = \omega_0$  (i.e.,  $\mathbf{q}$ -independent) and the Debye approximation for acoustic phonons is  $\omega_{\mathbf{q}} = v_s q$  where  $v_s$  is the sound speed of acoustic phonons. On the other hand, for electron-phonon interactions which involve zone edge phonons, such as intervalley scatterings, these intervalley phonons are assumed to be  $\mathbf{q}$ -independent as  $\omega = \omega_{ij}$  in which the  $i$  and  $j$  denote the indices of the valleys in the band structure.

Since the intervalley scatterings mainly result from the deformation potential of the zone-edge optical or acoustic phonons with nearly  $\mathbf{q}$ -independent nature, electron-phonon interaction matrices are generally expressed in a form similar to the case of deformation potential of the zone-center optical phonons (also nearly  $\mathbf{q}$ -independent) as

$$|M_{ij}|^2 = |M_{ij\mathbf{q}}|^2 V_n = \frac{D_{ij}^2 \hbar^2}{2\rho_L \hbar \omega_{ij}}. \quad (\text{A11})$$

For Si with the conduction band edge located at near the X-point along the  $\Delta$ -direction, it will involve the intervalley of  $D_{\Gamma\Delta}$  and  $\hbar\omega_{\Gamma\Delta}$ . Similarly, for Ge with the conduction band edge located at the L-point, it will involve the intervalley of  $D_{\Gamma L}$  and  $\hbar\omega_{\Gamma L}$ . The exact nature of  $D_{ij}$  and  $\hbar\omega_{ij}$  is a rather complicated issue itself and is always subjugated to the constraints of symmetry. The details are well described in Ridley's work<sup>1</sup> and thus will not be repeated here.

The interaction Hamiltonian  $H_{\text{int}}$  between electrons and photons comprises of two parts as

$$H_{\text{int}} = -\frac{e}{m_0} \mathbf{A} \cdot \mathbf{p} + \frac{e^2}{2m_0} \mathbf{A}^2 = H_{\mathbf{A} \cdot \mathbf{p}} + H_{\mathbf{A}^2}. \quad (\text{A12})$$

$H_{\mathbf{A}^2}$  is associated with two-photon processes which will not be discussed in this work. The magnetic potential of photons  $\mathbf{A}$  in Eq. (A12) is given by its quantization form as

$$\mathbf{A}(\mathbf{r}, t) = \sum_{\mathbf{q}} \hat{\mathbf{e}}_{\mathbf{q}} \sqrt{\frac{\hbar}{2\varepsilon\omega_{\mathbf{q}}V_{\lambda}}} [\hat{a}_{\mathbf{q}} e^{i(\mathbf{q} \cdot \mathbf{r} - \omega_{\mathbf{q}}t)} + \hat{a}_{\mathbf{q}}^\dagger e^{-i(\mathbf{q} \cdot \mathbf{r} - \omega_{\mathbf{q}}t)}]. \quad (\text{A13})$$

Here,  $\hat{\mathbf{e}}_{\mathbf{q}}$  is the unit vector indicating the direction of polarization and  $\varepsilon$  is the material permittivity.  $\hbar\omega_{\mathbf{q}}$  is the photon energy which is a function of the vibration wave vector  $\mathbf{q}$  (i.e., the dispersion relation).  $\hat{a}_{\mathbf{q}}$  and  $\hat{a}_{\mathbf{q}}^\dagger$  denote the annihilation and creation operators resulting from field quantization. If the momentum of photons, compared to electrons, is small enough to be neglected, i.e.,  $\mathbf{k}' = (\mathbf{k} \pm \mathbf{q}) \approx \mathbf{k}$ , then the following approximation (named as dipole approximation) can be applied:

$$\langle n' \mathbf{k}' | \hat{\mathbf{e}}_{\mathbf{q}} \cdot \mathbf{p} e^{i\mathbf{q} \cdot \mathbf{r}} | n \mathbf{k} \rangle \approx \langle n' \mathbf{k}' | \hat{\mathbf{e}}_{\mathbf{q}} \cdot \mathbf{p} | n \mathbf{k} \rangle. \quad (\text{A14})$$

As a result, the interaction matrices associated with  $H_{\mathbf{A} \cdot \mathbf{p}}$  becomes

$$|\langle n' \mathbf{k}' | H_{\mathbf{A} \cdot \mathbf{p}} | n \mathbf{k} \rangle|^2 = \begin{cases} |M_{\mathbf{q}}(\mathbf{k})|^2 N_{\mathbf{q}} \delta_{\mathbf{k}, \mathbf{k}'}, & \text{absorption} \\ |M_{\mathbf{q}}(\mathbf{k})|^2 (N_{\mathbf{q}} + 1) \delta_{\mathbf{k}, \mathbf{k}'}, & \text{emission,} \end{cases} \quad (\text{A15})$$

where

$$|M_{\mathbf{q}}(\mathbf{k})|^2 = \frac{\hbar^2 e^2}{2\varepsilon m_0^2 \hbar \omega_{\mathbf{q}} V_{\lambda}} |\hat{\mathbf{e}}_{\mathbf{q}} \cdot \mathbf{p}_{n'n\mathbf{k}}|^2, \quad (\text{A16})$$

with the momentum matrix element defined as

$$\mathbf{p}_{n'\mathbf{k}} = \langle u_{n'\mathbf{k}} | \mathbf{p} | u_{n\mathbf{k}} \rangle = \int_{\text{unit cell}} d^3\mathbf{r} u_{n'\mathbf{k}}^*(\mathbf{r}) \mathbf{p} u_{n\mathbf{k}}(\mathbf{r}). \quad (\text{A17})$$

For notation simplification, a volume-independent interaction matrices  $|M_\lambda|$  is preferred to be used in this work. In addition, the notation for wave vector  $\mathbf{q}$  is replaced by wave-length  $\lambda$  whenever possible in order to avoid the confusion from electron-phonon interactions

$$|M_\lambda|^2 \equiv |M_{\mathbf{q}}(\mathbf{k})|^2 V_\lambda = \frac{\hbar^2 e^2}{2\epsilon\hbar\omega_\lambda m_0^2} |\hat{\mathbf{e}}_\lambda \cdot \langle \mathbf{v}\mathbf{k} | \mathbf{p} | \mathbf{c}\mathbf{k} \rangle|^2. \quad (\text{A18})$$

The momentum matrix  $|\hat{\mathbf{e}}_\lambda \cdot \langle \mathbf{v}\mathbf{k} | \mathbf{p} | \mathbf{c}\mathbf{k} \rangle|^2$  can be calculated from first principles if the band structure is completely known. Alternatively, for bulk semiconductors incident with unpolarized light, the momentum matrix element is usually assumed to be anisotropic and  $\mathbf{k}$ -independent at the zone center of the  $\mathbf{k}$ -space and thus be simply characterized by an energy parameter  $E_p$  as

$$|\hat{\mathbf{e}}_\lambda \cdot \langle \mathbf{v}\mathbf{k} | \mathbf{p} | \mathbf{c}\mathbf{k} \rangle|^2 = p_{\text{cv}}^2 = \frac{m_0}{6} E_p. \quad (\text{A19})$$

In the case of a direct-band-gap material such as GaAs, the interband electron-photon interaction occurs at the  $\Gamma$  point, and this energy parameter can be further calculated by

$$E_p = \left( \frac{m_0}{m_c} - 1 \right) \frac{E_g(E_g + \Delta_{\text{so}})}{(E_g + 2\Delta_{\text{so}}/3)}, \quad (\text{A20})$$

where  $m_c$  is the effective mass of the conduction band at the  $\Gamma$ -point band edge,  $E_g$  is the band gap energy, and  $\Delta_{\text{so}}$  is the spin-orbit split-off energy. In fact, Eq. (A20) results from the  $\mathbf{k} \cdot \mathbf{p}$  theory for the conduction band where

$$E_{\mathbf{c}\mathbf{k}} = E_c + \frac{\hbar^2 k^2}{2m_0} + \frac{\hbar}{m_0} \mathbf{k} \cdot \langle u_{\mathbf{c}0} | \mathbf{p} | u_{\mathbf{c}0} \rangle + \frac{\hbar^2}{m_0^2} \sum_{n \neq c} \frac{|\mathbf{k} \cdot \langle u_{\mathbf{c}0} | \mathbf{p} | u_{n0} \rangle|^2}{E_c - E_n} = E_c + \frac{\hbar^2 k^2}{2m_c}. \quad (\text{A21})$$

Here,  $\langle u_{\mathbf{c}0} | \mathbf{p} | u_{\mathbf{c}0} \rangle \approx 0$  is usually assumed for the s-orbit nature of the  $\Gamma$ -point conduction band edge. If the problem is limited to four bands at the  $\Gamma$ -point band edge: conduction, heavy hole, light hole, and spin-orbit, then  $n = \text{hh}, \text{lh}$ , so in the summation notion of Eq. (A21); consequently,

$$\begin{aligned} & \frac{\hbar^2 k^2}{2m_0} + \frac{\hbar^2 k^2}{m_0^2} \\ & \times \left( \frac{|\langle u_{\mathbf{c}0} | \mathbf{p} | u_{\text{hh}0} \rangle|^2}{E_c - E_{\text{hh}}} + \frac{|\langle u_{\mathbf{c}0} | \mathbf{p} | u_{\text{lh}0} \rangle|^2}{E_c - E_{\text{lh}}} + \frac{|\langle u_{\mathbf{c}0} | \mathbf{p} | u_{\text{so}0} \rangle|^2}{E_c - E_{\text{so}}} \right) \\ & = \frac{\hbar^2 k^2}{2m_c}. \end{aligned} \quad (\text{A22})$$

Furthermore, from the mixing nature of the p-orbits at the  $\Gamma$ -point valence band edge, the following assumption can be presumably expected:

$$|\langle u_{\mathbf{c}0} | \mathbf{p} | u_{\text{lh}0} \rangle| \approx |\langle u_{\mathbf{c}0} | \mathbf{p} | u_{\text{so}0} \rangle| \approx |\langle u_{\mathbf{c}0} | \mathbf{p} | u_{\text{hh}0} \rangle| = p_{\text{cv}}. \quad (\text{A23})$$

With the definition regarding the band energies,  $E_c - E_{\text{hh}} = E_c - E_{\text{lh}} = E_g$  and  $E_c - E_{\text{so}} = E_g + \Delta E_{\text{so}}$ , Eq. (A22) thus becomes

$$p_{\text{cv}}^2 \left( \frac{1}{E_g} + \frac{1}{E_g} + \frac{1}{E_g + \Delta E_{\text{so}}} \right) = \frac{m_0}{2} \left( \frac{m_0}{m_c} - 1 \right), \quad (\text{A24})$$

which then yields the results for Eqs. (A19) and (A20). However, the approximation of Eq. (A23) is rather simplified. Details regarding the momentum matrix elements  $p_{\text{cv}}$  will not be discussed here.<sup>19</sup>

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