

Unified quantum field theory of light absorption by defect centers

Ze Cheng

Department of Physics, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

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Trapped electrons in crystals are responsible for many important effects on crystals: lattice relaxation, electron-ion correlation, lattice-frequency shift, and so on. These electron-phonon interaction effects cause peak shifts and give rise to various multiphonon structures in the absorption and emission spectra of trapped electrons. The present treatment for interactions of trapped electrons with a crystal does not include the standard second-quantized field theory, which neglects the quantum many-body effects of crystals. Therefore, up to now no universal light-absorption theory includes various effects of trapped electrons on crystals. For this reason, a unified, second-quantized field theory of optical absorption, which contains both linear and quadratic electron-phonon interactions is established. In this field theory we derive a universal, analytical spectral function of the absorption coefficient, which describes the whole absorption spectrum of an arbitrary color center. [S0163-1829(99)02547-3]

I. INTRODUCTION

Pure alkali halide crystals are transparent throughout the visible region of the spectrum. The crystals may be colored in a number of ways, for example, by the introduction of an excess of the metal atom. A color center is a lattice defect that absorbs visible light. A prototype of color center is the F center, which was suggested as an electron bound at a negative ion vacancy by de Boer in 1937.¹ The main absorption band of F centers is a strong, wide, bell-shaped band that lies in the visible region of the spectrum. In the same year, Pohl² recognized that the considerable widths of the characteristic absorption curves of F centers are caused by the coupling of the electronic motion in the F center to the ionic lattice.

Recently there has been a growing interest in developing color-center lasers.³ The motive is prompted by the realization of soliton propagation of picosecond pulses from a mode-locked color-center laser in an optical fiber.⁴ In the present optical communication systems, the transmitters all use coherent pulses of laser light and the transmission media are single-mode silica-glass fibers. There are two main physical effects that limit the transmission of pulses in optical fibers: loss and dispersion. Since the zero-dispersion wavelength is $1.32 \mu\text{m}$, this has become the wavelength of choice for optical fiber communication. However, typical commercial silica fibers have a minimum loss of 0.2 dB/km at the wavelength $1.55 \mu\text{m}$. Hasegawa pointed out that nonlinearity of the index of refraction could be used to compensate the pulse broadening effect of dispersion in low-loss optical fibers, i.e., soliton effects.⁵ To observe soliton effects in low-loss optical fibers, we have to work in the loss minimum at $1.55 \mu\text{m}$. Mode-locked color-center lasers are the only candidates capable of tuning over the wavelength region near $1.55 \mu\text{m}$. After color centers are optically excited by a pump source, their emission band is Stokes-shifted towards the infrared region from the absorption band in the visible region.

Although the basic mechanism underlying the absorption of color centers is clear, no quantitative theory of the absorption curves had been given. In 1950, Huang and Rhys ac-

quired in quantum-mechanical theory the first line-shape function of the main optical absorption band of F centers,⁶ but they only considered the linear interaction of the electron with longitudinal-optical phonons of a single frequency, leading to a discrete spectrum due to multiphonon transitions. In 1952, Lax first adopted the generating function method to generalize the Huang-Rhys work to all phonon modes, and introduced the moments of the absorption band, which can determine the values of theoretical parameters from experimental absorption band shapes.⁷ In 1953, O'Rourke made an artificial assumption that the photon-induced electronic transition accompanies a small change in the lattice vibration frequencies, and thereby he followed the approach of Lax to show variation of the frequency of the light-absorption maximum with temperature.⁸ In 1954, Kubo and Toyozawa developed a universal form of the theory of multiphonon transitions with the generating function method, the universal form that does not depend on a concrete physical model of color-center structures.⁹ With this theoretical form they discussed the shape of the absorption band and the probability for nonradiative transition of a trapped electron.

If the defect site is a center of inversion, the linear electron-phonon interaction will vanish by symmetry for the vibration modes of odd parity. In 1965, Keil presented the quantum treatment of optical-absorption line shapes due to the quadratic interaction of the electron of such a defect center with odd-parity modes.¹⁰ In 1978 and 1979, Barrie and Chow¹¹ and Barrie¹² calculated the optical-absorption line shapes of defect centers in the case of both linear and quadratic electron-phonon interactions. However, the lattice part of their Hamiltonian was not second-quantized according to the standard quantum-field theory, because each vibrational mode was represented by a pair of raising and lowering operators for phonons.¹³ When calculating with this Hamiltonian, they met many difficulties: neglect of the virtual parts of the Hamiltonian having two raising or lowering operators, which obviously loses much information, no ability to obtain an analytical expression for the line-shape function from the generating function, and so on.

As we have seen, the above-noted authors all under some

approximation discussed a partial effect of multiphonon transitions due to electron-phonon interactions. The present theories of light absorption by defect centers bear the following four shortcomings. (1) Most of the theories do not deal with quadratic electron-phonon interactions. (2) The theories cannot treat the linear and quadratic electron-phonon interactions simultaneously. (3) One just obtains the line-shape function of the fundamental absorption band of an F center. (4) One still cannot describe the whole absorption spectrum of an arbitrary color center. In view of these circumstances, we want to develop a unified, second-quantized field theory of optical absorption, which contains both linear and quadratic electron-phonon interactions. In this field theory one can derive a universal spectral function of light absorption by defect centers, which can reproduce the above-mentioned various approximate results. The present paper is completed just under the guidance of this idea.

The universal spectral function of the absorption coefficient is finally reduced into an analytical expression in the configurational coordinate model. This spectral function possesses the following three advantages: (1) it includes a weakly nonlinear electron-phonon interaction that prevails in all color-center crystals; (2) it can describe many absorption bands of an arbitrary color center; (3) it includes all phonon modes via an effective frequency. One will see that this spectral function cannot be derived in classical quantum mechanics.

The remainder of this paper is organized as follows. Section II describes our physical model and derives the second-quantized Hamiltonian of the model system. The expression of the absorption coefficient in terms of a temperature-dependent double-time Green's function is obtained in Sec. III. In Sec. IV, by calculating the Green's function, we find the spectral function of the absorption coefficient. In Sec. V, a general solution of the overlap integrals is acquired and its simplified forms under several approximations are discussed. In Sec. VI, we find the expression of the spectral function in the weak nonlinear case and, as an example, use this expression to describe the light-absorption band shape of F_A centers. The summary and discussion are given in Sec. VII.

II. HAMILTONIAN OF THE MODEL SYSTEM

We first establish a model system for discussion. A general concentration of defect centers in crystals is about 5×10^{16} centers/cm³, and so the mean separation between defect centers is about 270 Å. Since 270 Å is much larger than the extension of the wave function of a trapped electron in polar crystals, the interaction between defect centers in polar crystals must be very small. Thereby, we ignore this interaction and consider a single defect center in polar crystals. Because a single-electron transition is the simplest case for the study of photon absorption, our model system consists of an electron bound at a defect center in a polar crystal.

Let the perfect crystal lattice have N primitive cells and each cell have r basis atoms, so that the number of degrees of freedom of the lattice is $3Nr$. Introduction of a single defect center into the lattice decreases its number of degrees of freedom by a quantity s , and so the imperfect crystal lattice has the number of degrees of freedom $f = 3Nr - s$. In the dynamical theory of crystal lattices, this crystal lattice con-

tains f vibration modes and under the harmonic approximation the f vibration modes correspond to f quasiparticles or harmonic oscillators. Our model system is therefore reduced to a coupled system consisting of a trapped electron and f harmonic oscillators. In the discussion of this section, we always adopt the Schrödinger picture and neglect the electronic spin coordinate. At present, we take the orthonormal vector $|\vec{r}, \{q_\mu\}\rangle$ as the basis vector of the coordinate representation for the electron and f harmonic oscillators. Under these prescriptions, the Hamiltonian operator of the system is

$$\hat{H} = \hat{H}_e(\vec{r}, \hat{p}) + \hat{H}_p(q, \hat{p}) + \hat{H}_I(\vec{r}; q). \quad (2.1)$$

Here $\hat{H}_e(\vec{r}, \hat{p})$ is the Hamiltonian operator of the trapped electron, which includes the electronic kinetic energy and the potential energies of the electron in the perfect-crystal and defect fields, and \vec{r} and \hat{p} are the position coordinate and momentum operator of the electron. $\hat{H}_p(q, \hat{p})$ represents the Hamiltonian operator of crystal vibrations, where q and \hat{p} stand for the sets of canonical coordinates and canonically conjugate momentums of vibration modes, namely, $q = \{q_\mu\}$ and $\hat{p} = \{\hat{p}_\mu\}$, $\mu = 1, 2, 3, \dots, f$. Under the harmonic approximation for interatomic potential energy, one finds

$$\hat{H}_p(q, \hat{p}) = \sum_{\mu=1}^f \left(\frac{1}{2} \hat{p}_\mu^2 + \frac{1}{2} \omega_\mu^2 q_\mu^2 \right), \quad (2.2)$$

where ω_μ is the frequency of the μ th vibration mode. $\hat{H}_I(\vec{r}; q)$ is the interaction energy of the electron with the vibrating crystal. Expanding it to the quadratic term in q leads to

$$\hat{H}_I(\vec{r}; q) = - \sum_{\mu=1}^f \hat{a}_\mu(\vec{r}) q_\mu + \frac{1}{2} \sum_{\mu, \mu'=1}^f \hat{\omega}_{\mu\mu'}(\vec{r}) q_\mu q_{\mu'},$$

where the zeroth-order term $\hat{H}_I^{(0)}(\vec{r})$ has been already incorporated in $\hat{H}_e(\vec{r}, \hat{p})$ in advance.

In order to proceed with the practical discussion, we make an assumption that $\hat{\omega}_{\mu\mu'}(\vec{r}) = 0$ when $\mu \neq \mu'$. This assumption is a rather crude approximation, as it neglects the eigenvector effect of ions, the effect that the eigenvectors of ions change from those of the perfect lattice, particularly for ions in the vicinity of the defect. Under the assumption, we have

$$\hat{H}_I(\vec{r}; q) = - \sum_{\mu=1}^f \hat{a}_\mu(\vec{r}) q_\mu + \frac{1}{2} \sum_{\mu=1}^f \hat{\omega}_{\mu\mu}(\vec{r}) q_\mu^2. \quad (2.3)$$

Insertion of Eqs. (2.2) and (2.3) into Eq. (2.1) produces the total Hamiltonian operator as

$$\begin{aligned} \hat{H} = & \hat{H}_e(\vec{r}, \hat{p}) + \sum_{\mu=1}^f \left(\frac{1}{2} \hat{p}_\mu^2 + \frac{1}{2} \omega_\mu^2 q_\mu^2 \right) - \sum_{\mu=1}^f \hat{a}_\mu(\vec{r}) q_\mu \\ & + \frac{1}{2} \sum_{\mu=1}^f \hat{\omega}_{\mu\mu}(\vec{r}) q_\mu^2. \end{aligned} \quad (2.4)$$

Hamiltonian (2.4) describes the coupled motion of the trapped electron and the lattice ions. There exists an adiabatic approximation to separate the electronic and ionic mo-

tion. In second-quantized field theory,¹⁴ the adiabatic approximation indicates that the electronic and ionic motion can be described by two coordinate-dependent field operators. If we express the electronic operators in Hamiltonian (2.4) in the second-quantized form, the total Hamiltonian operator is given by

$$\begin{aligned} \hat{H} = & \int \Psi^\dagger(\vec{r}, t) \left[\hat{H}_e(\vec{r}, \hat{p}) - \sum_{\mu=1}^f \hat{a}_\mu(\vec{r}) q_\mu \right. \\ & \left. + \frac{1}{2} \sum_{\mu=1}^f \hat{\omega}_{\mu\mu}(\vec{r}) q_\mu^2 \right] \Psi(\vec{r}, t) d\vec{r} + \sum_{\mu=1}^f \left(\frac{1}{2} \hat{p}_\mu^2 + \frac{1}{2} \omega_\mu^2 q_\mu^2 \right), \end{aligned} \quad (2.5)$$

where $\Psi(\vec{r}, t)$ is the electronic field operator, namely, the second-quantized wave function of the electron. The electronic field operator meets the equal-time anticommutation relations:

$$[\Psi(\vec{r}, t), \Psi^\dagger(\vec{r}', t)]_+ = \delta(\vec{r} - \vec{r}'),$$

$$[\Psi(\vec{r}, t), \Psi(\vec{r}', t)]_+ = [\Psi^\dagger(\vec{r}, t), \Psi^\dagger(\vec{r}', t)]_+ = 0.$$

To discuss the following problems we employ a mixed representation in which the occupation number representation is used for the electron, and the coordinate representation is used for the harmonic oscillators. A complete orthonormal set of solutions to the classical time-independent Schrödinger equation of the electron is given by $\{u_i(\vec{r})\}$, where $u_i(\vec{r})$ satisfies the equation

$$\hat{H}_e(\vec{r}, \hat{p}) u_i(\vec{r}) = \varepsilon_i u_i(\vec{r})$$

and ε_i is the i th energy level of the electron. We now expand the electronic field operator in terms of $u_i(\vec{r})$ according to

$$\Psi(\vec{r}, t) = \sum_i \hat{a}_i(t) u_i(\vec{r}). \quad (2.6)$$

Here $\hat{a}_i(t)$ and $\hat{a}_i^\dagger(t)$ are the annihilation and creation operators for the i th electron state and obey the equal-time anticommutation relations:

$$[\hat{a}_i(t), \hat{a}_{i'}^\dagger(t)]_+ = \delta_{ii'}, [\hat{a}_i(t), \hat{a}_{i'}(t)]_+ = [\hat{a}_i^\dagger(t), \hat{a}_{i'}^\dagger(t)]_+ = 0.$$

Putting Eq. (2.6) into Eq. (2.5), we obtain the Hamiltonian operator in the mixed representation as follows:

$$\begin{aligned} \hat{H} = & \sum_i \varepsilon_i \hat{a}_i^\dagger \hat{a}_i - \sum_{\mu=1}^f \sum_{i, i'} a_{ii'} \hat{a}_i^\dagger \hat{a}_{i'} q_\mu \\ & + \frac{1}{2} \sum_{\mu=1}^f \sum_{i, i'} \omega_{ii'} \hat{a}_i^\dagger \hat{a}_{i'} q_\mu^2 + \sum_{\mu=1}^f \left(\frac{1}{2} \hat{p}_\mu^2 + \frac{1}{2} \omega_\mu^2 q_\mu^2 \right), \end{aligned} \quad (2.7)$$

where we have used the notation

$$a_{ii'} = \int u_i^*(\vec{r}) \hat{a}_\mu(\vec{r}) u_{i'}(\vec{r}) d\vec{r},$$

$$\omega_{ii'} = \int u_i^*(\vec{r}) \hat{\omega}_{\mu\mu}(\vec{r}) u_{i'}(\vec{r}) d\vec{r}.$$

In the mixed representation, the complete orthonormal basis vector of the Hilbert subspace of the electron is $|i\rangle = \hat{a}_i^\dagger |0\rangle$, where $|0\rangle$ stands for the vacuum state, while this vector of the Hilbert subspace of the f harmonic oscillators is $|\{q_\mu\}\rangle$. Therefore, the complete orthonormal basis vector of the mixed representation is given by $\hat{a}_i^\dagger |0\rangle |\{q_\mu\}\rangle$.

Equation (2.7) is not diagonal in the Hilbert subspace of the electron, and the nondiagonal matrix elements are as follows:

$$\langle i | \hat{H} | i' \rangle = \sum_{\mu=1}^f \left(-a_{ii'} q_\mu + \frac{1}{2} \omega_{ii'} q_\mu^2 \right), \quad i \neq i'.$$

In static coupling theory,¹⁵ these are just the perturbation operators of nonradiative transitions of the trapped electron. In a nonradiative transition, the electronic energy change is compensated entirely by multiphonon emission or absorption. As we take only account of radiative electronic transitions, we have reason to omit the nondiagonal matrix elements. This approximation is equivalent to the Condon approximation adopted in a theory for radiative electronic transitions in solids. In this theory, the electronic wave functions are functions of oscillator coordinates, and thereby the electric dipole matrix elements between the electronic states depend on oscillator coordinates. The Condon approximation states that the dependence of the electric dipole matrix elements on oscillator coordinates is neglected. As a result of our approximation, the total Hamiltonian operator diagonal in the Hilbert subspace of the electron is obtained as

$$\begin{aligned} \hat{H} = & \sum_i \varepsilon_i \hat{a}_i^\dagger \hat{a}_i - \sum_{\mu=1}^f \sum_i a_{ii\mu} \hat{a}_i^\dagger \hat{a}_i q_\mu \\ & + \frac{1}{2} \sum_{\mu=1}^f \sum_i \omega_{ii\mu} \hat{a}_i^\dagger \hat{a}_i q_\mu^2 + \sum_{\mu=1}^f \left(\frac{1}{2} \hat{p}_\mu^2 + \frac{1}{2} \omega_\mu^2 q_\mu^2 \right). \end{aligned} \quad (2.8)$$

The particle number operator for the i th electron state is defined as $\hat{N}_i = \hat{a}_i^\dagger \hat{a}_i$, whose eigenvalues are $n_i = 0, 1$. Since we are concerned with the single-electron problems, the total particle-number operator is yielded as

$$\hat{N} = \sum_i \hat{a}_i^\dagger \hat{a}_i = 1. \quad (2.9)$$

Substitution of Eq. (2.9) into Eq. (2.8) results in

$$\begin{aligned} \hat{H} = & \sum_i \varepsilon_i \hat{a}_i^\dagger \hat{a}_i + \sum_i \hat{a}_i^\dagger \hat{a}_i \\ & \times \sum_{\mu=1}^f \left[\frac{1}{2} \hat{p}_\mu^2 + \frac{1}{2} (\omega_\mu^2 + \omega_{ii\mu}) q_\mu^2 - a_{ii\mu} q_\mu \right]. \end{aligned} \quad (2.10)$$

Setting

$$\omega_{i\mu}^2 = \omega_\mu^2 + \omega_{ii\mu}, \quad (2.11)$$

$$\Delta_{i\mu} = \frac{a_{ii\mu}}{\omega_{i\mu}^2}, \quad (2.12)$$

Eq. (2.10) reduces to

$$\begin{aligned} \hat{H} = & \sum_i \left(\varepsilon_i - \sum_{\mu=1}^f \frac{1}{2} \omega_{i\mu}^2 \Delta_{i\mu}^2 \right) \hat{a}_i^\dagger \hat{a}_i + \sum_i \sum_{\mu=1}^f \hat{a}_i^\dagger \hat{a}_i \\ & \times \left[\frac{1}{2} \hat{p}_\mu^2 + \frac{1}{2} \omega_{i\mu}^2 (q_\mu - \Delta_{i\mu})^2 \right]. \end{aligned} \quad (2.13)$$

Again letting

$$E_i = \varepsilon_i - \sum_{\mu=1}^f \frac{1}{2} \omega_{i\mu}^2 \Delta_{i\mu}^2, \quad (2.14)$$

$$q_{i\mu} = q_\mu - \Delta_{i\mu}, \quad (2.15)$$

Eq. (2.13) is of the form

$$\hat{H} = \sum_i E_i \hat{a}_i^\dagger \hat{a}_i + \sum_i \sum_{\mu=1}^f \hat{a}_i^\dagger \hat{a}_i \left(\frac{1}{2} \hat{p}_\mu^2 + \frac{1}{2} \omega_{i\mu}^2 q_{i\mu}^2 \right). \quad (2.16)$$

Equation (2.16) shows that the Hamiltonian operator of the system is resolved into two parts. The first part represents the renormalized Hamiltonian operator of the trapped electron, and the second one is the Hamiltonian operator of the f harmonic oscillators coupled with the electronic states.

As we can see from the above discussion, the interaction between the trapped electron and the lattice vibrations has three effects. (1) The lattice relaxation effect: the electron induces a force on the lattice ions, causing a nonuniform displacement of the ionic equilibrium positions. The equilibrium displacement of the μ th vibration mode is given by $\Delta_{i\mu}$ in Eq. (2.12), which is different for each electronic state. The lattice relaxation effect is due to the linear electron-phonon interaction. (2) The electron-ion correlation effect: owing to lattice relaxation, the electron readjusts its probable distributions so that the electronic self-energy is at a minimum. The renormalized electronic self-energy is given by E_i in Eq. (2.14). $\sum_{\mu=1}^f \frac{1}{2} \omega_{i\mu}^2 \Delta_{i\mu}^2$ is the elastic energy required by lattice relaxation and characterizes the coupling strength of the electron with the lattice vibrations. The electron-ion correlation effect is also due to the linear electron-phonon interaction. (3) The lattice-frequency shift effect: the electron modifies the forces between the ions, leading to a shift in the vibration frequencies of the lattice. The lattice-frequency shift depends on the electron states and the renormalized lattice frequencies $\omega_{i\mu}$ are given by Eq. (2.11). As shown by Eq. (2.16), the energy of the electron-phonon system is the sum of the electronic and vibrational energies. Since the system's energy is constant in thermal equilibrium, the conservation of energy requires that the phonon energy increase when the electron energy decreases from ε_i to E_i , so that $\omega_{i\mu} > \omega_\mu$. If the energy E_j of the electron state j is higher than the energy E_i of the electron state i , the conservation of energy still requires that the phonon energy $\omega_{j\mu}$ pertinent to the state j be lower than the phonon energy $\omega_{i\mu}$ pertinent to the state i , i.e., $\omega_{j\mu} < \omega_{i\mu}$. This energy relation will be used

in the future discussion. The lattice-frequency shift effect is due to the quadratic electron-phonon interaction.

In the above-mentioned mixed representation, if we express the operators of the f harmonic oscillators in the Hamiltonian (2.16) in the second-quantized form, the Hamiltonian operator reads

$$\begin{aligned} \hat{H} = & \sum_i E_i \hat{a}_i^\dagger \hat{a}_i + \sum_i \sum_{\mu=1}^f \hat{a}_i^\dagger \hat{a}_i \int \hat{\phi}_\mu^\dagger(q_\mu, t) \\ & \times \left(\frac{1}{2} \hat{p}_\mu^2 + \frac{1}{2} \omega_{i\mu}^2 q_{i\mu}^2 \right) \hat{\phi}_\mu(q_\mu, t) dq_\mu, \end{aligned} \quad (2.17)$$

where $\hat{\phi}_\mu(q_\mu, t)$ is the field operator of the μ th harmonic oscillator uncoupled with the i th electronic state. The field operators satisfy the equal-time commutation relations:

$$[\hat{\phi}_\mu(q_\mu, t), \hat{\phi}_\mu^\dagger(q'_\mu, t)]_- = \delta(q_\mu - q'_\mu),$$

$$[\hat{\phi}_\mu(q_\mu, t), \hat{\phi}_\mu(q'_\mu, t)]_- = [\hat{\phi}_\mu^\dagger(q_\mu, t), \hat{\phi}_\mu^\dagger(q'_\mu, t)]_- = 0.$$

In the following, we also employ the occupation number representation for the f harmonic oscillators in addition to the electron. A complete orthonormal set of solutions to the classical time-independent Schrödinger equation of the μ th harmonic oscillator coupled with the i th electron state is of the form

$$X_{i\mu n}(q_{i\mu}) = \left(\frac{\alpha_{i\mu}}{\pi^{1/2} 2^n n!} \right)^{1/2} H_n(\alpha_{i\mu} q_{i\mu}) e^{-\alpha_{i\mu}^2 q_{i\mu}^2 / 2}, \quad (2.18)$$

where $\alpha_{i\mu} = (\omega_{i\mu} / \hbar)^{1/2}$, $H_n(x)$ is the Hermite polynomial of order n , and $X_{i\mu n}(q_{i\mu})$ satisfies the equation

$$\left(\frac{1}{2} \hat{p}_\mu^2 + \frac{1}{2} \omega_{i\mu}^2 q_{i\mu}^2 \right) X_{i\mu n}(q_{i\mu}) = (n + \frac{1}{2}) \hbar \omega_{i\mu} X_{i\mu n}(q_{i\mu}).$$

We can say in images that the n th energy eigenstate of the μ th harmonic oscillator coupled with the i th electron state is occupied by n quasiparticles, i.e., phonons, whose energy is $\hbar \omega_{i\mu}$ while $\frac{1}{2} \hbar \omega_{i\mu}$ is the corresponding zero-point energy. Therefore, the electron-lattice interaction is called frequently the electron-phonon interaction. We now expand the field operator $\hat{\phi}_\mu(q_\mu, t)$ in terms of $\{X_{i\mu n}(q_{i\mu})\}$ as

$$\hat{\phi}_\mu(q_\mu, t) = \sum_{n=0}^{\infty} \hat{b}_{i\mu n}(t) X_{i\mu n}(q_{i\mu}). \quad (2.19)$$

Here $\hat{b}_{i\mu n}$ and $\hat{b}_{i\mu n}^\dagger$ are the annihilation and creation operators for the n th eigenstate of the μ th harmonic oscillator coupled with the i th electronic state. They obey the equal-time commutation relations:

$$[\hat{b}_{i\mu n}, \hat{b}_{i\mu' n'}^\dagger]_- = \delta_{\mu\mu'} \delta_{nn'},$$

$$[\hat{b}_{i\mu n}, \hat{b}_{i\mu' n'}]_- = [\hat{b}_{i\mu n}^\dagger, \hat{b}_{i\mu' n'}^\dagger]_- = 0.$$

The phonon-number operator for the n th harmonic oscillator eigenstate is given by $\hat{N}_{i\mu n} = \hat{b}_{i\mu n}^\dagger \hat{b}_{i\mu n}$. Since we are considering the second quantization of a single

harmonic-oscillator wave field, the total phonon-number operator for the μ th harmonic oscillator is the identity operator

$$\hat{N}_{i\mu} = \sum_{n=0}^{\infty} \hat{b}_{i\mu n}^{\dagger} \hat{b}_{i\mu n} = 1.$$

Substituting Eq. (2.19) into Eq. (2.17), one acquires the Hamiltonian operator in the whole occupation-number representation as

$$\hat{H} = \sum_i E_i \hat{a}_i^{\dagger} \hat{a}_i + \sum_i \hat{a}_i^{\dagger} \hat{a}_i \sum_{\mu=1}^f \sum_{n=0}^{\infty} \hbar \omega_{i\mu} (n + \frac{1}{2}) \hat{b}_{i\mu n}^{\dagger} \hat{b}_{i\mu n}. \quad (2.20)$$

In the whole occupation-number representation, the Hilbert subspace of the electron is spanned by the complete orthonormal basis vectors $|i\rangle = \hat{a}_i^{\dagger}|0\rangle$, while the Hilbert subspace of the f harmonic oscillators is spanned by the complete orthonormal basis vectors $|\{n_{\mu}\}\rangle = \prod_{\mu=1}^f \hat{b}_{i\mu n_{\mu}}^{\dagger}|0\rangle$. Therefore, the whole occupation-number representation has the complete orthonormal basis vectors

$$|i, \{n_{\mu}\}\rangle = \hat{a}_i^{\dagger} \prod_{\mu=1}^f \hat{b}_{i\mu n_{\mu}}^{\dagger} |0\rangle. \quad (2.21)$$

The set $\{\hat{N}_i\}$ of electron-number operators, the set $\{\hat{N}_{i\mu n}\}$ of phonon-number operators, and the Hamiltonian operator \hat{H} constitute a complete set of commuting dynamical variables determining the system, and the common eigenvectors of this complete set are $|i, \{n_{\mu}\}\rangle$. In the eigenstates $|i, \{n_{\mu}\}\rangle$, the energy eigenvalues of the Hamiltonian operator \hat{H} given by Eq. (2.20) yield

$$E(i, \{n_{\mu}\}) = E_i + \sum_{\mu=1}^f (n_{\mu} + \frac{1}{2}) \hbar \omega_{i\mu}. \quad (2.22)$$

The eigenvalues and eigenstates of the electron-phonon system in the adiabatic approximation are often called vibrational-electronic, or vibronic levels and states.

III. EXPRESSION OF THE ABSORPTION COEFFICIENT

Let a beam of monochromatic light of frequency ω enter an isotropic dielectric crystal. The electric field of the light can be written in the complex number form

$$\vec{E}(t) = \vec{E} e^{-i\omega t}. \quad (3.1)$$

The electric polarization $\vec{P}(t)$ in the crystal and the exciting electric field $\vec{E}(t)$ satisfy the causal relation

$$\vec{P}(t) = \epsilon_0 \int_{-\infty}^t f(t-t') \vec{E}(t') dt', \quad (3.2)$$

where ϵ_0 is the permittivity of vacuum and $f(t)$ represents the complex linear response function of the crystal to the electric field. Putting Eq. (3.1) into Eq. (3.2) gives $\vec{P}(t) = \epsilon_0 \chi(\omega) \vec{E}(t)$, where we define a complex, frequency-dependent, electric susceptibility

$$\chi(\omega) = \int_0^{\infty} f(t) e^{i\omega t} dt.$$

The corresponding complex dielectric function is given by $\epsilon(\omega) = 1 + \chi(\omega)$.

We further assume that the monochromatic light is a plane wave propagating in the z direction,

$$\vec{E}(t) = \vec{E}_0 \exp[i(kz - \omega t)], \quad (3.3)$$

where k is the complex wave number and obeys the relation $k^2 = (\omega/c)^2 \epsilon$. If we introduce the complex refractive index N by $N^2 = \epsilon$, then $k = (\omega/c)N$. Separating the real and imaginary parts of the dielectric function and the refractive index,

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega), \quad (3.4)$$

$$N(\omega) = n(\omega) + iK(\omega), \quad (3.5)$$

where n is the real refractive index and K is the extinction coefficient, the two relations below follow:

$$\epsilon_1 = n^2 - K^2, \quad \epsilon_2 = 2nK.$$

The complex wave number acquires the following expression from Eq. (3.5):

$$k = \frac{n\omega}{c} + i \frac{\omega K}{c}. \quad (3.6)$$

Substituting Eq. (3.6) into Eq. (3.3) leads to

$$\vec{E}(t) = \vec{E}_0 \exp\left(-\frac{\omega K}{c} z\right) \exp\left[i\left(\frac{n\omega}{c} z - \omega t\right)\right]. \quad (3.7)$$

As seen from the last equation, the light wave is damped, K describes the absorption of the wave in the medium, and n its dispersion.

At this point, the cycle-averaged intensity of the electromagnetic wave is obtained from the electric field as

$$I = \frac{c}{2n} \epsilon_0 \epsilon_1 E_0^2 \exp(-\eta z), \quad (3.8)$$

where η is the absorption coefficient of light defined by $\eta = 2\omega K/c$. By use of the relations $\epsilon_2 = 2nK$ and $\epsilon = 1 + \chi$, the absorption coefficient is reexpressed as

$$\eta(\omega) = \frac{\omega \text{Im} \chi(\omega)}{nc}, \quad (3.9)$$

where Im denotes the imaginary part. As known from the above discussion, the absorption spectrum of the electromagnetic wave energy in the dielectric crystal is determined completely by the absorption coefficient, and again the absorption coefficient is decided by the imaginary part of the electric susceptibility. In what follows, we formulate the electric susceptibility adopting Kubo's linear response theory.¹⁶

Now we conceive a statistical ensemble, of which every system is just the model system that we have discussed in Sec. II. The natural motion of the system is determined by the Hamiltonian operator \hat{H} in Eq. (2.20), the statistical ensemble in an equilibrium state is described by the density

operator $\hat{\rho}$, and both operators satisfy the relation $[\hat{H}, \hat{\rho}]_- = 0$. If the model system is acted upon by the electric field of the light polarized along the x direction, the system gets a perturbation energy

$$\hat{H}'(t) = -\hat{p}_x E_x(t), \quad (3.10)$$

where $\hat{p}_x = -ex$ is the x component of the electric dipole moment of the trapped electron and the position vector \vec{r} of the electron with respect to the defect center has a component x . For simplicity, in Eq. (3.10) the local electric field at the defect center is replaced by the macroscopic electric field.

In the presence of the external perturbation expressed by Eq. (3.10), the motion of the statistical ensemble is described by the density operator $\hat{\rho}'(t)$, which obeys the Liouville equation

$$\frac{\partial}{\partial t} \hat{\rho}'(t) = \frac{1}{i\hbar} [\hat{H} + \hat{H}'(t), \hat{\rho}'(t)]. \quad (3.11)$$

Assuming the adiabatic condition $E_x(t = -\infty) = 0$, then the system at $t = -\infty$ is in a thermal equilibrium state. The corresponding density operator of the ensemble is given by

$$\hat{\rho}'(t = -\infty) = \hat{\rho} = \frac{\exp(-\beta\hat{H})}{\text{Tr} \exp(-\beta\hat{H})}, \quad (3.12)$$

where $\beta = 1/k_B T$ and T is the temperature. It is supposed that the light field is sufficiently weak that we can expand $\hat{\rho}'(t)$ as

$$\hat{\rho}'(t) = \hat{\rho} + \Delta\hat{\rho}(t).$$

Since we consider only the linear response, the second-order small amount in $\Delta\hat{\rho}(t)$ can be neglected when we substitute the above expansion into Eq. (3.11). After doing that, one can obtain the differential equation with an initial condition

$$\begin{aligned} \frac{\partial}{\partial t} \Delta\hat{\rho}(t) &= \frac{1}{i\hbar} [\hat{H}, \Delta\hat{\rho}(t)] - \frac{1}{i\hbar} E_x(t) [\hat{p}_x, \hat{\rho}], \\ \Delta\hat{\rho}(t = -\infty) &= 0, \end{aligned} \quad (3.13)$$

where Eq. (3.10) has been used.

Equation (3.13) is an inhomogeneous linear differential equation of first order about $\Delta\hat{\rho}(t)$, whose solution is easily found to be

$$\begin{aligned} \Delta\hat{\rho}(t) &= -\frac{1}{i\hbar} \int_{-\infty}^t \exp[-i(t-t')\hat{H}/\hbar] [\hat{p}_x, \hat{\rho}] \\ &\quad \times \exp[i(t-t')\hat{H}/\hbar] E_x(t') dt'. \end{aligned}$$

Therefore, the change $\Delta p_x(t)$ of the x component \hat{p}_x of the electric dipole moment due to the electric field of the light is statistically given by

$$\begin{aligned} \Delta p_x(t) &= \text{Tr}[\Delta\hat{\rho}(t)\hat{p}_x] = -\frac{1}{i\hbar} \text{Tr} \left\{ \int_{-\infty}^t \exp[-i(t-t')\hat{H}/\hbar] \right. \\ &\quad \left. \times [\hat{p}_x, \hat{\rho}] \exp[i(t-t')\hat{H}/\hbar] \hat{p}_x E_x(t') dt' \right\} \\ &= \frac{i}{\hbar} \int_{-\infty}^t \langle [\hat{p}_x(t-t'), \hat{p}_x] \rangle E_x(t') dt'. \end{aligned} \quad (3.14)$$

Here, we have utilized the average notation $\langle \hat{A} \rangle = \text{Tr}(\hat{\rho}\hat{A})$ and $\hat{p}_x(t)$ is the operator in the Heisenberg picture defined by

$$\hat{p}_x(t) = e^{i\hat{H}t/\hbar} \hat{p}_x e^{-i\hat{H}t/\hbar}.$$

$\Delta p_x(t)$ is called the linear response of the physical quantity \hat{p}_x to the external field $E_x(t)$. Let C be the number of defects per unit volume; then the x component of the electric polarization in the crystal is given by $P_x(t) = C\Delta p_x(t)$.

After we insert the electric field of the linearly polarized, monochromatic, incident light, $E_x(t) = E_x \exp(-i\omega t)$, into Eq. (3.14), the x component $P_x(t) = C\Delta p_x(t)$ of the induced electric polarization can be conveniently written in the form

$$P_x(t) = \epsilon_0 \chi(\omega) E_x(t), \quad (3.15)$$

where the electric susceptibility is expressed as

$$\chi(\omega) = \frac{iC}{\hbar \epsilon_0} \lim_{\epsilon \rightarrow 0^+} \int_0^{\infty} \langle [\hat{p}_x(t), \hat{p}_x] \rangle e^{i\omega t - \epsilon t} dt,$$

and the infinitesimal positive ϵ is used to assure the convergence of the integral. Considering that the orientation of the electric dipole moment of the trapped electron is arbitrary, the expression above has to be averaged over the three directions x, y, z , so that we have

$$\chi(\omega) = \frac{iC}{3\hbar \epsilon_0} \lim_{\epsilon \rightarrow 0^+} \int_0^{\infty} \langle [\hat{p}(t), \hat{p}] \rangle e^{i\omega t - \epsilon t} dt, \quad (3.16)$$

where $\hat{p} = -e\vec{r}$ is just the electric-dipole-moment vector of the electron.

Now, the electric susceptibility $\chi(\omega)$ as given by Eq. (3.16) is closely related to a temperature-dependent double-time Green's function. These Green's functions were first introduced by Bogoliubov *et al.*¹⁷ The retarded Green's function $\langle\langle \hat{A} | \hat{B} \rangle\rangle_{\omega}$ for operators \hat{A} and \hat{B} is defined in a complex ω plane by

$$\langle\langle \hat{A} | \hat{B} \rangle\rangle_{\omega} = \frac{1}{2\pi i} \int_0^{\infty} dt e^{i\omega t} \langle [\hat{A}(t), \hat{B}] \rangle, \quad \text{Im } \omega > 0 \quad (3.17)$$

where $\hat{A}(t)$ is the Heisenberg operator with

$$\hat{A}(t) = e^{i\hat{H}t/\hbar} \hat{A} e^{-i\hat{H}t/\hbar}.$$

One can show that the Green's function $\langle\langle \hat{A} | \hat{B} \rangle\rangle_{\omega}$ as defined by Eq. (3.17) is one branch analytic function of ω in the upper half plane outside the real axis and that it obeys the equation of motion

$$\omega \langle \langle \hat{A} | \hat{B} \rangle \rangle_{\omega} = \frac{1}{2\pi} \langle [\hat{A}, \hat{B}] \rangle + \frac{1}{\hbar} \langle \langle [\hat{A}, \hat{H}] | \hat{B} \rangle \rangle_{\omega}. \quad (3.18)$$

By comparison of Eq. (3.16) with Eq. (3.17), we can immediately see the relation

$$\chi(\omega) = -\frac{2\pi C}{3\hbar\epsilon_0} \lim_{\epsilon \rightarrow 0^+} \sum_{\alpha} \langle \langle \hat{p}_{\alpha} | \hat{p}_{\alpha} \rangle \rangle_{\omega+i\epsilon}, \quad (3.19)$$

where $\alpha = x, y, z$ and ω takes real values.

Next, we put Eq. (3.19) into Eq. (3.9) and introduce the spectral function $F(\omega)$ of the absorption coefficient by

$$F(\omega) = -\frac{4m_e\omega}{3\hbar e^2} \lim_{\epsilon \rightarrow 0^+} \text{Im} \sum_{\alpha} \langle \langle \hat{p}_{\alpha} | \hat{p}_{\alpha} \rangle \rangle_{\omega+i\epsilon}, \quad (3.20)$$

where m_e is the electron mass. Therefore, the absorption coefficient $\eta(\omega)$ has a simple expression

$$\eta(\omega) = \frac{\pi C e^2}{2ncm_e\epsilon_0} F(\omega).$$

This reveals that the absorption coefficient is completely determined by its spectral function. The dipole-moment operator \hat{p}_{α} in Eq. (3.20) is expressed in the electronic coordinate representation. We need the expression of \hat{p}_{α} in the electronic occupation-number representation. Using the second-quantized formalism in Sec. II, we can write the dipole-moment operator in the form

$$\hat{p}_{\alpha} = \sum_{i,j} p_{\alpha ij} \hat{a}_i^{\dagger} \hat{a}_j, \quad (3.21)$$

where $p_{\alpha ij}$ is the matrix element of the dipole-moment operator of the electron between the two electronic states i and j ,

$$p_{\alpha ij} = \int u_i^*(\vec{r}) (-e\vec{r})_{\alpha} u_j(\vec{r}) d\vec{r}.$$

Substituting Eq. (3.21) into Eq. (3.20) immediately leads to

$$F(\omega) = -\frac{4m_e\omega}{3\hbar e^2} \lim_{\epsilon \rightarrow 0^+} \text{Im} \sum_{\alpha, i, j} \sum_{i', j'} p_{\alpha ij} p_{\alpha j' i'} \times \langle \langle \hat{a}_i^{\dagger} \hat{a}_j | \hat{a}_{j'}^{\dagger} \hat{a}_{i'} \rangle \rangle_{\omega+i\epsilon}, \quad (3.22)$$

so that the Green's functions $\langle \langle \hat{a}_i^{\dagger} \hat{a}_j | \hat{a}_{j'}^{\dagger} \hat{a}_{i'} \rangle \rangle_{\omega+i\epsilon}$ determine the absorption spectrum. In the following section, we shall give an explicit evaluation of these Green's functions by utilizing the Hamiltonian operator \hat{H} in Eq. (2.20), the density operator $\hat{\rho}$ in Eq. (3.12), and the equation of motion in Eq. (3.18).

IV. EVALUATION OF GREEN'S FUNCTIONS

If we use the equation of motion (3.18) for Green's functions directly to calculate $\langle \langle \hat{a}_i^{\dagger} \hat{a}_j | \hat{a}_{j'}^{\dagger} \hat{a}_{i'} \rangle \rangle_{\omega}$ where ω takes complex values, this equation will lead in the familiar way to a coupled hierarchy of equations for Green's functions of higher and higher order. The reason for this difficulty lies in the fact that in the commutator $[\hat{a}_i^{\dagger} \hat{a}_j, \hat{H}]$ of this equation,

the Hamiltonian operator \hat{H} given by Eq. (2.20) has the symmetry with respect to the electron and phonon operators while $\hat{a}_i^{\dagger} \hat{a}_j$ does not.

In order to avoid this difficulty, we introduce the creation and annihilation operators $\hat{b}_{\mu p}^{\dagger}, \hat{b}_{\mu p}$ of free harmonic oscillators, where the word ‘‘free’’ means the vibrational eigenstates independent of electronic states. These operators meet the identity relation in the state space of interest,

$$\sum_{p_1} \cdots \sum_{p_f} \hat{b}_{1p_1}^{\dagger} \cdots \hat{b}_{fp_f}^{\dagger} \hat{b}_{fp_f} \cdots \hat{b}_{1p_1} = 1.$$

Thereby, one can make a transformation¹⁸

$$\begin{aligned} & \langle \langle \hat{a}_i^{\dagger} \hat{a}_j | \hat{a}_{j'}^{\dagger} \hat{a}_{i'} \rangle \rangle_{\omega} \\ &= \sum_{\{p_{\mu}\}} \langle \langle \hat{a}_i^{\dagger} \hat{a}_j | \hat{b}_{1p_1}^{\dagger} \cdots \hat{b}_{fp_f}^{\dagger} \hat{b}_{fp_f} \cdots \hat{b}_{1p_1} | \hat{a}_{j'}^{\dagger} \hat{a}_{i'} \rangle \rangle_{\omega}. \end{aligned} \quad (4.1)$$

A complete orthonormal set of eigenfunctions $X_{\mu p}(q_{\mu})$ of the μ th free harmonic oscillator has the same functional structure as Eq. (2.18). The field operator $\hat{\varphi}_{\mu}(q_{\mu}, t)$ of the μ th harmonic oscillator can be also expanded in terms of $\{X_{\mu p}(q_{\mu})\}$ as

$$\hat{\varphi}_{\mu}(q_{\mu}, t) = \sum_{p=0}^{\infty} \hat{b}_{\mu p}(t) X_{\mu p}(q_{\mu}). \quad (4.2)$$

From Eqs. (2.19) and (4.2) it follows that $\hat{b}_{i\mu n}$ and $\hat{b}_{\mu p}$ are linearly related by

$$\hat{b}_{\mu p} = \sum_{n=0}^{\infty} C_{pn}^{i\mu}(\Delta_{i\mu}) \hat{b}_{i\mu n}, \quad (4.3)$$

with

$$C_{pn}^{i\mu}(\Delta_{i\mu}) = \int_{-\infty}^{\infty} X_{\mu p}^*(q_{\mu}) X_{i\mu n}(q_{\mu} - \Delta_{i\mu}) dq_{\mu}.$$

Putting Eq. (4.3) into Eq. (4.1), we arrive at

$$\begin{aligned} & \langle \langle \hat{a}_i^{\dagger} \hat{a}_j | \hat{a}_{j'}^{\dagger} \hat{a}_{i'} \rangle \rangle_{\omega} \\ &= \sum_{\{m_{\mu}\}} \sum_{\{n_{\mu}\}} \prod_{\mu} C_{m_{\mu} n_{\mu}}^{ij\mu}(\Delta_{ji\mu}) \\ & \times \langle \langle \hat{a}_i^{\dagger} \hat{a}_j | \hat{b}_{i1m_1}^{\dagger} \cdots \hat{b}_{ifm_f}^{\dagger} \hat{b}_{jfn_f} \cdots \hat{b}_{j1n_1} | \hat{a}_{j'}^{\dagger} \hat{a}_{i'} \rangle \rangle_{\omega}, \end{aligned} \quad (4.4)$$

where $\Delta_{ji\mu} = \Delta_{j\mu} - \Delta_{i\mu}$ denotes the relative equilibrium displacement of the μ th vibration mode between the two electronic states i and j , and $C_{mn}^{ij\mu}(\Delta_{ji\mu})$ are called the overlap integrals between the vibrational eigenfunctions appropriate to the electronic states i and j ,

$$\begin{aligned} C_{mn}^{ij\mu}(\Delta_{ji\mu}) &= \sum_{p=0}^{\infty} C_{pm}^{i\mu*}(\Delta_{i\mu}) C_{pn}^{j\mu}(\Delta_{j\mu}) \\ &= \int_{-\infty}^{\infty} X_{i\mu m}^*(q_{\mu}) X_{j\mu n}(q_{\mu} - \Delta_{ji\mu}) dq_{\mu}. \end{aligned} \quad (4.5)$$

Now, we can apply the equation of motion (3.18) for Green's functions directly to evaluate the Green's function on the right of Eq. (4.4). The equation of motion for this Green's function reads

$$\begin{aligned} & \omega \langle \langle \hat{a}_i^\dagger \hat{a}_j \hat{b}_{i1m_1}^\dagger \cdots \hat{b}_{ifm_f}^\dagger \hat{b}_{jfn_f} \cdots \hat{b}_{j1n_1} | \hat{a}_j^\dagger \hat{a}_{i'} \rangle \rangle_\omega \\ &= \frac{1}{2\pi} \langle \langle [\hat{a}_i^\dagger \hat{a}_j \hat{b}_{i1m_1}^\dagger \cdots \hat{b}_{ifm_f}^\dagger \hat{b}_{jfn_f} \cdots \hat{b}_{j1n_1}, \hat{a}_j^\dagger \hat{a}_{i'}] \rangle \rangle \\ &+ \frac{1}{\hbar} \langle \langle [\hat{a}_i^\dagger \hat{a}_j \hat{b}_{i1m_1}^\dagger \cdots \hat{b}_{ifm_f}^\dagger \hat{b}_{jfn_f} \cdots \hat{b}_{j1n_1}, \hat{H}] | \hat{a}_j^\dagger \hat{a}_{i'} \rangle \rangle_\omega. \end{aligned} \quad (4.6)$$

The commutator with \hat{H} on the right of Eq. (4.6) gives rise to no higher-order Green's functions, because the first term in this commutator possesses the largest symmetry with respect to the electron and phonon operators. In fact, this commutator yields a term proportional to the first term in this commutator.

Because it is for a single electron and harmonic oscillator whose wave fields were second quantized, there is only one "particle" in the electronic and each mode's subspaces of the state vectors in the trace. As a result of this fact, one can easily find the two relations¹⁹

$$\hat{a}_i^\dagger \hat{a}_j \hat{a}_k^\dagger \hat{a}_l = \delta_{jk} \hat{a}_i^\dagger \hat{a}_l, \quad (4.7)$$

$$\hat{b}_{i\mu n}^\dagger \hat{b}_{i\mu m} \hat{b}_{i\mu l}^\dagger \hat{b}_{i\mu p} = \delta_{ml} \hat{b}_{i\mu n}^\dagger \hat{b}_{i\mu p}.$$

Furthermore, we need to carry out the statistical average of operator products concerned. In the absence of external fields, the electron-phonon system is in a statistical equilibrium state described by the density operator $\hat{\rho}(\hat{H})$ in Eq. (3.12). The action of $\hat{\rho}$ on the vibronic states (2.21) in the trace can be written as

$$\hat{\rho}(\hat{H})|i, \{n_\mu\}\rangle = \rho(E(i, \{n_\mu\}))|i, \{n_\mu\}\rangle,$$

where the energy eigenvalues $E(i, \{n_\mu\})$ are given by Eq. (2.22) and we will use the abbreviation $\rho(E(i, \{n_\mu\})) = \rho(i, \{n_\mu\})$. In what follows, we undertake calculation of the statistical average of the typical operator product,

$$\begin{aligned} & \langle \langle \hat{a}_i^\dagger \hat{a}_j \hat{b}_{i1m_1}^\dagger \cdots \hat{b}_{ifm_f}^\dagger \hat{b}_{jfn_f} \cdots \hat{b}_{j1n_1} \rangle \rangle \\ &= \sum_{k, \{l_\mu\}} \langle k, \{l_\mu\} | \hat{\rho}(\hat{H}) \hat{a}_i^\dagger \hat{a}_j \rangle \\ &\quad \times \hat{b}_{i1m_1}^\dagger \cdots \hat{b}_{ifm_f}^\dagger \hat{b}_{jfn_f} \cdots \hat{b}_{j1n_1} | k, \{l_\mu\} \rangle = \sum_{\{l_\mu\}} \rho(i, \{l_\mu\}) \\ &\quad \times \langle \langle \{l_\mu\} | \hat{b}_{i1m_1}^\dagger \cdots \hat{b}_{ifm_f}^\dagger \hat{b}_{jfn_f} \cdots \hat{b}_{j1n_1} | \{l_\mu\} \rangle \rangle \delta_{ii'}. \end{aligned}$$

To continue, we consider the expansion of the field operator of the μ th harmonic oscillator in the eigenfunction sets appropriate to the electronic states i and j ,

$$\begin{aligned} \hat{\varphi}_\mu(q_\mu) &= \sum_{n=0}^{\infty} \hat{b}_{j\mu n} X_{j\mu n}(q_\mu - \Delta_{j\mu}) \\ &= \sum_{p=0}^{\infty} \hat{b}_{i\mu p} X_{i\mu p}(q_\mu - \Delta_{i\mu}). \end{aligned}$$

From these two expansions it follows that $\hat{b}_{j\mu n}$ and $\hat{b}_{i\mu n}$ are linearly related by

$$\hat{b}_{j\mu n} = \sum_p C_{pn}^{ij\mu*}(\Delta_{ji\mu}) \hat{b}_{i\mu p},$$

where $C_{pn}^{ij\mu}(\Delta_{ji\mu})$ are the overlap integrals defined by Eq. (4.5). With use of this relation, the statistical average considered is finally found as

$$\begin{aligned} & \langle \langle \hat{a}_i^\dagger \hat{a}_{i'} \hat{b}_{i1m_1}^\dagger \cdots \hat{b}_{ifm_f}^\dagger \hat{b}_{jfn_f} \cdots \hat{b}_{j1n_1} \rangle \rangle \\ &= \sum_{\{l_\mu\}} \sum_{\{p_\mu\}} \rho(i, \{l_\mu\}) \left[\prod_\mu C_{p_\mu n_\mu}^{ij\mu*}(\Delta_{ji\mu}) \right] \\ &\quad \times \langle \langle \{l_\mu\} | \hat{b}_{i1m_1}^\dagger \cdots \hat{b}_{ifm_f}^\dagger \hat{b}_{jfn_f} \cdots \hat{b}_{i1p_1} | \{l_\mu\} \rangle \rangle \delta_{ii'} \\ &= \rho(i, \{m_\mu\}) \delta_{ii'} \prod_\mu C_{m_\mu n_\mu}^{ij\mu*}(\Delta_{ji\mu}). \end{aligned} \quad (4.8)$$

Equations (4.7) and (4.8) are repeatedly used in the following derivation.

With the help of Eqs. (4.7) and (4.8), the first term on the right of Eq. (4.6) is easily calculated as

$$\begin{aligned} & \frac{1}{2\pi} \langle \langle [\hat{a}_i^\dagger \hat{a}_j \hat{b}_{i1m_1}^\dagger \cdots \hat{b}_{ifm_f}^\dagger \hat{b}_{jfn_f} \cdots \hat{b}_{j1n_1}, \hat{a}_j^\dagger \hat{a}_{i'}] \rangle \rangle \\ &= \frac{1}{2\pi} [\rho(i, \{m_\mu\}) - \rho(j, \{n_\mu\})] \delta_{ii'} \delta_{jj'} \prod_\mu C_{m_\mu n_\mu}^{ij\mu*}(\Delta_{ji\mu}). \end{aligned} \quad (4.9)$$

The next task is to compute the commutator with \hat{H} on the right of Eq. (4.6). The Hamiltonian operator \hat{H} of the electron-phonon system is given by Eq. (2.20). Utilization of the relations (4.7) straightforwardly produces the result,

$$\begin{aligned} & [\hat{a}_i^\dagger \hat{a}_j \hat{b}_{i1m_1}^\dagger \cdots \hat{b}_{ifm_f}^\dagger \hat{b}_{jfn_f} \cdots \hat{b}_{j1n_1}, \hat{H}] \\ &= \hbar \left\{ \omega_{ji}^* + \sum_\mu [(\omega_{j\mu} - \omega_{i\mu})(n_\mu + \frac{1}{2}) \right. \\ &\quad \left. + \omega_{i\mu}(n_\mu - m_\mu)] \right\} \hat{a}_i^\dagger \hat{a}_j \hat{b}_{i1m_1}^\dagger \cdots \hat{b}_{ifm_f}^\dagger \hat{b}_{jfn_f} \cdots \hat{b}_{j1n_1}, \end{aligned}$$

where $\omega_{ji}^* = (E_j - E_i)/\hbar$ represents the renormalized transition frequency of the electron from the state i to j in the absence of multiphonon transitions. This result shows that the operator product in normal-ordering form, i.e., the number of lattice quasiparticles and electrons, is conserved by the interaction. Inserting this result into the second term on the right of Eq. (4.6) immediately yields

$$\begin{aligned} & \frac{1}{\hbar} \langle \langle [\hat{a}_i^\dagger \hat{a}_j \hat{b}_{i1m_1}^\dagger \cdots \hat{b}_{ifm_f}^\dagger \hat{b}_{jfn_f} \cdots \hat{b}_{j1n_1}, \hat{H}] | \hat{a}_j^\dagger, \hat{a}_{i'} \rangle \rangle_\omega \\ &= \left\{ \omega_{ji}^* + \sum_\mu [(\omega_{j\mu} - \omega_{i\mu})(n_\mu + \frac{1}{2}) + \omega_{i\mu}(n_\mu - m_\mu)] \right\} \\ & \quad \times \langle \langle \hat{a}_i^\dagger \hat{a}_j \hat{b}_{i1m_1}^\dagger \cdots \hat{b}_{ifm_f}^\dagger \hat{b}_{jfn_f} \cdots \hat{b}_{j1n_1} | \hat{a}_j^\dagger, \hat{a}_{i'} \rangle \rangle_\omega. \end{aligned} \quad (4.10)$$

This reveals that the equation of motion for Green's functions contains only Green's functions of the one kind, i.e., is self-contained, and can be solved to any desired order in the

interaction strength. Combining Eqs. (4.9) and (4.10) into Eq. (4.6), we get

$$\begin{aligned} & \left\{ \omega - \omega_{ji}^* - \sum_\mu [(\omega_{j\mu} - \omega_{i\mu})(n_\mu + \frac{1}{2}) + \omega_{i\mu}(n_\mu - m_\mu)] \right\} \\ & \quad \times \langle \langle \hat{a}_i^\dagger \hat{a}_j \hat{b}_{i1m_1}^\dagger \cdots \hat{b}_{ifm_f}^\dagger \hat{b}_{jfn_f} \cdots \hat{b}_{j1n_1} | \hat{a}_j^\dagger, \hat{a}_{i'} \rangle \rangle_\omega \\ &= \frac{1}{2\pi} [\rho(i, \{m_\mu\}) - \rho(j, \{n_\mu\})] \delta_{ii'} \delta_{jj'} \prod_\mu C_{m_\mu n_\mu}^{ij\mu*}(\Delta_{ji\mu}). \end{aligned} \quad (4.11)$$

As shown by Zubarev,¹⁷ the solution of Eq. (4.11) compatible with the definition of Green's functions is given by

$$\begin{aligned} & \langle \langle \hat{a}_i^\dagger \hat{a}_j \hat{b}_{i1m_1}^\dagger \cdots \hat{b}_{ifm_f}^\dagger \hat{b}_{jfn_f} \cdots \hat{b}_{j1n_1} | \hat{a}_j^\dagger, \hat{a}_{i'} \rangle \rangle_\omega = \frac{1}{2\pi} [\rho(i, \{m_\mu\}) - \rho(j, \{n_\mu\})] \delta_{ii'} \delta_{jj'} \prod_\mu C_{m_\mu n_\mu}^{ij\mu*}(\Delta_{ji\mu}) \\ & \quad \times \left\{ \omega - \omega_{ji}^* - \sum_\mu [(\omega_{j\mu} - \omega_{i\mu})(n_\mu + \frac{1}{2}) + \omega_{i\mu}(n_\mu - m_\mu)] \right\}^{-1}. \end{aligned} \quad (4.12)$$

According to Eq. (4.4), the original Green's function is expressed as a sum over the set of Green's functions of the type (4.12),

$$\begin{aligned} & \langle \langle \hat{a}_i^\dagger \hat{a}_j | \hat{a}_j^\dagger, \hat{a}_{i'} \rangle \rangle_\omega = \frac{\delta_{ii'} \delta_{jj'}}{2\pi} \sum_{\{m_\mu\}} \sum_{\{n_\mu\}} [\rho(i, \{m_\mu\}) - \rho(j, \{n_\mu\})] \prod_\mu |C_{m_\mu n_\mu}^{ij\mu}(\Delta_{ji\mu})|^2 \\ & \quad \times \left\{ \omega - \omega_{ji}^* - \sum_\mu [(\omega_{j\mu} - \omega_{i\mu})(n_\mu + \frac{1}{2}) + \omega_{i\mu}(n_\mu - m_\mu)] \right\}^{-1}. \end{aligned} \quad (4.13)$$

Substituting Eq. (4.13) into Eq. (3.22), we obtain the spectral function of the absorption coefficient as

$$\begin{aligned} F(\omega) &= -\frac{2m_e\omega}{3\hbar e^2\pi} \sum_{i,j} \sum_{\{m_\mu\}} \sum_{\{n_\mu\}} |\vec{p}_{ij}|^2 [\rho(i, \{m_\mu\}) - \rho(j, \{n_\mu\})] \\ & \quad \times \prod_\mu |C_{m_\mu n_\mu}^{ij\mu}(\Delta_{ji\mu})|^2 \operatorname{Im} \left\{ \lim_{\varepsilon \rightarrow 0^+} \frac{1}{\omega - \omega_{ji}^* - \sum_\mu [(\omega_{j\mu} - \omega_{i\mu})(n_\mu + \frac{1}{2}) + \omega_{i\mu}(n_\mu - m_\mu)] + i\varepsilon} \right\}, \end{aligned}$$

where ω takes real values. By using the asymptotic formula

$$\lim_{\varepsilon \rightarrow 0^+} \frac{1}{x \pm i\varepsilon} = \mathcal{P} \left(\frac{1}{x} \right) \mp i\pi \delta(x),$$

where \mathcal{P} denotes the Cauchy principal value, the above expression is reduced to

$$\begin{aligned} F(\omega) &= \frac{2m_e\omega}{3\hbar e^2} \sum_{i,j} \sum_{\{m_\mu\}} \sum_{\{n_\mu\}} |\vec{p}_{ij}|^2 [\rho(i, \{m_\mu\}) - \rho(j, \{n_\mu\})] \\ & \quad \times \prod_\mu |C_{m_\mu n_\mu}^{ij\mu}(\Delta_{ji\mu})|^2 \\ & \quad \times \delta \left\{ \omega - \omega_{ji}^* - \sum_\mu [(\omega_{j\mu} - \omega_{i\mu})(n_\mu + \frac{1}{2}) \right. \\ & \quad \left. + \omega_{i\mu}(n_\mu - m_\mu)] \right\}. \end{aligned} \quad (4.14)$$

Because of the relation $\hat{p} = -e\vec{r}$, it is now more convenient to introduce the matrix element of the electronic position vector \vec{r} between the electronic states i and j ,

$$\vec{r}_{ji} = \int u_j^*(\vec{r}) \vec{r} u_i(\vec{r}) d\vec{r}. \quad (4.15)$$

It is still necessary to introduce the bare transition frequency $\omega_{ji} = (\varepsilon_j - \varepsilon_i)/\hbar$ of the electron from the state i to j in the absence of multiphonon transitions. Thereby, we can set

$$f_{ji} = \frac{2m_e}{3\hbar} \omega_{ji} |\vec{r}_{ji}|^2. \quad (4.16)$$

f_{ji} is a real dimensionless number, characteristic of the $i \leftrightarrow j$ transition, and called the oscillator strength of this transition. Oscillator strengths satisfy the following sum rule:

$$\sum_j f_{ji} = 1.$$

Through oscillator strengths, the spectral function (4.14) can be rewritten in a neat form

$$F(\omega) = \sum_{i,j} \sum_{\{m_\mu\}} \sum_{\{n_\mu\}} \frac{\omega}{\omega_{ji}} f_{ji} [\rho(i, \{m_\mu\}) - \rho(j, \{n_\mu\})] \times \prod_{\mu} |C_{m_\mu n_\mu}^{ij\mu}(\Delta_{ji\mu})|^2 \times \delta \left\{ \omega - \omega_{ji}^* - \sum_{\mu} [(\omega_{j\mu} - \omega_{i\mu})(n_\mu + \frac{1}{2}) + \omega_{i\mu}(n_\mu - m_\mu)] \right\}. \quad (4.17)$$

Since there is no light amplification in the physical configuration under investigation, the absorption coefficient $\eta(\omega)$ or $F(\omega)$ must be positive. This poses an inequality $\rho(i, \{m_\mu\}) > \rho(j, \{n_\mu\})$ to Eq. (4.17). The inequality means that the vibronic states $(i, \{m_\mu\})$ are of lower energy and the vibronic states $(j, \{n_\mu\})$ are of higher energy. Therefore, the spectral function $F(\omega)$ given by Eq. (4.17) includes two contributions. The first part $F^a(\omega)$ is due to stimulated absorption, the second part $F^e(\omega)$ is due to stimulated emission, and the spectral function is the difference between both, $F(\omega) = F^a(\omega) - F^e(\omega)$. In any thermal equilibrium case, $F^e(\omega)$ is negligible compared with $F^a(\omega)$, so that the spectral function is mainly determined by stimulated absorption,

$$F(\omega) = \sum_{i,j} \sum_{\{m_\mu\}} \sum_{\{n_\mu\}} \frac{\omega}{\omega_{ji}} f_{ji} \rho(i, \{m_\mu\}) \times \prod_{\mu} |C_{m_\mu n_\mu}^{ij\mu}(\Delta_{ji\mu})|^2 \delta \left\{ \omega - \omega_{ji}^* - \sum_{\mu} [(\omega_{j\mu} - \omega_{i\mu})(n_\mu + \frac{1}{2}) + \omega_{i\mu}(n_\mu - m_\mu)] \right\}. \quad (4.18)$$

As seen from Eq. (4.18), the spectral function $F(\omega)$ assumes the form that it takes the thermal average over all the initial states $(i, \{m_\mu\})$ of transition and sums up all the final states $(j, \{n_\mu\})$ of transition but the δ function guarantees conservation of energy during transition processes.

$\rho(i, \{m_\mu\})$ is the probability of finding the electron-phonon system in a vibronic state $(i, \{m_\mu\})$. The probability distribution in the initial states of transition is given by

$$\rho(i, \{m_\mu\}) = \frac{\exp \left\{ -\beta \left[E_i + \sum_{\mu=1}^f \hbar \omega_{i\mu} (m_\mu + \frac{1}{2}) \right] \right\}}{\text{Tr} \exp(-\beta \hat{H})}.$$

Now we introduce the probability distribution $\rho(i)$ in the electronic states and the probability distribution $\rho_i(\{m_\mu\})$ in the vibrational states by

$$\rho(i) = \frac{\exp(-\beta E_i)}{\sum_k \exp(-\beta E_k)},$$

$$\rho_i(\{m_\mu\}) = \frac{\exp \left[-\beta \sum_{\mu=1}^f \hbar \omega_{i\mu} \left(m_\mu + \frac{1}{2} \right) \right]}{\sum_{\{l_\mu\}} \exp \left[-\beta \sum_{\mu=1}^f \hbar \omega_{i\mu} \left(l_\mu + \frac{1}{2} \right) \right]}, \quad (4.19)$$

where the vibrational probability depends on the electronic state i . Under the decoupling approximation, the probability of the total system is decoupled into the product form of the electronic and vibrational probabilities,

$$\rho(i, \{m_\mu\}) = \rho(i) \rho_i(\{m_\mu\}).$$

The decoupling approximation is based on the following argument: An electronic state i is separated from other electronic states by energy much larger than the phonon energies. The vibrational states can change only slowly near an electronic state i , while the electronic states respond adiabatically to all the vibrational states. The probability distribution $\rho(i)$ in the electronic states shows that in thermal equilibrium, the initial state i of transition chooses the ground state of the trapped electron with a maximum probability. In view of this fact, if $i=0$ signifies the ground state, in Eq. (4.18) we can set $i=0$ for all the quantities except $\rho(i)$ and then obtain the sum rule $\sum_i \rho(i) = 1$. Thereby, Eq. (4.18) becomes

$$F(\omega) = \sum_j \sum_{\{m_\mu\}} \sum_{\{n_\mu\}} \frac{\omega}{\omega_{j0}} f_{j0} \rho_0(\{m_\mu\}) \times \prod_{\mu} |C_{m_\mu n_\mu}^{0j\mu}(\Delta_{j0\mu})|^2 \delta \left\{ \omega - \omega_{j0}^* - \sum_{\mu} [(\omega_{j\mu} - \omega_{0\mu})(n_\mu + \frac{1}{2}) + \omega_{0\mu}(n_\mu - m_\mu)] \right\}. \quad (4.20)$$

In Sec. III, for convenience we assumed the incident light to be a monochromatic light with a fixed frequency ω . In this case, Eq. (4.20) gives the composite strength of a single absorption line at frequency ω due to transitions from the ground state $i=0$ to all the excited states j . In fact, one often uses a quasimonochromatic light of a central frequency in solid-state spectroscopy. If the incident central frequency matches the peak transition frequency Ω_{j0}^* of the electron from the ground state to a particular excited state j , then the probabilities of all other transitions almost go to zero. In this case, since the factor ω/ω_{j0} slowly varies near unity, Eq. (4.20) is turned into the following normalized line-shape function:

$$f_j(\omega) = \sum_{\{m_\mu\}} \sum_{\{n_\mu\}} \rho_0(\{m_\mu\}) \prod_{\mu} |C_{m_\mu n_\mu}^{0j\mu}(\Delta_{j0\mu})|^2 \times \delta \left\{ \omega - \omega_{j0}^* - \sum_{\mu} [(\omega_{j\mu} - \omega_{0\mu})(n_\mu + \frac{1}{2}) + \omega_{0\mu}(n_\mu - m_\mu)] \right\}. \quad (4.21)$$

When the variable ω in Eq. (4.21) varies in the frequency range of quasimonochromatic light, Eq. (4.21) describes a single absorption peak centered at Ω_{j0}^* . Equation (4.21) is reminiscent of the well-known Bethe-Sommerfeld formula

for one absorption band. The present paper will emphasize the case when the incident light is a polychromatic light, whose frequency range covers all the peak transition frequencies $\{\Omega_{j0}^*\}$. As the variable ω in Eq. (4.20) varies in the frequency range of the polychromatic light, Eq. (4.20) depicts a series of absorption peaks corresponding to different frequencies Ω_{j0}^* . The composite absorption curve $F(\omega)$ manifests itself as a linear superposition of the component absorption curves $f_j(\omega)$ with weight factor f_{j0} ,

$$F(\omega) = \sum_j \frac{\omega}{\omega_{j0}} f_{j0} f_j(\omega), \quad (4.22)$$

where $f_j(\omega)$ is given by Eq. (4.21). Equation (4.22) is the line-shape formula for many absorption bands and reveals that $F(\omega)$ is normalized to unity over ω , i.e.,

$$\int F(\omega) d\omega = 1.$$

This result represents the important law of constant area.

As we know from Eq. (4.21), the transition from the vibronic state $|i=0, \{m_\mu\}\rangle$ to the vibronic state $|j, \{n_\mu\}\rangle$ produces an absorption line at frequency

$$\omega = \omega_{j0}^* + \sum_{\mu=1}^f [(\omega_{j\mu} - \omega_{0\mu})(n_\mu + \frac{1}{2}) + \omega_{0\mu}(n_\mu - m_\mu)]. \quad (4.23)$$

When a photon of frequency ω is absorbed, the electron obtains the energy ω_{j0}^* to assist the transition from the electronic state $i=0$ to j . In the meanwhile, the crystal lattice undergoes a transition from the vibrational state $\{m_\mu\}$ to $\{n_\mu\}$. The initial vibrational state possesses the phonon energy $\sum_\mu \omega_{0\mu}(m_\mu + \frac{1}{2})$, the final vibrational state has the phonon energy $\sum_\mu \omega_{j\mu}(n_\mu + \frac{1}{2})$, and the net emitted or absorbed phonon energy is given by the second term on the right of Eq. (4.23). At zero temperature, the initial vibrational state must be the ground state $\{m_\mu=0\}$ and the quantum number n_μ of the final vibrational state gives the phonon number emitted in the μ th mode. The zero-phonon line $\{n_\mu=0\}$ determines a cutoff on the low-energy side of one absorption band. The absorption band of the $0 \rightarrow j$ electronic transition consists of the zero-phonon line and a series of emitted multiphonon lines. At finite temperature, we first consider the linear electron-phonon interaction when $\omega_{j\mu} = \omega_{0\mu}$. According to Eq. (4.23), the absorption frequency depends only on the net phonon numbers $p_\mu = n_\mu - m_\mu$. Because of the summation over $\{m_\mu\}$ and $\{n_\mu\}$ in Eq. (4.21), we always have the set $\{p_\mu=0\}$ which corresponds to the zero-phonon line, we also have the set $\{0, p_\alpha = \pm 1, 0\}$ where α refers to a certain mode and the plus or minus sign corresponds to the emitted or absorbed one-phonon line, and so on. The absorption spectrum of the $0 \rightarrow j$ electronic transition consists of the zero-phonon line and a series of emitted or absorbed multiphonon lines. For the nonlinear electron-phonon interaction when $\omega_{j\mu} \neq \omega_{0\mu}$, however, the absorption frequency still depends on the phonon excitation numbers $\{n_\mu\}$ besides $\{p_\mu\}$.

Therefore, there is a lot of additional phonon excitation lines between the previous two adjacent multiphonon lines. Since in Sec. II we have inferred the relation $\omega_{j\mu} < \omega_{0\mu}$, the zero-phonon line is shifted to a lower energy $\omega_{j0}^* - \frac{1}{2}(\omega_{0\mu} - \omega_{j\mu})$, the high-energy tail becomes narrower, and the low-energy side gets wider. To sum up, the quadratic electron-phonon interaction produces the two effects: (1) the absorption lines become denser and (2) the absorption spectrum is extended asymmetrically towards lower energy. The strength of the absorption line at frequency (4.23) is proportional to the coefficient in front of the δ function in Eq. (4.21), while this coefficient is determined by the overlap integrals $C_{mn}^{0j\mu}(\Delta_{j0\mu})$. In the next section, we will make a concrete calculation of $C_{mn}^{0j\mu}(\Delta_{j0\mu})$.

V. CALCULATION OF OVERLAP INTEGRALS AND SEVERAL APPROXIMATE CASES

For simplicity, we temporarily write $C_{mn}^{0j\mu}(\Delta_{j0\mu})$ as $C_{mn}^{0j}(\Delta_{j0})$. On substituting the vibrational wave functions (2.18) into Eq. (4.5), the overlap integrals become

$$C_{mn}^{0j}(\Delta_{j0}) = \left(\frac{\alpha_0 \alpha_j}{\pi 2^{m+n} m! n!} \right)^{1/2} \int_{-\infty}^{\infty} \exp \left[-\frac{1}{2}(\alpha_0 q)^2 - \frac{1}{2} \alpha_j^2 (q - \Delta_{j0})^2 \right] H_m(\alpha_0 q) H_n(\alpha_j (q - \Delta_{j0})) dq. \quad (5.1)$$

We multiply both sides of Eq. (5.1) by $t_0^m t_j^n (m! n!)^{-1/2}$, sum over m and n , use the generating function for Hermite polynomials

$$e^{2xt - t^2} = \sum_{n=0}^{\infty} H_n(x) \frac{t^n}{n!},$$

and hence obtain

$$\begin{aligned} & \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} C_{mn}^{0j}(\Delta_{j0}) \frac{t_0^m}{(m!)^{1/2}} \frac{t_j^n}{(n!)^{1/2}} \\ &= \left(\frac{\alpha_0 \alpha_j}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} \exp \left[-\frac{1}{2}(\alpha_0 q)^2 - \frac{1}{2} \alpha_j^2 (q - \Delta_{j0})^2 \right] \\ & \times \exp \left[2(\alpha_0 q) \left(\frac{t_0}{\sqrt{2}} \right) - \left(\frac{t_0}{\sqrt{2}} \right)^2 \right] \\ & \times \exp \left\{ 2 \left[\alpha_j (q - \Delta_{j0}) \right] \left(\frac{t_j}{\sqrt{2}} \right) - \left(\frac{t_j}{\sqrt{2}} \right)^2 \right\} dq. \end{aligned}$$

Then, one performs the integrals over q , expands the result into a power series in t_0 and t_j , and therefore gains

$$\begin{aligned}
\sum_{m=0}^{\infty} \sum_{n=0}^{\infty} C_{mn}^{0j}(\Delta_{j0}) \frac{t_0^m}{(m!)^{1/2}} \frac{t_j^n}{(n!)^{1/2}} &= \left(\frac{2\alpha_0\alpha_j}{\alpha_0^2 + \alpha_j^2} \right)^{1/2} \exp \left[-\frac{\alpha_0^2\alpha_j^2\Delta_{j0}^2}{2(\alpha_0^2 + \alpha_j^2)} \right] \\
&\times \sum_{k_1=0}^{\infty} \sum_{l_1=0}^{\infty} \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \sum_{p=0}^{\infty} (-1)^{l+l_1} \left[\frac{\alpha_0^2 - \alpha_j^2}{2(\alpha_0^2 + \alpha_j^2)} \right]^{k+l} \\
&\times \left(\frac{\sqrt{2}\alpha_0\alpha_j^2\Delta_{j0}}{\alpha_0^2 + \alpha_j^2} \right)^{k_1} \left(\frac{\sqrt{2}\alpha_0^2\alpha_j\Delta_{j0}}{\alpha_0^2 + \alpha_j^2} \right)^{l_1} \left(\frac{2\alpha_0\alpha_j}{\alpha_0^2 + \alpha_j^2} \right)^p \frac{t_0^{2k+k_1+p} t_j^{2l+l_1+p}}{k_1!l_1!k!l!p!}.
\end{aligned}$$

If we let $m=2k+k_1+p$ and $n=2l+l_1+p$ in the above equation, then it follows that

$$\begin{aligned}
\sum_{m=0}^{\infty} \sum_{n=0}^{\infty} C_{mn}^{0j}(\Delta_{j0}) \frac{t_0^m}{(m!)^{1/2}} \frac{t_j^n}{(n!)^{1/2}} &= \left(\frac{2\alpha_0\alpha_j}{\alpha_0^2 + \alpha_j^2} \right)^{1/2} \exp \left[-\frac{\alpha_0^2\alpha_j^2\Delta_{j0}^2}{2(\alpha_0^2 + \alpha_j^2)} \right] \\
&\times \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \sum_{p=0}^{\min(m,n)} \sum_{k=0}^{[(m-p)/2]} \sum_{l=0}^{[(n-p)/2]} \left[\frac{\alpha_0^2 - \alpha_j^2}{2(\alpha_0^2 + \alpha_j^2)} \right]^{k+l} \\
&\times \left(\frac{\sqrt{2}\alpha_0\alpha_j^2\Delta_{j0}}{\alpha_0^2 + \alpha_j^2} \right)^{m-2k-p} \left(\frac{\sqrt{2}\alpha_0^2\alpha_j\Delta_{j0}}{\alpha_0^2 + \alpha_j^2} \right)^{n-2l-p} \\
&\times \left(\frac{2\alpha_0\alpha_j}{\alpha_0^2 + \alpha_j^2} \right)^p \frac{(-1)^{n-l-p} t_0^m t_j^n}{(m-2k-p)!(n-2l-p)!k!l!p!}. \tag{5.2}
\end{aligned}$$

Here $\min(m,n)$ means the lesser of m and n , and $[(m-p)/2]$, $[(n-p)/2]$ signify $(m-p)/2$, $(n-p)/2$ when $m-p$, $n-p$ are even numbers and $(m-p-1)/2$, $(n-p-1)/2$ when $m-p$, $n-p$ are odd numbers. Now we equate equal powers of t_0 and t_j on both sides of Eq. (5.2) and acquire for the overlap integrals

$$\begin{aligned}
C_{mn}^{0j}(\Delta_{j0}) &= \left(\frac{2\alpha_0\alpha_j}{\alpha_0^2 + \alpha_j^2} \right)^{1/2} \exp \left[-\frac{\alpha_0^2\alpha_j^2\Delta_{j0}^2}{2(\alpha_0^2 + \alpha_j^2)} \right] \sum_{p=0}^{\min(m,n)} \sum_{k=0}^{[(m-p)/2]} \sum_{l=0}^{[(n-p)/2]} \frac{(-1)^{n-l-p} (m!n!)^{1/2}}{(m-2k-p)!(n-2l-p)!k!l!p!} \\
&\times \left[\frac{\alpha_0^2 - \alpha_j^2}{2(\alpha_0^2 + \alpha_j^2)} \right]^{k+l} \left(\frac{\sqrt{2}\alpha_0\alpha_j^2\Delta_{j0}}{\alpha_0^2 + \alpha_j^2} \right)^{m-2k-p} \left(\frac{\sqrt{2}\alpha_0^2\alpha_j\Delta_{j0}}{\alpha_0^2 + \alpha_j^2} \right)^{n-2l-p} \left(\frac{2\alpha_0\alpha_j}{\alpha_0^2 + \alpha_j^2} \right)^p. \tag{5.3}
\end{aligned}$$

The so general expression of the overlap integrals is deduced for the first time, whereas the previous researchers all made a variety of assumptions to calculate the overlap integrals. In what follows, we will discuss several approximate cases of this expression.

A. Neglecting the lattice relaxation effect

Since the equilibrium displacement $\Delta_{i\mu}$ of a vibrational mode characterizes the lattice relaxation effect, we let $\Delta_{0\mu} = \Delta_{j\mu} = 0$, so that the relative equilibrium displacement $\Delta_{j0\mu} = \Delta_{j\mu} - \Delta_{0\mu} = 0$. This is the case of so-called quadratic modes. If the defect site is a center of inversion, the linear electron-phonon interaction will vanish by symmetry for the vibrational modes with odd parity. In this case, a quadratic electron-phonon interaction will dominate.

In the series (5.3), the nonzero term is the zeroth power of Δ_{j0} and therefore one has $m-2k-p=0$ and $n-2l-p=0$. The two relations dictate that m, n, p be either all even or all odd. For m and n , when one index is odd and the other

even, Eq. (5.3) produces $C_{mn}^{0j}(0)=0$. When m and n are either both even or both odd, and as $\alpha_i = (\omega_i/\hbar)^{1/2}$, Eq. (5.3) is reduced to

$$\begin{aligned}
C_{mn}^{0j}(0) &= \left[\frac{4\omega_0\omega_j}{(\omega_0 + \omega_j)^2} \right]^{1/4\min(m,n)} \sum_{p=0,1}^{(m+n)/2} (-1)^{(n-p)/2} \\
&\times \frac{(m!n!)^{1/2}}{\left(\frac{m-p}{2}\right)! \left(\frac{n-p}{2}\right)! p!} \left[\frac{\omega_0 - \omega_j}{2(\omega_0 + \omega_j)} \right]^{(m+n)/2-p} \\
&\times \left[\frac{4\omega_0\omega_j}{(\omega_0 + \omega_j)^2} \right]^{p/2}, \tag{5.4}
\end{aligned}$$

where p is even when m, n are both even and p is odd when m, n are both odd. Equation (5.4) embodies conservation of the parity of the vibrational states during transition processes of the electron-phonon system.

Setting $x = (\omega_0 - \omega_j)/(\omega_0 + \omega_j)$, then Eq. (5.4) becomes

$$C_{mn}^{0j}(x) = \left[(1-x^2)^{1/2} \frac{m!n!}{2^{m+n}} \right]^{1/2} (-1)^{n/2} x^{(m+n)/2} \\ \times \sum_{p=0,1}^{\min(m,n)} \frac{2^p}{\left(\frac{m-p}{2}\right)! \left(\frac{n-p}{2}\right)! p!} \left[-\frac{(1-x^2)}{x^2} \right]^{p/2}. \quad (5.5)$$

The overlap integrals in Eq. (5.5) can be expressed as several mathematical functions. In the theory of mathematical functions,²⁰ we will develop the most compact expression of the overlap integrals. In doing so, we further let $z = i(1-x^2)^{1/2}x^{-1}$. When m and n are both even, i.e., $m = 2\alpha$ and $n = 2\beta$, Eq. (5.5) can be written in the form,

$$C_{2\alpha,2\beta}^{0j}(x) = \left[(1-x^2)^{1/2} \frac{(2\alpha)!(2\beta)!}{2^{2\alpha+2\beta}} \right]^{1/2} \\ \times (-1)^\beta x^{\alpha+\beta} (\alpha!\beta!)^{-1} F(-\alpha, -\beta; \frac{1}{2}; z^2), \quad (5.6)$$

where $F(a,b;c;z)$ is the Gauss hypergeometric series and the Gauss series reduces to a polynomials of degree n in z when a or b is equal to $-n$ ($n=0,1,2,\dots$). With the help of a property of the hypergeometric function, Eq. (5.6) can be rewritten in the most compact form,

$$C_{2\alpha,2\beta}^{0j}(z) = (\pi/2)^{1/2} (-1)^{\alpha/2-\beta/2} \\ \times [(2\alpha)!(2\beta)!]^{-1/2} z^{1/2} P_{\alpha-\beta-1/2}^{\alpha+\beta+1/2}(z), \quad (5.7)$$

where $P_\nu^\mu(z)$ is the associated Legendre function of the first kind of degree ν and order μ . The associated Legendre function possesses the following properties: When μ and ν are half integers, P_ν^μ is a polynomial in z . When μ and ν are integers and if $\mu > \nu$, P_ν^μ is identically zero.

Now we turn to the case when m and n are both odd, i.e., $m = 2\alpha + 1$ and $n = 2\beta + 1$. In this case, Eq. (5.5) may be written in terms of the hypergeometric function

$$C_{2\alpha+1,2\beta+1}^{0j}(x) = \left[(1-x^2)^{3/2} \frac{(2\alpha+1)!(2\beta+1)!}{2^{2\alpha+2\beta}} \right]^{1/2} \\ \times (-1)^{\beta+1} x^{\alpha+\beta} (\alpha!\beta!)^{-1} \\ \times F(-\alpha, -\beta; \frac{3}{2}; z^2),$$

and in terms of the associated Legendre function

$$C_{2\alpha+1,2\beta+1}^{0j}(z) = (\pi/2)^{1/2} (-1)^{\alpha/2-\beta/2} \\ \times [(2\alpha+1)!(2\beta+1)!]^{-1/2} \\ \times z^{1/2} P_{\alpha-\beta-1/2}^{\alpha+\beta+3/2}(z). \quad (5.8)$$

We further consider m and n where one index is odd and the other even. In this case, $m/2 + n/2 + \frac{1}{2}$ and $m/2 - n/2 - \frac{1}{2}$ are integers and $m/2 + n/2 + \frac{1}{2} > m/2 - n/2 - \frac{1}{2}$, so that

$$P_{m/2-n/2-1/2}^{m/2+n/2+1/2}(z) = 0. \quad (5.9)$$

At this point, Eqs. (5.7), (5.8), and (5.9) may be combined into a single expression,

$$C_{mn}^{0j}(z) = (\pi/2)^{1/2} (-1)^{m/4-n/4} (m!n!)^{-1/2} \\ \times z^{1/2} P_{m/2-n/2-1/2}^{m/2+n/2+1/2}(z), \quad (5.10)$$

where m and n are arbitrary positive integers.

If one puts the $C_{m_\mu n_\mu}^{0j\mu}(z_\mu)$ given by Eq. (5.10) into Eq. (4.21), in principle one can calculate the line-shape function of quadratic modes. Since the expression (4.21) is so complicated and the parameters are so numerous, however, without further simplification it is practically impossible to undertake the calculation. For the further treatment of simplification, please see Ref. 10.

B. Neglecting the lattice-frequency shift effect

As known in Sec. II, the quadratic electron-phonon interaction causes a shift in the vibration frequencies of the lattice, and the renormalized lattice frequencies $\omega_{i\mu}$ depend on the electronic states. Now, let $\omega_{0\mu} = \omega_{j\mu} = \omega_\mu$ and correspondingly $\alpha_{0\mu} = \alpha_{j\mu} = \alpha_\mu$. This means that we consider only the linear electron-phonon interaction.

In this situation, we have $k=l=0$ in Eq. (5.3), so that Eq. (5.3) is reduced to

$$C_{mn}^{0j}(\Delta_{j0}) = \exp\left(-\frac{\alpha^2 \Delta_{j0}^2}{4}\right) \sum_{p=0}^{\min(m,n)} (-1)^{n-p} \\ \times \frac{(m!n!)^{1/2}}{(m-p)!(n-p)! p!} \left(\frac{\alpha \Delta_{j0}}{\sqrt{2}}\right)^{m+n-2p}.$$

Next, one lets $r = \min(m,n) = \frac{1}{2}(m+n-|m-n|)$, makes the summation-index transformation $k = r - p$, and obtains for the overlap integrals

$$C_{mn}^{0j}(\Delta_{j0}) = (-1)^{(1/2)(n-m+|m-n|)} \\ \times \left[\frac{r!}{(r+|m-n|)!} \right]^{1/2} \left(\frac{\alpha \Delta_{j0}}{\sqrt{2}}\right)^{|m-n|} \\ \times \exp\left(-\frac{\alpha^2 \Delta_{j0}^2}{4}\right) L_r^{|m-n|} \left(\frac{\alpha^2 \Delta_{j0}^2}{2}\right), \quad (5.11)$$

where

$$L_r^{|m-n|}(x) = \sum_{k=0}^r (-1)^k \frac{(r+|m-n|)!}{(|m-n|+k)!(r-k)!} \frac{x^k}{k!}$$

is the generalized Laguerre polynomial of degree r .

If one substitutes the $C_{m_\mu n_\mu}^{0j\mu}(\Delta_{j0\mu})$ given by Eq. (5.11) into Eq. (4.21), one will easily find the line-shape function of linear modes. First one needs to perform the thermal average using $\rho_0(\{m_\mu\})$ in Eq. (4.19). Then, we change the index n_μ of summation into $p_\mu = n_\mu - m_\mu$ where $p_\mu = 0, \pm 1, \pm 2, \dots$, alter the index m_μ of summation into $r_\mu = \frac{1}{2}(n_\mu + m_\mu - |p_\mu|)$, and acquire for the line-shape function,

$$\begin{aligned}
f_j(\omega) &= \sum_{\{p_\mu\}} \prod_{\mu} \left\{ \sum_{r_\mu=0}^{\infty} \frac{r_\mu!}{(r_\mu + |p_\mu|)!} \right. \\
&\quad \times \left. \left(e^{-\beta\hbar\omega_\mu} r_\mu \left[L_{r_\mu}^{p_\mu} \left(\frac{\alpha_\mu^2 \Delta_{j0\mu}^2}{2} \right) \right]^2 \right) \right\} \\
&\quad \times \left(e^{\beta\hbar\omega_\mu} (p_\mu - |p_\mu|)^{1/2} (1 - e^{-\beta\hbar\omega_\mu}) \left(\frac{\alpha_\mu^2 \Delta_{j0\mu}^2}{2} \right)^{|p_\mu|} \right) \\
&\quad \times \exp \left(-\frac{\alpha_\mu^2 \Delta_{j0\mu}^2}{2} \right) \delta \left(\omega - \omega_{j0}^* - \sum_{\mu} \omega_\mu p_\mu \right).
\end{aligned} \tag{5.12}$$

For the series of Laguerre polynomials in the braces in Eq. (5.12), we utilize a theorem in the theory of mathematical functions,²¹

$$\begin{aligned}
&\sum_{m=0}^{\infty} \frac{m!}{(m+n)!} t^m [L_m^n(x)]^2 \\
&= \frac{(x^2 t)^{-n/2}}{1-t} \exp \left(-\frac{2xt}{1-t} \right) I_n \left(\frac{2xt^{1/2}}{1-t} \right),
\end{aligned}$$

where $I_n(z)$ is the modified Bessel function of the first kind of order n and $I_{-n}(z) = I_n(z)$ for n a natural number. As a result of the theorem, Eq. (5.12) is simplified as

$$\begin{aligned}
f_j(\omega) &= \sum_{\{p_\mu\}} \exp \left[-\sum_{\mu} (2\bar{n}_\mu + 1) \frac{\alpha_\mu^2 \Delta_{j0\mu}^2}{2} \right] \prod_{\mu} \left(\frac{\bar{n}_\mu + 1}{\bar{n}_\mu} \right)^{p_\mu/2} \\
&\quad \times I_{p_\mu} \left\{ 2 \left(\frac{\alpha_\mu^2 \Delta_{j0\mu}^2}{2} \right) [\bar{n}_\mu (\bar{n}_\mu + 1)]^{1/2} \right\} \\
&\quad \times \delta \left(\omega - \omega_{j0}^* - \sum_{\mu} \omega_\mu p_\mu \right),
\end{aligned} \tag{5.13}$$

where

$$\bar{n}_\mu = \frac{1}{e^{\beta\hbar\omega_\mu} - 1}$$

is the mean phonon number excited thermally per mode. Note that Eq. (5.13) applies to either sign of the various p_μ .

In principle, Eq. (5.13) can be used to calculate the line shape due to the linear electron-phonon interaction. Since the number f of vibrational modes of the lattice is so large (10^{23} per cm^3), however, such numerical calculations are impossible. Fortunately, the present laser-active color centers all belong in the molecule-type color center, in which the defect electron has very weak coupling with the body vibrational modes of the lattice, but interacts strongly with a very small number of local modes that surround the defect center. The local modes have frequencies in the gap between the acoustical and optical branches and above the optical branches. In this situation, we may conveniently take only several local modes to undertake the calculation of line-shape functions. The extreme situation is the configurational coordinate model, which assumes that there is only one ‘effective’ frequency associated with the local modes. This

model is superior in many respects to the Huang-Rhys case to be discussed in the following.

Huang-Rhys case

In this case, all the modes have a single frequency $\omega_\mu = \omega_l$, where ω_l is the frequency of longitudinal optical phonons. Correspondingly we have $\alpha_\mu = \alpha = (\omega_l/\hbar)^{1/2}$ and $\bar{n}_\mu = \bar{n} = (e^{\beta\hbar\omega_l} - 1)^{-1}$. Therefore, Eq. (5.13) is reduced to

$$\begin{aligned}
f_j(\omega) &= \sum_{\{p_\mu\}} \exp \left[-(2\bar{n} + 1) \sum_{\mu} \frac{\alpha^2 \Delta_{j0\mu}^2}{2} \right] \left(\frac{\bar{n} + 1}{\bar{n}} \right)^{(\sum_{\mu} p_\mu)/2} \\
&\quad \times \prod_{\mu} I_{p_\mu} \left\{ 2 \left(\frac{\alpha^2 \Delta_{j0\mu}^2}{2} \right) [\bar{n}(\bar{n} + 1)]^{1/2} \right\} \\
&\quad \times \delta \left(\omega - \omega_{j0}^* - \omega_l \sum_{\mu} p_\mu \right).
\end{aligned} \tag{5.14}$$

Now we introduce the Huang-Rhys factor $S_j = \sum_{\mu} \frac{1}{2} \alpha^2 \Delta_{j0\mu}^2$. The factor can be cast into the form

$$S_j = \frac{\sum_{\mu} \frac{1}{2} \omega_l^2 \Delta_{j0\mu}^2}{\hbar \omega_l}.$$

The numerator is just the elastic energy of lattice relaxation released during the transition process from the electronic ground state to its j th excited state, and the denominator is the phonon energy, so that S_j can be understood as the lattice relaxation energy expressed in terms of phonon numbers. The factor S_j is used to characterize the coupling strength between the defect electron and the linear modes. The net phonon number emitted by all the lattice modes is $P = \sum_{\mu} p_\mu$. Applying the relation

$$p_f = P - \sum_{\mu=1}^{f-1} p_\mu,$$

we change the index p_f of summation into P , so that the new index set of summation is $\{p_1, p_2, \dots, p_{f-1}, P\}$. In this way Eq. (5.14) becomes

$$\begin{aligned}
f_j(\omega) &= \sum_{P=-\infty}^{\infty} e^{-(2\bar{n}+1)S_j} \left(\frac{\bar{n}+1}{\bar{n}} \right)^{P/2} \\
&\quad \times \left(\sum_{p_1=-\infty}^{\infty} \cdots \sum_{p_{f-1}=-\infty}^{\infty} I_{P-\sum_{\mu} p_\mu} \right) \\
&\quad \times \left\{ 2 \left(\frac{\alpha^2 \Delta_{j0f}^2}{2} \right) [\bar{n}(\bar{n}+1)]^{1/2} \right\} \\
&\quad \times \prod_{\mu=1}^{f-1} I_{p_\mu} \left\{ 2 \left(\frac{\alpha^2 \Delta_{j0\mu}^2}{2} \right) [\bar{n}(\bar{n}+1)]^{1/2} \right\} \\
&\quad \times \delta(\omega - \omega_{j0}^* - \omega_l P),
\end{aligned} \tag{5.15}$$

where the prime on the summation symbol means excluding $\mu=f$. Using the integral representation of the modified Bessel function of the first kind of order n , where n is a natural number,

$$I_n(z) = \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{z \cos t + int} dt,$$

one can easily verify that

$$\begin{aligned} & \sum_{p_1=-\infty}^{\infty} \cdots \sum_{p_{f-1}=-\infty}^{\infty} I_{P-\sum_{\mu} p_{\mu}} \left\{ 2 \left(\frac{\alpha^2 \Delta_{j0f}^2}{2} \right) [\bar{n}(\bar{n}+1)]^{1/2} \right\} \\ & \times \prod_{\mu=1}^{f-1} I_{p_{\mu}} \left\{ 2 \left(\frac{\alpha^2 \Delta_{j0\mu}^2}{2} \right) [\bar{n}(\bar{n}+1)]^{1/2} \right\} \\ & = I_P \{ 2S_j [\bar{n}(\bar{n}+1)]^{1/2} \}. \end{aligned}$$

Substituting the last result into Eq. (5.15), finally we obtain

$$\begin{aligned} f_j(\omega) &= \sum_{P=-\infty}^{\infty} e^{-S_j(2\bar{n}+1)} \left(\frac{\bar{n}+1}{\bar{n}} \right)^{P/2} \\ & \times I_P \{ 2S_j [\bar{n}(\bar{n}+1)]^{1/2} \} \delta(\omega - \omega_{j0}^* - \omega_l P). \end{aligned} \quad (5.16)$$

Equation (5.16) is exactly the well-known Huang-Rhys line-shape function.

Originally, Huang and Rhys expanded the oscillator wave functions $X_{n_{\mu}}(q_{\mu} - \Delta_{j0\mu})$ in the overlap integrals with respect to $\Delta_{j0\mu}$, retained the first-order terms in the two series, and then employed statistical mechanics to derive Eq. (5.16). Afterwards, Lax utilized the generating function method and also obtained this result. Here the present author strictly calculates the overlap integrals so as to acquire the line-shape function too.

With the aid of the generating function of the modified Bessel function

$$\exp \left[\frac{1}{2} z \left(t + \frac{1}{t} \right) \right] = \sum_{n=-\infty}^{\infty} t^n I_n(z),$$

it is easily shown that

$$\sum_{P=-\infty}^{\infty} e^{-S_j(2\bar{n}+1)} \left(\frac{\bar{n}+1}{\bar{n}} \right)^{P/2} I_P \{ 2S_j [\bar{n}(\bar{n}+1)]^{1/2} \} = 1.$$

Thereby, the line-shape function $f_j(\omega)$ is normalized to unity over ω ,

$$\int f_j(\omega) d\omega = 1.$$

C. Weak nonlinear effect

The two extreme cases discussed in Secs. V A and V B are rarely encountered in realistic color-center crystals. Most of color-center crystals are of a weak nonlinearity. By the weak nonlinearity, we mean that the linear electron-phonon interaction is predominant and the quadratic electron-phonon interaction is weak. In this case, when calculating the normalized line-shape function as given by Eq. (4.21), for the overlap integrals we neglect the dependence of the lattice frequencies $\omega_{i\mu}$ on the electronic states i , but for the arguments of the δ functions we retain this dependence. Consequently, the treatment of the overlap integrals in Eq. (5.3) is

the same as Sec. V B, whereas we keep the factor $\omega_{j\mu} - \omega_{0\mu}$ in the arguments of the δ functions in Eq. (4.21).

Owing to the quadratic electron-phonon interaction, the renormalized phonon energy after the transition of electronic states becomes smaller than that before the transition, i.e., $\omega_{j\mu} < \omega_{0\mu}$, which is discussed in Sec. II. Thereby, we can let $\omega_{0\mu} - \omega_{j\mu} = \rho_{j\mu} \omega_{0\mu}$, where $\rho_{j\mu}$ is a phenomenological parameter and satisfies the relation $0 < \rho_{j\mu} < 1$. Then, for the two factors $\rho_{j\mu} \omega_{0\mu}$ and $\omega_{0\mu}(n_{\mu} - m_{\mu})$ in the δ functions in Eq. (4.21) we assume $\omega_{0\mu}$ to be independent of the electronic ground state $i=0$, i.e., $\omega_{0\mu} = \omega_{\mu}$. Concomitantly, the normalized line-shape function in Eq. (4.21) is evaluated as

$$\begin{aligned} f_j(\omega) &= \sum_{\{P_{\mu}\}} \exp \left[- \sum_{\mu} (2\bar{n}_{\mu} + 1) \frac{\alpha_{\mu}^2 \Delta_{j0\mu}^2}{2} \right] \\ & \times \prod_{\mu} \left(\frac{\bar{n}_{\mu} + 1}{\bar{n}_{\mu}} \right)^{P_{\mu}/2} \\ & \times I_{P_{\mu}} \left\{ 2 \left(\frac{\alpha_{\mu}^2 \Delta_{j0\mu}^2}{2} \right) [\bar{n}_{\mu}(\bar{n}_{\mu} + 1)]^{1/2} \right\} \\ & \times \delta \left\{ \omega - \omega_{j0}^* - \sum_{\mu} \left[-\rho_{j\mu} \omega_{\mu} (\bar{n}_{\mu} + \frac{1}{2}) + \omega_{\mu} P_{\mu} \right] \right\}, \end{aligned} \quad (5.17)$$

which is the modified form of Eq. (5.13). In the arguments of the δ functions in the last equation, we have replaced the quantum number n_{μ} with the mean phonon number \bar{n}_{μ} . The reason for this is that the summation over r_{μ} in Eq. (5.12) means to take the thermal average, and through the relation $n_{\mu} = r_{\mu} + \frac{1}{2} |p_{\mu}| + \frac{1}{2} p_{\mu}$ this causes us to take the thermal average over n_{μ} .

As seen from Eq. (5.17), the shape and strength of light absorption are all unchanged in comparison with the linear case, and only the absorption frequencies are redshifted. The absorption frequency of a P -phonon line, which is defined by $P = \sum_{\mu} p_{\mu}$, is now given by

$$\omega_P = \omega_{j0}^* + \sum_{\mu} \left[-\rho_{j\mu} \omega_{\mu} (\bar{n}_{\mu} + \frac{1}{2}) + \omega_{\mu} p_{\mu} \right]. \quad (5.18)$$

Since \bar{n}_{μ} increases with temperature, the frequency Ω_{j0}^* of the absorption peak shifts to lower frequency as the temperature increases, which is in agreement with the experimental result.

At the moment, one needs to adopt the configurational coordinate model, which assumes that the electron interacts only with one effective local mode. That is to say, we must set $\omega_{\mu} = \omega_{ef}$ for all μ , where ω_{ef} is the frequency of the effective local mode. To include acoustical phonons, the frequency ω_{ef} of the effective local mode must be smaller than the frequency ω_l of longitudinal optical phonons. If we further introduce a macroscopic phenomenological parameter $B_j = \sum_{\mu} \rho_{j\mu}$, then the line-shape equation (5.17) becomes

$$f_j(\omega) = \sum_{P=-\infty}^{\infty} e^{-S_j(2\bar{n}+1)} \left(\frac{\bar{n}+1}{\bar{n}} \right)^{P/2} \times I_P \{ 2S_j [\bar{n}(\bar{n}+1)]^{1/2} \} \times \delta[\omega - \omega_{j0}^* + B_j \omega_{ef}(\bar{n} + \frac{1}{2}) - \omega_{ef}P]. \quad (5.19)$$

Here, the Huang-Rhys factor S_j and the mean phonon number \bar{n} are redefined as

$$S_j = \frac{\sum_{\mu} \frac{1}{2} \omega_{ef}^2 \Delta_{j0\mu}^2}{\hbar \omega_{ef}}, \quad \bar{n} = \frac{1}{e^{\beta \hbar \omega_{ef}} - 1}.$$

Correspondingly, the absorption frequency of a P -phonon line is simplified from Eq. (5.18) as

$$\omega_P = \omega_{j0}^* - B_j \omega_{ef}(\bar{n} + \frac{1}{2}) + \omega_{ef}P. \quad (5.20)$$

It is worthy to note that in the case discussed in Sec. V B light-absorption frequencies are independent of temperature. This is exactly the result due to the linear electron-phonon interaction. Therefore, the redshift of light-absorption frequency with temperature is characteristic of the quadratic electron-phonon interaction.

VI. WEAK NONLINEAR SPECTRAL FUNCTION AND ITS APPLICATION IN F_A CENTERS

As shown in Sec. V, in the presence of both linear and quadratic electron-phonon interactions, a general analytic expression of line-shape functions $f_j(\omega)$ is hard to derive, while this expression of $f_j(\omega)$ can be found under the weak nonlinear approximation. Indeed, so far some researchers have employed a variety of modified Huang-Rhys line-shape functions to describe the main absorption band of F color centers. However, such a description fails for a more complex color center and for a polychromatic incident light, which will induce a series of absorption bands. In this case, we must make use of the spectral function $F(\omega)$ to describe many absorption bands of various color centers. If one substitutes the line-shape equation (5.19) for the j th absorption band into Eq. (4.22), the weak nonlinear spectral function $F(\omega)$ is acquired as

$$F(\omega) = \sum_j \frac{\omega}{\omega_{j0}} f_{j0} \sum_{P=-\infty}^{\infty} e^{-S_j(2\bar{n}+1)} \left(\frac{\bar{n}+1}{\bar{n}} \right)^{P/2} \times I_P \{ 2S_j [\bar{n}(\bar{n}+1)]^{1/2} \} \times \delta[\omega - \omega_{j0}^* + B_j \omega_{ef}(\bar{n} + \frac{1}{2}) - \omega_{ef}P]. \quad (6.1)$$

In form, Eq. (6.1) signifies the summation over infinite excited states j of the trapped electron and thus $F(\omega)$ is hard to evaluate. Since the frequency width of the polychromatic incident light is finite and can be controlled at will, we can always select the frequency width such that it just covers several particular peak-transition frequencies Ω_{j0}^* . In reality, Eq. (6.1) represents a finite sum and the $F(\omega)$ in this case is easy to calculate. On the other hand, the oscillator strength f_{j0} gives a transition probability of the electron from the

ground state $i=0$ to the j th excited state. The probability f_{j0} falls off rapidly with increasing of the excited state j . Take the F center in KCl as an example: the oscillator strength $f \approx 0.81$ for the F band, $f \approx 0.1$ for the K band, and $f \approx 0.01$ for the L band. Therefore, in Eq. (6.1) we just consider the summation over the first several excited states j .

Since the strengths of many absorption peaks induced by a polychromatic incident light are modulated by oscillator strengths f_{j0} , we need to know the details of f_{j0} . According to Eq. (4.16), f_{j0} is determined by the dipole matrix element \vec{r}_{j0} defined by Eq. (4.15). Further, the concrete evaluation of \vec{r}_{j0} depends on our knowledge of the electronic structure of the color center being investigated. The simplest electronic defect is the F center. Although not laser-active itself, it serves as an important building block for the formation of all laser-active F aggregate centers. As the potential energy in the Hamiltonian $\hat{H}_e(\vec{r}, \vec{p})$ of the F -center electron is spherically symmetric, $\hat{H}_e(\vec{r}, \vec{p})$ has the eigenfunctions $u_j(\vec{r}) = R_{nl}(r)Y_{lm}(\theta, \phi)$, where the state index $j=(nlm)$, $R_{nl}(r)$ is the radial function, and $Y_{lm}(\theta, \phi)$ is the spherical harmonic. The corresponding energy eigenvalues $\varepsilon_j = \varepsilon_{nl}$ are in the forbidden energy gap. The level ε_{nl} is independent of the magnetic quantum number m and $(2l+1)$ -fold degenerate. The ground state of F centers is an $i=1s$ state and the electric dipole transition selection rules only allow optically excited states to be the $j=np$, $n \geq 2$ states, which are threefold degenerate. A $1s \rightarrow 2p$ transition gives rise to the F band, which is called the fundamental absorption transition. The superposition of $1s \rightarrow np$, $n \geq 3$ transitions leads to the K band. The L band arises from transitions of the electron from the ground state to states that are degenerate with conduction states. When an F center is perturbed strongly, its threefold degenerate $2p$ level is splitted into two components, so that the main F band now consists of two bands in absorption. There exist two internal perturbation methods. When one of the nearest-neighbor cations of an F center is replaced by a cationic impurity, the F_A center forms. The F_2^+ center consists of two anion vacancies binding one electron.

The color center systems, which so far have been successfully operated as broadly tunable continuous-wave infrared lasers, can be divided into two characteristic groups: F_A and F_A -like centers, and F_2^+ and F_2^+ -like centers. As an example, we now apply our theory of light absorption to F_A centers, because in comparison with F_2^+ centers, they possess simpler structures and were found earlier.

When an alkali halide crystal contains a predominant content of extrinsic alkali ions of smaller size than the host alkali ion, F_A centers are formed. According to the F_A model put forward by Lütty,²² the F_A center consists of an F center attached to a small alkali ion on a $\langle 100 \rangle$ nearest-neighbor site, as shown in Fig. 1. There are two distinct types of F_A centers. A representative of type-I F_A centers is the F_A center in a Na^+ -doped KCl crystal, and a representative of type-II F_A centers is the F_A center in a Li^+ -doped KCl crystal. The $1s \rightarrow 2p$ transitions of $F_A(\text{I})$ and $F_A(\text{II})$ centers produce similar double-peak absorption spectra, which are called F_A bands. The $F_A(\text{I})$ centers exhibit a depolarized emission with the linewidth and Stokes shift similar to the F center case. However, the $F_A(\text{II})$ centers show a polarized emission with a very narrow linewidth and a very large

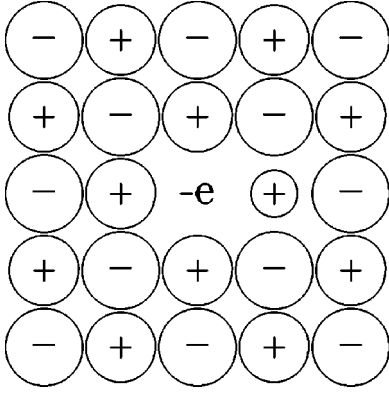


FIG. 1. Ionic structure of the ground state configuration of F_A centers. The $-e$ represents one excess electron bound at the vacancy.

Stokes shift. Consequently, the $F_A(\text{II})$ centers are laser-active but the $F_A(\text{I})$ centers are not. In the following the F_A centers refer to the $F_A(\text{II})$ centers.

The splitting of a single F band into two F_A bands may be easily understood in group-theoretical terms. The F and F_A centers have the same $1s$ singlet ground state. The F center in alkali halide crystals has the symmetry of a full octahedral group O_h . The $2p$ triplet excited states of F centers transform according to the irreducible representation T_{1u} of the group O_h . The resulting F_A center from an F center possesses the symmetry of a tetragonal group C_{4v} , with the symmetry axis being in the $\langle 100 \rangle$ direction. Since C_{4v} is a subgroup of O_h , the three-dimensional representation T_{1u} of O_h reduces to the sum of two irreducible representations A_1 and E of C_{4v} with dimensions one and two, respectively. The $2p_x$ and $2p_y$ states of F_A centers are twofold degenerate E states and the $2p_z$ state is a singlet A_1 state. The E level lies close to the T_{1u} level of F centers whereas the A_1 level is shifted to a lower energy below it. In this way, the triply degenerate T_{1u} level of F centers splits into an E doublet and an A_1 level of F_A centers. Assume the electric field vector of a polarized light incident in the F_A center crystal is not parallel to a $\langle 100 \rangle$ direction, the irradiation will lead to the appearance of two main absorption bands of F_A centers. The low-energy absorption band, labeled by F_{A1} , corresponds to the $1s \rightarrow A_1$ transition of an F_A electron, where the electric-dipole transition vector is along the symmetry axis of the center which passes through the impurity cation. The high-energy absorption band, labeled by F_{A2} , corresponds to the $1s \rightarrow E$ transition of an F_A electron, where the electric-dipole transition vector is normal to the symmetry axis of the center.

Integration of absorption spectra of F_A centers shows that the F_{A1} transition has the same oscillator strength as each of the twofold F_{A2} transitions. Let $f_{2p,1s}$ stand for this oscillator strength. Next, we need to find the Huang-Rhys factors for the F_{A1} and F_{A2} transitions, which are determined by the relative displacements of the equilibrium configurations of the lattice in the electronic ground and excited states. According to the Franck-Condon principle, during the $1s \rightarrow A_1$ and E transitions of F_A electrons, the lattice ions keep the equilibrium configuration $\Delta_{1s,\mu}$ ($\mu = 1, 2, \dots, f$) in the electronic $1s$ ground state, where $\Delta_{i\mu}$ are introduced in Eqs.

(2.12) and (2.13). When the electrons reach the A_1 and E excited states, the lattice ions having the ground-state configuration $\Delta_{1s,\mu}$ are in the vibration excited state. The lattice has to reach the vibration ground state by relaxing into a saddlepoint configuration, in which the two vacancies form a double-well potential for the center electron, separated by a high central barrier formed by the anion. Consequently, the $1s$ ground state and A_1 , E excited states of the single-well potential are transformed into the lowest symmetric state ψ_S and lowest asymmetric state ψ_A of the double-well potential, respectively. The transition from the relaxed excited state ψ_A to the lowest symmetric state ψ_S leads to a single polarized emission. The F_A center in the ψ_S state will relax into either its original lattice place or into a reoriented F_A center. Let $\Delta_{2p,\mu}$ represent the equilibrium configuration of the lattice in the relaxed excited state ψ_A . The relative displacement of the equilibrium configurations of the ψ_A and $1s$ states is given by $\Delta_{2p,1s;\mu} = \Delta_{2p,\mu} - \Delta_{1s,\mu}$. Therefore, the F_{A1} and F_{A2} transitions have the same Huang-Rhys factor $S_{2p} = (\sum_{\mu} \frac{1}{2} \omega_{ef}^2 \Delta_{2p,1s;\mu}^2) / \hbar \omega_{ef}$. Similarly, we may assume that the A_1 and E excited states have the same macroscopic phenomenological parameter B_{2p} .

In Sec. IV, we have introduced the three transition frequencies of the electron from the ground state to the j th excited state: ω_{j0} , ω_{j0}^* , and Ω_{j0}^* . ω_{j0} represents the bare transition frequency without multiphonon transitions. ω_{j0}^* denotes the transition frequency renormalized by the electron-ion correlation effect, in the absence of multiphonon transitions. ω_{j0} and ω_{j0}^* have a negligible difference and cannot be measured directly in optical absorption experiments, because electronic transitions always accompany multiphonon transitions. Ω_{j0}^* stands for the transition frequency at an absorption peak in the presence of multiphonon transitions, only which can be determined directly in optical absorption experiments. Let $\omega_{A_1,1s}^*$ and $\omega_{E,1s}^*$ denote the renormalized frequencies of the F_{A1} and F_{A2} transitions, respectively. At this point, the spectral function of the main F_A bands is obtained from Eq. (6.1) as

$$\begin{aligned}
 F(\omega) = & \sum_{P=-\infty}^{\infty} f_{2p,1s} e^{-S_{2p}(2\bar{n}+1)} \left(\frac{\bar{n}+1}{\bar{n}} \right)^{P/2} \\
 & \times I_P \{ 2S_{2p} [\bar{n}(\bar{n}+1)]^{1/2} \} \\
 & \times \left\{ \frac{\omega}{\omega_{A_1,1s}^*} \delta \left[\omega - \omega_{A_1,1s}^* + B_{2p} \omega_{ef} (\bar{n} + \frac{1}{2}) - \omega_{ef} P \right] \right. \\
 & \left. + 2 \frac{\omega}{\omega_{E,1s}^*} \delta \left[\omega - \omega_{E,1s}^* + B_{2p} \omega_{ef} (\bar{n} + \frac{1}{2}) - \omega_{ef} P \right] \right\}. \quad (6.2)
 \end{aligned}$$

In the last equation, for the factor ω/ω_{j0} we have replaced the bare frequency ω_{j0} with the renormalized frequency ω_{j0}^* , and the prefactor 2 of $\omega/\omega_{E,1s}^*$ is the degeneracy of the E level.

Based on Eq. (6.2), we now want to calculate $F(\omega)$ as a function of frequency ω and temperature T . According to Eq. (5.20), ω only takes on the discrete values when P goes

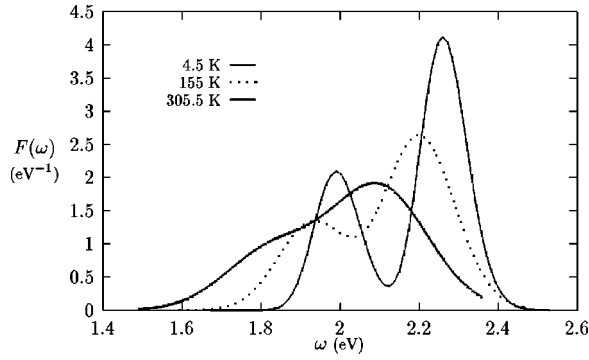


FIG. 2. Theoretical absorption curves of F_A centers in a Li^+ -doped KCl crystal for different temperatures.

through all possible integers, and so the frequency spacing of absorbed photons is the effective phonon frequency ω_{ef} . The δ functions in Eq. (6.2) obviously have the values

$$\delta[\omega - \omega_{j0}^* + B_j \omega_{ef}(\bar{n} + \frac{1}{2}) - \omega_{ef}P] = \begin{cases} \frac{1}{\omega_{ef}} & \omega = \omega_{j0}^* - B_j \omega_{ef}(\bar{n} + \frac{1}{2}) + \omega_{ef}P, \\ 0 & \text{otherwise.} \end{cases} \quad (6.3)$$

The data concerned in a Li^+ -doped KCl crystal are given as follows.²² The effective phonon frequency $\omega_{ef} = 1.86 \times 10^{13} \text{ s}^{-1}$ while the frequency of longitudinal optical phonons $\omega_l = 4.02 \times 10^{13} \text{ s}^{-1}$. One can derive $f_{2p,1s} = 0.27$ from the oscillator strength of the F band. The peak transition frequencies at $T = 4.5 \text{ K}$ are $\Omega_{A_1,1s}^* = 1.99 \text{ eV}$ and $\Omega_{E,1s}^* = 2.26 \text{ eV}$. Although $\omega_{A_1,1s}^*$ and $\omega_{E,1s}^*$ cannot be measured experimentally, they are independent of temperature and satisfy the relation $\omega_{E,1s}^* - \omega_{A_1,1s}^* = \Omega_{E,1s}^* - \Omega_{A_1,1s}^*$. If we choose suitably $S_{2p} = 22.4$, $\omega_{A_1,1s}^* = 1.77 \text{ eV}$, and $\omega_{E,1s}^* = 2.04 \text{ eV}$, the theoretical and experimental values of the peak transition frequencies at $T = 4.5 \text{ K}$ are the same. $B_{2p} = 8.2$ is used in order to fit the dependence of the peak transition frequencies on temperature.

We can plot the theoretical absorption curves of F_A centers for different temperatures in Fig. 2. Figure 2 shows four features: (1) at low temperature there are two partly overlapping absorption bands; (2) the F_{A2} peak is about twice as high as the F_{A1} peak; (3) both peaks broaden and shift to lower energies with rising temperature; (4) at high temperature both absorption bands merge into a single whole. The second and third features are in good agreement with the observed dichroic absorption spectra. The first and last features can be revealed if the incident light is not linearly polarized or the electric field of the polarized light is not parallel to a $\langle 100 \rangle$ direction of the crystal.

VII. SUMMARY AND DISCUSSION

In this section we first summarize the innovations made in the present paper. In Sec. II, we systematically develop a quantum field theoretical method to second-quantize the system's Hamiltonian with both linear and quadratic electron-phonon interactions. This method possesses the following

four characteristics. (1) We use the adiabatic approximation to second-quantize the electronic wave field, while the lattice ions are in the coordinate representation. (2) The Condon approximation equivalently omits the nondiagonal matrix elements of the system's Hamiltonian in the electronic Hilbert subspace. (3) We directly introduce the creation and annihilation operators of harmonic oscillators to fulfill the second quantization of lattice vibrations. (4) The linear and quadratic electron-phonon interactions give rise to the three effects: lattice relaxation, electron-ion correlation, and lattice-frequency shift. In the Hamiltonian for a linearly interacting electron-phonon system, the lattice vibrations are usually quantized by introducing the raising and lowering operators of harmonic oscillators. Such a Hamiltonian both disagrees with the second-quantized field theory and cannot describe any multiphonon transition effects correctly. As shown in Ref. 18, by the transition from the raising and lowering operators to the creation and annihilation operators of harmonic oscillators, the Hamiltonian obtained still cannot describe any multiphonon transition effects correctly. Our method gains by comparison.

In Sec. III, we use the linear response theory to derive the expression of the absorption coefficient, which is found to be determined by a temperature-dependent double-time Green's function. In Sec. IV, we apply the system's Hamiltonian obtained in Sec. II to the calculation of the temperature-dependent double-time Green's function. During the calculative process, we insert an identity operator in the Green's function so as to avoid the truncation approximation to the chain of equations for Green's functions. Owing to a quadratic electron-phonon interaction, we have to make the decoupling approximation to the probability distribution in the initial vibronic states of transition, the approximation that is unnecessary for a linear electron-phonon system. Consequently, we acquire the spectral function expression for many absorption bands, which resembles the generalization of the Bethe-Sommerfeld formula for a single absorption band.

In Sec. V, we deduce the first general expression of the overlap integrals and discuss its two approximate cases: quadratic and linear modes. After the overlap integrals of linear modes are obtained, we utilize a new technique to recover the Huang-Rhys line-shape function for one absorption band. The line-shape function of linear modes cannot explain the experimental fact that the one-band absorption peak broadens and shifts to lower energies with rising temperature. In order to remedy this defect, we propose the concept of weak nonlinear modes and acquire their line-shape function. The one-band line-shape function cannot describe the whole absorption spectrum of color centers, which has to be depicted by the spectral function of the absorption coefficient. In Sec. VI, we find the expression of the spectral function of weak nonlinear modes and apply this spectral function to the F_A center in a Li^+ -doped KCl crystal. The spectral function of the F_A bands is simplified by the Franck-Condon principle. Our numerical calculation gives successfully the first theoretical explanation of the absorption spectral features of the F_A center.

One of the greatest advantages of our treatment method is that the starting point is the Hamiltonian with linear and quadratic electron-phonon interactions and thereby a unified

framework is established. However, most of the previous researchers started from the Bethe-Sommerfeld formula for one absorption band and then made the adiabatic and Condon approximations. This method lacks a clear physical picture and strong systematicness.

In the discussion of the present paper, we do not touch upon the degeneracy of the vibronic states. If so, we should consider the nonradiative transition between two vibronic states which differ in electronic energy but have the same total energy. This transition is a resonant effect. The previous discussion also does not relate to the degeneracy of the electronic states, which is described by the Jahn-Teller theorem such that the configuration of atoms surrounding the defect will tend to distort to remove any electronic orbital degeneracy. The Jahn-Teller effect leads to partial broadening of an absorption band.²³ We have assumed no interaction between defect centers. In reality, the interacting defect centers of a sufficient concentration will cause splitting of vibronic levels and thereby produce inhomogeneous broadening of absorption bands. Furthermore, the author neglects broadening of absorption bands due to the lifetime of an excited state

and the self-bandwidth of a measuring instrument. In deriving the expression of the absorption coefficient, we have assumed an optically isotropic crystal. For a noncubic crystal, this expression of the absorption coefficient deviates somewhat from the experimental results.

It is worthwhile to point out that the coefficient $\omega_{ii'\mu}$ of the quadratic electron-phonon interaction in Eq. (2.7) is rather formal. Hitherto we have no concrete models to determine it and hence our theory waits for a further development. If one will know the microscopic mechanism of a quadratic electron-phonon interaction, one can calculate $\omega_{ii'\mu}$, the phenomenological parameter B_j for the weak nonlinear effect, and the Huang-Rhys factor S_j . Finally, we want to formulate the moments of various order of optical absorption bands by temperature-dependent double-time Green's functions and thereby to calculate these moments.

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