

## Optical absorption spectra of bipolarons

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The absorption of large bipolarons is investigated using the path-integral method. The response of a bipolaron to an external electromagnetic field is derived in the framework of the memory-function approach. The bipolaron optical absorption spectrum consists of a series of relatively narrow peaks. The peculiarities of the bipolaron optical absorption as a function of the frequency of the electromagnetic field may be attributed to the transitions involving relaxed excited states and scattering states of a bipolaron.

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### I. INTRODUCTION

The optical and kinetic properties of polar and ionic solids are substantially influenced by the polaron coupling. Large polarons have been most clearly manifested by investigations of the transport phenomena in a magnetic field (see the recent review on polarons<sup>1</sup>).

When two electrons (or two holes) interact with each other simultaneously through the Coulomb force and via the electron-phonon interaction, either two independent polarons can occur or a bound state of two polarons—the bipolaron—can arise (see Refs. 2–7 on large bipolarons and a comprehensive review<sup>8</sup> concerning small bipolarons). Whether bipolarons are stable or not, depends on the competition between the repulsive forces (the Coulomb interaction) and the attractive forces (mediated through the electron-phonon interaction). Verbist *et al.*<sup>5,6</sup> analyzed the large bipolaron using the Feynman path-integral formalism.<sup>9,10</sup> They introduced a “phase diagram” for the polaron-bipolaron system on the basis of a generalization of Feynman’s trial action and showed that the Pekar-Fröhlich coupling constant as high as 6.8 is needed in three dimensions (3D) to allow for bipolaron formation. Furthermore, in Refs. 5,6 it was shown that the large bipolaron formation is facilitated in 2D as compared to 3D. Experimental evidence for bipolarons, e.g., from the data on magnetization and electric conductivity in Ti<sub>4</sub>O<sub>7</sub>, as well as in Na<sub>0.3</sub>V<sub>2</sub>O<sub>5</sub> and polyacetylene, was discussed by Mott.<sup>11</sup>

In the framework of the renewed interest in bipolaron theory,<sup>2–5,7,8</sup> a preliminary analysis of the absorption of large bipolarons without a magnetic field was given.<sup>12</sup> A variational treatment of both spin-singlet and spin-triplet states of large bipolarons (in 2D) and for sufficiently strong coupling in high magnetic fields has been presented in Ref. 13. In Ref. 14, the path-integral approach for a bipolaron<sup>5</sup> was generalized to the case of a bipolaron in a magnetic field for all values of the Pekar-Fröhlich coupling constant and for all magnetic field strengths. It was demonstrated<sup>14</sup> that the magnetic field favors bipolaron formation. The first investigations of the optical absorption spectrum of large bipolarons in a magnetic field were performed in Refs. 15,16.

### II. APPROACH

We investigate here the optical properties of a bipolaron using the path-integral memory-function technique, developed in Refs. 17,18 (see also Ref. 16). The path-integral variational principle gives excellent results for the free energy of the electron-phonon systems (see, e.g., Refs. 19,20). Hence, these models adequately describe the physical properties (including the energy spectra) of the polaron and of the bipolaron, respectively.

The Hamiltonian of two electrons, interacting with longitudinal optical (LO) phonons and between each other in an external electric field  $\mathbf{E}(t)$ , is

$$\hat{H} = \sum_{j=1,2} \left[ \frac{\mathbf{p}_j^2}{2m} + e\mathbf{r}_j(t) \cdot \mathbf{E}(t) \right] + \frac{e^2}{\epsilon_\infty |\mathbf{r}_1 - \mathbf{r}_2|} + \sum_{\mathbf{q}} \hbar \omega_{\text{LO}} \left( \hat{a}_{\mathbf{q}}^+ \hat{a}_{\mathbf{q}} + \frac{1}{2} \right) + \sum_{j=1,2} \sum_{\mathbf{q}} (V_{\mathbf{q}} \hat{a}_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}_j} + V_{\mathbf{q}}^* \hat{a}_{\mathbf{q}}^+ e^{-i\mathbf{q} \cdot \mathbf{r}_j}) \quad (1)$$

with the interaction amplitudes<sup>18</sup>

$$V_{\mathbf{q}} = \frac{\hbar \omega_{\text{LO}}}{iq} \left( \frac{2\sqrt{2}\pi\alpha}{V} \right)^{1/2} \left( \frac{\hbar}{m\omega_{\text{LO}}} \right)^{1/4}, \quad (2)$$

where  $\alpha$  is the electron-phonon coupling constant,  $m$  is the electron band mass,  $V$  is the volume of the crystal,  $\epsilon_\infty$  is the high-frequency dielectric constant, and  $\omega_{\text{LO}}$  is the LO-phonon frequency.

We consider the equation of motion for the vector function  $\mathbf{R}(t)$  which has the sense of the average coordinate response per one electron

$$\mathbf{R}(t) \equiv \frac{1}{2} \left\langle \sum_{j=1,2} \mathbf{r}_j(t) \right\rangle_s. \quad (3)$$

Here, the symbol of averaging denotes the path-integral average over trajectories of the electrons (see Ref. 21)

$$\langle F[\bar{\mathbf{r}}(t), \bar{\mathbf{r}}'(t)] \rangle_S \equiv \frac{\int D\bar{\mathbf{r}}(t) \int D\bar{\mathbf{r}}'(t) F[\bar{\mathbf{r}}(t), \bar{\mathbf{r}}'(t)] \exp\{(i/\hbar)S[\bar{\mathbf{r}}(t), \bar{\mathbf{r}}'(t)]\}}{\int D\bar{\mathbf{r}}(t) \int D\bar{\mathbf{r}}'(t) \exp\{(i/\hbar)S[\bar{\mathbf{r}}(t), \bar{\mathbf{r}}'(t)]\}} \quad [\bar{\mathbf{r}} \equiv (\mathbf{r}_1, \mathbf{r}_2)] \quad (4)$$

with the action functional

$$S[\bar{\mathbf{r}}(t), \bar{\mathbf{r}}'(t)] = S_e[\bar{\mathbf{r}}(t)] - S_e[\bar{\mathbf{r}}'(t)] - i\hbar\Phi[\bar{\mathbf{r}}(t), \bar{\mathbf{r}}'(t)], \quad (5)$$

where  $S_e[\mathbf{r}_1(t), \mathbf{r}_2(t)]$  is the action of two interacting electrons in an external electric field,

$$S_e[\bar{\mathbf{r}}(t)] = \int_{-\infty}^{\infty} \left\{ \sum_{j=1,2} \left[ \frac{m\dot{\mathbf{r}}_j^2(t)}{2} - e\mathbf{r}_j(t) \cdot \mathbf{E}(t) \right] - \frac{e^2}{\varepsilon_\infty |\mathbf{r}_1(t) - \mathbf{r}_2(t)|} \right\} dt, \quad (6)$$

and  $\Phi[\bar{\mathbf{r}}(t), \bar{\mathbf{r}}'(t)]$  is the ‘‘influence phase’’ of the phonon subsystem<sup>16</sup>

$$\begin{aligned} \Phi[\bar{\mathbf{r}}(t), \bar{\mathbf{r}}'(t)] &= - \sum_{\mathbf{q}} \frac{|V_{\mathbf{q}}|^2}{\hbar^2} \int_{-\infty}^{\infty} dt \int_{-\infty}^t dt' [\rho_{\mathbf{q}}(t) - \rho'_{\mathbf{q}}(t')] \\ &\quad \times [T_{\omega_{\mathbf{q}}}^*(t-t')\rho_{-\mathbf{q}}(t') \\ &\quad - T_{\omega_{\mathbf{q}}}(t-t')\rho'_{-\mathbf{q}}(t')]. \end{aligned} \quad (7)$$

This influence phase describes both a retarded interaction between different electrons and a retarded self-interaction of each electron due to the elimination of the phonon coordinates. It contains the Fourier components of the electron density operator

$$\rho_{\mathbf{q}} = \sum_{j=1,2} e^{i\mathbf{q}\cdot\mathbf{r}_j} \quad (8)$$

and the phonon Green’s function

$$T_{\omega}(t) = \frac{e^{i\omega t}}{1 - e^{-\beta\omega}} + \frac{e^{-i\omega t}}{e^{\beta\omega} - 1}, \quad \beta \equiv \frac{\hbar}{k_B T}, \quad (9)$$

where  $T$  is the temperature.

We have calculated the optical absorption coefficient for a bipolaron in the memory-function approach<sup>16-18</sup>

$$\Gamma(\omega) = - \frac{4\pi n_0 e^2}{cn} \frac{\omega \text{Im} T(\omega)}{m [\omega^2 - \text{Re} T(\omega)]^2 + [\text{Im} T(\omega)]^2}, \quad (10)$$

where  $c$  is the velocity of light,  $n$  is the refractive index of the crystal,  $n_0$  is the electron density. The memory function  $T(\omega)$  has the form<sup>16</sup>

$$\begin{aligned} T(\omega) &= \sum_{\mathbf{q}} \frac{|V_{\mathbf{q}}|^2 q^2}{3\hbar} \int_0^{\infty} (e^{i\omega t} - 1) \\ &\quad \times \text{Im}[T_{\omega_{\mathbf{LO}}}^*(t) \langle \rho_{\mathbf{q}}(t) \rho_{-\mathbf{q}}(0) \rangle_{S_0}] dt. \end{aligned} \quad (11)$$

It is expressed in terms of the two-point correlation function  $\langle \rho_{\mathbf{q}}(t) \rho_{-\mathbf{q}}(0) \rangle_{S_0}$  of the electron density operators. The correlation function is calculated as the path-integral average [see Eq. (4)] with the model action functional  $S_0[\bar{\mathbf{r}}(t), \bar{\mathbf{r}}_f(t), \bar{\mathbf{r}}'(t), \bar{\mathbf{r}}'_f(t)]$  :

$$\langle F \rangle_{S_0} \equiv \frac{\int D\bar{\mathbf{r}}(t) \int D\bar{\mathbf{r}}'(t) \int D\bar{\mathbf{r}}_f(t) \int D\bar{\mathbf{r}}'_f(t) F \exp\{(i/\hbar)S_0[\bar{\mathbf{r}}(t), \bar{\mathbf{r}}_f(t), \bar{\mathbf{r}}'(t), \bar{\mathbf{r}}'_f(t)]\}}{\int D\bar{\mathbf{r}}(t) \int D\bar{\mathbf{r}}'(t) \int D\bar{\mathbf{r}}_f(t) \int D\bar{\mathbf{r}}'_f(t) \exp\{(i/\hbar)S_0[\bar{\mathbf{r}}(t), \bar{\mathbf{r}}_f(t), \bar{\mathbf{r}}'(t), \bar{\mathbf{r}}'_f(t)]\}}. \quad (12)$$

The model system consists of two electrons harmonically interacting with two fictitious particles and between each other. The model action functional  $S_0[\bar{\mathbf{r}}(t), \bar{\mathbf{r}}_f(t), \bar{\mathbf{r}}'(t), \bar{\mathbf{r}}'_f(t)]$  has the form

$$\begin{aligned} S_0[\bar{\mathbf{r}}(t), \bar{\mathbf{r}}_f(t), \bar{\mathbf{r}}'(t), \bar{\mathbf{r}}'_f(t)] \\ = \int_{-\infty}^{\infty} [L_0(\dot{\bar{\mathbf{r}}}, \dot{\bar{\mathbf{r}}}_f, \bar{\mathbf{r}}, \bar{\mathbf{r}}_f) - L_0(\dot{\bar{\mathbf{r}}}', \dot{\bar{\mathbf{r}}}'_f, \bar{\mathbf{r}}', \bar{\mathbf{r}}'_f)] dt, \end{aligned} \quad (13)$$

with the Lagrangian

$$\begin{aligned} L_0(\dot{\bar{\mathbf{r}}}, \dot{\bar{\mathbf{r}}}_f, \bar{\mathbf{r}}, \bar{\mathbf{r}}_f) &= \sum_{j=1,2} \left( \frac{m\dot{\mathbf{r}}_j^2(t)}{2} + \frac{M\dot{\mathbf{r}}_{fj}^2(t)}{2} \right) \\ &\quad - \frac{k}{2} \sum_{j=1,2} (\mathbf{r}_j - \mathbf{r}_{fj})^2 - \frac{k'}{2} [(\mathbf{r}_1 - \mathbf{r}_{f2})^2 \\ &\quad + (\mathbf{r}_2 - \mathbf{r}_{f1})^2] + \frac{K}{2} (\mathbf{r}_1 - \mathbf{r}_2)^2, \end{aligned} \quad (14)$$

where  $M$  is the mass of a fictitious particle,  $k, k'$ , and  $K$  are the elastic constants. The oscillator potentials in the Lagrangian (14) imitate the electron-phonon interaction and the electron-electron Coulomb repulsion. In Refs. 5,6, the aforesaid model has been first introduced in order to calculate the bipolaron ground-state energy by the Jensen-Feynman variational method.<sup>9,10</sup> The variational functional of Refs. 5,6 for the bipolaron free energy contains four variational parameters:  $M, k, k'$ , and  $K$ . It is convenient to use instead of them four other independent parameters: (i) three eigenfrequencies of the internal bipolaron motion  $\Omega_i$  ( $i=1,2,3$ ) (see Ref. 6),

$$\Omega_1 = \frac{m+M}{mM}(k+k'), \quad (15)$$

$$\Omega_{2,3}^2 = \frac{1}{2} \left\{ \frac{m+M}{mM}(k+k') - \frac{2K}{m} \pm \left[ \left( \frac{M-m}{mM}(k+k') - \frac{2K}{m} \right)^2 + \frac{4}{mM}(k-k')^2 \right]^{1/2} \right\} \quad (16)$$

and (ii) the frequency

$$v = \left( \frac{k+k'}{M} \right)^{1/2}, \quad (17)$$

which is analogous to the Feynman parameter  $w$  in the single-polaron problem.<sup>10</sup> It is seen from Eqs. (15)–(17), that the inequality  $\Omega_1 \geq \Omega_2 \geq v \geq \Omega_3$  is fulfilled for the variational frequency parameters. By the variational procedure of Ref. 6, the optimal values of those variational parameters are found for the physical system of two electrons interacting with the phonon field and between each other.

In the zero-temperature limit  $T=0$ , we have derived from Eq. (11) the analytical expressions for the real and imaginary parts of the memory function for a bipolaron in three dimensions:

$$\begin{aligned} \text{Re } T(\omega) &= \frac{4\sqrt{2}\alpha}{3} \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \frac{[1+(-1)^{k+l}]}{n!k!l!} s_1^n s_2^k s_3^l \\ &\times [f_{n+k+l}(\omega-1-n\Omega_1-k\Omega_2-l\Omega_3) \\ &+ f_{n+k+l}(-\omega-1-n\Omega_1-k\Omega_2-l\Omega_3) \\ &- 2f_{n+k+l}(-1-n\Omega_1-k\Omega_2-l\Omega_3)], \quad (18) \end{aligned}$$

$$\begin{aligned} \text{Im } T(\omega) &= -\frac{4\sqrt{2}\alpha}{3} \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \frac{[1+(-1)^{k+l}]}{n!k!l!} s_1^n s_2^k s_3^l \\ &\times [g_{n+k+l}(\omega-1-n\Omega_1-k\Omega_2-l\Omega_3) \\ &- g_{n+k+l}(-\omega-1-n\Omega_1-k\Omega_2-l\Omega_3)]. \quad (19) \end{aligned}$$

From here on, we use the system of units where  $\hbar=1$ ,  $m=1$ ,  $\omega_{\text{LO}}=1$ . The factors  $s_i$  ( $i=1,2,3$ ) in Eqs. (18),(19) have the sense of oscillator strengths corresponding to the eigenmodes of the internal motion of a bipolaron. The aforesaid factors are expressed through variational frequency parameters of the bipolaron model functional (15)–(17),

$$s_1 = \frac{\Omega_1^2 - v^2}{\Omega_1^3}, \quad s_2 = \frac{\Omega_2^2 - v^2}{\Omega_2(\Omega_2^2 - \Omega_3^2)}, \quad s_3 = \frac{v^2 - \Omega_3^2}{\Omega_3(\Omega_2^2 - \Omega_3^2)}. \quad (20)$$

The functions  $f_n(\omega)$  and  $g_n(\omega)$  are given by the expressions

$$\begin{aligned} f_n(\omega) &= (-1)^n \frac{|\omega|^{n+1/2}}{B^{n+3/2}} e^{-A\omega/B} \Theta(-\omega) \\ &- \frac{\Gamma(n+\frac{1}{2})}{\pi A^{n+1/2} B} {}_1F_1\left(1, \frac{1}{2} - n, -\frac{A\omega}{B}\right), \quad (21) \end{aligned}$$

$$g_n(\omega) = \frac{\omega^{n+1/2}}{B^{n+3/2}} e^{-A\omega/B} \Theta(\omega), \quad (22)$$

with the parameters

$$\begin{aligned} A &= \frac{\mu}{m\Omega_1} + \frac{a^2}{\Omega_2} + \frac{b^2}{\Omega_3}, \quad \mu = \frac{\Omega_1^2 - v^2}{\Omega_1^2}, \\ a &= \sqrt{\frac{\Omega_2^2 - v^2}{\Omega_2^2 - \Omega_3^2}}, \quad b = \sqrt{\frac{v^2 - \Omega_3^2}{\Omega_2^2 - \Omega_3^2}}, \quad B = \frac{v^2}{\Omega_1^2}. \quad (23) \end{aligned}$$

The optical conductivity for a 2D bipolaron is related to that for a 3D bipolaron, which is given by the formulas (18) and (19), by the scaling relation (see Ref. 1):

$$\text{Re } \sigma_{2\text{D}}(\omega, \alpha) = \text{Re } \sigma_{3\text{D}}\left(\omega, \frac{3\pi}{4}\alpha\right). \quad (24)$$

It follows from Eqs. (18) and (19) that the eigenfrequencies  $\Omega_2$  and  $\Omega_3$  appear in the optical absorption spectra only in such combinations ( $k\Omega_2 + l\Omega_3$ ) that  $(k+l)$  is an even integer. This selection rule is determined by the symmetry of these eigenmodes (a schematic picture of the internal motion of the bipolaron model system see, e.g., in Ref. 16). The only normal coordinates of eigenmodes with the frequencies  $\Omega_2$  and  $\Omega_3$  (let us denote these coordinates as vectors  $\mathbf{Q}_2$  and  $\mathbf{Q}_3$ ) are antisymmetric with respect to the permutation of electrons  $r_1 \rightleftharpoons r_2$ . Both the exact and model Lagrangians are symmetric with respect to this permutation. As a result of this symmetry, we obtain the selection rule

$$\left\langle \prod_{i=1,2,\dots} \prod_{k=x,y,z} [\mathcal{Q}_{2k}^{m_{ki}}(t_i) \mathcal{Q}_{3k}^{m'_{ki}}(t'_i)] \right\rangle_{S_0} = 0,$$

when

$$\sum_i \sum_{k=x,y,z} (m_{ki} + m'_{ki}) = \text{odd}. \quad (25)$$

Hence, only the combinations ( $\prod_{i=1,2,\dots} \prod_{k=x,y,z} [\mathcal{Q}_{2k}^{m_{ki}}(t_i) \mathcal{Q}_{3k}^{m'_{ki}}(t'_i)]$ ) with an even number  $n = \sum_i \sum_{k=x,y,z} (m_{ki} + m'_{ki})$  can give a nonzero contribution into the average  $\langle \rho_{\mathbf{q}}(t) \rho_{-\mathbf{q}}(0) \rangle_{S_0}$  of Eq. (11). The operator of an oscillator coordinate  $\mathcal{Q}_{jk}$  describes quantum transitions be-

tween energy levels of the corresponding oscillator with the frequency  $\Omega_j$  ( $j=1,2,3$ ). Consequently, the aforesaid combinations of coordinates provide the transitions, which change the energy of the model system by values  $(k\Omega_2 + l\Omega_3)$  with even  $(k+l)$ .

### III. OPTICAL ABSORPTION SPECTRA

In order to give a physical interpretation of the calculated bipolaron optical absorption spectra, we refer first to a description of those for a polaron in Refs. 17,18. In the polaron optical absorption spectra, for intermediate and large  $\alpha$ , there is an intense (zero-phonon) absorption peak corresponding to a transition from the ground state to the first relaxed excited state (RES). The relaxed excited state is created if the electron in the polaron is excited while the lattice readapts to a new electronic configuration.<sup>18</sup> A shoulder at the low-frequency side of the RES peak is attributed to one-phonon transitions through the scattering states (ScS): excitations of the polaron system characterized by the presence of a finite number of real phonons along with the polaron.<sup>18</sup> A broad peak, positioned at a higher frequency than the RES peak, is attributed to transitions to Franck-Condon (FC) states: internal excited polaron states for which the lattice polarization is that of the polaron in its ground state.<sup>18</sup> This picture is well-founded physically and is in agreement with the prediction of the aforesaid peaks, which was formulated within the strong-coupling approach.<sup>22</sup>

In Fig. 1, the real  $\text{Re } T(\omega)$  and imaginary  $\text{Im } T(\omega)$  parts of the memory function for a 3D (2D) bipolaron are plotted as a function of frequency  $\omega$  for  $\alpha=7$  (2.971). These values of  $\alpha$  are close to the minimal possible  $\alpha$  for the bipolaron formation:  $\alpha_{\min}=6.8$  (2.9) (see Ref. 16). The peaks of the imaginary part of the memory function are positioned near the points (explicitly indicated in Fig. 1)

$$\omega_{nkl} \equiv n\Omega_1 + k\Omega_2 + l\Omega_3 + 1, \quad (26)$$

where  $n, k, l$  are the non-negative integers ( $k+l = \text{even integer}$ ).

Analogously to the case of polaron optical absorption,<sup>18</sup> the peaks of the bipolaron optical absorption spectra (Fig. 2) correspond to (i) peaks of  $\text{Im } T(\omega)$  and (ii) roots of the equation  $\omega^2 - \text{Re } T(\omega) = 0$  [the crossing points of solid and dotted curves in panel (a) of Fig. 1]. Following the physical interpretation developed in Refs. 17,18, we suggest that the peaks corresponding to zeros of  $[\omega^2 - \text{Re } T(\omega)]$  can be attributed to transitions to bipolaron relaxed excited states. Due to a larger number of the internal degrees of freedom for a bipolaron, than that for a polaron, there are several types of RES for a bipolaron.

The positions of peaks of the optical absorption coefficient, corresponding to those of  $\text{Im } T(\omega)$ , are close to the values  $\omega_{nkl}$  determined by Eq. (26), so that  $\omega_{nkl}$  have the sense of the frequencies of transitions from the ground state to certain internal states of a bipolaron. Following the physical interpretation developed in Refs. 17,18, we can attribute these peaks to transitions into Franck-Condon (FC) bipolaron states [in the case when at least one of the numbers  $(n, k, l) \neq 0$ , i.e., for *excited* states of a bipolaron]. Within the same

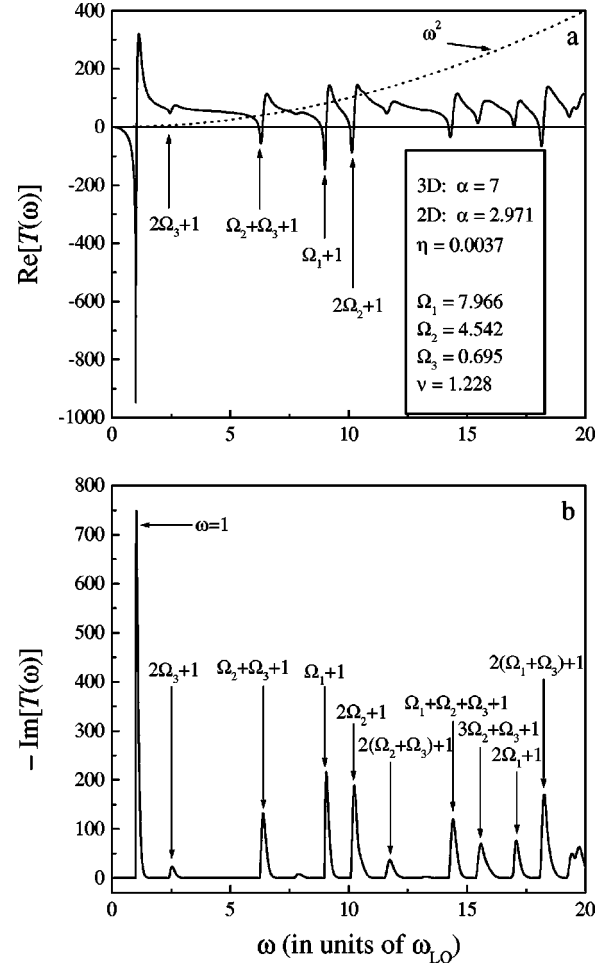


FIG. 1. Real (a) and imaginary (b) parts of the memory function  $T(\omega)$  for the optical absorption coefficient of a 3D (2D) bipolaron for  $\alpha=7$  (2.971),  $\eta=0.0037$ . The optimal values of the variational frequencies are indicated in the figure.

picture, we suggest that the low-intensity peak at  $\omega=1$  is provided by the transition into the lowest *scattering* state of a bipolaron. It is worth mentioning that the main resonances in oscillator strength are RES.

In order to classify peaks of the bipolaron optical absorption spectra, we have calculated transition frequencies to several bipolaron RES and FC states within the strong-coupling (adiabatic) approach. The results are shown in Table I. The transitions are classified with respect to the symmetry of states of the internal bipolaron motion and of the motion of a bipolaron as a whole (labeled, respectively, by small and capital letters within standard denotations of states with different orbital moments). ‘‘S’’ and ‘‘s’’ denote the states with the orbital momentum  $l=0$ , while ‘‘P’’ and ‘‘p’’ are those with  $l=1$ . The trial wave functions are of the same type as those used for the treatment of polarons in Ref. 18.

Comparing the peak positions of Fig. 2 with the results of Table I (which are obtained in the framework of the adiabatic approach, and therefore can be applied only approximately), we have attributed several optical absorption peaks to transitions to RES and FC states of a definite symmetry, as shown at the figure. It should be mentioned, that every RES

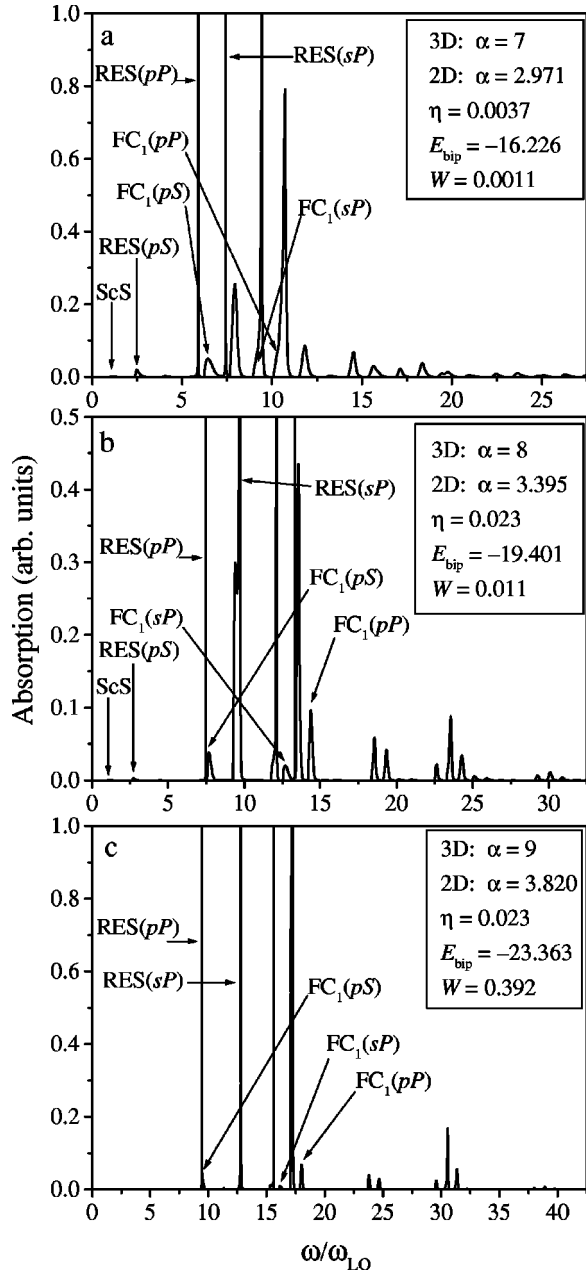


FIG. 2. Optical absorption spectra of a 3D (2D) bipolaron for  $\alpha=7$  (2.971),  $\eta=0.0037$  (a), for  $\alpha=8$  (3.395),  $\eta=0.023$  (b), and for  $\alpha=9$  (3.820),  $\eta=0.023$  (c).

TABLE I. Transition frequencies (in units of the LO phonon frequency) to bipolaron RES and FC states calculated within the adiabatic strong-coupling theory.

$\alpha$	RES			FC		
	$pS$	$sP$	$pP$	$pS$	$sP$	$pP$
7	2.2171	5.9877	5.7282	5.4633	9.9396	12.5210
8	2.8957	7.8207	7.4818	7.1328	13.0008	16.3627
9	3.6648	9.8981	9.4686	8.9364	16.2629	20.4673
10	4.5243	12.220	11.6895	11.1019	20.1550	25.4065

peak has a lower frequency, than the corresponding FC peak, since the lattice relaxation leads to a lowering of the energy of the electron-phonon system.

The linewidth of peaks of bipolaron optical absorption spectra is determined by the bipolaron recoil in the scattering process. Every FC peak is described by a function  $g_{n+k+l}(\omega - \omega_{nkl})$  of Eq. (19), where  $g_n(\omega)$  is given by Eq. (22). Consequently, the linewidth of a FC peak can be estimated, using the following characteristic of the function (22):

$$\sigma[g_n(\omega)] = \sqrt{\langle \omega^2 \rangle - \langle \omega \rangle^2}, \quad \langle \omega^k \rangle \equiv \frac{\int_0^\infty \omega^k g_n(\omega) d\omega}{\int_0^\infty g_n(\omega) d\omega}. \quad (27)$$

Performing the integrations over  $\omega$  analytically, we find that

$$\sigma[g_n(\omega)] = \frac{B}{A} \left( n + \frac{3}{2} \right)^{1/2},$$

where the parameters  $A$  and  $B$  are given by Eq. (23). The ratio  $A/B$  is of the same order as  $[2(M+1)]$ , which is used for estimation of the bipolaron effective mass.<sup>23</sup> Therefore, the characteristic linewidth of a FC peak corresponding to a definite frequency  $\omega = \omega_{nkl}$  can be qualitatively estimated as

$$\Gamma_{nkl}^{(FC)} \propto \frac{1}{2(M+1)} (n+k+l+3/2)^{1/2}.$$

Since the bipolaron effective mass is larger than that of a polaron, the bipolaron optical absorption spectrum consists of a series of peaks which are narrower in comparison with those of the polaron absorption spectrum.

Let us define  $N(\omega, \Delta\omega)$  as the number of possible combinations of  $(n, k, l)$  for which the frequencies  $\{\omega_{nkl}\}$  occupy the interval  $\omega \leq \omega_{nkl} \leq \omega + \Delta\omega$ . The higher is  $\omega$  (at a fixed interval length  $\Delta\omega$ ), the larger is  $N(\omega, \Delta\omega)$ . Hence, the density of the FC peaks increases with increasing frequency. Starting from a definite frequency range [where  $N(\omega, \Delta\omega) \propto \Gamma_{FC}(\omega)\Delta\omega$ ], FC peaks merge into a continuous band.

In the limiting case  $\omega \gg 1$ , the imaginary part of the memory function (19) asymptotically behaves as

$$\text{Im } T(\omega)|_{\omega \gg 1} \propto -\frac{2\alpha}{3} \omega^{1/2}. \quad (28)$$

Hence, the bipolaron absorption coefficient in the limiting case of high frequencies has the same asymptotic behavior as the polaron absorption coefficient<sup>17,18</sup> (this asymptotic behavior was also derived in Ref. 24 for the weak-coupling polaron optical absorption):

$$\Gamma(\omega)|_{\omega \gg 1} \propto \omega^{-5/2}. \quad (29)$$

This behavior has a clear physical explanation: in the high-frequency limit, only one-phonon scattering processes give a contribution into the optical absorption by the electron-phonon system. In this limit, the optical absorption coefficients for bipolarons and polarons at arbitrary coupling

strength are described by *one and the same* asymptotic dependence. It was emphasized in Refs. 17,18,24, that the frequency dependence (29) of the polaron optical absorption coefficient at  $\omega \gg 1$  differs from the Drude-like dependence  $\Gamma^{(\text{Drude})}(\omega)|_{\omega \gg 1} \propto \omega^{-2}$ .

For the bipolaron, the optical absorption spectrum turns into a continuous band at substantially higher frequencies, than for the polaron, due to a comparatively large effective mass of a bipolaron. This frequency region is not presented in Fig. 2. The bipolaron absorption coefficient in this region is very small when compared with that shown in Fig. 2.

#### IV. SUM RULES AND CONCLUSIONS

From the general analytical properties of the memory function, for the real part of the optical conductivity per one electron

$$\text{Re } \sigma(\omega) = -\frac{e^2}{m} \frac{\omega \text{Im } T(\omega)}{[\omega^2 - \text{Re } T(\omega)]^2 + [\text{Im } T(\omega)]^2} \quad (30)$$

the following sum rule was derived in Ref. 25:

$$\frac{\pi e^2}{m^*} + \int_{\varepsilon \rightarrow +0}^{\infty} \text{Re } \sigma(\omega) d\omega = \frac{\pi e^2}{2m}, \quad (31)$$

where  $m^*$  is the polaron effective mass. For the bipolaron optical absorption, the same equation (31) is valid with  $m^*$  the bipolaron effective mass. Our numerical test of the sum rule (31) has confirmed, that Eq. (31) is fulfilled within the chosen relative accuracy (up to  $10^{-3}$ ).

In Ref. 26, the ground-state theorem for a *polaron* has been derived which relates the polaron ground-state energy to the first moment of the optical absorption spectra. The extension of this theorem to the bipolaron can be performed in the same way as in Ref. 26. The analog of Eq. (25) from Ref. 26 for a *bipolaron* is

$$\begin{aligned} E_0(\alpha_2, \eta) - E_0(\alpha_1, \eta) \\ = -\frac{3m\hbar}{\pi e^2} \int_{\alpha_1}^{\alpha_2} \frac{d\alpha}{\alpha} \int_0^{\infty} \text{Im } \chi_{jj}(\omega, \alpha, \eta) d\omega, \end{aligned} \quad (32)$$

where  $\alpha_1$  and  $\alpha_2$  are two arbitrary values of  $\alpha$ ,  $\eta = \varepsilon_{\infty}/\varepsilon_0$  is the ratio of the high-frequency and static dielectric constants,  $\chi_{jj}(\omega, \alpha, \eta)$  is the current-current correlation function.<sup>26</sup> For a bipolaron, we choose  $\eta$  and both  $\alpha_1$  and  $\alpha_2$  within the region of the bipolaron stability. The function  $\text{Im}\chi_{jj}(\omega)$  for a bipolaron is expressed through the memory function  $T(\omega)$  as

$$\text{Im}\chi_{jj}(\omega) = \frac{2\omega^2 \text{Im } T(\omega)}{\omega^4 - 2\omega^2 \text{Re } T(\omega) + |T(\omega)|^2}. \quad (33)$$

In Fig. 3, the ground-state theorem (32) is illustrated numerically. The solid curve shows the difference between the

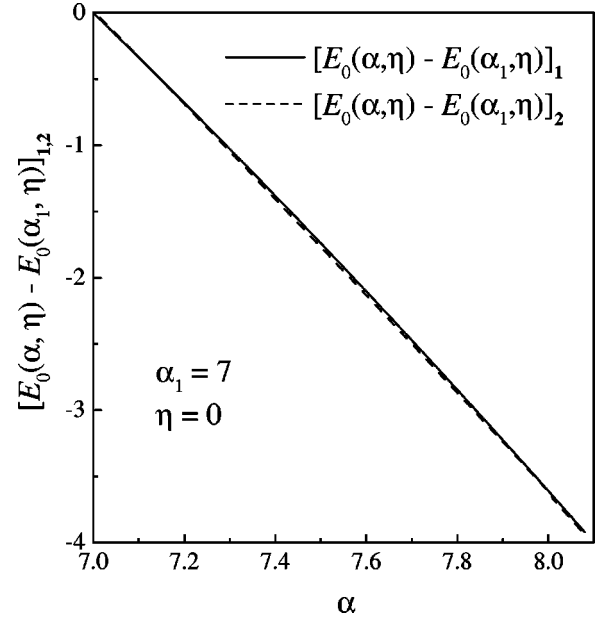


FIG. 3. Illustration of the ground-state theorem (32) for the bipolaron optical absorption. The index ‘‘1’’ denotes the ground-state energies calculated by the variational method [the left-hand side of Eq. (32)], while the index ‘‘2’’ denotes the ground-state energies calculated by integration of the bipolaron optical absorption spectra [the right-hand side of Eq. (32)].

ground state energies  $E_0(\alpha_2, \eta) - E_0(\alpha_1, \eta)$  (calculated by the variational method using the variational functional of Ref. 6) for two values of  $\alpha$  at  $\eta = 0$ . The value  $\alpha_1$  is taken  $\alpha_1 = 7$ . The dashed curve shows the values of the right-hand side of Eq. (32). As seen from Fig. 3, there exists an excellent agreement between the quantities entering the independently calculated left-hand and the right-hand sides of Eq. (32).

In the present paper, we have treated the bipolaron optical absorption within the memory-function path-integral approach. The derived optical absorption spectra demonstrate a rich structure of relatively narrow peaks, which is clearly related to the internal states of a bipolaron. We have attributed those peaks of the bipolaron optical absorption spectra to transitions from the ground state to (i) scattering states, (ii) relaxed excited states, (iii) Franck-Condon states. Every RES peak is shifted to a lower frequency with respect to the corresponding FC peak. This interpretation is performed within a unified approach to the polaron and bipolaron problems, which takes its origin in Refs. 17,18. The sum rules, developed for the polaron optical conductivity,<sup>25,26</sup> are extended to the case of a bipolaron.

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