A theory of the subgap photoemission in one-dimensional electron-phonon systems. An instanton approach to pseudogaps.

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For a one-dimensional electron-phonon system we consider the photon absorption involving electronic excitations within the pseudogap energy range. Within the adiabatic approximation for the electron - phonon interactions these processes are described by nonlinear configurations of an instanton type. We calculate intensities of the photoelectron spectroscopy PES including the momentum resolved one ARPES and supplement to known results for the optical subgap absorption. We start with the generic case of a one dimensional semiconductor with pronounced polaronic effect. In details we consider the Peierls model for a half-filled band of electrons coupled to the lattice which describes the polyacethylene and some commensurate Charge Density Waves. Particular attention was required for studies of momentum dependencies for the ARPES where we face an intriguing interference between the time evolution and the translational motion of the instantons.

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I. INTRODUCTION.

This article is devoted to theory of pseudogaps in electronic spectra as they can be observed by means of the Photo Electron Spectrography (PES) or the Angle Resolved Photo Electron Spectroscopy (ARPES). Notion of a pseudogap (PG) refers to various systems where a gap E_g in their bare electronic spectra is partly filled showing subgap tails. The best known examples are the tails in the Density of States (DOS) due to disorder[1] or the Urbach tails in the subgap optical absorption due to thermal fluctuations[2]. But the PG is especially pronounced in cases where the bare gap is opened spontaneously as a symmetry breaking effect which was the subject of detailed experimental studies[3–7]. In quasi-1D conductors it is known as the Peierls-Fröhlich instability leading to the Charge Density Wave (CDW) formation, as well as to analogous spin-Peierls and Spin Density Wave states[8]. Here the picture of the PG has been suggested theoretically[9] in relation to absence of the long range order (LRO) in 1D CDWs. Similarly in High-T_c materials the gap opening mechanisms (still of a disputable origin) which are not stabilized yet by the LRO are considered. They are supposed to be responsible for the pseudogap which opens at higher energy scale than the sharp gap appearing below the transition temperature to the superconducting state[10]. We shall consider generic 1D semiconductors and concentrate on systems with the dimerized ground state like the well known polyacethylene $(CH)_x$[11,12] or some CDWs with the 2-fold commensurability like NbS_3[6]. Properties of incommensurate CDWs (blue bronzes, tri- and tetra-chalcogenides of transition metals)[8] are further complicated by interference of the gapless collective mode and we shall consider them separately.

For 1D systems with only a discrete symmetry an absence of the LRO is not drastically important at low enough temperatures. At finite temperature there is a remnant concentration $n_s \sim \exp[-E_s/T]$ of topological solitons (kinks with the energy E_s) commuting different domains of the order parameter $\sim \pm\Delta_0$. The midgap electronic states associated with these solitons create a finite DOS $\sim n_s$ at the former Fermi level $E = 0$ and originate related optical features (see[11,12] for a review and[13] for a systematic theory), hence there is no true gap at finite T. Neglecting this exponentially freezing contribution, we are left, at first sight, with a sharp electronic gap $E_g^0 = \Delta_0$. But what happens instead is that, even at $T = 0$, rather smeared edges appear at $\pm\Delta_0$ while the spectrum extends deeply inwards the gap. This effect is particularly pronounced in 1D because of the edge singularity $\sim (E - E_g^0)^{-1/2}$ at $E \approx E_g^0$ in the bare DOS which smearing is considered to be the most evident signature of the PG formation below E_g. In the Peierls state the PG effect is further enhanced by strong electron-phonon (*e-ph)* interactions between electrons and

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quantum fluctuations of the gap amplitude $\delta = \Delta(x,t) - \Delta_0$. Stationary excitations (eigenstates of the total *e-ph* system) are now the selftrapped states, polarons or solitons, which energies W_p or W_s are fractions of Δ_0, see the review[14]. The states close to the bare electron edge Δ_0 can be observed only via instantaneous measurements like optical or X-ray absorptions or tunneling. The spectra of these nonstationary states fill the range $\Delta_0 > E > W_p$ for single electronic (PES) or $2\Delta_0 > \omega > 2W_s$ for $e-h$ (optics) processes. Particularly near Δ_0 the states resemble free electrons in the field of uncorrelated quantum fluctuations of the lattice[15]. Here the selftrapping has not enough time to be developed. But approaching the exact threshold they evolve towards eigenstate which are selftrapped states accompanied by excitations of their dress. This picture describes coexistence of the PG region $\Delta_0 > |E| > W_p, W_s$ and the exact gap $|E| < W_p, W_s$ in a similarity with the High-T_c superconductors.

It should be stressed in this respect that there *cannot be a common PG* for processes characterized by different time scales. We should distinguish (as stated in[16] and stressed also in several reviews, e.g.[14]) between short living states observed in optical, EPS (and may be tunneling) experiments and long living states (amplitude solitons, phase solitons) contributing to the spin susceptibility, NMR relaxation, heat capacitance, conductivity, etc. States forming the optical PG are created instantaneously: over times which are shorter than the inverse phonon frequencies $\tau_{opt} \sim \hbar/E_g < \omega_{ph}^{-1}$ and many orders of magnitude beyond the life times required for current carriers, and even much longer times for thermodynamic contributions. It follows then that the analysis of different groups of experimental data within the same model[17] must be reevaluated.

While experimental techniques of PES and ARPES are still less accurate than the traditional optics, their very fast progress through the last decade allows to rely upon a required accuracy already today or in nearest future. An apparent advantage of the ARPES is its access to the momentum distributions of spectral densities. Another particular feature of both PES and its ARPES version in our applications is its decoupling from the final state Coulomb interactions which affect drastically the optical intergap absorption. In this respect the PES differs also from the traditional spectroscopy by internal absorption from a core level; their the final state interaction between the band particle and the remnant hole, originates a seminal problem of the X-ray edge singularity in metals[18].

A theory of the subgap absorption in optics has been developed already: for a general type of polaronic semiconductors[2] with an emphasis to long range Coulomb effects and for the one dimensional Peierls type system with an emphasis to solitonic processes[11,20] - the last work is closest to our targets. Here we shall address the PES and ARPES in $1D$ systems. Methodologically all these studies deal with quantum transitions between distant field configurations which generalize the WKB method for a single degree of freedom. These classically forbidden nonlinear processes, well localized in space and time, are described by extremal trajectories called the instantons. The methods of optimal trajectories in the functional space have been initiated by the problem of quantum decay of a metastable state[19] (that is of a "false vacuum"[21]) and for quantization of solitons[22] (see the book[23] for a review). The relevant article on this line[24] was devoted to selftrapping barriers for transformation of a bare electron to the polaron in $3D$ systems.

The plan of our article is the following. In Sec. II we describe a general scheme for calculating the ARPES probabilities within the adiabatic approximations, that is based on smallness of typical phonon frequencies with respect to energies of electron transitions. In Sec. III we explore applications to particular models. In Sec. IIIA we consider a tutorial zero- dimensional model for an electron coupled to a single oscillator mode and show that results of the adiabatic approximation coincide with exact calculations. In Sec. IIIB we study the transition rate for shallow subgap states in a $1D$ system, both near the bare gap and at the polaronic threshold. In Sec. IIIC we consider in details the Peierls model in the half-filled band case. In Sec. IIID we present the ARPES theory for this model. Beyond the PES, in Sec. IIIE we also extend earlier calculations[25,20] for the intragap optical absorption related to creation of kinks pairs. In Sec. IIIF we consider relations of the general approach to the model of quantum instantaneous disorder. Finally Sec. IV is devoted to discussions conclusions.

II. GENERAL RELATIONS.

A. Adiabatic approximation.

The ARPES[5] means an absorption of a high energy Ω_0 photon taking off an electron from the crystal which is then analyzed in energy E_{out} and momentum P_{out}. Thus one obtains an information on the spectral density of the hole left beyond. The transition rate $I(\Omega, P)$, where $\Omega = \Omega_0 - E_{out}$ and $P = -P_{out}$, is proportional to the imaginary part of the single-electron retarded Green function

$$I(P,\Omega) \propto Im \int dx e^{-iPx} \int_0^\infty dT e^{i\Omega T} G(x,T,0,0). \tag{1}$$

(Since now on we shall omit all constant factors and take the Plank constant $\hbar = 1$; Ω will be measured with respect to a convenient level: the band edge or the middle of the gap.) The simple PES nonresolved in momenta measures the integrated absorption intensity $I(\Omega) = \int dp I(p, \Omega)$.

We shall use the adiabatic (Born-Oppenheimer) approximation. Electrons are moving in the slowly varying phonon potential, e.g. $Q(x,t)$, so that at any instance t their energies $E_j(t)$ and wave functions $\psi_j(x,t)$ are defined from the stationary Schroedinger equation for the instantaneous lattice configuration and they depend on time only parametrically. The intensity can be written in the form of a functional integral $D[Q(x,t)]$ over lattice configurations $Q(x,t)$

$$I(\Omega, P) \propto \int dx e^{-iPx} \int_0^\infty dT \int D[Q(x,t)] \Psi_0(x, T; [Q]) \Psi_0^*(0, 0; [Q]) \exp(-S[Q]) \tag{2}$$

This equation is already written in the Euclidean space $it \to t$ which is adequate for studies of classically forbidden processes[2,23,24]. Here $\Psi_0(x,t;[Q])$ is the wave function of the added $(N+1)$th particle in the instantaneous field $Q(x,t)$ which corresponds to the energy level $E_0(t) = E_0[Q(x,t)]$ inside the gap. The effective action $S = S[Q(x,t)]$ is expressed via Lagrangians L_j as

$$S = \int_\infty^0 dt L_0 + \int_0^T dt (L_1 - \Omega) + \int_T^\infty dt L_0 \tag{3}$$

where indices $j = 1, 0$ label systems with and without the additional particle state (actually the hole). Their typical structure is

$$L_j = \int dx \ \frac{\mu}{2} (\partial_t Q)^2 + V_j(Q) \, , \ \mu = const \sim \omega_0^{-2} \tag{4}$$

where ω_0 is a bare phonon frequency (implying the dispersionless phonon branch). A nature of the field Q, its potentials $V_j(Q)$ and the action upon electrons differ for various models as described in Sec.III. Usually

$$V_j[Q(x,t)] = \int dx \frac{Q^2}{2g^2} + \epsilon_j[Q] \, , \ \mu g^2 = \omega_0^{-2} \tag{5}$$

which contains the bare harmonic term $\sim Q^2$ and the adiabatic contribution from the energy of the electron system in the j-th excited state. The electronic terms $j = 0, 1$ correspond to adiabatic ground states of N and $N-1$electrons in the instantaneous field $Q(x)$. For calculations of subgap processes only lowest localized states $j = 0, 1$ are relevant, while other states belong to the continuum spectrum above the gap. Then Ψ in (2) is the wave function Ψ_0 of the split off singly filled electronic state with the energy level E_0 inside the gap and $V_1 = V_0 + E_0$.

Within the PG region the main contribution to I comes from the saddle points of the action S: $\delta S/\delta Q = 0$ $\partial S/\partial T = 0$, the last equation determines the value $T = T(\Omega)$ as

$$L_1(T) - L_0(T) = E_0(T) = \Omega. \tag{6}$$

(The same relation holds at the point $t = 0$ if one substitute $0, T \to t, t+T$ in Eq. (3) and find the minimum over t). We shall find also, in Sec. IIID devoted to particularities of the ARPES, circumstances when the extremum must be determined for the whole expression under the integral in the definition (2), including the wave functions in the prefactor of (2). Any nonzero contribution requires for a finite action $S_0 < \infty$ which selects configurations $Q(x,t)$ deviating from the ground state only within a finite space-time region. Such extremal solutions with finite actions are called the instantons[23], their trajectories correspond to tunneling in the real time.

B. Translational mode.

Within the saddle point approximation the transition rate is given by

$$I(p, \Omega) = I_0 \exp(-S_0), \tag{7}$$

The prefactor $I_0 = I_T I_X \ldots$ comes from integration over deviations δQ, δT around the extremal solution. E.g. the factor $I_T = \left(\partial^2 S/\partial T^2\right)^{-1/2} = \sqrt{dT/d\Omega}$ comes from the integration over T. Usually it can be taken after the extremal is determined. But there are cases when I_0 should be determined selfconsistently, like in statistical physics looking for

the minimum of a free energy, rather then simply of an energy. This option appears naturally in comparison of PES and ARPES where it comes from treatment of the translational invariance. Apparently an essential contribution to the action from the "quantum entropy" $\delta S = -\ln I_0$ may come only from integration over particular zero modes appearing because of continuous degeneracy. The contribution of usual nondegenerate modes must be small by definition of a well defined extremum.

The extremal solution can be written as $Q_0(x-X,t)$, $\Psi_0(x-X,t)$ where the collective coordinate X of the instanton corresponds to the translational invariance which originates one zero mode in the functional integration around the saddle point solution. We expand the field $Q(x,t)$ in the vicinity of instanton solution as

$$Q(x,t) = Q_0(x - X(t), t) + \eta(x - X(t), t) \tag{8}$$

with the orthogonality condition $\int dx Q_0 \eta = 0$, where $\eta(x,t)$ contains only nonzero modes. Integrating over the zero mode is carried out by means of Faddeev-Popov[26] method inserting the identity

$$1 = \int D[X(t)]\delta(\int dx \eta_0(x - X(t), t)Q(x,t))J, \quad J = \prod_t \int dx \partial_x \eta_0(x - X(t), t)Q(x,t), \tag{9}$$

where $\eta_0 = \partial_x Q_0(x - X(t), t)/\sqrt{\int (\partial_x Q)^2 dx}$ is the normalized zero mode eigenfunction. The integration over $X(t)$ can be done exactly. Taking into account only terms containing $X(t)$ we rewrite (2) as

$$I_X \propto \int dx e^{-iPx} \int_0^\infty \int D[X(t)] J \Psi_0(x - X(T), T; [Q]) \Psi_0^*(-X(0), 0; [Q]) \exp\left[-\frac{1}{2}\int dt M(t) \dot{X}^2(t)\right], \tag{10}$$

where $J = \prod_{t_i} \sqrt{M(t_i)}$, and $M(t)$ is the translational effective mass of the instanton at a given moment t:

$$M(t) = \mu \int dx (\partial_x Q)^2.$$

Introducing the integration over $X_1 = X(0)$, $X_2 = X(T)$ one obtains

$$I_X \propto \int \frac{dX_1}{\sqrt{M(0)}} \frac{dX_2}{\sqrt{M(T)}} \int dx e^{-iPx} \int_0^\infty \int D[Q(x,t)] \Psi_0(x - X(T), T; [Q]) \Psi_0^*(-X(0), 0; [Q]) I_1 I_2 I_3, \tag{11}$$

where

$$I_1 = \int_{X(-\infty)=0}^{X(0)=X_1} D[X(t)] \prod_{t_i \in (-\infty, 0)} \sqrt{M(t_i)} e^{-\int_{-\infty}^0 dt M \dot{X}^2/2}, \; I_2 = \int_{X(0)=X_1}^{X(T)=X_2} D[X(t)] \prod_{t_i \in (0,T)} \sqrt{M(t_i)} e^{-\int_0^T dt M \dot{X}^2/2},$$

$$I_3 = \int_{X(T)=x_2}^{X(\infty)=0} D[X(t)] \prod_{t_i \in (T,\infty)} \sqrt{M(t_i)} e^{-\int_T^\infty dt M \dot{X}^2/2}.$$

Each integral I_i is easy calculated, after the transformation $M\dot{X}^2 = \dot{Y}^2$, with the help of the result[22]

$$\int_{x(0)=x_1}^{x(T)=x_2} D[x(t)] e^{-\int_0^T (\dot{x}^2 + V(x))dt} = \left|\frac{\partial^2 S_0}{\partial x_1 \partial x_2}\right|^{1/2} e^{-S_0},$$

where S_0 is the saddle point action. After simple integrations over dx, dX_1, dX_2 we arrive at

$$I_X \propto \mid \Psi_P(T) \mid^2 \exp\left[-\int_0^T dt \frac{P^2}{2M(t)}\right], \tag{12}$$

where Ψ_p is the Fourier transform of the wave function Ψ_0.

Contrary to stationary solutions, the solitons (polarons, kinks), here $M(t)$ depends on time along the instanton trajectory $Q_0(x,t)$. The exponential term in (12) gives the contribution to the total action which is important at very large P because generally it is of the order of $M^{-1} \sim \omega_0^2$. It provides an important, sometimes leading effect upon the edge shape: it is singular along the instanton term with M vanishing at large $|t|$ when the space localization is week and $M^{-1}(t)$ diverges.

C. Zero dimensional reduction.

As a rule the space-time differential nonlinear equations for extremals are not solvable, hence one is bound to variational procedures. We shall use the following ansatz which is actually an one-parameter reduction of the functional space. The instanton trajectory must satisfy the condition (6) which means that there is an electron level $E_0 = \Omega$ at times $t = 0, T$. It seems reasonable that the trajectory with only one local level inside the gap will be a good approximation for the extremal action. There is also a special advantage that for models considered below we know exact solutions of the stationary problem $Q_0(x, a)$ depending on some continuous parameter a with the local level $E_0(a)$ inside the gap. Therefore we shall search the instanton (time-dependent) solution in the form $Q_0(x, a(t))$. After integration around saddle point $Da(t)$ we find finally for ARPES intensity

$$I(P, \Omega) \propto \sqrt{\frac{dT}{d\Omega}} \mid \Psi_p(a_T) \mid^2 e^{-S_0}, \tag{13}$$

where S_0 is the instanton action which is extremum over $T, a(t)$ of

$$S = \int_{-\infty}^{\infty} dt[f(a)\dot{a}^2 + \frac{P^2}{2M(a(t))} + V(a(t)], \tag{14}$$

where

$$f(a) = \frac{\mu}{2} \int dx \left(\frac{\partial Q_a(x,t)}{\partial a(t)} \right)^2 \tag{15}$$

is the variable effective mass, $V(a(t)) = V_1(a(t)) - \Omega$, for $\in [0, T]$, or $V(a(t)) = V_0(a(t))$ otherwise.

In some cases the form-factor Ψ_P^2 gives the main contribution to the function $I(P, \Omega)$. Then we must find the extremal solution for a modified action $S \to S - \log \mid \Psi_P \mid^2$. Such a possibility will be considered in details in Sec. IIID.

Since the PES intensity is obtained simply by integration of ARPES one, we obtain

$$I(\Omega) \propto \left(\int \frac{dp}{2\pi} e^{-p^2 l^2/4} \mid \psi_p(T) \mid^2 \right) \sqrt{\frac{dT}{d\Omega}} \exp[-S_0], \tag{16}$$

where

$$l^2 = \int_0^T \frac{dt}{M(a(t))},$$

and S_0 is the extremum of the action (14) without the kinetic term $P^2/2M$. The form-factor $F = \int dP \mid \psi_p(T) \mid^2 \exp(-P^2 l^2/2)$ in (16) provides a kind of Debye-Waller reduction of intensity. Thus for small l in compare to the localization length ξ of Ψ (short times near the free edge) $F \approx 1$ while for large $l \gg \xi$ (long times T near the absolute threshold) $F \sim |\Psi_{P=0}(T)|^2 \sim \xi/l$ with ξ being the polaronic width. In our examples typically it will hold $l \ll \xi$.

For typical potentials $V(a)$ (see Fig. 1 - 4 below) the extremum solution with a finite action exists only in some region of Ω where the potential curve $V_1(a) - \Omega$ (or $V_1(a) - \Omega + P^2/2M(a)$ for the case of ARPES) crosses both the curve $V_0(a)$ and $V = 0$. It takes place if the minimum of the potential $V_1 - \Omega$ (or $V_1 - \Omega + P^2/2M$) is placed below the minimum of the potential V_0 (min $V_0 = 0$). If a_T is the point where

$$V_0(a_T) = V_1(a_T) - \Omega \quad \text{(PES)}, \qquad V_0(a_T) = V_1(a_T) - \Omega + P^2/2M(a_T) \quad \text{(ARPES)}, \tag{17}$$

and a_f is the solution of

$$V_1(a_f) - \Omega = 0 \quad \text{(PES)}, \qquad V_1(a_f) - \Omega + P^2/2M(a_f) = 0 \quad \text{(ARPES)}, \tag{18}$$

then the extremal solution is the closed trajectory, described by the equation

$$f(a)\dot{a}^2 = \tilde{V}(a), \tag{19}$$

where $\tilde{V} = V_0(a)$, $a \in [0, a_T]$, and $\tilde{V} = V_1(a) - \Omega + P^2/2M(a)\}$, $a \in (a_T, a_f]$ for ARPES, or the same expression without the kinetic potential $P^2/2M$ for PES. The Eq. (17) is a consequence of the Eq. (6), it implies a continuity of the velocity $\dot{a}$ at the point a_T. The Eq. (18) reads that the velocity $\dot{a} = 0$ at the point a_f.

The instanton equation (19) describes the motion of some particle of zero energy with variable mass $2f(a)$ in the inverted potential $-\tilde{V}$. The trajectory starts at $t=-\infty$ from the point $a=0$, reaches the points a_T at $t=0$, a_f at $t=T/2$, after which the particle moves back across the point a_T at $t=T$ to the initial point $a=0$ at $t\to\infty$. The instanton action (for ARPES) can be expressed as

$$S_0 = 4\int_0^{q_T} dq\sqrt{fV_0} + 4\int_{q_T}^{q_f} dq\sqrt{f(V_1-\Omega+P^2/2M(a))}. \tag{20}$$

III. RESULTS FOR ABSORPTION INTENSITIES.

A. Zero-dimensional case

We shall start with a tutorial example where the general approximate scheme can be compared with exact calculations. Consider a particle interacting with a single quantum oscillator at zero temperature. Physically it can be a problem of the Jahn-Teller center or a zero order approximation for the small radius polaron. The total Lagrangian is

$$L = \frac{m}{2}\dot{q}^2 - \frac{m}{2}\omega_0^2 q^2 - gqN, \tag{21}$$

where q is the oscillator coordinate, m is its mass, g is the interaction constant, and N is the electron's occupation number. The potentials V_0 and V_1

$$V_0 = \frac{m\omega_0^2}{2}q^2, \qquad V_1 = \frac{m\omega_0^2}{2}q^2 - gq = \frac{m\omega_0^2}{2}(q-q_0)^2 - W_0\,;\; q_0 = \frac{g}{m\omega_0^2}\,,\; W_0 = \frac{g^2}{2m\omega_0^2}.$$

are shown in Fig. 1. In compare to $N=0$, for $N=1$ the oscillator states n are shifted by q_0 in coordinate and by $-W_0$ in energy. Adiabatically allowed transitions take place only at the given q that is they explore the region $q=0$, $\Omega=0$. Taking into account the quantum character of the coordinate q, the transitions are found to the lower energies down to W_0. The region $0>\Omega>-W_0$ corresponds to pseudogaps in more complex systems.

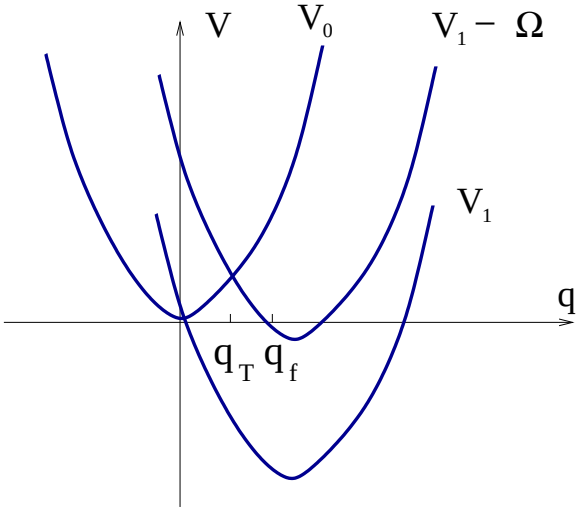

FIG. 1. Potentials V_0, $V_1-\Omega$.

The solutions of (17), (18) read

$$q_T = -\Omega/g, \qquad q_f = 2g/(m\omega_0^2).$$

The instanton action is easy calculated and for the absorption rate we arrive at

$$I(\Omega) \propto \frac{1}{\sqrt{\Omega + W_0}} \exp(-\frac{W_0}{\omega_0}) \exp\left[\frac{\Omega + W_0}{\omega_0} \log \frac{eW_0}{(\Omega + W_0)}\right]. \tag{22}$$

Expanding the exponent near the extremum point $\Omega = 0$ we obtain

$$I(\Omega) \propto \exp\left[-\frac{\Omega^2}{2W_0\omega_0}\right]. \tag{23}$$

which describes smearing of the adiabatically allowed electronic edge. This is the Gaussian with the width $\delta\Omega = \sqrt{W_0\omega_0} \gg \omega_0$ which justifies the adiabatic approximation. At the lower boundary $\Omega = -W_0$ of the exact spectrum the probability has a finite exponentially small value which is approached with an infinite slope.

For this simple example $W(\Omega)$ can be calculated exactly in the representations of eigenstates. Indeed,

$$I(\Omega) = \sum_n |\langle n, 1|\Psi^+|0, 0\rangle|^2 \delta(\Omega - E_n + E_0), \tag{24}$$

where $|0, 0\rangle$ is the ground-state of the system without electron with the energy $E_0 = \hbar\omega_0/2$, and $|n, 1\rangle$ is the n-th excited state ($n = 0, 1, ...$) with one electron and the energy $E_n = \hbar\omega_0(n + 1/2) - W_0$. The wave functions are the ones for the harmonic oscillator which are centered at $q = 0$ for $|0, 0\rangle$ and at $q = q_0$ for $|n, 1\rangle$. In the limit $\omega_0 \to 0$ and $n = (\Omega + W_0)/\omega_0 \gg 1$ we find

$$I(\Omega) = \frac{\exp[^{-(\delta y)^2/2}]}{\sqrt{2\pi n}\omega_0} \exp\left[n \log \frac{e(\delta y)^2}{2n}\right], \tag{25}$$

where $\delta y = g/\sqrt{m\omega_0^3}$. This equation reproduces the result (22).

B. Shallow states in a 1D system.

Consider the electron (hole) states in a 1D dielectric near an edge of a conducting (valence) band. We shall take into account the dispersionless phonon field $Q(x, t)$ with the bare frequency ω_0 which interacts locally with the electron via the deformation potential with a coupling g. Within the adiabatic approximation the action has the form (again at imaginary time)

$$S = \int dx \left\{ \int_{-\infty}^{+\infty} dt \left(\frac{1}{2\omega_0^2} \left(\frac{\partial Q}{\partial t} \right)^2 + \frac{1}{2} Q^2 \right) + \int_0^T dt \left(\frac{1}{2m} \left| \frac{\partial \Psi}{\partial x} \right|^2 + gQ\Psi^\dagger\Psi - \Omega \right) \right\}, \tag{26}$$

It is well known that the stationary ($\dot{Q} = 0$) extremum of S corresponds to the selftrapped state (the polaron)[32]. We arrive directly at Eqs. 4,5 with E and Ψ as solutions of the Schrödinger equation:

$$-\frac{1}{2m}\frac{d^2\Psi}{dx^2} + gQ\Psi = E\Psi\,,\ E = E(t) = E[Q(x, t]_t. \tag{27}$$

The minimum of the initial potential $\min V_0 = 0$ is achieved at the uniform configuration $Q = 0$. The minimum of V_1 takes place at the polaron state $\min V_1 = W_p = -W_0 = -mg^2/24$. The minimum of $V_1 - \Omega$ must be lower than the minimum of V_0, hence $-W_0 < \Omega < 0$.

Since the exact solution of the complete time dependent extremal equations is not known, we shall follow a variational approach. We will search for the instanton solution in the form which simulates the stationary solution but with the variable time dependent parameter $B(t)$ which we chose as the inverse localization length:

$$Q(x, t) = -\frac{B^2(t)}{mg} \frac{1}{\cosh^2 B(t)x}, \qquad \Psi = \sqrt{\frac{B(t)}{2}} \frac{1}{\cosh B(t)x}, \qquad E(t) = -\frac{B^2}{2m}. \tag{28}$$

The stationary solution corresponds to $B(t) = B_0 = mg^2/2$. In terms of $b(t) = B(t)/B_0$ the Lagrangians become

$$L_0 = W_0 \left[\frac{C_0}{\omega_0^2} b\dot{b}^2 + 2b^3\right]\,,\ L_1 = W_0 \left[\frac{C_0}{\omega_0^2} b\dot{b}^2 + 2b^3 - 3b^2\right], \tag{29}$$

where $C_0 = 4 + 2\pi^2/15 \approx 5.3$. The instanton equation describes the motion of a zero energy particle, with a coordinate b and with a variable mass $f \sim b$, in the inverted potentials

$$V_0 = W_0 2b^3 \text{ and } V_1 - \Omega = W_0 \left[2b^3 - 3b^2\right] - \Omega.$$

which are shown in Fig. 2.

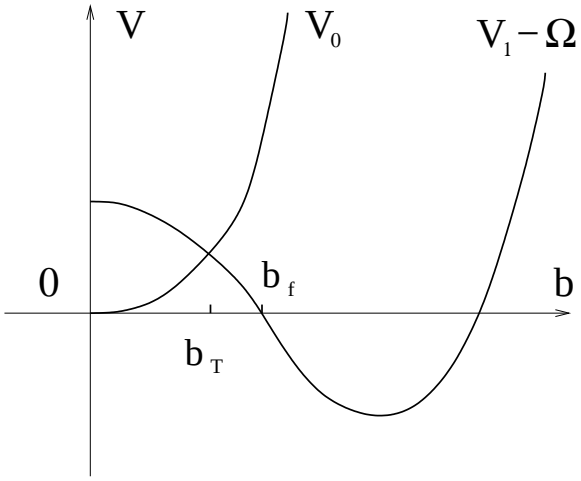

FIG. 2. Potentials V_0, $V_1 - \Omega$.

The value $b_T = \sqrt{|\Omega/E_0|}$, the value b_f at the turning point is determined by the condition $V_1(b_f) - \Omega = 0$. For the PES the action is

$$S_0 \approx 4\sqrt{C_0}\frac{W_0}{\omega_0}\left[\int_0^{b_T}\sqrt{2}b^2 db + \int_{b_T}^{b_f}\sqrt{(2b^3 - 3b^2 - \frac{\Omega}{W_0})}\, b\, db\right]$$

and we arrive at the following results.

Near the free electronic edge $\Omega = 0$ we have

$$I(\Omega) \propto |\ \Omega\ |^{-1/4}\exp\left[-\frac{8}{9}\sqrt{\frac{C_0}{6}}\frac{(-\Omega)^{3/2}}{\omega_0 W_0^{1/2}}\right] \tag{30}$$

The characteristic width of the edge is $\delta\Omega \sim (\omega_0^2 W_0)^{1/3} \gg \omega_0$ which justifies the adiabatic approximation.

In the vicinity of the absolute edge $\Omega \approx -W_0$ we obtain

$$I(\Omega) \propto \frac{1}{\sqrt{\Omega + W_0}}\exp[-2\frac{W_0}{\omega_0}]\exp\left[2\sqrt{\frac{C_0}{3}}\frac{\Omega + W_0}{\omega_0}\ln\frac{e(\sqrt{3}-1)^2 W_0}{(\Omega + W_0)}\right]. \tag{31}$$

In this limit the probability is finite, exponentially small in the adiabatic parameter W_0/ω_0 and it shows a weak singularity in its derivative. The prefactors in above formulas come from $I_T \sim (d^2S/d\Omega^2)^{1/2}$. The form-factor is

$F \approx 1$ according to Sec. II. Indeed, in spite of a formal divergence of l, within limits of the adiabatic approximation ($|\Omega| \gg \omega_0$ or $(\Omega + W_0) \gg \omega_0$) it stays below the localization length ξ. Thus $l/\xi \sim (\omega_0/\Omega)^{1/2} \ll 1$ for small Ω and $l/\xi \sim (\omega_0 \ln[W_0/(\Omega + W_0)])^{1/2}$ for $\Omega \approx -W_0$.

Peculiarities of the ARPES will be studied in the next section within a richer Peierls model.

C. The Peierls model

We consider now the PES absorption spectrum in the gap region for a half-filled Peierls model. In the ground state the electron spectrum has the form $E^2 = v_F^2 p^2 + \Delta_0^2$ and since now on we shall put the Fermi velocity $v_F = 1$. The gap $2\Delta_0 \sim \epsilon_F \exp[-1/\lambda]$ is opened as a result of symmetry breaking lattice deformations. We shall consider the case of a dimerization (trans-Polyacethylene, Spin-Peierls systems) which is described by the model with the real order parameter Δ taking equilibrium values $\pm\Delta_0$. The excited states are solitons (kinks), polarons and bisolitons (kink-antikink pairs) which are characterized by electron levels localized deeply within the gap (see the review[14]). The adiabatic approximation is valid when the electron transition energies are much larger than the phonon frequency $\omega_0 \ll |E_i - E_j|$. For characteristic $|E_i - E_j| \sim \Delta_0$ this constraint coincides with the applicability condition for the Peierls model in general[15]. Away from the ground state the field $\Delta(x,t)$ extends a role of the field Q from the

previous section. The first difference is that $\Delta \neq 0$ already in the ground state. The second one is that the whole sea of electrons at $E < -\Delta_0$ contributes to the selftrapping energy[14] and to the instanton terms.

The effective Euclidean action S consists of the kinetic and the bare potential lattice energy and of the sum over filled electron levels E_α.

$$S\{\Delta(x,t)\} = \int dx L_j dt, \quad L_j = \int dx \frac{\dot{\Delta}^2}{\pi\lambda\omega_{ph}^2} + V_j[\Delta(x,t)].$$

where $\omega_{ph} = \sqrt{\lambda}\omega_0$ is the bare frequency of the phonon responsible for the dimerization while ω_0 is the amplitude mode frequency in the dimerized state $\Delta \neq 0$. The index j characterizes perturbations in the set $\{\alpha_j\}$ of filled electronic states in the field Δ. The potential energy in the j-th electronic state is

$$V_j[\Delta(x,t)] = \int dx \frac{\Delta^2}{\pi\lambda} + \sum_{\alpha_j} E_{\alpha_j}\{\Delta(x,t)\} - W_{gs},$$

which we have defined relative to the ground state energy W_{gs} at $\Delta(x,t) = \Delta_0$ for a system of $N = N_a$ electrons (N_a is the number of sites in the chain).

The PES absorption adds one particle (hole) to the system, then the polaron state is formed by local deformations of the field $\Delta(x)$ which originate the pair of split off electronic levels $\pm E_0$ localized deeply in the gap. In optical absorption[20] an electron is excited across the gap, then a pair of distant kinks is formed with electron level placed exactly in the center of the gap ($E_0 = 0$). The crossover solution describing the states with just one pair of localized electronic levels $\pm E_0$ is known[29,30]:

$$\Delta_s(x) = \Delta_0(1 - \tanh a[\tanh(\Delta_0 x \tanh a + \frac{a}{2}) - \tanh(\Delta_0 x \tanh a - \frac{a}{2})]). \tag{32}$$

Depending on the parameter a it describes evolution from the shallow polaron at $a \to 0$ to the pair of kinks at $a \to \infty$. In the first case the parameter $a \ll 1$ becomes equivalent to b from the previous section. In the second case $a \gg 1$ becomes a distance between divergent kinks. For the configuration 32 the potential energy functional V and the energy of the local level E_0 are given by

$$V_\nu(a) = \nu E_0 + \frac{4}{\pi}\sqrt{\Delta_0^2 - E_0^2} - \frac{4}{\pi}E_0 \cos^{-1}\frac{E_0}{\Delta_0}\,, \; E_0 = \frac{\Delta_0}{\cosh a}, \tag{33}$$

where $\nu = 0, 1, 2$ is the number of particles (electrons and holes) added to the system. The wave function of the intragap state can be written as[27] $\Psi_0(x) \propto \sqrt{\Delta_0^2 - \Delta_s(x)^2}$.

The case $\nu = 0$ describes the state which evolves from the ground one without perturbing the occupation numbers: the level $-E_0$ is doubly filled while the level E_0 is empty. Naturally the minimum of V_0 corresponds to the uniform configuration $\Delta(x) = \Delta_0$ at $a = 0$ without a split-off level. The function $V_0(a)$ monotonically increases from $V_0(0) = 0$ to $V_0(\infty) = 2W_s$, ($W_s = 2/\pi\Delta_0$ is the total soliton energy) with the asymptotic behavior.

$$V_0(a) \approx \frac{4}{3\pi}\Delta_0 a^3, \quad a \to 0, \quad V_0(a) \approx 2W_s - 2E_0(a), \quad a \to \infty. \tag{34}$$

For the polaron $\nu = 1$ (either one electron at E_0 or one hole at $-E_0$) the equilibrium state corresponding to the minimum of V is achieved at $a = a_0$ where

$$\sinh a_0 = 1\,, \; \min V_1 = V(a_0) = W_p = 2^{3/2}\Delta_0/\pi\,, \; E_0 = \Delta_0/\sqrt{2}.$$

The limiting values of $V_1(a)$ are $V_1(0) = \Delta_0$, $V_1(\infty) = 2W_s$.

The case $\nu = 2$ corresponds to either an exciton (one electron and one whole at $\pm E$ that is each of these levels is singly occupied) or to electron or hole bipolarons (all states $\pm E$ are either filled or empty). The excitonic state plays a principal role in the subgap optical absorption problem[20,25]. The equilibrium state is achieved at $a = \infty$ where $V = 2W_s$ and $E_0 = 0$. The function $V_2(a)$ decreases monotonically from $V_2(0) = 2\Delta_0$ to $V_2(\infty) = 2W_s$. The dependencies $V_\nu(a)$ are shown in Fig. 3.

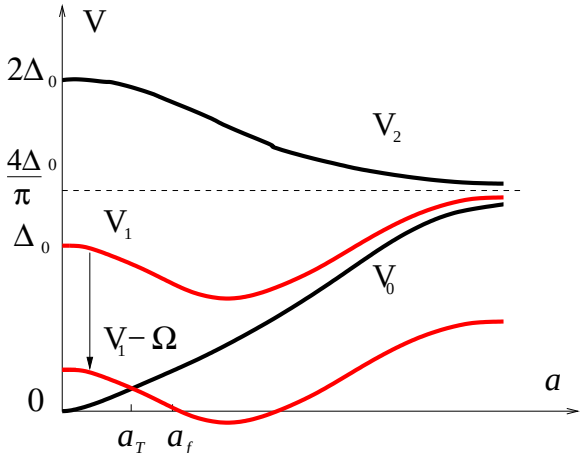

FIG. 3. Plots of $V_\nu(a)$ for $\nu = 0, 1, 2$.

The above $a-$ dependent family of solutions is the only one which provides exactly one pair of discrete levels in the gap. Its perturbations originate only shallow levels located near the edges $\pm\Delta_0$ which are not important for the described processes. Therefore we will choose the configuration $\Delta(x,t) = \Delta_s(x, a(t))$ of (32) taken with the time dependent parameter a. The kinetic term in the Lagrangian becomes $f(a)\dot{a}^2$ with

$$f(a(t)) = \frac{1}{\pi\omega_0^2}\int dx \left(\frac{\partial\Delta_s}{\partial a}\right)^2. \tag{35}$$

The function $f(a)$ increases from $f(0) = 0$ reaching the maximum value $f \approx 1.55\Delta_0/(\pi\lambda\omega_0^2)$ at $a \approx 0.78$, and then decreases with asymptotics

$$f(a) \approx \frac{2}{3}\frac{C_0}{\pi}\frac{\Delta_0 a}{\omega_0^2},\ a \to 0; \qquad f(a_0) \approx \frac{1.53\,\Delta_0}{\pi\omega_0^2}; \qquad f(\infty) = \frac{2}{3}\frac{\Delta_0}{\pi\omega_0^2}. \tag{36}$$

with the same coefficient C_0 as in the previous section.

The translational mass becomes

$$M(a) = \frac{2}{\pi\omega_0^2}\int dx \left(\frac{\partial\Delta}{\partial x}\right)^2 = \frac{8\Delta_0^3}{g^2\omega_0^2}\left[\frac{\tan^3 a}{3} - \frac{a\cosh a - \sinh a}{\cosh^3 a}\right]. \tag{37}$$

The function $M(a)$ monotonically increases with asymptotics

$$M(a) \approx C_M\frac{\Delta_0^3}{\omega_0^2}a^5, \quad C_M = \frac{32}{15}, \quad a \to 0; \qquad M(a_0) \approx 0.49\frac{\Delta_0^3}{\pi\omega_0^2}; \qquad M(\infty) = \frac{16}{3\pi}\frac{\Delta_0^3}{\omega_0^2}. \tag{38}$$

Following the prescriptions of Sec. II, we can describe now the PG region $W_p < \Omega < \Delta_0$. In the limiting cases the results are qualitatively similar to the ones for the shallow polaron.

Near the free edge, $\Omega \approx \Delta_0$ we find

$$I(\Omega) \sim (\Delta_0 - \Omega)^{-1/4}\exp\left[-\frac{32\sqrt{C_0}}{9\pi}\frac{(\Delta_0 - \Omega)^{3/2}}{\omega_0\sqrt{\Delta_0}}\right]. \tag{39}$$

with the same coefficient C_0 as in (29).

Near the polaronic energy $\Omega \approx W_p$ we find

$$I(\Omega) = const\frac{1}{\sqrt{\Omega - W_p}}\exp\left[-C_1\frac{\Delta_0}{\omega_0}\right]\exp\left[C_2\frac{(\Omega - W_p)}{\omega_0}\log\frac{C_3\Delta_0}{(\Omega - W_p)}\right] \tag{40}$$

Here the numerical coefficients $C_1 = 0.34$, $C_2 = 5.2$, $C_3 = 0.1$.

D. ARPES intensities.

For case of ARPES the potential V_1 acquires an additional term $P^2/2M$, therefore the closed trajectory is allowed in the region (Ω, P) where (See Fig. 4)

$$\tilde{V}_1(a_m) = V_1(a_m) + P^2/2M(a_m) - \Omega < 0\,,\; d\tilde{V}_1/da|_{a=a_m} = 0 \tag{41}$$

Here the value a_m is the point of a minimum of the potential $\tilde{V}_1(a)$, which exists for any value of the momentum P. In the limit $P = 0$ we have $a_m = a_0$. For other Ω, P there are no solutions with a finite action so that the transition rate is zero. In contrast to the PES case, the closed trajectory exists for any frequency $\Omega > W_p$ in the region of the momentum P satisfying the condition (41).

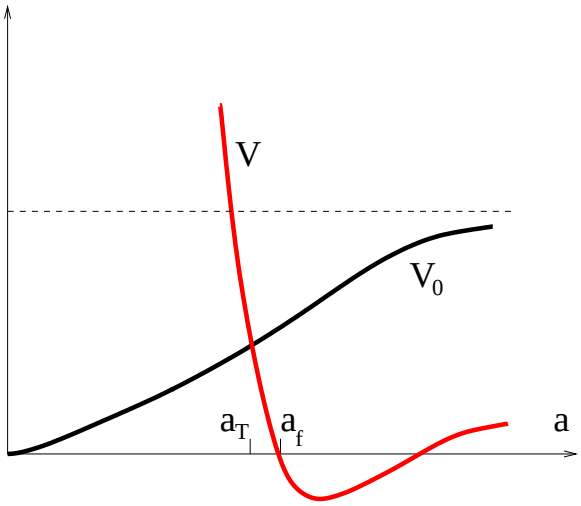

FIG. 4. Plots of $V_0(a)$ and $V_1 + P^2/2M(a) - \Omega$.

Consider most important cases where analytical solution can be found.

A. In a vicinity of the absolute edge $\Omega \approx W_p$ the absorption appears at $\Omega \geq V_1(a_m) + P^2/2M(a_m) \equiv \tilde{W}_p$. Here, near the polaron edge, the translational mass is almost constant staying near $M(a_m)$ hence the momentum appears simply through the shift $\Omega \Rightarrow \Omega - P^2/2M(a_m)$.

$$I(P,\Omega) \propto \frac{1}{\sqrt{\Omega - \tilde{W}_p}} \exp[-S_0]. \tag{42}$$

with

$$S_0 = \frac{\tilde{C}_1}{\sqrt{\pi\lambda}}\frac{\Delta_0}{\omega_0} + \left[\tilde{C}_2 \frac{(\Omega - \tilde{W}_p)}{\sqrt{\pi\lambda}\omega_0} \log \frac{\tilde{C}_3\Delta_0}{(\Omega - \tilde{W}_p)}\right]. \tag{43}$$

The result for the absorption looks like the Eq. (40) for the PES with $W_p \Rightarrow W_p(P)$ but the coefficients C_j become functions of P: $\tilde{C}_1, \tilde{C}_2, \tilde{C}_3$. They are defined as

$$\tilde{C}_1 = 4\sqrt{\pi\lambda}\frac{\omega_0}{\Delta_0}\left[\int_0^{a_T} da\sqrt{f(a)V_0(a)} + \int_{a_T}^{a_f} da\sqrt{f(a)(\tilde{V}_1 - W_p)}\right],$$

$$\tilde{C}_2 = \sqrt{\pi\lambda}\omega_0 \frac{2^{3/2}\sqrt{f(a_m)}}{\sqrt{\tilde{V}_1''(a_m)}}\,,\; \tilde{C}_3 = \frac{e}{2}(a_f - a_T)^2\frac{\tilde{V}_1''(a_m)}{\Delta_0}.$$

and at $P \to 0$ they coincide with the numerical ones C_1, C_2, C_3 defined above in Sec. IIIC.

B. A vicinity of the free edge $\Omega \approx \Delta_0$ is very particular for the ARPES. It is dominated by shallow fluctuations determined by small $a \ll 1$ where the kinetic energy diverges as $P^2/M \sim a^{-5}$ according to (38). The form-factor $\mid \Psi_P \mid^2$ acquires an explicit form

$$\mid \Psi_P \mid^2 \approx \frac{\pi}{\Delta_0 a_T} \cosh^{-2} \frac{\pi P}{2\Delta_0 a_T} \tag{44}$$

To simplify appearance of cumbersome relations we shall use below dimensionless units $\Delta_0 = 1$ for the momentum P and energies which also will be counted with respect to Δ_0. In the limit a_t, $a_f \ll 1$ equations (17), (18) are reduced to

$$-\epsilon - \frac{a_T^2}{2} + \frac{\omega_0^2 P^2}{C_M a_T^5} = 0, \tag{45}$$

$$-\epsilon + \frac{4}{3\pi} a_f^3 - \frac{a_f^2}{2} + \frac{\omega_0^2 P^2}{C_M a_f^5} = 0, \tag{46}$$

where $\epsilon = (\Omega - \Delta_0)/\Delta_0$ and the term $-a_T^2/2$ comes from the expansion of the local level energy E_0. A simple analysis of (45), (46) shows that $a_f - a_T = o(a_T)$, and first term gives the main contribution to the action (20), so that

$$S_0 = \frac{8\sqrt{2C_0}}{9\pi} \frac{\Delta_0}{\omega_0} a_T^3. \tag{47}$$

The general constraint is $S_0 \gg 1$ hence $a_T \gg \omega_0^{1/3}$. It assures us also in the condition $M \gg \Delta_0$ (the mass M must stay above the free band edge mass) which requires for a weaker inequality $a_T \gg \omega$.

We have different regions where one of terms of Eq. (45) is small in comparison with others.

B1. Consider at first the region lying deeply enough within the PG:

$$(\omega_0 P)^{4/7} \ll -\epsilon \ll 1$$

Here the characteristic values of a_T are not too small so that one can neglect the kinetic energy $\sim P^2\omega_0^2/a_T^5$ in compare to the energy $-a_T^2/2$ of the localized level: $P^2\omega_0^2/a_T^5 \ll a_T^2$. Then $a_T \approx \sqrt{-2\epsilon}$, $S \sim |\epsilon|^{3/2}/\omega_0$ and $d\Omega/dT \sim a_T$. The momentum dependence comes only from the form-factor (44) but it can be still appreciable: P/a_T is limited by a big quantity ($P/a_T \ll \epsilon^{5/4}/\omega_0 \gg \omega_0^{-1/6}$) that is allowed to be large.

The total intensity is

$$I(\epsilon, P) \propto \frac{1}{\mid \epsilon \mid^{3/4}} \exp\left[-\frac{32\sqrt{C_0}}{9\pi\omega_0} \mid \epsilon \mid^{3/2} - \frac{\pi P}{\mid 2\epsilon \mid^{1/2}} \right] \tag{48}$$

In the limit $-\epsilon \ll \sqrt{P\omega_0}$ the contribution from $\mid \Psi_p \mid^2$ (the second term in the exponent) dominates, while in the opposite case the main contribution comes from the term S_0. The line of the maximum intensity $-\epsilon \sim \sqrt{\omega_0 P}$ will show up in the ARPES plots as a *quasi spectrum* which intensity decreases exponentially with growing momentum: $I(P) \sim P^{-3/8} \exp[-const P^{3/4} \omega_0^{-1/4}]$.

B2. Consider a marginal frequency lying very close to the free edge $\epsilon = 0$ for both signs of ϵ:

$$\omega_0 \ll |\epsilon| \ll (\omega_0 P)^{4/7} \ll 1 \text{ for } P \gg \omega_0^{2/5}.$$

In this case the instanton kinetic energy and the binding of the electron almost compensate each other: $P^2/2M \approx a_T^2/2 \gg |\epsilon|$ which gives us $a_T = \left((\omega_0 P)^2/C_M\right)^{1/7}$ and we obtain

$$I(\epsilon, P) \propto \frac{1}{P^{3/7}} \exp\left[-\pi \frac{\pi (C_M)^{1/7}}{\omega_0^{2/7}} P^{5/7} - \frac{8\sqrt{2C_0}}{9\pi (C_M)^{3/7} \omega_0^{1/7}} P^{6/7} \right] \tag{49}$$

The form-factor Ψ_P^2 gives the main contribution (the first term) to the exponent of (49) .

B3. Consider now a new region of positive frequencies $\epsilon > 0$:

$$\epsilon \gg (\omega_0 P)^{4/7} \text{ but } \epsilon \ll \omega_0^{1/3} P^2.$$

The first inequality ensures that the excess frequency is absorbed mainly by the kinetic energy with a negligible ($a_T^2/2 \ll \epsilon$) contribution from the electronic state which is still localized. The second inequality supports the adiabatic condition $S_0 \gg 1$. We find

$$a_T \approx \frac{(\omega_0 P)^{2/5}}{(2C_M\epsilon)^{1/5}}, \quad \frac{dT}{d\Omega} \propto \frac{P^{6/5}}{\epsilon^{13/5}}.$$

The ARPES intensity becomes

$$I(\epsilon, P) \propto \frac{P^{1/5}}{\epsilon^{11/10}} \exp\left[-\frac{\pi(2C_M)^{1/5}}{\omega_0^{2/5}} P^{3/5}\epsilon^{1/5} - \frac{8\sqrt{2C_0}\omega_0^{1/5}}{9\pi(2C_M)^{3/5}} \frac{P^{6/5}}{\epsilon^{3/5}}\right] \tag{50}$$

The form-factor contribution, the first term in the exponent, always dominates but the second term is also big thus contributing to the dependence $I(\epsilon, P)$. The total expression in the exponent of (50) looks non monotonous similar to the case B1 but now the minimal is not physical: its position $\epsilon \sim (\omega_0 P)^{3/4}$ would fall too low, into the region B2. Contours of constant intensity are close to the descending line $\epsilon \sim \omega_0^2/P^3$. The contribution (50) from the *fast moving instantons* can be observable only below the intensive free electronic absorption at $\epsilon \approx P^2/2$ that is at $P \gg \omega_0^{2/5}$ (a similar constraint already appeared for the case B2).

For the ARPES intensities we must, in principle, minimize the total effective action with the prefactor term $\mid \Psi_P \mid^2$, since in some cases this term gives a main contribution to the exponent. Then the action is changed as

$$S \to S - \log \mid \Psi_P \mid^2$$

The extremal solution, as before, satisfies the Eq. (19). The turning point a_f is not changed and is defined by the Eq. (18), but the equation defining the point a_T becomes more complicated. Instead of the Eq. (17) we obtain

$$V_0(a_T) - \tilde{V}_1(a_T) = \frac{1}{2}\frac{\partial \log \mid \Psi_P \mid}{\partial a}\left(\sqrt{\frac{V_0}{f}} + \sqrt{\frac{\tilde{V}_1}{f}}\right)\Bigg|_{a=a_T}. \tag{51}$$

This equation leads to the discontinuity of the potential $\tilde{V}$ at the point a_T and, due to the equation of motion (19), leads also to the discontinuity of the "velocity" $\dot{a}$. The expression for the ARPES intensity has the same form (19) with the action (20). The only difference is the shift of the point a_T due to Eq. (51).

For a considered in B1-B3 regions the point a_T is defined by (45) with the additional term $\sim P\omega_0/a_T$. The simple analysis shows that this term is small in comparison with the kinetic part $P^2/2M$ or with the term $a^2/2$, therefore it can be neglected. Thus, the main contribution to the action is not changed, and all above results are retained.

E. Optical absorption: effects of confinement.

The same method is applicable to the subgap optical absorption problem which was basically studied already in[11,20]. We shall see that more details can be easily obtained. In this case we must use the potential V_2, defined in (33), instead of V_1. The term V_2 describes the first excited state when the optical photon, assisted by a lattice quantum fluctuation, creates an $e-h$ pair with levels $\pm E(t)$ spanning the whole interval $|E| < \Delta_0$. The transition rate is given by the modified Eq. (7). For the vicinity of the free electronic edge $\Omega \sim 2\Delta_0$ we easily find, in analogy with (39), that

$$I(\Omega) \propto \exp\left[-\frac{16\sqrt{2C_0}}{9\pi}\frac{(2\Delta_0 - \Omega)^{3/2}}{\omega_0\sqrt{\Delta_0}}\right]. \tag{52}$$

This law was noticed in[20], while with a different coefficient in the exponent. Actually it was obtained already in[15] by another method which was later reproduced in[17]. Near the absolute absorption edge $\Omega \approx 2W_s = 4\Delta_0/\pi$ we obtain

$$I(\Omega) \propto \exp[6\sqrt{f(\infty)}\sqrt{\Omega - 2W_s}] \tag{53}$$

where $f(\infty)$ is given by Eq. (36). Near this edge the absorption is due to tunneling to the final state formed by the two diverging kinks with the distance parameter $a \to \infty$. (This regime was studied for the first time in[20] but the above analytical asymptotics was not found.) The law (53) is different from (40) which was typical for all polaronic

thresholds. The particularity is related to a very fast, $\sim \exp[-a]$, decrease of interactions for diverging solitons which determine the threshold. In terms of the effective particles the difference is that near the polaronic threshold the turning point approaches the potential extremum while for the solitonic threshold it climbs asymptotically to the plateau (the dashed line at the Fig.3).

While the law (40) is very robust, e.g. the same as for shallow polarons, the solitonic threshold is extremely sensitive to perturbations. The most drastic effect comes from the confinement energy $\delta V_\nu = Fa$ with the constant confinement force F originated by lifting of the ground state degeneracy. The confinement is always produced by the interchain coupling[28]. But even for a single chain it appears in cases of a build-in alternation of unit cells which interferes with the spontaneous dimerization like in $cis-(CH)x$[29,27]. In principle, the solitonic terms for this problem have been found exactly in the frame of the microscopic model of the "combined Peierls state"[29,27] and they can be used in our calculations for an arbitrary strength of the force $F = \gamma\Delta_0/\xi_0$. But here we shall consider only a weak confinement $\gamma \ll 1$ which preserves the local structure of solitons but prevents their divergence at large a. This effect can be taken into account by adding the term $\gamma\Delta_0 a$ to the potentials V_0, V_2 taken in zero order in $\gamma \ll 1$. (For the PES this effect is not relevant since the minimum of the polaronic potential V_1 is achieved at finite value a_0 where confinement is not important yet.) As a result the minimum of the potential V_2 is shifted to the finite point $a_\gamma \approx \log(16/\pi\gamma)/2$, where $V_2''(a_\gamma) = 2\gamma$. The optical absorption edge is shifted up to $W_\gamma = 4\Delta_0/\pi + \gamma\Delta_0 \log(16/\pi\gamma)/2$ and the transition rate $I(\Omega)$ is given by Eq. (40) if substitute $W_p \to W_\gamma$, $V1 \to V2$, $a_0 \to a_\gamma$, $a_1 \to \cosh^{-1}(\pi/2)$.

The problem of solitonic absorption, without the confinement, was considered in[25,20] by means of a different quasi-classical approaches. Our results supply the absent analytical asymptotics in this case and provide a new description for the general case of confinement. Further complications are coming from the long range Coulomb interactions which must be studied before comparison with existing experiments.

F. Quantum fluctuations as an instantaneous disorder.

In a one dimensional system the X-ray or optical absorption near the band edge can be viewed as the one in a system with a quenched disorder which is emulated by instantaneous quantum fluctuations. This conclusion was achieved[15] by analysis of the perturbation series for the polarization operator which is not the most efficient way to do. Later applications of this idea did not add any prove[17]. Here we shall derive this result within the approach of functional integrals which will provide a model independent limit for over approximate analysis of more complicated regimes and systems.

Consider a particle interacting with a media of harmonic oscillators. This model embraces the shallow polaron case of Sec.B and the limit of $\Omega \approx \Delta_0$ of Sec.D. The probability is given by the action

$$S\{Q,\Psi;T) = \int d^D x \int_{-\infty}^{+\infty} dt \left(\frac{1}{2\omega_0^2} \left(\frac{\partial Q}{\partial t} \right)^2 + \frac{1}{2} Q^2 \right) \tag{54}$$

$$+ \int d^D x \int_0^T dt \left(\frac{1}{2m} \left| \frac{\partial \Psi}{\partial x} \right|^2 + g Q \Psi^\dagger \Psi \right). \tag{55}$$

We can integrate out the field Q at all x and t to arrive at the action which is defined only at the interval $(0,T)$, c.f.[2]:

$$S\{\Psi;T) = \int d^D x \left[\int_0^T dt \left(\frac{1}{2m} \left| \frac{\partial \Psi}{\partial x} \right|^2 \right) - \frac{1}{4} g^2 \omega_0 \int_0^T dt_1 \int_0^T dt_2 \rho(x,t_1)\rho(x,t_2) \exp[-\omega_0 |t_1 - t_2|] \right]$$

where $\rho = |\Psi|^2$. The result will prove that the characteristic energy scale δ_D is much larger than ω_0 which takes place only at $D < 2$. Then the whole time interval is short $T\omega_0 \sim \omega_0/\delta_D \ll 1$ and we can neglect the retardation: $\exp[-\omega_0|t_1 - t_2|] \to 1$. Now the last term in $S\{\Psi;T)$ can be decoupled back by the Hubbard-Stratonovich transformation via the *time independent* auxiliary field ζ to give us

$$S\{\Psi,\zeta;T) = \int d^D x \left[\int_0^T dt \left(\frac{1}{2m} \left| \frac{\partial \Psi}{\partial x} \right|^2 \right) + \zeta(x) \int_0^T dt_1 \rho(x,t) + \frac{1}{g^2\omega_0} \zeta^2(x) \right]$$

Finally we can integrate over Ψ to arrive at the transition probability

$$I(\Omega) \sim \int D[\zeta(x)] \int dT \exp\left[-\frac{1}{g^2\omega_0} \zeta^2(x) + T(E[\zeta(x)] - \Omega) \right]$$

After rotation to the real time it becomes

$$\int D[\zeta(x)\delta(E[\zeta(x)]-\Omega)\exp\left[-\frac{1}{g^2\omega_0}\zeta^2(x)\right]$$

where $E[\zeta(x)]$ is the eigenfunction in the random field ζ

$$\frac{-1}{2m}\left(\frac{\partial}{\partial x}\right)^2\Psi+\zeta\Psi=E\Psi$$

Clearly the dispersion $\delta_0=g\sqrt{\omega_0/2}$ of the field ζ is just the mean square of quantum fluctuations of the phonon field $gQ(x,t)$. The well known results for the DOS of disordered systems[1,31] confirm our direct calculations for the time dependent processes in the pseudogap region and extend them to the nonexponential part of the spectrum of $\Omega>0$. For $D=0$ ($m=\infty$) and $D=1$ we arrive correspondingly at the widths $\delta_0\sim g\sqrt{\omega_0}$ and $\delta_1\sim(g^2\omega_0)^{2/3}$ to find that in both cases the condition $\delta_D\gg\omega_0$ is satisfied at low enough ω_0. (This condition is not satisfied at higher dimensions hence at $D\geq 2$ the quantum fluctuations are not reduced to the random static field but rather become resolved phonon assistant processes.[16]) An additional peculiarity of the Peierls model is that, in microscopic units of Δ_0 and ξ_0 the coupling constant $g=1$, then the band edge smearing is given by $\delta_1=(\Delta_0\omega_0^2)^{1/3}$.

IV. DISCUSSION AND CONCLUSIONS

Electronic properties of quasi one - dimensional conductors in the Peierls state are quite peculiar in several respects. In general it is due to a strong interaction of CDW deformations with normal electrons which leads to their fast self trapping. The stationary excited states of the model are solitons (kinks) and polarons with energies $E_s,E_p<\Delta_0$. The processes related to these nonlinear excitations determine the true gaps $2E_s,2E_p$ placed within the pseudogap $2\Delta_0$. The single particle gap, as measured in absorption or tunneling, is opened by polarons which should exist also in $1D$ systems without symmetry breaking, like the majority of conjugated polymers[29,27]. The effect is very common because in $1D$ semiconductors the selftrapping of free electrons takes place for any type of e-ph interactions[32] while in higher dimensions the long range interactions are required. Here the minimal role of the Peierls effect, or at least its partial contribution, is to ensure a presence of the strong e-ph coupling. The optical threshold exists at $2E_p$ in general. But for systems with degenerate ground states like the polyacethylene there is also a lower gap at $2E_s$ because the lowest excitations are now topological solitons (kinks)[16,33,34]. A weak interchain coupling[35] preserves the polaronic effects, while creating a shallow barrier with respect to the selftrapping, thus allowing for metastable free electronic states and corresponding transitions. The $3D$ effects on solitonic transitions are more drastic because of the confinement effect[28,35].

Presented results recover the stretch exponential dependencies near the PG edge (for both PES and optics)

$$I\sim\exp\left[-\left(\frac{\Omega}{\delta_D}\right)^{\nu_D}\right],\ \delta_D\sim\omega_0^{1/\nu_D} \tag{56}$$

with different powers $\nu_D>1$. Near the absolute threshold at $\delta\Omega=\Omega-W_p\ll W_p$ we find the same (for the PES) law

$$I\sim\exp\left[-C\frac{W_p}{\omega_0}-C'\frac{\delta\Omega}{\omega_0}\ln\frac{W_p}{\delta\Omega}\right] \tag{57}$$

which differ only by numerical coefficients among different models. The first constant term in the exponent describes the adiabatic reduction for the probability of creation of the stationary polaron at W_p. The second term gives the law for approaching this threshold. At first sight, this quasi linear dependence of the exponent $\sim\frac{\delta\Omega}{\omega_0}\ln\frac{W_p}{\delta\Omega}$ is weaker than the one $\sim\ln\frac{W_p}{\delta\Omega}$ coming from the pre-exponential factors $\sim(\delta\Omega)^{-n}$ but it is not true: by definition we are working at $\delta\Omega$ which can be small only in compare to W_p but must be large in compare to ω_0. Hence $\frac{\delta\Omega}{\omega_0}\ln\frac{W_p}{\delta\Omega}\gg\ln\frac{W_p}{\delta\Omega}$ and the exponential term determines the profile near the absolute threshold. The same law holds for the two particle process (the internal optical absorption) if the ground state is nondegenerate. But for a system with a spontaneous symmetry breaking like the Peierls model for the polyacethylene the threshold dependence of the exponent changes from $\sim\delta\Omega\ln\delta\Omega$ to a stronger one $\sim\sqrt{\Omega-2W_s}$ with the threshold $2W_s$ being the energy of a solitonic pair.

The momentum dependence of the intensity $I(\Omega,P)$ as recovered by the ARPES shows a rich variety of regimes. Only near the absolute threshold the law (57) is simply generalized by adding the polaron kinetic energy: $W_p\Rightarrow W_p+P^2/2M_p$. But the region near the free electronic threshold $\Omega\approx E_g$ demonstrates several nontrivial regimes. The

differences come from two effects achievable for shallow states. One is the momentum dependence of the form factor - the momentum distribution of the split off state. Another one is the inertial part of the action coming from a drastic dependence of the kinetic mass on the localization parameter which evolves in time along the instanton process. One of unexpected results is that at large P the law (56) changes to a non monotonous function of Ω which would show itself as a quasi spectrum (a line of maxima of $I(\Omega, P)$) within the pseudogap. Another result is an appearance of optimal localized fluctuations at an elevated kinetic energy so that they show up above the PG region at $\Omega > 0$. These observations may be more general than the studied one dimensional adiabatic models.

In conclusion, we have calculated intensities of subgap photo electronic transitions by means of a functional integration over the lattice oscillation modes. By this virtue we have studied the problem of photoemission from the pseudogap region for typical one-dimensional models. We have found general expressions for the transition rate and studied the asymptotic behaviors near absorption edges, both below the free electronic edge and approaching the lower true one. It was shown that the main contributions to the transition rates comes from instanton configurations of the phonon field. The Peierls model was investigated in particular details in relation with its numerous applications. Peculiarities of the ARPES regime are coming from unexpected effects of the instanton motion.

For the intragap optical absorption problem we have calculated the asymptotic behavior of the absorption coefficient near the threshold for creation of pairs of solitons and studied effects of confinement.

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