I. INTRODUCTION

Putting an electron into a crystalline lattice, it will interact with the dynamical deformations of that latter. Depending on the type of material we are dealing with—such as ionic polar crystals, covalent materials or simple metals—the form of the electron-lattice coupling as well as the relevant lattice modes being involved in this coupling will be different. The mutual interaction between the electron and the lattice deformations, which in general is of a highly complex dynamical nature, results in composite entities of electrons surrounded by clouds of virtual phonons which, in a dynamical way, correlate the position of the electron and the associated local lattice deformation. Such entities are referred to as polarons, which can be either spatially quite extended “large polaron”, or rather constraint in space “small polarons”. Large polarons generally are itinerant entities, while small polarons in real materials, have a tendency to self-trap themselves in form of localized states. By far the most spectacular manifestation of such electron-lattice interactions in the weak coupling large polaron limit is the classical phonon mediated superconductivity.

The earliest indications for polarons came from F centers—electrons trapped in negative ion vacancy positions in alkali halides—which led Landau to the concept of localized strong coupling polarons. Subsequently, the field was developed mainly in connection with scenarios where the materials could be characterized by a continuous elastic medium and specifically for:

(i) ionic crystals, where positively and negatively charged ions oscillate out of phase around their equilibrium positions and thus give rise to large electric polarization fields in form of longitudinal optical modes, which then strongly couple back onto the conduction band electrons,

(ii) covalent materials, where local dilations of the material couple the electrons to corresponding deformation potentials and

(iii) simple metals, characterized by high frequency plasma modes which, because of strong charge density fluctuations, renormalize into acoustic modes.

With the arrival of new materials since the late sixties, the necessity to consider the microscopic lattice structure for the polaron formation became more and more crucial and initiated the theoretical work on the transition between large and small polarons and the question of polaron localization.

After reviewing the different kinds of electron-lattice coupling leading to polaron formation we shall discuss the fundamental issues of the cross-over between large and small polarons, the question of continuous versus discontinuous transition and the difference of the polaron self-trapping with respect to localization in systems with attractive interaction potentials. We then present examples of a few decisive experiments on polarons which, early on, shed some light on their dynamical formation and disintegration.

II. THE FRÖHlich LARGE POLARON

A. Polarons in ionic crystals

Let us to begin with consider the case of an ionic crystal where longitudinal optical phonons strongly couple to the electrons. A single electron in such a dielectricum induces via its charge an electric displacement field

\[ D(r, r_{el}) = -\text{grad} \frac{e}{|r - r_{el}|} , \]  

at a spatial coordinate \( r \) with \( r_{el} \) denoting the position of the electron. This displacement field couples to the dynamics of the lattice which can be described in terms of a polarization field \( P(r) \) of the dielectric medium and which (via Poisson’s equation \( \text{div} \, D(r) = 4\pi e \delta(r - r_{el}) \)) can be expressed in terms of a polarization potential \( \Phi(r) \) such as:

\[ P(r) = \frac{1}{4\pi} \text{grad} \Phi(r), \quad \Phi(r_{el}) = -\frac{1}{e} \int d^3r \, D(r, r_{el}) \cdot P(r) . \]
We assume for simplicity the absence of any shear and vorticity in the elastic medium forming the dielectricum.

The standard way to describe the physics of polarons is to introduce measurable material quantities such as the frequency dependent dielectric constant \( \varepsilon(\omega) \), defined by \( \mathbf{D} = \varepsilon(\omega) \mathbf{E} \), in order to account for the dynamics of the dielectric medium via the frequency dependence of the polarization field, related to \( \mathbf{E} \) via \( 4\pi \mathbf{P}(\mathbf{r}) = \mathbf{D}(\mathbf{r}) - \mathbf{E}(\mathbf{r}) \). \( \mathbf{D}(\mathbf{r}) \) being exclusively determined by the point charge is independent on \( \varepsilon(\omega) \). In a crude sense one can consider the response of the dielectric medium as being given by a superposition of two contributions: (i) a high frequency contribution in the ultraviolet regime \( \varepsilon_\infty \), arising from the electron clouds oscillating around the ionic positions and (ii) a low frequency contribution \( \varepsilon_0 \) in the infrared regime, arising from the oscillations of the positive and negative ions against each other. This separates the polarization field \( \mathbf{P}(\mathbf{r}) \) into two contributions \( \mathbf{P}(\mathbf{r}) = \mathbf{P}_0(\mathbf{r}) + \mathbf{P}_\infty(\mathbf{r}) \) which in the low and high frequency limits are determined by:

\[
\mathbf{P}_0(\mathbf{r}) = \frac{1}{4\pi} \left( 1 - \frac{1}{\varepsilon_0} \right) \mathbf{D}(\mathbf{r}),
\]

\[
\mathbf{P}_\infty(\mathbf{r}) = \frac{1}{4\pi} \left( 1 - \frac{1}{\varepsilon_\infty} \right) \mathbf{D}(\mathbf{r}),
\]

considering the fact that the low frequency contribution of the polarization field remains unaffected by high frequency perturbations. The determinant contribution to the polaron dynamics, arising from the low frequency polarization field is hence given by

\[
\mathbf{P}_0(\mathbf{r}) = \frac{1}{4\pi} \left( \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0} \right) \mathbf{D}(\mathbf{r}) = \frac{1}{4\pi\varepsilon_\infty} \mathbf{D}(\mathbf{r}).
\]

Before entering into a detailed discussion of the intricate nature of the dynamics of this problem let us consider certain limiting cases and start with the picture of an electron inside a dielectric continuous medium being constraint to a finite small volume in a sphere of a certain radius \( R_1 \) to be determined.

We consider an electron, moving inside such a sphere of radius \( R_1 \) with a velocity \( \mathbf{v} \), to be fast compared to the characteristic time of the atomic oscillations \( (2\pi/\omega_0) \) (given by the longitudinal optical lattice modes). The polarization field induced in the medium by the motion of the charge carrier can then be considered as static for distances much greater than \( 2\pi v/\omega_0 \) and being described by a static Coulomb potential. Inside this sphere the test charge can be considered as being uniformly distributed and hence the potential as being constant. We thus have:

\[
E_{\text{pot}} = -e^2/\varepsilon R_1 \quad (r < R_1), \quad E_{\text{pot}} = -e^2/\varepsilon r \quad (r \geq R_1).
\]

Determining the size of the polaron in a purely static fashion, considering the electron kinetic energy inside this sphere as being given by \( E_{\text{kin}} \simeq (2\hbar^2)/(2mR_1^2) \), we find by minimizing the total energy with respect to \( R_1 \):

\[
R_1 = (2\pi\hbar)^2 \varepsilon/\omega_0.
\]

Determining the size of the polaron radius in a dynamical fashion we require that the characteristic wavelength \( 2\hbar/mv \) of the electron must be smaller than \( 2\pi v/\omega_0 \). This implies that the typical radius \( R_2 \) of the trapping potential is determined by the distance for which \( \hbar/mv \simeq v/\omega_0 \), or in other words:

\[
R_2 = 2\pi (\hbar/m\omega_0)^{1/2}.
\]

From these simple arguments it follows that the interaction between the displacement field and the polarization field, arising from the dynamics of the lattice, (the polar coupling between the electron and the longitudinal optical phonons) is of the order of \( E_{\text{pot}} = -e^2/\varepsilon R_2 \).

The potential energies for the two limiting cases where the dielectric medium is considered (i) as static and (ii) as dynamic, are given by

\[
-\frac{U_1}{\hbar\omega_0} = \left( \frac{U_2}{\hbar\omega_0} \right)^2 = \frac{1}{2\pi^2} \alpha_{Fr}^2,
\]

where \( \alpha_{Fr} \) is a dimensionless coupling constant introduced by Fröhlich

\[
\alpha_{Fr} = \frac{e^2}{\varepsilon \sqrt{2}} \sqrt{\frac{m}{\hbar^3\omega_0}}.
\]
The value for $\alpha_F$ can vary over one decade in the interval $\sim [0.1, 5]$ depending on the material. Large values of $\alpha$ favor the static picture, while smaller ones favor the dynamical one. For most standard materials (polar and ionic crystals) the typical phonon frequency is of the order of $10^{-14}$ seconds and the electrons can be assumed to be essentially free electrons. This results in a value for $R_2$ which is much bigger than the lattice constant and hence justifies the continuum approach described above permitting to treat the dielectric constant as wave vector independent. Within such an approach Fröhlich first formulated this polaron problem in a field theoretical form and proposed a corresponding Hamiltonian for it, designed to describe the so called large polarons.

Let us now briefly sketch the derivation of the corresponding Hamiltonian\footnote{3}. To within a first approximation the dynamics of the polarization field can be described by harmonic oscillators driven by the electric displacement fields. Dealing with the polaron problem on the basis of the continuum model of a dielectricum one is restricted to consider waves of the polarization field with wave length much bigger than the inter-atomic distance and moreover to limit oneself in this problem to frequencies well below the optical excitations which would result from the deformations of the ions rather than from their motion. Under those conditions one can limit the discussion of the dynamics of the polarization field to the infrared longitudinal component of it, being driven by a source term due to its coupling with the electric displacement field. Using a simple Ansatz in form of a harmonic motion of the polarization field one has

$$
\left( \frac{d^2}{dt^2} + \omega_0^2 \right) P_0(\mathbf{r}) = \frac{1}{\gamma} D(\mathbf{r}, \mathbf{r}_\text{el}).
$$

The coefficient $\frac{1}{\gamma} = \equiv \frac{\omega_0^2}{2\mathbf{D}(\mathbf{r}, \mathbf{r}_\text{el})}$ of $D(\mathbf{r}, \mathbf{r}_\text{el})$ on the rhs of this equation is determined from its static limit, following eqs.\footnote{4}. To this equation of motion for the polarization field one has to add the term which describes the motion of the electron and which is controlled by the interaction energy $e\Phi(\mathbf{r})$, given in eq.\footnote{2}, i.e.,

$$
m \frac{d^2}{dt^2} \mathbf{r}_\text{el} = -e \text{grad} \Phi(\mathbf{r}_\text{el}).
$$

Considering $\gamma P_0(\mathbf{r})$, $m \mathbf{r}_\text{el}$ and $\gamma \dot{P}_0(\mathbf{r})$, $\mathbf{p}_\text{el} = m \mathbf{r}_\text{el}$ as a set of generalized coordinates and conjugate momenta $(Q, \partial L/\partial \dot{Q})$ the corresponding Hamiltonian is given by

$$
H = \frac{1}{2} \int d^3r \left[ \dot{\mathbf{P}}_0^2(\mathbf{r})/\omega_0^2 + \omega_0^2 \mathbf{P}_0^2(\mathbf{r}) \right] - \int d^3r D(\mathbf{r}, \mathbf{r}_\text{el}) \mathbf{P}_0(\mathbf{r}) + \frac{1}{2} m \dot{\mathbf{r}}_\text{el}^2.
$$

In order to obtain a quantum field theoretical formulation of this problem one introduces habitually the vector field representation for the polarization fields

$$
\mathbf{B}(\mathbf{r}) = \sqrt{\frac{\omega_0}{2\hbar}} \left( \mathbf{P}_0(\mathbf{r}) \pm \frac{i}{\omega_0} \dot{\mathbf{P}}_0(\mathbf{r}) \right) = \frac{1}{N} \sum_{q, \lambda} \frac{q}{q} \left( e^{-iqr} a_{q, \lambda}^+ + e^{iqr} a_{q, \lambda} \right),
$$

with the phonon annihilation (creation) operators $a_{q, \lambda}^{(+)}$ with $[a_{q, \lambda}, a_{q', \lambda'}^+] = \delta_{q, q'} \delta_{\lambda, \lambda'}$.

For ionic polar crystals the dominant contribution of the polarization field comes from longitudinal optical phonons. We shall in the following restrict ourselves to those modes only. Introducing the quantized form of the electron momentum $\mathbf{p}_\text{el} \equiv \frac{\hbar}{i} \partial/\partial \mathbf{r}_\text{el}$ with $[\mathbf{p}_\text{el}, \mathbf{r}_\text{el}] = -i\hbar$, we rewrite the Hamiltonian, eq.\footnote{13} in terms of the phonon creation and annihilation operators and the electron coordinates and conjugate momenta as

$$
H = \frac{p_\text{el}^2}{2m} + \hbar \omega_0 \sum_{q, \lambda} \left( a_{q, \lambda}^+ a_{q, \lambda} + \frac{1}{2} \right) + \sum_{q, \lambda} V_{q, \lambda}^{\text{opt}} (a_{q, \lambda}^+ e^{-iqr} \mathbf{r}_\text{el} - a_{q, \lambda} e^{iqr} \mathbf{r}_\text{el}),
$$

where the effective electron lattice coupling constant is

$$
V_{q, \lambda}^{\text{opt}} = i\sqrt{4\pi\alpha(\hbar/2\omega_0 m)^2} \hbar \omega_0 / (1/q).
$$

Upon introducing dimensionless electron coordinates as well as phonon wave vectors $\tilde{\mathbf{r}}_\text{el} = (2m\omega_0/\hbar)^{\frac{1}{2}} \mathbf{r}_\text{el}$ and $\tilde{q} = (2m\omega_0/\hbar)^{\frac{1}{2}} q$, $H/\hbar \omega_0$ turns out to be exclusively controlled by the unique parameter $\alpha_F$.

Replacing in the expression for the Hamiltonian, eq.\footnote{15}, the Fourier transform $e^{iqr}$ of the electron density $\rho(\mathbf{r}) = \sum_{\mathbf{r}_\text{el}} \delta(\mathbf{r} - \mathbf{r}_\text{el})$ by its second quantization form $\sum_{k \sigma} c_{k, \sigma}^\dagger c_{k, \sigma}$ we finally obtain what is generally called the Fröhlich Hamiltonian

$$
H = \sum_{k \sigma} \varepsilon_k c_{k, \sigma}^\dagger c_{k, \sigma} + \sum_{q, \lambda} \hbar \omega_0 (a_{q, \lambda}^+ a_{q, \lambda} + 1/2) + \sum_{q, \lambda} V_{q, \lambda}^{\text{opt}} (c_{k+q, \sigma}^\dagger c_{k, \sigma} a_{q, \lambda} - a_{q, \lambda}^+ c_{k, \sigma}),
$$

$\varepsilon_k = D - t \gamma_k$, $\gamma_k = \frac{1}{2} \sum_{\delta} \exp(i\mathbf{k} \cdot \delta)$ denotes the bare electron dispersion (with $\delta$ being the lattice vectors linking nearest neighboring sites) and $D = zt$ is the band half-width and $z$ the coordination number.
B. Polarons in non-polar covalent materials

A structurally very similar Hamiltonian is obtained for covalent materials when the density of charge carriers is very low and screening effects can be neglected. The electron lattice interaction then can be derived within the so-called deformation potential method where it is assumed that the electron dispersion of the rigid lattice \( \varepsilon_k^0 \) gets modified due to some elastic strain which, in the simplest case, amounts to a dilation. This then results in a shift of the electron dispersion \( \varepsilon_k = \varepsilon_k^0 + C \Delta \) with

\[
\Delta(x) = \frac{\partial u''}{\partial x'} = i \frac{1}{\sqrt{N}} \sum_q \frac{q}{\sqrt{2M\omega_q}} (a_q e^{iq\cdot x} - a^+_q e^{-iq\cdot x}).
\]

(18)

The dilation, being exclusively related to longitudinal acoustic phonons \((a_q, a^+_q)\) with a phonon frequency \(\omega_q\) and \(M\) denoting the ion mass, the constant \(C\) can be estimated from pressure measurements and is typically of the order of 10 eV. The effective electron-lattice interaction in that case is then similar to that derived above for ionic crystals and is described by the Hamiltonian eq. (17) upon replacing \(V^\text{opt} \) by

\[
V_{q}^{ac} = iC \frac{q}{\sqrt{\frac{1}{2}M\omega_q}}.
\]

(19)

C. Polarons in metals

A yet very different approach is required to treat the electron-lattice coupling in metals. The electrons at the spatial coordinate \(x\) experience a pseudopotential \(V(x - R_i)\) exerted on them by the positively charged ions situated at lattice sites \(R_i\). The major effect giving rise to the coupling of the electrons to the lattice now comes from the spatial coordinate \(x\) and is described by the Hamiltonian eq. (17) in the form

\[
H = \int dx \psi^+(x) \left[ -\frac{\nabla^2}{2m} + \sum_i V(x - R_i) \right] \psi(x) + \sum_i \frac{p_i^2}{2M} + \frac{1}{2} \sum_{i,j} \hat{V}(R_i - R_j)
\]

\[
+ \frac{1}{2} \int dx dx' \psi^+(x) \psi^+(x') \frac{e^2}{|x - x'|} \psi(x') \psi(x),
\]

(20)

where \(p_i^2/2M\) denotes the kinetic energy of the ions at site \(i\). Using the standard expansion of the lattice displacements \(u_i\) in terms of the phonon operators

\[
u_i = \frac{1}{\sqrt{N}} \sum_q \epsilon_{q\lambda} e^{i\mathbf{q}\cdot R_i} \left( \frac{\hbar}{2M\Omega_{q\lambda}} \right)^{3/2} (a_{q\lambda} + a_{-q\lambda}^+) \).
\]

(21)

\((\epsilon_{q\lambda} \) denotes the polarization vectors and \(\Omega_{q\lambda}\) the eigen-frequencies of the various phonon branches) one can write the above Hamiltonian in the form

\[
H = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^+ c_{k\sigma} + \sum_{q\lambda} \hbar \Omega_{q\lambda} (a_{q\lambda}^+ a_{q\lambda} + \frac{1}{2}) + \sum_{q} \frac{4\pi e^2}{q^2} \rho_q \rho_{-q} + \sum_{q\lambda} V_{q\lambda}^{\text{met}} \rho_q (a_{q\lambda} + a_{-q\lambda}^+),
\]

(22)

where \(\rho_q = \frac{i}{N} \sum_{k\sigma} c_{k+q\sigma}^+ c_{k\sigma}\) is the charge density fluctuation operator for the electrons and \(V_{q\lambda}^{\text{met}} = -i(N/2M\hbar \Omega_{q\lambda}) \hat{q} (\epsilon_{q\lambda} V(q))\). The relevant phonon modes arising from the ion-ion interaction are the practically dispersion-less ionic plasma modes with frequencies \(\Omega_{q\lambda}\). However, these modes being coupled to the electron charge fluctuations, this results in a strong renormalization leading to: (i) a longitudinal acoustic branch with a
correspondingly phonon frequency $\omega_{q}^{ac} = \frac{q}{\sqrt{m/3Mv_{F}}}$ ($v_{F}$ denoting the Fermi velocity) and (ii) to a corresponding dressed electron-phonon coupling given by

$$\tilde{\epsilon}_{q\lambda} = -i \frac{\sqrt{N}}{2M \omega_{q\lambda}} (q \cdot e_{q\lambda}) \frac{\Lambda(q) V(q)}{\varepsilon(q) Z_{c}}. \quad (23)$$

$\varepsilon(q)$ denotes a wave vector dependent dielectric constant, $\Lambda(q)$ the Coulomb screened renormalization of the bare ion potential and $Z_{c}$ the spectral weight renormalization constant of the electron quasi-particle spectrum.

In spite of the diversity of the physical systems considered above, the various Hamiltonians describing them are of rather general form. The main message which they contain is that, because of the electron-lattice interaction $V_{q}$, the electrons will be accompanied by a lattice deformation. In the weak coupling limit, this is restricted to simply a single phonon accompanying the electron. Within a lowest order perturbative approach this leads to states of the form

$$c_{k\sigma}^{+} |0\rangle + \sum_{q} V_{q} c_{k-q\sigma}^{+} q_{a}^{+} |0\rangle = \frac{1}{(\hbar \omega_{q} + \varepsilon_{k} - \varepsilon_{q})}, \quad (24)$$

where $|0\rangle$ denotes the vacuum state for the electrons as well as of the phonons. This expression clearly indicates that electrons carry with them an electrical polarization field or, in other terms, the electrons are accompanied by a phonon. This feature reflects the fact that the total wave-vector

$$K = \sum_{k\sigma} k_{k\sigma} c_{k\sigma}^{+} + \sum_{q\lambda} q_{q\lambda} a_{q\lambda}^{+}, \quad (25)$$

is a conserved quantity. The most spectacular consequence of this lies in the formation of Cooper pairs\textsuperscript{7}, as evidenced by the isotope effect of their binding energy\textsuperscript{7} and the ultimately resulting phonon mediated BCS theory of superconductivity\textsuperscript{7}. Electron pairing then can be understood by a process in which the passage of a first electron polarizes the lattice and where subsequently a second electron reabsorbs that polarization. The effective interaction Hamiltonian for this pairing is given by second order perturbation theory:

$$H_{cl-cl} = \sum_{kkq} |V_{q}|^{2} c_{k\sigma}^{+} c_{k+q\sigma}^{+} c_{k-q\lambda} c_{k+q\lambda}^{+} \frac{\hbar \omega_{q}}{(\varepsilon_{k} - \varepsilon_{k-q})^{2} - (\hbar \omega_{q})^{2}}. \quad (26)$$

This effective electron-electron interaction shows that within a small region around the Fermi surface i.e., $|\varepsilon_{k} - \varepsilon_{k+q}| \leq \omega_{q}$ this interaction is attractive and therefore leads to an instability of the Fermi surface resulting in a superconducting ground state via Cooper pair formation in k-space.

This present discussion of the continuum approach to the coupling between the electrons and the lattice-deformations has shown interaction Hamiltonians which, depending on the underlying materials, show either a coupling between the phonon coordinates $(a_{q} + a_{-q}^{+})/\sqrt{2}$ and the electron charge density $p_{q} = \frac{1}{N} \sum_{k} c_{k+q/2}^{+} c_{k-\pi/2}$ (metals) or between the conjugate phonon momenta $(a_{q} - a_{-q}^{+})/i\sqrt{2}$ and the charge current density $p_{q} = \frac{1}{N} \sum_{k} q_{q} c_{k+q/2}^{+} c_{k+\pi/2}$ (polar and covalent materials). Formally these interaction terms can be written in a unifying way by rotating the phonon coordinate into the phonon momenta and vice versa by a suitable unitary transformation $U = \exp(-i\frac{\pi}{2} a_{q}^{+} a_{-q})$.

### III. THE HOLSTEIN SMALL POLARON

The systems discussed in the previous section are characterized by long range electron-lattice coupling which show up in form of (i) a moderate mass renormalization of charge carriers in their band states, (ii) an equally moderate reduction in their mobility due to the scattering of the electrons on the lattice vibrations and (iii) the emergence of phonon sidebands in optical absorption spectra.

The fundamental theoretical question which posed itself in the context of polaron physics ever since Landau\textsuperscript{8} proposed self-trapped localized polarons was to establish whether in such systems one would have a local lattice instability upon increasing the coupling constant $q_{F}$, passing from large mobile Fröhlich polarons for weak coupling to localized polarons when the coupling strength exceeds a certain critical value. This question could not be addressed within the continuum approach since it requires a physics which is related to the dynamics of the local lattice deformations on the scale of the unit cell. On the experimental side, more and more new materials where synthesized in the mean time which clearly showed polaronic effects on such short length scales. It was for these reasons that a scenario was introduced which could describe such lattice polarons.
The generic model to capture such a situation, generally referred to as the Holstein molecular crystal model\(^7\) treats the problem consequently in real space. Its corresponding Hamiltonian is given by

\[
H = D \sum_{i\sigma} n_{i\sigma} - t \sum_{i\neq j} (c_{i\sigma}^+ c_{j\sigma} + h.c.) - \lambda \sum_i n_i u_i
+ \sum_i \frac{M}{2} \left( \dot{u}_i^2 + \omega_0^2 u_i^2 \right) + \sum_i U n_{i\uparrow} n_{i\downarrow},
\]

(27)

where \(n_{i\sigma} = c_{i\sigma}^+ c_{i\sigma}\) \((n_i = \sum_{\sigma} n_{i\sigma})\) denotes the density of charge carriers having spin \(\sigma\) at molecular sites \(i\). The electrons are assumed to be coupled to the intra-molecular deformations \(u_i\) via charge density fluctuations and the coupling constant is denoted by \(\lambda\). The dynamics of the lattice is treated purely locally with Einstein oscillators describing the intra-molecular oscillations with frequency \(\omega_0\). \(M\) denotes the mass of the atoms making up the diatomic molecular units. The additional Hubbard \(U\) intra-molecular repulsion is introduced sometimes in order to account for possible correlation effects in conjunction with the purely polaronic features. We shall not consider the effect of this term in this present discussion, but several specific lectures in this school will be devoted to it.

This model is capable of describing the self-trapping of charge carriers which arises from a competition between the energy gain coming from the itinerancy of the electrons and that coming from the potential energy due to the induced localization of the charge carriers.

\[
\text{In the limit of small coupling } \varepsilon_p \ll D, \text{ the form of the Hamiltonian, given in eq. (28) is reminiscent of one which describes itinerant electrons in a static potential, given by } V^\text{sc}(\{u_i\}) = -\lambda (u_i) c_{i\sigma}^+ c_{i\sigma} d_i^+ d_i \text{ with } \langle u_i \rangle = \lambda/M \omega_0^2 \text{ and } d_i^+ d_i \text{ representing the density of some fictitious particles. Solving the eigenvalue problem for the ground state energy } E_0, \text{i.e.,}
\]

\[
\frac{\lambda^2}{M \omega_0^2} \sum_k \frac{1}{\varepsilon_k - E_0} = 1
\]

(29)

predicts a splitting off of the ground state energy from the bottom of the free itinerant band \((E_0 < 0)\), resulting in a localization of the charge carriers.

In the limit of strong coupling, for large values for \(\lambda\) such that \(\varepsilon_p \geq D\), the adiabatic approach tells us to ignore the electron itinerancy and assume the electron to be fixed at a particular lattice site. This then results in an adiabatic potential for the electron given by \(V^\text{ad}(\{u_i\}) = -\varepsilon_p n_i + \frac{M}{2} \omega_0^2 
\left( u_i - \frac{\lambda n_i}{M \omega_0^2} \right)^2 \), which follows directly from the form of the Hamiltonian given in eq. (28). If one requires that this potential is deep enough to bind the electron in the first place, the self-consistency of the adiabatic approach is guaranteed and leads to localized states in this strong coupling limit where the time derivatives of the local deformations can be neglected. As \(\lambda\) is varied, these potentials for the weak and strong coupling limits are expected to join up smoothly. Depending on the strength of the coupling \(\lambda\),
this small exercise shows that one can have a situation where the energies of the two configurations are degenerate. In this intermediary coupling regime one should expect a coexistence of small localized polarons and weakly bound electrons. It has become customary in the theory of small polarons to introduce two dimensionless parameters: 

\[ \alpha \equiv \sqrt{\frac{\varepsilon_p}{\hbar \omega_0}} \]  

measuring the strength of the interaction and \( \gamma = t / \hbar \omega_0 \) the adiabaticity ratio (\( \alpha \) has nothing to do with the dimensionless coupling constant \( \alpha_F \), used in the theory of large polarons and introduced in section [1]). We then can rewrite the potential \( V^{\infty}(u_i) \) in a compact form in terms of those parameters and a dimensionless local lattice deformation \( u_i = u_i \sqrt{\omega_0/2\hbar} \). Its variation with \( \alpha \) and \( \gamma \) as a function of \( u \) illustrated in fig. [1].

This picture of the polaron physics, widely used and appreciated until the nineteen sixties (see ref. [7]), although intuitively very appealing is qualitatively incorrect - as we shall see in the next section. There we shall show that a polaron, although self-trapped, remains delocalized for any dimension.

A formal and correct treatment of this problem was first initiated by Holstein and collaborators [7] and in a very elegant and efficient way in terms of a unitary transformation by Firssov and collaborators [7], given by

\[ \hat{H} = e^S \hat{H} e^{-S}, \quad S = \alpha \sum_{i,\sigma} n_i \sigma (a_i - a_i^+) \]  

which transform the electron operators \( c_{i\sigma}^{(+)} \) into operators which describe charge carriers rigidly tied to local lattice deformations

\[ \tilde{c}_{i\sigma}^+ = c_{i\sigma}^+ X_i^+ + c_{i\sigma}^- X_i^-, \quad X_i^\pm = e^{\mp \alpha(a_i - a_i^+)} \]  

and which correspond to localized polaronic self-trapped states

\[ X_i^+ |0\rangle_i = \sum_n \frac{e^{\mp 2\alpha n}}{\sqrt{n!}} |n\rangle_i. \]  

\( |n\rangle_i \) denotes the \( n \)-th excited oscillator states at a molecular site \( i \) and \( X_i^+ |0\rangle_i \) signifies an oscillator ground state whose equilibrium position is shifted by an amount \( \lambda / M \omega_0^2 \). The corresponding transformed Hamiltonian is consequently given by

\[ \hat{H} = \sum_i (D - \varepsilon_p) c_{i\sigma}^+ c_{i\sigma} - t \sum_{i \neq j \sigma} (c_{i\sigma}^+ c_{j\sigma}^+ X_j^- + H.c.) + \sum_i (U - 2\varepsilon_p) c_{i\uparrow}^+ c_{i\downarrow} c_{i\downarrow} c_{i\uparrow} + \hbar \omega_0 \sum_i (a_i^+ a_i + \frac{1}{2}). \]  

Such an approach to the polaron problem is particularly useful in the limit of large \( \alpha \) where \( \varepsilon_p \geq D \) and for a small adiabaticity ratio \( \gamma \). In the strong coupling limit and anti-adiabaticity (\( \gamma < 1 \)), the term \( X_i^+ X_j^- \) in the transformed Hamiltonian can be averaged over the bare phonon states which, for zero temperature, results in an effective polaron hopping integral \( t^* = t e^{-\alpha^2} \). This is justified a posteriori since then \( t^* \ll \omega_0 \), where the local lattice deformations can be considered to adapt themselves quasi instantaneously to the slowly in time varying positions of the electrons. Such an approximation implies that the number of phonons in the phonon clouds surrounding each charge carrier remains largely unchanged during the transfer of a charge carrier from one site to the next, while processes where the number of phonons in the clouds change give rise to a polaron damping. Neglecting such damping effects, one obtains well defined Bloch states for the polaronic charge carriers (defined by \( c_{i\sigma}^+ X_i^+ \)), albeit with a much reduced hopping
integral $t^*$, while at the same time the electrons lose practically all of their coherence and thus their quasi-particle features. In order to illustrate that, let us consider the Green’s function for a single localized polaron, respectively for a single localized electron by putting $t^* = 0$. For the polaron retarded Green’s function we have

\[
G_p^\text{ret}(t) = -\theta(t)(0|X_i^-[e^{iHt}\gamma^+(0)e^{-iHt}\gamma(0)]X_i^+[0]) = -\theta(t)\sum_n e^{i(\varepsilon_n - n\hbar\omega_0)t}|(0|X_i^-(\varepsilon_n(0)|n))|^2 \delta_{n,0} = -\theta(t)e^{i\varepsilon_p t}|(0|\gamma^+(0)|0)|^2
\]

(34)

which after Fourier transforming becomes

\[
G_p^\text{ret}(\omega) = \lim_{\delta \to 0} \frac{1}{\omega + i\delta + \varepsilon_p}
\]

(35)

and displays a spectrum which consists of exclusively a coherent contribution. On the contrary, the electron retarded Green’s function

\[
G_{\text{el}}^\text{ret}(t) = -\theta(t)(0|X_i^-[e^{iHt}\gamma^+(0)e^{-iHt}\gamma(0)]X_i^+[0]) = \sum_{n=0}^{\infty} e^{i(\varepsilon_n - n\hbar\omega_0)t}|(0|X_i^-(\varepsilon_n(0)|n))|^2
\]

(36)

displays a spectrum given by its Fourier transform

\[
G_{\text{el}}^\text{ret}(\omega) \simeq \lim_{\delta \to 0} \sum_{n=0}^{\infty} \frac{e^{-\alpha^2} \alpha^{2n}}{n!} \frac{1}{\omega + i\delta + \varepsilon_p - n\hbar\omega_0}.
\]

(37)

The spectral weight of the coherent part is now reduced to $\exp(-\alpha^2)$, corresponding to the term $n = 0$ in eq. (36), while the major part of the spectrum is made up by the incoherent contributions which track the structure of the composite nature of the polaron.

Generalizing these results by including the itinerancy of the charge carriers leads to very similar results\(^7\) for the electron Green’s function for a many polaron system, which in this strong coupling anti-adiabatic limit reduces to a system of small polarons in band states and where the Green’s function for the electrons with wavevectors $\mathbf{k}$ is given by

\[
G_{\text{el}}^\text{ret}(\mathbf{k}, \omega) = \lim_{\delta \to 0} \frac{e^{-\alpha^2}}{\omega + i\delta + \varepsilon_p - \varepsilon_\mathbf{k}} + \lim_{\delta \to 0} e^{-\alpha^2} \sum_{n=1}^{\infty} \frac{\alpha^{2n}}{n!} \sum_{\mathbf{k}'} \left[ \frac{f(\varepsilon_\mathbf{k}^*)}{\omega + i\delta - \varepsilon_\mathbf{k}^* + n\hbar\omega_0} + \frac{1 - f(\varepsilon_\mathbf{k}^*)}{\omega + i\delta - \varepsilon_\mathbf{k}^*, - n\hbar\omega_0} \right]
\]

(38)

and where $\varepsilon_\mathbf{k}^* = e^{-\alpha^2}\varepsilon_\mathbf{k}$. These characteristic spectral properties of small polarons can be tested by photo-emission spectroscopy and present crucial tests which permit to distinguishing between different mechanisms leading to heavily dressed composite quasi-particles. The Poisson type phonon distribution was particularly well demonstrated early on in such experiments on simple molecules such as $\text{H}_2$ molecules\(^7\) and carbon rings\(^7\), on localized polaron states in the manganites by neutron spectroscopy\(^7\) and in the cuprate superconductors by infrared absorption measurements\(^7\).

The localized, or almost localized, nature of such small polarons is apparent in their electron occupation number distribution illustrated in fig. 2 showing an almost flat distribution covering the whole Brillouin zone, i.e.,

\[
n_{\mathbf{k}\sigma} = \langle \gamma^+_{\mathbf{k}\sigma}\gamma_{\mathbf{k}\sigma} \rangle = (1 - e^{-\alpha^2})n_\sigma + e^{-\alpha^2}n_\sigma(\varepsilon_\mathbf{k}^*)
\]

(39)

There is a qualitative difference between the weak coupling and the strong coupling limit discussed here. We have seen that in the weak coupling limit of the Fröhlich Hamiltonian the electrons are accompanied by phonons with which they continuously exchange the momentum such as to keep the total momentum of electron plus phonon constant. In the strong coupling limit the electrons are surrounded by real lattice deformations which in terms of phonons means clouds of phonons and which in the limit of extreme strong coupling, where the electrons can be considered as localized on a given site, have a Poisson distribution. The new feature now is that this deformation corresponds to a local mass inhomogeneity capable of carrying true momentum rather than the pseudo-momentum as is the case for weak coupling. Again, as we shall see below, the momentum between the electron and this deformation is perpetually
FIG. 2: Occupation number $n_{k\sigma}$ for a system of itinerant small polarons for $\alpha \gg 1$. The dashed and dotted curves indicate the case $n = 1$ for $\alpha \approx 1$ and $\alpha \ll 1$ respectively (after ref. 7).

exchanged as the polaronic charge carrier moves through the lattice, leading to a space-time dependent interaction between the charge carrier and the deformation associated to it. This effect will be particularly important in the cross-over between the weak coupling adiabatic and the strong coupling anti-adiabatic regime, discussed in the next section.

A key point which occupied the field of polaron theory for several decades was to try to establish if a large delocalized polaron changes discontinuously or continuously—although abruptly—into a small self-trapped polaron as the electron-lattice coupling is increased beyond a certain critical value. We shall review this issue in the following.

IV. SELF-TRAPPING

We shall in this section discuss the meaning of self-trapping. For that purpose let us go back for a moment to the semi-classical approach of the polaron problem (discussed in section III above) and the adiabatic lattice potential which goes with it. On the basis of such an approach, amounting to treat the polaron problem as a potential problem, it is tempting to conclude localization of charge carriers as their coupling to the lattice degrees of freedom increases. As we shall see below, the polaron problem cannot be treated as a potential problem. Its intrinsic dynamics of the local lattice deformations is determinant in correlating the dynamics of the charge and the lattice degrees of freedom, thus resulting in itinerant delocalized states of electrons surrounded by clouds of phonons whose density varies and increases as we go from the adiabatic weak coupling to the anti-adiabatic strong coupling limit. For that reason the lattice degrees of freedom must be treated in a quantized version.

Let us start with the weak coupling limit for which we can assume a polaron state in the form

$$\psi_{k} = \frac{1}{\sqrt{N}} \sum_{ij} e^{i\mathbf{k} \cdot \mathbf{r}_i} \left[ c_{i0}^+ \delta_{ij} + f_{kj}^k c_{j0}^+ \right] |0\rangle,$$

which is the real space version of the state previously discussed, i.e., eq. (24). Diagonalizing the Hamiltonian within such a subspace of zero and respectively one phonon present, leads to the following selfconsistent equations for the eigenvalues and parameters $f_{ij}^k$:

$$E_k = \varepsilon_k - (\alpha \hbar \omega_0)^2 \frac{1}{N} \sum_{k'} \frac{1}{\varepsilon_k - \varepsilon_{k'} - E_k + \hbar \omega_0},$$

$$f_{ij}^k = \alpha \hbar \omega_0 \frac{1}{N} \sum_{k'} e^{i\mathbf{k'} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \varepsilon_{k} - \varepsilon_{k'} - E_k + \hbar \omega_0.$$

Considering the solution for the ground state ($k = 0$) of this problem, one notices that its corresponding eigenvalue $E_0$ falls below the bottom of the free electron band ($E_0 \leq 0$). This signals a bound state which is characterized by an exponential drop-off of the spatial correlation between the electron and the accompanying phonon, which for a 3D system is given by:

$$f_{ij}^0 = \frac{\alpha \hbar \omega_0 m}{2\pi \hbar} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} e^{-\sqrt{2m(\varepsilon_k + \hbar \omega_0)} |\mathbf{r}_i - \mathbf{r}_j|},$$

($v$ denoting the unit cell volume) and which indicates that the dynamically (not thermally!) excited phonons accompanying the electron remain in its immediate vicinity. The exponential drop-off does not depend on any dimensionality (in contrast to the semi-classical approach outlined in section III) and gives us a first indication for the intricate
correlation between the inherent dynamics of lattice fluctuations and the charge dynamics. Hence, already in this weak coupling limit, the polaron problem can not be reduced to an effective (adiabatic) potential problem.

Let us next turn to the strong coupling limit, where on the basis of such an adiabatic approach one would expect self-trapped lowest energy eigenstates of the form

$$|\Psi_k\rangle = \frac{1}{\sqrt{N}} \sum_{i} e^{ikr_i} c_k^+|\Phi_k(\{u_j\})\rangle ,$$  \hspace{1cm} (44)

where $\Phi_k(\{u_j\})$ denotes a function of the ensemble of oscillator coordinates $u_j$ situated at sites $j$ in the vicinity of site $i$ where the electron is located. Guided by the semi-classical picture of the adiabatic potential, resulting in the strong coupling limit, one can try an intuitively appealing Ansatz for the lattice wavefunction in form of a series of displaced oscillators around the site where the electron is situated and which, for the ground state, can be assumed to be of the form

$$|\Phi_{k=0}(\{u_j\})\rangle = e^{-\alpha \sum_j (f_j \sigma_j^+ f_j \sigma_j)} |0\rangle .$$  \hspace{1cm} (45)

Determining the parameters $f_j$ variationally\(^7\) leads to solutions which change discontinuously in the intermediary coupling regime. Associated with that is a discontinuous change of the mass of the corresponding quasi-particles amounting to a change-over from a practically free band dispersion with a electron mass $m_{el}$ to an effective polaron mass $m_p$ given by $m_p/m_{el} = e^{\alpha^2}$ (see fig. 4).

It has been a matter of dispute for many decades and up to the 1960-ties whether this discontinuity is a real effect or is an artifact of the theory. From the experimental side, small polarons where found to be localized and have ever since, for the presently available materials, shown a mobility via hopping rather than Bloch like band motion and metallic conductivity. The theoretical results obtained for the cross-over regime between large and small polarons on the basis of the semi-classical description in terms of an adiabatic lattice potential with two minima of comparable energy (see the discussion in section III), suggest already that in this regime one should have particularly strong fluctuations of the local lattice displacements which could possibly be modeled by some effective lattice wave function in terms of a superposition of two sorts of oscillator states: one practically undisplaced and one displaced oscillator state on the site $i$ situated at sites $j$ in the vicinity of site $i$.

All these approaches converge to a lattice wave function for the ground state which can be approximated by

$$|\Phi_p(\{u_j\})\rangle = [e^{-\alpha \sum_j (f_j \sigma_j^+ f_j \sigma_j)} + \eta e^{-\alpha \sum_j (g_j \sigma_j^+ g_j \sigma_j)}] |0\rangle .$$  \hspace{1cm} (46)

This results (after variationally determining the parameters $f, g$ and $\eta$) in a smooth, but nevertheless very abrupt, cross-over between the weak and strong coupling features and a change-over from a quasi-free electron band mass to a strongly enhanced one (see fig. 5). The form of eq. (46) represents for any electron situated on a given site to be associated with an oscillator wave function on this site, illustrated in fig. 4. It indicates an essentially undisplaced oscillator for weak coupling, a displaced one for strong coupling and a superposition of such two oscillator states for the cross-over regime between those two limits. This latter has led to the suggestion of strong retardation effects between the dynamics of the electron and that of the local lattice deformation which could possibly result in a dynamically disordered system and subsequent localization, a scenario which we shall return to in the lecture “From Cooper-pairs to resonating Bipolarons”.

Let us here consider this point in more detail and investigate this cross-over behavior in terms of the strong dynamical correlation which act between the charge and the lattice degrees of freedom. We shall demonstrate that on hand of a polaron toy problem, such as a two-site system involving two adjacent diatomic molecules whose individual oscillations are uncorrelated with each other and an electron with spin $\sigma$ hopping between those two molecular units. The Hamiltonian, eq. (27), for that then reduces to

$$H = t(n_{1\sigma} + n_{2\sigma}) - t(c_{1\sigma}^+ c_{2\sigma} + c_{2\sigma}^+ c_{1\sigma}) - \lambda (n_{1u_1} + n_{2u_2})$$
$$+ \frac{M}{2} [ (\tilde{u}_1^2 + \tilde{u}_2^2) + \omega_0^2 (u_1^2 + u_2^2) ] .$$  \hspace{1cm} (47)

Upon introducing the variables

$$X = \frac{u_1 - u_2}{\sqrt{2}}, \quad Y = \frac{u_1 + u_2}{\sqrt{2}}$$  \hspace{1cm} (48)
FIG. 3: The effective mass versus the electron-lattice coupling $u (= \alpha^2(\gamma^2z)^{-1}$ in our notation), after ref. 7, for oscillator trial wave functions $\Psi^I$ and $\Psi^{II}$ such as given by eqs. (45), (46).

FIG. 4: The variation of the oscillator wave function on a given site (after ref. 7) as a function of $\{u, W_0\} (= \{\alpha^2(\gamma^2z)^{-1}, \alpha^2\}$ in our notation) for oscillator trial wave functions $\Psi^{II}$ such as given by eq. (46) and with $x = \frac{1}{\sqrt{2}}(a_i^+ + a_i)$.

This Hamiltonian separates into two contributions $H_X$ and $H_Y$ depending respectively on lattice coordinates $X$ and $Y$. $Y$ couples exclusively to the total number of charge carriers in the system, i.e. $(n_{1\sigma} + n_{2\sigma})$. It presents an in-phase oscillation of the two molecules and couples to the relative charge distribution $(n_{1\sigma} - n_{2\sigma})$. The Hamiltonian for this subspace which describes the intertwined dynamics of the charge and the lattice deformations is

$$H_X = t(n_{1\sigma} + n_{2\sigma}) - t(c_{1\sigma}^+c_{2\sigma} + c_{2\sigma}^+c_{1\sigma}) - \frac{\lambda}{\sqrt{2}}(n_{1\sigma} - n_{2\sigma})X + \frac{M}{2} \left[\dot{X}^2 + \omega_0^2X^2\right].$$

(49)

The term proportional to $\lambda$ in this Hamiltonian clearly indicates how the charge fluctuations between the two molecules induces a coupling between the oscillators of those two molecules and which ultimately couples back to the dynamics of the charge transfer. This generates, as we shall see, a new dynamical lattice deformation mode which accompanies the transfer of charge from one to the other molecule. The Hamiltonian for this subspace which describes the intertwined dynamics of the change and the lattice deformations is

$$|GS\rangle_\sigma = \frac{1}{\sqrt{2}} \left[|\psi_1^0(X)\rangle + |\psi_2^0(X)\rangle\right].$$

(50)

$|\psi_1^0(X)\rangle$ denote oscillator states in real space when the electron is either situated on site 1 or site 2, similar to the oscillator wave functions illustrated in fig. 4. In particular, in the cross-over regime, these oscillator wave-functions reflect the bimodal probability distribution of the equilibrium positions of the oscillator where the electron sits. Let us next investigate the evolution in time of the charge transfer together with that of the inter-molecular deformation, given by the correlation functions:

$$\chi_{nn}(\tau) = \theta(\tau)[(n_{1\sigma}(\tau) - n_{2\sigma}(\tau))|n_{1\sigma}(0) - n_{2\sigma}(0)|]$$

(51)

$$\chi_{XX} = \theta(\tau)(X(\tau)X(0))$$

(52)

The results of this are reproduced in fig. 5 for a fixed value of $\alpha$ (which in the present notation corresponds to $\alpha = \sqrt{2}\cdot1.2 = 1.70$) and where we cover the cross-over from the strong coupling anti-adiabatic limit ($\gamma = 0.1$) to the strong coupling adiabatic limit ($\gamma = 2.0$) upon increasing the adiabaticity ratio.
FIG. 5: The evolution in time (in units of $\omega_0^{-1}$) of the charge and intra-molecular distance transfer between two adjacent molecular units for a two-site one-electron system (after ref. 7) in the anti-adiabatic ($\gamma = 0.1$), the adiabatic ($\gamma = 2.0$) and in the cross-over regime ($\gamma = 1.1$) and for (in the present notation) a coupling strength $\alpha = 1.2\sqrt{2} \approx 1.7$.

The anti-adiabatic limit is characterized by a smooth and slowly in time varying transfer of charge from one molecule to the next. This charge transfer then *slaves* the inter-molecular deformation $X$ by subjecting it to a slowly in time varying driving force $-\frac{\lambda}{\sqrt{2}}[n_{1\sigma}(\tau) - n_{2\sigma}(\tau)]X(\tau)$. This in turn leads to a slowly in time varying sinusoidal intermolecular deformation, onto which are superposed the local intrinsic oscillations of the individual molecules with a frequency of the order of $\omega_0$. This is the exact opposite of what happens in the extreme other limit, when we approach the adiabatic situation.

In this adiabatic regime, considering here an adiabaticity ratio $\gamma = 2.0$, the slowly in time varying quantity is now the inter-molecular deformation (showing almost no fluctuations of the individual molecules with frequency $\omega_0$), which *slaves* the intermolecular charge transfer characterized by $[n_{1\sigma}(\tau) - n_{2\sigma}(\tau)]$. Averaged over several periods of oscillations of frequency $\approx 1/t$, this charge transfer adiabatically follows again the slowly in time varying potential $-\frac{\lambda}{\sqrt{2}}[n_{1\sigma}(\tau) - n_{2\sigma}(\tau)]X(\tau)$.

These results show that in these two extreme limits of adiabaticity and anti-adiabaticity the slowly in time varying component of the charge transfer processes and of the inter-molecular deformation dynamics are completely locked together. This is no longer the case in the cross-over regime between these two extreme limits, here shown in fig. 6 for the adiabaticity ratio 1.1. One can clearly distinguish phase-slips occurring between the correlated motion of the charge and the deformation transfer, which, in a large system where many body effects become important, could possibly lead to a dynamically induced localization of the charge carriers.

V. SOME EARLY EXPERIMENTAL INSIGHTS

The local character of small polaronic charge carriers requires specific experimental probes able to track the polaron induced lattice as well as charge excitations on a short spatial ($\approx 5$ Å) as well as time ($10^{-13} - 10^{-15}$ sec) scale. Generally such probes are quite adequate for insulating polaronic systems with either charge ordered bipolarons (Ti$_4$O$_7$), bipolaronic Mott type insulators (WO$_3$-x, the manganites and nickelates) and low density polaron systems arising from photo-induced or chemical doping and situated on the verge of a quantum phase insulator-superconductor transition (high $T_c$ cuprates). Concerning the cuprates, manganites and nickelates we refer the reader to the lectures by T. Egami and N. L. Saini in this volume, dealing with pulsed inelastic neutron scattering techniques and EXAFS as well as XANES. Here we shall restrict ourselves to the discussion of more classical probes such as optical absorption which can select specific local polaron-sensitive lattice modes.

As we have seen in the discussion presented above, one of the major issue here is to track the disintegration and...
reconstruction of a polaron during its transfer from one site to the next. This process implies a gradual stripping off of the electron’s phonon cloud upon leaving a given site and a subsequent rebuilding of this phonon cloud on the new site where the electron eventually ends up. Another important issue in the polaron problem is connected to the physics of Many-Polaron system, caused by the polaron induced local attraction which can bind two polarons on a given effective site into a bipolaron. We shall now discuss specific experiments which can illustrate these two characteristic polaron features.

Shortly after Anderson’s suggestion* of localized bipolarons in amorphous chalcogenide glasses, exhibiting a natural diamagnetism resulting from covalent bonding in locally deformed lattice structures, a variety of systems were found where bipolarons existed in more or less dense situations. Examples for dense bipolaronic systems, exhibiting spatially symmetry broken states related to bipolaron ordering are: Ti$_{4-x}$V$_x$O$_7$, and Na$_x$V$_2$O$_5$. An example for a dilute bipolaron systems is WO$_{3-x}$[7]. In those systems the bipolarons form on adjacent cations, such as Ti$^{3+}$-Ti$^{3+}$, V$^{4+}$-V$^{4+}$ and W$^{5+}$-W$^{5+}$ bonds in strongly deformed octahedral ligand environments. Those bipolaronic units are imbeded in a corresponding background of Ti$^{4+}$-Ti$^{4+}$, V$^{5+}$-V$^{5+}$ and W$^{6+}$-W$^{6+}$ molecular units, which together with the bipolaronic entities, constitute those crystalline materials.

A. Bipolaron dissociation and recombination in WO$_{3-x}$

Bipolarons can be dissociated with light which, in the case of WO$_{3-x}$, leads to the creation of isolated W$^{5+}$ cation sites in vibrationally excited states of the ligand environments and whose concentration can be tracked by electron spin resonance (ESR) signals coming from those W$^{5+}$ sites. Optical absorption measurements[7] in non-illuminated samples show a peak in the spectrum centered around 0.7 eV coming from pre-existing isolated W$^{5+}$ cations sites. When the crystal is illuminated with a broad spectral band centered around a suitable frequency (1.1 eV in this case) the optical absorption coming from the W$^{5+}$ cations sites increases while, concomitantly, an intrinsic shoulder of the absorption band at around 1 eV—attributed to the absorption coming from the intrinsic bipolaronic W$^{5+}$-W$^{5+}$ bonds—decreases correspondingly. After the illumination is shut off, the single-polaron vibrationally exited W$^{5+}$ units relax to bipolaronic ones, as can be tracked by ESR measurements as a function of time (see fig. 6).

The time evolution of this relaxation follows a bimolecular recombination process controlled by a rate equation given by

$$\frac{dn_W}{dt} = -B(t)n_W^2,$$

where $n_W$ denotes the density of the W$^{5+}$ ions and $B(t)$ is a function describing diffusion limited reactions. This relaxation behavior is clearly distinct from that of mono-molecular process which describe relaxation processes from vibrationally excited single polaron units to their ground state. Such time resolved studies permit to investigate the
rebuilding of the phonon cloud for a bipolaron after its separation into two separate polarons, much as would be expected for processes of bipolarons hopping between neighboring sites.

B. Photo-induced polaronic charge carriers in high \( T_c \) cuprates

A somewhat related in spirit technique was used in the study of polaronic features in the high \( T_c \) cuprates. It was based on examining the variation in the optical absorption spectrum upon doping those materials in the semiconducting phase with electron-hole pairs using so-called photo-induced doping. The idea was to use laser illumination with photon energies bigger than the semiconductor gap in the pump laser beam. In the specific case of the high \( T_c \) cuprates this meant a photon energy of typically 2 to 2.5 eV and which created an estimated density of charge carriers of about \( 10^{19} \) per cm\(^3\). The injected photoinduced charge carriers modify locally the lattice symmetry and, by doing so, lead to the activation of corresponding local phonon modes (the 434 cm\(^{-1}\) out of plane mode and the 500 cm\(^{-1}\) axial [Cu-O\(_4\)] stretching mode). These modes can be made evident as the steady state response of the system to the photo illumination in the absorption spectrum tested by a probe infrared beam (see fig. 3). In such an experimental set up, the 590 cm\(^{-1}\) mode with the tetragonal symmetry (being associated with the undistorted lattice which characterize the non-illuminated materials) loose in intensity (bleaching effect) in the absorption spectrum after the samples have been illuminated. Examining the response of the system at higher frequencies, covering the energy range of the semiconducting gap and higher, by photo-modulation techniques (which test the photo-induced charge carriers by their absorption of light in a narrow frequency window) visualizes the excitations with a life time which is inversely proportional to this frequency. The corresponding absorption spectra show an activation of charge excitations over a broad background, covering the energy region of the semiconducting gap, and a bleaching for energies above that frequency (see fig. 4). These results imply a shift of spectral weight upon illumination from the states above the gap in the non-illuminated samples into in-gap states. The intensity of the absorption of the activated phonon modes as well as of the activated electronic in-gap excitations turns out to scale like the square root of the intensity of the laser pulse illuminating the sample. This suggests that (in analogy with studies on WO\(_{3-\chi}\) discussed above) those excitations relax via bimolecular recombination processes. Since the studies on photo-induced charge carriers have features similar to those in low doped systems, obtained by chemical substitution, it has been tempting to conclude that the charge carriers in the low doped superconducting samples have resonant bipolaronic features of a finite lifetime rather than corresponding to well defined stable bipolaronic entities. Such entities can nevertheless condense into a superconducting state and are controlled by phase rather than amplitude fluctuations as discussed in my lecture: “From Cooper pairs to resonating bipolarons” in this volume.

C. Bipolaronic charge ordering in Ti\(_4\)O\(_7\)

A particularly interesting and physically very rich example of a dense bipolaronic system is Ti\(_4\)O\(_7\). It exhibits a low temperature phase (\( T \leq 140 \) K) where bipolarons are in a symmetry broken ordered state, consisting of diamagnetic \( T^{3+} - T^{3+} \) bipolaronic diatomic pairs with sensibly reduced intra-molecular distances as compared to \( T^{4+} - T^{4+} \) pairs with which they alternate in quasi 2D slab like structures. Upon increasing the temperature, there is a small interval, [140 K \( \leq T \leq 150 \) K], were these bipolaronic electron pairs are dynamically disordered and eventually break up into individual electrons and a metallic phase for \( T > 150 \) K. The experimental measurements of this material involved x-ray diffraction, resistivity, susceptibility and specific heat measurements as well as electron paramagnetic resonance (EPR) studies, summarized in ref. The two low temperature phases in the regimes \( T \leq 140 \) K and 140 K \( \leq T \leq 150 \) K are semiconducting with a conductivity characterized by comparable activation energies of the order of 0.16 eV. The phase transition between those two semiconducting phases can be attributed to an order-disorder phase transition where the bipolarons are essentially the same as in the low temperature ordered phase, as evident from the absence of any change in the magnetic susceptibility as well as intra-molecular distance of the bipolarons when going through this phase transition. The transition to the high temperature phase at \( T = 150 \) K is characterized by a breaking up of the bipolarons into itinerant electrons leading to a metal with an enhanced Pauli susceptibility and a substantial decrease in the unit-cell volume (see fig. 5). Both transitions are first order and the entropy change in the high temperature transition is due, in roughly equal amounts, to electronic and lattice contributions. The most important feature of this system is however that the disordered bipolaronic phase is a dynamical rather than static disorder as evidenced from EPR experiments which show a vanishing of the EPR line upon entering this phase from the low temperature ordered phase. It was on the basis of these experimental findings that the possibility of a condensation of bipolarons was initially proposed. This broke with a traditionally severely guarded doctrine and stimulated to look for superconducting materials which (i) were oxides, (ii) have reduced dimensionality, (iii) are close to insulating parent compounds and (iv) are generally poor rather than good metals in the normal phase.
FIG. 8: The electrical conductivity for Ti$_4$O$_7$ (after ref.7) showing with increasing $T$ a transition from a low temperature activated hopping regime to a different activated hopping regime at $T \approx 140$ K followed by a second transition from that to a metallic phase at $T \approx 150$ K. The magnetic susceptibility, shown in the inset, does not change at the low temperature transition.

On the basis of such a scenario and the Hostein model one could expect for such systems a superfluid state of bipolarons, albeit with a very small critical temperature, since being inversely proportional to the bipolaron mass which is typically several orders of magnitude bigger than the electron band mass. The real difficulty to observe this type of superfluidity in crystalline materials might however be related to the fact that the standard polaron models, generally based on harmonic lattice potentials, totally neglect any relaxation processes. High $T_c$ cuprates are clearly not candidates for this extreme case of Bipolaronic Superconductivity but are likely to contain localized bipolarons as resonant states inside the Fermi sea of itinerant electrons which could result in a superconducting state controlled by phase rather than amplitude correlations.

VI. SUMMARY

In this introductory lecture I briefly reviewed various kinds of electron-lattice couplings, characterizing different classes of materials and which give rise to two distinct categories of polarons: large Fröhlich and small Holstein polarons. The importance of treating the phonons as quantum rather than classical variables became evident in connection with the question of itinerancy of the polaronic charge carriers. The dynamics of the polaron motion, exemplified in real time, shows a highly non-linear physics involving the dynamics of coupled charge and the lattice fluctuations which mutually drive each other. The present discussion was restricted to the single polaron respectively bipolaron problem and to limiting cases (such as strong coupling anti-adiabatic limit) where the Many Polaron problem can be decomposed into a band of single polaron states with different wave vectors. The fundamental questions of the polaron problem which pose themselves today, are evidently beyond the topics touched upon in this preliminary discussion. These are questions which concern the cross-over between the adiabatic and anti-adiabatic regimes, the polaron induced residual interactions in a Many Polaron system and its dependence on the range of electron-lattice coupling as well as on the density of charge carriers, which can result in possible transitions between insulating and metallic behavior of polarons. At this stage, in order to tackle this kind of problems we have to resort to highly sophisticated numerical techniques, which will be presented in this school. The hope is that eventually this will give us some insight into this complex Many Body problem so that sooner or later we can formulate this polaron physics in a way where analytical approaches can capture its main qualitative features.

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