Resonating bipolarons

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Abstract. – Electrons coupled to local lattice deformations end up in self-trapped localized molecular states involving their binding into bipolarons when the coupling is stronger than a certain critical value. Below that value they exist as essentially itinerant electrons. We propose that the abrupt crossover between the two regimes can be described by resonant pairing similar to the Feshbach resonance in binary atomic collision processes. Given the intrinsically local nature of the exchange of pairs of itinerant electrons and localized bipolarons, we demonstrate the occurrence of such a resonance on a finite-size cluster made out of metallic atoms surrounding a polaronic ligand center.

The phenomenon of resonant pairing between nucleons, atoms and molecules, characterized by a strongly enhanced scattering amplitude, has received considerable attention in the past few years, primarily in connection with the study of ultracold dilute atomic gases exhibiting various forms of condensed macroscopic coherent quantum states. The basic requirement for such so-called Feshbach resonant pairing [1, 2] is that two incident particles have nearly the same energy as that required to form a shallow bound state between them. The efficiency to convert two uncorrelated atoms into a molecular state over short time intervals is then dramatically enhanced. As a result, two atoms near such a resonance oscillate between essentially uncorrelated pairs of atoms and diatomic molecular states. Experimentally such a situation can be created, provided the atoms can exist in two different spin states permitted by spin-orbit coupling. Different spin alignments of the two atoms (in form of spin singlet or triplet states) give rise to different inter-atomic interactions, which lead to either bound or scattering states. Favoring the one over the other can be monitored by applying a magnetic field which shifts the respective interaction potentials with respect to each other.

We shall illustrate in this letter, that similar effects are bound to play a role in strongly coupled electron-lattice systems with polaronic and bipolaronic charge carriers. The recently much studied high-$T_c$ cuprates, the colossal magneto-resistance manganates, the nickelates as well as the fullerenes are examples where such effects are likely to occur. It is however not our aim here to devote the present study to such specific cases and we shall limit ourselves to purely theoretical questions.

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It has been known for quite some time that a single electron in a lattice which is coupled to local lattice deformations undergoes, upon changing the electron-lattice coupling and/or the adiabaticity ratio, a rapid crossover between a well-defined itinerant quasi-particle (describable in terms of a weak coupling Born-Oppenheimer approach) and a predominantly incoherent excitation in form of a self-trapped small polaron [3–6]. A similar feature applies to a single pair of electrons in such a lattice. In the narrow crossover regime this involves two-electron states in a superposition of uncorrelated itinerant electrons in an essentially undeformed lattice and localized bipolaronic bound states, i.e., electron pairs which are self-trapped in their strongly deformed local lattice environments. How such effects, involving a single electron or a single pair of such electrons, will be carried over into a dense electron system has occupied much theoretical work over the past decades [7]. A great variety of different and highly sophisticated many-body techniques has been employed to shed light on the polaron physics in such dense systems. Particular features which emerge from such studies are the metal-insulator transition [8] driven by electron pairing into bipolarons and the transitions driven by a stripping off of the lattice polarization upon increasing the density of charge carriers [9]. Our goal here is to unravel the underlying physics behind such crossover phenomena, respectively phase transitions, which is to some extent hidden in the extremely complex numerical studies sofar used in this context. We shall show that the phenomenon leading up to such a crossover behavior is caused by the formation of resonating bipolaron states, according to a mechanism bearing great similarities with the Feshbach resonant pairing in atomic gases.

Let us illustrate this physics on the basis of a model system composed of small plaquette clusters consisting of i) a ring of four atoms on which the electrons behave in a tight binding itinerant fashion, and ii) a central site made up of a strongly deformable diatomic molecule described by a harmonic oscillator. Such clusters can be imagined being linked together to form a lattice by sharing the atoms at the corners of the square plaquettes. This makes the system a bipartite lattice with itinerant electrons on one sublattice and localized bipolarons on the other one. Our system can thus be envisaged as a band of tight-binding electrons with a localized bipolaronic level inside this band. Electrons with an energy close to this bipolaronic level will scatter in and out of the central molecular sites and thus acquire polaronic features, at the same time pairing up in form of short-lived bipolarons. This mechanism has an evident similarity with the Feshbach resonant pairing in ultracold atomic gases. The electrons moving on the sublattice made up of the rings mimic the incident scattering states of the atoms. When the electrons meet on the central site, they are momentarily bound into an electron pair (in the language of atomic physics, via so-called closed-channel collisions), before fluctuating back onto the ring. In a Feshbach low energy binary collision process the wave function of the corresponding Schrödinger equation is a superposition of i) the incident scattering states, characterized by spin singlet configurations of the pair of atoms with a repulsive inter-atomic interaction, and ii) closed channel states, characterized by spin triplet configurations with an attractive inter-atomic interaction. In the polaron problem the equivalent of these spin configurations are two configurations of the oscillator on the molecular site: i) one with a practically undisplaced intra-molecular distance, inciting the electrons to remain on the ring and hence uncorrelated and ii) one with a displaced shortened intra-molecular distance, inciting the electrons to pair up on the molecular site.

The essential physics of this resonance problem is already contained in the electronic and vibrational properties of a single isolated cluster. This is because the efficiency of converting the bipolarons into resonating electron pairs involves predominantly short-range interactions and thus concerns only the immediate vicinity of the polaronic sites, i.e., the atoms on the rings around them. Let us now pursue our investigation on the basis of a single cluster, for
which we have the following Hamiltonian:

\[
\begin{align*}
H &= -t \sum_{i \neq j=1\ldots4, \sigma} [c_{i\sigma}^\dagger c_{j\sigma} + H.c.] - \\
&\quad -t' \sum_{i=1\ldots4, \sigma} [c_{i\sigma}^\dagger c_{5\sigma} + H.c.] + \Delta \sum_{\sigma} c_{5\sigma}^\dagger c_{5\sigma} + \\
&\quad + \hbar \omega_0 \left[a_5^\dagger a_5 + \frac{1}{2}\right] - \hbar \omega_0 \alpha \sum_{\sigma} c_{5\sigma}^\dagger c_{5\sigma} \left[a_5 + a_5^\dagger\right].
\end{align*}
\]

Here \( c_{i\sigma}^{(\dagger)} \) denote the annihilation (creation) operators for electrons with spin \( \sigma \) on the site \( i \), \( i = 1, \ldots, 4 \) denoting the sites on the ring and \( i = 5 \) the central molecular site, while \( a_5^{(\dagger)} \) denote phonon annihilation (creation) operators on the latter. \( t \) and \( t' \) denote the hopping integrals on the ring and between the ring and the central site, respectively. \( \Delta \) is the bare energy level of the central site, \( \alpha \) the dimensionless electron-phonon coupling constant and \( \omega_0 \) the bare local phonon frequency. Expressing the energies in units of \( t \), we choose \( t' = 0.5 \) and \( \Delta = 1.5 \).

Approximating the full set of phonon states on the central site by a truncated Hilbert space, we diagonalize the above Hamiltonian for the case of two electrons. Describing the electrons on the ring in terms of their wave vectors \( q = 0, \pm \pi/2, \pi \) we find that the ground-state energy \( E_0(\alpha) \) is very close to \( E_0(\alpha = 0) \) up to a value of \( \alpha \) where the energy of the localized bipolaron state \( \varepsilon_{BP}(\alpha) = 2\Delta - 4\alpha^2 \hbar \omega_0 \) drops below the ground-state energy \( E_0(\alpha = 0) \) of the itinerant electrons on the ring. This value of \( \alpha \), \( \alpha_c = \frac{\ln(2\Delta - E_0(\alpha = 0))}{\hbar \omega_0} \), determines the crossover regime between itinerant and localized behavior. For \( \alpha \geq \alpha_c \), \( E_0(\alpha) \) drops off like \( \varepsilon_{BP}(\alpha) \). This crossover is characterized by a strong enhancement around \( \alpha_c \) (see fig. 1) of the static correlation function \( F_{el-bip}(\tau = 0) = \langle c_{5\uparrow}^\dagger c_{5\downarrow}^\dagger c_{q=0\uparrow} c_{q=0\downarrow} | 0 \rangle \), which measures the efficiency to convert two uncorrelated electrons on the ring into a bipolaron on the central site (here \( | 0 \rangle \) denotes the two-particle ground state). Unlike the case of the Feshbach resonance in atomic collision processes, the interaction leading to the conversion of itinerant electrons into localized bipolarons and vice-versa is time dependent and involves the building up and dismantling of a
The dynamical correlator $A_{\text{el-bip}}(\omega)$ for a fixed adiabaticity ratio $\omega_0/t = 0.5$ and various electron-phonon couplings $\alpha$. It describes the scattering of two itinerant electrons into localized bipolaronic states and keeps track of resonant scattering near $\alpha_c = 1.87$.

local lattice deformation. This effect is visible in the behavior of the time-dependent features of the above correlator $F_{\text{el-bip}}$, described by the corresponding spectral function

$$A_{\text{el-bip}}(\omega) = -\frac{1}{\pi} \text{Im} \int_0^\infty d\tau e^{i\omega\tau} \langle 0| c_5^\dagger(\tau)c_5^\dagger(\tau)c_{q=0}\dagger(0)c_{q=0}(0)|0\rangle.$$  \hspace{1cm} (2)

This is illustrated in fig. 2 in the adiabatic limit (for a specific choice of $\omega_0/t = 0.5$) and for several values of the electron-phonon coupling $\alpha$ in the crossover regime. We notice a spectral behavior which in the weak coupling regime ($\alpha \leq 1.85$) corresponds to well-defined coherent features describing two itinerant uncorrelated electrons on the ring, being dressed by a few harmonic overtones coming from the accompanying phonons. In the strong-coupling regime ($\alpha \geq 1.89$), we observe a spectral behavior typical of localized bipolarons which approaches a spectral distribution given by $e^{-4\alpha^2(2\alpha)^{2n}/n!}(\omega + \epsilon_{\text{BP}}(\alpha) - n\hbar\omega_0)$. Near and at the crossover, around $\alpha \simeq \alpha_c = 1.87$, we notice a superposition of a coherent contribution, coming from the two electrons freely moving on the ring, and an incoherent one coming from those two electrons when they stick together for a short time on the central site in form of a bipolaron.

Let us now further specify the features of the crossover regime. Going through the resonance upon increasing $\alpha$, the oscillator on the central site will show modifications in the intra-molecular distance $\langle 0|\hat{X}|0\rangle$ with $\hat{X} = \sqrt{\hbar/2M\omega_0}(a_5^\dagger + a_5)$ ($M$ denoting the mass of the molecule) as well as in the phonon frequency $\omega_0$. For weak coupling this distance remains essentially unshifted from its $\alpha = 0$ value, while for strong coupling it tends to that associated with the presence of a localized bipolaron, i.e., $X_0 = 4\alpha\sqrt{\hbar/2M\omega_0}$. At the resonance
Fig. 3 – The pair distribution function \( \rho(X) \) for the oscillator site as a function of the intra-molecular distance \( \xi = X \sqrt{M\omega_0/\hbar} \) for a fixed adiabaticity ratio \( \omega_0/t = 0.5 \) and various electron-phonon couplings \( \alpha \). The bipolaron resonance at \( \alpha_c = 1.87 \) is manifest in the appearance of a double-peak structure in a narrow regime around \( \alpha_c \).

we observe a superposition of the two. This behavior is illustrated in fig. 3, where we plot the pair distribution function (PDF) \( \rho(X) = \langle 0 | \delta(x - X) | 0 \rangle \), measuring the probability to find a certain value \( X \) for the intra-molecular distance. This is done by taking the real-space representation of the two-particle ground state \( | 0 \rangle \) in terms of the excited harmonic oscillator wave functions. The plot in fig. 3 signals the resonance by the appearance of a double-peak structured PDF. Below and above this resonance the PDF is singly peaked either around \( X \approx 0 \) or \( X \approx X_0 \). The analogous feature in Feshbach resonant pairing of atoms is a distribution function measuring the probability for singlet and triplet components of the atomic pair wave function. Above the resonance it would be given by predominantly triplet bound pairs and below it by singlet components of the two incident atoms. At the resonance it would correspond to a superposition of the two.

In order to get a resonance behavior in the two-particle channel making the \textit{a priori} uncorrelated particles stick together for some substantial time (which in the case of the atomic gases in traps can be as long as a fraction of a second), the dynamics of the attractive interaction in the present polaron problem must be significantly slowed down as compared to the characteristic frequency \( \omega_0 \). This is precisely what happens, as can be seen by inspection of the phonon spectral function

\[
B(\omega) = -\frac{1}{\pi} \text{Im} \int_0^\infty d\tau e^{i\omega\tau} \langle 0 | X(\tau)X(0) | 0 \rangle,
\]

whose behavior is illustrated in fig. 4. The bare phonon frequency \( \omega_0 \) is reduced to \( \omega_0^* \) by more than an order of magnitude upon approaching the resonance at \( \alpha = \alpha_c \), while at the same time its spectral weight is significantly enhanced. These are the features which control the
Fig. 4 – The phonon spectral function $B(\omega)$ for a fixed adiabaticity ratio $\omega/t = 0.5$ and various electron-phonon couplings $\alpha$, as indicated on the right $y$-axis. Upon approaching the resonance at $\alpha_c$, it shows a substantial softening and a simultaneous increase in spectral weight (given by the length of the vertical bars).

Physics leading to bipolaron resonant states. The lifetime of such resonating bipolarons is of the order of $\pi/\omega_0^*$, which is about an order of magnitude longer than the characteristic time of the intrinsic molecular oscillation, i.e., $\pi/\omega_0$. The electrons then oscillate with a frequency $\omega_0^*$ between an uncorrelated behavior on the ring and a trapped bipolaronic one on the molecular site. This fluctuation of the electrons in and out of the polaronic site is associated with the oscillation of the intra-molecular distance, a sluggish mode of the oscillator switching back and forth between two different bond lengths of the molecule. Increasing $\alpha$ slightly above $\alpha_c$ keeps the electrons bound as bipolarons, while a decrease of $\alpha$ below $\alpha_c$ makes them turn into itinerant quasi-particles. The mechanism of tuning the system via $\alpha$ between the different regimes is fully equivalent to the tuning across the Feshbach resonance in atomic gases by applying an external magnetic field. Experimentally, tuning in electron-phonon coupled systems could be achieved by either changing the electron density or the phonon frequency $\omega_0$ (via isotope substitution of the molecular units responsible for bipolaron formation) such as to modify the difference between the chemical potential and the energy level of the bipolarons.

This letter aimed to attract attention to a possible resonant pairing in polaronic systems in the intermediate-coupling regime. A particularly suited scenario for that is represented by systems composed of a lattice of metal atoms being surrounded by their ligand environments. The latter provide the local dynamical deformations which lead to self-trapped polaronic entities. Our contention is that global features (such as superconductivity or insulating behavior)
emerge from the local physics already contained in appropriately chosen clusters. An infinite system composed of such clusters, interconnected by electron hopping, can be treated by real space contractor plaquette renormalization group methods, which have been successfully applied to the Hubbard problem [10] in order to capture the relevant local physics of the correlation problem for an infinite lattice system.

The hallmark of such resonant pairing is a strongly enhanced conversion between localized bipolarons on the ligand and itinerant electrons in their immediate vicinity — a feature which we illustrated here on the basis of an isolated cluster. For an infinite lattice, composed of such interconnected clusters, the electrons which partially fill a tight binding band will overlap with the level of the localized bipolarons, describing the situation when the electrons find themselves momentarily on the ligands. Hence there will always be a degeneracy of uncorrelated pairs of itinerant electrons and localized bipolarons such that such a resonance behavior can occur. For this reason the particular choice of our parameter ∆, fixing the level of the localized electrons on the ligands will not influence the resonant pairing phenomenon on a qualitative level since by changing the electron lattice coupling (or alternatively by changing the band filling) we can always bring the energy level of the localized bipolarons $\varepsilon_{\text{BP}}$ inside the filled part of the tight-binding electron band.

Finally, we should point out that the phonon softening, indicative of the resonant pairing, is qualitatively similar to what has been obtained for the single-impurity Anderson-Holstein model analyzed by NRG [11] as well as for the Holstein model at half filling within DMFT [12, 13]. Given the electron-phonon interaction $-\hbar \omega_0 a \sum_{\sigma} (c_{5\sigma}^{\dagger} c_{5\sigma} - \frac{1}{2})[a_5 + a_5^\dagger]$ used in those studies and an impurity level coinciding with the Fermi energy, the resulting degeneracy of empty and doubly occupied impurity sites favors a Kondo resonance in charge space, whose dynamics shows up in phonon softening similar to that of the Feshbach-like resonance discussed here. Away from this limiting situation this Kondo resonance disappears [11], while the resonance discussed in this letter is expected to remain away from half-filling, for a bare energy ∆ of the polaronic sites not coinciding with the Fermi level, and for the usual form of the electron-phonon interaction.

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