Excitons in Mott insulators

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Motivated by recent Raman and resonant inelastic X-ray scattering experiments performed for Mott insulators, which suggest formation of excitons in these systems, we present a theory of exciton formation in the upper Hubbard band. The analysis based on the spin polaron approach is performed in the framework of an effective t-J model for the subspace of states with one doubly occupied site. Our results confirm the existence of excitons and bear qualitative resemblance to experimental data despite some simplifications in our approach. They prove that the basic underlying mechanism of exciton formation is the same as that which gives rise to binding of holes in weakly doped antiferromagnets.

The electronic properties of Mott insulators, like high temperature superconductors in the limit of low doping, belong to the most intriguing questions which faces contemporary condensed matter physics. Properties of such systems are determined by the large onsite Coulomb interaction $U$ or the charge transfer energy $\Delta$ of removing an electron from the $p$ orbital of oxygen and putting it into the $d$ orbital of the transition metal. The structure of occupied electronic states has been intensively investigated by means of the angle-resolved photoemission spectroscopy (ARPES) and much is already known about the electronic structure below the insulating gap. Natural probes of unoccupied states above the gap are Raman [1] and resonant inelastic X-ray scattering [2] (RIXS).

The Raman scattering provides information about excitations at $k = 0$. If we ignore polaritonic effects the cross section for the Raman scattering may be obtained directly from the golden rule. The final formula contains matrix elements $\langle f | M_R | i \rangle$ evaluated between an initial state $i$ and a final state $f$. In the case of the Mott insulator in two dimensions (2D) described by the Hubbard model at half-filling in the limit of strong correlations (large $U$), which is a natural framework to discuss such a system, the initial state $i$ is just the ground state of the quantum antiferromagnet (AF) in 2D, while the final state may be identified as an excitation in the AF state. The electronic states $|n\rangle$ above the insulating gap appear at the intermediate stage of the Raman process, which may be seen from the explicit formula for $\langle f | M_R | i \rangle$,

$$\langle f | M_R | i \rangle = \sum_n \frac{\langle f | \hat{j}_{-k_i} \cdot \hat{e}_i | n \rangle \langle n | \hat{j}_{-k_i} \cdot \hat{e}_i | i \rangle}{\epsilon_i - \epsilon_n - \hbar \omega_f + i \delta},$$

(1)

$\epsilon_i$ and $\epsilon_f$ are energies of the initial and final states, while $\hbar \omega_f$, $\epsilon_i$ and $\epsilon_f$ represent energies and polarizations of incident and outgoing photons. The current operator for the Hubbard model on the square lattice is given by,

$$\hat{j}_k = i \hbar \sum_{i, \delta, \sigma} \delta c_{i+\delta, \sigma}^\dagger c_{i, \sigma}.$$  

(2)

The summation is carried over lattice sites $i$, vectors $\delta$ which connect each site with its four nearest neighbors and spin polarizations $\sigma$. The Hubbard model in the lower Hubbard band at half-filling in the limit of strong correlations is equivalent to the Heisenberg model which action is restricted to the Hilbert space spanning states that correspond to configurations in which each site is occupied by a single spin-1/2 fermion. The current operator acting on the antiferromagnetic state, shifts a fermion to a nearest neighbor site that is already occupied, which means that it couples lower and upper Hubbard bands (LHB, UHB). The newly created hole and the double occupancy (DO) of a site reside on nearest neighbor sites. We conclude, that in order to contribute some substantial weight to the Raman spectra, the intermediate state should be a bound state of some sort, which is formed by the hole and the DO that plays the role of a particle. In other words, we expect formation of excitons in the UHB. The current operator at $k = 0$ is a vector and obeys a dipole selection rule.

The ground state of the quantum AF is fully symmetric, the current operator couples it only with excitons of $p$-wave symmetry.

The RIXS process may be interpreted in a slightly similar way, which in addition requires explicit consideration of the orbital structure of involved states. According to a most likely scenario for the undoped cuprates [3, 4] 3d electrons interact with the $1s$ core hole created during the dipole transition of an $1s$ electron to the $4p$ orbital which accompanies the absorption of an incident photon. This strong interaction gives rise to a shift of the $3d$ electrons across the gap. In the last step, the $4p$ electron returns to the $1s$ orbital and an outgoing photon is emitted. The RIXS process like the Raman scattering creates a particle-hole pair in the UHB which carries energy and in addition has non-vanishing momentum. It is easy to imagine three dispersing modes in the UHB with a single hole which might be relevant to the RIXS physics,
a positively charged spin polaron related with the hole, a negatively charged spin polaron related with the DO and a bound state of these two entities (exciton). Our calculation will clarify the mechanism of formation and propagation of such objects.

Since we are concerned with the the Hubbard model in the large-$U$ limit we choose a standard way of separating Hubbard bands by means of a unitary transformation. A version of an effective Hubbard bands by means of a unitary transformation of such objects.

States spanned by the fermionic Hilbert space may be obtained by acting on $|N\rangle$ with products of $c_{\sigma(i)}^d$ or $c_{\sigma(i)}^+ \equiv \bar{d}_i^\dagger$. They invert a spin (create a magnon), create a hole or a DO at the site $i$. The representation in terms of products will be unique if each index $i$, which refers to a site, appears in all products no more than once. Since the effective Hamiltonian obtained by Eskes et al. corresponds to the second-order perturbation expansion it acts maximally on three sites which lie in row in the lattice and hence affects only three operators in the above mentioned products. For the same reason only a single hole-creation operator and a single DO-creation operator may be involved in the action of the effective Hamiltonian. In (9-15) the action of the $t$-$J$ model in the UHB with a single hole is represented by means of states which are coupled by this operator. Relations (14-15) actually demonstrate how the action of the effective Hamiltonian interchanges pairs or trios of creation operators represented by $\tilde{O}$ and $\tilde{O}'$ between product representations like $\tilde{A}\tilde{O}B|N\rangle$ and $\tilde{A}\tilde{O}'B|N\rangle$ of these states, ($A$ and $B$ denote products of operators which act on different sites than those involved in the action of $\tilde{O}$ and $\tilde{O}'$). Lack of an operator for a given site $i$ in the product is formally represented by the identity operator $\tilde{1}_i$. In this case the site $i$ is occupied by a single spin which points in the direction determined by the original Néel configuration. The value of the matrix element of the Hamiltonian is given in (15) after a colon. The energy of the Néel state is chosen as a point of reference from which we count the diagonal contributions to the Hamiltonian. A different description of relations (15) is that they represent a sum over states with factors given by amplitudes presented after colons. That sum is created by action of the Hamiltonian on a given state represented by a product. Each component of the sum may be obtained by exchanging operators on two or three sites according to the rules represented by (15). Processes in (15) represent hopping, or in other words shifts of a hole or a DO accompanied by creation or annihilation of a magnon. In (15) anti-parallel spins on a pair of nearest sites are simultaneously inverted. (15) are related with the rise in the contribution to diagonal matrix elements of the Hamiltonian (which play the role of potential energy), in comparison to the vanishing contributions from (15), which appears if nearest sites are not occupied by parallel spins. That rise is higher if such a pair is occupied by a hole and a DO, which may be seen in the second term in (15). On the other hand in such a case an additional process is possible that may lower the energy, namely the exchange of the hole and the DO which may be seen in (15). Processes described by formulas (14-15) represent exchange, rotations and shifts of the hole-DO pair between nearest links which in some cases are accompanied by a shift of a magnon.

$$\tilde{h}_i^d \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{s}_i^d \tilde{\sigma}_{i+\delta} : t; \quad \tilde{d}_i^\dagger \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{s}_i^d \tilde{\sigma}_{i+\delta} : t$$

(3)

$$\tilde{i}_i^\dagger \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{s}_i^\dagger \tilde{\sigma}_{i+\delta} : J/2$$

(4)

$$\tilde{i}_i^\dagger \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{i}_i \tilde{\sigma}_{i+\delta} : 0; \quad \tilde{s}_i^\dagger \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{s}_i \tilde{\sigma}_{i+\delta} : 0$$

(5)

$$\tilde{i}_i \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{i}_i \tilde{\sigma}_{i+\delta} : J/2; \quad \tilde{i}_i \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{i}_i \tilde{\sigma}_{i+\delta} : J/2$$

(6)

$$\tilde{s}_i^\dagger \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{s}_i^\dagger \tilde{\sigma}_{i+\delta} : J/2; \quad \tilde{i}_i \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{i}_i \tilde{\sigma}_{i+\delta} : J/2$$

(7)

$$\tilde{d}_i^\dagger \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{d}_i^\dagger \tilde{\sigma}_{i+\delta} : J; \quad \tilde{d}_i^\dagger \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{d}_i^\dagger \tilde{\sigma}_{i+\delta} : J$$

(8)

$$\tilde{h}_i^d \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{d}_i^\dagger \tilde{\sigma}_{i+\delta} : -J/2$$

(9)

$$\tilde{h}_i^d \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{h}_i^d \tilde{\sigma}_{i+\delta} : J/4$$

(10)

$$\tilde{h}_i^d \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{h}_i^d \tilde{\sigma}_{i+\delta} : J/4$$

(11)

$$\tilde{h}_i^d \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{h}_i^d \tilde{\sigma}_{i+\delta} : -J/4$$

(12)

$$\tilde{h}_i^d \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{h}_i^d \tilde{\sigma}_{i+\delta} : -J/4$$

(13)

$$\tilde{d}_i^\dagger \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{d}_i^\dagger \tilde{\sigma}_{i+\delta} : -J/4$$

(14)

$$\tilde{d}_i^\dagger \tilde{\sigma}_{i+\delta} \leftrightarrow \tilde{d}_i^\dagger \tilde{\sigma}_{i+\delta} : -J/4$$

(15)

The duality between the hole and the DO may be clearly seen in (15). We may also notice the similarity with the $t$-$J$ model acting in LHB. The main differences are that the rise of the potential energy is only $J/2$ if a hole pair occupies nearest sites and not $J$ like for a hole-DO pair and that in the LHB only one kind of charged particles (holes) is present. Nevertheless, one may expect that the possible mechanism of binding of a hole and a DO in the UHB is similar to the mechanism of hole pairing in the LHB.

Much is already known about binding of holes in
weakly doped antiferromagnets \[10\]. We will use these insights to analyze formation of an exciton in the UHB. 

Fast motion, with the rate \( \sim t \), mediated by terms \([3]\) of a hole or a DO created at some site in the Néel state produces magnons which lie on the track of the hole or the DO and contribute to the rise in the potential energy (terms \([5\,5\,5]\)). Strings consisting of magnons are pinned to the site where these objects have been initially created and form a potential well for a hole and a DO which confines their motion. Much slower processes related to the process of inverting a pair of anti-parallel spins at nearest-neighbor sites (process \(4\)) at the begin of the string, produces magnons which lie on the track of the hole or a DO. For a pair of particles created an nearest-neighbor sites \(\langle \alpha, \delta \rangle\) we just apply the generalization of a single hole or a DO has been moving and \(H_{\text{DO}}(i,j)\) as a sum over states which may be reached by hopping of a hole and a DO created at the sites \(i\) and \(j\),

\[
\Psi_{i}^{H(\text{DO})} = \sum_{\mathcal{P}_{i}, \mathcal{P}_{j}} \alpha_{\mathcal{P}_{i}} \mathcal{P}_{i}^{H(\text{DO})}, \tag{16}\]

\(\mathcal{P}_{i}\) parameterizes the geometry of a path along which the hole or a DO has been moving and \(\mathcal{P}_{i}^{H(\text{DO})}\) is a state which has been created in this way. To be precise, at this stage of our considerations we analyze an ”unperturbed” Hamiltonian which consists of terms symbolized by relations \([3\,3\,3]\) and \([5\,5\,5]\) and represents fast oscillations of a hole or a DO in the vicinity of the initial site. Slower processes are neglected in this phase of analysis. “Orbital” states of polarons created at all possible sites exhaust, in principle, the relevant portion of the Hilbert space. In practice, the calculation may be confined to some low excited states or even to the polaron ground state. The concept of spin polarons may be extended to the description of paths \(\mathcal{P}_{i}\) and \(\mathcal{P}_{j}\), and thus \(\alpha_{\mathcal{P}_{i}} = \alpha_{\mathcal{P}_{j}}\) for polarons in the ground state will depend only on the lengths \(\mu, \nu\) of paths \(\mathcal{P}_{i}\) and \(\mathcal{P}_{j}\), by calculating the matrix elements of the full Hamiltonian in the polaron basis we derive an effective Hamiltonian expressed in the polaron language. Some processes, like oscillations of the hole or the DO in the vicinity of a polaron center, are already incorporated into the eigenenergy of polaron states. The rest which we discuss now either renormalizes the eigenenergies of polarons or gives rise to off-diagonal matrix elements in the polaron Hamiltonian. The latter circumstance occurs in the case of shortening of strings attached to a single particle. This process governs propagation of a single hole or a single DO in an antiferromagnetic spin background. Formation of bipolarons, and, in particular, strings that connect a hole and a DO, is an effective way of lowering the energy. A compromise between two opposite tendencies to minimize the kinetic energy of holes and DOs and to reduce the disturbance of the antiferromagnetic background is reached in this way. By shrinking at one end and expanding at the opposite end, a string may move, while keeping a moderate length. The physics of interaction between a hole and a DO is richer than just for two holes, because it incorporates processes described by relations \([5\,5\,5]\), but the method of deriving the Hamiltonian in the polaron language is the same as for one kind of particles \([10]\). Instead of dwelling on details we present now an explicit form of the effective Hamiltonian \(H_{\text{eff}}\). \(h_{i}^{\dagger}\) and \(d_{i}^{\dagger}\) are fermionic operators which create a hole and a DO spin-polaron at the site \(i\). They obey the relation \(h_{i}^{\dagger}d_{i}^{\dagger} = 0\) because none of sites may be simultaneously occupied by a hole and a DO. The bipolaron \(\Psi_{(i,j)}^{H(\text{DO})}\) is created by the pair \(h_{i}^{\dagger}d_{j}^{\dagger}\) where \(i\) and \(j\) are nearest-neighbor sites.

\[
H_{\text{eff}} = E_{1} \sum_{i} (h_{i}^{\dagger}h_{i} + d_{i}^{\dagger}d_{i}) + 2\chi_{1} \sum_{i,\delta,\delta',\delta'' \neq \delta} h_{i+\delta+\delta'}^{\dagger}h_{i} + 2\chi_{1} \sum_{i,\delta,\delta',\delta'' \neq \delta} d_{i+\delta+\delta'}^{\dagger}d_{i} + \sum_{i,\delta} (d_{i+\delta}^{\dagger}h_{i+\delta} + H.c.) + (E_{2} - 2E_{1}) \times \sum_{i,\delta,\delta',\delta'' \neq \delta} (d_{i}^{\dagger}d_{i+\delta}h_{i+\delta}^{\dagger}h_{i} + H.c.) + (E_{2}\omega_{1} + \tau_{1} + \i/2) \times \sum_{i,\delta,\delta',\delta'' \neq \delta} (d_{i}^{\dagger}d_{i+\delta}h_{i+\delta}^{\dagger}h_{i} + H.c.) + (E_{2}\omega_{2} + \tau_{2}) \times \sum_{i,\delta,\delta',\delta'' \neq \delta} (d_{i}^{\dagger}d_{i+\delta}h_{i+\delta}^{\dagger}h_{i+\delta} + H.c.)
\]

The meaning of symbols is the same as in the case of single particles. At this stage of considerations we prohibit, by definition, the hole and the DO to follow along the track left by the accompanying particle and solve the Schrödinger equation in this restricted Hilbert space for an ”unperturbed” Hamiltonian, which takes into account only hopping of the hole or the DO and the diagonal ”potential” contribution to the energy from the magnetic \(J\)-term in the \(t-J\) model. By means of that restriction we achieve that spin bipolarons are localized and we may proceed as in the case of a single hole. We make a further approximation and neglect some path details including the possibility of path crossing. It is self-evident that the coefficients \(\alpha_{\mathcal{P}_{i}}\) and \(\alpha_{\mathcal{P}_{j}}\) for polarons in the ground state will depend only on the lengths \(\mu, \nu\) of paths \(\mathcal{P}_{i}\) and \(\mathcal{P}_{j}\).
\[ + \frac{i}{2} \sum_{i,\delta} d_i^\dagger h_{i+\delta} h_i + \frac{i}{2} \sum_{i,\delta,\delta' \neq \delta} d_i^\dagger h_{i+\delta} h_{i+\delta'} h_i + \frac{i}{2} \sum_{i,\delta,\delta' \neq \delta} d_i^\dagger h_{i+\delta} h_{i+\delta'} h_i + 2 \chi_1 \sum_{i,\delta,\delta' \neq \delta} d_i^\dagger h_{i+\delta} h_{i+\delta'} h_i + 2 \chi_1 \sum_{i,\delta,\delta' \neq \delta} d_i^\dagger h_{i+\delta} h_{i+\delta'} h_i + \chi_2 \sum_{i,\delta,\delta',\delta'' \neq \delta,\delta' \neq \delta'} (d_i^\dagger h_{i+\delta} d_i^\dagger h_{i+\delta'} h_i + H.c.). \tag{18} \]

\( E_1 \) and \( E_2 \) denote the eigenenergies of the spin polaron and the bipolaron which represent the energy of a particle or two particles pinned to starting-point sites by strings, while the rest of parameters is either related with overlap between polaron states at different sites or processes that couple polaron states:

\[ \omega_1 = \sum_{\mu=0,\nu=1} (z-1)^{\mu+\nu-1} \alpha_{\nu,\mu} \alpha_{\nu-1,\mu+1}, \tag{19} \]

\[ \omega_2 = \sum_{\mu=0,\nu=2} (z-1)^{\mu+\nu-2} \alpha_{\nu,\mu} \alpha_{\nu-2,\mu+2}, \tag{20} \]

\[ \tau_1 = t \sum_{\mu=1} (z-1)^{\mu-1} \alpha_{\mu,0} \alpha_{\mu-1,0}, \tag{21} \]

\[ \tau_2 = t \sum_{\mu=1} (z-1)^{\mu-2} \alpha_{\mu,0} \alpha_{\mu-2,0}, \tag{22} \]

\[ \chi_1 = J/2 \sum_{\mu=2} (z-1)^{\mu-2} \alpha_{\mu,\mu}, \tag{23} \]

\[ \chi_2 = J/2 \sum_{\mu=2} (z-1)^{\mu-2} \alpha_{\mu,\mu}, \tag{24} \]

\[ \iota = J/2(\alpha_{0,0})^2. \tag{25} \]

As we have mentioned before polaron states are not necessarily orthogonal and in order to find eigenenergies of the system one has to diagonalize the operator \( O_{eff} H_{eff} \), where the operator \( O_{eff} \) represents overlap between polaron states,

\[ O_{eff} = 1 + \omega_1 \sum_{i,\delta,\delta',\delta'' \neq \delta} (d_i^\dagger h_{i+\delta} h_i + H.c.) + \omega_2 \sum_{i,\delta,\delta',\delta'' \neq \delta,\delta' \neq \delta'} (d_i^\dagger h_{i+\delta} h_{i+\delta'} h_i + H.c.). \tag{26} \]

The Hamiltonian \([18]\) and the overlap operator \([21]\) for a hole and a DO are very similar to operators that represent interaction of holes in the LHB. Thus the underlying mechanisms of exciton formation, if it occurs, and pairing of holes should be very similar. Fig.\([4]\) depicts the energy dispersion of eight states with lowest energies obtained by solving the eigenvalue problem for the operators \([18]\) and \([26]\) in the case of a single hole and a single DO. The line in the upper part of Fig.\([4]\) represents the lower boundary for the energy of scattering states. There exist three bound excitonic states at the wave vector \( \mathbf{k} = (0,0) \). The ground state has \( d \)-wave symmetry. The pair of bound states with higher energy has \( p \)-wave symmetry, which guarantees that they may take part in dipole transitions and contribute to Raman spectra.

![Energy dispersion of eight lowest states in the UHB with a single hole on a cluster of 32 x 32 sites for J/t = 0.4.](image-url)

For other values of the wave vector up to five exciton states at different energies may exist. The typical distance between the hole spin-polaron and the DO spin-polaron in the exciton state is one lattice spacing which indicates that they are tightly bound and constitute a bipolaron. Among dispersion curves which form in Fig.\([4]\) one may identify bands which shape agree with the form of energy-dispersion curves for the particle-hole excitation measured by Hasan et al. in the RIXS experiment, but the bandwidth in the theoretical approach for a reasonable hopping parameter \( t = 0.35 \text{ eV} \) seems to be much to small, which should be attributed to the fact that we have neglected the possibility of direct hopping to further neighbors. Additional analysis is also needed to understand the dependence of spectral intensity on the position of the wave vector in the Brillouin zone.

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