A toy model to investigate the existence of excitons in the ground state of strongly-correlated semiconductor

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Abstract. Excitons, quasiparticles associated with bound states between an electron and a hole and are typically created when photons with a suitable energy are absorbed in a solid-state material. We propose to study a possible emergence of excitons, created not by photon absorption but the effect of strong electronic correlations. This study is motivated by a recent experimental study of a substrate material SrTiO$_3$ (STO) that reveals strong exitonic signals in its optical conductivity. Here we conjecture that some excitons may already exist in the ground state as a result of the electronic correlations before the additional excitons being created later by photon absorption. To investigate the existence of excitons in the ground state, we propose to study a simple 4-energy-level model that mimics a situation in strongly-correlated semiconductors. The four levels are divided into two groups, lower and upper groups separated by an energy gap, $E_g$, mimicking the valence and the conduction bands, respectively. Further, we incorporate repulsive Coulomb interactions between the electrons. The model is then solved by exact diagonalization method. Our result shows that the toy model can demonstrate band gap widening or narrowing and the existence of exciton in the ground state depending on interaction parameter values.

1. Introduction

Strongly-correlated systems have attracted attention of researchers for decades because of their exotic phenomena. Just to mention some examples, colossal magnetoresistance effect (CMR) in several manganites that describes a large change of the electrical resistance in an applied magnetic field [1], high temperature superconductivity in several cuprates [2], metal-insulator-transitions as observed e.g. in magnetite [3] or certain vanadites, are due to strong electronic correlations.

A number of investigations over the past decades have demonstrated that Coulomb repulsive interactions among electrons dominate the nonlinear optical response of semiconductors [4]. Arita et al [5] have done experimental study using angle-resolved photoemission spectroscopy (ARPES) that reveals the transition from semiconductor into metal in FeSi as temperature increases, which has been attributed to strong correlations among thermally induced carriers near the Fermi energy.

In semiconductors, there are conditions where an electron is excited from the valence band to the conduction band, leaving a hole in the valence band, but the electron and the hole undergo Coulomb attractive interaction. If screening effect of the environment is weak, the electron and the hole may form a bound state acting as a neutral quasiparticle called exciton [6]. This quasiparticle is known to have an important role in determining the properties of semiconductors, especially energy transport. Excitonic signals usually appear on optical absorption and emission of direct-gap semiconductors [7]. A recent experimental study [8] of manganite thin film deposited on a substrate material SrTiO$_3$ (STO) has revealed anomalous excitonic signal in its optical conductivity. Some of these excitonic signals are
found to have energy above the band-gap edge. Based on the study, we conjecture that some excitons may already exist in the ground state as a result of the electronic correlations before the additional excitons being created later by photon absorption. Here, we propose to do a theoretical study to prove, at least in principle, the possibility of existence of excitons in the ground state of strongly correlated semiconductors through a simple model we refer to as a toy model.

In this study we hypothesize that, due to the presence of repulsive Coulomb interactions between electrons, especially the intra-band interactions, electrons would not feel the most comfortable configuration by fully occupying the valence band all the time, while the conduction band is left empty. As a result, the most stable electron configuration, i.e. corresponding to the ground state energy of the system, would be that some electrons are excited to the conduction band leaving some holes in the valence band. We also hypothesize that each electron-hole pair is bound to form an exciton. Our results show that the toy model can demonstrate the band gap widening and narrowing depending on the criteria of parameter values of interaction among electrons. We also find the criteria in which excitonic state occurs in the ground state of our model.

2. Model and computational method

The actual problem we would like to solve may be represented by the following Hamiltonian:

\[
H = \sum_{n\in\{v,c\}} \sum_{\sigma} \epsilon_{n,k,\sigma} \hat{a}_{n,k,\sigma}^\dagger \hat{a}_{n,k,\sigma} + \frac{1}{2} \sum_{n,m,n',m'} \sum_{kk'q} U_{n,m,n',m'}(q) \sum_{\sigma,\sigma'} \hat{a}_{m,v,kr-\mathbf{q},\sigma}^\dagger \hat{a}_{n,kr',\sigma'} \hat{a}_{m,c,k+\mathbf{q},\sigma'} \hat{a}_{n,k,\sigma} \hat{a}_{m,k',\sigma'}
\]

(1)

Here \(n, m, n', m'\) are indices denoting the valence (\(v\)) and the conduction (\(c\)) bands. \(k\) and \(k'\) represent momenta of the electrons, while \(q\) is the transfer momentum between two interacting electrons. \(\sigma\) is the spin index denoting the up (\(\uparrow\)) and the down (\(\downarrow\)) spin components. \(\epsilon_{n,k}\) is the energy of an electron in band \(n\) with momentum \(k\). \(U_{n,m,n',m'}(q)\) is the Coulomb interaction defined in momentum space between two electrons initially in band \(n\) and \(m\) that are scattered off each other into band \(n'\) and \(m'\), with transfer momentum \(q\). The Coulomb interaction couplings \(U_{n,m,n',m'}(q)\) are predicted to be much larger in magnitude for the intra-band (\(n = m = n' = m'\)) scatterings compared to those for inter-band (\(n \neq m, n' \neq m'\)) scatterings.

In the real problem of semiconductors we have to deal with a large number of electrons. It is then practically impossible to solve the actual problem exactly. We consider to restrict our goal to demonstrate the effect of exciton creation due to strong electron correlations only qualitatively. For this purpose, we propose to replace the actual problem with a “toy” model in which we drastically reduce the number of single-electron states to a minimum number that still accommodates possible transitions of electron states, both intra and inter-bands. Here, we define four \(k\) states named 1, 2, 3, and 4, with the corresponding energies \(\epsilon_1, \epsilon_2, \epsilon_3,\) and \(\epsilon_4\), respectively. We group these four energies into two bands (lower and upper) mimicking the valence and the conduction bands as shown in Fig. 1.

![Figure 1. Electronic configuration of actual semiconductor (a) and electronic configuration of the toy model (b) in \(k\)-space.](image)

Each two states in the same band may be considered to be nearly degenerate, that is, \(\epsilon_1 \equiv \epsilon_2, \epsilon_3 \equiv \epsilon_4\). Incorporating the spin degree of freedom, we now have \(2 \times 4 = 8\) single-electron states.
Since we are interested in the half-filling case, we set the number of electrons to be \( \frac{1}{2} \times 8 = 4 \) electrons. With these four electrons distributed among the eight single-electron states, the dimensionality of our 4-electron Hilbert space becomes: 
\[ \#_4 = \frac{8!}{4!(8-4)!} = \frac{8 	imes 7 	imes 6 	imes 5}{4 	imes 3 	imes 2 	imes 1} = 70. \]

Thus, the corresponding 4-electron Hamiltonian matrix is of size 70 \( \times 70 \), which can be easily constructed and diagonalized numerically using standard exact diagonalization subroutine. Now that we only deal with 4 energy levels in our toy model, equation (1) can be reduced into
\[ H = \sum_{\sigma,\sigma'} \varepsilon_{\sigma,\sigma'} \hat{a}_{\sigma}^\dagger \hat{a}_{\sigma'} + \sum_{m,n} \frac{1}{2} U_{mn}\langle \sigma \rangle \sum_{\sigma''} \hat{a}_{\sigma''}\hat{a}_{m\sigma'}\hat{a}_{n\sigma''}\hat{a}_{\sigma''}. \]  

In our model, we assume that the interaction between electrons in the lower band and that between electrons in the upper band has the same strength, we have
\[ U_{\text{lower-upper}}(q = 0) = U_{\text{upper-upper}}(q = 0) = U_{\text{intra-direct}} \]
\[ U_{\text{lower-upper}}(q \neq 0) = U_{\text{upper-upper}}(q \neq 0) = U_{\text{intra-exchange}}. \]

We also make abbreviations
\[ U_{\text{lower-upper}}(q = 0) \equiv U_{\text{inter-direct}} \text{ and } U_{\text{lower-upper}}(q \neq 0) \equiv U_{\text{inter-exchange}}. \]

To examine how parameter values affect the band gap in our model, we use mean field approximation (MFA) where we assume that an electron 'feels' the mean field caused by the presence of other electrons in certain states. The mean field value which is felt by an electron depends on the mean occupation number of other electrons lying in a particular state. Using the MFA we have
\[ n_i n_j = \langle n_i n_j \rangle - \langle n_i \rangle \langle n_j \rangle = \langle n_i \rangle \langle n_j \rangle. \]

Assuming that mean occupation number of each orbital \( \langle n_i \rangle = 2 \), \( \langle n_2 \rangle = 2, \langle n_3 \rangle = 0, \) and \( \langle n_4 \rangle = 0, \) we can derive the criterion for the widening of band gap due to the presence electron-electron interactions
\[ 4U_{\text{inter-direct}} + U_{\text{intra-exchange}} > 3U_{\text{intra-direct}} + 2U_{\text{inter-exchange}}. \]

Before we solve the Hamiltonian in Eq. (2), we want to find an approximate criterion such that the ground-state electron configuration has the existence of one exciton. We do this by applying MFA again and comparing the total energy of state where the valence band is fully occupied by four electrons (i.e. no exciton), \( E_0 \), and the total energy of the excitonic state in which there are three electrons in the lower band and an electron in the upper band (i.e. one exciton), \( E_1 \). To have an exciton in the ground state we need \( E_1 < E_0 \). Application of MFA gives us the criterion we need
\[ 6U_{\text{intra-direct}} - 2U_{\text{inter-exchange}} > E_0 + 3U_{\text{intra-direct}} + 3U_{\text{inter-direct}} - U_{\text{inter-exchange}} - 2U_{\text{inter-exchange}}. \]

We can apply this criterion to tune our interaction parameters in the Hamiltonian Eq. (2) so that the ground-state electron configuration will have an exciton, then obtain the ground-state energy and the corresponding eigen state by means of numerical exact diagonalization.

After we have obtained the ground-state configuration with one exciton, we may calculate its binding energy. We propose an approximate way to calculate the exciton binding energy, that is
\[ E_{\text{Binding}} = \langle \Psi | H_{\text{MF}} - H_{\text{g}} | \Psi \rangle \]

With \( | \Psi \rangle \) being the eigen vector of the excitonic ground state of the system, \( H_{\text{MF}} \) is the MFA version of the Hamiltonian, and \( H_{\text{g}} \) is the Hamiltonian stated in Eq. (2).

To display the exact diagonalization results in terms of the density of states (DOS), we need to construct the corresponding retarded Green function through Lehmann representation [9]. For zero temperature the expression is
\[ G_{i\sigma}(\omega + i0^+) = \frac{1}{Z} \left\{ \sum_{l=1}^{\#_{\text{N-1}}} \frac{\left| \langle l | \hat{a}_{i\sigma}^\dagger \hat{a}_{l\sigma} | \rangle \right|^2}{\omega + i0^+ - (E_l(\sigma) - E_{\text{g}}(\sigma))} \right\} + \frac{1}{\sum_{n=1}^{\#_{\text{N-1}}} \frac{\left| \langle n | \hat{a}_{i\sigma}^\dagger \hat{a}_{n\sigma} | \rangle \right|^2}{\omega + i0^+ - (E_n(\sigma) - E_{\text{g}}(\sigma))}. \]

The DOS can then be obtained through the relation
\[ \text{DOS}(\omega) = -\frac{1}{\pi} \sum_{l=1}^{\#_{\text{N-1}}} \text{Im} \, G_{i\sigma}(\omega + i0^+). \]

Further, the corresponding chemical potential or the Fermi energy can be extracted by solving
\[ \int d\omega \, \text{DOS}(\omega) f(\mu, T, \omega) = N, \]
where \( f(\mu, T, \omega) = \frac{1}{e^{\frac{\mu - \omega}{k_B T}} + 1} \) is the Fermi distribution function, and \( N = 4 \).
3. Results and discussion

3.1. Band gap
In this section we want to examine our model on how the resulting band gap depends on the value of interaction parameters. The table below lists the parameters we use in the calculation of DOS to see the band gap narrowing and widening based on the criterion we have presented before.

Table 1. Parameters used to calculate DOS in band gap widening and narrowing

| Physical Parameters | Value (eV) | Physical Parameters | Value (eV) | Value (eV) |
|---------------------|------------|---------------------|------------|------------|
| \( \varepsilon_1 \)  | 0          | \( U_{\text{intra-direct}} \) | 1.5        | 1.5        |
| \( \varepsilon_2 \)  | 0          | \( U_{\text{inter-direct}} \) | 1          | 1.25       |
| \( \varepsilon_3 \)  | 3          | \( U_{\text{intra-exchange}} \) | 0.003      | 0.003      |
| \( \varepsilon_4 \)  | 3          | \( U_{\text{inter-exchange}} \) | 0.002      | 0.0021     |

Using the interaction parameters listed in Table 1 we obtain the results as shown in Fig. 2. The figure clearly shows an energy shift due to the presence of interactions. The DOS in Fig. 1a gives chemical potential about 6.26 eV, while in Fig. 1b around 5.76 eV, which are inside the band gap as expected. By comparing the band gap of the two conditions we see that Fig. 1a exhibits the band gap narrowing while Fig. 1b shows the band gap widening.

![Figure 2. DOS of interacting system (black) and non-interacting system (red) showing the narrowing (a) and the widening (b) of the band gap.](image)

3.2. Ground state of strongly-correlated system
Earlier we have proposed the condition for obtaining the ground state with the presence of one exciton. Here we vary the interaction parameters to examine the criterion we presented before.

Table 2. Parameters used to investigate the existence of exciton in the ground state with band gap narrowing and widening.

| Physical Parameters | Value (eV) | Physical Parameters | Value (eV) | Value (eV) |
|---------------------|------------|---------------------|------------|------------|
| \( \varepsilon_1 \)  | 0          | \( U_{\text{intra-direct}} \) | 3.5        | 4.6        |
| \( \varepsilon_2 \)  | 0          | \( U_{\text{inter-direct}} \) | 2.5        | 3.5        |
| \( \varepsilon_3 \)  | 3          | \( U_{\text{intra-exchange}} \) | 0.0055     | 0.008      |
| \( \varepsilon_4 \)  | 3          | \( U_{\text{inter-exchange}} \) | 0.004      | 0.007      |

Figure 3 shows the calculated DOS using interaction parameters in Table 2. We can see the difference of DOS using MFA and the exact solution. Figure 3a shows that there is a gap narrowing, but the DOS shows splitting of the energy level in both bands. The exact solution gives the chemical...
potential about 11.67 eV with an electron in the upper band and three electrons in the lower band. Using Eq. (6) we find the exciton binding energy of 2.49 eV. Although the parameter values we use exhibit excitonic state, we see that there is a gap narrowing in the energy band spectrum. This is because the parameter values satisfy the condition needed for excitonic state, but do not satisfy the condition for the gap widening. Figure 3b shows the situation when the parameter values meet both criteria for the emergence of an exciton in the ground state and the widening of the band gap. In this case the exciton binding energy is 3.41 eV and the chemical potential of the system is at 15.46 eV.

Figure 3. DOS of interacting system (black) with an exciton in the ground state and non-interacting system (red) showing narrowing (a) and widening (b) of the band gap.

4. Conclusion
We have presented our theoretical study to investigate the existence of excitons in the ground state of a toy model mimicking strongly-correlated semiconductor. The toy model can predict both band gap widening and narrowing due to the interaction of electrons in the system based on the criterion we obtain using MFA. In addition, we have also presented the criterion for the parameter values that yields an exciton in the ground state. We have proposed a way to calculate the exciton binding energy and implemented the formula for certain parameter values. The exciton binding energies we obtained in these calculations happen to be much larger than typical exciton binding energy. However, this should not be too surprising, as we did the calculations on the toy model, not the actual semiconductor. Overall, we believe that our toy model and method of calculations can give us some physical insight about the mechanism of exciton formation in the ground state of a strongly-correlated semiconductor.

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