Remarks on the Role of Excitonic Renormalization in the Metal-Insulator Transition

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The existence of a phase transition to an excitonic state has been predicted theoretically many years ago. Efforts to observe this transition were concentrated on semi-metals under the effect of external pressure. These experiments could not confirm the theoretical predictions. Recently it has been claimed that an excitonic transition occurs in a doped narrow-band-gap semiconductor at moderate pressures. We have studied the possibility of an excitonic transition in the presence of hybridization in a two-band model. We show that a true phase transition never occurs in the presence of hybridization since the one-body mixing term acts as a conjugate field to the order parameter of the excitonic phase. We study the dependence of the zero temperature order parameter on: i) the relation between the effective masses of the two-bands, ii) the strength of the hybridization and iii) the intensity of the electron-hole attraction.

I. Introduction

Recently Wachter and colaborators[1] have claimed to observe a transition to an excitonic insulator in a doped narrow-band-gap semiconductor at moderate pressures. They detected the excitonic state at the semimetal- semiconductor transition monitoring the resistivity when the gap is continuously closed by external pressure. The resistivity at low temperatures showed a huge peak as a function of applied pressure which they attibuted to the long predicted excitonic phase transition[2]. They also presented data of the Hall constant which reveals that this resistivity anomaly is caused by a condensation of free carriers, related to an excitonic insulating ground state. An excitonic state corresponds to a bound state formed when electrons in the conduction band and holes in the valence band attract each other, so that they cannot contribute to the conductivity of the materials[3−7]. Knox[3] also argued about this anomaly in the case of an indirect-band-gap semiconductor: the difference between the energy gap E_G and the binding energy E_B of an exciton corresponds to the minimum energy necessary to create an exciton in a semiconductor. In a process in which E_G is reduced by external pressure but retains the excitonic energy E_G, as soon as $E_G < E_B$ the conventional insulating ground state would be unstable against the formation of excitons and excitonic insulator would result. Despite many efforts to observe this transition, mainly concentrated on semi-metals under pressure[6], the existence of the excitonic insulator has never been observed.

With renewed interest in this subject and motivated by recent challenging experiments[1], we investigate the possibility of this excitonic transition in presence of hybridization in a two-band model. We point out that no sharp excitonic phase transition occurs when external pressure is applied. The reason is that the hybridization, which depends on pressure, acts as a conjugate field to the order parameter of the excitonic phase and destroys this transition[8]. The effect is similar to that of a ferromagnetic system in the presence of an uniform external magnetic field which destroys the ferromagnetic transition.

In this paper we study the dependence of the zero temperature order parameter of the excitonic phase as function of: i) the relation between the effective masses of the two-bands, ii) the strength of the hybridization and iii) the intensity of the electron-hole attraction.

Some years ago Nünez-Regueiro and Avignon[9] have studied the effect of excitonic terms in the renormalization of hybridization V close to a valence transition. In their work the most relevant interaction is the Coulomb repulsion between the electrons in the localized f-level and those in the conduction d-band. In our approach, we are interested in the metal-insulator transition which occurs as function of pressure. For a semi-metal with two- electrons per site we have shown that in a two-band model such a transition requires a critical value of hibridization V_c to occur[10]. We are interested in studying this problem close to V_c, where the gap is small and therefore the dominant contribution of the Coulomb interaction is the electron-hole attraction.

II. Hamiltonian and excitonic phase

The Hamiltonian which describes the dynamics of our system is:

$$H = \sum_k \epsilon_k^a a_k^\dagger a_k + \sum_k \epsilon_k^b b_k^\dagger b_k + \sum_k V_k (a_k^\dagger b_k + b_k^\dagger a_k) - \sum_{k,k',q} G(q) a_{k+q}^\dagger a_k b_{k'-q}^\dagger b_{k'} \tag{1}$$

where ϵ_k^a and ϵ_k^b represent the energies for electrons in the large conduction band and in the narrow localized band which we from now on we refer to generically as an a-band and b-band, respectively. The operators $a_k^\dagger$, a_k create and destroy electrons in the wide band and $b_k^\dagger$, b_k are creation and annihilation operators of electrons in the narrow band. G is the effective attractive interaction between spinless electrons and holes and V is the mixing term, which arises from the crystalline potential. If it were not for the attractive term, the Hamiltonian above could be exactly diagonalized giving rise to two hybrid bands[11]. However the many-body term due to the effective attractive interaction G makes this a difficult problem for which an approximation must be introduced. We shall employ the equation of motion method[12] to calculate the order parameter associated with the excitonic phase written as $\langle b_k^\dagger a_k \rangle$. For this purpose we introduce initially the frequency-dependent Green's function $\langle\langle a_k ; b_k^\dagger \rangle\rangle_\omega$, which obeys the following equation of motion

$$\omega \langle\langle a_k ; b_{k'}^\dagger \rangle\rangle_\omega = \epsilon_k^a \langle\langle a_k ; b_k^\dagger \rangle\rangle_\omega + V_k \langle\langle b_k ; b_k^\dagger \rangle\rangle_\omega - \sum_{k',q} G(q) \langle\langle a_{k-q} b_{k'-q}^\dagger b_{k'} ; b_k^\dagger \rangle\rangle_\omega \tag{2}$$

In the equation above, new propagators were generated due to both the mixing term and the attractive interaction. For the mixing generated propagator we have the following equation of motion

$$\omega \langle\langle b_k ; b_k^\dagger \rangle\rangle_\omega = 1 + \epsilon_k^b \langle\langle b_k ; b_k^\dagger \rangle\rangle_\omega + V_k \langle\langle a_k ; b_k^\dagger \rangle\rangle_\omega - \sum_{k',q} G(q) \langle\langle a_{k'+q}^\dagger a_{k'} b_{k+q} ; b_k^\dagger \rangle\rangle_\omega \tag{3}$$

For the second Green's function $\langle\langle a_{k-q} b_{k'-q}^\dagger b_{k'} ; b_k^\dagger \rangle\rangle_\omega$ which appears due to the many-body interaction, we use a convenient mean-field approximation:

$$\langle\langle a_{k-q}b^{\dagger}_{k'-q}b_{k'};b^{\dagger}_{k}\rangle\rangle_{\omega} \approx \langle a_{k-q}b^{\dagger}_{k'-q}\rangle\langle\langle b_{k'};b^{\dagger}_{k}\rangle\rangle_{\omega}$$

$$\langle\langle a^{\dagger}_{k'+q}a_{k'}b_{k'+q};b^{\dagger}_{k}\rangle\rangle_{\omega} \approx -\langle a^{\dagger}_{k'+q}b_{k+q}\rangle\langle\langle a_{k'};b_{k}\rangle\rangle_{\omega} \tag{4}$$

We have now a closed system of equations given by

$$(\omega-\epsilon^{a}_{k})\langle\langle a_{k};b^{\dagger}_{k}\rangle\rangle_{\omega} = V_{k}\langle\langle b_{k};b^{\dagger}_{k}\rangle\rangle_{\omega} - \sum_{k',q} G(q)\langle a_{k-q}b^{\dagger}_{k'-q}\rangle\langle\langle b_{k'};b^{\dagger}_{k}\rangle\rangle_{\omega} \tag{5}$$

and

$$(\omega-\epsilon^{b}_{k})\langle\langle b_{k};b^{\dagger}_{k}\rangle\rangle_{\omega} = 1 + V_{k}\langle\langle a_{k};b^{\dagger}_{k}\rangle\rangle_{\omega} - \sum_{k',q} G(q)\langle a^{\dagger}_{k'+q}b_{k+q}\rangle\langle\langle a_{k'};b^{\dagger}_{k}\rangle\rangle_{\omega} \tag{6}$$

After solving this system of equations for $q=0$ and, for simplicity, neglecting the k-dependence of V, we obtain

$$\langle\langle a_{k};b^{\dagger}_{k}\rangle\rangle_{\omega} = \frac{\tilde{V}_{k}}{[(\omega-\epsilon^{a}_{k})(\omega-\epsilon^{b}_{k})-\tilde{V}^{2}_{k}]} \tag{7}$$

where $\tilde{V}_{k} = V + G\Delta_{k}$, with $\Delta_{k} = \langle b^{\dagger}_{k}a_{k}\rangle$. The new energies of excitation of the system are given by the poles of the propagator above, which means they are the roots of the equation

$$(\omega-\epsilon^{a}_{k})(\omega-\epsilon^{b}_{k}) - \tilde{V}^{2}_{k} = 0 \tag{8}$$

so that

$$\omega_{1,2}(k) = \frac{1}{2}\left\{\epsilon^{a}_{k}+\epsilon^{b}_{k} \pm \sqrt{(\epsilon^{a}_{k}-\epsilon^{b}_{k})^{2}+4\tilde{V}^{2}_{k}}\right\} \tag{9}$$

The excitonic propagator can be rewritten as:

$$\langle\langle a_{k};b^{\dagger}_{k}\rangle\rangle_{\omega} = \frac{\tilde{V}_{k}}{\omega_{1}(k)-\omega_{2}(k)}\left\{\frac{1}{\omega-\omega_{1}(k)} - \frac{1}{\omega-\omega_{2}(k)}\right\} \tag{10}$$

From which we obtain the following expression for the excitonic order parameter:

$$\Delta_{k} = \frac{\tilde{V}_{k}}{|\omega_{1}(k)-\omega_{2}(k)|}\int d\omega f(\omega)\{\delta[\omega-\omega_{1}(k)] - \delta[\omega-\omega_{2}(k)]\} \tag{11}$$

In order to obtain explicit results for the excitonic order parameter we adopt the homothetic band model[13] which consists in taking

$$\begin{cases} \epsilon^{b}_{k} = \epsilon_{k} \\ \epsilon^{a}_{k} = \alpha\epsilon_{k} + \beta \end{cases}$$

The quantity $\alpha(\alpha<1)$ may be interpreted as taking into account the different effective masses of the electrons in the narrow a-band and the large b-band, i.e. $(m_{b}/m_{a}) = \alpha$. The quantity β gives the shift of the narrow band with respect to the large band.

Now we introduce two new functions $g_{1}(\omega)$ and $g_{2}(\omega)$ [10] through the following equation

$$[\omega-\omega_{1}(k)][\omega-\omega_{2}(k)] = \alpha[g_{1}(\omega)-\epsilon_{k}][g_{2}(\omega)-\epsilon_{k}] \tag{12}$$

from which we get

$$g_{2,1}(\omega) = \frac{1}{2\alpha}\left\{(1+\alpha)\omega - \beta \pm \sqrt{[(\alpha-1)\omega+\beta]^{2}+4\alpha\tilde{V}^{2}}\right\} \tag{13}$$

The energies of the bottom of the hybrid bands correspond to $g(E^{i}_{B}) = 0$ with $i = 1,2$

$$E^{2,1}_{B} = \frac{1}{2}\{\beta \pm [\beta^{2}+4\tilde{V}^{2}]^{1/2}\} \tag{14}$$

while the energies of the top are obtained when $g(E_T^i) = D$, where D is the bandwidth of the large conduction b-band,

$$E_T^{2,1} = \frac{D}{2}\left\{(1+\alpha) + \frac{\beta}{D} \pm \left[\left((\alpha-1)+\frac{\beta}{D}\right)^2 + 4\left(\frac{\tilde{V}}{D}\right)^2\right]^{1/2}\right\} \tag{15}$$

For $\tilde{V} = 0$, we have $E_B^1 = 0$, $E_T^1 = D$, $E_B^2 = \beta$ and $E_T^2 = \alpha D + \beta$, which are in agreement with the definitions of α and β. Considering the new functions $g_i(\omega)$ we obtain the following equation for the excitonic order parameter

$$\Delta = \frac{1}{\alpha}\int d\omega \frac{\tilde{V}}{|g_1(\omega) - g_2(\omega)|} f(\omega)\{N[g_1(\omega)] - N[g_2(\omega)]\} \ , \tag{16}$$

where

$$N(\omega) = \sum_k \delta(\omega - \epsilon_k)$$

$$|g_1(\omega) - g_2(\omega)| = \frac{1}{\alpha}\left[(\omega(1-\alpha)-\beta)^2 + 4\alpha\tilde{V}^2\right]^{1/2}$$

and $f(\omega)$ is the Fermi function.

We also obtain an expression for the gap Δ_G between the two bands as a function of the hybridization V and the electron-hole interaction G. It corresponds to the difference in energy between the top of the first hybrid band E_T^1 and the bottom of the second E_B^2 :

$$\frac{\Delta_G}{D} = \frac{1}{2}\left\{\left[\left(\alpha - 1 + \frac{\beta}{D}\right)^2 + 4\left(\frac{\tilde{V}}{D}\right)^2\right]^{1/2} + \left[\left(\frac{\beta}{D}\right)^2 + 4\left(\frac{\tilde{V}}{D}\right)^2\right]^{1/2} - (1+\alpha)\right\} \tag{17}$$

Consequently for a two-band system the opening of a hybridization gap, contrary to what occurs for the Anderson lattice model, requires a critical value of renormalized hybridization V_c given by

$$\frac{\tilde{V}_c}{D} = \frac{1}{2}\left\{\frac{\left[2\alpha - \frac{\beta}{D}(\alpha-1)\right]^2}{(1+\alpha)^2} - \left(\frac{\beta}{D}\right)^2\right\}^{1/2} \ . \tag{18}$$

III. The divalent semi-metal

To study the possibility of an excitonic transition in the presence of hybridization we first investigate the case of two square symmetric bands with respect to the Fermi level fixed at $\mu = \frac{3}{4}D$, such that $\alpha = 1$ and $\beta = D/2$. This corresponds to a divalent semi-metal with two electrons per site, where μ is at the crossing of the bands[8]. In this case, we have the following expression for the excitonic order parameter

$$\Delta = \frac{(\tilde{V}/D)}{2[(1/4)^2 + (\tilde{V}/D)^2]^{1/2}}\left\{1 - 2\int_0^{E_T^1} N_1(\omega)d\omega\right\} \ , \tag{19}$$

where

$$E_T^1 = D\left\{\frac{5}{4} - \left[\left(\frac{1}{4}\right)^2 + \left(\frac{\tilde{V}}{D}\right)^2\right]\right\}^{1/2} \ , \tag{20}$$

so that we have a very simple analytical expression for the excitonic order parameter at $T = 0$:

$$\Delta = \frac{V}{G - G_c} \ . \tag{21}$$

We notice there is a critical value for the electron-hole attraction $G_c = D$, for which the excitonic order parameter is different from zero in the absence of hybridization. This is formally similar to an Stoner-like criterion for the appearance of magnetic order in a metallic system, where, in the present case, the hybridization plays the role of magnetic field conjugate to

the order parameter Δ. Consequently we do not expect a sharp phase transition to an excitonic to occur in presence of hybridization in spite of what the mean- field equation above suggests. Strictly there is no singularity in any physical quantity when G approaches to G_c whenever $V \neq 0$ and the order parameter should obey a scaling relation as $\Delta = |g|^{\beta} f[V/|g|^{\phi}]$, where $g = G - G_c$ and β and ϕ are critical cxponents. At $G = G_c$, one has $\Delta \propto V^{1/\delta}$ with $\delta = \phi/\beta$.

In practice however V and G vary with external pressure differently from the magnetic case where the magnetic field is completely independent of the parameters of the system as the density of states and Coulomb repulsion. The only zero temperature phase transition occuring in our model for the divalent semi-metal is a metal-insulator transition associated with the opening of a gap at the Fermi level for a critical value of the hybridization given by

$$\frac{V_c}{D} = \frac{\sqrt{3}}{4} - \frac{G}{D}\Delta \tag{22}$$

where due to the excitonic correlations this value is renormalized with respect to that of the non-interacting system[8]. Substituting equation (21) in (17) for the symmetric case, we obtain the following expression for the renormalized gap:

$$\frac{\Delta_G}{D} = \left[\frac{1}{4} + 4\Delta^2\right]^{1/2} - 1 \ . \tag{23}$$

Let us now study the symmetric case for two parabolic bands at $T = 0$. As before the Fermi level is at $\frac{3}{4}D$ and the conduction band is centered at $D/2$. In this case we obtain the following equation for the excitonic order parameter

$$\begin{aligned}
\Delta &= \frac{1}{2}\frac{\tilde{V}/D}{[(1/4)^2 + (\tilde{V}/D)^2]^{1/2}} \left\{ 1 - \frac{2}{\pi} \left\{ \frac{3}{4} - \left[\left(\frac{1}{4}\right)^2 + \left(\frac{\tilde{V}}{D}\right)^2 \right]^{1/2} \right\}^{1/2} \right. \times \\
&\times \left\{ \frac{3}{2} \left[\left(\frac{1}{4}\right)^2 + \left(\frac{\tilde{V}}{D}\right)^2 \right]^{1/2} - \frac{3}{8} - \left(\frac{\tilde{V}}{D}\right)^2 \right\}^{1/2} \\
&+ \left. \frac{1}{2\pi} \arcsin \left\{ \frac{3}{2} - 2 \left[\left(\frac{1}{4}\right)^2 + \left(\frac{\tilde{V}}{D}\right)^2 \right]^{1/2} \right\} + \frac{9}{200\pi} \right\} \ .
\end{aligned} \tag{24}$$

We solve this equation self-consistently and observe that there is a critical value for the renormalized electron-hole interaction, which also is independent of the one-body mixing term V. We emphasize again that there is no real phase transition or singularities at G_c due to the presence of the hybridization.

IV. General case

Finally we investigate the case of two bands at $T = 0$ for which α and β do not have any particular values and the Fermi level is at μ. In this case we have

$$\begin{aligned}
\Delta &= \frac{1}{\alpha} \left\{ \int_{E_B^1}^{\mu} d\omega \frac{\tilde{V}}{[g_1(\omega) - g_2(\omega)]} N[g_1(\omega)] \right. \\
&- \left. \int_{E_B^2}^{\mu} d\omega \frac{\tilde{V}}{[g_2(\omega) - g_2(\omega)]} \right\}
\end{aligned} \tag{25}$$

where the bottoms of the two bands $E_B^{1,2}$ are given by equation (14). For square bands the expression for the excitonic order parameter $\Delta(\alpha, \beta)$ is

$$\Delta(\alpha,\beta) = \frac{V}{D(1-\alpha)} \ln \frac{\mathcal{A}(\alpha,\beta)}{\mathcal{B}(\alpha,\beta)} \left\{ 1 - \frac{G}{D(1-\alpha)} \ln \frac{\mathcal{A}(\alpha,\beta)}{\mathcal{B}(\alpha,\beta)} \right\}^{-1} \tag{26}$$

where

$$\mathcal{A}(\alpha,\beta) = E_B^2(1-\alpha) - \beta + \{[E_B^2(1-\alpha)-\beta]^2 + 4\alpha\tilde{V}^2\}^{1/2}$$

and

$$\mathcal{B}(\alpha,\beta) = E_B^1(1-\alpha) - \beta + \{[E_B^1(1-\alpha)-\beta]^2 + 4\alpha\tilde{V}^2\}^{1/2} \quad (27)$$

with $E_B^{1,2}$ given before and

$$\tilde{V}(\alpha,\beta) = V + G\Delta(\alpha,\beta) \ .$$

We notice that $\Delta(\alpha,\beta)$ is independent of μ and for $\beta = D/2$ and in the lim $\alpha \to 1$ this expression reduces correctly to that for the symmetric case. It is interesting to observe that the expression which gives $\Delta(\alpha,\beta)$ can be cast in a form which resembles the Stoner criterion. The expression for the gap is given by equation 17.

The set of equations above can be used to treat a situation where for $V = 0$ one has a localized level ($\alpha = 0$) separated from a band of conduction states ($\beta > D$). In this case, even for a fixed value of hybridization, it is possible to drive a semiconductor-metal transition, i. e. $\Delta_G = 0$, through a variation of G/D which in principle can be accomplished through external pressure.

V. Conclusions

We have introduced a two-band model to investigate the possibility of the existence of an excitonic phase transition in presence of hybridization. The dominant interaction was taken to be the electron-hole attraction. We found differently from the Anderson lattice approach, that there is a critical value of the hybridization parameter for a gap to appear. This value is renormalized by the presence of excitonic correlations. We have argued however that a phase transition for an excitonic phase never occurs, since the one-body hybridization acts as a conjugate field to the order parameter of this phase. We have shown that hybridization induces the same correlations which characterize this excitonic phase. Finally we have obtained a set of equations (Eq. 26-28) which can describe the physical situation of the experiments of Wachter and colaborators[1]. Even in the absence of an excitonic phase transition, excitonic correlations should play a fundamental role on the interpretation of their experiments.

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