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LETTER TO THE EDITOR

Excitonic phase transitions in electronic systems

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Abstract. Although predicted theoretically, excitonic phase transitions have never actually been observed. Recently it has been claimed that they can occur in some strongly correlated materials. We study the possibility of an excitonic transition in a two-band model and show that a true phase transition never occurs in the presence of hybridization. We suggest an alternative interpretation for these experiments based on the opening or closing of a hybridization gap at a critical pressure.

Recently Wachter and collaborators [1, 2] have claimed to observe a transition to an excitonic insulator in a doped narrow-bandgap semiconductor at moderate pressures and in a strongly correlated metal [2]. The evidence for this transition is obtained by monitoring the resistivity close to the metal–insulator transition, as a bandgap is continuously closed or opened by external pressure. The resistivity at low temperatures showed a huge peak as a function of applied pressure which they attributed to the long-predicted excitonic phase transition [3]. They also presented data on the Hall constant which reveals that this resistivity anomaly is caused by a reduction in the number of carriers.

With interest in this subject renewed by these challenging experiments [1, 2] and the close connection of the materials which have been investigated with Kondo insulators [4], we study the possibility of this excitonic transition in the 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 for this is that the hybridization which depends on pressure acts as a conjugate field for the order parameter of the excitonic phase and destroys this transition [5]. The effect is similar to that of a ferromagnetic system in the presence of a uniform external magnetic field. The mixing term, however, is strongly renormalized by excitonic correlations. We suggest an interpretation for the experiments of Wachter *et al* on $Sm_{0.75}La_{0.25}S$ [2] on the basis of a metal–insulator (MI) transition associated with the appearance of a hybridization gap at a critical pressure. This metal–insulator transition is in the universality class of the *density-driven transitions*, for which the relevant critical exponents have been obtained previously [5]. This seems to hold even in the presence of correlations, as we find here, as long as the MI transition is not accompanied by the appearance of long-range magnetic order [5]. A characteristic feature of this transition is that the gap opens or closes linearly with pressure near the critical pressure. This is a direct consequence of the fact that the gap exponent [5] assumes the value $\nu z = 1$.

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The Hamiltonian which describes 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 narrow *a band* and in the large conduction *b band*, respectively. The operators $a_k^\dagger$, a_k create and destroy electrons in the narrow band and $b_k^\dagger$, b_k are creation and annihilation operators for electrons in the wide conduction band. V is the mixing term, which arises from the crystalline potential and G is the effective attractive interaction between spinless electrons and holes [6]. For the situation that we are interested in this is the most important interaction. Note that we should have taken into account in equation (1) the Coulomb repulsion between the electrons in the narrow a band. Since, however, as we argued before [5] these interactions are irrelevant, in the renormalization group sense, for the metal–insulator transition we are going to study we do not consider it, for simplicity. In fact within the approximation that is generally used to treat the Hamiltonian above [3] and that we also use in this letter, these interactions merely shift the energy of the *a electrons*.

We point out that we adopt here a different approach to the excitonic problem [3]. Instead of starting with two hybridized bands and the electron–hole attraction [3], we include explicitly the hybridization in the starting Hamiltonian to imply that it should be treated together with the many-body correlations and not separately. The main difference is that within our approach the gap which eventually opens or closes as will be shown below and is *experimentally accessible* turns out to be a truly many-body quantity. In the standard treatment [3] where the bands are diagonalized separately from the correlations one arrives at the artificial situation where the gap is a simple one-body effect.

If it were not for the attractive term, the Hamiltonian given by equation (1) could be exactly diagonalized giving rise to two hybrid bands [7]. 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 Green's function method [8] to obtain the order parameter associated with the excitonic phase, namely, $\Delta = \sum_k \langle b_k^\dagger a_k \rangle$. When calculating the equation of motion for the Green's function $\langle\langle a_k; b_k^\dagger \rangle\rangle_\omega$ we find it gives rise to new propagators. Introducing a a convenient mean-field approximation [3]:

$$\begin{aligned} \langle\langle a_{k-q} b_{k'-q}^\dagger b_{k'}; b_k^\dagger \rangle\rangle_\omega &\approx \langle a_{k-q} b_{k'-q}^\dagger \rangle \langle\langle b_{k'}; b_k^\dagger \rangle\rangle_\omega \\ \langle\langle a_{k'+q}^\dagger a_{k'} b_{k'+q}; b_k^\dagger \rangle\rangle_\omega &\approx -\langle a_{k'+q}^\dagger b_{k+q} \rangle \langle\langle a_{k'}; b_k \rangle\rangle_\omega . \end{aligned} \tag{2}$$

we obtain a closed set of equations which can be solved to yield

$$\langle\langle a_k; b_k^\dagger \rangle\rangle_\omega = \frac{\tilde{V}_k}{[(\omega - \epsilon_k^a)(\omega - \epsilon_k^b) - \tilde{V}_k^2]} \tag{3}$$

where $\tilde{V}_k = V + G\Delta_k$, with $\Delta_k = \langle b_k^\dagger a_k \rangle$. We have neglected the k-dependence of G and V for simplicity. The new energies of excitation of the system are given by the poles of the above Green's function, i.e., by the roots of the equation

$$(\omega - \epsilon_k^a)(\omega - \epsilon_k^b) - \tilde{V}_k^2 = 0 \tag{4}$$

and so

$$\omega_{1,2}(k) = \frac{1}{2}\left\{ \epsilon_k^a + \epsilon_k^b \pm \sqrt{(\epsilon_k^a - \epsilon_k^b)^2 + 4\tilde{V}_k^2} \right\}. \tag{5}$$

The excitonic propagator can be rewritten as

$$\langle\langle a_k; b_k^\dagger\rangle\rangle_\omega = \frac{\tilde{V}_k}{\omega_1(k) - \omega_2(k)} \left\{ \frac{1}{\omega - \omega_1(k)} - \frac{1}{\omega - \omega_2(k)} \right\} \tag{6}$$

from which we obtain

$$\Delta_k = \frac{\tilde{V}_k}{|\omega_1(k) - \omega_2(k)|} \int \mathrm{d}\omega \; f(\omega) \{\delta[\omega - \omega_1(k)] - \delta[\omega - \omega_2(k)]\} \tag{7}$$

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

In order to obtain explicit results for the excitonic order parameter we adopt the homothetic band model [9] which consists in taking

$$\epsilon_k^b = \epsilon_k \qquad \epsilon_{k\sigma}^a = \alpha\epsilon_k + \beta.$$

The quantity α ($\alpha < 1$) 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 $g_2(\omega)$ [7] through the following equation:

$$[\omega - \omega_1(k)][\omega - \omega_2(k)] = \alpha[g_1(\omega) - \epsilon_k][g_2(\omega) - \epsilon_k] \tag{8}$$

from which we get

$$g_{2,1}(\omega) = \frac{1}{2\alpha} \left\{ (1+\alpha)\omega - \beta \pm \sqrt{[(\alpha-1)\omega + \beta]^2 + 4\alpha\tilde{V}^2} \right\}. \tag{9}$$

The energies of the bottoms of the hybrid bands correspond to $g_i(E_B^i) = 0$ with $i = 1, 2$

$$E_B^{2,1} = \frac{1}{2}\{\beta \pm [\beta^2 + 4\tilde{V}^2]^{1/2}\} \tag{10}$$

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

$$E_T^{2,1} = \frac{D}{2} \left\{ (1+\alpha) + \frac{\beta}{D} \pm \left[\left((\alpha - 1) + \frac{\beta}{D} \right)^2 + 4 \left(\frac{\tilde{V}}{D} \right)^2 \right]^{1/2} \right\}. \tag{11}$$

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:

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

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

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

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:

$$\frac{\Delta_G}{D} = \frac{1}{2} \left\{ \left[\left(\alpha - 1 + \frac{\beta}{D} \right)^2 + 4 \left(\frac{\tilde{V}}{D} \right)^2 \right]^{1/2} + \left[\left(\frac{\beta}{D} \right)^2 + 4 \left(\frac{\tilde{V}}{D} \right)^2 \right]^{1/2} - (1+\alpha) \right\}. \tag{12}$$

Consequently for a two-band system the opening of a hybridization gap—contrary to what occurs for the Anderson lattice model [10]—requires a critical value of the renormalized hybridization $(\tilde{V}/D)_c$ given by

$$\left(\frac{\tilde{V}}{D}\right)_c = \frac{1}{2}\left\{\frac{[2\alpha - (\beta/D)(\alpha-1)]^2}{(1+\alpha)^2} - \left(\frac{\beta}{D}\right)^2\right\}^{1/2}. \tag{13}$$

Notice that for $\alpha \to 0$, $\tilde{V}_c \to 0$ as expected for a collection of localized levels. In this case also $\Delta_G \propto \tilde{V}^2$ [10] contrary to in our two-band problem where close to $(\tilde{V}/D)_c$ we find

$$\frac{\Delta_G}{D} = \left|\left(\frac{\tilde{V}}{D}\right) - \left(\frac{\tilde{V}}{D}\right)_c\right|$$

so the gap opens or closes linearly near $\tilde{V}_c$, i.e. $\nu z = 1$, as in the non-interacting case [5]. Within the assumption that $|(\tilde{V}/D) - (\tilde{V}/D)_c| \propto |P - P_c|$ where P_c is the critical pressure, this result, i.e. $\Delta_G \propto |P - P_c|$, describes the observed behaviour for $Sm_{0.85}La_{0.15}S$ [2]. We emphasize that the relevant variable here is $(\tilde{V}/D)$. This can increase or decrease with pressure, for a given pressure range, so a gap can either open or close depending on the relative pressure dependence of the hybridization and bandwidth. So our approach may also be useful for describing the metal–insulator transition in the compound SmB_6 [11, 12].

In order to study the possibility of an excitonic transition in the presence of hybridization we 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 [5]. In this case, we get a simple expression for the $T = 0$ excitonic order parameter

$$\Delta = \frac{V}{G - G_c}. \tag{14}$$

Then there is a critical value for the electron–hole attraction G_c, $G_c = D$, for which the excitonic order parameter is different from zero even in the absence of hybridization. This is formally similar to a Stoner-like criterion for the appearance of ferromagnetic order in a metallic system. In the present case, the hybridization plays the role of the uniform magnetic field conjugate to the order parameter Δ. The fact that a k-independent, local hybridization V acts as the conjugate field of the excitonic order parameter, independently of any particular approximation, can be directly seen from the Hamiltonian, equation (1), with the one-body mixing term written as $V\sum_k (a_k^\dagger b_k + b_k^\dagger a_k) = V\Delta$. This shows that V couples directly to Δ. For the case of d–f hybridization there are different mechanisms, for example involving phonons, which can provide local mixing between these orbitals with different symmetries [13]. Consequently we do not expect a sharp phase transition to an excitonic phase to occur whenever an external parameter which changes the hybridization—external pressure for example—is varied. There is no singularity in any physical quantity when G approaches G_c, whenever $V \neq 0$, contrary to what the simple mean-field equation above suggests. However, we expect strong renormalization of the physical quantities, such as the hybridization, due to excitonic correlations for $G \approx G_c$. The only zero-temperature phase transition which can occur in our model as pressure is varied is a metal–insulator transition associated with the opening of a hybridization gap at a critical value of the ratio $(V/D)_c$. For the divalent semi-metal discussed above this occurs at $(V/D)_c = [(\sqrt{3}/4) - (G/D)\Delta]$, where due to the excitonic correlations this value is renormalized with respect to that of the non-interacting system [5].

For completeness we give the self-consistency equation for the renormalized hybridization for general α and β and square bands:

$$V = \tilde{V}\left[1 - \frac{G}{D(1-\alpha)} \ln\left|\frac{\mathcal{A}}{\mathcal{B}}\right|\right] \tag{15}$$

with

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

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

with E_B^1 and E_B^2 given before. We notice that this is independent of μ and for $\beta = D/2$ and in the limit $\alpha \to 1$ it gives correctly the previous equation for Δ in the symmetric, divalent semi-metal case. In the limit $\alpha \to 0$, it reduces to the expression for the renormalized hybridization in the Anderson lattice, i.e., for a collection of local levels [13, 14].

We give now the scaling results for the properties of the Fermi liquid in the metallic phase close to the metal–insulator transition. We find that the thermal mass m_T, defined as the coefficient of the linear term of the specific heat, scales as $m_T \propto |P - P_c|^{d/2-1}$ and in three dimensions vanishes as $m_T \propto |P - P_c|^{1/2}$. The same scaling is found for the uniform susceptibility χ_0, the compressibility κ and the density of states at the chemical potential. The number of carriers $n_c \propto |P - P_c|^{d/2}$. The behaviour of the thermal mass obtained above is opposite to that found for heavy fermions [15], where it is enhanced as the system approaches the critical point. The characteristic or coherence temperature in the metallic phase scales as $T_c \propto (P - P_c)$ since $\nu z = 1$. The existence of a small coherence temperature close to the density-driven phase transition gives rise in the presence of electron–electron interactions to a significant T^2-term in the resistivity even in wide-band materials such as Yb [16]. If we write $\rho \approx \rho_0 + AT^2$ for $T \ll T_c$, then the coefficient A scales as $A \propto {T_c}^{-2} \propto (P - P_c)^{-2}$.

At the critical pressure, $P = P_c$, we find non-Fermi-liquid behaviour with the specific heat vanishing with temperature as $C \propto T^{3/2}$ and $\chi_0 \propto T^{1/2}$. In actual systems, states in the tails of the density of states due to impurities or disorder and which give rise to a saturation of the resistivity at the lowest temperatures may spoil this simple behaviour.

In conclusion the possibility of an excitonic phase transition in a two-band model has been investigated. The dominant interaction was taken to be the electron–hole attraction. We argued that a phase transition to an excitonic phase never occurs in the presence of hybridization since the one-body mixing term acts as a conjugate field for the order parameter of this phase. We suggested an alternative interpretation of the experiments of Wachter *et al* on $Sm_{0.75}La_{0.25}S$. Our approach gives rise to a gap that varies linearly close to the critical pressure, i.e., $\Delta_G \propto (P - P_c)$ as observed [2, 11]. We have derived the properties of the Fermi liquid in the metallic phase close to the transition and predicted non-Fermi-liquid behaviour at the critical pressure.

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