# Electronic mechanism for the production of heavy charged and neutral bosons in variable-valence systems

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A collective branch of two-particle excitations might form in a two-band model of a crystal in a state of thermodynamic equilibrium. This branch would result from an interband electron-electron interaction.

Mechanisms for the production of quasilocal two-particle excitations—centers with a negative correlation energy—in a state of thermodynamic equilibrium have been under discussion for a fairly long time now (see, for example, the bibliography in Ref. 1). Interest in this topic stems in particular from results obtained in a study of

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doped IV-VI semiconductors[1)] (Ref. 2), and more recently interest has become particularly strong because of the discussion of possible scenarios for the high-temperature superconductivity in metal-oxide ceramics.[3]

1. A fundamental feature of the two-band model discussed below is the pronounced difference between the effective masses of the electrons in the different bands. Light-band states form valence bonds, while the heavy band (which is completely filled or empty in the Hartree-Fock approximation) contributes essentially nothing to the binding energy of the crystal. We will assume below that the heavy band is filled in the initial state; in the opposite case, the entire discussion can be carried out in a corresponding way in terms of holes. Upon the transition of electrons from the heavy band to the light band, excitation energy is expended. For light particles, on the other hand, an attractive potential proportional to the number of heavy particles which have left the center arises in a cell. There can be a situation in which a change in the structure of the valence electrons in the field of this potential is advantageous in terms of the total energy. Because of the nonlinear dependence on the potential, this advantage turns out to be greater for a two-particle configuration at a single center than for two single-particle configurations at different centers. The result is the formation of a branch of two-particle excitations (heavy bosons). This branch stabilizes the Fermi level, since the number of valence electrons increases upon two-particle transitions; the kinetic energy of these electrons also increases, thereby preventing a further development of the process. This effect is known as "Fermi-level pinning."[4]

2. We write the Hamiltonian of the problem in the form[5]

$$H = H_{band} + \sum_j H_{loc}(\mathbf{R}_j), \tag{1}$$

$$H_{loc}(\mathbf{R}_j) = (E_0 - \mu)\sum_\sigma n_{\sigma j} + U \sum_{\sigma,\sigma',\mathbf{k},\mathbf{k}'} (n_{\sigma j} - 1)\,\psi^+_{\mathbf{k}\sigma'}\psi_{\mathbf{k}'\sigma'} \exp i(\mathbf{k}-\mathbf{k}')\mathbf{R}_j$$
$$+ \frac{1}{2} J \sum_\sigma (n_{\sigma j} - 1)(n_{-\sigma j} - 1) + \sum_{\mathbf{k},\sigma} \{ V(\mathbf{k}) \exp(i\mathbf{k}\mathbf{R}_j)\,\psi^+_{\mathbf{k}\sigma} b_{\sigma i} + \text{c.c.}\} \tag{2}$$

$$H_{band} = \sum_{\sigma,\mathbf{k}} [\epsilon(\mathbf{k}) - \mu]\,\psi^+_{\mathbf{k}\sigma}\psi_{\mathbf{k}\sigma}. \tag{3}$$

Here $\epsilon(\mathbf{k})$ is the dispersion law of the light particles, in which, strictly speaking, we should incorporate the self-consistent redistribution of the density of these particles for various configurations of the heavy particles at the center. This can be done in a crude way by introducing a configuration dependence of the interband interaction potential[2)] $U$. In addition, $E_0$ is a seed single-particle level of heavy particles; $\mu$ is the chemical potential; $J$ is the Hubbard repulsive potential of the heavy particles in cell $j$; and $V(\mathbf{k})$ is the matrix element of single-particle hybridization [the requirement that the Wannier functions of the light and heavy particles in cell $\mathbf{R}_j$ must be orthogonal leads to the necessary condition $\int V(\mathbf{k})d\mathbf{k} \equiv 0$]. All the rest of the notation is standard.

We restrict the analysis to the single-cell approximation of an effective medium,[6] which is valid, strictly speaking, for the case of a dilute alloy. It will serve as a starting point for constructing a strong-binding scheme for systems with a regular arrangement of heavy particles. We assume that a heavy particle is in cell $\mathbf{R}_0$ and that its interaction

with the continuum is described by the Hamiltonian $H = H_{\text{band}} + H_{\text{loc}}(\mathbf{R}_0)$, which is formally the same—when a level $E_0$ is singly occupied—as the Hamiltonian[7] in the problem of the x-ray photoemission of electrons from deep levels in metals. The thermodynamics of the problem with a single occupation of $E_0$ has been studied by Newson and Piseborough[8] for the case $V(\mathbf{k}) = 0$. We will discuss (also ignoring hybridization, for now) the situation which arises when $E_0$ is doubly occupied. We make use of the circumstance that in the limit $V(\mathbf{k}) \to 0$ the occupation numbers $n_{\sigma j}$ are integrals of motion. We can thus calculate the thermodynamic potential of the system exactly (the entire analysis is carried for $T = 0$):

$$\Omega(n_{\sigma 0}) = \langle H \rangle = \Omega_0(\mu) + \tilde{E}_0 \sum_\sigma (n_{\sigma 0} - 1) + \frac{1}{2} \tilde{J} \sum_\sigma (n_{\sigma 0} - 1)(n_{-\sigma 0} - 1), \quad (4)$$

where $\Omega_0(\mu)$ is the thermodynamic potential for the case of a two-electron occupation of $E_0(n_{\uparrow 0} + n_{\downarrow 0} = 2)$ and for a fixed value of $\mu$;

$$\tilde{E}_0 = E_0 + \Delta E_0(U) - \mu, \quad (5)$$

$$\tilde{J} = J + \Delta E_0(2U) - 2\Delta E_0(U), \quad (6)$$

$$\Delta E_0(U) = (2\pi)^{-1} \operatorname{Im} \int_{-\infty}^{0} 2\omega U [\partial F(\omega)/\partial \omega][1 + UF(\omega)]^{-1} d\omega = \Delta_0(U)$$
$$+ \pi^{-1} \int_{-\mu}^{0} \omega \frac{\partial}{\partial \omega} \{ \arctan \pi UN(\omega)/1 + UI(\omega) \} d\omega, \quad (7)$$

$$F(\omega) = \sum_{\mathbf{k}} [\omega - \epsilon(\mathbf{k})]^{-1} = I(\omega) + i\pi N(\omega). \quad (8)$$

The difference $\tilde{J}$ between the thermodynamic potentials of the two-particle configuration (two holes at a single center) and the one-particle configuration (two holes at different centers) is determined by the particular function $\epsilon(\mathbf{k})$, which determines the shape of the light-particle state density $N(\omega)$; and $\Delta_0$ is the energy of the bound state (if such a state exists) which has split off from the band edge.

Under the assumption of a small band occupation level ($\mu \ll W$, where $W$ is the band width), we use the approximation $N(\omega) = N_0(\omega/W)^{1/2}$ near the bottom of the band. In the absence of a bound state ($2UN_0 < 1$), the entire advantage in terms of binding energy results from the change in the local state density of light particles:

$$\Delta E_0(U) \approx -W (UN_0/1 - 2UN_0)(2/3)(\mu/W)^{3/2}, \quad (9)$$

where we have assumed $UN_0(\mu/W)^{1/2} \ll |1 - 2UN_0|$. When there is a shallow bound state ($2UN_0 > 1$, $|\Delta_0| \ll W$), and with the same limitations on $\mu$, the main contribution comes from the splitting off of the level:

$$\Delta E_0(U) \approx -|\Delta_0| = -W \frac{4}{\pi^2} [(2UN_0 - 1)/UN_0]^2. \quad (10)$$

Finally, if a deep level splits off ($|\Delta_0| \gg W$), the particular details of the functional dependence $N(\omega)$ are inconsequential. Replacing $N(\omega)$ by an average value over the band, $N_0$, we find, under the condition $UN_0 \gg 1$,

$$\Delta E_0(U) \approx -WUN_0\,(1-{}^1/UN_0). \tag{11}$$

It follows from (9)–(11) that in all the cases considered the contribution to the correlation energy satisfies $\Delta E_0(2U) - 2\Delta E_0(U) < 0$, and if the repulsive potential $J$ is not moderately strong, then we also have $\tilde{J} < 0$. In other words, the two-particle configuration at a center is preferred.

In a situation in which the chemical potential $\mu^*$ is pinned at a two-particle level, the thermodynamic potentials $\Omega(2)$ and $\Omega(0)$ must be equal,

$$\Omega(2) - \Omega(0) = -2(E_0 - \mu^*) + \Delta E_0(2U) + J = 0, \tag{12}$$

and the one-particle excitation is separated by a gap:

$$\Omega(1) - \Omega(0) = -\tilde{J} > 0. \tag{13}$$

3. In the absence of a light-particle bound state in the potential $2U$ (or if there is a shallow impurity level, with $|\Delta_0| \ll W$), there is just a slight redistribution of their density near the site occupied by two heavy holes. Because of the overlap of the wave functions at different sites, even if the concentration of impurities centers is small (and especially in a regular lattice), the excess electron density is "smeared out" over the crystal. The localized charge at a site is thus essentially equal to $+2|e|$; i.e., a heavy charged boson forms. At the same time, if there is a deep level, $|\Delta_0| \gtrsim W$, its localization may not occur, and a neutralizing electron charge of $-2|e|$ will remain at the site. The result will be the formation of a heavy neutral boson: a localized biexciton with a binding energy $-|\Delta_0(2U)|$. Correspondingly, for a single-particle configuration of a heavy particle, either a heavy-fermion level (in this case, a level of heavy holes) or a level of heavy neutral bosons—excitons with a binding energy $-|\Delta_0(U)|$—may form.

The hybridization of $V(\mathbf{k})$ is renormalized in different ways for the cases of two- and one-particle configurations. As a result, the widths of the bands of the corresponding excitation branches are different. For one-particle configurations, according to Refs. 7 and 9, the effective hybridization is $t(U) = V(\omega_{\max}/W)^{g^2}$, under the condition $g = UN_0 \ll 1$, while for two-particle configurations an analysis by the approach of Ref. 7 yields $t(2U) = t^2(2U)/|\tilde{J}| \ll t(U)$ (here $\omega_{\max} = \max\{T, \mu - \tilde{E}_0, \langle V^2\rangle^{1/2}\}$).

4. A discussion of the experimental justification of the application of our model to IV-VI systems and also of possible superconductivity scenarios goes beyond the scope of this letter. We simply note that in addition to the scenarios which are being widely discussed (Bose condensation of heavy pairs and Cooper pairing of light particles due to the exchange of heavy one- or two-particle excitations), there are some other possible mechanisms, more exotic, which involve a mutual induction of superconducting order parameters in the heavy and light subsystems. The presence of two such subsystems can lead to significant deviations from the standard BCS model. (One of the scenarios, for example, has the specific heat increasing near the point of the Bose condensation of heavy pairs directly in the superconducting phase of light particles; there is an unusual relation between the magnitude of the superconducting gap and the transition temperature; etc.)

[1)]The electrical activity of impurities in them is apparently related to a change in the electronic configuration of Sn in PbSe from $s^2p^2$ to $s^0p^4$ or of In and Tl in PbTe and SnTe from $s^2p^1$ to $s^0p^3$.

[2)]A more rigorous approach would have to incorporate the interaction of light particles with each other directly in Hamiltonian (1); all of the results remain qualitatively correct, however.


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