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LETTER TO THE EDITOR

Crystal structure effects upon the mass of an exciton

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Abstract. The Mattis–Gallinar effect predicts that the scalar mass of an exciton depends upon its internal kinetic energy, and that the exciton mass may be larger than the sum of the masses of the electron and the hole. I generalize this effect to the tensorial case of a crystal structure which is not necessarily cubic. By assuming that the electron and hole share the same band structure, I find that

$$M_{ij}^{-1} = -(1/4)\sum_{R} R_i R_j K_R$$

where K_R represents an internal excitonic kinetic energy associated to the vector R of the crystal lattice, and M_{ij}^{-1} is the ijth component of the inverse mass tensor of the exciton. Thus, if the exciton becomes localized in the sense that $K_R \to 0$, the mass tensor $\mathbf{M}$ may become arbitrarily large.

According to the Mattis–Gallinar effect the scalar effective mass M of an exciton in a cubic crystal is given by [1–5]

$$M = (m_e + m_h)/(1 - (K/W)) \tag{1}$$

where $m_e + m_h$ is the sum of the masses of the electron and hole, K the internal kinetic energy of the exciton and W the average of the electron and hole bandwidths.

Experimental verification of formula (1) was given by Cafolla, Schnatterly and Tarrio [6] from transmission electron-energy-loss measurements, for the cubic semiconductors NaF and CuCl, and more recently [7] for solid (cubic) krypton.

Although well established [6–8] for cubic crystals, the result† embodied in equation (1) has not been generalized to other lattice structures [8]. It is the purpose of this contribution to do so.

Thus, in the following, I will show that equation (1) can be extended in a non-trivial—yet very simple—manner to non-cubic structures, provided one makes the simplifying assumption that the electron and hole *share the same band structure*‡.

In effect, consider the reasonably general [3] lattice excitonic Hamiltonian H, consisting of kinetic energy for the electron and the hole, plus potential attractive energy $\mathcal{V}(R)$, of the form [3]

$$H = E_e(-i\Delta_e) + E_h(-i\Delta_h) + \mathcal{V}(R_e - R_h)$$

† Namely a theoretical interpolation between the extreme cases of the Mott–Wannier and the Frenkel-type excitons.

‡ The band structure being otherwise quite general, and not necessarily restricted to nearest-neighbour 'hops' as for equation (1).

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with the kinetic energy

$$E_e(k_e) = \sum_R C(R)e^{ik_e \cdot R} \tag{2}$$

for the electron of wavevector $k_e = -i\Delta_e$; and kinetic energy

$$E_h(k_h) = \sum_R V(R)e^{ik_h \cdot R} \tag{2'}$$

for the hole having wavevector $k_h = -i\Delta_h$. Associated to the lattice vector R, $C(R)$ and $V(R)$ represent the 'hopping' matrix elements for the electron and hole, respectively.

The two-particle state of the exciton $|\psi\rangle$ can be written as [2]

$$|\psi\rangle = \sum_{R_e, R_h} \psi(R_e, R_h)|R_e, R_h\rangle \tag{3}$$

where the $|R_e, R_h\rangle$ denotes the orthonormal basis states in which the electron is localized at lattice site R_e, and the hole at site R_h, and $\psi(R_e, R_h)$ is the corresponding wavefunction.

By making the centre-of-mass transformation, one writes [2]

$$\psi(R_e, R_h) = e^{-i(k/2)\cdot(R_e + R_h)} F(R_e - R_h) \tag{4}$$

where k is the wavevector of the centre of mass of the exciton, and $F(R_e - R_h)$ is some function of the relative coordinate $R_e - R_h$ only. Substitution of equations (3) and (4) into the eigenvalue equation of the exciton

$$H|\psi\rangle = E|\psi\rangle \tag{5}$$

leads, after some manipulations, to the following difference equation for the function $F(R_e - R_h) \equiv F(r)$; namely

$$\sum_R \left(e^{i(k/2)\cdot R} C(-R) + e^{-i(k/2)\cdot R} V(R)\right) F(r + R) = \left(E(k) - \mathcal{V}(r)\right) F(r). \tag{6}$$

To make further progress, I will now assume that the electron and hole share the same band structure, in the sense that $C(-R) = V(R)$ in equation (6), or, equivalently, that $E_e(k_e) = E_h(-k_e)$ in equation (2). With this simplifying assumption, equation (6) becomes

$$2\sum_R V(R) \cos\left(\frac{k \cdot R}{2}\right) F(r + R) = (E(k) - \mathcal{V}(r)) F(r). \tag{7}$$

From equation (7) one can now follow a line of reasoning similar (but somewhat simpler) to that used in previous references [1–3] to obtain the effective mass of the exciton.

In effect, introducing 'coupling' real parameters $\lambda(R)$, such that each $V(R)$ is renormalized to $\lambda(R)V(R)$, the energy eigenvalue $E(k)$ of the exciton, considered as a function of the $\lambda(R)$ parameters, will obey an obvious scaling relationship that follows from equation (7), namely,

$$E\left(k, \lambda(R_1), \lambda(R_2), \ldots\right) = E\left(0, \tilde{\lambda}(R_1), \tilde{\lambda}(R_2), \ldots\right) \tag{8}$$

provided the renormalised $\tilde{\lambda}(\boldsymbol{R})$ are given by

$$\tilde{\lambda}(\boldsymbol{R}) \equiv \lambda(\boldsymbol{R}) \cos(\boldsymbol{k} \cdot \boldsymbol{R}/2).$$

Then it is a simple matter to obtain the exciton mass by expanding the right-hand side of equation (8) in powers of $\boldsymbol{k}$ (up to $\boldsymbol{k}^2$). If $\{\lambda(\boldsymbol{R})\}$ denotes the set of the $\lambda(\boldsymbol{R})$s, one has by Taylor's expansion of all functions

$$E(\boldsymbol{k}, \{\lambda(\boldsymbol{R})\}) \simeq E\left(\boldsymbol{0}, \left\{\lambda(\boldsymbol{R}) - \lambda(\boldsymbol{R})\frac{(\boldsymbol{k} \cdot \boldsymbol{R})^2}{8}\right\}\right) \simeq \mathbf{E}(\boldsymbol{0}, \{\lambda(\boldsymbol{R})\})$$
$$- \sum_{\boldsymbol{R}} \lambda(\boldsymbol{R}) \frac{(\boldsymbol{k} \cdot \boldsymbol{R})^2}{8} \left(\frac{\partial E}{\partial \lambda(\boldsymbol{R})}\right). \tag{9}$$

By setting again $\lambda(\boldsymbol{R}) = 1$ in equation (9), the components of the inverse mass tensor $\mathbf{M}^{-1}$ of the exciton at $\boldsymbol{k} = \boldsymbol{0}$ can be obtained from equation (9), and from the definition

$$M_{ij}^{-1} \equiv \left(\partial^2 E(\boldsymbol{k})/\partial k_i \partial k_j\right)_{k=0}.$$

Finally, one finds that

$$M_{ij}^{-1} = -(1/8) \sum_{\boldsymbol{R}} \left(\frac{\partial E}{\partial \lambda(\boldsymbol{R})}\right) \frac{\partial^2[(\boldsymbol{k} \cdot \boldsymbol{R})^2]}{\partial k_i \partial k_j} = -(1/4) \sum_{\boldsymbol{R}} R_i R_j K_{\boldsymbol{R}} \tag{10}$$

with $K_{\boldsymbol{R}} \equiv \partial E/\partial \lambda(\boldsymbol{R})$. But according to the Hellmann–Feynman theorem, since $\lambda(\boldsymbol{R})$ is a real parameter, one then has

$$K_{\boldsymbol{R}} = \langle \partial H/\partial \lambda(\boldsymbol{R}) \rangle_{k=0}$$

where the expectation value is to be calculated with the eigenstates of H.

Thus,

$$K_{\boldsymbol{R}} = V(\boldsymbol{R}) \left\langle \mathrm{e}^{-\Delta_e \cdot \boldsymbol{R}} + \mathrm{e}^{+\Delta_h \cdot \boldsymbol{R}} \right\rangle_{k=0}$$

is a 'kinetic energy' associated† to the lattice vector $\boldsymbol{R}$; and the total 'internal' kinetic energy K of the exciton is

$$K \equiv \left\langle E_e(\boldsymbol{k}_e) + E_h(\boldsymbol{k}_h) \right\rangle_{k=0} = \sum_{\boldsymbol{R}} K_{\boldsymbol{R}} \geqslant 0.$$

It is a simple matter to show that equation (10) reduces to equation (1) for the cubic structures considered in previous works [1–3], when $m_e = m_h$ in equation (1) and only nearest-neighbour 'hops' are considered in equation (10). Furthermore, one expects that for the strongly bound Frenkel-type excitons, where localization is maximum [3], $K_{\boldsymbol{R}} = 0$ if $\boldsymbol{R} \neq 0$ (i.e. $K = K_0 = 2V(\boldsymbol{0})$) and the exciton mass tensor diverges in equation (10). For the loosely bound and highly delocalized Mott–Wannier excitons one will expect, on the

† This is a natural identification, since the displacement operators $\exp(\pm\Delta \cdot \boldsymbol{R})$ generate finite 'hops' of lattice vectors $\pm\boldsymbol{R}$.

contrary, that $K_R \simeq 2V(R)$ (i.e. $\langle e^{-ik_e \cdot R} \rangle = \langle e^{+ik_h \cdot R} \rangle \simeq 1$) and, thus, $M_{ij}^{-1} = (1/2)(m_h^{-1})_{ij}$, where

$$(m_h^{-1})_{ij} = -\sum_R R_i R_j V(R)$$

is the ijth component of the inverse mass tensor of the hole (or the electron). Thus, in both extreme cases one finds expected results†.

In summary, I have generalized in a very simple manner the Mattis–Gallinar effect [1, 6, 8], for the first time, to the tensorial case of a non-cubic crystal, and this for quite general, albeit similar, band structures for the electron and the hole. In the future, one would like to extend equation (10) to the case of different electron and hole masses ($m_e \neq m_h$), and to a more realistic multiband dispersion law.

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† In the Mott–Wannier case or continuum limit, one expects

$$K \sim 2\sum_R V(R) \sim 0.$$

In agreement then with equation (2'); since for $k_h = 0$, $E_h(0) = K/2 = 0$, as corresponds to a 'free-like' dispersion law.