The Heller - Marcus effect and the mass tensor of an exciton

1996 J. Phys.: Condens. Matter 8 3103

(http://iopscience.iop.org/0953-8984/8/17/020)

J. Phys.: Condens. Matter **8** (1996) 3103–3110. Printed in the UK

The Heller–Marcus effect and the mass tensor of an exciton

J-P Gallinar

Departamento de Física, Universidad Simón Bolívar, Apartado 89000, Caracas 1080-A, Venezuela

Received 6 December 1995

Abstract. As a generalization of the Mattis–Gallinar effect (which predicts that the mass of an exciton depends upon its internal kinetic energy), I derive a formula for the mass tensor $\mathbf{M}$ of the exciton that includes the effect of 'exciton hopping' or Heller–Marcus mechanism, which is particularly important for the mobility of Frenkel-like excitons. If M^{-1}_{ij} is the ijth component of the inverse mass tensor $\mathbf{M}^{-1}$, and if the mass tensors of the electron ($\mathbf{m}_e$) and hole ($\mathbf{m}_h$) are proportional, with $\mathbf{m}_e^{-1} = \alpha \mathbf{m}_h^{-1}$, then

$$M^{-1}_{ij} = -\sum_{\boldsymbol{R}} R_i R_j \left(\beta K_{\boldsymbol{R}} + H(\boldsymbol{R}) \frac{\langle H \rangle}{H_F} \right)$$

where $K_{\boldsymbol{R}}$ is an internal excitonic kinetic energy associated with the crystal lattice vector $\boldsymbol{R}$, $\beta \equiv \alpha/(1+\alpha)^2$ is the reduced mass tensor of the electron and hole divided by the total Wannier mass tensor, and $H(\boldsymbol{R})$ is a matrix element of the exciton-hopping energy operator H. If the exciton becomes Frenkel like or localized in the sense that the expectation value $\langle H \rangle \to H_F$, and that $K_{\boldsymbol{R}} \to 0$, then the inverse mass tensor in the Frenkel limit becomes

$$(M^{-1}_{ij})_F = -\sum_{\boldsymbol{R}} R_i R_j H(\boldsymbol{R}) \neq 0.$$

Thus, the (otherwise divergent) mass tensor of the Frenkel exciton remains finite as a consequence of the Heller–Marcus mechanism. On the other hand, for Wannier excitons one has $\langle H \rangle \to 0$, and

$$(-) \sum_{\boldsymbol{R}} R_i R_j K_{\boldsymbol{R}} \to (m_e^{-1} + m_h^{-1})_{ij}$$

which means that $\mathbf{M} = \mathbf{m}_e + \mathbf{m}_h$ in the Wannier limit. Finally, some comments are made about the various (experimental) predictions implicit in the above derived formula for the exciton's translational mass.

1. Introduction

The result that the translational mass of an exciton depends† upon the exciton's internal quantum state is well established by now [1, 2]. First predicted theoretically in 1984 by Mattis and Gallinar [1], this effect was then verified experimentally by Schnatterly and co-workers [3, 4] from transmission electron-energy-loss measurements in, for example, various substances such as NaF, CuCl and solid krypton. Although the samples studied [3, 4] have been in the form of cubic crystals, the effect has also recently [5] been theoretically extended to other crystalline lattices, where it has been shown [5] (for identical electron and hole masses) to hold in a somewhat similar form. In fact, as pointed out by Mattis [6], the conceptual reach of the Mattis–Gallinar effect [2, 3] should extend beyond the excitonic application to other two-particle composites such as the Cooper pair of the BCS theory of superconductivity or the bound-magnon pair of magnetism, and in general to the two-body 'problem' on a lattice.

† Mainly through the exciton's internal kinetic energy.

0953-8984/96/173103+08$19.50

Furthermore, one should add to this that three-body complexes (such as the 'trion' formed from a Frenkel exciton plus an electron (or hole)) have also been predicted [7] to exhibit a dependence of the total effective mass upon the internal energy of the bound complex. Whether every few-body composite with more than two particles defined on a lattice also exhibits this dependence, remains, however, an interesting unsettled question [6] to this day.

In the present work we purport to generalize the Mattis–Gallinar effect (for the two-body problem) by developing a formula for the mass tensor $\mathbf{M}$ of the exciton that takes account of the 'exciton hopping' [8] or Heller–Marcus mechanism, which is particularly relevant for the mobility of Frenkel-like excitons. The inclusion of the 'exciton-hopping' mechanism brings about a very desirable feature, namely that of endowing the Frenkel exciton with a finite mass [8, 9], yielding in this manner, in our formulation [8] for the exciton mass, a smooth interpolation between the two extreme limits of the Mott–Wannier and the Frenkel-type excitons.

The problem of interpolating between the Wannier and Frenkel limits is long-standing and difficult [4]. Although much original and important work, theoretical [10] as well as experimental [11], has been done in the detailed study of 'intermediate' [4] excitons [12], yet a sufficiently general (as well as simple) interpolating scheme for the specific property of the translational mass of the exciton was lacking prior to 1984. Thus, the Mattis–Gallinar result [1, 8] is important, as also is the need for further generalizations of it.

To this end, we also extend here our previous [5] formulation for non-cubic crystals to cases in which the mass tensors of the electron ($\mathbf{m}_e$) and hole ($\mathbf{m}_h$), although still proportional to each other, are, however, *not* necessarily *identical* as was previously [5] assumed. In turn, this requires (as will be seen below) somewhat more elaborate and interesting considerations in the derivation of the formula for the mass tensor $\mathbf{M}$ of the exciton.

2. Formalism and results

We consider the excitonic Hamiltonian $\mathcal{H}$ as

$$\mathcal{H} = E_e(\boldsymbol{k}_e) + E_h(\boldsymbol{k}_h) + \mathcal{V}(\boldsymbol{R}_e - \boldsymbol{R}_h) + H \tag{1}$$

with the kinetic energy

$$E_e(\boldsymbol{k}_e) = \sum_{\boldsymbol{R}} C(\boldsymbol{R}) \exp(\mathrm{i}\boldsymbol{k}_e \cdot \boldsymbol{R}) \tag{2}$$

for the electron of wavevector $\boldsymbol{k}_e = -\mathrm{i}\boldsymbol{\nabla}_e$, and the respective kinetic energy

$$E_h(\boldsymbol{k}_h) = \sum_{\boldsymbol{R}} V(\boldsymbol{R}) \exp(\mathrm{i}\boldsymbol{k}_h \cdot \boldsymbol{R}) \tag{3}$$

for the hole whose wavevector is $\boldsymbol{k}_h = -\mathrm{i}\boldsymbol{\nabla}_h$. Associated with the lattice vector $\boldsymbol{R}$, $C(\boldsymbol{R})$ and $V(\boldsymbol{R})$ represent the 'hopping' matrix elements for the electron and hole, respectively. In equation (1), $\mathcal{V}(\boldsymbol{R}_e - \boldsymbol{R}_h)$ is the attractive potential energy when the electron and hole are localized at lattice sites $\boldsymbol{R}_e$ and $\boldsymbol{R}_h$, respectively, with $|\boldsymbol{R}_e, \boldsymbol{R}_h\rangle$ denoting the corresponding orthonormal basis states of such localization; finally, H is the 'exciton hopping' [13] (or Heller–Marcus) energy [8].

The non-vanishing matrix elements of H are taken to be given by [8]

$$\langle \boldsymbol{R}', \boldsymbol{R}'|H|\boldsymbol{R}, \boldsymbol{R}\rangle \equiv H(\boldsymbol{R} - \boldsymbol{R}') \qquad \boldsymbol{R} \neq \boldsymbol{R}' \tag{4}$$

i.e. those for which $\boldsymbol{R}_e = \boldsymbol{R}_h$, with the electron and hole residing together (as a strongly bound Frenkel exciton) at the same lattice site [8]. $H(\boldsymbol{R} - \boldsymbol{R}')$ in equation (4) is thus the

matrix element for 'exciton hopping' of the exciton as a whole entity [8] between $\boldsymbol{R}$ and $\boldsymbol{R}'$ (or the initial and final sites of the 'hop').

A difference equation for the relative-coordinate wavefunction of the exciton, $F(\boldsymbol{R}_e - \boldsymbol{R}_h) \equiv F(\boldsymbol{r})$, can be obtained by a rather straightforward procedure which has been explained at length elsewhere [5, 8], resulting here in

$$\sum_{\boldsymbol{R}} \left[\exp\left(\mathrm{i}\frac{\boldsymbol{k}}{2}\cdot\boldsymbol{R}\right) C(-\boldsymbol{R}) + \exp\left(-\mathrm{i}\frac{\boldsymbol{k}}{2}\cdot\boldsymbol{R}\right) V(\boldsymbol{R}) \right] F(\boldsymbol{r}+\boldsymbol{R}) = (E(\boldsymbol{k}) - \mathcal{V}_{\boldsymbol{k}}(\boldsymbol{r}))F(\boldsymbol{r}) \tag{5}$$

where

$$\mathcal{V}_{\boldsymbol{k}}(\boldsymbol{r}) \equiv \mathcal{V}(\boldsymbol{R}_e - \boldsymbol{R}_h) + \delta_{\boldsymbol{r},\boldsymbol{0}} \sum_{\boldsymbol{R}\neq\boldsymbol{0}} H(\boldsymbol{R}) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}). \tag{6}$$

In equation (5), $E(\boldsymbol{k})$ is the energy eigenvalue of the exciton whose centre-of-mass wavevector is $\boldsymbol{k}$. Through equation (6) the effect of the 'exciton-hopping' mechanism is seen to give rise to an effective $\boldsymbol{k}$-dependent potential $\mathcal{V}_{\boldsymbol{k}}(\boldsymbol{r})$ binding the electron and hole together. One now writes

$$\epsilon_{\boldsymbol{k}}(\boldsymbol{R}) \equiv |\epsilon_{\boldsymbol{k}}(\boldsymbol{R})| \exp(\mathrm{i}\theta_{\boldsymbol{k}}(\boldsymbol{R})) \equiv \exp\left(\mathrm{i}\frac{\boldsymbol{k}}{2}\cdot\boldsymbol{R}\right) C(-\boldsymbol{R}) + \exp\left(-\mathrm{i}\frac{\boldsymbol{k}}{2}\cdot\boldsymbol{R}\right) V(\boldsymbol{R}) \tag{7}$$

and changes the phase of the wavefunction $F(\boldsymbol{r})$, through

$$F(\boldsymbol{r}) \equiv G(\boldsymbol{r}) \exp[-\mathrm{i}\varphi(\boldsymbol{k})\boldsymbol{r}\cdot\boldsymbol{k}]$$

where $\varphi(\boldsymbol{k})$ is to be suitably adjusted; thus we can rewrite equation (5) as

$$\sum_{\boldsymbol{R}} |\epsilon_{\boldsymbol{k}}(\boldsymbol{R})| \exp[\mathrm{i}\theta_{\boldsymbol{k}}(\boldsymbol{R})] \exp[-\mathrm{i}\varphi(\boldsymbol{k})\boldsymbol{k}\cdot\boldsymbol{R}] G(\boldsymbol{r}+\boldsymbol{R}) = (E(\boldsymbol{k}) - \mathcal{V}_{\boldsymbol{k}}(\boldsymbol{r}))G(\boldsymbol{r}) \tag{8}$$

where

$$|\epsilon_{\boldsymbol{k}}(\boldsymbol{R})| = \sqrt{V^2(\boldsymbol{R}) + C^2(-\boldsymbol{R}) + 2V(\boldsymbol{R})C(-\boldsymbol{R})\cos(\boldsymbol{k}\cdot\boldsymbol{R})} \tag{9}$$

and

$$\tan[\theta_{\boldsymbol{k}}(\boldsymbol{R})] = \frac{C(-\boldsymbol{R}) - V(\boldsymbol{R})}{C(-\boldsymbol{R}) + V(\boldsymbol{R})} \tan\left(\frac{\boldsymbol{k}\cdot\boldsymbol{R}}{2}\right). \tag{10}$$

To make further progress, we assume that electron and hole share a *similar* band structure, in the sense that $C(-\boldsymbol{R}) = \alpha V(\boldsymbol{R})$ ($\alpha > 0$) or, equivalently, that the mass tensors of the electron ($\mathbf{m}_e$) and the hole ($\mathbf{m}_h$) are proportional, with $(m_e^{-1})_{ij} = -\sum_{\boldsymbol{R}} R_i R_j C(-\boldsymbol{R}) = \alpha(m_h^{-1})_{ij}$, or $E_e(\boldsymbol{k}_e) = \alpha E_h(-\boldsymbol{k}_e)$ in equations (2) and (3). As a consequence of this simplifying assumption, the angle $\theta_{\boldsymbol{k}}(\boldsymbol{R})$ in equation (10) will depend upon $\boldsymbol{R}$ only through the combination $\boldsymbol{k}\cdot\boldsymbol{R}$, and thus the phase angle $\varphi(\boldsymbol{k})$ can be suitably adjusted so as to eliminate from the exponentials in equation (8) the linear $\boldsymbol{k}$-term in the net phase $\Phi(\boldsymbol{k}) \equiv \theta_{\boldsymbol{k}}(\boldsymbol{R}) - \varphi(\boldsymbol{k})\boldsymbol{k}\cdot\boldsymbol{R}$. With the choice $\varphi(\boldsymbol{k}) \equiv \frac{1}{2}[(\alpha-1)/(\alpha+1)]$, the net phase $\Phi(\boldsymbol{k})$ is thus at least of order k^3 (for $\boldsymbol{k}\to\boldsymbol{0}$) and, as will be seen below, can be left out of the calculation of the effective mass of the exciton.

One now introduces 'coupling' parameters $\lambda(\boldsymbol{R})$ and μ [5, 8], such that $V(\boldsymbol{R})$ and $C(-\boldsymbol{R})$ are renormalized to $\lambda(\boldsymbol{R})V(\boldsymbol{R})$ and to $\lambda(\boldsymbol{R})C(-\boldsymbol{R})$, respectively, while the entire Heller–Marcus term H in the Hamiltonian is renormalized by μ [8]. This, in turn, renormalizes $|\epsilon_{\boldsymbol{k}}(\boldsymbol{R})|$ by $|\lambda(\boldsymbol{R})|$ and $H(\boldsymbol{R})$ by μ, while leaving $\theta_{\boldsymbol{k}}(\boldsymbol{R})$ unchanged.

The energy eigenvalue $E(\boldsymbol{k})$ of the exciton considered (in a purely formal manner) as a function of the coupling parameters will obey a scaling relationship that follows from equation (8), namely

$$E(\boldsymbol{k};\mu,\lambda(\boldsymbol{R}_1),\lambda(\boldsymbol{R}_2),\ldots)=E(\boldsymbol{0};\tilde{\mu},\tilde{\lambda}(\boldsymbol{R}_1),\tilde{\lambda}(\boldsymbol{R}_2),\ldots) \tag{11}$$

provided that the renormalized parameters $\tilde{\lambda}(\boldsymbol{R})$ and $\tilde{\mu}$ are given by

$$\tilde{\lambda}(\boldsymbol{R})\equiv\frac{\lambda(\boldsymbol{R})|\epsilon_{\boldsymbol{k}}(\boldsymbol{R})|}{|V(\boldsymbol{R})+C(-\boldsymbol{R})|}\exp[\mathrm{i}\Phi(\boldsymbol{k})] \tag{12}$$

and by

$$\tilde{\mu}\equiv\frac{\mu h(\boldsymbol{k})}{h(\boldsymbol{0})} \tag{13}$$

where

$$h(\boldsymbol{k})\equiv\sum_{\boldsymbol{R}\neq\boldsymbol{0}}H(\boldsymbol{R})\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}).$$

The expansion of equations (12) and (13) in powers of $\boldsymbol{k}$ (up to $\boldsymbol{k}^2$) yields for equation (11) that

$$E(\boldsymbol{k};\mu,\{\lambda(\boldsymbol{R})\})\simeq E\Bigg(\boldsymbol{0};\mu-\mu\sum_{\boldsymbol{R}\neq\boldsymbol{0}}H(\boldsymbol{R})(\boldsymbol{k}\cdot\boldsymbol{R})^2/2h(\boldsymbol{0}),\left\{\lambda(\boldsymbol{R})-\frac{\lambda(\boldsymbol{R})V(\boldsymbol{R})C(-\boldsymbol{R})(\boldsymbol{k}\cdot\boldsymbol{R})^2}{2(V(\boldsymbol{R})+C(-\boldsymbol{R}))^2}\right\}\Bigg) \tag{14}$$

where $\{\lambda(\boldsymbol{R})\}$ denotes the set of $\lambda(\boldsymbol{R})$-values, and we have assumed [8] that $H(\boldsymbol{R})=H(-\boldsymbol{R})$. In obtaining equation (14), use has been made of the fact that in the expansion of equation (12) the net phase $\Phi(\boldsymbol{k})$ is at least of order k^3, and $\tilde{\lambda}(\boldsymbol{R})$ is thus real to the required order $\boldsymbol{k}^2$. The subsequent Taylor expansion of the right-hand side of equation (14) then gives to lowest order in $\boldsymbol{k}^2$ that

$$E(\boldsymbol{k};\mu,\{\lambda(\boldsymbol{R})\})\simeq E(\boldsymbol{0},\mu,\{\lambda(\boldsymbol{R})\})-\left(\mu\sum_{\boldsymbol{R}\neq\boldsymbol{0}}H(\boldsymbol{R})(\boldsymbol{k}\cdot\boldsymbol{R})^2/2h(\boldsymbol{0})\right)\frac{\partial E}{\partial\mu}-\sum_{\boldsymbol{R}}\frac{\lambda(\boldsymbol{R})V(\boldsymbol{R})C(-\boldsymbol{R})(\boldsymbol{k}\cdot\boldsymbol{R})^2}{2(V(\boldsymbol{R})+C(-\boldsymbol{R}))^2}\frac{\partial E}{\partial\lambda(\boldsymbol{R})}. \tag{15}$$

On the other hand, the components of the effective inverse mass tensor $\mathbf{M}^{-1}$ of the exciton at $\boldsymbol{k}=\boldsymbol{0}$ are defined through

$$M_{ij}^{-1}\equiv\left(\frac{\partial^2E(\boldsymbol{k})}{\partial k_i\partial k_j}\right)_{\boldsymbol{k}=\boldsymbol{0}}. \tag{16}$$

Setting again $\lambda(\boldsymbol{R})=\mu=1$ in equation (15), and inserting equation (15) into equation (16), one thus finds that

$$M_{ij}^{-1}=-\sum_{\boldsymbol{R}}R_iR_j\left(H(\boldsymbol{R})\frac{\langle H\rangle}{h(\boldsymbol{0})}+\frac{\alpha}{(1+\alpha)^2}K_{\boldsymbol{R}}\right). \tag{17}$$

In equation (17), use has been made of the Hellmann–Feynman theorem, according to which one has

$$\frac{\partial E}{\partial\mu}=\left\langle\frac{\partial\mathcal{H}}{\partial\mu}\right\rangle_{\boldsymbol{k}=\boldsymbol{0}}=\langle H\rangle$$

and

$$\frac{\partial E}{\partial \lambda(\boldsymbol{R})} = \left\langle \frac{\partial \mathcal{H}}{\partial \lambda(\boldsymbol{R})} \right\rangle_{\boldsymbol{k}=\boldsymbol{0}} \equiv K_{\boldsymbol{R}} = V(\boldsymbol{R})\langle \alpha \exp(-\boldsymbol{\nabla}_e \cdot \boldsymbol{R}) + \exp(\boldsymbol{\nabla}_h \cdot \boldsymbol{R})\rangle_{\boldsymbol{k}=\boldsymbol{0}} \tag{18}$$

the expectation values being calculated with the eigenstates of $\mathcal{H}$. Equation (18) defines $K_{\boldsymbol{R}}$ as a kinetic energy [5] associated with the lattice vector $\boldsymbol{R}$.

For Wannier excitons, one expects that $K_{\boldsymbol{R}} = (1+\alpha)V(\boldsymbol{R})$ (i.e. $\langle \exp(-\boldsymbol{\nabla}_e \cdot \boldsymbol{R})\rangle = \langle \exp(\boldsymbol{\nabla}_h \cdot \boldsymbol{R})\rangle \simeq 1$) and $\langle H\rangle \to 0$ [8]. Thus, equation (17) gives for Wannier excitons that $M_{ij}^{-1} = [\alpha/(1+\alpha)](m_h^{-1})_{ij}$ or $\mathbf{M} = \mathbf{m}_e + \mathbf{m}_h$, as expected.

On the other hand, for Frenkel-like excitons localized in the sense that $K_{\boldsymbol{R}} = 0$ (if $\boldsymbol{R} \neq \boldsymbol{0}$), one writes from equation (17) that

$$(M_{ij}^{-1})_F = -\sum_{\boldsymbol{R}} R_i R_j H(\boldsymbol{R}) \frac{H_F}{h(\boldsymbol{0})} \tag{19}$$

where $H_F \equiv \langle H\rangle_F$ is the value taken by $\langle H\rangle$ for a strongly bound Frenkel exciton of mass tensor $\mathbf{M}_F$. Thus, equation (17) can be conveniently rewritten as

$$M_{ij}^{-1} = -\beta \sum_{\boldsymbol{R}} R_i R_j K_{\boldsymbol{R}} + (M_{ij}^{-1})_F \frac{\langle H\rangle}{H_F}$$

with† $\beta \equiv \alpha/(1+\alpha)^2$. Identifying the strongly bound Frenkel exciton as one whose banding energy $E_F(\boldsymbol{k})$ can be written [8] as $E_F(\boldsymbol{k}) = E_0 + h(\boldsymbol{k})$, where E_0 is some constant [8], gives from equation (19) that $H_F = h(\boldsymbol{0})$, or finally

$$M_{ij}^{-1} = -\sum_{\boldsymbol{R}} R_i R_j \left(\beta K_{\boldsymbol{R}} + H(\boldsymbol{R}) \frac{\langle H\rangle}{H_F} \right) \tag{20}$$

ending our derivation.

3. Conclusions and discussion

We have derived in quite considerable detail a formula for the mass tensor $\mathbf{M}$ of an exciton (equation (20) above), that makes it depend on its internal quantum state, and which gives a non-trivial tensorial interpolation between the Wannier and Frenkel limits. A previous [5] result for non-cubic crystals is thus generalized in two different directions: firstly, by allowing in our formalism for the possibility of different electron and hole masses, and secondly by the inclusion of the Heller–Marcus 'hopping' mechanism. As pointed out in the abstract, this last yields from equation (20) a finite mass for the Frenkel exciton, instead of the infinite mass implied by the original [1] Mattis–Gallinar result.

It is a simple matter to show from equation (20) that, for cubic crystals, one recovers the result [8]

$$M^{-1} = (m_e + m_h)^{-1}\left(1 - \frac{K}{W}\right) + M_F^{-1}\frac{\langle H\rangle}{H_F} \tag{21}$$

for the diagonal components of $\mathbf{M}^{-1}$; with M_F^{-1} being the diagonal element of

$$(M_{ij}^{-1})_F = -\sum_{\boldsymbol{R}} R_i R_j H(\boldsymbol{R}) \neq 0.$$

† It is interesting to point out that β can also be written (more symmetrically) as $\boldsymbol{\mu}/\boldsymbol{\mathcal{M}}$ where $\boldsymbol{\mu}$ is the reduced mass tensor of the electron and hole (i.e. $\boldsymbol{\mu}^{-1} = \mathbf{m}_e^{-1} + \mathbf{m}_h^{-1}$), while $\boldsymbol{\mathcal{M}} = \mathbf{m}_e + \mathbf{m}_h$ is the total Wannier mass tensor.

In equation (21), W is the average of the electron and hole band widths, with only nearest-neighbour 'hops' being considered in the total internal kinetic energy K of the exciton:

$$K \equiv \sum_{\boldsymbol{R}} K_{\boldsymbol{R}} \geqslant 0.$$

As we have shown [9], the addition of the Heller–Marcus [13] term in equation (21) may bring about a 'qualitatively' [9] different behaviour for the mass of the exciton. Then, the inequality $M \geqslant m_e + m_h$ (which follows from the inequalities $0 \leqslant K \leqslant W$) does not necessarily hold, and the total mass M may be smaller [9] than the sum of the electron and hole masses. Likewise, one may surmise that the (quantum) interference between the kinetic energy and the Heller–Marcus term in equation (20) should bring about interesting and model-dependent (anisotropic) properties for the mass tensor **M**.

The explicit calculation of these anisotropies, as well as the experimental testing of equation (20) and of its predictions, are matters of future elucidation. However, a rough order-of-magnitude estimate of what kind of experimental effects to expect from our theoretical results can be obtained rather expeditiously. To this matter we now turn our attention and discussion in the rest of this work.

If we assume that the potential that binds the electron and hole together is approximately coulombic [4, 6] and is characterized by its usual quantum number $n = 1, 2, \ldots$ (with $n \to \infty$ in the continuum limit), one can estimate the n-dependent degree of anisotropy of the various components of M_{ij}^{-1} in equation (20). One evaluates the $\boldsymbol{R}$-dependent internal kinetic energy $K_{\boldsymbol{R}}$ appearing in equation (20) as an 'overlap' integral of the (relative-coordinate) wavefunction of the exciton, with wavefunctions centred on lattice points that differ by $\boldsymbol{R}$ (see the definition of $K_{\boldsymbol{R}}$ in equation (18)). Thus, if one *roughly* assumes a spherically symmetric exponentially localized wavefunction $F(\boldsymbol{r}) \simeq \exp(-r/a)$ for the exciton, with a localization radius on the order of a (in the coulombic wavefunctions, a increases linearly with increasing quantum number n, i.e. $a = na_0$, where a_0 is an appropriate 'Bohr' parameter or radius) one obtains that†

$$K_{\boldsymbol{R}} = (1+\alpha)V(\boldsymbol{R})\left(1 + \frac{|\boldsymbol{R}|}{a} + \frac{|\boldsymbol{R}|^2}{3a^2}\right)\exp\left(-\frac{|\boldsymbol{R}|}{a}\right) \tag{22}$$

for the n-dependent kinetic energy $K_{\boldsymbol{R}}$. In this description the Wannier limit is appropriately obtained by letting $n \to \infty$ for fixed a_0 (or also by letting $a_0 \to \infty$ for fixed n), while the Frenkel limit is obtained by letting $a_0 \to 0$.

On the other hand, for the Heller–Marcus term [13], one obtains by evaluating the corresponding integrals in spherical coordinates that

$$\frac{\langle H\rangle}{H_F} = 1 - \left(1 + \frac{2R_0}{a} + \frac{2R_0^2}{a^2}\right)\exp\left(-\frac{2R_0}{a}\right) \tag{23}$$

where R_0 (the nearest-neighbour lattice distance) is taken as the radius of a sphere centred on the origin ($\boldsymbol{r} = \boldsymbol{0}$), within the confines of which acts the Heller–Marcus operator H [13] (i.e. $\frac{4}{3}\pi R_0^3 \simeq v \equiv$volume of primitive cell; given that H acts in our approximation [13] only when the electron and hole are together in the same lattice cell). In (23), as in equation (22) for $K_{\boldsymbol{R}}$, the *exact* Wannier and Frenkel limits of the text are obtained by letting $n \to \infty$ and $a_0 \to 0$, respectively. Particularly noteworthy is the limit in the Wannier-like region (or continuum limit), for which one expects (22) and (23) to be better approximations than in the Frenkel-like region. In particular, the experimental results of Tarrio and Schnatterly [4] (for 4p excitons in solid Kr) were satisfactorily compared with our theory [1] in the

† The respective integral of overlap is here evaluated exactly in prolate spheroidal coordinates.

Wannier limit, where the virial theorem is approximately valid†. Thus, by taking the limit $n \to \infty$ (or $a_0 \to \infty$), one obtains, to lowest non-vanishing order in $|\boldsymbol{R}|/a$, that

$$(K_{\boldsymbol{R}})_n \simeq (1+\alpha)V(\boldsymbol{R})\left(1 - \frac{|\boldsymbol{R}|^2}{6a_0^2 n^2}\right) \tag{24}$$

for the n-dependent kinetic energy $K_{\boldsymbol{R}}$ while for the Heller–Marcus term one obtains from equation (23) that in the limit $n \to \infty$ (to lowest order in R_0/a)

$$\frac{\langle H\rangle_n}{H_F} \simeq \frac{v}{\pi(a_0 n)^3}. \tag{25}$$

The lowest non-vanishing terms that appear in (24) and (25) have characteristically *different* n-dependences. Equation (24) gives a total kinetic energy $K_n = \sum_{\boldsymbol{R}} K_{\boldsymbol{R}}$ that dies off as $1/n^2$, in agreement then with the virial theorem applied to the Coulomb potential. The Heller–Marcus term of equation (25), on the other hand, roughly vanishes as the ratio of the volume of the primitive cell with the volume of the sphere of localization‡. It must also be noted that the way in which the kinetic energy $K_{\boldsymbol{R}}$ behaves in (24) as $n \to \infty$ (here because there is no linear term in $|\boldsymbol{R}|/a$ in the expansion of (22) nor for that matter any cubic term $|\boldsymbol{R}|^3/a^3$ either) is more general than suggested by our rough calculation. This behaviour is also present in *exact* solutions of one-dimensional (exciton) models, with the Coulomb potential [14–16] defined on a lattice. It is interesting to remark that in these one-dimensional models [9, 16] the Heller–Marcus energy also behaves differently from the kinetic term. A $1/n$ dependence of the Heller–Marcus effect is found [9, 16] in the Wannier limit, due to the appropriate normalization of the one-dimensional wavefunction.

Noting then that (22) has no $1/n^3$ term, and inserting now (24) and (25) into equation (20), we can write our estimate for $\mathbf{M}^{-1}$ (up to order $1/n^3$), as

$$(M_{ij}^{-1})_n \simeq (M_{ij}^{-1})_\infty + \Delta(M_{ij}^{-1})_n \tag{26}$$

where $(M_{ij}^{-1})_\infty = [\alpha/(1+\alpha)](m_h^{-1})_{ij}$ is the Wannier result (i.e. $\mathbf{M} = \mathbf{m}_e + \mathbf{m}_h$); while the n-dependent correction $\Delta(M_{ij}^{-1})_n$ is given by

$$\Delta(M_{ij}^{-1})_n = \frac{\alpha}{1+\alpha}\sum_{\boldsymbol{R}} R_i R_j V(\boldsymbol{R})\frac{|\boldsymbol{R}|^2}{6a_0^2 n^2} + (M_{ij}^{-1})_F \frac{v}{\pi(a_0 n)^3}. \tag{27}$$

In the Wannier limit for which the Bohr-like parameter a_0 satisfies the condition $a_0 \gg |\boldsymbol{R}|$ for all relevant $\boldsymbol{R}$-values and given some experimental [4] or theoretical knowledge [13, 17] of the various matrix elements $C(\boldsymbol{R})$, $V(\boldsymbol{R})$ and $H(\boldsymbol{R})$, one expects equation (27) to provide a rough estimate with which to compare experimental results of the mass tensor for different members $n = 1, 2, 3, \ldots$ of a given excitonic series. Here n is, as previously indicated, the principal quantum number of the nth (excitonic) absorption peak of the series [4]. If the ground-state ($n = 1$) binding energy E_1 of the first peak in the series is known [4], then the Bohr-like parameter a_0 can be adjusted by the approximate relation [4] $E_1 \simeq K_1 \equiv \sum_{\boldsymbol{R}}(K_{\boldsymbol{R}})_{n=1}$, given by the virial theorem.

The Heller–Marcus matrix elements $H(\boldsymbol{R})$ (being amplitudes for the simultaneous 'hopping' of *both* the electron and the hole) are, on the other hand, expected [13, 17] on general grounds to be smaller than the electron's ($C(\boldsymbol{R})$) or hole's ($V(\boldsymbol{R})$) hopping elements. Thus, $(M_{ij}^{-1})_F$ in equation (27) and the entire Heller–Marcus term associated

† These workers did *not* consider, however, any Heller–Marcus effect in the interpretation of their experimental results.

‡ Mathematically, one also has that the square of the coulombic wavefunctions of *zero angular momentum* die off at the origin ($\boldsymbol{r} = \boldsymbol{0}$) as $1/n^3$.

with it with the $1/n^3$ dependence will be *weaker* than the corresponding kinetic term in (27) in the Wannier limit.

The precise details of equations (22), (23) and (27) cannot, of course, be expected to hold in general, given the rough approximations made in obtaining them. One does expect, however, the Heller–Marcus effect (*when present*) to die off as predicted by (27) for $a_0 \to \infty$, namely as the inverse volume of the sphere of localization of the exciton while, on the other hand, the kinetic term will decrease as $1/n^2$ because of the virial theorem requirements.

Future experimental works should, thus, have the last word on the applicability of the above equations, and on their novel and interesting predictions regarding the effective mass of an exciton.

Acknowledgments

The support of this research by Consejo Nacional de Investigaciones Científicas y Tecnológicas SPI scholarship 0244 is gratefully acknowledged.

References

[1] Mattis D C and Gallinar J-P 1984 *Phys. Rev. Lett.* **53** 1391
[2] Jeffries C 1991 *Encyclopedia of Physics* 2nd edn ed R G Lerner and G L Trigg (New York: VCH) p 359
[3] Cafolla A A, Schnatterly S E and Tarrio C 1985 *Phys. Rev. Lett.* **55** 2818
[4] Tarrio C and Schnatterly S E 1992 *J. Phys. Chem. Solids* **53** 1013, and references therein
[5] Gallinar J-P 1993 *J. Phys.: Condens. Matter* **5** L223
[6] Mattis D C 1986 *Rev. Mod. Phys.* **58** 361
[7] Gallinar J-P 1987 *Phys. Rev.* B **35** 6464
[8] Gallinar J-P and Mattis D C 1985 *Phys. Rev.* B **32** 4914
[9] Gallinar J-P 1987 *Phys. Rev.* B **36** 1782
[10] Altarelli M and Bassani F 1971 *J. Phys. C: Solid State Phys.* **4** L328
Andreoni W, Altarelli M and Bassani F 1975 *Phys. Rev.* B **11** 2352
[11] Baldini G 1962 *Phys. Rev.* **128** 1562
Bostanjoglo O and Schmidt L 1966 *Phys. Lett.* **22** 123
[12] Rashba E I 1982 *Excitons* ed E I Rashba and M D Sturge (Amsterdam: North-Holland), and references therein
Singh J 1994 *Excitation Energy Transfer Processes in Condensed Matter* (New York: Plenum)
[13] Heller W and Marcus A 1951 *Phys. Rev.* **84** 809
[14] Gallinar J-P 1984 *Phys. Lett.* **103A** 72
[15] Kvitsinsky A A 1992 *J. Phys. A: Math. Gen.* **25** 65
[16] El-Khoury J E and Gallinar J-P 1995 unpublished
[17] Callaway J 1974 *Quantum Theory of the Solid State* (New York: Academic)