Effect of exciton hopping upon the mass of an exciton

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A plausible formula derived in a previous paper for the mass M_n^* of an exciton in an nth bound state of the electron-hole binding potential is extended so as to include the effect of an exciton-hopping (or Heller-Marcus) mechanism upon M_n^*. If m_e^* and m_h^* are the electron and hole masses, we find that

$$M_n^* = \frac{m_e^* + m_h^*}{1 - \frac{K_n}{W} + \frac{m_e^* + m_h^*}{M_F^*}\frac{H_n}{H_F}} ,$$

where K_n and H_n are, respectively, the kinetic and exciton-hopping energies in the nth bound state; W is one-half the sum of the electron and hole bandwidths, and H_F is the value taken by H_n for a Frenkel exciton of finite mass M_F^*. For Wannier excitons, $K_n = H_n \cong 0$, so that $M_n^* \cong m_e^* + m_h^*$; while for Frenkel excitons, $K_n \cong W$ and $H_n \cong H_F$, so that the mass of the Frenkel exciton M_F^* is finite as a consequence of the Heller-Marcus mechanism.

INTRODUCTION

Recently, a plausible formula was derived[1] by us for the mass M_n^* of an exciton in the nth bound state of the potential that binds the electron and the hole together. We found[1] that

$$M_n^* = \frac{m_e^* + m_h^*}{1 - \frac{K_n}{W}} , \tag{1}$$

where m_e^* and m_h^* are, respectively, the electron and hole effective masses, W is one-half the sum of the electron and hole bandwidths, and K_n is the kinetic energy of the exciton in the nth bound state of the binding potential. As K_n varies from zero up to W, the mass M_n^* of the exciton changes from a value of $m_e^* + m_h^*$ (that which is appropriate for a Wannier exciton) up to infinity, which would then be the mass of an immobile or completely localized Frenkel exciton. Thus, formula (1) has the merit of being an interpolation—valid for a general electron-hole binding potential—between two extreme types of excitons, viz., the Wannier-Mott excitons and the Frenkel-type excitons. Although large, the mass of a Frenkel exciton need not, of course, be infinite.[2-4] The Frenkel exciton may, in fact, move and thereby acquire a finite mass through, for example, an "exciton-hopping" energy or so-called Heller-Marcus[2] mechanism. This is a process[2] by which the, otherwise, localized Frenkel exciton moves or diffuses by a resonance mechanism[1,2] which can be seen to be related to van der Waals (i.e., dipolar) forces. In the strongly bound or localized Frenkel exciton, the electron and the hole must "sit" together at the same place or site, and, hence, the usual one-particle matrix elements (embodied in the kinetic energy term) by which the electron *or* the hole moves (each independently of the other), become totally ineffective towards providing the exciton with some mobility. In such a situation it is necessary to introduce matrix elements (embodied in the Heller-Marcus mechanism) through which the electron *and* the hole (localized together at a given site) can move as a whole, together and simultaneously, and in that way *can stay together* in the course of their motion. This is what is required by the strongly bound condition of the localized Frenkel exciton; and this is the principal point that we wish to address in this paper. Thus, we allow the Frenkel exciton to become mobile (and have a given finite mass M_F^*) by introducing a simple (isotropic) exciton-hopping[2] or Heller-Marcus energy term into the Hamiltonian. In turn, this will allow us to obtain a nontrivial, yet simple, generalization of formula (1), with that one desirable feature of endowing the strongly bound Frenkel exciton with a finite mass M_F^*.

Thus, in the following section we begin this paper by obtaining a difference equation obeyed by a wave function associated to the exciton, and then, in the effective mass section, we derive the formula given in the abstract for the mass M_n^* of the exciton. Finally, we end with some comments about this formula.

DIFFERENCE EQUATION

As in Ref. 1, we find it convenient to use the theoreticians' "cubium" band structures in our derivation; namely, either the simple-cubic (sc) or the body-centered-cubic (bcc) band structures, appropriate for *nearest-neighbor*

hops of the electron or the hole on the corresponding cubic lattices. Furthermore, to include the exciton-hopping term in the Hamiltonian (or Heller-Marcus energy) we have found it illustrative here (in contrast with our earlier work[1]) to introduce the site representation. Thus, if we denote by $|\mathbf{n},\mathbf{m}\rangle$ the orthonormal basis states in which the electron is localized at site $\mathbf{n}$, and the hole at site $\mathbf{m}$, we write the "two-particle" state of the exciton $|\Psi\rangle$, as

$$|\Psi\rangle=\sum_{\mathbf{n},\mathbf{m}}\Psi(\mathbf{n},\mathbf{m})|\mathbf{n},\mathbf{m}\rangle\ , \tag{2}$$

wherein we shall make the customary separation of the center-of-mass motion from the relative coordinate motion by writing[4]

$$\Psi(\mathbf{n},\mathbf{m})=e^{i\mathbf{k}\cdot(\mathbf{n}+\mathbf{m})/2}F(\mathbf{n}-\mathbf{m})\ , \tag{3}$$

with $\mathbf{k}$ being the wave vector of the center of mass of the exciton, and $F(\mathbf{n}-\mathbf{m})$ being some function of the relative coordinate $\mathbf{n}-\mathbf{m}$ only. We shall write the Hamiltonian $\hat{\mathscr{H}}$, such that

$$\hat{\mathscr{H}}(\lambda,\mu)=\hat{K}+\lambda\hat{V}+\mu\hat{H}\ , \tag{4}$$

with $\hat{K}$ being the total positive kinetic energy appropriate to the cubium band structures previously mentioned, $\hat{V}$ is the *arbitrary* effective two-body potential that binds the electron and hole together, and $\hat{H}$ is the Heller-Marcus energy term. In Eq.(4) we have introduced *two coupling constants,* λ and μ, such that when $\lambda=\mu=1$, $\hat{\mathscr{H}}(\lambda,\mu)$ is, in fact, the Hamiltonian, i.e., $\hat{\mathscr{H}}(1,1)\equiv\hat{\mathscr{H}}$. The reason for introducing these coupling constants will readily become apparent in the text below.

We assume that the nonvanishing matrix elements of $\hat{\mathscr{H}}(\lambda,\mu)$ are the following

$$\langle\mathbf{n},\mathbf{m}|\hat{\mathscr{H}}(\lambda,\mu)|\mathbf{n},\mathbf{m}\rangle=W+\lambda V(\mathbf{n}-\mathbf{m}) \tag{5}$$

for the diagonal matrix elements. W in (5) is the combined half-bandwidth of the electron plus hole, since in (4) the kinetic energy of both the electron and hole are measured from their respective band extrema and are both positive. For the nondiagonal matrix elements, we take

$$\langle\mathbf{n},\mathbf{m}|\hat{\mathscr{H}}(\lambda,\mu)|\mathbf{n},\mathbf{m}+\boldsymbol{\delta}\rangle=-V \tag{6}$$

and

$$\langle\mathbf{n},\mathbf{m}|\hat{\mathscr{H}}(\lambda,\mu)|\mathbf{n}+\boldsymbol{\delta},\mathbf{m}\rangle=-C\ , \tag{7}$$

where $\mathbf{m}$, $\mathbf{m}+\boldsymbol{\delta}$ (or $\mathbf{n}$, $\mathbf{n}+\boldsymbol{\delta}$) are nearest-neighbor sites on the cubic lattices, V represents the usual valence-band width parameter associated with nearest-neighbor jumping of the hole, and C is the corresponding conduction-band width parameter associated to the electron. Finally, we introduce the exciton-hopping matrix elements given by

$$\langle\mathbf{m},\mathbf{m}|\hat{\mathscr{H}}(\lambda,\mu)|\mathbf{n},\mathbf{n}\rangle=\mu H(\mathbf{n}-\mathbf{m})\ ,\quad \mathbf{n}\neq\mathbf{m}\ . \tag{8}$$

This last matrix element is the one associated to the Heller-Marcus mechanism,[2-4] whereby the entire (Frenkel) exciton jumps as a whole entity between sites $\mathbf{n}$ and $\mathbf{m}$, with the amplitude $H(\mathbf{n}-\mathbf{m})$. Substitution of Eqs. (2)–(8), into the eigenvalue equation

$$\hat{\mathscr{H}}|\Psi\rangle=E|\Psi\rangle \tag{9}$$

leads, after some algebra, to the following difference equation for the function $F(\mathbf{n}-\mathbf{m})\equiv F(\mathbf{p})$, namely

$$[E(\mathbf{k})-V_{\mathbf{k}}(\mathbf{p})]F(\mathbf{p})=-\sum_{\boldsymbol{\delta}}\epsilon_{\mathbf{k}}(\boldsymbol{\delta})F(\mathbf{p}+\boldsymbol{\delta})\ , \tag{10}$$

where $E(\mathbf{k})$ is the energy eigenvalue of $|\Psi\rangle$.

$$V_{\mathbf{k}}(\mathbf{p})=V(\mathbf{p})+\delta_{\mathbf{p},0}\sum_{l\neq 0}H(l)e^{i\mathbf{k}\cdot l}+W \tag{11}$$

and

$$\epsilon_{\mathbf{k}}(\boldsymbol{\delta})=Ve^{-i\mathbf{k}\cdot\boldsymbol{\delta}/2}+Ce^{i\mathbf{k}\cdot\boldsymbol{\delta}/2}\ . \tag{12}$$

Thus, in Eq. (10) we have reduced the "two-body" problem of the exciton, to a one-body problem for the relative coordinate $\mathbf{p}=\mathbf{n}-\mathbf{m}$, which moves in the presence of the general $\mathbf{k}$-dependent potential $V_{\mathbf{k}}(\mathbf{p})$, and with a $\boldsymbol{\delta}$-dependent $\epsilon_{\mathbf{k}}(\boldsymbol{\delta})$ matrix element for jumping between nearest-neighbor sites.

EFFECTIVE MASS

Equation (10) is thus quite general and to derive it we have not yet explicitly assumed that the underlying lattice is either sc or bcc. To make further progress, we now make the simplifying assumption that the matrix elements $H(l)$ are isotropic,[3,4] i.e., $H(l)=H(|l|)\equiv H(l)$. With this assumption, the effective mass M_n^* of the exciton, as deduced from (10), will be a scalar[1,4] for a cubic lattice.[5] Hence, in Eq. (10) we can then *arbitrarily* assign the direction of the vector $\mathbf{k}$ in the derivation of the formula for

$$(M_n^*)^{-1}=\left[\frac{\partial^2 E(\mathbf{k})}{\partial k^2}\right]_{\mathbf{k}=0}\ .$$

The procedure that we now follow is that of choosing the direction of $\mathbf{k}$ so that $|\epsilon_{\mathbf{k}}(\boldsymbol{\delta})|$ becomes independent of $\boldsymbol{\delta}$, i.e., $|\epsilon_{\mathbf{k}}(\boldsymbol{\delta})|\equiv\epsilon(\mathbf{k})$ for such $\mathbf{k}$'s. As will be seen below, *only* for the sc and bcc of the cubic lattices can this be achieved. In fact, we have in general that

$$\epsilon_{\mathbf{k}}(\boldsymbol{\delta})=|\epsilon_{\mathbf{k}}(\boldsymbol{\delta})|e^{i\theta}\ , \tag{13}$$

with

$$|\epsilon_{\mathbf{k}}(\boldsymbol{\delta})|=[V^2+C^2+2VC\cos(\mathbf{k}\cdot\boldsymbol{\delta})]^{1/2} \tag{14}$$

and

$$\tan\theta=\left[\frac{C-V}{C+V}\right]\tan\left[\frac{\mathbf{k}\cdot\boldsymbol{\delta}}{2}\right]\ . \tag{15}$$

We now change the phase of the wave function $F(\mathbf{p})$ (corresponding to a relocation of the center of mass) by defining a new wave function $G(\mathbf{p})$ according to

$$F(\mathbf{p})\equiv e^{-i\mathbf{p}\cdot\mathbf{k}\varphi(\mathbf{k})}G(\mathbf{p})\ , \tag{16}$$

where $\varphi(\mathbf{k})$ is to be suitably adjusted. Substitution of (13) and (16) into (10), leads to

$$[E(\mathbf{k})-V_{\mathbf{k}}(\mathbf{p})]G(\mathbf{p})=-\sum_{\boldsymbol{\delta}}|\epsilon_{\mathbf{k}}(\boldsymbol{\delta})|e^{i\theta}e^{-i\boldsymbol{\delta}\cdot\mathbf{k}\varphi(\mathbf{k})}G(\mathbf{p}+\boldsymbol{\delta})\ . \tag{17}$$

For the sc lattice we choose $\mathbf{k}$ to be $\mathbf{k}=(1/\sqrt{3})(k,k,k)$, while for the bcc lattice we set $\mathbf{k}=(k,0,0)$. In each case the corresponding $|\boldsymbol{\delta}\cdot\mathbf{k}|$ is then constant, i.e., $\boldsymbol{\delta}\cdot\mathbf{k}$ changes *at most* in sign as $\boldsymbol{\delta}$ varies. Hence, we can choose $\varphi(\mathbf{k})$ to be given by $\varphi(\mathbf{k})=\theta/\boldsymbol{\delta}\cdot\mathbf{k}$, where $\varphi(\mathbf{k})$ is then, indeed, a function of $\mathbf{k}$ (independent of $\boldsymbol{\delta}$). With this choice for $\varphi(\mathbf{k})$, the phase factors in (17) then cancel out, and (17) becomes

$$[E(\mathbf{k})-V_{\mathbf{k}}(\mathbf{p})]G(\mathbf{p})=-\epsilon(\mathbf{k})\sum_{\boldsymbol{\delta}}G(\mathbf{p}+\boldsymbol{\delta})\ , \tag{18}$$

where $\epsilon(\mathbf{k})\equiv|\epsilon_{\mathbf{k}}(\boldsymbol{\delta})|$ is indeed independent of $\boldsymbol{\delta}$ for such $\mathbf{k}$'s. We remark at this point that for the face-centered-cubic (fcc) lattice, the derivation of (18) obviously fails, since there is then no direction for $\mathbf{k}$ that will make $|\boldsymbol{\delta}\cdot\mathbf{k}|$ constant for all $\boldsymbol{\delta}$'s; while, on the other hand, for a one-dimensional lattice the equivalent of (18) can be trivially obtained, since there are then no such directional problems. As will be seen below, the validity of Eq. (18) is crucial in the derivation that follows. We will now use the coupling constants λ,μ introduced in (4) for $\hat{\mathscr{H}}(\lambda,\mu)$ to obtain a relationship between $E(\mathbf{k})$ and $E(\mathbf{k}=0)$ for small $\mathbf{k}$'s. We will do this by the method of using the coupling constants λ,μ to express $E(\mathbf{k},\lambda,\mu)$ in terms of $E(0,\tilde{\lambda},\tilde{\mu})$, where $\tilde{\lambda}$ and $\tilde{\mu}$ will be suitably *renormalized* values of λ and μ. Ultimately, of course, λ and μ will be set equal to 1. Thus, if we consider in (18) the λ and μ dependence of $E(\mathbf{k},\lambda,\mu)$, we define a $u(\mathbf{k},\lambda,\mu)$ by

$$E(\mathbf{k},\lambda,\mu)-W\equiv\epsilon(\mathbf{k})u(\mathbf{k},\lambda,\mu)\equiv E'(\mathbf{k},\lambda,\mu)\ . \tag{19}$$

In terms of $u(\mathbf{k},\lambda,\mu)$, (18) becomes

$$\left[u(\mathbf{k},\lambda,\mu)-\frac{\lambda V(\mathbf{p})}{\epsilon(\mathbf{k})}-\frac{\mu\delta_{\mathbf{p},0}h(\mathbf{k})}{\epsilon(\mathbf{k})}\right]G(\mathbf{p})=-\sum_{\boldsymbol{\delta}}G(\mathbf{p}+\boldsymbol{\delta})\ , \tag{20}$$

where

$$h(\mathbf{k})\equiv\sum_{l\neq 0}H(l)e^{i\mathbf{k}\cdot\mathbf{l}}\ . \tag{21}$$

From (20), it easily follows that

$$u(\mathbf{k},\lambda,\mu)=u(0,\tilde{\lambda},\tilde{\mu})\ , \tag{22}$$

if

$$\tilde{\lambda}\equiv\frac{\lambda\epsilon(0)}{\epsilon(\mathbf{k})}\quad\text{and}\quad\tilde{\mu}\equiv\mu\left[\frac{\epsilon(0)}{\epsilon(\mathbf{k})}\right]\left[\frac{h(\mathbf{k})}{h(0)}\right]\ . \tag{23}$$

Hence,

$$E'(\mathbf{k},\lambda,\mu)=\frac{\epsilon(\mathbf{k})}{\epsilon(0)}E'(0,\tilde{\lambda},\tilde{\mu})\ , \tag{24}$$

where $\mathbf{k}=(1/\sqrt{3})(k,k,k)$ for the sc lattice, and $\mathbf{k}=(k,0,0)$ for the bcc lattice. Equation (24) above is fundamental for the derivation that follows. Its validity, in turn, follows from the form of Eq. (20), where a "single" $\epsilon(\mathbf{k})\equiv|\epsilon_{\mathbf{k}}(\boldsymbol{\delta})|$ appears.

We now expand, for small k, all functions which appear in (24) in powers of k, up to k^2. We have that,

$$\frac{\epsilon(\mathbf{k})}{\epsilon(0)}\cong 1+\frac{k^2\epsilon''}{2\epsilon(0)} \tag{25}$$

and

$$\frac{h(\mathbf{k})}{h(0)}\cong 1+\frac{k^2h''}{2h(0)}\ , \tag{26}$$

where

$$\epsilon''\equiv\left[\frac{\partial^2\epsilon}{\partial k^2}\right]_{k=0}\quad\text{and}\quad h''\equiv\left[\frac{\partial^2 h}{\partial k^2}\right]_{k=0}\ . \tag{27}$$

Thus

$$\tilde{\lambda}\cong\lambda\left[1-\frac{k^2\epsilon''}{2\epsilon(0)}\right]\ , \tag{28}$$

and

$$\tilde{\mu}\cong\mu\left[1-\frac{k^2\epsilon''}{2\epsilon(0)}\right]\left[1+\frac{k^2h''}{2h(0)}\right]\cong\mu\left[1+\frac{k^2}{2}\left[\frac{h''}{h(0)}-\frac{\epsilon''}{\epsilon(0)}\right]\right]\ . \tag{29}$$

Substitution of (25), (28), and (29) into (24) gives upon expansion that

$$E'(\mathbf{k},\lambda,\mu)\cong\left[1+\frac{k^2\epsilon''}{2\epsilon(0)}\right]E'\left[0,\lambda-\frac{\lambda k^2\epsilon''}{2\epsilon(0)},\mu-\frac{\mu k^2}{2}\left[\frac{\epsilon''}{\epsilon(0)}-\frac{h''}{h(0)}\right]\right]$$
$$\cong\left[1+\frac{k^2\epsilon''}{2\epsilon(0)}\right]\left[E'(0,\lambda,\mu)-\frac{\lambda k^2\epsilon''}{2\epsilon(0)}\frac{\partial E'}{\partial\lambda}(0,\lambda,\mu)-\frac{\mu k^2}{2}\left[\frac{\epsilon''}{\epsilon(0)}-\frac{h''}{h(0)}\right]\frac{\partial E'}{\partial\mu}(0,\lambda,\mu)\right]\ , \tag{30}$$

or

$$E'(\mathbf{k},\lambda,\mu)\cong E'(0,\lambda,\mu)+\frac{k^2}{2}\left[\frac{\epsilon''}{\epsilon(0)}E'(0,\lambda,\mu)-\frac{\lambda\epsilon''}{\epsilon(0)}\frac{\partial E'}{\partial\lambda}(0,\lambda,\mu)-\mu\left[\frac{\epsilon''}{\epsilon(0)}-\frac{h''}{h(0)}\right]\frac{\partial E'}{\partial\mu}(0,\lambda,\mu)\right]\ . \tag{31}$$

From (31) we can readily identify $(M^*)^{-1}$, as the factor in large square brackets on the right-hand side of (31), when evaluated for $\lambda=\mu=1$. Hence,

$$(M^*)^{-1}=\left[\frac{\epsilon''}{\epsilon(0)}\left[E(0,\lambda,\mu)-W-\lambda\frac{\partial E}{\partial\lambda}(0,\lambda,\mu)-\mu\frac{\partial E}{\partial\mu}(0,\lambda,\mu)\right]+\frac{\mu h''}{h(0)}\frac{\partial E}{\partial\mu}(0,\lambda,\mu)\right]_{\lambda=\mu=1}\ . \tag{32}$$

We now invoke the Hellmann-Feynman theorem to write that

$$\frac{\partial E}{\partial\lambda}(\mathbf{0},\lambda,\mu)=\left\langle\frac{\partial\hat{\mathscr{H}}(\lambda,\mu)}{\partial\lambda}\right\rangle_{\mathbf{k}=0}=\langle\hat{V}\rangle_{\mathbf{k}=0} \tag{33}$$

and

$$\frac{\partial E}{\partial\mu}(\mathbf{0},\lambda,\mu)=\left\langle\frac{\partial\hat{\mathscr{H}}(\lambda,\mu)}{\partial\mu}\right\rangle_{\mathbf{k}=0}=\langle\hat{H}\rangle_{\mathbf{k}=0}\,, \tag{34}$$

where the angular brackets in (33) and (34) denote the expectation value of the corresponding operators with respect to the eigenstates of $\hat{\mathscr{H}}(\lambda,\mu)$. Since

$$E(\mathbf{0},\lambda,\mu)=\langle\hat{K}\rangle_{\mathbf{k}=0}+\lambda\langle\hat{V}\rangle_{\mathbf{k}=0}+\mu\langle\hat{H}\rangle_{\mathbf{k}=0}\,,$$

Eq. (32) then becomes

$$(M^*)^{-1}=\left[\frac{\epsilon''}{\epsilon(\mathbf{0})}(\langle\hat{K}\rangle_{\mathbf{k}=0}-W)+\frac{h''}{h(\mathbf{0})}\mu\langle\hat{H}\rangle_{\mathbf{k}=0}\right]_{\lambda=\mu=1} \tag{35}$$

or, equivalently,

$$M_n^*=\frac{1}{\frac{\epsilon''}{\epsilon(\mathbf{0})}(K_n-W)+\frac{h''}{h(\mathbf{0})}H_n}\,, \tag{36}$$

where for $\lambda=\mu=1$, we have defined the notation

$$K_n\equiv\langle\hat{K}\rangle_{\mathbf{k}=0}\text{ and }H_n\equiv\langle\hat{H}\rangle_{\mathbf{k}=0} \tag{37}$$

to be, respectively, the kinetic energy and exciton-hopping energy in an nth bound eigenstate of $\hat{\mathscr{H}}$, for which the mass of the exciton is then M_n^*. But,

$$\epsilon(\mathbf{k})=[V^2+C^2+2VC\cos(\eta k)]^{1/2}\,, \tag{38}$$

where

$$\eta=\begin{cases}\frac{1}{2}\text{ for the bcc lattice}\\ \frac{1}{\sqrt{3}}\text{ for the sc lattice}\,,\end{cases}$$

and in (38) the length of the side of the conventional cubic cell is taken to be unity. Hence,

$$\frac{\epsilon''}{\epsilon(\mathbf{0})}=-\frac{VC\eta^2}{(V+C)^2}\,. \tag{39}$$

Analogously, for both the bcc and sc lattices we find

$$\frac{h''}{h(\mathbf{0})}=-\frac{1}{3}\frac{\sum_{l\neq0}l^2H(l)}{\sum_{l\neq0}H(l)}\,. \tag{40}$$

We now rewrite (36) in the form

$$M_n^*=\frac{\left[-\frac{\epsilon(\mathbf{0})}{\epsilon''W}\right]}{1-\frac{K_n}{W}-\left[\frac{h''}{h(\mathbf{0})}\right]\left[\frac{\epsilon(\mathbf{0})}{\epsilon''W}\right]H_n}\,, \tag{41}$$

and we see that, remarkably,

$$-\frac{\epsilon(\mathbf{0})}{\epsilon''W}=\frac{(V+C)^2}{VC\eta^2W}=\frac{1}{2C}+\frac{1}{2V}=m_e^*+m_h^*\,, \tag{42}$$

since $\eta^2W=2(V+C)$, for both the bcc and sc lattices; and the electron effective mass is $m_e^*=1/2C$, while $m_h^*=1/2V$ is the hole effective mass, independently (both) of the lattice in question.

If we identify the Frenkel exciton as that for which $K_n=W$, when $H_n=H_F$, by writing under such conditions that $M_n^*\equiv M_F^*$, we obtain from (41) that

$$M_F^*=\frac{h(\mathbf{0})}{h''H_F}\,, \tag{43}$$

so that we can finally write (41) as

$$M_n^*=\frac{m_e^*+m_h^*}{1-\frac{K_n}{W}+\frac{m_e^*+m_h^*}{M_F^*}\frac{H_n}{H_F}}\,, \tag{44}$$

which ends our derivation. Q.E.D.

At this point it is worthwhile to remark the following about Eqs. (43) and (44).

(a) Equation (43) can be understood very simply if we take the energy $E_F(\mathbf{k})$ of a Frenkel exciton to be[2]

$$E_F(\mathbf{k})=E_0+H_F(\mathbf{k})\,, \tag{45}$$

where E_0 is some constant[2] and

$$H_F(\mathbf{k})\equiv h(\mathbf{k})\,. \tag{46}$$

Equation (45) then expresses the energy of the strongly bound Frenkel exciton as that of a single particle that bands or hops among the lattice sites according to the exciton-hopping matrix elements $H(l)$ which appear in $h(\mathbf{k})$. Then we set $H_F\equiv H_F(\mathbf{k}=0)=h(\mathbf{0})$ and from (45) we obtain additionally that $M_F^*=(h'')^{-1}$. These values for M_F^* and H_F, are then clearly a solution of Eq. (43), as they should be.

(b) If, as is sometimes assumed,[3,4] the only nonvanishing $H(l)$ is that connecting first-nearest-neighbors, then H_F can be identified with a Frenkel exciton half-bandwidth, as derived from the band structure for $E_F(\mathbf{k})$ in (45). H_F in (44) is then the "analogue" of W in the same formula.

(c) Although the potential $V(\mathbf{n}-\mathbf{m})$ that binds the electron and hole together does not appear explicitly in (44), it must be realized that it will implicitly appear, of course, in the determination of the eigenstates of $\hat{\mathscr{H}}$ needed to calculate the expectation values K_n of the kinetic energy, and H_n of the exciton-hopping energy of the exciton. By the same token, the additional term [in the denominator of (44)] proportional to H_n is only *formally* additive. By this we mean that the presence of the exciton-hopping energy in the Hamiltonian $\hat{\mathscr{H}}$ in (4), will, obviously, affect the eigenstates of $\hat{\mathscr{H}}$ needed, in turn, to calculate the expectation value K_n of the kinetic energy which appears in our formula for M_n^*. The kinetic energy and exciton-hopping energy processes can then be said to interfere (in a quantum-mechanical sense) with each other and with the electron-hole binding potential.

In summary, we have derived in quite considerable detail a plausible equation [Eq. (44)] for M_n^*, the mass of an exciton in the nth bound state of an arbitrary[6] effective two-body potential between the electron and the hole. We have done so while taking into consideration the so-called exciton-hopping matrix elements,[2] which are essential[2–4] for the mobility of an otherwise localized[7,8] strongly bound Frenkel exciton, and which were omitted, for simplicity, in our previous work of Ref. 1.

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[5]As clearly shown in Ref. 2, without this assumption the mass of the Frenkel exciton can be a tensor, even for a cubic lattice. In such a case *our derivation* of formula (44) for M_n^* *ceases to be valid.*

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