Excitonic contribution to photoluminescence in amorphous semiconductors

Jai Singh \(^a\), T. Aoki \(^b\) & K. Shimakawa \(^c\)

\(^a\) Faculty of Site B-28, Northern Territory University, Darwin, Northern Territory, 0909, Australia
\(^b\) Department of Electronics and Computer Engineering and Joint Research Center of High Technology, Tokyo Institute of Polytechnics, Atsugi, 243-0297, Japan
\(^c\) Department of Electrical and Electronic Engineering, Gifu University, Gifu, 501-1193, Japan

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Excitonic contribution to photoluminescence in amorphous semiconductors

JAI SINGH†
Faculty of Site, B-28, Northern Territory University, Darwin, Northern Territory 0909, Australia

T. AOKI
Department of Electronics and Computer Engineering and Joint Research Center of High Technology, Tokyo Institute of Polytechnics, Atsugi 243-0297, Japan

and K. SHIMAKAWA
Department of Electrical and Electronic Engineering, Gifu University, Gifu 501-1193, Japan

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ABSTRACT

Applying the effective-mass approach, the energy eigenvalues of excitonic states in amorphous semiconductors are derived. It is shown that Wannier-Mott-type excitons can indeed be formed in amorphous solids. The results show that the occurrence of the double photoluminescence (PL) lifetime distribution peak, fast and slow, in hydrogenated amorphous silicon (a-Si:H) and hydrogenated amorphous germanium (a-Ge:H) can unambiguously be assigned to radiative recombinations from singlet and triplet excitonic states respectively. The dependence of PL peaks on the temperature and generation rate in a-Si:H and a-Ge:H is also discussed. The approach is general and simple and can be applied to study the charge-carrier transport and PL properties in any amorphous solid.

§1. INTRODUCTION

Considerable progress has been made in understanding photoluminescence (PL) in amorphous semiconductors in the last two decades, particularly in hydrogenated amorphous silicon (a-Si:H) (Fischer 1979, Street 1981, 1991) and amorphous chalcogenides (Street 1976, Murayama 1983). However, the origin of PL, particularly in a-Si:H, has become a controversial issue (Kemp and Silver 1992). Using the quadrature frequency-resolved spectroscopy (QFRS) technique, a double-peak PL lifetime distribution has been observed in a-Si:H by several groups (Boulitrop and Dunstan 1985, Searle et al. 1987, Ambros et al. 1991, Stachowitz et al. 1998). By deconvoluting the double-peak structure, Ambros et al. (1991) have found two lifetime peaks: firstly, a short-lived PL peak lasting for about 10 μs and, secondly, a
long-lived peak lasting for about 1 ms. This double-peak lifetime distribution cannot be explained on the basis of the widely accepted radiative tunnelling model (Street 1981).

Recently, Ishii et al. (2000) and Aoki (2000) have also observed a similar double-peak lifetime distribution in hydrogenated amorphous germanium (a-Ge : H) using the QFRS technique and found PL with a long lifetime of $10^{-4}$ s and a short lifetime of about 1 μs. These results suggest that the occurrence of the double-PL-peak lifetime distribution is probably a common feature in amorphous semiconductors, and therefore it should have a common origin, for example excitonic involvement. Although the involvement of excitons has also been indicated earlier (Yoshida et al. 1989, Stachowicz et al. 1998), no theories seem to exist to explain the occurrence of the double-peak structure.

Some work on excitonic states in disordered systems has been presented (Baranovskii and Efros, 1978, Brinkman et al. 1999, Sieh et al. 1999), but a theory that can explain the appearance of two PL peaks in a-Si : H and a-Ge : H has not yet been developed. It is therefore very timely and essential to develop a theory for the excitonic states in amorphous semiconductors that can be applied to study PL in amorphous semiconductors.

In this paper, a theory of Wannier–Mott excitonic states applicable to amorphous semiconductors is presented. An effective-mass approach (Singh 1994, 2000) is applied, and approximate analytical expressions for the effective mass of charge carriers are given. The expressions for the energy eigenvalues of both singlet and triplet excitonic states, and the splitting energy between singlet and triplet states are derived for a-Si : H and a-Ge : H.

In §2, a theory of excitonic states in the real coordinate space applicable to amorphous solids is presented, and then the effective mass approach is briefly described in §3, where approximate analytical expressions for electron and hole effective masses are also derived. In §4, the effective-mass approximation is applied to derive the energy difference between singlet and triplet excitonic states, and then the singlet–triplet splitting is calculated for a-Si : H and a-Ge : H. A discussion of our results is presented in §5.

§2. EXCITONIC STATES IN AMORPHOUS SOLIDS

As amorphous solids do not have long-range order or translational symmetry, we use the electronic Hamiltonian in the real coordinate space for such solids as (Singh 1994):

$$\hat{H} = \hat{H}_1 + \hat{H}_2,$$

where

$$\hat{H}_1 = \sum_{l,m,j,\sigma} E_{lmj} a_{jl}^+(\sigma)a_{jm}(\sigma),$$

$$\hat{H}_2 = \frac{1}{2} \sum_{l_1,j_1,\sigma_1 l_2,j_2,\sigma_2 l_3,j_3,\sigma_3 l_4,j_4,\sigma_4} \langle j_1, l_1, \sigma_1; j_2, l_2, \sigma_2 \rangle \langle j_3, l_3, \sigma_3; j_4, l_4, \sigma_4 \rangle \langle a_{j_1l_1}(\sigma_1) a_{j_2l_2}(\sigma_2) a_{j_3l_3}(\sigma_3) a_{j_4l_4}(\sigma_4) \rangle,$$

$$E_{lmj} = \langle j, l, \sigma | -\frac{\hbar^2 \nabla^2}{2m_e} + V(r) | j, m, \sigma \rangle.$$
and $|j, l, \sigma\rangle = |\phi_{j l}(\mathbf{r})\rangle$ is the ket vector of an electron in the electronic state $j$ of an atom localized at $l$ with spin $\sigma = +\frac{1}{2}$ or $-\frac{1}{2}$, $\phi_{j l}(\mathbf{r})$ is the corresponding electronic wavefunction and $m_e$ is the free-electron mass. $V(\mathbf{r})$ is the ionic periodic potential that an electron is subjected to, and $U(|r_1 - r_2|)$ is the repulsive potential between two electrons. These are given as

$$V(\mathbf{r}) = -\sum_n \frac{\kappa Ze^2}{|\mathbf{r} - \mathbf{R}_n|} = \sum_n V_n(\mathbf{r}),$$

where $Z$ is the atomic number, $\mathbf{R}_n$ is the position coordinate of the $n$th ion and

$$U(|r_1 - r_2|) = -\frac{\kappa e^2}{|r_1 - r_2|}, \quad \kappa = (4\pi\varepsilon_0)^{-1}.$$

The operators $a_{j l}^+(\sigma)$ and $a_{j l}(\sigma)$ are the creation and annihilation operators respectively of an electron with spin $\sigma$ in the electronic state $j$ of an atom localized at $l$.

For creating optical excitations in amorphous solids, we define a vacuum state vector $|0\rangle$ such that the valence states are completely occupied and conduction states are completely empty. The ket vector of an excited state with an electron (denoted by subscript $e$) in the conduction states denoted by $l$ and a hole (denoted by subscript $h$) in the valence states denoted by $0$ can be written as:

$$|1, 0\rangle = \sum_{l_e, l_h} C_{10}(l_e, l_h) \sum_{\sigma_e, \sigma_h} a_{l_e\sigma_e}^+(\sigma_e) d_{0h\sigma_h}^+(\sigma_h)|0\rangle,$$

where $C_{10}(l_e, l_h)$ is the probability amplitude coefficient for the electron localized at site $l_e$, and a hole at $l_h$. The creation (annihilation) operators, $d_{0l\sigma}^+(\sigma)$ ($d_{0l\sigma}$) of a hole localized at $l$ with spin $\sigma$ in the valence states are defined as (Singh 1994)

$$d_{0l\sigma}^+ = a_{0l\sigma}, \quad d_{0l\sigma} = a_{0l\sigma}^+$

for a singlet, and

$$\sum_{\sigma_e, \sigma_h} a_{l_e\sigma_e}^+(\sigma_e) d_{0h\sigma_h}^+(\sigma_h)|0\rangle = \frac{1}{2^{1/2}} \left[ a_{l_e\sigma_e}^+ \left( \frac{1}{2} \right) d_{0h\sigma_h}^+ \left( -\frac{1}{2} \right) + a_{l_e\sigma_e}^+ \left( -\frac{1}{2} \right) d_{0h\sigma_h}^+ \left( \frac{1}{2} \right) \right]|0\rangle$$

for a triplet.

Using equations (1)–(10), we solve the following eigenvalue problem:

$$\langle 1, 0 | \hat{H} | 1, 0 \rangle = W \langle 1, 0 | 1, 0 \rangle,$$
where \( W \) is the energy eigenvalue of the excitonic state. Thus we obtain

\[
W = W_0 + \sum_{\mathbf{l}_c, \mathbf{l}_h} C_{10}^{*}(\mathbf{l}_c, \mathbf{l}_h) C_{10}(\mathbf{l}_c, \mathbf{l}_h) E_{\mathbf{l}_c, \mathbf{l}_h} - \sum_{\mathbf{l}_c, \mathbf{l}_h, \mathbf{l}_2} C_{10}^{*}(\mathbf{l}_c, \mathbf{l}_h) C_{10}(\mathbf{l}_c, \mathbf{l}_h) E_{\mathbf{l}_c, \mathbf{l}_2, \mathbf{l}_1, \mathbf{l}_h; S),
\]

(12)

where \( W_0 \) represents the total energy of all electrons in the valence states before the excitation, and it is obtained as

\[
W_0 = \sum_{\mathbf{l}_c} \left( 2\langle 0, \mathbf{l}_1 | - \frac{\hbar^2 \nabla^2}{2m_e} + V(r)|0, \mathbf{l}_1 \rangle + \sum_{\mathbf{l}_2} \{2\langle 0, \mathbf{l}_2 | U|0, \mathbf{l}_2; 0, \mathbf{l}_1 \rangle \}
- \langle 0, \mathbf{l}_1; 0, \mathbf{l}_2 | U|0, \mathbf{l}_1; 0, \mathbf{l}_2 \rangle \right),
\]

(13)

\[
E_{\mathbf{l}_c, \mathbf{l}_1} = \langle 1, \mathbf{l}_c | - \frac{\hbar^2 \nabla^2}{2m_e} + V(r)|1, \mathbf{l}_1 \rangle + \sum_{\mathbf{l}_2} \{2\langle 1, \mathbf{l}_2 | U|0, \mathbf{l}_2; 1, \mathbf{l}_1 \rangle \}
- \langle 1, \mathbf{l}_2; 0, \mathbf{l}_1 | U|1, \mathbf{l}_2; 0, \mathbf{l}_1 \rangle \}
\]

(14)

\[
E_{\mathbf{l}_h, \mathbf{l}_1} = \langle 0, \mathbf{l}_h | - \frac{\hbar^2 \nabla^2}{2m_e} + V(r)|0, \mathbf{l}_1 \rangle + \sum_{\mathbf{l}_2} \{2\langle 0, \mathbf{l}_2 | g, \mathbf{l}_u|0, \mathbf{l}_2; 0, \mathbf{l}_1 \rangle \}
- \langle 0, \mathbf{l}_2; 0, \mathbf{l}_1 | U|0, \mathbf{l}_2; 0, \mathbf{l}_1 \rangle \}
\]

(15)

and

\[
E_b(\mathbf{l}_c, \mathbf{l}_2, \mathbf{l}_1, \mathbf{l}_h, S) = \langle 1, \mathbf{l}_c; 0, \mathbf{l}_2 | U|0, \mathbf{l}_h; 1, \mathbf{l}_1 \rangle - (1 - S) \langle 1, \mathbf{l}_c; 0, \mathbf{l}_2 | U|1, \mathbf{l}_1; 0, \mathbf{l}_h \rangle,
\]

(16)

where \( S = 0 \) for singlets and \( S = 1 \) for triplets. At 0 K, \( W_0 \) is the same as the Fermi energy. It is to be noted that equation (12) is obtained by applying the following condition:

\[
\sum_{\mathbf{l}_c, \mathbf{l}_h} [C^{*}(\mathbf{l}_c, \mathbf{l}_h) C(\mathbf{l}_c, \mathbf{l}_h)] = 1,
\]

(17)

which ensures that the excited pair of charge carriers is within the solid. The energy matrix elements \( E_{\mathbf{l}_c, \mathbf{l}_1} \) (equations (12) and (14)) and \( E_{\mathbf{l}_h, \mathbf{l}_1} \) (equations (12) and (15)) represent the energy transfer matrix element between sites at \( \mathbf{l}_c \) and \( \mathbf{l}_1 \) for an electron excited in the conduction states and that between sites \( \mathbf{l}_h \) and \( \mathbf{l} \) for a hole in the valence states respectively. The last term of equation (12) with the energy matrix element \( E_b(\mathbf{l}_c, \mathbf{l}_2, \mathbf{l}_1, \mathbf{l}_h; S) \) represents the interaction between the excited electron and hole as the electron moves from site \( \mathbf{l}_c \) to \( \mathbf{l}_1 \), and the hole moves from site \( \mathbf{l}_h \) to \( \mathbf{l}_2 \), as expressed in equation (16). Depending on the relative magnitude of this energy matrix element, an excited electron–hole pair may or may not form a bound state like an exciton. Therefore, the magnitude of this term in equation (12) contributes to the binding energy of an excited electron–hole pair. It is obvious from equation (16) that the binding energy depends on the spin of the excited pair. The first term of the binding energy is due to the Coulomb interaction, and the second is due to the exchange interaction. The exchange interaction between the electron and the hole vanishes for a triplet spin state \( (S = 1) \), and this means that the binding energy in a
Excitonic contribution to PL in amorphous semiconductors

859

Singlet state is usually less than that in a triplet state. In other words, a singlet bound state is usually formed at a higher energy than the triplet bound state.

§ 3. Effective-mass approach for amorphous solids

It is proposed here to express the probability amplitude coefficients in amorphous solids as

$$C_{10}(l, m) = N^{-1} \exp \left[ i(t_e \cdot l + t_h \cdot m) \right],$$  \tag{18}

where $t_e = [2m_e^*(E_e - E_c)]^{1/2}/\hbar$ and $t_h = [2m_h^*(E_v - E_h)]^{1/2}/\hbar$, with $m_e^*$ and $m_h^*$ being the effective masses of electron in the conduction states and hole in the valence states, respectively and $N$ is the total number of atoms in the sample. $E_c$ and $E_v$ are the electron and hole mobility edges respectively, and $E_e$ and $E_h$ are their corresponding energies. Equation (18) suggests that an electron with energy $E > E_c$ localized on any site can move to another site like a free wave but, if $E < E_c$, the electron can only tunnel through the barrier distance. Neglecting the Coulomb interaction, a similar complex energy–momentum relation has also been used to study the optical spectra of amorphous semiconductors in the $k$ space (Kramer et al. 1970, 1972).

Using equation (18) we obtain the last three terms of equation (12) as functions of $t_e$ and $t_h$, which can be expanded in a Taylor’s series about $t = 0$. The series of the first two terms are terminated at the quadratic terms in $t$, which give the kinetic energies of excited charge carriers. Comparing these terms with the usual expression of kinetic energy as $p^2/2m_e^*$ for an electron and $p^2/2m_h^*$ for hole with $p = \hbar k$ being the linear momentum, we obtain expressions for the electron and hole effective masses respectively, in the real coordinate space as (Singh 2000, Singh and Shimakawa 2002):

$$[m_e^*]^{-1} = -\hbar^2 N^{-1} \sum_{l \neq l'} (l_e - l)^2 E_{11},$$  \tag{19}

$$[m_h^*]^{-1} = -\hbar^2 N^{-1} \sum_{l \neq l'} (l_h - l)^2 E_{00}.$$

Although a similar expression for the effective mass of an electron in amorphous solids has been derived by Kivelson and Gelatt (1979), the approach followed here is relatively simpler and similar to that used for defining the effective mass of Frenkel excitons (Singh 1994) in crystalline solids. Applying the nearest-neighbour approximation, an analytical form of the electron effective mass in the conduction extended states is obtained as (Singh and Shimakawa 2002)

$$m_e^* = \frac{E_L}{2(E_2 - E_c)a^{1/3}} m_e,$$  \tag{21}

where $E_L = \hbar^2/m_e L^2$, with $L$ being the average nearest-neighbour separation. $E_2$ is the energy at which the imaginary part of the dielectric constant becomes a maximum and represents the middle of the extended states. Thus $2(E_2 - E_c)$ is the total width of the conduction extended states. $a = N_1/N$, where $N_1$ and $N$ are the number of atoms contributing to the extended states and total number of atoms in the sample respectively. Likewise the effective mass of an electron in the conduction tail states is obtained as:
Table 1. Effective masses of electrons calculated using equations (21) and (22) for samples of 
a-Si: H and a-Ge: H with 1 at.% weak bonds (i.e. \( a = 0.99 \) and \( b = 0.01 \)) giving rise to 
the tail states.

<table>
<thead>
<tr>
<th></th>
<th>( L ) (( \text{nm} ))</th>
<th>( E_2 ) (eV)</th>
<th>( E_C ) (eV)</th>
<th>( E_L ) (eV)</th>
<th>( E_C + E_{ct} ) (eV)</th>
<th>( m_e^* )</th>
<th>( m_{ct}^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si: H</td>
<td>0.235(^a)</td>
<td>3.6(^b)</td>
<td>1.80(^c)</td>
<td>1.23</td>
<td>0.8(^d)</td>
<td>0.34(m_e)</td>
<td>5.7(m_e)</td>
</tr>
<tr>
<td>a-Ge: H</td>
<td>0.245(^a)</td>
<td>3.6(^b)</td>
<td>1.05(^e)</td>
<td>1.14</td>
<td>0.22(m_e)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Morigaki (1999).
\(^b\) Ley (1984).
\(^c\) Street (1991).
\(^d\) Spear (1979).
\(^e\) Aoki et al. (1999).

\[
m_e^* = \frac{E_L}{(E_C - E_{ct})b^{1/3}} m_e,
\]

where \( E_{ct} \) is the energy of the end of the conduction tail states, giving \( E_C - E_{ct} \) as the 
total width of the tail states, and \( b = N_2/N \), where \( N_2 \) is the number of atoms in the 
amorphous solid contributing to its tail states. Thus one obtains different effective 
masses for an electron in extended and tail states. It is conceptually very important 
to realize that the tail states are localized and hence the associated effective mass 
should be larger. Effective masses of electrons thus calculated are given in table 1.

Following an analogous approach for a hole, we can derive its effective mass in 
the valence extended state from equation (20) as

\[
m_h^* = \frac{E_L}{2(E_v - E_{v2})a^{1/3}} m_e,
\]

and that in the valence tail states as:

\[
m_{ht}^* = \frac{E_L}{(E_{vt} - E_v)b^{1/3}} m_e,
\]

Figure 1. Schematic illustration of the energies \( E_2, E_C, E_{ct}, E_{vt}, E_v \) and \( E_{v2} \) used in the theory 
presented here. The shaded region represents the extended states.
where $E_{v2}$ represents the energy of the middle of the valence extended states, and $E_{vt}$ is that of the end of the valence tail states above $E_v$. Here $2(E_v - E_{v2})$ and $E_{vt} - E_v$ are the widths of the valence extended and tail states respectively. The energies $E_2$, $E_{ct}$, $E_{v2}$, $E_v$ and $E_{vt}$ are schematically shown in figure 1. It may, however, be noted that the electron and hole effective masses are expected to be the same in sp$^3$-hybrid amorphous semiconductors such as a-Si:H and a-Ge:H. In such semiconductors, as the conduction and valence states are two equal halves of the same electronic band, their widths are the same, and then one obtains $m_c^* = m_h^*$ from equations (21)-(24).

§4. ENERGY OF EXCITONIC STATES

Substituting equation (18) in equation (12) we obtain

$$W = W_0 + N^{-1} \sum_{l,e} \exp \left[ i \mathbf{t}_e \cdot (l - l_e) \right] E_{2l1} - N^{-1} \sum_{l,h} \exp \left[ i \mathbf{t}_h \cdot (l - l_h) \right] E_{0l1}$$

$$- N^{-2} \sum_{l,e,l,h,l} \exp \left[ i \mathbf{t}_e \cdot (l_1 - l_e) + i \mathbf{t}_h \cdot (l_2 - l_h) \right] E_{b}(l_1, l_2, l_1, l_1; S).$$

(25)

In the real coordinate space, equation (25) is similar to that obtained from the theory of Wannier excitons (Elliott 1962, Singh 1994) in the reciprocal-lattice vector space for crystalline solids. However, there are two marked differences.

(i) According to the definition of $t_e$ and $t_h$ given in equation (18), it is obvious that these are functions of energy. Thus the advantage of the present approach is that the probability amplitude coefficients (equation (18)), which are functions of the wave-vector $k$ in crystalline solids, become functions of energy in amorphous solids.

(ii) In the theory of Wannier excitons in crystalline solids, the exchange interaction between the excited electron–hole pair, which is the second term in equation (16), is neglected when solving equation (25) analytically. This is done on the assumption that the exchange interaction is of a short-range nature (Elliott 1962) and hence it can be neglected for large radii orbital excitons such as Wannier excitons in crystalline solids. This approximation makes equation (25) independent of spin, which is regarded to be quite valid for crystalline solids, but it is not so for amorphous solids. In amorphous solids, because of the lack of the translational symmetry, the situation may be quite different. The charge carriers in an excited pair, in relative terms, may not be able to move far away from each other, and hence the large radii orbital model cannot be applied to amorphous solids. Thus amorphous solids offer a kind of confinement to the transport of charge carriers.

However, equation (25) can still be solved in a way similar to that applied for crystalline solids (Singh 1994). Applying the effective-mass approximation for both the charge carriers we can write equation (25) as:

$$W \approx W_0 + E_i - E_0 + \frac{p_e^2}{2m_e^*} + \frac{p_h^2}{2m_h^*}$$

$$- N^{-2} \sum_{l,e,l,h,l} \exp \left[ i \mathbf{t}_e \cdot (l_1 - l_e) + i \mathbf{t}_h \cdot (l_2 - l_h) \right] E_{b}(l_1, l_2, l_1, l_1; S),$$

(26)
where $m_e^*$ and $m_h^*$ are the effective masses of the excited electron and hole as obtained in equations (21) and (23) respectively. If the excited charge carriers are in their tail states, one should use the corresponding effective masses given in equations (22) and (24) respectively. $E_1$ and $E_0$ are the average energy of excited electron and hole in the conduction and valence states given respectively by

$$E_1 = N^{-1} \sum_{l,l'} E_{1l,l'} \quad (27a)$$

and

$$E_0 = N^{-1} \sum_{l,l'} E_{0l,l'} \quad (27b)$$

The average optical energy gap $E_{\text{opt}}$, of an amorphous solid can be defined as $E_{\text{opt}} = E_1 - E_0$.

The last term of equation (26), which is the interaction energy term between the excited electron–hole pair, depends on both $t_e$ and $t_h$, and therefore it needs to be expanded in a Taylor series with respect to both. Let us denote it by $M(t_e, t_h, S)$ and expand it about $t_e = t_h = 0$ up to the second-order term to obtain

$$M(t_e, t_h, S) = -N^{-2} \sum_{l,l',l_1,l_2} \exp \left[ it_e \cdot (l_1 - l_1) + it_h \cdot (l_2 - l_2) \right] E_b(l_e, l_2, l_1, l_h; S)$$

$$\approx -N^{-2} \sum_{l,l',l_1,l_2} E_b(l_e, l_2, l_1, l_h; S)$$

$$- N^{-2} \sum_{l,l',l_1,l_2} \left[ t_e \cdot (l_1 - l_1) + t_h \cdot (l_2 - l_2) \right] E_b(l_e, l_2, l_1, l_h; S)$$

$$+ N^{-2} \sum_{l,l',l_1,l_2} \left\{ \left[ t_e \cdot (l_1 - l_1) \right]^2 + \left[ t_h \cdot (l_2 - l_2) \right]^2 \right\} E_b(l_e, l_2, l_1, l_h; S). \quad (28)$$

In equation (28), again the first-order term is zero, and the second-order term provides additional kinetic energy to the motion of the excited electron–hole pair owing to their mutual Coulomb interaction. It is interesting to note that this additional kinetic energy term does not seem to appear when the theory of Wannier excitons is developed in $k$ space for crystals (Singh 1994). As there is no translational symmetry in amorphous solids, the additional kinetic energy may be attributed to the confinement to the motion of charge carriers offered by the amorphousness of amorphous solids, as mentioned above. This supports further that the Wannier type of excitons in amorphous solids may not necessarily have large radii orbitals. However, the contribution of this term to the kinetic energy of the excited electron–hole pair is expected to be small, owing only to the Coulomb and exchange interaction energy between the excited pair, without any interaction with ions. Keeping this in mind, this term can be neglected for simplicity and thus only the zeroth-order term of equation (28) will be used for solving equation (26), which then becomes

$$W = W_0 + E_{\text{opt}} + \frac{P_e^2}{2m_e^*} + \frac{P_h^2}{2m_h^*} - N^{-2} \sum_{l,l',l_1,l_2} E_b(l_e, l_2, l_1, l_h; S). \quad (29)$$

The last term of equation (29) is difficult to evaluate analytically. However, some simplifications can help in understanding the main features of the problem. According to equation (16), $E_b(l_e, l_1, l_2, l_h; S)$ involves more than two-centre
integrals, which not only are difficult to evaluate but also may have magnitudes that are not very significant. Therefore, let us neglect three- and four-centre integrals and consider only terms with \( l_1 = l_1 \) and \( l_h = l_2 \) (two-centre integrals only). With this simplification, equation (29) reduces to

\[
W = W_0 + E_{\text{opt}} + \frac{\hbar^2}{2m_e} + \frac{\hbar^2}{2m_h} - N^{-2} \sum_{l_e, l_h} E_b(l_e, l_h; S),
\]

where \( E_b(l_e, l_h; S) \) is obtained from equation (16) by using \( l_e = l_1 \) and \( l_h = l_2 \) as

\[
E_b(l_e, l_h; S) = \langle 1, l_e; 0, l_h|U|0, l_h; 1, l_e \rangle - (1 - S)\langle 1, l_e; 0, l_h|U|1, l_e; 0, l_h \rangle,
\]

where the Coulomb integral in equation (31) can be written as

\[
\langle 1, l_e; 0, l_h|U|0, l_h; 1, l_e \rangle = \int \left| \phi_{l_h}(r') \right|^2 |\phi_{0_h}(r'_2)|^2 \times \frac{k\epsilon e^2}{|(l_e - l_h)||1 - (r'_1 - r'_2)/(l_e - l_h)|} d^3 r'_1 d^3 r'_2.
\]

Considering that \( |r'_1 - r'_2|/|l_e - l_h| \ll 1 \), the integral of equation (32) can be written as

\[
\langle 1, l_e; 0, l_h|U|0, l_h; 1, l_e \rangle \approx \int \left| \phi_{l_h}(r') \right|^2 |\phi_{0_h}(r'_2)|^2 \frac{k\epsilon e^2}{|l_e - l_h|} d^3 r'_1 d^3 r'_2.
\]

As \( r'_1 \) and \( r'_2 \) are electronic coordinates measured from their nuclei, and considering that all atoms in the solid are the same, \( |r'_1 - r'_2| \) will be nearly zero, and therefore the above approximation is quite justified. Using then Haken’s approximation applied for Wannier excitons (Singh, 1994, p. 24), we can write

\[
\int \left| \phi_{0_h}(r'_2) \right|^2 d^3 r'_1 = \int \left| \phi_{0_h}(r'_2) \right|^2 d^3 r'_2 \approx \frac{1}{\epsilon^{1/2}},
\]

where \( \epsilon \) is the static dielectric constant of the solid. In the theory of Wannier excitons, the static dielectric constant is introduced through the Bloch wavefunctions in the same way as introduced in equation (34) through the localized wavefunctions for amorphous solids. Using equation (34) in equation (33) we obtain an estimate of the Coulomb integral as

\[
\langle 1, l_e; 0, l_h|U|0, l_h; 1, l_e \rangle \approx \frac{k\epsilon e^2}{\epsilon |l_e - l_h|}.
\]

Likewise, the second term of equation (31), the exchange interaction, also depends on the inverse of the distance between the electron and the hole, but its magnitude is usually less than that of the Coulomb interaction. Let us assume that the second term can be approximated by

\[
\langle 1, l_e; 0, l_h|U|0, l_e; 1, l_h \rangle = \frac{k\epsilon e^2}{\alpha \epsilon |l_e - l_h|},
\]

where \( \alpha \) is a parameter to be determined later.

It should be quite clear that when an excited electron–hole pair forms a bound state owing to their Coulomb interaction, their separation in a particular energy state (orbital radius) will be fixed and will not change as they move in a bound hydrogenic state.
orbital. Therefore, we can assume that $|l_e - l_h|$ does not change much during the motion of an electron–hole pair inside the solid. Then using equations (31), (35) and (36), the binding energy term in equation (30) can be written as

$$N^{-2} \sum_{l_e, l_h} E_b(l_e, l_h; S) \approx \frac{\kappa e^2}{\varepsilon |l_e - l_h|} \left( 1 - \frac{(1 - S)}{\alpha} \right).$$

(37)

Using equation (37) in equation (30) we obtain

$$W = W_0 + E_{opt} + \frac{p_e^2}{2m_e^*} + \frac{p_h^2}{2m_h^*} - \frac{\kappa e^2}{\varepsilon'(S)|l_e - l_h|},$$

(38)

where $E_{opt} = E_e - E_h$ is the optical gap, and $\varepsilon'(S) = \varepsilon[1 - (1 - S)/\alpha]^{-1}$.

The last three terms of equation (38) represent the energy operator of an electron–hole pair interacting through their Coulomb interaction, exactly in the same way as that of a Wannier exciton in crystalline semiconductors (Singh 1994).

Replacing the linear momentum by the corresponding operators, $p \rightarrow -i\hbar \nabla$, and then transforming the coordinates to the centre-of-mass coordinate $R$ and relative coordinate $r$ according to

$$R = m_e^* l_e + m_h^* l_h \over M, \quad r = l_e - l_h,$$

(39)

the last three terms of equation (38) can be written as

$$- \frac{\hbar^2 \nabla^2_R}{2M} - \frac{\hbar^2 \nabla^2_r}{2\mu_x} - \frac{\kappa e^2}{\varepsilon'(S)r},$$

(40)

where $\nabla_R$ and $\nabla_r$ are the differential operators associated with $R$ and $r$ respectively. $M = m_e^* + m_h^*$, and $\mu_x$ represents the reduced mass of the excited electron–hole pair given by $\mu_x^{-1} = (m_e^*)^{-1} + (m_h^*)^{-1}$. The first term of equation (40) represents the kinetic energy operator associated with the centre of mass of the excited electron–hole pair, and the last two terms give the energy operator of an electron–hole pair bound in a hydrogenic state. Eigenfunctions of the operator in equation (40) can be written as (Singh 1994)

$$\psi(r, R) = V^{-1} \exp \left( \frac{i \cdot P \cdot R}{\hbar} \right) \phi_n(r),$$

(41)

where $V$ is the volume of the solid, $P$ is the linear momentum associated with the centre-of-mass motion of the exciton and $\phi_n(r)$ are eigenfunctions corresponding to the principal quantum numbers $n$ associated with the hydrogenic states energy operator given by

$$\left( - \frac{\hbar^2 \nabla^2_r}{2\mu_x} - \frac{\kappa e^2}{\varepsilon'(S)r} \right) \phi_n(r) = E_n(S) \phi_n(r),$$

(42)

where $r = |l_e - l_h|$ and

$$E_{ex}(S) = - \frac{\mu_x e^4 \kappa^2}{2\hbar^2 \varepsilon'(S)^2} \frac{1}{n^2}.$$  

(43)
The energy $E_{\text{ex}}(S)$ of an excitonic state can be calculated from equation (43) for any amorphous solid provided that the parameter $\alpha$ is known. A way of determining $\alpha$ is described below.

4.1. Determination of $\alpha$

The values of $\alpha$ are expected to be different for different solids. For instance $\alpha = 1$ allows no binding between the excited pair of charge carriers as the binding potential energy vanishes. It is necessary for binding that $\alpha$ must be greater than unity ($\alpha > 1$). It may also be noted that, for a very large value of $\alpha (\rightarrow \infty)$, the contribution of the exchange interaction becomes negligible and the binding energy reaches the large radii orbital limit at which the energy difference between singlet and triplet states vanishes. One way of determining $\alpha$ would be by evaluating the integrals in the Coulomb and exchange interaction in equation (16) numerically, but then also the result will depend on the sample size, kind of atomic wavefunctions chosen etc. Alternatively, as described below, $\alpha$ can be estimated from the experimental results.

We first derive the singlet–triplet splitting from equation (43) for the excitonic ground state ($n = 1$) as

$$\Delta E_{\text{ex}} = E_{1}(S = 0) - E_{1}(S = 1) = \left(1 - \frac{(\alpha - 1)^2}{\alpha^2}\right)C_{M},$$  \hspace{1cm} (44)

where

$$C_{M} = \frac{\mu_{\text{e}} e^4 \kappa^2}{2\hbar^2 \varepsilon^2},$$  \hspace{1cm} (45)

and compare it with that observed experimentally. Let us denote the observed splitting by $\Delta E_{\text{xp}}$, and then equate it to the splitting derived in equation (44), which gives $\alpha$ as

$$\alpha = \left[1 - \left(1 - \frac{\Delta E_{\text{xp}}}{C_{M}}\right)^{1/2}\right]^{-1},$$  \hspace{1cm} (46)

where only one of the signs of the square root is applicable for obtaining $\alpha > 1$.

Assuming that both an electron and a hole are excited in their extended states in a-Si:H and a-Ge:H, and using the corresponding effective mass from table 1, we obtain the excitonic reduced mass $\mu_{\text{e}} = 0.17m_e$ for a-Si:H and $\mu_{\text{e}} = 0.11m_e$ for a-Ge:H. Using then the static dielectric constant $\varepsilon = 12$ for a-Si:H (Cody 1984), we obtain $C_{M} = 16.12\, \text{meV}$ from equation (43), and for a-Ge:H we obtain $C_{M} = 5.87\, \text{meV}$ with $\varepsilon = 16$ (Conwell and Pawlik 1976). The observed singlet–triplet splitting $\Delta E_{\text{xp}}$, in a-Si:H can be rounded to $3\, \text{meV}$ (Aoki 2000), and in a-Ge:H to $1\, \text{meV}$ (Aoki 2000). Using these values in equation (44), we obtain $\alpha \approx 10$ for a-Si:H, and $\alpha \approx 11$ for a-Ge:H. As there are uncertainties in the experimental data, it is considered reasonable to use $\alpha = 10$ for both a-Si:H and a-Ge:H.

4.2. Energy difference between singlet and triplet excitonic states

Using $\alpha = 10$ in equation (44) for a-Si:H and a-Ge:H, we obtain the ground-state singlet–triplet energy splitting as

$$\Delta E_{n} \approx 0.2C_{M}.$$

\hspace{1cm} (47)
The Bohr radius of singlet \( a_{\text{ex}}(S = 0) \) and triplet \( a_{\text{ex}}(S = 1) \) excitonic states can also be estimated from equation (43) for a-Si:H and a-Ge:H. We thus find that

\[
a_{\text{ex}}(S = 0) = \frac{5}{4} a_{\text{ex}}(S = 1),
\]

and

\[
a_{\text{ex}}(S = 1) = \frac{\mu_e}{\mu_x} a_0, \quad a_0 = \frac{h^2}{\kappa \mu e^2},
\]

where \( a_0 \) is the Bohr radius and \( \mu \) the reduced mass of the electron in a hydrogen atom. Thus the Bohr radius of a singlet excitonic state is larger than that of a triplet excitonic state, and accordingly the binding energy of a triplet state is larger than that of a singlet state in a-Si:H and a-Ge:H.

Once \( \kappa \) is known, the theory developed above can be applied to study the details of photoluminescence in any amorphous solid. Here we shall focus mainly on a-Si:H and a-Ge:H, which are reasonably well studied and in which valence and conduction states are obtained from sp\(^3\) hybridization. For creating an excitation in amorphous solids, there are four possibilities.

(i) Both the electron and the hole are excited in their respective extended states.
(ii) The electron is excited in the conduction extended states and the hole in the valence extended states.
(iii) The electron is excited in the conduction tail and the hole in the valence tail states.
(iv) Both the electron and the hole are excited in their respective tail states.

![Figure 2. Arrhenius plots for the ratio of PL quantum efficiency \( \eta_2/\eta_1 \) for a-Si:H calculated from the data of Searle et al. (1987) (□) and of Schubert et al. (1993) (●), giving \( \Delta E_{\text{ex}} \approx 3.0 \text{ meV} \), and those for a-Ge:H from Aoki (2000) (○) with \( \Delta E_{\text{ex}} \approx 0.8 \text{ meV} \). \( \eta_1 \) denotes the PL quantum efficiency of the slow peak and \( \eta_2 \) that of the fast peak.](image-url)
It is therefore important to use the appropriate effective masses of the electron and the hole for calculating the singlet–triplet energy splitting in the PL originating from the different possibilities.

Using the estimated value of $\alpha = 10$, and $\mu_e = 0.17m_e$ for a-Si:H and $0.11m_e$ for a-Ge:H for an exciton created through the first possibility that both the electron and the hole are excited in their extended states, we obtain the energy difference between singlet and triplet excitonic states from equation (47) as $\Delta E_{\text{ex}} = 3.22$ meV for a-Si:H, and 1.17 meV for a-Ge:H. Aoki (2000) has recently estimated $\Delta E_{\text{ex}}$ in a-Ge:H to be 0.8 meV, as shown in figure 2. Our theoretical results are thus in close agreement with the experimental results for both a-Si:H and a-Ge:H. The agreement between the theoretical and experimental results is expected because $\alpha$ is determined by comparing the theoretical and experimental results. However, the important point is that the value of $\alpha$ is not expected to depend on the energy of exciting photons or to which states electrons and holes are excited. Therefore, once $\alpha$ is known, the PL observed through the other three possibilities can also be studied and analysed by applying the above theory. This will be described in the next section. Using equation (47), the calculated values of $\Delta E_{\text{ex}}$ in a-Si:H and a-Ge:H are given in table 2.

### Table 2. Values of $\Delta E_{\text{ex}}$ calculated from equation (47) for a-Si:H and a-Ge:H.

<table>
<thead>
<tr>
<th></th>
<th>$\mu_e$</th>
<th>$\epsilon$</th>
<th>$\Delta E_{\text{ex}}$ (meV)</th>
<th>$\Delta E_{\text{ex}}$ Experimental (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si:H</td>
<td>0.17$m_e$</td>
<td>12.0$^a$</td>
<td>3.22</td>
<td>3.0$^b$</td>
</tr>
<tr>
<td>a-Ge:H</td>
<td>0.11$m_e$</td>
<td>16$^c$</td>
<td>1.17</td>
<td>0.8$^b$</td>
</tr>
</tbody>
</table>

$^b$Aoki (2000).  
$^c$Conwell and Pawlik (1976).

### §5. Discussion

Applying the effective-mass approximation, a comprehensive theory of PL applicable to amorphous semiconductors is developed here. The radiative recombination from a singlet excited state is spin allowed and that from a triplet excited state is spin forbidden; therefore PL from a triplet is much slower than that from a singlet. This is attributed to the origin of the two PL peaks, fast and slow, appearing in the PL time distribution in a-Si:H and a-Ge:H. The short-time peak can be assigned to recombination from singlets and that at long time to recombination from triplets. Such excitonic states can be created in both the extended and the tail states. Therefore, as described above, four distinct possibilities exist for optical excitations in amorphous semiconductors: valence to conduction extended states, valence tail to conduction extended states, valence extended to conduction tail states and valence to conduction tail states. Accordingly, four different reduced masses of the excited electron–hole pairs are required to be used corresponding to the four different possibilities, giving rise to four singlet states and four triplet states. Therefore, there can be a few possible singlet–triplet splitting energies. For the first possibility, as given in table 2, we obtain the energy difference $\Delta E_{\text{ex}}$ between singlet and triplet
as 3.22 meV for a-Si: H, and 1.17 meV for a-Ge: H, in agreement with the experimental results (Aoki 2000).

One may argue that the good agreement between the theory and experiment for $\Delta E_{\text{ex}}$ is obtained because $\alpha$ is determined by comparing these data in the first place. This is probably true; however, as stated in §4.1, once $\alpha$ is determined, it can be used for all possible transitions. At present the only other way of determining $\alpha$ is to calculate it numerically by evaluating all the integrals in equation (16). The result will then, of course, depend on the kind of atomic electronic wavefunction used and the sample size. Moreover, firstly, the computing process is going to be very time-consuming and, secondly, the value of $\alpha$ thus determined may not be any more accurate than the present value, because of the choice of wavefunctions and limitations on sample size.

As mentioned above, in sp$^3$-bonded amorphous semiconductors, it is expected that $m^*_e = m^*_h$, and therefore in such materials the possibilities (ii) and (iii) in §4.2 will give the same value of the reduced mass, which according to equation (45) will give the same $C_M$, and hence the same $\Delta E_{\text{ex}}$. In a-Si: H, using $m^*_e = m^*_h = 5.7 m_e$ and $m^*_e = m^*_h = 0.34 m_e$, we obtain $\mu_{\text{ext}} = 0.32 m_e$, which gives $\Delta E_{\text{ex}} = 6.1$ meV. This is slightly higher than the experimental value of 3 meV. Such variations in $\Delta E_{\text{ex}}$ may be attributed to the broad PL peak in a-Si: H and a-Ge: H. As $\alpha$ is relatively large, any change in the effective mass causes only a small shift in the PL frequency.

Furthermore, depending on the experimental conditions, more than one singlet and triplet peaks can be observed in any amorphous semiconductor, producing different values for the singlet–triplet splitting. Thus a general expression for the ground excitonic state singlet–triplet splitting can be derived using equation (43) as:

$$\Delta E_{\text{ex}} = \left( \frac{\mu_x^1 - \mu_x^0 (\alpha - 1)^2}{\alpha^2} \right) C_M',$$

(50)

where $\mu_x^0$ and $\mu_x^1$ are the reduced masses corresponding to the four possibilities for transitions associated with the singlet and triplet states respectively, and $C_M' = C_M/\mu_x$. For $\mu_x^0 = \mu_x^1$, equation (50) reduces to equation (44). Thus one can expect to observe a few PL peaks using the time-resolved spectroscopy technique, as has recently been observed in chalcogenides.

Finally, the temperature dependence of PL in a-Si: H and a-Ge: H can also be addressed here. For a-Si: H, Searle et al. (1987) have found that at lower temperatures, from 4 to 65 K, the slow-time (low-frequency) PL peak is dominant in intensity but, as the temperature increases to 115 K and then to 150 K, the fast-time (high-frequency) peak becomes more pronounced than the slow-time peak. For a-Si: H, $\Delta E_{\text{ex}} \approx 3$ meV (table 2), which means that, when the temperature increases, the triplet excitonic states gain enough thermal energy to become converted into singlets, and hence the PL from the fast component (due to singlets) increases. However, at lower temperatures, the thermal energy is too small to convert triplets into singlets and hence the slow-time component remains dominant. Likewise, for a-Ge: H, from the double peak observed by Aoki (2000), one finds that the peak intensity of the fast peak increases when the temperature increases from 13 to 60 K. The same argument can be applied to a-Ge: H, where $\Delta E_{\text{ex}} \approx 1.0$ meV, and the fast peak starts to increase when the temperature is raised from 13 to 60 K.
The maximum of the lifetime distribution and associated quantum efficiencies depend on the generation rate of excitation. The long-time component remains constant at the smaller generation rate $G$ and then begins to decrease proportional to $G^{-0.5}$ when $G \geq 3 \times 10^{20} \text{ cm}^{-3} \text{ s}^{-1}$ for a-Ge:H. However, the short-time component is found to remain constant for a-Ge:H within the range of measurement. A similar trend in both the long- and the short-time components has been observed for a-Si:H as well, except that the short-time component also starts to decrease as $G^{-0.5}$ at a much higher concentration (Stachowitz et al. 1998). This can be explained as follows. At the low generation rate, the radiative processes are more efficient and hence dominant. In this regime, therefore the observed PL lifetime is nearly the same as the radiative lifetime of excitonic states, which is constant and independent of the generation rate. Consequently the PL quantum efficiency remains constant at lower $G$. At higher $G$, however, the non-radiative recombination becomes more efficient and dominant. In this case, an excitonic state can dissociate into an electron and a hole owing to the enhanced repulsive interaction between like charge carriers at a very high value of $G$. Using the phenomenological rate equation, it can be very easily shown that, in this situation, both the PL lifetime and the quantum efficiency decrease as $G^{-0.5}$. Stachowitz et al. (1998) have proposed that such decreases in the PL lifetime and quantum efficiency are due to Auger processes. It may be noted here, however, that, as both Auger and excitonic dissociation processes are bimolecular processes, they follow the same phenomenological rate equation. Nevertheless, Auger processes may be relevant in the low-temperature regime and at high generation rates but, at higher temperatures, excitonic dissociation is expected to dominate.

The decrease in the short lifetime at a much higher generation rate as observed for a-Si:H and nearly constant within the range of measurement for a-Ge:H can also be explained. As the singlet recombination is very fast, the radiative recombination from singlets remains dominant up to a much high generation rate before the non-radiative recombination takes over. For a-Ge:H, the radiative recombination from singlets is about an order of magnitude faster than that for a-Si:H, which means that the radiative recombination remains far more efficient than the non-radiative recombination during the whole range of measurement for a-Ge:H.

It may be desirable to comment on using equal effective masses for electrons and holes in sp³-hybrid systems such as a-Si:H and a-Ge:H. In these systems, valence and conduction bands are two halves of a single band and therefore have the same width. According to equations (21) and (23), as the effective mass is inversely proportional to the bandwidth, the effective masses of electron and hole become equal. This is different from crystalline solids where the effective masses $m_e^*$ and $m_h^*$ are not usually the same. However, this difference between amorphous and crystalline solids is similar to, for example, indirect and direct crystalline semiconductors but not amorphous semiconductors.

In conclusion, it may be stated that the effective-mass approach has proved to be very useful in studying the PL properties in amorphous solids. Its application shows that excitonic states can be formed in amorphous semiconductors in a way similar to excitons in crystalline solids. The radiative recombination from excitonic states is responsible for PL in amorphous solids. The double-peak structure observed in the PL time distribution can be attributed to radiative recombination from singlet and triplet excitonic states in amorphous solids.
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Note added in proof:—Abeles and Tiedje (1984) have used $m^*_e = 0.2m_e$ for a-Si:H, which is close to $0.34m_e$ obtained from the present theory.

REFERENCES


† An error was detected in determining $\Delta E_{ee}$ in this paper, which has been corrected in Aoki (2000).
Excitonic contribution to PL in amorphous semiconductors


