One-dimensional exciton in a two-band tight-binding model with long-range interactions

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The nature of an exciton in a one-dimensional system is clarified from numerical solutions for the electron-hole attraction varied from the weak (Wannier) limit to strong (Frenkel) limit by making use of a two-band tight-binding model having $1/r$ as well as on-site interactions. "Large" and "small" excitons are shown to respond to an increase in the strength of the long-range interaction relative to the on-site interaction in opposite manners: the size of an exciton is found to shrink for weak interactions, whereas the extension increases for strong interactions. This property is explained both intuitively and from an exact solution for a simplified model. We further show that the crossover between the large and small excitons should be observable in the optical properties.

A standard practice in studying excitons in semiconductors[1] is to classify them into Wannier[2] and Frenkel[3] excitons. The picture of the Wannier, or large, exciton, has been thought to be valid when the spatial extension of the exciton, R, is much larger than the dimension of the unit cell of the crystal, a. The Frenkel, or small, exciton, represents the opposite limit of strongly coupled excitons. There the exciton is regarded as an intra-atomic excitation which can migrate in the crystal, so that the model applies to the case of $R \ll a$. However, on the one hand, it is not obvious whether there is a clear theoretical way to distinguish the two models, and, on the other, the excitons observed in real materials should be somewhere between these extremes. Thus it becomes an important question to ask how the Frenkel exciton crosses over to the Wannier exciton as the coupling is gradually decreased.

A second essential factor in considering excitons is the dimensionality. The wave function of an exciton becomes spatially more strongly confined as we go to lower dimensions, so that the physical properties of excitons become intriguing as the dimensionality is reduced. Specifically, the problem of the crossover between Wannier and Frenkel excitons becomes particularly interesting in one-dimensional (1D) systems. Recently it has become experimentally possible to fabricate "natural" 1D semiconductors, i.e., σ-conjugated polymers as exemplified by polysilanes.[6] Several theoretical models have been introduced to study excitons in 1D systems.[4,5]

In the present Brief Report, the crossover of Wannier and Frenkel excitons in 1D systems such as polysilane is explored from first principles, by which we mean that we obtain numerical solutions of finite systems in a model with $1/r$ as well as on-site interactions in a crystal represented by the tight-binding model. Since the spatial extension of an exciton becomes extremely small, i.e., of the order of the lattice constant, in 1D, we consider that the employment of the tight-binding model on a discrete lattice should be adopted, as contrasted with continuum models. In a discrete model, the problem of the $1/r$ singularity in the Coulomb interaction does not arise either, while the singularity causes a catastrophe in 1D continuous models. Such a difficulty is circumvented in a different manner in quantum wires, which are another class of quasi-1D systems, i.e., one may consider that the electron-hole potential has a cutoff momentum arising from averaging the quantized envelope function in the transverse direction of the wire.[7,4] In contrast, we address ourselves to the problem of the Wannier/Frenkel crossover in lattice structures, in which the divergence of the electron-hole potential is inherently absent.

Here we employ the two-band model with long-range Coulomb interactions between electrons and holes. The long-range interaction is essential if one wishes to discuss the excited states of excitons, since only one exciton level (the $1s$ state in the Wannier picture) appears when the long-range electron-hole interaction is absent.

The Hamiltonian then reads

$$\begin{aligned}\mathcal{H} = & -t_e \sum_i (a_{i+1}^\dagger a_i + \text{H.c.}) - t_h \sum_i (b_{i+1}^\dagger b_i + \text{H.c.}) \\ & - \sum_{ij} U(i-j) a_i^\dagger a_i b_j^\dagger b_j \\ & - V_d \sum_i (a_{i+1}^\dagger b_{i+1}^\dagger b_i a_i + \text{H.c.}) , \end{aligned} \tag{1}$$

where a_i and b_i represent the annihilation operators of an electron and a hole at the ith site, respectively, and t_e and t_h are the transfer energy of electrons and holes, respectively.

The long-range Coulomb attraction between an electron and a hole is denoted by $U(r)$, where the distance r is measured in units of the lattice constant a. Here we consider low concentrations of excitons to neglect the screening of electron-hole interactions. Thus we employ the form

$$U(r) = \begin{cases} U_0 & (r=0) \\ U_1/|r| & (r \neq 0) \end{cases} \quad (U_0 > U_1 > 0) . \tag{2}$$

Here intracell attraction U_0, which is the interaction of an electron and a hole within the same unit cell, is a parameter reflecting the internal structure of the unit cell, while the coefficient of the long-range part, U_1, is basically dominated by the intercell spacing and the dielectric constant of the host material.

The last term in Eq. (1) comes from the electromagnetic dipolar coupling between atoms. This term has been shown to be indispensable for the mobility (dispersion) of excitons by Heller and Marcus.[9] An exciton in fact becomes immobile in the Frenkel limit ($U_0/t \to \infty$) if $V_d=0$.

Here we consider a single exciton (one electron and one hole), while we shall address ourselves to finite concentration of excitons in a separate paper. Thus we can neglect the spin of electrons and holes here. We have numerically diagonalized the above Hamiltonian for finite systems with periodic boundary conditions. We have taken sample sizes ($L \sim 600$) that are large enough to make the result size independent for each value of the parameters. A cutoff in the interaction range at $L/2$ is introduced.

We first define the binding energy of an exciton, E_B, which is the energy gained by turning on the electron-hole interaction. The result shows that, although the binding energy is reduced as the transfer energy is increased relative to $U(r)$, E_B never vanishes. Thus we confirm, in the present model, that an electron-hole pair is bound in 1D no matter how small the electron-hole interaction may be in contrast to higher-dimensional cases. For a fixed transfer energy, the binding energy increases with U_1. This result is reminiscent of the result by Ogawa and Takagahara,[4] who calculated the binding energy of an exciton in a continuous space confined in a tube having a finite thickness.

We now turn to the radius of an exciton, R, defined by the second moment of the wave function as

$$R \equiv \left\langle \sum_{ij} (i-j)^2 a_i^\dagger a_i b_j^\dagger b_j \right\rangle^{1/2} . \tag{3}$$

Hereafter we concentrate on the exciton with zero total momentum, k. This is because, first, we would like to single out the wave function of the relative motion of the electron and hole, and, second, because optical properties concern the $k=0$ states. The relevant parameters in this case are t_e+t_h, U_1, and U_0+2V_d. Hereafter we take U_0+2V_d as a unit of energy.

The result (Fig. 1) shows that R increases with t_e+t_h for any value of U_1. Conspicuously, however, the dependence of R on U_1 becomes the opposite as t_e+t_h is varied: For $t_e+t_h<1$, an exciton *expands* with increasing U_1, while it *shrinks* with U_1 for $t_e+t_h>1$. This is contrasted with the binding energy, which always becomes deeper with U_1.

As a reference, we can consider the limit of vanishing long-range interactions (i.e., $U_1=0$). Then we can readily obtain an exact solution for the whole range of parameters,[10] which gives a linear dependence of R on t,

$$R(U_1=0)=\sqrt{2}\frac{t_e+t_h}{U_0+2V_d} . \tag{4}$$

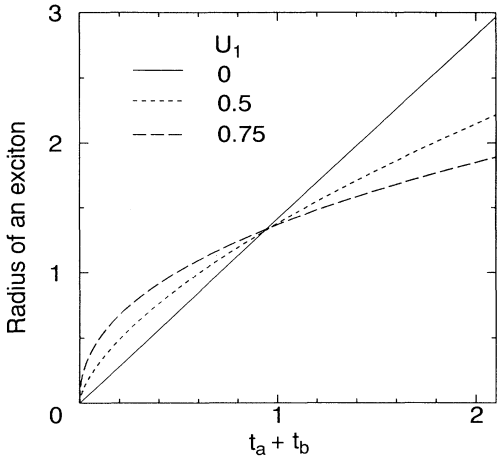

FIG. 1. The radius of the exciton, R, is shown as a function of t_e+t_h for $U_1=0$ (solid line), $U_1=0.5$ (dotted line), and $U_1=0.75$ (dashed line).

This happens to coincide with the random-phase-approximation (RPA) result by Egri for the two-band tight-binding model with only on-site electron-hole interactions considered in an analysis of Wannier and Frenkel excitons,[8] although the RPA is only justifiable for small interactions. As U_1 is turned on, the curve shifts above this straight line for $t_e+t_h<1$ and below the line for $t_e+t_h>1$.

We can call the former the Frenkel regime and the latter the Wannier regime. This behavior is nontrivial in that, while for the usual 3D excitons the Bohr radius is proportional to $t(\propto 1/m^*)$ for long-range $1/r$ interactions, for 1D excitons $R \propto t$ is realized for short-range interactions instead and for the long-range interactions R depends sublinearly (e.g, $R \propto t^{-0.48}$ for $U_1=0.8$) on the bandwidth.

Interestingly, the curves for R for various values of U_1 cross near, but not exactly at, a single point. Notably, even in the weak-coupling (Wannier) regime, R is comparable to the lattice constant, so that, first, our definition of a Wannier exciton differs from the conventional one, and, second, a continuum model would be inadequate to describe the region of Wannier/Frenkel crossover in 1D.

There are two ways to give physical explanations for the different responses to the variation in U_1. To give an intuitive one, we can reduce the problem of a single electron-hole pair to a one-body problem in a potential well for the relative motion. When the well is shallow, the wave function for the relative motion will spill out of the well, and the addition of a long-range potential will act to shrink the wave function. On the other hand, when the well is deep enough to confine the wave function within the well, addition of the long-range interaction will make the wave function spread out of the well.

This argument can be reinforced from an exact solution[10] for a two-band model having on-site and nearest-neighbor interactions with

$$U(r)=\begin{cases} U_0 & (r=0) \\ U_1 & (r=1) \\ 0 & (\text{otherwise}) \end{cases} \quad (5)$$

In this case, up to three exciton bound states appear, depending on the value of the parameters. The wave function of the lowest state for $U_0 > U_1 > 0$ is given as

$$|\Psi\rangle = \left[\sum_i a_i^\dagger b_i^\dagger + C \sum_{i \neq j} e^{-\kappa |i-j|} a_i^\dagger b_j^\dagger \right] |0\rangle \ , \quad (6)$$

where κ is determined from a cubic equation,

$$xyk^3+(x^2-y)k^2+(x+xy)k-x^2=0 \ , \quad (7)$$

with $x=(t_e+t_h)/(U_0+2V_d)$, $y=U_1/(U_0+2V_d)$, and $k=e^{-\kappa}$. The ground-state energy and the radius of exciton are given by

$$E=-2(t_e+t_h)\cosh\kappa \ ,$$

$$R=\left\{ \frac{C^2}{1+\dfrac{2(C^2-1)}{e^{2\kappa}+1}} \frac{1}{2\sinh^2\kappa} \right\}^{1/2} \ , \quad (8)$$

$$C=\frac{t_e+t_h}{t_e+t_h-U_1 e^{-\kappa}} \ .$$

R indeed increases (decreases) with U_1 in the strong-coupling (weak-coupling) regimes. The crossover of the two regimes is given here by $t_e+t_h=\sqrt{2+\sqrt{5}}/(1+\sqrt{5})\sim 0.64$. The critical value of t in this model is slightly smaller than that for the $1/r$ interaction, since, when R is as small as a, addition of the long-range interaction will expand the exciton, while addition of the nearest-neighbor interaction alone will compress the exciton.

Although the crossover has also been observed in the continuous model with a cutoff interaction, $U(r) \propto 1/(r+r_0)$,[4] the physics providing the crossover is essentially different for the following reason. We can translate the reciprocal of the reduced effective mass of the electron and hole in the continuous model into t in the tight-binding model. The crossover point in the former model occurs at a much lower point, $(1/m^*)_c \sim (1/10)U(0)$, than the present result of $t_c \sim U_0$. Since the spatial extension is of the order of the lattice constant in the strong-coupling regime with $t < U(0)$, the discrete atomic structure must be taken into account there, and the crossover point in the continuous model thus falls upon the region where the model breaks down.

As an observable property which can reflect the spatial extension of excitons we have calculated the optical absorption. Figure 2 shows the optical-absorption spectra when t_e+t_h is varied from the Frenkel to the Wannier regimes. As is experimentally observed in polysilanes[6] and is pointed out from a continuous model,[4] the band-edge absorption (across the valence-band top and the conduction-band bottom) is absent or very weak in 1D, which comes from the property that excitons exhaust the oscillator strength almost completely in 1D. The present

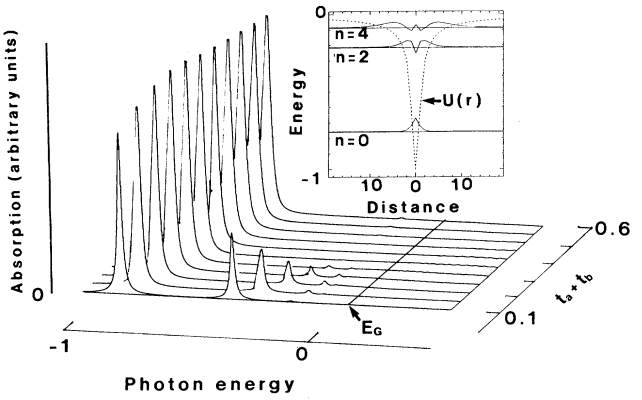

FIG. 2. Optical-absorption spectra are shown for $U_1=0.6$ and t_e+t_h varied from 0.1 to 0.6. The position of the band edge (separation of the conduction-band bottom and the valence-band top) is denoted by E_G. A Lorenzian width of $\Gamma=0.01$ is assumed in plotting the discrete absorption lines. The inset shows the envelope function of the lowest three excited states of exciton for $t_e+t_h=0.2$ and $U_1=0.6$.

result (Fig. 2) shows that this holds for the tight-binding model *in both Wannier and Frenkel regimes.*

Another feature in Fig. 2 is a remarkable difference for the *excited* states between the Frenkel and Wannier excitons. For the Wannier and intermediate excitons, the oscillator strength of the excited states of the exciton is too small (typically $\frac{1}{100}$ times of that of the lowest exciton for $t_e+t_h=0.25$) to give significant peaks at the energy of those states. Thus only one peak due to the lowest exciton state will be observable. This result for the weak-interaction regime is consistent with a theoretical result in a continuous model.[4]

If we now decrease the transfer energy, the peaks for excited states grow and become comparable with the peak for the lowest exciton state, as shown in Fig. 2. This is because the electron and hole in the excited states become bound tightly enough to give oscillator strengths comparable with that of the lowest state. More specifically, peaks appear when the wave function of the first excited state of the exciton is confined within the effective range of the dipole moment. The effective range of the dipole moment is defined as the spatial separation over which the matrix elements of the dipole moment between different atomic orbitals have significant values, and is of the order of the size of Slater orbitals.

This property provides an observable property specific to the Frenkel exciton. Noticeably, the critical value of $t(\sim 0.2)$, at which the peaks for the excited states become significant, is considerably slower than the crossover value of $t(\sim 1)$ in Fig. 1. Since the crossover for R is defined only in terms of the lowest exciton state, it is natural that the crossover for the optical absorption which involves the excited states (the inset of Fig. 2) should take place at a lower value of t.

In higher-dimensional systems, the excited states of an exciton have comparable oscillator strength even in the Wannier regime, so that the above property in the

Frenkel/Wannier crossover regime is *specific* to 1D systems.

Two-photon absorption (TPA) spectra are also calculated with conventional perturbational formula. Since the dominant TPA processes employ the lowest exciton state as the intermediate state, it is interesting to ask the relation of the peak value (f) of TPA for $\hbar\omega = E_1/2$ to the ratio of the ground-state energy and the excitation energy of an exciton, $\tau \equiv E_0/(E_1 - E_0)$, where E_0 and E_1 denote the excitation energy of the lowest exciton and the first excited state of the exciton, respectively.

We can see in Fig. 3 that f for a fixed value of $t_e + t_h$ decreases with τ as the lowest exciton state becomes off-resonant. For a fixed value of τ, the oscillator strength is peaked at a certain value of $t_e + t_h$ that falls upon the Frenkel regime. This peak arises when the spatial extension of the relative motion optimally fits into the effective range of the dipole moment (r_d). Namely, the first excited state of the exciton has an oscillating wave function with a node, and its dipole moment reaches maximum when its size is about r_d. Thus the situation, in which the optical absorption is dominated by the size of the excited excitons relative to r_d, is reminiscent of the appearance of one-photon absorption peaks for excited states revealed above. Since the above explanation is valid only when the size of an exciton is of the order of the lattice constant, it is again an important property of the 1D exciton in the crossover regime.

If we now apply the present results to polysilanes, we can determine the value of the parameters by fitting the experimental results[6,11] to the theory. Namely, the energy of the lowest exciton is deduced experimentally from the result for the one-photon absorption, and the energy of the first excited exciton state from the experimental result for two-photon absorption. We can combine these with the present result as well as with theoretical results for two-photon absorption[12] and for the bandwidth ($\propto t$) from the band calculation by Takeda and Shiraishi.[13] For polydihexylsilane (PDHS), we obtain $t_e + t_h = 2.5$ eV, $U_0 + 2V_d = 1.8$ eV, and $U_1 = 1.7$ eV. This gives $(t_e + t_h)/(U_0 + 2V_d) \approx 1.4$, so that the exciton is of Wannier type in PDHS in our definition. Experimentally, only one peak is observed in the optical absorption,[6] which indeed confirms our identification.

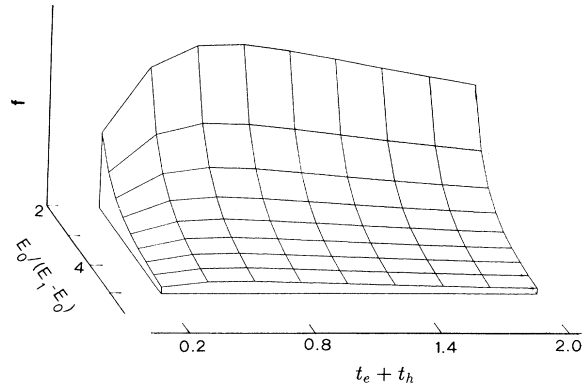

FIG. 3. The oscillator strength of two-photon absorption (f_{ex}) is shown as a function of $t_e + t_h$ and $\tau \equiv E_0/(E_1 - E_0)$. Here E_0 and E_1 are the energy of the lowest exciton and the first excited state of the exciton.

When the exciton size is $\sim a$, the notion of the charge-transfer exciton is sometimes evoked, in which the exciton is viewed as a charge transfer over atomic distances. To accurately discuss the behavior of such excitons, the effects of lattice distortions and Madelung energies will be necessary.

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