REVIEW

Exciton hybridization states in organic–semiconductor heterostructures containing quantum dots

Nguyen Que Huong

Marshall University, Huntington WV 25755, USA
E-mail: nguyenh@marshall.edu

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Abstract
The formation of a hybridization state of Wannier Mott and Frenkel excitons is theoretically studied for different heterostructure configurations involving quantum dots. At the interfaces of the semiconductor quantum dots and the organic medium, the hybridization states are formed, having complimentary properties of both kinds of excitons as well as large optical nonlinearities. The coupling at resonance is very strong, depending on the parameters of the systems (dot radius, dot separation, generation of the organic dendrites and the materials of the systems, etc). The hybrid excitons are as sensitive to external perturbation as Wannier–Mott excitons. Upon the application of magnetic and electric fields, the coupling term between the two kinds of excitons increases. The most important feature of this system is that by adjusting the system parameters as well as the external fields and their orientation, one can tune the resonance between the two kinds of excitons to get different regions of mixing to obtain the expected high nonlinearity.

Keywords: nanocrystals, semiconductors, organic material

Classification numbers: 3.00, 4.01, 4.03

1. Introduction

With the goal of designing a new generation of materials having applications in high-speed lasers, light sources and telecommunications, a large amount of experimental and theoretical research has been focusing on heterostructures combining organic and semiconductor materials [1–11]. Recent development of nanotechnology allows the possibility of the realization of low-dimensional systems containing both organic and inorganic materials, a new class of materials, giving us the opportunity to investigate the optical properties of organic–inorganic hybrid states for both fundamental background and opto-electronic device application purposes. This paper reviews the theoretical study of Wannier–Frenkel hybrid excitons in organic–semiconductor heterostructures containing quantum dots [5–10].

It is well known that there are two kinds of excitons in solids: the Frenkel exciton with an effective Bohr radius of approximately a lattice constant or less, and the Wannier–Mott exciton where the ground bound state has a radius of tens of lattice constants. Usually, ionic crystals and organic molecular materials have Frenkel type excitons, while semiconductors (CdS, ZnS, etc) have the Wannier type. The two kinds of excitons have very different and complementary properties. The Frenkel exciton is an excited electronic state, where the electron and the hole are situated in the same molecule or atom. Because of its small radius, the Frenkel exciton is usually considered to be a localized, tightly bound exciton with the exciton radius equal to the crystal lattice constant, about \( a \sim 5 \text{ Å} \), and the interaction between Frenkel excitons at different sites can be neglected in many cases. The Frenkel excitons have a very large oscillator strength, which is comparable to the oscillator strength of the molecule. The small radii of Frenkel excitons make it very difficult for their wavefunctions to overlap each other to reach the saturation density and exciton resonance, and it leads to their very
large saturation density so that the excitonic resonance in organic material is very difficult to achieve. In contrast, being an electron–hole bound state, the large-radius Wannier–Mott exciton in semiconductors is relatively weakly bound due to a typically large electron-hole distance with the Bohr radii \( d_B \sim 30–100 \, \text{Å} \). The interaction between Wannier–Mott excitons is very important while their oscillator strength is rather weak. Within the effective mass approximation, the Wannier–Mott exciton can be represented by a hydrogen-like wavefunction. The Wannier–Mott exciton wavefunctions overlap each other easily to achieve the exciton resonance, so the optical nonlinearity of the Wannier–Mott exciton can be large at rather low densities.

The different and complimentary properties of the Frenkel excitons of organic materials and the Wannier–Mott excitons of semiconductors lead to the idea of forming hybrid excitation states with complimentary properties of both kinds of excitons. The hybrid exciton is expected to have the large exciton radius of the Wannier exciton and the large oscillator strength of the Frenkel exciton at the same time. The hybrid state could then have a large optical resonance nonlinearity and a low exciton saturation density. With this proposal, scientists expect to have mixing states with the complimentary properties of both kinds of excitons [1]. Different geometrical configurations of organic-semiconductor materials have been proposed [1] where the Frenkel excitons of organic material and the Wannier–Mott excitons of semiconductors are in resonance with each other and interact with each other by the dipole–dipole interaction at their interface to form the mixing state. The model of nanostructure consisting of neighboring organic and inorganic quantum wells was proposed by Agranovich [2]. The strong interaction of two kinds of exciton at the interface of two 2D quantum wells at resonance forms a new state with a large exciton radius (typical for Wannier–Mott excitons) and a large oscillator strength (typical for the Frenkel excitons). The dipole–dipole coupling decreases quickly with increasing interwell distance. Another configuration studied in [3] was the exciton hybridization state in parallel neighboring organic and inorganic semiconductor quantum wires. For this geometry, the hybrid exciton state is different from zero even for a zero wavevector. The model of a single semiconductor quantum dot with an organic shell was also proposed in [4] and strong mixing was found for the weak confinement regime in the limit of dot radius \( R_D \gg a_B \) (exciton Bohr-radius).

Being confined in all three dimensions, excitons in quantum dots have the biggest quantum size effect and unique properties [12–27]. In a quantum dot, there is always competition between the electron–hole Coulomb interaction, the confinement potential and applied external fields. This competition leads to unique electronic structures and optical properties of the exciton in quantum dots, which could be used to build new materials. The system of a semiconductor quantum dot array embedded in a medium of organic material [5–7] and a dendrimeric structure with a dot at the center [8] have been considered by Huong and Birman. Such structures were reported to have been fabricated in several labs [23, 28]. For these models, the authors predict a large enhancement of nonlinearities at resonance, in some cases about two orders of magnitude in comparison with the traditional systems [5–7]. The effects of applying external electric and magnetic fields to the system that produces the quantum dot hybrid exciton have been studied for an organic-coated semiconductor spherical quantum dot [9]. An important result of this study is the possibility of tuning the Wannier–Frenkel exciton resonance with applied electric and magnetic fields.

In this review paper, we discuss the formation and properties of the Wannier–Mott–Frenkel hybrid exciton in different systems containing quantum dots with the possibility of tuning the system properties by parameters of the systems as well as the external electric and magnetic fields.

## 2. A lattice of semiconductor quantum dots embedded in an organic medium

An exciton is said to be confined in a quantum dot when the size of the dot is approaching the exciton Bohr radius. The energy has the same form as the energy of the free particle, only the wave vector is quantized by the spherical boundary conditions, and so the energy of the confined exciton in the dot has discrete values and is proportional to the inverse of the square of the dot radius. The effective band gap increases in the dot with respect to the bulk values. The oscillator strength of a quantum dot exciton increases proportionally to the radius of the dot as long as the quantum size effect still works. The exciton transition dipole moment is largest for the transition from the ground state to the lowest excited state. There exists some size of the quantum dot when the quantum size effect does not work any more, the exciton energy becomes continuous, and the nonlinearities stop increasing with the increasing size of the dot. This maximum value of the nonlinearities is the limitation that a pure dot cannot overcome.

When many semiconductor quantum dots are placed together in a three-dimensional lattice, Wannier–Mott excitons in different dots interact with each other through the multidipole interaction to form a Wannier transfer exciton inside the lattice. The Wannier exciton inside a quantum dot can then be considered not localized in that dot, but propagating through the lattice via the mechanism of the exciton transfer process [29]. That transfer process in the quantum dot array can help to obtain higher nonlinearities to overcome the above limitation of a single quantum dot. If this lattice of dots is placed in an organic medium, the interaction between this Wannier transfer exciton and the Frenkel exciton of the medium will take the place, and as a result, a new hybrid exciton, which is a mixing state of the excitons in the semiconductor dot lattice and in the organic medium, will appear in the system [5, 6].

In order to investigate the system, we consider a nanostructure consisting of a three-dimensional lattice of semiconductor quantum dots placed into some organic material as a host medium [5, 6]. The size of the system should be considerably smaller than the wavelength of light that corresponds to the transition between the ground states [29]. An ideal array of identical dots \( R \) and uniform dot–dotspacing \( d \) is used for the model. The excitations in inorganic semiconductor quantum dots are the Wannier–Mott excitons, and in the organic medium are the Frenkel excitons. The system is described by the following total Hamiltonian,

\[
H = H_W + H_F + H_{\text{int}},
\]
where $H_W$ is the Hamiltonian of the Wannier–Mott excitons in the dot lattice, $H_F$ is the Frenkel exciton in organic medium and $H_{int}$ is the interaction Hamiltonian between the two kinds of excitons.

$$H_W = \sum_{\vec{n},l} E_W^{\vec{n}} a_{\vec{n}l}^+ a_{\vec{n}l} + \sum_{\vec{n}',l'} t_{\vec{n}\vec{n}',l'l'} \left( \alpha_{\vec{n}l}' a_{\vec{n}'l}^+ + \text{h.c.} \right).$$  \hspace{1cm} (2)

$$H_F = \sum_{k,m} E_F^G(\vec{k}) b_{km}^+ b_{km}^-. \hspace{1cm} (3)

$$H_{int} = \sum_{m \vec{n}\vec{n}'} g_{m}(\vec{r}_{\vec{n}'}, \vec{k}) \left( a_{\vec{n}l}^+ b_{m\vec{k}m} + a_{\vec{n}'l} b_{m\vec{k}'m}^+ \right), \hspace{1cm} (4)

where $a_{\vec{n}l}^+$, $(a_{\vec{n}l})$, $b_{km}^+$, $(b_{km})$ are creation (annihilation) operators of the Wannier excitons in quantum dots and the Frenkel exciton in the organic medium, respectively. Indices $l$, $m$ label the exciton states with wave vector $\vec{k}$ and $\vec{n}$ indicating the sites of the dot in the dot lattice. The dots are distributed on sites of a three-dimensional lattice with the position $\vec{n} = (n_x, n_y, n_z)$ of each site in $(x, y, z)$ coordinates, where the distance between the sites (the “lattice” constant) equals $d$. For a cubic lattice, the number of dots in each direction $N_x$, $N_y$, $N_z$ is the same $N_x = N_y = N_z = N$. $E_W^G$ and $E_F^G$ are the excitation energies of Wannier excitons in the dots and the Frenkel exciton in the medium, respectively. For the Wannier excitons confined to a spherical dot, the oscillator strengths are concentrated mainly on the low excited states, therefore, with no loss of generality, only the interaction of the lowest states of excitons (the ground state and the lowest excited state) is taken into account. The resonance case of Wannier and Frenkel excitons is considered when the energy difference between the energy levels $E_V^G$ and $E_W^G$ is much smaller than the distance to other bands. $g_m(\vec{r}_{\vec{n}'}, \vec{k})$ is the coupling constant of Wannier–Mott and Frenkel excitons, and $t_{\vec{n}\vec{n}'l'l'}$ is the interaction (hopping) constant between Wannier–Mott excitons in different dots. This constant, in general, is different in different directions. The nearest dot interaction is assumed, so the hopping constants for the nearest dots in the $x$-, $y$- and $z$-direction are $t_x$, $t_y$, $t_z$, respectively. The model is studied in the regime where the dot radius is of the same order as the ground state exciton Bohr radius, only one exciton in each dot is assumed and the same-dot exciton–exciton interaction is omitted. We consider the exciton–exciton interaction and the hybridization as the principal effect and omit the potential scattering between the dot array and the medium.

The Wannier exciton Hamiltonian (2) consists of a free exciton term and the different-dot Wannier exciton–Wannier exciton interaction. Changing to $k$-space by Fourier transformation, we obtain the Hamiltonian for the Wannier–Mott exciton including the transfer exciton process in different dots.

$$H_W = \sum_{k,l} E_W^{G}(k) a_{kl}^+ a_{kl} + 2 \sum_{l} \sum_{k_1,k_2,k_3,k_4} t(k_{l}) \cos k_{x} d + t(k_{l}) \cos k_{y} d + t(k_{l}) \cos k_{z} d \right] a_{kl}^+ a_{kl}.$$

$$t(k_{l}) = t(k_{l}), \ \ t(k_{l}) = t(k_{l}), \ \ \text{respectively. Then the total Hamiltonian (1) is written in the form}$$

$$H = \sum_{k,l} E_W^{G}(k) a_{kl}^+ a_{kl} + \sum_{m} E_F^{G} \left(\vec{k}\right) b_{km}^+ b_{km}^-. \hspace{1cm} (6)

where $E_W^{G}(k, l)$ is the eigenenergy of the Wannier–Mott exciton Hamiltonian component (5), including the hopping transfer process. For $kd$ small, the transfer energy of the transfer Wannier excitons. In the quantum dot lattice, $E_W^{G}(k)$ has the form

$$E_W^{G}(k) = E_W^G + 2 \sum_{l} t(k_{l}) - d^2 \sum_{l} t(k_{l})k_{l}^2, \hspace{1cm} (7)

where $E_W^G$ is the band gap, $E_W^{G}(k)$ is the exciton binding energy, and $\gamma_{ext}$ is the nth zero of the spherical Bessel function, $J_{\gamma_{ext}}(x)$ of order $\gamma_{ext}$, which depends on the magnitude of the dot radius $R$. $M_x$ is the effective mass of the exciton. The lowest excitation in the dots will be the state with $l = 0$, $n = 1$. In writing the expression for $E_W^{G}(k)$, we are assuming that the dots are spherical as a good approximation to the actual shape.

Besides the exciton energy in single quantum dots, the energy (7) of the Wannier exciton in the quantum dot array also includes the large transfer energy between the quantum dots in the lattice. Notice here that because of confinement, the energy and the state of one quantum dot cannot be described by the wave vector. But the energy and the state of the transfer exciton in the quantum dot lattice have the $k$-vector dependence and we will need to include the dispersion relation for the transfer Wannier exciton energy. This energy strongly depends on the value of the hopping constant $t(k)$ and the direction of the polarization vector of the exciton. The presence of the transfer exciton allows us to manipulate the energy region of the resonance and also the optical properties of the hybrid exciton.

The system (6) of excitons in a lattice of dots embedded in an organic medium can be interpreted as follows. The Wannier–Mott excitons in the quantum dots interact with each other to form a transfer exciton propagating through the lattice. This transfer exciton in its turn couples at resonance with the Frenkel excitons in the organic medium to form a hybrid organic–inorganic exciton state. For the case when the energies of the Wannier and Frenkel excitons are comparable, i.e. the energy separation between the Wannier–Mott and the Frenkel excitons is much less than the distance to other exciton bands, and the mixing state is assumed only between the two nearest bands, we choose as the basis the mixing state such that when the Wannier–Mott exciton is excited, the Frenkel exciton is in its ground state, and when the Frenkel
exciton is excited, the Wannier–Mott exciton is in its ground state. We write the new hybrid excited state as

$$|\Psi(k)\rangle = u(k) f^F(0) |\Psi^W(k)\rangle + v(k) f^W(0) |\Psi^F(k)\rangle,$$  \hspace{1cm} (9)

where $|\Psi^W(k)\rangle$ and $|\Psi^F(k)\rangle$ are excited states and $f^W(0)$, $f^F(0)$ are ground states of the Wannier–Mott exciton in the dot array and Frenkel excitons in the medium, respectively. In terms of hybrid exciton operators $\alpha_k$, $\alpha_k^\dagger$, the Hamiltonian (6) can be written

$$H' = \sum_k E(k) \alpha_k^\dagger \alpha_k,$$  \hspace{1cm} (10)

with the energy $E(\vec{k})$ of the hybrid state given by the following dispersion relation:

$$E(\vec{k}) = 1/2 \left\{ E^F(\vec{k}) + E^W(\vec{k}) \right\}$$

$$\pm 1/2 \left\{ \left[ E^F(\vec{k}) - E^W(\vec{k}) \right]^2 + 4G^2(\vec{k}) \right\}^{1/2}.$$  \hspace{1cm} (11)

Due to the weak dependence of the Frenkel exciton energy upon the k-vector, the Frenkel exciton energy may be taken independent of the wave vector $k$, $E^F(k) = E^F(0)$.

From (11), it is noticed that the existence of the array of dots and the transfer exciton energy $E^W(\vec{k})$ enhances the coupling between these two kinds of exciton at resonance and enlarges the gap between two hybrid exciton branches. The coupling is strong when $E^F(\vec{k})$ and $E^W(\vec{k})$ are in resonance. The resonance coupling behavior depends strongly on the hopping coefficient $t(k)$ and the hybridization coefficient $G(k)$.

We will consider only the lowest excited states of the exciton, so from now on we will omit the indices $l$ and $l'$. The Bogoliubov transformation coefficients $u(k)$ and $v(k)$ have the following form:

$$u(k) = \frac{G(k)}{\left\{ [E^F(k) - E^W(k)]^2 + G^2(k) \right\}^{1/2}},$$

$$v(k) = \frac{E^F(k) - E^W(k)}{\left\{ [E^F(k) - E^W(k)]^2 + G^2(k) \right\}^{1/2}}.$$  \hspace{1cm} (12)

We can also obtain the average exciton radius of the new hybrid exciton,

$$a_{\text{hybrid}} = |u(k)|^2 a_W + |v(k)|^2 a_F,$$  \hspace{1cm} (13)

where $a_W$, $a_F$ are the radius of the Wannier–Mott exciton and Frenkel exciton, respectively. As previously mentioned, $a_W \gg a_F$, therefore for a strong hybrid state, we have a large hybrid exciton radius $a_{\text{hybrid}} \sim |u(k)|^2 a_W$. Since $u(k)$ depends on the coefficients $G(k)$ and $t(k)$, the hybrid exciton radius is also dependent on those coefficients.

Figure 1 shows the hybrid exciton dispersion curves plotted for ZnSe dots embedded in a standard organic material. The parameters were taken as $E^W(0) - E^F(0) = 5$ meV, $a_B = 30$ Å, $\mu_k = 5D$, $N = 5$. In figure 1, two branches of the hybrid exciton are plotted for an array of dots with radius $R = 40$ Å, and the dot lattice constant $d = 80$ Å.

The Wannier–Wannier exciton interaction coefficient $t(\vec{k})$, or the hopping constant, is estimated as the electrostatic interaction between excitons in dots. Each exciton confined in a dot has its transition dipole moment, which interacts with the corresponding moment of another dot when the distance between the two dots is comparable to the dot radius. As mentioned above, the oscillator strength of a dot exciton is concentrated mainly on the lowest excited states, therefore we assume that only the transition dipole moment to the lowest excited states is involved in the interaction for an array. This multipolar interaction is intrinsically strongly short range, and dependent upon the distance between dots, therefore the nearest neighbor approximation is suitable.

$$t(\vec{k}) = \left\langle W_i(\vec{k}) \right| H_{d-d} \left| W_j(\vec{k}) \right\rangle,$$  \hspace{1cm} (14)

where $W_i(\vec{k})$, $W_j(\vec{k})$ are the exciton wave functions in the two dots,

$$\left| W_i(\vec{k}) \right\rangle = \frac{1}{V_0} \int \phi(\vec{r}_i \psi(\vec{r}_i)) e^{i\vec{k} \cdot \vec{r}_i + i\vec{r}_i \cdot \vec{p}_i} / 2$$

$$\times \Psi_e(\vec{r}_i), \Psi_h(\vec{r}_i) d\vec{r}_i d\vec{p}_i |0\rangle.$$  \hspace{1cm} (15)

where $V_0$ is the dot volume, $\phi(\vec{r}_i \psi(\vec{r}_i))$ is the relative electron–hole motion function, and $\vec{r}_i$, $\vec{p}_i$, $(\vec{r}_i, \vec{p}_i)$ are the coordinates and creation operators of the electron (hole) in the dot, respectively. $\psi(\vec{r})$ is the exciton envelope function [1, 4],

$$\psi(\vec{r})_{\text{nlm}} = Y_{\text{lm}}(\theta, \phi) \frac{2^{1/2}}{R^{1/2}} J_{l+1}(\gamma \vec{R}_d / R).$$  \hspace{1cm} (16)

$H_{d-d}$ is the interaction Hamiltonian between two dipole moments in these two dots. In our case, where the distance between two dots is larger than the dot radius $d > R$, the ordinary dipole–dipole interaction can be used.

$$H_{d-d} = \int \frac{3(\vec{p}_1 \cdot \vec{p}_2)(\vec{r} \cdot \vec{p}_1) + (\vec{p}_1 \cdot \vec{p}_2) \vec{r}^2}{r^5},$$  \hspace{1cm} (17)

where $\vec{p}_1$, $\vec{p}_2$ are the polarization vectors of the Wannier–Mott excitons inside the two dots,

$$p_i = \mu_i \Psi_e(\vec{r}_i), \Psi_h(\vec{r}_i) + \text{h.c.},$$  \hspace{1cm} (18)
\( \mu^W_0 \) is the optical transition dipole moment of the Wannier–Mott exciton. For the transition dipole moment to the excited state \((n, l = 0, m = 0)\) of the spherical quantum dot,

\[
\mu^0 = \frac{(2)^{3/2}}{\hbar \pi} \phi_{1s}^0(r) p_{cv} R^{3/2}.
\]

(19)

As a result, the hopping coefficient between two spherical quantum dots has the form

\[
t(k) = \phi_{ns}^r(0)^2 \sum_{l=0} f_{ns} \{ (\hat{\mu}_{1s}^n \cdot \hat{\mu}_{2s}^n) - 3(\hat{\mu}_{1s}^n \cdot \hat{n}_{12})(\hat{\mu}_{2s}^n \cdot \hat{n}_{12}) \},
\]

(20)

where \( \hat{\mu}_{1,2}^n \) are transition dipole moments to the excited state \((n, l = 0, m = 0)\) for the quantum dot spheres 1 and 2, respectively, \( \hat{n}_{12} \) is the unit vector directed along the straight line connecting two excitons, which due to the small dot radius we can approximately treat as directed along the line connecting two dot centers. \( f_{ns} \) is an integral taken over the volumes of the two dots [5]. The hopping constant depends strongly on the polarization direction of the excitons, the direction of the \( k \)-vector and the relationship between the \( k \)-vector and the polarization mode of the exciton. The longitudinal and transverse modes have different energies. The hopping coefficient \( t \) also depends on \( R/d \), and one can tune the dot separation \( d \) with respect to the dot radius \( R \) in order to determine the optimum \( t \).

The organic medium can also be described as a lattice with organic molecules occupying every site and the Frenkel excitons moving between the sites. Because of the small ‘lattice constant’, the organic molecular lattice can be considered as a ‘microscopic’ lattice in comparison with the macroscopic size of the dot lattice. The organic lattice constant is in the order of 5 Å, while the dot radius is about 30–100 Å and the dot lattice constant is usually around 60–500 Å. The resonance coupling of Frenkel excitons in the medium and Wannier excitons in the dot array is determined by the interaction parameter [2],

\[
G(k) = \langle F, k | H_{int} | W, k \rangle,
\]

(21)

where the interaction Hamiltonian, similarly to [2], is taken as the product of the operator of the electric field \( E(r_n) \) created at point \( r_n \) in the organic medium by the excitons in quantum dots and the transition polarization operator \( P(r_n) \) of the Frenkel exciton at molecular site \( r_n \) of the organic medium.

\[
H_{int} = - \sum_n E(r_n) P(r_n).
\]

(22)

The Frenkel exciton wave function is written in the form

\[
\chi^f(r_n) = \frac{1}{N_F^{1/2}} \sum_n e^{i k \cdot r_n} \chi^f_n(r_n) b^\dagger_n |0\rangle.
\]

(23)

\( \chi^f_n(r_n) \) is the excited state of the molecule at site \( r_n \). The obtained expression for the hybridization coefficient of the semiconductor quantum dot and the organic medium has the following form:

\[
G(k) = \frac{3 \epsilon_1}{2 \epsilon_2 + \epsilon_1} \frac{\pi}{2} \sin \theta \sum_n \mu^0 \phi_{ns}(0) D_{ns}(k),
\]

(24)

where \( \theta \) is the angle between exciton transition dipole moments of the quantum dot and the organic molecule and

\[
D_{ns}(k) = \int \frac{d^3 r}{\sqrt{\pi}} e^{i k \cdot r} W_{s}(r) \rho_{cv}(r) R^{3/2}.
\]

D.

(25)

The value of \( \chi^{(3)}(\omega) \) at resonance may be very large. By changing the number of dots and other parameters of the array, one can control the value of the nonlinearity.

Figure 2 is the numerical results for ZnSe dots [5]. We use here the following typical parameters of organic and semiconductor materials: \( \nu^F = 100 \text{ Å} \), \( a_{\text{org}} = 5 \text{ Å} \), \( \mu^F = 5 \text{D} \),

\[
D_{ns}(k) \text{ is a double integral taken over the volume of the dot and the volume of the whole medium [5].}
\]

At resonance, the oscillator strength of the hybrid state is determined by its Frenkel exciton component and its exciton radius is determined by its Wannier component. As a result, the hybrid exciton has both a large exciton radius and a large oscillator strength. In addition, as already noted in [5, 29], the Wannier transfer exciton has a rather small translational mass, which depends on the hopping constant and the number of dots, and is a few times smaller than the ordinary reduced electron-hole mass. This small translational mass is one reason for a large coherence length, which is related to the homogeneous linewidth of the excitonic transition. The increase in the oscillator strength as well as the coherence length leads to a large figure of merit of the hybrid exciton. The large radius leads to a rather low saturation density, and the existence of the large oscillator strength and the low saturation density promises the large nonlinearities of the state. In the presence of the external electric field, neglecting contributions from the other nonresonant levels, the third order susceptibility has been calculated using the standard perturbation theory [30–33] and has the form

\[
\chi^{(3)}(\omega) \approx \frac{\mu^F}{V} \left( \frac{2 \sqrt{2} \gamma_\perp}{\pi^2} \right) \left( \frac{V_{\text{Medium}}}{V_{\text{cell}}} \right)^2 \frac{L}{d} \left( \frac{R}{d} \right)^6 \phi_{3}^f(0) \left( \frac{1}{(\omega - \tilde{\omega} + i \gamma_\parallel)^2} \right),
\]

(25)

Here, \( V_{\text{Medium}} \) is the volume of the organic host, and \( V_{\text{cell}} \) is the volume of one cell in the organic lattice, \( L \) is the coherence length, \( \gamma_\parallel \) and \( \gamma_\perp \) are the transverse and longitudinal relaxation constants of the excitonic transition, respectively, \( R \) is the dot radius, \( d \) is the dot to dot separation, \( a \) is the Bohr radius, and \( \hbar \omega \) is the lowest excitation energy of the hybrid exciton.

Figure 2 is the numerical results for ZnSe dots [5]. We use here the following typical parameters of organic and semiconductor materials: \( \nu^F = 100 \text{ Å} \), \( a_{\text{org}} = 5 \text{ Å} \), \( \mu^F = 5 \text{D} \),

\[
D_{ns}(k) \text{ is a double integral taken over the volume of the dot and the volume of the whole medium [5].}
\]
Figure 3. Imaginary part of the third order nonlinear susceptibility as a function of wavelength. The dotted curves correspond to \( R = 50 \, \text{Å} \) and \( d = 100 \, \text{Å} \), the dashed curves correspond to \( R = 50 \, \text{Å} \) and \( d = 150 \, \text{Å} \) and the solid curves correspond to \( R = 40 \, \text{Å} \) and \( d = 160 \, \text{Å} \). Gao et al [6].

The imaginary part of the susceptibility gives rise to the coefficient for the two-photon absorption \( a_2 \). The results for the two-photon absorption \( a_2 \) coefficient for the material with hybrid excitons shows that it significantly exceeds that of the other materials in the near infrared spectral region. For example, we obtain the values of \( a_2 \approx 5 \times 10^{-10} \, \text{m} \, \text{W}^{-1} \) for the array of quantum dots with \( R = 100 \, \text{Å} \) and \( d = 200 \, \text{Å} \) in an organic medium at a wavelength of 1060 nm. This value exceeds \( a_2 \) for the other materials in the visible and near infrared spectral regions.

Figure 3 shows the plot of the imaginary part of the third order susceptibility as a function of the wavelength.

3. Hybrid exciton state in a quantum dot–dendrimer system

Another efficient semiconductor dot–organic material combination is the quantum dot–dendrimer system. Dendrimers are nanosized, highly ordered and perfectly hyperbranched three-dimensional macromolecules with controlled structures, which have very strong potential for optimal energy funnels, gene and drug delivery applications. Dendrimers with controllable size and structure can be used as light emitters and can serve as building blocks in nanodevices [34–39].

A quantum dot–dendrimer system, where a semiconductor dot is placed inside a dendrimer structure during the synthesis process, is studied. The Wannier exciton in the dot and the Frenkel exciton in the dendrimer interact with each other through dipole–dipole interaction to form the mixing state. This hybrid exciton plays an important role in optical properties of the system. By changing the size and structure of the nanocrystal dendrimer, one can expect to tune the hybrid exciton properties and control optical processes of the system. The problem is solved in [8] using the Green’s function approach [40]. The double-time real space Green’s function with the diagram technique is very useful and important in solving problems with complicated structures.

A model of a quantum dot as a spherical core at the center, which is attached to three dendrimeric branches, is considered. Each dendrimeric branch consists of tertiary amine groups linked by three-carbon chains. The molecule at the end of each branch, called the branching point, in its turn, is attached to two protein branches, and so on, as in figure 4. We assume nearest neighbor interaction, i.e. there are couplings between the quantum dot and the first molecules of the attached protein branches, between the molecules in the same branches as well as between the molecule at a branching point and the protein chain attached to it, but no coupling between molecules of different branches.

The tight-binding Hamiltonian of the system can be written as

\[
H = \sum_{i=1}^{N} \varepsilon_i a_i^\dagger a_i + \sum_{i,j} V_{ij} a_i^\dagger a_j,
\]

where \( a_i^\dagger, a_i \) are exciton creation and annihilation operators, \( \varepsilon_i \) is the exciton energy at each site, and \( i \) labels the sites of the quantum dot and molecules at the end of each generation of the dendrimeric branch. At the quantum dot site, the energy will be the energy of the exciton confined in the dot [8] and for the molecular sites it will be the Frenkel exciton energy. \( V_{ij} \) is

Figure 4. A quantum dot–dendron ligand model. Huong and Birman [8].
the effective interaction integral between excitons of different dendrimer generations.

The double-time Green’s functions are written as
\[ G_{ij}(t) = \frac{2\pi}{\hbar} \langle [a_i(t), a_j^*(0)] \rangle \]
\[ = -\frac{2\pi}{\hbar} \Theta(t) \langle [a_i(t), a_j^*(0)] \rangle, \quad (27) \]
where \([\cdot]\) is a commutator, \(a(t)\) is the Heisenberg representation of the operator \(a\), \(\Omega(t)\) is the Heaviside function, and \((\ldots)\) is the thermal average over a grand canonical ensemble. Using the Fourier transformation to transfer the time Green’s functions to the energy variable, the Schwinger–Dyson equations for the Green’s functions have the form
\[ (E - \varepsilon_i)G_{ij}(E) - \sum V_{ik}G_{kj}(E) = \delta_{ij}. \quad (28) \]

Before solving this equation, the effective interaction \(V_{ik}\) between different generations, called the interaction at a macroscopic scale, is needed. This has been made from all interactions between the nearest neighboring molecules, called the interaction at the microscopic scale. For instance, for a chain in figure 4, we want to calculate the interaction between the quantum dot at the center, considered as the zero generation, and the molecule at the end of one of the first molecular chains, which is the first generation. In the chain, there are a number of molecules, so the quantum dot and the molecule finishing the first generation may be far apart and not interact directly with each other if we assume only nearest neighbor interaction. The exciton in the quantum dot interacts with the exciton in the first molecule of the first chain, the second molecule, and so on, and the next to last molecule interacts with the last molecule of the chain. Actually in this process the exciton in the quantum dot interacts with the exciton in the last molecule of the first chain indirectly through the effective superexchange interaction. This problem is very similar to the problem of electron transfer in a chain with one impurity [42, 43].

By solving the Dyson equation for the Huckel Hamiltonian of the linear chain,
\[ H = \sum_a \varepsilon_a a_a^\dagger a_a + \sum_{a,\beta} (a_a^\dagger a_\beta + a_\beta^\dagger a_a), \quad (29) \]
the effective interaction between the dendrimer generations is obtained [7]. As a result, the effective interaction between site 0 and site \(n\), i.e., between the exciton in the quantum dot at the core and the Frenkel excitation of the first dendrimeric generation, has the form
\[ V_{WF} = \frac{v_0}{E - vT} T^{n-1}, \quad (30) \]
where \(v_0\) is the interaction of the Wannier exciton at the core and the Frenkel excitation at the nearest molecular site, \(v\) is the interaction between two Frenkel excitations at the nearest sites, \(T\) is a transfer function [7] and \(E\) is the energy of the mixed state in this chain,
\[ E = \varepsilon_{WF} + \frac{v_0^2}{E - \varepsilon_{WF} - vT}, \quad (31) \]
Similarly, the effective interaction between the Frenkel excitons in the neighboring generations is obtained as
\[ V_{EF} = \frac{v}{E - vT} T^{n-1}, \quad (32) \]
with the energy
\[ E = \varepsilon_F + \frac{v^2}{E - \varepsilon_F - vT}. \quad (33) \]
The effective interaction coefficients (30) and (32) depend on the energies of the excitons, the nearest neighbor interaction coefficients, and also the number of molecules in each chain. Then each chain can be replaced by a site, and the interactions between the nearest neighbor chains are described by these effective interactions.

To solve the Schwinger–Dyson equations (28) for the dendrimer system with many generations, it is convenient to use the electron transfer graph method developed in [40, 41] where this method is used to study electron transfer between localized sites. The details of the diagram technique method can be found in [40, 41]. We just brieﬂy introduce the method to be used in our work. For the Schwinger–Dyson equation (28), every site corresponds to a graph vertex. A nondiagonal term \(V_{jk}\) of the Hamiltonian corresponds to an oriented edge originating at vertex \(j\) and ending at vertex \(k\) with the value of the edge equal to the interaction integral \(V_{jk}\). Diagonal terms \(E - \varepsilon_i\) of the Hamiltonian correspond to a loop attached to the vertex \(i\) and the value of the loop equals \(W_i = E - \varepsilon_i\). The value of the cycle is the product of the values of all edges in the cycle, with the sign being negative except for the loop for any cycle with a length of more than 1. The cyclic term is a set of cycles that have no common vertices and pass through every vertex. The value of the cyclic term \(O\) is a product of the value of all cycles of the cyclic term, and the cyclic value of the graph \(\Theta\) is the sum of all of the cyclic terms.

For a linear chain of sites, it is shown in [40, 41] that the Green’s function \(G_{ij}\) is equal to
\[ G_{ij} = \frac{\Theta_{i,i+1} P_{ij} \Theta_{j+1,i}}{\sum O^{(k)}} \quad (34) \]
where \(P_{ij}\) is the product of the edges along the pathway from vertex \(i\) to vertex \(j\),
\[ P_{ij} = V_{i,i+1} V_{i+1,i+2} \cdots V_{j-1,j} \quad (35) \]
with \(\Theta = \sum O^{(k)}(i, j)\) being the cyclic value of the graph and \(O^{(k)}(i, j)\) the cyclic term.

A very important feature of this method is the continuous fraction representation for sites with side groups attached. For the case where there are side groups attached to some site \(i\) of a linear path, all of the graph of the main chain remains the same; only the value of the loop at site \(i\) is different. It has been proved [40, 41] that the diagonal element of the Green’s function of the side graph can be expressed through the Green’s function of the subgraph in the continued fraction representation. The value of the loop with the side groups could be expanded into a continuous fraction of loops values of the extended side subgraph of the graph. Instead of the
original loop value $G^{-1}_j = E - \varepsilon_j$, the loop value of the site with side groups becomes

$$G^{-1}_j = (E - \varepsilon_j) - \sum_k V^2_{jk}(i) \frac{1}{\Theta_{kk}/\Theta_{ji}} = (E - \varepsilon_j) - \sum_k V^2_{jk}(i) G[\tilde{\gamma}_k(i)]_{kk}. \quad (36)$$

For instance, for the site chain in figure 5, the value of the loop at site 2 has the form

$$\tilde{W}_{22} = E - \varepsilon_2 - \frac{V_{2a}V_{a2}}{E - \varepsilon_a - (V_{ab}V_{ba}/(E - \varepsilon_b))}. \quad (37)$$

The above real space Green’s function method and its diagrammatic technique have been used to investigate the Wannier–Frenkel hybrid exciton in different quantum dot-organic dendrimeric configurations [7]. We discuss one of the systems, the nanocrystal–dendron ligand, a special structure of perfect symmetry with a dot at the center and a closely packed ligand shell.

Let us assume that a quantum dot is attached to three molecular branches, then each terminal molecule is attached to two other branches, and so on, as in figure 4. Using the diagram with continuous fraction representation, we can consider the ligand as a linear chain with sidegroups attached to each site.

At first we consider the first generation system with the quantum dot at the center attached to three chains of molecules in figure 6. For the dot-dendron of the first generation, the quantum dot is situated at chain 2, connected to molecules at chains 1, 3 and 2’. Considering this system as a linear chain of chain 1, chain 2 and chain 3, with chain 2’ is attached to chain 2. At chain 2 we have a Wannier exciton with energy $\varepsilon_w$, at chains 1, 3 and 2’ we have Frenkel excitons with energy $\varepsilon_F$. The Green’s functions of the system have the following form,

$$G_{11} = \frac{1}{\Theta} \left[ \left( E - \varepsilon_w - \frac{V_{WF}V_{FW}}{E - \varepsilon_F} \right) (E - \varepsilon_F) - V_{WF}V_{FW} \right],$$

$$G_{12} = \frac{1}{\Theta} V_{FW}(E - \varepsilon_F) = G_{21},$$

$$G_{13} = \frac{1}{\Theta} V_{FW}V_{WF} = G_{31},$$

$$G_{22} = \frac{1}{\Theta} (E - \varepsilon_F)^2,$$

$$G_{23} = \frac{1}{\Theta} (E - \varepsilon_F) V_{FW} = G_{32},$$

$$G_{33} = \frac{1}{\Theta} \left[ (E - \varepsilon_F) \left( E - \varepsilon_w - \frac{V_{WF}V_{FW}}{E - \varepsilon_F} \right) - V_{WF}V_{FW} \right]. \quad (38)$$

For the two generation quantum dot-dendron, we can consider the dendron of one generation with a side group attached to each of the terminal molecules in figure 6.

The loop values $\varepsilon_1$, $\varepsilon_2$, $\varepsilon_3$ become $\tilde{\varepsilon}_1$, $\tilde{\varepsilon}_2$, $\tilde{\varepsilon}_3$ with the side group values attached,

$$\tilde{\varepsilon}_1 = \varepsilon_1 - \frac{V_{11}V_{111}}{E - \varepsilon_{11}} - \frac{V_{12}V_{121}}{E - \varepsilon_{12}},$$

$$\tilde{\varepsilon}_2 = \varepsilon_2 - \frac{V_{22}V_{222}}{E - \varepsilon_{22}},$$

$$\tilde{\varepsilon}_3 = \varepsilon_3 - \frac{V_{33}V_{333}}{E - \varepsilon_{33}} - \frac{V_{32}V_{322}}{E - \varepsilon_{32}}, \quad (41)$$

Continuing this process of side group graphs attached to the chains, we can go further to any generation just by changing the loop values in equation (41). Since every branching point is attached to two branches, in going from the $n$th generation to the $(n + 1)$th generation, the value of the loop $i$ just needs to be added to the value of the two branches of the $(n + 1)$th generation attached to the $n$th generation of the loop. If we know the energy and Green’s functions of a dendrimer with $n$ generations, we can always find ones for the dendrimer with $(n + 1)$ generations. Because of the continuous fraction, from some generation, the effects of the $(n + 1)$th generation is small and can be treated as perturbations.

The energy of the Wannier–Frenkel hybrid exciton is the pole of the Green’s functions, which is the zeros of the Green’s function determinator $\Theta$. 

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**Figure 5.** (a) A quantum dot-molecule chain. (b) A molecular chain. Huong and Birman [8].

**Figure 6.** (a) A model of a quantum dot-dendron ligand with one generation. (b) A model of a quantum dot-dendron ligand with two generations. Huong and Birman [8].
For the dot–dendron ligand of one generation, the Wannier–Mot exciton energy is obtained in the form
\[ E_{WF}^{WF} = \frac{1}{2} \left[ \varepsilon_F + \varepsilon_W \pm \sqrt{(\varepsilon_F - \varepsilon_W)^2 + 8V_{WF}^2 V_{WF}^2} \right], \tag{42} \]
and for the energy of the hybrid exciton of the quantum dot–dendron ligand of two generations, we find
\[
E_{WF}^{WF} = \frac{1}{2} \left[ \varepsilon_F + \varepsilon_W + \frac{4V_{WF}^2}{E - \varepsilon_F} - \frac{2V_{WF}^2}{E - \varepsilon_W} \right] \pm \frac{\varepsilon_F^2 + \varepsilon_W^2 + 6\varepsilon_F \varepsilon_W}{E - \varepsilon_F} + \frac{16V_{WF}^4}{(E - \varepsilon_F)^2} - \frac{16V_{WF}^4}{(E - \varepsilon_F)^2} \frac{24V_{WF}^2 V_{WF}^2}{(E - \varepsilon_F)^2} + 8V_{WF}^2 \right]^{1/2}. \tag{43}\]

Notice here that using the continuous fractional diagram technique, each time when we have more generations, the values of \(2V_{WF}^2/(E - \varepsilon_F)\) are added to each branching point. This means that when one more generation is added, in equation (39) only the value of \(E\) will change for \(2V_{WF}^2/(E - \varepsilon_F)\) time some integers. Then when \(n\) is large, when it is difficult to solve equation (39) analytically, the self-consistent method is used to solve the equations. In this way, for quantum dot–dendron ligands of any generation, the expressions for the energy of the hybrid exciton can always be obtained. The Green’s functions also allow the calculation of other physical quantities of the hybrid states.

The structure of the dendrimer (i.e. the number of molecules in one branch and/or the number of the branches, the number of generations, etc) as well as its material affects the mixing region, energy and optical properties of the hybridization. In addition, the homogeneous broadening of the absorption lines could arise for different reasons, such as the surface roughness of the dots and the imperfect symmetry of the structure or the participation of the second or third-order interaction between molecular sites. It is shown in [7] that for the CdSe quantum dot, the exciton linewidth is much smaller than the exciton linewidth for the quantum well, about 0.12 meV [44]. For Frenkel excitons, there are organic substances with exciton linewidths of about 1 meV or smaller. Both of these linewidths are smaller in comparison with the hybridization parameter \(V_{WF}\) (\(\sim 5\) meV).

4. Optical nonlinearities of quantum dot–dendrimer systems

One of the main problems in the study of the optics of condensed matter systems is predicting the nonlinear optical response. Using the microscopic framework [33], which is based on the Heisenberg equations of motion for the variables determining the optical response, we calculate the linear and non-linear susceptibilities using the real space Green’s functions obtained above [9]. The calculation of optical response leads to the solution of the coupled nonlinear equations for variables \(\{a_i, a_i^*\}, \{a_i a_j a_k\}\), which under the local factorization approximation (LFA) [33] can all be represented by products of one-exciton Green’s functions.

Following [33], the first-order susceptibility has the form
\[ \alpha(E) = \bar{\mu}_a \bar{\mu}_m [G_{nn}(E) + G_{mn}(E)], \tag{44} \]
and the third-order susceptibility
\[ \gamma^{(3)}(-\omega_j, \omega_1, \omega_2, \omega_3) = -\frac{1}{2 \times 3!} \times \sum_m \sum_{m_1 m_2 m_3} \gamma_{nm_1 m_2 m_3}(-\omega_j, \omega_1, \omega_2, \omega_3), \tag{45} \]
where
\[
\gamma_{nm_1 m_2 m_3}(-\omega_j, \omega_1, \omega_2, \omega_3) = \frac{1}{6} \sum_{p, n', n''} \bar{\mu}_n \bar{\mu}_n^* \bar{\mu}_m^* \bar{\mu}_{m_1} \bar{\mu}_{m_2} \bar{\mu}_{m_3} \times [G_{nn'}(\omega_1) G_{n'n''}^*(\omega_j) G_{n''m_1}^*(\omega_2) G_{n' m_2}^*(\omega_3) \times \omega(\omega) \Gamma_{n'n''}^*(\omega_1 + \omega_2) + G_{nn'}^*(\omega_j) G_{n''m_1}^*(\omega_3) G_{n' m_2}^*(\omega_2) \times \omega(\omega) G_{n''m_1}^*(\omega_j) \Gamma_{n'n''}^*(\omega_1 - \omega_2)]. \tag{46} \]

Here, \(\Gamma_{n'n''}^*(\omega)\) is a two-exciton scattering matrix,
\[ \Gamma_{n'n''}^{-1}(\omega) = \frac{1}{2} \int \frac{d\omega'}{2\pi i} G_{n'n''}(\omega') G_{n'n''}(\omega - \omega'). \tag{47} \]
The susceptibilities depend on the energies of the excitons and the effective interaction \(V_{WF}\) and \(V_{WF}\) and those coefficients themselves depend on the parameters of the system, such as the dendrimer and the quantum dot materials, the size of each chain, and the number of generations, so they can be tuned by those parameters. The analytical solutions can be obtained for a dendrimer of any generation by the side group method. The numerical calculation for a standard dendrimERIC ligand of four generations with a quantum CdSe dot of radius 40 Å at the center and a distance of 80 Å between the links of different molecules shows an increase in the third order susceptibilities of about 400 times in comparison with the organic material. We also notice that the shorter the link, the larger the interaction coefficients and the larger the nonlinearities. By changing the size and parameter of the dendrimer, the region of resonance could be changed so that one could also tune the laser frequency \(\omega\).

5. Hybrid exciton under electric and magnetic fields

Since the hybrid Wannier–Frenkel exciton can be considered among the most promising materials for optical and electronic devices, it is helpful to study the effects of electric and magnetic fields on this mixed state. There are several theoretical works studying the composite organic–inorganic quantum wells in the presence of an electric field [45], a magnetic field [46], and mutually perpendicular electric and magnetic fields [47]. It was found that by tuning the applied fields, various interesting properties of dispersion laws were obtained [46, 47]. The quadratic Stark dependence of the hybrid exciton energy on the electric field was found as expected for the confined Stark effect for the hybrid exciton.

We consider a heterostructure of an inorganic semiconductor spherical quantum dot covered by a thin organic layer. The excitations in the quantum dot are Wannier–Mot excitons and in the organic layer the Frenkel excitons are moving between lattice sites. The
total Hamiltonian of the system under applied electric field $\vec{E}$ and magnetic field $\vec{B}$ is given by

$$H = H_{\text{F}} + H_{\text{W}}(\vec{E}, \vec{B}) + H_{\text{int}}(\vec{E}, \vec{B}).$$  \hspace{1cm} (48)

Here, $H_{\text{int}}$ is the interaction Hamiltonian between the two kinds of excitons, which will lead to a hybridization coupling constant that governs the hybridization,

$$\Gamma = \langle \Psi_f | H_{\text{int}} | \Psi_f \rangle.$$  \hspace{1cm} (49)

Because of the large Bohr radius of the Wannier–Mott exciton, the semiconductor quantum dot is more affected by the electric and magnetic fields and we can neglect the field effect on the organic layer due to localization of the Frenkel exciton. So in the Hamiltonian (48), the fields will change the second and third terms only. In this strong confinement limit, the effect of electric and magnetic fields has been calculated using perturbation theory, using the Hamiltonian of the Wannier exciton for the non-perturbation basic functions to give analytical values of the wavefunctions and energies. It is shown that perturbation theory works well for the small quantum dots with very little different from numerical calculation. The energies and wavefunctions of the Wannier–Mott excitons under the effects of the electric and magnetic fields are then calculated in the first and second orders of the perturbation.

The interaction $H_{\text{int}}$ in (49) is then estimated from the electric field and magnetic field operators produced by the molecular layer in the organic dot under the applied fields and then the coupling constant $\Gamma$ will be calculated on the basis of the Frenkel exciton wave function and the new Wannier exciton wavefunction. By this method, the Wannier–Mott–Frenkel hybrid exciton in the presence of the electric field is described by the coupling states. The hybridization is strong at the resonance region, and the region depends on the applied field. The resonance region where the Wannier and Frenkel excitons are strongly mixed is shifted by the values and orientation of the fields, so by tuning the field one can change the resonance region and the properties of the hybridization. The electric field reduces the exciton binding energy of the hybrid excitons. The Stark shift of the Wannier exciton energy levels and its wavefunction depending on the applied electric field have been obtained [8]. In addition to the spatial confinement of the quantum dot, the magnetic confinement of the electron and hole leads to more localization of the electrons and holes. From the results, it is shown [8] that the application of the field enhances the coupling between the two kinds of excitons and increases the gap between two branches of the hybrid exciton.

By tuning the magnitude and orientation of the fields, one could obtain different physics properties of the semiconductor-organic systems.

6. Conclusion

The possibility of creating systems using semiconductor quantum dots and organic materials offer a strong resonance coupling of Frenkel and Wannier excitons. The hybrid exciton states have special properties of both kinds of exciton, i.e. having large exciton radius as well as large oscillator strength. The energies and different optical properties of the semiconductor dot-organic systems can be tuned by changing the parameters of the systems, such as the number of dots, dot radius, dot–dot spacing, number of molecular branches and number of molecules in each branch. These results could help to create organic-semiconductor combined systems with expected optical and physical properties to be used in different applications.

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