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Quantum dot lattice embedded in an organic medium: Hybrid exciton state and optical response

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We propose a model to implement organic exciton–semiconductor exciton hybridization by embedding a semiconductor quantum dot array into an organic medium. A Wannier-Mott transfer exciton is formed when the exciton in each semiconductor dot interacts via multipole-multipole coupling with other excitons in the different dots of the array. A hybrid exciton appears in the system owing to strong dipole-dipole interaction of the Frenkel exciton of the organic molecules with the Wannier-Mott transfer exciton of the quantum dot array. This hybrid exciton has both a large oscillator strength (Frenkel-like) and a large exciton Bohr radius (Wannier-like). At resonance between these two types of excitons, the optical nonlinearity is very high and can be controlled by changing parameters of the system such as dot radius and dot spacing.

I. INTRODUCTION

The possibilities of using organic materials to embed semiconductor heterostructures led us to the expectation of having some system with unique physical properties. It has already been noted that a different type of excitonic state could be obtained by mixing Wannier-Mott and Frenkel excitons. In Refs. 1–4 the authors proposed structures of layers with organic-inorganic quantum wells, and parallel organic-inorganic quantum wires, where the Wannier and Frenkel excitons in neighboring layers interact with each other to form a type of exciton that has both the very large oscillator strength of the Frenkel exciton, and the high polarizability in an external field of a Wannier exciton. Recently, in Ref. 3 the interesting model of a single semiconductor quantum dot with an organic shell was also proposed and strong enhancement of the nonlinearity was found for the weak confinement regime in the limit of dot radius $R_D \gg a_B$ (exciton Bohr radius).

At present, quantum dots—which are three-dimensionally confined nanostructures—have been studied intensively theoretically and experimentally.[5–9] As a model for heterostructures where the resonant mixing of Wannier-Mott and Frenkel excitons can appear, we propose here the system of a semiconductor quantum dot array embedded in a medium of organic material. Such structures are reported to have been fabricated by several authors.[10,16] It is already known[11] that when many quantum dots are arranged together in an array, due to the multipole interaction of excitons in different dots, an exciton inside a quantum dot can be considered as not localized in that dot, but it can propagate through the lattice via the mechanism of exciton transfer processes. In our model, when we place such a dot array in an organic material, due to the interaction of this propagating exciton with the medium, a hybrid exciton will appear in the system. This hybrid exciton, which is a mixed state of the transfer exciton and the Frenkel exciton of the medium when these are at resonance, also has a large exciton radius (because of the large Wannier-Mott exciton radius) and a large oscillator strength (because of the large oscillator strengths of both the Frenkel and transfer Wannier-Mott excitons). The small mass of the transfer exciton then leads to a large coherence length of the system. This fact, as well as the hybridization, will give us a very large optical nonlinearity.

In Sec. II we present our model to get the hybrid exciton Hamiltonian. The hopping coefficient of the exciton in different dots and the Wannier-Frenkel exciton coupling constant are described in Secs. III and IV. The nonlinear optical susceptibility and its dependence upon the system parameters are obtained in Sec. V, along with an estimate of the magnitude of the nonlinear coefficient for a typical system.

II. THE MODEL

We consider a three-dimensional array of semiconductor quantum dots placed into some organic material as a host medium. The size of the system should be considerably smaller than the wavelength of light that corresponds to the transition between excited and ground state.[3] As an approximation, we will consider here the ideal array with dots of the same radius R and the same dot-dot spacing d.

The total Hamiltonian of the system will be taken as follows:

$$H=\sum_{\vec{n},l} E^W_{\vec{n}l} a^\dagger_{\vec{n}l} a_{\vec{n}l} + \sum_{\vec{k},m} E^F_m(\vec{k}) b^\dagger_{\vec{k}m} b_{\vec{k}m} + \sum_{ml\vec{n}\vec{k}} g_{lm}(\vec{r}_{\vec{n}},\vec{k})$$

$$\times(a^\dagger_{\vec{n}l} b_{\vec{k}m} + a_{\vec{n}l} b^\dagger_{\vec{k}m}) + \sum_{\vec{n}\vec{n}'ll'} t_{\vec{n}\vec{n}'ll'}(a^\dagger_{\vec{n}l} a_{\vec{n}'l'} + \text{H.c.}), \quad (1)$$

where $a^\dagger_{\vec{n}l}$ ($a_{\vec{n}l}$) are creation (annihilation) operators of Wannier excitons in quantum dots. The index l labels the exciton states and $\vec{n}$ indicates the sites of the dot in the dot lattice. Here we assume that 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 simplicity, we assume a cubic array, i.e., the number of dots in each directions N_x,N_y,N_z is the same, $N_x=N_y=N_z=N$. $b^\dagger_{\vec{k}m}$ ($b_{\vec{k}m}$) are creation (annihilation) operators for the Frenkel exciton in the organic medium with wave vector $\vec{k}$ in the mth exciton state. $E^W_{\vec{n}l}$ and $E^F_{\vec{k}m}$ are the excitation energies of Wannier excitons in the dots and the Frenkel exciton in the medium, respectively. For Wannier excitons confined to a dot, or quantum sphere, the oscillator strengths are concentrated mainly in the low excited states. So, with no loss of generality, and in order to simplify, we will consider only the interaction of the lowest states of excitons (the ground state and the lowest excited state). Also we assume that the energy difference between the energy levels E^F and E^W is much smaller than the distance to other bands. $g_{lm}(\vec{r}_{\vec{n}},\vec{k})$ is the coupling constant of Wannier and Frenkel excitons, and $t_{\vec{n}\vec{n}'ll'}$ is the hopping constant between Wannier excitons in the dots. This hopping constant, which has its origin in the multipolar interaction of excitons in different dots, in general is different in different directions because of the direction of polarization. Here we assume that only nearest dots interact with each other, so the hopping constants for the nearest dots in the x,y,z directions are t_x,t_y,t_z, respectively, where, e.g., $t_x=t_{\vec{n}\vec{n}'ll'}$ if $\vec{n}'$ is (n_x+1,n_y,n_z) and l,l' are the labels of the lowest energy levels, and similarly for t_y,t_z. Because the dot radius is approximately equal to the ground state exciton Bohr radius for the systems under consideration, we assume that there exists only one exciton in each dot, so we omit the exciton-exciton interaction in the same dot. Thus we have for the hopping term

$$H_{hop}=\sum_{ll'}\sum_{n_x,n_y,n_z}(t_x a^\dagger_{n_x+1,n_y,n_z;l}a_{n_x,n_y,n_z;l'} + t_y a^\dagger_{n_x,n_y+1,n_z;l}a_{n_x,n_y,n_z;l'} + t_z a^\dagger_{n_x,n_y,n_z+1;l}a_{n_x,n_y,n_z;l'}+\text{H.c.}). \tag{2}$$

Changing to k space by Fourier transformation, we obtain

$$a^\dagger_{n_x,n_y,n_z;l}=1/\sqrt{N^3}\sum_{k_x,k_y,k_z}[\exp i(n_xk_xd+n_yk_yd+n_zk_zd)]a^\dagger_{k_x,k_y,k_z;l}. \tag{3}$$

Here d is the distance between dots and $\vec{k}=\{k_x,k_y,k_z\}$ is the wave vector of the exciton in the coupled dots.

The Fourier transforms of t_x,t_y,t_z will be $t(k_x),t(k_y),t(k_z)$, respectively. The Fourier transformation for the dot-medium coupling constant $g_{lm}(\vec{r}_{\vec{n}},\vec{k})$ will be the following:

$$g_{lm}(\vec{r}_{\vec{n}},\vec{k})=\sum_{\vec{k}'}[\exp i(n_xk'_xd+n_yk'_yd+n_zk'_zd)]G_{lm}(\vec{k}',\vec{k}). \tag{4}$$

Notice here that if one makes the translational transformation with a lattice vector $\vec{L}$ in the lattice, due to the exponential forms of the Frenkel and Wannier exciton state functions, one will get, by translational invariance, $\Sigma_L \exp i(\vec{k}-\vec{k}')\vec{L}=\delta(k-k')$. So the coefficient $G_{lm}(\vec{k},\vec{k}')$ will be different from zero only if $k=k'$. Then instead of $G_{lm}(\vec{k},\vec{k}')$ we can write the coupling constant as $G_{lm}(\vec{k})$ and omit the sum over k'.

Then we get the total Hamiltonian (1) as

$$H=\sum_{l\vec{k}}E^W_l(\vec{k})a^\dagger_{l\vec{k}}a_{l\vec{k}}+2\sum_l\sum_{k_x,k_y,k_z,l}[t(k_x)\cos k_xd + t(k_y)\cos k_yd+t(k_z)\cos k_zd]a^\dagger_{l\vec{k}}a_{l\vec{k}}+\sum_{m\vec{k}}E^F_m(\vec{k})b^\dagger_{\vec{k}m}b_{\vec{k}m} + \sum_{ml\vec{k}}G_{lm}(\vec{k})(a^\dagger_{\vec{k}l}b_{\vec{k}m}+a_{\vec{k}l}b^\dagger_{\vec{k}m}). \tag{5}$$

In the perfect confinement approximation,[1,4] the exciton wave functions must vanish at the boundary of dots, and the energy of the Wannier exciton in the spherical quantum dot has discrete values according to the zeros of the Bessel function. That is, the energy of the Wannier exciton with quantum number $\{n,l\}$ is $E^W_{nl}(k)=E_g-E^b_{ext}+\hbar^2\gamma^2_{nl}/2mR^2$, where E_g is the band gap, E^b_{ext} is the exciton binding energy, and γ_{nl} is the nth zero of the spherical Bessel function $J_l(x)$ of order l, which depends on the magnitude of the dot radius R. Here m is the effective mass of the electron and the hole. The lowest excitation in the dot will be the state with $l=0,n=1$. In writing the expression for $E^W_{nl}(k)$ we are assuming the dot is spherical as a good approximation to the actual shape.

For kd small, the total Hamilton (5) can be written as

$$H=\sum_{\vec{k}}E^W_{tr}(\vec{k})+\sum_k E^F(k)b^\dagger_{\vec{k}}b_{\vec{k}}+\sum_k G(k)(a^\dagger_{\vec{k}}b_{\vec{k}}+a_{\vec{k}}b^\dagger_{\vec{k}}), \tag{6}$$

where $E^W_{tr}(\vec{k})$ is the transfer energy of the Wannier exciton of the semiconductor dot array:

$$E^W_{tr}(\vec{k})=E^W+2\sum_i t(k_i)-d^2\sum_i t(k_i)k_i^2, \tag{7}$$

where $i=\{x,y,z\}$.

Equation (6) describes the system of Wannier excitons and Frenkel excitons, interacting with each other. In addition to the exciton energy in single quantum dots, the energy of the Wannier exciton in the quantum dot array also includes the large transfer energy between the two closest quantum dots in the array.

We notice that, because of confinement, the energy and state of one quantum dot cannot be described by a wave vector. But the energy and state of a transfer exciton in the quantum dot array do have k-vector dependence and we will need to include the dispersion relation for the energy of this transfer exciton. This energy strongly depends on the value of the hopping constant $t(\vec{k})$ and the direction of the polarization vector of the exciton, which we will investigate in the next sections. The presence of the transfer exciton allows us to change the energy region of the resonance and also the optical properties of the hybrid exciton. So in our model the semiconductor quantum dot array embedded in an organic medium can be interpreted as follows. The Wannier excitons in quantum dots interact with each other to form a kind of transfer exciton propagating through the lattice. This transfer exciton in its turn is coupled at resonance with the Frenkel excitons in the organic medium to form a hybrid organic-inorganic exciton state.

In our model we consider the exciton-exciton interaction and the hybridization as the principal effect, so here we omit the potential scattering between the dot array and the medium and leave it for future reseach.

We write the hybrid excited state as follows

$$|\Psi(k)\rangle = u_l(k) f^F(0)\Psi_l^W(k) + v_{l'}(k) f^W(0)|\Psi_{l'}^F(k)\rangle, \quad (8)$$

where $\Psi^W(k)$ and $\Psi^F(k)$ are excited states and $f^W(0), f^F(0)$ are ground states of the Wannier exciton in the dot array and the Frenkel exciton in the medium, respectively. Since we will consider only the lowest excited states of the exciton, from now on we will omit the indices l and l'. The coefficients $u(k)$ and $v(k)$ have the following form:

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

$$v(k) = \frac{E^F(k) - E_{tr}^W(k)}{\{[E^F(k) - E_{tr}^W(k)]^2 + G^2(k)\}^{1/2}}. \quad (9)$$

Thus in terms of hybrid operators $\alpha_{\vec{k}}, \alpha_{\vec{k}}^\dagger$, the Hamiltonian in Eq. (6) can be written as

$$H' = \sum_k E(k)\alpha_{\vec{k}}^\dagger \alpha_{\vec{k}} \quad (10)$$

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

$$E(\vec{k}) = (1/2)[E^F(\vec{k}) + E_{tr}^W(\vec{k})] \pm 1/2\{[E^F(\vec{k}) - E_{tr}^W(\vec{k})]^2 + 4G^2(\vec{k})\}^{1/2}. \quad (11)$$

Because of the weak dependence of the Frenkel exciton energy upon the k vector, the Frenkel exciton energy may be taken as independent of the wave vector k, $E^F(k) = E^F(0)$. We can see from Eq. (11) that the existence of the array of dots, which results in the appearance of the transfer exciton energy $E_{tr}^W(\vec{k})$, enhances the coupling between these two kinds of exciton at resonance, i.e., the gap between two hybrid exciton branches becomes large. The coupling will be strong when $E^F(\vec{k})$ and $E_{tr}^W(\vec{k})$ are in resonance. So the resonance coupling behavior depends strongly on the hopping coefficient $t(\vec{k})$ and the hybridization coefficient $G(\vec{k})$, which we will investigate in the next sections.

III. HOPPING COEFFICIENT $t(\vec{k})$

The hopping coefficient $t(\vec{k})$ is in fact the transfer energy between the two closest dots in the dot array and plays an important role in the process occurring when a dot array is placed in an organic medium. The transfer energy is estimated as the electrostatic interaction between excitons in dots. Because of the existence of ‘‘confined’’ excitons, each dot has its transition dipole moment, which will interact with the corresponding moment of another dot when the distance between dots is comparable to the dot radius. As mentioned above, for one isolated quantum dot the oscillator strength is concentrated mainly in the lowest excited states and so we assume that only the transition dipole moments to the lowest excited states are involved in the interaction for an array. This multipolar interaction is intrinsically strongly short range and dependent upon the distance between dots, so we use here the nearest neighbor approximation.

Now consider the electrostatic interaction between excitons in two spherical quantum dots:

$$t(\vec{k}) = \langle W_i(\vec{k})|H_{d\text{-}d}|W_j(\vec{k})\rangle, \quad (12)$$

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

$$|W_i(\vec{k})\rangle = \frac{1}{V_0}\int \phi(\vec{r}_i^{\,eh})\varphi(\vec{r}_i)e^{i\vec{k}(\vec{r}_{ei}+\vec{r}_{hi})/2} \times \Psi_e^\dagger(\vec{r}_{ei})\Psi_h^\dagger(\vec{r}_{hi})d\vec{r}_{ei}d\vec{r}_{hi}|0\rangle, \quad (13)$$

where $\phi(\vec{r}_i^{\,eh})$ is the relative electron-hole motion function, $\vec{r}_i^{\,eh} = \vec{r}_{ei} - \vec{r}_{hi}$, $\varphi(\vec{r})$ is the exciton envelope function, and $\vec{r}_{ei}(\vec{r}_{hi})$, $\psi_e^\dagger(\vec{r}_{ei})[\psi_h^\dagger(\vec{r}_{hi})]$ are the coordinates and creation operators of the electron (hole) in the dot, respectively. V_0 is the spherical dot's volume.

The envelope function for the exciton inside a spherical dot depends on the radius of the dot and has the form[1,4]

$$\varphi(\vec{r}_i)_{nlm} = Y_{lm}(\theta_i, \phi_i)\frac{2^{1/2}}{R^{3/2}}\frac{J_{nl}(\gamma_{nl}r_i/R)}{J_{l+1}(\gamma_{nl})}, \quad (14)$$

where r_{eh} is the electron-hole relative coordinate and r is the center of mass coordinate of the exciton. $H_{d\text{-}d}$ is the interaction Hamiltonian between two dipole moments in these two dots. In our case the distance between two dots is larger than the dot radius, $d > R$, so the interaction can be considered approximately as the ordinary dipole-dipole interaction. But when the dot spacing is of the same order as the dot radius, we have to consider the multipolar interaction. Neglecting the higher orders, we obtain for the hopping coefficient between two spherical quantum dots

$$t(k) = \phi_{ns}(0)^2 f_{ns}\{(\vec{\mu}_1^w \cdot \vec{\mu}_2^w) - 3(\vec{\mu}_1^w \cdot \hat{n}_{12})(\vec{\mu}_2^w \cdot \hat{n}_{12})\}. \quad (15)$$

$\phi_{nl}(r)$ is the quantum dot exciton envelope function, $\vec{\mu}_{1,2}^w$ are transition dipole moments to the excited state $(n, l=0, m=0)$ for the quantum dot spheres 1 and 2, respectively, and $\hat{n}_{12}$ 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 the integral

$$f_{ns} = \int \varphi(\vec{r})_{ns} d^3r \int \frac{\varphi(\vec{r}\,')_{ns}}{|d + r + r'|^3} d^3r'. \quad (16)$$

The integrals are taken over the volume of the two dots.

For exciton polarization parallel to the direction connecting two dot centers,

$$t_\parallel = -\phi_{ns}(0)^2 f_{ns} 2(\mu^w)^2. \quad (17)$$

For exciton polarization perpendicular to the direction connecting two dot centers the hopping coefficient is equal to

$$t_\perp = \phi_{ns}(0)^2 f_{ns}(\mu^w)^2. \quad (18)$$

The hopping constant depends strongly on the polarization direction of the excitons. Also, the transfer energy (7) depends on 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.

For the transition dipole moment to the excited state $(n,l=0,m=0)$ of the spherical quantum dot we have

$$\mu^{w}=\frac{(2)^{3/2}}{n\pi}\phi_{1s}(0)p_{cv}R^{3/2}. \tag{19}$$

Hence, from Eqs. (15)–(19), the hopping coefficient t depends on R/d, so we can change the dot separation d with respect to dot radius R in order to determine the optimum t.

IV. HYBRIDIZATION PARAMETER $G(k)$

The organic medium can also be described as a lattice, with organic molecules occupying every site. The Frenkel exciton can move between the sites. Because of the small ''lattice constant'' here, 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 of order 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

$$G(k)=\langle F,k|H_{int}|W,k\rangle, \tag{20}$$

where the interaction Hamiltonian is taken similarly to Refs. 1, 3, and 4 as

$$H_{int}=-\sum_{n} E(r_n)P(r_n). \tag{21}$$

Here $E(r_n)$ is the operator of the electric field created at point r_n in the organic medium by the excitons in quantum dots and $P(r_n)$ is the transition polarization operator of the Frenkel exciton at molecular site r_n of the organic medium.

If the dielectric constant of the semiconductor dots is ϵ_1 and of the organic medium is ϵ_2, the field at some point r_n outside the dot created by the exciton in the dot located at r is

$$E(r-r_n)=\frac{3\epsilon_1}{2\epsilon_2+\epsilon_1}\frac{3\hat{n}\cos\theta-\hat{\mu}}{(r-r_n)^3}\mu^{D}[\hat{a}_{nl}^{\dagger}(r)+\hat{a}_{nl}(r)]. \tag{22}$$

$P(r_n)$ is the polarization operator of the Frenkel exciton at molecular site r_n,

$$P(r_n)=\vec{\mu}^{F}(\hat{b}_n^{\dagger}+\hat{b}_n). \tag{23}$$

$\vec{\mu}^{F}$ is the optical transition dipole moment of the organic molecule. The Frenkel exciton wave function is written in the form

$$F(k)=\frac{1}{N_F^{1/2}}\sum_{n} e^{ikr_n}\chi_s^{f}(r_n)b_n^{\dagger}|0\rangle. \tag{24}$$

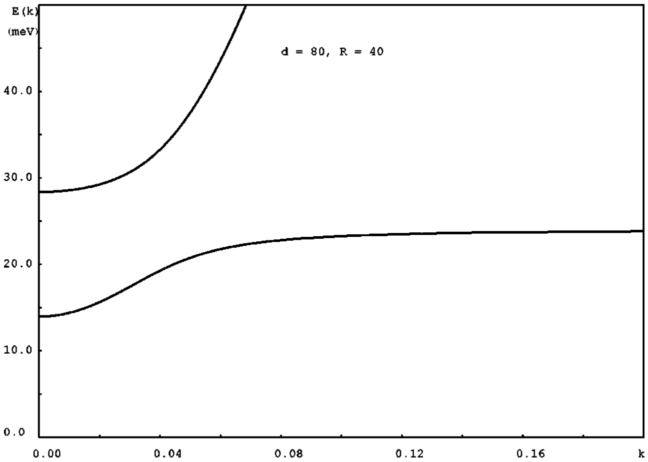

FIG. 1. Hybrid exciton dispersion calculated for ZnSe dots placed in an organic material. The dispersion curve is plotted for dot radius $R=50$ Å and dot spacing $d=200$ Å.

$\varphi_s(r_n)$ is the excited state of the molecule at site r_n. Putting Eqs. (21)–(24) into Eq. (20), we have the expression for the hybridization coefficient of the semiconductor quantum dot and the organic medium:

$$G(k)=\frac{3\epsilon_1}{2\epsilon_2+\epsilon_1}\frac{\pi}{2}\frac{\sin\theta}{(N^{F})^{1/2}}\mu^{F}\mu^{w}\phi_{ns}(0)D_{ns}(k), \tag{25}$$

where θ is the angle between the exciton transition dipole moments of the quantum dot and the organic molecule, and

$$D_{ns}(k)=\int_{medium}e^{ikr'}\chi_{ns}^{f}(r')d^3r'\int_{dot}\frac{\varphi_{nlm}(r)}{r|r-r'|^3}d^3r. \tag{26}$$

Reading from right to left, the first integral is taken over the dot and the second one is taken over the volume of the whole medium.

For illustration a numerical calculation was done for some samples. Figure 1 shows the hybrid exciton dispersion curves plotted for ZnSe dots embedded in a standard organic material. The parameters were taken as $E^{F}(0)-E^{W}(0)=5$ meV, $a_B=30$ Å, $\mu^{F}=5$ D, $N=5$. In Fig. 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.

V. NONLINEAR OPTICAL RESPONSE

As already noted in Ref. 11 and can be seen from Eq. (7), the Wannier transfer exciton has a rather small translational mass, which depends on the hopping constant and the number of dots. This small translational mass is one reason for a large coherence length, which is related to the homogeneous linewidth of the excitonic transition. In turn, this leads to a large figure of merit of the exciton, and, associated with it, large exciton resonance oscillator strength and nonlinearity.[11]

In the region of strong mixing, the oscillator strength of the hybrid exciton is determined as

$$f(\vec{k})=|u(\vec{k})|^2f^{F}+|v(\vec{k})|^2f^{W}+2|u(\vec{k})v(\vec{k})|(f^{F})^{1/2}(f^{W})^{1/2}. \tag{27}$$

Both components, the transfer Wannier and the Frenkel excitons, give contributions to the oscillator strength of the hybrid exciton. Due to the confinement effect of the exciton in one single dot as well as the transfer exciton coupling between dots in the array, the Wannier transfer exciton oscillator strength may achieve a value comparable to that of the Frenkel exciton, which is very big due to the small exciton radius and small molecular lattice constant. So placing many semiconductor dots in an organic medium leads to a large oscillator strength of the hybrid exciton. At resonance, the oscillator strength of the hybrid state is determined by its Frenkel exciton component.

In the presence of an electric field, the third-order susceptibility can be calculated using standard pertubation theory.[12–15] We introduce the decay constant γ and note that the two-body interaction here is considered to arise from the interaction of excitons in different dots. Considering only the resonance case and neglecting contributions from the other nonresonant levels, we have approximately the result for the lowest optical nonlinearity of the hybrid excitons:

$$\chi^{(3)}(w) \approx \frac{\mu_F^4}{V} \frac{(2\sqrt{2})^4}{\pi^2} \left(\frac{V_{medium}}{V_{cell}} \right)^2 l_c^3 \left(\frac{R}{d} \right)^6 \phi_{1s}^4(0) \times \left(\frac{1}{(w-\tilde{w}+i\gamma_\perp)^2 (w-\tilde{w}-i\gamma_\parallel)} \right). \tag{28}$$

The exciton coherence length l_c is given as[8]

$$l_c = \left(\frac{3\pi^2}{2^{1/2}} \right)^{1/3} \frac{\hbar}{(M\hbar\Gamma_h)^{1/2}}. \tag{29}$$

M is the exciton translational mass, which is inversely proportional to the transfer energy (7), which we can control by changing the system parameters, namely, dot radius and dot spacing. $\hbar\tilde{w}$ is the lowest excitation energy of the hybrid exciton. Γ_h is the linewidth of the exciton and $\gamma_\perp$ and $\gamma_\parallel$ are the transverse and longitudinal relaxation constants of the excitonic transition, respectively. V is the volume of the whole system, V_{medium} is the volume of the organic host, and V_{cell} is the volume of one cell in the organic lattice. Notice here that we consider the case where the sample size is smaller than the coherence length, so the size dependence appears as in Eq. (29).

The value of $\chi^{(3)}(w)$ in Eq. (28) 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.

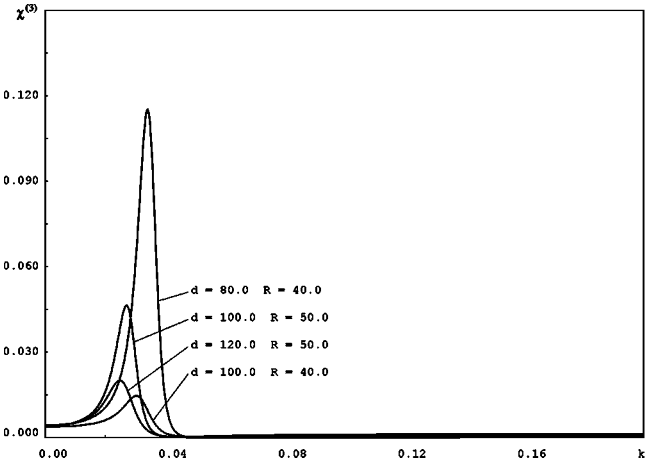

FIG. 2. Third-order nonlinear susceptibility for the hybrid exciton state of ZnSe dots in organic material. We plot the susceptibility versus wave vector. Note that there is a very significant enhancement of $\chi^{(3)}$. Plots are for different dot radius *R* and separation *d*.

Here we present some numerical results for ZnSe dots. In Fig. 2 the third-order nonlinear susceptibility of a ZnSe quantum dot lattice embedded in an organic material is plotted for several different dot radii and dot spacings. We use here the following typical parameters of organic and semiconductor materials: $v^F = 100$ Å, $a_{org} = 5$ Å, $\mu^F = 5$ D, $a_{1B} = 30$ Å, $E^F(0) - E^W(0) = 5$ meV. We see that at resonance, e.g., where the hybridization is strongest, we have a very high peak of nonlinear susceptibility with an enhancement of about five orders of magnitude in comparison with that of the Wannier exciton. The nonlinear coefficient is larger for smaller dots and closer spacing between them. Also, we expect that disorder in the semiconductor dot array will decrease the enhancement effect, but this has not yet been calculated.

VI. SUMMARY

In summary, we have presented here a model for creating systems that offer a strong resonance coupling of Frenkel and Wannier excitons to obtain an hybrid exciton state with the special properties of both kinds of exciton, i.e., having large exciton radius as well as large oscillator strength. In addition, we can control the expected resonance parameters by changing the number of dots, their radius, the distance between them, and the dot radius and dot separation relation. We are now investigating the system with randomness—i.e., a disordered distribution of dots, which is very interesting and important.

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