Nonlinear Optical Response of Hybrid Exciton State in Quantum Dot- Dendrite Systems

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Abstract. A “real space” Green’s function method and a diagrammatic technique are used to study the optical response of the semiconductor-organic hybrid exciton in quantum dot-dendrimer system. The energy of the hybrid exciton and the linear and non-linear susceptibilities have been calculated for a sample of quantum dot-dendron ligand. Enhanced non-linearity is obtained, which is controllable by the number of generations, the size and structure of the QD-dendrimer systems.

1. Introduction
Dendrimers, a group of nanosized, highly ordered and perfectly hyperbranched three-dimensional macromolecules with controlled structure, attracted remarkable interest in recent years. The dendrimer components such as a core, repeating branches (called generations) attached to the core, and monomer unit groups attached to those branches at the end of each generation, determine the size, shape and of course, physical and optical properties of the dendrimers.

Recent studies reported the preparation of systems of semiconductor quantum dots and organic dendrimer [3]. Semiconductor quantum dots have very strong quantum confinement effects, their electronic energy levels are discrete, their electronic states are widely separate and their optical properties and optical processes strongly depend on the dot size [4-5]. Since the optical properties and the emission regions can be controlled by the size of the quantum dots it is important to use the dot as a photoactive element at the center of the dendrimer. In these kinds of combinations, the optical processes in the quantum dot-dendrimer systems can be tuned by the dot size as well as the structure of the dendrimer [6-7].

In the quantum dot-dendrimer system, the Wannier exciton in the dot interacts with the Frenkel exciton in the dendrimer through dipole-dipole interaction to form a hybrid excitation [8]. As previously proposed systems such as the neighboring structure of organic and semiconductor quantum wells [9], neighboring organic and semiconductor quantum wires [10], a single dot coated by an organic layer [11], and a lattice of semiconductor dot embedded in an organic medium [12], this hybrid exciton of the dot-dendrimer structure has both the Wannier-Mott-like properties (large Bohr radius, weak oscillator strength) and Frenkel-like (small exciton radius, strongly localized, strong oscillator strength. Due to their complicated structures, it is very difficult to calculate electronic structures of dendrimer systems. In this paper we will use the real pace Green’s function approach and the diagram technique firstly proposed in [13-14] and developed in our previous paper [8] to study the non-linearity of the hybrid exciton. This method allows us to solve analytically for complicated systems with any generations.
2. The Quantum Dot-Dendrimer System

The model consists of a quantum dot as a spherical core at the center. The dot is attached to two dendrimeric branches, each of which consists of linked tertiary amine groups. The unit at the end of each branch (branching point) in its turn is attached to two other protein branches, and so on (Fig. 1). We assume only nearest neighbor interaction so the coupling between the quantum dot and the attached protein branches, between molecules in the same branches, as well as between the molecule at the branching point and the protein chain attached to it will be counted, and the coupling between molecules of different branches will be neglected. Nature of the coupling is dipole-dipole interaction between the excitons (Wannier or Frenkel) in the quantum dot and organic molecules. The Hamiltonian of the system in the tight-binding approximation has the form:

\[ H = \sum_{i=1}^{N} \mathcal{E}_i a_i^+ a_i + \sum_{i,j} V_{ij} a_i^+ a_j \]  

(1)

\[ a_i^+, a_i \] are exciton creation and annihilation operators, \( \mathcal{E}_i \) is the exciton energy at each site. When a quantum dot is allocated at a site, the energy will be the energy of the exciton confined in the dot [8] and at molecular sites it will be the Frenkel exciton energy. \( V_{ij} \), where \( i,j \) are the sites at the branching points, is the effective interaction integral between excitons of different dendrimer generations. Since each dendrimer generation consists of many linked molecules, the interaction between molecules in the same chain causes the effective interaction between dendrimer generations (Fig. 1). The effective interaction \( V_{WF} \) and \( V_{FF} \) of the excitons (Wannier-Mott-Frenkel and Frenkel-Frenkel, respectively) in neighboring dendrimer branches has been calculated in the previous paper [8]. The double-time Green's functions are written as

\[ G_{ij} = \frac{2\pi}{\hbar} \langle\langle a_i(t), a_j^+(0) \rangle\rangle = -i \frac{2\pi}{\hbar} \Theta(t) \langle [a_i(t), a_j^+(0)] \rangle \]  

(2)

where \( [\cdot, \cdot] \) is a commutator, \( a(t) \) is the Heisenberg representation of the operator \( a \), \( \Theta(t) \) is Heaviside function, \( \langle\langle \cdot \rangle\rangle \) is the thermal average over a grand canonical ensemble. Since the system consists of both Wannier and Frenkel excitons, the Green functions we consider here are the Green function of the hybridized state.

After transferring the time Green’s functions to the Green’s functions of the energy variable by the Fourier transformation, the Schwinger-Dyson equation for the Green’s functions of the Hamiltonian (1) can be solved using the “electron transfer graph” method developed by Malinsky.
and Magarshak [13-14]. As described in detail in [8], in this diagram technique every site of the system has been assigned to a graph vertex. A path is a sequence of graph edges with successive edges originating at the point where the previous one ends, and a cycle is a path with the last edge ending at the point where the first one originates. Diagonal terms $E - E_i$ of the Hamiltonian corresponds to a loop attached to the vertex $i$, the value of which equals $W_{ii} = (E - E_i)$. A non-diagonal 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 $V_{jk}$. The value $O$ of the cycle is defined as the product of the value of all edges in the cycle, with the sign being negative except for the loop for any cycle with length more than 1 (a length is the number of edges in the path with $P_{ij} = 1$). The cyclic term is a set of cycles which have no common vertex and pass through every vertex. The value of 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 the cyclic terms.

The Green’s function $G_{ij}$ is equal to

$$G_{ij} = \frac{\Theta_{i,j-1} P_{ij} \Theta_{j+1,n}}{\sum O^{(k)}}$$

where, as said above, $P_{ij}$ is the product of the edges along the path from vertex $i$ to vertex $j$; $\Theta = \sum O^{(k)} (i, j)$ is the cyclic value of the graph and $O_{ij}^{(k)}$ is the cyclic term.

One strong point of this diagrammatic technique which make it applicable to complicated dendrimeric system is the sidegroup graph [8,13-14]. As described in detail in [8], in this diagram technique every site of the system has been assigned to a graph vertex. A path is a sequence of graph edges with successive edges originating at the point where the previous one ends, and a cycle is a path with the last edge ending at the point where the first one originates. Diagonal terms $E - E_i$ of the Hamiltonian corresponds to a loop attached to the vertex $i$, the value of which equals $W_{ii} = (E - E_i)$. A non-diagonal 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 $V_{jk}$. The value $O$ of the cycle is defined as the product of the value of all edges in the cycle, with the sign being negative except for the loop for any cycle with length more than 1 (a length is the number of edges in the path with $P_{ij} = 1$). The cyclic term is a set of cycles which have no common vertex and pass through every vertex. The value of 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 the cyclic terms.

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where, as said above, $P_{ij}$ is the product of the edges along the path from vertex $i$ to vertex $j$; $\Theta = \sum O^{(k)} (i, j)$ is the cyclic value of the graph and $O_{ij}^{(k)}$ is the cyclic term.

3. The non-linear susceptibilities

Using the microscopic framework [15], 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 functions obtained above. The calculation of optical response leads to the solution of the coupled non-linear equations for variables $<a_i>$, $<a_i a_j>$, $<a_i a_j a_k>$, which under the local factorization approximation (LFA) [15] can all be represented by products of one-exciton Green functions. Then first order susceptibility has the form

$$\alpha(E) = \mu_n \mu_m [G_{nm}(E) + G_{nm}(E)]$$

and the third order susceptibility:

$$\gamma^{(3)}(-\omega_s, \omega_1, \omega_2, \omega_3) = -\frac{1}{2 \times 3} \sum_p \sum_{m_1 m_2 m_3} \gamma_{nm_1 m_2 m_3}(-\omega_s, \omega_1, \omega_2, \omega_3)$$

where

$$\gamma_{nm_1 m_2 m_3}(-\omega_s, \omega_1, \omega_2, \omega_3) = \frac{1}{6} \sum_p \sum_{n', n''} \mu_n^{*} \mu_{m_1}^{*} \mu_{m_2}^{*} \mu_{m_3}^{*} \times$$

$$\left[ G_{nm'}(-\omega_s) G_{n'm_3}^{*}(-\omega_3) G_{n''m_2}^{*}(-\omega_2) G_{n''m_1}^{*}(-\omega_1) \Gamma_{n'n''}^{*}(\omega_1 + \omega_2) \right]$$

$$+ \left[ G_{nm'}^{*}(-\omega_s) G_{n'm_3}^{*}(-\omega_3) G_{n''m_2}^{*}(-\omega_2) G_{n''m_1}^{*}(-\omega_1) \Gamma_{n'n''}^{*}(-\omega_1 - \omega_2) \right]$$
Here $\Gamma_{n,n'}(\omega)$ is a two-exciton scattering matrix:

$$\Gamma_{n,n'}^{-1}(\omega) = \frac{1}{2} \int \frac{d\omega'}{2\pi i} G_{n,n'}(\omega') G_{n',n}(\omega - \omega')$$

(7)

Recently several series of semiconductor nanocrystal-organic dendron ligands with perfect symmetry with the dot at the center, have been designed and synthesized [5].

As an example, for the two generation quantum dot-dendron, we can consider the dendron as linear chain of one generation with sidegroup attached to each of the terminal molecules. Continuing this process of sidegroup graph we can go farther to any generation by changing the value of the two attached branches of ($n$ branches, in going from the loop values [8]. Since every branching point of the dendron ligand is attached to two other molecules shows the increase of the third order susceptibilities about 400 times in comparison with the organic material. We also notice that the shorter the link, the larger the interaction coefficients, the larger the nonlinearities. By changing the size and parameter of the dendrimer, the region of resonance could be changed so one could also tune the laser frequency $\omega$.

At resonance the susceptibilities depend strongly on the effective interactions coefficients $V_{FF}$ and $V_{WF}$, which depend on the parameters of the system such as the size of each chain, the number of generation... so the system can be tuned by changing those parameters.

The analytical solutions can be obtained for dendrimer of any generation by side group method. The calculation for a standard dendrimeric ligand of four generations with a quantum CdS dot of radius 40 Å at the center and the distance of 80 Å between the links of different molecules shows the increase of the third order susceptibilities about 400 times in comparison with the organic material. We also notice that the shorter the link, the larger the interaction coefficients, the larger the nonlinearities. By changing the size and parameter of the dendrimer, the region of resonance could be changed so one could also tune the laser frequency $\omega$.

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