

## Fermion Excited States in One-Dimensional Molecular Aggregates with Site Disorder: Nonlinear Optical Response

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It is well known that Frenkel excitons are not true bosons or fermions. I show that the fundamental electronic excitations in a linear (noncyclic) one-dimensional molecular aggregate consisting of  $N$  coupled two-level absorbers with site disorder are in fact fermions, allowing one to calculate *all* of the  $2^N$  excited-state eigenfunctions and eigenenergies with a single  $N \times N$  matrix diagonalization. As an application, the third-order nonlinear absorption coefficient for a molecular aggregate with site disorder is calculated.

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One-dimensional Frenkel excitons on a site disordered lattice play a major role in the optical response of  $J$  aggregates [1], anisotropic molecular crystals such as 1,4 dibromonaphthalene [2] and polysilanes [3]. Much theoretical attention has been devoted to the effect of disorder on the linear optical response [4] where Frenkel one-excitons (one molecule on average is excited out of the total  $N$ ) can be accurately modeled as bosons. However, higher excited states with multiple electronic excitations (two-excitons, three-excitons, etc.) are major contributors to the nonlinear optical response which, consequently, depends strongly on the nonbosonic nature of Frenkel excitons—the Pauli exclusion principle forbids double occupation per site and as a result an  $n$ -exciton wave function is not decomposable into the product of  $N$  one-exciton wave functions. Recent investigations into the nonbosonic nature of elementary excitations in semiconductor quantum dots [5] and molecular aggregates [6,7] have led to some rather remarkable predictions regarding the size dependence of the nonlinear optical response; for small aggregates the third-order response has been shown to scale as  $N^2$  [5,6], but eventually crosses over to a linear dependence when the aggregate dimensions exceed an optical wavelength [6]. In this Letter, it is shown that the electronic eigenstates in a linear one-dimensional molecular aggregate with site disorder are, in fact, fermions, by employing a canonical transformation originally developed by Lieb, Schultz, and Mattis [8] in their analysis of the one-dimensional  $XY$  model of antiferromagnetically coupled spins. This allows one to immediately write down all  $2^N$  excited-state wave functions and energies for a system of  $N$  coupled two-level systems with site disorder, preparing the way for future nonperturbative investigations into the nonlinear response of confined excitons.

The Hamiltonian for a one-dimensional array of  $N$  coupled two-level molecules with *free* ends and site disorder is given by

$$H = \sum_{n=1}^N \hbar \omega_n b_n^\dagger b_n + \hbar V \sum_{n=1}^{N-1} \{b_n^\dagger b_{n+1} + b_{n+1}^\dagger b_n\}. \quad (1)$$

Here,  $\omega_n$  is the optical two-level transition frequency of the  $n$ th molecule and  $V$  is the near-neighbor dipole-dipole coupling ( $4V$  is the exciton bandwidth). The operators  $b_n^\dagger$  ( $b_n$ ) are Pauli raising (lowering) operators which satisfy the anticommutation relations

$$[b_n^\dagger, b_m]_+ = \delta_{mn} + (1 - \delta_{mn}) 2b_n^\dagger b_m, \quad (2a)$$

$$[b_n^\dagger, b_m^\dagger]_+ = (1 - \delta_{mn}) 2b_n^\dagger b_m^\dagger. \quad (2b)$$

When the excitations are limited to a single site they are fermions. However, when they are on different sites they obey Bose commutation relations. By utilizing the fermion transformation of Lieb, Schultz, and Mattis [8], we can rewrite  $H$  in terms of fermion operators. Defining the Fermi operators  $c_n$  and  $c_n^\dagger$  as

$$c_n = \exp \left[ \pi i \sum_{j=1}^{n-1} b_j^\dagger b_j \right] b_n, \quad (3a)$$

$$c_n^\dagger + b_n^\dagger \exp \left[ -\pi i \sum_{j=1}^{n-1} b_j^\dagger b_j \right]. \quad (3b)$$

$H$  can be rewritten in terms of the  $c$  operators. The result is identical to Eq. (1) but with the  $b$  operators replaced by the  $c$  operators. This is because  $c_n^\dagger c_{n+1} = b_n^\dagger b_{n+1}$  and  $c_n^\dagger c_n = b_n^\dagger b_n$  which can easily be verified by use of Eq. (3). Equation (1) is now in a quadratic form of Fermi operators and can be diagonalized by the canonical transformation  $\eta_\sigma^\dagger = \sum_{n=1}^N \phi_{\sigma n} c_n^\dagger$ , where  $\eta_\sigma^\dagger$  is also a Fermi operator, to the form

$$H = \sum_{\sigma=1}^N \hbar \Omega_\sigma \eta_\sigma^\dagger \eta_\sigma. \quad (4)$$

The coefficients  $\phi_{\sigma n}$  and eigenenergies  $\hbar \Omega_\sigma$  can be found from  $[\eta_\sigma^\dagger, H] = \hbar \Omega_\sigma \eta_\sigma^\dagger$ , which is equivalent to

$$\mathbb{A} \phi_\sigma = \Omega_\sigma \phi_\sigma, \quad (5)$$

where the  $N \times N$  matrix  $\mathbb{A}$  has elements  $A_{mn} = \omega_m \delta_{mn} + V(\delta_{m, n+1} + \delta_{m, n-1})$  and  $\phi_\sigma$  is the  $\sigma$ th normalized eigenvector with the  $n$ th element equal to  $\phi_{\sigma n}$ . Since  $\eta_\sigma^\dagger$  is a Fermi operator, the occupation number basis set contains

all of the  $2^N$  eigenfunctions of the system which are easily written down in terms of the Slater determinants. Thus the single exciton manifold is spanned by the eigenbasis  $\eta_\sigma^\dagger|0\rangle$ , which is equal to  $\eta_\sigma^\dagger|0\rangle = \sum_{n=1}^N \phi_{\sigma n}|n\rangle$  with energy  $\hbar\Omega_\sigma$  ( $|0\rangle$  is the vacuum state with no excitations and  $|n\rangle$  is the state with site  $n$  excited). In general, the eigenstates with  $m$  excitations result from the application of  $m$  creation operators on the ground state:

$$\eta_{\sigma_1}^\dagger \eta_{\sigma_2}^\dagger \cdots \eta_{\sigma_m}^\dagger |0\rangle = \sum_{n_1 > n_2 > \cdots > n_m} \det[\phi_{\sigma_1 n_1}, \phi_{\sigma_2 n_2}, \dots, \phi_{\sigma_m n_m}] |n_1 n_2 \cdots n_m\rangle. \quad (6)$$

Because the wave function is zero unless all the  $\eta_\sigma^\dagger$  are different and is independent of the order (up to a sign), the total number of eigenstates in the  $m$ th manifold is  $N!/m!(N-m)!$ . The eigenenergy of this state is simply given by

$$E_{\sigma_1, \sigma_2, \dots, \sigma_m} = \hbar \sum_{n=1}^m \Omega_{\sigma_n}. \quad (7)$$

Thus by diagonalizing a single  $N \times N$  matrix all  $2^N$  eigenfunctions and eigenenergies of a linear array of  $N$  coupled two-level systems with site disorder are immediately obtained.

In order to calculate the nonlinear optical response, the transition dipole matrix elements between the eigenstates are also needed. The transition dipole operator is given by  $\hat{\mu} \equiv \mu \sum_{n=1}^N e^{ik \cdot r_n} b_n^\dagger + \text{H.c.}$ , where  $\mu$  is the transition dipole moment between the ground and excited states of the two-level system. The only nonzero matrix elements of the transition dipole operator are those involving states which differ by a single excitation. Using Eq. (6) one obtains

$$\langle 0 | \eta_{\sigma_1} \cdots \eta_{\sigma_m} | \hat{\mu} | \eta_{\sigma'_1}^\dagger \cdots \eta_{\sigma'_{m-1}}^\dagger | 0 \rangle = \mu \sum_{i=1}^m \exp[ik \cdot r_{n_i}] \sum_{n_1 > n_2 > \cdots > n_m} \det[\phi_{\sigma'_1 n_1}^*, \phi_{\sigma'_2 n_2}^*, \dots, \phi_{\sigma'_m n_m}^*] \times \det[\phi_{\sigma'_1 n_1}, \dots, \phi_{\sigma'_{i-1} n_{i-1}}, \phi_{\sigma'_i n_i}, \dots, \phi_{\sigma'_{m-1} n_{m-1}}]. \quad (8)$$

Equations (6)–(8) contain all the information necessary to calculate the nonlinear optical response nonperturbatively for any degree of excitation. The major difficulty is evaluating the sums in Eq. (8).

In order to appreciate the simplification afforded by the above formalism consider, for example, the third-order hyperpolarizability for an aggregate of  $N$  molecules with site disorder. The third-order response requires only knowledge of the two-exciton eigenstates and energies [6]; since there are  $N(N-1)/2$  two-exciton states, a brute force numerical evaluation requires the diagonalization of an  $N(N-1)/2 \times N(N-1)/2$  matrix. However, by performing the canonical transformation to fermion

operators all of the one- and two-exciton eigenstates and energies (in fact, all of the  $2^N$  eigenstates and energies) are derived in a *single*  $N \times N$  matrix diagonalization requiring much less computer memory. One must still evaluate lengthy sums for the transition dipole moments, but for the third-order response Eq. (8) consists of only  $N(N-1)/2$  terms. Once the eigenstates, eigenenergies, and transition dipole moments are evaluated the third-order response can be derived from the sum over states procedure or, in a more compact form, by using reduced equations of motion [5]. For the third-order aggregate hyperpolarizability  $\gamma(-\omega; \omega, \omega, -\omega)$  in the rotating-wave approximation one obtains

$$\gamma(-\omega; \omega, \omega, -\omega) = \frac{1}{4\hbar^3} \left\langle \sum_{\sigma_1, \sigma_2, \sigma_3 > \sigma_4}^N \left\{ \frac{\mu_{\sigma_1}^2 \mu_{\sigma_2}^2}{\Delta\omega_{\sigma_1} + i\gamma_{\sigma_1}/2} - \frac{\mu_{0, \sigma_1} \mu_{\sigma_1, \sigma_3} \mu_{\sigma_3, \sigma_4} \mu_{\sigma_4, \sigma_2} \mu_{\sigma_2, 0}}{\Delta\omega_{\sigma_3} + \Delta\omega_{\sigma_4} + i\Gamma_{\sigma_3 \sigma_4}} \frac{\Delta\omega_{\sigma_2}}{\Delta\omega_{\sigma_2} + i\gamma_{\sigma_2}/2} \right\} \times \frac{1}{\Delta\omega_{\sigma_1} + i\gamma_{\sigma_1}/2} \frac{1}{-\Delta\omega_{\sigma_2} + i\gamma_{\sigma_2}/2} \right\rangle, \quad (9)$$

where  $\Delta\omega_\sigma \equiv \omega - \Omega_\sigma$ ,  $\mu_{0, \sigma} \equiv \langle 0 | \hat{\mu} \eta_\sigma^\dagger | 0 \rangle$ , and  $\mu_{\sigma_1, \sigma_2 \sigma_3} \equiv \langle 0 | \eta_{\sigma_1} \hat{\mu} \eta_{\sigma_2}^\dagger \eta_{\sigma_3}^\dagger | 0 \rangle$ . The quantities  $\gamma_\sigma$  and  $\Gamma_{\sigma\sigma'}$  are the coherence decay rates for the one- and two-exciton states, respectively. Equation (9) is strictly valid when the homogeneous broadening of the one- and two-exciton lines is much less than their separation. As a result, when radiative damping is dominant (superradiance), Eq. (9) is applicable only for small aggregates, where the aggregate length is smaller than an optical wavelength [6]. The damping rates are then simply proportional to the square of the transition dipole moments:  $\gamma_\sigma = (\mu_{0, \sigma}/\mu)^2 \gamma$  and  $\Gamma_{\sigma\sigma'} = \frac{1}{2} \gamma \sum_{\sigma''} (\mu_{\sigma\sigma''} \mu_{\sigma''\sigma'}/\mu)^2$ . These relations are valid for any degree of disorder as long as the aggregate remains

small. In this limit, Eq. (9) generalizes a previous expression [6] by including free-end effects and size disorder. The brackets  $\langle \cdots \rangle$  in Eq. (9) indicate an average over the site transition frequency distribution function. In the calculations below a Gaussian distribution  $P(\omega_n) = \pi^{-1/2} \Delta^{-1} \exp(-(\omega_n - \omega_0)/\Delta)^2$  is assumed, where  $\omega_0$  is the unbroadened transition frequency.

The nonlinear absorption spectrum for a cw laser of frequency  $\omega_L$  is proportional to  $\text{Im}[\gamma(-\omega_L; \omega_L, \omega_L, -\omega_L)]$ . The first term in Eq. (9) is responsible for exciton saturation when  $\omega_L \approx \Omega_{\sigma_1}$  while the second term represents two-photon absorption (TPA) to the two-exciton

states when  $2\omega_L = \Omega_{\sigma_3} + \Omega_{\sigma_4}$ . Equation (9) correctly reduces to the independent monomer result when either  $\Delta\omega_\sigma \gg V$  or  $\Delta \gg V$ .

All of the quantities in Eq. (9) can be derived analytically for the homogeneous aggregate ( $\Delta=0$ ). From Eq. (5), the one- and two-exciton eigenfunctions are the following:

$$\eta_k^\dagger|0\rangle = [2/(N+1)]^{1/2} \sum_{n=1}^N \sin[n\pi k/N+1]|n\rangle, \quad k=1, \dots, N,$$

and

$$\eta_{k_1}^\dagger \eta_{k_2}^\dagger|0\rangle = \frac{2}{N+1} \sum_{n_1 > n_2}^N \{ \sin[\pi n_1 k_1/N+1] \sin[\pi n_2 k_2/N+1] - \sin[\pi n_2 k_1/N+1] \sin[\pi n_1 k_2/N+1] \} |n_1 n_2\rangle,$$

$$k_1, k_2 = 1, \dots, N,$$

respectively, with the eigenenergies  $\Omega_k$  and  $\Omega_{k_1} + \Omega_{k_2}$ , where  $\Omega_k = \omega_0 + 2V \cos(\pi k/N + 1)$ . Here we have used the index  $k$  instead of  $\sigma$  to denote the  $k$ th Frenkel exciton. Evaluation of  $\mu_{0,k}$  from Eq. (8) gives  $\mu_{0,k} = [2/(N+1)]^{1/2} \cot[\pi k/2(N+1)]$  for odd  $k$  and zero for even  $k$ , which shows that the  $k=1$  exciton carries most of the oscillator strength (about 81% for an infinite aggregate).  $\mu_{k,k_1 k_2}$  can also be derived analytically, but the expression is quite lengthy. It is nonzero only if  $k_1 + k_2$  is odd, either of the two following conditions hold: (1)  $k = \pm k_1 \pm k_2$  [modulo  $2(N+1)$ ], in which case  $\mu_{k,k_1 k_2}$  scales like  $O(\sqrt{N}/k_1 + \sqrt{N}/k_2)$  for  $N \gg k_1, k_2$  or (if the first condition is not satisfied) (2)  $k = k_1$  or  $k = k_2$ , in which case  $\mu_{k,k_1 k_2}$  scales like  $O(\sqrt{N}/k_2)$  or  $O(\sqrt{N}/k_1)$ , respectively. In the homogeneous limit saturated excitonic absorption peaks occur at  $\omega_L = \Omega_1, \Omega_3, \dots$  and (negative) TPA peaks at

$$2\omega_L = \Omega_1 + \Omega_2, \Omega_1 + \Omega_4, \dots, \Omega_2 + \Omega_3, \Omega_2 + \Omega_5, \dots$$

Figure 1 shows the most prominent features of the nonlinear absorption spectrum for an aggregate with  $N=40$  and several values of  $\Delta$ , calculated by solving Eq. (5) and using Eq. (9). Several hundred configurations of site disorder  $\{\omega_1, \omega_2, \dots, \omega_N\}$  were used in the average. Figure 1(a) shows the dominant portion of the spectrum centered at  $\Omega_1$ ; the upper curve corresponds to the homogeneous aggregate ( $\Delta=0$ ) while the progressively broader curves corresponding to increasing values of  $\Delta$ . Note the strong  $k=1$  exciton bleaching resonance at  $\omega_L = \Omega_1$  and the much weaker (negative) two-exciton, TPA resonance when  $2\omega_L = \Omega_1 + \Omega_2$ . As the disorder increases, the bleaching line shape generally broadens and shifts to the red, which is also characteristic of the linear absorption spectrum [4]. Note that the linewidth is significantly less than  $2\Delta$  because of motional narrowing [9]. The TPA resonance also broadens but shifts to the blue. Figure 1(b) shows the second most prominent feature of the spectrum, centered at  $\Omega_3$ . Note that the  $k=3$  exciton bleaching line shape is about 100 times weaker than the  $k=1$  line shape, and undergoes an opposite (blue) shift with increasing disorder. Two TPA resonances appear to the red of the bleaching line shape, the first (largest redshift) involves excitation of the two-exciton with  $k_3, k_4 = 2, 3$  and the second involves excitation to

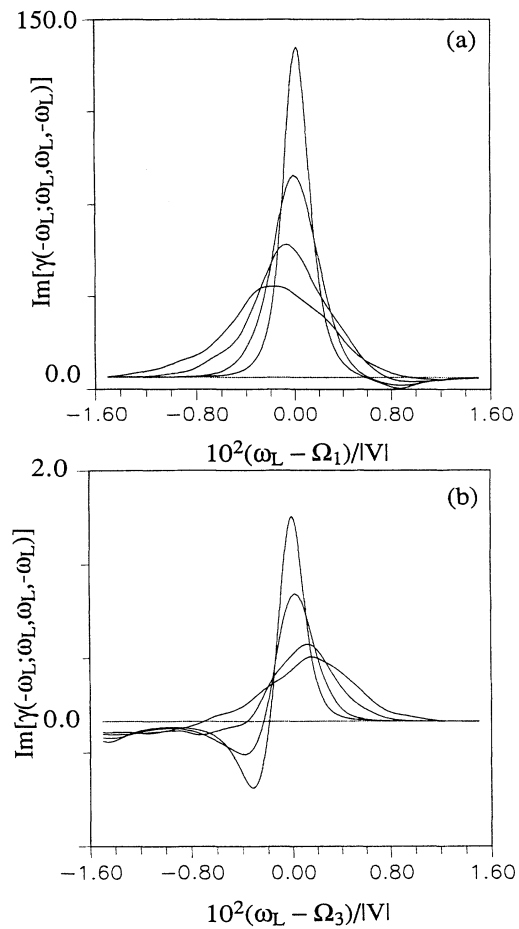


FIG. 1. The nonlinear absorption spectrum (in arbitrary units) for an aggregate with  $N=40$  and  $V < 0$  ( $J$  aggregate) calculated from Eqs. (5) and (9) for several values of  $\Delta$ .  $\Delta=0, 0.01|V|, 0.02|V|, \text{ and } 0.03|V|$  in the order of increasing spectral width. The damping rates used were simply  $\gamma_\sigma = \gamma_0$  and  $\Gamma_{\sigma\sigma'} = 2\gamma_0$ , with  $\gamma_0 = 2 \times 10^{-3}|V|$ . In (a) the spectrum is centered on  $\Omega_1$  and in (b) on  $\Omega_3$ . For  $\Delta=0$  these two portions constitute over 99% of the spectral area. Note that the spectrum is clearly dominated by the  $k=1$  exciton bleaching line shape for the values of  $\Delta$  considered here.

the two-exciton with  $k_3, k_4=1,4$ . Figures 1(a) and 1(b) represent the dominant contributions to the entire nonlinear absorption spectrum for the values of  $\Delta$  considered; as  $\Delta$  approaches values much greater than the exciton bandwidth, the monomer spectrum, a Gaussian line shape centered at  $\omega_0$  with standard deviation  $\Delta/\sqrt{2}$ , will result.

The formalism outlined here is quite general and will prove useful in studying the contributions of three and higher exciton states to the nonlinear optical response. Such states are necessary in understanding saturated absorption in the strong-field regime. Experiments of this type have recently been performed on  $J$  aggregates [10]. More fundamental questions regarding the nature of the disorder-induced coherence length and the validity of various factorization schemes (such as the local-field approximation) in strong fields can also be directly addressed.

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