Geometrical Effects on One-Dimensional Excitons

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The geometrical structures of linear chain systems are shown to be sensitively reflected on the optical spectrum of Frenkel and Wannier excitons. The effects of shape of the chain on the Frenkel exciton absorption spectrum are represented by the geometrical factor describing the global chain structure and the line broadening due to the structure fluctuations. The corner with the stronger curvature induces the stronger attractive potential on the Wannier exciton so that the bound states are formed.

While polydiolefin crystals such as as-polymerized polyDSP (2,5-distyrylpyrazine) are well known as rigid linear chains, many conjugated polymers and J aggregates of dyes show some globally deformed structures deviating from straight lines, both in solutions and in solids. We are interested in the problem of how much the responses of these systems to external forces are influenced by the topological structures of these systems. In this paper, we will investigate the geometrical effects on optical spectra of Frenkel and Wannier excitons in the chainlike systems.

First we investigate the absorption spectrum of Frenkel excitons. To see the modification of the selection rules, we use the fact that a transition matrix element is generically decomposed into some products of two factors: a *geometrical factor* and the matrix element of a *local operator*. This decomposition will have broad applications to general problems about geometrical effects, and the following derivation of the absorption spectra will offer a basic idea as well as a good example of its applications. We consider a system composed of N molecules in a one-dimensional chain. The Hamiltonian of the Frenkel exciton is given in terms of spin operators [1]:

$$H_s = \sum_j \hbar\omega_0 \hat{s}_j^z + \sum_{\langle i,j \rangle} \hbar\Omega_{i,j}(\hat{s}_i^+ \hat{s}_j^- + \hat{s}_j^+ \hat{s}_i^-), \tag{1a}$$

$$\Omega_{i,j} \equiv \frac{\mu^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|^3} [(\boldsymbol{\varepsilon}_i \cdot \boldsymbol{\varepsilon}_j - 3(\boldsymbol{\varepsilon}_i \cdot \mathbf{r}_{i,j})(\boldsymbol{\varepsilon}_j \cdot \mathbf{r}_{i,j})] , \tag{1b}$$

where $\mathbf{r}_j$ and $\mu\boldsymbol{\varepsilon}_j$ are the position and the transition dipole moment vectors at jth molecule, and both $\boldsymbol{\varepsilon}_j$ and $\mathbf{r}_{i,j} \equiv (\mathbf{r}_i - \mathbf{r}_j)/|\mathbf{r}_i - \mathbf{r}_j|$ are unit vectors. We assume the dipole moment vectors tend to be parallel to the tangent vectors of the chain. Geometrical perturbations are categorized into the following three groups: (1) the global and weak curving of the chain direction, (2) the local fluctuations of the polarization vectors which are of the short range, and (3) the kinks of the chain at which the excitation transfer is almost forbidden. The kinks will determine the coherent or localization length of the exciton, but we restrict ourselves to the first and the second

perturbations in this paper. Keeping only the nearest neighbor interactions, we start with the following Hamiltonian:

$$H_s = H_0 + H', \tag{2a}$$

$$H_0 \equiv \sum_{j=0}^{N-1} \hbar\omega_0 \hat{s}_j^z - \sum_{j=0}^{N-1} \hbar J_0(\hat{s}_j^+ \hat{s}_{j+1}^- + \hat{s}_j^- \hat{s}_{j+1}^+), \tag{2b}$$

$$H' \equiv \sum_{j=0}^{N-1} \hbar J_j'(\hat{s}_j^+ \hat{s}_{j+1}^- + \hat{s}_j^- \hat{s}_{j+1}^+), \tag{2c}$$

where $J_0 = J_0^{(0)} + J_0^{(1)}$, $J_0^{(0)} \equiv \mu^2/2\pi\epsilon_0 a^3$, $J_0^{(1)} \equiv -\mu^2 \overline{\rho^{-2}}/4\pi\epsilon_0 a$, and $J_j' \equiv (\mu^2/4\pi\epsilon_0 a)(\overline{\rho^{-2}} - \rho_j^{-2})$. Here a is a length between two adjacent sites, ρ_j is the radius of curvature of the chain at jth molecule, and $\overline{\rho^{-2}} \equiv N^{-1} \sum_j \rho_j^{-2} \simeq L^{-1} \int_0^L \rho^{-2}(s)ds$ with $L = Na$ and arc length s. $J_0^{(0)}$ is the exchange energy for a straight chain, $J_0^{(1)}$ is the energy shift due to the global deformation of the system, and J_j' reflects local fluctuations at jth molecule. Note that the stabilization energy $\hbar J_0$ of the Frenkel exciton decreases by $\hbar J_0^{(1)}$, which is proportional to the average of the squared curvature of the chain. As we confine ourselves to the case $|\rho_j| \gg a$, H' can be treated by perturbational methods. The one particle eigenstates (Frenkel exciton) of H_0 are obtained as $|k\rangle = N^{-1/2} \sum_j e^{ikja} \hat{s}_j^+ |\text{vac}\rangle$ with eigenenergy $\hbar\omega_k = \hbar(\omega_0 - 2J_0 \cos ka)$. Here $|\text{vac}\rangle$ denotes the ground state which corresponds to the state with all spin down. The absorption spectrum is given by

$$I_{ab}(\omega) = I_0 \, \text{Im}[\langle \text{vac}|H_{\text{int}}(\omega - H_s - i\gamma_\parallel)^{-1} H_{\text{int}}|\text{vac}\rangle],$$

$$= I_0 \sum_k |\langle \text{vac}|H_{\text{int}}|k\rangle|^2$$

$$\times \text{Im}[\langle k|(\omega - H_s - i\gamma_\parallel)^{-1}|k\rangle], \tag{3}$$

where $H_{\text{int}} = -\sum_j \boldsymbol{\varepsilon} \cdot \boldsymbol{\mu}_j(\hat{s}_j^+ + \hat{s}_j^-)$ describes the interaction between the present system and the external electromagnetic field with the unit polarization vector $\boldsymbol{\varepsilon}$, I_0 is a constant, $\gamma_\parallel$ is the longitudinal decay constant, and

here and hereafter we take $\hbar = 1$.

We have to evaluate the transition matrix element $T_{v;k} \equiv \langle \mathrm{vac}|H_{\mathrm{int}}|k\rangle$. We introduce the translation operator *along the chain*, $\hat{T}$, as $\hat{T}\hat{s}_j^{\pm}\hat{T}^{-1} = \hat{s}_{j+1}^{\pm}$. Since $\hat{T}$ commutes with H_0, $|k\rangle$ is simultaneously an eigenvector of $\hat{T}$: $\hat{T}|k\rangle = e^{-ika}|k\rangle$. Therefore,

$$T_{v;k} = \sum_j \boldsymbol{\varepsilon} \cdot \boldsymbol{\mu}_j \langle \mathrm{vac}|(\hat{s}_j^+ + \hat{s}_j^-)|k\rangle$$

$$= \sum_j \boldsymbol{\varepsilon} \cdot \boldsymbol{\mu}_j \langle \mathrm{vac}|\hat{T}^{-j}(\hat{s}_0^+ + \hat{s}_0^-)\hat{T}^j|k\rangle$$

$$= \sum_j \boldsymbol{\varepsilon} \cdot \boldsymbol{\mu}_j e^{-ikja} \langle \mathrm{vac}|(\hat{s}_0^+ + \hat{s}_0^-)|k\rangle$$

$$\equiv N\mu G(k)\langle \mathrm{vac}|\hat{x}_0|k\rangle.$$

Thus, we find $T_{v;k}$ is decomposed into two factors; a geometrical factor $G(k)$,

$$G(k) \equiv \frac{1}{N}\sum_j \boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}_j e^{-ikja} \simeq \frac{1}{L}\int_0^L \boldsymbol{\varepsilon} \cdot \mathbf{t}(s)e^{-iks}ds,$$
$$(4)$$

and a matrix element of a local operator $\hat{x}_0 \equiv \hat{s}_0^+ + \hat{s}_0^-$. Here $L \equiv Na$ is the total length of the chain and $\mathbf{t}(s)$ is the tangent vector of the chain at arc length s. The geometrical factor is determined by the configuration and symmetry of the system and independent of the details of the system Hamiltonian, while the matrix element of a local operator $\hat{x}_0$ is determined only by the local nature of the system. The matrix element of $\hat{x}_0$ is very simple for the photoexcitation of a Frenkel exciton: $\langle \mathrm{vac}|\hat{x}_0|k\rangle = N^{-1/2}$, and we get

$$|T_{v;k}|^2 = |\langle \mathrm{vac}|H_{\mathrm{int}}|k\rangle|^2 = N\mu^2|G(k)|^2. \qquad (5)$$

The effects of H' can be estimated with the self-energy $\Sigma_k(\omega)$ defined by $\langle k|(\omega - H_s - i\gamma_\parallel)^{-1}|k\rangle \equiv [\omega - \omega_k - \Sigma_k(\omega)]^{-1}$. The self-energy $\Sigma_k(\omega)$ is given in the Born approximation as $\Sigma_k(\omega) \simeq \langle k|H'(\omega - H_0 - i\gamma_\parallel)^{-1}H'|k\rangle = \sum_q |\langle k|H'|q\rangle|^2(\omega - \omega_q - i\gamma_\parallel)^{-1}$. We can use a similar decomposition in evaluating the matrix element $\langle k|H'|q\rangle$ and get $\Sigma_k(\omega) \simeq iP(k - q_0)\sigma(\omega)$. Here we neglect a small energy shift $\mathrm{Re}[\Sigma_k(\omega)]$ as the dominant geometrical effect is already taken into account by $J_0^{(1)}$ in the starting Hamiltonian. $\sigma(\omega)$ is the renormalized density of states of the system at $\omega \equiv \omega_{q_0}$ and $P(k - q_0)$ is the power spectrum of the fluctuation J'_j in the continuum limit:

$$P(k - q_0)$$
$$\equiv 2L^{-1}\int_0^L ds_1 \int_0^L ds_2 J'(s_1)J'(s_2)e^{i(k-q_0)(s_1-s_2)}.$$

By denoting $\gamma'(k,\omega) \equiv P(k - q_0)\sigma(\omega)$, we obtain

$$I_{ab}(\omega) = I_0\mu^2 N \sum_k |G(k)|^2 \frac{\gamma'(k,\omega)}{(\omega - \omega_k)^2 + \gamma'(k,\omega)^2}.$$
$$(6)$$

We have thus represented two effects of geometrical perturbation on the absorption spectrum of the Frenkel exciton. The first is the selection rule to the state with the finite wave number k, which is described by the geometrical factor $|G(k)|^2$. The second, which comes from the local fluctuations of polarization vectors, is the spectrum broadening proportional to the power spectrum of the fluctuation and the normalized density of states.

Figures 1(a)–1(e) show several examples of curved chains. The corresponding absorption spectra are schematically represented in Figs. 2(a)–2(e). For the straight chain 1(a), photoabsorption occurs only at $k = 0$, which satisfies the usual selection rule due to the momentum conservation for a translationally invariant system. However, since low spatial dimensional systems do not necessarily have three-dimensional translational symmetry, the momentum $\hbar k$ of the system is no longer a conserved quantity, so that Frenkel excitons with nonzero wave numbers can be generated. Actually, as is shown in
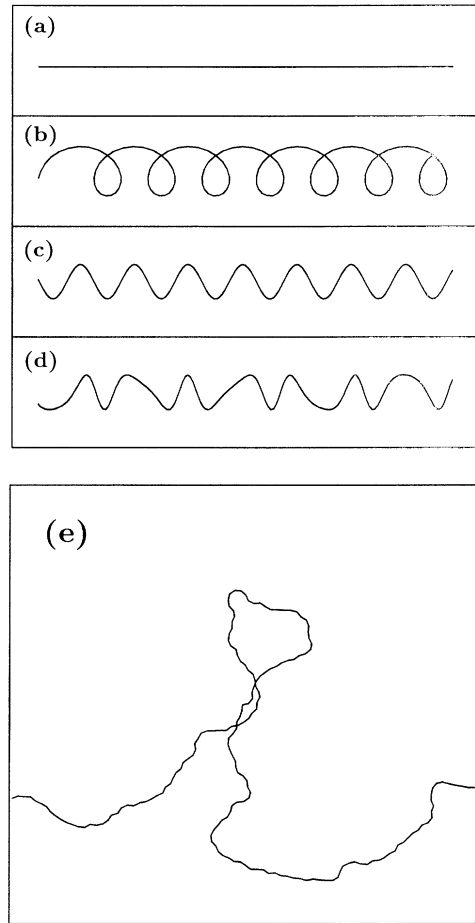

FIG. 1.   Examples of chains: (a) Straight line, (b) helix, (c) periodic chain, (d) quasiperiodic chain, (e) random chain with finite correlation length.
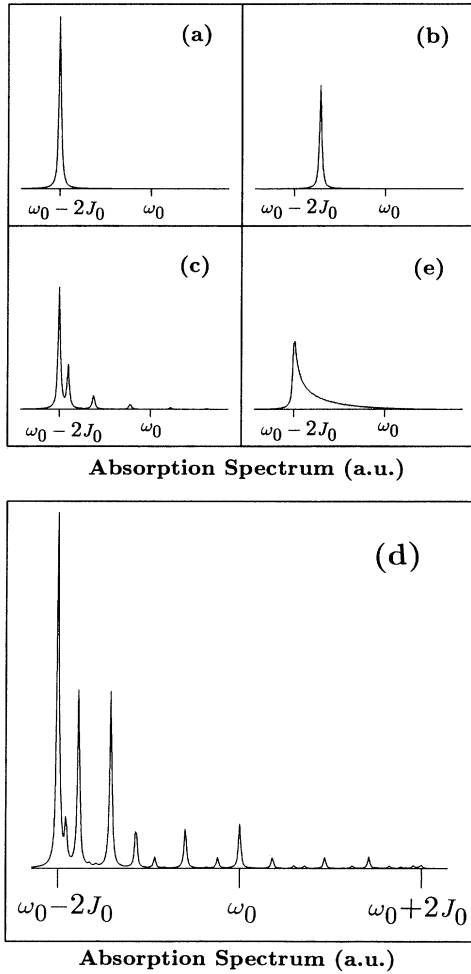
Absorption Spectrum (a.u.)

Absorption Spectrum (a.u.)

FIG. 2.   Schematic figures of absorption spectra of Frenkel excitons in the chains given in Figs. 1(a)–1(e). Polarization vector ε is assumed to be parallel to the average direction of the chain in (a),(c)–(e) and perpendicular to that in (b).

Fig. 2(b), we can selectively create the Frenkel exciton with an arbitrary wave number k by making the system in the helical structure with radius r and pitch λ which satisfy $k = (2\pi/\lambda)\sqrt{1 + (2\pi r/\lambda)^2}$, and using a linearly polarized light with ε perpendicular to its helical axis. The structures shown in Figs. 1(c) and 1(d) were conjectured to exist in polymers dissolved in chiral nematics [2]. For the periodic case with period λ, the excitons with wave number $k_n = 2n\pi/\lambda$ ($n = 0, \pm 1, \pm 2, \ldots$) are generated as shown in Fig. 2(c). For the quasiperiodic case with two periods λ_1 and λ_2, (d), the wave numbers are $k_{n,m} = 2n\pi/\lambda_1 + 2m\pi/\lambda_2$ ($n, m = 0, \pm 1, \pm 2, \ldots$) and dense in the whole spectrum. We can find self-similar structures typical for a quasiperiodic system in Fig. 2(d). Figure 1(e) shows a random chain with finite correlation length which is an ideal model of a polymer. The long absorption tail due to violation of the momentum con-

servation appears on the higher energy side in Fig. 2(e).

A Wannier exciton in a chain is expected to show geometrical effects different from the Frenkel exciton. Generally speaking, long-range Coulomb interactions break the symmetry of the system and our treatments presented above can no longer be applied. We assume that the chain is rather smoothly curved and that the effective mass approximation is still valid. The Schrödinger equation for a Wannier exciton is written in terms of the center-of-mass coordinate R and relative coordinate r along the chain as

$$\left[-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{8m}\kappa(R)^2 + V(R,r) \right] \Phi(R,r)$$

$$= E\Phi(R,r). \quad (7)$$

Here M (m) is the total (reduced) mass of a Wannier exciton, $\kappa(R) = 1/\rho(R)$ is the curvature at arc length R and the term proportional to κ^2 arises from the global deformation of the chain corresponding to the term with $J_0^{(1)}$ in Eqs. (2) for case of the Frenkel exciton. Note, however, that the stronger curvature gives more stability [3,4] to the Wannier exciton. The Coulomb potential $V(R,r)$ can be expanded in terms of r: $V(R,r) = (-e^2/\epsilon_0)[1/|r| + \kappa(R)^2|r|/4! + $ (higher order terms)] as long as the average electron-hole separation l is much smaller than $\rho(R)$. Note here that the stronger curvature gives again the deeper potential to the exciton. The higher order terms contain the derivatives of $\kappa(R)$ and torsion $\tau(R)$ with respect to R such as $\dot{\kappa}(R)^2|r|^3$ and $\kappa(R)^2\tau(R)^2|r|^3$. When the extent l is small enough to satisfy $l\dot{\kappa}, l\tau \ll \kappa$, we may approximate $\Phi(R,r) \simeq \phi(R)\psi(r)$ and the wave function for the center-of-mass coordinate obeys the following equation:

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{dR^2} - V_0\Delta\kappa(R)^2 \right] \phi(R) \simeq (E - E_r)\phi(R),$$

$$(8)$$

where $V_0 \equiv (\hbar^2/8m)(l/3a_B^* + 1)$, $a_B^* \equiv \epsilon_0\hbar^2/me^4$ is the bulk Bohr radius, $\Delta\kappa(R)^2$ is the deviation of $\kappa(R)^2$ from the mean value $\overline{\kappa^2}$, and E_r is the energy of the relative motion. When $\psi(r)$ is well approximated by the envelope function of a one-dimensional Wannier exciton obtained by Loudon [5], we find $l \simeq n^2 a_B^*$ ($n = 0, 1, 2, \ldots$). The lowest state $n = 0$ has an infinite binding energy and a zero extension $l \simeq 0$ for the electron-hole relative motion in the effective mass approximation. For the real system, however, there are several factors to give a finite binding energy and a finite extension l; the central-cell correction and a finite radius and potential strength in the transverse direction [6]. These values depend strongly on the precise model. Therefore we confine ourselves to the small frequency region around the lowest electron-hole relative motion and study the fine structures of this lowest state coming from the geometrical structures.
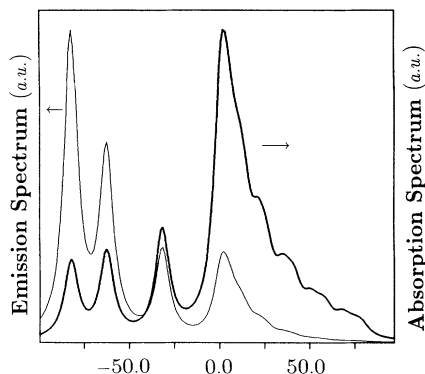
Equation (8) implies that the center-of-mass motion

FIG. 3. The emission (thin line) and absorption (thick line) spectra of Wannier excitons in the system described in the text. We take c as a unit of length ($c = 1.0$) and the unit of energy is thus $\hbar^2/2Mc^2$. Then, the values of the parameters used for the calculation are $b = 2.0$, $(2MV_0/\hbar^2)\kappa_0^2 = 3\pi$, and $(k_B T^*)^{-1} = 0.3$. The energy at the origin corresponds to the lowest energy of the internal state.

of the exciton feels attractive potentials in the regions with large curvature on the chain. Therefore we expect some trapped states to appear below the free exciton and can be observed in the absorption and emission spectra. In order to clarify the influence of the trapped states, we consider, as an idealized model, a random chain constituted by the segments with length b, in which every pair of the adjacent segments makes an equal angle and is combined by circular arcs with length c and curvature κ_0. Then, $\Delta\kappa^2(R)$ becomes a periodic function of R with period $b + c$ and we can analytically evaluate the eigenstates $\phi(R)$ for the center-of-mass motion and the optical spectra of this system. We show the absorption and emission spectra of this system in Fig. 3. We have assumed the photoemission was induced after the population of excitons had been thermalized in some effective lattice temperature T^*. The absorption peak due to the usual free exciton at $k = 0$ appears at the center in the figure of the absorption spectrum. It has a long absorption tail to the higher energy side due to the randomness of the directions of the segments. In addition, three trapped states appear on the lower energy side of the free exciton peak at $E = 0$ due to the 1D square-well potential for the center-of-mass motion described by the second term of Eq. (8) with the numerical values given in the caption of Fig. 3.

Since $\Delta\kappa(R)^2$ randomly fluctuate spatially in real ma-

terials, the center-of-mass motion $\phi(R)$ necessarily localizes in the thermodynamic limit. If $\Delta\kappa(R)^2$ can be regarded as the Gaussian random process with respect to R, its localization length λ_L can be estimated from the correlation length λ^* of $\Delta\kappa(R)^2$ by the standard arguments for fluctuations [7] as long as $\lambda_L^{-1} \ll k_0 \equiv [2M(E - E_r)/\hbar^2]^{1/2}$: $\lambda_L^{-1} \sim (M^2V_0^2/\hbar^4k_0^2\lambda^*L)\int_0^L dR\,[\Delta\kappa(R)^2]^2$. When λ_L is larger than the wavelength of the electromagnetic field, no essential effect of localization appears in the optical transitions and the previous discussions for Frenkel excitons can be applied. On the other hand, for λ_L less than the wavelength, in addition to the existence of the trapped states, the localization of Wannier excitons gives new effects on optical processes such as an enhancement of nonlinear susceptibility [8].

The effective-mass description of Wannier excitons discussed above may be justified for quantum wires of semiconductors in which the radii of the wires are small enough compared with the Bohr radius of the bulk exciton. For realistic polymers, we have to take the electronic natures of both valence and conduction bands into account microscopically, and the curvature κ in Eq. (8) shoud be replaced by the effective curvature which depends on these electronic natures and torsion of the chain. The essential features of the present results, however, will be kept without serious modifications.

[1] T. Tokihiro, Y. Manabe, and E. Hanamura, Phys. Rev. B **47**, 2019 (1993).

[2] T.C. Lubensky, T. Tokihiro, and S.R. Renn, Phys. Rev. Lett. **67**, 89 (1991).

[3] H. Jensen and H. Koppe, Ann. Phys. (N.Y.) **63**, 586 (1971).

[4] M. Ikegami and Y. Nagaoka, Prog. Theor. Phys. Suppl. **106**, 235 (1991).

[5] R. Loudon, Am. J. Phys. **27**, 649 (1959).

[6] L. Bániyai, I. Galbraith, C. Ell, and H. Haug, Phys. Rev. B **36**, 6099 (1987).

[7] R. Kubo, Rep. Prog. Phys. **29**, Part 1, 255 (1966).

[8] N. Taniguchi and E. Hanamura, Phys. Rev. B **47**, 12470 (1993).