A tight-binding model for the excitonic band structure of a one-dimensional molecular chain: UV-Vis spectra, Zak phase and topological properties

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Recently organic optics becomes a hot topic due to the rapid development of organic light-emitting diodes, organic solar cells, and organic photon detectors. The optical spectra of the molecular semiconductors are difficult to solve an model from first-principles because (i) the very large number of atoms in a unit cell and (ii) the accurate theoretical excited state is still under development. Here we present a tight-binding model of an exciton band structure in a molecular chain. We take into account the intra-molecule and charge-transfer excitation within a molecular dimer in a unit cell, then we apply the tight-binding model by including the coupling between two types of excitations. We not only found that our calculations can explain a body of UV-Vis optical spectra of transition-metal phthalocyanines, but also a one-dimensional excitonic topological band structure if we fine-tune the couplings in a dimerized molecular chain. We have found a large space to obtain the topological Zak phase in the parameter space, in which there is a simple linear relationship between the hopping integrals between cells and within cell.

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I. INTRODUCTION

The recent development of organic light-emitting diodes (OLED) and organic solar cells (OSC) has stimulate an unprecedented huge amount of experimental measurements and theoretical analysis of the optical properties of organic materials [1, 2]. The optical properties of the organic materials is very important because it can tell us the electronic structure, vibrational modes, and their potential for OLED and OSC. Normally people measure the UV-Vis optical spectra to tell the potential performance of organic materials for OLED and OSC. The comparison between experimental results and theoretical modelling is crucial to the understanding of the electronic-structure origin of the optical spectra, assessment of the potential of the organic materials for optical applications, and development of new materials according the theoretical analysis. It is well known that the organic materials is liable to form one-dimensional chains [3, 4], especially for the $\pi$-conjugated systems mainly due to the strong $\pi - \pi$ interactions that can stack the molecules along a particular spatial direction. Therefore, the main characteristics of the optical spectra of organic chain compounds such as transition-metal phthalocyanines originates from molecular chains [5]. We can then understand the optical properties of the organic chain compounds based on the optical simulation of molecular chains.

The optical properties of transition-metal phthalocyanines, a one-dimensional-chain organic compound, have been studied for a long time. There are mainly two UV-Vis absorption bands; one of them is B bands (at $\lambda \sim 350$ nm) while the others (at $\lambda \sim 650$ nm) are called Q-band [6]. Normally Q-band is split and very broad, which is controversial. A popular argument is that this is due to the Davydof splitting, however this effect is too small comparing with the experimentally observed splitting in Q-band. Another deeper understanding is that this is due to the coupling between the intra-molecular and charge-transfer excitations [7]. This opinion is more reasonable because (i) there indeed exist these two types of excitations and (ii) the coupling between them should be proportional to the conduction- or valence-bandwidth, which is close the splitting observed ($\sim 10^{-1}$ eV) [8].

The common methods for analysing the optical properties of molecules or finite-size nano-structure include configuration interaction (CI) [9], time-dependent Hartree-Fock (TDHF) [10], and time-dependent density-functional theory (TDDFT) [11], etc. CI is normally very expensive as the computational cost will increase with the number of atoms and basis set factorially. People normally choose TDHF and TDDFT to compute the excited states of the molecules or molecule clusters as they are much cheaper and the calculation results are reasonably good as compared with CI. In practice TDDFT is in general more accurate than TDHF although the exchange-correlation functional is empirical through fitting to the experimental values such as B3LYP [11]. For the excited state of solids, the related theoretical approaches are still under development. For example, in CRYSTAL code [12], people are trying to extend the idea of TDDFT to periodic solid-state structure. To the authors’ knowledge, it is rare [12] to deal with the optical properties of periodic solid from first-principles due to (i) the large amount of atoms in the unit cell and (ii) the large number of single-particle excited states to be taken into account.

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in the calculation of excited states in the solid state.

Recently the one-dimensional topological insulator arising from the alternating coupling in the dimer chains becomes a hot topic. The original work by Su, et. al., shows that there exists a topological soliton owing to the alternating coupling and the interaction with phonons. People have realized this type of topological electronic state by using finite atom chain or arrays on the Cu surface, in which we can see the topological state. Similarly, people have proposed that the similar topological state can exist in magnon, excitons, and phonons. Here we propose a one-dimensional excitonic model with alternating coupling due to the dimerization of molecular chains, which can easily happen in the molecular crystals.

Here we propose a tight-binding method for a one-dimensional periodic molecular chain to take into account the intra-molecule excitation, charge-transfer excitation, and the coupling between them. We show that we can not only qualitatively explain the optical spectra of molecule-chain compound, but also find the topological excitonic band structure if we can fine-tune the coupling in a dimerized molecular chain. The remaining discussion falls into three parts. In II we talk about the method used. In III we show our results and discuss them. In IV we draw some general conclusions.

II. METHODS

We mainly used the tight-bind model as shown in Fig.1 to perform the calculations. The related Hamiltonian reads

\[
\hat{H} = \sum_{n} t_{2}a_{IM1,n}^{\dagger}a_{CT1,n} + t_{1}a_{IM1,n}^{\dagger}a_{CT2,n-1} + \\
t_{1}a_{IM1,n}^{\dagger}a_{CT2,n} + t_{2}a_{IM2,n}^{\dagger}a_{CT1,n-1} + \\
t_{1}a_{IM2,n}^{\dagger}a_{CT1,n} + t_{2}a_{IM2,n}^{\dagger}a_{CT2,n-1} + \\
t_{2}a_{IM2,n}^{\dagger}a_{CT2,n} + a_{CT1,n}^{\dagger}a_{CT2,n-1} + \\
\frac{d}{4} a_{IM1,IM1} - \frac{d}{4} a_{IM2,IM2}^{\dagger} + \\
\frac{d}{4} a_{CT1,CT1} + \frac{d}{4} a_{CT2,CT2}^{\dagger} + h.c.
\]

(1)

Here \(a_{IM}^{\dagger}\) and \(a_{st}\) are the bosonic creation and annihilation operators for individual states \(s\), respectively as we consider singlet/triplet excitons.

The excited state properties, including excitation energies and oscillator strengths, can be computed by using the time-dependent density-functional theory module built in Gaussian 09 code. \(t_{1}\) and \(t_{2}\) are the couplings between the single-particle LUMO (lowest-unoccupied molecular orbital) and HOMO (highest-occupied molecular orbital) states respectively within the unit cell, while the \(t_{1}'\) and \(t_{2}'\) are for between cells. The couplings \(t_{1}\), \(t_{1}'\), \(t_{2}\), and \(t_{2}'\) are phenomenological, which can work as fitting parameters for the experimental results. We can also assume that there is a small energy gap \(d\) between the intra-molecular and charge-transfer excited states. We can then transform the Hamiltonian \(\hat{H}\) into the \(k\)-space to have \(\hat{H}_{k}\), as follows,

\[
\hat{H}_{k} = \begin{pmatrix}
-d/2 & 0 & t_{1} + t_{2}' e^{-i k} & t_{1} e^{-i k} + t_{2}' \\
0 & -d/2 & t_{1} e^{i k} + t_{2}' & t_{1} + t_{2}' e^{i k} \\
t_{1} + t_{2}' e^{i k} & t_{1} e^{i k} + t_{2}' & d/2 & 0 \\
t_{1} e^{i k} + t_{2}' & t_{1} + t_{2}' e^{i k} & 0 & d/2
\end{pmatrix}
\]

Then we can solve the eigenvalue problems for each \(k\)-points (assuming the lattice constant here is 1) by using the standard diagonalization technique.

III. RESULTS AND DISCUSSION

A. Mixture of the intra-molecular and charge-transfer excited states

We first solve the eigenvalue problem for a uniform molecular chain, and take \(t_{1} = t_{1}'\) and \(t_{2} = t_{2}'\). Here we take \(t_{1} = 0.15 \text{ eV}, \ t_{2} = 0.015 \text{ eV}\), the energy difference between the intra-molecular and charge-transfer states is 0.5 eV. The oscillator strengths for the IM and CT excited states are 0.5 and 0.02, respectively, as computed by using TDDFT in Gaussian 09 code. According to the eigenvector obtained, we can obtain the total oscillator strength across the first Brillouin zone from \(-\pi\) to +\(\pi\) for \(k\)-vector (here we assume the lattice constant is 1 in our periodic structure as show in Fig.1). As shown in Fig.2 we have computed the oscillator strength for the above parameters (black curve), and compare this with the calculation in which the coupling is turned off (red curve). When the coupling is turned off, we only have the strong transition for the IM excited state, whereas, when the coupling is turned on, we can see the lower-energy CT excited states will strengthen and become even stronger than the IM excited state. This is in consistent with
most of the optical spectra for the transition-metal phthalocyanines [21].

![Graph of oscillator strength vs wavelength](image)

**FIG. 2:** (Colour online.) The computed absorption spectra by using the parameters of Gaussian calculations (black curve) combined with our tight-binding model, which is in a qualitative agreement with the previous experimental results. Especially, we can see the longer-wave length has a stronger absorption than the shorter one. In comparison, we have also shown the computed optical spectra with coupling turned off (red curve).

We have computed the excitonic band structure as shown in below when taking \( t_1 = t'_1 = -0.5, t_2 = t'_2 = -0.1, d = -1 \) (alternatively, we use the gap between IM and CT as energy unit), in which we can see the bandwidth is large the top and bottom bands due to \( t_1 \).

We have also found these two interesting straight bands which seem not to be coupled to any other components. These bands are from the linear combination of the two pure IM or CT states, therefore they are purely the IM or CT excited states. However, the top and bottom bands contribute to the mixture between IM and CT excited states.

**B. Analogue to the Su-Schrieffer-Heeger model: molecular dimer model and topological phase**

1. **Topological band structure**

In addition to the uniform chain calculations \( (t_1 = t'_1 \text{ and } t_2 = t'_2) \), we can also tune the couplings between the intra-molecular and charge-transfer excited states to find the similar physics to the Su-Schrieffer-Heeger (SSH) model [13]. As shown in Fig[4], we have fixed the ratio between \( t'_1 \) and \( t_1 \) (and \( t'_2 \) and \( t_2 \)) to be 2, \( t_2 \) to -3, \( d \) to -1 and varied \( t_1 \). We can see the evolution of the band structure when tuning \( t_1 \) from -8 to -5 from (a)-(d) of Fig[4].

![Graph of energy vs k](image)

**FIG. 3:** (Colour online.) The excitonic band structure computed by using our tight-binding model when we take the same parameters as Fig[1].

We can see the band touching. This evolution of band structure as a function of the coupling between IM and CT excited states indicates the potential topological properties of molecular dimer chain through excitonic aspect.

2. **Zak phase**

We have also computed the total Zak phase [22] that reads \( z = i \int_{FBZ} dk \langle \phi_k | \partial_k \phi_k \rangle \) for the band structure, in which FBZ represents the first Brillouin zone and \( \phi_k \) is the Bloch function. We have summed up the total Zak phase by using \( \sum_i |z_i|/\pi \) for all the bands. Here we have fixed the ratios \( t'_1/t_1 \) and \( t'_2/t_2 \) to 2 and the energy gap \( d = -1 \). From the phase diagram as shown in Fig[5](a), the upper-left part is the topological phase, whereas the lower-right part for the trivial phase. We can also see that the phase transition happens when \( t_1/t_2 \simeq 2 \) as suggested by the green line. We have plotted the band structure for the parameters at blue, purple, and red squares in the trivial, phase transition, and topological phases, respectively. We can see the corresponding colour-coded band-structure evolution in Fig[5](b). The evolution follows band-gap closing and re-opening. As the band structure suggests, the model proposed here still maintains the chiral symmetry similar to the SSH model. However, the band-gap reopening happens for both the positive- and negative-energy bands separately, which is different from the band structure arising from the SSH model. This can be attributed to the involvement of the single-particle excited states.
FIG. 4: (Colour online.) The excitonic band structure computed by using our tight-binding model. We can see that the evolution of the band structure as a function of $t_1$. We can see the band touching when $t_1 = -6.1$.

FIG. 5: (Colour online.) The Zak-phase diagram is shown in (a) and the corresponding colour-coded band structures are plotted in (b) to illustrate the band-gap reopening after the phase transition. In the band structure, the energy is in arbitrary unit.
IV. CONCLUSIONS

We combined the first-principles TDDFT calculations for a molecular dimer with excitonic tight-binding model to analyse the optical spectra of molecular-chain compound. Especially we compare our theoretical modelling with the recent optical UV-Vis measurement of transition-metal phthalocyanines crystal. We found that our results are in a good agreement with the experimental results. The coupling between the IM and CT excited states indeed plays an important role to the explanation of the optical spectra of molecular chains. Based on these uniform-chain calculations, we have tuned the coupling to dimerize the molecules and found interesting band structures which is an analogue to the SSH model, but in the sense of excitonic interactions within a one-dimensional dimer chain. We found the band-structure evolution and the band touching as we tune the interaction parameters. These calculations show that the molecular dimer chain is a promising candidate for photonic topological insulator. In the future, we would like to improve the model by including the Coulomb interaction between excitons (two-electron integrals) into the model, which may bring new physics.

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