Theory of Photoinduced Phase Transitions

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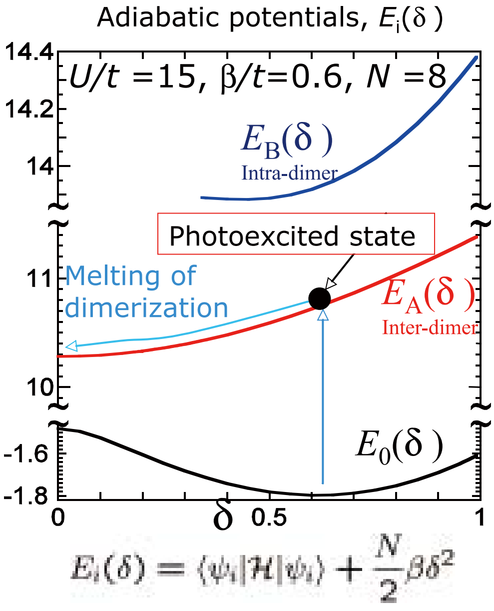
Photoirradiation of materials usually creates electrons and holes, which are often accompanied by local structural deformation. With the help of cooperativity, the electronic and/or structural deformation can proliferate to change the physical property such as conductivity, permittivity, and magnetic susceptibility. The resultant nonequilibrium phase may not be reached by changing temperature or pressure because the energy of a photon is much higher than thermal energies. Our theoretical researches are focused on the mechanisms and dynamics of photoinduced phase transitions, how they are controlled, and how the photoinduced electron-lattice states are different from those which are realized in thermal equilibrium.

1. Relaxation Processes in Photoinduced Neutral-Ionic Paraelectric-Ferroelectric Phase Transitions[1)]

To find characteristic properties of relaxation processes in the neutral-ionic, paraelectric-ferroelectric phase transition in the charge-transfer complex, tetrathiafulvalene-*p*-chloranil, we investigate stochastic processes in the classical spin-1 anisotropic Blume-Emery-Griffith model. Spins are assumed to obey the Markov process that is described by the master equation with the Arrhenius-type transfer probability. Time-evolution equations are derived from two standpoints. One is the mean-field approximation and the other is an extension of the Saito-Kubo treatment to the spin-1 and anisotropic case, which improves the mean-field approximation. Solving the equations numerically, we have found highly anisotropic relaxations during the neutral-to-ionic (thus, paraelectric-to-ferroelectric) transition: The interchain ordering develops much more slowly than the intrachain one. In contrast, the ionic-to-neutral (thus, ferroelectric-to-paraelectric) phase transition proceeds in a rather isotropic manner. This finding is relevant to the experimentally realized transition induced by intramolecular photoexcitations.

2. Charge-Transfer Excitations in One-Dimensional Dimerized Mott Insulators[2,3)]

Dynamical properties of photoexcited states are theoretically studied in a one-dimensional Mott insulator dimerized by the spin-Peierls instability. Numerical calculations combined with a perturbative analysis from the decoupled-dimer limit have revealed that the lowest photoexcited state without nearest-neighbor interaction corresponds to an interdimer charge-transfer excitation that belongs to dispersive excitations. This excited state destabilizes the dimerized phase, leading to a photoinduced inverse spin-Peierls transition (Figure 1). We propose a purely electronic origin of midgap states that are observed in a latest photoexcitation experiment of an organic spin-Peierls compound, potassium-tetracyanoquinodimethane (K-TCNQ).



$$E_i(\delta) = \langle\psi_i|\mathcal{H}|\psi_i\rangle + \frac{N}{2}\beta\delta^2$$

Figure 1. Adiabatic potentials of the ground state, the inter-dimer charge-transfer state, and the intra-dimer charge-transfer state.

The optical properties of one-dimensional dimerized Mott insulators are investigated further by using the one-dimensional dimerized extended Hubbard model, which contains nearest-neighbor interaction. Numerical calculations and a perturbative analysis from the decoupled-dimer limit clarify that there are three relevant classes of charge-transfer (CT) states generated by photoexcitation: interdimer CT unbound states, interdimer CT exciton states, and intradimer CT exciton states (Figure 2). This classification is applied to understanding the optical properties of an organic molecular material, 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA), which is known for its photoinduced transition from the dimerized spin-singlet phase to the regular paramagnetic phase. We conclude that the lowest photoexcited state of TTTA is the interdimer CT exciton state and the second lowest state is the intradimer CT exciton state.

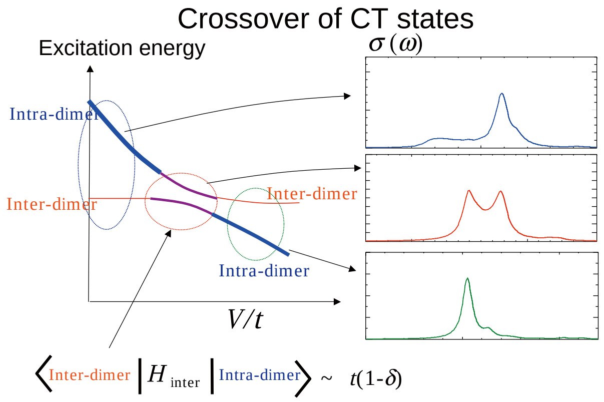


Figure 2. Energy diagram of relevant excited states. The solid (dotted) lines show the exciton (unbound) states, and the width of the lines indicate the strength of the spectral weight.

3. Effects of Electron Correlations and Lattice Distortions on Charge Order in Two-Dimensional Organic Salts[4,5)]

Charge ordering accompanied by lattice distortion in quasi-two dimensional organic conductors θ-(BEDT-TTF)$_2$X [BEDT-TTF = bis(ethylenedithio)-tetrathiafulvalene)] is studied by using a two-dimensional 3/4-filled extended Hubbard model with Peierls-type electron-lattice couplings first within the Hartree-Fock approximation. It is found that the horizontal-stripe charge-ordered state, which is experimentally observed in θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$, is stabilized by the self-consistently determined lattice distortion. Furthermore, in the presence of the anisotropy in nearest-neighbor Coulomb interactions, the horizontal charge order becomes more stable than any other charge patterns such as diagonal, vertical, and three-fold-type states. At finite temperatures, we compare the free energies of various charge-ordered states and find a first-order transition from a metallic state with three-fold charge order to the insulating state with the horizontal charge order. The role of lattice degrees of freedom in the realization of the horizontal charge order and the relevance to experiments on θ-(BEDT-TTF)$_2$X are clarified.

These combined effects of electron correlations and lattice distortions on the charge ordering in θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ are further investigated by means of the exact-diagonalization method. The findings are explained by the third-order perturbation theory from the strong-coupling limit. Electron-phonon interactions are found to be crucial to stabilize the horizontal-stripe charge order and to realize the low-symmetry crystal structure at low temperatures. Especially, modulations of transfer integrals not only by *c*- and *a*-axis molecular translations but also by molecular rotations are demonstrated to be important (Figure 3).

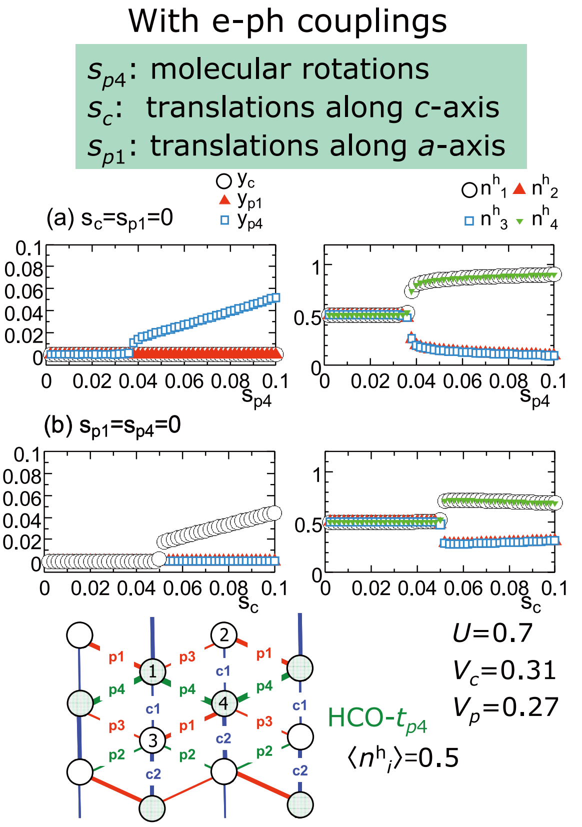


Figure 3. Electron-phonon coupling strength dependence of modulations of transfer integrals (left) and hole densities (right).

References

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