I-V Dimensional Crossovers and Excitation Spectra in Quasi-One-Dimensional Organic Conductors

In molecular materials including organic conductors and metal complexes, physical properties sensitively depend on electronic dimensionality, which is controlled by applying external or chemical pressure. Dimensional crossovers are classified according to whether one- or two-particle coherence in directions perpendicular to the highest conductivity is first restored by increasing dimensionality. The restoration of coherence depends on the asymptotic property of the corresponding one-dimensional system. For a one-dimensional gapless phase, interchain hopping easily restores the transverse one-particle coherence. If any excitation spectrum has a gap owing to electron correlation, the transverse one-particle process is so strongly suppressed that the transverse two-particle coherence is relatively easily restored. In quasi-one-dimensional organic conductors $(TMTTF)_2X$, the charge gap suppresses the transverse one-particle coherence and the antiferromagnetic transition takes place from a charge-localized phase. Even in the gapless phase of $(TMTSF)_2X$, effective dimensionality of the optical property is lowered by increasing energy scale. In mixed crystals $(DI\text{-}DCNQI)_2Ag_{1-x}Cu_x$ and $(DMe\text{-}DCNQI)_2Li_{1-x}Cu_x$, random potential scattering causes complex competition among the Mott-insulator, Anderson-insulator, and Fermi-liquid phases.

I-V-1 Quantum Phase Transitions and Collapse of the Mott Gap in the $d = 1 + \varepsilon$ Dimensional Hubbard Model with $2k_F$ Umklapp Scattering

KISHINE, Jun-ichiro

[*Phys. Rev. B* **62**, 2377 (2000)]

We study the low-energy asymptotics of the $d = 1 + \varepsilon$ dimensional Hubbard model with a circular Fermi surface where there is $2k_F$ umklapp scattering present *a priori*. Peculiarity of the $d = 1 + \varepsilon$ dimensions is incorporated through the imbalance between the elementary particle-particle and particle-hole (PH) loops: infrared logarithmic singularity of the PH loop is smeared for $\varepsilon > 0$. The one-loop renormalization-group flows indicate that a quantum phase transition from a metallic phase to the Mott insulator phase occurs at a finite on-site Coulomb repulsion U for $\varepsilon > 0$. We also discussed effects of randomness and obtained phase diagrams in terms of d, U, and strength of random backward scattering.

I-V-2 One– and Two–Band Hubbard Models in $d = 1 + \varepsilon$ Dimensions: Dimensionality Effects on the Charge and Spin Gap Phases

KISHINE, Jun-ichiro

[*J. Phys. Chem. Solids* in press]

To examine dimensionality effects on the charge/spin gap phases in quasi-one-dimensional, strongly correlated chain/ladder systems, we perform the one-loop renormalization-group analysis of the one- and two-band Hubbard models with circular Fermi surfaces in $d = 1 + \varepsilon$ dimensions. The renormalization-group flows indicate that raising dimensionality suppresses the charge and spin gap in the one and two-band cases, respectively. This result gives a clue to understand experimental indication: both the charge gap in the quasi-one-dimensional organic conductor $(TMTTF)_2Br$ and the spin gap in the doped ladder system $(Sr_2Ca_{12}Cu_{24}O_{41})$ are suppressed upon increasing pressure.

I-V-3 Interplay of Randomness, Electron Correlation, and Dimensionality Effects in Quasi-One-Dimensional Conductors

KISHINE, Jun-ichiro; YONEMITSU, Kenji

[*Phys. Rev. B* **62**, in press (2000)]

We study the interplay of randomness, electron correlation, and dimensionality effects in weakly coupled half-filled Hubbard chains with weak quenched random potentials, based on the renormalization-group (RG) approach. We perform a two-loop RG analysis of an effective action derived by using the replica trick, and examine the following crossovers and phase transitions from an incoherent metal regime: (1) a crossover to the Anderson localization regime, (2) an antiferromagnetic phase transition, and (3) a crossover to the quasi-one-dimensional weak-localization regime. The case of $d = 1 + \varepsilon$ ($\varepsilon \ll 1$) dimensions is also mentioned. Based on the result, we tried a simple simulation of the experimentally suggested successive crossovers [antiferromagnetic, Anderson localization to metallic phases] upon doping in $(DI\text{–}DCNQI)_2Ag_{1-x}Cu_x$.

I-V-4 Charge Gap and Dimensional Crossovers in Quasi-One-Dimensional Organic Conductors

YONEMITSU, Kenji; KISHINE, Jun-ichiro

[*J. Phys. Chem. Solids* in press]

Quasi-one-dimensional quarter-filled organic conductors, $(TMTTF)_2X$ and $(TMTSF)_2X$, show a dimensional crossover, and their electronic properties change accordingly. We describe this using the two-loop perturbative and density-matrix renormalization-group methods, the ε expansion around one dimension, and the random phase approximation. The effect of dimerization on the charge gap and interchain one-particle coherence is clarified. The effect of random potentials is also studied to describe Mott insulator, Anderson localization, and metallic phases of $(DCNQI)_2Ag_{1-x}Cu_x$ mixed crystals.

I-V-5 Dimensionality Effects on the Charge Gap in the Dimerized Hubbard Model at Quarter Filling: the Density-Matrix and Perturbative Renormalization-Group Approaches

YONEMITSU, Kenji; KISHINE, Jun-ichiro

[*J. Phys. Soc. Jpn.* **69**, 2107 (2000)]

We study dimensionality effects on the charge gap in the dimerized Hubbard model at quarter filling, with two approaches. First, we examine three chains coupled via the interchain one-particle hopping integral t_b, by the density-matrix renormalization-group (DMRG) method. Next, we consider the $d = 1 + \varepsilon$ dimensional model, using the perturbative renormalization-group (PRG) method. The dimensionality is controlled through t_b and ε, respectively. Both approaches lead to the conclusion that, for a finite dimerization ratio, the charge gap decreases as the dimensionality increases.

I-V-6 Intra- and Inter-Chain Dynamic Response Functions in Quasi-One-Dimensional Conductors

YONEMITSU, Kenji

[*Synth. Met.* in press]

Intra- and inter-chain excitation spectra are studied in a spinless fermion model on a two-leg ladder at half filling. Numerical results are obtained by application of the density-matrix renormalization-group technique to the quantum transfer matrix for infinite systems. Near the metal-insulator transition, the intra-chain Coulomb repulsion is found to affect local current correlations more sensitively in the rung direction than in the leg direction.

I-W Optical Excitations in Charge-Lattice-Ordered Phases of One-Dimensional Materials

Halogen-bridged binuclear metal complexes, which are often called MMX chains, have strong electron-lattice coupling and electron-electron interaction. Various charge and lattice ordering phases are found and depend on the ligand, the halogen ion and the counter ion. An alternate-charge-polarization phase is observed as well as a metallic phase for the ligand dta. Meanwhile, for the ligand pop, an averaged-valence Mott-insulator phase and a charge-polarization phase are observed as well as a well-known charge-density-wave phase. The competition among these electronic phases is qualitatively understood in a model with strong on-site repulsion, two types of electron-lattice couplings, and two types of elastic couplings. However, the optical properties sensitively depend on the long-range part of the electron-electron interaction. To explain both static and dynamical properties, we add nearest- and next-nearest-neighbor repulsion terms to the model in order to discuss the stability of each phase from the strong-coupling viewpoint and clarify the origin of each peak in the optical conductivity spectrum.

I-W-1 Charge Ordering and Lattice Modulation in Quasi-One-Dimensional Halogen-Bridged Binuclear Metal Complexes

KUWABARA, Makoto; YONEMITSU, Kenji

[*Mol. Cryst. Liq. Cryst.* **343**, 47 (2000)]

We have investigated ground state phase diagrams of the MMX chains in a one-dimensional dimerized 3/4-filled model by exactly diagonalizing 12-site clusters. In charged chains where counter ions are present, competition occurs among a uniform state, a charge-density-wave (CDW) state and a charge-polarization (CP) state. Experimentally observed phases are understood by strengths of a site-diagonal electron-lattice coupling β, the interdimer transfer integral t_{MXM}, and an elastic constant, whose variation is roughly estimated from the inter-atomic spacing, the species of the halogen ion. The CP state is relatively stable for small t_{MXM} and the CDW state for large β. In neutral chains where counter ions are absent, the dimer units can move almost freely. Dimers are alternately shifted to form tetramers because of a strong off-diagonal electron-lattice coupling, thus stabilizing an alternate-charge-polarization (ACP) state.

I-W-2 Charge Ordering and Lattice Modulation in MMX Chains

KUWABARA, Makoto; YONEMITSU, Kenji

[*J. Phys. Chem. Solids* in press]

Ground state phase diagrams for the MMX chains are studied in a one-dimensional two-band model by exactly diagonalizing 18-site clusters. Qualitative behavior of the phase diagrams is explained by the strong-coupling expansion. The relative stability between the charge-density-wave (CDW) and charge-polarization (CP) states observed in charged chains is determined by the kinetic energy gain through second-order processes with respect to intra-dimer charge transfer. Thus the relative stability is ascribed to competition between on-site Coulomb repulsion U and a diagonal electron-lattice coupling (β). The CP state is relatively stable for strong U and the CDW for strong β. In neutral chains, an alternate-charge-polarization (ACP) state is always more stable than the CP state by the energy gain through fourth-order processes with respect to interdimer transfer.

I-W-3 Charge Ordering and Optical Conductivity of MMX Chains

KUWABARA, Makoto; YONEMITSU, Kenji

[*Proc. LLD2K* submitted]

We study the optical conductivity of the halogen-bridged binuclear metal complexes, using a one-dimensional dimerized 3/4-filled-band model and the Lanczos method. The spectra are quite sensitive to the charge ordering pattern and the long-range Coulomb interaction. For instance, in a charge-polarization (CP) state two peaks are generally expected and ascribed to intra-dimer and interdimer charge excitations when long-range interactions are taken into account. However, when the interdimer Coulomb repulsion is weaker than the intra-dimer repulsion, only a single peak may be observed because the oscillator strength of the interdimer charge excitation is much weaker than that of the intra-dimer one. We clarify relations between the various ordering states and their optical conductivity spectra and compare them with experimental results.

I-W-4 Charge Excitations in an Alternate Charge Polarization Phase of a One-Dimensional Two-Band Extended Peierls-Hubbard Model for MMX Chains

KUWABARA, Makoto; YONEMITSU, Kenji

[*Synth. Met.* in press]

We investigate the optical conductivity of a halogen-bridged binuclear metal complex in an alternate-charge-polarization phase observed in $Pt_2(dta)_4I$ below 80 K, using a one-dimensional two-band extended Peierls-Hubbard model and the Lanczos technique, to study the dependence of three main peaks ascribed to intra-dimer, interdimer and halogen(X)-to-metal(M) charge excitations on model parameters. We show that effective energy difference between the M(Pt)-d_{z^2} and X(I)-p_z orbitals (Δ_{eff}) must be small in order to reproduce the optical conductivity spectra observed experimentally. Here Δ_{eff} is defined as $\Delta + U_{\mathrm{M}} - U_{\mathrm{X}} + 2V_{\mathrm{MM}} - 2V_{\mathrm{MX}}$, where Δ is the bare level difference, U_{M} (U_{X}) the on-site Coulomb repulsion at M (X) site, and V_{MM} (V_{MX}) the nearest-neighbor repulsion within a dimer (between M and X sites).

I-W-5 Highly Doped Nondegenerate Conjugated Polymers—A Theory Using the DMRG Method

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([1]Electron. Tech. Lab.)

[*Synth. Met.* in press]

Highly doped conjugated polymers with a non-degenerate ground state are investigated theoretically by using the density-matrix renormalization-group method. We pointed out a crossover between polaron- and bipolaron-lattice via formation of polaron-pairs. We also indicate that, at high doping concentration, the gaps in charge and spin excitations become negligibly small, while the bond alternation still survives.

I-X Magnetic and Optical Properties of Two-Dimensional Metal-Complex and Organic Conductors

Assembled metal complexes $Et_nMe_{4-n}Z[Pd(dmit)_2]_2$ are two-dimensional electronic materials and show rich phases including paramagnetic-insulator, antiferromagnetic–insulator, superconductor and metallic phases in different temperature and pressure regions and with different cations. The variety comes from the presence of HOMO and LUMO bands near the chemical potential and from strong dimerization of $Pd(dmit)_2$ molecules. The dependence of the ground state on the cation $Et_nMe_{4-n}Z$ was roughly interpreted on the Hückel basis and is now understood from the strong-coupling viewpoint, which enables us to show the correlation between the transport and magnetic properties and the stability criterion of the antiferromagnetic phase. On the other hand, two-dimensional organic conductors θ-$(BEDT\text{-}TTF)_2X$ have no or very weak dimerization, so that the long-range part of the electron-electron interaction causes charge ordering and consequently insulator phases with different magnetic properties. The charge-ordering and magnetic-coupling patterns are understood on the basis of the anion-dependent anisotropy of Coulomb repulsion strengths and transfer integrals. Some of the optical properties may indicate importance of electron-phonon interaction as well, so that both static and dynamical properties are studied in a consistent manner.

I-X-1 Collective Excitations around Charge Ordered States and Coexistent States with Different Orders

MORI, Michiyasu; YONEMITSU, Kenji

[*Mol. Cryst. Liq. Cryst.* **343**, 221 (2000)]

Some novel ground states have recently been studied in molecular conductors. One is the coexistence of a spin density wave (SDW) and a charge density wave (CDW) in $(TMTSF)_2PF_6$, which is quasi-one-dimensional and is basically a quarter-filled system with dimerization. Seo and Fukuyama[1)] and Kobayashi *et al.*[2)] have used the Hartree approximation for one-dimensional extended Hubbard models and found coexistence of a $2k_{\mathrm{F}}$ SDW with a $4k_{\mathrm{F}}$ CDW and that with a $2k_{\mathrm{F}}$ CDW, respectively. They claim that not only the on-site but also the nearest neighbor and the next-nearest-neighbor repulsive interactions are important, respectively. We study collective excitation spectra of such states with different orders. The excited states are

calculated in the random phase approximation for the one-dimensional extended Hubbard model at quarter filling. In the charge ordered state, a dominant excitation in the current-current correlation function has no charge density modulation. A dominant excitation in the charge uniform state originates from crossing the dimerization gap and modulates the charge density.

References

1) H. Seo and H. Fukuyama, *J. Phys. Soc. Jpn.* **66**, 1249 (1997).
2) N. Kobayashi, M. Ogata and K. Yonemitsu, *J. Phys. Soc. Jpn.* **67**, 1098 (1998).

I-X-2 Anisotropic Collective Excitations around Various Charge Ordering States

MORI, Michiyasu; YONEMITSU, Kenji

[*J. Phys. Chem. Solids* in press]

Among the family of $(ET)_2X$ (ET = BEDT-TTF), the θ-type salts have no evident dimeric structure and no antiferromagnetic insulating phase near the superconducting phase in contrast to the κ-type salts. In the paramagnetic insulating phase, charge ordering (CO) states are observed by the X-ray studies.[1)] We notice that the various CO states are indeed possible and the intersite repulsive interactions are important in the θ-type salts. It is still hard to distinguish the ground states among many CO candidates in the actual salts. We calculate absorption spectra for various charge ordering (CO) states in the two-dimensional extended Hubbard model at quarter filling with the random phase approximation. Each CO state has its own characteristic and anisotropic excitations. In principle, these features should be observed in the optical measurements and tell which CO state is realized in the θ-$(ET)_2X$ salts.

Reference

1) M. Watanabe, Y. Nogami, K. Oshima, H. Mori and S. Tanaka, *J. Phys. Soc. Jpn.* **68**, 2654 (1999).

I-X-3 Stability and Cation Dependence of Magnetic Orders in $(Et_nMe_{4-n}Z)[Pd(dmit)_2]_2$

MORI, Michiyasu; YONEMITSU, Kenji

[*Synth. Met.* in press]

Electronic states of $(Et_nMe_{4-n}Z)[Pd(dmit)_2]_2$ (Z = P, As, Sb) depend on the cations, although they are isostructural and have little differences in the lattice parameters. The experimentally observed Néel temperature is about 30 K for Me_4P and 18 K for Me_4Sb and Et_2Me_2P. For Et_2Me_2Sb, the antiferromagnetic (AF) phase transition is not observed above 5 K by the ESR measurement.[1)] The cation dependence of the magnetic phase transitions in the $Pd(dmit)_2$ salts is studied by calculating effective exchange interactions between spins on dimers in a two-band Hubbard model. The effective Hamiltonian in the low-energy region is reduced to a spin-1/2 AF Heisenberg model on the anisotropic triangular lattice. The existence/absence of the magnetic order is understood from the sublattice magnetization calculated within the linear spin wave theory, as shown in Figure 1. For Et_2Me_2Sb, the AF order is destroyed by magnetic frustration.

Reference

1) T. Nakamura, H. Tsukada, T. Takahashi, S. Aonuma and R. Kato, *Mol. Cryst. Liq. Cryst.* **343**, 187 (2000).

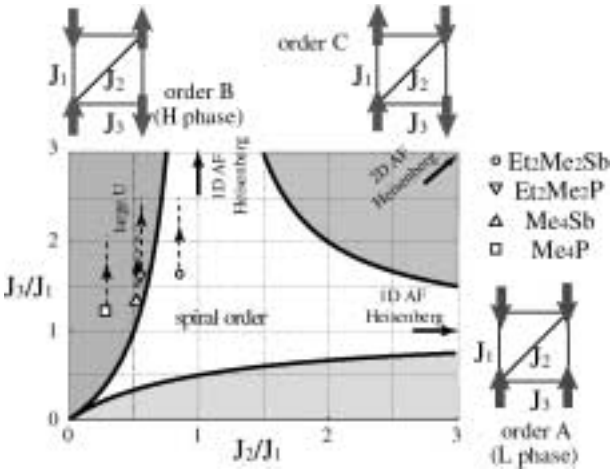

Figure 1. Magnetic phase diagram in the linear spin wave theory for the orders A, B and C. In each shaded region, the displayed magnetic order is stable. The salts with different cations are roughly located on the dashed lines. The position moves upward along the J_3/J_1 axis, as the on-site repulsive interaction is strengthened.

I-Y Multi-Phase Stability and Nonlinear Dynamics near Phase Boundary

In organic donor-acceptor compounds showing a neutral-ionic structural phase transition, each phase is locally stable and separated by a potential barrier from the other phase. To study photoinduced cooperative phenomena and dynamical processes, the high-energy part of the many-body potential is studied as well as the local minima. Techniques developed in molecular dynamics may be useful for such evolution of many-electron states. In conducting polymers possessing a non-degenerate bond-ordered ground state, electroluminescence involves recombination of excitons or polarons, which are produced by nonlinear processes of coupling between many electrons and phonons. Linear excitation analysis around such quasiparticles is useful to compare with experimental data.

I-Y-1 Influence of Short-Range Interference on Ionization Threshold Law

MIYASHITA, Naoyuki[1]; WATANABE, Shinichi[2]; MATSUZAWA, Michio[2]; MACEK, Joseph H.[3]
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[*Phys. Rev. A* **61**, 14901 (2000)]

Electron-impact ionization of the collinear $Z = 1/4$ model atom is investigated in order to examine a nonclassical behavior of the ionization cross sections. Slightly above the ionization threshold, ab initio calculations reveal a distinctive dip due to short-range dynamics. The dip is a strongly energy-dependent feature in the usually smooth and structureless ionization cross section and is foreign to treatments based on classical, as well as semiclassical mechanics. The $Z = 1/4$ model thus serves as a counterexample to the standard Wannier treatment of near-threshold ionization. The hyperspherical hidden-crossing theory is applied to identify the origin of the dip.

I-Y-2 Potential Analysis for Neutral-Ionic Phase Transition

MIYASHITA, Naoyuki[1]; YONEMITSU, Kenji
([1]GUAS)

Adiabatic potentials around neutral and ionic phases are studied in two-site and four-site extended-Hubbard models with varying energy difference between donor and acceptor sites. Mean-field solutions are searched under the constraints that the spin-density alternation amplitude and the degree of charge transfer take some fixed values. Unstable regions are numerically hard to access, so that we develop several iteration schemes.

I-Y-3 Localized Vibrational Modes of Excitations in Electroluminescent Polymers

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([1]Fudan Univ.; [2]Natl. Lab. Infrared Phys.)

[*Chin. Phys. Lett.* **16**, 836 (1999)]

The localized vibrational modes of an exciton and a polaron are investigated, and the results show that the frequencies of the three even parity modes of the exciton are very different from those of the polaron. For the exciton, three modes are distinctly separated, but, for the polaron, two modes with higher frequencies are close to each other. Then, it is possible to distinguish an exciton from a polaron by watching their Raman spectra. Therefore, the localized modes may be used to specify the exciton and the polaron in electroluminescent polymers.

I-Y-4 Photoinduced Polarization Inversion in a Polymeric Molecule

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[*Phys. Rev. Lett.* **84**, 2830 (2000)]

The polymeric molecule can exhibit a new photoinduced phenomenon where the electric dipole of the molecule with a bipolaron is reversed by absorbing one photon. This photoinduced polarization inversion occurring in a single molecule is an ultrafast process with a relaxation time of 200 fs.