

# Chapter 1

## Introduction

One of the most important goals, in spectroscopic studies of solids, is to clarify the dispersion-relation of the electronic energy-band, that is, the wavenumber-dependence of the energies of the one-body occupied and unoccupied states of electrons. Once we know how electrons occupy this band, it significantly helps us understand even the transport properties of the solid. Therefore, a lot of efforts to clarify this band structure have been made in both theoretical and experimental studies. Especially, it is well known that the photoemission and inverse-photoemission experiments can directly determine the band structure. Unfortunately, the energy resolution of the inverse-photoemission spectroscopy has not been significantly improved to date, being still about 0.5 eV or so. On the other hand, in the photoemission spectroscopy, it has been greatly reduced to as small as 1 meV, due to the rapid progress of the x-ray source. Therefore, we are now able to clarify the wavenumber-dependence of the one-body occupied states very precisely, by means of the so-called angle-resolved photoemission spectroscopy.

Such a rapid progress in the photoemission spectroscopy was, in some sense, caused by the discovery of exotic materials, in which the strong electron-electron interaction brings about unconventional and fascinating electronic properties. Usually, they are called the strongly correlated electron systems, and their unconventional electronic properties are not described by the single-particle picture. High-Tc superconductivity and colossal magneto-resistance are very good

examples. To clarify the origins of these unconventional electronic properties, the one-body occupied states, especially near the Fermi level, have been intensively investigated by the photoemission experiment. As a result, its energy and momentum resolution has been dramatically improved. However, as these improvements are realized, we have faced the serious problem that it is not so easy to catch the one-body state of these strongly correlated electron systems.

According to our conventional perturbation theory, the photoemission spectrum has been believed to consist of a sharp pole-like structure called the coherent component, and a broad sideband structure called the incoherent component. The coherent component represents the one-body state which the photo-emitted electron originally occupied, while the incoherent component reflects the collective motion of other surrounding electrons, induced by this photoemission. Usually, the coherent peak is believed to be very sharp and dominate the photoemission spectrum. Therefore, its wavenumber-dependence, if once observed, will be enough to determine the energy-dispersion relation of the one-body occupied states.

However, the real photoemission spectrum of the strongly correlated electron system turns out to be quite different from what is expected by this conventional picture. It has only a single broad peak, whose width is as large as 1 eV, and no other eminent structure has been observed inside this broad peak, despite the very fine experimental energy-resolution.

“Does this broad peak really show the one-body state, or the

band-like component ?” Obviously, to answer this question, we have to develop a more sophisticated theory than the conventional single-particle picture, so that we can include the electron correlation effects, almost completely.

In addition to the photoemission spectrum, a light absorption spectrum is another valuable observable, which determines the energy difference between the occupied and unoccupied states. In the visible region, the light absorption spectroscopy is one of the most reliable measurements, since its energy resolution is less than 1 meV. By combining the photoemission and light absorption spectra, we are able to obtain more precise information on the electron correlations of the solid. For example, in the conventional single-particle picture, the photoemission gap should be almost equal to half the optical gap. However, from the experimentally observed photoemission and light absorption spectra of the real one-dimensional Mott insulator,  $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_2$  (chxn=1R, 2R-cyclohexanediamine), we see that the photoemission gap is much smaller than half the optical gap.

“ Why are they so significantly different ? ” The conventional single-particle theory also cannot clarify this difference. To clarify the unconventional electronic states, it is quite important to get as many observables as possible, and construct a theory which can describe these different experiments, comprehensively.

This book aims to introduce the readers a new concept on the x-ray spectroscopy. As mentioned above, the conventional band picture works quite poorly on the strongly correlated materials. In this confused situation, the most reliable way for the breakthrough will be the direct comparison of the experimental and theoretical

results. Now, the experimental technique is sophisticated almost enough to detect the true electronic states. Therefore, to understand the complicated electronic states, we need the theories through which we can calculate the accurate spectral functions that include the electron correlation effects almost completely. Furthermore, we had better explain different experimental results of one material, in terms of the unified model.

In this book, we introduce a non-Grassmann path-integral theory for soft x-ray spectroscopy. The Coulomb repulsions, not only the short-range part but also the arbitrary long-range part, are reduced to only two kinds of one-body potentials through the path-integrals over two kinds of c-number fields, which represent quantum fluctuations of spins and charges, respectively. Therefore, the theory can treat arbitrary Coulomb repulsions exactly, even if they come from the Hubbard, extended Hubbard or Pariser-Parr-Pople-like models. The theory is applied to the photoemission, light absorption, inelastic x-ray scattering, and inelastic neutron scattering spectra of the strongly correlated electron systems. By clarifying the quantum fluctuation effects on these spectra, the nature of the correlated electrons will be revealed. The answers to the aforementioned questions are clearly given in connection with the strong quantum fluctuations. It will also be shown that the calculated photoemission and light absorption spectra reproduce well the experimentally observed spectra of the real materials, such as the Ni-Br complex and Cu-O compounds.

We do not have to take an unnecessarily large number of inner-shell electrons and nuclei explicitly into consideration, or in

other words, we do not have to construct the macroscopic model for electrons in solids from microscopic rules for elementary particles, since the collective properties of solids, constituted of numerous elementary particles, can be quite different from those of individual elementary particles. In this book, it will be shown that simple models, such as the Hubbard and extended Hubbard models, can well describe the experiments on the real strongly correlated materials. This success indicates that these models effectively contain the substance of the complicated many-electron systems, even if they seem too simple.

The electron correlation effects on the x-ray radiation spectrum are also clarified in this book. Generally speaking, the x-ray radiation spectrum has been believed to be constituted of two components, that is Raman and luminescence components. While the radiation energy of the Raman component depends on the incident photon energy, that of the luminescence component hardly depends on the incident photon energy, because of the dissipation process in the transition states. However, there has been no systematic explanation on why and how the x-ray radiation separates into the Raman and luminescence components. We will show that the electron-electron interaction brings about the luminescence component separated from the Raman component in the characteristic x-ray radiation spectrum. The calculated spectra agree well with the experiments on  $\text{YF}_3$  and  $\text{YCl}_3$ .

In addition to the electron correlation effects, phonon fluctuation effects on the soft x-ray radiation spectrum are studied. It will be shown that dissipation through the core hole-phonon coupling also

brings about a significant luminescence component in the soft x-ray radiation spectrum. Furthermore, we will show that the luminescence component strongly reflects the density of states of the valence band electrons, since the core level is localized and its energy dispersion hardly depends on the wavenumber.

The x-ray radiation measurements had been quite difficult for a long time, because the intensity of the second-order radiation was very weak. However, now, the brilliance of the synchrotron radiation is significantly increased, and therefore, the x-ray radiation spectroscopy is obviously widely-accepted every year.

We hope that the x-ray spectroscopy plays a more and more important role to clarify the natures of the new materials, and this book can make a contribution to the theoretical development of the x-ray spectroscopy.