Angle-Resolved Two-Photon Photoemission of Mott Insulator

Takami Tohyama

Institute for Materials Research (IMR)
Tohoku University, Sendai

Collaborators

IMR: H. Onodera, K. Tsutsui, S. Maekawa

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OUTLINE

Introduction

Mott insulator: Copper oxides

Why is the upper Hubbard band important?

Two-photon photoemission (2PPES)

The “$\omega$” and “$2\omega$” processes

The “simultaneous” and “cascade” processes

Angle-resolved 2PPES for insulating cuprates in two dimensions

Pump photon

Zhang-Rice singlet band

Non-bonding oxygen band

Predictions for future experiments
Crystal structures of insulating cuprates

La$_2$CuO$_4$ (two dimension)

Sr$_2$CuO$_3$ (one dimension)

CuO$_2$ plane

Cu$_{2+}$ 3$^d$\(^9\) 1 hole on each $x^2$-$y^2$ orbital

localized spin $\leftrightarrow$ antiferromagnetic exchange interaction

$J \sim 1000$K-2000K
Photo excitation: Band insulator vs. Mott insulator

Band

\[ E \]

\[ \varepsilon_F \]

conduction

electron

\[ k \]

hole

valence

Mott

\[ E \]

\[ \varepsilon_F \]

upper Hubbard

\[ k \]

lower Hubbard

exciton picture

\[ V_{\text{Band}}(r) \]

new concept !

\[ V_{\text{Mott}}(r) \]
Band structure of semiconductors

Si

Ge

GaAs

indirect gap
direct gap

Band structure of Mott insulators: Theoretical prediction

one dimension (14-site \(t-U\))

two dimension (4X4 \(t-t'-t''-U\))

- **direct gap**
- **indirect gap** because of \(t'\) and \(t''\)

Why is the upper Hubbard band (UHB) important?

UHB characterizes the “particle-hole” excitation.

It is necessary to understand its nature for future application of the Mott insulators.

We propose a method to see the momentum-dependent UHB.

Angle-resolved two-photon photoemission
(AR-2PPES)

cf. Inverse photoemission low-energy resolution
Electron-energy loss spectroscopy (EELS)
Resonant inelastic X-ray scattering (RIXS)

[2D cuprates: PRL83, 3705(1999); Science288, 1811(2000)]
Energy diagram for 2PPES

Time-resolved

Energy-resolved

Two-photon photoemission

- Image-potential states at metal surfaces and their decay
  
  **Time, energy- and angle-resolved modes**


- High-Tc cuprate superconductor: \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} \)

  **Time-resolved mode**


  **Energy-resolved mode**


  No experimental works in Mott insulators!
A: excitations from lower-Hubbard band
B: excitations from upper Hubbard band
C, D: excitations perpendicular to CuO$_2$
The “$2\omega$” and “$\omega$” processes

Information on occupied state

\[ E_{\text{kin}} = -e_{\text{OC}} + 2\omega \]

Information on unoccupied state

\[ E_{\text{kin}} = e_{\text{UO}} + \omega \]

Possible to separate the two states from the $\omega$ dependence
Formulation for two-photon photoemission

Three-level model

\[ H = \sum_{\alpha = i, m, f} \epsilon_{\alpha} |\alpha\rangle \langle \alpha| - \mu E(t) \]

\[ \mu = V_{m i} |m\rangle \langle i| + V_{m f} |f\rangle \langle m| + H.c. \]

Optical Bloch equation

\[ \frac{d}{dt} \rho_{\alpha\beta} = -i [H, \rho]_{\alpha\beta} - \Gamma_{\alpha\beta} \rho_{\alpha\beta} \]

\[ \rho = \begin{pmatrix} \rho^{(0)}_{ii} & \rho^{(1)}_{im} & \rho^{(2)}_{if} \\ \rho^{(1)}_{mi} & \rho^{(2)}_{mm} & \rho^{(3)}_{mf} \\ \rho^{(2)}_{fi} & \rho^{(3)}_{fm} & \rho^{(4)}_{ff} \end{pmatrix} \]

\[ \Gamma = \begin{pmatrix} 0 & \Gamma_{im} & \Gamma_{if} \\ \Gamma_{mi} & \Gamma_{mm} & \Gamma_{mf} \\ \Gamma_{fi} & \Gamma_{fm} & \Gamma_{ff} \end{pmatrix} \]

\( \rho \): density operator, where the superscript (#) denotes the order of the electric field.

\( \Gamma \): retaliation rate
**“simultaneous” process**

Virtual excitation to $|m\rangle$

$$\rho_{ii} \rightarrow \rho_{im} \rightarrow \rho_{if} \rightarrow \rho_{mf} \rightarrow \rho_{ff} \Rightarrow I^{(s)}$$

$$I^{(s)}_{2PPE}(E, \omega) = 2\pi \sum_{i,f} \rho^{(0)}_{ii} \left| \sum_m \frac{V_{im} V_{mf}}{\epsilon_m - \epsilon_i - \omega_1 - i\Gamma_{im}} \right|^2 \delta(\epsilon_f - \epsilon_i - \omega_1 - \omega_2) \delta(E - \epsilon_f)$$

$\Gamma_{im}$: phase-relaxation rate

**“sequence” or “cascade” process**

Real excitation to $|m\rangle$

$$\rho_{ii} \rightarrow \rho_{im} \rightarrow \rho_{mm} \rightarrow \rho_{mf} \rightarrow \rho_{ff} \Rightarrow I^{(c)}$$

$$I^{(c)}_{2PPE}(E, \omega) = (2\pi)^2 \sum_{imf} \rho^{(0)}_{ii} \left| \frac{V_{im}}{\Gamma_{mm}} \right|^2 \left| \frac{V_{mf}}{\Gamma_{mm}} \right|^2 \delta(\epsilon_m - \epsilon_i - \omega_1) \delta(\epsilon_f - \epsilon_m - \omega_2) \delta(E - \epsilon_f)$$

$\Gamma_{mm}$: energy-relaxation rate
Density of states for insulating cuprates

Upper-Hubbard band

Lower-Hubbard band

Mixing O2p and Cu3d

Emergence of a bound state:
Zhang-Rice singlet band
Mapping from three-band model to single-band model

- d^{10} state
- Zhang-Rice Singlet

Upper Hubbard band

Lower Hubbard band
$H = -t \sum_{\langle ij \rangle, \sigma} (c_{i,\sigma}^+ c_{j,\sigma} + \text{h.c.}) - t' \sum_{\langle ij' \rangle, \sigma} (c_{i,\sigma}^+ c_{j,\sigma} + \text{h.c.})$

$-t'' \sum_{\langle ij'' \rangle, \sigma} (c_{i,\sigma}^+ c_{j,\sigma} + \text{h.c.}) + U \sum_i n_{i,\uparrow} n_{i,\downarrow}$

$U/t = 10$

**Cuprates in 2D: Ca$_2$CuO$_2$Cl$_2$**

$t = 0.35$ eV, $t' = -0.12$ eV, $t'' = 0.08$ eV
Angle-resolved 2PPES for cuprates

“simultaneous” process

\[
I^{(s)}(\omega_1, \omega_2, E_{\text{kin}}, k) = \sum_F \sum_M \left\langle F \left| c_k | M \right\rangle \left\langle M | j_x | I \right\rangle^2 \frac{E_M - E_I - \omega_1 - i\Gamma_{IM}}{\Gamma_{MM}} \delta(\omega_1 + \omega_2 + E_I - E_F - E_{\text{kin}})
\]

“sequence” or “cascade” process

\[
I^{(c)}(\omega_1, \omega_2, E_{\text{kin}}, k) = \sum_F \sum_M \left\langle F \left| c_k | M \right\rangle \left\langle M | j_x | I \right\rangle^2 \delta \left( E_M - E_I - \omega_1 \right) \times \delta(\omega_1 + \omega_2 + E_I - E_F - E_{\text{kin}})
\]

The spectra are calculated for finite-size clusters such as a 4x4 lattice.

Initial state \( |I\rangle \): the standard Lanczos method

\( I^{(s)}, I^{(c)} \): the correction-vector method based on the conjugate gradient technique

\( \Gamma_{MM} = 2\Gamma_{IM} = 0.4t \), neglecting the pure dephasing
Calculation of spectrum in the second-order process

Correction-vector method

\[
I^{(s)}(\omega_1, \omega_2, E_{\text{kin}}, \mathbf{k}) = \sum_F \left| \sum_M \frac{\langle F | c_k | M \rangle \langle M | j_x | I \rangle}{E_M - E_I - \omega_1 - i\Gamma_{\text{IM}}} \right|^2 \delta(\omega_1 + \omega_2 + E_I - E_F - E_{\text{kin}})
\]

Correction vector:

\[
|\phi\rangle = \frac{1}{H - E_I - \omega_1 - i\Gamma_{\text{IM}}} j_x |I\rangle \quad \Rightarrow \quad (H - E_I - \omega_1 - i\Gamma_{\text{IM}}) |\phi\rangle = j_x |I\rangle
\]

This is evaluated by the conjugate-gradient method.

\[
I^{(s)}(\omega_1, \omega_2, E_{\text{kin}}, \mathbf{k}) = \sum_F \left| \langle F | c_k | \phi \rangle \right|^2 \delta(\omega_1 + \omega_2 + E_I - E_F - E_{\text{kin}})
\]

This is easily calculated by the standard Lanczos algorithm (recursion method).
Calculation of spectrum in the second-order process

\[ I^{(c)}(\omega_1, \omega_2, E_{\text{kin}}, k) = \sum_{F} \sum_{M} \frac{|\langle F | c_k | M \rangle|^2 |\langle M | j_x | I \rangle|^2}{\Gamma_{MM}} \delta(E_M - E_I - \omega_I) \times \delta(\omega_1 + \omega_2 + E_I - E_F - E_{\text{kin}}) \]

\[ \approx \sum_{F} \sum_{M'=1}^{M'_{\text{max}}} \frac{|\langle F | c_k | M' \rangle|^2 |\langle M' | j_x | I \rangle|^2}{\Gamma_{MM}} \delta(E_{M'} - E_I - \omega_I) \times \delta(\omega_1 + \omega_2 + E_I - E_F - E_{\text{kin}}) \]

\[ |M' \rangle: \text{approximate eigenstates with large value of } |\langle M' | j_x | I \rangle|^2, \text{ which are evaluated by the standard Lanczos algorithm } M'_{\text{max}} \approx 20 \]

For each \[ |M' \rangle \], we perform the Lanczos process.
Possible excitation due to the pump photon $\omega_1$

Excitation from Zhang-Rice singlet band

$\omega_1 \sim 2-3\,\text{eV}$

Current operator in the Hubbard model

$$j_x = i \sum_{\mathbf{k},\sigma} \alpha_{\mathbf{k}} c_{\mathbf{k},\sigma}^{\dagger} c_{\mathbf{k},\sigma}$$

$$\alpha_{\mathbf{k}} = -2t \sin k_x - 4t' \sin k_x \sin k_y + 2t'' \sin 2k_x$$
Excitation from Zhang-Rice band

4x4 Hubbard model

$U = 10t$
$t' = -0.343t$
$t'' = 0.229t$

Absorption spectrum

$\omega$

Excitation from Zhang-Rice band

$k = (\pi, 0)$
Single-particle excitation $A(\mathbf{k}, \omega)$ at half filling

Momentum dependence of $I^{(s)}$ at the two photon energies

$\omega_1 = 6t$

"2\omega"

Global feature is similar to that of LHB.

$\omega_1 = 9t$

"\omega"

Global feature is similar to that of UHB, but it is difficult to identify the bottom of UHB due to diffusive features.
Possible excitation due to the pump photon $\omega_1$

Excitation from non-bonding band

We assume no dispersion of NB and no interactions with other bands.

$\omega_1 \sim 4-5\text{eV}$

Electron-addition operator in the Hubbard model

$$j_x = \sum_{k,\sigma} \beta_k c_{k,\sigma}^+ b_{k,\sigma}$$

$$\beta_k = C \frac{\cos(k_x/2) \sin(k_y/2)}{\sqrt{1 - (\cos k_x + \cos k_y)/2}}$$

$$C = 2d_{\text{Cu-O}} T_{pd}$$

Momentum dependence comes from the construction of Wannier orbital, following by Zhang and Rice.
Excitation from non-bonding band

$A(k, \omega)$ in UHB

$\omega_1 = 2.4t + \varepsilon_p$

$20$-site $t$-$t'$-$t''$-$J$ model

$U = 10t$, $t' = -0.343t$, $t'' = 0.229t$

AR-2PPES: $I^{(s)}$

Emission from the $(0, \pi)$ state.

additional structures

"spin-wave" excitation

Absence in the spectral function

$|I\rangle$: $N$ (half-filling)

$|M\rangle$: $N+1$

$|F\rangle$: $N$
With increasing $\omega_1$, the highest-energy position follows UHB dispersion, but accompanied with the spin-related excitation.
Experimental conditions to detect the bottom of UHB at \((\pi,0)\)

**Maximum kinetic energy of photoelectron from the bottom of UHB**

\[
E_{\text{kin}}^{\text{max}} = \frac{E_{\text{gap}}}{2} + \omega_2 \\
E_{\text{gap}} = 4.8t \sim 2\text{eV}
\]

(i) From Zhang-Rice band \(\rightarrow\) Max. intensity appears at \(\omega_1\sim9t\sim3\text{eV}\).

If \(\omega_1 = \omega_2\), then \(E_{\text{kin}}^{\text{max}} \sim 4\text{ eV}\).

(ii) From non-bonding band \(\rightarrow\omega_1 = 2.4t + \varepsilon_p \sim 5\text{ eV}\).

If \(\omega_1 = \omega_2\), then \(E_{\text{kin}}^{\text{max}} \sim 6\text{ eV}\).

**Minimum kinetic energy necessary to reach \((\pi,0)\)**

From

\[
\frac{\hbar^2}{2m} k_{\parallel}^2 = (E_{\text{kin}} - E_{\text{vac}}) \sin \theta \quad , \quad E_{\text{kin}}^{\text{min}} \sim 6 \text{ eV}
\]

using \(d_{\text{Cu-Cu}} \sim 0.4\text{ nm}\) and \(E_{\text{vac}} \sim 4\text{ eV}\).

The case (ii) critically satisfies this condition.

If the condition \(\omega_1 < \omega_2\) is used, it is easy to observe the bottom of UHB.
We proposed angle-resolved two-photon photoemission spectroscopy (AR-2PPES) as a new technique to detect the location of the bottom of the upper Hubbard band (UHB) in two-dimensional insulating cuprates.

When the pump photon excites an electron from the Zhang-Rice singlet band, the bottom of UHB is less clear, because of diffusive features in the spectra.

When the pump photon excites an electron from the non-bonding band, the bottom of UHB can be clearly identified.

In addition to information of UHB, additional excitations related to spin degree of freedom emerge in the spectrum, which are characteristic of strongly correlated system.

To detect the bottom of UHB at $(\pi,0)$, it may be necessary to use either the excitation from non-bonding band or two photons with different energies.