interaction of the outgoing photo electron with the remaining hole) and second order response theory one obtains an expression of the Fermi golden rule form for the steady photo current (Schaich and Ashcroft, 1971; Bansil and Lindroos, 1999),

$$I(E_i, \hbar\omega) = \frac{2\pi e}{\hbar} \sum_{i,f} \left|\langle \psi_f|\hat{V}|\psi_i\rangle\right|^2 \delta(E_f - E_i - \hbar\omega)\,. \tag{5.22}$$

Here, ψ_i (ψ_f) are initial (final) states with energy E_i (E_f) of the semi-infinite solid, $\hat{V} = -e(\hat{\boldsymbol{p}} \cdot \boldsymbol{A} + \boldsymbol{A} \cdot \hat{\boldsymbol{p}})/(2mc)$ is the interaction with the electromagnetic field, and full initial as well as empty final states have been assumed. For localized electron orbitals, both the dipole selection rules and the transport to the surface determine the matrix elements $\langle \psi_f|\hat{V}|\psi_i\rangle$. Neglecting both its structure and assuming a featureless continuum of final states one can draw a direct connection between PES and the single-particle spectrum $A(E) = -\frac{1}{\pi}\mathrm{Im}\, G(E)$ (at temperature T):

$$I(E) \propto \int_{-\infty}^{\infty} \mathrm{d}E'\, A(E') \frac{1}{1 + \mathrm{e}^{-(E'-\mu)/(k_B T)}} R_\Delta(E - E') + B \tag{5.23}$$

Here, $R_\Delta(E - E') = \mathrm{e}^{-(E-E')^2/(2\Delta^2)}/\sqrt{2\pi\Delta^2}$ is a Gaussian broadening function associated with the experimental resolution,[17] and B a background contribution arising from photo electrons which have been inelastically scattered within the solid. We stress that (5.23) is at best a crude approximation for contributions arising from orbitals within a few top layers of the material. Photo electrons generated in the bulk cannot escape since the typical mean free path for photo electrons in the energy range of 10 to 100 eV in crystals is only a few nanometers. Within such a close distance to the surface, however, surface effects may be important, at least quantitatively. Partially, the importance of final-state and transport effects can be assessed by measuring the same spectra using different incident photon energies.

In Fig. 5.7, we compare theoretical PES calculated via (5.23) for $La_{1\text{-}x}Sr_xTiO_3$ with a broadening width $\Delta = 0.3$ eV (and $B = 0$) with two experimental results. In one experiment, polycrystalline samples of $LaTiO_{3.03\pm0.01}$, characterized by thermogravimetry analysis, were cooled down to $T = 80$ K, scraped in situ, and irradiated with photons of the energy $h\nu = 48$ eV. Here, the stated resolution is $0.2 - 0.3$ eV (Fujimori, Hase, Namatame, Fujishima, Tokura, Eisaki, Uchida, Takegahara and de Groot, 1992). In a more recent experiment, PES for the nominally same material grown by the floating-zone method were measured at 23 K and 150 K using a He discharge lamp ($h\nu = 21.2$ eV) with a nominal resolution of 30 meV (Yoshida et al., 2002).[18] Qualitatively, good agreement is observed for $U = 5$ eV, the strongest interaction value being shown in Fig. 5.7: both the peak position at -1.5 eV $\lesssim E \lesssim -1$ eV and the suppression of spectral weight near the Fermi energy are

[17] The spectra are also Lorentzian broadened by the finite lifetime of the final states, i.e., the decay of the photo holes left behind in the bulk.

[18] Note that here the authors claim to see antiferromagnetic order even for the doped system with $T_N \approx 112$ K. Thus, only the measurement at $T = 150$ K corresponds to the paramagnetic phase modeled in our simulations.