Real-Space Orbitals from Angle-Resolved Photoemission

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Abstract

The frontier electronic orbitals of molecules are the prime determinants of the respective compounds' chemical, electronic, and optical properties. Several experimental methods have enabled imaging of molecular orbitals under certain conditions. As has been shown in a number of recent publications, angle-resolved photoemission (ARPES) intensity maps of organic molecular layers are related to the Fourier transform of the initial state molecular orbital. However, the missing phase information impedes the back-transformation of the momentum maps of the orbital into real space. Here, we show how the absent phase information can be retrieved by applying an unbiased, iterative procedure which takes the experimental ARPES maps as input and only assumes a region of spatial confinement of the orbital. Thereby we obtain real-space images of several molecular orbitals for two proto-typical pi-conjugated molecules: the LUMO, HOMO, and HOMO-1 of pentacene, and the LUMO and HOMO of PTCDA. Our technique further emphasizes the capabilities of ARPES looking at real-space distributions of wave functions of adsorbed molecules thereby complementing data obtained from scanning probe methods.

Computation of Photoemission Intensity

We use the so called one-step-model, whereat the excitation occurs in a single step an from initial Bloch state to a so called "time reversed LEED state" final state. The ARPES intensity $I(\theta,\phi,E_{kin})$ is then given by a Fermi golden rule formula (1):

$$I(\theta, \phi; E_{kin}) \propto \sum_i \left| \langle \psi_f^*(\theta, \phi; E) | \mathbf{p} \cdot \mathbf{A} | \psi_i \rangle \right|^2 \times \delta\left(E_i + \Phi + E_{kin} - \hbar\omega\right)$$

By approximating the final state by a free electron state, the evaluation of the matrix elements is greatly simplified and turns out to be proportional to the Fourier transform of the initial state wave function (2). Thus, the square root of the measured photocurrent is proportional to the absolute value of the orbital in reciprocal space. Thereby, we have to take a hemispherical cut through the Fourier transformed molecular orbital with a radius proportional to the square root of the kinetic energy.
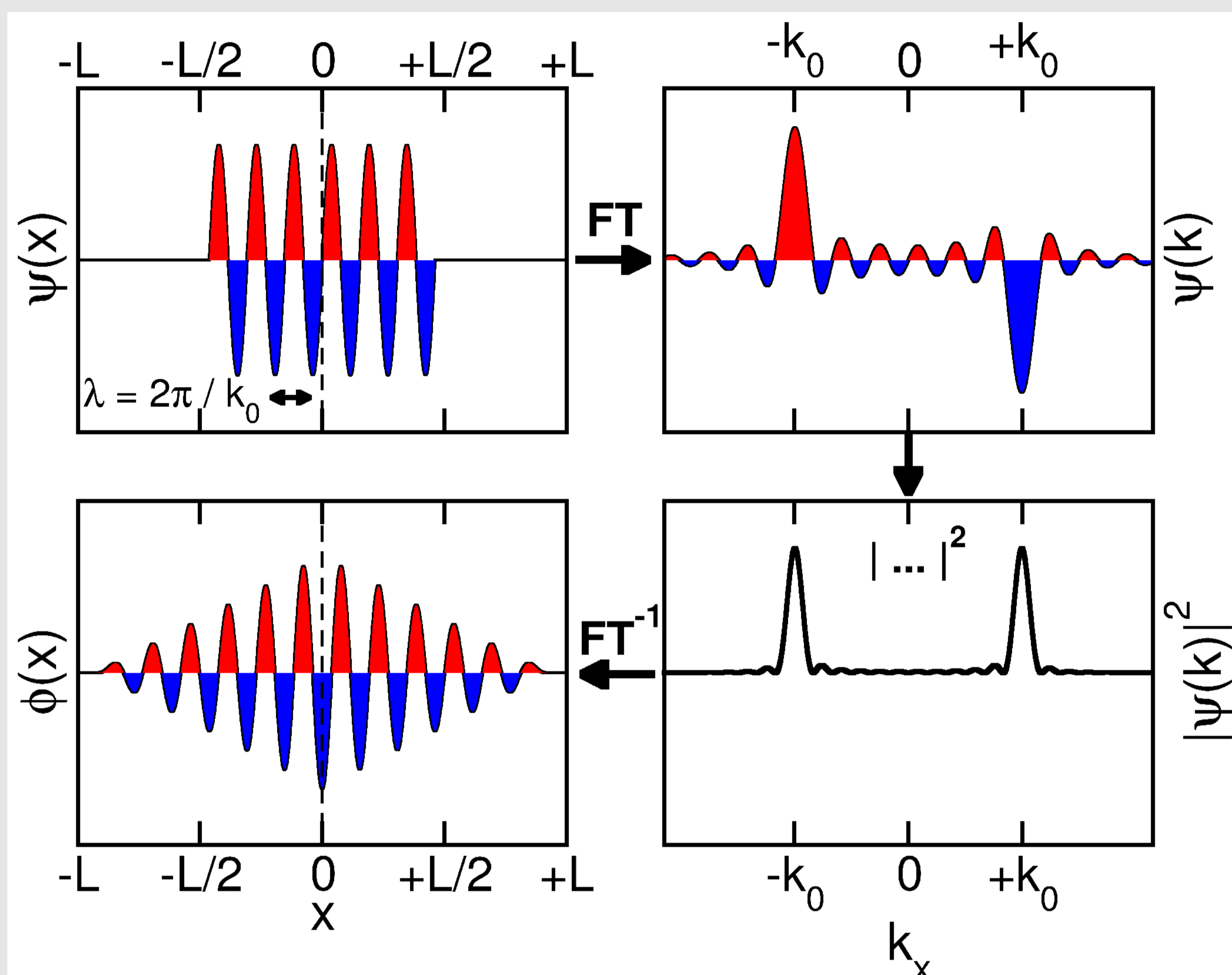
1. The Phase Problem

Illustration of the phase problem for a 1D-wave function. A model 1D wave function of sine-wave shape with wave number k_0 and spatial extent L (top left) is Fourier transformed (top right). When taking the absolute value in reciprocal space (bottom right) and subsequently transforming back to real space, the resulting function generally has the wrong phase and a spatial extent which is twice as large as the original wave function (bottom left).

2. Recovery of the Phase
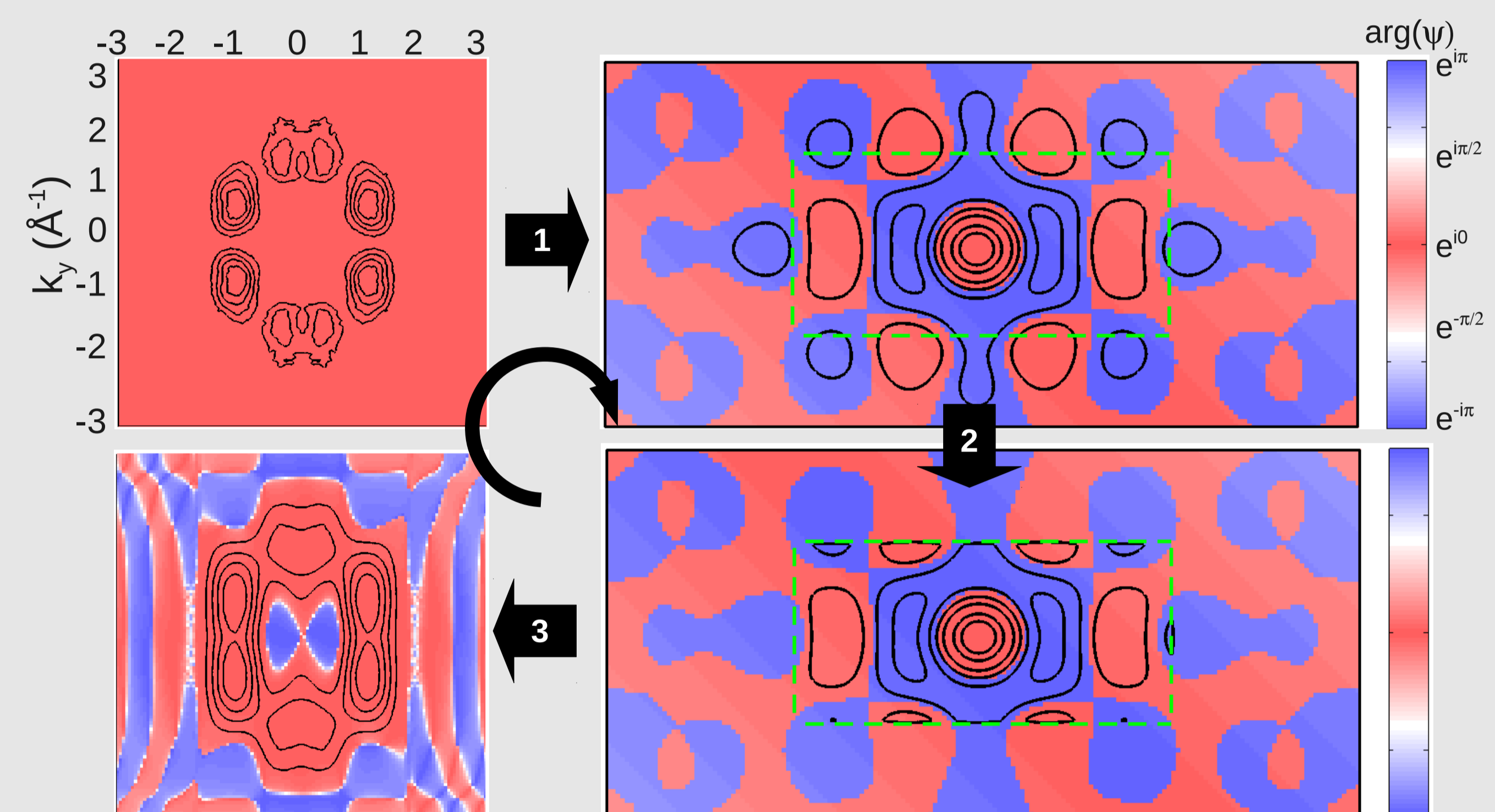
Iterative procedure to recover the phase information. The starting point is the experimental ARPES map (top left, HOMO-map of PTCDA/Ag(110)). Note that isolines denote the absolute value while the complex phase is shown as color map. In a first step, an inverse Fourier transform leads to the real space function shown in the top right. Now, the wave function outside a pre-defined spatial region (green rectangle) is diminished by a factor of ten (bottom right). A subsequent Fourier-transform leads to the image at bottom left. Note that for the next iteration, only the *phase* (color map) of this image is kept, while the *absolute value* (isolines) is restored according to the measured ARPES map.
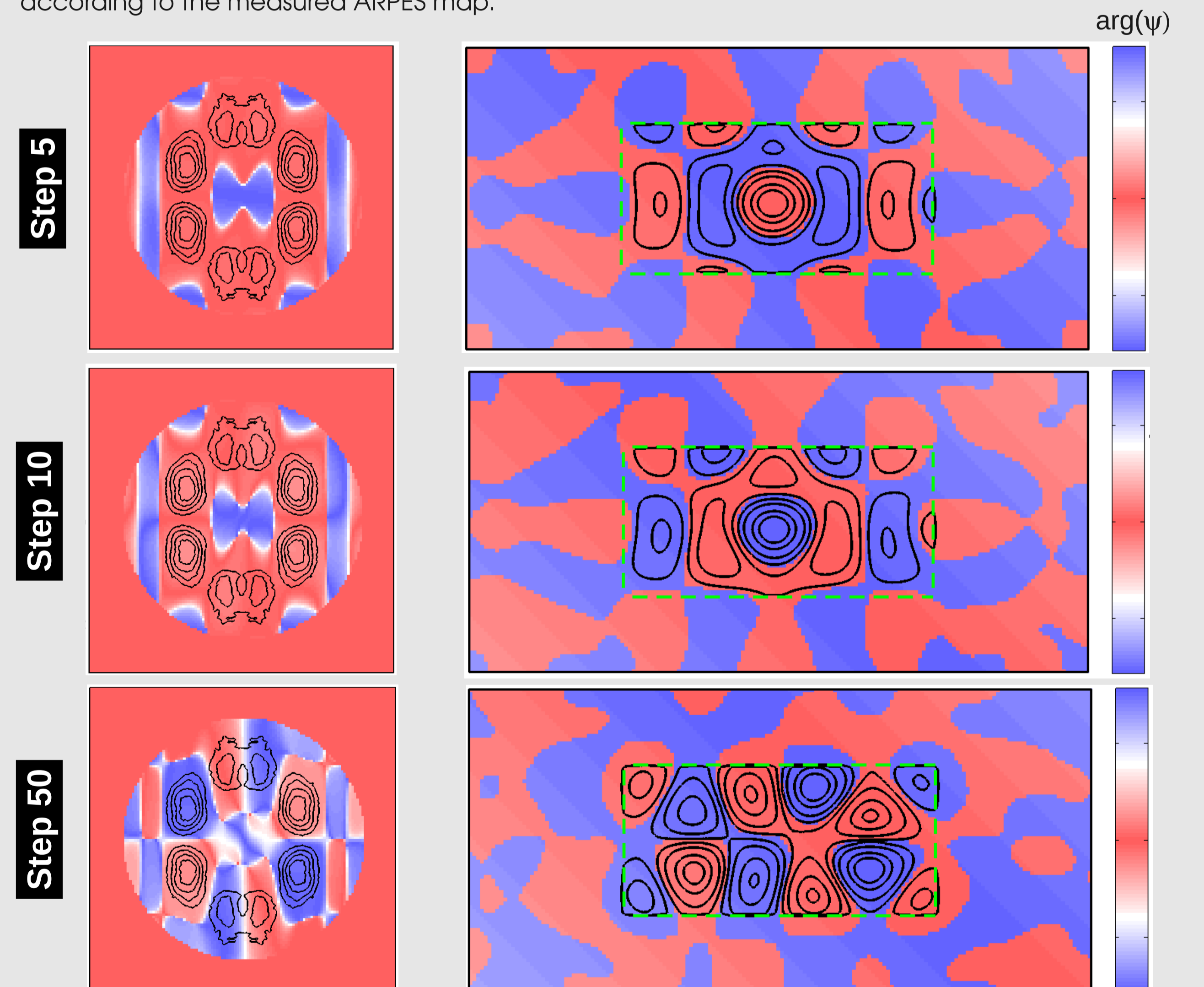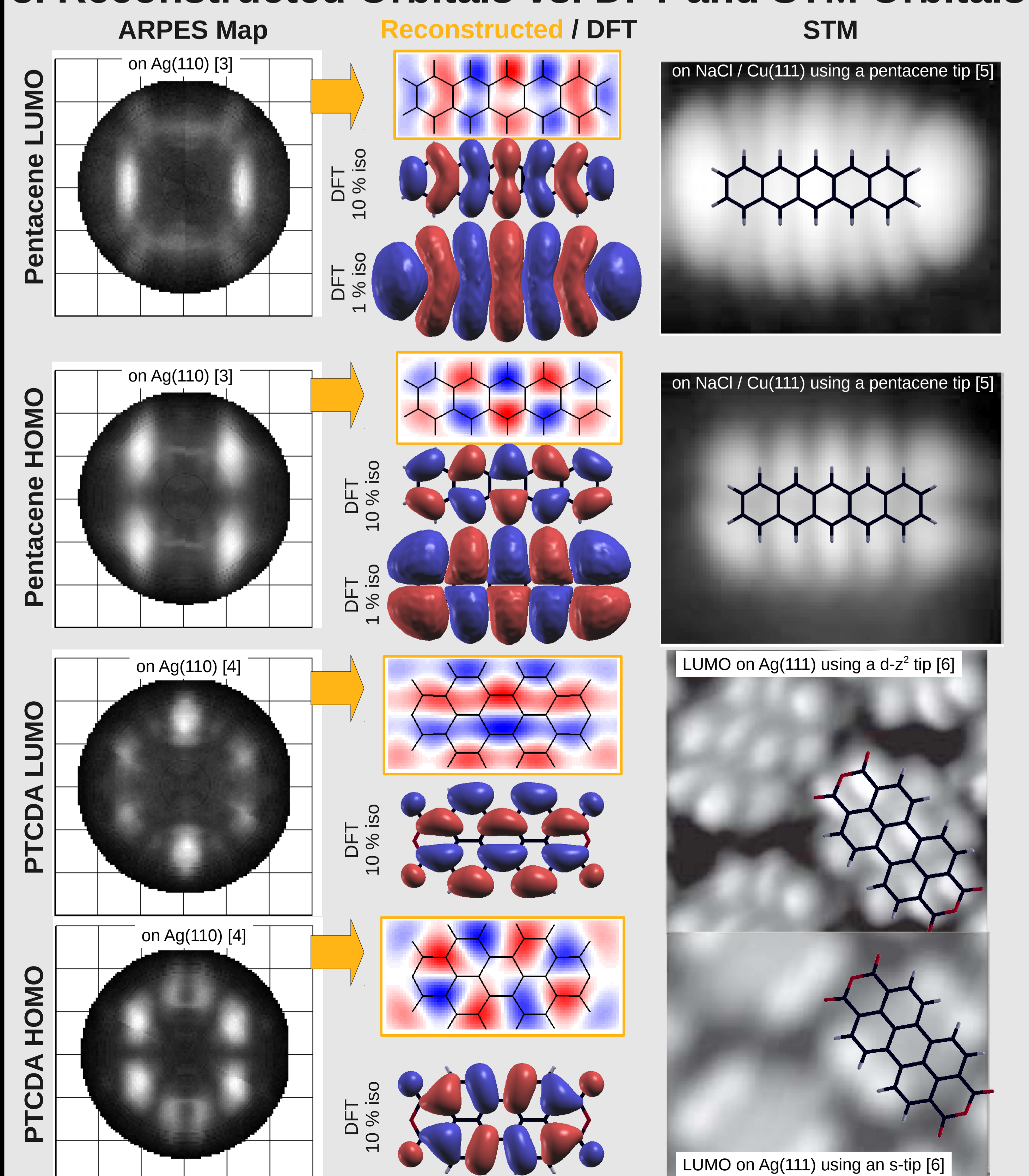

Gradual evolution of the phase during iterative phase recovery. Three steps during the iterative procedure are shown for reciprocal space (left column) and real space (right column).
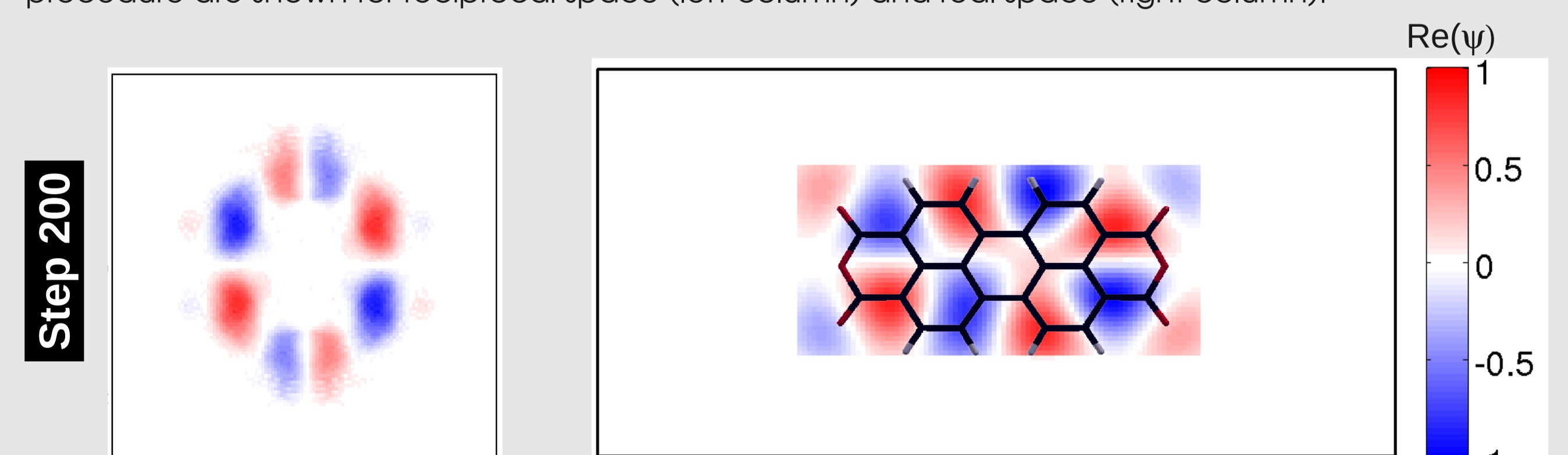
Representation of orbital. After convergence (200 steps) has been reached, the orbital information is presented in a more familiar way, by taking the real part of the wave function shown as a density plot, red indicating positive, blue negative values.

3. Reconstructed Orbitals vs. DFT and STM Orbitals

ARPES Map | Reconstructed / DFT | STM

Pentacene LUMO — on Ag(110) [3] — on NaCl / Cu(111) using a pentacene tip [5]
Pentacene HOMO — on Ag(110) [3] — on NaCl / Cu(111) using a pentacene tip [5]
PTCDA LUMO — on Ag(110) [4] — LUMO on Ag(111) using a d-z^2 tip [6]
PTCDA HOMO — on Ag(110) [4] — LUMO on Ag(111) using an s-tip [6]

References

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