Photoemission orbital tomography of excitons in organic semiconductors

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Excitons are realizations of a correlated many-particle wave function, specifically consisting of electrons and holes in an entangled state. Excitons occur widely in semiconductors and are dominant excitations in semiconducting organic and low-dimensional quantum materials. To efficiently harness the strong optical response and high tuneability of excitons in optoelectronics and energy-transformation processes, access to the full wavefunction of the entangled state is critical, but has so far been limited.

In our work [1], we show how time-resolved photoemission momentum microscopy can be used to gain access to the entangled wavefunction and to unravel the exciton's multiorbital electron and hole contributions. For the prototypical organic semiconductor buckminsterfullerene C_{60}, we exemplify the capabilities of exciton tomography and achieve unprecedented access to key properties of the entangled exciton state including localization, charge-transfer character, and ultrafast exciton formation and relaxation dynamics.

First, we shed light on the multiorbital contributions of excitons in C_{60}. Depending on the excitation energy and material properties, the exciton components may be spread over multiple energetically distinct molecular orbitals, and we demonstrate how the unique sensitivity of photoemission orbital tomography can be employed to probe the multiorbital nature of the hole component.

Second, we analyze the momentum distribution observed in photoemission orbital tomography in order to characterize the spatial properties of the exciton. This provides access to the exciton's localization, charge separation and inter-molecular charge transfer. For C_{60} specifically, we find that only the optically-active exciton at about 2.8 eV is of charge-transfer nature, while the lower-lying excitons are of Frenkel nature.

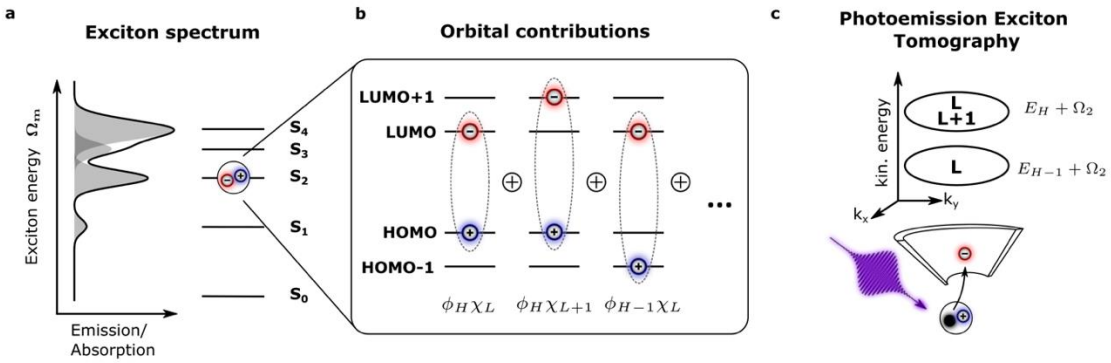

Fig. 1. The optical response of many semiconducting materials is described by the excitation of excitons. a) In the exciton picture, each excited state is described by an exciton energy Ω, which (for bright excitons) can be measured by optical spectroscopy. b) At the orbital level, however, each exciton is built up by an entangled sum of electron-hole pairs. In this description, the sum of orbital contributions provides complete access to the spatial properties of the exciton. c) Photoemission exciton tomography can be used to disentangle the multiple orbital contributions to the exciton.

[1] W. Bennecke, A. Windischbacher, D. Schmitt, J. P. Bange, R. Hemm, C. S. Kern, G. D`Avino, X. Blase, D. Steil, S. Steil, M. Aeschlimann, B. Stadtmueller, M. Reutzel, P. Puschnig, G. S. M. Jansen, S. Mathias, arXiv:2303.13904 (2023)