

## Advances in the Theory of Excitation of Correlated Materials

**Summary:** The absorption of light by materials proceeds through the formation of excitons, which are states in which an excited electron is bound to the valence hole it vacated. Understanding the structure and dynamics of excitons is important, for example, to developing technologies for light-emitting diodes or solar energy conversion. Recently, teaming up with X-ray experimentalists, the CMSN PCSCS collaborative research team has made important progress in resolving a decades-long debate on the nature of excitons in alkali halides by mapping out in detail their space-time propagation.

The excitation of correlated materials has been one of the grand challenges in the scientific community for decades. The difficulty originates from the strong interactions between the electrons in such materials, which modulate significantly the space and time propagation of the excitations beyond the free particle picture. One well known example is the formation of excitons, a bound pair of excited electrons and the holes left in the electronic system. Depending on the strength of the interaction, the binding between the electron and the hole can sometimes dramatically lower the exciton energy, shrink its size, and alter its mobility.

Typically, excitons are characterized into two limiting cases: weakly bound Wannier excitons [1] and strongly bound Frenkel excitons [2]. The former is formulated theoretically as an electron and hole orbiting each other at large distance, having small binding energy and good mobility. By contrast, the latter is constructed theoretically as a local intra-atomic excitation that occasionally hops to neighboring atomic sites. Interestingly, the first experimentally observed excitons (in the alkali halides NaCl, KBr, and LiF) do not quite fit into either picture, and their nature has thus led to a long-standing debate [3,4]. These excitons are strongly bound, similar to the Frenkel picture, but the excited electron (residing in alkaline  $p$  orbitals) and hole (residing in Halogen  $s$  orbital) are never on the same atom, thus inconsistent with Frenkel's construction.

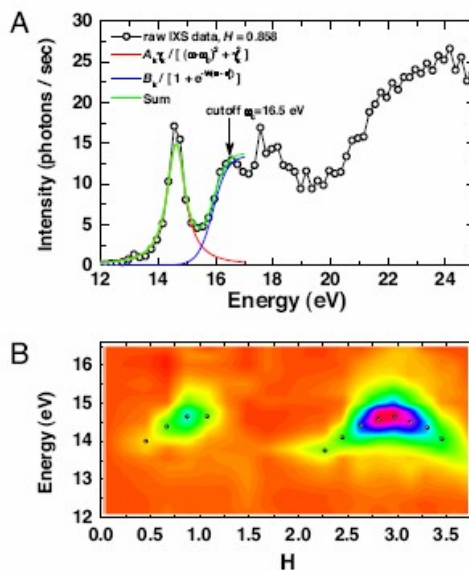


Fig. 1. Inelastic X-ray scattering spectrum of LiF. Upper panel illustrates the procedure to isolate the exciton signature from the rest of the excitations. Lower panel presents the measured (momentum, energy) dispersion of the exciton. Notice the very structured spectral weight focusing around momentum ( $H, 0, 0$ ) with  $H = 0.8$  and  $3$ . This information is then transformed to (space, time) domain to give exciton shape, size and space-time propagation.

This conceptual difficulty actually reflects a very general theoretical challenge in a large family of functional materials called “charge transfer” insulators, in which the low-energy excitations involve an electron and hole on different atoms, with kinetic energy of similar scale to the local interactions. Well known examples include cuprates with high temperature superconductivity, manganites with colossal magneto resistivity, and cobaltates with high thermoelectricity.

A broad PCSCS collaboration of eleven scientists from seven institutions has been working together to tackle this challenging problem of describing correlated charge-transfer insulators with the development of new theoretical and computational approaches. In a recent study [5], teaming up with X-ray experimentalists from University of Illinois and Advanced Photon Source, this PCSCS team has resolved the long standing problem of characterization of excitons of charge-transfer insulators, by mapping out the size, shape, and space-time propagation of the exciton in LiF.

Experimentally, direct observation of excitons is performed in reciprocal space via inelastic scattering, as shown in Fig. 1. A carefully designed procedure is then applied to transform the information into the space-time domain. Within the scale defined by the resolution, the size, shape, and the space-time propagation of the exciton can be mapped out.

Theoretically, the subtle charge transfer nature was treated using a new computational “super atom” approach. As illustrated in Fig. 2, local orbitals (so-called Wannier orbitals) in the crystal can be constructed [6,7] to fully capture the Hilbert space of the low-energy electron (Li-s) and hole (F-p) orbitals. By construction, the electron orbitals can be chosen to be centered at the F sites, forming a larger F-s-like orbital [8,9]. Effectively, this method transforms the charge transfer insulator into a Mott insulator consisting of only “super atoms” F that contains additional s-orbitals. In this approach, a large number of leading kinetic and potential effects can be encapsulated within a single super-atom, allowing an affordable many-body solution.

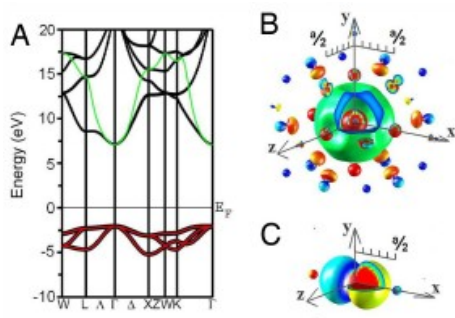


Fig. 2. Theoretical construction of Wannier functions for the super atom, including F-p orbitals in [-2,5] eV and Li-s orbitals around in [5,18] eV. Notice the Li-s is centered at F site by construction, as additional F-s orbital in the super F atom.

The description of the physics of strongly bound charge-transfer exciton now becomes that of an effective Frenkel exciton of the super atom. Indeed, as shown in Fig. 3A, taking the product of only a single pair of electron and hole orbital, the shape of the exciton in real space can already be obtained quite accurately. The precision is evident in reciprocal space, where the shape of the exciton (c.f. Fig. 3B and 3C) agrees quite well with the experimentally observed structured spectral weight.

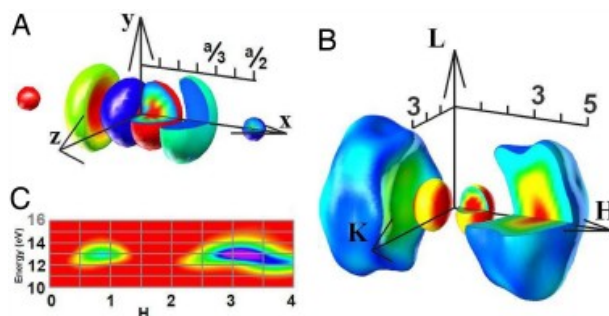


Fig. 3. Theoretical shape of the exciton in real space (A) and in reciprocal space (B). The latter produce the experimental spectral weight around  $H=0.8$  and  $3.0$ . (C) shows the theoretical dispersion.

With this effective Frenkel exciton picture, the propagation of the exciton can be estimated via hopping to neighbor sites. The theoretical team thus introduced a general-purpose concept of exciton kinetic hopping kernel [10] to capture both the propagation and decay into higher energy excitation. This leads to a very simple yet accurate Frenkel description of the complicated exciton spectra, as shown by comparing Fig. 3C with Fig. 1B.

This joint experimental and theoretical study, within the DOE Computational Materials Science Network, resolved an old controversy about strongly bound excitons in the alkali halides, by proposing a practically very useful theoretical concept of super atoms to treat the complications concerning charge transfer insulators. Further applications and extensions of this new theoretical method are expected to improve our basic understandings of excitations in correlated charge-transfer materials.

## REFERENCES

1. G. H. Wannier, Phys. Rev **52**, 191 (1937).
2. J. Frenkel, Phys. Rev. **37**, 17 (1931).
3. R. Hilsch and R. W. Pohl, Z Physik 48, 384 (1928).
4. N. F. Mott, Trans Faraday Soc 34, 500 (1938).
5. P. Abbamonte et al., PNAS 105, 12159 (2008).
6. Wei Ku, H. Rosner, W. E. Pickett, and R. T. Scalettar, Phys. Rev. Lett. **89**, 167204 (2002).
7. W. Yin, D. Volja, and Wei Ku, Phys. Rev. Lett. **96**, 116405 (2006).
8. W.-G. Yin and Wei Ku, unpublished <cond-mat/0702469>.
9. C.-C. Lee and Wei Ku, unpublished.
10. C.-L. Yeh, H.-C. Hsueh, and Wei Ku, unpublished.