

CMSN



Newsletter

Newsletter of the
*Computational Materials
Science Network*

Vol. 5, Number 3
Spring 2009

In this issue:

Research Highlight

- Advances in the Theory of Excitation of Correlated Materials

Conferences & Workshops

- Details from the Multiscale Simulation of Thermo-mechanical Processes in Irradiated Fission-reactor Materials Spring Coordination Meeting
- Details from Predictive Capability for Strongly Correlated Systems Fall Coordination Meeting

CMSN News

CMSN Information



Computational Materials Science Network
sponsored by the U.S. Department of Energy
Division of Basic Energy Sciences
*Coordinated and administered at the
Department of Physics
University of Washington, Seattle*



Research Highlight

In this issue of the *CMSN Newsletter*, we feature a research highlight from the Predictive Capability CRT: “Advances in the Theory of Excitation of Correlated Materials.”

Advances in the Theory of Excitation of Correlated Materials

PREDICTIVE CAPABILITY FOR STRONGLY CORRELATED SYSTEMS CRT

WEI KU AND PETER ABBAMONTE¹

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, for 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* orbitals) are never on the same atom, thus inconsistent with Frenkel’s construction.

¹ Adapted from full article, available at <http://www.pnas.org/cgi/doi/10.1073/pnas.0801623105>

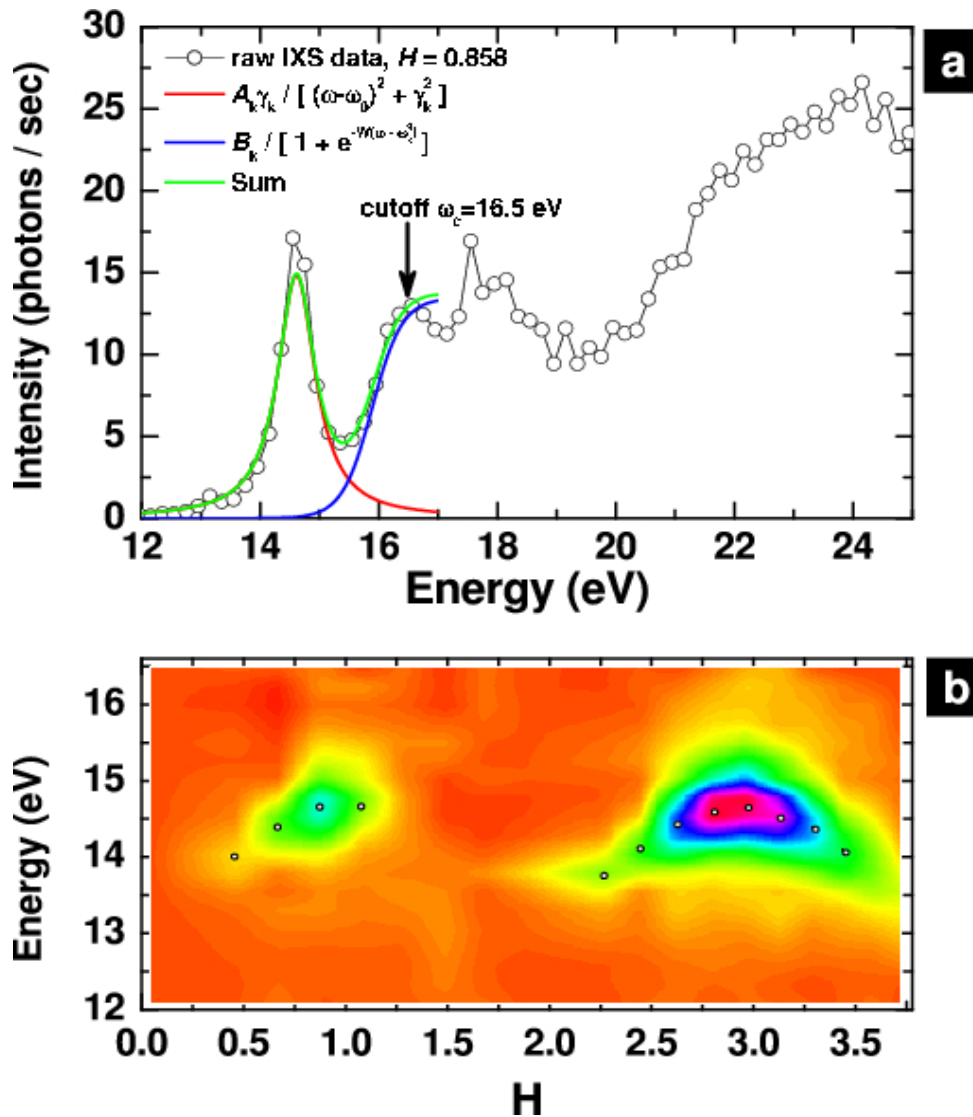


Fig. 1: Inelastic x-ray scattering spectrum of LiF. Upper panel illustrates the procedure to isolate the exciton signature from the rest of the excitations. Lower panel presents the measured (momentum, energy) dispersion of the exciton. Notice the very structured spectral weight focusing around momentum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

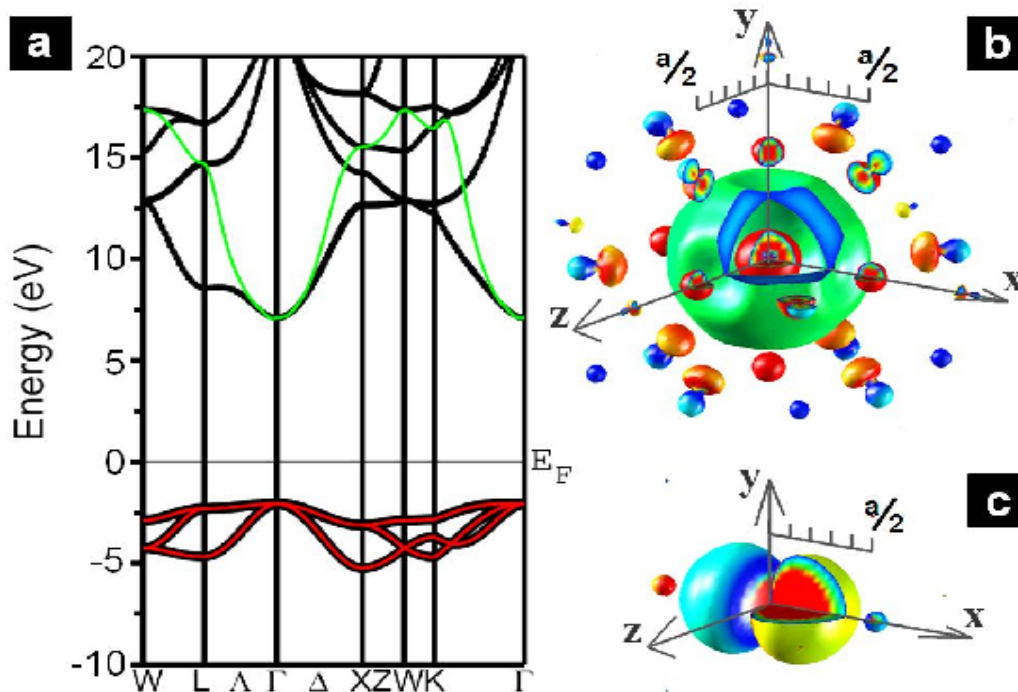
This conceptual difficulty actually reflects a very general theoretical challenge in a large family of functional materials called “charge-transfer” insulators, in which the low-energy excitations involve an electron and hole on different atoms, with kinetic energy of similar scale to the local interactions. 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, with the development of new theoretical and computational approaches, to tackle this challenging problem of describing correlated charge-transfer insulators. In a recent study [5], teaming up with x-ray experimentalists from the 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 (“super” fluorine), 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. Left panel shows the electronic band structure (black lines) and the subspace used to construct F-*p* Wannier orbitals (illustrated in panel C) in the range of [-2,5] eV (red lines) and Li-*s* Wannier orbitals (panel B) in the range of [5,18] eV (green lines). Notice the Li-*s* is centered at the F site by construction, as an additional F-*s* orbital in the super F atom.*

The description of the physics of a 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 orbitals, 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.

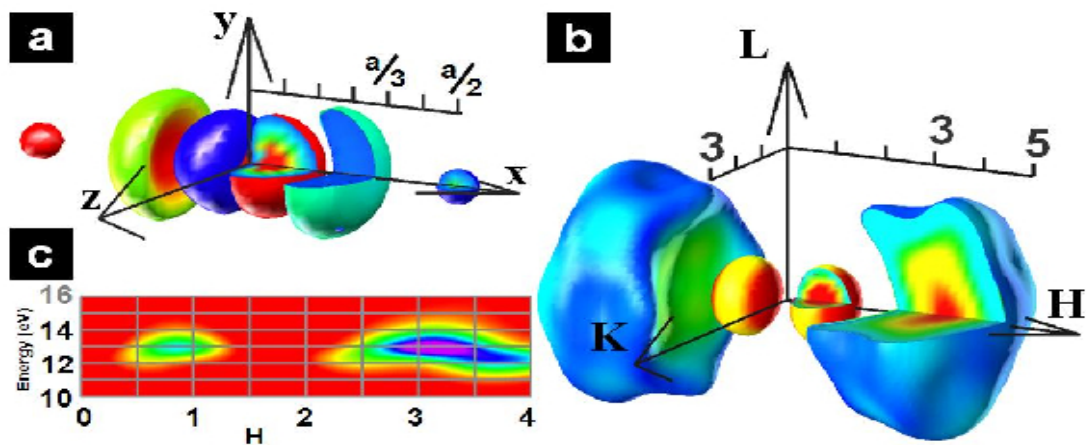


Fig. 3. Theoretical shape of the exciton in real space (A) and in reciprocal space (B). The latter produces the experimental spectral weight around $H = 0.8$ and 3.0 . (C) Shows the theoretical dispersion.

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, has 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 Phys. **48**, 384 (1928).
- [4] N. F. Mott, Trans. Faraday Soc **34**, 500 (1938).
- [5] P. Abbamonte, T. Graber, J. P. Reed, *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.

CMSN News

We expect to be putting out a call for proposals sometime this summer for the formation of new Cooperative Research Teams. Please check the CMSN web site (www.phys.washington.edu/~cmsn) periodically this summer for updates and further information.

Conferences and Workshops

- Information on the Multiscale Simulation of Thermo-mechanical Processes in Irradiated Fission-reactor Materials CRT Spring Coordination Meeting: <http://phillpot.mse.ufl.edu/cmsn/ufmarch2009.html>
- Details from the Predictive Capability for Strongly Correlated Systems CRT Fall Coordination Meeting:

On November 14-16 2008 the Predictive Capabilities for Strongly Correlated Systems CMSN Cooperative Research Team gathered at Oak Ridge National Laboratory. Experimental overviews on correlation physics of the cuprate superconductors, iron pnictide and heavy fermions were presented, along with discussions of the existing results and future prospects for neutron and inelastic x-ray scattering on quantum materials. Theoretical presentations included the topics of graphene, magnetism and superconductivity in iron pnictides, pseudogap physics, transition-metal oxides, plutonium, dense hydrogen, and the Yb valence transition.

Further information is available at:

<http://www.physics.ucdavis.edu/~savrasov/CMSN2008/Agenda.pdf>

Please consult the CMSN website for updated information on conferences and workshops, at <http://www.phys.washington.edu/~cmsn/>.

CMSN Information

CMSN's teams, oversight, and administration are listed below. Further information can be found at <http://www.phys.washington.edu/~cmsn>.

Cooperative Research Teams

Leaders

Dynamics and Cohesion of Materials
Interfaces and Confined Phases Under
Stress

Mark Asta (University of California at
Davis), Alain Karma (Northeastern),
and Anthony Rollett (Carnegie-
Mellon)

Predictive Capability for Strongly
Correlated Systems

Richard Scalettar and Warren Pickett
(UC-Davis)

Multiscale Simulation of Thermo-
mechanical Processes in Irradiated
Fission-reactor Materials

Dieter Wolf (INL) and Simon Phillpot
(University of Florida)

Resonant Inelastic X-Ray Scattering

Arun Bansil (Northeastern
University), Jim Freericks
(Georgetown University), Bob
Markiewicz (Northeastern
University), Michel van Veenendaal
(Northern Illinois University and
Argonne National Laboratory)

Predictive Modeling of the Growth and
Properties of Energy-Relevant Thin
Films and Nanostructures

Kai-Ming Ho (University of Iowa and
Ames Laboratory) and Zhenyu Zhang
(University of Tennessee and Oak
Ridge National Laboratory)

CMSN Oversight

CMSN Scientific Oversight Committee

Ellen Stechel (chair) (Sandia)
Samuel Trickey (Florida)
Juan Sanchez (University of Texas-
Austin)
Michael Weinert (University of
Wisconsin-Milwaukee)
Roberto Car (Princeton)

CMSN Coordinators

John J. Rehr (University of
Washington)
George F. Bertsch (University of
Washington)

CMSN Steering Committee

Ellen Stechel (Sandia)
Bruce Harmon (Ames Lab)

CMSN DOE Contact

Michael Lee (DOE-BES)

CMSN Editor & Administration
Department of Physics
University of Washington
Box 351560
Seattle, WA 98195-1560
Phone: (206) 616-3604
Fax: (206) 543-9523
Email: cmsn@phys.washington.edu

Rosemary Sult (University of
Washington)

For inquiries regarding CMSN, the CMSN Teams, the Newsletter and Newsletter submissions, send email to cmsn@phys.washington.edu. Contact information and other details can be found on the web at <http://www.phys.washington.edu/~cmsn>