Probing Fundamental Physics of Strongly Correlated Quantum Electron and Biomolecular Systems using LCLS-SLAC (both X-ray and e-beam) Facility

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I. Correlated Electron Physics (Hasan, Ong)

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Real-time observation of superconducting (Cooper) pair formation

II. Biomolecular physics (Austin, Hasan)

Protein Dynamics & Folding

Techniques of Interest

Inelastic X-ray Scattering (time-averaged flux)
X-ray Transient Grating Spectroscopy (XTGS)
Electron Spectroscopy under Pulsed Magnetic Field (LCLS e-beam)

Complex phenomena in condensed matter systems continues to be a major theme of physics in the 21st century. Steady improvements in materials quality and synthesis techniques have led to faster discovery of qualitatively new classes of universalities in physics. In case of quantum electron physics, many-body aspects as realized in the quantum hall effect, low dimensional magnetism and high temperature superconductivity have the potential to fundamentally change our view of the physical world and significantly impact the technology as well. Photon-in electron-out and photon-in photon-out spectroscopies have proven to be fundamental in understanding the complex electron or molecular behavior in solids. Hence, pushing the limits of inelastic scattering or X-ray time correlation spectroscopy or photoelectron spectroscopies will be crucial to gain fundamental insights into a variety of condensed matter phenomena ranging from the exotic electron pairing in superconductors to the mechanism of protein folding.

We describe a few fundamental pieces of science picked from areas (such as correlated electron behavior to the dynamics of bio-macromolecules) that could be potentially carried out using LCLS Facility at SLAC.

I. QUANTUM DYNAMICS OF CORRELATED ELECTRONS: A POTENTIAL PARADIGM SHIFT IN FUNDAMENTAL CONDENSED-MATTER PHYSICS

Collapse of Fermi-Dirac Statistics (Electron fractionalization)

The standard paradigm of condensed matter physics is Landau's Fermi liquid theory which states that elementary excitations in solids can be described by a quasiparticle (an effective electron) dressed with all types of interactions. The effect of interaction is to give it a finite lifetime and shift in energy. Within this so called standard model "quasielectron" still remains a fermion and obeys Fermi-Dirac statistics[1-4].

In last several years using electron spectroscopies and X-ray scattering techniques[5,6]it has been shown that in one dimensional compounds there are no quasielectrons. Electron rather undergoes a form of dynamic fractionalization call spin charge separation. It turns out that one dimensional systems are kinematically singular and can "afford" to allow for such fractionalization of an "elementary" particle. However, such singularlities are absent in two dimensional systems and it is not clear how a fractionalization can happen where electrons lose their Fermi-Dirac statistics and acquire a novel form of statistics.

Phil Anderson and others have proposed that electron fractionalization might be at play in causing high temperature superconductivity[3]. In its simplest form electron fractionalization means electron's charge and spin degrees of freedom are no longer coupled (no longer moving together) meaning the charge (e) velocity and the spin (h/2) velocity are different. Since the spin (1/2) is no longer attached to the charge there is no requirement for it to obey Fermi-Dirac statistics. However, this decoupling of charge are spin are dynamic in the sense that decoupled "charge" corresponds to a new collective charge mode and decoupled "spin" corresponds to a new collective spin mode.

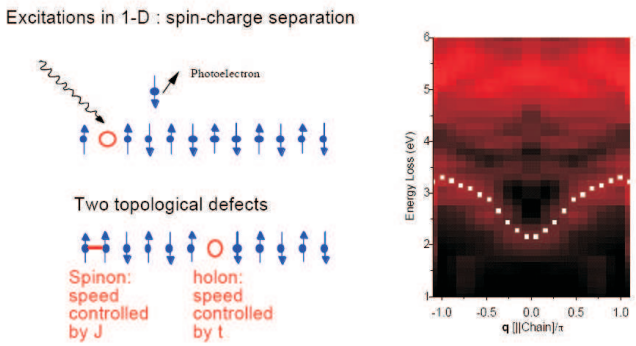

FIG. 1: Electron fractionalization in one dimensional magnets: Spinless charge (holon) could be detected in a recent work from APS [Advanced Photon Source Research Highlight (2004)]. Chargeless spin signal is two to three orders of magnitude weaker but can be detected using LCLS beam. Chargeless spin (1/2) and spinless charge collective modes can not be observed using neutron scattering but can be detected using LCLS beam and allow one to observe novel statistics beyond conventional Fermi-Dirac statistics.

X-ray scattering is clearly a natural tool to measure collective charge mode (similar to plasmons). We have recently carried out such studies at the Advanced Photon Source on one dimensional copper oxides (Adv. Photon Source Research Highlight, 2004)[7]. However, extending such studies to two dimensional copper oxides would be a challenge at APS since the collective mode is weaker and appear at even lower energies. We proposed several ideas how it can be addressed with LCLS facility.

In order to establish complete spin-charge separation one also needs to detect the spin collective mode. One could naturally think of neutron scattering a way to detect that but unfortunately it does not work since the spin collective mode has a quantum number of 1/2 not 1. In other words it is not magnon like. Since neutron scatters by flipping the spin net change is spin-1. One can make use of direct magnetic coupling of x-rays to study a spin-1/2 collective mode. Unfortunately, direct magnetic coupling of x-rays is weak[8] : *Spin couples through the curl of the photon operator (X-rays) :*

$$-(eh/mc)\sum_j s_j \cdot (\Delta X A_j) \rightarrow \mid (h\omega/mc^2) < f \mid \sum_j s_j exp(iq \cdot r_j) \mid i > \delta(...) \mid^2 \quad (1)$$

This pure magnetic term in the X-ray-matter interaction scales with $(h\omega/mc^2)^2 \sim 10^{-4}$ *which is several orders of magnitude weaker than charge scattering.*

One can make use of direct magnetic coupling of x-rays to directly detect a spin-1/2 collective mode for the first time ever with LCLS since the time-average flux of LCLS would be about 4 orders of magnitude than the 3rd generation synchrotrons. Furthermore, one could also try in an interference scattering mode by making use of resonance: using circularly polarized light, one can observe interference between the charge and magnetic channels. This term would be linear in spin coupling and of order $\sim (h\omega/mc^2) \sim 10^{-2}$ which would be even easier to observe.

This would directly allow us to measure the dispersion relations (E vs. q) of these new exotic particles (modes) that are fundamentally different from any other excitation modes observed or studied so far in condensed matter physics. Temperature dependence of form factors (intensities) measured over the -q space of these modes would allow us to detect/discover novel forms of quantum statistics beyond Fermi-Dirac or Bose-Einstein type. We should be able to detect subtle spin excitation with LCLS x-ray beam without spin-orbital coupling which is fundamental in studying electron fractionalizations.

Novel Symmetry-breaking Collective modes

Certain classes of theories known as guage theories (Patrick Lee et.al.)[9], high symmetry group based (Zhang et.al.)[10] unification schemes of high temperature superconductivity and quantum antiferromagnetism, or one dimensional self-organized fluctuating charge objects (Kivelson et.al.,)[11] suggests the existence of novel charged collective modes or charge oscillations in the range of 1 to 100 meV. Since these are collective in nature they are not directly observable in single-particle excitation spectroscopies like ARPES[12]. It is true that one can achieve energy resolution on the order of a millivolt with x-rays but current x-ray scattering capabilities (APS or Spring8) are out of parameter range for detection of such modes. Some sort of inelastic (ω-domain) or time domain (t-domain) X-ray studies (including momentum high-Q resolution) are vital for their detection. Their cross-section is about 2 to 3 orders of magnitude below the detectability level of charge scattering response from 3^{rd} generation synchrotrons. The electronic excitations

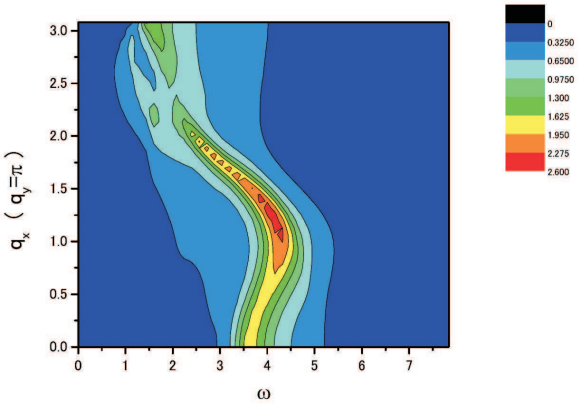

FIG. 2: X-ray form factor for a novel collective charge mode predicted in certain theories (RVB Gauge theory[9], P.Lee (2002)) of high Tc superconductivity

can be distinguished from phonon (lattice dynamics) scattering using the resonance technique since resonance will selectively enhance electronic scattering. Higher time averaged flux from LCLS would allow for their detection performed even in their conventional mode (Triple-axis inelastic scattering) however since the characteristic time scales for these modes are on the order of pico to femtosecond range LCLS is the only place for such studies. A combination of high momenta (high-Q) naturally achievable with X-rays, enormous flux (only LCLS) needed to get signals from these subtle collective modes and the time structure (pico to femtosecond) of these charge oscillations make LCLS essential to detect and study these modes in correlated electron systems. Study of such collective modes uniquely enabled by LCLS will certainly narrow down the spectrum of theories for high temperature superconductivity.

Real-time Observation of Superconducting Pair Formation (LCLS e-beam)

Traditional angle-resolved photoemission spectroscopy performed under conventional settings does not allow one to perform the measurement of electronic structure under an applied magnetic field[11]. since the field changes the trajectories of the exiting electron and the parallel momentum component is not uniformly conserved. A way out to do ARPES with an applied field could be to use the LCLS e-pulse to generate a field on the sample (similar to Siegmann, Stohr and collaborators measurements on magnetic switching[13]) and use a laser beam timed with the e-pulse to induce the photoemission event. The electron beam applies a magnetic field in the sample where it hits. This field dies away from the center. Suppose the center field is around 20-T and a couple of microns away field has dropped down to 11-T which is above the critical field (H_{C2}) for many superconductors such as electron doped cuprates (NCCO) or cobaltates[14]. At this location of the sample superconducting pairs are broken by the field. Shining laser at this point to look at ARPES signal would reveal that there is no coherence peak in the electron spectrum (absence of superconductivity), however shining laser at a nearby point where field has died out below the critical field will show the appearance of a coherence peak signalling Cooper pair formation. Such measurements may only work for high temperature superconductors. Hence by combining spatially resolved ARPES and the field applied by the e-beam from LCLS can allow to observe real-time formation or disintegration of superconducting pairs. Timing can also be done by ultra-fast time-binning the electron detector at a comparable rate (microsec.?) with the disappearnce of the applied field. Certain amount of R&D will be necessary to achieve these levels of precision. Since the potential pay-off is significant it might be worth pursuing such directions.

Response of superconducting condensate to ultra-fast magnetic field (LCLS e-beam)

The availability of intense field pulses with rise-times on the 50-250 femtosecond timescale opens up an interesting and exciting regime of research on superconductivity. We may now probe experimentally the question "How fast does it take a superconducting condensate to form and spread?" Assume that the pulse peak-field (estimated to be 10-20 Tesla) exceeds the upper critical field Hc2 of a superconductor. If it is switched off on an ultra-fast time-scale, the condensate will recover over an intrinsic time tS that can be measured. In our proposed experiment, we measure the voltage drop across a thin-film superconductor (NbTi) fabricated to achieve resistances R of 1-10 Ohms in the normal state. The onset of superconductivity is monitored by detecting the vanishing of R on ps (eventually fs) time scales. Because the field pulses are accurately periodic, we may use box-car gating techniques, synchronized to the field pulses,

to average over 100 or 1000 pulses. This vastly improves the experimental resolution over single-shot measurements. With present-day gating technology, tS may be resolved on the 1-10 ps time scale. Further improvements in high-speed electronics in the coming decade will allow tS to be resolved in the 1-10 fs time-scale.

In low-Tc superconductors, the pairing mechanism is phonon-mediated. The retarded potential created by the persistence of the polarization of the heavy ions is essential for establishing attractive interaction for Cooper pairing. Hence we expect the time scale to be set by the Debye frequency (tS $\sim$ 10-100 ps). The direct measurement of this time-scale in conventional superconductors would be a significant contribution to further understanding Cooper pairing. Extending these experiments to the novel superconductors (cuprates, ruthenates, heavy fermions and organic superconductors) would be very exciting. For mechanisms that are electron mediated, we expect the time scale to be much faster (tS $\sim$ fs), possibly dictated by the superexchange J in cuprates. We foresee using tS to categorize and classify various pairing mechanisms in a novel and experimentally testable way. The ability to discriminate the time scales in distinct classes of superconductors would resolve the some of the major controversies in the field. Such a technique can be applied to a whole new class of problems in fundamental condensed matter physics mostly generally one would like to have a real-time tracking of electrons as a system undergoes a quantum phase transition[15].

With recent advancements in ultrafast technologies (streak camera etc.) it is now becoming possible to study real-time lattice dynamics[16]as a system undergoes phase transition. LCLS time structure is a good match for many ultra-fast processes such as lattice role in colossal magnetoresistance (CMR) under a pulsed field in correlated electron physics could also be studied.

II. UNDERSTANDING PROTEIN MOTION : A FUNDAMENTAL STEP TOWARDS UNDERSTANDING THE WORKINGS OF LIFE

Protein Dynamics

Collective modes : The human genome has recently been completely sequenced. Understanding the working of proteins- the ultimate nano machines - represents a major scientific challenge for the post-genomic era. Established techniques such as X-ray diffraction and NMR allow one to determine the average (static) protein structure. However, proteins are dynamic objects, and it is not possible to understand their physiological functioning without characterizing their dynamical behavior[17-21].

Proteins exhibit collective modes ($\sim$ 3meV)[19] that resembles the "boson peak" observed in glasses[21] or polymers. The nature of the molecular motions responsible for this feature has not yet been established. Above a characteristic temperature ($\sim$ 200K), proteins undergo a dynamical transition from harmonic to strongly anharmonic behavior. These anharmonic fluctuations are believed to result from transitions among the large number of thermally accessible local minima of the energy landscape and to enable biological functioning. Water is required to activate these anharmonic fluctuations and the temperature of the dynamical transition depends strongly on solvent properties such as viscosity[20]. Although neutron scattering has played an important role in establishing many characteristics of protein dynamics, ultra-high resolution ($\sim$ 1 microvolt) inelastic X-ray scattering (currently unavailable at 3rd generation sources) or fast X-ray Transient Grating Spectroscopy (XTGS) have significant advantages. The ability to work with small sample volumes will allow the study of many interesting proteins that are simply not available in the gram quantities required for INS and the relative insensitivity of x-rays to hydrogen enables measurements in H_2O, rather than D_2O. Candidate proteins for these measurements will be the oxygen-binding protein myoglobin and the proton pump bacteriorhodopsin[22]. Both possess well-characterized light-driven reactions, so that in-situ measurements in the presence and absence of illumination could identify vibrational changes between well-defined states of the protein.

Structural info on membrane proteins via inelastic scattering(in collaboration with S. Doniach): Some 25% of gene sequences in the data bases code for expression of membrane proteins. Although structures for several thousand soluble proteins have been determined, only a handful of structures are known for membrane proteins owing to the difficulties of crystallizing proteins which are naturally stabilized by the hydrophobic environment of their surrounding lipids. It appears that the excitation spectra of lipid bilayers, as seen by IXS[23], are qualitatively different from those of proteins. In particular the high frequency peptide backbone bands[27] are not expected to be manifest in the lipid bilayers, which rather show overdamped, or highly damped, propagating sound modes characteristic of a viscous molecular liquid[23]. Thus it may well be possible to use the high frequency energy loss/energy gain sidebands of the main elastic scattering peak, to distinguish the protein contributions to the total scattering (i.e. integrated over energy) for a sample containing membrane proteins, from those of the lipids. Under the assumption that the magnitude of the scattering from the bond-stretch bands for lipids is relatively weak or can be removed by suitable background subtraction, reconstruction of the shape of a membrane protein can the be done by measuring the Q dependence of the inelastic scattering in the backbone peptide bond-stretch bands. Since bond-stretch scattering depends on

the relative distance between the atoms forming the bond, the dynamic scattering cross section is expected to vary as Q2S(Q), where S(Q) is the static scattering profile function. Hence an estimate of the scattering profile may be obtained by dividing the inelastic scattering cross section measured in the bond-stretch bands by Q2: Sprofile(Q) (1/ Q2)SIXS(Q, str), over a suitable range of Q values. The validity of this assumption, and the range of Q over which it gives reasonable results needs to be tested by simulations. Reconstruction of the pair distribution, p(r) using the program GNOM will enable an estimate of Rg to be made. Then shape reconstruction algorithms of the type of SAXS3d or DAMMIN may be applied to obtain a low resolution density map of the membrane protein[25]. The difference between the measured x-ray profile and the estimated protein component, Sprofile(Q) may be attributed to scattering from the lipids.: Slipid(Q) Stot(Q) - Sprofile(Q). Clearly of central importance in providing an underlying physical picture for these experiments will be the ability to perform reasonably accurate numerical simulations of the excitation spectra of proteins and of lipid bilayers both separately and for proteins dissolved in the bilayers. Given the huge number of sequences coding for membrane proteins, it seems likely that clues to structure associated with unknown membrane proteins will potentially be useful in guiding cellular studies.

Folding Kinetics : A more directly relevant protein dynamics lies at somewhat lower frequencies or slower time scales. Understanding the dynamics of the process where a protein finds its functional set of conformational states (the "folding problem") and the dynamics of transitions between the various functional states of the folded protein constitute a problem of very fundamental issue in life sciences[17]. In a recent x-ray scattering work Plaxco, Millet, Hasan and collaborators has demontrated[26]a universal scaling behavior in unfolded proteins. Is the denatured unfolded state a random coil? Spectroscopic studies suggest that many proteins exhibit measurable residual structure even under strongly denaturing conditions. The average dimension of the most unfolded proteins (except the ones with disuphide bridges) and peptides are well fitted by a power-law relationship with an exponent, 0.5850.014, that is effectively indistinguishable from the 0.588 expected for an ideal random coil. It appears that the mean dimensions of the significant majority of chemically denatured proteins are consistent with a completely unstructured unfolded state. The next question to ask how this universality ("physics limit") breaks down along the time axis, the folding time scale, which is the "chemistry limit" since each protein then has a unique functionality. Recent time-resolved SAXS work by Pollack, Gruner, Austin[27]and collaborators along these lines suggests a time snap-shot can be taken using a micro-channel fluid mixer[28]. However no dynamical information is obtained in such TR-SAXS measurements.

One can possibly pursue two new directions at LCLS to study the details of folding kinetics. One approach could be to use high energy resolution resolution beam (at the expense of flux) under SAXS geometry and resolved frequency of the scattered beam in addition hence gaining dynamical information. Of particular interest is to watch the evolution of the 180 meV vibrational line (protein backbone) as the protein folds. Radiation damage is reduced since to get down to 1 meV resolution incident beam one has already cut the flux by several orders of magnitude. The other approach to dynamics could be to use XTGS methods to access a relevant time scale. Since folding time scales vary from picosecond to hours one can match a class of proteins that has characteristic time-scale to that of the XTGS time scales achievable with LCLS.

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[1] C. Kittle, Introduction to Solid State Physics, Wiley, New York 5th Ed., (1976).
[2] D. Pines, The Theory of Quantum Liquids, Adv. Book Clas. Benjamin, NY, (1989).
[3] P.W. Anderson, Science 235, 1196 (1987).
[4] P.W. Anderson "Theory of High Temperature Superconductors", Princeton Univ. Press, (1997).
[5] C. Kim et al., Phys. Rev. Lett. 77, 4054 (1996).
[6] M.Z. Hasan et.al., Phys. Rev. Lett.,88, 177403 (2002).
[7] Adv. Photon Source "APS Science-2003" ANL(2004).
[8] S.W. Lovesey & S.P. Collins "X-ray scattering and absorption by magnetic materials" Oxford (1996).
[9] P.A. Lee et.al., "New collective modes in superconductors" cond-mat/0211699 (2002).
[10] S.C. Zhang, "A Unified Theory Based on SO(5) Symmetry of Superconductivity and Antiferromagnetism" Science 275, 1089 (1997).
[11] A. Damascelli et.al., Rev. Mod. Phys. 75, 473 (2003).
[12] Z.X. Shen et.al., Phil Mag. B 82, 1349 (2002).
[13] I. Tudosa et.al., Nature 428, 831 (2004).
[14] M. Z. Hasan et.al., Phys. Rev. Lett. 92, 246402(2004).
[15] S. Sachdev "Quantum Phase Transitions" Cambridge, NY (1999).
[16] A.M. Lindenberg et.al., Phys. Rev. Lett. 84, 111 (2000).
[17] H. Frauenfelder et.al., Annu. Rev. Biophys. Chem. 17, 451 (1988).
[18] J. King "The Unfolding Puzzle of Protein Folding",Technology Review, 58-61(1993).
[19] M. Diehl et.al., Biophys. J. 73, 2726 (1997).

[20] J.L. Rupley et.al., Trends Biochem. 8, 18 (1983).
[21] B. Frick et.al., Science 267, 451 (1995).
[22] J. Baudry et.al., "Molecular dynamics study of bacteriorhodopsin and the purple membrane" J. Phys. Chem. B 105(5), 905-918 (2001)
[23] S. H. Chen et.al., Phys. Rev. Lett. 86, 740 (2001).
[24] A. GoupilLamy et.al., "Vibrational inelastic neutron scattering: A new spectroscopic tool for globular proteins" J. Am. Chem. Soc. 119, 9268 (1997).
[25] D. Walther, F.E. Cohen and S. Doniach Reconstruction of low-resolution three-dimensional density maps from one-dimensional small-angle X-ray solution scattering data for biomolecules. J. Appl. Cryst 33(2), 350-363 (2000).
[26] J.E. Kohn et.al., APS Activity Report ANL-03/21 (2002)
[27] L. Pollack, M.W. Tate, A.C. Finnefrock, C. Kalidas, S. Trotter, N. C. Darnton, L. Lurio, R.H. Austin, C.A. Batt, S.G.J. Mochrie. "Time-resolved collapse of a folding protein observed with small angle x-ray scattering" Phys. Rev. Lett. 86, 4962-4965 (2001).
[28] J. B. Knight, A. Vishwanath, J. P. Brody, and R. H. Austin Hydrodynamic Focusing on a Silicon Chip: Mixing Nanoliters in Microseconds Phys. Rev. Lett. 80, 3863 (1998)

Scientific Team:

Zahid Hasan brings in experience in using various forms of synchrotron x-ray based photon-in/photon-out and photon-in/electron-out spectroscopies in correlated electron physics (superconductors and quantum magnets) and biomolecular (protein dynamics) physics. **Robert Austin** has been developing methods for using FELs to study protein dynamics specially energy transport along the hydrocarbon backbones along with the development of micro(fluid)mixers (and nanomixers) for kinetic studies of proteins using syncrotron beams (work done in collaboration with Sol Gruner). **Phuan Ong** is an expert on high magnetic-field studies of correlated electron systems and exotic superconductors - field-induced physics is an essential component of this proposal. Robert Cava, a leading chemist (a leading expert in advanced crystal growth techniques of new materials) will provide samples essential for these experiments proposed here. **Bill Brinkman** (recently joined Princeton) will bring in the certain theory components in terms of x-ray-matter interaction under extreme conditions reached at LCLS. **Phil Anderson** helps with interpreting novel aspects of the expected/unexpected results.

Robert H. Austin: *Professor of Physics* : Biophysics, Protein Dynamics using FELs. Protein-DNA interactions. Folding Kinetics using SR sources. Micro- and nano- mixers for kinetic studies. Time-resolved X-ray scattering. Web: $http://pupgg.princeton.edu/www/jh/research/Austin_Robert.htmlx$

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