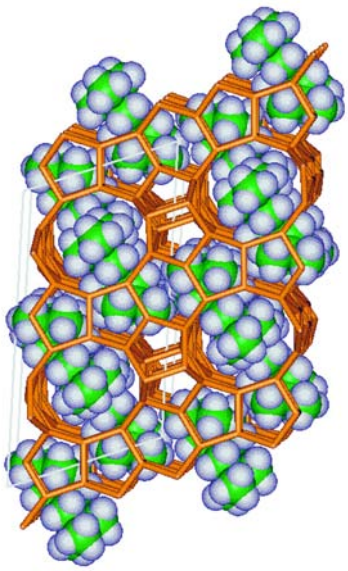

Computational Scattering Science 2010

Organizers

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Disclaimer

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Executive Summary

Over the past two decades, synchrotron x-ray sources, spallation and steady-state neutron sources, and electron microscopy facilities in the United States have had a major impact on basic research into many of our critical technologies. Discoveries are changing the way we understand the world around us from the perspectives of physics, materials, chemistry, biology, geosciences, engineering, life sciences and medicine, and the energy sciences.

Large-scale facilities in the U.S. include: the Lujan Center at Los Alamos National Lab, HFIR at Oak Ridge, NCNR at NIST, APS at Argonne, NSLS I (and soon II) at Brookhaven, SSRL at Stanford, ALS at Berkeley, CHESS at Cornell, and the newcomers LCLS at Stanford and the SNS at Oak Ridge. Current and future developments at these sources are poised to enable in situ and real time research on spatial domains from millimeters to below nanometers, and time domains from s to fs. Simultaneously, the developments in computational materials science have been no less remarkable, with game-changing advances in both hardware and in computational methods. Many state-of-the-art computations of structure and dynamics now address the same phenomena, at the same scales of space and time, as state-of-the-art experimental measurements.

Far less well developed are the interfaces between computational science and scattering experiments. While measurement capabilities are uncovering information on atomic length scales and on macroscopic functional scales, and discovering a myriad of excitations in condensed matter, the theoretical interpretations of these measurements lag far behind what is possible in principle. This is a loss of opportunity for scientific discovery. Efforts in the U.S. by scattering science to exploit the extraordinary advances in scientific computing are typically small scale with limited scope, steep learning curves, and the efforts are often repeated for each new investigation. The sophistication of our computational scattering science has remained about the same over the past decade. Unless we bring modern computational science to our scattering science, leadership will pass to Europe where computational scattering science is pursued aggressively.

The workshop attendees, with the support and endorsement from the NSF and DOE BES, assessed the relationship between computing and scattering science. Their focus was on how modern computation can leverage and grow the scientific output from scattering experiments by linking theory, modeling and simulation more closely with experimental scattering research. Ideas were also discussed for organizing software development, migration to new computer systems, maintenance, and user support. This combination of science drivers with possible software solutions proved stimulating and compelling. This report offers specific recommendations in many topical areas including correlated electrons, chemical processes far from equilibrium, structure and dynamics in nanostructures, engineering diffraction, fast and ultrafast phenomena, experimental simulations, optimization for complex physical modeling, software maintenance and support for multicore computing, software development and community expectations, education and career paths, and financial support.

Capital investments in some of our experimental facilities are well over a billion dollars. Ongoing operational investments approach a billion dollars each year, serving a community of over 14,000 researchers who perform world-class science. An incremental investment of approximately 15 M$/year would establish critically-needed companion capabilities in theory, modeling and simulation in a robust national effort distributed over national laboratories and universities. Coordination of existing efforts could begin earlier by establishing a computational scattering science steering committee. The time is right to do develop a computational science infrastructure that will expand the impact of the U.S. national user facilities for scattering research.

1. Introduction and Scope

1A. Trends in Scattering Research and Computing

Most of what we know today about atomic structures in the world around us was learned from x-ray and neutron scattering. With the highly successful U.S. investment in powerful new facilities, such experimental observations are poised for rich scientific rewards. Mesoscopic structures of macromolecules and microstructures of materials can now be determined with enough detail to develop insights into how and why materials and molecules possess properties of importance to engineering or life processes. At larger spatial scales, scattering measurements can quantify the mechanical behavior of materials through the continuum responses of its microstructure. Besides revealing structure over length scales from sub-Ångstroms to millimeters, scattering regularly probes the motions of electrons, atoms, molecules, and microstructures on time scales from 10^{-14} to 10^{-7} s, opening new windows into dynamics. Recent U.S. investments in user facilities for scattering have kept our experimental capabilities at the cutting edge, and the range of measurements continues to expand.

Computational scattering science is positioned to benefit from three major trends.

- Hardware performance has followed "Moore's law." Since 1980, performance per dollar has increased by more than a factor of a million, and computations that were unimaginable only 20 years ago are commonplace today.

- Computational materials science has grown and blossomed. Condensed matter theoreticians can now evaluate realistic quantum mechanical models for complex materials, and engage in productive interactions with their experimental colleagues. Many approaches are in use for calculating the structure and dynamics of materials, and their reliability is understood. Improvements in the efficiency of algorithms are giving a boost to computational performance beyond that of Moore's law.

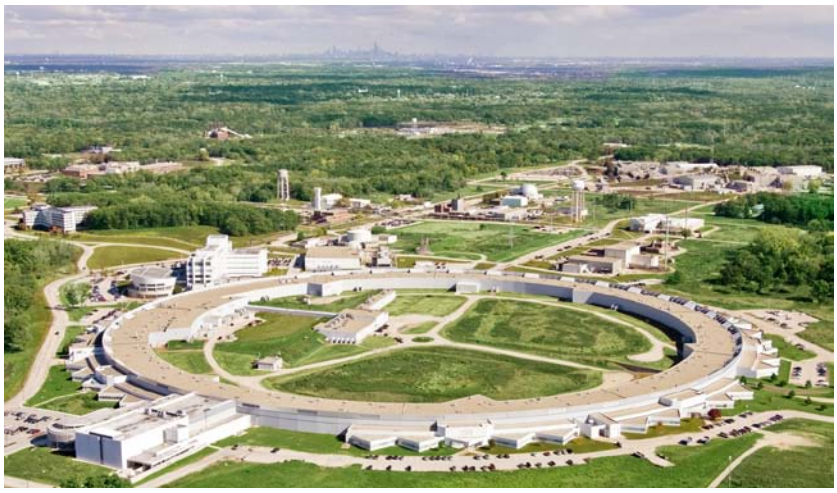
- Finally, developments in software engineering and cyberinfrastructure allow data, software, and hardware to be combined creatively, optimizing serendipity for scientific discovery. Professional practices of software development are established, and it is known how software modules can be designed to interoperate, and maintained into the future.

It is time to assess these advances in computing, and how they can work together with advances in experimental scattering methods to best enable scientific discovery. This sea change needs to be exploited to accelerate the discovery of new materials needed for alternative energy sources, materials benign for the environment, and materials to enhance industries related to electronics and transportation.

1B. Roles for Computing in the Scattering Sciences

Scattering measurements at x-ray synchrotrons and neutron sources are often described as "small science at big facilities." Unlike the monolithic efforts of high-energy physics, x-ray and neutron scattering facilities serve simultaneously numerous scientific investigations in biology, chemistry, engineering, geology, materials, and physics. The research groups typically consist of persons ranging in experience from students to senior scientists. The success of the x-ray and neutron facilities is measured in part by the number of the researchers who use the facilities, and by their scientific output of quality publications. Common computational support for a wide range of users includes data processing and the archiving of data so that users bring home physically meaningful results in the form of the intensity of scattering versus momentum (or spatial scale) and energy (or time). These $S(Q,E)$, $I(Q)$, or $I(E)$, corrected for instrument characteristics, are fundamental measurables of scattering experiments. It is generally the role of the user facilities to reduce data to these forms because the instrumental characteristics used in reduction are under facility control.

The next level of analysis is interpretation of the reduced data, $S(Q,E)$, $I(Q)$, or $I(E)$. Here the methods of interpretation follow the diversity of the underlying science. The "small science" style of scattering research can be a strength because it motivates innovation. It is also one of the weaknesses. The analysis software is typically developed to achieve narrow goals, and is not



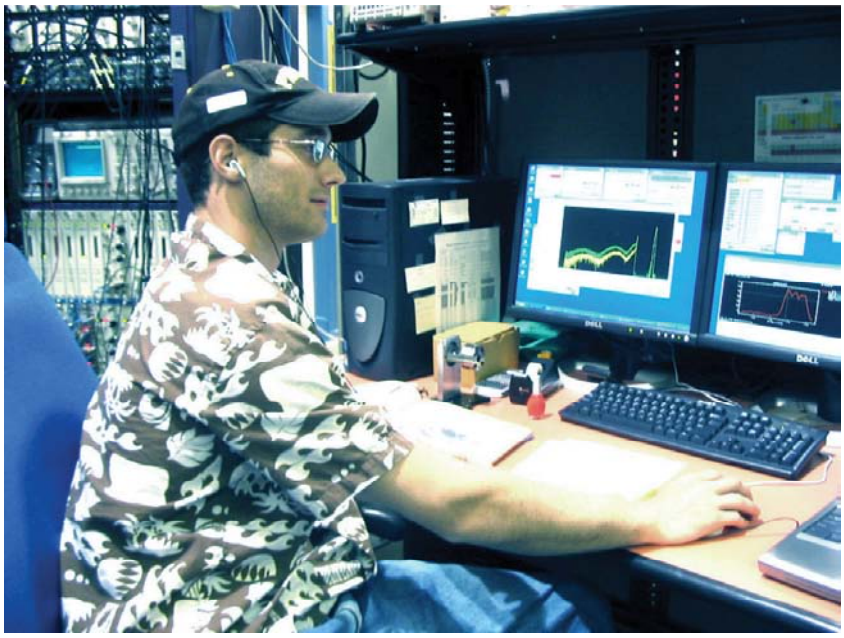
The Advanced Photon Source at the Argonne National Laboratory.

The Spallation Neutron Source at the Oak Ridge National Laboratory.

usually useful for others. Although good software is often passed down as legacy code within a research group, it rarely reaches professional standards of design or documentation. Further, research groups around the world replicate this kind of limited scope software many times over. Another tactic is to adapt or modify more professional software (for ab-initio, molecular dynamics, or finite element calculations, for example) to support a particular investigation. In this case as well, the researcher focuses on a particular result, and the working software is often brittle, breaking easily if modified, or when moved to a new computer. Owing in large part to the difficulty for a small research group to adapt their specialized codes for execution on modern supercomputers, supercomputing resources have seen little use for computational scattering science.

We learn about the structure and dynamics of the material by analysis of $S(Q,E)$, $I(Q)$, or $I(E)$. Computational approaches to these results include, for example, molecular dynamics, density-functional theory electronic codes, and finite-element elasticity. Iterative or Monte Carlo techniques for finding parameters of a computational model that best fit experimental data are also used across many fields of scattering science. Adapting these computational methods for calculating neutron scattering has been low-lying fruit for the DANSE project, and was one goal of the ASISI proposal. In adapting computational tools to the needs of scattering research, some of the biggest challenges are in software engineering, such as ensuring computational flexibility while minimizing the effort for installing, building, and using modern computational science codes. Today, a number of European groups are at the forefront in calculations of materials structure and dynamics for predicting experimental data from real instruments (see Appendix, and visit the new website for the European Theoretical Spectroscopy Facility http://www.etsf.eu/). It is noteworthy that their computations often provide information beyond what can be obtained by experiment alone, and the experimental data often provide corrections or guidance to the calculations.

The synergy between experiment and computation is often a new source of insight into nature, and is at the core of many recent high-profile publications. It is the focus of this Workshop Report. In what follows we present a strategic plan that assesses the state of computational scattering science today, presents a vision of where the field could be in five years, and offers a suggestion for the effort that would achieve this goal. The individual reports on science topics have similar structures.



Much of the time during experimental runs involves working with software for data reduction and visualization.

2. Strategic Plan for Computational Scattering Science

2.A. Where We Are Today

The individual workgroups assessed the status of their own fields, and their reports are in Section 3. Key findings, common across many groups, are summarized here.

2.A.1 Status of Computation in Scattering Science

Computation is required for even the most basic presentation and display of experimental scattering data. The ability to work interactively in real time with rich data visualization is needed for all experimental work. Reduction and visualization tools are facility responsibilities, however, because they reflect directly on the instrument performance and quality of measurement. The status and development of these tools lie outside the scope of the workshop and this report.

The next step of data analysis typically involves correcting for background, instrument resolution, and artifacts of scattering measurements. Some corrections, such as multiple scattering and multiphonon scattering, depend on the sample, and become a shared responsibility of the user and facility scientists. These corrections are generally required before publication because they affect error bars, for example. The quality of these corrections is variable, however, sometimes because there is a lack of convenient tools for the job.

Properly executed scattering experiments, while powerful, generally do not provide all the information required for scientific discovery. Considerably more detail is possible by combining experimental results from multiple types of scattering measurements, such as in a simultaneous analysis of x-ray and neutron diffraction data. Today these analyses include an underlying model of the structure, and the model is optimized through properly weighted fittings to the experimental data sets. Convergence can be tricky, and there are deeper statistical questions about how much information can be extracted with confidence from the experimental data sets. Although these issues have been known for decades, tools are still emerging for flexible optimizations, and mathematical rigor for statistical analyses is often lacking in the tools of today. Beyond diffraction measurements of atomic structure, there have been few attempts at co-refinement of different data sets. Using diffraction measurements to understand a dynamics model is usually done on an ad-hoc basis if at all, in part because the software tools are not modular and frustrate attempts to assemble new optimization workflows.*

All groups at the workshop found big opportunities for scientific discovery by interpreting experimental scattering data with methods of computational materials science that have emerged over the past decade or so. Successful agreement between computation and experiment is not the only measure of progress. Discrepancies and anomalies in the comparison between computation and experiment may also point the direction to discovery. Computational work can perform a service role to experimental work by predicting known contributions to the scattering that can be removed from experimental measurement to better reveal the phenomena of interest. Calculations of phonon scattering are useful for magnetic scattering experiments when they allow phonon contributions to be deleted. Spin-polarized DFT methods are capable of providing information on classical spin waves that can be removed from experimental studies of low-dimensional quantum magnetism, although this is frontier work today.

At larger scales of length and time, results from ab initio calculations can be used to parameterize force fields for molecular dynamics, and an ensemble of molecular dynamics trajectories can be used to parameterize Monte Carlo methods that efficiently access even longer times. Such approaches are typical of the growing effort in computational materials science to cross length and time scales. Scattering experiments can benefit from these methods, although to date there have been only a few efforts to do so.

Sometimes we do not know if the theoretical methods of today are capable of interpreting experimental data, or if we have entered a new realm of scientific phenomena. Are electron states in equilibrium with nuclear motions, for example? For ultrafast phenomena, correlated electron materials, and many complex materials, there may

** Sometimes comparisons to theory can correlate scattering results to other physical phenomena that are predicted by computational models. Are there ways to weight these other phenomena to improve the model?*

be no obvious path forward with the computational tools of today. The development of new methods lies beyond the scope of computational scattering science considered at this workshop. Nevertheless, we need a flexible way for using known computational approaches to predict scattering in frontier topics. Without trying some of today's methods, sometimes in combination, we may not be able to tell if observed phenomena are beyond our present understanding.

There are, of course, important topics, such as scattering studies of spin excitations in new superconductors, that we know are outside today's competence for quantitative interpretation. For such work it is productive to encourage collaborations between experimentalists and theorists. Unfortunately, the individual efforts by theorists and experimentalists are often done in isolation, but collaborations can be exciting for both. *

2.A.2 Software Development and Community Resources

Some trends can be learned from the record of scientific publications over the past two decades. The Appendix presents some statistical information obtained by searching the Web of Science for papers with the keywords "ab initio" AND "scattering" AND ("x-ray" OR "neutron"). The publication rates are increasing linearly with time, approximately starting from zero in 1990. The citation rate is increasing with a linear plus a quadratic trend, the latter indicating that earlier papers are still being cited. The average numbers of citations per paper are 17 and 22 for neutrons and x-rays, respectively. Although U.S. researchers were pioneers in this type of work, today the institutional dominance is European. The major players are the most scientifically productive European facilities, such as ESRF, ILL, ISIS, although Argonne places well. The Univ. of Washington has an anomalously high impact, owing to the group of J.J. Rehr.

To date, most software for computational scattering science has been developed in small efforts where individual research groups create their own analysis tools and "own" the software. They usually share it with others in their community with varying levels of responsiveness to requests for help or maintenance.

** Synergy between experimentalists and theorists stimulated many discussions at the Argonne workshop itself.*

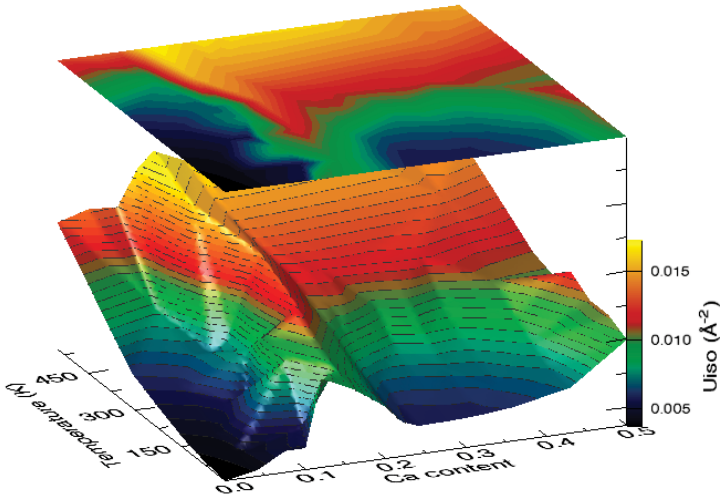
Nevertheless, there are many cases where software is withheld except to generate sales income, or withheld to provide a competitive advantage in the field. The workshop attendees found that scattering science is no longer well served by this cottage industry, which has been unable to scale up productivity over the past decades. Increased data volumes, the increased complexity of analyses, the deeper science of the computational tools, and the increased complexity of computing systems requires the coordination of more expertise than can be mustered by small individual activities. Especially when using computation to test new models of hypotheses, it is useful to interchange or rearrange computational building blocks. This requires that software packages interoperate in a modular way. The design patterns of object-oriented programming enable such flexibility, but are not so well known to the scattering science community. Furthermore, more complex systems require professional standards of testing, documentation, maintenance, and user support. Today there is no infrastructure for these services in computational scattering science.

High performance computing resources such as the Teragrid, Open Science Grid, and leadership computing facilities at national laboratories have been available for some time, but the scattering science community has not used them seriously. Despite improvements in middleware and development tools, the entry barrier is too high for a typical scientific software developer, who is likely a physical scientist driven by necessity to software development. The computational scattering science community is likely to suffer the same fate of underutilizing the emerging technologies of web services, cloud computing, and multiprocessor architectures. In the absence of targeted funding, the attendees of this workshop question whether computational scattering science can advance.

2.B Goal State

From the topic report on Correlated Electrons, "A clear issue is how to take the available theoretical efforts and cast them in a form that is useful for the analysis of experimental data."

The record of computational scattering science publications identifies an important set of software tools. One group includes predictive, computing-



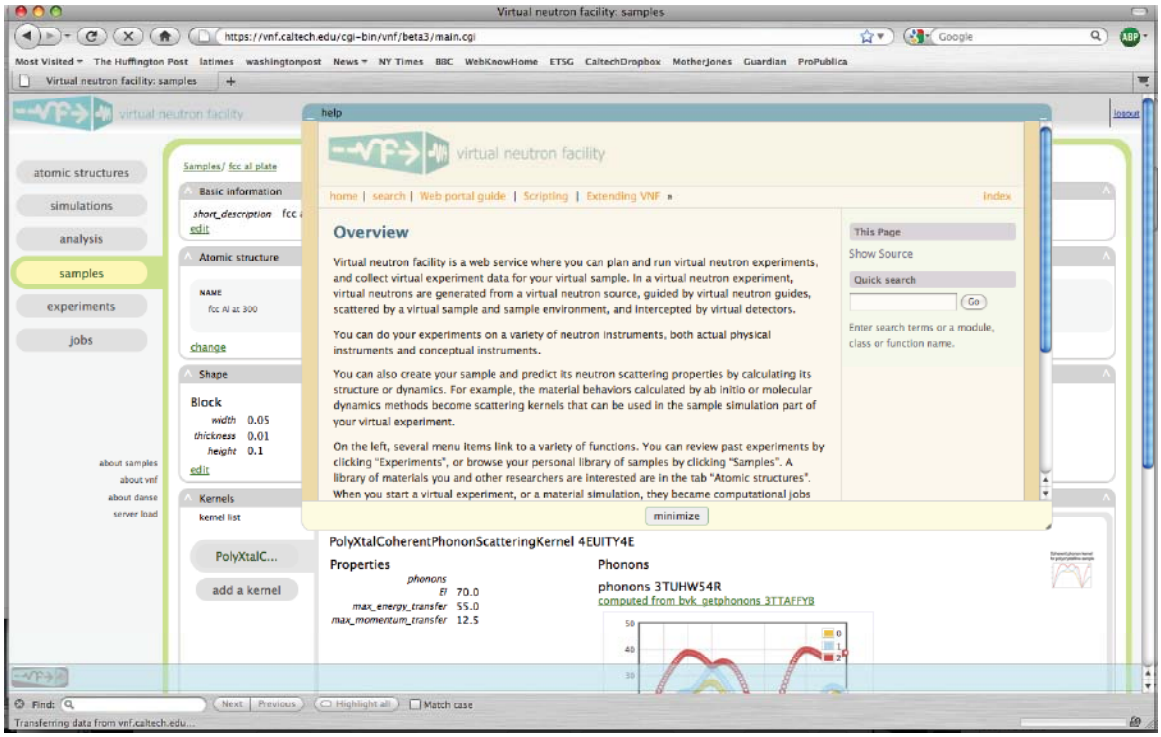
This figure shows the power of high throughput diffraction studies coupled with advanced computation. Local oxygen displacements in $La_{1-x}Ca_xMnO_3$ are presented as a function of x and T, showing fluctuations associated with a structural phase transition (the ridge around x=0.15), the disappearance of polarons (the blue valley at low temperature and x~0.3), and a competition between phases of similar energy (the small valley at around x=0.5 and 260 K).

intensive codes such as ab initio density functional theory, classical molecular dynamics, quantum molecular dynamics, kinetic Monte Carlo, and 3D finite element methods. Ab initio molecular dynamics will become more routine over the next five years; we need to plan for it today. Theoretical efforts in dynamical density functional theory need to be watched closely. Another group of important software tools is based around algorithms for optimization and iterative fitting. Over the next five years, tools for model refinements of crystal structure (e.g., Rietveld refinement), shapes, and scattering length density will continue to be important for fitting elastic scattering data. Analogous models for lattice and spin dynamics would be useful for inelastic scattering.

Combinations of methods, or comparisons of results between different methods and models, require modular tools that can be linked, interchanged, and rearranged without undue effort. Experimentalists need more flexible optimization strategies than are available today. Good predictions of scattering from realistic samples in realistic instruments can be done by simulation, or sometimes by corrections of experimental data, but in practice both routes have proved useful and should be made available for comparison. Again, modular tools are the key to such flexibility. Some such tools and a framework to use them have been developed in the DANSE project, although these have just been released in 2010.

Today we know how to modularize software with proper abstractions and encapsulations, making it easier to use the same code in different applications, and making it easier to maintain complex software applications. Modular software promotes the use of compatible structures and standards for data and metadata. There are tools for storing metadata in a relational database, a great convenience for users working with multiple datasets from measurements and computation, and for keeping track of prior work. Many of these new capabilities and conveniences will become available by using modern professional software development practices. Such practices include automated systems to build, test, and help document the software. These functions are even more important for distributed computing, although these automated systems demand development and maintenance themselves.

With more computing will come more demand for computing resources. As ab initio calculations and optimization problems come into broader use, they will stress the available resources even as the ongoing trends in computing hardware bring more capability. We expect that the national investment in cyberinfrastructure will continue, but planning for scattering science is needed now. Infrastructural needs of scattering science are not identical to the needs for astronomy, which handles data in volumes that are many orders larger than for scattering science. (Scattering science tends to be more processor-intensive and less data intensive.) Many scattering scientists will want to use commercial off-the-shelf products for their work, so software development must plan to accommodate changes in the commercial sector. As this is written, Apple Inc. has deleted the word "computer" from its name, and its products for content distribution and display are now its main source of profits. It is possible that the developments in consumer products, which were so helpful in the past, will diverge somewhat from the needs of scientific computing. With a stagnation of clock speed, CPU performance will increase with multicore architectures. Some algorithms do not deploy efficiently on multicore systems, and may fade in importance. The deployment of computations to remote services as offered by "web 2.0" technologies and cloud computing needs planning now. In five years, the productive environments for scientific computing may be



Browser window for the virtual neutron facility, a web service for computational neutron scattering science.

different from what we see today. More generally, migrating software to new platforms should be part of a planned and funded "maintenance" effort. This effort should also assess the cost-effectiveness of maintaining some of today's codes.

Several participants expressed concern that diffraction, scattering and crystallography are disappearing from the academic curriculum. These topics are not vanishing entirely, but with new topics being added to graduate programs, the depth of coverage of diffraction and scattering is shallower than in the past. Methods based on analytical mathematics, such as the Fourier-space Warren-Averbach method, are being replaced by computing-intensive methods such as Rietveld refinement. Herein lies an opportunity. Some computing tools are well suited to the dual purposes of education and research. These needs will also be served by modular design, where computational tools are properly encapsulated so that different interfaces are available to serve different users, from new graduate students to expert researchers. The technologies to do this are known today, but a complete solution requires customization for the workflows of different users. Simulations of experiments can play important roles in university coursework, and would be used more widely if individual instructors did not need to maintain the software themselves.

Teaching new scientists about scattering techniques would benefit from software tools, but over the next five years these will not replace human interactions. Much as a new user of an experimental method can benefit rapidly by collaboration with an instrument scientist, many experimentalists could benefit rapidly from interactions with a computational scattering scientist who is familiar with both the phenomena and the computational tools. Within a facility, the interaction of instrument scientists and computational scattering scientists will be mutually beneficial, and elevate the intellectual richness of the lab environment.

Computational scattering science can benefit by combining information from different experimental measurements. Multi-technique investigations will become more common, fostering new types scientific collaborations. The emergence of better communication and networking tools will help. Other capabilities, such as a distributed file system between national user facilities, and provisions for proper data staging and movement, may require some development by the scattering community. Software that works with data sets from multiple techniques may motivate distributed data handling. We may see growth of efforts to work with multiple types of data, especially if it includes more rigorous ways of handling the statistical significance of different parts of the data set.

Individual user facilities must maintain core competence for data archiving, data reduction into units of momentum transfer and energy, and

visualization tools. Software for these essential functions is needed at the instrument, and must be convenient, fast, and accurate. Such software can dominate the user experience with the instrument or the facility itself, so responsibility must reside at the facility. However a complete set of tools for computational scattering science, especially those deployed as web services, need not all be maintained by each facility, or even deployed locally, and these analysis software tools present opportunities to engage a wider community in scattering science research.

Computer systems with hundreds of processor cores are widely used by research groups today, and systems with thousands of cores will be commonplace in the near future.

2.C Path Forward

We recommend a national effort with high standards and coordinated work. We propose a Computational Scattering Science Steering Committee (CSSSC) to coordinate several teams that develop and test tools for computational scattering science, and work with the staff and scientific users of neutron, x-ray, and electron scattering facilities. This committee should include members of both the user community and facilities, because both are stakeholders in the path forward. Depending on the structure of the software development teams, the CSSSC membership could comprise the leaders of the software teams who are doing the work. An interim membership would serve for two or three years, but a proper succession mechanism needs to be developed.

In his book "The Mythical Man Month", Brooks argues that efficient software development teams comprise approximately seven persons with one team lead. Each development team, located at a national user facility or university, would be composed of approximately two scattering scientists, one lead developer or software architect, two software developers, one technical writer, one person for testing and team support, and one person for user support. Several such teams are needed to cover the field of computational scattering science. To minimize duplication of effort, different topical areas should be assigned to different user facilities. Assignment should be based on mission, but it is critical to also consider the expertise of the personnel. Computational scattering scientists are scientists, and their work is not interchangeable. Strong forces are needed to ensure coordination. Budget authority, or at least some of it, must be centralized with the CSSSC.

A computational scientist on the team would serve as a mentor for new users, a collaborator for intermediate users, and a peer for advanced users. For members of the scattering community, such persons would lower the entry barrier for using computational tools, and would build trust in computation for scattering research. A computational scattering scientist in the position of team leadership would ensure that the software development proves useful for scattering science. Most software project failures occur because the product requirements are not adequately communicated to the software developers. This is less of a concern when the developers are expert scientific users themselves, or if such persons are on the development team.

Professional standards for the process of software development need to include project management

tools for earned value, design reviews, repository management, and the tracking of bugs and feature requests.

Software teams must extend beyond software development and scientific computing, to maintenance, education, and user support. It is usually best to separate quality assurance from development functions, but planning for quality is needed in the software design. Automated testing will be essential, especially if new features are added frequently. Fortunately, tools for automated building and testing are becoming mature, but these systems require maintenance, adding to labor costs. An important ongoing function for the team will be responding to requests for bug fixes and feature requests. Having computational scattering scientists as part of the team will ensure correctness of the code, and they can best assess the cost and value of feature requests.

A total number of personnel of 60-70 would cover all of computational scattering science, and rapidly advance the field. A larger effort does not seem manageable. Assuming a distribution of positions from postdoctoral fellows to senior scientists, a set of eight teams of eight persons would require an annual budget of approximately M$ 15/year. A smaller effort could be started with fewer teams, but would cover fewer topics in computational scattering science. Expansion of effort should occur by adding new development teams, rather than changing team sizes. The distribution of these teams across topics, and their location at specific labs or universities, will require a more specific proposal than can be given here. We hope that both DOE BES and the NSF would entertain such a proposal.

3. Topic Reports

3.A. Correlated Electrons

Robert J. McQueeney, Mike Norman, Gabriel Kotliar

John Freeland, Bruce Harmon, Gabi Kotliar, Rob McQueeney, Mike Norman, Ray Osborn, Toby Perring

Background and Scope

Correlated systems are by definition materials that lie beyond the purview of standard electronic structure methods used to evaluate material structures and properties. In correlated materials, traditional concepts of solid-state physics break down. New ideas and methodologies are needed to put experimental results in a proper context. Many body theory provides this framework, and allows for the interpretation of various spectroscopic features. Theoretical ideas and novel algorithms and methodologies based on quantum many body theory are needed for accurately modeling, understanding, and exploiting new phenomena and materials such as high temperature superconductors, superhard ceramics, topological insulators, and better permanent magnets, catalysts, and ionic conductors.

By their nature correlated electron systems, where observed ground states result from a sensitive balance of multiple energy scales, pose a great challenge to theoretical methods. New theoretical approaches must develop in concert with state-of-the-art experimental techniques. This process can ultimately validate advanced theoretical models as appropriate and lead to a predictive description of novel material phenomena, or at least assess a model's shortcomings and point the way to the development of more refined models.

A wide variety of scattering techniques are applied to the study of correlated electron systems, such as single crystal and powder diffraction, inelastic neutron and x-ray scattering, ARPES, and STM. These techniques provide a detailed microscopic description of the myriad of magnetic, charge, and orbitally ordered states, and their fluctuations. Spectroscopic studies of the magnetic, electronic, and lattice energy scales give insight into the nature of the interactions that lead to novel behavior.

Current Status

It is beneficial to look at the present status of specific experimental techniques and some existing theoretical methodologies to assess the role of computation in the study of strongly correlated electronic systems. As the subject is a vast one, we chose to discuss two spectroscopies: elastic and inelastic neutron scattering, and resonant and non-resonant inelastic x-ray scattering.

Neutron scattering

Neutron scattering has the capability to measure lattice and magnetic excitations, and the scattering cross-sections can be related directly to the correlation functions obtained from linear response theory. For example, magnetic scattering of neutrons provides a window into how the spin and orbital moment is distributed in space and fluctuates in space and time. Neutrons therefore provide a powerful probe for validating theoretical models and, conversely, appropriate theoretical models can, in principle, predict neutron scattering cross-sections. Despite this direct association, the condensed matter community does not often take advantage of the coupling between frontier theoretical calculations and state-of-the-art scattering methods.

A typical approach by the neutron community is to work with simple model calculations or analytic forms for the response functions and determine where such simple data treatments fail, since this often indicates "anomalies" that could signify new and potentially interesting physics. Going beyond the mere identification of novel phenomena in scattering data to a deeper understanding of the underlying microscopic interactions requires close contact with theoretical efforts, and the data must be compared to the calculation or simulation of an appropriate correlated electron model. Such theoretical calculations can, for example, take the form of phonon or magnetic scattering derived from *ab initio* electronic structure calculations or could be numerical simulations from model Hamiltonians. These calculations often exist in the literature, however, significant effort is required to cast these calculations in a form that can be compared

directly to the scattering data. In the field of strongly correlated materials, much can be gained from a tighter coupling between theory and the output of scattering facilities. This is generic to all spectroscopies.

The elastic neutron scattering cross-section is traditionally factorized into a form factor and an autocorrelation function. The form factor can be measured directly even in materials which do not order magnetically by applying a magnetic field to induce a moment. The neutron scattering community compares the induced form factor measured with polarized neutrons against LDA calculations in itinerant systems, or against atomic physics calculations in materials containing localized electrons. This approach is insufficient in cases where the relevant electrons are not well treated by either a fully localized or fully itinerant model. For example in the Pu 115 material that holds the record for the highest superconducting critical temperature among the actinide materials, the measured form factor cannot be accounted for even at the qualitative level by either LDA calculations or by atomic physics calculations, requiring a more sophisticated DMFT treatment [1]. Similar issues occur for the cuprate compound Sr_2CuO_3. A recent study showed the importance of using advanced methods such as density matrix renormalization group along with an improved Wannier function technique that included oxygen covalency to extract a sensible interpretation of the data [2].

A second example of how a tighter coupling between theory and experiment will be beneficial to the scattering community is provided by the interplay of magnetism and unconventional superconductivity. The observation by neutrons of a sharp magnetic excitation (called the spin resonance) in the superconducting state of the cuprates [3] established a connection between magnetism and unconventional superconductivity. While many empirical details of the resonance are known, such as the relationship between the resonance and the energy gap, the nature of the resonance has many theoretical interpretations [4], and its role in superconductivity itself is debated. One interpretation considers the resonance as a bound-state exciton [5]. Within the random-phase approximation, the exciton approach has the capability to make quantitative predictions of neutron scattering data. Quantitative comparisons of calculations and neutron data have been done only in limited cases (e.g. Ref. [6]), owing to the dependence of the spectra on material-dependent details of the band dispersion and the strength of electronic correlations. The resonance has now been established as a general feature observed in a variety of unconventional superconductors, such as heavy fermions [7,8] and pnicitides [9,10]. A stronger coupling between experimental and theoretical studies of the resonance can lead to a greater understanding of the resonance, and the superconducting state itself, and help establish general trends that unite a variety of novel superconducting compounds.

In the normal state, it is possible to do system specific calculations of the frequency and momentum dependent susceptibility using variations of *ab initio* Green's function RPA methods. This captures the effects of itinerant magnetism (i.e. Stoner excitations) and collective excitations [11,12]. Early studies were limited to simple 3d-ferromagnets (Fe, Ni) [13,14]. Advances in computer power and numerical algorithms and advanced basis sets allowed a team to perform *ab initio* RPA-type calculations for more complicated systems (10-20 atoms per unit cell) as well as the iron pnictides. This theoretical tool development has been performed in close contact with the Ames neutron scattering group, and corresponding studies proved to be very well suited to each other. For instance, the theory uniquely determined the presence of damping due to electron-hole transitions that otherwise would have been hard to identify [15].

X-ray scattering

The increase in brilliance of modern x-ray sources opens new vistas in materials exploration. This is well known and has been documented in various DOE reports. It is less well known that advances in many body theory and computing power can enhance much further the insights that are obtained from the investment in instrumentation.

An important problem for the scattering community was the determination and understanding of the phonon spectra of plutonium. This material is challenging, as it is not well described by density functional theory due to the strong correlations present in the f shell. It is also challenging for experiment due to the availability of only small single

crystals. Application of the LDA+DMFT machinery to this problem resulted in a theoretical prediction of the phonon spectra of δ plutonium [16]. Interesting features were noted, for example softening of a phonon mode at the zone boundary and the near degeneracy of the acoustic and transverse branches over a broad region of the Brillouin zone. Inelastic x-ray scattering measurements in non-resonant mode [17] at the ESRF determined the phonon spectrum. The qualitative agreement between the predicted and observed spectra was excellent, in spite of the approximations involved in the calculations. Theory and experiment can now focus on the areas where the discrepancies are largest, instead of scanning blindly in parameter space.

Resonant scattering allows for further gains in signal to noise and element specificity. This is ideal for identifying complex ordered states in materials with strongly interacting electrons. In transition metal oxides, spectroscopy and scattering at the L edges are ideal since they directly probe the 3d states of interest. From valence orbital configurations in systems such as cuprate high temperature superconductors, to long range ordered states of charge and orbital order [18-27], these resonant techniques have provided tremendous insight into local electronic structure. However, the interpretation of these results is strongly dependent on theoretical interpretation of the resonant data, where the strong core-hole interaction can have a major influence on the outcome. In almost all cases, this is handled in the limit of quantum cluster calculations with a single transition metal atom coordinated by oxygen. Can one apply a more sophisticated approach to refine the local picture of the electronic properties? Can we extend *ab initio* methods, which give insight into the physical mechanisms behind the ordered state, to interpret these results? Combinations of DMFT and quantum chemical packages such as TT-muliplets are promising avenues as demonstrated by the recent work of M. W. Haverkort and colleagues at the Max Planck Institute in Stuttgart, Germany.

There has also been considerable progress in theories of x-ray spectra (both absorption and scattering) for non-strongly correlated systems. Perhaps the most successful of these is the GW/Bethe-Salpeter Equation (GW/BSE) method [28]. This approach builds in several key many-body effects crucial to a quantitative description, for example quasi-particle self-energy corrections of the photoelectron and hole, based on the Hedin GW approximation account for peak shifts and final state broadening. It also includes the screened interaction between the photoelectron and the hole that accounts for excitonic effects observed in many systems. At present, a number of GW/BSE codes have been developed both for valence and core spectra.

Future Developments

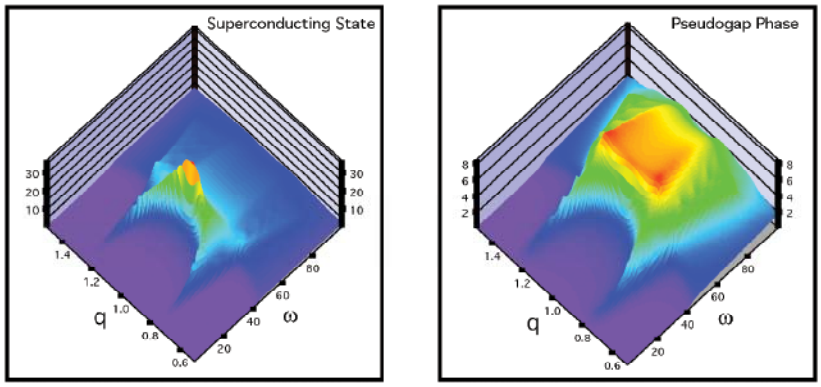
It should be clear from the above examples that computational materials science and the theory of strongly correlated electron systems has developed at a breathtaking pace. At the same time, the scattering community currently underutilizes these advances. As can be seen from the examples of the previous section, two steps are identified in the methodology of the analysis and interpretation of scattering data:

(1) Identification of novel unexpected phenomena or validation of theoretical suggestions in scattering data.

(2) Understanding the origin of novel phenomena by comparison to detailed theoretical models or *ab initio* calculations, or refinement of these approaches when the experiment was motivated or already well described by theory. Ideally this cycle should be iterated until a deeper understanding is reached.

Both steps could benefit from advances in computational scattering and require a closer involvement of the theoretical and computational community with the scattering community. For step (1), there is a strong desire to have a core set of routines for simple well-established analyses of scattering data. Such routines should be standardized as much as possible and made available at all of the scattering facilities whenever possible. Specific instruments should have such routines available and embedded with instrument specific computational routines, such as resolution convolution and matrix elements.

The resulting software suite will allow for more efficient use of instrumentation by providing a rapid assessment of where the interesting phenomena reside, thereby allowing experiment to focus on them. Examples of routines might include calculations of



Calculation of the dynamic spin susceptibility of a cuprate in the superconducting phase (left) and the pseudogap phase (right). These RPA calculations are based on dispersions derived from angle resolved photoemission data. Note the change from a commensurate spin resonance in the superconducting phase to incommensurate behavior in the pseudogap phase.

model and *ab initio* phonon dispersions, spin waves, crystalline electric field excitations, and simple forms for the response functions (such as long wavelength or symmetry imposed limits). Time-of-flight inelastic neutron scattering analysis suites, such as VNF, seem like the right approach, but only limited phonon models are available at this time and it should be expanded to include a fuller range of models.

There is a strong desire to use *ab initio* electronic structure approaches to deal with electronic, magnetic and phonon excitations. There is no doubt that even though the theoretical methods are approximate, they can give considerable insight into the experiments, helping separate the different contributions (lattice, electronic, magnetic) to the cross-section in a given material. Currently, most of the interpretation of magnetic excitations by experimental groups is done using simplified models that do not take into account the real electronic structure of materials.

The unambiguous identification of novel phenomena also requires that data analysis software be available to routinely make estimates of common "backgrounds" such as multiple scattering. Note that the "background" may also include single and multi-phonon scattering cross-sections if the magnetism is of interest (or vice versa). Analysis software should be able to provide accurate estimates of these scattering processes, many of which should be available in the set of core analysis routines.

In parallel with the development of more advanced theoretical tools, such as *ab initio* calculations of the dynamic susceptibility, we can start to ask more of the techniques themselves. A good example is the development of inelastic neutron scattering using polarized beams. Polarized beams allow for an unambiguous separation of magnetic and lattice signals, especially in regions where overlapping excitations occur and can mix, and can resolve the full susceptibility tensor. Modern TOF inelastic instruments with polarization capabilities are starting to become a reality. For example, the HYSPEC instrument at the SNS will offer polarization analysis using Heusler monochromators and a choice of either ^{3}He or supermirror polarizers offering energy transfers up to 100 meV. A suite of data reduction and analysis routines will be required for polarization studies. These more advanced experimental techniques should be used to validate theoretical developments that will later be used in the experimental facilities for further analysis. For example polarized neutrons should validate the theoretical phonon background subtraction used in the analysis of neutron scattering cross-sections.

The second step concerns computational efforts that allow one to go beyond the simple model analysis routines in order to better understand the origin of anomalous features found in the scattering data. In this case, the measured data must be compared to theoretical models that can be quite specialized and tailored for certain systems. Such computational approaches are available in some form in the theoretical community, and they continue to be generated in response to experimental data. A clear issue is how to take the available theoretical efforts and cast them in a form that is useful to the analysis of experimental data. As the theoretical approaches can be quite technical, and system specific, it is essential that this step involves close collaboration of experimentalists and theorists. These efforts may or may not require the use of high-performance computing. In cases that they do, computational resources should be made available for this purpose.

How Do We Get There?

How do we develop in parallel theoretical and experimental spectroscopies, building on the significant advances that have taken place and

continue to take place at an accelerated rate? How do we create and maintain community codes in the US that can describe correlated materials, building on the existent efforts in the US and in Europe? How do we make the expertise needed to compute the properties of correlated materials available to users of national facilities that need to have access to computation in order to provide a basic interpretation of their results? Given that computations in correlated electron materials, and the visualization of massive data sets requires a lot of computational power, how can this infrastructure be developed and made available to the users? These are serious issues that the DOE should address in order to maximize the benefit they receive from the experiments performed at their scientific facilities.

There are obvious paths forward to assist with step (1) of the previous section. One needs to standardize and combine with instrumentation specific details the computational tools of today which have proved their success in many instances, so that the community can use them more broadly. For step (2), it is essential to continue the investment in theory and computation, enhancing the ties with experiment, the development of codes, as well as the development of methods, concepts, and phenomenologies, thus sustaining and invigorating the experimental efforts. Close ties between theory and experiment have been the tradition in condensed matter theory in the US, and we should build on it to keep the US competitive in this area where Europe and Japan have taken the lead, and China is rapidly advancing. For example, methods such as single-site LDA+DMFT can now be applied to a very large class of systems, and comparisons of photoemission calculations to experiment have been done in several cases. There are strong European and Japanese efforts to incorporate all the recognized advances in electronic structure into codes for use by a small community as a development platform, and by a larger community as a platform for applications. GW and hybrid methods are now part of VASP, but require considerable sophistication and computer time on the part of the user to obtain meaningful results. The same is true for *ab initio* phonon calculations, and will be the case as well for single-site LDA+DMFT. No standardization of dynamic susceptibility calculations exists in these packages, but this development is certainly feasible in the GW/RPA context. The same applies to methods for evaluating exchange constants and crystal field splitting in localized materials. To summarize, there is an arsenal of methods that could be put at the disposal of the scattering community for routine use in their analysis of experimental data. While this is entirely feasible and well defined, it entails a substantial commitment of resources.

Other powerful techniques such as resonant elastic and inelastic x-ray scattering, and resonant photoemission spectroscopy, involve correlation functions containing two frequencies for their interpretation, as does time resolved photoemission spectroscopy. Theoretical approaches to model these responses in real materials are in their infancy, and thus not ready for standardization, but their development could be accelerated.

For materials where the correlations are highly non-local, many new methods are becoming available, are rapidly evolving, and are currently not available in standard software packages today. The formulation of these techniques is at the level of model Hamiltonians, but they should be followed carefully to accelerate their transition to the modeling of real materials. These include quantum Monte Carlo with improved fixed node approximations, density matrix renormalization group (DMRG) and attempts to extend this to higher dimensions (i.e., tensor renormalization group methods such as MERA and PEPS), exact diagonalization studies exploiting all symmetries, and numerous extensions of DMFT to a cluster of sites (DCA, CDFMT, and generalizations thereof), and functional renormalization group. Solutions of model Hamiltonians can be systematized and coded in a uniform format. Again, the main effort seems to be in Europe, for instance the ALPS project (http://alps.comp-phys.org). In this context, as in the development of electronic structure codes, the US is lagging behind.

Several complementary approaches can be followed to advance this scientific program:

- The facilities should develop a core set of analysis routines available in an easy to use computational framework.

- Analysis routines from users and other members of the materials community should be sought and modified to fit into this framework.

- This framework should also include the capability of

calculating instrumental effects, such as resolution, background, absolute scaling, and sample dependent effects, such as absorption and multiple scattering.

- And said framework should be professionally coded software and available remotely. Scientific computation groups at the facilities could be responsible for these tasks.

To establish a connection between experimental results and applicable theory, networks of theorists are needed. Teams from universities and national labs could form to tackle these challenges along the lines of the CMSN model. For weakly correlated materials, multiple scattering techniques developed by John Rehr in this framework has been successful thanks to continued funding over many cycles. Continuous dedicated funding is definitely needed to sustain software development efforts. There are many parallels between software development support and experimental facilities support.

Another avenue is having theorists reside for periods of time as visitors at national labs. A third alternative is to exploit the delocalized nature of computation, which could be distributed among different nodes and teams. This is the pattern followed by the European Theoretical Spectroscopy Facility (http://www.etsf.eu), which is managed exactly the same way as an experimental facility. Users submit proposals for calculations that require theoretical support, the proposals are ranked, and teams of experts and their postdocs at various universities provide theoretical support.

Access to high-performance computing will continue to be essential. Computational platforms are constantly changing. Today it seems most likely that further advances will come from massive parallelization rather than from increases in clock speed. However, it is not at all clear if this will take the form of GPU/CPU hybrids or simpler multicore architectures. Thus flexibility is essential. Different architectures may turn out to be much more successful for different algorithms and applications, and finding this will require direct experimentation with different machines and codes.

In addition to the supercomputer facilities, it is essential to support intermediate scale computing. The cost of these facilities is intermediate between those of a PC (1K) and that of teragrid facilities or other supercomputer facilities (1000K). Single investigators or small groups of investigators should have direct access to these resources to facilitate the development of codes for the new architectures. Many innovations are the outcome of small-scale research. The distributed structure of the computing effort would facilitate the selection of the most promising candidates.

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3.B. Chemical Processes Far from Equilibrium

Lin X. Chen

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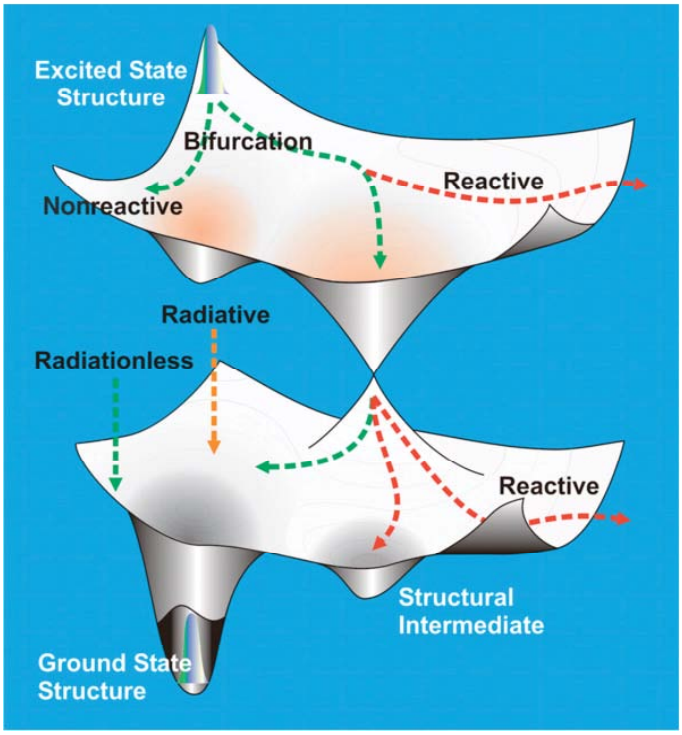
Chemical transformations often undergo pathways far from equilibrium. Understanding details of electronic and atomic movements under non-equilibrium conditions and their response to external driving forces that cause the transformation is crucial for chemical sciences in the 21st century [1]. Microscopically, an individual molecule is at a non-equilibrium state when it undergoes a chemical transformation, even through the ensemble of molecules may appear to be at equilibrium. Under the influence of a driving force, i.e. heat, pressure, light, electric field, reaction coordinates and energetics are dynamic, and constantly evolve on time scales from femtoseconds to seconds, and on length scales from sub-Ångstroms to nanometers or longer. Therefore, it is challenging to capture atomic and electronic structures of molecules when far from equilibrium unless one can either monitor a single molecule or particle, or synchronize the actions of all molecules in the chemical processes and utilize experimental tools with a time resolution sufficient to follow the molecular trajectories during the chemical transformation.

The advances in accelerator-based x-ray sources with high brilliance and short pulses open a new paradigm in imaging chemical processes far from equilibrium with multiple spatial and temporal resolutions. For example, transient structures of molecules, molecule/solvent complexes and solvent structures as a function of time after photo-excitation have been captured by combining local structural imaging with transient x-ray absorption spectroscopy (XAS) [2-5] and global structural imaging with transient small/wide-angle x-ray scattering (S/WAXS) [6-8]. An ultra-short pump laser induces an electronic redistribution that triggers an elemental chemical event synchronously among molecules. A subsequent probe x-ray pulse interrogates the time evolution of the event in the chemical process, following the initial trigger that pushes the chemical system far from equilibrium. This method synchronizes an otherwise randomly occurring chemical process among molecules in an ensemble, allowing their reaction trajectories to be monitored. Non-equilibrium chemical processes may also be triggered by sources other than light, or the pathways may be altered. Pressure or temperature causes phase transitions through a series of meta-stable structures, e.g. glass melting/cooling [9,10], and catalytic reactions on the surfaces of metal nanoparticles [11-13]. Transient x-ray studies, therefore, can provide unique and direct structural information on molecular structural rearrangements from reactants to products and solute/solvent interactions that are currently available only through theoretical quantum mechanical calculation and molecular dynamics simulation.

Computational studies on chemical processes far from equilibrium have made tremendous progress in past decades [14-15]. Molecular dynamics [16-19] and reverse Monte Carlo simulations [20-22] routinely produce the dynamic trajectories and trends of structural changes under pressure and temperature for systems from small molecules to small solids and interfacial systems. In a number of cases, incorporating structures along the dynamic trajectories with experimental x-ray scattering and absorption data gave successful agreements with experiments. Today, however, the majority of experimentalists have neither the computing facilities nor the expertise to couple commonly-used software packages together. In addition, there is still a huge gap in computation capabilities in producing trajectories long enough to be compatible with the time scale of the events to be simulated. For example, glass melting phenomena have been studied by x-ray and neutron scattering methods, and meanwhile have been simulated by molecular dynamics with 50,000 atoms. However, the currently achievable trajectory for such a system covers a ps time scale, while the event of interest takes place on s ms time scale – a gap in time by a factor of 10^9. A recent example of MD simulation of a platinum cluster (Pt_{10}) rolling on an aluminum oxide surface indicated that only when individual structures along the MD trajectory are included in the FEFF calculation can agreement with experimental data be obtained [23]. For laser pulse

pump and x-ray probe XAS, structures of valence-excited states can be calculated via TDDFT or *ab initio* QM methods, and compared with experimental data. Such calculations are far from routine, especially for systems with many atoms or heavy atoms. Nevertheless, the new transient structural results from the laser pump/x-ray probe studies promise to put to test theoretical models. Unfortunately, calculations with simultaneous core and valence excitations are few, but these will be necessary as the x-ray pulses from the new generation of sources push the time-resolution into femtosecond regime.



Schematic of the potential energy landscape of ground and excited states in complex molecular systems showing dark structures in molecular radiationless transitions determined by ultrafast diffraction [Srinivasan R, Feenstra JS, Park ST, Xu SJ, Zewail AH, Science 307, 558-563 (2005)].

Successful computations of the electronic configuration and geometry of molecules with excited valence electrons are needed urgently, especially for metal complexes. Calculations of the XANES spectra for molecules with excited valence electrons need to be conducted more routinely with consideration of the influence of the valence electron excitation on the core to continuum excitation in x-ray absorption spectroscopy. The existing software for x-ray absorption spectroscopy, such as FEFF [24-26], requires further development to calculate molecular systems with full quantum mechanical potentials connected to MD methods. Quantum mechanical software packages dealing with core excitations and valence excitation need to be developed to produce acceptable agreement with XANES and pre-edge regions for molecular systems. There is an urgent need to develop a quantum mechanical methodology and computational models for x-ray absorption spectra of the excited valence electron state, the influence on the nuclear geometry, and the interference between the valence and core level excitations. If the correlations between the electronic and nuclear structures of photo-excited states and the core and valence excitations can be modeled, our understanding of structural/functional correlations of molecules will be greatly enhanced.

These correlations can also be obtained with high-resolution single-crystal x-ray and polarized neutron diffraction to map the crystalline electron and spin densities. With advances in neutron and x-ray sources, it is becoming possible to collect x-ray and neutron data under the same conditions on the same crystal. This experimental breakthrough has initiated a renewed interest in the application of orbital-based scattering models. This method would use molecular orbital (MO) scattering factors derived from *ab initio* quantum chemical calculations and would adjust only the MO occupation numbers when performing fits to the data. The simultaneous interpretation of x-ray and neutron experiments will lead to an unprecedented flow of quantitative information on the valence electrons in paramagnetic materials and materials in photo-excited states. What is required is software to quickly and easily refine joint parameters (conventional structural, displacement, majority and minority spin density parameters) against combined data. Software that is easy to use and provides fast results can then be used to implement parametric studies of the dependence of the electronic structure of materials with temperature, pressure, chemical composition or photo-excitation to understand how changes in charge and spin density properties affect chemical activity. For solid phase non-equilibrium systems, combining refinement Monte Carlo processes with MD simulations will be a way of providing feedback from experiments into simulations.

Because both computational and experimental studies on chemical processes far from equilibrium are still at the forefront of chemical sciences, a significant growth of the community in next decade is expected to accompany the construction and operation of several new x-ray sources with femtosecond pulses. Therefore, the time is right to bring theoretical and experimental scientists together to establish frequent communications and fill the gap between the knowledge obtained from new facilities and newly gained computational capabilities. One-on-one collaborations in a center associated with a facility may be a way to attract people to form a critical mass tackling the challenges. For some software packages with a broad user community, such as FEFF, the continuous development, maintenance and update to meet the new experimental frontier should be supported.

In summary, proper simulations of chemical processes far from equilibrium require a combination of real-time density-functional theory/finite temperature molecular dynamics (DFT/MD) calculations and simulations of x-ray absorption spectra, for comparison to synchrotron radiation-based x-ray experiments. The availability of accurate first-principles techniques to simulate the dynamics of these chemically active systems offers new electronic and structural insights into the dynamics, electronic fluctuations, and ultimately the catalytic activity of these systems. In combination with recent advances in high-performance computing (HPC), computational approaches are now on the brink of revealing and exploiting the fundamental processes underlying the activity of nanoscale catalysts. This approach recognizes the importance of linking simulations to complementary experimental characterizations. This capability will enable the verification of the proposed structural and dynamical models by direct comparison with core-level spectroscopy experiments.

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3.C. Nanostructures: Structure and Dynamics

Joseph E. Curtis

Frank Bates, Joseph E. Curtis, Brent Fultz, Bruce Harmon, Ken Herwig, Dean Myles, Peter Rez, Franz Trouw

Introduction

The topic of nanostructures is a broad one that spans across different scientific disciplines as diverse as biology and hard-condensed matter physics. Nevertheless, there are some common themes. The ability to perform precise calculations on a small number of atoms has been extended to study much larger clusters, or individual nanoparticles. From the other direction, as materials dimensions become smaller, surface phenomena take on a larger role, and confinement effects become important at the nanoscale. The nanoscale is where quantum mechanics meets continuum mechanics, phonons become heat, spins become magnetism, and electronic excitations become conductivity. Computational tools at the level of electrons and computational tools at the continuum level meet at the nanoscale. Interfaces between different fields of study also occur at the nanoscale, for example, when there are physical interfaces between hard matter and soft matter or biomaterials.

Many of the Grand Challenges identified in Department of Energy reports over the past decade have identified that new technologies are going to require the creation of advanced materials that require the characterization of structure and dynamics of these materials at levels beyond our present reach [1-3]. Understanding complex materials with theory, computation and advanced simulation methods is essential to adequately increase the rate of discovery and innovation [1]. In fact, it has been concluded that nanoscale measurements require computational methods to describe observed behavior, otherwise the development of nanoscale technology will be seriously inhibited [2].

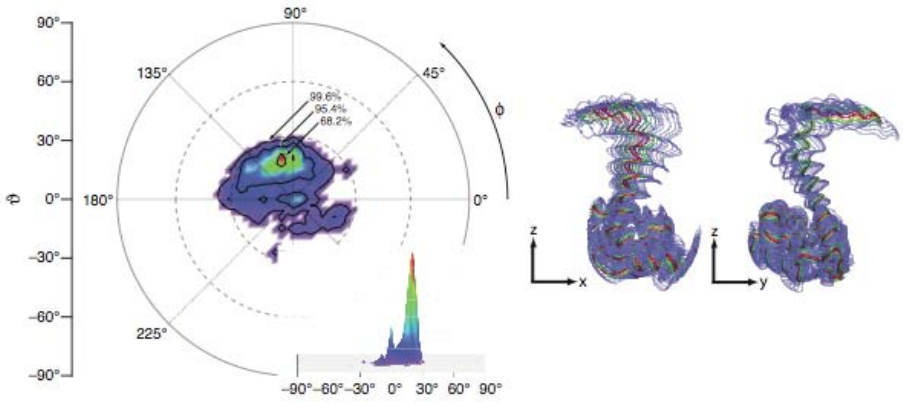
Nanoparticles: Structure

High resolution electron microscopy coupled with electron energy loss spectroscopy (EELS) at the atomic resolution level is a powerful technique for studying local changes in structure and bonding. These methods have undergone rapid advances with the development of aberration-corrected electron microscopes [4,5]. To get the most information from electron microscopy of nanostructures, we must move beyond just recording images, and use the data to quantitatively test models and hypotheses. Theory and computation should be used as the link between structure as determined by imaging, and bonding as measured by EELS.

Atomistic level modeling, using techniques such as *ab initio* and classical molecular dynamics (MD), is mature and routinely used with considerable impact on diverse scientific fields. For scattering experiments in soft materials at the nanoscale, molecular dynamics frequently addresses similar scales of length and time, and MD can be the technique of choice for modeling large assemblies of atoms.

The availability of such theoretical and computational methods does not guarantee that the techniques are used in an efficient manner. In our experience at various national laboratories and scattering user facilities, computational methods are typically used after data are collected, even though the entire experimental design, data acquisition, data analysis process would benefit by the application of computational scattering techniques throughout the experimental process. For example, recent studies of self-assembled multilayers of molecules exhibiting non-linear optical activity benefited from the post-experimental insights provided by both *ab initio* methods and molecular dynamics simulations. The application of theory in conjunction with x-ray and neutron scattering data had a dramatic impact on the molecular level understanding of the molecular conformation (shovel shape), self-assembly process, and the resulting disorder in the multilayer film. If computational methods could be augmented with scattering-specific features for materials science problems, the combination of theory and scattering experiments could have contributed to the decisions made during the early synthesis and self-assembly phases of the project. An investment in software development to create an efficient and user friendly theory suite of established techniques such as

quantum and classical computational chemistry and simulation methods focused on the modeling and interpretation of scattering experiments will yield large dividends in the understanding of scattering data, and allow us to use theory to guide the experiments while they are in progress.



The HIV-1 Gag multi-domain protein mediates assembly of new progeny viruses on the cell membrane of an infected host cell. The Matrix (MA) domain of Gag is responsible for targeting the protein to the membrane. Using neutron reflectivity and computational modeling, the orientation of MA, and therefore the binding interface of the protein to the membrane surface, was determined. These results provide important molecular insight into the interactions that drive membrane binding and specificity of Gag during viral assembly [Nanda, H., Datta, S. A. K., Heinrich, F., Losche, M., Rein, A., Krueger, S. Curtis, J. E. Biophys. J. 2010; 99, 2516.].

Many biological systems of interest span length scales that are well beyond those attainable using state-of-the-art simulation techniques. For example, the study of heterogeneous protein, nucleic acid, and lipid complexes are key components being studied by the systems biology research community. Many of these systems are studied using scattering methods. Software to design and interpret scattering data of such large and inherently flexible molecules is not easily accessible by biologists who study these important systems, and many methodological questions remain open. Biological scientists are typically not expert in scattering or computational methods. Thus, they face two barriers that prevent them from fully exploiting national scattering resources. Computational scattering science can address both of these issues by providing basic resources (accessible and user-friendly computer programs, case studies) to both educate users with biological applications, and to streamline both the pre- and post-experimental computational analysis methods.

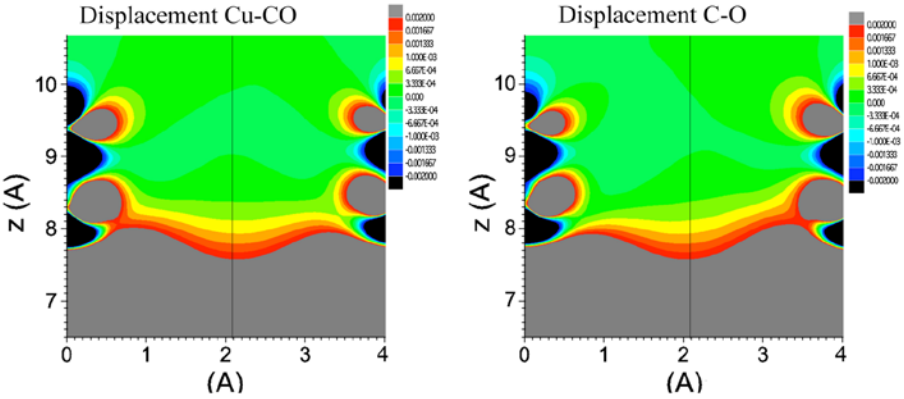
Nanoparticles: Dynamics

Studies on excitations are important for understanding the chemical reactivity and the stability of nanomaterials. High-resolution inelastic x-ray scattering studies of phonon excitations, and inelastic neutron scattering measurements have found large effects on the vibrational spectra, which were subject to various interpretations [6-16]. Evidence for 2-dimensional behavior is not found until extremely small particles are formed, of dimensions less than a few nanometers [15,16]. These particles are amenable to the molecular dynamics simulations of today, which revealed clear differences in vibrational characteristics of atoms at surfaces and in the bulk, and identified some of the unusual features of the vibrational spectra [14-16].

Another opportunity for computational scattering science is to incorporate lattice dynamics directly into calculations of surface phenomena, including rates of chemical reactions on surfaces. Except for molecular dynamics simulations, most methods assume the ion cores to be frozen, or include vibrational effects through diffusion pre-exponential factors or the local harmonic approximation. While vibrational entropic considerations may account for only about a tenth of the system free energy [17], they can play a critical role in determining system structural stability and phase transitions. Theory [14] and experiments [10,15], on the other hand, have revealed novel features in the vibrational density of states for nanoparticles and other nanostructures that have interesting consequences for thermal transport, temperature dependence of heat capacity, signatures of alloying, or measures of structural stability. Methodologies to include vibrational dynamics of surface phenomena are in prototype form, and can be adapted for computational scattering science studies of surfaces.

Computational software and algorithms to study the dynamics of soft-matter systems are quite mature, but unfortunately not directly accessible to the scattering community. There are many areas where computational methods could be applied to study the dynamics of soft-matter systems from times of femtoseconds to microseconds, but there are high

barriers to learning the applicable theory and implementation details for performing such calculations. Indeed, it has been noted that there needs to be an effort to remove the obstacles to effectively exploit existing high-end computational software, resources and facilities [3].



Substrate mediated CO-CO interaction resulting from charge density fluctuations induced by vibrational displacements patterns, at the Brillion zone boundary, of the CO internal stretch (ν_1) and the C-Cu stretch (ν_2) modes. The charge redistribution (left panel) led by ν_2 remains local as one CO does not feel that the neighboring CO is vibrating, while that led by ν_1 (right panel) has longer range and the neighboring CO molecules are affected by each others displacement. The differences in the dispersion of the two modes for a c(2x2) overlayer of CO on Cu(100), found in density functional perturbation theory calculations can be explained by the charge density distributions below. There is also good agreement with experimental data. More such work is needed for more complex systems provided resources are available [M. Alcántara Ortigoza, R. Heid, K. P. Bohnen, and T. S. Rahman, J. Phys. Chem., in press].

Major investments in instrumentation to measure the dynamics of nanostructures have been made at national laboratories and scattering facilities. The use of computational methods to aid in the interpretation of dynamical data requires close interaction between experimentalists and computational scientists. There are demonstrated successes with these types of collaborations, but the rate at which discoveries can be made would be increased dramatically if the computational methods were made more accessible to experimentalists. This point continues to be largely unaddressed, although it has been recognized that well designed modular software tools need to be developed for the efficient use of scattering resources [2].

Goal State

Scattering science has been unable to fully utilize the ongoing advances in computational methodologies and hardware technology. This inhibits the progress that could be made on Grand Challenge problems in nanomaterials. In a five-year timeframe, increasing the accessibility of established computational scattering codes would allow significant advances in computational scattering science. A primary goal should be to reduce the barriers that prevent the application of existing theoretical and computational methods by new and established scattering scientists.

Diffraction studies of nanostructures benefit from new tools such as the atomic pair distribution function (PDF) method, and hard x-ray free electron lasers (for example LCLS) may probe individual nanoparticles. Nevertheless, both methods face severe computational challenges for extracting structural information at the nanoscale.

Studies of nanostructured materials are often close to, or beyond, the information limit in the data, where the complexity of the structure solution is greater than the information content of diffraction data. This will require a new paradigm such as "complex" modeling [18], where multiple information sources are complexed in a single structure solution. Modular software frameworks are needed to implement such schemes because the computation changes with the problem being studied and the information being complexed. This new paradigm will demand both code development and scientific sophistication.

Modern diffractometers are generating huge quantities of data and high throughput studies are often needed to understand complex materials. A key bottleneck in the scientific process is getting from raw data to the scientific result. This requires sophisticated, robust, flexible, but user-friendly software.

Software to interpret experimental data should have an accessible component to predict, *a priori,* experimental scattering results using theoretical tools and atomistic modeling. This would allow for better utilization of national scattering resources; both in the review of scientific proposals for allocation of these resources, and in the stimulation of ideas by users of such facilities before the proposals are

finalized. This latter aspect could be easily adapted to provide training to new scattering users to allow for "what-if" questions both in individual and workshop environments.

These goals can be achieved through training programs, increasing the staffing of theoretical and computational scientists, increasing software support, and encouraging the development of robust, well designed open-source code to access and unify existing computational code that links atomistic simulations to experimental observations.

Path Forward

Many Grand Challenge problems in nanoscience and soft-matter science can be addressed more efficiently with investments in computational scattering resources.

Continued long-term improvements in computational methods are expected, but significant improvements can be made in the near term by increasing the efficient use of computational methods at scattering centers at the national laboratories. This can be achieved by reducing the barrier to access existing software, increasing outreach and training of new users to computational methods, increasing the interaction between theoreticians and computational scientists with users, and making core data analysis routines generally available at national scattering facilities.

A tremendous amount of computational software to simulate nanoscale structures and dynamics exists, so in many cases there is no need to reinvent this software. That said, there is a very strong need to improve the accessibility of this open-source code base and provide the link to the calculation of scattering observables. The link must include important instrument details (such as resolution functions, sampling, background correction, and must accommodate data file formats).

High-level computing languages allow access to a wide scale of computational software techniques have presented a unique opportunity to bridge often disparate computational methodologies. For example, one can write human readable code in a language such as Python, and in a few lines can call system functions, write an input file, run a computational chemistry package, extract the data, send the data to a scattering application, process the results, and then call a graphics program to display the data. Thus, there is an opportunity that was not technically feasible just a few years ago, to put the pieces together to tackle the barriers that prevent the full-use of computational scattering code and theoretical techniques.

In the past decade there has been an explosion of new computer science hardware and software development paradigms. Literally every aspect of our society is influenced by well-designed mature software that has an impact on our daily lives. Given the ubiquitous aspect of computers in our society, one should expect that users of national scattering resources are going to demand mature, user-friendly, software to analyze scattering data. Computational scattering science has to adopt professional software development methods so that modular, extensible code is developed that is user-friendly, open-source, validated, and can be maintained over the usable lifetime of the code.

Given these new developments in the tools that are now available to write code, we encourage the development of modular code that can be used at various levels of granularity so the general usefulness of computational scattering code is accessible from the command line to computer clusters, but also from web-driven software with multi-purpose graphical-user interfaces.

We suggest that workshops and scattering user-groups be utilized to encourage the interaction between software engineers, computational scattering scientists, instrument scientists and experimentalists such that a common community is developed. The face-to-face interactions will expedite progress.

Our recommendation echoes that of previous DOE reports in that we agree that support for the development of software to aid in the design and interpretation of scattering experiments allows software itself to be a "shared scientific instrument" [3]. Doing this would enhance the scientific impact of nanoscale science and improve the utilization of the scattering resources in the United States.

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3.D. Engineering Diffraction

Cev Noyan

Jan Ilavsky, Gabrielle Long, Matthew P. Miller, Cevdet Noyan, Peter Peterson, Brian Toby,

Overview

Engineering diffraction refers to the measurement of mechanical response of industrial (engineering) materials across an enormous range of length scales. It includes traditional diffraction-related topics such as residual stress and crystallographic texture [1-3], emerging areas such as three-dimensional orientation and lattice strain reconstructions on the grain scale using high-energy x-rays [4-7], and methods such as high resolution x-ray diffraction for measuring physical dimensions with nanometer resolution [8]. The measured data are Bragg peaks. The shape, FWHM and peak position of these profiles are then used to determine elastic strain tensor components, the active plastic deformation processes such as slip or twinning, line and planar defect types and densities. Depending on the scattering experiment, these data may be obtained from a single grain, an ensemble of grains with a common, parallel, lattice direction (a texture group), or from multiple such ensembles.

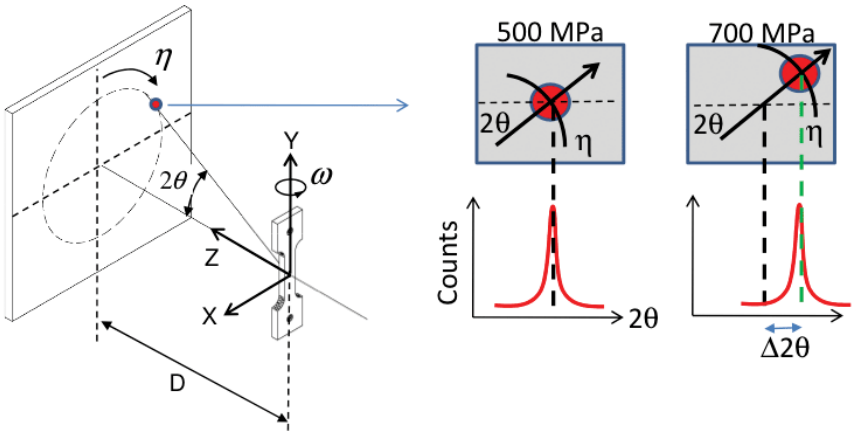
While strong interactions are currently being formed between diffraction and the material behavior modeling community, one of the primary challenges in this field is to model from the scattering event forward (forward modeling): given a particular alloy chemistry, strain distribution and defect density, can we predict the expected diffraction peak profiles at a given length scale? This is not generally achievable for common engineering alloys today. Instead, most experiment/simulation interactions have occurred from the "top down" – intensity values read from the detector and reduced to peak characteristics (intensity, position and FWHM), which are in turn interpreted within the context of material microstructure (lattice orientations and strains, dislocation densities). Comparisons are then made with the output from microstructural-based models.

The potential for linking all levels of modeling (mechanical response, microstructural configurations and intensity distributions) and introducing explicit representation of the scattering event is enormous. By initiating the model at the point of interaction between the x-ray and the material, we can transcend preconceived, centuries-old notions regarding links between microstructure and mechanical response. This approach would have the potential to assemble a virtual specimen based not on static, two-dimensional micrographs but on scattering data taken in real time in three dimensions; then to track the multiscale response of the material to external thermo-mechanical stimuli – again in real time. The structural complexity of modern engineering materials makes this a daunting challenge but the payoff in terms of improved material selection and mechanical design (greater efficiencies at significantly reduced "safety factors") justify the effort. In addition, recent advances at the interface of modeling and experiment have created a fertile intellectual environment for the inauguration of such a project. Significant progress can be made in these areas in the next five years by the judicious use of high power computing resources.

For such a multi-disciplinary effort, the creation of an enriched educational environment is crucial. It is key for the students to recognize the enormous potential that exists at this interface between mechanical behavior and computational scattering science.

Current Status

Diffraction of x-rays and neutrons has played a significant role in the general area of engineering materials. Currently, there is a broad range of interactions involving mechanical behavior models and the diffraction of x-rays and neutrons. This includes simple applications such as the representation of residual stresses in fatigue analysis as well as validation of highly sophisticated grain scale deformation behavior such as crystallographic slip in multiphase alloys [9] and twinning in slip-limited materials such as magnesium [10]. There is a natural interface between crystal-based micromechanical models such as self-consistent formulations [11-12] or finite element models [6,13] and diffraction data. At this size scale, however, it is not completely clear



(Left) Schematic of the experimental configuration in experimental station 1-ID-C at the APS. A point on the detector is defined by ω and 2θ, and the diffraction experiment is conducted at a particular specimen orientation (η). (Right) Depiction of the radial, 2θ "shift" in the intensity distribution associated with one reflection from one crystal within the loaded sample. This shift is converted into a normal lattice strain, which is associated with a particular scattering vector. [C. Efstathiou, D.E. Boyce, J.-S. Park, U. Lienert, P.R. Dawson, and M.P. Miller, Acta Materialia, 58(17):5806 – 5819, 2010.]

whether the simulation or the experimental data should serve as the standard. Moreover, there is an enormous amount of modeling between the intensity data taken from the detector and the physical quantity such as lattice strain or dislocation density. This fitting is typically done manually by highly trained experts. Comparison between experiment and simulation involves a trial and error process until the model output matches the measured data. At this point, the model is said to be **calibrated** by the diffraction data or the diffraction data are said to be **verified** by the model. A better idea would use all data simultaneously.

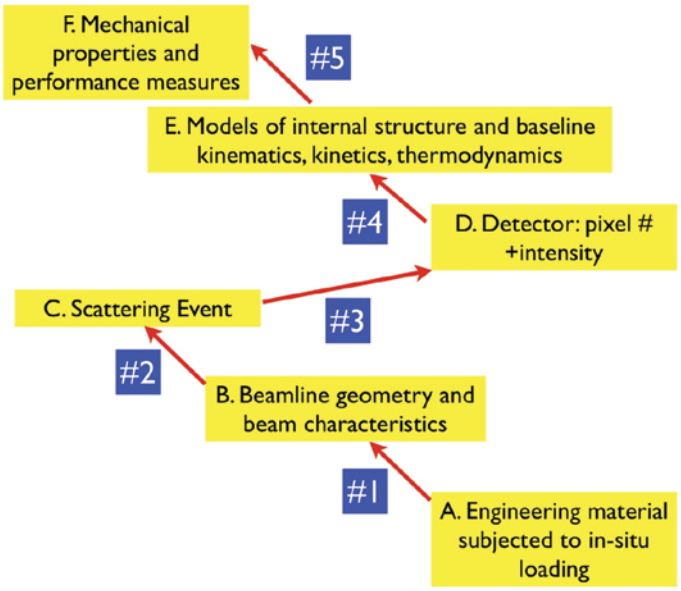
Two current applications of high-energy x-ray diffraction that are enjoying a large measure of success at the modeling interface are grain reconstruction experiments [14-16] and lattice strain measurements from individual crystals within a deforming polycrystal [17]. Three-dimensional grain reconstructions that rival those created using a destructive method such as serial sectioning with electron backscatter diffraction (EBSD) methods can be accomplished using high-energy x-rays with the detector in a "near field" configuration. These orientation domains can be discretized for a mechanical loading simulation or for grain growth / recrystallization studies. Alternatively, with the detector in a far field configuration, entire Debye rings containing hundreds of individual reflections are collected. The radial shift of each reflection is converted to a lattice strain within one of the deforming crystals. These data are ideal for comparison to crystal-based modeling formulations. For instance, stresses measured within individual crystals in deforming aggregates are seen to vary significantly from the macroscopic uniaxial condition [7,10,13]. These trends are captured well with a finite element modeling formulation, which was used to determine the single crystal elastic moduli [17]. Stress states at a subgrain level have even been measured, then corroborated using a viscoplastic self consistent (VPSC) model to investigate grain decomposition in twinning magnesium [10].

Microdiffraction using polychromatic x-rays have made it possible to create maps of orientation and residual lattice strains in engineering alloys and ceramics [18-19]. As the beams continue to shrink in size, the spatial resolution for such experiments continues to improve. Again, these highly resolved orientation maps can be used in the creation of virtual samples. As in-situ loading comes on line in this area, the possibility of highly resolved lattice strain fields becomes a reality. Acquisition time is one of the more serious barriers for collecting statistically significant datasets. This area needs significant work in algorithms and implementation.

A third group of solutions in use today address elastically deformed perfect single crystals. These codes are of limited industrial interest, but have the basic, rigorous, physics-based models for single-grain diffraction, which can be extended to the current effort [20]. We note that currently there is no dynamical diffraction solution for a single crystal with an arbitrary elastic strain state. This area is also in need of significant basic analysis.

Goals and Opportunities

X-ray and neutron diffraction experiments have several well-established roles central to characterization of most classes of engineering materials. The very nature of diffraction data makes them ideal for collaborative research with the computational mechanics community. A new class of



Schematic depicting the aspects (A-F) of a high-energy x-ray diffraction experiment designed to quantify the internal microstructure and micromechanical response of an engineering alloy.

experiment using high-energy x-ray diffraction, which is ideally suited for alloys, can be coupled with in situ loading to characterize orientation, lattice strain and position of literally every grain within a deforming polycrystalline aggregate [4]. These data are ideal for employment with crystal-based simulations.

Near field methods produce three-dimensional grain maps that rival current serial sectioning techniques. These maps can become virtual samples that are identical to the physical specimen. Far field methods with in-situ loading can be used to measure lattice strains within individual deforming crystals in an aggregate. Using polychromatic microbeams, three-dimensional orientations and lattice strains with sub-micron resolution are also becoming possible. Programs for novice users are coming on line at several light sources, which are effectively lowering the barriers to access for the mechanics community.

The general area of 3-dimension materials science has currently created a watershed moment for modeling engineering materials and the creation of new design tools. This success has unearthed some natural "soft spots" in our understanding and, more importantly, in the representations that we create for modeling the processing and performance of engineering materials. So while the area is enjoying incremental successes, there is a natural barrier to further improvements looming in the distance. Simply stated there is a general lack of self consistency from one "physical phenomena" to the next and from one aspect of the diffraction experiment to the next. Models and experiments currently exist as a series of hypotheses, experimental data and modeling representations – rarely with any feedback or self consistency check. We often apply our 21st century materials science data to 19th and 20th century theories.

An example of the challenges and possible outcomes from the area of high-energy x-ray diffraction is presented below. The figure provides a rough schematic depicting the individual aspects of an in-situ loading / high-energy x-ray diffraction experiment designed to understand structure-property relationships in a engineering alloy (A-E). The "connections" between these items are numbered 1-5. The current state of experiment/simulation research described in the previous section basically involves steps #1, #4 and #5 only. The proposed project would bring steps #2 and #3 into the modeling effort and would make explicit use of the diffraction data for redefining stage E and #5.

i. The scattering event itself, especially when in-situ loading is employed, is rarely modeled in engineering materials. Certainly detailed models of diffracted x-rays from loaded polycrystalline alloys currently do not exist. Steps #2 and #3 in the figure are blurred together with step #4. What is currently needed is a forward model that can simulate the angular variation of intensity of 1) diffraction peaks, and 2) diffuse scattering when different slip systems or twinning modes are activated within the sample, along with the concomitant change in the density of dislocations.

ii. We design the experiment with specific idealizations of material microstructure and assumptions regarding the true nature of dynamic processes such as single crystal elasticity and plasticity. We begin with aspects of E in mind and very specific hypotheses related to #5. In fact everything we know about E and #5 for engineering alloys, we learned from static micrographs taken pre- or post-mortem. Elastic and plastic deformations are dynamic phenomena yet our models of processes such as crystallographic slip, twinning and creep are based on static, "before and after" two dimension

observations – most of which were made decades ago. Our interpretation of the intensity distributions that we collect on the detector is based on these plausible but dated hypotheses. The real-time nature of high-energy x-rays and high speed detectors make it possible to adjust or even completely rethink the way an aggregate of crystals accommodates thermal and mechanical loading. That is, instead of corroborating existing theories at #5, we need to create the experiment and modeling framework to accommodate a new set of structure-property hypotheses.

iii. The figure is a drastic simplification – care must be chosen when we choose the first materials to avoid unwanted feedback in the intensity signal. In fact, it would be prudent to employ single or bi-crystals in early experiments. Eventually, we will want the flexibility to accommodate real-time structural evolution and actually "predict" changes in diffracted intensity. The models in part E will yield shape, strain and rotation information, which need to be translated backwards into dislocation distribution and atomic coordinates; the scattering kernel will take in this information and re-calculate the scattering profiles. This is a very important task: diffraction spots from deformed grains rarely exhibit regular Gaussian or Lorenzian profiles. In fact, most of the available peak-fitting routines are inapplicable for fitting such peaks. The shape of such peaks, on the other hand, carry information about the deformation distribution within the grains and a rigorous forward model would enable us to extract such information.

iv. Once such a model for a single grain is obtained, the code can be parallelized to solve the scattering from a set of contiguous grains that deform as an ensemble. The problem is then scaled up until the deformation characteristics of a representative volume element is computed, which should be comparable to the elasto-plastic or visco-plastic models in use today. A supercomputer such as Blue Gene is required for this effort. The results have the potential to yield a significant increase in our understanding of grain and subgrain scale phenomena, which will create a new generation of design tools for important classes of structural materials.

The scattering kernel described here will be applicable to creep, fatigue, fracture processes in most materials of engineering interest, and should have very widespread use in academia and eventually industry. It will also help provide desperately needed mechanical data at the size scale of the individual grain and below to aid the further development of experimentally verified micromechanical theories.

Path Forward

A project along the lines outlined above is incredibly ambitious. As stated previously, the possible benefits far outweigh the risks. The groups involved in this research will contain disparate capabilities across several universities and national laboratories, working together in a five-year effort. The first two to three years will be spent on optimizing the finite element codes to allow for the various plastic flow mechanisms (different slip systems, twinning modes, hardening parameters) and, in parallel, writing the scattering kernel based on atomic coordinates, and getting these two modules communicating with each other, and doing optimization and sensitivity tests. Years four and five would be spent on experimental testing, validation and documentation.

A key challenge for this and subsequent tasks at the interface of engineering and diffraction scattering science is the education of students. There are very few students or post-docs who have the required knowledge in both rigorous mechanics of materials and rigorous diffraction physics. In addition, diffraction courses are disappearing from university curricula. The codes that are being developed for this task can be incorporated into a web-based training course which will show both analytically and through simulation how x-ray and neutron scattering works for samples of different perfection in the kinematical regime.

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3.E. Fast and Ultrafast Phenomena

Fernando Vila

Lin X. Chen, J. Freeland, B. Harmon, M. Norman and F. Vila

Background

From chemical reactions to high-harmonic generation and quantum control, fast and ultrafast phenomena encompass a wide variety of scientific problems. For the past four decades, conventional optical probes such as pulsed lasers dominated the study of ultrafast phenomena. More recently, however, photon sources delivering ultra-short, coherent x-ray pulses have started to probe regimes that were previously unattainable, providing a more complete look into matter. Such sources give access to length scales small enough, and time scales fast enough, to capture atoms in motion, thus enabling researchers to observe chemical reactions as they occur and to monitor the structures directly.

These new instruments pose some significant challenges, both theoretically and computationally. First, fast and ultrafast phenomena usually involve transient electronic states with a wide range of lifetimes, allowing for different states of equilibrium between the dynamical degrees of freedom of a material. The methods currently available for the simulation of these transient states are, at present, not applicable to the complex systems studied in practice. Second, although computational methods for static x-ray spectroscopies such as EXAFS and XANES are well developed, their time-resolved counterparts lack the computational infrastructure required for simulation. Finally, even when the theoretical methodologies are available, the computational costs of the simulations are usually beyond the resources of most users.

Case Studies

Despite these issues, scientists are already combining the available theories and experiments to produce remarkable new insights into basic and applied problems. For instance, manganites are an important and convenient testing ground for studying electron correlation phenomena. In these systems, the strong interplay between charge, spin, orbital and lattice degrees of freedom results in rich phase diagrams. One of the most striking aspects of the physics of manganites is the occurrence of a number of metal-insulator transitions, initiated by perturbations of temperature, magnetic field, pressure, and irradiation with light. In the case of $Pr_{1-x}Ca_xMnO_3$ at the optimal doping level (x=0.3), the insulating phase adjoins a "hidden" metallic state characterized by enormous changes in resistivity. The metallic phase can be reached by application of external perturbations such as a magnetic field. An important development has been the demonstration that a first order insulator-metal phase transition can be induced optically, by the photoinjection of carriers into the insulating state. Even more remarkably, recent studies show that this transition occurs on a sub-ps time scale and can be initiated by the selective excitation of vibrational degrees of freedom.

More recently, solution-based x-ray transient absorption (XTA) experiments combined with a multidimensional interpolation were used to study molecular-level structural changes on Pt complexes accompanying an electronic transition induced by laser excitation. Fitting the XTA difference spectra from full multiple-scattering calculations to the experimental results revealed a Pt-Pt bond compression in the triplet excited state of the complex, consistent with transient production of a metal-metal bonding interaction. This Pt-Pt bond compression correlated well with that predicted by DFT simulations of the lowest triplet excited state of the system. The application of the multidimensional interpolation approximation approach to fitting the difference XTA spectrum is an alternative to conventional XAFS data analysis for extracting structural parameters.

Finally, in the case of the Pt nanoparticles on γ-alumina, a real-time approach based on a combination of density functional theory molecular dynamics (DFT/MD) and x-ray absorption (XAS) simulations showed that fast dynamical fluctuations (librational motion and internal flexing), driven by the interaction with the surface, can explain many of the unusual properties of these systems.

These fluctuations, coupled with fast changes in the electronic structure of the catalysts have potential implications for the understanding of the catalytic properties of these systems.

Goal State

The studies described above are not routine and represent special efforts by experts with custom computational tools. We believe, however, that it is possible to make these types of scientific computations widely available in the next few years. In that period it should be possible to:

1. Equip non-experts with user-friendly tools that would:

- Help in the construction of relevant models for the materials of interest. There are currently few free tools to build, visualize and manipulate the structural models that are the starting point of most simulations.

- Perform real-time simulations of the processes involved. We believe that DFT/MD and TDDFT (time-dependent density functional theory) simulations are key to understanding fast and ultrafast phenomena. At present, these simulations require specialized codes that are difficult to install and to use efficiently. Moreover, they are computationally very expensive.

- Calculate the necessary properties that will bridge theory and experiment. In our experience, a common barrier to the generation of knowledge arises from the lack of connection between the simulated quantities and the measured properties. In some cases this results from theoretical and computational deficiencies. In others, however, it arises simply from the lack of an adequate interface between modeling and experimental data.

2. Integrate these tools into an adaptable, self-sustaining research framework supported by theoreticians, experimentalists and software developers with experience in the areas of molecular dynamics, excited states physics, density functional theory, and optical and x-ray spectroscopy. This "ultrafast simulation framework" (UFSF) would ensure that tools are:

- Added when new experimental methods are developed.

- Efficiently integrated to facilitate research.

- Distributed and kept up to date.

- Optimized to achieve the best possible performance.

The UFSF would not be responsible for development, but would rather encourage groups to contribute their tools. In return, these groups would benefit from the scientific, computational and organizational expertise of the framework. At a minimum, the UFSF should include the following free tools: a graphical user interface for the manipulation of arbitrary materials, a DFT/MD code, a TDDFT code, a code capable of computing ground and excited state properties of condensed phases (including lattice dynamics) and codes capable of computing optical and x-ray properties. It should also include all the bridging software needed to facilitate, whenever possible, the exchange of structures, electron densities, potentials, dielectric and magnetic properties, etc.

Driven by the coordinated efforts of a more diverse group of researchers, we believe that an integrated framework with modular tools would result in new and better science in the area of fast and ultrafast phenomena.

Path Forward

To achieve the goals described above we envision the following areas of development:

Scientific:

- Encourage the theoretical developments needed to enable the simulation of excited states dynamics. At present this is one of the most important barriers for advancement in the field.

- Facilitate the transfer of expertise between the many areas involved in the study of ultrafast phenomena. Given that optical probes have been in use for the past few decades, we believe that the experience accrued with them will be extremely useful.

Software and Hardware Infrastructure:

- Promote the development of software tools. Work

with computer scientists to develop new algorithms or revamp those already available to increase the efficiency of the simulations. Researchers should plan in advance how to handle the large amounts of data that will be generated by both experiments and simulations and how to make it available quickly to facilitate further discovery.

- Optimize the usage of available hardware and explore new hardware. With the emergence of the infrastructure-as-a-service (IaaS) paradigm, we are at a crossroads similar to that experienced with the transition from supercomputers to commodity clusters. We believe IaaS could have significant impact for researchers with modest access to high performance computing resources. IaaS has the potential to change their computational approach and open new avenues for research and education.

Human:

- Fast and ultrafast phenomena cover a broad range of problems and experimental and theoretical methods that require training opportunities beyond those usually dedicated to a single method or instrument model. Educational opportunities could be driven by case studies.

- The combination of science and computing in this field offers considerable opportunities for building an exciting educational and outreach program involving scientists, students, educators and the general public. In particular, informal educational aspects such as the development of searchable public knowledge repositories should be explored.

3.F. Simulations of Experiments

Brent Fultz

Chris Benmore, Brent Fultz, Ray Osborn, Toby Perring, Peter Rez, Frans Trouw

The Situation Today

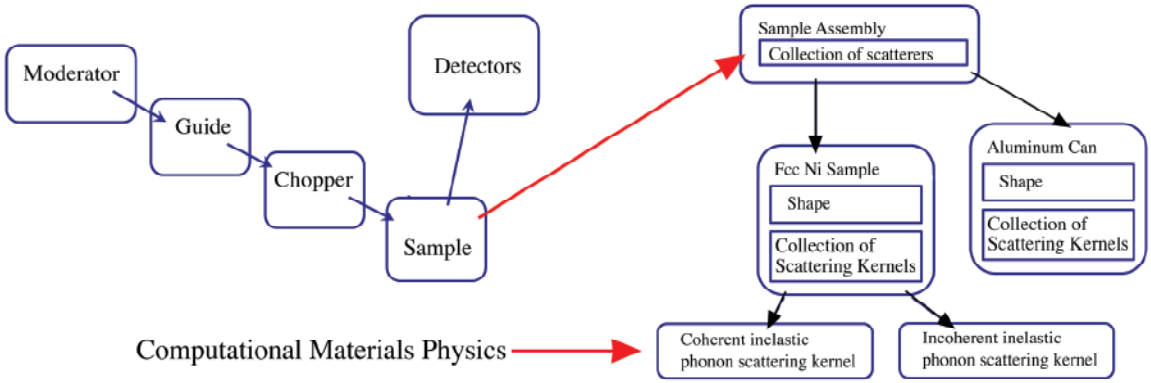
Computer simulations have been used to design instruments and beamlines for many years. Likewise, many methods of computational materials science have been developed to predict the structures and dynamics of materials that are studied by experiments using these instruments. Simulations of experiments that include the effects of instrument performance on the predicted scattering are a way to draw a tight connection between theory and experiment, and such simulations are emerging now.

Simulation tools for neutron instruments, such as McStas [1], VITESS, MCVINE [2], and NISP are commonly used for instrument design and optimization. For many neutron instruments, good Monte Carlo models are available, and these will become even more reliable as the SNS makes an effort to build accurate simulation models of its operating instruments. Today there are some successful examples of experimental simulations that connect simulated instruments with the simulated structure and dynamics in the sample [3]. A "virtual experiment" is a way to put theory and experiment on the same level for interpretation and comparison. Another role for scattering simulations is experiment planning, which could help when designing a new experiment. If computations were practical in real time, simulations would offer opportunities for guiding experimental work as it is underway. Instrument simulation tools are less general for x-ray and electron scattering, largely because the source brightness and optical performance vary with time. Nevertheless, the flexibility of changing the experimental configurations for x-ray and electron scattering experiments may offer opportunities for simulations to optimize the measurements. Today measurements on standard samples can provide much of the resolution information for x-ray and electron scattering, so computational scattering results can be modified appropriately with resolution, backgrounds, weighting by Q, E, T, and instrumental artifacts [4,5].

Computational science has expanded the scientific value of experimental measurements in different ways. The successes are not necessarily ones where the simulations and measurements are in agreement, although this is often a goal. For example, an electron energy loss spectrometry (EELS) study of the oxygen K-edge in SiO_2 showed states in the band gap when the SiO_2 layers were 1.5 nm or smaller [6]. This result has important implications for the sizes of CMOS electronic devices, but it was not clear if the results were an artifact. Electronic structure calculations by density functional theory showed that EELS measurements of features at the O K-edge should be reliable. Similar types of electronic structure calculations were used to help interpret the charge transfers accompanying Li insertion into the battery cathode materials $LiCoO_2$ and $Li(Co,Ni,Mn)O_2$ [7,8]. In these materials the electronic structure around the O atoms undergoes a larger change than around the Co, Ni or Mn during Li insertion and de-insertion. A consequence is that the compositional ratios of Co, Ni, and Mn need not be in fixed ratios to accommodate the valence changes of these metals.

In many cases computer simulation provides a powerful tool to access important aspects of the physics of materials that cannot be deduced from the experimental data alone. For example, the structures of heavy and light water at ambient conditions were investigated with the combined techniques of x-ray diffraction, neutron diffraction, and computer simulation [8]. The simulation extracted detailed information on the magnitude of quantum mechanical hydrogen bonding effects buried in the diffraction data, providing essential information regarding the intra- and inter-molecular forces present in liquid water.

The development of aberration-corrected transmission electron microscopes has extended studies of structure and bonding to unprecedented levels of resolution. Examples are the determination of 3D shapes of catalyst nanoparticles [10] and the measurement of interface roughness and transition metal charge



Simulation of an inelastic neutron scattering experiment on phonons with a chopper spectrometer. Blue arrows on left denote neutron paths. Black arrows at right indicate software dependencies. Red arrows highlight connections between instrument simulation and sample, and between computational science and sample.

state in perovskite superstructures [11]. Theory and computational support for these efforts has not kept pace with the developments in instrumentation. The aberration corrected microscopes form electron probes with large convergence angles. Analyzing images on a column by column basis is no longer reliable. This brings both challenges and opportunities. The high convergence angles open up the possibility of determining 3 dimensional (as opposed to projected 2 dimensional structures) by confocal microscopy. At the same time, the larger scattering wave vectors mean that it is no longer possible to evaluate energy loss fine structures on the basis of dipole approximation (using the same codes as for x-ray absorption).

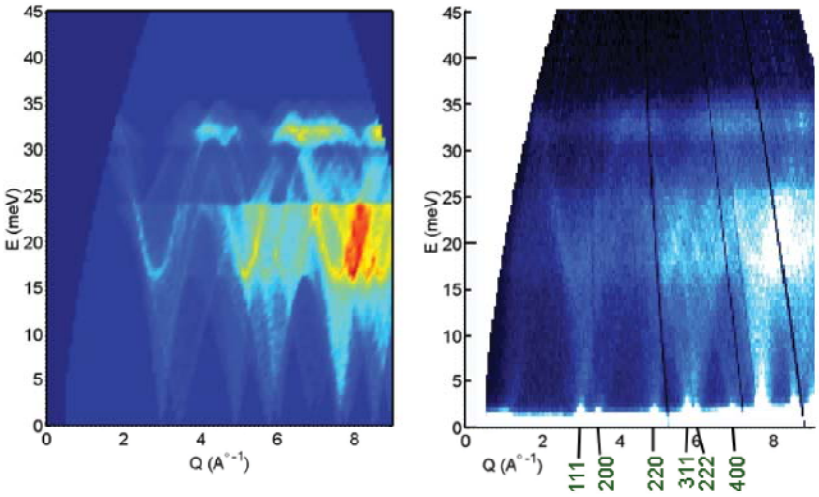
Where can we go from here?

Combining results or constraints from different measurements can expand scientific insights. For example, the interpretation of dynamics measurements requires knowledge of the underlying structure. Diffraction studies of crystal structure often benefit from measurements with different types of radiation, such as with both neutron and x-ray diffraction, or input from EXAFS on local structure. At larger length scales, it is often useful to combine results from the small angle scattering of both x-rays and neutrons. Combining the results from different measurements, or from different computational models, can often be done by changing some components of the simulations in the figure. For example, it should be possible to change a neutron scattering kernel to one appropriate for x-rays.

Computation can provide contributions to the scattering that can be removed from measured results to better reveal the phenomena of interest. For example, calculations of phonon dynamics can often be performed with accuracy, converted to a scattering intensity including multiphonon processes, and subtracted from experimental measurements to reveal the magnetic scattering. Techniques for doing so are particularly important for studies of magnetism in single crystals with chopper spectrometers, where the kinematical requirement for higher incident energies increases the likelihood of multiphonon scattering. For another example, when phonon spectra can be calculated with high accuracy by *ab initio* methods, the cubic anharmonicity tensor may also be used to obtain the phonon linewidth broadening from phonon-phonon interactions. The remaining phonon broadening can be attributed to electron-phonon interactions, for example. Separating phonon-phonon from electron-phonon effects is not possible by experimental methods alone.

Pressure effects are relatively easy to compute by *ab initio* methods. Such calculations are especially useful for interpreting scattering data measured at extreme conditions, which are usually of lesser quality. The conjugate thermodynamic to pressure is volume, and volume is straightforward to vary in simulations of electronic structure. Such calculations allow identifications of the electronic levels that change with pressure, and may underlie structural or magnetic phase transitions.

Simulations of experimental data from phase interference measurements, such as performed with electron holography, neutron spin echo instruments, or x-ray speckle imaging, are not mature. This is not a fundamental limitation, since *ab initio* methods can generate exit wavefunctions from materials. The exception is phase contrast transmission electron microscopy, where image simulations must be compared to experimental images to obtain quantitative results. These image simulation tools



Comparison between computed (left) and measured (right) inelastic scattering of neutrons by phonons in polycrystalline fcc Ni-Fe.

have become routine. Unfortunately, the theoretical efforts in transmission electron microscopy have withered somewhat, slowing progress in some of the modern spectroscopy work with aberration corrected instruments. To get the most information from electron microscopy of nanostructures, we must move beyond just recording images, and use the data to quantitatively test models and hypotheses. Theory and computation based on ab-intio DFT calculations offer a link between structure as determined by imaging, and bonding as measured by electron energy loss spectrometry (EELS).

Neutron, x-ray, and electron experiments can often benefit from the same material models of the structure and dynamics of the atoms, electron density, and electron spins. The coupling between the materials simulations and the measurements is through a imulated sample, which includes kernels* for different scattering processes. The figure shows how different scattering kernels can be combined to predict the scattering of neutrons into a detector of a simulated instrument. It suggests how straightforward it should be to interchange sample assemblies in a virtual instrument, or change the scattering kernels in a sample.

Exploiting the interplay between the results from experiments and their simulations requires software modularity. Computational codes cannot be run in isolation, especially without conversion to experimental measurables, and accounting for the sample environment and instrument distortions. We know today how to modularize software with proper abstractions and encapsulations, which also makes it easier for code reuse in other applications. Appropriate interfaces for scattering kernels also facilitate the computation of materials properties on remote or distributed resources that can be selected for the capabilities of their hardware or software. Compatible data structures are also enabled by adhering to common standards for data and metadata. The metadata can be stored in a relational database, which is a great convenience for users working with multiple datasets from measurements and computation. Software development for the scattering community did not address these design issues until relatively recently, as in the DANSE project. Some information on usage patterns of modular software is available today, but it is already clear that flexibility is necessary to satisfy the needs of many users. A modular toolkit is the approach of choice.

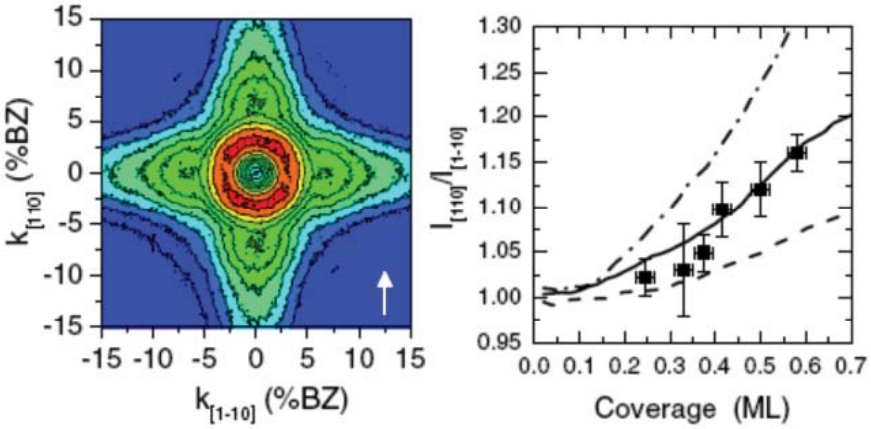
** A scattering kernel gives the probability of an energy and momentum transfer per unit length of the neutron trajectory through the material of the sample.*

How do we get there expediently?

Much as a new user of an experimental method can benefit rapidly by collaboration with an instrument scientist, many experimentalists could benefit from interactions with a computational scattering scientist who is familiar with the phenomena and the computational tools. A computational scientist on the facility staff could serve as a mentor for new users, a collaborator for intermediate users, and a peer for advanced users. For many scientists in the scattering community, such persons would lower the entry barrier for using computational tools, and would build trust in the value of these tools for augmenting scattering research. An initial effort is underway to provide some such support for DANSE software at the SNS.

Some priorities for the development of tools for computational scattering science can be identified today. Density functional theory codes and classical molecular dynamics codes are obvious candidates for use in scattering simulations. *Ab initio* molecular

dynamics is a capability that will become more routine over the next five years, and we need to plan for it today. Not all research requires a full simulation of the instrument plus materials computations, but modularity is needed so that different parts of the problem can be compared and interchanged between computation and experiment.



Contour plot of the calculated diffraction intensity after deposition of 60% ML of Cu on Cu(100), averaged over 128 simulations at grazing incidence of 80º at a temperature of 250 K at deposition rate of 0.6 ML/min. The simulation used empirical potentials with dispersive forces. The arrow indicates the deposition direction. Right-hand side: Anisotropy of the diffraction intensity as a function of coverage [F. Rabbering, Phys. Rev. Lett. 103, 096105 (2009)]. These simulations used molecular dynamics and kinetic Monte Carlo methods that would not have been feasible without the extraction of a condensation rule from experiments. Such calculations could be performed using more accurate and efficient methods if there were closer collaborations between experiment and theory.

The first priority is for computational tools that predict the main contributions to experimental scattering. Nevertheless, as experimental data improve in resolution and statistical quality, physical phenomena that could be neglected previously may now need consideration. Computation can play a valuable role in determining if these effects are small, or if they provide new scientific insights. The priority for predicting a phenomenon such as magnetovibronic coupling, for example, needs to be considered on a case-by-case basis.

An organizational model along the lines of the European Theoretical Spectroscopy Facility (ETSF) may be appropriate. The ETSF maintains a number of "Theoretical Beamlines" in which advanced computer codes are used to simulate various spectroscopies, including optics, energy loss spectroscopy, photoemission spectroscopy, and x-ray spectroscopy. Each of the beamlines is charged with the development of appropriate software. This model fosters a close collaboration with users of various European synchrotron facilities, which stimulates new developments and spurs progress.

In the U.S., software development for virtual scattering experiments would need to have personnel located at each scattering facility. Each facility needs to take responsibility for its own instruments, whose configuration is under facility control. Ensuring correctness of instrument models requires experimental tests of the simulations. It would be natural for these simulated scattering experiments to reflect the scattering experiments done at the facility. Some types of calculations are more appropriate for either x-ray scattering or neutron scattering facilities, although some like density functional theory codes are common to both. Time scales, energy scales, and length scales of emphasis can be useful for deciding which facility is most natural to host a software development group. If the software development group were an ideal number of seven or eight persons [12], however, one group could address only a fraction of the types of materials simulations proposed here. There is more than enough work to go around. The number of opportunities extends beyond what can be done by one group or at one user facility. A national coordination of effort will be required.

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3.G. Optimization Techniques with Complex Physical Models

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Present Status

One of the ultimate goals of the physical material sciences is the development of detailed models that allow us to understand the properties of matter. While models may be developed from *ab initio* theory or from empirical rules, often models are fit directly to experimental results. Crystallographic structural analysis has pioneered model fitting; direct fitting of crystal structure models to diffraction datasets has been used routinely since the middle of the last century. In the past two decades, direct model fitting has been applied to other scattering techniques such as PDF analysis and x-ray spectroscopies. Combinations of experiments and theory to derive a single physical model is a broad frontier for scattering science. In a few fields this is practiced today; the combined use of x-ray and neutron diffraction is nearly routine [1]. On the other hand, the combined fitting of EXAFS and diffraction data is novel and relatively uncommon.

Models that use physically meaningful parameters may not be *well-conditioned* (meaning that the minimum is narrow and easily missed). Likewise, using parameters that are physically meaningful may result in problems that are not *well-posed* – meaning that there may not be a unique solution, since the effect of changing one parameter may be offset by adjustment to another. Despite this, models with physical parameters are most valuable for interpreting experimental measurements. In some cases there may be many model descriptions that provide equivalent fits, within experimental uncertainty. It is then not sufficient to identify a single minimum, since this leads to the misapprehension that this single answer has been proven. Identification of all such minima allows for the design of new experiments, or calculations to differentiate between them.

The algorithmic process by which models are fit to data is called optimization, which is an active research field in computational science. However, materials researchers gravitate towards the Newton-Raphson least squares method, even though the preferred BFGS algorithm was developed in 1970. Since then a wide variety of both derivative-directed and heuristic algorithms have been developed, but these are not commonly used by the x-ray and neutron scattering community. Where more sophisticated algorithms are applied, this likely to be done using a commercial programming environment such as Matlab, which produces code that is neither scalable nor easily distributable. Examples of more modern optimizers can be found in the DAKOTA package [2], but it is useful only for certain types of work. Likewise, a wealth of optimizers are available in the NEOS Server project [3], which can be accessed via web services, but again this appropriate only for some types of projects. The Mystic package [4] is an example of a python-based optimizer package that is of great interest, but it has only recently been released.

Goal State

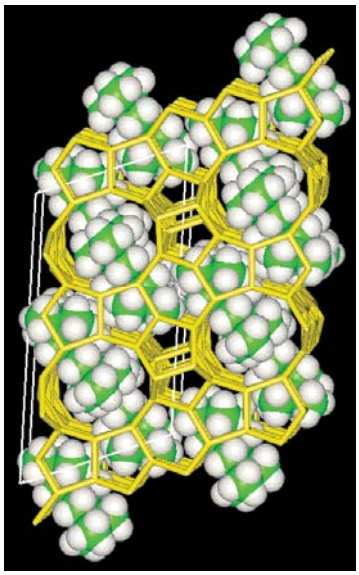
The fundamental scientific limitation that has prevented more widespread deployment of model fitting has been that, until recently, relatively few types of measurements could be simulated at the level where quantitative agreement with experiments can be obtained. When simulations can directly reproduce experimental results, then parameters in the model can be optimized to improve the fit. However, to obtain unique solutions that are not overly affected by statistical noise, one needs to have many more observations than varied parameters (the crystallographic rule-of-thumb is 10:1). While accurate simulation of many types of experiments is now possible, the experimental data may not offer a sufficient number of observations to allow fitting of a very complex model. This changes when different types of experiments are combined, since each experiment may be sensitive to different aspects of the model. In addition to the advances in computation, modern user facilities now offer a wide assortment of experimental probes. Theory too can be added to the mix. It is clear that the frontier over the next decade will be to develop codes that optimize a single model

to fit all types of data for a material – rather than to develop a different model from each experiment.

The task of model determination from pair distribution function (PDF) data has gained considerable interest because it is one of few techniques giving detailed short-, medium- and long-range structural information for materials without long-range order. However, the task of automated model derivation is exceedingly more difficult without the assumption of a periodic lattice [5]. One approach is to use a greater range of experimental techniques in modeling. The combined use of x-ray and neutron diffraction has been done for decades in crystallography, but new studies are demonstrating that the pairing of specific techniques (cf., [6]), generates a result that could not be obtained from a serial study. The challenge, thus, is to develop a computational framework that allows for simulation of a variety of experiments and theory combined with a powerful, scalable optimizer for model optimization. This area will benefit from greater access to minimization algorithms and interactions with computational scientists.

For example, optimization plays a central role in the three-part process of powder diffraction crystallography – a major research area at all DOE neutron and x-ray user facilities. The first task is to index the lattice from an unknown material, potentially in the presence of peaks from multiple phases. This is an ill-conditioned problem where a large volume of parameter space must be searched for solutions with extremely sharp minima.

The second task is structure solution. Many approaches have been successful for identifying minima, though none has been shown to be universally applicable. Structure solution is often an ill-posed problem; crystallographic methodology assumes that if a well-behaved and plausible solution is identified, this solution is unique. An unusual counter example is [7], where molecular modeling was used to identify all possible physical models to fit the neutron and x-ray diffraction and neutron spectrometry data. Such studies should be routine rather than heroic. Two advances are vital for structure solution. 1) As powder diffraction problems grow in complexity and more physical constraints are built into models, exhaustive searches of the structure solution space become a significant challenge. 2) Current methodology requires identification of a space group, but this can seldom be determined directly, so combinatorial approaches are needed.



Location of structure-directing cations in the pores of zeolitic material CIT-1, as determined in ref. [7]. This model was found to be the only possible fit to both data and theory. This determination required multiple rounds of experimental fitting and molecular modeling. Improved optimization strategies, along with improved modeling frameworks, will allow direct development of globally optimized models and will allow such techniques to be accessible to a wider range of scientists.

Finally, once a set of solutions is identified, structural refinement techniques are needed to optimize the structural model for the best fit to the measurements. The necessary developments are to build optimizers that improve the software utility in the hands of non-specialists. At present, it is expected that the software user will direct the introduction of variables into the optimization to maintain a stable fit, will identify when multiple datasets do not have a common minimum (indicating incompatible experiments), and will know when models are likely incomplete. Expertise is also needed for reducing complexity when the model description is ill-posed. A high level challenge for this technique is to transition increasing levels of expertise into software. The combined impact of the partner GSAS [8] and EXPGUI packages [9] is approximately 6,000 citations, with the vast majority coming in the last five years – at the same time as crystallography is disappearing from the academic curriculum.

In another area of structure analysis, grazing-incidence small-angle scattering (GISAS) currently enables a statistical description of samples over macroscopic length scales. This method has been

applied to a variety of systems, such as nanostructured polymer thin films, nanoparticle-polymer composites, and supported nanoislands. However, due to the complexity of data processing involving the distorted-wave Born approximation (DWBA), most GISAS analyses are either qualitative or performed by a DWBA theory simplified for a single layer or supported nanoislands. These methods and analysis models are often unsatisfactory when the nanostructures of interest significantly perturb the scattering potentials, or when the size of the nanostructures is comparable to the electric field variation patterns. Researchers need to solve the two-dimensional structure within a three-dimensional matrix. Because of wave-guiding effects between multiple interfaces, most current DWBA theories can only explain scattering data either well below the film critical angle or above the substrate critical angle, and fail to give quantitative analyses between these two critical angles. Most importantly, it is exactly the scattering data in this range that reveals the depth-dependent information that is required to understand the structures in 3D. To overcome current limitations, the challenge is to develop diffuse differential cross-sections using the DWBA for multilayer films with embedded nanostructures, where discretized multilayer DWBA theory can be readily reduced to the conventional scattering theories under the particular scattering circumstances. The goal is to achieve a robust analysis method analogous to Parratt's recursive formalism for x-ray reflectivity of thin films.

Another goal is to reduce the technique-specific expertise needed to perform optimizations. As one example, parameters must be added carefully to crystallographic refinements where the recipe varies with data and model. It takes considerable training to overcome the weaknesses of the optimization method. Current optimizer technology can automatically direct the fitting strategy. Optimizers can also examine the reliability of the resulting model by identifying where multiple solutions exist. They can automatically perform leverage tests on constraints and sensitivity analysis on parameters to help address model reliability and assess parameter uncertainty.

Path Forward

Collaborations between computational scientists and physical scientists with interest in software development would identify the most valuable new optimizer technologies. Case studies where optimization techniques fail will provide a wealth of research problems for computational development and may help toward the grand-challenge goal of self-adaptive minimizers that can analyze the shape of the parameter space and monitor the minimization process to automatically select the most appropriate algorithm at different stages of the fitting. While both physical and computational scientists will benefit from the interactions, the research cannot be completed without cross-disciplinary funding strategies that foster such collaborations.

Modular, plug-in optimization toolkits are needed for commonly used platforms for scientific software development, but these codes also need to be scalable to applications that require large-scale computation. Having optimizer libraries that share a common application interface (such as what is offered by Mystic) allows multiple optimizers to be interchanged with only minor programming cost. Likewise an optimizer that can be deployed on a laptop, but can scale to a supercomputer, encourages the development of codes that can be validated on small-scale tasks, but can be expanded to grander challenges.

The subject of how to best choose an optimization strategy is obscure to most non-computational scientists. Educational approaches such as workshops and media are also needed to explain how to choose optimizers and how to best parameterize models. The process for integrating a simulation module into a model-fitting package can also be improved considerably, and this will further foster growth of multi-technique modeling approaches by lowing the energy barrier. Optimizers can also identify where the best-fit parameter sets are in conflict between datasets, suggesting where experiment design needs review. It is clear that in the future, scientists will need to demonstrate that their model is not only consistent with their experiments, but also that the parameters in their model are optimized against all observations. Improvements to the usage of optimization strategies in the physical sciences are a prerequisite for this major advance.

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3.H. Software Maintenance, User Support, and Emerging Hardware

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Scientific software is basic scientific infrastructure, so planning, implementation, review and funding need attention like other scientific infrastructure. Software development and maintenance differs from instrument and hardware development in significant ways, however, and requires a different style of management and planning. Over its life cycle, software needs a large investment of labor for initial development, testing, documentation, updates and maintenance. Experience teaches us that successful and widely accepted software often lives for decades (e.g. GSAS). This far exceeds the lifespan of the platforms (software and hardware) on which it was first developed. The maintenance and transition to new platforms and software environments needs to be an integral part of the software maintenance and upgrade planning and funding.

Some future trends of computing hardware are emerging. Today it seems that multicore computing – either using multicore CPUs or using CPU/GPU combinations -- is the future of commonly available resources (desktop and notebook computers) for most users. On the high performance side of computing, we again see multicore computing in supercomputers and cloud computing. We do not know in detail the characteristics of the computers of the next decade or two, but we do expect computing to move to the exascale with an increasing number of processor cores, and not with an increase in clock speed that has been the trend to date. Some characteristics may include a heterogeneous mix of specialty processors in the same system, and a mismatch by today's standards of processor capabilities over memory, bus, and storage performance. Such hardware architectures will favor some algorithms over others, as is the case for petascale computing. Software needs to be periodically optimized for these new resources and new platforms, not just at the high performance end, but also for personal computers with new architectures.

Other changes expected in the environment for computational scattering science are increasing data volumes and new analysis methods, both of which may be enabled by new high-performance architectures, and may also drive the adoption of those architectures. Data placement may also prove to be different than today. Overcoming these challenges will require a larger, more professional, and more carefully managed software maintenance.

Today software maintenance is largely performed by the "owners" of the software packages, who have various motivations for this work. Commercial vendors have business plans for providing up-to-date products, and sometimes these plans change unexpectedly. Open source software for scattering science is often a secondary effort by dedicated individuals, and their motivations and interests may also change over time. Open source software, be it compilers (such as gcc and gfortran), high-level languages (such as Python) and graphics packages (such as pgplot, BLT and matplotlib), and more specialized libraries (such as optimizers or cctbx) are essential infrastructure for the construction of modern scientific applications. Considering the dependence of the scientific community on these tools, should we not contribute to them and steer their development? There is no central organization to assess the needs for software maintenance and feature requests in computational scattering science.

Likewise, today there is no coordinated effort or common model for user support; user help and training occurs through the documentation, instrument scientists at national user facilities, and communications with the owners of the software. These types of user support are unlikely to be successful as the complexity and capability of software continues to advance. Using computing resources increasingly involves understanding issues of cybersecurity, and working with cybersecurity policies can be challenging even when they are understood. Cybersecurity requirements can be a disincentive for some users, so help with these requirements could be important. A lack of user support tends to suppress the use of more advanced tools for computational scattering science. Users are also needed to help

design the software workflow. The final design of software packages benefits from interactions between the developers and users. This interaction identifies bugs and features, and enhances usability and productivity.

Goal State: Using Future Hardware

Making the best use of the emerging computing hardware landscape requires some rethinking of how scattering calculations are done. The emergence of multi-core computing, both on conventional CPUs and on GPUs, will provide the computational scattering community with vast amounts of computational power. Unfortunately, very few of today's codes will be able to harness this power without major re-engineering. Many codes in use by the scattering science community are designed to run on single processors, and much of their improvement in performance has depended on improvements in clock speed. Some large software packages such as *ab initio* calculations or molecular dynamics codes do take full advantage of the computational power provided by clusters, although only few codes scale well beyond a few dozen processors.

More exciting is the prospect that cheap and plentiful computing power may enable the design of algorithms that are unthinkable on a single core. Stochastic methods, speculative calculations, optimization and inverse problems, are essentially parallel techniques that require vast amount of computing power as they try numerous cases on different processors. On the other hand, they are easily dismissed as impractical in traditional computing environments. A clear example of how transformative the available computing power can be is provided by *ab initio* molecular dynamics codes. Calculations that would be unthinkable a few years ago are now routinely done by a wide community of researchers on dozens of computing facilities around the country. The computational scattering community should seek to identify the scientific problems of broad interest that can benefit from highly concurrent algorithms.

Goal State: Maintenance Functions

It is perhaps reasonable to use the present style of ownership for specialized software packages with a small user base. Nevertheless, there are a number of types of software packages from computational materials science that have broad use for many types of studies. Some of these have their own communities that perform maintenance and updates, and are likely to be supported this way into the future. On the other hand, there are connections between the structure and dynamics results from these simulations and the scattering profiles of samples that are not expected to be maintained by the theoretical community supporting a molecular dynamics package, for example. This is even more difficult when the scattering kernels are connected to instrument simulations that predict countrates at detectors. Nevertheless, such packages have the potential for broad use across many types of instruments and beamlines.

There is a need to coordinate the support of software packages that are not "owned" by commercial enterprises or small groups, in part to avoid duplication of effort and unnecessary branching of the codes. The organization for maintenance could set quality standards and select the software packages to be maintained and supported. Such an organization would include a committee representing the scattering community, as acceptance implies a long-term commitment of resources. A second necessary function of such a committee of stakeholders is the decision to cease the support level for a package as it is superseded by better or alternative approaches. This will require the development of objective metrics to measure the impact and success of a package for the scattering community.

The organization should publish guidelines emphasizing that software must be developed within a set of quality guidelines. These guidelines would likely require a planned test structure, documentation, anticipated maintenance needs, bug handling, patches, and their documentation.

There could be a variety of levels of maintenance and support for a package depending on the needs and impact of the software. This could range from formal quality assurance and testing to providing for distribution only, and this level of support should be clearly communicated.

Quality assurance, automated testing, and documentation should be essential prerequisites for the acceptance of a package into the project. Tools

for software testing will be essential for ensuring that deployment to a diverse set of architectures does not impact the correctness of the results. Another essential function of the maintenance group will be porting codes to new architectures to leverage the continued improvements in computational hardware. This will require members of the team with expertise in both hardware and software.

A primary continuing function of the maintenance team will be to respond to requests for bug fixes, and the acceptance of patches to enhance and correct deficiencies in the code. It is essential that a domain expert be a member of the maintenance team for each package, to ensure continued correctness of the code and the continuing development of novel features. Succession planning for domain experts will ensure no disruption of maintenance and support.

Deployment and installation support will be another vital function of the maintenance group. A seamless, consistent and straightforward installation process is essential for broad acceptance within the community. This function will require considerable effort, and should leverage the successful approaches developed within other similar community projects.

A national committee for scattering science software could promote the sharing of codes, code libraries, common tools, and runtime or development frameworks. This type of work will require professional staff that understands the algorithms and architectures. Reuse of common code should result in a significant reduction of development time, cost, and effort for new capabilities. Timeliness and quality of maintenance and development is crucial. Today this is often possible by using commercial packages, where a company provides upgrades and maintenance at a cost of licensing to users. This can be highly efficient for the programmer, although the costs of licensing can restrict software distribution. The development of the package is outside the control of the community, however, and therefore it may be difficult to control and influence. Also, there is potential for failure of the commercial entity and therefore catastrophic loss of the support and development. An open platform is preferable.

Goal State: User Support

A prerequisite for user support is effective documentation of the science underlying the package and training materials that include a wide range of examples. It will be essential to document the limitations and the potential pitfalls that can lead to incorrect results.

Support will be needed at a number of levels of sophistication. At the highest level the domain expert will need to be available to respond to queries requiring his scientific expertise and detailed knowledge of the package, while a community forum will suffice for more general requests for information and help. Defining a workable process for escalating requests to the appropriate level will be critical for establishing effective user support.

To be most useful, scientific software should be as user-friendly as possible. Pre-optimized codes, which are accessible to users, and tools like graphical user interfaces, are important for scientific productivity. It is also important to have consultants available to help users utilize the software most efficiently. Indeed, today many codes owe some of their popularity to these characteristics, for example the VASP electronic structure code and the FEFF x-ray spectroscopy code. It will become increasingly important to have high performance versions of such codes available to users at dedicated computer centers, likely at the various user facilities.

Workshops are a very effective method for disseminating expertise within a community. The use support team should be responsible for developing and holding workshops for interested groups at locations such as regional centers, or scientific workshops and meetings.

Ideally, maintenance and user support should be organizationally and financially separate from the development of new software packages. A formal separation of development and support will minimize the risk of committing resources to an inherently risky software development project.

Path Forward

Computational scattering scientists must make a clear case about the scientific cost of missing the opportunities offered by the emerging computing resources. They can plan a path forward with help from the expertise from other fields that have benefited

from techniques and algorithms that are designed for efficient and scalable concurrency. Professional programmers, software designers, and computer scientists can help identify the opportunities and set the path forward. Having a leading institution or support group providing them with such support would be highly valuable. It is time to get started.

Software maintenance and user support are important for user productivity, but it is unlikely that sufficient support can be obtained without dedicated personnel with a funded mission to provide these services. Typical software is currently developed as part of a specific scientific project (funded by the project grant) or possibly funded as separate grant. But like an investment in a beamline at a synchrotron or neutron source, funding for this software package cannot end after a few years if the software is to be used. A mechanism for maintenance should be planned and made available. Continued funding for this software package should be dependent on periodic peer review of usefulness and the impact of the software package. At the time of review, future funding should be decided – for example reduced or eliminated when software is not being used, kept if the functionality is appropriate, or even increased if there is interest from the community and maintainers to expand capabilities or make major upgrades or updates, such as porting to new multicore hardware.

Large scientific user facilities (synchrotrons, neutron sources, and electron microscopy facilities) are primary users and disseminators of the scientific software in the community. They should be expected to carry responsibilities for software maintenance, user support, teaching and dissemination. National labs also support high performance computing facilities. Today the experimental user facilities have few links to HPC facilities at the same labs, but there is interest on both sides of changing this situation because of obvious mutual benefits. Some coordination within a national laboratory would help promote such interaction, but the scattering community needs a broader effort than one within a particular laboratory. Nevertheless, a national laboratory group with a mission to provide support for computational scattering science would complete the path to publication of results from scattering experiments. The user facilities could provide full services for working with experimental data: collect, reduce, analyze, and publish, and the different facilities could maintain different specializations. This approach offers the potential for the fullest scientific impact of our synchrotrons, neutron sources, and electron microscopy facilities.

3.I. Software Development and Community Expectations

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Current Status

Over the years, most scientific software has been developed in small research efforts, with individual research teams creating the analysis tools as needed. Recently, scientific interest groups (SIG) have formed at x-ray and neutron facilities to consider the scientific software needs of their communities, and these frequently develop roadmaps for the software needs within their specialized areas. Successful larger efforts are few, and even the implementation of SIG planning requires more resources than those that have been made available. In addition to these efforts, larger projects are taking place that require communication of technical detail across development teams. Outputs from these, such as the DANSE project, are just now reaching realization.

At the U.S. x-ray and neutron facilities, funding for software development often competes with experimental beamline demands for operating funds. The attendees of this computational scatting workshop question whether the compelling need for computational scattering science can be met in the absence of targeted funding. In our collective experience, all of the large, grand-challenge science projects we are familiar with require the support of a coordinated theory, modeling and simulation effort to enjoy realization. Finally, one might consider avenues to stimulate and develop successful international cooperation in software development for scattering science.

There are many useful scientific software packages in use today. These are maintained and updated by dedicated individuals who "own" the software and share it with the communities where they collaborate. This has been both effective and efficient in the past. Unfortunately, after a period of time, when the software owner moves on to other areas, the analysis capabilities often become degraded and lost, only to be reinvented at a later date. A resource where software is maintained and upgraded with the latest understanding of the science is required to avoid the loss of important capabilities.

What is Needed

Software for data analysis, modeling, and simulation at x-ray and neutron facilities begins after data reduction and instrumental corrections are complete. An essential software capability is a "quick" analysis of data as it is being collected, to ensure that the investigators actually acquire the information they will need for the analysis. More sophisticated calculations can then give quantitative comparisons with experimental results. These more sophisticated calculations can often enhance the effectiveness of the experimental measurements, so it would be ideal if they could be done at the time of measurement.

For many problems in scattering science, it is nearly inconceivable that data can be modeled or fit without a highly specialized package, developed by experts in the scattering technique. The developers of such codes have responsibility to the scientific community and to the scientific process. They must recognize that a result is not accepted unless others can reproduce it. This favors scientific software that is disclosed (open source) so that formulae and algorithms can be validated. Proprietary software for science is troubling, unless there are multiple independent implementations of a method (preferably at least one that is open source, since different commercial codes have sometimes share the same computational code). A "secret" computational methodology invalidates the scientific principal of validation by reproduction.

Today much software is produced as a voluntary contribution by motivated scientists. In such cases, the community can expect little more than what is outlined above (and often less) from code developers, since the work is already a gift to the community. In contrast, if software development is funded, higher standards can be expected. Developers should provide documentation for users and documentation for developers, a test suite and possibly tools for automated testing, version control, packaging of software for easy installation, bug and feature management, maintenance of codes for continued operation on new platforms, and outreach to educate

the community in the use of the packages. In other words, scientific software developers can be expected to work at a higher level of software professionalism, and adopt many well-established commercial practices. Some of these expectations mean that funding must be provided on a long-term basis, since much of the effort described above takes placed after the nominal completion of the coding and the delivery of the "product." For scientific software, development is an on-going process and *rigor mortis* sets in as soon as development and support stops.

It is always desirable that codes be "platform-independent," which is usually taken to mean that they will run on the variety of common computers. Likewise, when a program may have utility for computations that span a large range in computational demand, it is valuable to have scaleable implementation, so that the user with access to only simple hardware such as an isolated laptop can still obtain a result, but the user at the forefront will be able to take advantage of parallelization on a computer cluster. Modern developments such as web services and cloud computing offer access to high performance computing for users with a laptop environment, for example enabling their use of modern codes of computational materials science.

In return for providing their tools and service to the scientific community, scientist-programmers should expect from the community the recognition that comes to all intellectual contributors to the scientific process: the citation of the specialized computer program as an integral part of the intellectual chain that led to the current work. Anything less is ethically suspect.

Roadmap for the Future

The DOE Office of Science supports operational activities of the facilities as well as scientific research divisions at the laboratories, and NSF supports scientific research efforts originating with universities and to a lesser extent the construction of new experimental capabilities at the facilities. Starting with the x-ray and neutron facilities, we propose that each facility have a strong and experimentally engaged computational theory group, numbering perhaps ten. These individuals must be experienced in leading theory, modeling and simulation efforts, and must be deeply engaged in the experimental data analysis. They should be pleased to attend science seminars at the facilities, engage in the science, and work with laboratory staff and scientific users on data interpretation. The members of the scientific software groups have a dual mission. Part of their mission is to create new data analysis software, models and simulations for leading-edge grand-challenge research. Once developed, this analysis capability becomes part of the portfolio of capabilities at the facility. The other part of their mission is to maintain and upgrade the large base of software that is currently used by facility researchers. In this manner, scientific software becomes, like the experimental measurement facilities themselves, part of the world-class science capabilities of the x-ray or neutron facilities.

Looking toward the future, we recommend the development of facility networks to make data available to users after they leave the facilities, and to enable multiple-technique data intensive and collaborative science, bringing together the research data requiring multi-techniques. Today's portal based utilities are not sufficient to meet the requirements for the growing multi-technique applications. The idea is to enable data movement, caching, and mirroring for neutron and x-ray facilities in the U.S.

For most of the theory-intensive grand challenge scattering and spectroscopy-based science described in this report, it is difficult to imagine that the required software can be developed by means of anything less than an institute-based software effort. Such an institute would include theoretical and experimental scientists from many disciplines, software engineers, and programmers. A strong visitor's program including distinguished theorists, postdoctoral associates and students would enable longer-term access to institute capabilities, as well as bring to the institute expertise from disciplines not represented.

3.J. Education and Career Paths

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Scope of Topic

The major x-ray, neutron, and electron facilities funded by the DOE and NSF represent a substantial public investment in materials science that provide the US with state-of-the-art tools for advancing scientific discovery. Historically, these facilities have been used by specialists in scattering, imaging, and spectroscopy, but as experimental techniques mature, it is imperative that they are made available to the broader scientific community to address the full range of scientific and technological challenges facing society today. Such an expansion of the facilities' user base requires the development of educational tools that inspire scientists to explore these scientific opportunities and guide them in the planning, execution, and analysis of their first experiments. This section will discuss how an expanded investment in software is essential to achieving these educational goals. It also addresses how to ensure that those involved in software development have opportunities for career advancement that are commensurate with their value to the scientific enterprise.

Where Are We Today?

There is currently a dearth of educational opportunities to learn about the capabilities of x-ray, neutron, and electron science. In universities, courses on diffraction are being discontinued because of the perception that modern laboratory-based diffractometers and the automated structural analysis they provide no longer require extensive training. Although there are online resources that offer simple tutorials to basic crystallographic concepts, none give a comprehensive introduction to scattering theory or the advanced capabilities at large-scale facilities at a level that would inspire scientists to explore such research opportunities more deeply. The educational resources that do exist, including graduate courses offered by several national facilities, require a considerable commitment in time and effort. The challenge is to offer educational material that is easy for non-experts to access and assimilate, but is sufficiently detailed to give a clear idea how these facilities can address specific scientific problems.

New users also face obstacles when they plan and perform their first experiments. The major facilities have a responsibility to provide software for the basic reduction of instrumental data, but it is typically the responsibility of the scientific user to perform the subsequent analysis that allows appropriate scientific interpretation. With the software commonly available to the user community, this can be a formidable barrier to the inexperienced user and can impede the publication of results. Although progress has been made in providing more sophisticated tools through initiatives like the DANSE project, there is much more that can be done to provide tools for experiment planning, visualization of results, and interpretation of results with modern materials theory.

At present, software tends to be developed in a haphazard fashion within individual experimental teams, usually by post-doctoral associates or junior scientists, for specific types of science. Again, the DANSE project has attempted a more ambitious fusion of such efforts, but the work is still performed by those at the start of research careers. There are two problems with this approach; increasingly complex software is being developed by those who still need to learn the principles of software design, and the time devoted to software development can harm future career prospects by reducing their scientific productivity.

Scientific software development often gets less respect than experimental or theoretical work, even if it has broad impact. An important measure of impact is journal citation rate. Unfortunately, software developments are not appropriate for publication in many research journals, and software descriptions are often relegated to specialty publications that are not tracked today by services such as the ISI Web of Science. The case of the program, SHELX, which is widely used in single crystal x-ray scattering, illustrates some of the inconsistency between software impact and citation impact. In 2007 the

Attendees of the National School on Neutron and X-Ray Scattering, Argonne and Oak Ridge National Laboratories, at the entrance of the Advanced Photon Source June 2010.

author, George Sheldrick, was invited to publish a retrospective article describing the thirty-year evolution of his program [1]. Users, armed with a proper article to cite, did so and generated more than 6600 citations by mid-2009. This pushed the impact factor of the Journal, Acta Crystallographica A, from its usual value factor of 2.5 up to 50. Not all software stories have such happy endings, and scientific software development is considered a career risk.

Where Should We Go?

Software can play a significant role in introducing both students, undergraduate and graduate, and scientists in other fields, to the potential value of x-ray, neutron, and electron scattering for their own research. Web-based courses, if well-designed, can provide tutorials introducing concepts in scattering theory, including dynamical diffraction, that go beyond current introductions to reciprocal space and basic crystallography and include other fields, such as diffuse scattering, engineering diffraction, inelastic scattering, spectroscopy, and imaging (e.g., tomography, coherent diffraction imaging). The kinds of online simulations that could help a student gain insight into the theory of such techniques could also be extended to provide realistic tools for those planning experiments on specific systems, provided they were coupled to databases of source parameters, instrumental configurations, cross-sections, and scattering kernels. These databases should also have access to recent calibration data and other relevant metadata to allow detailed optimization of future experiments.

There is considerable overlap between the needs for advanced data analysis techniques that offer both novice and experienced users rapid visualization, preferably in real space, of experimental results, and the needs of simulation software that educate the next generation of scattering scientists. Such comprehensive experiment simulations can also be a great help in deepening the interaction with theorists, particularly for experiments that require advanced *ab initio* modeling, allowing them to understand the uncertainties and approximations that affect the interface between materials properties and experimental design. With careful design, web services could fulfill the needs of both research and education.

However, the benefits of such synergies can only be realized by a considerable investment that couples expertise in scientific computing, algorithm development, applied mathematics, statistical software engineering, and interface design. The software needs to be well-designed, robust, platform-independent, well-maintained, well-documented, and long-lasting. It is not clear that we currently have the infrastructure that allows such a comprehensive union of such different fields of expertise.

We need to develop means of linking such disparate communities in ways that ensure adequate career opportunities for all groups involved. In the past, funding has been provided by bodies that require rigorous peer-review of individual investigators, and there have been barriers that prevent joint initiatives involving multiple fields. For example, it can be difficult to couple funding for scientific goals, typically by DMSE in the DOE or by the NSF, and computational science goals by ASCR, particularly if the latter is seen as merely providing a service to the former. There would be value in breaking down such barriers to provide a stronger coupling between, for example, the major scattering facilities and the leadership computing facilities.

What Efforts Would Expedite Progress?

Since there is typically an "impedance mismatch" between experts in the divergent fields of materials science, computational science, and software engineering, we need to develop organizational structures that provide intensive interactions between these groups. These have often been in the form of virtual communities that are easier to establish and have the potential of combining a wider range of expertise. They have the disadvantage of having much less frequent and more formalized interactions that can impede the development of mutual understanding.

Another possible model is one or more organizations run jointly by a university and a national laboratory, with joint funding by DOE and NSF to reflect both the scientific and educational scope. Coupling software development to educational goals could produce significant advantages by also linking these communities to those with educational expertise. The challenges of providing advanced educational tools that simulate realistic experiments overlap considerably with those of enhancing analysis tools for scattering experts.

Such an organization would contain a mixture of academic researchers from materials science and computational science and professional software engineers, whose career paths are not dependent on performing peer-reviewed research. It could then draw on recent experience with instrument simulations and enhance their usability by providing innovative interfaces for both novice and experienced users. It would also offer a stable home for legacy software and build on the mechanisms developed as part of the DANSE project of allowing diverse code bases to be combined into integrated data analysis and visualization.

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3.K. Organization and Financial Support

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Current Status

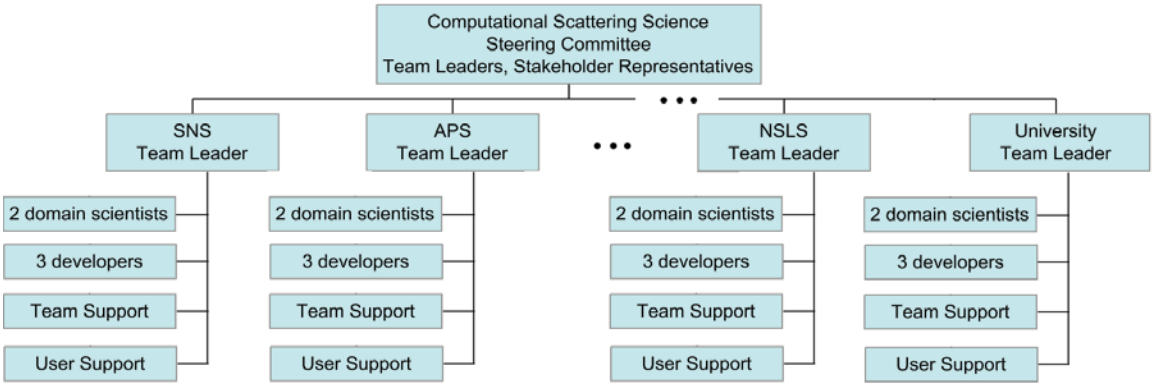
The large DOE scattering facilities are world class, and we contend that they could be made more efficient and productive by incorporating a computational science component that takes advantage of the great advances in software and computer hardware. Today at US x-ray and neutron facilities, computational scattering science and analysis software development compete for funds with experimental beamline support and other operational expenses. Although the facilities have developed some software for data reduction and visualization, robust computational science has not emerged through operations support. The attendees of this Workshop are concerned that the compelling need for computational scattering science will most likely not be met unless there is targeted funding, separate from the facilities' operations budget. A degree of independence of the computational scattering science would also allow this effort to adapt and fill the gap between the scattering science performed at the facility, and the large computational science efforts at the host national laboratory.

Without targeted attention, we in the US risk losing pre-eminence to Europe, where there are serious innovations. The European Theoretical Spectroscopy Facility (ETSF) is a knowledge center for theoretical spectroscopy carrying out state-of-the-art research on theoretical and computational methods for studying electronic and optical properties of materials. The ETSF gathers the experience and know-how of a network of more than 200 researchers in Europe and the United States, facilitating collaborations and rapid knowledge transfer. They have pushed the frontiers of optical response theory, and have developed many of the best modern codes. The ETSF is co-funded by the EU under the FP7 Capacities program. In Germany, DESY has put forward a high data rate initiative to address scientific software needs. The plan includes data management and real time data processing, data analysis, modeling, and simulation. They anticipate a partnership in which DESY joins other German scientific institutes, each contributing resources. The plan is for 32 FTE from DESY over 5 years, with an overall plan for 64 FTE. They will begin with biological crystallography, followed by microtomography, SAXS, WAXS, and others.

The US computational scattering science efforts tend to be small, and are not coordinated. Their visibility and attraction to theorists and experimentalists is generally low, although there are some wonderful individual success stories. What is needed is a common mission and broad planning to bring together theory, modeling and simulations to experiments. Some of the potential benefits of computational scattering science described in this Report are clear today, and these will only grow and improve with advances in computing resources and algorithms. Here we address how such an effort could be organized to meet the needs of today and tomorrow, and what it might cost to operate.

What is Needed

Software for data analysis, modeling, and simulation at x-ray and neutron facilities begins after data reduction is complete, but there are often important connections between data analysis and data reduction. Some computer simulations require close connections to specific instruments, and for these it is essential for computational scattering scientists to work with experimental scientists. A model we endorse would embed a computational scattering science team at each major national user facility. To balance these team efforts, reduce duplication, and promote sharing of successful products and processes by all teams, these efforts should be coordinated by a central governing panel of community experts, derived from across all the facilities and stakeholders in the scattering science community. Beyond that, there is the additional opportunity to create a grand challenge institute that can address specific research opportunities, accelerating the field of computational scattering science.



Organization of computational science teams at different facilities, with national coordination.

An optimal size for a software development team is approximately seven individuals [1], including an architect or lead developer, developers, systems administrator or technical support person, software tester, writer and user liaison, and administrator; this number becomes slightly larger when we add scattering scientists into the mix. Communication is burdensome for larger teams, and division of labor is a problem for smaller teams. A team of 8 or 9 persons can take responsibility for a topic such as interfacing density functional methods to scattering codes and refinement methods, interfacing molecular dynamics packages for predictions of x-ray and neutron scattering, finite element methods for mesoscale models, or optimization of structural models to fit diffraction data. These responsibilities would include adapting accepted software packages for predictions of scattering, documentation of special features, release management, user support, and strategic planning for new capabilities. The team would not have a core mission of developing molecular dynamics codes, for example, although modifying them would be expected. The team would also support interfaces to simulations of the facility instruments. As scientific collaborators, team members would interact with the instrument scientists and the user community of the facility. Another part of their mission would be to plan and execute the maintenance and upgrades of the large base of software that is currently used by facility researchers. Scientific software would become, like the experimental facilities themselves, part of the world-class science capabilities of the x-ray or neutron facilities, and additionally would have the distinct advantage of being shared and distributed among all of the different facilities.

The efforts of the teams should be coordinated at the national level to help balance the support for different fields of science, and ensure that important algorithms and software packages are shared. The figure depicts a concept for an organizational structure. Coordination would ensure that the analysis capabilities developed as part of the portfolio of capabilities at one facility could also serve other facilities. The national organization could work with the different teams to run a robust visitors program. The national organization would help direct the effort of the individual computational science teams, but it may be reasonable for the local teams to make their own proposals of technical effort, and the Steering Committee could work with the sponsors to arrange a review of the technical plans. We suggest that after 3 years, a renewal proposal will be submitted by each team, and their prior work and proposed work be reviewed for its success, productivity and for its value to the missions of the facility, national lab, and scattering community. The national coordination of these development teams needs to be firm, with the national organization playing a role in setting the budgets of the computational science teams. If the scope is divided appropriately between the teams, there should be few problems at their boundaries.

Looking toward the future, we recommend the development of facility networks to make data available to users after they leave the facilities, and to enable multiple-technique and collaborative science, bringing together the research data requiring multi-techniques. Today's portal based utilities are not sufficient to meet the requirements for the growing multi-technique applications. The idea is to enable data movement, caching, and mirroring for neutron and x-ray facilities in the U.S. Simulation and analysis tools could follow a similar model.

Roadmap for the Future

Augmentation of facility operations support, with periodic reviews of the computational science activity, may sound like a tempting path forward because it could be built incrementally. Unfortunately, even an embryonic effort has not yet developed under

this model, and we doubt it can. The priority for an operations-based software group will naturally be to support operations, which are focused toward data reduction, calibrations, and data visualization. Data analysis by computational scattering scientists needs to be a separate activity. Even an enlarged local software group under operations support could not support all science that occurs at the facility, so national coordination, such as shown in organizational chart, is needed to distribute the computational science efforts between facilities and avoid duplication. Some specialization will follow naturally from the expertise and interests of the computational scattering scientists at a facility, so there is an opportunity for different facilities to specialize in different types of computational science. Perhaps some of the local style could follow the interests of the theory groups in the nanoscience centers at DOE labs. The nanoscience centers are often nearby, and some sharing of personnel and resources could be possible. Again, sharing these capabilities between labs would require national coordination.

The proposed structure could be built modularly. A thorough analysis is required to prioritize topics and plan the computational science teams, but our estimate today is that there should be ultimately about eight such teams. With some program management personnel and team support functions, we expect that the full effort would cost about M$ 15/year. This could be built incrementally, since computational scattering science teams could be added to cover different topics. It would seem unwise to start with only one team, however, since the national coordination should be developed early.

Not all of the teams need to be centered at national user facilities. Today the SNS and ISIS facilities are outsourcing development work on data reduction software to a private firm, Tessella, through the Mantid project. A steering committee works closely with the Tessella developers, however, so some facility oversight is necessary. Data analysis software could be developed by a private company if the personnel had sufficient computational science expertise, and worked closely with computational scattering scientists at the facility. Such arrangements occurred with software for interpreting high resolution images from the earlier generation of transmission electron microscopes. Private firms have not yet offered analogous products for the new generation of aberration-corrected and monochromated instruments, however, and the financial incentive may not be sufficiently strong to do so.

A university-based team may contribute effectively to a computational scattering science activity, assuming quality standards are met. Some important data analysis software packages have emerged from, and have been maintained by, university groups. University-based users could become better invested in the scattering facilities by participating in computational scattering science efforts. The DOE Office of Science supports operational activities of the facilities as well as scientific research divisions at the laboratories, and NSF supports scientific research efforts originating with universities and to a lesser extent the construction of new experimental capabilities at the facilities. Perhaps a shared sponsorship is possible.

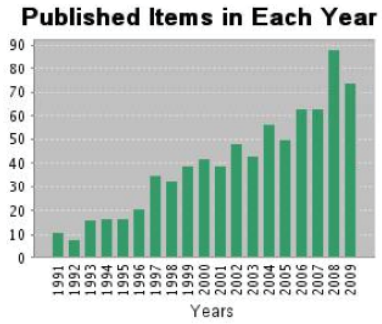
For some of the most theory-intensive grand challenge scattering science described in this Report, it is difficult to imagine that the required software can be developed by anything less than the scale of an institute-based effort. Such an institute would include theoretical and experimental scientists from many disciplines, software engineers, and programmers. A strong visitor's program including distinguished theorists, postdoctoral associates and students would enable longer-term access to institute capabilities, as well as bring to the institute expertise from disciplines not represented.

Reference

[1] F. Brooks, The Mythical Man Month: Essays on Software Engineering, (Addison-Wesley, 1995).

Appendix: Analysis of Literature on Computational Scattering Science

A keyword search was performed with the ISI Web of Science database in October, 2010, using the words (***ab initio* AND scattering AND neutron**).
Some 802 papers were found. Additional results are shown below.



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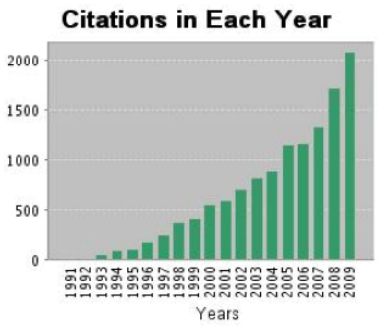
View Citing Articles
View without self-citations

Average Citations per Item [?] : 17.95

h-index [?] : 51

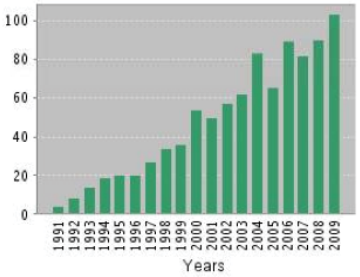


Field: Institution Name	Record Count	% of 802
INST MAX VON LAUE PAUL LANGEVIN	69	8.6035 %
RUTHERFORD APPLETON LAB	55	6.8579 %
ARGONNE NATL LAB	22	2.7431 %
MAX PLANCK INST FESTKORPERFORSCH	19	2.3691 %
CNRS	18	2.2444 %
POLISH ACAD SCI	18	2.2444 %
RUSSIAN ACAD SCI	18	2.2444 %
JOINT INST NUCL RES	17	2.1197 %
UNIV PARIS 06	17	2.1197 %
LOS ALAMOS NATL LAB	15	1.8703 %
OAK RIDGE NATL LAB	15	1.8703 %
CEA SACLAY	14	1.7456 %
FORSCHUNGSZENTRUM JULICH	14	1.7456 %
UNIV MONTPELLIER 2	14	1.7456 %
UNIV REGENSBURG	14	1.7456 %
CSIC	12	1.4963 %
DELFT UNIV TECHNOL	12	1.4963 %
FORSCHUNGSZENTRUM KARLSRUHE	12	1.4963 %

Field: Source Title	Record Count	% of 802
PHYSICAL REVIEW B	135	16.8329 %
JOURNAL OF CHEMICAL PHYSICS	70	8.7282 %
JOURNAL OF PHYSICS-CONDENSED MATTER	46	5.7357 %
JOURNAL OF PHYSICAL CHEMISTRY B	30	3.7406 %
JOURNAL OF PHYSICAL CHEMISTRY A	29	3.6160 %
CHEMICAL PHYSICS	25	3.1172 %
PHYSICAL REVIEW LETTERS	19	2.3691 %
JOURNAL OF MOLECULAR STRUCTURE	18	2.2444 %
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY	15	1.8703 %
JOURNAL OF NON-CRYSTALLINE SOLIDS	14	1.7456 %
PHYSICAL CHEMISTRY CHEMICAL PHYSICS	12	1.4963 %
JOURNAL OF ALLOYS AND COMPOUNDS	10	1.2469 %
JOURNAL OF PHYSICAL CHEMISTRY	10	1.2469 %
MACROMOLECULES	10	1.2469 %
RT A-MOLECULAR AND BIOMOLECULAR SPECTROSCOPY	10	1.2469 %
EUROPHYSICS LETTERS	9	1.1222 %
PHYSICA B-CONDENSED MATTER	9	1.1222 %
CHEMICAL PHYSICS LETTERS	8	0.9975 %

A keyword search was performed with the ISI Web of Science database in October, 2010, using the words (***ab initio* AND scattering AND x-ray**).
Some 982 papers were found. Additional results are shown below.

Published Items in Each Year



Results found: 982

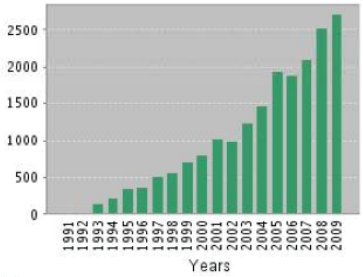
Sum of the Times Cited [?] : 22,173

View Citing Articles
View without self-citations

Average Citations per Item [?] : 22.58

h-index [?] : 59

Citations in Each Year



Field: Institution Name	Record Count	% of 982
EUROPEAN SYNCHROTRON RADIAT FACIL	60	6.1100 %
UNIV WASHINGTON	59	6.0081 %
RUSSIAN ACAD SCI	43	4.3788 %
CNRS	39	3.9715 %
UNIV PARIS 06	37	3.7678 %
CHINESE ACAD SCI	22	2.2403 %
ARGONNE NATL LAB	21	2.1385 %
DESY	21	2.1385 %
IST NAZL FIS NUCL	21	2.1385 %
OAK RIDGE NATL LAB	20	2.0367 %
FREE UNIV BERLIN	19	1.9348 %
BROOKHAVEN NATL LAB	17	1.7312 %
LAWRENCE LIVERMORE NATL LAB	16	1.6293 %
UNIV CALIF BERKELEY	16	1.6293 %
UNIV SAO PAULO	16	1.6293 %
STANFORD UNIV	15	1.5275 %
UNIV CAMERINO	15	1.5275 %
UNIV PARIS 11	15	1.5275 %
CEA	14	1.4257 %
GUNMA UNIV	14	1.4257 %

Field: Source Title	Record Count	% of 982
PHYSICAL REVIEW B	191	19.4501 %
JOURNAL OF PHYSICAL CHEMISTRY B	45	4.5825 %
JOURNAL OF CHEMICAL PHYSICS	43	4.3788 %
PHYSICAL REVIEW LETTERS	35	3.5642 %
JOURNAL OF PHYSICS-CONDENSED MATTER	30	3.0550 %
JOURNAL OF SYNCHROTRON RADIATION	22	2.2403 %
BIOPHYSICAL JOURNAL	19	1.9348 %
JOURNAL OF PHYSICAL CHEMISTRY A	18	1.8330 %
JOURNAL OF APPLIED CRYSTALLOGRAPHY	14	1.4257 %
JOURNAL OF BIOLOGICAL CHEMISTRY	14	1.4257 %
JOURNAL OF MOLECULAR BIOLOGY	13	1.3238 %
PHYSICAL CHEMISTRY CHEMICAL PHYSICS	13	1.3238 %
ACTA CRYSTALLOGRAPHICA SECTION A	12	1.2220 %
SURFACE SCIENCE	12	1.2220 %
JOURNAL OF ALLOYS AND COMPOUNDS	11	1.1202 %
JOURNAL OF APPLIED PHYSICS	11	1.1202 %
CTRON SPECTROSCOPY AND RELATED PHENOMENA	10	1.0183 %
JOURNAL OF MOLECULAR STRUCTURE	10	1.0183 %
JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS	10	1.0183 %

How the Workshop was Organized

Topics and Scope

The emphasis of the workshop was on evaluating how modern computations of the structure and dynamics of materials can provide results of importance to scattering science. Some general questions addressed were:

- Where are the best opportunities for leveraging the most science for the most scattering scientists?
- For enabling scientific discovery, what are the most effective ways to combine computation and experiment today, and over the next 2-5 years?
- In what fields of scattering science can computation deliver the maximum impact with minimum effort?
- How should these opportunities be assessed in terms of realistic resources and time to achieve them?
- How can the results of such efforts be assessed (what metrics are useful in doing so)?
- Who should make strategic and tactical decisions in this dynamical field?

Workshop Logistics

The workshop occurred at the Argonne National Lab for 3 days (July 7-9), with an extra day for preparation (July 6). Before the meeting, the attendees indicated their preferences for 3 topical groups. The organizers made assignments to the topical groups and picked leaders. Several leaders initiated an early effort by email to better define the topics for discussion, and started developing a plan to discuss issues and opportunities. The topic leaders suggested another person or two (with encouragement for women and members of underrepresented groups) for invitation, and the organizers invited most of them.

The emphasis was on how today's methods for calculating the structure and dynamics of materials can be connected to scattering research, and what new developments in computation or scattering could impact these capabilities over a time horizon of 5 years or less. The approach was to develop a strategic plan that included three pieces: 1) an assessment of where we are today, 2) a picture of where we want to be in 5 years, and 3) a path to get there. Each subgroup prepared a strategic plan for their topic, included in this report.

The Report will be sent to the management of the national user facilities for x-ray, neutron, and electron scattering, and to university-based facilities such as CHESS. The SNS and the APS will post the report on their web sites. The attendees of the workshop will be encouraged to post the Report locally, and email it to interested colleagues. The workshop organizers and attendees will communicate the Report to attendees of the NSSD User meeting in 2010, and neutron and x-ray scattering meetings as appropriate.

Agenda

Tuesday July 6

1 PM Meeting of organizers and group leaders
- Flash presentations of 15 topics
- Discussion of logistics for main meeting

Wednesday July 7

8:30 Introductions and Overview
9:00 Presentations of topics by group leaders
7 topics: 15 minutes+5 min for questions each. Allowance for 20 min break.
12:00 Lunch
1 PM Presentations of topics by group leaders
6 topics: 15 minutes+5 min for questions each. Allowance for 20 min break.
3:40 PM General Discussion
4:30 PM Planning for Day 2

Thursday July 8

8:30 AM Four Parallel Topical Sessions
Correlated Electron Problems/Complex Materials. Rob McQueeney (ISU)
Chemical Processes Far from Equilibrium. Lin Chen (Northwestern U and ANL)
Nanostructures – Structure and Dynamics. Joseph E. Curtis (NCNR)
Large-Scale Finite Element Methods. Cev Noyan (Columbia)
Computing Resources, Data and their Management. Mark Hagen (SNS)
9:30 AM Five Parallel Topical Sessions
Fast and Ultrafast Phenomena. Fernando Vila (UW)
Materials Simulations and Scattering Cross-sections. Brent Fultz (Caltech)
Technology for Heuristic Optimization of Complex, Ill-conditioned Models. Brian Toby (ANL)
Multicore Computing Architecture. Jan Ilavsky (ANL)
10:30 break
11:00 AM Four Parallel Topical Sessions
Software Development and Community Expectations. Gabrielle G. Long (APS)
Software Maintenance and User Support. Frans Trouw (LANL)
Education and Career Paths. Ray Osborn (ANL)
Financial Support. Kenneth W. Herwig (SNS)
12:00 Lunch
1:00 PM Four Parallel Writing sessions
Correlated Electron Problems/Complex Materials. Rob McQueeney (ISU)
Chemical Processes Far from Equilibrium. Lin Chen (Northwestern U and ANL)
Nanostructures – Structure and Dynamics. Joseph E. Curtis (NCNR)
Large-Scale Finite Element Methods. Cev Noyan (Columbia)
Computing Resources, Data and their Management. Mark Hagen (SNS)
2:00 PM Five Parallel Writing sessions
Fast and Ultrafast Phenomena. Fernando Vila (UW)
Complex Matter. Robert McQueeney (ISU)
Materials Simulations and Scattering Cross-sections. Brent Fultz (Caltech))
Technology for Heuristic Optimization of Complex, Ill-conditioned Models. Brian Toby (ANL)
Multicore Computing Architecture. Jan Ilavsky (ANL)
3:00 break
3:30 Four Parallel Writing sessions
Software Development and Community Expectations. Gabrielle G. Long (APS)
Software Maintenance and User Support. Frans Trouw (LANL)
Education and Career Paths. Ray Osborn (ANL)
Financial Support. Kenneth W. Herwig (SNS)

Friday July 9

8:30 Presentations of writings by topic leaders
10 minutes each, allowing for 30 minute break
12:00 Lunch
1 PM Discussion
1) common themes,
2) how to assess opportunities for best value,
3) how to measure success.
3 PM Closeout

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