MS.62.3

Acta Cryst. (2008). A**64**, C109

Relaxed averaged alternating reflections for diffraction imaging

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We report on progress in algorithms for iterative phase retrieval. The theory of convex optimisation is used to develop and to gain insight into counterparts for the nonconvex problem of phase retrieval. We propose a relaxation of averaged alternating reflectors and determine the fixed point set of the related operator in the convex case. A numerical study supports our theoretical observations and demonstrates the effectiveness of the algorithm compared to the current state of the art.

Keywords: phase retrieval, projection, inconsistent feasibility

MS.62.4

Acta Cryst. (2008). A**64**, C109

Reduced-rank extension of BLUE and deep lipschitzian gradient projector for inverse problems

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This talk is divided into 2 parts as follows. In the 1st part of this talk, we introduce one of the central ideas of the MV-PURE (Minimum-Variance Pseudo-Unbiased Reduced-Rank Estimator), by Yamada and Elbadraoui (2006) and Piotrowski and Yamada (2008), which is a novel estimator for ill-conditioned inverse problems. The MV-PURE is a reduced-rank extension of the Gauss-Markov estimator (BLUE: Best Linear Unbiased Estimator) and defined as a closed form solution of a hierarchical nonconvex constrained optimization problem. The MV-PURE achieves the minimum variance among all solutions of the first stage optimization problem for minimizing, under a rank constraint, simultaneously all unitarily invariant norms of an operator applied to the unknown parameter vector in view of suppressing bias of the estimator. The MV-PURE offers a unified view for many estimators including the well-known estimators: the Gauss-Markov (BLUE) estimator, the generalized Marquardt's reduced-rank estimator and the minimum-variance conditionally unbiased affine estimator subject to linear restrictions. In the 2nd part of this talk, we introduce an idea of the deep lipschitzian gradient projector which is defined by Yamagishi and Yamada (2008) as the metric projection onto the level set of the best lower bound of a convex function which is assumed to be (i) bounded below, and (ii) differentiable and its derivative is lipschitzian. The deep lipschitzian gradient projector is computationally efficient and can approximate the level set of the convex function better than the subgradient projector, hence it can improve many computational methodologies employing the subgradient projector as one of their key players.

Keywords: inverse problem, MV-PURE, lipschitzian gradient projector

MS.62.5

Acta Cryst. (2008). A**64**, C109

Solution to the phase problem for surface X-ray diffraction

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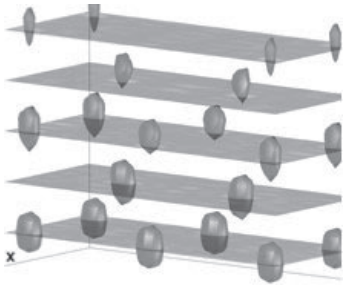
Directly inverting x-ray data requires determining the unmeasured phases (the "phase problem"). We propose a general solution to the phase problem for surface x-ray diffraction (SXRD) termed the *phase and amplitude recovery and diffraction image generation method* (PARADIGM); atomic structures from a single surface domain or from multiple, symmetry-related domains on a known bulk structure may be recovered. Diffraction *rods* in reciprocal space may be *oversampled* relative to the Nyquist frequency of the height of the selvedge. An iterative algorithm alternately satisfies known constraints of the oversampled data in real and reciprocal space, and progressively determines the amplitudes and phases of the surface structure factors. A Fourier transform then constructs an "image" of the selvedge. Using this method, the atomic positions on a Au(110)-(2x1) surface have been visualized directly from the data. (See figure.) This breakthrough allows an automated, model-independent way to determine unknown surface structures. We have applied this method to several heretofore unknown surface phases: Sb/Au(110)-c(2x2) and even the multi-domain Sb/Au(110)-($\sqrt{3}$x$\sqrt{3}$)R54.7° structure.



Keywords: phase determination methods, real-space refinement methods, surface reconstruction

MS.63.1

Acta Cryst. (2008). A**64**, C109-110

Photoreduction of metalloprotein active sites by synchrotron radiation

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X-ray damage to protein crystals is assessed on the basis of the degradation of diffraction intensity, yet this measure is not sensitive to the rapid changes that occur at photosensitive groups, such as the active sites of metalloproteins. X-ray absorption spectroscopy (XAS) has been used to study the x-ray dose-dependent photoreduction of crystals of the [Fe(2)S(2)]-containing metalloprotein, putidaredoxin. A dramatic decrease in the rate of photoreduction, followed through changes in the XAS edge structure, is observed in crystals cryocooled with liquid helium at 40 K as compared to those cooled with liquid nitrogen at 110 K, showing structural changes consistent with active site cluster reduction at 110 K, but not at 40 K, even after an eight-

fold increase in dose. Comparing structural results from EXAFS to those from crystallography on this and similar proteins, show that x-ray induced photoreduction has impacted the crystallographic data and subsequent structure solutions. These results indicate the importance of using LHe-based cooling for metalloprotein crystallography in order to limit changes at the metalloprotein active sites. The study also illustrates the need for direct measurement of redox states of the metals, through XAS, simultaneously with the crystallographic measurements. The work was performed at SSRL with support from the NIH NCRR BTP program and the US DOE BER. SSRL operations are funded by the US DOE BES.

Keywords: radiation damage, metallo-enzymes, X-ray absorption spectroscopy

MS.63.2

Acta Cryst. (2008). A**64**, C110

Crystallography with X-ray and optical spectroscopies for metalloproteins structural studies

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Metalloproteins constitute a significant fraction (> 30%) of a genome and use the redox properties of metals to perform essential catalytic processes. The accuracy with which information is required is often not available through X-ray crystallography (1). Furthermore, the effect of intense X-ray beams now available at most synchrotrons on redox centres is very severe and it is not easy to obtain information of the redox state of the metal from a structure. In both of these context, use of XAS will be discussed with some recent examples. In addition, the advantage of combining on-line optical spectroscopy with XAS and crystallography are demonstrated with a specific example of copper nitrite reductase(ref 2).

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Keywords: metalloproteins, radiation damage, redox states

MS.63.3

Acta Cryst. (2008). A**64**, C110

X-ray absorption spectroscopy for the structure determination of copper transport proteins

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All organisms, from prokaryotes to plants and mammals have evolved complex mechanisms to efficiently acquire and properly utilize copper (Rosenzweig, O'Halloran 2000;Wintz, Vulpe 2002). The past ten years have assisted the discovery of many pieces of the sophisticated machinery which is used to efficiently acquire and utilize copper. (Elam et al. 2002;Rosenzweig 2001) At CERM we have focussed our work on the study of copper transport proteins in different organisms by x-ray crystallography and by coupling NMR and x-ray absorption (XAS) spectroscopic techniques that, combined, offer the possibility to achieve the complete structure determination of a metalloprotein in solution and provide unique information on the electronic structure of the metal ion and on how it influences its binding to the protein (Arnesano et al. 2003; Banci et al. 2003; Banci et al. 2004; Banci et al. 2005a,b; Banci et al. 2006). The most recent applications of the NMR-XAS approach to the structure determination of copper proteins involved in the assembly of bacterial and human cytochrome C oxidase will be presented and discussed as well as the comparison with crystallographic results.

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Keywords: copper proteins, X-ray absorption, NMR spectroscopy

MS.63.4

Acta Cryst. (2008). A**64**, C110−111

Structure in the local environment of Zn^{2+} ion in the anti-termination protein of *Bacillus subtilis*

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HutP is an RNA-binding protein that regulates the expression of the histidine utilization (hut) operon in Bacillus subtilis, by binding to cis-acting regulatory sequences on hut mRNA. Our crystal structure of the quaternary complex (HutP- L-histidine-Mg^{2+}-21-mer RNA) showed that three Nε atoms of imidazole rings of His residues, the backbone nitrogen and carboxyl oxygen atoms of L-histidine, and a water molecule coordinate the Mg^{2+} ion to form the typical octahedral polyhedra1). Further studies showed that not only Mg^{2+} ion but also several other divalent cations, except Cu^{2+}, Yb^{2+}, Hg^{2+} cations, are effective, and the structures of HutP- L-histidine-Mn^{2+} and HutP-L-histidine-Ba^{2+} revealed to be very similar to that of the HutP-L-histidine-Mg^{2+} complex2). We recently solved the crystal structure of the HutP- L-histidine-Zn^{2+} complex, because Zn^{2+} is the best among divalent cations for mediating RNA-binding and probably antitermination process as well2). Our complex (HutP-L-histidine-Zn^{2+}) revealed that imidazole Nε atoms of not only His residues of HutP but also of the L-histidine ligand undergo four-fold Zn^{2+} coordination, which differs from the case of octahedral coordination found in our previous complex (HutP-L-histidine-Mg^{2+}). To obtain further insight into the Zn^{2+}-binding site, X-ray absorption both near-