PS02.09.07 QUANTUM CRYSTALLOGRAPHY AND FRAGMENT CALCULATIONS. Jerome Karle, Lulu Huang, Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D. C. 20375-5341, Lou Massa, Hunter College and Graduate Center of City University, New York, NY 10021-5024

Quantum crystallography concerns the intimate interrelationship of quantum mechanics and crystallographic data.* Its purpose is to obtain wave functions that are consistent with data measured in an X-ray diffraction experiment. Fragment calculations are purely quantum mechanical ones and their implementation, in accordance with our procedure, is feasible to good accuracy with the currently available program, Gaussian 94. The fragment calculations can generate wave functions for rather complex molecules in a free state or in a crystalline environment. The connection between quantum crystallography and fragment calculations resides in our approach to quantum crystallography which is based on the use of a single, idempotent density matrix (a projector matrix). In starting the process of optimizing the fit of the quantum mechanical model to the X-ray scattering data, it is valuable to have a good projector matrix. This is obtainable from an ab initio calculation. The fragment calculation is required when the structure of interest is too large for the ab initio calculation of the entire structure to be performed all at once. In that case, it can be carried out in a stepwise fashion with the results of the individual steps combined in a way that gives the desired result for the entire structure. The theoretical basis for the fragment calculation arises from examination of the theoretical description of quantum crystallography. A successful test of the fragment calculation has been reported for a cyclic hexapeptide. Results of further testing will be given. Over the past year, quantum crystallography (QCr) has also been subjected to much testing. Although QCr has been developing over some years, our approach is novel and requires careful initial attention to a variety of matters. These have concerned, for example, the character of the minima associated with least-squares calculations applied to the projector matrix, the handling of anisotropic vibrational information derived from experiment, the relationship of the results to those from ab initio calculations and purely crystallographic experiments, and, importantly, the discovery of suitable computing facilities and related programming adjustments. Matters such as these will be discussed in the presentation. *L. Massa, L. Huang and J. Karle, Intern. J. of Quantum Chem.Symp. No. 29, 371-384 (1995).

PS02.09.08 CuKβ-RADIATION APPLICATION FOR DETERMINATION OF X-RAY PARAMETERS OF CRYSTALS G. A. Kuznetsova, Irkutsk State University, Irkutsk, Russia

The Kβ-line doubling of monochromatic X-ray radiation often was the obstacle which carried the certain difficulties and noncontrollable errors in the final results at the X-raying. Kβ-line monochromatization has been fulfilled according to the modern apparatus possibility which allows to obtain the highintensive lines of characteristic spectrum.Then it was used to solve some structural analysis.

The CuKβ X-rayograms had the almost zero background level, which remained constant all through the diffractional angles 2θ range over 4π. Maximum positions were not displaced relative to the weight center of reflection, so measurements were simplified a lot.

The possibility of obtaining of great number of reflections in the certain angular range without replacement X-ray tube allows to construct the electron density crystal projections and determine atom coordinates or their changes depending on the physical factor influence.The diffractional maxima were determined to become more narrow at the experimental projections.The often coincident with maximum of Si tetrahedral oxygen maximum became now more sharp.

On using CuKα-radiation in combination with the second moment-method for the measurement of the crystallite dimension and fine-film polycrystal material microstrain good results were also obtained.According to these results CuKα -radiation would be perspective in X-raying.

PS02.09.09 MOLECULAR REPLACEMENT: A NEW DENSITY MODIFICATION STRATEGY USING A SUBTRACTIVE ALGORITHM. Philip D. Martin, Jacqueline Vitali, Brian F. P. Edwards, Wayne State University, Detroit, MI 48201

When more than one molecule lies in the crystallographic asymmetric unit, more often than not only one of the unknown molecules is readily found by molecular replacement. Repeating the search using Fo-Fc coefficients is frequently unsuccessful because of the noise, due to inaccurate positions and B values of the known molecule, at this level of analysis. However, if the known molecule is refined crystallographically it can be used to phase a 2Fo-Fc map which may be 'correct enough' to roughly visualize the unknown portions of the asymmetric unit plus the image of the known molecule used for phasing. If all the electron density within 2 Å of the known molecule is then zeroed from the map, and the map inverted, a new, modified, set of structure factors that does not contain noise from the known molecule is produced. If another molecular replacement search is then initiated with the modified structure factors, the search can reveal the next molecule, and the process can be repeated until the structure is solved. We will show how the method was used to find: (1) a second thrombin molecule in a mutant peptide/thrombin complex with a dimer in the asymmetric unit; (2) the kringle 2 portion of a des-F1-meizothrombin structure with a dimer in the asymmetric unit; and (3) a second molecule of a thrombin dimer with an exocite peptide bound (Vitali, J., Martin, P. D., Malkowski, M. G., *et al., Acta Crystallogr . (1996)*. In Press). *This work was supported in part by NIH grant GM33192. J. V. was supported by NIH training grant T32 HL07602.*

PS02.09.10 SOLVING SMALL PROTEIN STRUCTURE USING EXPERIMENTAL TRIPLET PHASES IN DIRECT METHODS. Mathiesen, R.H. & Mo, P. Dept. of Physics, Norwegian University of Science and Technology-NTNU, N7034 Trondheim, Norway

Triplet phases (TP's) can be determined from 3-beam diffraction experiments with protein crystals [1]. We are investigating the potential for using such measurements in combination with direct methods to solve protein structures. Unlike the MIR and MAD techniques, this method does not require the presence of heavy atoms.

Pancreatic trypsin inhibitor, a small protein with 58 amino acid residues (V=50 111 Å^3), was originally solved from 1Å resolution data [2]. In our study small sets of TP's, each assigned a value $\phi_3=n\cdot\pi/4$ closest to its refined equivalent were used to initiate phase expansion and refinement; ϕ_3 defines the mean direction of the corresponding von Mises distribution. Structure solution, revealing 95% of the backbone atoms, was obtained in a recycling process both with data at 1.55 and 1.75Å. By employing single phases obtained from linear equations in the assigned ϕ_3-values, the problem of numerous possible solutions was avoided leaving only 4 different phase models to be examined in both cases. Crucial in this process was the derivation of a new figure of merit which is sensitive both for the initial selection and the ensuing expansion of a structure fragment.

References:

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