Acta Cryst. (2002). A**58** (Supplement), C54

STRUCTURAL TRANSITIONS IN AMORPHOUS SILICON AT HIGH AND LOW DENSITY

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We recently used synchrotron x-ray diffraction combined with raman scattering to study pressure-induced amorphisation in silicon compressed to above 10-15 gpa. The high pressure amorphous form was in a high-density state. During decompression, a transformation occurred to the normal tetrahedrally coordinated amorphous semiconductor form. We suggest that the amorphous-amorphous transition is linked to an underlying phase transition in the liquid state. We now have evidence for further 'polyamorphism' in amorphous silicon, between 'continuous random network' and 'clathrate cage-like' amorphous tetrahedral states. Structural information including x-ray diffraction, nmr and vibrational spectroscopy, will be presented, along with a possible 'metastable phase diagram' including the amorphous silicon states.

Keywords: AMORPHOUS SILICON HIGH PRESSURE POLYAMORPHISM

Acta Cryst. (2002). A**58** (Supplement), C54

QUANTUM CRYSTALLOGRAPHY: AN OVERVIEW

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The term quantum crystallography (QCr) describes the combination of structural, mainly crystallographic, information with quantum-mechanical theory. The objective is to facilitate the theoretical calculations and thereby enhance the information that may be derived from a crystallographic experiment. This concept has a long history and, in recent years, has been receiving increased attention as a consequence of the advances in theory and computational facilities. Examples of the information that becomes available are electron density distributions, difference electron densities showing the nature of the bonding, charges on atoms, electrostatic potentials, various energies and geometry optimization on structures that are close to optimal.
In a study of quantum crystallography applied to maleic anhydrate, which considered two approaches, namely, the use of atomic positions to facilitate quantum mechanical calculations and, instead, use of the structure factor magnitudes from which the atomic coordinates were obtained, it was concluded that the use of coordinates was quite preferable and may well be true in general. In the course of this study, we also found a rather useful method for using quantum mechanics to correct, in a statistical fashion, systematic errors in the experimental structure factor magnitudes. The question arises concerning what role crystallography may play in the future of quantum crystallography. Crystallography can furnish atomic coordinates when a molecule is too large for geometry optimization to proceed, even if the free molecule approximation is valid. Crystallography can furnish coordinates and packing when there is enough interaction between molecules to make the free molecule approximation unacceptable. Crystallography can validate or throw doubt on the mode or bias set used for the quantum mechanical calculation.

Keywords: QUANTUM MECHANICS, BASIS SETS, SYSTEMATIC ERRORS

Acta Cryst. (2002). A**58** (Supplement), C54

COMPUTATIONAL CHEMISTRY OF MACROMOLECULES

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We have invented a method of doing the quantum crystallography of large biochemical molecules. The computational difficulty of representing the system increases only linearly with the number of atoms. These calculations are carried out on modern parallel supercomputers, for example an IBM SP2, in the Laboratory for Quantum Crystallography at Hunter College. This combination of theoretical modeling and computational power makes it possible to visualize an attack upon heretofore unrealizable applications in a host of areas, such as rational drug design, active sites of proteins, site directed mutagenisis, agricultural biotechnology, and enzyme catalysis. Our method entails refinement of the elements of a normalized, Hermitian, projector density matrix that is guaranteed to be obtainable from a solution of the Schrodinger equation. By adopting the approximation that a full biological molecule can be broken into smaller fragments, consisting of a kernel of atoms and its neighborhood of atoms, a simplified representation is obtained which reduces the number of parameters required. The kernels are each extracted from their fragments by rules patterned on those of Mulliken population analysis. The fundamental feature that explains the applicability of the kernel approximation is the vanishing of the orbital overlap as the distance between orbital centers increases. Our method has been tested, for example, using a cyclic hexapeptide trihydrate, and a linear hexadecapeptide Leu Zervamicin, and has been found to be accurate.

Keywords: WAVE FUNCTION, ELECTRON DENSITY, PROJECTOR

Acta Cryst. (2002). A**58** (Supplement), C54

HIGH-RESOLUTION COMPTON SCATTERING AS A PROBE OF CORRELATION AND BONDING EFFECTS

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Compton scattering is one of the few spectroscopies, which directly probes the ground state momentum density in materials. The advent of third generation synchrotron light sources has brought a renewed interest in the technique as a tool for investigating electronic structure, fermiology and bonding properties of wide classes of materials on the one hand, and as a unique window on hitherto inaccessible correlation effects in the electron gas on the other. We provide a brief overview of the field and highlight some of the progress that has been made with examples drawn from our recent work on a variety of metals and alloys, including: Li, Be, Cu and Al; Li-Mg, Ni-Cu, Ni-Co and Al-Li disordered alloys; La-Sr-Cu-O high-T_c superconductor; and the La-Sr-Mn-O CMR compound. Notably, these studies reveal fundamental limitations to the conventional local density approximation (LDA) based description of the ground state electron momentum density in solids. These and other relevant issues are discussed and a few problem areas where Compton scattering would be especially suited for making a significant contribution are touched upon.

Keywords: COMPTON SCATTERING, CORRELATION EFFECTS, FERMIOLOGY