14-Diffraction Physics and Optics

14.02 – Electron Densities at the Forefront of Chemistry and Solid State Physics

OCM–14.02.01

POSITIVE AND NEGATIVE SIDES TO CHARGE DETERMINATION. By Kersti Hermansson, Department of Chemistry, Uppsala University, Box 531, S-75121 Uppsala, Sweden

Molecular modelling - molecular mechanics, Monte Carlo and molecular dynamics calculations - is gaining ground in all branches of condensed matter chemistry. The success of these methods stands and falls with the quality of the force field used. For polar and van der Waals systems the electrostatic interaction is a major contributor to the overall interaction. The derivation of reliable electrostatic parameters - atomic charges, distributed charges, dipoles etc. - is a difficult enterprise. The atomic charges built into different commercial molecular modelling packages vary widely and give rise to large differences in the computed electrostatic interaction energies for a pair of molecules.

In the talk I will discuss:
- the role of atomic charges in computer simulations
- methods to derive atomic charges (from experiment and theory)
- models "beyond atomic charges", e.g. distributed multipoles, polarisable atoms, etc.

OCM–14.02.02
CHARGE DENSITY STUDIES WITH THE MAXIMUM ENTROPY METHOD. By R.Y. de Vries, W.J. Briels and D. Feil. *Chemical Physics Laboratory, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands.*

In many fields, the Maximum Entropy Method (MEM) has become the standard method to obtain images from incomplete and noisy data. In crystallography, there are only a few studies for which the MEM has been applied to obtain charge density maps from Fourier data. Sakata & Sato (*Acta Cryst.* (1990). A46, 263-270) applied the MEM to the very accurate *Pendellösung* data on silicon, where they showed that the method handles the series termination effect very well.

We have developed a computer program to maximize the entropy subject to $\chi^2 = \sum_k^M \frac{(F_k - D_k)^2}{\sigma_k^2} = M$, where D_k is the measured structure factor, F_k is the structure factor calculated from the electron density, σ_k is the standard deviation of the measured reflection and M is the total number of reflections. The program was based on the work of Bryan & Skilling (*Mon. Not. R. Astr. Soc.* (1984) 211,111-124).

We present a study of the MEM on hypothetical crystals. Structure factors were calculated from *ab initio* wave functions. Noise was added to these structure factors to simulate the experimental situation. We discovered that when less accurate data are available problems arise due to the fact that the constrained optimization of the entropy does not lead to a proper χ^2-distribution. In the obtained Electron Density Distribution (EDD) the calculated value of (a few) low order reflections tend to deviate much from the measured value causing the high order reflections of the obtained EDD to be exactly equal to their measured values. The resulting EDD deviates uncomfortably much from the original distribution. A weighting scheme is suggested which leads to a better χ^2-distribution and a much improved EDD.

Whereas in the MEM deviations from a flat distribution are only allowed as far as is necessary to satisfy the constraints imposed by the observations, in the Minimum Cross-Entropy Principle the deviations from a *a priori* distribution are minimized. The results of the two methods will be compared.

OCM–14.02.03
MAGNETIC COMPTON SCATTERING, PROGRESS AND PROSPECTS. M. J. Cooper, Department of Physics, University of Warwick, Coventry CV47AL, UK.

It is only comparatively recently that studies of HoFe$_2$, which has dominant orbital magnetisation, have confirmed that magnetic Compton scattering, in the impulse approximation, is indeed only sensitive to the spin magnetisation. The experiment yields a projection of the momentum distribution of the unpaired spin component and this magnetic Compton profile is characteristic of the electron's atomic origin. Thus for example in HoFe$_2$ the 4f and 3d contributions can be easily separated and their relative contribution to the spin moment deduced. It is also possible to study the nature of the diffuse component which in this material appears to be associated with the Ho site; it does not change in magnitude significantly between room and low temperature in contradiction to unpublished neutron data. Unfortunately appropriate band calculations are not yet available to be tested by these data. The establishment of an absolute scale, for example by measuring a stanadard ferromagnet such as Fe then allows the individual moments to be assigned; furthermore combination of these data with bulk magnetisation measurements allows the orbital moments to be determined. In the same material the magnetic Compton profile has been measured at temperatures down to 10K and an estimate of the spin compensation point (200 ± 10K) made. This work clearly shows that magnetic Compton scattering provides a large amount of detailed information data with which models of the electron density distribution can be tested, even in a material for which the net magnetic scattering effect is only 0.05% of the charge scattering. Other experiments, in which high resolution magnetic profiles have been obtained and the spin sub-band momentum distributions separated, will be reviewed and the implications for future work considered.

OCM–14.02.04
HIGH RESOLUTION COMPTON SCATTERING FOR MOMENTUM DENSITY AND FERMI SURFACE DETERMINATION. By A. Bansil, Department of Physics, Northeastern University, Boston, Mass. 02115, USA. and N. Shiotani, Tokyo University of Fisheries, Kounan, Minato, Tokyo 108, Japan.

The energy profile of the Compton scattered x-rays is well known to probe the electron distribution of the target in momentum space, i.e. the momentum density n(p) of the electron system. For investigating bulk electronic states, the Compton experiment does not suffer the drawback of surface sensitivity of UV photoemission, or of defect sensitivity of the dHvA and positron annihilation spectroscopies. Further, especially in complex unit cell materials (e.g. the high-T$_c$'s), the signals associated with different pieces of the Fermi surface can be suppressed or enhanced in various other spectroscopies as a result of matrix element and other effects. On the other hand, the Compton scattering samples all the electron states with equal weight. These facts make the Compton scattering a valuable complement to other k-resolved spectroscopies. In principle thus, the Compton technique can provide unique information concerning the Fermi surface parameters and spectral properties of the electron states at and near the Fermi energy in ordered as well as disordered crystals.

The realization of the considerable potential of the Compton spectroscopy has however been hampered in practice due primarily to the fact that the best momentum resolution possible via γ-ray sources and solid state detectors is about 0.4 au, which is too limited to explore delicate Fermiology related issues in materials. But the advent of synchrotron radiation sources capable of providing high energy, high flux and well-defined polarization offers revolutionary new opportunities since momentum resolution of 0.1 au has been demonstrated and better resolution should be possible.

Bearing these considerations in mind, the Commission on Charge, Spin and Momentum Density has recently started a new project, "Fermiology of High T_c Superconductors via High Resolution Synchrotron-based Compton Scattering Spectroscopy". This effort is particularly timely since the third generation synchrotron sources are at various stages of development around the world (ESRF in France, APS in USA and Spring-8 in Japan). The plan is to proceed in two steps, exploring simpler systems first, as a prelude to developing the Compton technique fully in order to investigate complex materials, the goal being the High-T_c's. This talk will discuss the objectives of this new Commission Project, giving an overview of the important theoretical questions to be addressed, and discuss the experimental challenges facing the Compton community towards this end. Some very recent relevant theoretical and experimental results will also be presented.

OCM–14.02.05

UNIFIED DESCRIPTION OF ELECTRONIC STRUCTURE BY DENSITY MATRICES FROM THEORY AND EXPERIMENT. By Vedene H. Smith, Jr.* and Hartmut Schmider, Dept. of Chemistry, Queen's University, Kingston K7L 3N6, Ontario, Canada; Wolf Weyrich, Fak. für Chemie, Universität Konstanz, D-W-7750 Konstanz, Fed. Rep. of Germany; Winfried Schülke, Inst. für Physik, Universität Dortmund, D-W-4600 Dortmund, Fed. Rep. of Germany.

The one-particle reduced density matrix (ODM) is the carrier of all single-particle information about a chemical system, and plays therefore a central rôle in the theoretical description of the latter. Both charge and momentum densities are respectively a cut and a transformed projection of this function, and are directly or indirectly accessible by experiment. The attempt to reconstruct the ODM from these densities or directly from experimental data in the framework of a given basis set is the subject of this paper. To this end, a methodology employing a restrained least-squares technique that ensures so-called $N - representability$ conditions has been developed and tested. Applications to atomic and molecular systems, including isotropic and directional data from both spaces are presented. The impact of the combination of complementary information and the necessity of partial inclusion of correlation effects are discussed. The quality of the results is judged employing suitable representations of the ODM and its functionals. It is emphasized that a *direct* experimental access to projections of nondiagonal elements of the ODM in momentum space becomes feasible for highly perfect crystalline solids by means of coherent Compton scattering. Thus an additional experimental test for the quality of the ODM reconstruction is available.

PS–14.02.06   STANDING WAVE INELASTIC SCATTERING FROM Si
By A. Kaprolat* and W.Schülke, Institute of Physics, University of Dortmund, Germany; K. Sturm, Forschungszentrum Jülich GmbH, Germany

Conventional inelastic scattering experiments using x-rays are known to yield information about electron correlations in space and time. For momentum transfers comparable to reciprocal characteristic length's of the system (inelastic x-ray scattering spectroscopy **IXSS**), the experiments yield the dynamical structure factor $S(\vec{q},\omega)$, a quantity connected to diagonal elements of the inverse dielectric matrix ε^{-1}, wherefrom electronic properties such as plasmon dispersion and excitation spectra can be calculated.

An extension to this experimental technique is to use a coherent superposition of two plane waves, forming a standing wave field, rather than one single plane wave as initial photon state of the scattering process. These experiments (coherent **IXSS**) yield the nondiagonal dynamical structure factor, connected to nondiagonal elements of ε^{-1}, so one has at least in principle experimental access to the full dielectric matrix.

We present an experimental setup for coherent **IXSS** using synchrotron radiation. Experimental results for coherent inelastic scattering from single-crystal Si-samples are shown and discussed within the framework of a two-plasmon-band model. The results show for the first time direct experimental evidence for the existence of a bulk plasmon band structure showing a band gap for scattering vectors close to the [111]-Brillouin zone boundary in **Si** (A. Kaprolat, W. Schülke, Phys. Rev. Lett., 1991, 67, 879). It is shown that using coherent **IXSS**, the line shape of the two plasmons at the Brillouin zone boundary can be reconstructed (K. Sturm, W. Schülke, Phys. Rev. B, 1992, 46, 7193).

PS–14.02.07 ELECTRON DENSITY DISTRIBUTIONS IN ATOMS, MOLECULES AND CRYSTALS. A NEW APPROACH OF ANALYZING INTRA- AND INTERMOLECULAR INTERACTIONS. By W.H.E. Schwarz*, J.E. Niu, and S. Irle. Theoretical Chemistry Group, The University, Siegen, Germany.

Electron density distributions $\rho(r)$ contain three types of features, which give rise to a new natural approach of analyzing ρ with respect to chemical bonding. These features are 1) the very large, nearly spherical atomic core densities, defining the geometric structure, 2) the smaller multipolar atomic valence densities, defining the orientation and population of partially filled p- and d-shells of the "independent atoms" in the molecule or crystal, and 3) the very small density deformations due to the interatomic interactions.

The valence shell parameters (orientation and shape of independent atoms in the promolecule or procrystal) and the Chemical Deformation Densities are determined theoretically and experimentally for molecules and crystals. The features are brought in relation to intramolecular and intermolecular interactions. The atomic shapes correlate well with the intermolecular bond type. Intramolecular interactions affect the atomic orientations. Positive chemical deformation densities are found on all covalent bonds including those to F and O atoms. Previous results have been published by Schwarz et al. in J. Mol. Struct. **225** (1992) 435 and Ber. Bunsenges. Phys. Chem. **96** (1992) 1545.