surfaces and electric field lines are drawn and discussed in some cases of chemical reactivity prediction for molecules in the solid state. The topology of the electrostatic potential exhibits novel atomic basins where the total charge is zero. The quantum theory of Bader is used to establish the atomic bonding structures and chemical reactivity relationship. Finally, the interatomic force (pressure) [3] concept is introduced: the Ehrenfest and Feynman forces are computed for a set of chosen molecules to emphasize their contributions for a better molecular reactivity understanding.

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[2] N. Bouhmaida, . M. Dutheil, N. E. Ghermani & P. Becker, J. Chem. Phys., 2002, 116, No14, 6196.
[3] N. Bouhmaida & N. E. Ghermani PCCP, 2008, in press.

Keywords: molecular reactivity, electrostatic potential and electric field, ehrenfest & feynman forces.

MS.05.4

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Structural chemistry of 2-aza-1,3-dienes

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Since the solution of crystal structure of leading compound 1 ($Ph_2C(1)$=N-C(2)(H)=C(3)X_2, X=Cl) we focused our attention on its capability of acting as a target for both the nucleophilic and the electrophilic attacks. One of the phenyl groups is roughly coplanar with azadienic chain suggesting so an extended pi-conjugation. The calculated electronic structure of 1 (B3LYP/6-311G) is compatible with that of butadiene, but shows a significant contribution of Cl atoms to the HOMO. The first nucleophilic attack occurs on C(2) atom with alkoxydes, cyanide and pyrrol anion, but C(3) carbon is preferred with thiolates and OPh. Such a regio - selectivity is rationalized by the hardness of incoming nucleophile calculated with DFT (hard nucleophile attacks on C(2) and the soft one on C(3)). A mentioned pi-conjugation of one phenyl ring with azadienic chain seems to operate in several molecules with X = Cl, OPh, SPh ... where the dihedral angles Ph/C(1)NC(2)C(3) fall in the range of 10 to 38 deg. This effect is much stronger for free molecules (gas phase) as calculated with DFT (range of angles is 1 to 8 deg). Thus, the packing in the crystals partially leaves this conjugation. An oxidative addition of 1 on one Pt atom and on two Pd atoms (A-frame structure) is observed. The terminal chloride in Pt sigma-alkenyl complex may be substituted with a neutral (xylyl)NC ligand rising a spectacular linear pi-system delocalized on some 20 atoms. Substituted azadienes with X = SPh and SiPr act as the ligands in complexes with Re, Mn, Cu, Hg, Pt and Pd. Generally, the chelates with five membered S,N-metallacycles are formed. Orthometallation reactions predicted by DFT calculations are also observed in some cases.

Keywords: azadienes, chemical hardness, organometallics

MS.05.5

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Iridium catalyzed hydrogenation with chiral ferrocenyl P-S ligands. X-ray structure of precatalysts

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Iridium complexes of the new chiral ferrocenyl (P,SR) ligands CpFe[1,2-C5H3(PPh2) (CH2SR)] (R = Et, tBu, Ph, etc.), were successfully used in the hydrogenation of diphenylacetylene and in asymmetric hydrogenation simple ketones with high activities (turnover numbers up to 915 and global turnover frequencies up to ca. 250 h^{-1}) and enantioselectivities (ee up to 99%). The X-ray structural characterization of the precatalyst Ir complexes allowed to reveal that the coordination geometry of chlorocyclooctadieneiridium ligand adducts is delicately controlled by the nature of the R substituent, yielding five or four-coordinate complexes featuring then a dangling thioether group. Moreover, the ligand chirality controls the geometry at the sulfur and iridium atoms, producing single diastereomers.

Ref.
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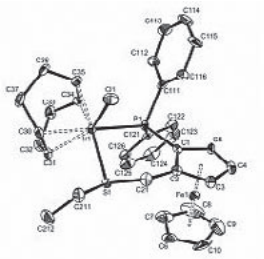

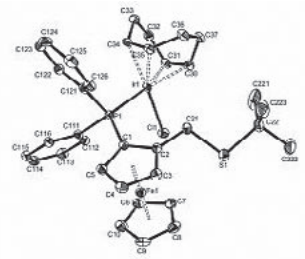

Keywords: structural ferrocene chemistry, asymmetric catalysis by iridium, catalysts optimization

MS.06.1

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Macromolecular refinement at subatomic resolution with interatomic scatterers

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The study of accurate electron-density distributions in molecular crystals at subatomic resolution (better than 1.0 Å) requires more detailed models than those based on independent spherical atoms. We present a simple model composed of conventional independent spherical atoms augmented by additional scatterers to model bonding effects at high resolution. Refinement of these mixed models for several benchmark data sets gives results that are comparable in quality with the results of multipolar refinement and superior to those for conventional models. The application of this method to several data sets of both small molecules and macromolecules will be described as well as its implementation in the general-purpose macromolecular refinement module, phenix.refine, in the PHENIX software package.

Keywords: fefinement, high-resolution, subatomic

MS.06.2

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Macromolecular model-building and validation using Coot

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Coot [1] is a molecular graphics application for macromolecular model building against X-ray data. Coot provides a modern interface drawing from usability paradigms of popular desktop applications. In so doing, it has become increasingly popular [2], particularly in the UK and parts of Europe. Coot provides several tools which can be used to build, refine and protein structures and other models. In the last year, there has been more focus on developments to better handle lower resolution data, these include the fitting of alpha helices and beta strands for model building and the addition of extra restraints and modification of restraints when refining. Also to be discussed are the tools for validation for the detection of model-building errors and feature outliers.
[1] Emsley & Cowtan (2004) “Coot: Model-Building Tools for Molecular Graphics”, Acta Cryst D 60, 2126-2132.
[2] But not close to the popularity of a more established application.

Keywords: map fitting, molecular graphics, model building

MS.06.3

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Advances in automatic model building and structure completion in the context of ARP/wARP

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Automated protein model building procedures are becoming better and better in building partial initial models with minimum user intervention. Manual interactive building is in many cases needed only in the final stages of model building. A natural trend for automatic building developments, is thus to spend more effort towards providing a more complete model. The ARP/wARP software suite is build around the concept of a hybrid model, a partial protein model supplemented by unrestrained atoms used to model the rest of the ordered electron density. The model is iteratively build by recycling the information contained in the restraints of the partial model to obtain better phases estimates through model refinement. Here we present three types of improvement to the automated model building procedure in ARP/wARP:
Improved procedures that allow sequence assignment to the main chain in a more effective manner, using pattern classification algorithms that use the free atoms and rotamer fit to the electron density;
Algorithms to assign conditional restraints to the free atoms (the ones that do not have chemical identity yet). The goal is to enhance further model refinement by providing additional observation in the form of restraints and improve the derived electron density. This approach enables ARP/wARP to reach a more complete model faster;
A program that uses both statistical knowledge of protein main chain structure and electron density, to build missing loops connecting main chain fragments already docked in sequence. This algorithm uses hierarchical filtering and only considers local electron density as a loose selection criterion. That allows both for speed and makes the procedure relatively unaffected by partial disorder of the residues to build.

Keywords: model building, loop building, protein crystallography

MS.06.4

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MAIN 2008: Real space model fitting - as good as it gets

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After an initial model of a macromolecular crystal structure has been generated it goes through cycles of refinement and manual corrections until the structure is done. In order to speed up this process cycling through visual inspection and manual manipulation of the model needs to be efficient and swift. When finalizing the MAIN 2008 release the combined use of automated model rebuilding tools and the user guidance were in focus. The conjugate gradient minimizer has been rewritten. Energy minimization in combination with rotational searches of side chain and main chain conformations, fragmented rigid body minimizations can now rebuild molecular models to correspond to electron density map to the level of an expert user and better, thus as good as it gets. The role of the user is to inspect the model (guided by validation tools or own choice) and trigger appropriate functions on appropriate model parts either using mouse clicks or keyboard shortcuts. With this the manual guidance of atoms and residues into desired positions during model rebuilding became essentially obsolete. It used to be that after model building step R-value increases, however, with the new MAIN reals space fitting and minimization procedures, the R-value decreases after each model rebuilding cycle. Clearly the quality of the electron density maps defines the success of real space minimization, nevertheless properly configured procedures can be used at any resolution range at any stage of model building including the very initial stages. The current limitation of the toolbox is that it does not work with multiple conformations, but only chooses the “best” one at a certain density contour level. (See “http://www-bmb.ijs.si/”).

Keywords: automated model rebuilding, real space refinement, density fitting

MS.06.5

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Beyond crystallographic refinement: Broader application of TLSMD to model protein dynamics

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TLS (Translation/Libration/Screw) models provide a useful