algorithms for the determination of substructures (*phenix.hyss*), the refinement of macromolecular structures (*phenix.refine*), and the underlying "hybrid" open-source software framework, *cctbx*.

The *Phenix* Hybrid Substructure Solution (*phenix.hyss*) combines Patterson methods and dual-space direct methods, automatic substructure comparisons and simple substructure refinement into a highly integrated algorithm. The *Phenix* refinement tools include Cartesian dynamics simulated annealing, a novel robust bulk-solvent correction procedure including overall anisotropic scaling, maximum likelihood refinement with and without experimental phases, and isotropic and anisotropic refinement of displacement parameters.

Both *phenix.hyss* and *phenix.refine* are designed to minimize the need for tedious and error-prone manual intervention. Development of the required tools is made practical by the tight integration of a scripting language (Python) with a compiled language (C++), and maximization of source code reuse through a library-based approach.

[1] Adams P.D., Gopal K., Grosse-Kunstleve R.W., Hung L.-W., Ioerger T.R., McCoy A.J., Moriarty N.W., Pai R.K., Read R.J., Romo T.D., Sacchettini J.C., Sauter N.K., Storoni L.C., Terwilliger T.C., *J. Synchrotron Rad.*,2004, **11**, 53-55.
Keywords: macromolecular refinement, substructure solution, cctbx

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MS63 CHEMICAL INSIGHTS FROM ELECTRON DENSITY STUDIES AND WAVEFUNCTIONS
Chairpersons: Nour Eddine Ghermani, Peter Blaha

MS63.28.1
Acta Cryst. (2005). A**61**, C82
Quantum Mechanical Basis of Conceptual Chemistry
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Science is observation, experiment and theory. This is the path that led to the development of the molecular structure hypothesis - that a molecule is a collection of atoms with characteristic properties linked by a network of bonds that impart a structure – a concept forged in the crucible of nineteenth century experimental chemistry. One hundred and fifty years of *experimental* chemistry underlie the realization that the properties of some total system, molecule or crystal, are the sum of its atomic contributions. The lecture will demonstrate that this conceptual basis of chemistry is recovered in its entirety by the Quantum Theory of Atoms in Molecules, [1] a theory grounded in the quantum mechanics of an open system and given physical expression in terms of a system's measurable [2] charge distribution.

[1] Bader R. F. W., *"Atoms in Molecules: A Quantum Theory"*, Oxford University Press, Oxford UK, 1990. [2] Coppens, P., *"X-Ray Charge Densities and Chemical Bonding"*, IUCR Texts on Crystallography.4. Oxford University Press, Oxford UK, 1997.
Keywords: atoms, electron density, quantum mechanics

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Construction or Refinement of Approximate Reduced Density Matrices
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One electron density matrices (1RDM) are useful tools since they convey information concerning charge, spin and momentum densities. Their determination from ab-initio calculations is nowadays straightforward for simple systems. However, few attempts have been made to construct a semi-empirical 1RDM from data originating from different experiments [1]. One difficulty is the lack of a generic model, generalizing the Hansen-Coppens approach for charge density refinements. Furthermore, when reaching large systems, such as those encountered in biology or pharmacology, ab-initio methods turn out to be both cumbersome and sometime "too" precise [2].

After a brief review, we will propose, for those two issues, some suggestions and tracks that are or can be fruitfully explored.

[1] Gillet J.M., Becker P., *J.Phys. Chem Solids*, 2004, **65**, 2017. [2] Ragot S, Gillet J.M., Becker P., *Physical Review B*, 2002, **65**, 235115.
Keywords: ab-initio calculations, density matrices, refinement

MS63.28.3
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Atomic and Bond Topological Properties of Strained Carbon Ring and Cage Systems
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The discovery of the fullerenes in the 80s brought a new class of carbon cage compounds with unusual structural properties into the scope of chemical research, similarly as happened with Cope systems in the 60s, where, for example, bullvalene with its unique property to exist in more than 1.2 million isomers [1], raised considerable attention. Not only preparative chemists, but also nature was able to generate complicated oligocyclic carbon cages, as for example, for several opioide derivatives. They all have in common to contain carbon atoms in very unusual steric arrangements and to exhibit C-C bonds of unusual lengths. Distances far beyond normal single bond lengths are then in question whether or not a covalent bond exists. We have analyzed experimental and theoretical electron densities of a number of strained carbon cages from the compound classes mentioned above. We could derive quantitative atomic and bond topological properties making use of Bader's AIM formalism [2]. The existence/non existence of bond critical points and the analysis of the Laplacian function allowed also the characterization of bond/no bond regions in a [1.1.1]propellane and a related bicyclo [1.1.1]pentane derivative. Electron densities on bond critical points allowed bond orders to derive which were found remarkably smaller than one in several strained cages, for example in halogenated C_{60} derivatives.

[1] Doering W.E. von, Roth W.R., *Tetrahedron*, 1963, **19**, 715. [2] Bader R.F.W., *Atoms in Molecules*, Clarendon Press, Oxford, 1990.
Keywords: electron density, topological analysis, carbon cages

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Chemical Bonding in Hypervalent Silicon and Germanium Compounds
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On the basis of the analysis of experimental and calculated electron density distribution functions of different atranes and monochelated compounds we have investigated the nature of the chemical bonding in their axial D-M-X (D = O, N; M=Si, Ge; X = Cl, OH, OH_2) fragment.

Both in crystal and isolated molecules the hypervalent D…M bonds are characterized by the intermediate type of interatomic interaction in terms of R. F. Bader's "Atoms in Molecules" theory. The transition of molecules of this type from crystal to isolated state leads to a noticeable decrease of electron density and potential energy density values in critical points (3, -1) of D…M hypervalent bonds that implies the weakening of this bonds. The extent of such weakening depends on the nature of D, M and X atoms.

The usage of the same theoretical background and periodic DFT calculations allow us to reveal the influence of intermolecular interactions on the geometry of M atom coordination centre.

On the basis of topological analysis and NBO population analysis we have estimated the strength of hypervalent bonds in monochelated compounds and atranes. For instance, in a number of six-membered cyclic compounds (X=Hal, OAlk) the strength of D…O bonds (1.96 ÷2.45 Å) varies in the range 4 - 29 kcal/mol.
Keywords: charge density distribution, topological properties of charge, theoretical crystal calculations