

proposed as more suitable indices. However, both matrices are generally not directly amenable to experimental determination.

Recently, it has been shown [1-3] how the sign of  $\nabla^2\rho$  at  $\mathbf{r}'$  determines whether this point acts as a *source* or as a *sink* for  $\rho$  at any other point  $\mathbf{r}$  in a system, with the effectiveness as a source or as a sink being related to  $|\nabla^2\rho|$  and to the inverse of the distance between the two points,  $\rho(\mathbf{r}) = \int (1/4\pi)\nabla^2\rho(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{-1}\cdot d\mathbf{r}' = \int \text{LS}(\mathbf{r}, \mathbf{r}')\cdot d\mathbf{r}'$ .

The profile of the *local source function* LS ( $\mathbf{r}, \mathbf{r}_{\text{bcp}}$ ) along the bond path is here used to unravel the different mechanisms by which covalent bonding between light or heavy atoms realizes in crystals.

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**Keywords:** chemical bonding theory, electron density studies, topological properties of charge distributions

### MS34.26.3

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#### Thermal Motion Analysis via Modern Probability Methods

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Interesting statistical theory advances with crystallographic application possibilities continue to appear. Examples follow:

The Gram-Charlier anharmonic atom model might be replaced by a saddlepoint expansion [1] or a mixture of linear & angular Gaussians.

The refinement matrix from a structure-factor equation in logarithmic form contains a Fisher information matrix [2] with geometric information about interatomic motion coupling.

A stationary Levy stochastic process [3] along a crystal chemistry interaction network may allow atomic displacement models with Levy-jump intramolecular components and Levy-drift intermolecular rigid-body-motion components.

Spatial point processes [4], e.g. the familiar Gibbs process, allow attraction/avoidance calculation for point particle systems. More general marked point process [4] network node systems with thermal ellipsoid pair Radon-Nikodym derivative[5] couplings seem feasible.

Feasibility studies for a subset of the examples will be discussed.

[a] ORNL operated by UT-Battelle, LLC, under DOE DE-AC05-00OR22725.

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**Keywords:** anharmonic refinement models, stochastic processes, fisher information matrix

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#### Images of Unpaired Electron Density in Molecular Crystals Obtained using Experimentally Constrained Wavefunctions

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Unpaired electrons are responsible for many of the magnetic properties of crystalline systems. Traditionally, unpaired electrons in crystalline systems have been imaged using the technique of polarised neutron diffraction (PND). However, these experiments are difficult, and relatively few data are obtained compared with X-ray diffraction measurements.

In this talk I will present and compare images of unpaired electron density in molecular crystals. These images are obtained from a molecular or cluster Hartree-Fock wavefunctions, which have been constrained to reproduce X-ray diffraction data, to reproduce PND data, and to reproduce both of these data simultaneously.

Two crystalline systems will be considered: a system displaying the photomagnetic LIESST effect, and a simple molecular magnetic system. The difficulties and results will be discussed, including the physical meaning of the orbital energies, and their shapes.

**Keywords:** quantum crystallography, unpaired electron density, constrained wavefunctions

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#### Holographic Principles of Molecular Structure and Electron Density Calculations

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Electron densities of molecules obey a holographic principle: in a non-degenerate ground state any small positive volume of the electron density cloud contains the complete information about the entire molecular structure [1]. This holographic theorem provides the constraint on the applications of various electron density fragmentation methods, including fuzzy density fragmentation methods aimed at potential advances in the crystallographic structure refinement process [2], the analysis of quantum chemical functional groups of molecules [3], detailed molecular shape analysis [4], and providing the foundations for linear scaling, ab initio quality macromolecular quantum chemistry computational methods, applied to various proteins [5-7]. Some new advances in these fields will be reviewed.

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**Keywords:** holographic theorem, molecular shape, fuzzy density fragments

### MS35 POLYTYPISM AND TWINNING

*Chairpersons:* Giovanni Ferraris, Elena Belokoneva

#### MS35.26.1

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#### Recent Aspects of the Theory of Oriented Crystal Associations

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Despite its long history, twinning is far from having disclosed all its secrets. Although the definition of twinning is unambiguous, it is still sometimes used in a less appropriate way. The typical example is that of "cell-twinning", a phenomenon by which homogeneous modular structures derive from iso- or heterochemical archetypes with a possible chemical modification at the interface. Modules in cell-twins are related by space-groupoid operations (defined in point space) and the edifice is homogeneous, whereas individuals in twins are related by point group operations (defined in vector space) and the edifice is heterogeneous [1].

The classical reticular theory of twinning had to be extended to include cases not fitting the original classification, leading to a finer subdivision of Friedel's categories [2]. The most recent extension concerns the coexistence of up to three sublattices, which correspond to different types of non-merohedric twinning resulting in an effective twin index (degree of quasi-overlap of lattice nodes) significantly higher than the classical twin index [3].

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