structures

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Coherent Diffraction Imaging is a technique for the three-dimensional reconstruction of single objects using coherent X-ray nano-beams. This technique, when used on Bragg reflections [1-5], can be used to recover both the shape and strain inside the objects.

In semi-conductor nanowires (NWs), the knowledge of the exact strain state is essential for the tuning of the physical properties (conduction, photo-emission). While ensemble-averaged studies can provide quantitative information about the shape and strain state [6], this is only possible in the case of a very low dispersion of the structural properties. This presentation will be focused on the study of small (diameter<200nm) homogeneous and heterogeneous NWs and strained Silicon-On-Insulator lines, which have been studied using Coherent Bragg Imaging (CBI) [7,8].

In the case of heterogeneous nanowires, we will show that it is possible to use the small size of existing nano-beams (e.g. 300x500 nm^2 using a Fresnel Zone Plate on beamline ID01 of the ESRF) to perform CBI measurements on different parts of heterogeneous nanowires, and therefore analyze the strain state near the interface.

We will also discuss the current challenges presented by the method: (i) the requirement to determine the amplitude and phase of the incident focused X-ray beam, (ii) the difficulties of keeping a single object inside a nano-beam while rotating it over ~1° to record the 3D scattering pattern , and (iii) the effects of radiation damage due to the high flux (>10⁴ ph/s/nm^2) on the sample.

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Bulk dislocation core dissociation probed by coherent X Rays in silicon

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We present a new approach to probe bulk dislocations by using coherent x-ray diffraction. Coherent X rays are particularly suited for bulk dislocation studies because lattice phase shifts induce typical diffraction patterns which strongly depend on the fine structure of dislocation cores. The strength of the method is demonstrated by performing coherent diffraction of a single dislocation loop in silicon. The measured dissociation is proved to be unusually large compared to known dissociations. This work opens a route for the study of

dislocation cores in a static and dynamical regime, and under various external constraints.

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Predicting the behaviour of lone-pair electrons

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If one defines the bonding strength of an ion as the valence of a typical bond, the valence matching rule states that stable bonds will be formed only between ions having bonding strengths that do not differ by more than a factor of two. This rule limits the range of compounds that can form and indicates that weak cations bond only to weak anions and strong cations only to strong anions. This rule is obeyed in all compounds whose atoms can be assigned a formal cation or anion charge (valence) regardless of whether the bonding is ionic or covalent, with only two exceptions: the presence of steric stress or electronic anisotropies. Ions with lone pairs, namely cations in lower oxidation states and anions, also obey this rule in compounds in which the lone pairs are described as 'inactive'. However, the presence of lone pairs in the valence shell provides a flexibility not available to normal ions. An ion with lone pairs can bond to a counterion with a bonding strength greater than twice its own bonding strength if the lone-pair electrons in the region of the bond are converted to bonding electrons. This allows the ion to form a stronger bond to match the larger bonding strength of the counterion. To conserve the number of lone pairs, bonding electrons on the opposite side of the ion are converted to lone pairs, leading to the characteristic asymmetry associate with stereoactive lone pairs. This model leads to a number of conclusions. It it is possible to predict when and how lone pairs result in asymmetric coordination, it reveals that 'dative' bonds do not involve lone pairs but usually result from hydrogen bonding, and it predicts that monovalent anions bonded to electron-rich cations (those with bonding strengths greater than 1.0 vu (valence units)) will necessarily form finite molecules containing bonds of exactly 1.00 vu, i.e., electron-pair bonds. Although such bonds are generally considered to be prototypical covalent bonds, they are predicted as a special case of the ionic model.

Keywords: bond, valence, lone-pairs

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Revealing electron conjugation through an observable

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The Source Function (SF) [1,2] enables one to view chemical bonding and other chemical paradigms under a new perspective and using only information from the electron density observable, ρ, and its derivatives. Being completely independent from the tools used to get ρ, the SF represents a very useful descriptor, able in some cases to bridge the gap between the rich information one gains from an *ab-initio*

wavefunction of an ideal system and that, quite often more limited, but referred to a real system, obtained from an experimental ρ derived from X-ray diffraction data.

The potential uses of the SF are, however, yet not fully explored. In a preliminary work, we addressed the question of whether the SF is or is not capable to reveal electron conjugation [3]. Question arose because of a recent claim [4] according to which "π-electron delocalization in the benzene ring is not manifest in the SF when the reference point (*rp*) - the point at which the atomic sources for its density are calculated - is taken at the C-C bond critical point (bcp)". Reasoning behind this statement is the null contribution from π molecular orbitals (MOs) to ρ in their nodal plane. However, since σ- and π-distributions are not independent, but self-consistently interrelated, we conjectured that some, albeit small, effect of electron conjugation could also be manifest when the *rp* lies in the π-nodal plane, even though π-orbitals do not obviously yield *direct* contributions to ρ in that plane. Results on a series of increasingly π-conjugated systems demonstrate that *this is actually the case*. By looking at the C-C bcp electron density for the shortest bond(s) in cyclohexene, cyclohexadiene, benzene, i.e. those bonds with largest double-bond character, one observes that both the SF and the SF% contributions of the C atoms other than those directly involved in such a bond increase with decreasing double bond character and electron localization of the bond. The enhanced S% value then becomes largely more evident when analysed using *rps* for which the effect of π-electron conjugation takes place directly through π-electron distribution rather than, indirectly, through σ-π electron interdependency.

In this work, the analysis is extended to more complex systems, formed by more than one ring, with fully conjugated or partially interrupted sequence of formal double-bonds and with planar or non planar geometry. In the case of benzene, the analysis is also performed on a ρ derived through multipole refinement of a set of X-ray diffraction data taken on a benzene molecular crystal. In the inspected cases and regardless of the theoretical or experimental origin of ρ, the SF reveals capable to detect electron conjugation. Such an ability is independent from a σ and π separation of ρ, since the SF tool was applied to the *total* ρ. This observation is important in view of the possibility to recover electron conjugation effects *using both ρ's derived experimentally* (hence without σ and π separation being allowed) and ρ's where *the departure from symmetry inhibits a proper separation* of σ and π contributions. Using a MO approach, the σ and π contributions to the SF values can also be revealed and quantified.

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Descriptors of charge density for estimating the energy of coordinate bonds

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Various quantum descriptors have been employed in establishing the QSAR/QSPR relationship in chemistry and biochemistry, but the main objective of this approach is to relate the electronic properties derived from calculations for isolated molecules with their macroscopic properties. The useful bridge between these two steps is the investigation of experimental charge density distribution function (ρ(r)) via high-resolution X-ray diffraction analysis and extracting the

necessary quantum descriptors of charge density from this data to relate them with more sound physical quantities.

The quantum theory of *Atoms in Molecules* [1] together with Espinosa's correlation scheme [2] provides the unique opportunity of estimating the energy of weak closed-shell interactions from first principles on the basis of one of the descriptors of molecular structure, namely, the value of potential energy density (*v(r)*) in the corresponding bond critical point. Recently the application of this approach was extended to the case of strong hydrogen bonds, in other words, the interactions of intermediate type [3]. The topological analysis of various coordination bonds based on the experimental ρ*(r)* showed the similarity of strong hydrogen bonds and semipolar bonds of a moderate strength from the quantum descriptors' point of view[4].

We tested the applicability of this approach to estimate the dissociation of AuCl·PPh$_3$ complex [5]. The Au-P bond energy estimated via Espinosa correlation (57.9 kcal/mol) was close to the dissociation energy of the complex according to MP2 calculation (53.2 kcal/mol). This finding as well as the recent data for lanthanide complexes [4] showed this approach can be used at least for the semi-quantitative description of the coordination bonds.

To generalize the usage of quantum descriptors for the estimation of the metal-to-ligand binding energies, we performed the systematic high-resolution XRD analysis of a wide range of coordination and organometallic complexes and examined the relative strength of different metal-ligand bonds. Results will be presented for ruthenocene [6], cymantrene [7], and various coordination complexes of titanium, copper, zinc, palladium, and cadmium [8]. They cover a wide range of interactions - from the weakest metal…hydrogen ones to strong metal-carbon bonds. We also investigated the influence of intermolecular interactions on the bonding within first coordination sphere of metal atoms.

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The atomic energy as *the* descriptor for the stereoelectronic interactions

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The term 'stereoelectronic effect' comes from the molecular mechanics approach and defines a conformational preference not explainable in terms of steric effects. One of the most fundamental of such effects is the generalized anomeric effect which dictates that in the R-X-C-Y systems, where X is bearing a lone pair (lp), and Y is more electronegative than carbon atom, the gauche conformation is generally the most stable [1]. It is explained in terms of lp—X—C—Y stereoelectronic interaction (SEI): the charge transfer from X's lone pairs to the σ*$_{C-Y}$ antibonding orbital. Until recently the study of energetic characteristics of SEI was limited to second-order perturbation analysis