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An X-ray constrained wavefunction (XCW) is a wavefunction constrained to reproduce the structure factors from X-ray charge density experiment [1]. XCW's have primarily been used to obtain accurate images of the electron density in molecular crystals [1]. In this talk the XCW method is extended to the calculation of linear and non-linear optical response properties for several molecular crystals [2]. The theory used for the calculation of bulk (crystalline) susceptibilities and refractive indices from molecular polarisabilities will be reviewed. Results for several systems will be presented and discussed. I will also outline a method for improved structure determination based on using aspherical atomic densities obtained from quantum mechanical calculations. The new method allows the determination of ADP's for hydrogen atoms from the X-ray data alone [3]. The possibility of using such aspherical densities in everyday structure refinement will be discussed.

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Characterization of weak chemical bonds in highly strained and hypervalent compounds

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To characterize chemical bonds in highly strained and hypervalent compounds have been attractive target of theoretical study. However, it is not rare that some researcher derive different result from other researchers, who study the same compound, especially for such weak chemical bonds. While, if such compounds are synthesized and crystallized, we can perform charge density analysis using accurate X-ray diffraction data, which shows electron density distribution as it is. We report here bonding characters of strained cyclopentyne and 5- and 6-coordinate carbon compounds. Small cyclic alkynes are, in general, unstable because of ring strain. Recently, 1-zirconacyclopent-3-yne complexes, viz 5-membered cyclic alkynes, were synthesized and crystallized.[1] The experimental electron density analysis clarifies that both of the eta2-pi,pi and eta4-pi,pi structures contribute to the bonding not only the former structure.[2] In the case of the 5- and 6-coordinate carbon compounds, we showed dative character of the hypervalent bonds.[3, 4]

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How and why elemental boron undergoes self charge transfer between 19 and 89 GPa

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Boron has nearly 20 polymorphs with non-trivial chemical bonding, complex structures and similar energies. It is the only light element for which the ground state is not experimentally established at ambient conditions. Using high-pressure experiments and an *ab-initio evolutionary methodology*, the structural stability of boron under pressure was explored.¹ At low pressures (<19 GPa) boron adopts covalent structures based on icosahedral B₁₂ clusters, and at high pressures (>89 GPa) it forms a superconducting α -Ga-type phase. At intermediate pressures a *new insulating phase*, γ -B, has been found to be stable.¹ Its structure consists of distorted B₁₂ clusters and B₂ pairs: (B₂)^{Δ+}(B₁₂)^{Δ-}, with a significant charge transfer (CT), substantiated by several theoretical measures and physical properties. Using Bader's theory, δ amounts to ≈ 0.34 - 0.48 , based on either PAW or DFT-LCAO densities. Electron charge flows from B₂ to B₁₂ units for their corresponding frozen 3D sublattices act as *n*-doped and *p*-doped semiconductors, respectively. The CT occurring in this unique phase affects its physical properties (electronic band gap, infrared absorption, dielectric properties, etc.) and results from the Lewis acid-base interaction of the B₁₂ and B₂ groups. It is the ability of boron to form clusters with very different electronic properties and the very low packing efficiency of icosahedral structures (34% for α -B₁₂) which leads to γ -B, the *first experimentally established autoionized form of an element*. An analysis of bonding within and between the B₂ and B₁₂ subunits and its relationship with the observed CT in γ -B is also outlined.

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Advances in quantum *ab initio* calculations with the CRYSTAL code

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