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.


Keywords: constrained wavefunction, charge density, linear and non-linear optics

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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 isocahedral B$_2$ 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 B$_2$ clusters and B$_2$ pairs : (B$_3$)$_n$ (B$_3$)$_n$, with a significant charge transfer (CT), substantiated by several theoretical measurements and physical properties. Using Bader’s theory, $^5$ amounts to ~0.34-0.48, based on either PAW or DFT-LCAO densities. Electron charge flows from B$_2$ to B$_2$ 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 B$_2$ and B$_2$ groups. It is the ability of boron to form clusters with very different electronic properties and the very low packing efficiency of isocahedral structures (34% for α-B$_2$) which leads to γ-B, the first experimentally established autoionized form of an element. An analysis of bonding within and between the B$_2$ and B$_2$ subunits and its relationship with the observed CT in γ-B is also outlined.$^1$


Keywords: charge density and properties, chemical bond, high pressure

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

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