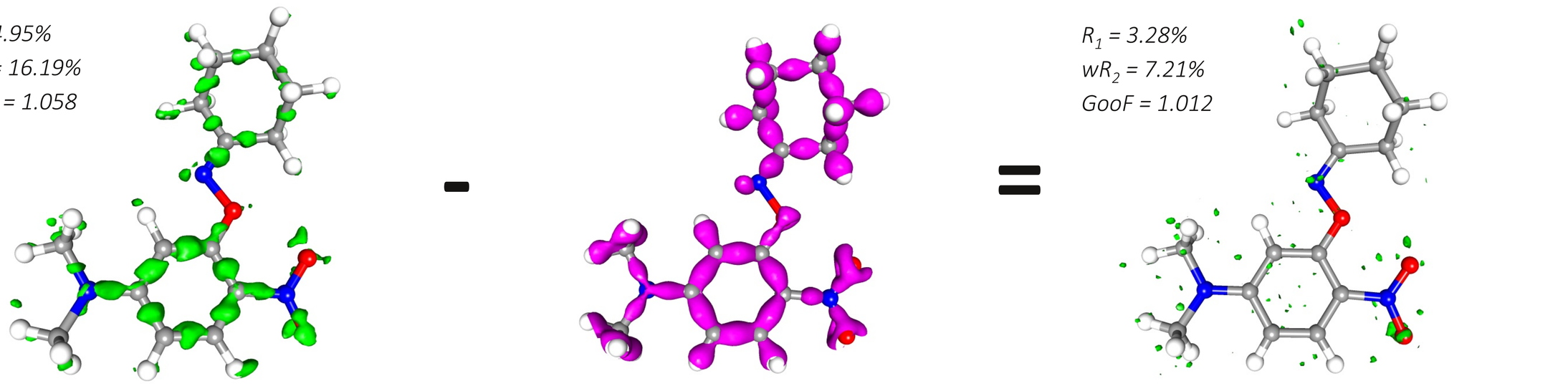
Experimental electron densities from accurate X-ray diffraction data

Thomas Fellowes and Jonathan White
School of Chemistry and Bio21 Institute

• Chemical structure and reactivity are determined by electron density, so valuable insight into a system can be gained by calculating or measuring the electron density.

• X-rays are scattered by electron density, the bulk of which is concentrated in a small volume centered on the atomic coordinates (core electron density), while the remainder is distributed in bonds and lone pairs (valence electron density).



Residual electron density from SHELXL refinement of a high quality dataset is shown in green. Bonding electron density and lone pairs are visible.

Aspherical scattering factors are incorporated into the model. These can be calculated from quantum mechanics or refined against diffraction data, and are shown in magenta.

Residual electron density after incorporating aspherical scattering factors is shown in green. The remaining density is simply experimental noise.

Charge density refinement

• Valence electron density is modelled using a series of atom centered spherical harmonic functions, similar to atomic orbitals.

• The population, size, and orientation of each of these functions can be refined in a typical least-squares refinement procedure.

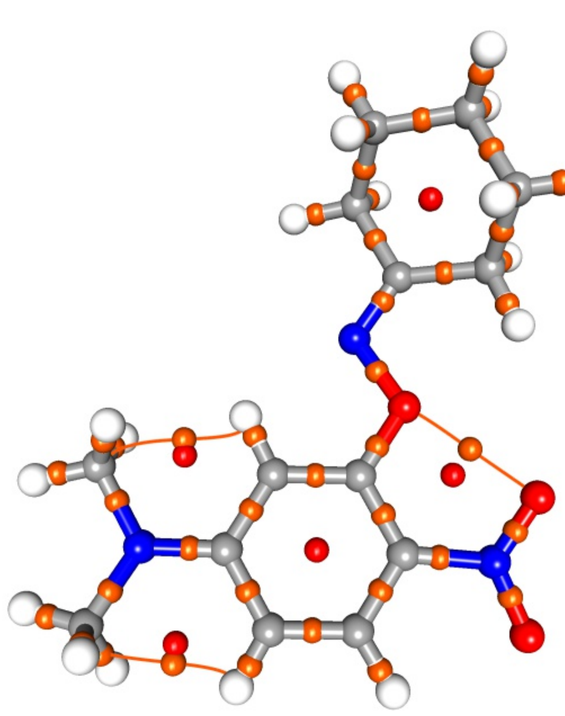
• Anisotropic displacement parameters are strongly correlated with valence electron density, leading to unstable refinement. Accurate atomic coordinates must first be derived from high angle data or neutron diffraction.

Results from experimental density

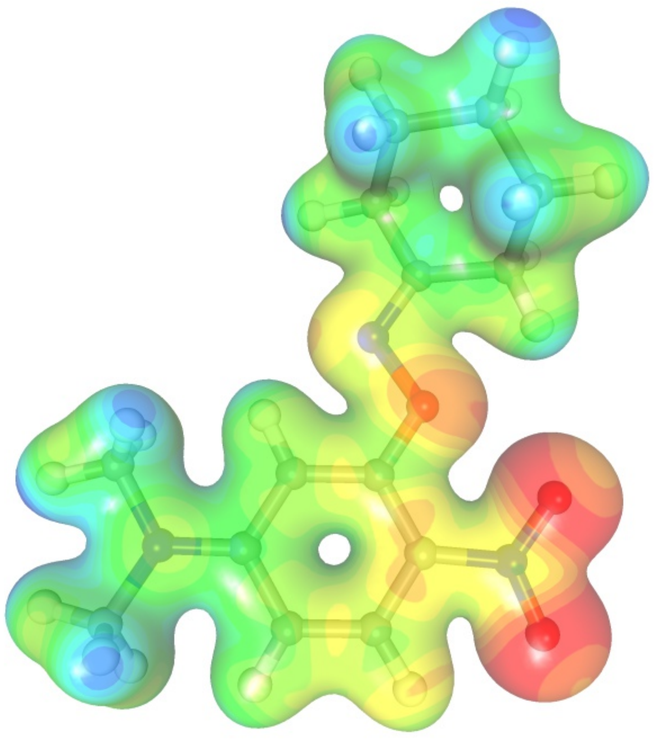
• Bader's Quantum Theory of Atoms In Molecules (QTAIM) characterises molecules based solely on the electron density, and provides a mathematically rigorous definition of bonding and intermolecular forces.

• Electrostatic potential can be calculated, which reveals likely nucleophilic/electrophilic sites on a molecule.

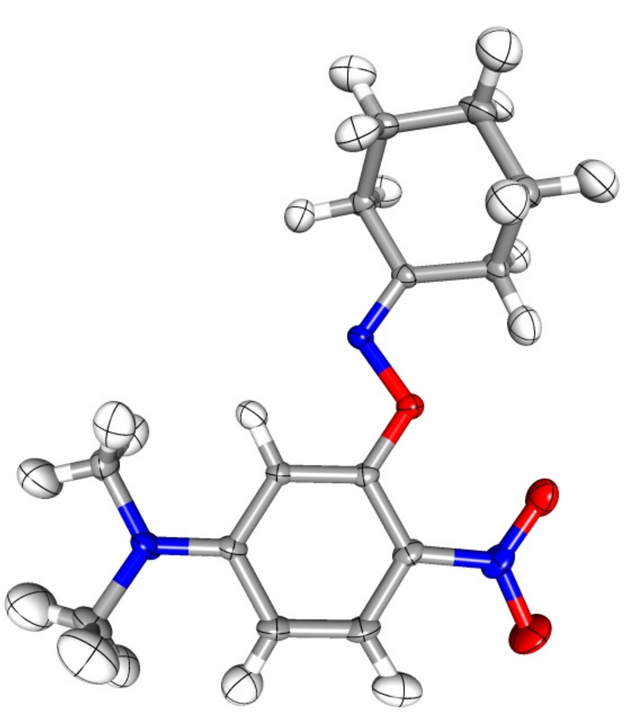
• Improved atomic scattering factors lead to better refinement statistics and lower estimated standard deviations on geometric parameters.



QTAIM bond paths and critical points are shown, based on the experimental electron density. This analysis reveals an unexpected interaction between the oxygens of the nitro group and oxime.



Experimental electrostatic potential is mapped on the 0.1 a.u. electron density isosurface. The red colour indicates an unusually electron rich nitro group.



Bond lengths involving hydrogen are lengthened to neutron distances, as the strongly anisotropic electron distribution around the H atom is included in the model. H atoms may also be refined anisotropically.