

# Charge Densities Come of Age

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In 1915, just three years after the discovery of X-ray diffraction by Von Laue, Peter Debye noted that “*the scattering from light atoms should get more attention, since along this way it should be possible to determine the arrangement of electrons in crystals*”.<sup>[1]</sup> Debye’s statement preceded the development of quantum mechanics and Born’s definition of electron probability distribution, but correctly assumed that the electron distribution was an observable that had become accessible. Interestingly, it took the better part of a century for this vision to be realized and for X-ray charge-density analysis to become a true analytical technique that was capable of providing quantitative insight into controversial issues and sufficiently rapid to be applicable to a series of related problems. In 1990 we wrote, “At present, charge-density analysis is far from a routine technique”, pointing out the need for time-consuming collection of large data sets and the limitations in accuracy of the experimental measurements.<sup>[2]</sup> These limitations have now to a large extent been overcome as a result of the development of more-intense X-ray sources, sensitive area detectors that allow rapid (and redundant) data collection, much improved cryogenic techniques, and last, but not least, the dramatic increase in computing power. As a result, not only has the accuracy improved but the analysis can be fast and precise, as demonstrated by Koritsanszky et al. in 1998 with the determination of accurate

experimental electronic properties of DL-proline monohydrate within 1 day.<sup>[3]</sup> It illustrates the disappearance of time limitations, making the time required for experimental charge-density analysis comparable with that for theoretical calculations. Of course, the experiment yields the charge density for the molecule in the solid state rather than the isolated molecule or complex, thus incorporating in the case of molecular crystals the small but subtle effects of the molecular environment. It must also be kept in mind that the charge distribution and not the wave function is accessible, a crucial distinction, though recently wave functions derived from experiment have been obtained by constraining Hartree–Fock variational calculations to fit the experimental structure factor amplitudes.<sup>[4]</sup> However, the theory of “atoms in molecules”, as pioneered by Richard Bader, which provides a quantitative link between the total electron density and the all-important physical properties of a molecule, bypasses the wave function in the analysis.<sup>[5]</sup> Topological analysis of the total density has been exploited to obtain net atomic moments, including charges, and to infer the nature of chemical bonding directly from the electron-density distribution. The chemical bond analysis derives much of its power from the characteristics of the topological bond path between atoms, including the density ( $\rho$ ) at the bond critical point (BCP) and the Laplacian of the electron density at the BCP and in other regions around the atoms. At the BCP,  $\rho$  is a minimum along the bond path but is a maximum along the perpendicular directions.

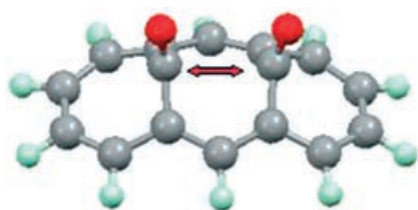
The results recently reported by Luger and co-workers on the bonding in a [1,1,1]propellane with its inverted

carbon atoms<sup>[6]</sup> are a culmination of a series of careful studies of charge density on strained hydrocarbons<sup>[7]</sup> and other small molecules<sup>[8]</sup> from Luger’s laboratory. The work on the propellane addresses the important issue of the nature of this relatively short ( $< 1.6 \text{ \AA}$ ) C–C interaction, which has been the subject of earlier theoretical<sup>[9]</sup> and experimental<sup>[10]</sup> studies. The analysis showed the presence of a bond path between the two inverted carbon atoms with a significant electron density at the BCP, corresponding to a bond order of 0.71, as derived with Bader’s empirical relationship, in very good agreement with theory. The agreement is less close for the value of the Laplacian ( $\nabla^2\rho(r_{\text{BCP}})$ ) at the BCP, which is much more positive according to the experiment, and indicates a closed-shell rather than a shared interaction. To assess this discrepancy, it must be realized that the experimental Laplacian, being a second derivative, is quite sensitive to the functions used in both the experimental and theoretical analyses. To obtain precise experimental information on a second-derivative function such as the Laplacian, very high order X-ray data would be needed. These are weak or even absent as the X-ray scattering falls off with scattering angle as a result of interference and the effects of thermal motion. The experimental Laplacian may therefore be rather dependent on the functions used in the fitting of the experimental observations.<sup>[11]</sup> Similarly, the theoretical Laplacian may vary with the nature of the basis set and its completeness. In this context it is relevant that the X-ray refinement on which the static density is based is performed with Slater-type functions, while Gaussian functions are used in the theoretical computation with which comparison is made. So the dis-

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agreement between the experimental and theoretical Laplacians in the bridgehead bonds may be less surprising than appears at first glance.

The results from Luger and co-workers may be compared with another unusual C–C interaction. Topological analysis of the experimental electron density of *syn*-1,6:8,13-biscarbonyl-[14]annulene (Figure 1),<sup>[12]</sup> derived from high-resolution data at 19 K, shows a bond path between the two bridgehead carbon atoms across the central ring, as



**Figure 1.** The *syn*-1,6:8,13-biscarbonyl-[14]annulene molecule.<sup>[12]</sup> The bridgehead carbon atoms between which a bond path was found are indicated by the arrow.

indicated by the arrow in Figure 1, even though the C···C distance is much longer than that for the bridgehead bond in the [1.1.1]propellane (2.593 Å versus 1.579 Å). Also,  $\rho(r_{\text{BCP}})$  is much smaller for the annulene (0.116(3) versus 1.31(3)  $\text{e}\text{\AA}^{-3}$ ), whereas the Laplacian  $\nabla^2\rho(r_{\text{BCP}})$  has a value of 1.53(1)  $\text{e}\text{\AA}^{-5}$  for the annulene at the BCP compared to  $\nabla^2\rho(r_{\text{BCP}}) = 10.3(1) \text{e}\text{\AA}^{-5}$  for the [1.1.1]propellane. In the annulene, no BCPs were found along other transannular lines although the distances are shorter (by about 0.1 Å) than the distance between the bridgehead atoms. Such results demonstrate the need for additional criteria for judging the nature of atomic interactions. Several such criteria have been applied in particular to bonds involving heavier atoms, for which the radial shape of the atomic Laplacian makes this function less useful in characterizing the bonding interaction.<sup>[13]</sup> In the classification proposed initially by Cremer and Kraka,<sup>[14]</sup> and extensively applied in later work,<sup>[15]</sup> covalent interactions are characterized

by local excess of the negative potential-energy density  $V(r)$ , over the positive kinetic-energy density  $G(r)$ . Thus the total energy density,  $H(r) = G(r) + V(r)$ , will be negative at the BCP for covalent bonds. A second, most useful measure is the electron-localization function (ELF),<sup>[16]</sup> which provides information on the pairing of electrons in the bonding region. This function can be obtained approximately from the experimental density<sup>[17]</sup> by the use of a functional proposed by Kirshnitz.<sup>[18]</sup> As the functional is approximate, the experimental ELF is often referred to as the “approximate ELF” (AELF). The AELF contains a number of undesirable artifacts, but its features are in broad agreement with the ELF.<sup>[19]</sup> A third function that has been successfully used in the analysis of M–M bonding (M = metal) but can only be obtained from the pair density distribution is the delocalization index  $\delta(A,B)$  of Bader and Stephens,<sup>[20]</sup> which corresponds to the number of electron pairs delocalized between atoms A and B. In a combined experimental/theoretical analysis of the M–M bonding in  $[\text{FeCo}(\text{CO})_8]^-$ , Macchi et al. compared the various criteria upon the (hypothetical) fluxional rearrangement of the CO coordination from terminal to bridging.<sup>[21]</sup> For the Fe–Co bond,  $\delta(\text{Fe},\text{Co})$  varies smoothly along the fluxional rearrangement path, even though the topological bond path disappears somewhere along the transition from the terminal to the ligand-supported conformation, which suggests the shortcomings of a sole reliance on the bond path criterion. When the M–M BCP is present, the energy density is small but nevertheless negative.

Clearly, although much progress has been made in recent years, the characterization of the chemical bond is not a closed subject. Experimental studies of unusual bonds, as presented in the recent report by Luger and co-workers, demonstrate how new light can be shed on longstanding issues in chemical bonding.

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