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Chemical bonding in crystals: new directions

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Abstract. Analysis of the chemical bonding in the position space, instead of or besides that in the wave function (Hilbert) orbital space, has become increasingly popular for crystalline systems in the past decade. The two most frequently used investigative tools, the Quantum Theory of Atoms in Molecules and Crystals (QTAIMAC) and the Electron Localization Function (ELF) are thoroughly discussed. The treatment is focussed on the topological peculiarities that necessarily arise from the periodicity of the crystal lattice and on those facets of the two tools that have been more debated, especially when these tools are applied to the condensed phase. In particular, in the case of QTAIMAC, the physical and chemical significance of the bond paths for the very weak or the supposedly repulsive interactions, the distinctive features and the appropriateness of the several schemes that have been proposed to classify chemical bonds, and, finally, the relative importance of the local and integrated electron density properties for describing intermolecular interactions. In the case of the ELF, particular attention is devoted to how this function is formulated and to the related physical meaning, and to how can the ELF be chemically interpreted and properly analysed in crystals. Several examples are reported to illustrate all these points and for critically examine the answers obtained and the problems encountered. The discussed examples encompass the case of molecular crystals, Zintl phases, intermetallic compounds, metals, supported and unsupported metal-metal bonds in organometallics, ionic solids, crystal surfaces, crystal defects, etc. Whenever possible joint ELF and QTAIMAC studies are considered, with particular emphasis on the comparison of the bond description afforded by the ELF and the Laplacian of the electron density. Two recently proposed functions, the Localized Orbital Locator (LOL) and the Source Function in its integrated or local form are also presented, in view of their potential interest for studies of chemical bonding in crystals. The use of approximated ELF and LOL, as derived from the density functional form of the positive kinetic energy density, is also discussed.

Introduction

Studies of chemical bonding in solids have experienced a true blossoming over the past decade. The situation has clearly changed since when, in 1988, Roald Hoffman provocatively observed [1] that "many solid chemists have isolated themselves from their organic or even inorganic colleagues by choosing not to see bonds in their materials". Many are the reasons behind this change and many are the grafts from other scientific disciplines that have contributed to renovating the interest towards a local description of bonding in solids beyond the tremendously successful, though empirical, Zintl-Klemm concept [2-4]. A reason, on the one hand, is the continuously increasing complexity (and reduced size) of new materials and the ensuing necessity to understand their properties at an atomistic level, if the materials' potentialities are to be fully exploited and the materials' performances significantly improved. A decisive scientific graft is, on the other hand, the technical developments that are still continuing and that have made X-ray diffraction a unique tool for mapping the charge density in crystals [5-7]. The accessibility to intense short-wavelength synchrotron sources, the availability of commercial devices for low-temperature experiments, the advent of area detectors, all have led to a significant increase of the redundancy of measurements and hence of the X-ray data quality one may attains [5-8]. Parallel progresses have also been made in the refinement of these data, by using improved aspherical-atom multipole models to describe the distortion of atomic clouds due to bonding, and by adopting suitable formalisms to deconvolute thermal motion effects from the X-ray amplitudes [5-8]. Presently, the final outcome is a static crystalline electron density, which most often represents a faithful extrapolation to infinite resolution from the finite set of experimental data and which may be so compared with the corresponding density from theory. Deconvolution of the thermal motion has become quite effectual as recently testified by a multi-temperature experiment showing that identical atomic multipole parameters can be obtained, irrespective of the acquisition temperature [9], provided the data are collected to high resolution and below 200 K. All these progresses have made electron densities derived from X-ray diffraction data of comparable [8] or, in some cases, of even better quality [10] than those obtained from the ab-initio periodic approaches, whose capabilities have

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nevertheless also largely been improved over the last decade [11]. This has provided a unique opportunity for a comparison and mutual validation of the theoretical and experimental techniques [6, 10], a comparison that goes far beyond the atomic positions or the visual inspection of electron and deformation densities [5, 6, 8-10]. Indeed, being the electron density the observable common to the two approaches, it has become a natural consequence and a common practice to adopt *density-based* topological tools for confronting them [5-8]. This allows for a *real* space quantitative description of the chemical bonding in crystals instead of the conventional bonding analysis in the space of the specific and different mathematical functions used to expand the wavefunction or the multipolar model. If one would simply stop at this conventional level of analysis, neither a proper comparison between experiment and theory, nor an unbiased description of bonding within either approaches could be achieved, since the nature of functions that are chosen to represent the system would "determine the *flavour* of the bonding model to a too large extent" [12].

The Quantum Theory of Atoms in Molecules [13] is certainly the most complete density-based topological tool for chemical bonding studies. Although extensively applied to gas-phase systems since the early 1980's, it was only in the last decade that, thanks to the progresses in experimental and theoretical densities, has this tool been increasingly applied to crystalline systems. Indisputably, the Quantum Theory of Atoms in Molecules has nowadays been elected by the X-ray density community as the primary standard theory to discuss bonding in crystals [6–8, 14].

However, the charge density alone does not describe bonding in its entirety, especially the mechanism of electron pairing, despite the famous Hohenberg-Kohn theorem [15] had established a one-to-one correspondence between the electron density and the wave function of a system. The structure of the whole one-electron density matrix (ODM) has been shown to be crucially influenced by covalent chemical bonding [16, 17]. Yet, the general difficulty of visualizing the underlying function, except for linear molecules, has led quantum chemists to propose new convenient functions, defined in the real space and intimately related to electron pairing. Examples are the Electron Localization Function [18], the Localized Orbital Locator [19], or, in the Quantum Theory of Atoms in Molecules, the Fermi hole [13] and the ensuing delocalization indices [20-22]. These functions are derived from the ODM or from the pair density and can thus be obtained from the X-ray diffraction experiment only through approximations [23-26] or by suitably combining information from X-ray data and *ab-initio* calculations [27, 28]. Due to the unique ability to yield easily understandable, chemically informative patterns of bonding, the Electron Localization Function has undoubtedly become the standard tool of analysis within the solid state chemist's community.

Basically, this review is aimed at discussing the main approaches that are currently being used for the study of chemical bonding in crystals, with a particular emphasis on the Quantum Theory of Atoms in Molecules and on the Electron Localization Function. All the discussed tools have been originally proposed for the gas phase systems and, later on only, has their use been extended to the condensed phase. For this reason, presentation of each approach is far from being complete. It is rather focused on those aspects which make each approach particularly important for the study of chemical bonding in crystals or on those facets that are still a matter of debate and, occasionally, of misuse or misinterpretation. Several examples are reported to illustrate all these points and to critically examine the answers one obtains and the problems one is facing when applying the various tools. Whenever possible, a comparison between the descriptions provided by different approaches is outlined. The presented applications encompass the case of bonding in molecular crystals, Zintl phases, intermetallic compounds, metals, organometallics, ionic solids, crystal surfaces, crystal defects, etc. In spite of the over 290 bibliographic citations, many other important studies could have been certainly reported in this review. The choices I made reflect the kind of topics I have addressed, the intrinsic didactic character of the selected examples and, quite often, simply my own knowledge of the literature. Needless to say, I'm more familiar with the studies in which I've been personally involved or to some extent related and I sincerely apologize if this has resulted in an excessive emphasis on my own work and/or in a too biased exposition.

There are also important thematic omissions in this review. The comparison between theoretical and experimental descriptions of bonding is only touched upon occasionally, since excellent reviews have already appeared covering this subject [6, 8]. The role of X-ray data quality as for a quantitative analysis of the bonding details is not discussed. An enlightening test case study has recently been published [29].

Traditional investigations of bonding, based on the LCAO theory of periodic structures and on the breakdown into atomic orbital contributions of the ensuing band structure or density of states, retain an undisputed importance for many interpretive and predictive aspects of bonding in crystals. Use of these tools has been largely documented in the literature and it is not reported here. The reader is referred to the several excellent books on this subject [1, 30]. Although not often common in the literature, use of such techniques, in combination with the tools presented in this review, should be strongly encouraged in several instances.

Quantum theory of atoms in molecules [13, 31]

This is not merely an instrument for studying the chemical bond, but rather a complete theory defining, in the real space, the boundaries of the atoms forming a system and enabling to evaluate their properties. The theory, due to Richard Bader and coworkers, is often simply referred to as the theory of Atoms in Molecules (AIM). The term Quantum Theory of Atoms In Molecules (QTAIM) or, in this context, Quantum Theory of Atoms In Molecules And Crystals (QTAIMAC) is to be preferred to emphasize that definition of atomic subsystems is fully rooted in quantum mechanics and that the theory applies with no significant changes to gas and condensed phase systems, be it possible or not to recognize molecular entities within them.

Apart from the amply surmised merit of yielding a faithful mapping of the chemical concepts of atoms, bonds, and structure, one of the most important reasons explaining the popularity [5, 6] of QTAIMAC for the study of chemical bonding in crystals is that a large part of this theory uses, operationally, only information contained in the electron density $\rho(\mathbf{r})$. Being this latter a quantum observable, the theory permits the investigation of related systems on a common basis, regardless their electron density has been obtained through experiment or theory and is being expressed in terms of different functional basis, or even numerically. Quite obviously, this is an important advantage in the study of chemical bonding in crystals. The unbiased comparison between experimental and theoretical densities may provide information on the quality of the experimental data and the suitability of the multipolar model used to project the reciprocal (diffraction) space representation of o to its real-space representation [32, 33]. On the other hand, it may evidence deficiencies of the theoretical approach like a poor treatment of the electron correlation, the use of a not enough flexible basis set or the adoption of a pseudopotential with a too crude core-valence separation [8, 10, 32]. Moreover, when comparing theoretical densities, use of QTAIMAC allows for an unambiguous assessment of how matrix effects influence chemical bonds on passing from the isolated molecules, to their cluster aggregations (dimers, trimers, etc.) and then to their regular packing in twodimensional (surfaces or slabs) or three-dimensional crystal systems [34]. This is achieved using one single theory despite the quantum chemical treatment of systems of different dimensionality might necessarily involve the use of specifically shaped basis sets for each level of matter aggregation [35].

As for any periodic scalar field defined on the unit cell [36], the periodicity of a crystal lattice is at the origin of a set of peculiarities in the topology of the charge density [37]. A description of how these specific topological features characterize the application of QTAIMAC to crystal-line systems is reported in the next two paragraphs. The remaining paragraphs in this section deal with those aspects of QTAIMAC that have been more debated and/or are of greater interest when studying the chemical bonding in crystals. Specific examples are also reported. The basic tenets of the theory are assumed to be familiar to the reader.

Atoms in crystals. Shape of atomic basins

An atom in a molecule is defined as that portion of the molecular space that obeys the condition of being delimited by a surface S through which the gradient of the density has zero flux at any point of S,

$$\nabla \varrho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \quad \forall \mathbf{r} \in S(\mathbf{r}_s)$$

 $\mathbf{n}(\mathbf{r})$ being a unit vector normal to the surface at \mathbf{r} . The atom in a molecule is the union of a nucleus and of the basin enclosed by the surface *S*. Fulfillment of this boundary condition ensures that the atom in a molecule is a

proper open system, one to which quantum mechanics applies [13]. This same boundary condition analogously defines an atom in a crystal as a quantum object [34, 37, 38]. There is however an important difference between atoms in a molecule and atoms in a crystal. The space domain for an in-vacuum molecule and hence for its associated electron density ρ is the ordinary space R^3 . This is an open domain, which has no boundaries and it is infinite in every direction. On the contrary, a 3D-lattice is mapped on S^3 [36], the 3-torus, which is the simplest example of a finite 3-dimensional surface (a 3-dimensional object which has no boundaries but it is finite).¹ Therefore, contrary to the case of gas-phase molecules, whose atomic basins have generally infinite volume, every atomic basin is finite in a perfectly periodic crystal. Obviously this is not exactly the case of a real crystal [39], whose atoms in the bulk are finite, whereas those on the outermost surface layer(s) have infinite volume, an example being reported later in Fig. 31c of this review.

The fact that in crystals atomic basins are finite has important consequences for the interpretation of their *shape*, as explained below. The treatment that follows combines the general survey of the possible types of gradient paths in any 3D scalar field outlined in Ref. [40] with the analysis of the fundamental properties of the topology of the electron density in ionic materials presented in Ref. [37].

An atom in a molecule or in a crystal may be defined in terms of its boundary as above, or alternatively as the union of a nucleus and the basin traversed by all the paths of steepest ascent through the electron density which terminate at the nucleus. These paths, including those which do not have a nucleus acting as their 3D sink (terminus), are called gradient paths (GPs) and naturally partition a molecule or a crystal into disjoint subspaces, the atomic basins. Each GP has a distinct origin and terminus, which are necessarily critical points (CPs) in the density, that is points where $\nabla \varrho = 0$. Contrary to general points, which for definition are passed through by one GP only, a CP may act as a source or a sink of more than one GP and its capability of sending or receiving GPs depend on its type, as shown below. CPs of any scalar field are classified in terms of the rank (r), the number of nonzero eigenvalues of the Hessian of the field, and of the signature (s), the sum of the signs of the Hessian eigenvalues. CPs are then designated by the pair (r, s) and the four types of rank 3 CPs in 3D are denoted as (3, -3), (3, -1), (3, +1) and (3, +3). The (3, -3) CPs are local maxima, the (3, +3)CPs local minima, and the (3, -1) or the (3, +1) CPs are saddle points in one or two dimensions. In the case of the *q* scalar field, they have been associated to the nuclei, the cages, the bonds and the rings of the molecular structure, respectively [13]. A CP will receive GPs only from direc-

¹ A 2-D lattice is mapped on the 2-torus, the surface of a torus, which may be obtained by folding the 2D-cell so as to form a cylinder and then bending the cylinder by joining its top with its bottom surface. The 3-torus can be constructed by starting with a cube (called the fundamental domain of the 3-torus) and then conceptually joining opposite faces: the top and bottom, the left and right and the front and back.

Table 1. Dimension of the topological object (manifold) generated by the set of steepest ascent gradient paths (GPs) connecting each of the nine possible pairs of critical points in any 3D scalar field.^a

Origin →	Din	Dimensionality ^b		Example
Terminus	OR	TE	MA	-
$(3, +3) \to (3, +1)$	3	1	1	Ring line
$(3, +3) \to (3, -1)$	3	2	2	Interatomic. surface
$(3,+3) \rightarrow (3,-3)$	3	3	3	Atomic basin
$(3,+1) \rightarrow (3,+1)$	2	1	1	
$(3,+1) \rightarrow (3,-1)$	2	2	2	
$(3,+1) \rightarrow (3,-3)$	2	3	2	Ring surface
$(3,-1) \rightarrow (3,+1)$	1	1	1	
$(3,-1) \rightarrow (3,-1)$	1	2	1	
$(3,-1) \rightarrow (3,-3)$	1	3	1	Bond path

a: adapted from Table 1 of Ref. [40]

b: OR = origin; TE = terminus; MA = manifold; OR is the number of directions in which the CP can "send" GPs, while TE is the number of directions in which the CP can "receive" GPs. MA is the dimension of the connecting topological object, 1 for curve, 2 for surface, 3 for basin.

tions associated to the negative eigenvalues for which the scalar field at the CP is a maximum, while it will send GPs only to those directions that are associated to the positive eigenvalues and for which the scalar field at the CP is a minimum. Hence, a (3, -3) CP will act as a 3D sink, while a (3, +3) CP will act as a 3D source for the steepest ascent GPs. The topological object (curve, surface or basin) generated by the single GP or by the set (bundle) of GPs connecting a given pair of CPs, is called a manifold, whose possible dimensions are listed in Table 1, for the nine types of GPs in any 3D scalar field [40]. The dimension of the manifold is related to the minimum of the dimensionality of the source CP and the dimensionality of

Table 2. Topological objects created by collecting the Primary Bundles (PBs) sharing the same (3, -3) or the same (3, +3) CP. Mapping of these objects on the atomic and repulsion polyhedra, respectively, is highlighted.^{*a*}

PBs sharing	Name	Mapping
Same (3, -3)	Basin of attraction of a nucleus (atomic basin)	Attraction or atomic polyhedron \rightarrow atomic shapecages \rightarrow verticesBcps \rightarrow faces ^b Rcps \rightarrow edges ^b
Same (3, +3)	Basin of repulsion of a cage	Repulsion or coordinationpolyhedron \rightarrow bonding networkNuclei \rightarrow verticesRcps \rightarrow faces ^c Bcps \rightarrow edges ^c

a: Ref. [37]

the sink CP. It is immediately clear that the only bundle of GPs that is able to fill the 3D space, and hence form the atomic basins, is that originating from the (3, +3) CPs and terminating at the (3, -3) attractors. All other sets of connecting GPs form topological objects that have a lower dimensionality, like for instance the interatomic surfaces or the bond paths.

In vacuum, the presence of a cage CP is not a necessary condition for the existence of a 3D manifold and hence of an atomic basin. In this case there is a "sea" of CPs at infinity all of rank zero, which altogether behave exactly as (3, +3) cage critical points. An infinite number of GPs originate at infinity, most of which are being attracted to a nucleus. On the contrary, in a perfectly periodic crystal, these cage-like points at infinity are no longer present and the only 3D manifolds of GPs are those originating from the true cage CPs. This is a profound difference, since in a unit cell there is a non-zero finite number of cages and hence a finite number of origins for the 3D manifolds. Each of these manifolds, which have been called primary bundles (PBs) by Martín Pendás et al. [37], is itself bounded by a zero-flux surface, for the very definition of a GP, and it represents a partition of space into smaller regions than those normally associated to atomic basins in Bader's theory.² The most basic topological structure of the crystal is thus that of its distinct PBs and of their interconnections. Analogously to the origin and terminus of the PB, the (3, -1) and (3, +1) CPs must necessarily stay on the surface of the PB, since any GP in the interior of the PB can only terminate at its (3, -3)attractor. PBs can then be collected to form larger zeroflux bounded regions, Table 2. Indeed, the interior of the union of all the PBs sharing the same maximum is nothing else than the basin of attraction of the nucleus, that is the atomic basin (Fig. 1). All CPs that, in any way, are related to this nucleus are to be found on the surface of its associated atomic basin. It has been shown that there is a homeomorphism between a PB and a convex polyhedron, whose vertices are the CPs [37, 41]. The union of all PBs sharing the same (3, -3) CP can also be mapped on a polyhedron, the attraction or atomic polyhedron, with each cage being associated to a vertex, each face to the 2D basin of attraction of a (3, -1) bond critical point (bcp) and each edge to the 1D basin of attraction of a (3, +1) ring critical point (*rcp*). An atomic polyhedron with m vertices is composed of m primary bundles and each of its faces is the interatomic surface (IAS) associated to a bond. So, an atomic basin will map on an atomic polyhedron with as many faces as are the atoms the atom is bonded to in the crystal (Fig. 1).

All polyhedrons have to share faces and edges with other polyhedrons in the crystal to fill the space completely, which physically corresponds to each IAS being shared by the two associated connected atoms and each ring axis being common to all atoms forming the ring.

b: The 2D basins of attraction of (3, -1) bond critical points (bcps) are mapped on the faces, while the 1D basins of attraction of (3, +1) ring critical points (rcps), are mapped on the edges of the atomic polyhedron.

c: The 2D basins of repulsion of rcps are mapped on the faces, while the 1D basin of attraction of (3, -1) bcps are mapped on the edges of the repulsion polyhedron.

 $^{^2}$ In vacuo the PB would be generally a 1D object, being any of the GPs emanating from the points at infinite and terminating at a given nucleus. The union of these GPs with the PBs associated to the cage points, if present, and with the given nucleus, would form the atomic basin.



Fig. 1. (a) Attraction basins and (b) coordination polyhedrons for the LiI cubic structure. Top. Attraction (atomic) basins of I (left) and Li (right). Atomic basins highlight atomic shapes. Notice the great difference in size between I and Li atoms. The associated weighted proximity polyhedrons (WPP), not shown here, are a very good approximation to the atomic basins in this simple case. Each Li is bonded to six I atoms and its shape is that of a slightly bumped regular cube, with each vertex being a cage CP, each midpoint of the 12 edges being a ring CP and each center of the 6 faces being a bcp, the face being the 2D basin of attraction (interatomic surface) of the bcp. Besides bonding to Li, each I atom has secondary bonding interactions with 12 I atoms along (110) lines. The square faces are associated to the six Li-I bonds and the hexagonal faces to the 12 I-I bonds. Bottom. Coordination polyhedrons. The 18-fold coordination of the I atoms yields the truncated cube, while the sixfold bonding of the Li atoms produces a regular octahedron. Cage points are located inside the polyhedrons, while the nuclei are the vertices of the polyhedrons. The edges are bond paths and the faces the 2D basins of repulsion of each ring CP. (Modified from Fig. 2 and 3 with permission from Ref. [37], Martín Pendás, A.; Costales, A.; Luaňa, V., Phys. Rev. B55 (1997) 4275-4284. Copyright 1997 by the American Physical Society).

Since the PBs are quantum objects, one may also imagine different partitions of the crystal space. The most natural alternative to the atomic basins is the basin of repulsion of a cage, which is obtained by collecting all the PBs sharing the same cage, Table 2. The cage minimum is at the interior of the basin, which may be mapped on a repulsion polyhedron where the nuclei are the vertices, the faces are the 2D repulsion basins of the rcps and the edges the bond paths associated to the bcps (Fig. 1). Mapping the real basins on the associated atomic and repulsion polyhedrons yields a very clear and complementary chemical picture. Attraction polyhedrons represent the atomic shape with as many faces as bonds connecting this atom to the lattice, while repulsion polyhedrons provide the coordination index of an atom in a crystal and correspond to its associated coordination polyhedron (Fig. 1). These polyhedrons show directly the bonding network of the crystal structure, as it is described by QTAIMAC.

Mapping atomic basins on atomic polyhedrons enable one to have an intuitive understanding of the shape of an atomic basin and allow classifying its changes in a series of related crystal systems. Martín Pendás et al. [37] have used weighted proximity polyhedrons (WPPs), as approximations to the real topological basins. The WPPs are generalized Wigner-Seitz cells with cage points defining the number and position of their vertices. Martín Pendás et al. [42] and Luaňa et al. [41, 43] have applied this kind of analysis on several classes of inorganic ionic crystals, like the B1 and B2 phases of the alkali halides and the 120 alkali halide perovskites. These studies have great interest as for the concept of ionic radius, which within this approach is generally direction dependent, and for the various correlations among atomic properties, i.e. electronegativities, deformabilities, etc., that it induces. A detailed report on these extremely profound and far-reaching studies is far beyond the scope of the present review and the reader is referred to the numerous original papers [37, 41-45].

With relation to the definition of atomic and molecular shapes in crystals, Martín Pendás *et al.* [46] have used a simple algebraic model to show that in condensed phases Hirshfeld surfaces [47, 48] are good approximations to the QTAIMAC interatomic surfaces, for most molecular solids. Contrary to the QTAIMAC surfaces, Hirshfeld surfaces have the pro to be easily computed and visualized. This study [46] provides a physical foundation to the wellestablished ability [48–50] of Hirshfeld surfaces to visualize and inform about molecular interaction in condensed phases.

Morse relations, critical points and crystal symmetry

Space group symmetry restricts the possible positions and types of CPs.³ When the domain space of the electron density (or of any single-valued scalar function) is R^3 , the

³ The CP analysis presented in this paragraph is not specific to the electron density or to QTAIMAC, but it generally applies to any single-valued function defined over a unit cell, such as the Electron Localization Function, the Localized Orbital Locator, etc. (see *infra*).

number and type of CP's must satisfy the Euler or Poincaré-Hopf relation

$$n-b+r-c=1$$

where n, b, r and c are the total number of nuclear, bond, ring and cage points. Conversely, for a single-valued function defined over a unit cell, the Morse relations [36, 51] for an L-dimensional closed domain hold. For the 3-torus they read as follows [36]:

$$\begin{split} & n-b+r-c = 0\,; \\ & c \geq 1\,, \quad r \geq 3\,, \quad b \geq 3\,, \quad n \geq 1\,. \end{split}$$

As noted earlier, at least one cage point must be present in the unit cell to ensure the occurrence of one PB and hence of an atomic basin.

Point-group symmetry also plays an important role as for the location of the CPs, since these necessarily occur at each Wyckoff position of the crystal space group having three fixed coordinates [37, 52]. Wyckoff positions with the cubic site symmetries for tetrahedral and octahedral point groups are even more restricted, since these positions can accommodate only *n* or *c* because of their bodydiagonal 3-fold axes [52]. The remaining 27 point group site symmetries in a space group can accommodate any of the 4 type of CPs. Morse's relation implies that the minimum number of CPs possible in a crystallographic unit cell is 8 (1c + 3r + 3b + 1n).

Morse's relation enables one to either accept or reject a set of CP's, when constructing an automatic CP search procedure within the cell. However, fulfillment of Morse's relation just ensures that a set of compatible CPs has been determined, while it not implies that all the unique CPs within the cell have been recovered. Table 3 shows one of such cases. The set of CPs (16n, 26b, 18r and 8c) found in the first QTAIMAC study [34] of urea crystal fulfilled Morse's relationship. Yet, that set didn't include the bcps and *rcps* related to the shorter of the two unique $N \cdots N$ contacts which have been later on recovered [53] using a more careful CP search procedure.⁴ The new topology (16n, 34b, 26r and 8c) also fulfils Morse's relation and it agrees with a recent experimental determination, using synchrotron diffraction data and a detailed multipolar analysis ([54, 55] and supplementary material of Ref. [55]).⁵ Data in Table 3 confirm the necessary occurrence of CPs

Table 3. Fulfillment of Morse's relation in urea crystal.^a

Wyckoff pos.	Multiplicity	CP type	Element
с	2	(3, -3)	С
С	2	(3, -3)	0
е	4	(3, -3)	Ν
е	4	(3, -3)	Η′
е	4	(3, -3)	Η″
С	2	(3, -1)	C-0
е	4	(3, -1)	C-N
е	4	(3, -1)	N-H'
е	4	(3, -1)	N-H''
е	4	(3, -1)	$O \cdots H^\prime$
е	4	(3, -1)	$O\cdots H^{\prime\prime}$
d	4	(3, -1)	$N \cdots N$, 4.3 Å
С	2	(3, +1)	Ring
е	4	(3, +1)	Ring
е	4	(3, +1)	Ring
f	8	(3, +1)	Ring
е	4	(3, +3)	Cage
a	2	(3, +3)	Cage
b	2	(3, +3)	Cage
i	n-b+r-c=1	16 - 26 + 18 - 8	= 0
f	8	(3, -1)	N…N, 3.4 Å
f	8	(3, +1)	Ring
i	n-b+r-c=1	16 - 34 + 26 - 8	= 0

a: Data from the study discussed in Ref. [34]. Reported in bold are the data for the additional critical points (CPs) found in the more detailed CP search [53]. Both CP sets fulfill Morse's relation. For the sake of precision, neither the ring and cage CPs, nor the bcp related to the longer $N \cdots N$ interaction are listed in Table 4 of Ref. [34] (specification added upon request of a referee).

at the fixed Wyckoff's positions (a and b) of the $P42_1m$ group.

The occurrence of CPs at locations other than fixed Wyckoff's positions depend both on the system that is being studied and on the method used to obtain its electron density. One may classify series of related systems according to their density topologies [41-44, 56], which are defined through the location, the number and type of ρ CPs. CPs of the same type and at equal Wyckoff sites, but with different free fractional coordinates, yield equivalent topologies. In general, a given topology is stable against small perturbations, like the geometry differences between experiment and theory or the differences in the electron density due to changes in the computational or experimental approach. This is especially so if the chemical interactions within the system are well characterized and strong enough. Systems exhibiting very flat valence electron densities for most of the internuclear region, like the alkali and alkali-earth metals, exhibit a pronounced tendency towards topological changes that clearly distinguish them from ionic, covalent and molecular crystals [53, 56-58]. Changes occur either by smoothly varying the interatomic distance or by changing the computational approach. The most detailed and conclusive study is due to Luana et al. [57, 59] who detected, in a 0.5 Å interval around the experimental lattice parameter, as many as 10 different topol-

⁴ For the sake of precision, even the *bcp* data for the longer $N \cdots N$ contact were not reported in Table IV of Ref. [34], although this *bcp* was actually recovered during the CP search. At that time, we thought it worth to publish only the *bcp* data for the intramolecular and the main intermolecular (H-bonds) interactions in the crystal. Furthermore, neither the ring, nor the cage recovered CPs were reported in Table 4 of Ref. [34]. This footnote was requested by a referee.

feree. ⁵ The experimental charge density at the two unique $N \cdots N$ *bcps* amounts to 0.018 and 0.004 $e/Å^3$, for the shorter and longer contact, respectively. These values [55] are, respectively, below or well below the unavoidable uncertainty (0.05 $eÅ^{-3}$) in the experimental electron density distributions [6] and, although very similar to the corresponding theoretical values, must be taken with caution. A referee pointed out that the *bcp* corresponding to the longer $N \cdots N$ contact vanishes when the same experimental data set is refined with the Hansen-Coppens, rather than with the Stewart's model ([7] and references therein).

ogies for Li bcc using a FPLAPW/GGA approach, and a distinct topology for each of the four different computational methods they scrutinized at the experimental geometry. This result may at a first sight seem discouraging as for the physical meaning one may attach to these changes of topological regime. However, when examined in a wide range of interatomic distances, the electron density of every alkali metal was found to follow a well-defined topological sequence, with strong similarities across the five metals [57, 59]. The feature that mostly distinguishes one metal from another is the different extent of compression which is required to pass from one topological regime to another one, a result of interest as for the effect on the bonding patterns of an applied external pressure. Although all alkali metals undergo phase transitions upon compression, the main features of the topological regimes found for the bcc structure should be essentially translated to the metastable structures these metals adopt under pressure. Indeed, a parallel comparative analysis of the topologies of alkali metal clusters and dimers, suggests that it is essentially the internuclear distance that drives the change from regime to regime [57, 59].

The behavior of alkali metals contrasts with what observed for the ionic systems, like the cubic alkali halides, where the topological scheme at the equilibrium geometry is maintained for a wide range of values of the crystal cell parameter a. This is likely related to the fact that the ionic radii of anions and cations change linearly with a, while their ratios remain essentially constant [41].

Bond paths and chemical interactions in crystals

Defining and characterizing a chemical bond through the existence of, and the properties at the associated bond critical point (bcp) is at the core of the QTAIMAC study of chemical bond in crystals [6, 60]. However, this approach is and will continue to be also a source of controversy, misinterpretation and misuse. In this paragraph and in the one specifically devoted to intermolecular interactions, some issues, which have been raised against this approach, will be closely examined and hopefully clarified.

According to Bader [13, 61], the presence of a line linking two atoms and along which the electron density is a maximum with respect to any neighboring line, is a necessary condition for the two atoms to be *bonded* to one another when the system is in a stationary state (energy minimum at a given nuclear configuration).⁶ Persistence of this line when the system is also in a stable electrostatic equilibrium (no net forces acting on nuclei), ensures both a necessary and a sufficient condition for bonding in the "usual chemical sense of the word" [61]. In this case, the lines of maximum density, which are generally termed interaction lines, are called *bond paths* and their network defines the molecular or crystal graph. This latter isolates the pair-wise interactions which are present in a crystal and which are deemed to determine and characterize its

general properties [60].7 The topological definition of a bonded interaction is universal [61].8 A bond path can be associated with all kinds of interatomic interactions, from weak to strong, including those between atoms with a large deficiency of electrons relative to the number of bonding orbitals, typical of metals and alloys [53, 57, 58, 62], and also those between entities with completely filled shells, typical of ionic crystals [41–45], host-guest crystal structures [63], hydrogen-bonded crystals [6, 34, 64-76] and solids formed by non polar molecules [60]. Indeed, as pinpointed by Bader [61], the use of a bond path to denote a bonded interaction frees the definition of bonding from the constraints of the Lewis pair model [77], a model that is unable to describe the bonding in metals and in condensed phases composed of closed shell atoms or neutral or charged molecules.

Adoption of a single criterion to define a bonding interaction in crystals is challenging, for in many crystals ionic, covalent, metallic and van der Waals-like interactions are all simultaneously present [30]. Performing an analysis of these bonds on the same footing and within a single theoretical approach, besides being a practical advantage, is an obvious requirement for a meaningful comparison. However, use of the bond path as a universal indicator [61] of bonding in crystals also makes the structural chemists to feel often bewildered, for not saying, quite uncomfortable. In general, difficulties have arisen when a bond path is associated with closed-shell rather than shared interactions. This is the case of what have been termed "nonbonded" [78] interactions or of what have been described even as "repulsive" contacts [79]. An example of the former are the intra and inter-molecular bond paths which have been found to link neighboring H...H atoms at distances below the sum of their van der Waals radii [78], although recent experimental and theoretical studies on crystals of organoammonium tetraphenylborates [80] and on benzenoids systems [81] have brought together evidences in favor of considering also these $H \cdots H$ contacts as true bonds (see infra). Secondary interactions between ions of similar charge in ionic crystals are, instead, the classical example of seemingly "repulsive" contacts [79]. Bond paths associated to these contacts have often been encountered, both in the experimental and theoretical crystalline electron density distributions (EDDs) of ionic solids, albeit their occurrence would not be a topolo-

⁶ Significant electron pairing has however been found also between pair of atoms not linked by a bond path (see *infra*).

⁷ This assertion should be very cautiously interpreted when referred to the realm of the very weak interactions which are, e.g., so ubiquitous in molecular crystals. Polymorphs with hardly distinguishable energies might differ in number and kind of pair of connected atoms. Formation of bond paths is in this case to be seen more the result of molecules interacting as a "whole" than the cause determining their interaction [181].

⁸ As discussed in the following, the notion of a bond path as a universal indicator of bonding does not follow from first principles in QTAIMAC. It is rather the result of a reasonable, though arbitrary, extension to the polyatomic case of what occurs in diatomics where the formation of the bond path and of the virial path leads at equilibrium to the balancing of the forces of repulsion on the nuclei and to the lowering of the total molecular energy. The *universal* attribute for the bond path indicator simply denotes that atom-atom interactions with a very different nature share, as a common feature, the occurrence of a bond path.



Fig. 2. LiH crystal. $\nabla \rho$ gradient paths on the [001] plane. Bond paths (BPs) link the bulky hydride ions, besides those linking cations to anions. Bond paths associated to secondary interactions are frequent but not a topological necessity in ionic solids. The most usual situation is that of a bond between neighboring anions. In few cases, secondary cation-cation interactions have instead been observed [41].

gical necessity [41]. The most usual feature is that of a bond between neighboring anions, because these ions have a more diffuse distribution than cations and hence a greater ionic radius resulting in anion-anion contacts in the crystal and the formation of associated bond paths. This is shown for LiH crystal in Fig. 2 where besides the Li–H paths, bond paths are found to connect the bulky hydride ions, rather than linking the small lithium cations or being absent. Now, the question is of whether and how can the formation of these peculiar bond paths be reconciled with the "common" thinking of a chemical bond. Bader's [61] and author's views on this matter are here merged as follows:

A. One has first to consider that the crystal is at electrostatic equilibrium and the Hellmann-Feynman force acting on each nucleus must necessarily be zero. There cannot be net repulsive forces in the crystal, since the only operative forces in a bound state are the attractive forces restoring the system to its equilibrium geometry once the nuclei have been displaced from equilibrium as it occurs along vibrational modes. For instance, in ionic crystals, there is sufficient accumulation of density between each pair of anions to not only balance the attractive restoring force when they are displaced from equilibrium. If net repulsive forces were present, the crystal would be unstable and would either atomize or distort to an equilibrium geometry of lower energy.

B. The existence of a bond path between two atoms in a crystal does not imply that the two atoms would be

bonded if taken in isolation. At a nuclear separation as in the crystal, their electron distribution would be necessarily different from the one in the crystal, as would it be their nuclear equilibrium distance (if any), due to the lack of any matrix effect. Indeed, the atoms linked by a maximum density interaction line in a crystal are defined as bonded on a multi-dimensional Born-Oppenheimer potential energy surface (PES) and when the system is at local minimum on this surface. Translating the properties of an atom-atom interaction defined on a multi-dimensional PES, on the one-dimensional PES associated to a diatomic system is a rough approximation, one that tacitly assumes that the energy of the crystal could be decomposed in terms of additive mutually independent pairwise contributions.⁹ Bonding between any pair of atoms is a physical mechanism involving these two sole atoms only in the limit of a diatomic molecule in vacuum. Rigorously speaking, the question whether a given atom-atom interaction is attractive or repulsive at an equilibrium geometry appears as a non-sense but for diatomics. The source function (see infra), is a practical tool to evaluate the contributions to the density at a *bcp* from atoms other than the bonded atoms [82, 83]. Generally, the less strong and covalent is an interaction, the more is the indirect involvement of other system's atoms in producing such an interaction [83].

C. If, at equilibrium, the electron density accumulates along a given internuclear axis, as it is between the hydrides ions in LiH, this is because it gives a more stabilizing (or a less destabilizing) contribution to the energy than if it would distribute differently. The electron distribution reached at equilibrium is to be seen as the best compro*mise* yielding the lowest energy for the system as a whole, not necessarily for each single pair of atoms embedded in the crystal. Nevertheless, Keith, Bader and Aray, have shown that the negative of the virial field, $-V(\mathbf{r})$, is in general structurally homeomorphic to the electron density over all of the nuclear configuration space [84]. This has an important physical consequence for the present discussion, one that entails that the lines of maximum density in a field are to be matched by corresponding lines of maximal density in the other field. The virial field $V(\mathbf{r})$ is the virial of the Ehrenfest force exerted on the electron density at **r** by the nuclei and by the average distribution of the remaining electrons in the total system [13]. It defines the electronic potential energy density of an electron at **r**, integrates to the total potential energy V and provides the most short-ranged description that it is possible for the local electronic potential energy. If every bond path is mirrored by a *virial path*, this implies that besides the former path, simultaneously present at equilibrium is a line linking the same nuclei and along which the potential energy density is maximally negative (i.e. maximally stabilizing) with respect to any neighboring lines. This is the same mechanism operating for the interaction in a diatomic, where it is the formation of the bond and the virial paths, with the specific features these paths have at equilibrium

⁹ Note 46 of Ref. [61] details why a rigorous calculation of the potential energy of interaction between a pair of linked atoms is physically unfeasible in a multi-atom system.

that leads to the balancing of the forces of repulsion on the nuclei and to the lowering of the molecule's total energy. This balancing results in attractive restoring forces for any displacement from equilibrium position. By mere analogy with the diatomic case, any pair of atoms linked by a virial and a bond path in a crystal at equilibrium is termed as bonded in the "usual chemical sense of the word", within QTAIMAC. Indeed, it is the analysis of the nature of such a bond, as for instance summarized by its bond critical point density properties, that enables one to qualitatively assess whether a bonding interaction is really important in determining the structure and properties of the crystal or just marginal or even possibly "repulsive", within an atom-atom view.

Energy lowering at equilibrium does not necessarily imply formation of secondary anion-anion interactions in all ionic crystals. Rarely, secondary cation-cation interactions have been observed, instead [41]. This is, for instance, the case of CsSrF₃ and CsBaF₃, two out of 120 investigated alkali halide perowskites where Cs-Cs secondary interactions form, owing to the comparatively large cation/anion size ratio and to the close contact of Cs⁺ ions arising from the large size of the Sr and Ba cations. Although the switching from anion-anion to cation-cation secondary interactions seems in this case to be very much related to geometrical considerations only, one can not ignore that the minimal energy EDD complies with lines of maximum density and maximally negative potential energy linking the cations rather than the anions.

D. Considering the simultaneous occurrence of a bond and a virial path as a universal indicator of bonding does not require abandoning the common thinking of associating the pairing of electrons with bonding.¹⁰ But one has to distinguish between pairing and electron pair. Indeed, any chemical interaction results from the *local* pairing of the densities of opposite spin and the formation of a bond and a virial path. It is a matter of degree and of how such pairing realizes that differentiates one kind of interaction from another. The conditional pair density for same-spin electrons [18, 85] expresses such local pairing, the Laplacian of ρ or the Electron Localization Function (ELF) [18] being convenient 3D indirect measures of the pairing [85], as discussed later in this review. In general, the localization of the pair density is less than that required to accommodate individual pairs of electrons and it may realize in more than a single spatial region along the bond. Pairing occurs maximally between the two atomic basins for a shared covalent interaction and within each atomic basin for closed-shell interactions, as are those taking place in crystals between ions of similar or different charge.

As a concluding remark of this paragraph, it is worth mentioning that Martín Pendás *et al.* [86] and Blanco *et al.* [87, 292] have recently proposed a new, practical and efficient method for partitioning the total energy of a system

into self-basin energy and basin-basin interaction energy terms.¹¹ This approach, which is presently in its early development stages and which has only been presented for very simple gas-phase molecular systems [87, 292], will possibly pave the way to operationally define and evaluate "bonding" and "non-bonding" energy contributions to the total energy within QTAIMAC. Bonding and non-bonding contributions would correspond to the interaction energy terms between atomic basins linked and respectively not linked by a bond path. For a given pair of bonded atoms in a crystal one could compare the sum of their mutual interaction energy and of their self-basin energies (atomic net energies) with the sum of the energies of the two atoms when isolated. If this latter sum is higher in magnitude than the former sum, it is the energy lowering due to the "non-bonding" interactions that stabilizes the bonded atom pair in the crystal, while if the opposite is true, it is the mutual interaction alone, besides the changes in the self-basin energies of the two atoms due to crystallization, that stabilizes these bonded atoms in the crystal phase.¹² Matta et al. [81] have discussed hydrogen-hydrogen bonding, which is bonding between hydrogen atoms bearing the same or similar net charges, as stabilizing interactions in molecules and crystals. Their analysis, which has been performed for benzenoid hydrocarbons in the gas-phase, defines the H-H stabilization energy as the lowering of the energy of the H involved in H-H bonding in the bay areas of condensed benzenoid hydrocarbons with respect to the average energy of the H atoms in the corresponding linear isomers. Each H-H interaction was found to make a stabilizing contribution of up to 10 kcal mol^{-1} to the energy of the molecule in which it occurs. Whether this energy lowering is due to the H-H bonding interaction alone rather than to favorable "non-bonding" interactions of the H-H bonded atoms with the remaining atoms in the system or to an increase of the magnitude of the H self-basin energies, is presently unknown. The approach proposed by Martín Pendás et al. [86] and Blanco et al. [87, 292] could shed light on cases like this where the common belief of a crystallographer is that of an atom-atom repulsive interaction due to $H \cdots H$ distances much shorter (~ 1.9 Å) than twice the standard van der Waals radius of 1.2 Å for the H-atom.

 $^{^{10}}$ Indeed, there are pair of atoms that, even if not linked by a bond path, exhibit a relevant electron pairing, as denoted by the value of their delocalization indices (see *infra*). Conversely, extremely low delocalization indices may be observed between "bonded" atoms.

¹¹ The method has a quite broad formulation since it is based on general one-electron and two-electron density matrix partitions, that can be performed either in real space or in Hilbert space. In this context, we are interested in the formulation that combines Bader's partitioning with the theory of the electronic separability due to McWeeney [123]. Two-electron integrations over atomic basins are computed using a procedure that generalizes the conventional multipolar approach to the case of overlapping densities [86]. The resulting method [86, 87, 292] allows for a partitioning of the total two-electron energy in a sum of regional contributions (intra-basin and basin-basin), while in the usual implementation of Bader's method this same energy can be only partitioned in atomic basin contributions and using Hartree-Fock wavefunctions solely.

¹² It may also occur that the two bonded atoms have atomic energies in the crystal that are smaller in magnitude than when the atoms are in isolation. If this is the case, the outlined comparison would serve to distinguish whether it is the interaction among the non-bonded atoms or the combination of the self-pair interaction and of the two self-basin energies that is mainly responsible for the energy destabilization of the two bonded atoms in the crystal.

Classification of chemical interactions in crystals

Chemical interactions between pair of atoms involve complex electron density redistributions, which account for the changes in the shape, the volume and the EDD of the atomic basins with respect to the superposition of atomic densities. When two atoms are bonded, they necessarily share an interatomic surface (IAS) whose point of maximum electron density is at *bcp*. Properties evaluated on the IAS contain information on bonding, since surface and atomic basin properties are known to be interdependent [88]. Indeed, an atomic expectation value is the result and may be equated to a sum of "bond" contributions in terms of a corresponding sum of surface integrals on each of the IASs the atom forms upon bonding. Each surface contribution reflects the formation of its associated bond, yet the one occurring when all other bonding interactions within the system concomitantly form. Although the IAS properties are likely to be increasingly exploited as an investigative tool [89], more common practice is to simply make use of properties at *bcps* as a mean to classify and summarize the nature of chemical interactions. This recipe is however not unique since it depends on the subset of examined properties and on how these properties are ordered in a hierarchical classification procedure. In keeping with this, one has to be extremely cautious in drawing conclusions on bonding on the basis of the properties at one single point (*bcp*), whatever representative it may be. The existing bond classifications are discussed below. In what follows properties at *bcp* will be denoted by the subscript b for bond.

The dichotomous classification based on the sign of the Laplacian of the electron density

Probably the simplest and earliest proposed classification [90] is that based on the local expression of the virial theorem [13, 91], which in atomic unit (a.u.) reads as follows,

$$\frac{1}{4}\nabla^2 \varrho(\mathbf{r}) = 2G(\mathbf{r}) + V(\mathbf{r}) \tag{1}$$

with $\nabla^2 \rho(\mathbf{r})$ being the Laplacian of the electron density, $G(\mathbf{r})$ the positive definite kinetic energy density and $V(\mathbf{r})$ the potential energy density introduced earlier. Since $G(\mathbf{r})$ is positive everywhere and $V(\mathbf{r})$ is negative everywhere, the theorem states that the sign of $\nabla^2 \rho(\mathbf{r})$ determines which energy contribution, potential or kinetic, is in local excess relative to their average virial ratio of minus two. A negative Laplacian reveals that the potential energy is in local excess, while a positive Laplacian denotes that the kinetic energy is locally prevailing. According to the divergence theorem [92], the sign of the Laplacian of a scalar function indicates whether a net flux of the gradient of the scalar is entering (sign -) or leaving (sign +) an infinitesimal volume centered on a given point. It so highlights whether the function, the electron density in our case, is concentrating/compressing or diluting/expanding at the point. The Laplacian equals the sum of the three principal curvatures of a scalar. At a *bcp*, two electron density curvatures $(\lambda_{ib}, i = 1, 2)$ are negative and define a plane tangent to the IAS at the bcp, while the remaining curva-

ture, λ_{3b} , is positive and its associated eigenvector is tangent to the bond path at *bcp*. Using the Laplacian at *bcp*, $\nabla^2 \rho_b$, one then interprets the formation of an IAS and a bond path as a result of a competition between the perpendicular compression of the density toward the bond path, as conveyed by the two negative curvatures, and its expansion in a direction parallel to the path away from the IAS, as given by the positive curvature λ_{3b} . The sign of $\nabla^2 \rho_b$ determines which of the competing effects is dominant. Putting all together, one has that, generally, shared chemical interactions (covalent and polar bonds) are characterized by negative $\nabla^2 \varrho_b$ values and hence dominant negative curvatures, with lowering of the potential energy arising from the charge being concentrated between the nuclei along the bond path. Conversely, closed-shell interactions (ionic bonds, hydrogen bonds, van der Waals molecules) have positive $\nabla^2 q_b$ values and hence a dominant positive λ_{3b} curvature, with energy stability attained from the electronic charge being separately concentrated within the atomic basins, rather than being shared between them. Closed-shell interactions are dominated by the kinetic energy in the IAS region, with a particularly high value for the parallel component, $G_{b\parallel}$. These interactions are characterized by relatively low values of ρ_b because the density is contracting away from the IAS in requirement to the Pauli exclusion principle. When comparing closed shell and shared interactions, it is therefore advisable to place the kinetic energy on an absolute footing by using the quantity G_b/ρ_b , the kinetic energy per electron. Closed shell interactions generally have $G_b/\varrho_b > 1$, $G_{b\parallel} \gg G_{b\perp}$ (perpendicular component of G_b), $|\lambda_{1,2;b}|/\lambda_{3b} \ll 1$, and a small ρ_b value, while shared interactions exhibit $G_b/\rho_b < 1$, $G_{b\parallel} \ll G_{b\perp}, |\lambda_{1,2;b}|/\lambda_{3b} > 1$ and a large ϱ_b value (see Table 4, top). Needless to say, this kind of classification is very general and apparently dichotomous in nature. Chemical interactions in crystals exhibit properties that range smoothly from those of purely closed-shell (rocksalt) to those of purely covalent interactions (diamond). Rigorously, comparing a given property at *bcp* from one bond to another yields meaningful information provided the nuclei participating in the bond are the same. Interesting and informative trends, can also be observed if the bonds are in some way "chemically related", as for instance the $X-H\cdots Y$ bonds, with X = O, N, C and Y = O, N. Therefore, the classification reported on top of Table 4 is to be simply meant as a useful set of quantitative indices, whose variations along a series of chemically related compounds or following an environment's change pinpoint the effect these perturbations have on the nature of a given atomatom interaction. For instance, if on passing from the gas to the crystal phase, G_b/ϱ_b and λ_{3b} are decreasing, while $\varrho_b, -\nabla^2 \varrho_b$, and $|\lambda_{1,2;b}|/\lambda_{3b}$ are all increasing, this implies that the associated interaction has become more covalent in nature upon crystallization, the opposite being true if the reversed changes would occur. This kind of criteria was applied to the chemical interactions in urea, in the first published topological study [34] of crystal field effects on molecules. As shown in Table 5, on passing from the molecule to the bulk, the C–N bond has its ρ_b , $-\nabla^2 \varrho_b$ values increased and its parallel curvature decreased, the opposite being true for the C-O bond. The

Table 4. Classification of atomic interactions.

The dichotomous classification ^a based on the sign of $ abla^2 arrho_b$							
Property	Shared shell, $\nabla^2 \varrho_b < 0$ Covalent and polar bonds	Closed-shell, $\nabla^2 \varrho_b > 0$ Ionic, H-bonds and vdW molecules					
$\overline{\lambda_{I}}$	$\lambda_{1,2}$ dominant; $ \lambda_{1,2} / \lambda_3 > 1$	λ_3 dominant; $ \lambda_{1,2} / \lambda_3 \ll 1$					
VSCC ^b	The VSCCs of the two atoms form one continous region of charge concentration	$\nabla^2 \rho > 0$ over the entire interaction region. The spatial display of $\nabla^2 \rho$ is mostly atomic-like					
Q_b	Large	Small					
Energy lowering	By accumulating ϱ in the interatomic region	Regions of dominant $V(\mathbf{r})$ are separately loca- lized within the boundaries of interacting atoms					
Energy components	$2G_b < V_b ; G_b/\varrho_b < 1; G_{b\parallel} \ll G_{b\perp}; H_b < 0$	$2G_b > V_b ; G_b/\varrho_b > 1, G_b \gg G_{b\perp}; H_b$ any value					

Bond polarity is increasing ------

-----Bond covalency is increasing

The classification^{*c*} based on the adimensional $|V_b|/G_b < 1$ ratio

Shared shell (SS)	Transit region, incipient covalent bond formation	Closed-shell (CS)
$ V_b /G_b > 2$	$1 < V_b /G_b < 2$	$ V_b /G_b < 1$
$H_b < 0; abla^2 arrho_b < 0$	$H_b < 0; abla^2 arrho_b > 0$	$H_b>0; abla^2arrho_b>0$
Bond degree (BD) = $H_b/\varrho_b \equiv$ Covalence degree (CD)	$BD \equiv CD$	$BD \equiv Softness degree (SD)$
BD large and negative	BD negative and smaller in magnitude than for SS interactions	SD positive and large
The larger is BD the more covalent is the bond	BD Approaching zero at the boundary with CS region	The larger is SD the weaker and closed-shell in nature is the bond

The classification^d based on the atomic valence shell and on both the local (bcp) and integral properties

	Q_b	$ abla^2 arrho_b$	G_b/ϱ_b	H_b/ϱ_b	$\delta(A,B)$	$\oint_{AB} \varrho(\mathbf{r}_s) \mathrm{d}\mathbf{r}_s$
Bonds between light atoms						
Open-shell (covalent bonds); e.g. C–C, C–H, B–B	Large	$\ll 0$	<1	$\ll 0$	\sim Formal bond order	Large
Intermediate interactions (polar bonds, donor-acceptor bonds; e.g. C–O, H ₃ B–CO	Large	any value	≥ 1	≪0	< Formal bond order	Large
Closed-shell (ionic bonds, HBs, van der Waals interactions; e.g. LiF, HO, NeNe	Small	>0	≥ 1	> 0	~ 0	Small
Bonds between heavy atoms						
Open-shell (e.g. Co-Co)	Small	~ 0	<1	< 0	Formal bond order (unless bond delocalisation occurs)	Medium/large
Donor acceptor (e.g. Co-As)	Small	>0	~ 1	<0	< Formal bond order	Medium/large

a: according to Ref. [90].

b: VSCC is the Valence Shell Charge Concentration, that is the valence region of the isolated atom where the Laplacian is negative [13]

c: according to Ref. [93]

d: according to Ref. [109]; the lower part of this Table is an adaptation of Table 5 and Table 4 of Ref. [109] and Ref. [97], respectively. Ref. [109] defines as heavy atoms the atoms having more than three atomic shells, i.e. from K atom onwards.

N–H bonds undergo a negligible ρ_b decrease and a significant λ_{3b} increase. These changes denote that the C–O and N–H bonds are becoming more polar and weaker, while the C–N bond is increasing its covalency and strength upon formation of N–H···O hydrogen bonds in the crystal. Being related to second derivatives of the electron density, $\nabla^2 \rho_b$ and λ_{3b} seem more sensitive indicators of crystal field effects than are the ρ_b values since the reported changes of the former quantities are at least one

order of magnitude greater than those of ρ_b . The bond ellipticity, $\varepsilon = (\lambda_{1b}/\lambda_{2b}) - 1$, is related to the deviation of charge distribution from cylindrical symmetry at *bcp* and, hence, for bonds like C–O and C–N to their π -character [13]. Bond ellipticity changes in urea, upon crystallization, indicate that the C–N (C–O) bond is acquiring (loosing) double bond character, in agreement with the variation of the other *bcp* indicators. The *bcp* displacements upon change of phase (Δr_x values in Table 5), are larger for the

Table 5. Percentage changes in the *ab-initio* bond critical properties of urea upon crystallization.^{*a*, *b*}

X-Y	ΔR_x	$\Delta \varrho_b$	$\Delta(-\nabla^2\varrho_b)$	$\Delta\lambda_3$	$\Delta \varepsilon$
С-О	-1.0	-2.9	-67.0	+14.9	-2370.
C-N	+2.0	+2.3	+18.3	-37.7	+53.
N-H'	+1.5	-0.3	+1.5	+11.4	-26.
$N-H^{\prime\prime}$	+2.8	-0.6	+2.5	+18.4	-53.

a: Ref. [34]

b: Data refer to $6-31G^{**}$ basis and, for both systems, at the geometry as in the crystal. For a given property *P*, the percentage change ΔP is evaluated as $[P_{crystal} - P_{molecule})/P_{crystal}] \times 100$. R_x is the *bcp* distance from the *X* atom, while ε is the bond ellipticity, $\varepsilon = (\lambda_1/\lambda_2) - 1$.

less polar interactions since these may be more easily polarized by the crystal field. Displacements are such as to decrease the size of hydrogen atoms and make them more positively charged. In fact, all heavy atoms increase their basin electron population in the crystal by about 0.1 e, while the H atoms have their population correspondingly decreased. The net result is a more polarized molecule, yielding a molecular dipole moment enhancement of about 37%.¹³ This has been shown to be a common behaviour for several H-bonded molecular crystals, as summarized in Ref. [8] and discussed later on in this review for the case of the weak CH···O bonds.

The classification based on the adimensional $|V_b|/G_b$ ratio

Espinosa, Alkorta, Elguero and Molins have recently reexamined [93] the dichotomous classification of bonding yielded by the sign of the Laplacian at bcp, with the aim of identifying a transit region associated to incomplete or incipient covalent bond formation. Their analysis refers to the $H \cdots F$ interaction in a series of 79 neutral, positively and negatively charged $X - H \cdots F - Y$ gas-phase systems with $H \cdots F$ distances d ranging from 0.8 to 2.5 Å. These complexes are known to exhibit a wide variety of strengths, so enabling the study of bcp properties over a nearly complete range of interactions. By analysing the dimensionless $|V_h|/G_h$ ratio as a function of d, Espinosa et al. [93] identified (Table 4, middle) three characteristic bonding regimes: (i) a pure closed-shell (CS) interaction region, with $|V_b|/G_b < 1$ and hence positive $\nabla^2 \varrho_b$; (ii) a pure shared-shell (SS) interaction region with $|V_b|/G_b > 2$ and thus negative $\nabla^2 \rho_b$; and *(iii)* an intermediate *transit* region, associated to the formation of the H-F bonding molecular orbital, and characterized by a $|V_b|/G_b$ ratio between 1 and 2, implying positive $\nabla^2 \rho_b$ values. By introduc-

ties upon crystallization can be found in Ref. [34].

ing the electronic energy density¹⁴ [94] at the bcp, $H_b = V_b + G_b$, the transit region is characterized by negative H_b values as does the SS region. The transit region has an upper $H_b = 0$ limit, defining the boundary with the CS region, and a lower $\nabla^2 \varrho_b = 0$ limit marking its boundary with the SS region. It is worth noting that long time ago, Cremer and Kraka [94] already suggested that negative H_b values should be considered as a sign of covalency. The H_b values were then put by Espinosa *et al.* [93] on an absolute footing, by defining H_b/ϱ_b as a bond degree (BD) parameter (Table 4, middle). This parameter expresses the total energy per electron at *bcp* and exhibits a monotonic behaviour against d. The BD is negative inside the SS and the transit region, and the greater is its magnitude, the more covalent and stronger is the bond. Conversely, the BD is positive in the CS region and the larger is its value, the more closed-shell and weaker in nature is the interaction. For these reasons, the BD has been termed softening degree (SD) in the CS regions and covalence degree (CD) in both SS and transit regions [93].

The classification proposed by Espinosa et al. (Table 4, middle) has the merit of identifying precise d intervals for given bonding regimes. The transit region should be definable for any kind of interaction, since one expects the $\nabla^2 \varrho_b$ and thus the $|V_b|/G_b$ values monotonically decreasing and respectively increasing with decrease in d over a large d interval (see e.g. ref. 56). However, to be rigorous, the transit region has thus far been proved to correspond to the bonding molecular orbital formation only for the $H \cdots F$ interaction. The interval where this association takes place could be more or less displaced towards the SS or the CS regions, according to the nature of the interacting atomic pair. One anticipates that the above correspondence should hold true for chemically related interactions like the NH \cdots O, OH \cdots O and CH \cdots O hydrogen bonds.

Use of Espinosa's et al. approach [93] for classifying the nature of metal-metal bond in crystals, has been recently proposed. Gervasio et al. [95] used the available information from literature to plot the BD parameters versus the $|V_b|/G_b$ ratios for the metal-metal bond in metals (theoretical data only) and in organometallic complexes (both experimental and theoretical data). Interestingly, for both kinds of systems the metal-metal bonds were all found to lie in the transit region and to span a narrow range of CD values. According to Espinosa's classification, the metal-metal bond is thus typically different from a pure covalent and a pure closed-shell bond. However, the association of the transit region with that where the bonding molecular orbital is forming is to be verified and not taken automatically for granted for this kind of interactions also. Studies of the metal-metal bond, using the

¹⁴ The electronic energy density, when integrated over the whole space, yields the total electronic energy of a system, which equals the total molecular energy when there are no forces acting on any of the nuclei in the system. In the following, $H(\mathbf{r})$ will be simply referred to as the energy density. $H(\mathbf{r})$ may exhibit both negative and positive values, with positive values indicating a point wherein the potential energy, while stabilizing, is locally dominated by a larger kinetic energy.

Electron Localization Function, provide further insight on the peculiar partial "covalency" features of this bond (*see infra*).

The classifications introduced so far relate the bond nature to bcp properties, with the advantage of being rather simple and the drawback of emphasizing the role of one spatial point only. Mori-Sánchez, Pendás, Luanã [96] and Macchi and Sironi [97] have proposed classifications of bonding that, although being very different in spirit between each other, are both placing the bcp properties on a less dominant role.

The classification of bonding in solids based on dimensionless indices reflecting the whole EDD

The simpler to use is that of Mori-Sánchez et al. [96] that explicitly focus on bonding in solids and deliberately employs classifying indices that are obtainable from $\rho(\mathbf{r})$ only. It may be so applied directly to either experimental or theoretical densities. Two others features characterize the three proposed classifying indices, namely to be dimensionless and to reflect the whole 3D distribution of the electron density across the crystal. The first index measures the valence electron density *flatness* and it is given by the ratio $f = \rho_c^{\min} / \rho_b^{\max}$, where ρ_c^{\min} is the absolute minimum of the electron density, which necessarily occurs at a cage critical point in a periodic lattice, and ρ_h^{max} is the maximum electron density found among the bcps. In practice, this f index assumes that the most relevant portion of the valence electron density starts at the highest density bcp and ends up at the lowest density cage critical point. The index separates metals, having a large f value, from non metals with f approaching zero. Indeed, a flat electron density throughout the valence region has been early recognized as one of the most characteristic features of metals and it is at the basis of the ability of the crude Drude-Sommerfeld electron gas model in accounting for the electric and heat transport properties of metals [98]. Alkaline metals (Li-K) show the highest values of f, 0.89-0.95, followed by the alkaline-earth metals, with f between 0.64 and 0.75 and then by most other metallic elements and alloys with f close to 0.5. Typical semiconductors (GaAs, GaP, etc.) have f values lower than 0.1 as most ionic solids, while molecular crystals exhibit, in general, f values negligibly different from zero. Complex systems are composed by regions exhibiting quite different f values. Gervasio et al. [95] evaluated the flatness index for the orthorhombic and triclinic forms of the $Co_2(CO)_6(\mu-CO)(\mu-C_4O_2H_2)$ transition metal complex [99, 100]. f has a value of 0.97 when computed on the Co-Co-C 3-membered rings of this complex, whereas it is as small as 0.21 when evaluated on the lactonic ring, which has bonds only between C and O atoms. The "metallic" and the "organic" part of the complex are clearly distinguished in terms of their separate *f* values.

As a second independent index, Mori-Sánchez *et al.* [96] introduced an adimensional global measure of the average charge transfer occurring between the atoms forming a crystal. It is defined as

$$c = \frac{1}{N} \sum_{\Omega=1}^{N} \frac{q(\Omega)}{\operatorname{OS}(\Omega)}$$

where $q(\Omega)$ is the net charge of atom Ω , $OS(\Omega)$ is its nominal oxidation state and the sum runs over all atoms forming the unit cell of the crystal. $q(\Omega)$ is obtained by subtracting the basin electron population $N(\Omega)$ from the nuclear charge $Z(\Omega)$, $q(\Omega) = Z(\Omega) - N(\Omega)$. Contrary to other net charge estimates, QTAIMAC charges are known to approach the OS values in most ionic molecules and crystals [13, 37, 41]. Accordingly, each term of the sum yielding the global charge-transfer index c, should provide a faithful measure of the departure of the net charge of a given basin Ω from that anticipated by the ideal ionic model. Each term in the sum will approach 1 in this limit, yielding a global c value close to 1 for an ideal ionic crystal. In reality, one finds values of c around 0.9 for typical ionic crystals, like the alkali halides, simple oxides as MgO and even some nitrides as AlN. Crystals such as zincite and rutile are also found largely ionic with $c \approx 0.75$, while most III–V crystals and nitrides have c ranging in the 0.3-0.6 interval. Covalent compounds and van der Waals molecular solids have much lower c values, while most crystals made of a single element have $OS(\Omega) = q(\Omega) = 0$ and are assigned c = 0 as a default. The case of systems exhibiting maxima in their electron density distribution at positions other than nuclei deserves a special comment. These non-nuclear maxima (NNM) [101], behave as pseudoatoms [102], trapping most of the valence electron density of the metallic atoms, and have been located between two or more nuclei in several alkaline [103, 57, 58] and alkaline-earth metals [62, 53, 104]. These metals have the structure formed by nearly spherical positively charged metallic cores linked through negatively charged pseudoatoms, which completely fill the interstitial space. They appear as prototypical images of the Drude-Sommerfeld model. It is therefore not surprising that these metals show a nonzero charge-transfer c value, with well defined trends within the alkaline (0.83, 0.53, 0.53)0.40 for Li, Na and K), and alkaline-earth metals (0.88, 0.74, and 0.17 for Be, Mg, and Ca, respectively).¹⁵ The values of c in crystals are therefore to be regarded as "a measure of the ability of some elements to lose electrons either to other elements such as in ionic or polar compounds or to the interatomic space such as in the prototypical Drude-Sommerfeld metals" [96]. One should note, however, that the reported trends for c in the alkaline and alkaline-earth metals series is opposite to what expected from the electronegativity scale. As shown by Luaňa et al. [57], the occurrence and extent of NNMs in these series depend heavily on the atomic number, being the lighter elements fare more prone to show them. Moreover, the presence of NNMs is not a necessary condition for metallic behaviour [105] and some of the most characteristic metals, like Al, Cu and Fe, lack any NNMs at normal pressure because their equilibrium interatomic distance is largely exceeding the distance at which they would eventually appear [56, 57]. Inspection of the trend of c with

¹⁵ Although these metals are made of a single element, their net charge is far different from zero because of the presence of pseudoatoms. For calculating c, a value equal to their number of valence electrons (1 and 2 for alkaline and alkaline-earth metals, respectively) is assigned to OS.

increasing pressure, could serve as a measure of a metal's enhanced ability of losing electrons to its interatomic space and of increasing Drude-Sommerfeld-like behaviour upon compression.

The third independent index coined by Mori-Sánchez *et al.* is called the *molecolarity* μ . It is aimed at differentiating the 3D covalent crystals from the molecular crystals, which are both clustered around the covalent corner (*f* and *c* both approaching zero) of the flatness versus charge-transfer diagram. The molecolarity μ is defined as

$$\begin{split} \mu &= (\varrho_b^{\max} - \varrho_b^{\min})/\varrho_b^{\max} \quad \text{if} \quad \nabla^2 \varrho_b^{\max} \cdot \nabla^2 \varrho_b^{\min} < 0 \\ \mu &= 0 \,, \text{ otherwise} \end{split}$$

with $0 \le \mu \le 1$. The prototypical 3D covalent solids, like diamond, are characterized by a network of connected regions of charge concentration ($\nabla^2 \rho < 0$) extending over the whole crystal and hosting all bcps inside. The molecolarity is therefore 0. In contrast, prototypical molecular crystals exhibit not connected regions of charge concentration, associated to covalent bonds within molecules. These regions are then linked together through closed-shell type interactions, having $\nabla^2 \varrho_b > 0$. The molecularity is in this case very close to 1 since the $\nabla^2 \varrho_b^{\text{max}} \cdot \nabla^2 \varrho_b^{\text{min}} < 0$ condition is fulfilled and the intra- and intermolecular interactions have q_b values that may typically differ by one order of magnitude. Compounds with μ values in the range 0.8-1.0 comprise crystal of molecules like N₂, Cl₂ and N₂O₄, but also include ionic crystals with molecular-like anions as NaNO₃, MgCO₃.

More than providing a novel classification for chemical interactions, the three indices f, c, and μ are aimed at classifying a crystal as a whole. Any crystal may be associated to a point on a 3D f-c- μ diagram, which has the shape of a triangular prism, since $\mu + f \leq 1$ (by combining their expressions). Indeed, this diagram may be thought as an electron density-based evolution of the classical van Arkel and Ketelaar classification of binary crystals [106–108], consisting in an ionic-covalent-metallic triangular diagram obtained through electronegativity scales.

Many of the solids that are most interesting from a chemical and materials' point of view have a more complex bonding than the ionic, covalent, metallic and molecular solids prototypes and their position within triangular prism will reflect some average of the bonding types occurring in their crystals. Generally, the approach of Mori-Sánchez et al. has the merit of providing a classification that accounts for more complex intermediate situations. However, in some cases, the set of three indices is not flexible enough to treat even simple situations. One of such cases is graphite, which is described to be a molecular crystal ($\mu \approx 0.99$) because the 2D graphene sheets formed by covalent C-C bonds interact among each other through weak, $\nabla^2 \varrho_b > 0$, closed-shell interactions. It is well known, instead, that graphite is better thought as a 1D molecular crystal and as a 2D covalent crystal with non-negligible 2D semi-metal conducting features (despite a small flatness, f = 0.06). Another kind of problems could arise with crystals of polar molecules, since some of them are known to exhibit positive $\nabla^2 \varrho_b$ values at their intramolecular bonds. This would erroneously place these solids among the 3D covalent crystals, the molecular CO crystal being one of such cases.¹⁶

The classification based on the valence atomic shell and on both local (*bcp*) and integral properties

Analogously to the first two approaches discussed earlier in this paragraph, the bonding classification proposed by Macchi et al. [97, 109] applies to single atom-atom interactions.¹⁷ Yet, it is aimed at extending and adapting to the 'heavy' atoms systems, the bonding topological indices borrowed from the simpler 'light' atoms chemistry.¹⁸ This extension is of relevance to this review, since most interesting crystalline materials are totally made of, or at least contain, heavy atoms. One has to premise that Macchi's et al. classification was admittedly formulated in a narrower area, namely that of metal-ligand and metal-metal bonding in crystals of transition metal carbonyl clusters and dimers. However, many facets behind this classification stand for interactions between heavy atoms in general, and are here outlined to warn the reader against a too simplistic extension of the first two classification schemes reported in Table 4 to this kind of interactions also. Interpretation of bonding is in this case a less straightforward task, one that is currently debated and increasingly investigated [6, 8, 95, 110-112]. Heavy atoms and in particular those giving rise to metals, are characterized by diffuse valence density, causing low electron densities and concentrations in the bonding regions. This generally complies with very low ρ_b values and $\nabla^2 \rho_b$ magnitudes, a fact, which makes the sign of $\nabla^2 \rho_b$ quite indeterminate and the use of $\nabla^2 \varrho_b$ as the only classification index, rather deceiving. This scenario becomes even more complicate for transition metal atoms, which are characterized by the simultaneous involvement in bonding of their diffuse ns and contracted (n-1)d electrons. Furthermore, the oneto-one correspondence of the $\nabla^2 \rho$ distribution with the shell structure of isolated atoms is lost for all the d-block elements [113, 114]. The form of the Laplacian for second-row and third row elements reflects the shell structure of an atom by exhibiting a corresponding number of pairs of spherical shells of alternating charge concentration and charge depletion [13]. Instead, from Sc to Ge, the N shell becomes indistinguishable from the M shell, and the corresponding regions of charge depletion and concentration are missing. M and N shells separate again from As up to Kr, but the sign of the Laplacian at the outermost minimum is found to be positive, rather than negative as for the other minima. Similar trends were observed for the successive rows, with five being the number of maximum distinguishable shells [113]. In practice, for most heavy atoms, either the last atomic shell is not resolved or, when

¹⁶ I was made aware of this problem by Dr. Piero Macchi.

 $^{^{17}}$ Data reported in this paragraph, and related to Ref. [97, 109], were taken only from Ref. [97], where few errors in the calculations of the properties from the multipolar model have been suitably corrected (see footnote 4 of Ref. [97]).

¹⁸ Ref. [109] defines as heavy atoms the atoms having more than three atomic shells, i.e from K atom onwards.

Table 6. Comparison of metal-metal and me-
tal-ligand bond properties with corresponding
properties for some prototype bonding inter-
actions. a, b, c

Bond	Q_b	$ abla^2 \varrho_b$	H_b/ϱ_b	G_b/ϱ_b	$\oint_{AB} \varrho(\mathbf{r}_s) \mathrm{d}\mathbf{r}_s$	$\delta(A,B)$
H ₃ C-CH ₃	0.241	-0.566	-0.844	0.256	2.16	1.01
HC≡CH	0.394	-1.124	-1.425	0.711	3.70	2.85
C≡O	0.473	0.842	-1.759	2.203	3.17	1.80
Na-F	0.043	0.358	0.288	1.785	0.46	0.27
Na-Na	0.008	-0.002	-0.160	0.080	0.50	1.00
Ne-Ne	0.002	0.015	0.593	1.514	0.02	0.002
Co-Co	0.034	0.001	-0.30	0.31	1.56	0.47
Co-C	0.145	0.535	-0.38	1.31	2.21	1.06

a: Data from Ref. [97], calculated at QCISD (quadratic configuration interaction using single and double excitations) level.

b: All quantities in atomic units.

c: local and integral properties, according to the bond classification approach proposed in Ref. [97] and Ref. [109] and listed in Table 4 (bottom part), are reported.



Fig. 3. Evolution of bonding properties along the terminal-to-bridging CO reaction path in the metal carbonyl cluster $[FeCo(CO)_8]^-$. The reaction coordinate is taken as the Fe–Co–C₁ angle α . The intervals of existence of the terminal ($Co-C_1$ bonding), the asymmetrically bridged and the symmetrically bridged coordination modes are shown. The minimum energy geometry occurs at $\alpha = 56^{\circ}$. By decreasing α from 90° down to the value ($\alpha = 49^{\circ}$) at which a symmetry trically bridged conformation is attained, a Fe-C1 bond path and a Fe–Co–C₁ ring appear at $\alpha \approx 70^{\circ}$. The ring cp then disappears at $\alpha = 64^{\circ}$ and the Co–Fe bond breaks. (a) delocalization indices δ for the relevant pairwise interactions. $\Sigma \delta_{Me\cdots C}$ represents the sum of all the metal-proximal carbonyl delocalization indices other than $\delta_{\text{Fe}\cdots\text{C1}}$ and $\delta_{Co\cdots C1}$. Regardless of the structural discontinuities along the bond path, all δ values exhibit smooth trends. The summation of $\Sigma \delta_{Me...C}$ with the delocalization indices involving the two metal atoms remains almost constant to 2.0 electron pairs throughout the whole reaction path. (b) electron density at the *bcp*, ρ_b , for the relevant pairwise interactions. When a *bcp* is missing (dashed line), the ρ_b value refers to the electron density at the internuclear axis midpoint. (Adjusted from Fig. 7 and Fig. 9 with permission from Ref. [121], Macchi, P.; Garlaschelli, L.; Sironi, A., J. Am. Chem. Soc. 124 (2002) 14173-14184. Copyright 2002 American Chemical Society).

it is not so, it lacks of any charge concentration region, being $\nabla^2 \rho$ always positive there. One must therefore be extremely cautious in applying to heavy atoms the simple criterion of positive $\nabla^2 \rho_b$, as a clear-cut sign of a closedshell interaction.

In keeping with this and with the general low ρ and $\nabla^2 \rho$ values in the bonding regions, Macchi *et al.* [97, 109] have proposed that other clues of bonding besides the properties at *bcps* be considered in these cases (see Table 4, bottom). Integrated properties within atomic basins and on interatomic surfaces, as well as the analysis of Laplacian distribution along the bond path, help in disclosing these additional bonding signs. One of the most interesting clue is the *delocalization index* for a pair of atoms, $\delta(A, B)$, which yields the number of pairs of electrons that are exchanged or shared between them and it so provides a physical measure of a property that classical models of bonding associate with covalency. It was introduced long time ago by Bader and Stephens [115] and resumed later on by Ponec and Uhlik [20], Fradera et al. [20], Bochicchio et al. [22] and Ángyán et al. [116]. It is the integral over two atomic basins of the so-called exchange part of the pair density [117], the integration of this same density over a single atomic basin A determining its localization index $\delta(A)$, i.e. the number of electron pairs localised inside an atomic basin [21, 118]. The increasing interatomic charge transfer in the progression of bonding from shared to polar to ionic is accompanied by an increased localization of electrons within atomic basins and as a result $\delta(A, B)$ is found to decrease, while $\delta(A)$ and $\delta(B)$ both increase along this bonding sequence. The sum of localization and half of the delocalization indices equals the number of electrons in a system $\left(N = \sum_{A} \left[\delta(A) + \sum_{B \neq A} \delta(A, B)/2\right]\right)$ and thus, in

the ionic limit, $\delta(A)$ and $\delta(B)$ have to approach the corresponding basin electron populations N(A) and N(B). Table 6 reports $\delta(A, B)$ values for some prototypical systems to be compared with those (Co–Co and Co–C) typical for metal-metal and metal-ligand interactions in crystals of metallorganic compounds.¹⁹ These indices qualitatively

¹⁹ The indices reported in Table 6 have been obtained from correlated calculations which, at variance with Hartree-Fock approach,

agree with those anticipated from Lewis theory for reference systems like ethane and acetilene. They serve to immediately distinguish a typical metal-metal interaction, [Na–Na, δ (Na, Na) = 1], from a pure closed-shell interaction, [Ne–Ne, δ (Ne, Ne) = 0.002], despite their similar low ρ_b and $\nabla^2 \rho_b$ values. Furthermore, $\delta(A, B)$ is found to be pretty close to zero for ionic Na-F, as expected. Interestingly, the C \equiv O bond has a significant δ (C, O) value, despite its large positive $\nabla^2 \rho_b$ value (see *infra*). Yet, $\delta(C, O)$ is reduced to 1.8, respect to the formal bond order of 3, in agreement with the large charge transfer $(1.16 e^{-})$ and reduced covalency of this molecule.²⁰ Similar $\delta(C, O)$ values are found in crystals of transition metal carbonyl clusters [97]. The Co-C bond, even if it shows large positive $\nabla^2 \rho_b$, has more than one shared electron pair, while the Co-Co bond, characterized by vanishing Laplacian, has nearly half of an electron pair shared. These electronsharing features of Na-Na and Co-Co bonds are therefore secreted in the traditional classification based on the $\nabla^2 \rho_b$ sign, but are put to the fore by the H_b/ρ_b ratio (Table 6) and, in particular, by the $\delta(A, B)$ values. It is worth noting that pairs of non linked atoms may also exhibit delocalization indices significantly different from zero [22, 81, 118-120], thus reflecting that exchange "electron communication" [97] or, said in other words, through space electron delocalization,²¹ is taking place to some extent. Electron exchange may be responsible of a significant interatomic interaction, even when a bond path and a virial path, along which the potential energy density is maximally negative, are both absent. Interestingly, the electron pair formally associated to the Co-Co interaction in $Co_2(CO)_8$ may be almost exactly recovered by adding to $\delta(Co, Co)$, the electron pairs being shared between each metal atom and all its vicinal carbonyls through 1,3 Co-C interactions [97].²²

Macchi *et al.* have used the delocalization indices to get insight on how the Me–Me interaction in the crystals of organometallics compounds is affected by the coordination mode of the CO ligands [97, 121]. By analysing the frequency of occurrence of geometries of dimeric and polinuclear species present in the Cambridge Structural Database [122], Macchi *et al.* found no substantial discontinuity between terminal (I) and symmetrical bridging (III) coordination modes [121]. The asymmetric bridging (II) occurs in the 2.0–3.0 Å M···C distance range and, though conformations I and III are reasonably well defined in the correlation plot, a clear distinction between the three bonding modes appears not possible on the basis

of the structure-correlation method only [121]. According to the available theoretical calculations, the molecular graph corresponding to coordination mode I always exhibits a M-M bond path, which is instead ever missing in symmetric bridging coordination III and either present or missing in coordination mode II [97]. To shed further light on the continuity/discontinuity features of the Me $-(\cdots)$ Me and Me $-(\cdots)$ C interactions in the crystals of these transition metal carbonyl clusters, Macchi et al. analysed theoretically [121] the evolution of the delocalisation indices and of other bonding properties along the terminal-to-bridging CO reaction path for the gas-phase compound $[FeCo(CO)_8]^-$. Macchi *et al.* choose the Fe-Co-C₁ angle α as a simplified reaction coordinate, finding a minimum at $\alpha = 56^{\circ}$, with no Fe–Co bond path and an asymmetrically bridged C1O (see Fig. 3 for atomic labeling). The asymmetric bridging coordination mode II found from theory was confirmed by a new structural experimental determination of $[FeCo(CO)_8][N(PPh_3)_2]$, reported in the same study [121]. Fig. 3 displays the theoretical ρ_b and delocalization indices δ as a function of the α angle for the Co-C₁, Co-Fe, and Fe-C₁ interactions, with the ρ_b value being the density value at the internuclear axis midpoint when the *bcp* is missing. By decreasing α from 90° down to the value ($\alpha = 49^{\circ}$) at which the symmetrically bridged conformation III is formed, a $Fe-C_1$ bond path and a Fe–Co–C₁ ring appears at an α angle of about 70°. This ring CP then disappears at $\alpha \leq 64^{\circ}$ and the Co–Fe bond breaks. Despite these structural discontinuities, the delocalization indices for both the Co-Fe and the M-C1 (M = Co, Fe) pair of atoms exhibit a substantial continuity (Fig. 3), with $\delta_{\text{Fe-Co}}$ smootly decaying and $\delta_{\text{Fe-C1}}$ more rapidly growing with the decreasing α angle. The sum of all the other metal-proximal carbonyl delocalization indices, $\Sigma \delta_{M \cdots C}$, stays almost constant. Similarly, the summation of $\Sigma \delta_{M \cdots C}$ with the delocalization indices involving the two metal atoms remains close to 2 electron pairs throughout the whole reaction path, while the ρ value at the Fe-Co bcp and, after the bond rupture, at the Fe-Co midpoint, decreases slowly and smoothly with the decrease of α . When the ring is formed $\rho_b(\text{Fe}-\text{C}_1) < \rho_b(\text{Fe}-\text{Co})$, but $\rho_b(\text{Fe}-\text{C}_1)$ then rapidly increases up to the value of a symmetric bridging coordination, where $\rho_b(\text{Fe}-\text{C}_1)$ $\approx \rho_b (\text{Co}-\text{C}_1)$. Analysis of the trend of the delocalization indices suggests that the $[Co(CO)_3]$, $[C_1O]$ and $[Fe(CO)_4]^$ fragments are held together, along the whole reaction path, by four electron distributed over three major interactions (Fe-Co, Fe-C₁ and Co-C₁) and over the small metalproximal carbonyl interactions. The discontinuities in the structure are neither mirrored in the delocalization indices nor in the ρ_b values, which both exhibit continuous and generally smooth trends. This is in keeping with the continuum of conformations observed in the solid state for these systems and with their commonly observed carbonyl fluxionality. Analysis of the delocalization indices enables one to characterize the bonding in these systems in terms of a mutual interplay of direct M-M and M-CO and indirect $M \cdots M$ and $M \cdots C$ interactions.

Delocalization indices are very powerful indicators of bonding mechanisms and are clearly grounded on physics. However, the knowledge of the pair distribution function

somewhat reduce the number of electrons that are shared between two atoms respect to the pairing predicted by the Lewis model. At the Hartree Fock level, the Fermi hole is the only source of correlation between the electrons. Introduction of Coulomb correlation, disrupts the sharing of electron pairs between the atoms and its effect is therefore most pronounced for shared interactions [20].

²⁰ The small and reversed ($C^{-}\equiv O^{+}$) dipole moment of CO is the result of the atomic polarization contribution overwhelming that due to charge transfer (see *infra*).

²¹ The 'through bond' and 'through space' terms are here used to distinguish electron delocalisation between linked and not linked atoms.

atoms. ²² This is a case where "bond delocalization" occurs for bonds between "open-shell" heavy atoms (see Table 4, bottom).

[123], or, at the Hartree Fock level, of the one-density matrix is needed for their evaluation.²³ This seriously hampers the use of these indices, since they are neither directly amenable to experimental determination through X-ray elastic diffraction, nor has, to the best of author's knowledge, their evaluation from a thoretical periodic wavefunction been yet implemented. Jayatilaka *et al.* [27, 28, 124] have recently devised an efficient technique to obtain wavefunctions constrained to experiment, which might in the near future represents a viable route to 'experimental' δ estimates.

As clearly shown in Table 6, a direct correlation between the number of shared electron pairs and the value of ρ_b does not subsist. Nor is $\delta(A, B)$ directly related to the bond strength, unless bonds between the same pair of atoms are considered, as in the ethane, ethylene, acetylene series [13]. In general, ρ_b values will depend on the (relative) diffuseness of the valence atomic shells of the two interacting atoms and on the nature of bonding, which is essentially conveyed by the $\delta(A, B)$ value. Keeping with this and with the discussion on the peculiarities of the Laplacian distribution for heavy atoms, atomic interactions were conveniently grouped by Macchi et al. [97, 109] in bonds between light atoms and bonds between heavy atoms (Table 4, bottom). Bonds between a light atom and a heavy atom will generally show intermediate features. Use of the electron density integrated over the whole interatomic surface, $\oint \varrho(\mathbf{r}_s) d\mathbf{r}_s$, counteracts to some extent the size effect on q_b . This surface integral is exceedingly small only for interactions with negligible electron sharing and no charge transfer, like those occurring in noble gases. Instead, for a bond like Co-Co (Table 6), the integral has a value comparable in magnitude to that of covalent bonds between light atoms, despite a ρ_b value that is about one order of magnitude lower than for these cova-

Generally, delocalisation indices are related to bonding mechanisms and only indirectly to the interaction strength. This is, instead, typically revealed by large charge transfer for ionic bonds or large ρ_b and $\oint_{AB} \rho(\mathbf{r}_s) d\mathbf{r}$ values and largely negative H_b , $\nabla^2 \rho_b$ values, for covalent bonds. In a covalent bond between light atoms, the *bcp* usually lies in

lent bonds.

a region where the valence shells of charge concentrations (VSCCs) of the interacting atoms have merged to give a single region of charge concentration. $\nabla^2 \varrho_b$ is highly negative and the *bcp* lies between the two $-\nabla^2 \rho$ VSCC maxima, one for each atom, and generally located along or nearby the bond path. When the bond is highly ionic (e.g. NaF), the cation looses its outermost shell, due to a charge transfer close to the formal value, and the bcp occurs in the valence shell charge depletion of the anion, characterized by flat and positive $\nabla^2 \rho$. For (partially) polar interactions or for bonds between heavy atoms, it is more instructive and meaningful to look at the full profile of $\nabla^2 \rho$ along the bond path. In the case of polar interactions, the VSCC of the more electronegative atom overwhelms progressively the other atom's VSCC, upon bond polarity increase. The bcp shifts towards the less electronegative atom and normally occurs close to the nodal surface $(\nabla^2 \rho = 0)$ that separates the single VSCC lying in the basin of the more electronegative atom from the outermost core depletion shell of the less electronegative atom. In this case, due to the core proximity, both the sign and magnitude of $\nabla^2 q_b$ are very sensitive to very small perturbations and change of sign from negative to positive and vice versa should not be regarded as particularly indicative.

The *bcp* for non polar bonds between heavy atoms has usually a very low $\nabla^2 \varrho_b$ value, as it lies in a region with very flat and low $|\nabla^2 \varrho|$ because of the diffuseness of the valence atomic shells. The sign of $\nabla^2 \varrho$ may be either negative or positive in these cases, depending essentially on whether the two interacting atoms possess or miss their outermost VSCCs, when isolated. This is why non polar bonds between transition metal atoms have generally a small positive Laplacian, despite their partial covalency (see Table 6).

To conclude this paragraph, use of highly positive $\nabla^2 \varrho_b$ value as sign of non-shared bonding character may be truly deceptive, as clearly illustrated by the well-known case of CO [13, 125]. This bond, either in the isolated molecule or in crystals of transition metal carbonyl clusters [97], has generally²⁴ a large positive $\nabla^2 \varrho_b$ value (about 0.8 a.u.). In fact, the bcp lies in the core charge depletion region of the carbon L shell and close to the nodal $\nabla^2 \rho$ surface separating this region from the single VSCC concentration lying in the oxygen basin. $\nabla^2 \rho_b$ is largely positive, although the negative curvatures of the density at *bcps* are almost as large in magnitude as in N_2 . Despite the large charge transfer (typically 1.1-1.3e), there are no indications of ionic-like behaviour in CO. The large $\delta(C, O)$ value and negative density curvatures at *bcp*, and the fact that density contours up to about 0.5 a.u. encompass both nuclei, are indication of a shared interaction, even if incomplete [125]. Indeed, a high charge trans-

²³ The localization index $\delta(A)$ is given by $\delta(A) = |F(A,A)|$, the magnitude of the total correlation contained within the atomic basin of A, while the delocalization index $\delta(A,B)$ is given by $\delta(A,B) = |F(A,B)| + |F(B,A)|$, the sum of magnitudes of the total correlation shared between basins A and B and viceversa. Total correlation includes Fermi and Coulomb correlation, the latter vanishing when integrated over the whole space [13, 20]. Localization and delocalization indices are related to the average number of electron pairs that are, respectively, contained within a basin A or shared between two basins A, B, through the expressions: $D_2(A, A) = \int_A d\mathbf{r}_1 \int_A d\mathbf{r}_2 \varrho(\mathbf{r}_1, \mathbf{r}_2) = [N^2(A) + F(A, A)]/2; D_2(A, B) = \int_A d\mathbf{r}_1 \int_B d\mathbf{r}_2 \varrho(\mathbf{r}_1, \mathbf{r}_2) = [N(A) N(B) + F(A, B)]/2$, where $\varrho_2(\mathbf{r}_1, \mathbf{r}_2)$ is the pair density or the diagonal part of the second-order density matrix [123]. At the Hartree-Fock level, where

the second-order density matrix [123]. At the Hartree-Fock level, where only Fermi correlation is taken into account, F(A, A) and F(A, B) are given by very simple expressions in terms of the spin orbitals' overlaps S_{ij} over basins A and B: F(A, A) = $\sum_{i} \sum_{j} S_{ij}^{2}(A)$ and F(A, B) = $\sum_{i} \sum_{j} S_{ij}(A) S_{ij}(B)$ with *i* and *j* running over the subsets of α or β spin orbitals.

²⁴ Occasionally, experimental, but not theoretical densities, recovered a negative $\nabla^2 \varrho_b$ value in some transition metal carbonyl clusters, as likely the result of an exaggerate shift of the *bcp* towards the oxygen atom, upon metal-ligand bond formation [97, 109]. This provides further evidence to the extreme sensitivity of the $\nabla^2 \varrho_b$ sign for this kind of partially polar interactions and once more suggests a very cautious use of this index alone, when assessing the bond nature.

fer would denote an A-B ionic bond only when sufficient to give atomic distributions approaching the ionic limit, that is $\delta(A)$ and $\delta(B)$ close in values to N(A) and N(B), respectively. As shown earlier, this is what happens in typically ionic compounds like NaF, where, in fact, just a minimal part of the valence density is shared in bonding since only density contours with values less than 0.05 a.u. are found to encompass both nuclei [13, 125]. The small and reversed ($C^{-}\equiv O^{+}$) dipole moment of CO is the result of the atomic polarizations contribution overwhelming that due to charge transfer [13]. Interatomic charge transfer is generally accompanied by polarization of atomic densities in counter direction, a response that is particularly noteworthy for C in CO, due to a large polarization of the remaining carbon valence density into the non bonded region [13, 126]. This yields in turn a pronounced nonbonded charge concentration, one which is associated to the lone pair of C and which accounts for the well reckoned ability of CO to act as ligand in metal carbonyl complexes. The reported case of bonding in CO serves as a warning in using classification schemes on a too strict basis, even for bonds between light atoms. Of late, a paper promoting the Voronoi deformation density atomic charges has claimed that QTAIMAC charges in CO are too large since they "would falsely suggest an ionic bond in CO" [127]. This assertion ignores the physical mechanisms of polarizations accompanying the interatomic charge transfer and determining the peculiar chemistry of CO [125]. Moreover, the claim of too large QTAIMAC charges in CO is manifestly confuted by the evidences on the partial shared character of the CO bond obtained from this same theory.

Strength, weakness and applicability of the discussed bond classifications

At this point, a reader could reasonably ask himself which of the outlined bond classifications should one preferentially adopt within QTAIMAC. Apart from the scheme of Mori-Sanchez et al., which is aimed at classifying the bonding interactions in a crystal as a whole and cannot in general provide information on a single interaction, there is not a simple recipe, if any selection has to be made, on how to choose among the other classification schemes. Any of the three outlined schemes has its strength, weakness and range of applicability, as discussed earlier and summarized below. Moreover, either a suitable mixture of information from the three schemes could be a viable recipe in some case, or the use of different or further criteria could alternatively be proposed. For instance, criteria like the charge transfer between the interacting atoms, the extent and direction of their atomic dipole moments [13], and the quantitative departure from spherical symmetry of their EDDs [13, 63], could be reasonable additional criteria, although of not so simple use when at least one of the interacting atoms is involved in more than one kind of bond. Inspection of which density contours encompass both interacting nuclei is another valuable factor (see the reported case of bonding in CO).

The dichotomous classification based on the sign of the Laplacian has the merit of being rather simple, but it is

often unacceptable if used on an absolute scale, especially when the outermost shell regions of charge depletion and concentration are missing in the atomic Laplacian description of the interacting atoms.²⁵ On the other hand, if applied on a relative scale, the dichotomous classification provides a set of quantitative indices (Table 4, top) whose changes along a series of chemically related compounds allow to neatly establishing whether a given interaction is increasing or decreasing its shared/not-shared character along the series. The same criterion has proved useful to rationalize the variations occurring in bonding upon change of phase [34]. The dichotomous classification does not require knowledge of the system's wavefunction and may be so easily applied both to experimentally and theoretically derived densities. Quantities like G_b , V_b and H_b are in principle computable only from the first order density matrix, but may also be approximately obtained in terms of ϱ_b and $\nabla^2 \varrho_b$ (see *infra*). These approximations are usually poor, but probably acceptable when the dichotomous classification is used on a relative scale.

The scheme proposed by Espinosa *et al.* has the pro of identifying a transit region between the pure closed shell (CS) and the shared shell (SS) regimes. However, the association of the transit region with incomplete or incipient covalent bond formation has been proved only for $H \cdots F$ bonds. The interval where this association takes place could be more or less displaced towards the SS or the CS regions, according to the atomic species of the interacting partners. Use of this classification should be supported with a Natural Bond Order (NBO) analysis [128] or with a calculation of delocalisation indices for bonds other than $H \cdots F$. The proposed bond indices, softness degree and bond degree, are both numerically not bounded, the former from above and the latter from below. They are probably useful only when applied on a relative scale along a series of chemically related systems.

Three important marks set the strength of the classification put forward by Macchi et al. Namely, the use of the localization/delocalisation indices, the combination of *bcp* and atomic properties, and the attention paid to the principal quantum number(s) of the valence shell of the two interacting atoms. Delocalisation indices have a fundamental physical meaning, intimately related to the mechanism of bonding. Their numerical value yields precise information applicable to any bond on an absolute scale, regardless of the nature of bonding and of the atomic species of the interacting atoms. Moreover, delocalisation indices may be evaluated between any pair of atoms, being these linked or not linked by a bond path. Unfortunately, these indices cannot be (generally) computed from experimental densities, nor are they presently computable from periodic wavefunctions. Use of atomic properties, along with the conventional properties at *bcp*, has the important advantage of decreasing the role of one spatial point only in determining the nature of a bond, however representative might this point be. The classification of bonds between a

²⁵ In this case, the change in $\nabla^2 \varrho_b$ with respect to the sum of the isolated atom values at the same distance from the two nuclei as \mathbf{r}_b , can provide some information.

heavy and a light atom deserves special attention, since only the Me–C interaction has been fully explored within the scheme proposed by Macchi *et al.* In general, one has to remember that this scheme has been formulated within the area of metal-ligand and metal-metal bonding in crystals of transition metal carbonyl clusters. Extension to other kind of systems can be certainly done, but it may deserve a proper tuning.

New tools for bond classification

The paragraph on the classification of chemical bonds in crystals is concluded by briefly mentioning two recently proposed methodologies aimed at better elucidating complex bonding patterns, like the multi-center bonds and the multiple (triple, quadruple, etc.) bonds. These tools are the so-called *generalized population analysis*, mainly due to Ponec and Bochicchio [20, 22, 118, 129–133], and the analysis of *domain averaged Fermi holes*, formulated by Ponec *et al.* [112, 134–136]. To the best of the author's knowledge, these methodologies have never been extended and applied to crystalline systems, although the analysis of chemical bonding in crystals could clearly benefit from their use.

The generalized population analysis is based on the idempotency property [123] of SCF density matrix expressed by the identity: $(2^{k-1}) \operatorname{Tr} (PS)^k = N$ where P is the usual density or charge density-bond order matrix [137], S the overlap matrix and N the total number of electrons in the system. Depending on the value of the exponent k, the identity above can be partitioned into mono-, bi- and generally *k*-center contributions: $N = \sum_{A} [\Delta_{A}]_{k} + \sum_{A < B} [\Delta_{AB}]_{k}$ + $\sum_{A < B < C} [\Delta_{ABC}]_{k} + \dots \sum_{A < B < C \dots < K} [\Delta_{ABC \dots K}]_{k}$, to which an appealing physical or chemical meaning can be attributed [118, 131]. For k = 1, the partitioning yields only monoatomic contributions, equal to Mulliken's or to QTAIMAC electron atomic populations, according to whether the generalized population analysis is performed in the framework of a Mulliken-like (basis set based) or of a QTAIMAC (real space based) partitioning of the molecular space. Similarly, for k = 2, the partitioning yields mono- and biatomic contributions corresponding to the well-known Wiberg-Mayer indices [138, 139] or to the QTAIMAC localization and delocalization indices [20-22], depending on the adopted partitioning framework. New descriptors of chemical bonding, the k-center bond indices, come to the play for k > 2. Within the QTAIMAC framework, these indices can be seen as the extension of the delocalization indices to more than two centers [118]. The main advantage of multi-center indices is that they allow for a direct detection of multi-center bonding, whereas the occurrence of non negligible delocalization indices between atoms not linked by a bond path yields only indirect evidences of a non standard bonding pattern. It is worth noting that, regardless of the framework used, the multicenter (k > 2)bond indices were found significantly different from zero only for the systems where the presence of multicenter bonds was expected and only for those $\Delta_{ABC...K}$ contributions involving the centers supposedly involved in the multicenter bonding [22, 118, 130]. The most typical example is that of diborane molecule, where in keeping with the presence of two 3-center bonds in BHB fragments, only two non-negligible 3-center contributions, and involving two BHB fragments, exist for k > 3 [20, 118]. Applications of the generalized population analysis to much more complex bonding situations have been reported [130, 140, 141] including the evidence for a 5-center 4-electron (5c-4e) bonding in a C···H···C ···H···C array [141]. In the case of 3-center bonding, positive values for Δ_{ABC} have been related to 3c-2e bonding, while negative values for this same quantity denote the presence of 3c-4e bonds [142].

The Fermi hole is a 3D distribution function defined relative to an uncorrelated pair density. It determines the *decrease* in the probability of finding an electron with the same spin as some reference electron, relative to a given position of the reference electron [13, 31]. However, fixing the reference electron in a single point is not very compatible with the probabilistic description of the electron distribution. A more realistic picture may be obtained by allowing the reference electron to vary its position within a certain region [134]. The *domain averaged* Fermi hole, $h_{\Omega}(\mathbf{r}_1)$, is thus obtained by averaging the Fermi hole, $h_{\mathbf{r}_2}(\mathbf{r}_1)$, over a given integration domain Ω

$$h_{\Omega}(\mathbf{r}_1) = \int\limits_{\Omega} h_{\mathbf{r}_2}(\mathbf{r}_1) \,\mathrm{d}\mathbf{r}_2$$

with \mathbf{r}_2 representing the position of the reference electron. The analysis of $h_{\Omega}(\mathbf{r}_1)$ is generally performed on the charge-weighted domain averaged Fermi hole $g_{\Omega}(\mathbf{r}_1)$ $= N(\Omega) h_{\Omega}(\mathbf{r}_1)$, where the scaling factor $N(\Omega)$ takes into account that the region Ω is populated not by one but by $N(\Omega)$ electrons [112, 134, 135]. The analysis of $g_{\Omega}(\mathbf{r}_1)$ is generally made by diagonalizing the matrix \mathbf{G}^{Ω} , which represents the hole in the basis of atomic orbitals, $g_{\Omega}(\mathbf{r}_1)$ $=\sum \mathbf{G}_{\mu\nu}^{\Omega}\chi_{\mu}(\mathbf{r}_{1})\chi_{\nu}(\mathbf{r}_{1})$. Since the Fermi holes associated with a region Ω are predominantly localised in the same region, the eigenvalues and eigenvectors resulting from such diagonalisation provide a specific information about the structure of the region. Domains defined according to the QTAIMAC recipe have usually been considered [112, 134, 135]. If the region Ω corresponds to a single atom, the diagonalization of \mathbf{G}^{Ω} provides the information about the actual valence state of the atom in a molecule [134-136, 143]. Similarly, one may analyse a more complex domain formed by the union of several atomic regions [112, 134, 140]. In this case diagonalization of the corresponding hole, yields information about the bonding within the fragment and the interactions this fragment has with the rest of the molecule. Applications of the analysis of domain averaged Fermi holes to the central atom in some "hypervalent" molecules YL_m (Y = P, S, C; L = F or Li, m = 4-6) have been recently reported [135, 136, 140, 143]. These studies were aimed at verifying whether the picture of bonding in these molecules is consistent or not with the traditional hypervalent model assuming the existence of *m* localized (albeit very polar) bonds around the central atom. An interesting application of the domain averaged Fermi hole analysis to more complex domains has been recently reported by Ponec et al. to unravel the nature of multiple metal-metal bonding in transition metal compounds [112]. Systems representative of triple, quadruple and higher than quadruple metal-metal bonding were analysed. Eigenvalues and eigenvectors of G^{Ω} were generally found to be consistent with the expectations based on simple MO models, but the study also revealed important exceptions. For instance, V₂ exhibits a quintuple V–V bond as anticipated from MO models, whereas Mo₂, rather than the expected sextuple Mo–Mo bond, was found to have a quadruple bond only.

Intermolecular and weak interactions in crystals

In addition to providing information on standard chemical bonds, electron distributions in crystals represent an amazing and potentially immense source of information for the weak and/or the less conventional atom-atom interactions. Comparison of bonding indices from this continuously growing data bank is, therefore, a logic investigative endeavour, one which has however been systematically performed only for H-bonds, due to their ubiquitous occurrence and to their dominant role in determining the energy of stabilization of molecular crystals. Bonding indices are not collected for the only sake of internal comparison under (slightly) different crystal or bonding environments, but also in view of relating these indices to other physical properties characterising the bond, like spectroscopic data (IR, NMR, etc.), bond distances, bond energies, etc [144, 145]. Typical of molecular crystals is the recurrent interplay between intermolecular and intramolecular interactions, with properties of both being mutually affected. Topological indices may serve as a tool to detail and quantitatively characterize this interplay, as e.g. performed in recent studies of the matrix effect on intramolecular $C=O\cdots HC$ hydrogen bonds [73] or on molecular dipole moment enhancement [72].

Selected examples from experiment and theory

Topological *bcp* properties are listed in Table 7 for a number of weak to moderate strength atom-atom interactions. This list is clearly not exhaustive, but it serves as an example of the wide class of atomic contacts that have been detected and investigated, either theoretically or experimentally, or, in most cases, by comparing outcomes from the two approaches. Important technological applications are behind the study of most of these interactions. The bonding examples shown in Table 7 are illustrated below.

The first entry in the table concerns the strong and covalent (negative Laplacian) intramolecular Resonance Assisted H-bond in the 8 K structure of benzoylacetone [66]. The structure is characterized by the enol hydrogen having an asymmetric position between the two oxygen atoms²⁶ in the otherwise quite symmetrical molecule. Topological features reveal [146] a rather strong H-bond also in the crystal of potassium hydrogenoxalate (II, Table 7) – the most widely addressed example of $O^{\delta-}H\cdots O^{\delta-}$ interanionic interactions – despite the supposedly repulsive interaction between the two negatively charged oxygen

atoms. Interestingly, gas phase calculations on dimers proved unable to suitably describe this H-bond [146], because the (H-oxalate)⁻ fragment is largely polarized in the crystal by the electrostatic interactions with the K cations and by the formation of two H-bonds per fragment. The third example in Table 7 refers to a comparison between neutral and ionic intramolecular H-bonds in Schiff bases. The topological features confirm the geometrical evidence of the neutral H-bond being stronger than the charge-assisted ones in this class of compounds [74]. The next three entries in Table 7 report results for the weak to the very weak $CH \cdots X$ (X = O, H) H-bonds. Case IV concerns the average properties of the unique 19 intermolecular and 4 intramolecular CH···O bonded interactions found in the 3,4-bis(dimethylamino)-3-cyclobutene-1,2-dione (DMACB) molecular crystal [73]. This system represents an interesting test case for analysing the characteristics of these weak interactions in solids, since no other kind of stronger, and thus successfully competing H-bond, is present. By using the bond path criterion to distinguish between bonded and nonbonded CH···O contacts, it was found [73] that the 23 unique bonded contacts are characterized by a large and nearly constant ($\sim 140^{\circ}$) C-H-O angle, denoting the importance of the electrostatic contribution to such interactions (Fig. 4). Instead, the nonbonded contacts are all more bent and some of them are even folded down below 90°. Interestingly, the $CH \cdots O$ angular distribution observed for $H\!\cdots\!O$ separations greater than 2.7 Å is only apparently isotropic, since such isotropy visibly disappears when the bonded and nonbonded contacts are identified and their angular distribution separately analysed (Fig. 4).



Fig. 4. C–H–O angles (α_{CHO} , deg) vs $d_{H...O}$ distances for CH···O contacts with $d_{H...O}$ below 3 Å in the 3,4-bis(dimethylamino)-3-cy-clobutene-1,2-dione (DMACB) molecular crystal. The CH···O contacts that do not exhibit an associated bond path are enclosed in a square box. This crystal represents a case system for studying the weak CH···O interactions in solids, since no other kind of stronger and thus successfully competing H-bond, are present [73]. The 23 unique bonded contacts are characterized by a large and nearly constant (~140°) C–H–O angle, while the nonbonded contacts are much more bent. If the nonbonded contacts are identified and separately analysed, the CH···O angular distribution remains isotropic even beyond $d_{H...O} > 2.7$ Å. (Reprinted from Fig. 3 with permission from Ref. [73], Gatti, C.; May, E.; Destro, R.; Cargnoni, F., J. Phys. Chem. A106 (2002) 2707–2720. Copyright 2002 American Chemical Society).

 $^{^{26}}$ OH distances are 1.14 and 1.31 Å according to the neutron diffraction study.

Table 7. Bcp data for a number of bonding interactions of moderate to weak strength.^{a, b}

Bond		R_e , Å	Q_b	$ abla^2 \varrho_b$	$\lambda_3/\lambda_{(1, 2) av}$
O−H···O=	Ι	1.329(11)	0.113(4)	-0.187(8)	1.4
$O^{\delta-}H\cdots O^{\delta-}$	II	1.457(2)	0.080(4)	0.084(4)	_
$N^{+}H \cdots O^{-}$	III	1.849(0)	0.019(1)	0.128(4)	_
$NH \cdots O$	III	1.665(0)	0.064(4)	0.207(4)	_
$CH \cdots O$	IV	2.219-2.248	0.018 - 0.017	0.084 - 0.080	5.1-6.7
CH···O	IV	2.351-2.969	0.011-0.003	0.059-0.018	6.3-14.6
$(C-)H\cdots Ph$	V	2.89(7)	0.007(1)	0.017(5)	_
$(C-)H\cdots H(-C)$	VI	2.37(11)	0.008(1)	0.021(5)	_
$C \cdots C$	VII	2.59	0.017(0)	0.063(0)	17.3
$\mathbf{C}\cdots\mathbf{C}$ $(\pi\cdots\pi)$	VIII	3.32-3.55	0.002 - 0.004	0.013-0.023	15.0-25.0
$Cl\cdots Cl$	IX	3.284	0.006	0.008	_
$I \cdots (:N)$	Х	2.780(1)	0.035(0)	0.081(1)	4.9
$Si \cdots (:N)$	XI	1.970	0.074(2)	0.321(1)	5.0
$Co \cdots (:N)$	XII	1.966(0)	0.074(1)	0.502(4)	6.5
C_{β} - H_{β} ···Ti	XIII	2.096(2)	0.025(1)	0.069(0)	_
$Sr \cdots Ge(Ga)$	XIV	3.38(7)	0.012(1)	0.025(5)	5.8(16)
$Ba \cdots Ge(Ga)$	XIV	3.59(13)	0.010(0)	0.013(6)	3.4(17)
Na···NNA	XV	2.70	0.004	0.005	8.0

a: All quantities in atomic units, if not otherwise stated.

b: This footnote details each bond listed in column 1 according to the bond's identifying roman number listed in column 2 of the Table.

I: O-H···O=C intramolecular Resonance Assisted H-bonds in the crystal structure (8 K) of benzoylacetone, Ref. [66].

II: Interanion OH...O interaction in single crystals of potassium hydrogenoxalate, Ref. [146].

III: Ionic vs neutral Intramolecular Hydrogen Bonding in Schiff Bases, Ref. [74].

IV: Intramolecular (first line) and Intermolecular (second line) $C-H\cdots O$ bonds in the crystal structure (20 K) of 3,4-bis(dimethylamino)-3-cyclobutene-1,2-dione, Ref. [73]. The range of bond distances and associated bcp properties for each series of bonds is reported. Only periodic calculations results are listed here.

V: $C-H \cdots Ph$ bonds in the crystal structure of organoammonium tetraphenylborates. The average values for 13 bonds are reported (in parentheses, standard deviations over this series), Ref. [80].

VI: Non polar Dihydrogen bonds in the crystal structure of organoammonium tetraphenylborates. The average values for $15 \text{ H} \cdots \text{H}$ bonds are reported (in parentheses, standard deviations over this series), Ref. [80].

VII: *Bcp* midway between the two C atoms of the carbonyl bridges in the crystal structure (19 K) of *syn*-1,6:8,13 biscarbonyl [14] annulene, Ref. [147].

VIII: $\pi \cdots \pi$ stacking interactions in 2,2'-EthylnylenediBenzeneBoronic Acid, periodic Hartree Fock calculations, Ref. [148]. The range of bond distances and associated *bcp* properties is reported.

IX: Shortest secondary Cl···Cl interaction in the molecular crystal of Chlorine, Ref. [60], experimental results.

X: Halogen bonding (halogen atoms interacting with Lewis Bases) in the crystal structure (90 K) of a donor-acceptor complex, Ref. [151].

XI: Si...(:N) dative bond in a hexacoordinated (hypervalent) Silicon Complex, experimental data from Ref. [155].

XII: Co···(:N) dative bond in Lithium Bis(tetramethylammonium) Hexanitrocobaltate(III), experimental data from Ref. [156].

XIII: β -agostic Me···H interaction in the crystal structure (105 K) of [EtTiCl₃(dmpe)][dmpe = 1,2-bis(dimethylphophino)ethane], Ref. [157].

XIV: Guest-Host metal-framework interactions in type I inorganic clathrates. Data refer to the average properties of the bonds between the Ge(Ga) atoms forming the 24-atom cages and the metal guest encapsulated in each of the six 24-atom cages in the unit cell. Standard deviations, within this series of bonds, in parentheses. Periodic first principle calculations, Ref. [63].

XV: Bond between a Na atom and the non-nuclear attractor (NNA) associated to the F center in sodium electrosodalite. Periodic first principle calculations, Ref. [170].

Case V refers to the average properties for $13 \text{ C}-\text{H}\cdots\text{Ph}$ H-bond interactions in a number of organoammonium tetraphenylborates [80]. The coexistence of these very weak H-bonds with N-H···N, N-H···Ph H-bonds and with almost neutral dihydrogen bonds (DBs) (Case VI, Table 7) in each of the investigated structures, led Robertson *et al.* [80] to establish the relative strength hierarchy of these bonds (N-H···N > N-H···Ph > C-H···Ph > DBs), using a topological classification.²⁷ More importantly, all the 15 recovered DBs were found to be well characterized in terms of stable bond paths and bcps [80], with bond lengths always shorter than the sum of van der Waals radii (2.6 Å), the shortest bond being 2.18 Å and the average bond length amounting to 2.37(11) Å. The bonding contacts exist primarily between phenyl hydrogens of neighbouring B(Ph)4- anions and may be classified essentially as weak van der Waals interactions of induced dipole-induced dipole type since these bonding contacts are recovered even between like or symmetry-related H atoms. Case VI represents an interesting source of DBs of nominally zero or close to zero polarity and should therefore be classified, according to Matta et al. [81], as hydrogen-hydrogen (HH) bonds. Robertson et al. [80] also made the interesting observation that the simultaneous occurrence of intermolecular H-bonds and DBs (or HHs) in the three

²⁷ Assessment of the relative strength of these bonds was given on the basis of the different ϱ_b and $\nabla^2 \varrho_b$ values at similar bonding distances or, viceversa, on the basis of the different bonding distances at which similar ϱ_b and $\nabla^2 \varrho_b$ values occur. This criterion is to be taken with some caution when comparing bonds where one of the two bonded atoms is varying.

structures they examined makes every phenyl hydrogen to be either a donor or an acceptor of a proton in a DB(HH) and (or) in an H-bond. This was considered as an excellent demonstration of the principle of exhaustive bonding in crystal structures containing such kinds of bonds.

The next two entries in Table 7 concern $C \cdots C$ bonded contacts. The well-defined bcp (case VII, Table 7) found between the two C atoms of the carbonyl bridges in the crystal structure of syn-1,6:8,13 biscarbonyl [14] annulene is not an artifact due to a short $C \cdots C$ contact since no bcps were found between closer transannular carbon atoms in the 14 C-membered ring [147]. Rather, it appears related to the preferred (70%) thermal decomposition of the annulene through deoxygenation, which occurs via the intermediate 1,2-dioxetane obtained by chemical bonding the two oxygen and the two carbon atoms of the carbonyl bridges. This example reveals a relationship between charge density topology and incipient molecular reactivity in this compound. The presence of a $C \cdots C$ bond path linking the two C atoms of the carbonyl bridges has also been confirmed by gas-phase calculations, ruling out the hypothesis of a pure solid state effect. The $C \cdots C$ bonded contacts (case VIII, Table 7) related to $\pi \cdots \pi$ stacking interactions in 2,2'-EthylenediBenzeneBoronic acid exhibit [148] among the lowest ϱ_b and the highest $\lambda_3/\lambda_{(1,2)}$ av values in the Table, denoting the weakness and the closedshell nature of these intermolecular contacts. Interactions between parallel π systems are known to play an important role in diverse phenomena, among which the packing of aromatic molecules in crystals [149]. It is therefore gratifying that also these kinds of contacts may be recovered and classified through the EDD topology, and not just through geometrical considerations. These interactions are generally most favourable for an offset π -stacked geometry [150] as it is more a $\pi \cdots \sigma$ rather than a $\pi \cdots \pi$ electron interaction that seems to be preferentially favoured. The data reported in the Table refers to four bcps, one connecting two carbon atoms of two parallel phenyl rings in an offset π -stacked geometry and three associated to interactions between the C atom of a phenyl ring and the C atoms of an alkyne bond [148]. Bond path lengths are between 3.3 and 3.6 Å, which is slightly below the van der Waals separation between two carbon atoms (3.7 Å).

Case IX (Table 7) regards secondary Cl...Cl interactions in solid molecular Chlorine [60]. Each Cl atom is linked by bond paths to 12 other atoms within the crystal. The strongest interaction (Fig. 5) is a shared one (negative $\nabla^2 \rho_b$, large ρ_b) giving a well defined Cl₂ unit, while the remaining bonds (secondary interactions) exhibit much longer bond path lengths and have topological features (ρ_b values 20–40 times smaller and positive $\nabla^2 \varrho_b$ values) representing the opposite extreme of bonding. The shortest among the five unique secondary interactions, the one reported in Table 7 and imparting the characteristic layered structure to the crystal, results from the alignment of a non bonded charge concentration $(\nabla^2 \varrho < 0)$ in the VSCC of one Cl atom with the charge depletion ($\nabla^2 \rho > 0$) in the VSCC of another Cl atom (Fig. 5), [60]. Each atom participates in two of these interactions, as a base in one interaction and as an acid in the other interaction with other Cl atoms in the same layer (Fig. 5). Recently, Tsirelson and



Fig. 5. The Laplacian distribution for the (100) plane of solid chlorine (solid contours denoting negative values for $\nabla^2 \varrho$), [60]. Bond paths and section of the interatomic surfaces on the (100) plane are displayed for one atom in the crystal. Three *bcp* are found in this plane: point *a* defining the intramolecular bond, points *f* and *f'* defining the shortest secondary contact (reported in Table 7) and point *b*, the weaker in-plane interaction. The shortest secondary contact, which imparts the characteristic layered structure to the crystal, results from the alignment of a non bonded charge concentration $(\nabla^2 \varrho > 0)$ in the VSCC of one Cl atom with the charge depletion $(\nabla^2 \varrho < 0)$ in the VSCC of another Cl atom. (Adjusted from Fig. 4 with permission from Ref. 60], Tsirelson, V. G.; Zou, P. F.; Tang, T.-H.; Bader, R. F. W., Acta Cryst. **A51** (1995) 143–153. Copyright 1995 International Union of Crystallography).

Stash [24] reported a similar key-and-lock mechanism for the intermolecular interactions in solid Cl_2 using the ELF.

The next three entries in Table 7 refer to dative bonding interactions between I, Si, Co and the nitrogen atom. Case X represents an example of a donor-acceptor complex [(E)-1,2-Bis(4-pyridyl)ethylene with 1,4-Diiodotetrafluorobenzene] where the donor and the acceptor are connected by intermolecular I...N halogen bonding into infinite 1D chains [151]. The four F atoms on each benzene ring withdraw electronic charge from the iodine atom, which becomes almost neutral and which may then act as the acid moiety in the donor-acceptor complex. Halogen bonds represent valuable synthons to build up supramolecular structures due to their relative strength, high directionality and selectivity [152]. Therefore, the main target of the study by Bianchi et al. [151] was to characterize the nature of the halogen bond in search for analogies and differences with the more conventional H-bonds. Bianchi et al. [151] found that the halogen bond has many features in common with the medium strength H-bond [153], in terms of their similar ρ_b , $\nabla^2 \rho_b$, G_b and V_b values. The electrostatic contribution seems to play the dominant role in the halogen bonding interaction, with a charge transfer between the two moieties of about 0.4e and, surprisingly, with the acidic molecule being the negatively charged fragment due to the presence of the halogen-activat-



Fig. 6. Method-dependency of the β -agostic Ti····H interaction in [EtTiCl₃(dmpe)][dmpe = 1,2-bis(dimethylphophino)ethane] [158]. (a) Theoretical (B3LYP/AE-TZ/BPW91/AE-TZ level) bond paths and $\nabla^2 \rho$ contour map in the Ti– C_{α} – C_{β} – H_{β} plane. Bcps are denoted by filled circles and the ring CP by a black square. (b) As in (a), but at the B3LYP/AE-TZ theoretical level. A slight change in the gas-phase geometry yields to a merging of the ring and Ti···H_{\beta} CPs and to the vanishing of the Ti···H_{\beta} interaction line. (c) Experimental X-ray density, using an updated version [161, 162] of the XD code, see note 97 of Ref. [158]. The Ti···H_{\beta} CP is lacking at variance with what found in Ref. [157], using a previous version [163] of the multipolar code on the same X-ray data set. (Reprinted from Fig. 10 with permission from Ref. [158], Scherer, W.; McGrady, G. S., Angew. Chem. Int. Ed. **43** (2004) 1782–1806. Copyright 2004 Wiley-VCH Verlag).

ing electron-withdrawing F atoms [151]. Bianchi et al. [154] recently reported a study on another halogen-bonded complex where the $I \cdots O$ halogen bonding reveals features basically similar to those found for the $I \cdots N$ halogen bond. Case XI illustrates the use of experimental EDD topology, rather than of the conventional structural approach, to shed light on whether silicon is hypervalent or just highly coordinated in an organosilicon compound having six substituents at the central silicon atom [155]. Difluorobis[N-(dimethylamino)phenylacetimidato-N,O]silicon was chosen as a convenient example, as it contains three different sets of polar silicon-element bonds (Si-E, E = N, O, F). The experiment revealed predominantly ionic bonding and much less covalent contribution than is commonly believed [155]. Analysis of the ρ_b , $\nabla^2 \rho_b$, H_b properties at *bcps* and of the Laplacian distribution along the different bond paths rules out any hypervalency of silicon atom in this compound [155]. In particular, the Si \cdots N bonds (Table 7) are definitely characterized as dative ones, with completely different properties than found in shorter nondative Si-N bonds. Case XII presents [156] the bonding interactions between the central Co atom and the NO₂⁻ ligands in the crystal of an octahedral CoIII complex. The bonding features at *bcps* are those typical of closed-shell interactions and quite similar to those found for the Si ··· N bonds in the previous example. The study revealed [156] a close parallel between the orbital model description of the aspherical distribution of Co 3d-electrons due to the ligand field and the shape of an observable, the experimental and theoretical Laplacian distribution around the Co atom.²⁸

The next entry in Table 7 (case XIII) is related to the Me····H contact in the crystal structure of [EtTiCl₃(dmpe)], [dmpe = 1,2-bis(dimethylphophino)ethane], a prototypical case of a β -agostic interaction [157]. This latter is characterized "by the distortion of an organometallic moiety that brings an appended C–H bond into close proximity with the metal centre" [158]. Agostic interactions are of particular interest in organotransition-metal chemistry, in view

of their potential role in important processes like C-H activation in catalytic reactions. Proper characterization of agostic bonding according to structural or spectroscopic measurements or theoretical studies is often fraught with difficulty [158, 159], and the presence of a Me \cdots H CP had thus been proposed [160] as a convenient, alternative mean of identifying these interactions. A Me · · · H CP had indeed been identified [157] in both the [EtTiCl₃(dmpe)] crystal (X-ray experiment) and molecule (gas-phase ab-initio calculations). However, the bcp and the intervening ring CP inside the TiC_{α}C_{β}H_{β} fragment were found to be proximal and with quite similar electron density values [157]. The negative curvature (λ_2) at the *bcp*, associated to the axis directed at the ring CP, was almost vanishing and the two CPs were close to merge into a singularity in ρ , a sign of an incipient bond catastrophe [13]. Systems with weaker agostic interactions were therefore expected and found to miss the Me···H bcp [158, 159]. Even for case XIII, the *bcp* has now been shown to disappear (Fig. 6) when suitable corrections/updates [161, 162] to the multipolar model program [163] used in the experimental charge density study,²⁹ or changes in the level of theory employed in the theoretical study, are introduced [158]. Therefore, other more robust topological indices, like the analysis of bond ellipticity profile along the $C_{\alpha}-C_{\beta}$ bond, the charge concentrations (CCs) at the carbon atoms which form the alkyl ligand and the ligand-induced CCs (LICCs) at the transition metal center have recently been scrutinized for establishing agostic interactions [158, 159]. These indices provide a general method for quantifying the extent of the hyperconiugative delocalization of the M–C bonding electron density into the C_{α} – C_{β} bonding regions. Indeed, this delocalization has been proved to be the actual driving force behind agostic interactions in the d^0 metal alkyl complexes [158, 159].

 $^{^{28}}$ see discussion of this point in the section entirely devoted to the Laplacian distribution.

²⁹ As detailed in note 97 of Ref. [158], the occurrence of a $Me \cdots H$ CP in the earlier study of [EtTiCl₃(dmpe)] [157] was simply due to a software bug in the official XD-14 release [163]. This bug has now been corrected in the most recent version of the XD code [162].

The next two examples [63] in Table 7 refer to the guest-host chemical interactions in type I inorganic clathrates, $A_8Ga_{16}Ge_{30}$ (A = Sr, Ba). Metal atoms (Sr, Ba) are hosted in oversized 20-atom or 24-atom cages formed by Ge and Ga atoms. These open framework structures have recently aroused a surge of interest as new promising thermoelectric materials [164-166], since the loosely bound heavy metal atoms rattling in the oversized cages may efficiently suppress the material's thermal conductivity without affecting the electron conduction that takes place mostly in the framework. The thermoelectric properties are heavily dependent on the nature of the guest-host interaction. Guest atoms donate electrons to the framework and are almost fully ionized [Sr: +1.67(2); Ba: +1.75 (3)], [63]. The interaction is mostly ionic in nature [63], but the fact that guest atoms have generally been found [167, 168] highly far off the cage center and with displacements and vibrational frequencies differing from guest to guest and, for a given guest, from the large to the small cage, is a sign of partial covalency, however small it might be [63]. Indeed, by relaxing the idealized fully symmetric $Pm\bar{3}n$ structure of the clathrate to the most stable P1 structure [169], the ρ_b value of guest-host interactions increases on average by 50% (Sr) and 16% (Ba), respectively, while the number of bonded interactions is more than halved [63]. The higher rattling frequencies found for A = Srwith respect to A = Ba comply with the higher q_b and $\nabla^2 \varrho_b$ values in the Sr than in the Ba clathrate (Table 7), [63, 168]. Similar reasoning was used to explain why the rattling frequencies of Sr (Ba) are higher (lower) in the large than in the small cages [63, 168].

The last example in Table 7 concerns [170] the bonding interaction between a Na atom and the F center in sodium electrosodalite, Na₈(AlSiO₄)₆. The sodalite framework is a bcc array of β cages consisting of regularly alternating SiO₄ and AlO₄ tetrahedrons (Fig. 7a). To balance the formal negative charge of the framework, each β cage contains three positive sodium atoms. When exposed to sodium vapour the sodalite gradually changes colour, becoming eventually black [171]. The colour change has been ascribed to the formation of F centers in the Na_4^{3+} clusters containing the three existing sodium ions and the excess sodium atom absorbed in each β cage. The resulting structure is named sodium electrosodalite, with the Na₄³⁺ clusters having perfect tetrahedral arrangement and with one unpaired electron per cage in the ferromagnetic phase. The F center is found [170] to manifest itself as a maximum in the electron density at a non-nuclear position [13, 101], that is as a pseudoatom consisting of a nonnuclear attractor (NNA) and of its associated basin (Fig. 7b). The F center thus possesses a separate identity and behaves quantum mechanically as an open system [170]. Each NNA is linked to its 4 neighboring Na atoms and it is located at the center of the Na_4^{3+} clusters. The electron density at the bcp is very low (Table 7). The F center is characterized by an extremely flat electron distribution and contains almost solely unpaired electron density, with 97% of its 0.711e population being spin α electrons. This is pictorially shown in Fig. 7b and 7c, where the total density and the spin density distribution in the sodalite cage are compared.



Fig. 7. F-center in sodium electrosodalite [170]. (a) Schematic drawing of a cubic symmetry $(P\bar{4}3n)$ sodalite framework. The circles correspond to regularly alternating aluminium and silicon atoms bridged by an oxygen atom. The Na₄³⁺ clusters are located inside each β cage, with each unit cell containing two β cages and two unpaired electrons (ferromagnetic phase). The non-nuclear attractors (NNAs) associated to the F centers are located at the center (2a site) of the Na_4^{3+} clusters. (b) Total electron density and (c) spin density distribution in the sodalite cage, in the (1, 1, 0) plane. Contour levels at 2, 4, and $8 \cdot 10^n$ a.u., with *n* ranging from 0 to -3 for the total density, and from 0 to -4 for the spin density. In the spin density the first line is the zero contour. The locations of the Na-NNA and Na-O bcps are denoted by dots. The contour level closest to the NNA has similar shapes and equal value (0.004 a.u) in both maps, since the F centre contains almost solely unpaired electron density. (Modified from Fig. 1 and Fig. 2 with permission from Ref. [170], Madsen, G. K. H.; Gatti, C.; Iversen, B. B.; Damjanovic, L.; Stucky, G. D.; Srdanov, V. I., Phys. Rev. B59 (1999) 12359-12369. Copyright 1999 by the American Physical Society).

The illustration given in this paragraph of few selected examples of weak to moderate strength atom-atom interactions in crystals is followed, in the next paragraph, by the presentation of some of the interesting and controversial aspects related to the QTAIMAC study of these interactions.

Energetics, characterization and relevance of intermolecular interactions in crystals from topological properties

The characterization of the energetic features of intermolecular interaction in crystals, using topological properties at the relevant *bcps*, has in the recent past been introduced [172, 153,173, 93]. It has aroused great interest and it is now routinely applied.

In a study of 83 experimentally observed *bcps* for $X-H\cdots O$ (X = O, N, C) interactions in crystals, Espinosa *et al.* found [172], Eq. 2–3, that G_b and $-V_b$ both follow a negative exponential dependence on the $d_{H\cdots O}$ distance over the examined range of 1.6 Å to 3.0 Å:

$$G_b = 12(2) \cdot 10^3 \exp\left[-2.73(9) \cdot d_{\mathrm{H}\cdots 0}\right],$$
 (2)

$$V_b = -54(18) \cdot 10^3 \exp\left[-3.65(18) \cdot d_{\rm H...0}\right]$$
(3)

with G_b , V_b in kJ/mol per atomic unit volume and $d_{H\cdots O}$ in Å.

A relation between local energy densities at *bcp* and hydrogen bond dissociation energies D_e cannot be rigorously defined. Therefore, Espinosa *et al.* [172] computed *ab initio* D_e values for a series of gas phase hydrogen bond systems, spanning the same $d_{\text{H}\cdots\text{O}}$ range of the experimental data set. The distribution of the D_e data was also found to follow an exponential law, with the exponential factor of the resulting fitting curve, Eq. (4),

$$D_e (\text{kJ/mol}) = 23(5) \cdot 10^3 \exp \left[-3.54(10) \cdot d_{\text{H}\cdots\text{O}}\right]$$
 (4)

being statistically equivalent to the corresponding factor in the potential energy density curve, Eq. (3). By fixing, somewhat arbitrarily, both exponential factors at -3.6, and by fitting only the multiplier factors, the following equations were obtained for D_e and V_b as a function of the $d_{\rm H...O}$ distance:

$$V_b = -50(1.1) \cdot 10^3 \exp\left[-3.6 \cdot d_{\rm H...0}\right],\tag{5}$$

$$D_e (\text{kJ/mol}) = 25.3(6) \cdot 10^3 \exp[-3.6 \cdot d_{\text{H}\cdots\text{O}}].$$
 (6)

Inspection of Eq. 5–6 led Espinosa *et al.* [172] to propose the following approximate relationship between V_b and the hydrogen bond energy, E_{HB} :

$$-D_e \equiv E_{\rm HB} = 0.5 V_b; \tag{7}$$

with the proportionality factor being in volume atomic units.

A. The G_b and V_b values entering in these equations were estimated³⁰ by using Abramov's approach [174], since the rigorous evaluation of these quantities would imply the knowledge of the full one-electron density matrix and not just of its experimentally available diagonal elements, yielding $\rho(\mathbf{r})$. By combining the semiclassical Thomas-Fermi equation [175] with the total form of Kirzhnitz's [176] gradient quantum corrections, Abramov provided [174] a simple approximate expression for directly relating $G(\mathbf{r})$ to $\rho(\mathbf{r})$, as given by Eq. 8 (all quantities in a.u.):

$$G(\mathbf{r}) = ({}^{3}/{}_{10}) (3\pi^{2})^{2/3} \varrho(\mathbf{r})^{5/3} + ({}^{1}/{}_{72}) [\nabla \varrho(\mathbf{r})]^{2}/\varrho(\mathbf{r}) + ({}^{1}/{}_{6}) \nabla^{2} \varrho(\mathbf{r}).$$
(8)

This equation becomes even simpler at *bcp* since $\nabla \rho_b$ vanishes and G_b is thus derived by knowing ρ_b and $\nabla^2 \rho_b$ only. Espinosa *et al.* [172] then obtained V_b values through Eq. 1, assuming that the multipole derived electron distributions obey the local virial theorem, though they do not, of course. Eq. (8) gives a relatively accurate description in the medium-range behaviour ($\sim 1-4$ a.u. from the atomic nucleus) of $G(\mathbf{r})$, which corresponds to the region where most bcps lie. Agreement with the "exact" $G(\mathbf{r})$ values was found to be nearly quantitative [173, 174] for closed-shell interactions, having *bcps* at large distances from nuclei, while the agreement was only qualitative and often rather poor - with differences as large as 300% – for typical shared interactions [174]. These were results from gas-phase calculations. The range of $d_{H...O}$ distances spanned by the Espinosa et al. data set [172], with *bcps* lying 0.5 to 1.2 Å from the H nucleus and 1.0 to 1.6 Å from the O nucleus, should in this case ensure a nearly quantitative reproduction of G_b values by Eq. 8.³¹

B. Since the electron density in intermolecular regions is known to be close to the model density of non-interacting atoms (promolecular or Independent Atom Model, IAM, density) [7], one is wondering whether the promolecular model also fulfils the same correlations found by Espinosa et al. [172] for the experimental data set. Although hydrogen bond interactions have been theoretically proved [177] to yield a small, yet recognizable, effect on the Bragg intensities - with the low angle simulated structure factors being affected to less than 1% – this remains an important question since such a small effect could be hardly recognizable in real space, at hydrogen bond CP. The question has been convincingly addressed by Spackman [178]. Indeed, by using Abramov's approach, the Eq. 1 and a simplified promolecular model given by the sum of the spherical densities of only the H and O atom engaged in the hydrogen bond, Spackman could reproduce the exponential dependence of G_b and V_b on the $d_{H\cdots O}$ distance. This remarkable result is illustrated in Fig. 8a [178]. The

These results (Eqs. (2)–(4) and (7)) are interesting in their own right and of a practical use since, regardless of the nature of X, they disclose general relationships between energetic features and $d_{\text{H}\dots\text{O}}$ distance and enable one to estimate (Eq. (7)) the hydrogen bond energy using only a topological index (V_b) at a single point. However, few important *caveats* should be borne in mind when using Eqs. (2)–(7):

³⁰ Although this is essentially a minor point, it is introduced here because it serves for discussing the other more important caveats.

³¹ In a study of CH···O interactions, Gatti et al. [73] found differences of about 10% for G_b and, consequently, of about 20% for V_b , at $d_{\text{H}...0} = 2.2$ Å, by comparing the exact values obtained from the Hartree-Fock periodic calculation with the G_b and V_b estimates obtained from use of Eq. 8 and Eq. 1. These differences were smaller for the larger $d_{\text{H}...0}$ distances. G_b and V_b estimates were always smaller in magnitude than the "exact" values.



Fig. 8. Properties of hydrogen-bond *bcps* from a simple model of overlapping spherical atoms [178] and from experimental densities. (**a**) Dependence of kinetic energy density, G_b , and potential energy density, V_b (both in kJ mol⁻¹ per a.u. volume), on $d_{H...0}$ distance (Å). Solid lines correspond to results from the simple model and are thus *not* fitted to experimental data. Experimental data are taken from the Espinosa *et al.* [172] data set, supplemented with additional 26 contacts to achieve a better distribution of points in the whole range of $d_{H...0}$ distances considered. (**b**) $\nabla^2 q_b$ vs q_b . Solid lines correspond to results from the simple model and the experimental data (filled squares) are from the same data set used in (a). (Adjusted from Fig. 1 and Fig. 4 with permission from Ref. [178], Spackman, M. A., Chem. Phys. Lett. **301** (1999) 425–429. Copyright 1999 by Elsevier Science B.V.).

Espinosa *et al.* [172] data set is supplemented in this figure with additional 26 contacts so as to have a better distribution of points in the whole range of $d_{\text{H}\dots\text{O}}$ distances considered, while the solid lines correspond to results from the simple model of overlapping spherical atoms and are thus *not* fitted to experimental data. Spackman [178] showed that the two-atom model successfully accounts for

the behaviour of G_b over the entire range of $d_{H...O}$ distances. And it does so even better than the curve (Eq. (2)) fitted on the Espinosa et al. subset of experimental data a curve that systematically underestimates G_b at large distances $(d_{H\dots 0} > 2.2 \text{ Å})$. On the other hand, V_b is generally overestimated in magnitude by the two-atom model, except for separations greater than 2.2 Å where most of the weak $C-H\cdots O$ interactions occur. These contrasting results suggest that G_b is barely affected by redistribution of density due to bonding in the examined range of distances, with its value being basically determined by the exponential decay of the overlap of the H and O undistorted densities. On the other hand, V_b turns out to be overestimated in magnitude because the two-atom model underestimates $\nabla^2 q_b$, except at large distances. This is an expected result. As shown in Fig. 8b, deviation from experiment of the $\nabla^2 q_b$ values obtained with the Spackman's model generally increases with increasing ρ_b and decreasing separation. This is because the bond covalent nature, which cannot be described by the promolecular model, is obviously becoming more and more important with decreasing $d_{H...O}$. Since the promolecular model nicely reproduces G_b and since $\nabla^2 \rho_b$ is everywhere positive in the investigated range of distances, use of Eq. (1) to get V_b yields to too negative values for this quantity. Overall, Spackman's analysis raises the question of whether or not the experimental results at H-bond bcps are providing "more than noise about a trendline determined by the promolecular electron distribution" [178]. At large separations $(d_{\rm H} \dots \rho > 2.2 \text{ Å})$, where ρ_b is close to or below the unavoidable uncertainty $(0.05 \text{ e}\text{\AA}^{-3})$ in the experimental EDDs [6], both V_b and G_b values can be hardly distinguished from those of a promolecular electron distribution. Hence, the relevance of these energetic bonding indices as well as of the $E_{\rm HB}$ values obtained through Eq. (7), appears in this case rather questionable. A similar conclusion is likely to hold for both experimental and theoretical data and if a true IAM model density, instead of the simple two-atom model density, is used in the comparison. This matter has been addressed by Gatti et al. [73] in the earlier mentioned study of the properties of $CH \cdots O$ interactions $(2.2 \le d_{\rm H...0} \le 3.0 \text{ Å})$ in the DMACB molecular crystal. It was found that the IAM densities miss some of the CH...O *bcps* recovered by the corresponding multipolar or theoretical densities.³² However, for those remaining intermolecular CHO contacts, which are identified as bonded in both IAM and crystal densities, the values of V_b and G_h obtained from either density were very much alike. This result prompted Gatti et al. [73] to investigate whether other regions of the crystal space and different topological indices bear more information on these weak intermolecular interactions. As shown in Fig. 9a, the differences between promolecular and crystal densities are at a minimum at intermolecular bcps and in nearby regions, while they are much larger (well) inside the atomic basins

 $^{^{32}}$ Not unexpectedly, the presence or lack of a *bcp* in the IAM density was found to be also related to the kind of adopted spherical atom densities. Eight and only two unique *bcps* were missing, with respect to the experimental and theoretical densities, in their related IAM densities [73].





Fig. 9. (a) Deformation (crystal-promolecular) and (b) interaction (crystal-procrystal) RHF/6–21G densities contour plots in the 3,4bis(dimethylamino)-3-cyclobutene-1,2-dione (DMACB) crystal [73]. Contour levels at \pm (2,4 and 810^{*n*} a.u.) with *n* ranging from 0 to –3. Dotted lines denote negative contour levels. Bond paths from the H-atoms to their acceptor O-atoms (a, b, c: $d_{H...O} = 2.453$, 2.907 and 2.942 Å, respectively) are depicted as heavy lines and the associated *bcps* as dots. Deformation and interaction densities reach their minimal values in magnitude at and nearby the intermolecular *bcps*. (Reprinted from Fig. 8 with permission from Ref. [73], Gatti, C.; May, E.; Destro, R.; Cargnoni, F., J. Phys. Chem. A106 (2002) 2707–2720. Copyright 2002 American Chemical Society).

of the H and O atoms involved in the intermolecular interaction. This observation holds true also when the procrystal density [7], the sum of non-interacting molecular densities, is compared to the crystal density, though the differences between the two densities are in this case much lower, of course (Fig. 9b). The sign of a weak intermolecular interaction, rather than in the local properties at the corresponding *bcp*, has thus to be sought in changes of the integral properties of the atomic basins involved in the bonding. Some time ago, Koch and Popelier [179] proposed a set of criteria to establish and characterize hydrogen bonds, among which the mutual penetration³³ of H and acceptor atoms and the changes in a number of H-atom integral properties upon H-bond formation. These changes include a decrease of the H electron population, atomic moment or dipolar polarization and volume, and an increase of its energy. These criteria, besides that of the existence of the H-bond CP, had been proved in the gasphase for several kinds of hydrogen-bonded systems but had never been applied as a whole to a molecular crystal. Gatti et al. [73] found these criteria to be extremely well fulfilled by the intermolecular CH···O bonded contacts occurring in the DMACB crystal, with just one outlier out of a 114 values data set (6 criteria times 19 intermolecular H-bonds). In particular, the sufficient criterion [179] of mutual penetration of the H and of the O acceptor atoms was satisfied by all interactions. A conclusive take-home message of the study [73] was that the signature of weak intermolecular interactions, like CH ··· O bonds, is actually more evident in the charge rearrangements occurring inside the atomic basins, than it is in the local changes at *bcps*, despite the fact that the former changes were taken with respect to the density of the isolated molecules (Koch's and Popelier's approach) and the latter with respect to that of isolated atoms (IAM density). All that speaks for the efficacy of Koch's and Popelier's criteria to establish H-bonds in molecular crystals, especially when the H-bonds are rather weak. In keeping with this, it is worth mentioning that are the changes in the H-atoms and O-atoms populations upon H-bond formation that give the dominant contribution to the extremely large enhancement (>70%) of the molecular dipole moment found in the crystal [72].

As shown later on in this review, the analysis of the local contributions from the whole space to the density at the bcp of weak intermolecular interactions might represent another interesting way for pinning down the subtle features of these bonding contacts [180].

C. Dissociation and hydrogen-bond energies in eqs. 5 and 7 were evaluated in the gas-phase by assuming the H...O separation as the reaction coordinate for dissociation [172]. This is generally a reasonable approximation for gas-phase systems, but it might be quite far from reality for an H-bond in the crystal where many H-bond interactions take simultaneously place and where H or acceptor atoms are often involved in more than one interaction at a time. The $E_{\rm HB}$ values given by Eq. 7 using $V_{\rm b}$ values in the crystal must thus be taken with caution, since it is a rough approximation in this case to envisage the H-bond energy as essentially depending on a single internuclear distance. This observation is particularly true for the weaker H-bonds and is tied to the more general question of whether intermolecular recognition and cohesion is to be seen more as driven by the atom-atom interactions involving the peripheral atoms of the molecules, or rather in terms of the less localized molecule-molecule or

³³ This is estimated, for either H or O atoms, as the difference between their bonded and nonbonded radius. The bonded radius of *X* (*X* = O, H) is the distance from the nucleus *X* to the H-bond critical point, while the nonbonded radius of *X* is calculated as the distance of its nucleus to the 0.001 a.u. contour in the isolated molecule [13].

even supramolecular interaction processes [181] Quite obviously, the "right" choice between these two contrasting views depend on the nature of the interacting molecules. In the limiting case of molecular recognition and crystal formation among non-polar molecules, it is probably more instructive to seeing the whole molecule that "bonds" to another molecule than discussing and justifying cohesion in terms of thousands of unavoidable weak atom-atom contacts. Formation of bond paths among couples of facing atoms is in this case more likely the result than the cause of molecular interaction. These ideas form the basis of the PIXEL method, due to Gavezzotti [183, 182] and illustrated in this same issue [184]. In the PIXEL approach, the interaction energy between molecules in crystals is explicitly calculated from the whole EDDs of the isolated molecules in terms of electrostatic, polarization, dispersion and repulsion lattice contributions. The more conventional atom-atom potentials approach to the calculation of lattice energies of organic crystal is completely abandoned in the PIXEL method.

Use of topological indices other than the properties at *bcps*, is another way to get over the simple atom-atom view of intermolecular interaction, since a larger portion of the molecular space comes into the play. This is for instance the case of Koch's and Popelier's criteria [179], which take into account the mutual effect of intra- and intermolecular-interactions on the whole EDDs of the H and acceptor atom basins. The Source Function (see *infra*) [82, 83, 180] represents another alternative to characterize how relevant is the contribution to a given intermolecular interaction from any atom within a system.

D. Due to their large uncertainty, the H-bond energy estimates given by Eqs. (6)–(7) are at best only qualitative and the data obtained from these two equations are often seriously inconsistent among each other, especially for the weak H-bonds. Gatti et al. [73] addressed this problem in their study of the CH···O contacts in the DMACB crystal. It was found that estimates obtained through Eq. (7) are about twice as large as the estimates given by Eq. (6) for the interactions falling in the range of distances considered by Espinosa et al. [172] and even more so for longer $H \cdots O$ distances. The discrepancy found at large H...O distances was not surprising since Eqs. (6)-(7) have been fitted to energy and topological data pertaining to shorter CH...O bonds. Less clear was why a significant difference between the two estimates had also been found in the "safer" interval. Possible causes include first the much larger number of, and generally the shorter $H \cdots O$ distances spanned by the $OH \cdots O$ and $NH \cdots O$ interactions in the Espinosa data set, as compared to the CH···O ones. This lack of balance is likely to result in poorer fits for the $CH \cdots O$ bonds. Secondly, use of a common fixed exponential factor in Eqs. (3)-(4) to obtain Eqs. (5)–(6) and then Eq. (7), might not be necessarily warranted. A careful analysis of the causes of discrepancy between estimates given by Eqs. (6) and (7), led Gatti et al. [73] to conclude that the H-bond energies significantly deviate from $0.5V_b$ in the range of the large H···O distances ($2.2 \le d_{H \dots O} \le 3.0$ Å). New relationships, fitted on $CH \cdots O$ bonds only, were proposed in this case.

Overall, Eq. 7 may be viewed as a way of ranking the strength of the hydrogen bonds present in a crystal on a

relative scale, rather than as a tool for providing precise estimates of their energies, no matter how can these be defined. Eqs. (4) and (6) indicate that, at least in the gasphase, the H-bonds energy ordering is already provided by their $d_{H...O}$ distances, without the need of resorting to any topological index. In the solid state, one of the most interesting use of Eqs. (2)-(3), (5), (7) could be that of carefully exploring those cases where similar $d_{\rm H...O}$ distances occur for significantly different V_b (and/or G_b) values or where similar V_b (and/or G_b) values are found for significantly different H-bond geometries. This analysis could reveal subtle features of the H-bonds in crystals that are not simply related to geometrical considerations only: the hydrogen-bond cooperativity effects, the presence of acceptor atoms involved in multiple or competing H-bonds and the crystal-field effects, in general. Ref. [76] presents the case of the 5,6,7-trhydroxyflavone crystal where two OH...O hydrogen bonds were found to exhibit very dissimilar G_b and $\nabla^2 \rho_b$ values, despite their H···O distances differ by only 0.001 Å. The discrepancy was interpreted in terms of the possibility of a resonance-assisted hydrogen bond mechanism in only one of the two bonds.

The Electron Localization Function

The Electron Localization Function (ELF) has proved to yield easily understandable, pictorially informative patterns of the chemical bond and is therefore widely used to describe and visualize bonding in molecules and solids [185, 186]. A precious source on several theoretical and practical aspects of this function is the ELF *official* website [186], where a reasonably updated literature on the development and applications of the ELF can also be found.

Despite the general immediacy of the various graphical representations that have been adopted for the ELF [185, 187–189], the deep physical understanding of this function is not trivial and, for a number of aspects, it is still a matter of continuing research and debate [190, 191]. References [186] and [192] detail common misconceptions on the meaning of the ELF and mistakes on its use, disseminated through the literature.

The first two paragraphs in this section summarize the key points concerning the physical and chemical interpretation of the ELF. A paragraph on the application of this function to the solid state and one on the derivation of "experimental" ELF follow.

The physical interpretation

One of the major concerns with the ELF is what does it physically means [185, 186, 190, 191]. The ELF has several different interpretations, but all of them are indirectly related to the Pauli principle. If a single Slater determinant description is adopted, these interpretations fortunately share a unique mathematical expression for the ELF, while beyond this approximation the definition of the ELF becomes not unique. The two most popular interpretations are here discussed. The ELF function $\eta(\mathbf{r})$ has the general formula

$$\eta(\mathbf{r}) = 1/[1 + \chi(\mathbf{r})^2], \qquad (9)$$

Fig. 10. (a) The Pauli kinetic energy densities t_p (solid line) and t_{ph} (dashed line) for the potassium atom. (b) The ELF for the potassium atom. The capital letters indicate the shells. The atomic shell structure emerges only when t_p is divided by t_{ph} as in the ELF formula. (Reprinted from Fig. 1 and Fig. 2 with permission from Ref. [194], Kohout, M.; Savin, A., J. Comp. Chem. **18** (1997) 1431–1439. Copyright 1997 by John Wiley & Sons, Inc.).

where $\chi(\mathbf{r})$ is the relevant kernel of ELF, while the scaling of η respect to $\chi(\mathbf{r})$ is just a way to bound the η values between 0 and 1 and to give a suitable sharpness in the η regions of most interest.³⁴ In the original formulation of Becke and Edgecombe (BE) [18], the relevant kernel is the ratio $\chi_{\rm BE}(\mathbf{r}) = D(\mathbf{r})/D_h(\mathbf{r})$ where $D(\mathbf{r})$ is the curvature of the spherically averaged same-spin conditional pair density and $D_h(\mathbf{r})$ is the corresponding expression for a uniform electron gas of the same electron density as at the examined point **r**. The same-spin conditional pair density $P_{\rm cond}^{\sigma\sigma}$ (**r**, **r**') expresses the probability of finding one electron at r' when another electron with the same-spin is certainly located at r. To switch from a 6D to a manageable 3D scalar quantity, BE introduced the spherically averaged conditional same spin probability density $P_{\text{cond}}^{\sigma\sigma}$ (**r**, *s*), which gives the probability density to find a same-spin electron at a distance s from r. This probability density may be expressed by Taylor expanding $P_{\text{cond}}^{\sigma\sigma}$ (**r**, *s*) around the reference point \mathbf{r} . For small values of s, the leading term in the expansion is the quadratical term $D(\mathbf{r})$, the curvature of the spherically averaged same-spin conditional pair density, since the first term (s independent) and the linear term both vanish because of the Pauli principle.³⁵ Therefore the smaller is $D(\mathbf{r})$, and hence $P_{\text{cond}}^{\sigma\sigma}(\mathbf{r}, s)$, the larger is the Pauli repulsion between two same-spin electrons and the higher is the electron localization. While $D(\mathbf{r})$ is an actual measure of the electron localization, the ELF kernel $\chi_{BE}(\mathbf{r})$ is *not* because it depends through $D_h(\mathbf{r})$ on the electron density as well (in fact: $D_h(\mathbf{r}) \propto \rho^{\sigma}(\mathbf{r})^{5/3}$). The ELF is only a *relative* measure of the electron localization. The essential quantity for the derivation of the BE ELF formula [18] is the use of the Hartree-Fock samespin pair density to express $D(\mathbf{r})$. Multi-determinantal wavefunctions would yield different ELF expressions, within the BE approach. Starting from quite different premises, Savin et al. [193] showed that for closed-shell systems the ratio $\chi_{\rm S}(\mathbf{r}) = t_p(\mathbf{r})/t_{ph}(\mathbf{r})$ yields an expression that is formally identical with that of $\chi_{BE}(\mathbf{r})$, when this latter is evaluated within the Hartree-Fock approximation.³⁶ In the formula above, $t_p(\mathbf{r})$ is the Pauli kinetic energy, that is the increase in the kinetic energy due to the redistribution of the electrons according to the Pauli principle (or analogously the excess of kinetic energy with respect to a bosonic system) and $t_{ph}(\mathbf{r})$ is the Pauli kinetic energy density of a uniform electron gas of the same electron density. In this interpretation, the ELF is a measure of the influence of Pauli principle, as mirrored in $t_p(\mathbf{r})$, relative to the effect this same principle produces in a uniform electron gas of the same density. Analogously to $\chi_{\rm BE}(\mathbf{r})$, the ELF kernel $\chi_{\rm S}({\bf r})$ depends through $t_{ph}({\bf r})$ on the electron density as well $(t_{ph}(\mathbf{r}) \propto \varrho(\mathbf{r})^{5/3})$ and so, also within this interpretation, the ELF is only a relative measure of the effects due to the Pauli principle. However, the interpretation of the BE ELF formula given by Savin et al. has the great conceptual advantage of being based on the kinetic energy density,³⁷ which may be obtained from the first-order density matrix for any kind of wavefunction. It thus frees the interpretation of the BE ELF formula from its intimate connection with the Hartree Fock method only.

While $D(\mathbf{r})$ and $t_p(\mathbf{r})$, and not $\chi_{BE}(\mathbf{r})$ and $\chi_S(\mathbf{r})$, are both guided by the Pauli principle, they do not reveal the same spatial structuring as does the ELF kernel $\chi(\mathbf{r})$ [194]. It is only the use of the homogeneous electron gas as a reference and thus the somewhat arbitrary division of $D(\mathbf{r})$ and $t_p(\mathbf{r})$ by $D_h(\mathbf{r})$ and $t_{ph}(\mathbf{r})$, respectively, that results in attractive, meaningful chemical pictures. Disappointingly enough, one gains chemical insight when loses a more direct physical significance! For instance, in the case of the potassium and many other atoms, t_p is a monotonically decaying function, but, when divided by t_{ph} , as in the ELF formula, the atomic shell structure in real space visibly emerges (Fig. 10) [194]. It is only the "arbitrary" reference to the homogeneous gas that makes the ELF capable of recognizing the inner-, the outer-core, the valence and the lone pair basins in atoms and the distortions and evolutions exhibited by these basins in molecules and crystals. Indeed, Bader and Heard [85], have claimed that this same reference is the cause of the incomplete homeomorphism found between the ELF (but not $D(\mathbf{r})$) and the Laplacian of the sum of the conditional same-spin pair density for α



³⁴ Due to the mathematical relationship in Eq. 9, $\chi(\mathbf{r})$ and $\eta(\mathbf{r})$ share the same number, space-position and kind of critical points.

³⁵ The conditional probability density to find two same-spin electrons at the same position \mathbf{r} is zero (a minimum) and hence so is its gradient (the linear term in the expansion).

 $^{^{36}}$ This identity holds true for an open shell system also, provided that the kinetic energy densities are computed for corresponding spin parts only (see *infra*).

³⁷ $t_p(\mathbf{r})$ is given by $t_p(\mathbf{r}) = t(\mathbf{r}) - t_b(\mathbf{r})$ where $t(\mathbf{r})$ is the kinetic energy density of the system and t_b is the kinetic energy density for the bosonic system. t_b is expressed in terms of the electron density and its gradient only. $t(\mathbf{r})$ corresponds to $G(\mathbf{r})$ (see earlier, QTAIMAC part).

and β spins, $\theta(\mathbf{r}_1, \mathbf{r}_2) = P_{\text{cond}}^{\alpha \alpha}(\mathbf{r}_1, \mathbf{r}_2) + P_{\text{cond}}^{\beta \beta}(\mathbf{r}_1, \mathbf{r}_2)$. The Laplacian of $\theta(\mathbf{r}_1, \mathbf{r}_2)$, as a function of \mathbf{r}_2 for a fixed position \mathbf{r}_1 of a reference pair, determines the spatial localization of the pair density, which is mirrored in $D(\mathbf{r})$ but not necessarily in the ELF. Instead, the Laplacian of $\theta(\mathbf{r}_1, \mathbf{r}_2)$ exhibits a complete homeomorphism with the Laplacian of the electron density [85]. This homeomorphism approaches an isomorphic mapping of one field onto the other as the reference electron pair becomes increasingly localized to a given region of space [85]. Since the Laplacian of ρ has been generally, but not always, found homeomorphic with the ELF [195, 85], Bader and Heard [85] concluded that the charge concentrations displayed by the Laplacian give a faithful and hence more physical mapping of the regions of partial pair condensation - regions with greater than average probabilities of occupation by a single pair of electrons – than does the ELF.³⁸ Very recently, however, Silvi [190] and Kohout [191, 293] have reestablished to some extent the physical credit of the ELF. These authors have independently shown that the reference to the uniform electron gas made by BE was certainly arbitrary but, inadvertently, compatible with new proposed measures of electron localizability avoiding this reference.39

It is clear that the studies of Silvi and Kohout allow for a deeper physical insight into the meaning of an ELF result than that attainable with BE's or Savin's interpretations. Reference to the adopted interpretive framework, provided this is compatible with the modeling approach followed to compute the ELF, should perhaps become a necessary premise when discussing this function. Few basic points to be considered and/or mistakes to be avoided when adopting BE's or Savin's interpretations are summarized below:

A. The ELF cannot reveal any information about the actual *magnitude* of the local Pauli repulsion, in both interpretations. The $\eta(\mathbf{r})$ value is neither directly related to the value of the Pauli kinetic energy density t_p , nor to the curvature of the spherically averaged pair density. ELF values below 0.5 only mean that the Pauli repulsion in the analyzed region is higher *relative* to that in a uniform gas of the same density, while values above 0.5 mean just the opposite. ELF values close to 1 correspond to a situation where the local Pauli repulsion is very small compared to

that in a uniform gas. Yet, the magnitude of this repulsion does not need to be small at all, as it is the case of the region close to a nucleus where the ELF and the Pauli repulsion both attain high values. Analysis of ELF should be generally done in terms of "high/low η values", not of "high/low electron localization" [186]. When $\eta(\mathbf{r}) = 0.5$, the Pauli repulsion at that position has the same value as in a uniform electron gas of the same density, but the system can not be equated with this gas⁴⁰ nor can it be described as "perfectly delocalized" at that position, despite this has been sometimes reported in the literature [196].⁴¹

B. Low values of $\eta(\mathbf{r})$ bear no direct relation with low values of $\varrho(\mathbf{r})$, although this also has been reported in the literature. For instance, in the outer regions of the alkali metal atoms $\eta(\mathbf{r})$ and $\varrho(\mathbf{r})$ reach asymptotically 1 and 0, respectively. In fact, since $D(\mathbf{r})$ approaches zero, the ELF tends asymptotically to 1 in regions dominated by a *single* orbital containing an unpaired electron (alkali metals) or a couple of perfectly paired electrons [18].

C. In the case of spin-polarized systems, the definition of the ELF is not unique and one should always specify which formula has been used. The BE formulation deals with one spin part only, implying the evaluation of two *separate* $\eta^{\sigma}(\mathbf{r})$ functions, one for each spin ($\sigma = \alpha, \beta$) [18, 197, 198]. When the kinetic energy densities are com-

where k is a constant and where the index i runs over all occupied orbitals φ_i . The magnitude of a given $|\nabla \varphi_i(\mathbf{r})|$ is generally larger the closer the point \mathbf{r} is to an orbital node. Therefore, from a qualitative point of view, ELF assigns high values to a point in space where ρ is high, but with few or no orbital nodes passing through the point. Conversely, ELF assigns lower values to points that either have low ρ or through which enough nodes from one or more occupied orbitals pass so that these nodes can overcome the contribution of the density to the ELF at those points. This interpretation is only qualitative and hides the basic understanding of the ELF as of a relative measure of the electron localization. Rather, it describes electrons as localized at points where there is significant ϱ , but few nodes, from all the occupied orbitals. Interestingly, the approximate ELF kernel used by Burdett and McCormick in their qualitative interpretation of the ELF, yields to an ELF expression formally equal to that of the LOL (see infra). Indeed, the appellative "Localized Orbital Locator, LOL" comes from the ability of this function to single out the regions where a single dominating orbital becomes extremal (i.e. has zero gradient and is far from its nodes), yielding large LOL values. On the other hand, the LOL becomes low when the orbital gradients are sizeable and one is moving from a region dominated by one localized orbital to a region dominated by another localized orbital. In this transit region orbital nodes occur. The Burdett and McCormick interpretation of the approximate ELF and the interpretation of the LOL coincide since molecular orbitals may be always transformed to some set of localized orbitals, while leaving the one-electron density matrix, and hence the LOL or the approximate ELF, invariant.

 $^{^{38}}$ This statement is however based on empirical grounds being the result of a series of observations, not of a mathematical proof. 39 Kohout has introduced the Electron Leasting 100 million of the

³⁹ Kohout has introduced the Electron Localizability Indicator (ELI) which is based on a functional of the same-spin electron pair density yielding the average number of same-spin electrons pairs in a region Ω enclosing a *fixed* charge. The larger is this number, the lower is the electron localizability within Ω . In the Hartree-Fock approximation, the Taylor expansion of the Kohout's functional can be related to the BE ELF without using an arbitrary reference to the uniform electron gas.

Silvi has studied several spin-pair compositions, defined as ratios of the same-spin electron pair density to the antiparallel, to the total and to the ideal fully localized pair densities, all these pair densities being integrated in a given region Ω . These ratios are size- dependent, but may be converted into size-independent quantities by studying their asymptotic dependence on the electron population of Ω with decreasing the volume of Ω . A common, approximate expression for these size-independent quantities closely resembles the BE ELF.

 $^{^{40}}$ In the homogeneous electron gas, $\nabla \varrho$ is everywhere zero, whereas, in atoms and molecules, $\nabla \varrho$ is almost everywhere very different from zero.

⁴¹ Burdett and McCormick [196] describe the homogeneous electron gas as the "fully-delocalised reference state" and the ELF value of 0.5 as the value indicating "perfect delocalisation", within the BE interpretation of the ELF. As pointed out by Kohout *et al.* [192], this would lead to the dilemma of how to classify electrons in region with ELF values less than 0.5. Nevertheless, Burdett and McCormick [196] have in the same paper proposed an interesting qualitative interpretation for high/low values of the ELF, based on the nodal properties of the occupied orbital of a system. By assuming that locally the bosonic kinetic energy is negligible with respect to the actual kinetic energy of the system, the ELF kernel is approximated by $\chi \cong k \varrho^{-5/3} \sum |\nabla \varphi_i|^2$



Fig. 11. *F*-centre in sodium electrosodalite [170] (see Fig. 7a for structure). The ELF function in a spin-polarized system: (a) η^{α} and (b) η^{β} : The first dashed contour is the zero contour, and the increase is 0.05 per contour up to 0.45. The first full contour has the value of 0.50 and the increase is 0.05 per contour up to 1.00. (c) $\eta^{\alpha} - \eta^{\beta}$. The first full contour is the zero contour. The increase is 0.05 per contour up to 1 and the first dashed contour is the -1 contour and the increase is 0.05 up to -0.05. (Reprinted from Fig. 4 with permission from Ref. [170], Madsen, G. K. H.; Gatti, C.; Iversen, B. B.; Damjanovic, L.; Stucky, G. D.; Srdanov, V. I., Phys. Rev. **B59** (1999) 12359–12369. Copyright 1999 by the American Physical Society).

puted for corresponding spin parts only, BE's and Savin's interpretations lead to a formally equivalent ELF expression for the open shell systems. For instance, this is the approach coded in the current version of the TOPOND-98 package [199]. On the other hand, Savin's interpretation opens the possibility to define a *single* ELF function for the spin polarized systems. Kohout and Savin (KS) have introduced [197] a spin-polarized ELF formula defined as $\chi_{\mathrm{KS}}(\mathbf{r}) = [t_{p,a}(\mathbf{r}) + t_{p,\beta}(\mathbf{r})]/[t_{ph,a}(\mathbf{r}) + t_{ph,\beta}(\mathbf{r})]$ where the Pauli kinetic energy densities are split into their spin-dependent parts. KS adopted this approach for studying the atomic shell structure for the atoms Li to Sr using a single formula and compared their results with those obtained for each spin separately [197]. Use of two separate $\eta(\mathbf{r})$ functions formula may reveal subtle spin-polarization effects in crystals. Fig. 11 displays $\eta^{\alpha}(\mathbf{r})$ and $\eta^{\beta}(\mathbf{r})$ plots in the (1, 1, 0) plane of the sodium electrosodalite cage, which in the ferromagnetic phase formally contains one unpaired α electron associated to an F-center (see earlier) [170]. The Na-NNA (Non-Nuclear Attractor) electron density bcps lie close to the $0.5\eta^{\alpha}(\mathbf{r})$ contour and, by moving towards the center of the sodium tetrahedron, $\eta^{\alpha}(\mathbf{r})$ increases monotonically up to 1 at the NNA location (Fig. 11a). The Fcenter region is dominated by a single, localized α -spin orbital, yielding a local vanishing of D^a and thus an ELF value close to 1. This is confirmed by Fig. 11b, where on moving from the Na-NNA critical point towards the center of the tetrahedron, $\eta^{\beta}(\mathbf{r})$ decreases monotonically and reaches its minimum value of zero at the NNA position. New features emerge when the difference $[\eta^{\alpha} - \eta^{\beta}]$ is portrayed (Fig. 11c). The plot reveals areas pointing towards the F-center where the β electrons have higher η values than the α electrons. Behind these areas, a contiguous region around the oxygen atoms is formed, where η^{α} is greater than η^{β} . The strong relative localization of α electrons in the *F*-center leads to ripples in the $[\eta^{\alpha} - \eta^{\beta}]$ function. Although related to the mechanism of interactions among the spins of the *F*-center electrons in the crystal, the interpretation of $[\eta^{\alpha} - \eta^{\beta}]$ is somewhat tricky since this function is a difference between two relative quantities.

For the sake of completeness, this paragraph is concluded by mentioning that a thermodynamic interpretation for the ELF has also been reported [200], by expressing the various kinetic energy densities entering in $\chi_{S}(\mathbf{r})$ in terms of their associated local temperatures.

The ELF topology and chemical interpretation

The topological analysis of the ELF is formally similar to that performed on ρ and $\nabla^2 \rho$, being the ELF a continuous and differentiable scalar field in 3D space. In addition, due to their almost complete homeomorphism, the ELF and $\nabla^2 \rho$ share similar topological features and, as a consequence, technical tools of analysis. Contrary to the usual case of the ρ topology, there is generally more than one basin associated to each nucleus and there normally are basins shared between two or more atoms (see *infra*). A basin is the spatial region given by all points whose gradient paths end at the same (3, -3) ELF CP attractor. Division of the 3D space in basin domains - regions where ELF exhibits maxima - characterizes and isolates "pair regions" [185], or regions dominated by a single unpaired electron, within a system [18, 170].42 The occurrence and location of attractors and basins, in molecules and crystals, is related to the shell structure [197] of the constituting atoms and to the deformations of the atomic shell structure due to bonding [185, 192]. As shown in Fig. 10, the ELF for an atom reveals a radial sequence of spherical attractors (ELF maxima), one for each atomic shell, with a spherical repellor (an ELF minimum) between any two consecutive attractors defining the surface (separatrix) separating the atomic shell basins associated to these attractors [197]. At variance with the shell structure obtained with $\nabla^2 \rho$ (see earlier), the electron populations of the ELF atomic shells generally agree with those expected from the Aufbau principle, and especially so for the valence shell where the electron populations are equal within 0.1 electron to the valence number known by chemists [197]. The ELF basins' populations have therefore an important che-

⁴² Keeping in mind, however, all provisos given earlier on the physical interpretation of the ELF. This is why the term "localization" will always appear within quotation marks in the following.





mical significance, despite the ELF basin doesn't have itself, differently from the QTAIMAC basin, a quantum mechanical basis [186]. Upon chemical bonding, the atomic shell basins decompose into several smaller basins, interconnected by separatrices. The topology of the gradient field of the ELF evidences two type of basins, the *core basins* C around nuclei with Z > 2 and the *valence basins* V in the remaining space [201, 188]. Generally, the valence basins closely match the electronic domains defined by Gillespie in the VSEPR model [202, 203] and therefore the ELF gradient field topology provides a reliable mathematical model for Lewis's valence theory [77] as well as for VSEPR. Similar properties are shared by the topology of $\nabla^2 \rho$, at least for light elements [13].

Among the most interesting chemical features of a valence basin in a molecule or a crystal, are its space location and shape [185], and its electron population value and fluctuation [188, 204]. If the valence basins are roughly spherically distributed around the cores, this is a clear sign of either an ionic-like or a van der Waals-like interaction. As expected, the anions show larger deviation from spherical symmetry than the cations. In the NaCl crystal, a region of high localization is found around the anion and no attractors can be found between the Na and Cl atom pairs [185]. Instead, the valence attractors align as expected from the VSEPR or the ligand field theory. The six attractors around the chloride ion are directed precisely between the Na neighbours. When the covalency of a bond is increasing, the migration of the attractor between the interacting centres becomes progressively more evident. Indeed, ELF investigations of the diamond structure for the element carbon, silicon, germanium, and tin show the interesting trend of a reduction of "localization" along the bond accompanied by a continuous increase of "localization" in the interstitial regions (Fig. 12).

The space location and shape of a valence basin is also related to its *synaptic order* [188, 205], which is the number of core basins that have a common separatrix with it.⁴³ Valence basins can be asynaptic, monosynaptic, disynaptic

or polysynaptic and are denoted as V(A, B, C...) where A, B, C... are the atomic labels of the cores to which they are connected. A proton within a valence basin increases its synaptic order by one. Asynaptic basins have synaptic order zero and correspond to unusual chemical entities such as the F-centres in crystals [170] and on surfaces [206]; monosynaptic basins are the signature of lone pairs, disynaptic basins of the two-center bonds and polysynaptic basins of the multicenter bonds. For instance, the water molecule in the gas-phase consists of four valence basins, the two disynaptic basins V(O, H) related to the OH bonds and the two monosynaptic basins V(O) associated to the lone pairs, besides the core basin C(O). This description is complementary to the valence viewpoint, since one is considering the number of centers which are connected to a given valence basin, rather than counting the neighbours of a given atomic centre [205]. The occurrence, the location and the synaptic order of valence basins have proved to be extremely useful tools for distinguishing among several possible bonding patterns in complex crystal structures (see infra) [185, 192, 207-217). The synaptic order of a valence basin allows for a clearcut "chemical" distinction between conventional 2-center-2electron (2c-2e) bonds and more complex bonding patterns, like the 3c-2e bonds [205]. The synaptic order is related to and complements the information provided by the QTAIMAC delocalisation index introduced earlier, whereas the presence of a bond path - although depending on the whole set of interactions within a system - is always topologically associated to a two-body interaction only.44 In this respect, the synaptic order and the delocalisation index (or, even better, the multicenter generalization of this index proposed by Bochicchio et al. [118]) appear as more direct and "useful" indicators of unconventional bonds than is the bond path. For instance, in the ELF picture, the β -agostic interaction is signalled by the occurrence of a trisynaptic basin $V(C_{\beta}, H_{\beta}, Metal)$, that is by a proton embedded in a valence basin already sharing boundaries with two cores [205]. This situation is topologically

⁴³ These core basins must however be surrounded by the same localization domain (*see infra*).

 $^{^{44}}$ The bond path is for construction made of two and only two $\nabla \varrho$ trajectories.

similar to that occurring in diborane and, accordingly, Silvi has proposed to generalize the concept of agostic bond to any bond for which there is a polysynaptic basin involving a proton [205]. In this view, there would be a double agostic bond in diborane with the protonation of two-centre bonds.

It often occurs, especially for systems containing metalmetal interactions, that the ELF values at the attractors of a set of valence basins are hardly distinguishable from the values at the separatrices between the basins themselves [205]. In these cases, rather than considering the individual basins, it is more convenient to take the union of these basins as the most chemically useful entity to discuss bonding, also because the number and synaptic order of the merged basins may strongly depend on the adopted level of calculation [205]. These multi-basins have been called *superbasins* [205] or *basin sets* [192]. For instance, in the [Mo₃S₄Cl₃(PH₃)₆]⁺ cation, a 4-membered trisynaptic superbasin gathering three V(Mo, Mo) disynaptic basins and a trisynaptic V(Mo, Mo, Mo) basin nicely accounts for the 3*c* metal-metal bond in this system [205].

Another convenient concept used in the visualization and analysis of the ELF is that of the *f-localization do*main [201, 218]. This is the region in space bounded by the isosurface $\eta(\mathbf{r}) = f$ and with the restriction that each point inside the domain has $\eta(\mathbf{r}) > f$. An f-domain may have holes to satisfy this restriction (see infra). Three main types of domains can be distinguished according to the nature of the attractors within them. A core domain contains the core attractor(s) of given atoms, a valence domain only valence attractors and a composite domain contains both types of attractors. For any system there exists a low value of f defining a unique composite parent domain. By increasing f, the initial parent domain first splits into core domains and a single valence domain containing all the valence attractors [188, 189]. This valence domain has the shape of a hollowed volume with as many holes as atomic cores in the molecule, and with each hole containing a core domain. An f-localization domain is called *irreducible* if it contains just one attractor, otherwise it is *reducible*; this implies that an irreducible domain is a subset of a basin whereas a reducible one is the union of subsets of different basins. One may order the f values at which the splitting of reducible domains occurs until a final high f value is reached where all domains are irreducible [188, 189]. Ordering these splitting points enables one to build *tree diagrams* reflecting the hierarchy of the basins [188, 189, 205, 219]. The reduction of reducible domains is a powerful method for isolating regions of increasing "localization" and for recognizing chemical subunits - like molecules, functional groups, lone pairs, etc. within a complex system. With little exception, such a use of the *f*-localization domains has been so far exploited in the gas phase only. In the studies of chemical bond in crystals, the *f*-localization domains are normally calculated to simply visualize chemically meaningful regions with "localization" equal to or above a given threshold. Application of tree diagrams to molecular crystals could provide interesting insight on which are and which is the nature of the interactions that really govern the molecular packing in a given crystal. A complementary view to the QTAIMAC

or the PIXEL [184] approaches could be afforded in this way.

The valence basin electron populations are often used to characterize lone pairs and bonds in crystals, but their use deserves some caution. An ELF study of representative conjugated organic molecules has shown that the bond basin population (N_b) is a convenient measure of bond order $(0.5N_b)$, while the relative population fluctuation – the quantum mechanical uncertainty on N_b divided by N_b – serves as a sensitive criterion of electron delocalisation [188]. However, when atoms of differing electronegativity are involved or lone pairs are nearby, this simple picture becomes more complex [220-222]. Chesnut, in a study on gas-phase systems, has proposed to derive the formal bond order of two atoms from a comparison of the valence basin bond populations of the same two atoms in differing states of bond multiplicity [223]. A formal bond order of two is assigned to a reference double bond and the bond orders of the other bonds involving the same pair of atoms are estimated by twice the ratio of their bond populations to that in the reference double bond. The common practice in solid state studies is akin to but simpler than Chesnut's approach. Basin bond populations are generally compared on a relative basis, in series of related systems, and involving even pair of different atoms, as a tool for structural elucidation (bond connectivity) or characterization of the bond nature [185, 224-226].

Shape, volume, and electron population of the valence basins are very much depending on whether the ELF is computed from the total density (all-electron ELF), or from the valence density only (valence-only ELF) [192, 194], or from any other "chemically" convenient subset of orbitals [227]. The same holds true for the value of the ELF within the basins. Earlier applications of the ELF to solid state used valence-only or frozen core approaches [185, 193] and this is still often the case when crystalline systems containing heavy atoms are investigated. Use of the valence-only ELF often affords pictures that apparently convey simpler and more intuitive representations of chemical bonding. However, on the basis of the formula for the ELF, it is not possible [194] to rigorously separate this function into a valence and a core part.45 The valence-only ELF turns out to be similar to the all-electron ELF in the bond region only when in this region the core orbitals are not appreciably contributing to the electron density and to its gradient [194]. This is the case of bonding between light elements, as illustrated in Fig. 12 where the valenceonly ELF for the diamond structure of C, Si, Ge and Sn is compared to the all-electron ELF for the same crystals. For C and Si, ELF undergoes only small changes in the valence region, the only big difference between the total and valence representations being the presence of the core shells in the former and the occurrence of the corresponding holes in the latter [194]. For heavier elements, having d electrons in the outermost shell of the core (Ge and Sn,

⁴⁵ The electron density and the kinetic energy densities can be divided into orbital contributions, but this is not possible for the Pauli kinetic energy because of the term proportional to $(\nabla \varrho)^2/\varrho$. For this same reason, the recently proposed [227] separation of the ELF in a σ and a π contribution in aromatic systems yields $\text{ELF}_{\sigma} + \text{ELF}_{\pi} \neq \text{ELF}_{\text{total}}$.



Fig. 13. ELF for the binary III–V compounds, GaAs and InSb, in the sphalerite structure. The figures in the upper row are computed from the valence density, in the lower row from the total density. (Adjusted from Fig. 13 with permission from Ref. [194], Kohout, M.; Savin, A., J. Comp. Chem. 18 (1997) 1431–1439. Copyright 1997 by John Wiley & Sons, Inc.).

Fig. 12), the *d*-subshell tends to penetrate the valence region and exclusion of this subshell produces values for the ELF that are too high when compared with those obtained from all-electron calculations. Inspection of Fig. 12 reveals that the inclusion of the core density yields a flattening of the ELF in the bond region, with a rather regular localization and a much less high "localization" along the bond axis [194]. Similar changes are found for polar bonds. Figure 13 shows the changes in the ELF portraits upon inclusion of the core for the two binary III-V compounds, GaAs and InSb. The ELF value in the bond region drops from 1 to 0.7 and this area converts from a reasonably localized region along the bond axis to a narrow area bent in the direction of the anion when the core density is also taken into account [194]. This effect of the *d* electrons persists even if only one of the elements involved in the bonding possesses occupied *d*-orbitals [194].

The participation of transition-metal *d* electrons in chemical bonding is accompanied by a significant structuring of the ELF in the outer-core regions [192]. If the occupation of the *d*-subshell is not complete, a significant structuring also occurs in the valence shell. These properties of the ELF have been used to discuss bonding in crystals containing transition-metal atoms [192]. To start with, it is instructive to compare the ELF plots of an early first-row transition element, like the Sc atom $(3s^{2}3p^{6}3d^{1}4s^{2})$, when all 3*d* orbitals are equally occupied (Fig. 14a) and when only the $3d_{xz}$ orbital is occupied (Fig. 14b) [192]. The symmetry breaking due to the occupation of a particular *d* orbital results in a clear structuring of the outer core (M-shell) and of the valence (N-shell) regions (Fig.14b). The incomplete filling of *d*-orbitals yields high ELF val-



Fig. 14. ELF for the Sc $(3s^23p^63d^14s^2)$ and the Ge atom. (a) all the Sc 3d orbitals are equally occupied (0.2e). The ELF has spherical symmetry and nicely mirrors, in real space, the K, L, M and N shells predicted by the Aufbau principle. (b) only the Sc $3d_{xz}$ orbital is occupied (1e). Both the outer-core and valence regions reveal pronounced structuring. Three ELF saddle points are marked: $\eta(r_1)$ connecting two outer core basins; $\eta(r_2)$ between two valence basins; $\eta(r_3)$ connecting a valence and an outer core basin, with $\eta(r_1) > \eta(r_2)$ > $\eta(r_3)$. f-localization domains with $f = \eta(r_1)$ and $f = \eta(r_2)$ would correspond to a single outer core and a single valence superbasin, respectively. An *f*-localization domain with $f = \eta(r_3)$ would unify the outer core and the valence superbasins into one single superbasin. (c) Ge atom: fully occupied 3d orbitals. The ELF scale used in all the diagrams is at the bottom. (Reprinted from Fig. 1 with permission from Ref. [192], Kohout, M.; Wagner, F. R.; Grin, Y., Theor. Chem. Acc. 108 (2002) 150-156. Copyright 2002 by Springer-Verlag Heidelberg).

ues in the outer core region of Sc (Fig. 14a) and in case of uneven *d*-orbitals occupation the ELF still achieves high values in some parts of this region, depending on the occupied *d* orbitals. The maximum of the ELF in the outercore shell basin is known to decrease with the increasing, evenly distributed, occupation of the *d* orbitals [197]. The ELF plot for Ge (Fig. 14c), an atom from the same row of Sc but with a filled 3*d* shell, clearly shows the contraction of the outer core region (M-shell) and the significant decrease of its ELF maximum. We now apply to crystals what we have learnt from the ELF distribution in the free atoms. The iso-structural crystal compounds LaM_2Ge_2 (M = Mn, Fe, Co, Ni, Cu) crystallize in the ThCr₂Si₂ type



Fig. 15. (a) The structure of LaM_2Ge_2 showing half of the crystallographic unit cell along the c direction; the complete unit cell is given by applying the mirror plane located at $z = \frac{1}{2}c$. The yellow 0.77localization domains reveals the characteristic structuring of the outer core regions for M = Mn, Fe, Co, whereas the small light-blue 0.387localization domains enclose the ELF attractors associated to the M-M bond; (b) ELF slice through the planar nets of M = Mn. An ELF attractor is found at the Mn-Mn midpoint. The outer core region ELF maxima point in between the four bonded partners. The corresponding plots for M = Fe, Co exhibit similar topological features. (c) ELF slice through the planar nets of M = Ni. There is no ELF attractor in the valence region and the ELF outer-core region is nearly spherical. The corresponding plot for M = Cu exhibits similar topological features. Same ELF scale as for Fig. 14. (Adjusted from Figs. 7-9 with permission from Ref. [192], Kohout, M.; Wagner, F. R.; Grin, Y., Theor. Chem. Acc. 108 (2002) 150-156. Copyright 2002 by Springer-Verlag Heidelberg).

of structural family and are characterized by planar nets formed by condensed four-membered M_4 rings with quite similar M-M distances ($d_{M-M} = 2.90-2.99$ Å). The question addressed by Kohout *et al.* [192] was if any directed bonding interaction exists between the transition metal ions in these rings. As shown in Fig. 15a, the ELF distribution for M = Mn, Fe and Co exhibits, in the valence region, local maxima between the transition metal atoms, along with a significant structuring of the outer-core regions, which have ELF maxima pointing between the four bonded partners of each M atom. All these features comply with a direct interaction between the transition-metal atoms in these compounds (Fig. 15b for M = Mn). Conversely, neither a valence ELF attractor, nor a significant structuring of the outer core region could be detected for M = Ni and Cu (Fig. 15c, M = Ni), despite M-M distances hardly distinguishable from the M = Mn, Fe, Co case [192]. Lack of these topological elements, rules out any significant directed interaction between nearest-neighbor metal atoms, mediated by d electrons, for M = Ni and Cu. The nearly spherical outer core distribution of ELF around the Ni and Cu centres reveals their ionic nature.

Applications of the ELF to the solid state

Few examples of ELF studies on crystals have already been outlined in the previous paragraph as a convenient way to introduce the chemical interpretation of the ELF. In the following, further applications of the ELF are mentioned for illustrating how this function is typically used for the study of chemical bonding in the solid state.

ELF and QTAIMAC joint studies

Few cases where the ELF and QTAIMAC approaches were combined together are first presented to show how these investigative tools, rather than convey contrasting chemical insights, may often complement each other when properly applied.

Gomes et al. [224] have used ELF and QTAIMAC approaches to study the metal-support interaction on oxide surfaces, taking Pd adsorbed on Mg (001), α -Al₂O₃ (0001) and SiO₂ surfaces as examples of simple ionic, complex ionic and covalent oxide surfaces, respectively. As expected, the nature of bonding of the Pd atom to the oxide substrate is a function of the kind of surface and of the adsorption site. For instance, in the case of Pd on the MgO (001) surface the interaction energy is rather weak if the Pd adsorption occurs above the cationic site, while a moderately large interaction is predicted for adsorption on the basic sites. These energetic differences are consistent with the QTAIMAC and ELF descriptions. For Pd adsorbed on the Mg site, the QTAIMAC finds a very small charge transfer (CT) towards the surface (0.04e), whereas a somewhat larger CT and directed towards the Pd atom is observed when the Pd is adsorbed above the oxygen. The excess charge on Pd (0.19e) comes from the nearest neighbor oxygen atom, whose population is lower than that of the other oxygen atoms by 0.31e. The Pd-Mg and Pd-O *bcp* properties are different, with ρ_b and $\nabla^2 \rho_b$ values being about five times larger for Pd-O (0.081 a.u., 0.376 a.u.) than for Pd-Mg (0.015, 0.068). These values suggest that Pd is weakly bound to the surface when adsorbed on the Mg site, while a somewhat stronger bonding interaction, with an ionic character and an appreciable CT to the adsorbed atom, characterizes the Pd adsorption on the anionic site. As shown in Fig. 16, the two bonding schemes are well differentiated by the ELF. For the case of Pd at the Mg adsorption site, the electron density assigned by QTAIMAC to Pd is entirely located in the ELF core basin, suggesting a [Kr] d^{10} local configuration of Pd. This is revealed by the almost spherical C(Pd) core do-



Fig. 16. The ELF isosurfaces for Pd adsorption on MgO(001). Color code is: magenta (core); red (valence monosynaptic); green (valence polisynaptic). The Pd is the topmost atom in all figures. (a) Pd on Mg site, ELF = 0.75; (b) Pd on the O site, ELF = 0.75. At variance with adsorption on the Mg site, note the distortion from spherical symmetry of the Pd core domain; (c) Pd on the O site, ELF = 0.25. The green Pd valence shell domain, mostly located on Pd, is formed by joining four valence V(Pd, Mg) disynaptic basins. (Reprinted from Fig. 1 with permission from Ref. [224], Gomes, J. R. B.; Illas, F.; Silvi, B., Chem. Phys. Lett. **388** (2004) 132–138. Copyright 2004 by Elsevier B.V.).

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main in the representation of the ELF $\eta = 0.75$ isosurface (Fig. 16a). In the case of Pd adsorption on the oxygen, the Pd core domain has lost the spherical symmetry (Fig. 16b) and a Pd valence shell, formed by 4 disynaptic V(Pd, Mg) basins, surrounds the core with four bulges directed towards the Mg atoms of the surface, as shown by the $\eta = 0.25$ isosurface (Fig. 16c). The C(Pd) population is 42.69, consistent with a core structure dominated by the [Kr] d^6 configuration, while each V(Pd, Mg) basin con-

tains 1.05e. Depletion of charge is observed along the Pd–O line, in accord with the absence of a V(Pd, O) basin, the formation of the 4 V(Pd, Mg) basins, the flow of electronic charge towards Pd, and the facing of two negatively charged (Pd and O) atoms. The valence shell of Pd, the green domain in Fig. 16c, rather than being shared between Pd and the "surface", is very much located on Pd. All this speaks against any significant Pd–Mg covalent interaction. Instead, a visible internal polarization of both



Fig. 17. QTAIMAC and ELF analysis of Pt-Pt bonding interaction in the ground state and in the lowest triplet state of the $[Pt_2(H_2P_2O_5)_4]^{4-}$ ion. (a) $\nabla \rho$ trajectories in the plane defined by Pt1, Pt2 and P6 for the ground state. The bond paths are indicated by heavy lines and the bcps are denoted by filled circles. (b) As in (a) but for the triplet state. A bond path linking the two Pt atoms is present in either electronic states. (c) The ELF isosurfaces $(\eta = 0.815, \text{ gray}; \eta = 0.658, \text{ yellow})$ for the ground state. The two surfaces are shown separately in the upper and lower part of the drawing, for the sake of clarity. (d) The ELF $\eta = 0.30$ isosurface for the triplet state. The Pt-Pt electron pairing region is displayed in solid gray, whereas all other regions of ELF are colored in transparent yellow. (Adjusted from Fig. 7 and 9 with permission from Ref. [228], Novozhilova, I. V.; Volkov, A. V.; Coppens, P., J. Am. Chem. Soc. 125 (2003) 1079-1087. Copyright 2003 American Chemical Society).

the core and the valence of the Pd atom occurs, consistent with the charges on the neighboring ions and a partly ionic description of the metal-support interaction. As found in previous examples, the bond path descriptor is intrinsically unable to reveal this multi-center character of the interaction, if taken alone. The reader is referred to the original paper [224] for the detailed discussion of the other examples of metal-support interactions. The main conclusion is that the presence of chemical bonding on the most energetically favored sites is signaled by the occurrence of polysynaptic basins. Their electron populations are however very low in the case of the two ionic oxides, whereas on the E' center, \equiv Si[•], of the SiO₂ surface a polysynaptic basin with about 2 electrons is observed. The Pdoxide interaction thus exhibits a large variety of bonding schemes whose unraveling greatly benefits from suitably combining the QTAIMAC and ELF topological analyses.

Novozhilova et al. [228] have compared the ELF and QTAIMAC approaches in a joined theoretical (relativistic DFT) and experimental (Time-resolved X-ray and Spectroscopy) study on the excited states of transition metal complexes. Because of their chemical reactivity and their role as intermediates in photochemically induced reactions and electron transfer, a full understanding of the nature of these excited states is an important goal to be reached. In the case of the $[Pt_2(H_2P_2O_5)_4]^{4-}$ ion, both theory and experiment predict a Pt-Pt bond shortening and a slight Pt-Pt lengthening upon excitation to the lowest triplet state. Experimentally, the Pt-Pt bond length decreases by about 0.2 Å, with respect to the ground state (gs) value of 2.92 Å. A bond path between the Pt atoms is found in both the ground and excited state, whereas the ELF topology indicates weak Pt-Pt covalent bonding for the excited state only (Fig. 17). These results are apparently in contrast, but a closer inspection reveals that, presumably, they are more consistent within one another than they appear at a first sight. The topological indices at the bcp for the ground and the excited state ($\varrho_b = 0.035$ and 0.051; $\nabla^2 \varrho_b = 0.033$ and 0.048; $V_b = -0.016$ and -0.032; $H_b = -0.004$ and -0.010; $H_b/\varrho_b = -0.114$ and -0.196, all quantities in a.u.) suggest that both bonds are essentially in the transition regime between a closed-shell interaction and an incipient covalent-bond formation (Table 4), with topological indices in the triplet state being somewhat closer to (weak) covalency than in the gs. Indeed, the bond in the triplet state has V_b and H_b values twice as big as and more significantly different from zero than in the gs. Not surprisingly, the ELF analysis reveals a very small, compact V(Pt-Pt) domain along the Pt-Pt axis in the triplet state and no such a domain in the gs. The "electron pairing" region in the triplet state has a very low ELF maximum ($\eta = 0.33$), which may be attributed either to the lowering of the ELF caused by a nearly filled d-shell [197, 229], and/or to the influence of the two relatively close Pt core regions. The former interpretation would imply a uniform occupation of the 5d orbitals [192], while the vicinity of core regions was proposed to interpret the low ELF value found for the Re-Re bond in the $Re_2(CO)_{10}$ molecule [192]. What it is more important, however, is that, due to its smallness, the V(Pt-Pt) domain should contain a very small number of electrons,

probably much less than one. This basin population was however not reported in the paper. Due to the generally observed homeomorphism between the ELF and $\nabla^2 \rho$, it would be worth investigating whether a $-\nabla^2 \rho$ Laplacian attractor (a local minimum within a positive $\nabla^2 \rho$ region) is present in the triplet state along the Pt-Pt axis and absent in the gs. If so, this result would further reconcile the QTAIMAC and ELF views on the Pt-Pt interaction in the two states. Another point deserves attention. As discussed earlier, the basin domains of the ELF isolate "pair regions", or regions dominated by a singly occupied orbital [18]. Therefore, the occurrence of the V(Pt-Pt) domain could also partly result from the single occupation of the LUMO orbital in the triplet state [228].46 In fact, this orbital has major contributions from the p_z atomic orbitals on the Pt atoms and it is bonding in the Pt-Pt region.

Novozhilova *et al.* [230] also investigated the Rh–Rh interaction in the *gs* and the lowest triplet excited state of the $[Rh_2(1,3-diisocyanopropane)_4]^{2+}$ ion. Analogously to the Pt–Pt case, apparently contrasting QTAIMAC and ELF views were reported in this very interesting study.

Silvi and Gatti have used the ELF and QTAIMAC tools in a study aimed at a direct space representation of the metallic bond [105]. Indeed, the standard description of the bonding in metals relies on the band structure theory and implies, as a necessary but not sufficient condition [231],⁴⁷ the closure of the energetic gap between the valence and conduction bands [232]. This combined energyorbital picture is related to the reciprocal space representation of the crystal and, in the absence of a direct space representation, it becomes uneasy to include the metallic bond in any general chemical theory of the bonding. For instance, Lewis has not considered the metallic bond in his classic textbook [77], while Pauling describes it as a partial covalent bond between nearest neighbor atomic centers [233]. This covalent description, which has been more recently advocated in order to remove the metallic bond from the vocabulary of chemistry [234, 235], raises however the question of the bond (de)localization as well as that of its directionality.⁴⁸ As clearly pointed out by

⁴⁶ The molecular orbital analysis of the gs reveals that the HOMO level is d_{z2} -metal like in character and antibonding in the Pt–Pt region, whereas the LUMO has major contributions from the p_z atomic orbitals on the Pt atoms and is bonding in this region [230]. This is in line with the common interpretation of the Pt–Pt bond shortening as due to an antibonding to weakly bonding transition. The ordering of the orbitals in the excited-state remains the same as in the *gs*. ⁴⁷ Though the closure of the gap between the valence and con-

[&]quot;' Though the closure of the gap between the valence and conduction band is considered as the signature of the conducting state, it has been shown that the insulating state does not require an energy gap (see. Ref. 231). According to W. Kohn "the insulating characteristics are a strict consequence of electronic localization" [231]. In the spirit of Kohn's paper, delocalization means that the wavefunction "breaks up into a sum of functions which are localized in disconnected regions of the many-particle configurational space" [231]. The ELF is another tool enabling to decide if the electrons are localized.

⁴⁸ Anderson, Burdett and Czech (ABC) [234] have presented an interesting analysis which concludes that there is no special type of chemical bonding associated with "metallic bonding". According to ABC, this term should be dropped from the literature, because fully encompassed by molecular orbital and band theory and the broader concept of covalent bonding. The metals would be simply those struc-



Fig. 18. ELF Localization domains for: (a) bcc Li metal, (b) bcc Na metal. Two bounding isosurfaces are drawn in order to show the valence attractors (dark green) and the network of channels (light green) extending throughout the crystal (see text). The two green isosurfaces correspond to *n* values very close to and just little less than the ELF value at the valence attractors and the ELF value at which the irreducible valence domains merge into a single reducible one, respectively. Color code: magenta = core. Green: valence polysynaptic. (Adjusted from Fig. 2 with permission from Ref. [105], Silvi, B.; Gatti, C., J. Phys. Chem. A104 (2000) 947-953. Copyright 2000 American Chemical Society).

Savin et al. [185], the metallic bond is "one of the most homogeneous of all bonding classes with respect to differences in electron localization, but at the same time one of the most complex regarding the variety of bonding forms that are simultaneously present in a structure". Silvi and Gatti [105] performed periodic ab-initio calculations on the bcc lattices of Li, Na, K, V and on the fcc lattices of Al, Ca, Sc and Cu. All systems were found conductors in terms of the closure of the gap between the valence and conduction band. A first conclusion of the study was that the existence of non-nuclear attractors (NNAs) of the electron charge density field, firstly evidenced in lithium clusters [101, 102] and alkali metals [103], is not a prerequisite for metallic behavior. Indeed, NNAs do not occur in V and Cu metals. Secondly, Silvi and Gatti compared the valence localization domains of a typical covalent insulator, like the diamond, with those of the metals they studied, by introducing the concept of localization window. This window is defined as the interval $[\eta(\mathbf{r}_a), \eta(\mathbf{r}_s)]$ between the ELF value, $\eta(\mathbf{r}_a)$, at the valence attractor and that, $\eta(\mathbf{r}_s)$, at which the irreducible valence domains merge into a single reducible one. In the diamond $\eta(\mathbf{r}_a)$ is close to one (0.97) and the localization window is as large as 0.31. In the metals, $\eta(\mathbf{r}_a)$ is typically much lower, close to the homogenous gas value (0.5), and the localization window is generally much smaller than for insulators. For instance, in the Li metal, $\eta(\mathbf{r}_a)$ equals 0.637 and $\eta(\mathbf{r}_s)$ 0.635,

with a localization window as low as 0.002. According to the ELF, a metallic system is thus characterized by a rather low value of the valence attractor and by a narrow localization window, which is the signature of a very large delocalization between the valence basins. A third conclusion of the study concerned the variety of the observed ELF topologies. Because of the flatness of the ELF function in the interstitial valence region,49 the ELF critical points (CPs) are characterized by small eigenvalues in this region and a rather weak perturbation may therefore change both the nature and location of the CPs. Fig. 18a-b displays the localization domains of Li and Na. Two ELF bounding isosurfaces are shown in the figure, corresponding to η values very close to $\eta(\mathbf{r}_a)$ and just little less than $\eta(\mathbf{r}_s)$, respectively. The valence attractors of Li are at the center of the faces of the cube and the valence basins are truncated octahedra sharing the boundaries with six core basins. Their synaptic order is thus six. Conversely, each valence attractor of Li is split into 4 new attractors in Na, with each basin having a synaptic order of 4.50 More importantly, for both metals, the isosurface with η value just little less than $\eta(\mathbf{r}_s)$ marks the boundary of an infinite three-dimensional network of channels within which the localization function is almost constant. As a conclusion, Silvi and Gatti pointed out that the analysis of the ELF provides a picture of the metallic bond generalizing that of Pauling [233]. The metallic bond is to be seen as a partial covalent bond, which is often multicentric and where the adjective "partial", rather than indicating any possible ionic contribution, stands for basin populations that are always very low (typically much less than 1e). This is due to the high coordination of the atoms in the crystal and to the strong Pauli repulsion arising from the cores, which both tend to increase the number of the synaptic order of the valence attractors. The reducible valence localization domain forming an infinite network over the whole crystal

tures possessing partially filled energy bands, without the option of a transformation to a localized (Wannier) representation or, analogously, with the impotence of 3D Peierls distortions to open a gap at the Fermi level, creating an insulator or a semiconductor. Allen and Capitani (AC) [235] have strengthened the conclusions of ABC, using arguments based on the van Arkel-Ketelaar triangles [107, 108]. A referee has pointed out the possible inherent deficiency of the ELF method for describing bonding features in free-electron-like metals and has drawn my attention to these ABC and AC studies, challenging the traditional concept of metallic bond. The description of bonding in metals presented in the following is simply aimed at characterizing the features of electron "localization/delocalization" in these systems, as revealed by the ELF. These features appear indeed peculiar and quite distinct from conventional covalent bonding. Whether these differences justify or not a special category of bonding may be a matter of discussion. Being the ELF a direct space approach to bonding, the main bias one may introduce in the analysis is that related to the translation of the topological features in a "chemical" qualitative language. This may also be a matter of discussion.

⁴⁹ Compare this flatness of the ELF in the interstitial region with the high values for metals of the valence electron density *flatness* index introduced by Mori-Sánchez *et al.* [96] (see earlier).

⁵⁰ Due to the negligible difference between the ELF value of the 4 valence attractors and that of the separatrices between their basins, this is one of those cases (see earlier) where, rather than considering the individual basins, one should take the union of the basins (a superbasin) as the most chemically useful entity.

may be considered as a network of channels through which the electron conduction takes place. An argument in favor of this interpretation is provided by the calculation of anisotropic conductors, such as gallium, for which the channels form parallel 2D networks [105].

The last reported example of a joined QTAIMAC and ELF study concerns the characterization of oxygen vacancies (F centers) in ionic oxides. Using QTAIMAC, Mori-Sánchez et al. [206] found that charged and neutral oxygen vacancies in bulk MgO and on perfect and defective surfaces of MgO are associated to non-nuclear basins. These are chemically bonded to the host lattice and contain most of the charge left by the removed oxygen atoms. The non-nuclear basins were found to behave as coreless or valence-only anions and to share an important number of properties with the host oxides they replace, including basin size, net charge and topology. Analysis of the ELF also showed attractors at the vacancy sites. The η values at the attractors are close to 1, revealing a true Lewis pair and an unpaired electron in the F and F^+ -centre cases, respectively. The irreducible vacancy domain merges with the valence domains of the nearest oxygen atoms to form polyatomic O_n superanions, whose properties depend on the formal charge and the coordination of the vacancy. QTAIMAC and ELF descriptions were found to complement each other and to agree on the fact that oxygen vacancies are not to be seen as vacancies but rather as coreless pseudo-anions.

ELF and chemical bonding in Zintl phases

The ELF is well known for its ability of pictorially visualizing chemist's intuitive ideas of single and multiple bonds as well as non-bonding electron pair in molecules. Because of this, the ELF has been extensively applied to the study of chemical bonding in the Zintl phases, i.e. extended solids where atoms fulfill the valence rules, and in intermetallic compounds where localized electrons predominantly occur in the form of lone pairs and where covalent, ionic and delocalized interactions may simultaneously be present [185, 208]

The structure of phases which are formed by an electropositive metal and a semi-metal of Group 13 to 15 (Zintl phases) can be rationalized by formal transfer of the valence electrons from the electropositive metal to the more electronegative component and applying, as for molecules, valence concepts like the 8-N rule⁵¹ to the resulting polymeric Zintl anion [185, 208]. Hence, only 2c-2e bonds and lone pairs of electrons are possible states for the valence electrons. The resulting structure may be easily understood in terms of these Zintl anions surrounded by cations of the electropositive metals through the lone pairs of electrons. The ELF analysis has been used to either confirm this qualitative picture, or to assign a structural formu-



Fig. 19. The $[Si_4]^{4-}$ Zintl anion. (a) 3D-isosurface of ELF ($\eta = 0.80$) for the valence electron density of an isolated $[Si_4]^{4-}$ unit. (b) As in (a) but for the $[Si_4]^{4-}$ unit in the solid NaSi. For the sake of comparison, the isosurface of Fig. 19a is represented in Fig. 19b as grid lines. (Reprinted from Fig. 3 with permission from Ref. [208], Fässler, T. F., Chem. Soc. Rev. **32** (2003) 80–86. Copyright 2003 by The Royal Society of Chemistry).

lation to the anionic moieties when more than one is possible, or also, to verify whether a given compound may be actually described as a Zintl phase. We present, in this order, a simple example for each of these three cases.

In the binary phase NaSi, the resulting Si¹⁻ anion has five valence electrons, with the tetrahedral $[Si_4]^{4-}$ unit forming the anionic building block of the structure. The ELF of an isolated $[Si_4]^{4-}$ unit and of such a unit in the solid NaSi is shown in Fig. 19 [208]. There are six maxima outside the tetrahedron and located above the six edges, representing 2c-2e bonds, and four much larger regions corresponding to the lone pairs located at each Si atom, in agreement with the well-known VSEPR rule stating that lone pairs occupy more space than bonding electron pairs. The bond maxima are not along the internuclear axis because of the ring strain in the three-membered rings of the tetrahedron. The ELF regions of the isolated [Si₄]⁴⁻ unit are superimposed as grid lines on the corresponding ELF isosurfaces (in yellow) for the solid NaSi. The bond pattern is obviously the same, but the "localization" domains are more contracted in the solid as compared to the case of isolated ions in the gas phase. The effect originates from the repulsive interactions between electron pairs and it is particularly evident for the lone pair regions. A very recent application of the ELF to the dimeric ion [Ge₉-Ge₉]⁶⁻ provides another example of the use of this function to disclose the kind of bonding in the anionic moieties of the Zintl compounds. The ELF reveals a localized 2c-2e bond connecting the clusters of the dimeric unit [236].

The structure of the ternary silicide $Ba_2Mg_3Si_4$ contains Si_2 pairs and Si_6 chains. The latter are in the *cistrans* conformation and planar. The possible formulations of $Ba_2Mg_3Si_4$ imply non-completely saturated anion moieties to achieve charge balance [185]. The two most likely proposals are $(Ba^{2+})_4(Mg^{2+})_6(Si_2^{6-})(Si_6^{14-})$ and $(Ba^{2+})_4(Mg^{2+})_6(Si_2^{4-})(Si_6^{16-})$ with an unsaturated sixmembered chain (e.g. $[Si-Si-Si=Si-Si-Si]^{14-}$ with 36 valence electrons) in the former case and a $[Si=Si]^{4-}$ pair in the latter. The ELF analysis was used to discriminate which of the two bonding patterns realizes [185]. Fig. 20 shows an ELF plot in the $Ba_2Mg_3Si_4$ plane that contains Si_2 pairs and Si_6 chains. In the lower part of the figure are

⁵¹ The 8-N rule of elementary chemistry states that the number of electron pair bonds that an atom will form with its neighbors is equal to 8-N, where N is the group number. Elements found in groups 4 to 7 (don't call them groups 14-17 to apply this rule) are most likely to obey this 8-N rule. Therefore, usually, halogens have 1 bond, O has two bonds, N, P has three bonds, C, Si has four bonds, etc.



Fig. 20. The Ba₂Mg₃Si₄ Zintl phase. Top: ELF plot in the plane containing the Si₂ pairs and Si₆ chains. Note the direct relationship between the Mg centres and the lone pair electrons of the Zintl anions; the coordination of the Ba cations at the Zintl anions is far less evident. Bottom: ELF cross sections of the various Si–Si bonds of the Si₂ pairs and Si₆ chains. Labelling of bonds is given in the upper figure. Only bonds in the Si₆ chains exhibit some π character. This is very distinctive in the central bond II, weaker in III, and almost absent in IV. ELF colour scale as in Fig. 12 and 13. (Reprinted from Fig. 11 with permission from Ref. [185], Savin. A.; Nesper, R.; Wengert, S.; Fässler, T. F., Angew. Chem. Int. Ed. Engl. **36** (1997) 1809– 1832. Copyright 1997 by Wiley-VCH Verlag).

shown ELF cross sections through the various Si-Si bonds, labeled as I, II, III and IV in the upper part of the figure. There is a rotationally symmetric Si-Si bond in the Si₂ unit (Fig. 20, I), which clearly features the characteristics of a σ bond, while the central bond in the chain shows an elliptical form, typical of π character, and has a larger "localization" region (Fig. 20, II). The next bond in the chain (Fig. 20, III) is distorted towards the Mg centers but also shows an elliptical shape in the central, relatively compact region, whereas the bond to the terminal Si atom is almost rotationally symmetric and hence has no π character (Fig. 20, IV). Thus, the ELF analysis suggests a delocalized [Si-Si-Si=Si-Si-Si]14- structure for the Si_6^{14-} ion and a $(Ba^{2+})_4(Mg^{2+})_6(Si_2^{6-})(Si_6^{14-})$ formulation for Ba₂Mg₃Si₄. These findings were corroborated by a detailed analysis of the underlying band structure [237]. Fig. 20 also shows the direct relationship between the Mg centers and the lone pair electrons of the anionic units, whereas the coordination of the Ba cations at the Zintl anions appears as far less pronounced.

MgB₂ shows superconductivity at 39 K [238], which is almost two times of the transition temperature T_c of the old record holder for intermetallic compounds showing BCS superconductivity. The magnesium diboride phase exists near the nominal composition with a defect occupation (about 95%) of the magnesium position [225]. Assuming a definite composition MgB₂, the compound may be written in terms of the Zintl concept as Mg²⁺(B₂)²⁻ by considering the graphite-like nets of three bonded boron atoms in the structure (Fig. 21) [225]. In this view, each Mg atom would transfer two electrons to the more electro-



Fig. 21. Magnesium diboride (Mg: big blue, B small green balls): the $\eta = 0.75$ ELF isosurface (valence electrons only). The maxima of the ELF are localized on the B–B bonds. The population of the V(B, B) valence disynaptic basins yields a bond order of 1.25 rather than the 1.33 value that one would expect from the Zintl count. MgB₂ is not a Zintl phase, according to the ELF analysis. (Reprinted from Fig. 6 with permission from Ref. [225], Schmidt, J. Schnelle, W.; Grin, Y.; Kniep, R., Solid State Sci. **5** (2003) 535–539. Copyright 2003 by Elsevier SAS).

negative boron network. The ELF was calculated on stoichiometric MgB₂ to confirm or disprove this electron counting [225]. The $\eta = 0.75$ isosurface shows maxima on the B–B bonds and integration of ρ in the corresponding disynaptic valence basins gives 2.5 electrons per bond, with a bond order of 1.25. This value is less than the value of 1.33 that one would expect from the Zintl count. This means that for the stabilization of the covalently bonded part of the structure (the anions B_2^{2-}) not all the valence electrons of magnesium are needed and only 0.75 of the magnesium atom per formula unit would be necessary, yielding $(Mg^{2+})_{0.75}(B_2)^{1.5-}$. Assuming a 0.23 excess of the Mg with respect to the Zintl count, as found in the case of $Al_{0.9}B_2$ [226], would give the formula $(Mg^{2+})_{0.98}(B_2)^{1.5-}(0.46 e^{-})$, in nice agreement with the experimental stoichiometry. According to the ELF analysis, the magnesium diboride is not a Zintl phase and deviation from the nominal 1:2 composition may easily occur [225]. Analogous conclusions were drawn for AlB₂ where only two electrons, rather than the three anticipated by the Zintl count, are transferred to the anionic B_2 unit [226].

ELF and chemical bonding in intermetallic compounds

The ELF has also been extensively used to give insight in the chemical bonding of polar intermetallic compounds [185, 208]. These may roughly be described as formed by



Fig. 22. Bonding in NaSn₅, a system at the border between valence and intermetallic compounds. (a) Structural detail of NaSn₅. (b) The ELF $\eta = 0.80$ 3D-isosurface. Bonding electron pairs between Sn1 and Sn2 are designated by 1, whereas polar bonds between the Sn2 and Sn3 atoms are labelled as 2. Non bonding electron pairs as 3. (c) LMTO (linear muffin tin orbital)-band structure and density of states on the basis of density functional theory. Yellow area corresponds to filled states up to the Fermi level E_{F} (Reprinted from Fig. 6 with permission from Ref. [208], Fässler, T. F., Chem. Soc. Rev. **32** (2003) 80–86. Copyright 2003 by The Royal Society of Chemistry).

a covalent and a "metallic" substructure. Localised chemical bonds occur in the form of bonding and non-bonding electron pair domains. Lone pairs are predominantly located on empty cavities, or cavities that are occupied by the more electropositive atoms. We report two simple cases [208], NaSn₅ and BaSn₅, both belonging to the binary phases of tin and electropositive metals. Tin has the outstanding property that there exists a metallic (β -Sn) and nonmetallic (α -Sn) allotrope almost equal in stability, with the α form being more stable by only 2 kJ mol⁻¹. The MeSn (Me = alkaline or alkaline earth metal) phases also show a variety of bonding patterns, from structures that are typical for valence compounds to structures that are typical for intermetallic compounds through structures that are intermediate between the two classes and which possess both structural motives [239]. NaSn₅ is one of these intermediate cases [208]. It has a tin network with alternate tetravalent atoms (Sn1 and Sn2 atoms in Fig. 22a) and tin atoms with five-fold coordination (Sn3 atoms, Fig. 22a). The 4-bonded (4b) atoms form a 2D net of 5-membered rings connected to the slightly corrugated quadratic net of the five-bonded (5b) atoms. The Sn-Sn separations between 4b atoms are close to the value of 2.81 Å in α -Sn, in which all Sn–Sn contacts correspond to localized 2c-2e bonds, whereas the atom-atom separations of 5b atoms are in the range of the values of the metallic β -Sn modification (3.02 and 3.18 Å). Fig. 22b shows 3D ELF isosurfaces for NaSn₅ isolating regions with $\eta > 0.8$ between Sn1 and Sn2 and featuring 2c-2ebonds between these atoms (region 1); the region between Sn2 and Sn3, labeled as 2 in Fig. 22b, is much closer to Sn2 than to Sn3, denoting a polar bond between these atoms. No local maximum can be observed along the Sn3-Sn3 vector, whereas a lone-pair region (indicated as 3 in Fig. 22b) is evident at the Sn3 atoms. This region is directed toward the electropositive Na atom. The band structure and DOS calculations (Fig. 22c) show that NaSn₅ is an anisotropic conductor, with metallic conductivity propagating predominantly over states with in-plane p_x and p_y Sn3 orbital contributions. The ELF thus affords a clear-cut distinction of the structure parts with localized and delocalized bonds. Interestingly, localized electron domains, interpretable as lone pairs, occur also at those atoms that form the 'metallic' substructure.

BaSn₅ covers, instead, the case [208] of a true intermetallic system that becomes even superconducting at temperatures below 4.4 K. The Sn1 tin atoms in BaSn₅ form pairs of graphite-like layers (honeycomb) (Fig. 23a), which built a slab of hexagonal prisms, centered by additional Sn2 atoms. These atoms have 12 nearest neighbors of Sn1 atoms. The slabs are separated by Ba atoms above and below the center of each tin hexagon. The 3D-isosurface of ELF ($\eta = 0.77$) indicates the presence of lone pairs at Sn1 (labeled as 2 in Fig. 23b). These are located



Fig. 23. Bonding in the intermetallic compound BaSn₅. (a) Structural detail of BaSn₅. (b) The ELF $\eta = 0.77$ 3D-isosurface. The localised Sn–Sn bond is designated by 1, whereas the non-bonding electron pair domains at Sn1 and Sn2 are labelled as 2 and 3, respectively. (c) LMTO-band structure and density of states on the basis of density functional theory. Yellow area corresponds to filled states up to the Fermi level E_{F} . (Reprinted from Fig. 8 with permission from Ref. [208], Fässler, T. F., Chem. Soc. Rev. **32** (2003) 80–86. Copyright 2003 by The Royal Society of Chemistry).

above and below the hexagonal prisms; other two lone pair regions are located above and below the centring Sn2 atoms, whereas small regions of localized bonds (indicated as 1 in Fig. 23b) occur along the vectors joining the nearest neighbors Sn1 atoms within each pair of graphite-like layers. The band analysis shows that the lone pairs form narrow bands, which are energetically located at the Fermi energy E_F and associated with the density of states maximum at E_F (Fig. 23c).⁵² Lone pairs are directed perpendicular to the hexagonal layers towards the lone pairs of adjacent layers. The lattice vibrations will modify the interaction of two adjacent layers, with repulsive interaction between the lone pairs raising the energy of the filled band. Since the lone pairs are located close enough at E_F , the repulsive interaction will shift them above E_F and the electrons of these localized states will be so transferred to 'metallic' bands (disperse bands crossing E_F), which now lie lower in energy. Lattice vibrations may thus induce electron transfer from localized to delocalized bands and vice versa. The occurrence of localized electrons in the form of lone pairs in intermetallic compounds is thus related to the electron-phonon interactions leading to the phenomenon of superconductivity in these systems. This study, along with other similar studies on SrSn3 and K_5Pb_{24} , shows how the ELF may provide insight for a chemical view of superconductivity in intermetallic compounds [208].

ELF and chemical bonding changes under pressure

The major improvements of the last decade in the highpressure experimental techniques have resulted in many high-pressure crystal structures of elemental solids being successfully solved [211]. In this respect, the ELF analysis has proved useful in elucidating the changes in bonding due to pressure. Of course, this has only been possible because of the parallel progress in the accuracy and capabilities of first principle methods that, for these high pressure phases, usually lead to structural predictions in excellent agreement with experiment [240]. Ormeci and Rosner [214] have recently reported an interesting application of the ELF to Sb-II, the high-pressure phase of antimony between 8.5 and 28 GPa, whose exact structure has been a matter of controversy for a long time. A tetragonal model with space group P4/n containing 10 atoms per cell and with two inequivalent Wyckoff sites forming host-guest sublattices was suggested in 1990 [241]. The host sublattice is made up by a 3D framework of Sb atoms, whereas the guest sublattice forms chains of Sb running through the channels provided by the 3D framework. Sb-II is now known to be formed by two incommensurate host-guest Sb sublattices, with first order modulation waves in both of them [242]. Analysis of the ELF shows that the relatively high total energy of the structure with commensurate sublattices can be easily explained by the lack of chemical bond between the chain atoms. This kind of bonding becomes instead clearly visible in a model structure approximating the modulated incommensurate Sb-II phase [214]. The ELF has also been applied to depict bonding changes in high T or high-pressure modifications of several intermetallic and Zintl compounds [207, 213, 243].

ELF in minerals

Of late, the electron density, the electron density Laplacian and the ELF topological analysis have started to be exploited for problems of relevance to mineralogy and geosciences [244–257]. In particular, the ELF analysis has been used as a tool for locating favorable proton docking sites in the silica polymorphs coesite, quartz and stishovite [252, 257]. The proton docks in the vicinity of the lonepair electrons and the lone pair features have always been found to correspond with the docking positions determined in careful FTIR studies. As an example, Fig. 24b



Fig. 24. (a) ELF Isosurfaces of the Si–O bonding regions and of the nonbonding regions on the bridging oxide anion calculated for geometry optimized $H_6Si_2O_7$ molecules with their SiOSi angles fixed at values ranging from 110° to 180°. The *red* spheres represent O and the *green* spheres represent Si. (b) ELF isosurfaces for the Si–O bonding regions and the nonbonding regions of the bridging oxide anions comprising the SiOSi-bonded interactions in coesite [252]. In both figures, the ELF isosurface value is set at the 98% of the local maximum in the nonbonding region. (Reprinted from Fig. 1 and Fig. 7 with permission from Ref. [252], Gibbs, G. V.; Cox, D. F.; Boisen Jr., M. B.; Downs, R. T.; Ross, N. L., Phys. Chem. Minerals **30** (2003) 305–316. Copyright 2003 by Springer-Verlag).

⁵² The importance of saddle points in the band structure [36] and the associate van Hove singularities in the DOS (local maximum) is generally applied to cuprate superconductors. Inspection of the band structure in Fig. 23c shows that the van Hove scenario can also be discussed for intermetallic superconductors. The ELF provides a chemical view and a link to the qualitative picture of the electron-phonon interaction responsible of superconductivity (see infra).

shows the ELF isosurfaces for the Si-O bonding regions and the nonbonding regions of the bridging oxide anions comprising the SiOSi-bonded interactions in coesite [252]. Fig. 24a shows similar regions calculated for geometry optimized H₆Si₂O₇ molecules with their SiOSi angles fixed at values ranging from 110° to 180°. In both figures (24a and 24b), the η value is set at the 98% of the local maximum in the nonbonding region. As the SiOSi angle widens (Fig. 24a), the local maxima of the banana-shaped isosurfaces on the bridging oxide anion decrease in value as these isosurfaces progressively wrap around the bridging oxide anion until about 170° where the bonding and nonbonding isosurfaces merge. This suggests that the narrower the SiOSi angle, the larger is the ability of a nonbonding region on the bridging oxide anions to act as a proton-docking site. There are five unique bridging oxide anions in coesite; the O1 anion is involved in a 180° SiOSi angle whereas the remaining four anions are involved in narrower angles that range in value between 137.6° and 149.7° (Fig. 24b). FTIR spectra recorded for several protonated coesite crystals indicate [258] that the hydrogen atoms in the structure avoid O1 and protonate the others four anionic sites, with relative accuracy for the proton location being largest for the smallest (O5) and smallest for the largest (O4) SiOSi angle. These results nicely fit the trend, as a function of the SiOSi angle, of the shapes of the non-bonding ELF isosurfaces shown in Figs. 24a and 24b. Not surprisingly, the maxima in $-\nabla^2 \rho$ associated to lone pairs were found to be in close correspondence with the non-bonding maxima displayed by the ELF [252, 256]. As an anticipated result, Ross et al. proved how the $-\nabla^2 \rho$ topology, just like the ELF topology, is able to locate favorable proton-docking sites in high-pressure silicates [256].

ELF from "experiment"

The ELF applications discussed thus far used orbitals determined from first-principles calculations to evaluate the ELF for a given chemical system. Recently, there have been attempts to calculate the ELF using information from the experimental electron density determinations, so as to exploit the chemical interpretive capabilities of the ELF in this kind of studies also [24, 28, 259]. Basically, the ELF has been derived either inserting a model functional for the unknown dependence of the positive kinetic energy density on the electron density in the Savin's expression for the ELF, or constructing an approximate wavefunction and then using the Becke-Edgecombe, $\chi_{BE}(\mathbf{r})$, or Savin's, $\chi_{\rm S}({\bf r})$, formulas. Although these methods afford a determination of the ELF, the obtained function should not be regarded as an experimental ELF, since, besides the information from experiment, both methods are at best adopting the same quantum mechanical models the ab-initio methods use. According to the language of the electronic structure theory, the ELF so obtained should be better regarded as a "semi-empirical" ELF [186].

Two studies have recently proposed the use of "semiempirical" ELF and both report, among others, results for the crystal of urea. Tsirelson and Stash [24] used the Savin's $\chi_{\rm S}(\mathbf{r})$ formula for the ELF and evaluated $t_p(\mathbf{r})$ by calculating the positive kinetic energy density G(r) with the Kirzhnits approximation (see earlier) [176]. Conversely, Jayatilaka and Grimwood [28] obtained their ELF distribution from a X-ray constrained Hartree-Fock wavefunction [27, 124], where the Hartree-Fock solution for the superposition of isolated molecules, placed as in the crystal, is constrained to reproduce the X-ray scattering data from experiment. In the following, we call these two semiempirical ELF as approximate ELF (AELF) and Constrained Hartree-Fock ELF (CHFELF), respectively.53 AELF and CHFELF differ in important features in the molecular plane of urea, as shown in Fig. 25. In the AELF (Fig. 25a), the C-N bond region shows a double peak along the covalent bonds, instead of the single bonding regions found both in accurate Hartree-Fock wave function-based ELF [24] and in the CHFELF (Fig. 25b). Furthermore, the AELF shows more contracted electron lone-pair regions respect to CHFELF and displays around the H atom a shell structure, which is instead totally absent in the CHFELF and in the isolated molecule. Interestingly, Tsirelson and Stash [24] have claimed that the shell structure around H atoms forms the basis of the three-dimensional H-bonding network in urea, which has each oxygen atom involved in 4 hydrogen bonds. A key-lock mechanism is operative, with the four non-bonding ELF attractors on the oxygen atom pointing towards the four ELF holes, one behind each H nucleus, in the electron shell of the four H atoms bonded to the oxygen. This explanation of the peculiar H-bonding network in urea is reminiscent of the key-lock mechanism described earlier by Gatti *et al.* [34] in terms of the $\nabla^2 \rho$ distribution,⁵⁴ once more confirming the analogies between the ELF and $\nabla^2 \rho$. The discrepancies observed between the AELF and CHFELF distributions in the crystal of urea are rather indicative. On the one hand, Kirzhnits' gradient expansion of the kinetic energy density seems to be performing too poorly for covalent bonding and, on the other hand, the constrained Hartree-Fock wavefunction, in the superposition of isolated molecules model, appears as still not sufficiently flexible to reproduce adequately subtle crystal field effects.⁵⁵ Lyssenko et al. [259] have recently used AELF and $-\nabla^2 \rho$ to discuss a dative transannular $\mathbf{B} \cdots \pi$ -system interaction in the crystal of a borabicyclo[3.3.1]nonane

⁵³ Jayatilaka and Grimwood [28] calculated also the AELF from their X-ray constrained Hartree-Fock wavefunction.

⁵⁴ Gatti *et al.* [34] showed that it is the lengthening of the C–O bond in the solid state that leads to the splitting of the $-\nabla^2 \varrho$ saddle point between the two non-bonded concentrations of the oxygen in two $-\nabla^2 \varrho$ saddle points located above and below the molecular plane of urea. These saddle points are seen as maxima by hydrogens atoms lying in a plane perpendicular to the molecular plane of urea. The oxygen atom may thus form 4 hydrogen bonds in the crystal, by simultaneously exploiting the two non bonded charge concentrations formed upon C–O bond lengthening.

⁵⁵ For the sake of correctness, one has however to mention that the AELF obtained by Jayatilaka and Grimwood [28] from the X-ray constrained Hartree-Fock wavefunction closely resembles the AELF obtained by Tsirelson and Stash [24] from the multipolar model density. Comparison of the CHELF with the ELF from a very accurate periodic *ab-initio* calculation on urea should clearly help in clarifying all this matter.



b

Fig. 25. "Semi-empirical" ELF distributions for urea (a) approximate ELF (AELF) in the plane (110) of crystalline urea from a multipolar analysis of X-ray diffraction data. Solid lines correspond to values $\eta \ge 0.5$ (interval is 0.05); dashed lines are specified in the map. Solid arrows show the hydrogen bonds. (b) constrained Hartree-Fock ELF (CHFELF) in the molecular plane of urea. [Adjusted from Fig. 4 with permission from Ref. [24], Tsirelson, V.; Stash, A., Chem. Phys. Lett. 351 (2002) 142-148. (Copyright 2002 by Elsevier Science B.B.) and from Fig. 1 with permission from Ref. [28], Jayatilaka, D.; Grimwood, D. J., Acta Cryst. A60 (2004) 111-119. (Copyright 2004, International Union of Crystallography)].

compound. For this kind of non-covalent interactions, Kirzhnits' gradient expansion, and hence the AELF, should behave more adequately [174].

Gadre et al. [260] and Fuentealba [261] have proposed modified versions of the ELF that do not depend on the orbitals and are thus computable exclusively from the knowledge of the electron density and the electrostatic potential. Although these modified ELFs retain most of the properties and qualitative features of the ELF, their conceptual interpretation is somewhat different and less intuitive. Their use for obtaining modified ELFs from experiment has never been reported, to the best of the author's knowledge.

The Localized Orbital Locator (LOL) function

Few years ago, Schmider and Becke [19, 12] introduced a function, which, as the ELF and the Laplacian of the density, is also highly indicative of details of atomic and molecular structure. The function, named localized orbital locator (LOL) is able to reflect common chemical concepts such as atomic shells, molecular bonds and lone pair regions in a quite intuitive way. Use of the LOL for the study of the chemical bonding in crystal is in its earlier stages [25], but the popularity of the LOL seems to be largely increasing, especially among crystallographers, due to the simple physical interpretation of the LOL in terms or "fast" and "slow" electron regions. Indeed, contributions to the kinetic energy from the bond regions is usually decreasing upon bonding and it is highly desirable to use a function, like the LOL, that incorporates a measure of the local kinetic energy as an indicator of bond effects. The LOL function v is given by $v(\mathbf{r}) = t(\mathbf{r})/[1 + t(\mathbf{r})]$, an expression that formally resembles the formula for the ELF. Here $t(\mathbf{r})$ is simply the inverse ratio between the kinetic energy density of the system and that of a homogeneous electron gas with electron density $\rho(\mathbf{r})$. Since the kinetic energy density is not uniquely defined, Schmider and Becke [19] solved pragmatically the problem by choosing its positive definite definition, $G(\mathbf{r})$. As for the ELF, the introduction of a suitable reference introduces some arbitrariness into the LOL, but it serves the purpose to enhance greatly the salient features of the bonding, which are hardly visible in $G(\mathbf{r})$ because the regions with high charge density, i.e. the cores, tend to dominate this function. The ratio $t(\mathbf{r})$ is bounded by zero from below, since the positive kinetic energy density can never become negative by definition, but it is not bounded from above. Division by $[1 + t(\mathbf{r})]$ in the LOL formula thus serves to map the semi-infinite range of $t(\mathbf{r})$ onto the finite interval [0, 1].

The LOL is a measure for the relative value of the local kinetic energy. A value of v = 0.5 indicates that the kinetic energy content of the corresponding region is what would be expected from a spin-neutral electron gas of that density. The LOL becomes larger than 0.5 for regions where the kinetic energy is smaller compared with the uniform electron gas model, and smaller than 0.5 for regions where it is greater. One may view the v = 0.5 isosurface as the boundary separating the slow from the fast regions and thus defining a simple means to identify bonds. A covalent bond is denoted by a v = 0.5 isosurface enclosing a region with very large values of v, with a maximum between the bound centers. Conversely, the closed shell interactions, like the strongly ionic bonds, exhibit separate regions of large v on both centers, and a region along the bond axis with low values of v and a saddle-point. Lone electron pairs are characterized by a characteristic "kidney" shaped v = 0.5 isosurface, which encloses a region with very large values of v and with a local maximum in the "kidney" center. The Localized Orbital Locator appellative for v comes from the observation that the kinetic energy density becomes small and hence v becomes close to 1 when a single dominating orbital has zero gradient, i.e. when a localized orbital becomes extremal (typically, a maximum).⁵⁶ Therefore, one may relate regions with high v values with regions associated with localized orbitals, whereas low v values indicate that the orbital gradients are sizeable and one is moving from a region dominated by one localized orbital to a region dominated by another localized orbital. The chemical information in $v(\mathbf{r})$ is similar to that in the ELF and both are in some way dependent on the relative kinetic energy density. Contrary to the ELF in the BE formulation, the LOL is not founded on consideration of the electron pair density. The physical interpretation of the LOL is therefore certainly simpler than and not as dependent on the kind of adopted wave-function as it is the ELF.

Tsirelson and Stash [25] used Kirzhnits' [176] gradient expansion of $G(\mathbf{r})$ to obtain an approximate LOL from electron densities derived from X-ray diffraction data. By illustrating few simple applications of the LOL, Tsirelson and Stash convincingly advocated the importance of this function for studies of the bonding in the solid state also. Figure 26 shows the approximate LOL profiles along the nearest interatomic lines in crystalline Kr and Ge. These crystals represent two extreme cases of bonding. Ge forms a crystal with covalent bonded atoms, whereas Kr is crystallised at 99 K via van der Waals atomic interactions. To interpret Figure 26, one has to know that, analogously to the ELF and differently from $\nabla^2 \rho$, the LOL is able to faithfully retrieve the atomic shell structure of free atoms, by exhibiting alternating maxima and minima corresponding to intra-shell and inter-shell regions, respectively [12, 19]. The approximate LOL was found to replicate qualitatively the "exact" LOL [25]. Kr and Ge atoms have the same number of electronic shells in a free state and, accordingly, their LOL profiles show 4 maxima and 4 minima (Fig. 26). In the Kr crystal (Fig. 26) eight $(4 + 4 \rightarrow 8)$ LOL maxima along the bond axis are separated by seven $(4 + 4 \rightarrow 7)$ minima, with the deepest minimum being located at the Kr-Kr midpoint. This means that the outermost LOL minima in the isolated atoms have merged upon crystallization. On the contrary, the LOL along the bond axis in the Ge crystal reveals seven $(4 + 4 \rightarrow 7)$ maxima separated by six $(4 + 4 \rightarrow 6)$ minima, with the widest maximum at the bond mid-point. In this case, the outermost LOL maxima have merged to form the covalent bond, while the outermost atomic minima have disappeared. Comparison with the procrystal distributions in Fig. 26 indicates that upon crystal formation v is increasing at the bond mid-point in the case of Ge, and decreasing, at the same point, in the case of Kr. Owing to the constructive interference of the outermost atomic orbitals, the relative kinetic energy density lowers with respect to the procrystal when the covalent bond is formed



Fig. 26. LOL profiles along the nearest interatomic lines in crystalline krypton (a) and germanium (b). LOL profiles for the procrystal and for their atomic contributions are also reported. (Reprinted from Fig. 1 with permission from Ref. [25], Tsirelson, V.; Stash, A., Acta Cryst. **B58** (2002) 780–785. Copyright 2002 International Union of Crystallography).

in Ge, while for Kr the relative electron velocity is increasing respect to the procrystal, because of Pauli repulsion. A comparison between a typical ionic crystal (LiF) and a molecular crystal, benzene, is shown in Fig. 27. In LiF, the outer LOL maxima of atoms have merged to yield only 3 maxima along the Li-F line and with the valence maximum shifted to the fluorine atom. Ions are well separated in space, with $\nu = 0.5$ isosurfaces enclosing nearly spherical regions around each nucleus. This implies near closed-shell ionic electron configurations for LiF in the solid state. The $\nu = 0.55$ isosurface reveals covalent C–C bond in crystalline benzene. The covalent region is separated from the atomic cores by minima, similarly to the Ge crystal. The surface $\nu = 0.5$ encloses the skeleton of the whole molecule, denoting the higher relative speed and the delocalization of electrons over the benzene circle. The LOL distribution in a plane perpendicular to the molecular plane and bisecting two opposite C-C bonds shows an elongated area with $\nu > 0.5$, which is indicative

⁵⁶ One can always transform the molecular orbitals to localized orbitals, while leaving the one-electron density matrix, and hence the LOL, invariant. The interpretation of v as a localized orbital locator persists to any possible unitary transformation of the orbitals [12].



Fig. 27. (a) LOL distribution in the LiF crystal. The boundaries of the $\nu = 0.5$ isosurface are denoted by heavy lines. (b) LOL in the benzene molecular crystal. A single molecule removed from the crystal is shown. The LOL isosurface $\nu = 0.55$ is depicted in yellow, whereas the $\nu = 0.5$ isosurface is shown as a gray dotted net. (c) LOL contour lines in a plane going through the middle points of two opposite C–C bonds. The contour interval is 0.1 for $\nu < 0.5$ (dashed lines) and 0.05 for $\nu > 0.5$ (solid lines). (Adjusted from Fig. 2 and 3 with permission from Ref. [25], Tsirelson, V.; Stash, A., Acta Cryst. **B58** (2002) 780–785. Copyright 2002 International Union of Crystallography).

of the π -character of the C–C bond. Tsirelson and Stash also reported on the difference between the Sr–O and the Ti–O bonds in the cubic perovskite SrTiO₃ [25]. According to their analysis, the LOL is also able to discriminate clearly between the polar covalent (Ti–O) and ionic (Sr–O) bonds, whereas the Laplacian of the electron density would not have such a capability. This view, which is not entirely justified as far as $\nabla^2 \rho$ is concerned, should be further verified with more LOL studies as for the claimed ability of this function. Additional work would also be required to prove that the Kirzhnits' gradient expansion of $G(\mathbf{r})$ is not introducing spurious features in the approximated LOL, as found for the approximated ELF [24, 28].

Further properties and applications of the Laplacian of the electron density

The importance of the Laplacian of the electron density for the study of chemical bonding in crystals has already been outlined in this review. On the one hand, the dominant role that $\nabla^2 \rho$ has in providing a classification of intermolecular interactions and, via the local form of the virial theorem, in pinpointing the regions where either the kinetic ($\nabla^2 \rho > 0$) or the potential energy ($\nabla^2 \rho < 0$) contributions to the local energy density are dominating. On the other hand, the capability of $\nabla^2 \varrho$ to single out the regions of localized single or paired electrons, due to its empirical homeomorphism with the Laplacian of conditional same-spin pair density for α and β spins, and, in most cases, with the ELF also [85, 195]. Besides, contrary to these two latter functions and to the LOL, $\nabla^2 \rho$ requires the knowledge of the only electron density for its evaluation, a fact rendering the use of this function particularly advisable in charge density experimental studies. The $\nabla^2 \rho$ is not defined relative to an arbitrary reference as are the ELF, the LOL and the deformation density functions, but likewise the electron density it is an observable [262]. The availability of $\nabla^2 \rho$ is not a real problem even when the electron density, rather than being known analytically as in multipole models, it is just sampled on 3D grids, as it is the case of densities derived from the maximum entropy method applied to X-ray diffraction data. To this end, Katan et al. [263] and Rabiller et al. [264] have recently developed an efficient and accurate code, named InteGriTy, able to perform the topological analysis of a gridded electron density and to obtain its associated $\nabla^2 \varrho$ distribution. InteGriTy adopts a 3rd order polynomial interpolation method of the density grid points [263].

In view of the importance, lack of arbitrariness and easy availability of $\nabla^2 \varrho$, other properties of this function and examples of its application to problems of relevance for chemical bonding in crystals are sketched below.

The Laplacian distribution and the reactive surface

Local maxima and local $\nabla^2 \rho$ minima in the Valence Shell Charge Concentration (VSCC) of an atom are intimately related to its chemical reactivity [13, 31]. There is a parallel between the generalized acid-base principle of Lewis and the $\nabla^2 \rho$ distribution. A local charge concentration is a Lewis base or a nucleophile, whereas a local charge depletion is a Lewis acid or an electrophile. It has been shown that a convenient way to give an effective description of the qualitative affinity of the various molecular portions toward Lewis acids and bases is to display the *reactive surface* of the molecule, defined as the $\nabla^2 \rho = 0$ isosurface [13, 265]. A first example of a reactive surface in a molecular organic crystal was obtained by Roversi *et al.* [266] from an X-ray diffraction study of the charge density in citrinin at 19 K. This molecule, when treated with alkali,



Fig. 28. Experimental reactive surface $(\nabla^2 \varrho = 0$ isosurface) for the dihydropyrane ring (see scheme) of the citrinin molecular crystal. Atom C8 is predicted to be the most suitable site for nucleophilic attack in keeping with the known chemical reactivity of the molecule in alkali. The isosurface from the multipolar model C [266] is shown. (Adjusted from Fig. 8 with permission from Ref. [266], Roversi, P.; Barzaghi, M.; Merati, F.; Destro, R., Can. J. Chem. **74** (1996) 1145–1161. Copyright 1996 by National Research Council of Canada).

is converted into an alcohol by a reaction involving a nucleophilic attack at the C8 carbon atom in the citrinin dihydropyrane ring, whose chemical formula and $\nabla^2 \rho = 0$ isosurface are shown in Fig. 28. Some of the carbon atoms exhibit holes through which the inner zero surfaces between core charge concentration and core charge depletion become clearly visible. No VSCC region is encountered while moving away from these carbon atoms along the viewing direction. This feature results particularly evident around atom C8, which is therefore predicted to be the most suited site for nucleophilic attack in this portion of the molecule, in full agreement with the known chemical reactivity of citrinin in alkali.

The Laplacian distribution and the metal atom asphericity in metallorganic compounds

The Laplacian distribution has also been studied [156, 267-269] to neatly reveal the asphericity of the metal electron distribution that results from an incomplete filling of the *d*-shell of metal atoms in the crystals of transition metal clusters [270]. As detailed below, such an approach

sheds light on the correspondence between an observable and the expectations of the ligand field theory (LFT).57 For instance, the octahedral field is known to split the five d orbitals into three t_{2g} orbitals of lower energy and two e_g orbitals of higher energy. The total t_{2g} orbital charge density has eight lobes on the diagonal of a cube, whereas that associated with e_g orbitals has six lobes pointing towards the faces of a cube [270]. Fig. 29a-b shows the electron density and the Laplacian distribution generated by the Cr $(t_{2g})^6$ configuration [97]. The electron density isosurface (q = 0.09 a.u.) has a cubic shape with density accumulations along the diagonals of the cube and holes at the center of the faces, as expected. The Laplacian distribution emphasizes these features and shows eight maxima of $-\nabla^2 \rho$ along the diagonal of the cube. For the isosurface $-\nabla^2 \rho = 0.083$ a.u. the vertexes of the cube correspond to the eight $-\nabla^2 \varrho$ maxima of the outermost core Cr shell (3rd shell). Generally, if the filling of the d-orbitals is incomplete, a preferential occupation of t_{2g} orbitals will occur, yielding an electron distribution around the metal atom whose shape will reflect the uneven d-orbital occupation. Bianchi, Gatti et al. [156] were probably the first who verify such a prediction using experimental and theoretical Laplacian distributions in crystals. Fig. 29d-e shows maps of ϱ and $\nabla^2 \varrho$ in a plane containing four of the six N atoms coordinated around the cobalt atom in the crystal structure of lithium bis(tetramethylammonium) hexanitrocobaltate (III). The map is a section of a cube around the octahedrally coordinated Co, bisecting four edges and containing the center of four faces. The $\nabla^2 \rho$ distribution around the Co atom is aspherical, clearly revealing a preferential occupation of the t_{2g} orbitals. It also shows how the four charge concentrations associated to the lone pairs of the nitrogen atoms are oriented towards and complement the charge depletions on the Co atom arising from the (partial) emptiness of the Co e_g orbitals.⁵⁸ These features are not evident in the ρ map. It is now a general observation [6, 271] that the donor-acceptor interaction between a metal atom and the surrounding negatively charged ligands may be visually interpreted in terms of a key-lock mechanism, one which involves a matching of a $-\nabla^2 \varrho$ 'lump' on the ligand (Lewis base) with a $-\nabla^2 \rho$ hole on the metal (Lewis acid). Fig. 29c gives a pictorial illustration [97] of this mechanism for the prototypical case of the Cr(CO)₆ molecule, using two different $-\nabla^2 \rho$ isosurfaces for the metal and the ligands. The topological mechanism shown in Fig. 29c and 29e is to be contrasted with the one usually found for AY_n when A is a main group element. In this case, the charge concentrations of the A VSCC are directed towards the ligands and neither lie between two neighboring ligands nor are opposite lo-

⁵⁷ The asphericity of the metal electron distribution may be also detected by analysing the deformation density (crystal density minus the sum of atomic densities) or the *d*-orbital populations [6–8]. The advantage of using an observable like $-\nabla^2 \rho$ is that any resort to an unphysical reference (the sum of spherical atomic densities) or to an orbital model is *a priori* avoided.

⁵⁸ The Co atom has a basin population of 25.27*e* and, hence, a net charge of +1.73 (QTAIMAC value, periodic Hartree-Fock wavefunction). This implies a *d* population of 7.27*e*, if the Co 4s electrons have been fully transferred to the ligands.



Fig. 29. Electron distribution around the metal atom in transition metal compounds. (a) $\rho = 0.09$ a.u. isosurface for the Cr $(t_{2g})^6$ configuration [97]. (b) $\nabla^2 \rho = -0.083$ a.u isosurface for the Cr $(t_{2g})^6$ configuration; the eight vertexes of the cube surrounding Cr correspond to the eight local $-\nabla^2 \rho$ maxima in the outermost core shell (3rd shell) [97]. (c) The key-lock mechanism of the metal-ligand interaction in the Cr(CO)₆ molecule. Two isosurfaces are drawn: metal ($\nabla^2 \rho = -12.45$ a.u.); ligands ($\nabla^2 \rho = -0.083$ a.u.) [97]. (d) Map of ρ [156] in a plane containing four of the six coordinated N atoms around the cobalt atom in the Lithium Bis(tetramethylammonium) Hexanitrocobaltate (III) crystal. Periodic Hartree-Fock wavefunction. The contour values (a.u.) increase from the outermost one inwards in steps of 2×10^n , 4×10^n , and 8×10^n , with *n* beginning at -3 and increasing in steps of 1. (e) The same as (d) for the $\nabla^2 \rho$ distribution [156]. Dashed and solid contours denote positive and negative $\nabla^2 \rho$ values, respectively. The key-lock mechanism of the metal-ligand interaction is clearly evident. See Ref. [156] for the corresponding experimental maps. [Adjusted from Fig. 4 with permission from Ref. [97], Macchi, P.; Sironi, A., Coordination Chem. Rev. **238–239** (2003) 383–412 (Copyright 2003 by Elsevier Science B.V.) and from Fig. 4 with permission from Ref. [156], Bianchi, R.; Gatti, C.; Adovasio, V.; Nardelli, M., Acta Cryst. **B52** (1996) 471–478. (Copyright 1996 International Union of Crystallography)].

cated (LOCC, Ligand-Opposed Charge Concentrations) [271]. This reflects the change of the nature of bonding between A and Y in the two cases. A similar topological change was reported earlier when discussing the ELF topological changes on passing from the covalent to the closed-shell bonding in simple crystals.

Scherer et al. [158, 159] have recently examined the polarization occurring in the metal VSCC for a series of d^0 metal (M) ethyl compounds, using either theoretical or experimental $\nabla^2 \rho$ densities. In all these compounds it is the (n-1) quantum shell that acts as VSCC and that is distorted by the presence of the ligands. For M = (Ca, Ti), the metal-carbon (M-C) bond shows some degree of covalency [159]. Accordingly, a bonded charge concentration (BCC) on the C_{α} atom of the alkyl group is found to face an induced BCC on the metal, analogously to the typical covalent bonding scheme in the main group molecules. However, concomitant to the M-C bond formation is the appearance of three pronounced ligand induced charge concentrations (LICCs) on the metal VSCC, one opposed to the ligand (trans-LICC) and other two, denoted as cis-LICC, forming an angle of about 90° with the vector joining the two BCCs. Fig. 30 shows these LICCs for

 $Et-TiCl_3(dmpe)$ [dmpe = 1,2-bis(dimethylphosphino)ethane], as obtained for the first time from a careful multipolar analysis of an experimental density [159]. Results shown in the figure represent an important achievement, for they demonstrate cis-LICCs to be observable not just by gasphase calculations, but also from analysis of the experimental crystalline density. The complex distortion occurring in the metal VSCC has been related to the relative ease by which a β -agostic interaction may develop in these d^0 transition-metal alkyl complexes as a function of the nature of the other ligands bounded to the metal. In fact, an area of significant charge depletion (CD) and enhanced Lewis acidity, lying between the BCC and the cis-LICC region pointing toward the alkyl fragment, is formed on the metal upon Me–C bond formation (Fig. 30). The β -agostic interaction involves the matching of this metal CD region with a CC (a 3, -1 CP in $-\nabla^2 \varrho$) at C_{β} and, albeit less important, at the H_{β} atom also. Since the π -acceptor ligands enhance the Lewis acidity of the metal CD region, they are found to encourage the β -agostic interaction of the metal with the alkyl fragment, whereas the σ - and π donor ligands hinder this same interaction because they decrease the Lewis acidity of the CD region [158, 159].



Fig. 30. Metal VSCC polarization in [EtTiCl₃(dmpe)][dmpe = 1,2bis(dimethylphosphino)ethane] [158]. (a) Contour plot of $-\nabla^2 \rho$ in the Ti-C_a-C_b plane from experiment. The $-\nabla^2 \varrho = 227$ and 233 (eÅ-5) values refer to the two cis-Ligand Induced Charge Concentrations (cis-LICCs). The BCC on C_{α} , facing the BCC on Ti, is present but not marked in the plot. (b) Experimental envelope map $(\nabla^2 \rho = -160 \text{ e}\text{\AA}^{-5})$ showing the ligand-induced polarization at the Ti atom. The CD region, lying between BCC and the cis-LICC, is clearly evident. The β -agostic interaction involves the matching of this metal CD region with a charge concentration (a 3, -1 CP in $-\nabla^2 \varrho$) at C_{\beta} and, albeit less important, at the H_{\beta} atom also. σ - and π -donor ligands decrease the Lewis acidity of the metal CD region, hindering the development of the β -agostic interaction. (Adjusted from Fig. 3 with permission from Ref. [159], Scherer, W.; Sirsch, P.; Shorokhov, D.; Tafipolsky, M.; McGrady, G. S.; Gullo, E., Chem. Eur. J. 9 (2003) 6057-6070. Copyright 2003 by Wiley-VCH Verlag).

The Laplacian distribution and the chemical bonding of silicon reconstructed surfaces

The final reported example concerns the re-bonding occurring in the topmost surface layers upon cleavage of bulk silicon. While several experimental techniques are presently available to get a qualitative information on the geometrical reconstructions occurring at semiconductor surfaces, their detailed electronic structure is less evidently experimentally detectable, not to say of their accurate electron density distribution [272–274]. Use of *ab-initio* techniques and of wavefunction interpretive tools is in this case mandatory if a detailed understanding of the interplay between geometrical reconstructions and electronic relaxations is to be gained [275]. Cargnoni *et al.* [39] and Cargnoni and Gatti [276] have performed a QTAIMAC directspace analysis of the Si-Si bonding patterns in the H-covered and clean Si(111) (1 \times 1) surface, and in the π bonded chain reconstructed Si(111) (2×1) surface, using ab-initio periodic slab model wavefunctions. The clean surface, where the dangling bonds of the threefold-coordinated atoms of the first layer (Si1L, Fig. 31a) are not allowed to form bonds, is an ideal surface, which is not present in nature and which serves for comparison purposes in this example. The (2×1) reconstruction, according to the Pandey's π -bonded chain model [277], is the surface structure one obtains upon cleavage in ultra-high vacuum below 600 K [273]. This reconstruction affords two buckled layers of chain-bonded surface atoms: a top layer of threefold (Si1 and Si2, Fig. 31b) and a lower layer of fourfold-coordinated atoms (Si3 and Si4, Fig. 31b). As shown for Si1 and Si4 in Fig. 31c, only the atoms of the topmost layer have an infinite volume (true "surface" atoms), whereas the atoms of the second layer (Si3 and Si4) are already finite though their atomic and bonding properties largely differ from those of the silicon atom in the bulk [276]. The fundamental physical feature of the π -bonded chain reconstruction is that the surface dangling bonds are on nearest neighbor sites rather than on next-nearest neighbor sites as in the clean surface. The zigzag chain of adjacent p_z orbitals can, in principle, π -bond as in organic materials, leading to the formation of bonding and antibonding surface π states. Indeed, in the clean surface, the dangling sp^3 orbital of the three-fold coordinated Si1L atoms manifests itself as a non-bonded charge concentration (NBCC) pointing outwards the surface (Fig. 31d) [39]. This NBCC has 60% of the $|-\nabla^2 o|$ value exhibited by the four bonded charge concentrations (BCCs) of Si along the Si-Si linkages in the bulk.⁵⁹ On the contrary, in the reconstructed surface, only Si1 exhibits a NBCC, whose value is about 20% less than the $|-\nabla^2 \rho|$ value at the NBCC in the clean surface [276]. Thus, upon reconstruction, the single electrons associated with the nominal dangling bonds of the threefold coordinated atoms either participate entirely in bond reconstruction (Si2) or, differently from the Si1L atoms in the clean surface, become at least partially involved in rebonding. Fig. 31e shows the whole surface bonding network in the reconstructed surface, as portrayed by the $-\nabla^2 \rho$ distribution, while Fig. 31f-i displays the ellipticity profiles along the bond path for each pair of bonded atoms. Results refer to the LEED geometry for the surface [278]. The Si1-Si2 bond electron distribution, although displaying the largest deviation from the cylindrical symmetry and the greater accumulation of charge in the π direction, is highly asymmetric along the bond path, in agreement with the differences in the atomic properties found for these two atoms [276]. Significant bond ellipticities are also present for the neighbouring bonds, thus indicating that the π -conjugation is not strictly localized along the topmost layer chains, but that it rather extends over a 2D array of bonds between the topmost and the lower surface layers [276]. Adoption

 $^{^{59}}$ This is in keeping with the single electron nature of this NBCC.



Fig. 31. Si(111) surface reconstruction [39, 276]. (a) Stick-and-ball representation and atomic numbering of the Si(111) (1×1) unrelaxed surface. SiXL (X = 1, 2,...) label the atoms of the X-layer. (b) Stick-and-ball representation and atomic numbering of the Si(111) (2 \times 1) reconstructed surface according to Pandey's π -bonded chain model. Upon reconstruction, the surface dangling bonds are on nearest neighbor rather than on next-nearest neighbor sites. There are two layers of chain-bonded surface atoms: a top layer (Si1 and Si2) of threefold and a lower layer (Si3 and Si4) of fourfold-coordinated atoms. (c) $\nabla \rho$ gradient paths in the mirror plane normal to the Si(111) (2 × 1) surface and containing Si1 and Si4 nuclei. Only the basin of the atoms of the topmost layer (Si1 and Si2) have a non finite volume, while those of the atoms of the lower surface layers all have a finite volume, analogously to the single atomic basin in the bulk. (d) $-\nabla^2 \rho$ contour plots in a plane normal to the unrelaxed Si(111) (1 × 1) surface and containing Si1L through Si5L nuclei. The dangling sp^3 orbital of the three-fold coordinated Si1L atoms manifests itself as a non bonded charge concentration (NBCC) pointing outwards the surface. This NBCC has half the $-\nabla^2 \rho$ value exhibited by the four bonded charge concentrations (BCCs) of Si along the Si–Si linkages in the bulk. (e) $-\nabla^2 \rho$ contour plots in a plane normal to the reconstructed Si(111) (2×1) surface and containing the unique bond paths among the atoms of the two outermost layers. Contour plots in five different planes are juxtaposed so as to reveal the whole surface bonding network. Only atoms Si1 exhibit a NBCC, denoting the partial involvement in rebounding of the single electron associated with the nominal dangling bond of Si1 (and Si2) atoms. (f-i) Bond ellipticity profiles along the bond path of each pair of bonded atoms in the two outermost layers of the Si(111) (2×1) surface. Results at the LEED geometry [278] and using either Unrestricted Hartree-Fock (UHF/LEED) or restricted HartreeFock (RHF/LEED) models. Ellipticity profiles denote the asymmetry of π -conjugation in the topmost layer and shows that this conjugation is not strictly localized along the topmost layer chains, but that it rather extends over a 2D array of bonds between the topmost and the lower surface layers. [Adjusted from Fig. 3 with permission from Ref. [39], Cargnoni, F.; Gatti, C.; May, E.; Narducci, D., J. Chem. Phys. 112 (2000) 887-899. (Copyright 2000, American Institute of Physics) and from Fig. 1,3 and 4 with permission from Ref. [276], Cargnoni, F.; Gatti, C., Theor. Chem. Acc. 105 (2001) 309-322. (Copyright 2001 by Springer-Verlag)].

of a spin-polarized, instead of a conventional non-polarized RHF solution, leads to a smaller differentiation within each pair of bonded atoms (Fig. 31f–i) and to a more efficient surface bonds delocalization, which yields in turn a significant energy lowering for the reconstructed surface [276]. Analysis of the *bcp* properties of the Si–Si bonds in the first two layers of the Si(111) (2 × 1) surface suggests that these bonds are, on average, as strong as in the bulk, in contrast to what found for the unrelaxed surface where the related Si1L–Si2L bonds are slightly weakened [39, 276].

These studies on silicon surfaces [39, 276], along with other investigations on bond [279] and interstitial defects in silicon [280], reveal the capability of the QTAIMAC and of the $-\nabla^2 \rho$ topological analysis to quantitatively detail the changes in bonding and atomic properties upon

perturbation of the regularly periodic crystal structure. Very enlightening results on the interpretation of rebounding at surfaces have also been reported by Fässler *et al.* [281], Savin *et al.* [185], and by De Santis *et al.* [282, 283] using an ELF approach. Empirical connection of the ELF pictures with the scanning tunnel microscopy images of surfaces at subatomic resolution has also been established [281, 185].

The source function

A few years ago, Bader and Gatti [82] introduced a function to view the electron density ρ at any point **r** within a molecule to consist of contributions from a local source operating at all other points \mathbf{r}' . When this local source is evaluated over regions Ω satisfying the QTAIMAC definition of an atom or group of atoms in a molecule [13], the density at **r** may be equated to a sum of atomic contributions SF($\mathbf{r}; \Omega$), each of which is termed as the source *function* (SF) from the atom Ω to $\rho(\mathbf{r})$. Such decomposition enables one to view the properties of the density from a new perspective and establishes the SF as a novel interesting tool to provide chemical insight. For instance, the density within an atom may be envisaged as being determined solely by an internal SF self-contribution and by SF contributions from the remaining atoms or groups of atoms within the molecule. One of the main advantages of the SF is that it discloses important facets of the local and non-local character of the electron density distributions without requiring knowledge of the 1-particle or of the 2-particle density matrix. Only the system's electron density (and derivatives) is needed for evaluating the SF, which should therefore be easily obtainable from a chargedensity quality X-ray diffraction experiment also.

For a gas-phase molecule, the density at a point \mathbf{r} in terms of a local source (LS) contribution is given by:

$$\varrho(\mathbf{r}) = \int \mathrm{LS}(\mathbf{r}, \mathbf{r}') \cdot d\mathbf{r}' = \int_{\Omega} \mathrm{LS}(\mathbf{r}, \mathbf{r}') \cdot d\mathbf{r}' + \sum_{\Omega' \neq \Omega} \int_{\Omega'} \mathrm{LS}(\mathbf{r}, \mathbf{r}') \cdot d\mathbf{r}'.$$
(10)

The local source LS (\mathbf{r}, \mathbf{r}') has the following expression:⁶⁰

$$LS(\mathbf{r},\mathbf{r}') = -\binom{1}{4\pi} \cdot \frac{\nabla^2 \varrho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
(11)

with

$$\int_{\Omega} \mathrm{LS}\left(\mathbf{r},\mathbf{r}'\right) \cdot \mathrm{d}\mathbf{r}' \equiv \mathrm{SF}\left(\mathbf{r},\Omega\right) \tag{12}$$

and where $(4\pi \cdot |\mathbf{r} - \mathbf{r}'|)^{-1}$, a Green's function, may be seen [92] as an *influence function* representing the effectiveness of how the *cause* $\nabla^2 \varrho(\mathbf{r}')$ gives rise to the *effect* $\varrho(\mathbf{r})$. For a system with no boundaries at infinite, like for example an atom or group of atoms in a crystal, Eq. (10) takes another operative form. The contributions to $\varrho(\mathbf{r})$, within a given atomic basin or superbasin Ω , from the other infinite atoms in the system, are replaced (Eq. (13)) by just the flux through the boundary surface of Ω , $S_{\Omega}(\mathbf{r})$, of the electric field density at \mathbf{r} , $\boldsymbol{\varepsilon}(\mathbf{r} - \mathbf{r}_s)$, due to the density at the surface point \mathbf{r}_s , $\varrho(\mathbf{r}_s)$:

$$\varrho(\mathbf{r}) = \left\{ \int_{\Omega} \mathrm{LS}\left(\mathbf{r},\mathbf{r}'\right) \cdot \mathrm{d}\mathbf{r}' + \left(-\frac{1}{4}\pi\right) \oint_{S_{\Omega}} \mathrm{d}S(\mathbf{r}_{S}) \cdot \varepsilon(\mathbf{r}-\mathbf{r}_{S}) \right\}.$$
(13)

The SF should enable one to detail quantitatively the effect of a perturbation, such as a chemical substitution or a change of geometry, phase, etc., on the contributions to the electron density at given points. These may typically be the bond critical points, as the least biased choice one may conceive for a point representative of bonding. Using the SF one may quantify how local or non local, with respect to a given chemical bond, is the effect of a given perturbation.

In spite of its promising features, few applications of the SF have however appeared in literature up to now [82, 83, 180, 284] and only one [180] using a crystalline electron density. We report two examples, selected on the basis of their potential interest for the study of the chemical bond in crystals. Application of the SF to the $OH \cdots O$ hydrogen bonded systems reveals [83, 284] that this function enables one to classify the hydrogen bonds (HBs) in terms of characteristic SF contributions to the density at the HB critical point arising from the H atom involved in this bond, the H-atom donor D and the H-atom acceptor A. The five H-bond classes defined by Gilli & Gilli [285] using chemical and geometrical considerations have quite distinctive quantitative features in terms of the SF [83]. As pictorially shown in Fig. 32, the source contribution from the H appears as the most characteristic marker of the Hbond strength, being highly negative for isolated H-bonds, slightly negative for polarized assisted H-bonds, close to zero for resonance-assisted H-bonds and largely positive for charge-assisted H-bonds.⁶¹ The contributions from atoms other than H, D and A was found to be strongly increasing with decreasing H-bond strength, consistently with the parallel increased electrostatic character of the interaction. This SF analysis of the H-bond seems more informative than the standard analysis in terms of the Hbond critical point properties. Further details can be found in the original paper [83], where a parallel between the

 $^{^{60}}$ At variance with Ref. 82 the term $-1/(4\cdot\pi)$ is here included in the definition of the local source.

⁶¹ The LS is positive in regions where $\nabla^2 \rho$ is negative and negative in regions where $\nabla^2 \varrho$ is positive. Hence the regions where the electron density is concentrated ($\nabla^2 \rho < 0$) and the potential energy $V(\mathbf{r})$ dominates over the kinetic energy $G(\mathbf{r})$ act as source for the electron density at a point \mathbf{r} , whereas regions where $G(\mathbf{r})$ dominates over $V(\mathbf{r})$ act as a sink for $\rho(\mathbf{r})$. The SF contribution from an atomic basin to the density at **r** is always positive for an isolated atom since $\rho(\mathbf{r})$ is ≥ 0 everywhere. In general, for a system with more than one atomic basin, the positive LS contributions dominate over the negative LS contributions to the density at bcps; however it is possible for an atom to act as a *sink* rather than as a *source* in special cases. This is what happens to the H atom involved in the weak and the moderate strength HBs. The shape of the H basin and of the Laplacian distribution along the $OH \cdots O$ axis is highly asymmetric for these bonds, with regions of negative Laplacian surrounding the O-H bcp and with the H-bond critical point being instead located in a pronounced region of positive Laplacian.



Fig. 32. The hydrogen bond (HB) description in terms of the percentage atomic source contributions to the electron density at the HB critical point. Sources are displayed as circles whose size is proportional to the percentage contribution from each atom, with positive sources in blue and negative sources, i.e. "sinks", in yellow. The black dot indicates the HB critical point position where the sources are evaluated. Hydrogen bonds are classified below, according to Gilli & Gilli [285]. 1: The symmetrical $[H_2O \cdots H \cdots OH_2]^+$ dimer, a positive Charge Assisted H-bond (+)CAHB, $d_{O \dots H} = 1.204$ Å; **2**: The open form of the formic acid-formate anion complex, a Negative Charge Assisted H-bond (–)CAHB, $d_{O \dots H} = 1.216$ Å; **3**: Malonaldeyde, Cs equilibrium form, a Resonance-Assisted H-Bond, RAHB, $d_{O \dots H} = 1.639$ Å; **4**: Malonaldeyde, C_{2v}, Transition State for the Hatom transfer between the two oxygen atoms, $d_{O...H} = 1.209 \text{ A}$; 5: The cyclic homodromic water trimer, a Polarization Assisted H-bond, PAHB, $d_{O \dots H} = 1.850$ Å; **6**: The linear water dimer, an Isolated HB, IHB, of moderate strength, $d_{O \dots H} = 2.077$ Å. The source contribution from the H involved in the OH...O bond is highly negative for IHBs, 6, small and negative for PAHBs, 5, close to zero for RAHBs, 3, large and positive for CAHBs, 1 and 2. The source contributions from atoms other than the $OH \cdots \overline{O}$ triad are as large as 50% in the H-bond dominated by electrostatics, $\underline{6}$, and are negligibly small in the essentially covalent H-bonds, $\underline{2}$ and $\underline{1}$. (Adjusted from Fig. 7 with permission from Ref. [83], Gatti, C.; Cargnoni, F.; Bertini, L., J Comput Chem 24 (2003) 422-436. Copyright 2003 by Wiley Periodicals, Inc.)

classifications of the H-bonds given by the SF and by the ELF [219] is also highlighted.

The other reported application uses the local form of the source function, LS, to explore the features of the interaction density $\delta \varrho(\mathbf{r})$ in H-bonded molecular crystals [180].⁶² Analogously to $\varrho(\mathbf{r})$, one may define a local source for $\delta \varrho(\mathbf{r})$ to analyse how the overall charge-density polarization occurring upon H-bond formation concurs in determining the interaction density in the H-bond region and, in particular, at the H-bond CPs. For the weak H-bonds, the interaction density generally reaches absolute minimum values in regions close to the HB CPs and is therefore not very informative [73, 180], as discussed earlier in this review. Instead, the analysis of the LS profiles along the juxtaposition of the D-H and $H \cdots A$ bond paths clearly shows that the largest contributions to $\delta \varrho(\mathbf{r})$ at the HB CP occur far from this point and in regions that enclose a large portion of the H basin [180]. For instance, in the case of the NH \cdots O bonds in urea, the LS contributions at the HB CP from points close to the H nucleus are one order of magnitude larger than those from points close to the *bcp*. Their associated local $|\delta \nabla^2 \varrho|$ difference of about 0.3 a.u. (6 e $Å^{-5}$) should be surely detectable in an accurate experimental study. This result is of potential interest for judging the data quality of a charge-density experimental determination. Rather than directly inspecting $\delta \rho(\mathbf{r})$ in the H-bond region, one could more precisely assess the quality of the interaction density in this same region by analysing how other parts of the crystalline space contribute to $\delta \rho(\mathbf{r})$. Certainly, further work is required to prove whether the SF and its local form can be of some utility in the study of chemical bonding in crystals.

Conclusions and outlook

During the past decade, direct space analysis of chemical bond has grown into a mature field. Several interpretive tools have been proposed, often complementing each other, if properly applied and combined. Application to crystals has revealed fascinating bonding patterns in many classes of extended solids and disclosed subtle bonding features of the intermolecular bonding in molecular crystals. Extension of direct space analysis of bonding to crystalline systems was made possible by a number of technical developments including, on the theoretical side, the increased availability of efficient *ab-initio* periodic packages and, on the experimental side, the largely enhanced X-ray data quality and the improvements in the charge density models used in the data refinement. No study on crystals would have however been possible if several software packages implementing the QTAIMAC and the topological analysis of various scalar functions related to bonding had not been developed, documented and made generally available in the past decade (see Ref. [263] and Ref. [186] for a not exhaustive list).

But, given the present situation, where are we going now? A number of possible directions are tentatively listed:

a) Many important technological materials have properties that crucially depend on their defective structure. The X-ray experiment yields the space-time averaged structure and electron density. The topological analysis of the thermally smeared electron density obtained by the maximum entropy method (MEM) is an emerging technique, which may unambiguously reveal the partial occupancies of the main atomic sites and the locations and relative populations of the interstitial defective atoms in a structure. This technique may also disclose subtle bonding ef-

⁶² As reported earlier in this review, the interaction density is given by the difference between the electron density in the crystal and that given by the superposition of non-interacting molecules placed as in the crystal.

fects due to dynamical disorder. A recent synchrotron powder diffraction and MEM study on thermoelectric zinc antimonide confirms the potential power of this combined approach for the study of defective structures [286]. Standard ab-initio techniques can not deal with partial occupancies, but geometrical and energetic considerations derived from the *ab-initio* calculations may be used to unravel a composing mixture of cells compatible with the observed defective structure. Analysis of bonding and properties of each of these composing structures may then yield information on the resulting properties in the defective material. This kind of approach was successfully applied to the understanding of thermoelectric properties of zinc antimonide in the same study referred to above [286].

- b) Electronic transport properties and the electronic contribution to thermal transport properties are both related to the valence and conduction electron band structure [287], which depends in turn on chemical bonding. Temperature dependency of the transport properties is also tied up with chemical bonding and to how this evolves with temperature. Boltzmann's transport theory allows to quantitatively relating the band structure with the electron transport properties and their dependency with temperature [287, 288]. One may reasonably hope that the direct space analysis of chemical bond might contribute to find a similarly powerful link between these fundamental material properties and the underlying bonding features.
- c) Time-resolved experiments and computational modelling of time-dependent phenomena will likely set the standard of studies on condensed matter within the coming decades. If the related electron densities and/or wavefunctions will be(come) available, direct space analysis of bonding will be a convenient tool to follow the time-evolution of the system, thanks to the immediate and chemically informative visualization this approach may provide. Application of QTAIMAC to neutral to ionic phase transitions in charge transfer salts has already been reported [289].
- d) Electron correlation effects in crystals are poorly described by the presently available theoretical methods, while the multipole models, fitted on the elastic part of the X-ray scattering, are only indirectly influenced by these effects. Significant progresses are expected in the near future from both theory and experiment. On the theoretical side, the development of post-Hartree-Fock methods [11], using well-localized Wannier functions, or the availability of improved functionals for the weak interactions in the periodic DFT approach. On the experimental side, the use of joint refinements on several set of experimental data (including elastic and inelastic scattering information) [290] or, alternatively, the use of these data sets in a constrained variational optimization of a theoretical (periodic) wavefunction [27]. The direct space analysis of chemical bonding will benefit from these improvements (more interpretive

functions will become directly available) and will serve as a very suitable tool to detail the subtle effects introduced by a better treatment of electron correlation.

e) New useful functions for chemical bonding studies. A list of candidates, mostly taken from density functional theory has been recently reported by Tsirelson and Stash [291]. Use of the Fermi hole mobility function to map an energy surface for electron transfer in crystals (see possible relation with point *b*) was recently proposed by Jayatilaka and Grimwood [28]. Extension to crystalline systems of the generalized population analysis [20, 22, 118] and of the domain averaged Fermi holes methodology [134] can be reasonably envisaged.

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