TOPOND14

User's Manual
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Chapter 1

Introduction

TOPOND performs the topological analysis of the electron density, according to the Quantum Theory of Atoms in Molecules (QTAIM) developed by Richard Bader and coworkers. [1] Its first implementation for systems periodic in 0 to 3 dimensions was made through the TOPOND code [2] interfaced to both CRYSTAL94 and CRYSTAL98 code [3].

A useful survey on the application of QTAIM and of other real-space topological analyses to periodic systems, in particular to crystals, may be found in Ref. [4]. More recent developments are described in [5–7], and in several chapters of a recent book on Modern Charge Density Analysis. [8]

TOPOND has currently been incorporated into CRYSTAL14 and it is accessible through the keyword **TOPO** of its **Properties** part. While retaining all the functionalities of TOPOND98, this new keyword enables the user to perform a topological analysis of the periodic electron density directly in CRYSTAL, thereby avoiding the use of an interface between CRYSTAL and TOPOND and the creation of external files with information from CRYSTAL. On top of this, there is no longer the need to resize the code as a function of the dimension of the investigated system since all variables are dynamically allocated as in other parts of the CRYSTAL code.

Ongoing developments, like the Source Function analysis [6,9] will be included in a next release of the code. The required citation for this work is:

C. Gatti, V. R. Saunders and C. Roetti, *Crystal field effects on the topological properties of the electron density in molecular crystals. The case of urea*, J. Chem. Phys. 101, 10686-10696 (1994).

C. Gatti and S. Casassa, **TOPOND14 User's Manual**, CNR-ISTM of Milano, Milano, 2013.

If the parallel version of the code is used, the developers would appreciate the following additional reference:

S. Casassa, A. Erba, J. Baima, R. Orlando, *Electron density analysis of large (molecular and periodic) systems: A parallel implementation*, Journal of Computational Chemistry 36, 1940-1946, (2015).

1.1   Topological analysis: steps and sections

The QTAIM topological analysis of the electron density may involve different steps which correspond to different sections of the code and are customarily performed separately, but that may be also suitably chained according to a reasonable sequence given in input. In general, this sequence may have any order of steps, but there may be limitations, depending on the analysed system and on the required kind of analyses, within each step.

A first section deals with the topological analysis of the electron density (ρ) scalar field (keyword **TRHO**). It provides the Critical Points (CPs),$\mathbf{r}_c$, of this field, that is the points where the gradient of the density, $\boldsymbol{\nabla}\rho$, vanishes. The critical points may be classified in terms of their type (r,s) where r is the rank and s the signature. The rank is given by the number of non-zero eigenvalues of the Hessian matrix of the scalar at $\mathbf{r}_c$. Stable structures are characterized by all their critical points of ρ being of rank 3. The CPs of ρ may be put in one to one correspondence with the elements of the "chemically" recognizeable structures (nuclei, (3,-3), bonds (3,-1), ring (3,+1), cages (3,+3)) in a crystal, thus providing a chemical structure of a crystal based on the properties of an observable. [4] Characterization of the nature of the bonds is made in terms of several properties at the bond (3,-1) CP. A very detailed and reasoned summary of the various schemes of classification of bonds in terms of properties at the (3,-1) CP is reported in Ref. [4].

A second section concerns the topological analysis of the Laplacian of the electron density ($\nabla^2\rho$) scalar field (keyword **TLAP**). The atomic shell structure is not visible through the topology of ρ, but it becomes generally so when that of $\nabla^2\rho$ is analysed [1], which serves as a magnifying lens. When applied to atoms in chemical combination (like those in a crystal) the topology of $\nabla^2\rho$ reveals the electron pairs (shared, partially shared, or not shared "lone pairs") of the Lewis model [1]. A careful analysis of the bonding in a crystal should involve both the TRHO and TLAP steps (for an illustrative example on the Urea crystal, see Ref. [3] and [10]). Comparison of bond properties for isolated molecules, simple clusters of molecules (dimers, trimers, etc.) and crystals, enable one to evaluate the effects on intramolecular and intermolecular bonding of crystal packing. [3, 4]

A third section (keyword **ATBP**) deals with the determination of atomic basins and of their properties. An atomic basin Ω is defined as a portion of space bounded by a surface $S(\Omega, \boldsymbol{r}_s)$ whose points $\boldsymbol{r}_s$ all fulfil the condition $\boldsymbol{\nabla}\rho(\boldsymbol{r_s}) \cdot \boldsymbol{n}(\boldsymbol{r_s}) = 0$, where $\boldsymbol{n}(\boldsymbol{r_s})$ is a unit vector normal to the surface. The atomic surfaces are thus called zero-flux surfaces, ZFSs. [1, 4] Atomic basins are necessarily finite in crystals, while they may have a finite or infinite volume at lower periodicity. [4] The topological definition of an atom in a molecule, polymer, slab or crystal provides the boundary condition for the extension of quantum mechanics to an open system. [1] Thus, within QTAIM, the average value of some observable for the total system may be given in terms of well defined atomic contributions. In general every atomic property, like the electron population, the kinetic energy, etc. can be expressed in terms of a corresponding three-dimensional density distribution that can be integrated over Ω to obtain its average value. [1]

The last session (keywords **PL2D** and **PL3D**) prepares the required information for a number of useful 2-dimensional plots and 3-dimensional visualizations, respectively.

1.2 Input cards

There are five different keywords that can be used and that will be explained in the following chapters of the Manual. They are summarized in table 1.1.

- **Warning:** if not otherwise stated, the length unit used throughout the input depends on the value of INF(72) adopted in CRYSTAL14 run. Namely:

  INF(72)=0, ANGSTROM,   **keyword ANGSTROM** (default)

  INF(72)=1, AU (bohr)   (1Å=0.529177 bohr) **keyword BOHR**

- **Warning:** the TOPOND option must always been the last of a **Properties** run and must end with the **END** keyword

value	meaning	chapter (pag)
TRHO	topological analysis of $\rho(\boldsymbol{r})$	2 (7)
TLPA	topological analysis of $\nabla^2\rho(\boldsymbol{r})$	3 (19)
ATBP	atomic basins properties	4 (28)
PL2D	plot section (2D)	5 (36)
PL3D	plot section (3D)	5 (36)

Table 1.1: Main input cards

A single test, **Urea Bulk**, will be used through all the Sections of the Manual to explain the various keywords in detail. This is a molecular crystal containing 5 atoms in the asymmetric part of the unit cell for a total of 16 atoms in the reference one. In order to get the wavefunction (fort.9) to perform a **Properties** calculation with the **keyword TOPO** the Input file for CRYSTAL14 is provided in appendix C.

Chapter 2

Topological Analysis of the Electron Density

2.1 Topological analysis of $\rho(\boldsymbol{r})$ (TRHO)

This section deals with the topological analysis of the electron density (ρ) scalar field (keyword **TRHO**). It provides the Critical Points (CPs), $\mathbf{r}_c$, of this field, that is the points where the gradient of the density, $\boldsymbol{\nabla}\rho$, vanishes. The critical points may be classified in terms of their type (r, s) where r is the rank and s the signature. The rank is given by the number of non-zero eigenvalues λ_i (i=1,3; $\lambda_1 \leq \lambda_2 \leq \lambda_3$) of the Hessian matrix of the scalar at $\mathbf{r}_c$. Stable structures are characterized by all their critical points of ρ being of rank 3. The CPs of ρ may be put in one to one correspondence with the elements of the "chemically" recognizeable structures (nuclei, (3,-3), bonds (3,-1), ring (3,+1), cages (3,+3)) in a crystal, thus providing a chemical structure of a crystal based on the properties of an observable. [4] Characterization of the nature of the bonds is made in terms of several properties at the bond (3,-1) CP. The union of the two steepest ascent $\boldsymbol{\nabla}\rho$ paths originating at a (3,-1) CP (a **bond critical point, bcp**) and ending at the nuclei (3,-3 maxima) of these two bonded atoms, is called a **bond path** (rigorously when the system is at equilibrium, i.e. no net forces are acting on the nuclei).

The CPs of ρ may be searched according to four different strategies (**IAUTO** variable in the Table below) and using either the standard Newton Raphson (NR) or the more sophisticated eigenvector following (EF) *numerical procedure*. [11–13] By *strategy* we mean the criteria used to select the starting points for locating the various CPs of the system, whereas the numerical procedure refers to the algorithm which is used to locate the CPs from given starting points. The EF procedure is a NR-like algorithm, but with a suitable, locally defined shift for the NR step so as to take into account the type of CP is sought for. In practice, the EF method seeks for the CPs of a given type, regardless of the structure of the Hessian of ρ at the starting point of the search.

More specific CP searches - along a line or starting from a given set of points are also possible. A search along a line may be required when the automated starting point for a bonding interaction is not appropriate for that specific interaction (for instance the **bcp** is notably displaced from the mid-point or **non-nuclear attractors** are present. [1, 4] The **non-nuclear attractors are (3,-3) maxima of** ρ at non-nuclear positions, [4, 14] with important consequences on the **molecular graph** (the collection of bond paths). However, note that IAUTO=0 and IMETH=0 (see *infra*) enable one to displace at will the starting point of the (3,-1) CP search. Finally, it is possible to evaluate a number of properties $(\rho(\boldsymbol{r}), \nabla^2\rho(\boldsymbol{r}), \lambda_3, \epsilon = \lambda_2/\lambda_1 - 1$, the so called bond ellipticity) along a line (joining two points or two nuclei) without explicit search for a CP. This may be useful either for profiling these quantities along the line (for instance, if the line corresponds or is close to a bond path these properties serve to characterize in more detail the nature of the bond) or to have a closer insight on the features of the density along a line when an expected (3,-1) CP, hence a bonding interaction, is, instead, seemingly missing.

The search options, summarized in table 2.1 (**IAUTO** variable) are described in the following sections.

IAUTO	Meaning	section (pag)
Global searches		
-2	fully automated and chain-like search strategy for all kind of CPs, using at each stage the EF step suitable for the kind of CP searched for. By chain- like, it is meant that (3,-3), (3,-1), (3,+1) and (3,+3) CPs are separately searched for, according to this listed sequence The search is performed within a finite region of space, which encloses a finite molecular cluster built-up around a specified seed point. Size and origin of the cluster are given in input.	2.1.1 (9)
-1	Same search strategy as for IAUTO=-2. However, when IAUTO=-1, the search region is defined as the union of the regions of space obtained by building-up molecular clusters centered at each of the non-equivalent atom (NEA) of the unit cell. This allows to automatically explore the various symmetry unique parts of the system. Size of clusters is given in input.	2.1.2 (10)
0	automated CPs search between unique atom pairs. This options normally recovers the (3,-1) CPs only but occasionally other CP types may be located	2.1.3 (11)
3	CPs are sought for using a brute force approach (search on a grid in the asymmetric unit of the crystalline cell). If the grid size is small enough, this procedure normally recovers all unique CPs in the cell. It may be useful when one needs to verify the fulfilment of the Morse relationship, relating the type and number of CPs in the unit cell (see Ref. [4] for a working example on urea crystal). Normally used only for 3D periodic systems. It may be computationally expensive.	2.1.6 (14)
Specific searches		
1	CPs search started from a given set of points	2.1.4 (12)
2	CPs search along the line joining nuclei A and B or two points a and b	2.1.5 (13)
Profiles of properties		
4	Calculates the profiles of ρ, $\nabla^2\rho$, λ_3 and ϵ along the axis joining nuclei A and B or two points a and b. Information is saved on file SAVEPRO.DAT	2.1.7 (15)

Table 2.1: ρ topology: summary of the search options

2.1.1 IAUTO=-2

●*	IAUTO	-2	global search strategy type, see table 2.1
●*	IEXT	0	Only properties depending on ρ and on its derivatives are evaluated at each unique CP
		1	Properties (kinetic energy densities, virial density, Electron Localization Function, ELF [15]) depending on the non-diagonal elements of the first-order density matrix are also evaluated at each unique CP [4]
	ICRIT	0	all kind of CPs are searched for
		1	chain-like search stopped after $(3,-3)$ and $(3,-1)$ CPs search stages. This option saves the largest part of CPU time required by the automatic search (particularly useful for defective systems) or very large unit cells
	IBPAT	0	Bond paths or atomic interaction line (AIL) [1,3] lenghts and termini are not evaluated. The bond paths are the AILs at geometric equilibrium (no net forces acting on the nuclei)
		1	Bond paths (or AILs) lengths and termini are evaluated numerically for each unique (3,-1) CP. This evaluation increases by about 1-2 orders of magnitude the CPU time of the CP search
	IPRINT	0	normal printing
		1	debug printing during CP search
	NSTEP	m	max. number of EF steps along each search. A reasonable value is about 15-20, but difficult cases may require a larger value
	NNB	n	● NNB is the maximum number of symmetry-related stars of atoms to be included in the clusters generated around the seed point. NNB must be low (2-5) for very symmetric environments around the seed point, whereas it may be significantly larger (10-20) for asymmetric environments ● NNB is also the number of neighbors in the nearest neighbor analysis around each unique CP located
	RMAX	r	maximum radius of the clusters. RMAX may reduce the actual value of NNB
	TH	$\neq 0.$	(3,-1) CP search is performed among all the unique atom pairs whose internuclear distance falls below TH
		0.	the default value is used $(5\mathring{A})$ in the (3,-1) CP search stage
●*	IFRA	0	coordinates of the "seed point" (centre of the cluster) in **bohr**
		1	coordinates of the "seed point" in fractionary units (conventional cell)
	x,y,z	x,y,z	coordinates of the "seed point"

2.1.2 IAUTO=-1

•*	IAUTO	-1	global search strategy type, see table 2.1
•*	IEXT	0	Only properties depending on ρ and on its derivatives are evaluated at each unique CP
		1	Properties (kinetic energy densities, virial density, Electron Localization Function, ELF [15]) depending on the non-diagonal elements of the first-order density matrix are also evaluated at each unique CP [4]
	ICRIT	0	all kinds of CPs are searched for
		1	chain-like search stopped after the (3,-3) and (3,-1) CPs search stages. This option saves the largest part of CPU time required by the automatic search (particularly useful for defective systems or very large unit cells).
	IBPAT	0	Bond paths or atomic interaction line (AIL) [1,4] lenghts and termini are not evaluated. The bond paths are the AILs at geometric equilibrium (no net forces acting on the nuclei)
		1	Bond paths (or AILs) lengths and termini are evaluated numerically for each unique (3,-1) CP. This evaluation increases by about 1-2 orders of magnitude the CPU time of the CP search
	IPRINT	0	normal printing
		1	debug printing during CP search
	NSTEP	m	max. number of EF steps along each search. A reasonable value is about 15-20, but difficult cases may require a larger value
	NNB	n	•NNB is the maximum number of symmetry-related stars of atoms to be included in the clusters generated around each NEA. NNB must be low (2-5) for very symmetric environments around the various NEAs, whereas it may be significantly larger (10-20) for asymmetric environments •NNB is also the number of neighbors in the nearest neighbor analysis around each unique CP located
	RMAX	r	Maximum radius of the clusters. Each cluster includes all atoms within a sphere of radius RMAX, centered around the NEA. RMAX may reduce the actual value of NNB
	TH	$\neq 0.$	(3,-1) CP search is performed among all the unique atom pairs whose internuclear distance falls below TH
		0.	the default threshold value ($5\mathring{A}$) is used in the (3,-1) CP search stage

2.1.3 IAUTO=0

●*	IAUTO	0	global search strategy type, see table 2.1
●*	IMETH	0	NR algorithm adopted in the CP search
		1	EF algorithm adopted in the CP search
	IEXT	0	Only properties depending on ρ and on its derivatives are evaluated at each unique CP
		1	Properties (kinetic energy densities, virial density, Electron Localization Function, ELF [15]) depending on the non-diagonal elements of the first-order density matrix are also evaluated at each unique CP [4]
	IBPAT	0	Bond paths or atomic interaction line (AIL) [1,4] lenghts and termini are not evaluated. The bond paths are the AILs at geometric equilibrium (no net forces acting on the nuclei)
		1	Bond paths (or AILs) lengths and termini are evaluated numerically for each unique (3,-1) CP. This evaluation increases by about 1-2 orders of magnitude the CPU time of the CP search
	IPRINT	0	normal printing
		1	debug printing during CP search
	NSTEP	m	max. number of NR (IMETH=0) or EF (IMETH=1) steps along each search. A reasonable value is about 15-20, but difficult cases may require a larger value
	NNB	n	● (3,-1) CPs are searched among all the unique pairs generated from a set of nuclei. The set is generated by constructing clusters of atoms around each non-equivalent atom (NEA) of the unit cell. NNB is the maximum number of symmetry-related stars of atoms to be included in the clusters generated around each NEA. NNB must be low (2-5) for very symmetric environments around the various NEAs, whereas it may be significantly larger (10-20) for asymmetric environments ● NNB is also the number of neighbors in the nearest neighbor analysis around each unique CP located
	RMAX	r	Maximum radius of the clusters. Each cluster includes all atoms within a sphere of radius RMAX, centered around the NEA. RMAX may reduce the actual value of NNB
●*	TH	$\neq 0.$	(3,-1) CP search is performed among all the unique atom pairs whose internuclear distance falls below TH
		0.	the default threshold value ($5\overset{\circ}{A}$) is used
		if IMETH=0 insert the following record	
●*	PC	$\neq 0.$	if a CP is not found between an A-B pair, the starting point of the NR search is displaced - along the internuclear axis - from the mid-point of the axis to the following two positions: $\mathbf{r'}_{start} = \mathbf{r}_A + PC * (\mathbf{r}_B - \mathbf{r}_A); \mathbf{r''}_{start} = \mathbf{r}_A + (1. - PC) * (\mathbf{r}_B - \mathbf{r}_A)$
		0.	the default value is used ($PC = 0.4$)

2.1.4   IAUTO=1

●*	IAUTO	1	global search strategy type, see table 2.1
●*	IMETH	0	NR algorithm adopted in the CP search
		1	EF algorithm adopted in the CP search
	IEXT	0	Only properties depending on ρ and on its derivatives are evaluated at each unique CP
		1	Properties (kinetic energy densities, virial density, Electron Localization Function, ELF [15] depending on the non-diagonal elements of the first-order density matrix are also evaluated at each unique CP [4]
	IBPAT	0	Bond paths or atomic interaction line (AIL) [1,4] lenghts and termini are not evaluated. The bond paths are the AILs at geometric equilibrium (no net forces acting on the nuclei)
		1	Bond paths (or AILs) lengths and termini are evaluated numerically for each unique (3,-1) CP. This evaluation increases by about 1-2 orders of magnitude the CPU time of the CP search
	IPRINT	0	normal printing
		1	debug printing during CP search
	NSTEP	m	max. number of NR (IMETH=0) or EF (IMETH=1) steps along each search. A reasonable value is about 15-20, but difficult cases may require a larger value
	NNB	n	NNB is the number of neighbors in the nearest neighbor analysis around each unique CP located
	RMAX	r	Maximum radius of the cluster in the nearest neighbor analysis around each unique CP located. RMAX may reduce the actual value of NNB
**if IMETH=1 insert the following record**
●*	ITYPE	0	(3,-3) CP search
		1	(3,-1) CP search
		2	(3,+1) CP search
		3	(3,+3) CP search
**Always insert the following record**
●*	NGUE	n	number of starting points for CPs search
	IFRA	0	coordinates in **bohr**
		1	coordinates in fractionary units (conventional cell)
**if NGUE>0, insert NGUE records**
●*	XS,YS,ZS	x,y,z	x,y,z starting point coordinates (**bohr** or fract. units, see IFRA)

2.1.5 IAUTO=2

•*	IAUTO	2	global search strategy type, see table 2.1
•*	IMETH	0	NR algorithm adopted in the CP search (heavily suggested for IAUTO=2, because the starting point of the CP search is moved slightly and smoothly along a line and one is normally interested in locating all CPs along the line and not just one peculiar type of CP (if this is instead the case use IMETH=1)
		1	EF algorithm adopted in the CP search
	IEXT	0	Only properties depending on ρ and on its derivatives are evaluated at each unique CP
		1	Properties (kinetic energy densities, virial density, Electron Localization Function, ELF [15]) depending on the non-diagonal elements of the first-order density matrix are also evaluated at each unique CP [4]
	IBPAT	0	Bond paths or atomic interaction line (AIL) [1,4] lenghts and termini are not evaluated. The bond paths are the AILs at geometric equilibrium (no net forces acting on the nuclei)
		1	Bond paths (or AILs) lengths and termini are evaluated numerically for each unique (3,-1) CP. This evaluation increases by about 1 order of magnitude the CPU time of the CP search
	IPRINT	0	normal printing
		1	debug printing during CP search
	NSTEP	m	max. number of NR (IMETH=0) or EF (IMETH=1) steps along each search. A reasonable value for IAUTO=2 is about 5-10, because the starting point of the CP search is moved slightly and smoothly along a line. Higher values are indeed useless and force the code to keep locating the same CPs.
	NNB	n	NNB is the number of neighbors in the nearest neighbor analysis around each unique CP located
	RMAX	r	Maximum radius of the cluster in the the nearest neighbor analysis around each unique CP located. RMAX may reduce the actual value of NNB
		if IMETH=1 insert the following record	
•*	ITYPE	0	(3,-3) CP search
		1	(3,-1) CP search
		2	(3,+1) CP search
		3	(3,+3) CP search
		insert always the following record	
•*	NTYP	0	CP search along the internuclear axis joining nuclei A and B
		1	As above, but along the axis joining two points a and b
		if NTYP=0, insert the following records	
•*	IA1,IA2	n,m	**IA1**, n, in the progressive number of unique atom A (1≤n≤number of non-equivalent atoms) **IA2**, m, is the atom B, that is the m-th neigbor of A (m is the "NEW" number in the "Cluster around each of the non-equivalent atom" printing at the beginning of the TOPOND output).
		elseif NTYP=1 insert the following two records	
•*	X1,Y1,Z1	x,y,z	coordinates (**bohr**) of point a
•*	X2,Y2,Z2	x,y,z	coordinates (**bohr**) of point b

2.1.6   IAUTO=3

•*	IAUTO	3	global search strategy type, see table 2.1
•*	IMETH	0	NR algorithm adopted in the CP search (**heavily suggested** for IAUTO=3, because the starting point of the CP search is moved slightly and smoothly during the search on a grid. On top of this, the general interest is in locating all CPs in the asymmetric unit, rather than one peluliar type of CP. If this is instead the case, use IMETH=1)
		1	EF algorithm used in the CP search
	IEXT	0	only properties depending on ρ and on its derivatives are evaluated at each unique CP
		1	Properties (kinetic energy densities, viral density, Electron Localization Function, ELF [15]) depending on the non-diagonal elements of the first-order density matrix are also evaluated at each unique CP [4]
	IBPAT	0	Bond paths or atomic interaction line (AIL) [1,4] lenghts and termini are not evaluated. The bond paths are the AILs at geometric equilibrium (no net forces acting on the nuclei)
		1	Bond paths (or AILs) lenghts and termini are not evaluated numerically for each unique(3,-1) CP. This evaluation increases the CPU time of the CP search, altrough it is performed only for the unique(3,-1) recovered CPs
	IPRINT	0	normale printing
		1	debug printing during CP search
	NSTEP	m	max. number of NR (IMETH=0) or EF (IMETH=1) steps along each search. A reasonable value for IAUTO=3 is about 5-10, because the starting point of the CP search is moved slightly and smoothly along the grid. Higher values are indeed useless and force the code to keep locating the same CPs.
	NNB	n	NNB is the number of neighbors in the nearest neighbor analysis around each unique CP located
	RMAX	r	maximum radius of the cluster in the nearest neighbor analysis around each unique CP located. RMAX may reduce the actual value of NNB
		0.	the default threshold value (5Å) is used
if IMETH=1 insert the following record			
•*	ITYPE	0	(3,-3) CP search
		1	(3,-1) CP search
		2	(3,+1) CP search
		3	(3,+3) CP search
insert always the following record			
•*	XMI	r	Fractional coordinate intervals: minumum value of X
	XMA	s	Fractional coordinate intervals: maximum value of X
	XINC	t	Fractional coordinate intervals: grid interval along X
•*	YMI	r'	Fractional coordinate intervals: minumum value of Y
	YMA	s'	Fractional coordinate intervals: maximum value of Y
	YINC	t'	Fractional coordinate intervals: grid interval along Y
•*	ZMI	r''	Fractional coordinate intervals: minumum value of Z
	ZMA	s''	Fractional coordinate intervals: maximum value of Z
	ZINC	t''	Fractional coordinate intervals: grid interval along Z
•*	NCONS	n	number of constraints, if any, among the values of the x,y,z fractional coordinates
if NCONS > 0 insert NCONS records			
•*	ICO	n	conventional number of constraint type, see Table 2.2
	ACO	a	value of a in constraint ICO, see Table 2.2

If a certain number of constraints (namely **NCONS** > 0) has to be defined, reference can

be made to Table 2.2.

Constraint number	Constraint type
1	X≤ay
2	X≤(a+y)/2
3	Y≤ax
4	Y≤min [a-x,(a+x)/2]
5	Y≤min (x,a-x)
6	Y≤min (2x,a-x)
7	Y≤a-x
8	Z≤ay
9	Z≤a+y
10	Z≤min (y, a-x)

Table 2.2: IAUTO=3: type of constraints among the values of x,y,z fractional coordinates

2.1.7 IAUTO=4

●*	IAUTO	4	global search strategy type, see table 2.1
●*	NTYP	0	Scalar function profile along the internuclear axis joining nuclei A and B
		1	As above, but along the axis joining two points a and b
		if NTYP=0, insert the following record	
●*	IA1,IA2	n,m	**IA1**, n, is the progressive number of unique atom A (1≤n≤number of non-equivalent atoms) **IA2**, m, is the atom B, that is the m-th neighbor of A (m is the "NEW" number in the "Cluster around each of the non-equivalent atom" printing at the beginning of the TOPOND output)
		elseif NTYP=1 insert the following two records	
●*	X1,Y1,Z1	x,y,z	coordinates (**bohr**) of point a
●*	X2,Y2,Z2	x,y,z	coordinates (**bohr**) of point b
● *	PPDISP	n	percentage step s along A-B or a-b [if n=1, $s=0.01*R_{A-B}$(or R_{a-b}); if n=100 $s=1*R_{A-B}$(or R_{a-b})]
	JUNIT	0	ρ, $\nabla^2\rho$ and λ_3 values in **bohr** (note: ϵ is dimensionless); profiles of ρ, $\nabla^2\rho$, λ_3 and ϵ are saved on file SAVEPRO.DAT
		1	ρ in $e/\mathring{A}^3$, $\nabla^2\rho$ and λ_3 values in $e/\mathring{A}^5$; profiles of ρ, $\nabla^2\rho$, λ_3 and ϵ are saved on file SAVEPRO.DAT

2.2 Input examples

With reference to Urea bulk 6-12g∗∗.

EX 1 Fully automated and chain-like search strategy for all kinds of CPs, using at each stage the EF step suitable for the kind of CP searched for. The search is performed within a finite region of space, around the seed point located on the nucleus of the carbonyl oxygen O3. Bond paths lenghts and their termini are not evaluated.

```
TOPO
TRHO
−2                          IAUTO=-2
0, 0, 0, 0, 20, 15, 10., 0.   IEXT,ICRIT,IBPAT,IPRINT,NSTEP,NNB,RMAX,TH
1, 0., −0.5, −0.4047        IFRA (coordinates of the "seed point" in fractionary units);
                            Coordinates of the "seed point" (O3)
```

NOTE: the (3,-3) cps associated to nuclei are found; all intramolecular bcps are found save one of the two unique N-H bcps; the two hydrogen bonds N-H9··O and N-H13··O are found; the intermolecular N··N interactions are not recovered. Only 3 unique rcps and 1 unique ccp are found (in urea crystal there are 5 unique rcps, 3 unique ccps, see Ref. [4])

EX 2 Fully automated and chain-like search strategy for (3,-3) and (3,-1) CPs, using at each stage the EF step suitable for the kind of CP searched for. The search region is defined as the union of the regions of space obtained by building-up molecular clusters centered at each of the non-equivalent atom (NEA) of the unit cell. Bond paths lenghts and their termini are evaluated. Kinetic energy densities, virial density and ELF values are evaluated at the recovered bcps

```
TOPO
TRHO
−1                          IAUTO = −1
1, 1, 1, 0, 20, 10, 7., 0.   IEXT, ICRIT, IBPAT, IPRINT, NSTEP, NNB, RMAX, TH
```

NOTE: the (3,-3) cps associated to nuclei are found; all intramolecular bcps are found; the two hydrogen bonds N-H9··O and N-H13··O are found; the shorter, 3.44 $\mathring{A}$ intermolecular N··N interaction is recovered.

EX 3 Automated CPs search between unique atom pairs. This option normally recovers the (3,-1) CPs only, but occasionally other CP types may be located. The NR algorithm (IMETH=0) is used for locating CPs and the starting poin of the search is displaced from the internuclear axis midpoint if the CP is not recovered. Bond paths lenghts and their termini are evaluated. Kinetic energy densities, virial density and ELF values are also evaluated at the recovered bcps

```
TOPO
TRHO
0                           IAUTO = 0
0, 1, 1, 0, 20, 7, 5.        IMETH, IEXT, IBPAT, IPRINT, NSTEP, NNB, RMAX
0.                          TH
0.                          PC
```

NOTE: the (3,-3) cps associated to nuclei are found; all intramolecular bcps are found; the two hydrogen bonds N-H9··O and N-H13··O are found; 2 unique rcps are found.

EX 4 CPs are sought for using a brute force approach (search on a grid in the asymmetric unit of the crystalline cell. It is useful for locating all unique CPs in the unit cell and to so verify the fulfilment of the Morse's relationship. The NR algorithm (IMETH=0) is used for locating CPs. Bond paths lenghts and their termini are evaluated. Kinetic energy densities, virial density and ELF values are also evaluated at the recovered bcps

```
TOPO
TRHO
3                 IAUTO = 3
0, 1, 1, 0, 10, 7, 5.    IMETH, IEXT, IBPAT, IPRINT, NSTEP, NNB, RMAX
0., 0.5, 0.025     XMI, XMA, XINC
0., 0.5, 0.025     YMI,YMA, YINC
0., 1., 0.025      ZMI, ZMA, ZINC
1                 NCONS
7, 0.5             ICO (ICO=7, see Table 2.2), ACO
```

NOTE: All the 21 unique CPs of bulk urea are recovered. There are 5 (3,-3) cps associated to nuclei; 8 unique (3,-1) bcps, 4 of them due to intramolecular bonds (C-O, C-N, N-H13 and N-H9) and other 4 due to intermolecular bonds (N-H9··O, N-H13··O, N··N shorter and longer interactions) 5 (3,+1) rcps and 3 (3,+3) ccps. By taking into account their multiplicity (taken from their Wyckoff positions), one finds that the recovered set of CPs fulfills Morse's relationship (see Table 3, Ref. [4]).

EX 5 CPs search started from a given set of points (Wyckoff special positions were selected). The EF metod is used (IMETH=1) and (3,-1) CP are searched for (ITYPE=1). Bond paths lenghts and their termini are evaluated. Kinetic energy densities, virial density and ELF values are also evaluated at the recovered bcps

```
TOPO
TRHO
1                 IAUTO = 1
1, 1, 1, 0, 10, 7, 5.    IMETH, IEXT, IBPAT, IPRINT, NSTEP, NNB, RMAX
1                 ITYPE
4, 1               NGUE,IFRA
                  (4 starting points and starting coordinates in fractionary units)
0., 0., 0.         coordinates of the first starting point (Wyckoff position : a)
0., 0.5, 0.4       coordinates of the second starting point (Wyckoff position : c)
0., 0., 0.5        coordinates of the third starting point (Wyckoff position : b)
0., 0., 0.25       coordinates of the fourth starting point (Wyckoff position : d)
```

NOTE: two ccps, C-O bcp and the C and O nuclei (3,-3) CPs are found.

EX 6 CPs search along the line joining nuclei C1 (0,0,0) and N5 (0,1,0). The EF metod is used (IMETH=1) and (3,-1) CP are searched for (ITYPE=1). Bond paths lenghts and their termini are evaluated.

```
TOPO
TRHO
2                 IAUTO = 2
1, 0, 1, 0, 5, 7, 5.    IMETH, IEXT, IBPAT, IPRINT, NSTEP, NNB, RMAX
1                 ITYPE
0                 NTYP
1, 2               IA1,IA2
```

NOTE: the C-N bcp and the C and N nuclei (3,-3) CPs are found

EX 7 CPs search along the line joining nuclei N5 (0,0,0) and N6 (0,0,0) (intermolecular N··N long interaction, 4.263 Å). The EF metod is used (IMETH=1) and (3,-1) CP are searched for (ITYPE=1). Bond paths lenghts and their termini are evaluated.

```
TOPO
TRHO
2                  IAUTO = 2
1, 0, 1, 0, 5, 7, 5.   IMETH, IEXT, IBPAT, IPRINT, NSTEP, NNB, RMAX
1                  ITYPE
1                  NTYP
1.534, −3.724, 1.563   coordinates, au, of N5 (0, 0, 0)
−1.534, 3.724, 1.563   coordinates, au, of N6 (0, 0, 0)
```

NOTE:the longer (4.263 $\mathring{A}$) N··N intermolecular interaction is recovered. It is correctly assigned to an N··N interaction after the bond path evaluation, which identifies the N5(0,0,0) and N6(0,0,0) nuclei as termini of the bond path.

EX 8 Calculates the profiles of $\rho, \nabla^2\rho, \lambda_3$ and ϵ along the axis joining nuclei C1(0,0,0) and N5 (0,1,0).
The values of these functions are printed in the output and on file SAVEPROP.DAT.

```
TOPO
TRHO
4        IAUTO = 4
0        NTYP
1, 2     IA1,IA2
2, 0     PPDISP (percentage step, 2 %, along the internuclear axis), JUNIT (in au)
```

Chapter 3

Topological analysis of the Laplacian

3.1 Topological analysis of $\nabla^2\rho(\boldsymbol{r})$ (TLAP)

This section deals with the topological analysis of the Laplacian ($\nabla^2\rho$) of the electron density scalar field (*keyword* **TLAP**). It provides the Critical Points (CPs), $\mathbf{r}_c$, of this field, that is the points where the gradient of $\nabla^2\rho$, $\boldsymbol{\nabla}(\nabla^2\rho)$, vanishes. The critical points may be classified in terms of their type (r, s) where r is the rank and s the signature, analogously to the case of the ρ field. [1,4] The Laplacian of a scalar field, like ρ, has an important physical significance. A positive (negative) $\nabla^2\rho$ ($\mathbf{r}$) value denotes that the electron density at $\mathbf{r}$ is lower (higher) in value than it is on average in an infinitesimal volume around $\mathbf{r}$. Regions with positive Laplacian are so locally charge depleted, while regions characterized by a negative Laplacian are locally charge concentrated. The $\nabla^2\rho$ has a dominant role in providing a classification of chemical interactions [1,4,6] and, via the local form of the virial theorem, [1] 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 dominate. The $\nabla^2\rho$ is also able 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. [4] Bonded or non-bonded charge concentrations (lone pairs) are in general associated to (3,-3) maxima in -$\nabla^2\rho$ (but see more general cases in Refs. [3,4,6]).

Note that in TLAP a topological analysis of $L(\boldsymbol{r}) = -\nabla^2\rho$ **is performed**, so as to associate a positive value of a function, $L(\boldsymbol{r})$, with an electronic charge concentration and a negative value for this same function with a charge depletion.

The CPs of $L(\boldsymbol{r}) = -\nabla^2\rho$ may be searched according to an automated strategy (**IAUTO=0** variable in the Table below) and using either the standard Newton Raphson (**NR**) or the more sophisticated eigenvector following (**EF**) *numerical procedure*. [11–13]

The strategy used to locate the CPs of $L(\boldsymbol{r})$ is different from that used for the CPs of ρ, as the CP search is in this case "atom's-based". It is, therefore, performed only on the non-equivalent atoms in the cell. Non Nuclear Attractors, **NNA**, [1,4,14] may be also added to the list of unique atoms. The chosen strategy takes into account that, upon chemical combination, the topology of $L(\boldsymbol{r})$ may be generally seen as a perturbation of the Valence-Shell Charge Concentration [1] (**VSSC**)of the isolated atom (though also the innermost shells may be slightly perturbed). The deviation from spherical symmetry due to bonding, is made evident by the formation of CPs in the VSCC region. The CP search may, however, also be performed on different regions (valence depletion region, core concentration or depletion regions, etc.) based on the chosen value for the variable **RSTAR**. The EF numerical procedure is a NR-like algorithm, but with a suitable, locally defined shift for the NR step so as to take into account the type of CP is sought for. In practice, the EF method seeks for the CPs of a given type, regardless of the structure of the Hessian of $\nabla^2\rho$ at the starting point of the search.

More specific L($\boldsymbol{r}$) CP searches, starting from a given set of points, IAUTO=1, or along a line, IAUTO=2, are also possible. The search options are summarized in Table 3.1 (IAUTO variable):

IAUTO	meaning	section (pag)
	Global search	
0	automated L($\boldsymbol{r}$)= -$\nabla^2\rho$ CP's search within the concentration (or depletion) shells of each of the non-equivalent atom (NEA) and of the non-nuclear attractors (NNAs) given in input. Usually the search is performed in the valence shell charge concentration (VSCC) of each NEA. Which shell is sampled, depends however on the RSTAR value given in input (see below)	3.1.1 (21)
	Specific search	
1	CPs search started from a given set of points	3.1.2 (23)
2	CPs search along the line joining nuclei A and B or two points a and b	3.1.3 (25)

Table 3.1: $\nabla^2\rho$ topology: summary of search options

3.1.1   IAUTO=0

•*	IAUTO	0	global search strategy type, see table 3.1
•*	IMETH	0	NR algorithm adopted in the CP search
		1	EF algorithm adopted in the CP search
	IEXT	0	Only properties depending on ρ and on its derivatives are evaluated at each unique CP
		1	Properties (kinetic energy densities, virial density, Electron Localization Function, ELF [15]) depending on the non-diagonal elements of the first-order density matrix are also evaluated at each unique CP [4]
	IBPAT	0	Atomic graph line (**AGL**) [1] lenghts and termini are not evaluated.
		1	AGL lengths and termini are evaluated numerically for each unique $L(\boldsymbol{r})$ (3,-1) CP. The AGL is the union of the unique pair of $\boldsymbol{\nabla}(-\nabla^2\rho)$ trajectories that originate at the (3,-1) $L(\boldsymbol{r})$ CP and terminate at neighbouring (3,-3) $L(\boldsymbol{r})$ CPs maxima. Evaluating the AGLs is computationally expensive as it may increase the CPU time of the CP search by 1-2 orders of magnitude
	IPRINT	0	normal printing
		1	debug printing during CP search
	NSTEP	m	max. number of NR (IMETH=0) or EF (IMETH=1) steps along each search. A reasonable value is about 15-20, but difficult cases may require a larger value
	NNB	n	NNB is the number of neighbors around each unique CP
	RMAX	r	Maximum radius of sphere in the nearest neighbor analysis around each unique CP. Considered as neighbors will be only those atoms whose nuclei are within a sphere of radius RMAX, centered on the investigated CP. RMAX may reduce the actual value of NNB
if IMETH=1 insert the following record			
•*	ITYPE	0	(3,-3) $L(\boldsymbol{r})$ CP search
		1	(3,-1) $L(\boldsymbol{r})$ CP search
		2	(3,+1) $L(\boldsymbol{r})$ CP search
		3	(3,+3) $L(\boldsymbol{r})$ CP search
always insert the following records			
•*	NT,NP	n,m	CPs search is started from points located on the surface of a sphere centered on the nucleus of a given non-equivalent atom (NEA) or at the Non Nuclear Attractor (**NNA**) location. The number of starting points is determined by the intervals n, m chosen for the polar coordinates θ and φ, respectively. The suggested values for n, m depend on the sphere radius RSTAR (see table 3.2). For RSTAR<1, n=12 and m=18 is generally a reasonable choice For 1< RSTAR<2, n=18 and m=24 is a more appropriate choice
•*	NNA	n	the number of NNAs to be considered in the $L(\boldsymbol{r})$ CP search

			insert this(these) record(s)
			for each NEA and for each of the considered NNAs
●*	IYES	0	no L(r) CP search is performed for this current NEA or NNA
		1	L(**r**) CP search for this current NEA or NNA is performed
			if IYES=1 and if this search is around a NNA insert also
●*	X1,Y1,Z1	x,y,z	coordinates (**bohr**) of the current NNA
			if IYES=1, insert also for the current NEA or NNA
●*	NMAX	0	Standard L(r) CP search over the angular grid for the current NEA or NNA
		m	if IMETH=1, the L(r) CP search for the current NEA or NNA is stopped when m different CPs of the required type (variable ITYPE) are found
	RSTAR	0.	the default sphere radius, given in **bohr** in Table 3.2, is adopted in the CP search. This radius is taken equal to the distance from the nucleus to the spherical surface where L(**r**) attains its maximum value in the VSCC of the isolated atom. Note that there is not a default value for NNAs.
		r	the sphere radius is taken to be equal to r (to be given in Å or **bohr** accordingly to the set value of INF(72) i.e. keyword ANGSTROM or BOHR). This is a mandatory input for NNAs and a necessary input datum when shells other than the VSCC are sampled or when the NEA is an ion. If the NEA is a cation (anion) RSTAR will be significantly smaller (larger) than the default value for this NEA. Note also that the default value for Hydrogen is that for an hydride.

3.1.2 IAUTO=1

●*	IAUTO	1	global search strategy type, see table 3.1
●*	IMETH	0	NR algorithm adopted in the CP search
		1	EF algorithm adopted in the CP search
	IEXT	0	Only properties depending on ρ and on its derivatives are evaluated at each unique CP
		1	Properties (kinetic energy densities, virial density, Electron Localization Function, ELF [15]) depending on the non-diagonal elements of the first-order density matrix are also evaluated at each unique CP [4]
	IBPAT	0	Atomic graph line (AGL) [1] lenghts and termini are not evaluated.
		1	AGL lengths and termini are evaluated numerically for each unique L($\boldsymbol{r}$) (3,-1) CP. The AGL is the union of the unique pair of $\boldsymbol{\nabla}(-\nabla^2\rho)$ trajectories that originate at the (3,-1) L($\mathbf{r}$) CP and terminate at neighbouring (3,-3) L($\mathbf{r}$) CPs maxima. Evaluating the AGLs is computationally expensive as it may increase the CPU time of the CP search by 1-2 orders of magnitude
	IPRINT	0	normal printing
		1	debug printing during CP search
	NSTEP	m	max. number of NR (IMETH=0) or EF (IMETH=1) steps along each search. A reasonable value is about 15-20, but difficult cases may require a larger value.
	NNB	n	NNB is the number of neighbors in the nearest neighbor analysis around each unique CP located.
	RMAX	r	Maximum radius of sphere in the nearest neighbor analysis around each unique CP located. Considered as neighbors will be only those atoms whose nuclei are located within a sphere of radius RMAX, centered on the located CP. RMAX may reduce the actual value of NNB
if IMETH=1 insert the following record			
●*	ITYPE	0	(3,-3) L($\boldsymbol{r}$) CP search
		1	(3,-1) L($\boldsymbol{r}$) CP search
		2	(3,+1) L($\boldsymbol{r}$) CP search
		3	(3,+3) L($\boldsymbol{r}$) CP search
insert always the following record			
●*	NGUE	m	number of starting points for L($\boldsymbol{r}$) CPs search
	IFRA	0	coordinates in **bohr**
		1	coordinates in fractionary units (conventional cell)
	NMAX	0	Standard L($\boldsymbol{r}$) CP search from the starting points given in input
		m	if IMETH=1, the L($\boldsymbol{r}$) CP search is stopped when m different CPs of the required type (variable ITYPE) are found.
if NGUE>0 insert NGUE records			
●*	XST,YST, ZST	x,y,z	starting point coordinates (**bohr** or fractional units depending on the value of IFRA)

3.1.3 IAUTO=2

●*	IAUTO	2	global search strategy type, see table 3.1
●*	IMETH	0	NR algorithm adopted in the CP search (heavily suggested option for IAUTO=2, because the starting point of the CP search is moved slightly and smoothly along a line and one is normally interested in locating all CPs along the line and not just one peculiar type of CP. If this is instead the case, use IMETH=1)
		1	EF algorithm adopted in the CP search
	IEXT	0	Only properties depending on ρ and on its derivatives are evaluated at each unique CP
		1	Properties (kinetic energy densities, virial density, Electron Localization Function, ELF [15]) depending on the non-diagonal elements of the first-order density matrix are also evaluated at each unique CP.
	IBPAT	0	Atomic graph line (**AGL**) [1] lenghts and termini are not evaluated.
		1	AGL lengths and termini are evaluated numerically for each unique L($\boldsymbol{r}$) (3,-1) CP. The AGL is the union of the unique pair of $\boldsymbol{\nabla}(-\nabla^2\rho)$ trajectories that originate at the (3,-1) L($\boldsymbol{r}$) CP and terminate at neighbouring (3,-3) L($\boldsymbol{r}$) CPs maxima. Evaluating the AGLs is computationally expensive as it may increase the CPU time of the CP search by 1-2 orders of magnitude
	IPRINT	0	normal printing
		1	debug printing during CP search
	NSTEP	m	max. number of NR (IMETH=0) or EF (IMETH=1) steps along each search. A reasonable value for IAUTO=2 and L($\boldsymbol{r}$) CP search is about 10, because the starting point of the CP search is moved slightly and smoothly along a line. Higher values are indeed useless and force the code to keep locating the same L($\boldsymbol{r}$) CPs.
	NNB	n	NNB is the number of neighbors in the nearest neighbor analysis around each unique CP located
	RMAX	r	Maximum radius of sphere in the nearest neighbor analysis around each unique CP located. Considered as neighbors will be only those atoms whose nuclei are located within a sphere of radius RMAX, centered on the located CP. RMAX may reduce the actual value of NNB
			If IMETH=1 insert the following record
●*	ITYPE	0	(3,-3) L($\boldsymbol{r}$) CP search
		1	(3,-1) L($\boldsymbol{r}$) CP search
		2	(3,+1) L($\boldsymbol{r}$) CP search
		3	(3,+3) L($\boldsymbol{r}$) CP search
			insert always the following record
●*	NTYP	0	L($\boldsymbol{r}$) CP search along the internuclear axis joining nuclei A and B
		1	L($\boldsymbol{r}$) CP search along the axis joining two points a and b
			if NTYP=0 insert the following record
●*	IA1,IA2	n,m	**IA1**, n, is the progressive number of unique atom A ($1\leq n\leq$ number of non-equivalent atoms) **IA2**, m, is the atom B, that is the m-th neighbor of A (m is the NEW number in the Clusters around each of the non-equivalent atom printing at the beginning of the TOPOND output).
			elseif NTYP=1 insert the following two records
●*	X1,Y1,Z1	x,y,z	coordinates (**bohr**) of point a
●*	X2,Y2,Z2	x,y,z	coordinates (**bohr**) of point b
			insert the following record
●*	NMAX	0	Standard L($\boldsymbol{r}$) CP search along the line
		m	if IMETH=1, the L($\boldsymbol{r}$) CP search along the line is stopped when m different CPs of the required type (variable ITYPE) are found.

Atom	r	Atom	r	Atom	r	Atom	r	Atom	r	Atom	r
H	1.139	**Ne**	0.500	**K**	4.938	**Ni**	0.559	**Rb**	5.516	**Pd**	0.865
He	0.64	**Na**	3.436	**Ca**	3.773	**Cu**	0.535	**Sr**	4.369	**Ag**	0.830
Li	2.494	**Mg**	2.549	**Sc**	0.834	**Zn**	0.510	**Y**	1.204	**Cd**	0.802
Be	1.594	**Al**	2.081	**Ti**	0.779	**Ga**	0.487	**Zr**	1.140	**In**	0.770
B	1.188	**Si**	1.760	**V**	0.731	**Ge**	0.466	**Nb**	1.082	**Sn**	0.740
C	0.942	**P**	1.522	**Cr**	0.691	**As**	2.175	**Mo**	1.031	**Sb**	0.713
N	0.776	**S**	1.341	**Mn**	0.652	**Se**	1.833	**Tc**	0.984	**Te**	0.688
O	0.658	**Cl**	1.198	**Fe**	0.618	**Br**	1.652	**Ru**	0.940	**I**	2.228
F	0.569	**Ar**	1.080	**Co**	0.587	**Kr**	1.503	**Rh**	0.901	**Xe**	2.00

Table 3.2: Default **RSTAR** values in **bohr** for most atoms. See **Note** 1 and 2 for details.

Notes to Table 3.2

Note 1. Radius r (**RSTAR** value in **bohr**) of the sphere where, on its surface, $L(r)$ attains its maximum value in the VSCC of the isolated atom. The data, from Li to Xe, were taken from Table 1 of Ref. [16]. The outermost (valence) shell is missing for some atoms, using the $L(r)$ descriptor. In that evenience, the datum refers to the outermost (core) shell visible through $L(r)$. The datum for H refers to $H^{(-1)}$. Typical values for the cages CPs around the H are 0.7 **bohr**. [3]

Note 2. If not otherwise stated, these data refer to the neutral atoms. If the atoms are largely ionized in the crystal, the radius need to be reduced (increased) for a cation (for an anion).

3.2 Input Examples

With reference to Urea bulk 6-12g∗∗.

EX 1 Automated $L(\mathbf{r}) = -\nabla^2 \rho$ CP's search within the concentration shells of each of the five non-equivalent atoms (NEA), using NR algorithm. Atomic graphic lines (AGL) are evaluated.

```
TOPO
TLAP
0                 IAUTO=0
0,0,1,0,20,7,5.   IMETH, IEXT, IBPAT, IPRINT, NSTEP, NNB, RMAX
12,18             NT,NP (angular grid)
0                 NNA=0
1                 search over the VSCC shell of the first NEA, that is C1
0,0.              NMAX,RSTAR
1                 search over the VSCC shell of the second NEA, that is O3
0,0.              NMAX,RSTAR
1                 search over the VSCC shell of the third NEA, that is N5
0,0.              NMAX,RSTAR
1                 search over the VSCC shell of the fourth NEA, that is H9
0,0.38            NMAX,RSTAR (since H is largely positive, the value 0.38 Å is used
                  rather than the much larger default values reported for the hydride
                  in Table 3.2)
1                 search over the VSCC shell of the fifth NEA, that is H13
0,0.38            NMAX,RSTAR
```

Note: many $L(\mathbf{r}) = -\nabla^2 \rho$ CPs are recovered. Namely 24, 10, 15, 11, 10 following the CP search in the VSCC of the C, O, N, H9 and H13, respectively. In the case of C, a large part belongs to the C VSCC, but clearly not all. A detailed analysis requires to

evaluate their location, value, type, distance from the C nucleus (see Ref. [3] for an help). The search around the O atom locates three (3,-3) charge concentration maxima (two non bonded and associated to the lone pairs and one bonded along the C-O bond) as anticipated by the sp^2 hybridization of the O; the other 3 (3,+1) and 4 (3,-1) CPs all fall in the VSCC of the O; the search over the N VSCC recovers 5 (3,-3) charge concentrations (3 bonded concentrations associated to the two N-H bonds and to the C-N bond and two non bonded concentrations above and below the N nucleus associated to the lone pair); the remaining 10 CPs all fall in the N VSCC, except the last one; in the case of the two H most of the recovered CPs are located far from the H and not in the VSCC; the real interesting ones are the (3,+3) CPs located at about 0.614 **bohr** from the nucleus and directed towards the carbonyl oxygen. The hydrogen bond formation may be explained in terms of an acid-base mechanism, due to the interaction between these (3,+3) charge depletions on the H with the (3,-3) charge concentrations of the carbonyl oxygen lone pairs (see Ref. [3]).

EX 2 Automated L($\boldsymbol{r}$)= $-\nabla^2 \rho$ CP's search within the concentration shell of the carbonyl oxygen atom. EF algorithm is used and search of (3,-3) L($\boldsymbol{r}$) CPs is requested. Due to the sp^2 hybridization of the O, three (3,-3) charge concentration maxima (two non bonded and associated to the lone pairs and one bonded along the C-O bond) are expected. The input thus requires that the search be stopped after the recovery of three (3,-3) CPs.

TOPO	
TLAP	
0	IAUTO= 0
1,0,0,0,20,7,5.	IMETH, IEXT, IBPAT, IPRINT, NSTEP, NNB, RMAX
0	ITYPE [(3,-3) L($\boldsymbol{r}$) CP search]
12,18	NT,NP (angular grid)
0	NNA=0
0	no search over the VSCC shell of the first NEA, that is C1
1	search over the VSCC shell of the second NEA, that is O3
3,0.	NMAX (3) ,RSTAR
0	no search over the VSCC shell of the third NEA, that is N5
0	no search over the VSCC shell of the fourth NEA, that is H9
0	no search over the VSCC shell of the fifth NEA, that is H13

Note: The search around the O atom locates three (3,-3) charge concentration maxima (two non bonded and associated to the lone pairs and one bonded along the C-O bond) as anticipated by the sp^2 hybridization of the O and as explicitly required in input. This is a "targeted', very efficient, search of an important chemical feature of the Lapalcian distribution around the O.

EX 3 CPs search along the line joining C1 (0,0,0) and O3 (0,0,1), using NR algorithm.

TOPO	
TLAP	
2	IAUTO= 2
0,0,0,0,10,7,5.	IMETH, IEXT, IBPAT, IPRINT, NSTEP, NNB, RMAX
0	NTYP
1,1	IA1,IA2
0	NMAX

Note: The search along the C-O bond recovers a (3,-3) charge concentration in the Oxygen VSCC and a (3,-1) CP in the core depletion region of the C.

Chapter 4

Atomic basins and their properties

4.1 Atomic basins properties (ATBP)

This section deals with the determination of atomic basins and of their properties. An atomic basin Ω is defined as portion of space bounded by a surface S(Ω, $\mathbf{r}_s$) whose points $\mathbf{r}_s$ all fulfil the condition $\boldsymbol{\nabla}\rho(\boldsymbol{r_s})\cdot\boldsymbol{n(r)} = 0$, where $\boldsymbol{n(r)}$ is a unit vector normal to the surface. The atomic surfaces are thus called zero-flux surfaces, ZFSs. [1, 4] Atomic basins are necessarily finite in crystals, while they may have a finite or infinite volume at lower periodicity. [4] This means that every point of the ZFSs is within a finite distance from the associated nuclei in crystals, while a part of them may be at infinite distance in systems of lower periodicity. In this case, information is required to "bound" the atoms at a finite distance, in order to get their properties by integration. In general every atomic property, like the electron population, the kinetic energy, etc. can be expressed in terms of a corresponding three-dimensional density distribution that can be integrated over Ω to obtain its average value. [1] Integration over each non equivalent atom (NEA) Ω is essentially performed in two main steps: a) ZFSs determination and b) integration within the volume bounded by the ZFSs. The ZFSs determination is performed according to the algorithm devised by T.A. Keith. [17] It is a time-consuming algorithm, but generally safe, that determines within a given accuracy (variable **ACC**) the lengths of the rays starting from the nucleus of the integrated atom and ending up at their intersections with the ZFSs, and associated to all possible pairs (θ_l, φ_j) of the angular grid. The computational time required by the ZFS determination is, therefore, proportional to **ITH*IPHI**, i.e. to the product of the number of θ and φ angular points, repectively. In some peculiar case, a given integration ray may intersect the ZFSs more than once. This typically happens with the rays emanating from an atom Ω lying close to a cation. [17] If this is the case, the search for the second ZFSs intersections should be performed (NOSE=1) to get meaningful integration results (otherwise a small or large portion of Ω would be missed in the integration).

Once the ZFSs have been so determined, the integration of properties within Ω is divided in two parts, integration within the so-called β-sphere and integration in the remaining part of Ω. The β-sphere is a sphere surely located within Ω and where the electron density and other properties slightly deviate from spherical symmetry. Integration within this sphere, does not obviously require the evaluation of the length of the integrating radii, being all automatically defined by the single value of the β-sphere radius. The latter needs to be lower than the distance from the nucleus (of the atom being integrated) to its closest bond critical point. The angular grid, due to the supposed slight departure from spherical symmetry, does not need to be very thick for integration within the β-sphere. If the departure from spherical symmetry is, instead, appreciable, one needs to adopt a more dense grid (see input). The β-sphere radius needs to be provided in input for any NEA atom and Non-Nuclear Attractor (NNA) in the cell, even if they are not required to be integrated. In fact, the information on the β-sphere

radius information is also used in the ZFSs determination to distinguish regions of space that are certainly attributable to a given atomic basin or NNA. Integration in the remaining part of Ω is then performed, using for each pair (θ_l, φ_j) the length of the associated radius minus the length of the β-sphere radius. If second intersections were found in the ZFS determination step, then the code automatically takes into account them, by integrating from the nucleus to the first intersection and then from the second intersection up to the ZFS.

The accuracy of the integration step depends on the size of the angular grid and on the number of radial points along each ray. As a rule of thumb, use a dense and larger angular grid in the region outside the β-sphere and the highest possible number of radial points inside the β-sphere. The integration step has a negligible (about 1%) computational cost compared to that (about 99%) of the ZFSs determination step. So the overall (surface determination and integration) computational time is dominated by the size of the angular grid in the region outside the β-sphere. On top of this, the larger is the ZFSs accuracy requested, i.e. the smaller is the value of **ACC**, the larger will be the computational time for a given angular grid in the region outside the β-sphere. Since the ZFSs determination step is computationally demanding and dominating, it may be advisable to save the results of the ZFSs step, i.e. the lengths of the integration radii, for subsequent integrations (with the same angular grid in the region outside the β-sphere), skipping in this way the time-consuming ZFS determination step or reducing considerably its computational time . This may be useful, if a change of model or basis set is performed (in this case the integration radii of another model hamiltonian or basis set are used as good starting guess for the radii associated to the new model/basis set) or if one desires to make an integration within the same basin, but using a different density matrix (e.g. that of the IAM model, **PATO** option in **Properties**, or an energy-weigthed density matrix, **PDIDE** option in **Properties**).

4.2   Input cards

Due to the fact that this is usually the most time demanding step of any topological analysis, in the new version of the code three alternative procedures for the atoms selection have been implemented. A different keyword anticipates different input structures:

UNI   the integration is performed for all the non-equivalent atoms of the unit cell;

STD   the same integration parameters are used to integrate over the basin of all the non-equivalent atoms of the unit cell so no other input parameters are required;

SEL   the integration is performed on a given set of atoms.

4.2.1 Integration over the basin of all the non-equivalent atoms

record	variable	value	Meaning
•*	UNI		atomic properties are evaluated for all the non-equivalent atoms

begin loop over the non-equivalent atoms (NEA)

insert this (these) card(s) for each NEA			
•*	IYES	0	atomic properties for this NEA are not evaluated
		1	atomic properties for this NEA are evaluated
	TOL	R	size of the the β sphere for this NEA (required value, even if the atoms is not integrated, see explanation in the introduction to this program section). The β sphere radius is conveniently taken equal to the distance from the nucleus of the atom to its nearest BCP.
if IYES=1, insert also for the current NEA			
•*	NVI	N	number of stars of neighbors of the NEA being integrated which have to be considered as possible attractors of the $\nabla\rho$ paths launched from points along the IRs. It is suggested to define n so as to include at least the neighbours bonded to such NEA. However, it may often be required an higher number of neighbors, because of the numerical character of the ZFSs determination procedure and because of the general non-smooth nature of the ZFSs.
	IRSUR	0	Default
		1	the lengths of the IRs obtained in a previous run are read from fortran READSUR.DAT (fortran unit 97) and used as an initial guess for the IRs lengths. The program selects the proper surface information in the file on the basis of the perfect matching with the kind of integrated atom, the value of its coordinates and the required angular grid size. This option may be useful when using a different basis set or a different Hamiltonian with respect to a previous run on the same system. Clearly one has to adopt the same angular grid of the previous run.
		-1	The lengths of the IRs are kept fixed to those obtained in a previous run and read from unit READSUR.DAT (fortran unit 97). This is a particularly useful option whenever one desires to keep the ZFS obtained in a previous run and use instead, in the integration step, a different density matrix (e.g that of an independent atom model, PATO option, or a specific energy-weighted density matrix, PDIDE option)
	IWSUR	0	Default
		1	the lengths of the IRs are saved on unit SAVESUR.DAT (fortran unit 99).Saving the IRs is mandatory if one desires to use IRSUR $\neq 0$ in a subsequent run (see above). Data for different unique atoms and with different angular grid sizes for each atom may be saved on SAVESUR.DAT. Each surface information in the file is labelled with the kind of atom it belongs, the coordinates of such atom and the selected angular grid size.
	IPRINT	0	normal printing
		1	debug printing
•*	IPHI	M	Angular integration outside β-sphere: number of φ values (max 120). Suggested values: H atoms, $m = 48$; from second row atoms on, $m = 64$. H atoms involved in H-bonds may require a better integration, ($m = 64$)
	ITH	N	Angular integration outside β-sphere: number of θ values (max 96). Suggested values: H atoms, $n = 32$; from second row atoms on, $n = 48$. H atoms involved in H-bonds may require a better integration, ($n = 48$)
	IBETP	L	radial integration inside β-sphere: number of r values (max 120). Suggested values: H atoms, $l = 96$; other atoms $l = 120$

	IMUL	I	radial integration outside β-sphere and angular integration inside β-sphere. These values are a function of the length of the current IR minus the value of the β-sphere radius. I=0 default values. I=n: the default values are roughly multiplied by n (the values are set to their maxima, φ=120, θ=96, radial=120 if they would exceed them)
	IEXT	0	Only properties depending on ρ and on its derivatives are evaluated
		1	Properties (kinetic energy densities) depending on the non-diagonal elements of the first-order density matrix are also evaluated [4]
	NOSE	0	Default (no search of a second intersection of each IR with a ZFS [17])
		1	Second intersections are searched for (warning: very costly!!!). To be exploited only when poor integrations have obtained with NOSE=0
	ACC	0.	The standard very high accuracy in the determination of ZFS is adopted. Such accuracy means that each IR length is determined within 0.001 **bohr**. If "simple" quantities like the atomic populations are only searched for, such accuracy is generally excessive. It may be safely lowered to 0.005 or even to 0.01 **bohr**, with great saving of CPU time.
		X	The IR lengths are determined within X **bohr**.
**if IYES=1 and .NOT. 3D (crystal) system,** **insert the following card for the current NEA**
•*	SIZ	R	the minimum IR length that must be reached to make sure that a given IR does not have a finite intersection with the ZFS. If the periodicity dimension of the system is < 3, the atomic basins may (but may also not) have an infinite volume (see general ATBP explanation section above). A given IR may have therefore an infinite length and one has to define both the minimum length (the value r of SIZ) to classify this IR as infinite in the ZFS search and the actual length used in the numerical integration step (the value s of TIN, see below). Typical value for SIZ is 5 Å.
	TIN	S	the IR length to be used in the radial integration when the IR does not have finite intersections with the ZFS (typical value 5-8Å)

end loop over the NEAs

**Insert the following card**
•*	NNA	0	non-nuclear attractors (NNAs) are not present
		m	there are m NNAs to be considered as possible attractors of $\nabla\rho$ trajectories

begin the loop over the NNAs

**If NNA>0,insert the following cards for each NNA**
•*	XNNA YNNA ZNNA	x,y,z	NNA coordinates (**bohr**)
•*	IYNNA	0	atomic properties for this NNA are **not** evaluated
		1	atomic properties for this NNA are evaluated
	TOL	R	size of the capture sphere for this NNA when another NEA or NNA is integrated. This value should be about the radius of the β-sphere. This radius should be roughly taken equal to the distance from the NNA to its nearest BCP.
**if IYNNA=1 insert for the current NNA the same kind of information** **given for each integrated (IYES=1) NEA**

end of loop over the NNAs

4.2.2 Integration over the basin of all the non-equivalent atoms, adopting standard parameters

The integration is performed over all the NEA with the following parameters: NVI = 10, IRSUR, IWSUR, IPRINT = 0, IPHI = 64, ITH = 48, IBETP = 96, SIZ = 5.0, TIN = 8.0. The size of the β sphere for each atom is selected accordingly to the value reported in Table 4.1.

record	variable	value	Meaning
•*	STD		atomic properties are evaluated for all the non-equivalent atoms
Insert the following card			
•*	NNA	0	non-nuclear attractors (NNAs) are not present
		m	there are m NNAs to be considered as possible attractors of $\nabla\rho$ trajectories
begin the loop over the NNAs			
If NNA>0,insert the following cards for each NNA			
•*	XNNA YNNA ZNNA	x,y,z	NNA coordinates (**bohr**)
•*	IYNNA	0	atomic properties for this NNA are **not** evaluated
		1	atomic properties for this NNA are evaluated
	TOL	R	size of the capture sphere for this NNA when another NEA or NNA is integrated. This value should be about the radius of the β-sphere. This radius should be roughly taken equal to the distance from the NNA to its nearest BCP.
if IYNNA=1 insert for the current NNA the same kind of information given for each integrated (IYES=1) NEA			
end of loop over the NNAs			

Atom	r	Atom	r	Atom	r	Atom	r	Atom	r	Atom	r
H	1.139	**Ne**	0.500	**K**	4.938	**Ni**	0.559	**Rb**	5.516	**Pd**	0.865
He	0.64	**Na**	3.436	**Ca**	3.773	**Cu**	0.535	**Sr**	4.369	**Ag**	0.830
Li	2.494	**Mg**	2.549	**Sc**	0.834	**Zn**	0.510	**Y**	1.204	**Cd**	0.802
Be	1.594	**Al**	2.081	**Ti**	0.779	**Ga**	0.487	**Zr**	1.140	**In**	0.770
B	1.188	**Si**	1.760	**V**	0.731	**Ge**	0.466	**Nb**	1.082	**Sn**	0.740
C	0.942	**P**	1.522	**Cr**	0.691	**As**	2.175	**Mo**	1.031	**Sb**	0.713
N	0.776	**S**	1.341	**Mn**	0.652	**Se**	1.833	**Tc**	0.984	**Te**	0.688
O	0.658	**Cl**	1.198	**Fe**	0.618	**Br**	1.652	**Ru**	0.940	**I**	2.228
F	0.569	**Ar**	1.080	**Co**	0.587	**Kr**	1.503	**Rh**	0.901	**Xe**	2.00

Table 4.1: Default **TOL** values in **bohr** for most atoms.

4.2.3 Integration over a given set of atoms

With the keyword SEL, followed by an integer number n, it is possible to perform the integration over the basin of n selected atoms, defining all the computational parameters by input as in the UNI case.

In the input file the only difference with respect to the UNI case is that the IYES card is not any more a switch (perform or not perform the integration) but univocally identify the selected atom with its progressive number in the *irreducible* unit cell numeration (reported in the CRYSTAL output).

record	variable	value	Meaning
●*	SEL		atomic properties are evaluated for a set of selected atoms
●*	NSEL	N	the selected atoms are N

begin loop over the N selected atoms

Insert the following card			
insert this (these) card(s) for each atom			
●*	IYES	NA	sequential number of the selected atom in the irreducible unit cell order
	TOL	R	size of the the β sphere for this NE (required value, even if the atoms is not integrated, see explanation in the introduction to this program section). The β sphere radius is conveniently taken equal to the distance from the nucleus of the atom to its nearest BCP.

Then, the input parameters follow as for the UNI keyword

4.3   Input Examples

With reference to Urea bulk 6-12g∗∗.

EX 1 Boundary surface determination and integration over the resulting atomic basin for each of the five NEA

TOPO	
ATBP	
UNI	
1,0.43	integration over C1 atom,TOL (size of the beta and capture spheres)
10,0,1,0	NVI, IRSUR, IWSUR(the surface data are saved on SAVESUR.DAT, fortran unit 99), IPRINT
64,48,120,2,1,0,0.002	IPHI, ITH, IBETP, IMUL, IEXT, NOSE, ACC
1,0.8	integration over O3 atom,TOL (size of the beta and capture spheres)
10,0,0,0	NVI, IRSUR, IWSUR,IPRINT
64,48,120,2,1,0,0.002	IPHI, ITH, IBETP, IMUL, IEXT, NOSE, ACC
1,0.74	integration over N5 atom,TOL (size of the beta and capture spheres)
10,0,1,0	NVI, IRSUR, IWSUR (the surface data are saved on SAVESUR.DAT), IPRINT
64,48,120,2,1,0,0.002	IPHI, ITH, IBETP, IMUL, IEXT, NOSE, ACC
1,0.24	integration over H9 atom,TOL (size of the beta and capture spheres)
10,0,0,0	NVI, IRSUR, IWSUR, IPRINT
48,32,96,2,1,0,0.002	IPHI, ITH, IBETP, IMUL, IEXT, NOSE, ACC
1,0.24	integration over H13 atom,TOL (size of the beta and capture spheres)
10,0,0,0	NVI, IRSUR, IWSUR, IPRINT
48,32,96,2,1,0,0.002	IPHI, ITH, IBETP, IMUL, IEXT, NOSE, ACC
0	NNA (no NNA is present)

EX 2 Boundary surface determination and integration over the resulting atomic basin for the carbon atom C1 and the Nitrogen atom N5, requiring a greater accuracy (0.001 **bohr**) for the ZFS than in the example 1 and reading as an initial guess the ZFS determined in the example 1.

```
TOPO
ATBP
UNI
1, 0.43                integration over C1 atom,TOL (size of the beta and capture spheres)
10,1,1,0               NVI,IRSUR (previous ZFS information read from READSUR.DAT,
                       fortran unit 97, and used as an initial guess), IWSUR (final ZFS
                       information written on file SAVESUR.DAT), IPRINT
64,48,120,2,1,0,0.     IPHI,ITH,IBETP,IMUL,IEXT,NOSE,ACC (default value)
0, 0.8                 no integration over O3 atom,TOL (size of the beta and capture
                       spheres)
1, 0.74                integration over N5 atom,TOL (size of the beta and capture spheres)
10,1,1,0               NVI,IRSUR  (previous   ZFS   information   read   from   file
                       READSUR.DAT), IWSUR (final ZFS information written on
                       file SAVESUR.DAT), IPRINT
64,48,120,2,1,0,0.     IPHI,ITH,IBETP,IMUL,IEXT,NOSE,ACC (default value)
0, 0.24                no integration over H9 atom,TOL (size of the beta and capture
                       spheres)
0, 0.24                no integration over H13 atom,TOL (size of the beta and capture
                       spheres)
0                      NNA (no NNA is present)
```

EX 3 Integration over the atomic basin for the carbon atom obtained in step 2, but using the PATO density matrix

```
PATO
0  0
TOPO
ATBP
UNI
1, 0.43                integration over C1 atom,TOL (size of the beta and capture spheres)
10,-1,0,0              NVI,IRSUR    (IRSUR=-1    previous    ZFS    information    read
                       READSUR.DAT and used unmodified), IWSUR,IPRINT
64,48,120,2,1,0,0.     IPHI,ITH,IBETP,IMUL,IEXT,NOSE,ACC (default value)
0, 0.8                 no integration over O3 atom,TOL (size of the beta and capture spheres)
0, 0.74                no integration over N5 atom,TOL (size of the beta and capture spheres)
0, 0.24                no integration over H9 atom,TOL (size of the beta and capture spheres)
0, 0.24                no integration over H13 atom,TOL (size of the beta and capture spheres)
0                      NNA (no NNA is present)
```

EX 4 Boundary surface determination and integration over the resulting atomic basin for each of the five NEA with standard parameters

```
TOPO
ATBP
STD
0        NNA (no NNA is present)
```

EX 5 Boundary surface determination and integration over the oxygen and two non equivalent hydrogen atoms

```
TOPO
ATBP
SEL
3
2,0.8                      integration over O3 atom,TOL (size of the beta and capture spheres)
10,0,0,0                   NVI, IRSUR, IWSUR,IPRINT
64,48,120,2,1,0,0.002      IPHI, ITH, IBETP, IMUL, IEXT, NOSE, ACC
4,0.24                     integration over H9 atom,TOL (size of the beta and capture spheres)
10,0,0,0                   NVI, IRSUR, IWSUR, IPRINT
48,32,96,2,1,0,0.002       IPHI, ITH, IBETP, IMUL, IEXT, NOSE, ACC
5,0.24                     integration over H13 atom,TOL (size of the beta and capture
                           spheres)
10,0,0,0                   NVI, IRSUR, IWSUR, IPRINT
48,32,96,2,1,0,0.002       IPHI, ITH, IBETP, IMUL, IEXT, NOSE, ACC
0                          NNA (no NNA is present)
```

Chapter 5

Plotting Utilities and Options

5.1 Plotting functions in 2 dimension (PL2D)

This section prepares the required information for a number of useful 2-dimensional (2D) plots on a plane defined through 3 points or nuclei or a suitable combination of points and nuclei. The 2D plots include: contour plots of the electron density, the electron spin density, the Laplacian or the minus Lapalcian of the electron density, the magnitude of the electron density gradient, two kinds of kinetic energy densities, the virial field density, the ELF and the gradient paths.

Moreower, also *deformation densities* and *interaction density* can be obtained and plotted.
Deformation density refers to the difference between the computed electron density and the density given by the superposition of undistorted atomic densities. The electron density (or other scalar functions) for the model of non deformed atoms is obtained by inserting the PATO keyword in **properties** before running the topological part.
Interaction density is the difference between the computed electron density and that of non interacting molecules. The electron density (or other scalar functions) for the model of non interacting molecules is obtained by running TOPOND on a wavefunction evaluated through the MOLSPLIT keyword in the CRYSTAL14 Manual. [18]

The cumulative information prepared by PL2D and stored in the files listed in Table 5.1 can be post-processed in two different way:
(i) by an external code, *p2dtopo.f* (author C. Gatti) downloadable from the CRYSTAL website. *p2dtopo.f* produces graphic files in HP-GL (Hewlett Packard Graphic Language) that are easily translated by the UNIX program hp2xx (part of GNU software) in several format (PDF file, PCX image, etc.);
(ii) by mean of CRYSPLOT, a free visualization environment available on the crys-plot.crystalsolutions.eu web site.

5.1.1 Gradient Paths

There are several options to obtain gradient paths in PL2D. The user may trace:

- all downhill gradient paths originating from the (3,-3) CP attractors (including nuclei and NNAs) and from the 2-dimensional manifold of the (3,-1) BCP associated to the two Hessian eigenvectors defining the interatomic surface at the BCP. In the latter case the interatomic surface needs to be on the plotting plane or at least to be initially contained in it;

- those gradient paths yielding the molecular or crystal graph and the atomic basin boundaries (intersections of the ZFS with the XY plot plane). There are two uphill gradients paths originating from each (3,-1) BCP lying in the XY plot plane and forming the bond

path and two downhill gradient paths originating from each (3,-1) BCP and marking the intersections of the interatomic ZFSs with the XY plot plane;

- those gradients paths yielding the molecular or crystal graph only (that is the collection of bond paths).

When the plot plane is not a symmetry plane the gradient paths will leave the plane, even if they have an origin (or a terminus) on that plane. The user may force a projection of the gradient paths on the plot plane through the TR1 and IPLANE variables. This may lead to unphysical crossing of gradient paths if the plot plane significantly departs from the condition of being a symmetry plane. When such a deviation is minimal, gradient path projection may be conveniently used to ensure a proper filling of the XY plot plane with gradient paths. In order to facilitate this task, either when the gradient paths lie in the plane or when the plot plane is not a "perfect" symmetry plane, the user may define a window, which is larger than the area of the plot, from which may originate gradient paths. This option allows for tracing those gradient paths that lie and traverse the plot area, but have their origin (or terminus) outside the plot area.

5.1.2   The $p2dtopo.f$ program

Based on information stored in the files prepared by PL2D section and by the value of an option selected by the user, $p2dtopo.f$ may produce contour plots of scalar functions, gradient path plots or a suitable combination of both, by overlaying the selected gradient paths over the contour plots. $p2dtopo.f$ may also evaluate contour plots for the sum or difference of the various computed scalar functions. Also these plots may be overlaid with gradient paths. For instance $p2dtopo.f$ enables to evaluate the contour plot deformation density and to overlay this contour plot with the molecular graph and interatomic surface boundaries of the computed electron density. Analogously one may obtain the corresponding plots for the interaction density overlaid with these same gradient paths.

A self-explained *bash* script, TOPLOT, can be downloaded from the web site. It performs all the steps, summarized in appendix D, which, starting from the $*.DAT$ files produced by the PL2D keyword and summarized in Table 5.1, yield to the corresponding postscript files.

M	Scalar function (or $\nabla\rho$ plot) type		File name
1	Electron density	ρ	SURFRHOO.DAT
2	Spin density	$(\rho_\alpha - \rho_\beta)$	SURFSPDE.DAT
3	Laplacian of the electron density	$\nabla^2\rho$	SURFLAPP.DAT
4	Negative of the Laplacian of the electron density	$-\nabla^2\rho$	SURFLAPM.DAT
5	Magnitude of the gradient of ρ	$\|\boldsymbol{\nabla}\rho\|$	SURFGRHO.DAT
6	Hamiltonian Kinetic energy density	K	SURFKKIN.DAT
7	Lagrangian Kinetic energy density	G	SURFGKIN.DAT
8	Virial field density	V	SURFVIRI.DAT
9	ELF (Becke electron localization function)		SURFELFB.DAT
10	$\boldsymbol{\nabla}\rho$ trajectories (except molecular/crystal graph)		TRAJGRAD.DAT
11	Molecular/crystal graph(and atomic basin boundaries)		MOLGRAPH.DAT
12	$\boldsymbol{\nabla}\rho$ trajectories (including molecular/crystal graph)		TRAJMOLG.DAT
	Other files		
Any M	Common information for the XY plot		P2DCRYIN.DAT

Table 5.1: Each function is stored on a formatted fortran files. M is the value which has to be inserted in the P2DCRYIN.DAT file to process the correspondig functions.

5.2 Input cards for 2D

rec	variable	value	Meaning
Three points (A,B,C) or nuclei (A,B,C) must be given to define the plot plane			
•*	KA	0	A is not a nucleus
		m	atom label of nucleus A
if KA=0 insert			
•*	XA, YA, ZA	x,y,z	coordinates (**bohr**) of point A
if KA>0 and.NOT.MOLECULE insert			
•*	LA, MA, NA	l,m,n	indeces (direct lattice) of the cell where A is located.
Insert			
•*	KB	0	B is not a nucleus
		m	atom label of nucleus B
if KB=0 insert			
•*	XB, YB, ZB	x,y,z	coordinates (**bohr**) of point B
if KB>0 and .NOT.MOLECULE insert			
•*	LB, MB, NB	l,m,n	indeces (direct lattice) of the cell where B is located.
Insert			
•*	KC	0	C is not a nucleus
		m	atom label of nucleus C
if KC=0 insert			
•*	XC, YC, ZC	x,y,z	coordinates (**bohr**) of point C

			if KC>0 and .NOT.MOLECULE insert
●*	LC,MC,NC	l,m,n	indeces (direct lattice) of the cell where C is located.
			Insert
●*	ISHFT	0	origin as in the original frame.
		1	origin of the plot is translated to a point lyring on ABC plane
		2	origin of the plot is put at the barycentre of the nuclei (points) which define the ABC plane. A mass equal to 1 is assigned to all nuclei (and/or points).
		3	the origin of the plot lies along the A-B axis (taken as the x axis of the plot) and its actual position is defined by VMOD (see below).**This is the suggested and most practical choice for ISHFT**
		4	the origin of the plot is set at nucleus (point)A
			NOTE: A warning message is issued if, as a consequence of a given choice of the origin, the nuclei (points) A,B,C do not longer lie in the XY plot plane.
			if ISHFT=1, insert
●*	X0,Y0,Z0	x,y,z	origin coordinates (**bohr**)
			if ISHFT=3, insert
●*	VMOD	r	if $r=0$, the origin is at A; if $r=1$ the origin is at B. Intermediate r values shift the origin along A-B. Negative r values or values greater than 1 may also be assigned, with obvious meaning.
			Insert
●*	NSTA	m	number of stars of neighbors of A,B,C used in the cluster construction around A,B and C atoms or points. From these clusters, the atoms whose nuclei lie in the ABC plane are selected and their position denoted with the sign * in the plots. For the other atoms, a + sign designs their position projection in the plot plane. The NSTA variable is also used in other parts of the code. It determines: a) the atom pairs considered in the evaluation of the molecular (crystal) graph on the ABC plane; b) the number of origins (nuclei) for tracing the downhill $\nabla\rho$ trajectories (gradient paths) on the ABC plane
	RMAX	r	maximum radius of each cluster (see NSTA explanation); RMAX may, locally, reduce the actual value of NNB
●*	ICONT	0	test run to check if the choice of the ABC plane was made correct. The program stops after printing the coordinates in the plot frame of the A,B,C nuclei or points (and of the nuclei belonging to their clusters).
		1	normal run
			if ICONT=0, STOP else insert the following lines
●*	XMI, XMA, XIN	r,w,t	the plot plane is XY; XMI and XMA are the minimum and maximum X value, while XIN is the grid interval along X (plot frame coordinates)
●*	YMI, YMA, YIN	s,q,p	as above for the Y coordinate
●*	IFU(M),M=1,12	0	the M-th scalar function (or $\nabla\rho$ plot)is not evaluated
		1	the M-th scalar function (or $\nabla\rho$ plot) is evaluated. Table 5.1 lists the names of the files which contain the values of each computed function (variable IFU). Common information for the XY plot (system geometry, Euler rotation angles from crystal to plot frame, plot size, etc.) is saved in file P2CRYIN.DAT. These files are the input for the external *p2dtopo.f* program.
		2	if K=9, $\text{ELF}^{\beta\beta}$ instead of $\text{ELF}^{\alpha\alpha}$ is saved on SURFELFB file

•A80	NAME		plot title
•*	SCALE	r	plot scale ($\AA$/cm or **bohr**/cm, according to the keyword ANGSTROM or BOHR selected in the CRYSTAL run)
if IFU(10) or IFU(11) or IFU(12) equal 1 insert			
•*	TOLER	r	an atom in the XY plot plane is considered as an origin of downhill gradient paths or as a terminus of an atomic interaction line (AIL) if: a) its distance from the plot border is < TOLER b) its |z-plot coordinate| is <TR1. $\boldsymbol{\nabla}\rho$ trajectories are projected on the XY plot plane
	TR1	w	plot $\boldsymbol{\nabla}\rho$ trajectory segment if the current |z-plot coordinate| is <TR1
	IPLANE	0	normal tracing of $\boldsymbol{\nabla}\rho$ trajectories
		1	the starting point of each $\boldsymbol{\nabla}\rho$ trajectory segment is forced on the XY plot plane
if IFU(11)=1 or IFU(12)=1 insert			
•*	THR	r	the maximum distance between bonded atomic pairs which is taken into account during the automated tracing of the molecular (crystal) graph.
	IL(K), K=1,3	l,m,n	the $\boldsymbol{\nabla}\rho$ trajectories that originate at bond critical points (BCPs) and have as initial direction the K-th eigenvector of the Hessian of ρ at BCPs [1], are traced out (IL(K)=1) or skipped (IL(K)=0). The K-th eiegenvector is associated to the K-th eigenvalue $\lambda_K(\lambda_1 \leq \lambda_2 \leq \lambda_3)$[1]
if IFU(10)=1 or IFU(12)=1, insert			
•*	NPATH	N	number of downhill $\boldsymbol{\nabla}\rho$ trajectories originating from each (3,-3) attractor (suggested value: 36)
	NEXTR	0	no other attractors are considered as origins of downhill $\boldsymbol{\nabla}\rho$ trajectories.
		M	other NEXTR attractors, like the non-nuclear attractors (NNAs) or the 2D attractors associated to a BCP, must be considered as origins of downhill $\boldsymbol{\nabla}\rho$ trajectories (this latter is the case where the associated interatomic surface lies or at least originates in the plane of the plot).
If (NEXTR.NE.0) insert NEXTR cards			
•*	R(K),K=1,3	x,y,z	x,y,x coordinates (**bohr**) of each additional origin

5.3 2D Input Examples

With reference to Urea bulk 6-12g∗∗.

EX 1 Preparation of files for 2D plots in the N6 (0,-1,0), N5 (0,0,0) and O3 (0,-1,1) plane (XY plane of the plot). The origin of the plot is placed at mid-point of the N6(0,-1,0)-N5(0,0,0) axis (it is selected as the X axis of the plot, ISHFT=3 and VMOD=0.5). This is only a test job (ICONT=0) to check the correct choice of the plotting plane and the coordinates of atoms in the transformed frame to verify which atoms lie on the XY plane of the plot.

```
TOPO
PL2D
6           N6 in 0,-1,0
0,-1,0
5           N5 in 0,0,0
0,0,0
3           O3 in 0,-1,1
0,-1,1
3           ISHFT=3
0.5         VMOD=0.5
30,15.0     NSTA=30, RMAX=15.
0           ICONT=0
END
```

EX 2 As in example 1 but now the files for 2D plots are actually prepared by the code (ICONT=1). It is here required to evaluate the electron density, the Laplacian of the electron density, the crystal graph and the projection of atomic basin boundaries on the selected plane and the gradient path trajectories (IFU(1)=1, IFU(3)=1, IFU(11)=1, IFU(12)=1)). In tracing the gradient paths, TOLER set to 2.0 defines the extra frame area, with respect to the plotting area, to be included as a possible origin or terminus of gradient paths, and only gradient paths lying on the XY plot plane are traced out (TR1=0.0, IPLANE=0).

```
TOPO
PL2D
6                                N6 in 0,-1,0
0,-1,0
5                                N5 in 0,0,0
0,0,0
3                                O3 in 0,-1,1
0,-1,1
3                                ISHFT=3
0.5                              VMOD=0.5
30,15.0                          NSTA=30, RMAX=15.
1                                ICONT=1
-4.,4.,.025                      XMI,XMA,XIN
-3.3,4.7,.025                    YMI,YMA,YIN
1,0,1,0,0,0,0,0,0,0,1,1          IFU
urea 6-21gss bulk/ molecular plane   PLOT TITLE
0.55                             SCALE=0.55
2.,0.0,0                         TOLER=2., TR1=0.0 , IPLANE=0
2.2,1,1,1                        THR=2.2, IL vector all set to 1
36,0                             NPATH=36, NEXTR=0
END
```

5.4   Plotting functions in 3 dimension (PL3D)

Three-dimensional (3D) grid files of a number of scalar functions can be evaluated in a box defined by the user in terms of either cartesian or fractional coordinates. The computed functions are listed in Table 5.3, along with the names of the corresponding data files. There are two main possibilitis for the output format:

(i) the first, which represents the historical format, produce files (*.DAT) in which the information is saved as detailed in Table 5.2. These units can be post processed by the **NCI-milano** [19] public code. This program also allows the study of non-covalent interactions

through the reduced electron density gradient tool; [20]

(ii) the second possibility is to produce CUBE format files that can be visualized by several graphic programs, as for istance **Jmol**, www.jmol.org, an open-source Java viewer for chemical structures in 3D.

5.5 Input cards for 3D

To produce files in the DAT format the input is the following:

rec	variable	Value	Meaning
•*	IFRA		Units used in the definition of 3D grids
		0	**bohr** or $\mathring{A}$, according to INF(72) value
		1	fractionary units (conventional cell)
•*	XMI, XMA, XIN	r,w,t	XMI and XMA are the minimum and maximum X value, while XIN is the grid interval along X (or the a axis, if IFRA=1)
•*	YMI, YMA, YIN	s,q,p	as above for the Y coordinate is the grid interval along Y (or the b axis, if IFRA=1)
•*	ZMI, ZMA, ZIN	e,f,g	as above for the Z coordinate is the grid interval along Z (or the c axis, if IFRA=1)
•*	IFU(M),M=1,9	0	the M-th scalar function is not evaluated (see functions and corresponding file names listed in Table 5.1). File content is as explained in Table 5.2.
		1	the M-th scalar function is evaluated (see Table 5.3)
		2	If M=9, $ELF^{\beta\beta}$ instead of $ELF^{\alpha\alpha}$ is saved on file 3DELFB.DAT

To produce files in the CUBE format, the input is as follows:

rec	variable	Value	Meaning
•*	IFRA		Units used in the definition of 3D grids
		0	**bohr** or $\mathring{A}$, according to INF(72) value
•*	XMI, XMA, XST	r,w,t	XMI and XMA are the minimum and maximum X value, while XSP is the step interval along X
•*	YMI, YMA, YSP	s,q,p	as above for the Y coordinate is the step interval along Y
•*	ZMI, ZMA, ZSP	e,f,g	as above for the Z coordinate is the step interval along Z
•*	IFU(M),M=1,9	0	the M-th scalar function is not evaluated (see functions and corresponding file names listed in Table 5.1). File content is as explained in Table 5.2.
		1	the M-th scalar function is evaluated (see Table 5.3)
		2	If M=9, $ELF^{\beta\beta}$ instead of $ELF^{\alpha\alpha}$ is saved on file 3DELFB.DAT

rec	Content	Format
1	Number of points along x, y and z, (NX, NY, NZ)	3I4
2	xmi,xma,xin (in **bohr**)	3(E15.8,1X)
3	ymi,yma,yin (in **bohr**)	3(E15.8,1X)
4	zmi,zma,zin (in **bohr**)	3(E15.8,1X)
5-xx	Values of the scalar which are written in bunches of NX values with 8 values per record. So for instance if NX=34, the bunches will contain 34 values and be made by 5 records per bunch (4 records with 8 values each and the final record of the bunch with 2 values only) The total number of points is given by NPOINT=NX*NY*NZ: NX=(xma-xmi)/xin +1.1D0 (NX is integer!) NY=(yma-ymi)/yin +1.1D0 (NY is integer!) NZ=(zma-zmi)/zin +1.1D0 (NZ is integer!) The NPOINT values are written with the innermost do loop on X and the outermost do loop on Z, starting from xmi,ymi,zmi. DO 200 L=1,NZ DO 201 K=1,NY DO 202 J=1,NX	8(E15.8,1X)

Table 5.2: Content of the data files, for each plotted (IFU(M)=1) scalar function.

M	Scalar function type		File name
1	Electron density	ρ	3DRHOO.DAT//CUBE
2	Spin density	$(\rho_\alpha - \rho_\beta)$	3DSPDE.DAT//CUBE
3	Laplacian of the electron density	$\nabla^2\rho$	3DLAPP.DAT//CUBE
4	Negative of the Laplacian of the electron density	$-\nabla^2\rho$	3DLAPM.DAT//CUBE
5	Magnitude of the gradient of ρ	$|\boldsymbol{\nabla}\rho|$	3DGRHO.DAT//CUBE
6	Hamiltonian Kinetic energy density	K	3DKKIN.DAT//CUBE
7	Lagrangian Kinetic energy density	G	3DGKIN.DAT//CUBE
8	Virial field density	V	3DVIRI.DAT//CUBE
9	ELF (Becke electron localization function)		3DELFB.DAT//CUBE

Table 5.3: Computed functions and name of the data files.

5.6   3D Input examples

With reference to Urea bulk 6-12g∗∗.

EX 1 Electron density, Laplacian of the electron density and ELF$^{\alpha\alpha}$ are plotted in a box defined in terms of fractional coordinates (IFRA=1) and will result in the corresponding 3D grid files.

```
TOPO
PL3D
1                 IFRA=1
0.,0.5,0.01       XMI,XMA,XIN
0.,0.5,0.01       YMI,YMA,YIN
0.,1.0,0.01       ZMI,ZMA,ZIN
1 0 1 0 0 0 0 0 1  electron density, its Laplacian and ELF^{\alpha\alpha}
END
```

EX 2 Alle the functions are plotted in a volume corresponding to the conventional unit cell and the result is a set of CUBE format files.

```
TOPO
PL3D
0
0.,5.565,0.2      XMI,XMA,XSTEP
0.,5.565,0.2      YMI,YMA,YSTEP
0.,5.565,0.2      ZMI,ZMA,ZSTEP
1 1 1 1 1 1 1 1 1  all the functions are evaluated inside the unit cell volume
END
```

Appendix A

Atomic properties evaluated by TOPOND

Populations		
Atomic population	N	$N(\Omega) = \int_\Omega \rho(\boldsymbol{r})d\tau$
Net charge	q	$q(\Omega) = Z(\Omega) - N(\Omega)$
α-Atomic population (α-electrons population)	N_A	$N_A(\Omega) = \int_\Omega \rho_\alpha(\boldsymbol{r})d\tau$
β-Atomic population (β-electrons population)	N_B	$N_B(\Omega) = \int_\Omega \rho_\beta(\boldsymbol{r})d\tau$
Excess of up-spin over down-spin atomic popultation	E_{SAP}	$E_{SAP} = N_A(\Omega) - N_B(\Omega)$
Energies		
Atomic Lagrangian: the error in L is a measure of the accuracy of the numerical integration	L	$L(\Omega) = -1/4 \int_\Omega \nabla^2 \rho\, d\tau$
Kinetic energy in terms of the dot product of the momentum operator $\rightarrow$ integration of the lagrangian kinetic energy density distribution	G	$G(\Omega) = 1/2 \int_\Omega (\boldsymbol{\nabla} \cdot \boldsymbol{\nabla'})\Gamma^{(1)}(\boldsymbol{r},\boldsymbol{r'})\vert_{r=r'}\, d\tau = $ $= L(\Omega) = K(\Omega) - G(\Omega)$
Kinetic energy in terms of the Laplacian operator $\rightarrow$ integration of the hamiltonian kinetic energy density distribution	K	$K(\Omega) = -1/4 \int_\Omega (\nabla^2 + \nabla'^2)\Gamma^{(1)}(\boldsymbol{r},\boldsymbol{r'})\vert_{r=r'}d\tau$
Atomic energy E=-E$_{kin}$ corrected for the virial ratio	E_G	$E_G(\Omega) = G(\Omega) \cdot (1 + V/T)$
	E_K	$E_K(\Omega) = K(\Omega) \cdot (1 + V/T)$
Atomic value of nuclear-electron potential energy with its own nucleus; $\boldsymbol{R}_\Omega$ is the position vector of Ω in the system frame	V_{NEO}	$V_{NEO}(\Omega) = -\int_\Omega (Z_\Omega/r_\Omega)\,\rho(\boldsymbol{r})d\tau\ \boldsymbol{r}_\Omega =$ $= \boldsymbol{r} - \boldsymbol{R}_\Omega;\ r_\Omega \equiv \vert\boldsymbol{r}_\Omega\vert$
Atomic value of nuclear-electron potential energy with all nuclei in the system (only for molecular systems); $\boldsymbol{R}_B$ is the position vector of nucleus B in the molecular frame	V_{NET}	$V_{NET}(\Omega) = -\int_\Omega \sum_B (Z_B/r_B)\,\rho(\boldsymbol{r})d\tau\ \boldsymbol{r}_B =$ $= \boldsymbol{r} - \boldsymbol{R}_B;\ r_B \equiv \vert\boldsymbol{r}_B\vert$
Corrected values of nuclear-electron potential energies for the virial ratio	V_{NEOC}	$V_{NEOC} = 2 \cdot V_{NEO} \cdot (1 + T/V)$
	V_{NETC}	$V_{NETC} = 2 \cdot V_{NET} \cdot (1 + T/V)$

Forces		
Atomic force components: force on nucleus of atom Ω by the electron density of atom Ω; x_Ω, y_Ω, z_Ω: components of $\boldsymbol{r}_\Omega$	F_{AXA} F_{AYA} F_{AZA}	$F_{AXA}(\Omega) = \int_\Omega (Z_\Omega/r_\Omega^3)\, x_\Omega\, \rho(\boldsymbol{r})d\tau$ $F_{AYA}(\Omega) = \int_\Omega (Z_\Omega/r_\Omega^3)\, y_\Omega\, \rho(\boldsymbol{r})d\tau$ $F_{AZA}(\Omega) = \int_\Omega (Z_\Omega/r_\Omega^3)\, z_\Omega\, \rho(\boldsymbol{r})d\tau$
Atomic force components: it is the sum of forces on all nuclei but Ω by the electron density of Ω; only for molecular systems; x_B, y_B, z_B comp. of $\boldsymbol{r}_B$	F_{BXA} F_{BYA} F_{BZA}	$F_{BXA}(\Omega) = \int_\Omega \sum_{B\neq\Omega}(Z_\Omega/r_B^3)\, x_B\, \rho(\boldsymbol{r})d\tau$ $F_{BYA}(\Omega) = \int_\Omega \sum_{B\neq\Omega}(Z_\Omega/r_B^3)\, y_B\, \rho(\boldsymbol{r})d\tau$ $F_{BZA}(\Omega) = \int_\Omega \sum_{B\neq\Omega}(Z_\Omega/r_B^3)\, z_B\, \rho(\boldsymbol{r})d\tau$
"Radial" atomic expectation values		
Atomic expectation value of the operator r_Ω^n	R(-1) R(+1) R(+2) R(+3) R(+4)	$R^N(\Omega) = \int_\Omega r_\Omega^n\, \rho(\boldsymbol{r})\, d\tau$
Atomic expectation values of r_Ω^n averaged over $\boldsymbol{r}_\Omega \cdot \boldsymbol{\nabla}\rho$. It reflects the distortion of the $\boldsymbol{\nabla}\rho$ field of the charge density that is caused by the formation of chemical bond. For n=0 and for a free atom (or a perfectly spherical atom in a molecule or in a crystal) is equal to -3N(Ω) (see pages 241-242 of Reference [1])	GR(-1) GR(0) GR(1) GR(2)	$GR^N(\Omega) = \int_\Omega r_\Omega^n\, \boldsymbol{r}_\Omega \cdot \boldsymbol{\nabla}\rho(\boldsymbol{r})d\tau$
Atomic volumes and related populations		
Volume of the region of the atomic basin where ρ is greater or equal 0.001 **bohr**; $d\tau_{0.001}$ are infinitesimal volume elements where ρ exceeds or is equal to 0.001 **bohr**	V_{001}	$V_{001}(\Omega) = \int_\Omega d\tau_{0.001}$
Electron population in the V_{001} region	N_{001}	$N_{001}(\Omega) = \int_\Omega \rho(\boldsymbol{r})\, d\tau_{0.001}$
Ratio of electron populations in V_{001} and in the atomic basin	R_{001}	$R_{001} = N_{001}/N$
Volume of the region of the atomic basin where Ω is greater or equal 0.002 **bohr**	V_{002}	$V_{002}(\Omega) = \int_\Omega d\tau_{0.002}$
Electron population in the V_{002} region	N002	$N_{002}(\Omega) = \int_\Omega \rho(\boldsymbol{r})\, d\tau_{0.002}$
Ratio of electron populations in V_{002} and in the atomic basin	R_{002}	$R_{002} = N_{002}/N$
Total atomic volume (only for 3D systems)	V_{TOT}	$V_{TOT}(\Omega) = \int_\Omega d\tau$

Atomic dipole and quadrupole moments		
Atomic dipole components	D_X	$D_X(\Omega) = -\int_\Omega \rho(\boldsymbol{r})\, x_\Omega d\tau$
$x_\Omega, y_\Omega, z_\Omega$ components of $\boldsymbol{r}_\Omega$	D_Y	$D_Y(\Omega) = -\int_\Omega \rho(\boldsymbol{r})\, y_\Omega d\tau$
	D_Z	$D_Z(\Omega) = -\int_\Omega \rho(\boldsymbol{r})\, z_\Omega\, d\tau$
Atomic dipole magnitude, where $\mathbf{D}_M(\Omega)$ is the atomic dipole vector	D_M	$D_M(\Omega) = |\mathbf{D}_M(\Omega)|$
Components of atomic displacement vector	D_{CX}	$D_{CX} = -D_X/N(\Omega)$
	D_{CY}	$D_{CY} = -D_Y/N(\Omega)$
	D_{CZ}	$D_{CZ} = -D_Z/N(\Omega)$
Coordinates of the centroid of negative charge	C_X	$C_X = D_{CX} + X_\Omega$
$X_\Omega, Y_\Omega, Z_\Omega$, components of $\boldsymbol{R}_\Omega$	C_Y	$C_Y = D_{CY} + Y_\Omega$
	C_Z	$C_Z = D_{CZ} + Z_\Omega$
Atomic quadrupole moment traceless tensor components	Q_{XX}	$Q_{XX}(\Omega) = -\int_\Omega [3x_\Omega^2 - r_\Omega^2]\, \rho(\boldsymbol{r})\, d\tau$
	Q_{XY}	$Q_{XY}(\Omega) = -\int_\Omega [3x_\Omega\, y_\Omega]\, \rho(\boldsymbol{r}) d\tau$
	Q_{XZ}	$Q_{XZ}(\Omega) = -\int_\Omega [3x_\Omega - z_\Omega]\, \rho(\boldsymbol{r}) d\tau$
	Q_{YY}	$Q_{YY}(\Omega) = -\int_\Omega [3y_\Omega^2 - r_\Omega^2]\, \rho(\boldsymbol{r}) d\tau$
	Q_{YZ}	$Q_{YZ}(\Omega) = -\int_\Omega [3y_\Omega - z_\Omega]\, \rho(\boldsymbol{r}) d\tau$
	Q_{ZZ}	$Q_{ZZ}(\Omega) = -\int_\Omega [3z_\Omega^2 - r_\Omega^2] \rho(\boldsymbol{r}) d\tau$
Eigenvalues and eigenvectors of the atomic quadrupole moment traceless tensor		by diagonalizing the Q matrix
Atomic Shannon information entropy		
Atomic information, I, (missing information function) is the integral of $\rho' \ln \rho'$, where: ρ' is the *un*-normalized electron density (UN) $\rightarrow I_{UN}$ or	I_{UN}	$I_{UN}(\Omega) = \int_\Omega \rho'(\boldsymbol{r})\, ln\, \rho'(\boldsymbol{r})\, d\tau$
ρ' is the normalized electron density to unity over the atomic basin [21] (NO) $\rightarrow I_{NO}$	I_{NO}	$I_{NO}(\Omega) = \int_\Omega \rho(\boldsymbol{r})\, ln\, \rho(\boldsymbol{r})\, d\tau$

Appendix B

Acronyms used in the input description

Acronym	Meaning
QTAIM	Quantum Theory of Atoms In Molecules [1]
$\rho, \rho_\alpha - \rho_\beta$	electron density; electron spin density
$\nabla^2\rho$	Laplacian ($\boldsymbol{\nabla} \cdot \boldsymbol{\nabla}\rho$)
G	Lagrangian kinetic energy density [1]
K	Hamiltonian kinetic energy density [1]
V	Virial field density [1]
ELF	Electron Localization Function [4, 15]
$\boldsymbol{H}(\rho)$	The Hessian matrix of ρ [1] (3x3 symmetric matrix collecting the second derivatives of ρ)
λ_k	Eigenvalues ($\lambda_1 \leq \lambda_2 \leq \lambda_3$) of $\boldsymbol{H}(\rho)$
CP(s)	Critical Point(s) [1]: a point $\mathbf{r}$ where a given scalar f has $\boldsymbol{\nabla}f(\boldsymbol{r}) = 0$
(m, n) CP	A critical point with **rank** m and **signature** n. The rank is the number of non-zero eigenvalues of $\boldsymbol{H}(\rho)$ at the CP, the signature is the difference between the number of positive and negative eigenvalues of $\boldsymbol{H}(\rho)$ at the CP [1]
BCP	Bond Critical Point, [1,4] a (3,-1) CP in the ρ scalar field
ZFS	Zero-Flux-Surface S. It is the surface whose points $\boldsymbol{r}_s$ fulfill the condition $\boldsymbol{\nabla}\rho(\boldsymbol{r}_s)\cdot\boldsymbol{n}(\boldsymbol{r}_s) = 0$ where $\boldsymbol{n}(\boldsymbol{r}_s)$ is a unit vector normal to the surface at $\boldsymbol{r}_s$. [1] Interatomic surfaces are ZFS in QTAIM.
Atomic basin	The space traversed by all the uphill $\boldsymbol{\nabla}\rho$ paths which terminate at a nucleus, which acts as a 3D attractor for its basin. The atomic basin is also the portion of space enclosed by a ZFS and including a nucleus [1]
NNA	Non-nuclear attractor: a (3,-3) CP of ρ at a position other than that of a nucleus [4, 6, 14]
NEA	Non-Equivalent Atom (see CRYSTAL Manual)
AIL	Atomic interaction line (a curved path joining two nuclei along which ρ is a maximum with respect to any lateral displacement). The density minimum along the atomic interaction line (AIL) is reached at the (3,-1) ρ CP. At an equilibrium geometry (no Hellman-Feynmann forces acting on nuclei), the AIL is named Bond Path and the associated (3,-1) CP is named Bond Critical Point (BCP) [1, 4]
Molecular Graph	The network of AIL(s) in a given nuclear configuration [1]
AGL	Atomic graph line (a curved path joining two $-\nabla^2\rho$ (3,-3) CPs along which $-\nabla^2\rho$ is a maximum with respect to any lateral displacement [1])
VSCC	Valence shell charge concentration (the atomic valence shell region having negative $\nabla^2\rho$ values [1])
IR	Integration Ray (it is used in the atomic properties evaluation)
EF	Eigenvector Following method (CP search) [11–13]
NR	Newton-Raphson method (CP search) [11–13]

Appendix C

Urea bulk Input file

Input file for Urea Bulk.

```
TEST12 - UREA BULK BASE 6-21 + POLARIZATION
CRYSTAL
0 0 0
113
5.565  4.684
5
6  0.0          0.5          0.326
8  0.0          0.5          0.5953
7  0.1459       0.6459       0.1766
1  0.2575       0.7575       0.2827
1  0.1441       0.6441      -0.0380
SETPRINT
1
3 1
END
6  4
2 0 6  2.  1.
2 1 2  4.  1.
2 1 1  0.  1.
2 3 1  0.  1.
7   4
2 0 6 2. 1.
2 1 2 5. 1.
2 1 1 0.   1.
2 3 1 0.  1.
8  4
2 0 6 2.  1.
2 1 2 6.  1.
2 1 1 0.  1.
2 3 1  0.  1.
1 3
2 0 2 1. 1.1
2 0 1 0.  1.1
2 2 1 0. 1.
99   0
END
SHRINK
2 2
TOLDEE
7
END
```

Appendix D

P2DTOPO PROGRAM

P2DTOPO is a Fortran program that anables to process any of the SURF* and TRAJ* data files, obtained by the PL2D keyword of TOPOND, to obtain HPGL format files. The whole machinery works as follows:

1. P2DTOPO program needs the following files:
   (i) the **input** file, named P2DCRYIN.DAT,
   (ii) the **data files**, whose names, in accordance to the value (0 or 1) assigned to the element of vector IFU, are summarized in Table D.1.

2. The **data files** have to be linked to the correct fortran unit:

P2DCRYIN.DAT	plotting information	unit 5
SURF*.DAT	scalar functions	unit 11
SURF*.DAT	density difference plots	unit 10
TRAJ*.DAT	molecular graph or $\nabla\rho$ trajectories	unit 12

   In Table D.3 the whole set of files and possible combination is presented. SURF*1.DAT and SURF*2.DAT refer to model system 1 and 2, respectively, in case of density differences (NFUN=9-11).

3. The user has to select the proper value of NFUN and modify the 8th row of the P2DCRYIN.DAT file by substituting one of the values reported in Table D.2, in order to obtain the corresponding **plot file** in HPGL format.

4. Then, the plot files can be processed by any device (printer, plotter, etc.) which is able to deal with HPGL files. A free-ware converter from HPGL to postscript files may be obtained from the URL: **ftp://ftp.rz.uni-duesseldorf.de/pubgnu/hp2xx**.

Warning: Dashed (full) lines indicate negative (positive) contours. ELF is shifted in the P2DTOPO program by 0.5, so that ELF is portrayed as follows:

$$0 \leq \text{ELF} \leq 0.5 \qquad \text{dashed contours}$$
$$0.5 \leq \text{ELF} \leq 1.0 \qquad \text{full lines}$$

A self-explained bash script is provided, *toplot*, **which performs all these steps. It can be downloaded from** $http://www.crystal.unito.it/topond$

File content	Name
Information file for plot	P2DCRYIN.DAT
$\rho(\boldsymbol{r})$	SURFRHOO.DAT
$\nabla^2\rho$	SURFLAPP.DAT
$-\nabla^2\rho$	SURFLAPM.DAT
$|\boldsymbol{\nabla}\rho|$	SURFGRHO.DAT
ELF	SURFELFB.DAT
V	SURFVIRI.DAT
G	SURFGKIN.DAT
K	SURFKKIN.DAT
$\rho_\alpha - \rho_\beta$	SURFSPDE.DAT
Molecular graph	MOLGRAPH.DAT
$\boldsymbol{\nabla}\rho$ trajectories (except mol. graph. and atom. boundaries)	TRAJGRAD.DAT
Molecular graph $+\boldsymbol{\nabla}\rho$ trajectories	TRAJMOLG.DAT

Table D.1: Full names of the files are listed and depend on the element of IFU.

NFUN	Content of HPGL files
1	$\rho(\boldsymbol{r})$
2	$\pm\nabla^2\rho$
3	$|\boldsymbol{\nabla}\rho|$
4	ELF
5	Virial field density
6	Lagrangian Kinetic energy density $G(\boldsymbol{r})$
7	Hamiltonian Kinetic energy density $K(\boldsymbol{r})$
8	Spin density $\rho_\alpha - \rho_\beta$
9	Electron density difference $\rho_1 - \rho_2$
10	Laplacian density difference $\nabla^2\rho_1 - \nabla^2\rho_2$
11	ELF Function difference
12	$\rho+$ superimposed molecular graph
13	$\pm\nabla^2\rho+$ superimposed molecular graph
14	molecular graph
15	$\boldsymbol{\nabla}\rho$ trajectories (or $\boldsymbol{\nabla}\rho$ traj.+molecular graph)

Table D.2: Value of NFUN.

Fortran unit	File name	NFUN
5	P2DCRYIN.DAT	1-15
11	SURFRHOO.DAT	1
11	SURFLAPP.DAT	2
11	SURFLAPM.DAT	2
11	SURFGRHO.DAT	3
11	SURFELFB.DAT	4
11	SURFVIRI.DAT	5
11	SURFGKIN.DAT	6
11	SURFKKIN.DAT	7
11	SURFSPDE.DAT	8
11	SURFRHOO.DAT	9
10	SURFRHOO2.DAT	
11	SURFLAPP.DAT	10
10	SURFLAPP2.DAT	
11	SURFLAPM.DAT	10
10	SURFLAPM2.DAT	
11	SURFELFB.DAT	11
10	SURFELFB2.DAT	
11	SURFRHOO.DAT	12
12	MOLGRAPH.DAT	
11	SURFLAPP.DAT	13
12	MOLGRAPH.DAT	
11	SURFLAPM.DAT	13
12	MOLGRAPH.DAT	
12	MOLGRAPH.DAT	14
12	TRAJGRAD.DAT	15
12	TRAJMOLG.DAT	15

Table D.3: Fortran units, file name and **NFUN** value.

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