

Ab-initio structure solution **without** the use of atomicity

Gábor Oszlányi & András Sütő

*Research Inst. for Solid State Physics and Optics
Budapest, Hungary*

two papers on
the charge-flipping algorithm:

Acta Cryst. A **60**, 134 (2004)

Acta Cryst. A **61**, 147 (2005)

The phase problem

$F = Ae^{i\varphi}$ — is complex

A is known \Rightarrow find out φ

-
-
- *single crystal x-ray diffraction*
 - *single wavelength*
 - *high-resolution data*
 - *real electron density*
 - *truly ab-initio approach*

For practical crystallography
of small molecules

well known software
of direct methods

(SHELX, SIR,...) work well.

Do we need another algorithm ?
the answer is: YES

1. Sufficiently different algorithms can work in different cases.
2. Simplicity is an advantage for teaching and mathematical treatment.
3. Learn more about the phase space and the working/limitation of other methods.

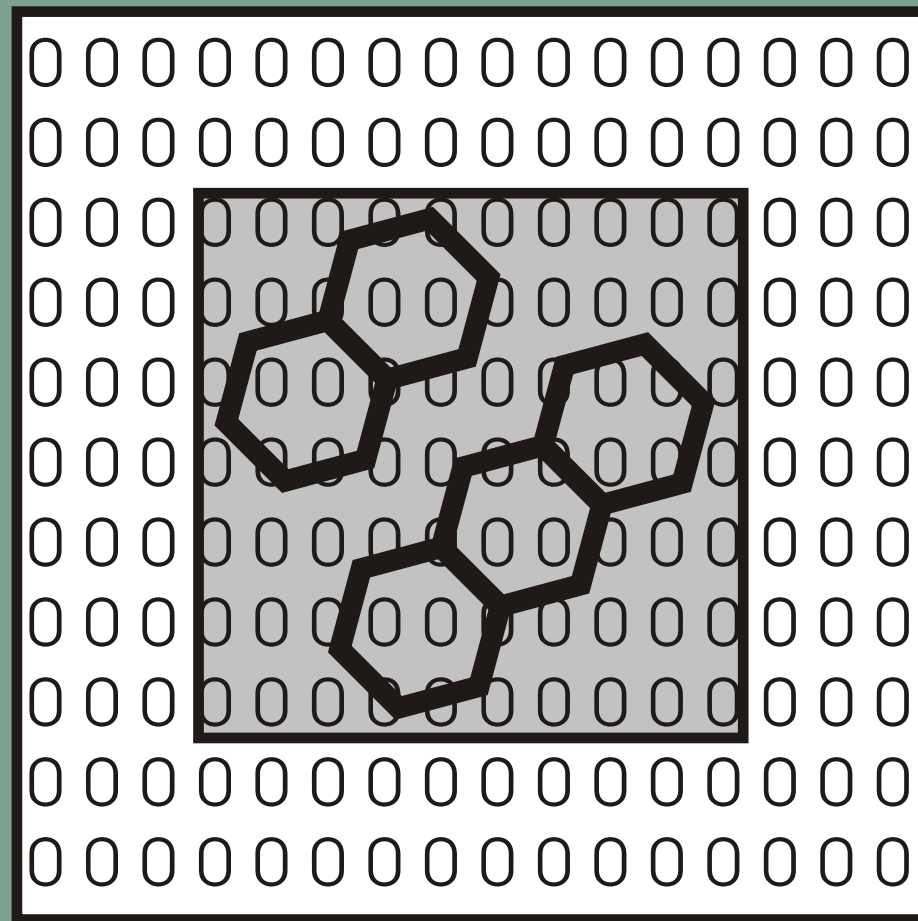
Phase retrieval in optics

Gerchberg-Saxton (1972) & Fienup (1982)



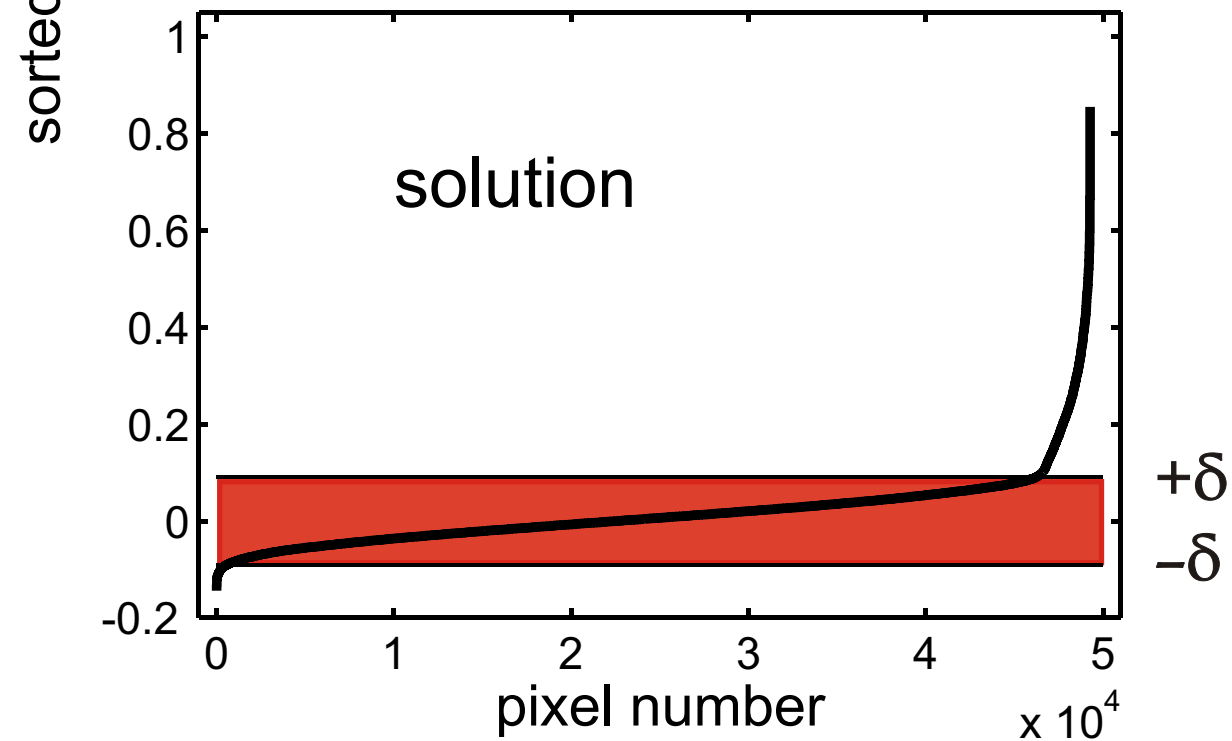
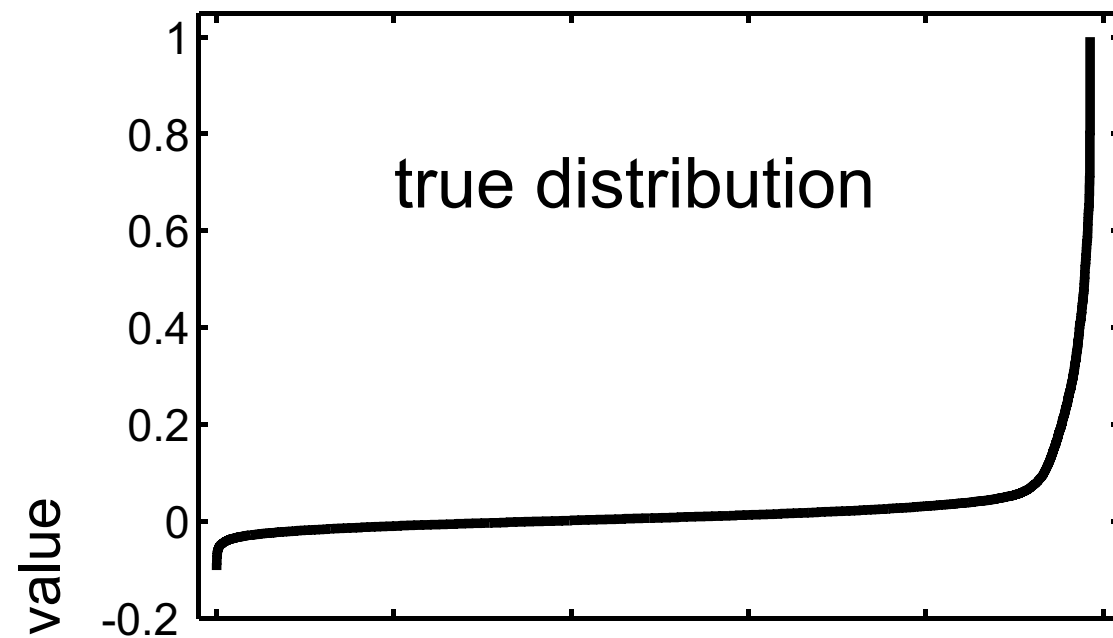
Phase retrieval in optics

Gerchberg-Saxton (1972) & Fienup (1982)



Groundwork

1. The unit cell is mostly empty.
2. At finite resolution negative electron density is naturally present.
3. Reduce the number of variables.
(with sufficient data)
Low electron density can be utilized to obtain high electron density.



grid = 0.4 \AA
res = 0.8 \AA

History & Ingredients

Low-density elimination:

Shiono-Woolfson

Solvent flipping:

Abrahams-Leslie

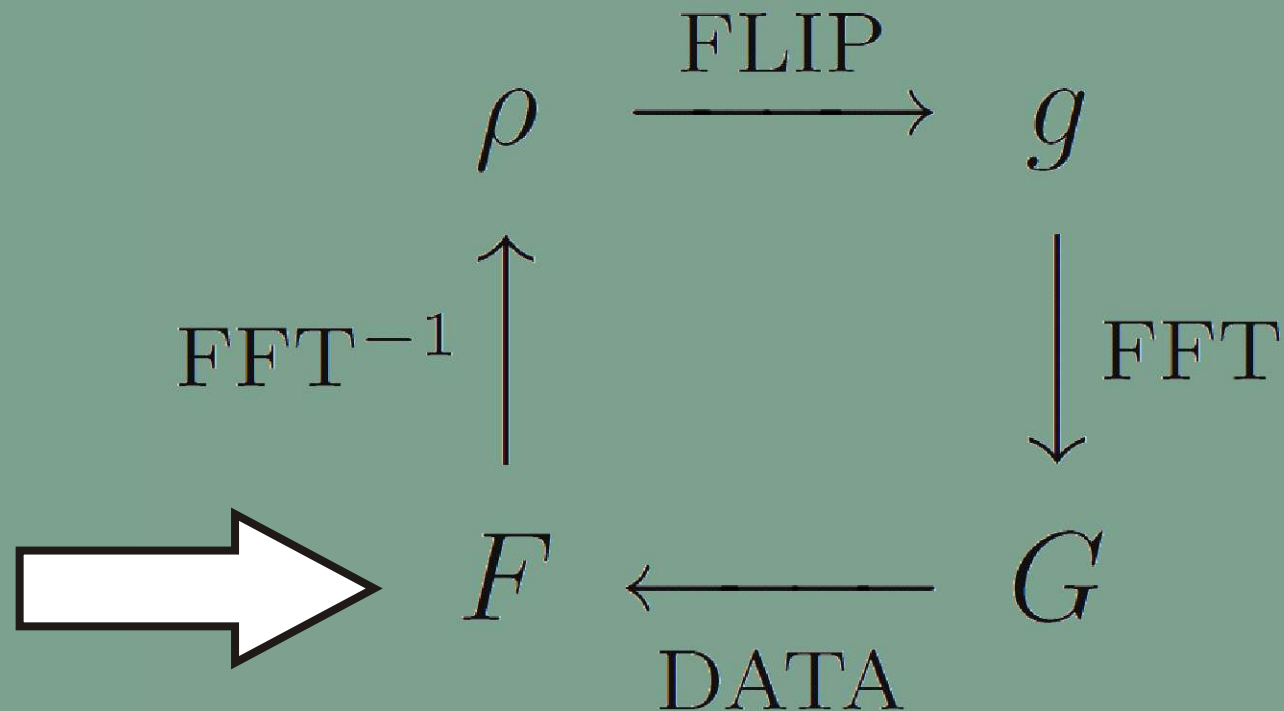
Use of the P1 spacegroup:

Sheldrick-Gould, Burla, ...

Some other details:

$F(0)$, resol. shell, sharpening, ...

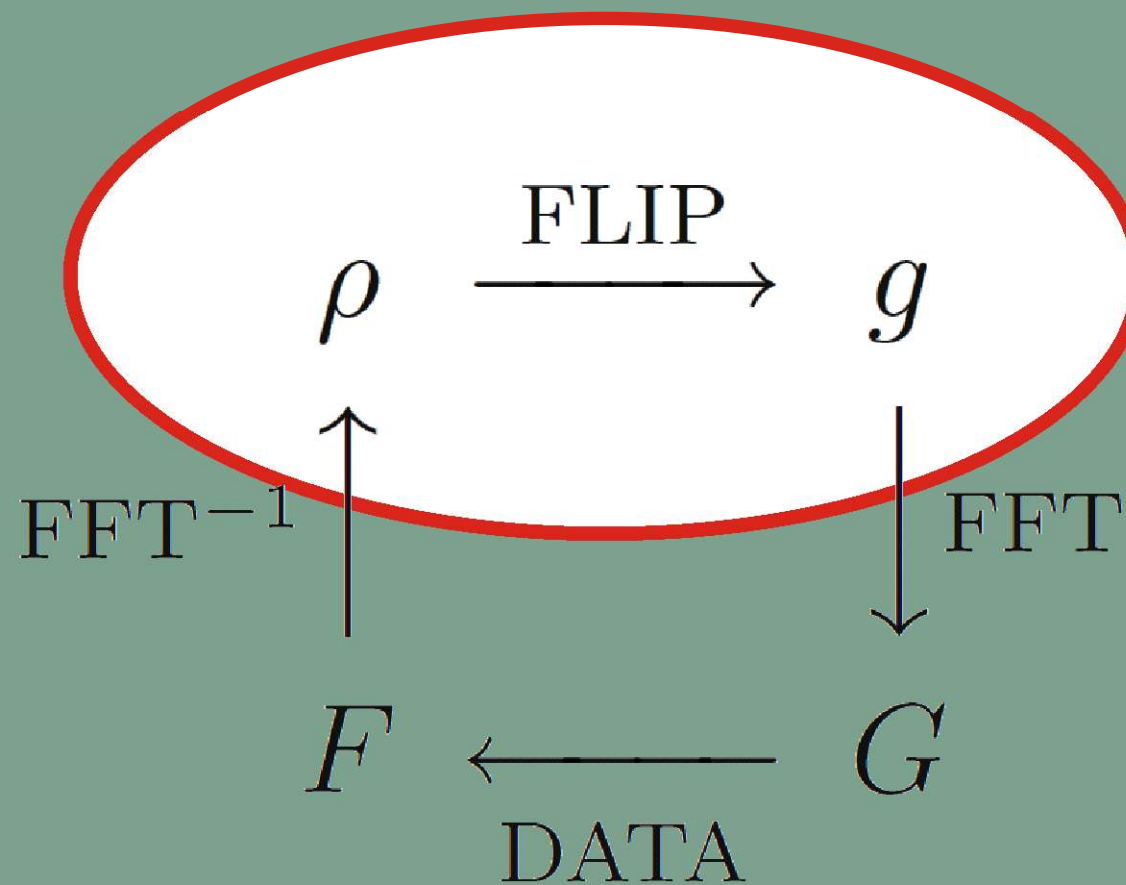
The iteration cycle:

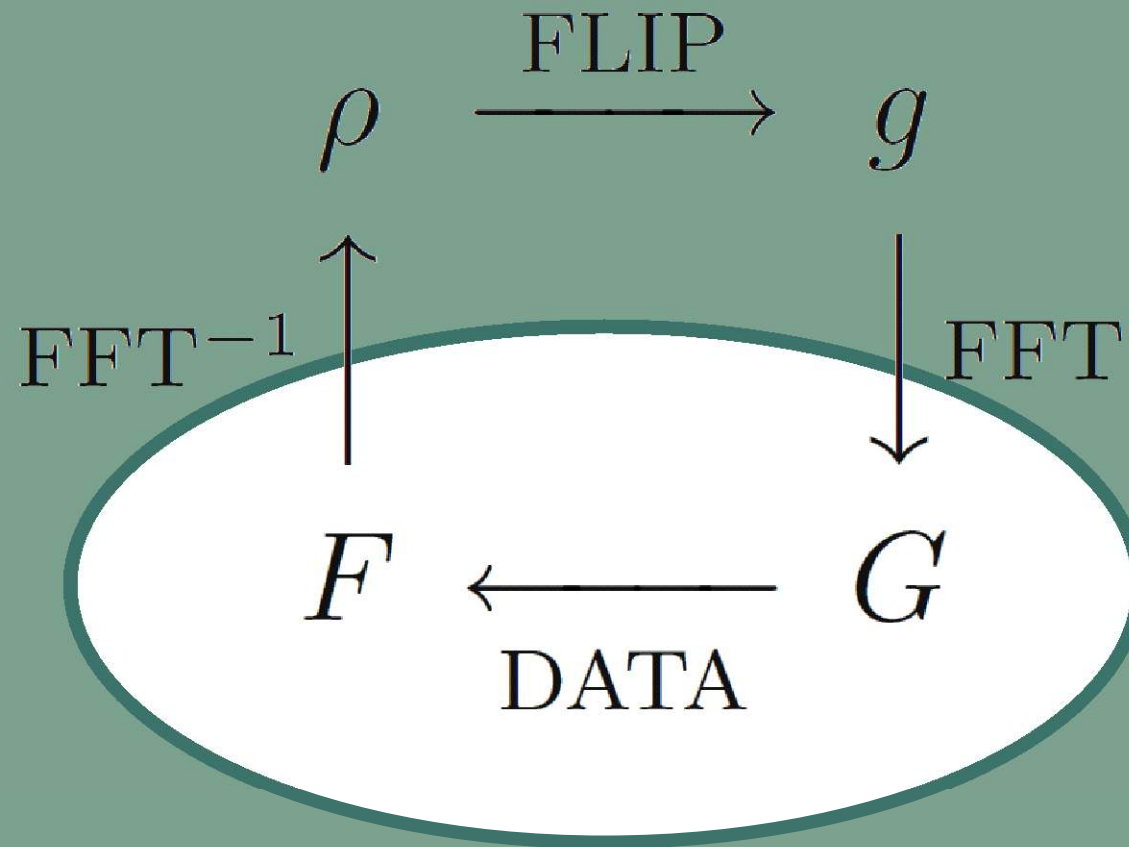


START:

random phases & $F(0)=0$

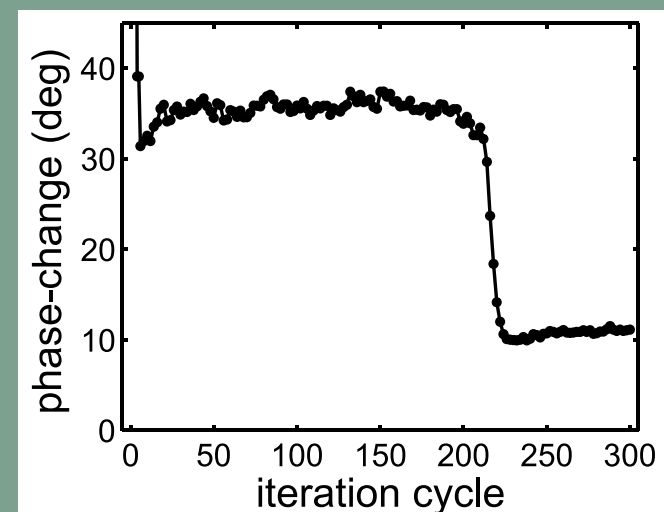
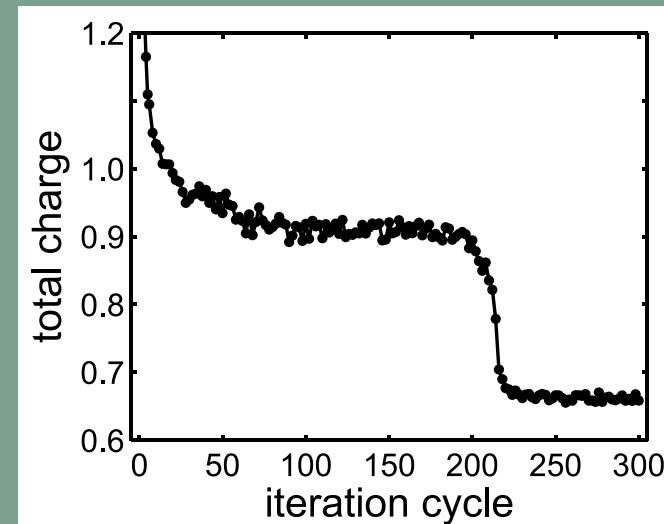
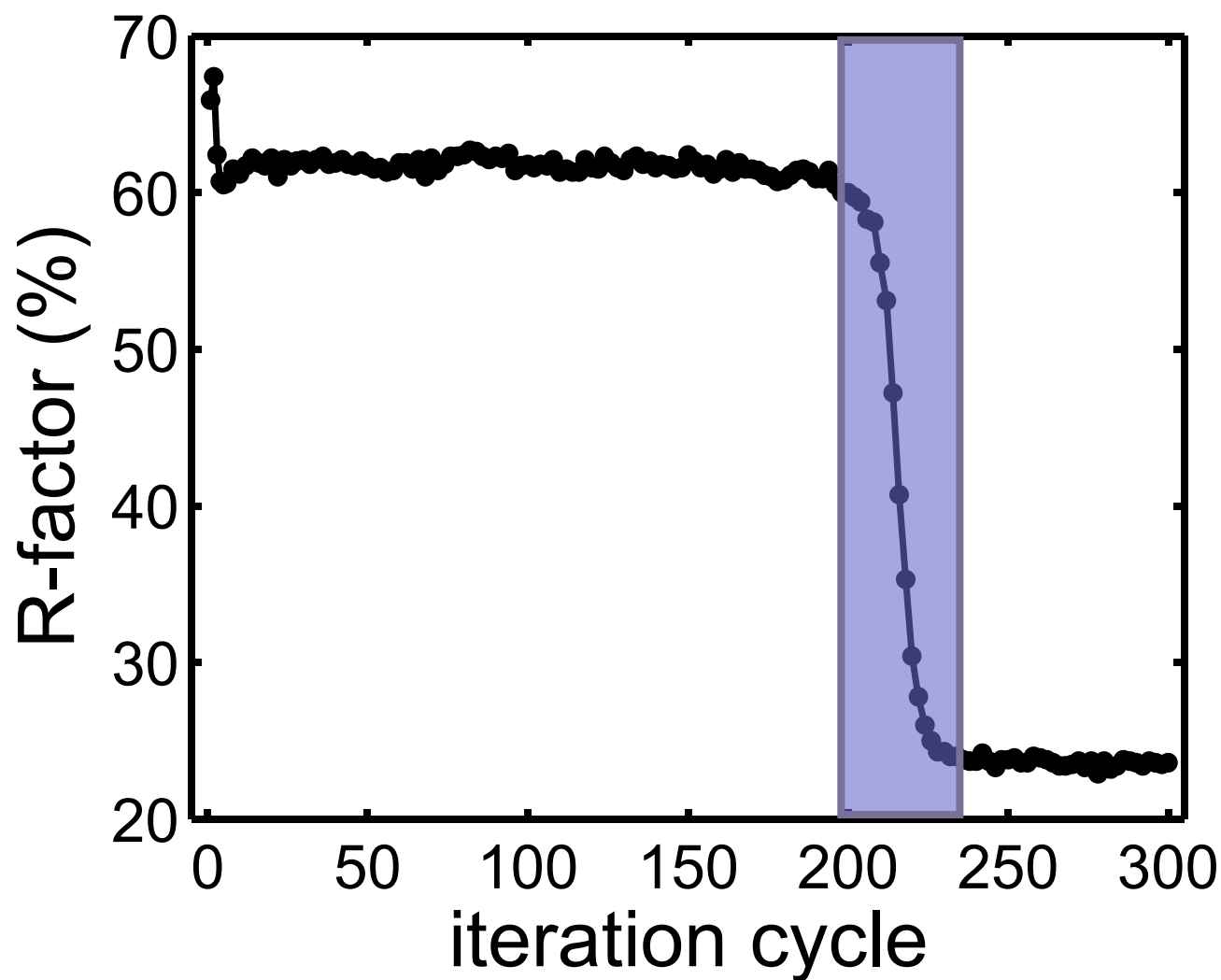
real space: if $\rho < \delta$ then $\rho = -\rho$





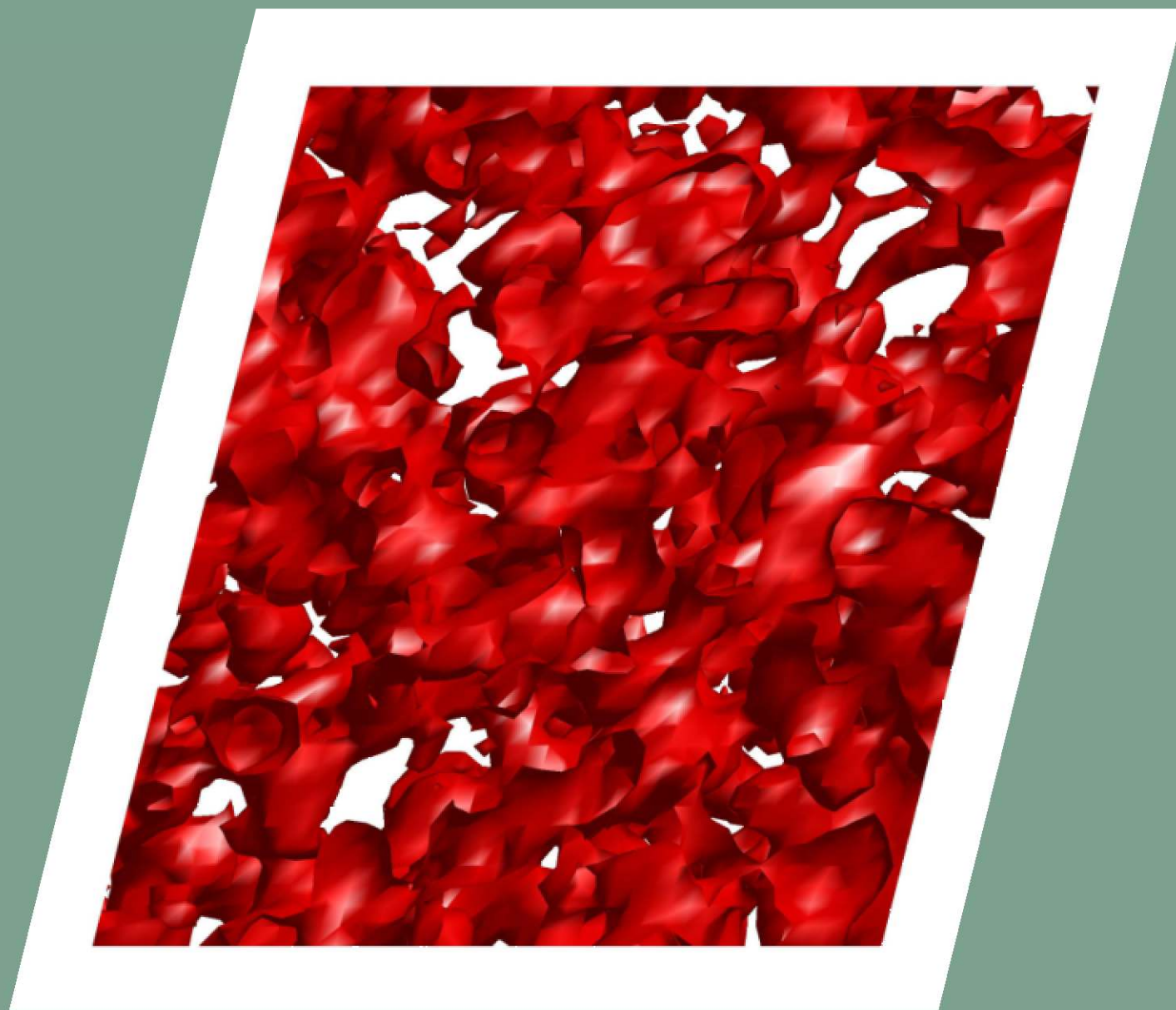
reciprocal space: $F = A_{\text{obs}} e^{i\varphi_{\text{calc}}}$

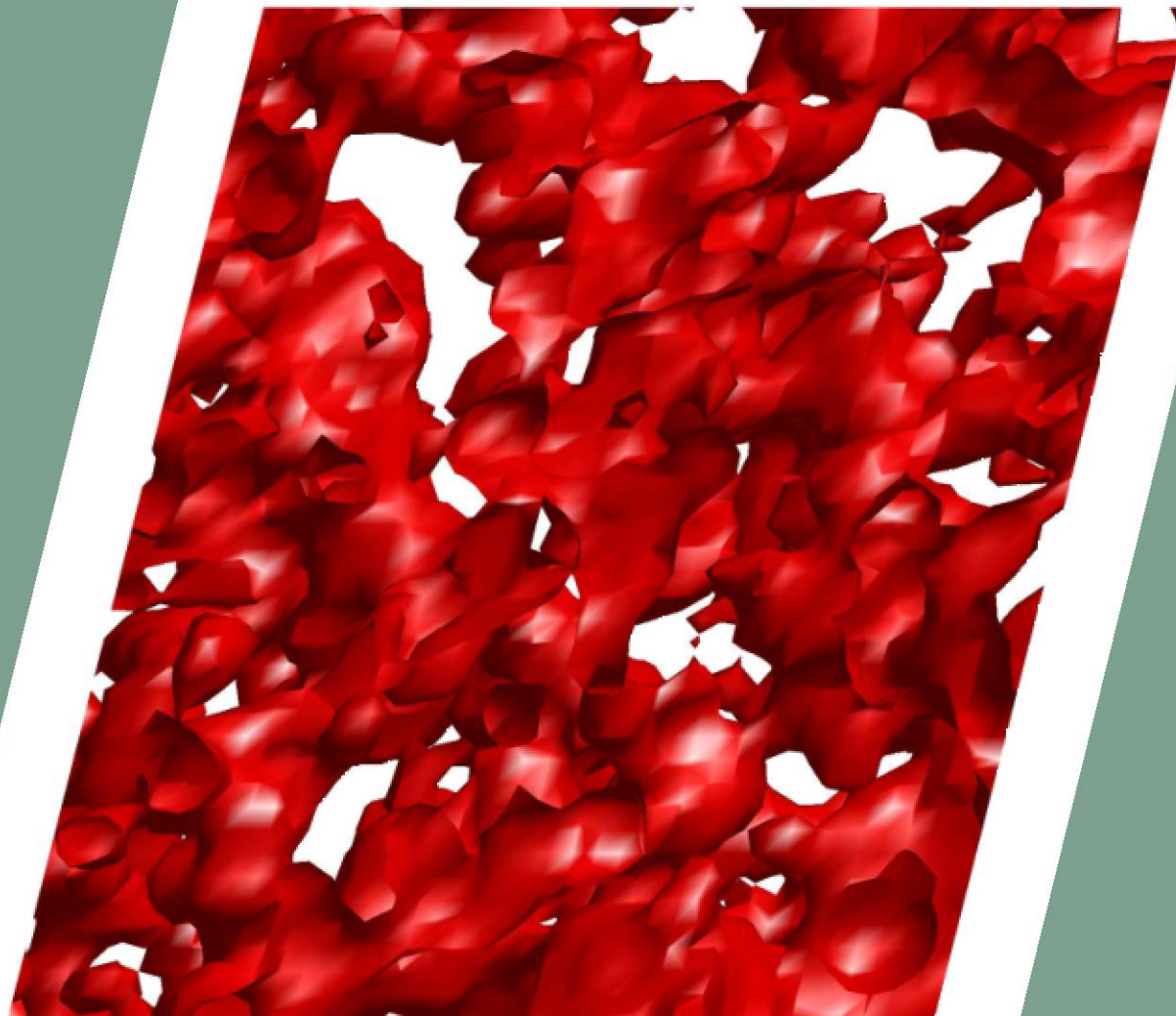
When should we stop ?

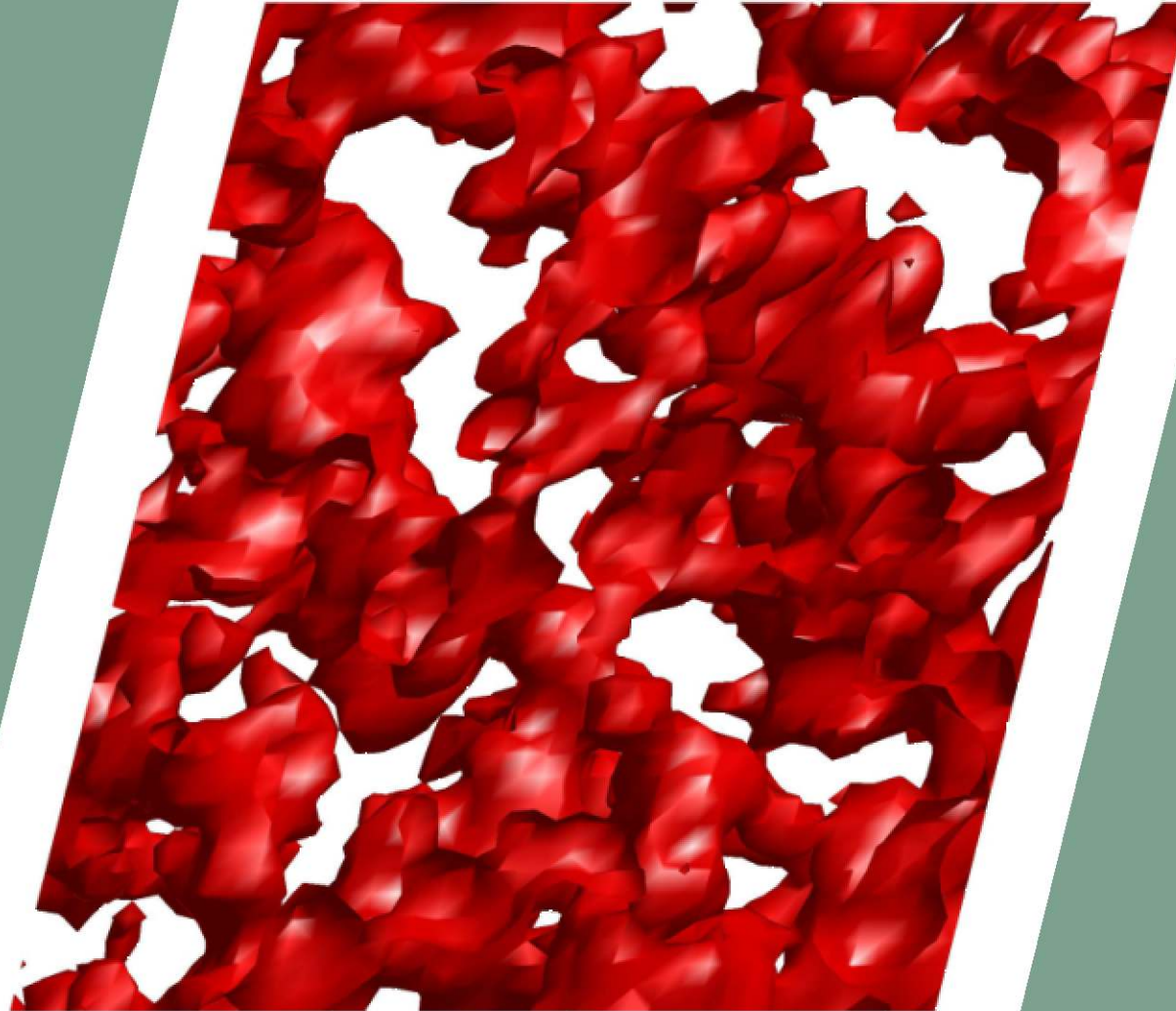


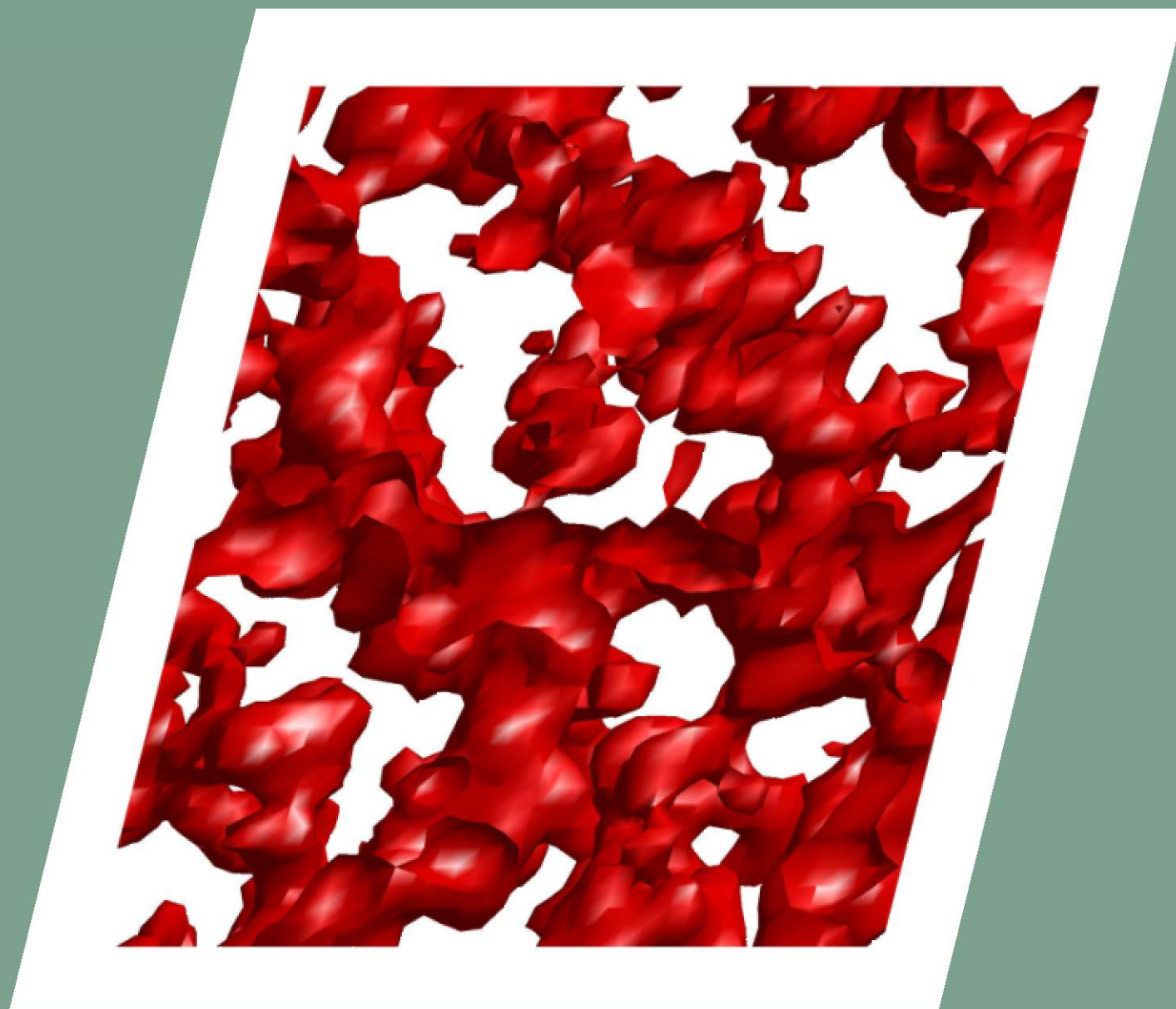
Some properties

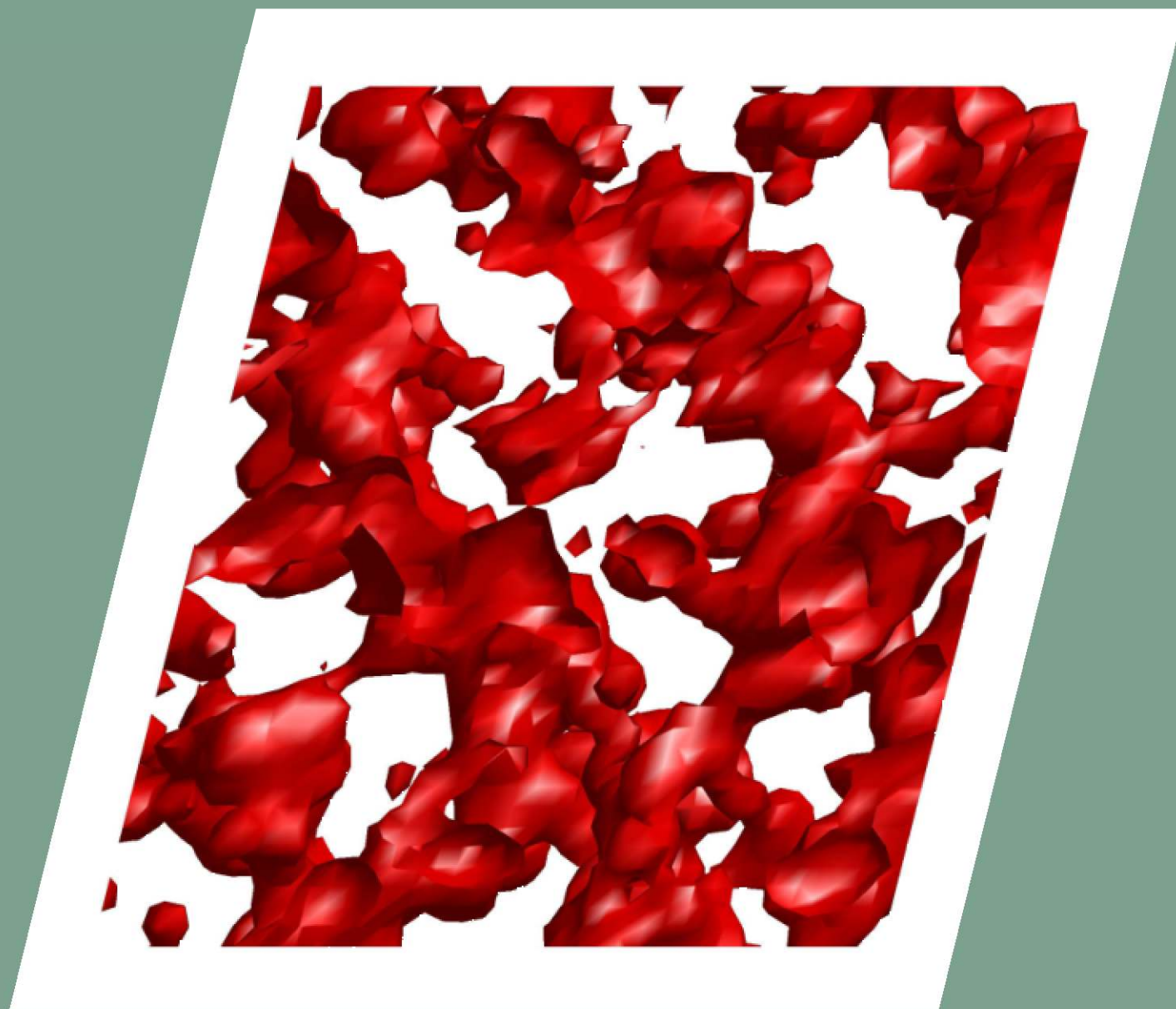
- electron density on a grid (2D/3D/...)
- limited positivity (δ threshold)
- no use of atomicity
- no atom types / chemical composition
- no use of symmetry
- all structures are let to float in P1
- no tangent formula / weighting
- no use of a cost function
- deterministic / unconditional process
- leading to an approximate solution

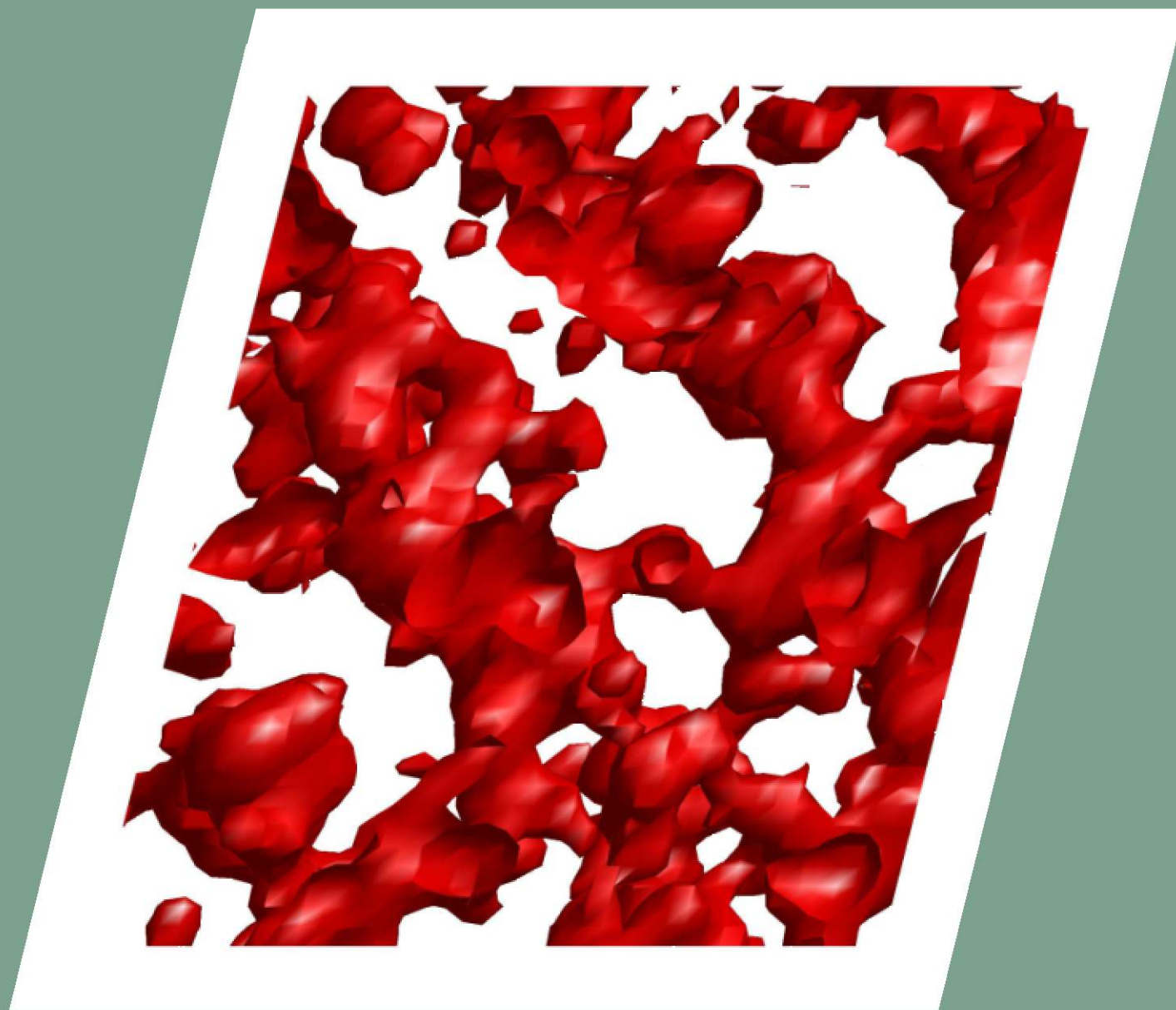


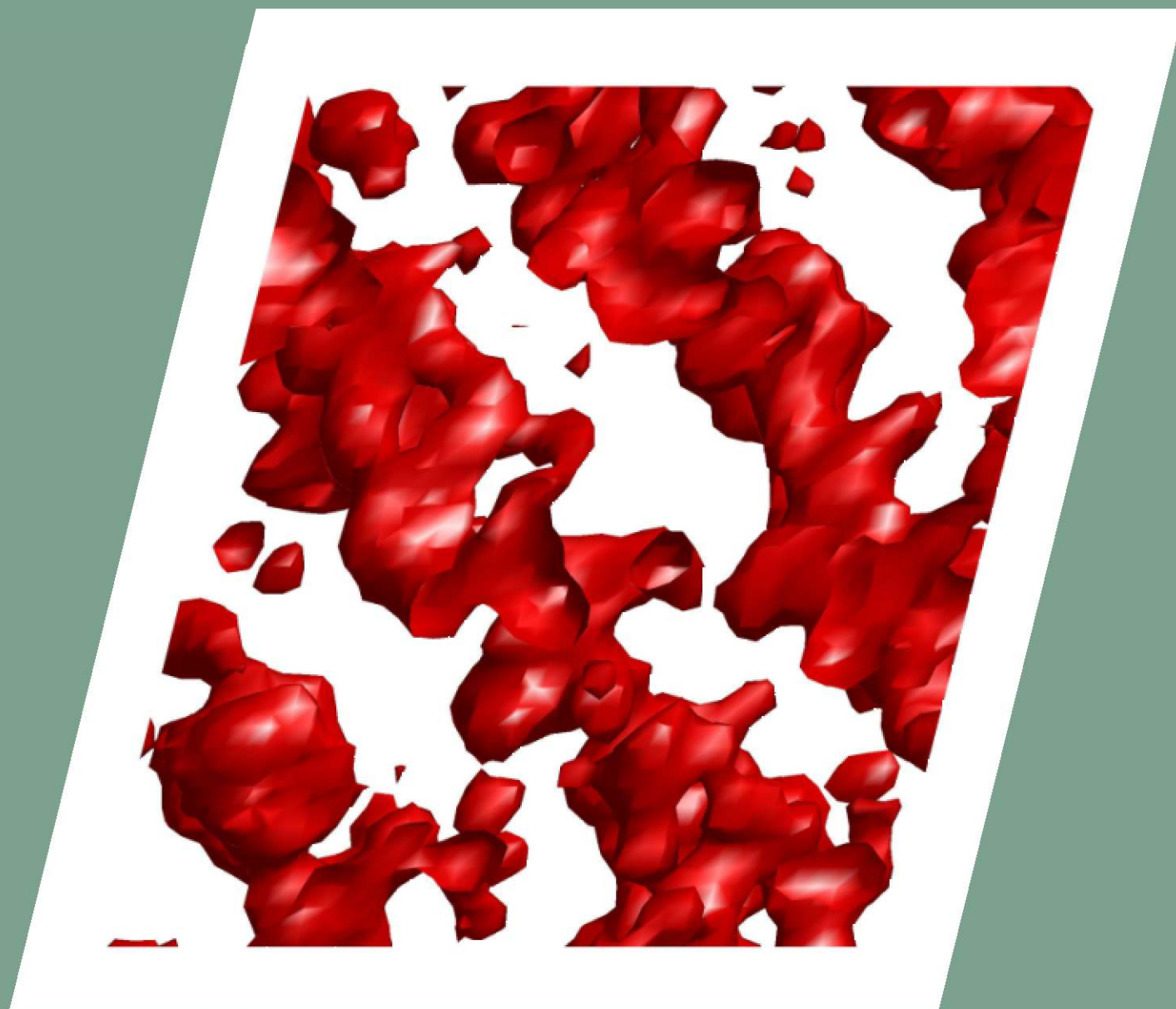


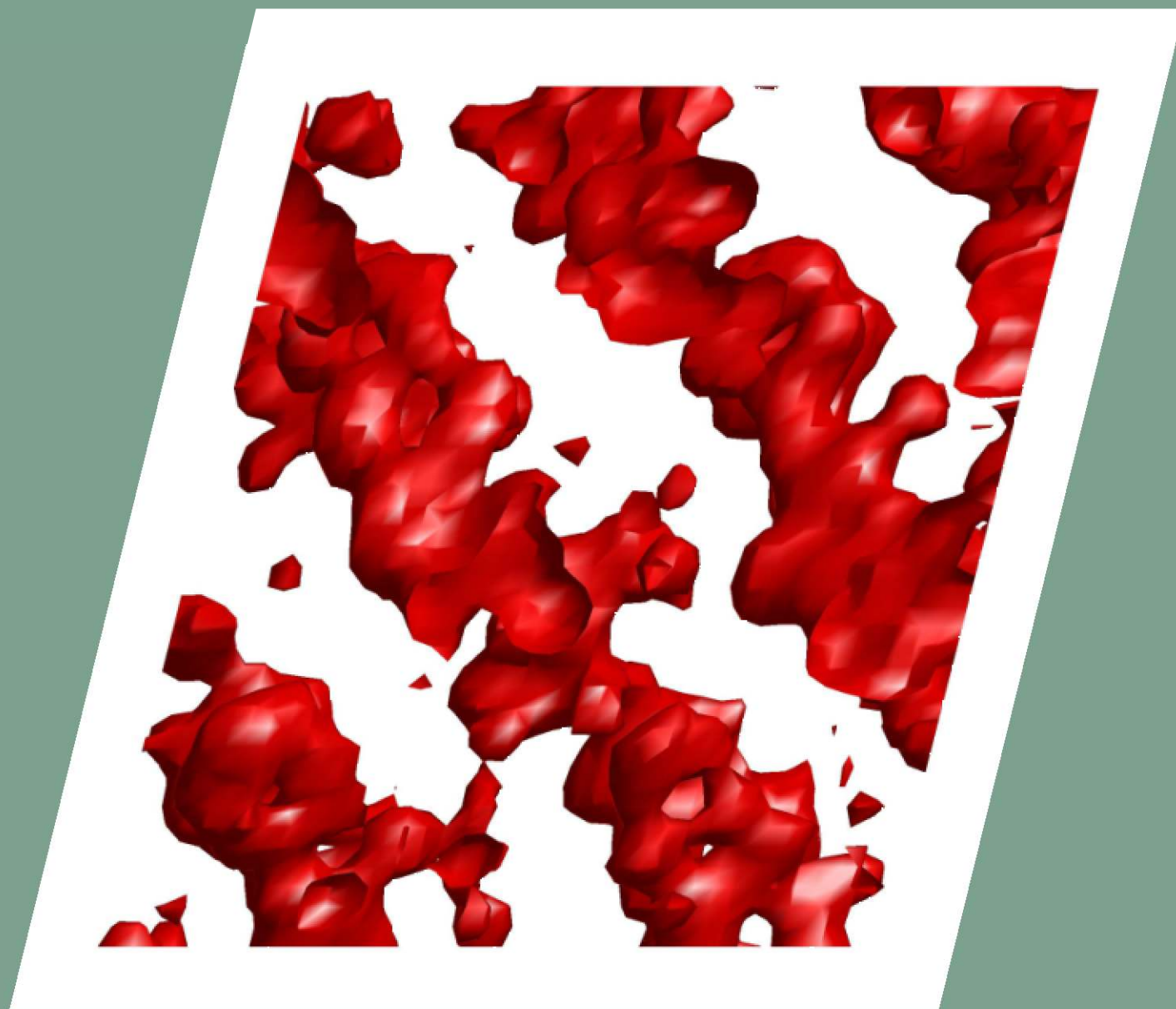


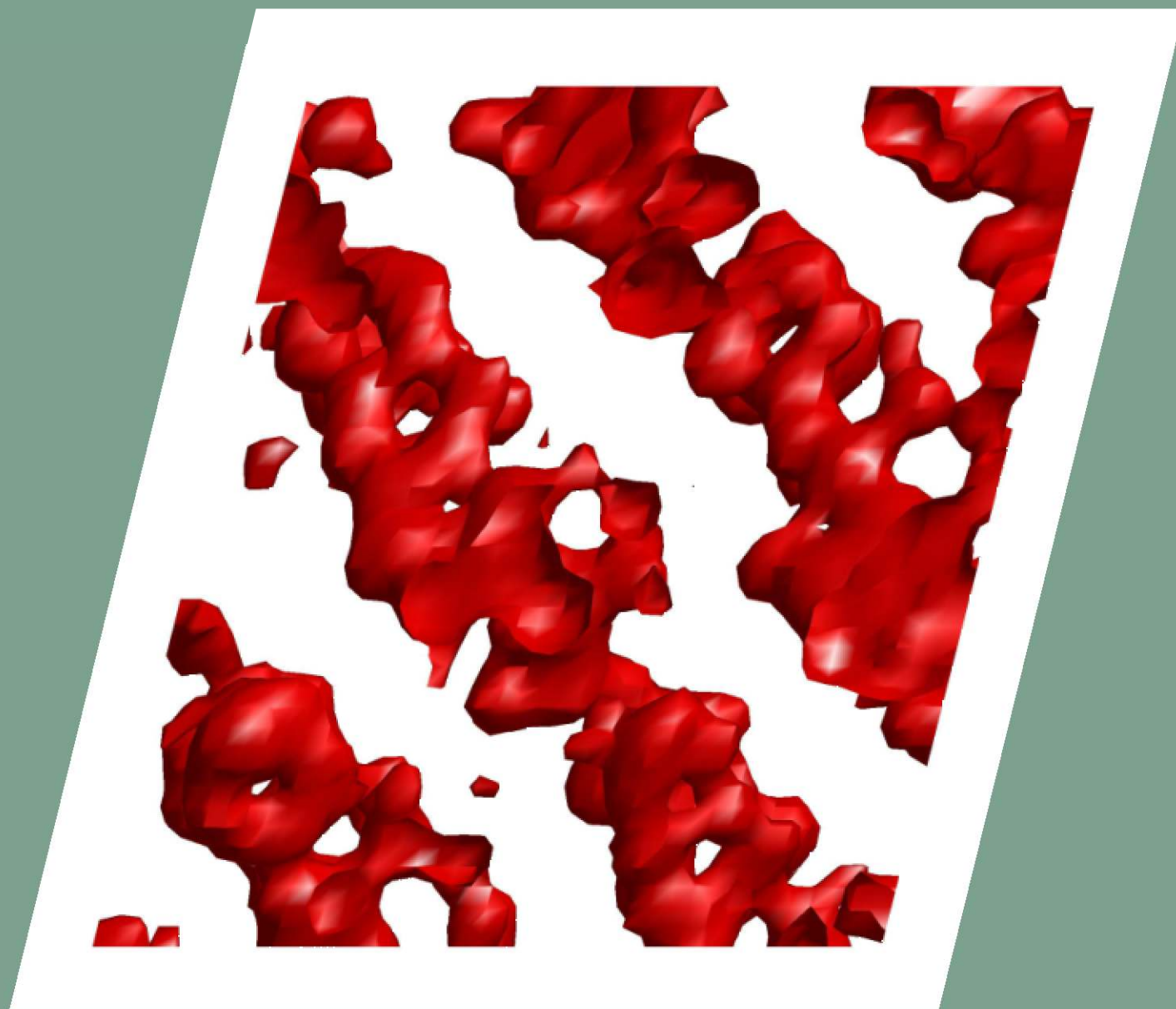


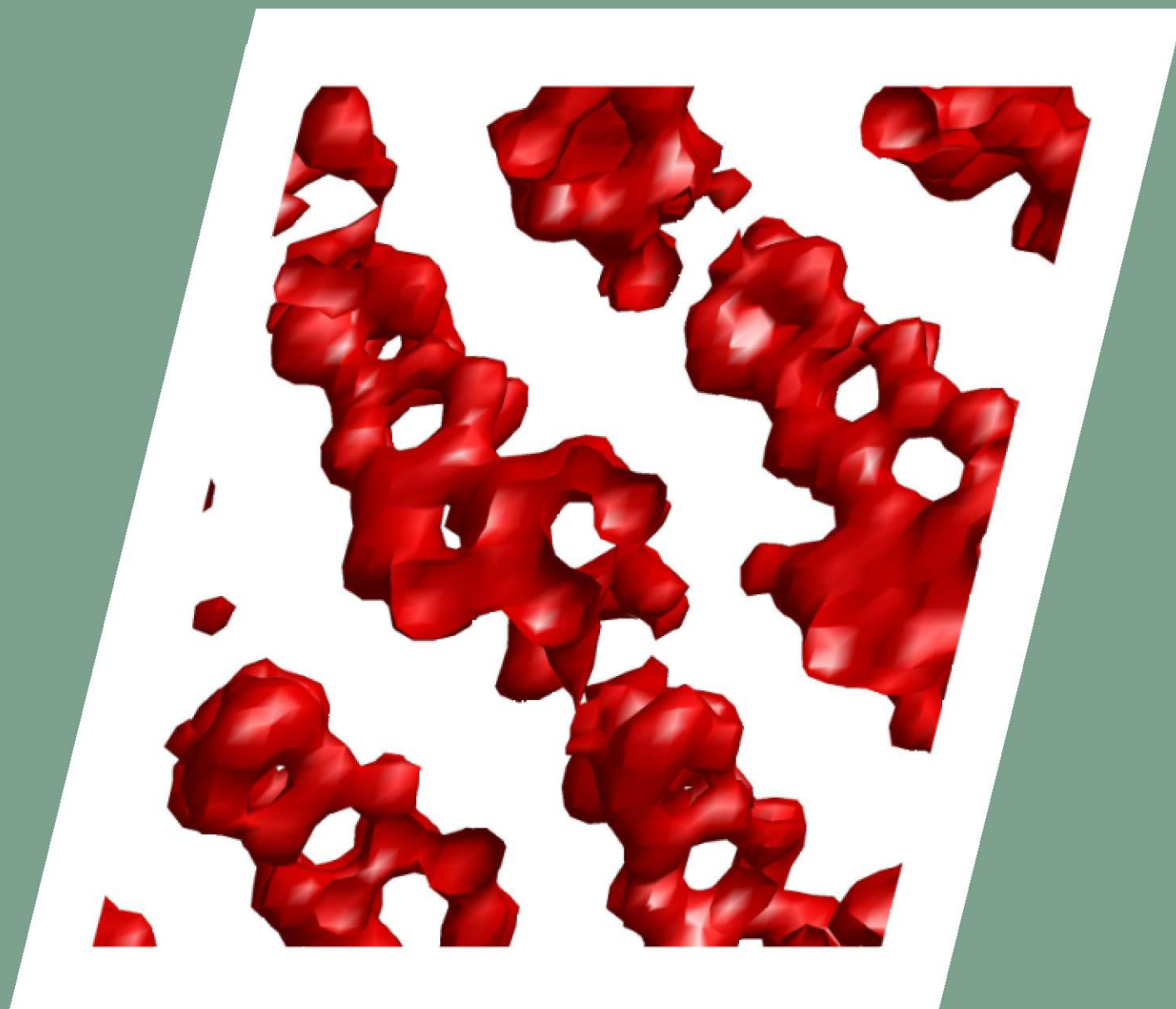


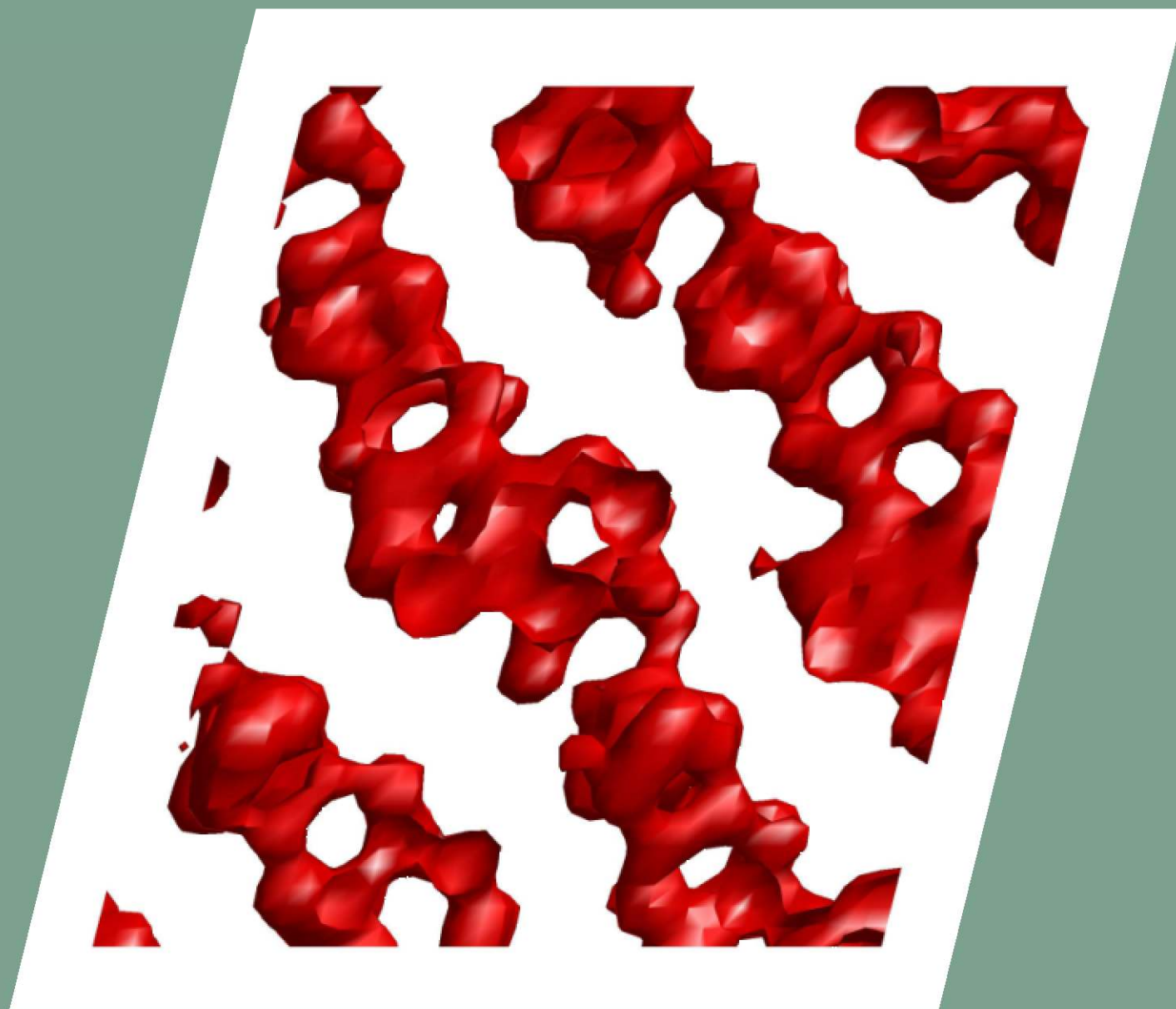


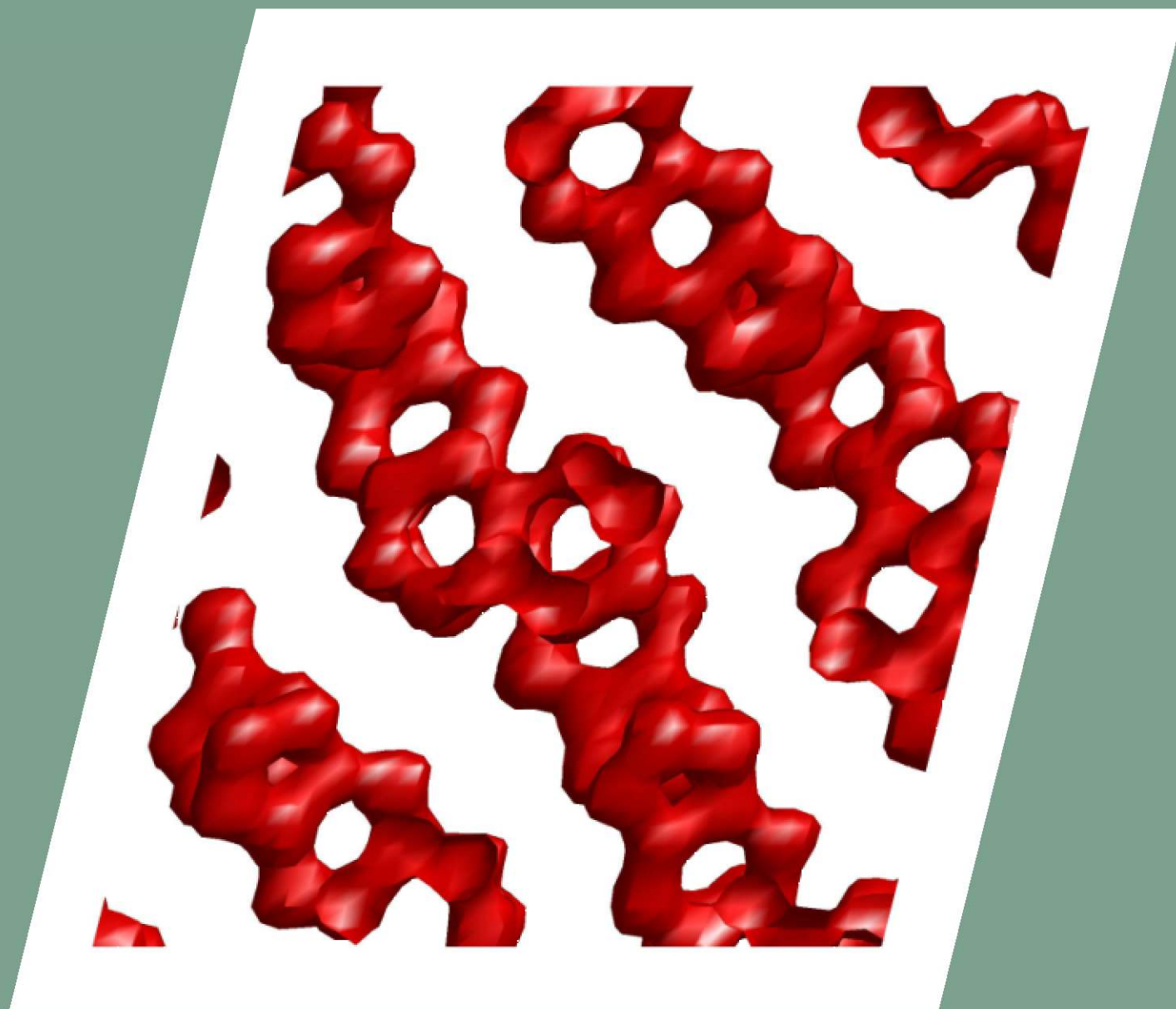


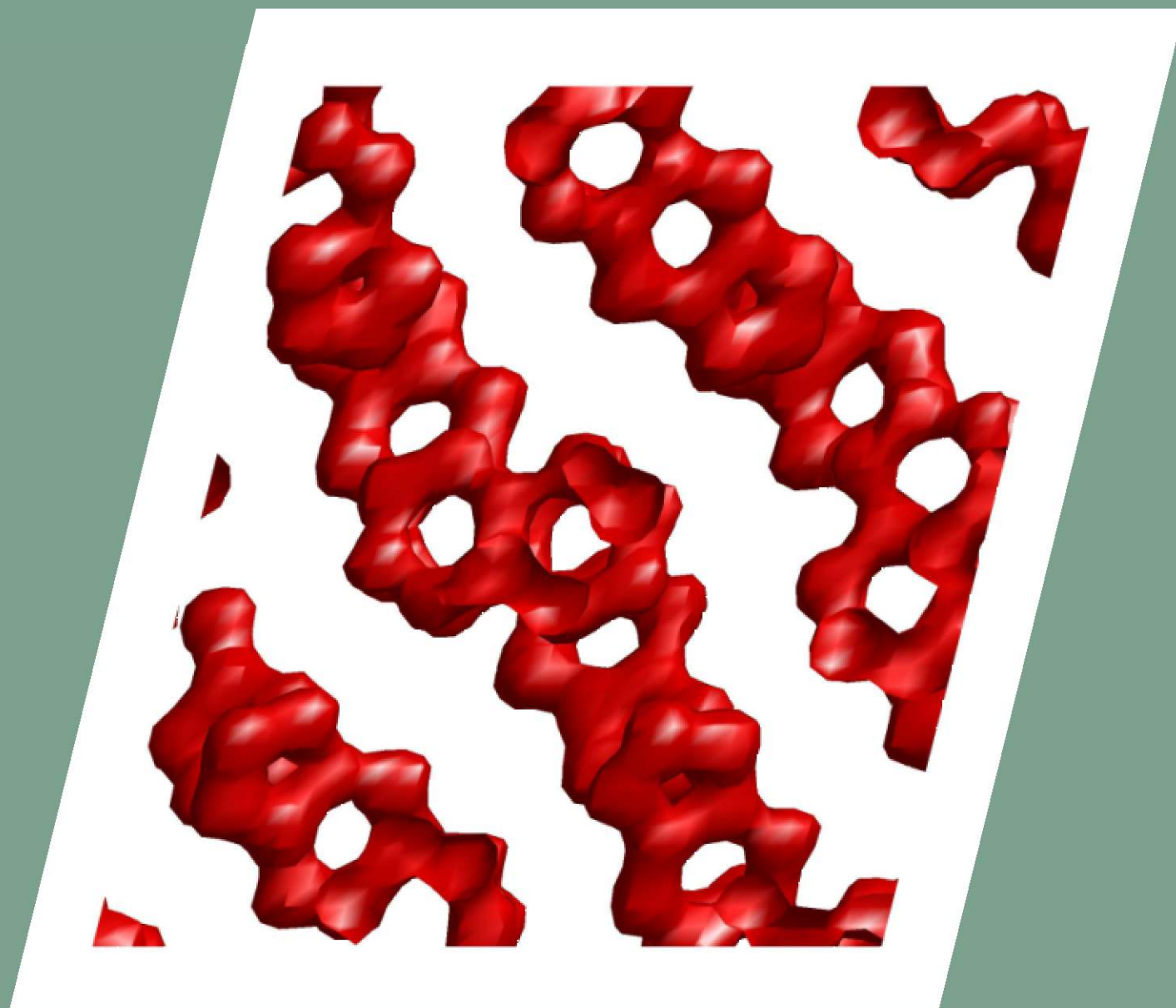




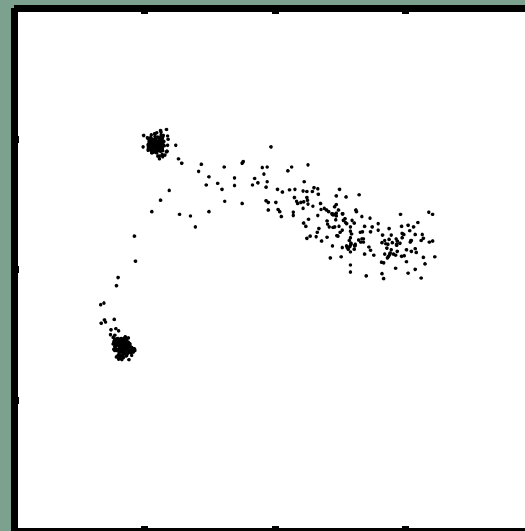
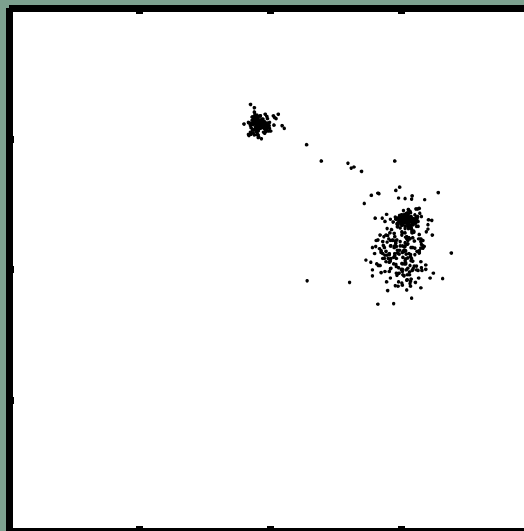
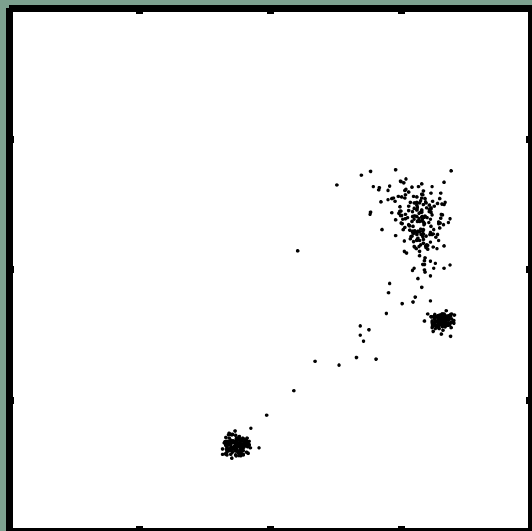
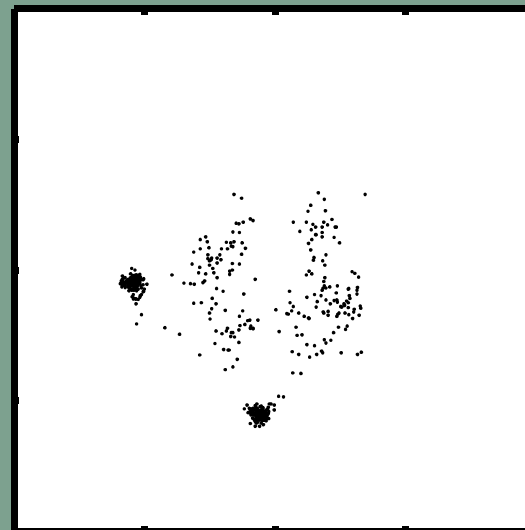
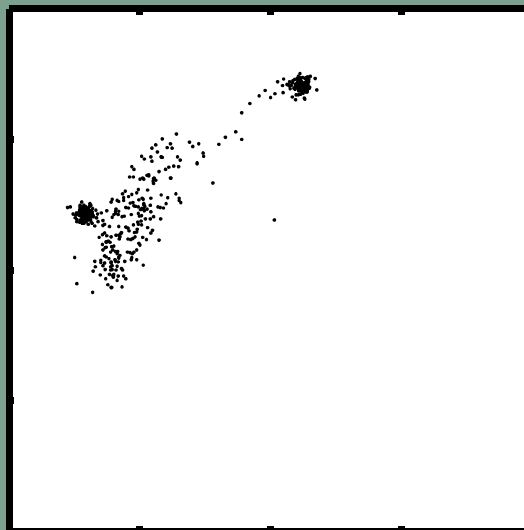
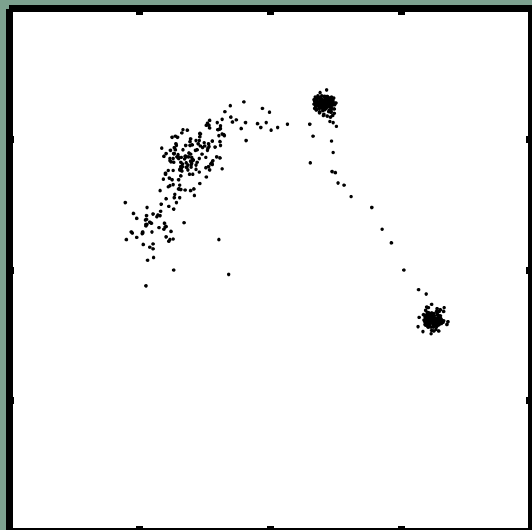




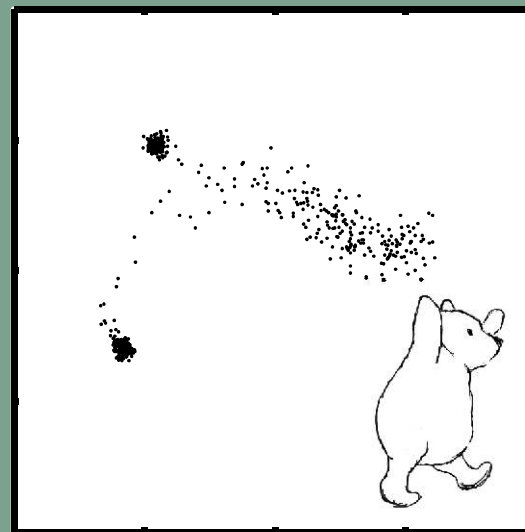
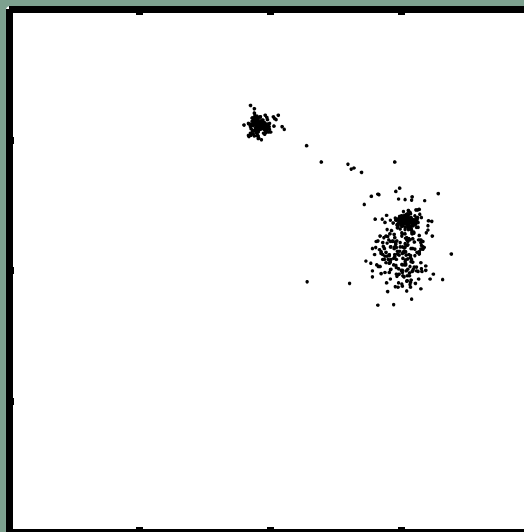
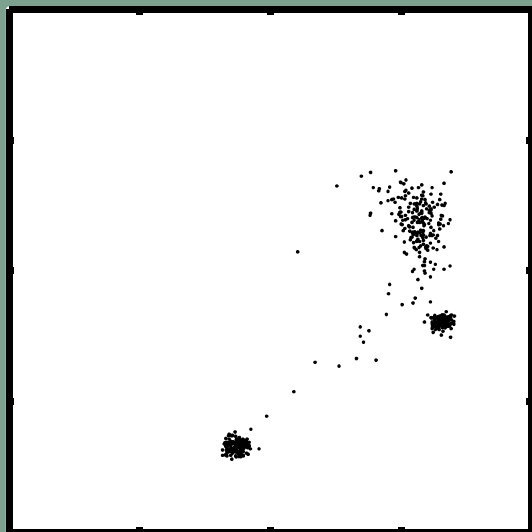
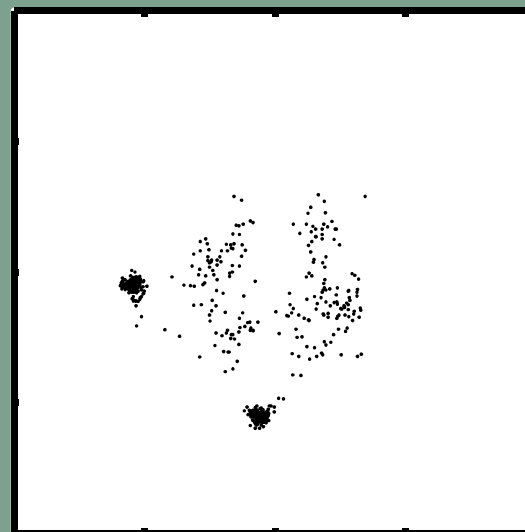
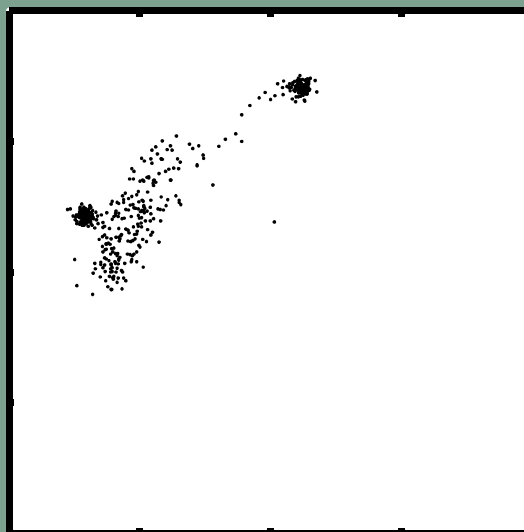
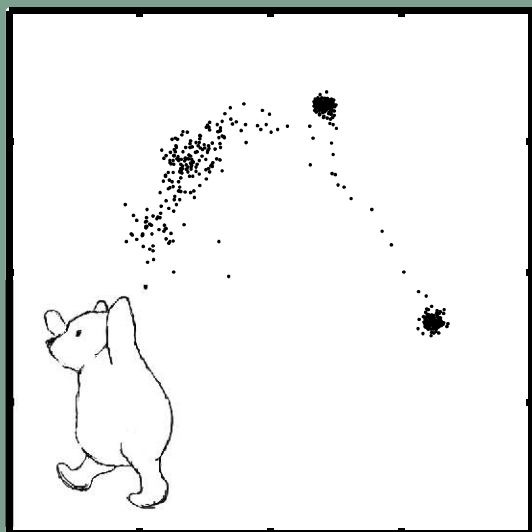




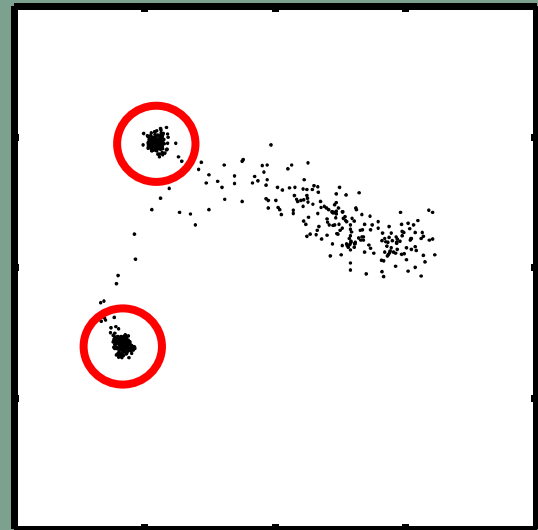
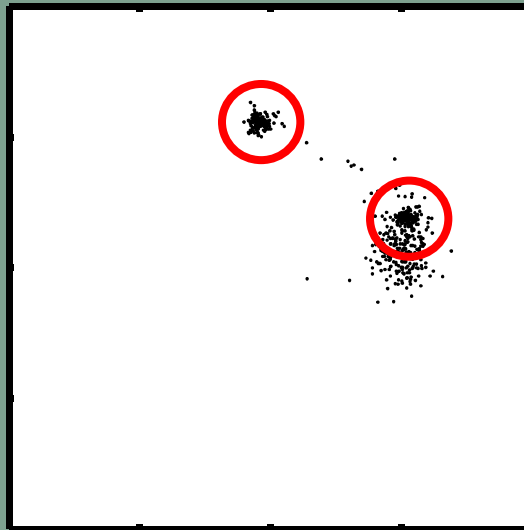
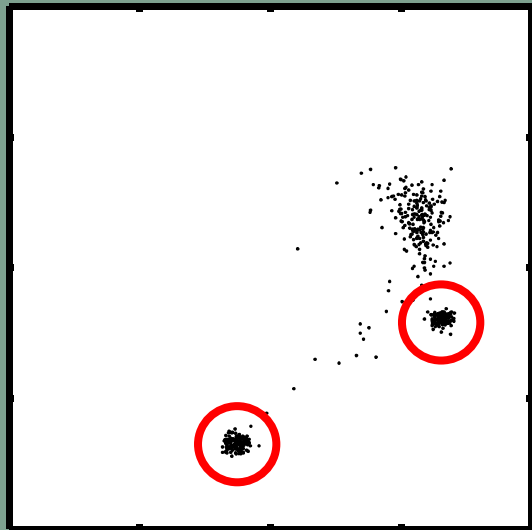
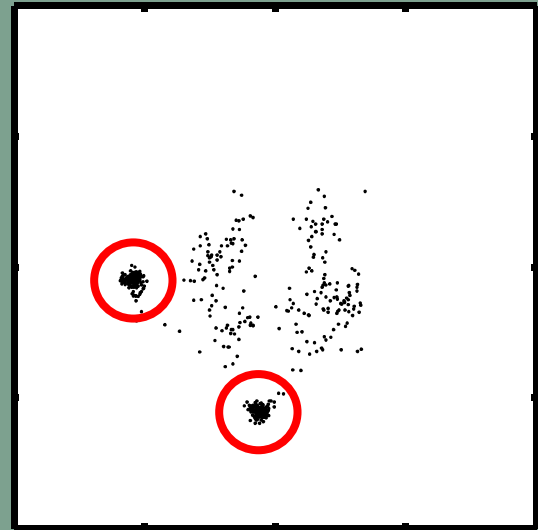
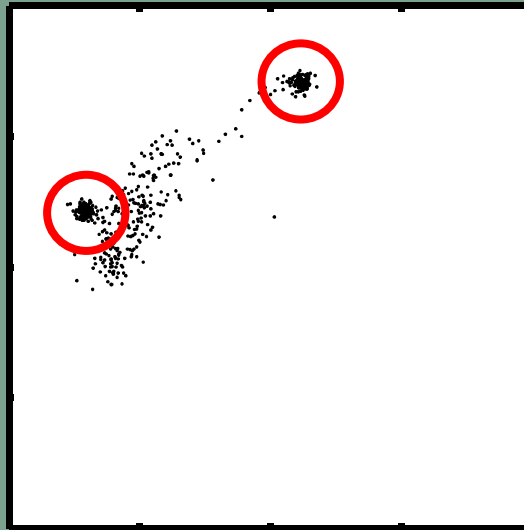
What is this ?

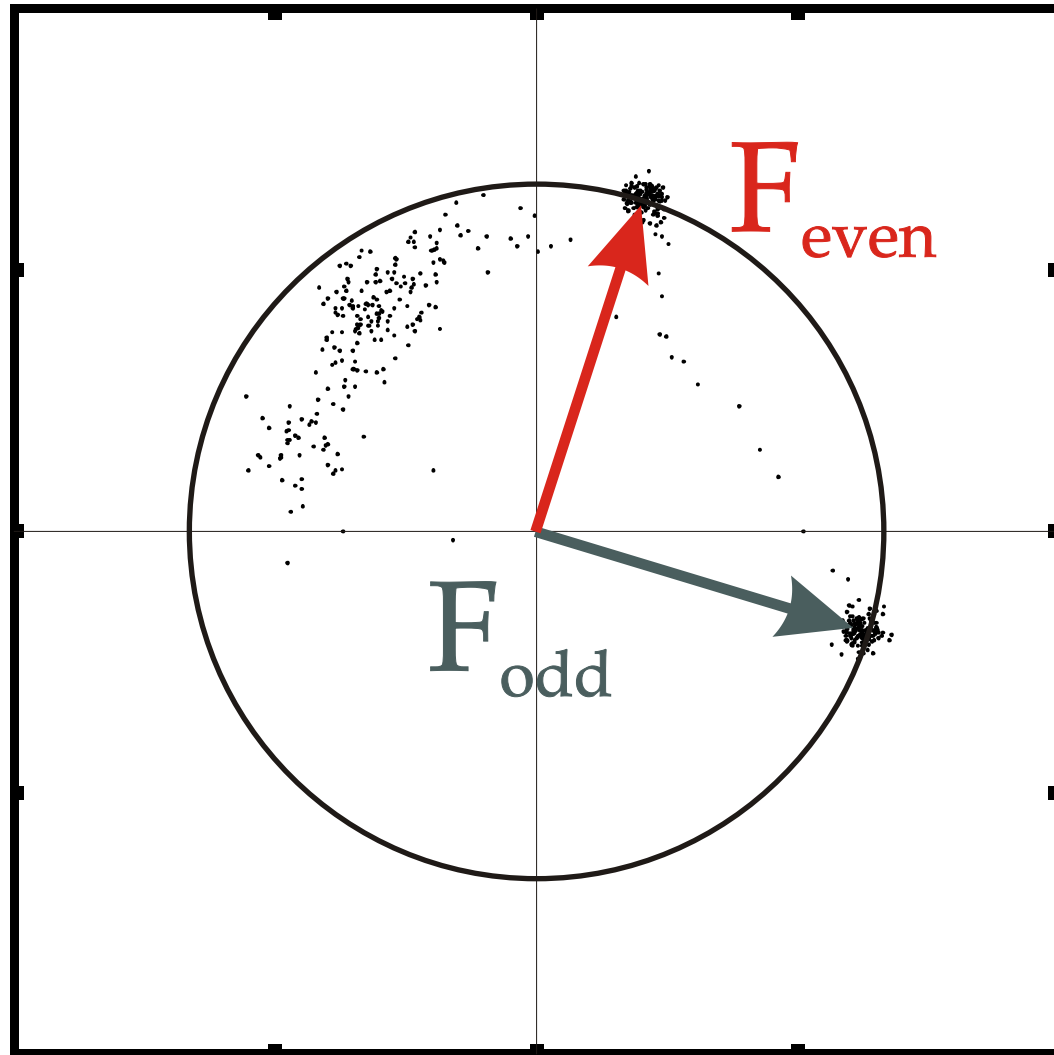


What is this ?



Evolution of strong reflections





converged
to a
limit cycle
not a
fixed point

Table 1

Example structures; columns: CSD code and original reference, space group, number of non-hydrogen atoms and chemical formula per unit cell.

	Code and reference	Space group	N	Unit-cell content
1	feryoq (<i>a</i>)	$P\bar{1}$	172	$2\cdot\text{C}_{80}\text{N}_1\text{O}_5$
2	rawtoy (<i>b</i>)	$P\bar{1}$	216	$2\cdot\text{C}_{88}\text{N}_4\text{O}_{16}$
3	ibeyap (<i>c</i>)	$P\bar{1}$	220	$2\cdot\text{C}_{96}\text{N}_1\text{O}_{13}$
4	cotgib (<i>d</i>)	$P\bar{1}$	244	$4\cdot\text{C}_{53}\text{Cu}_1\text{O}_5\text{P}_2$
5	sisyey (<i>e</i>)	$P\bar{1}$	326	$2\cdot\text{C}_{98}\text{Cl}_2\text{Mn}_{12}\text{N}_1\text{O}_{50}$
6	valino (<i>f</i>)	$P1$	156	$2\cdot\text{C}_{54}\text{N}_6\text{O}_{18}$
7	pawveo (<i>g</i>)	$P1$	164	$2\cdot\text{C}_{72}\text{N}_4\text{O}_6$
8	gofmod (<i>h</i>)	$P1$	188	$2\cdot\text{C}_{77.5}\text{N}_4\text{O}_{12.5}$
9	qarpuu (<i>i</i>)	$P1$	220	$2\cdot\text{C}_{105}\text{N}_4\text{Pd}_1$
10	qibbuy (<i>j</i>)	$P1$	240	$1\cdot\text{C}_{181}\text{Cl}_{24}\text{N}_6\text{O}_{26}\text{P}_3$

Table 2

Solution statistics of the example structures; columns: δ normalized by the height of an oxygen peak, success rate, mean/minimum/maximum number of iterations.

	δ	Success	Mean	Min.	Max.
1	0.080	0.99	338	55	2005
2	0.074	1.00	301	55	1650
3	0.080	1.00	90	30	205
4	0.098	1.00	101	15	230
5	0.111	1.00	143	70	300
6	0.074	0.95	1040	115	4220
7	0.080	1.00	106	35	345
8	0.080	1.00	268	40	1645
9	0.111	1.00	198	75	690
10	0.125	1.00	441	85	4115

100 runs, 5000 iterations

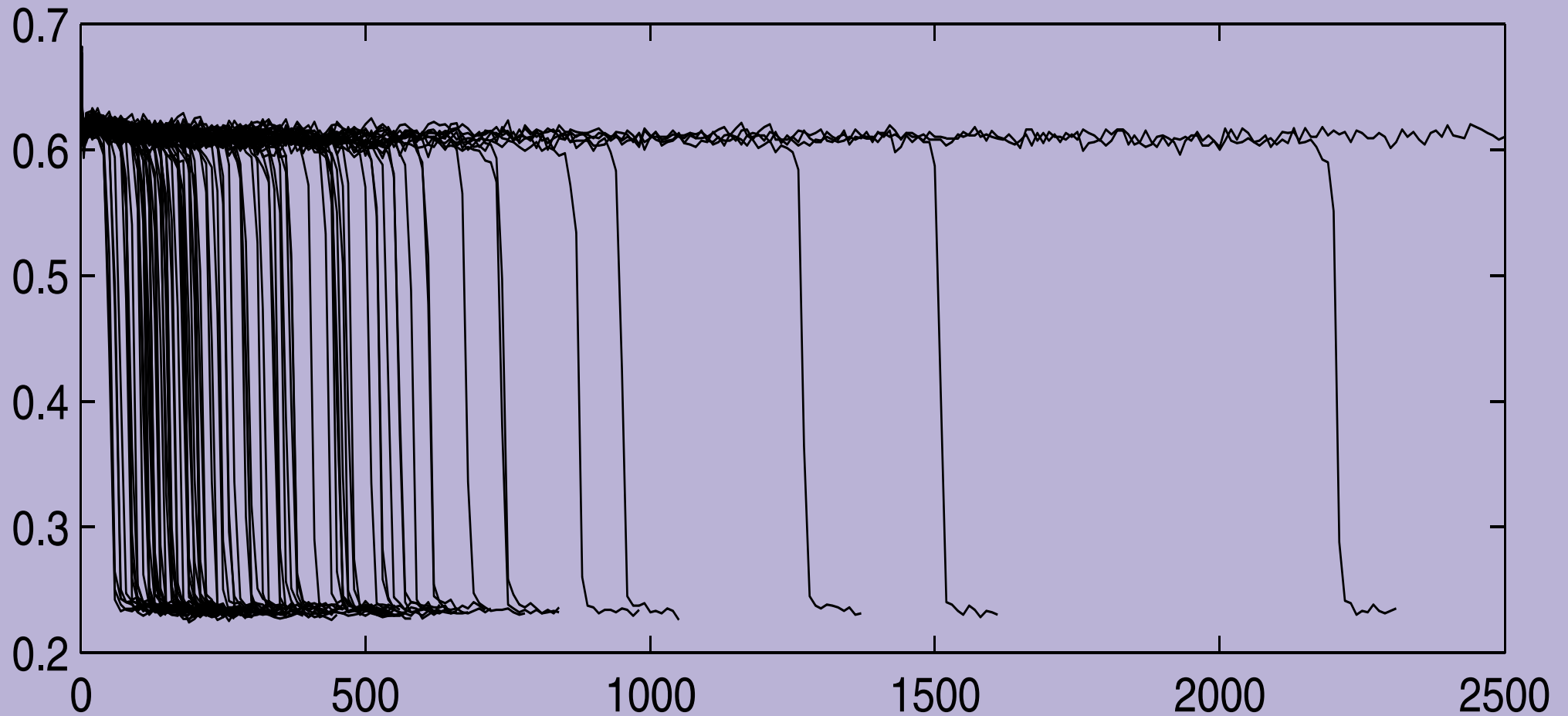
Table 2

Solution statistics of the example structures; columns: δ normalized by the height of an oxygen peak, success rate, mean/minimum/maximum number of iterations.

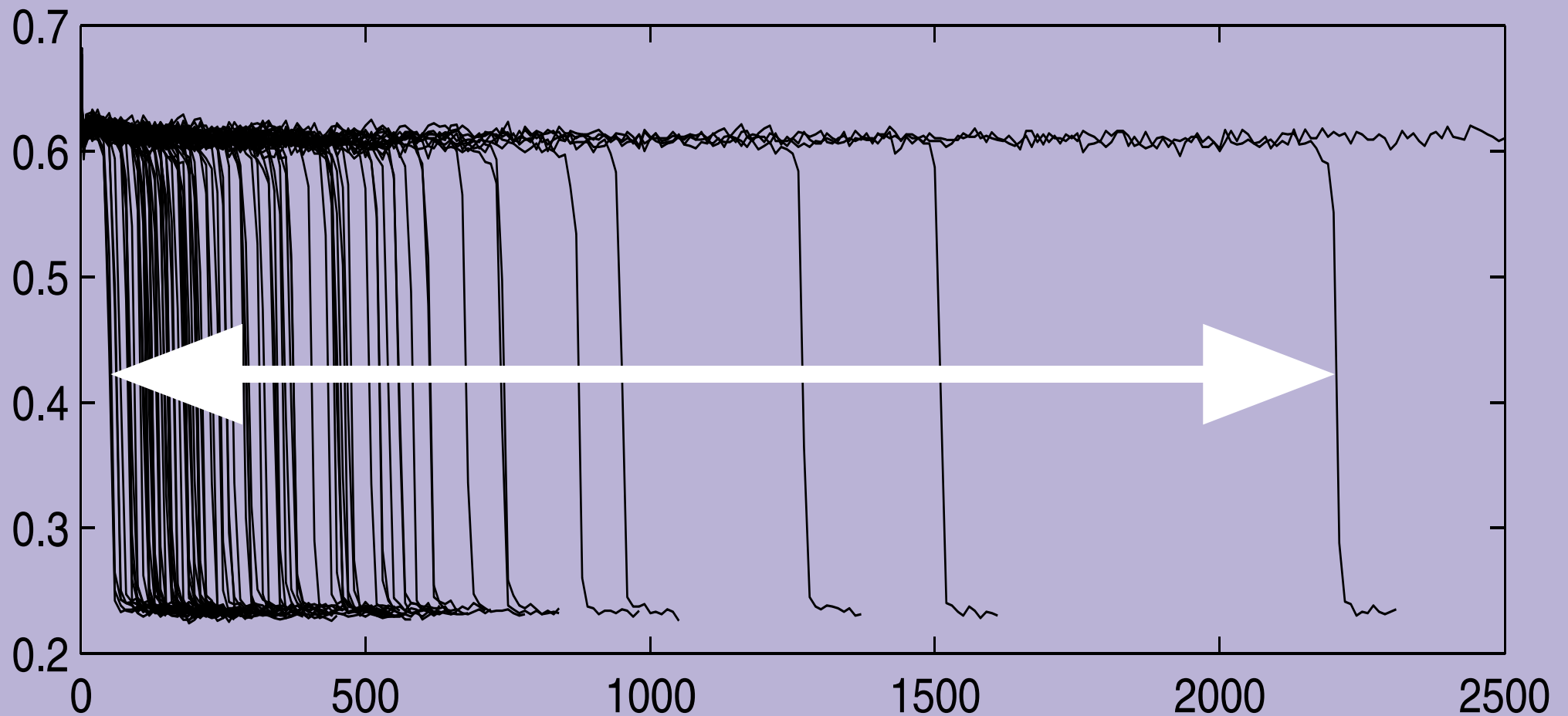
	δ	Success	Mean	Min.	Max.
1	0.080	0.99	338	55	2005
2	0.074	1.00	301	55	1650
3	0.080	1.00	90	30	205
4	0.098	1.00	101	15	230
5	0.111	1.00	143	70	300
6	0.074	0.95	1040	115	4220
7	0.080	1.00	106	35	345
8	0.080	1.00	268	40	1645
9	0.111	1.00	198	75	690
10	0.125	1.00	441	85	4115

100 runs, 5000 iterations

Chaotic behaviour



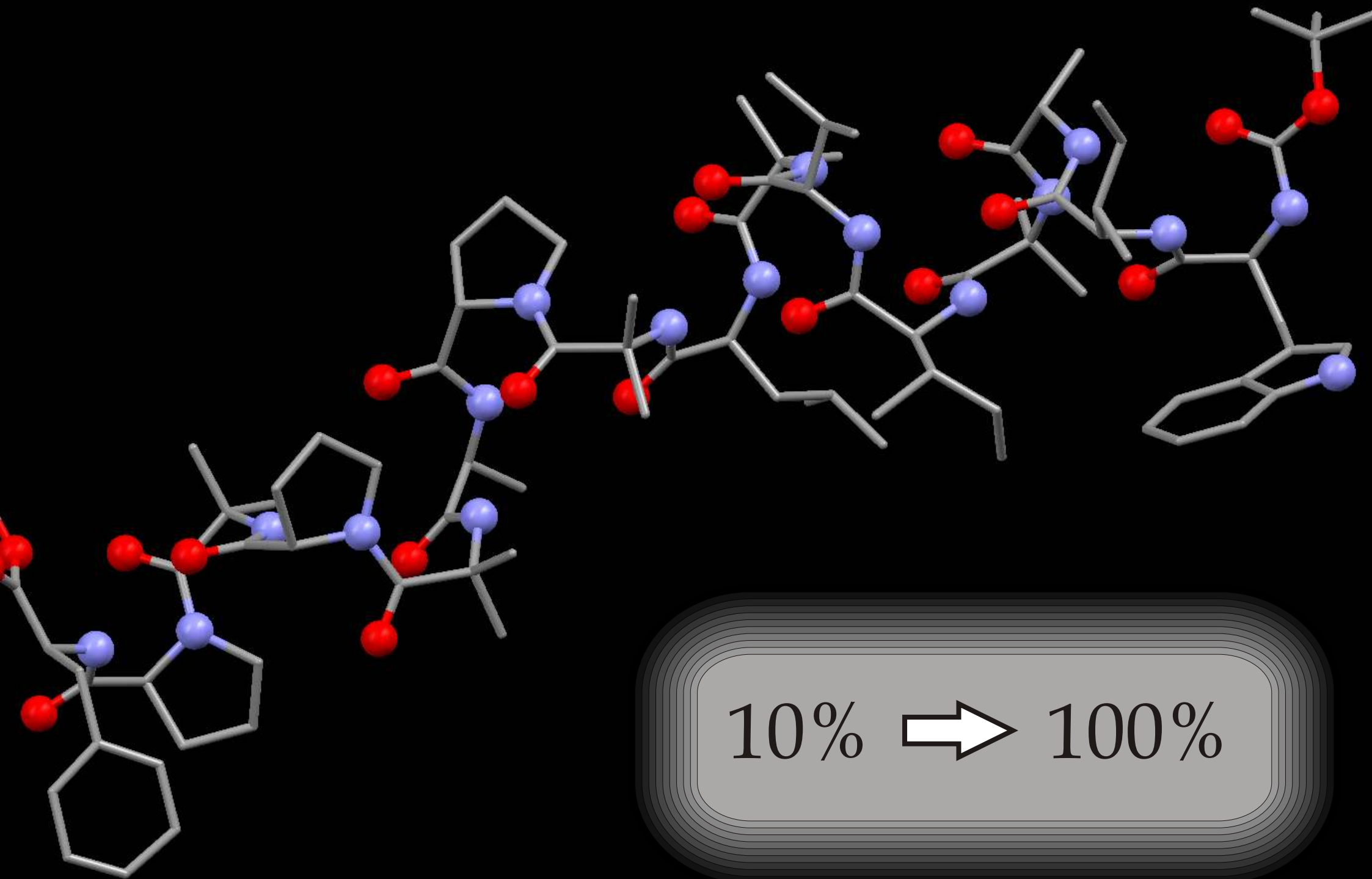
Chaotic behaviour



last bit of a single phase

Hard-to-solve structures

- non-centrosymmetric
- many atoms
- all-light atoms
- random looking
- dense
- no fragments



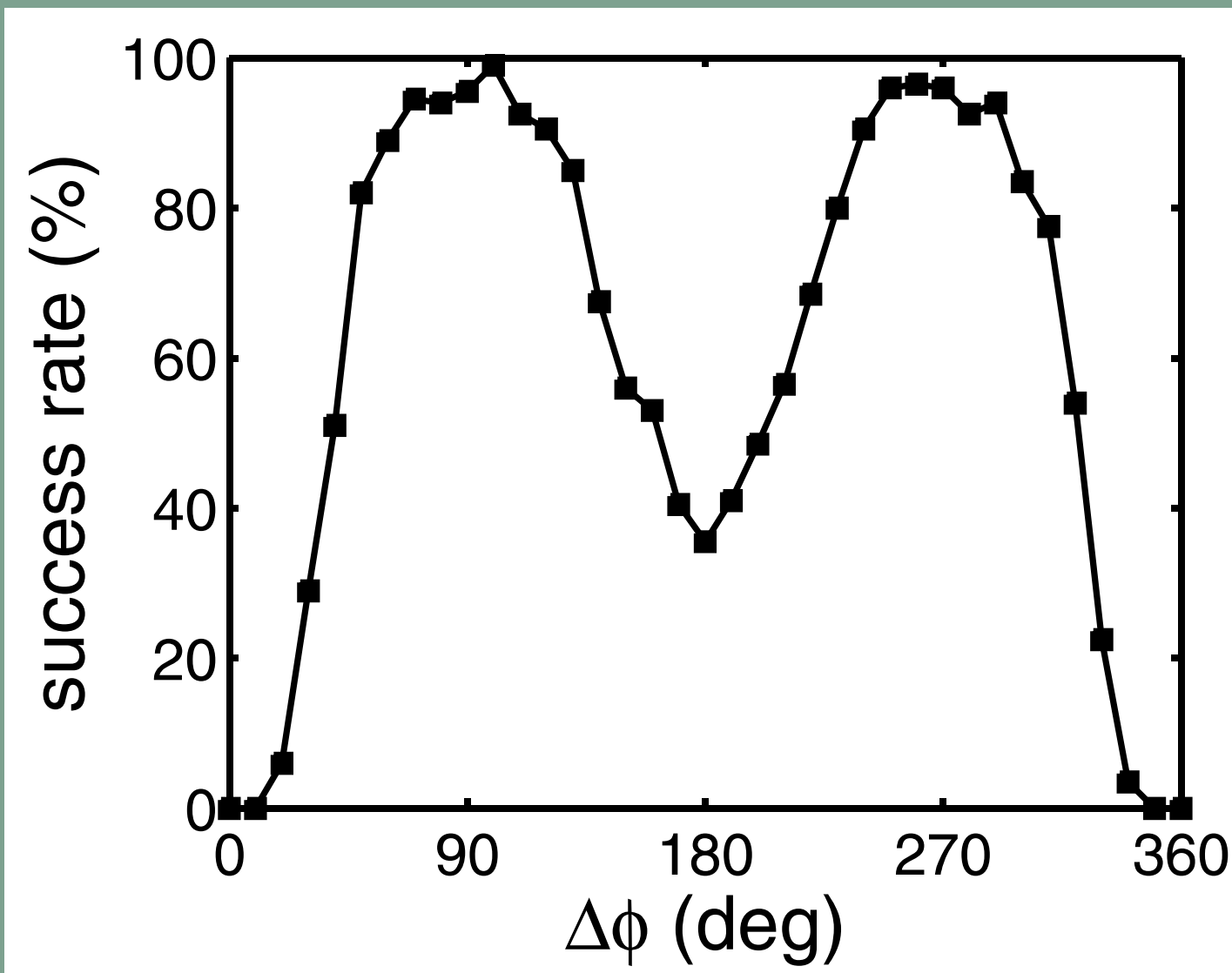
Can we improve the efficiency ?
Yes.

In the reciprocal half cycle
weak reflections can be utilized
to obtain the strong structure factors.

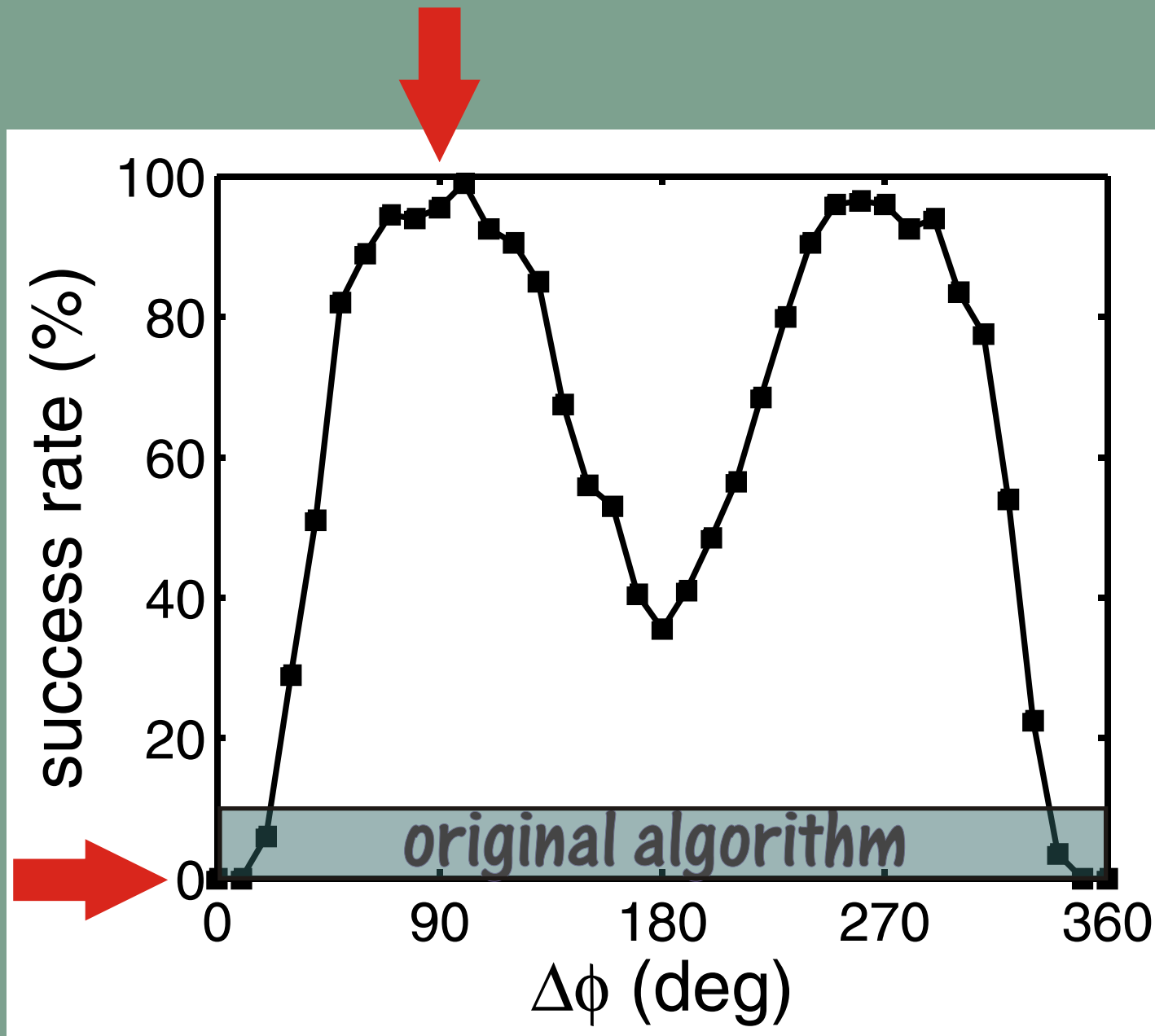
This is complementary to
what we do in real space.

Modified charge flipping:

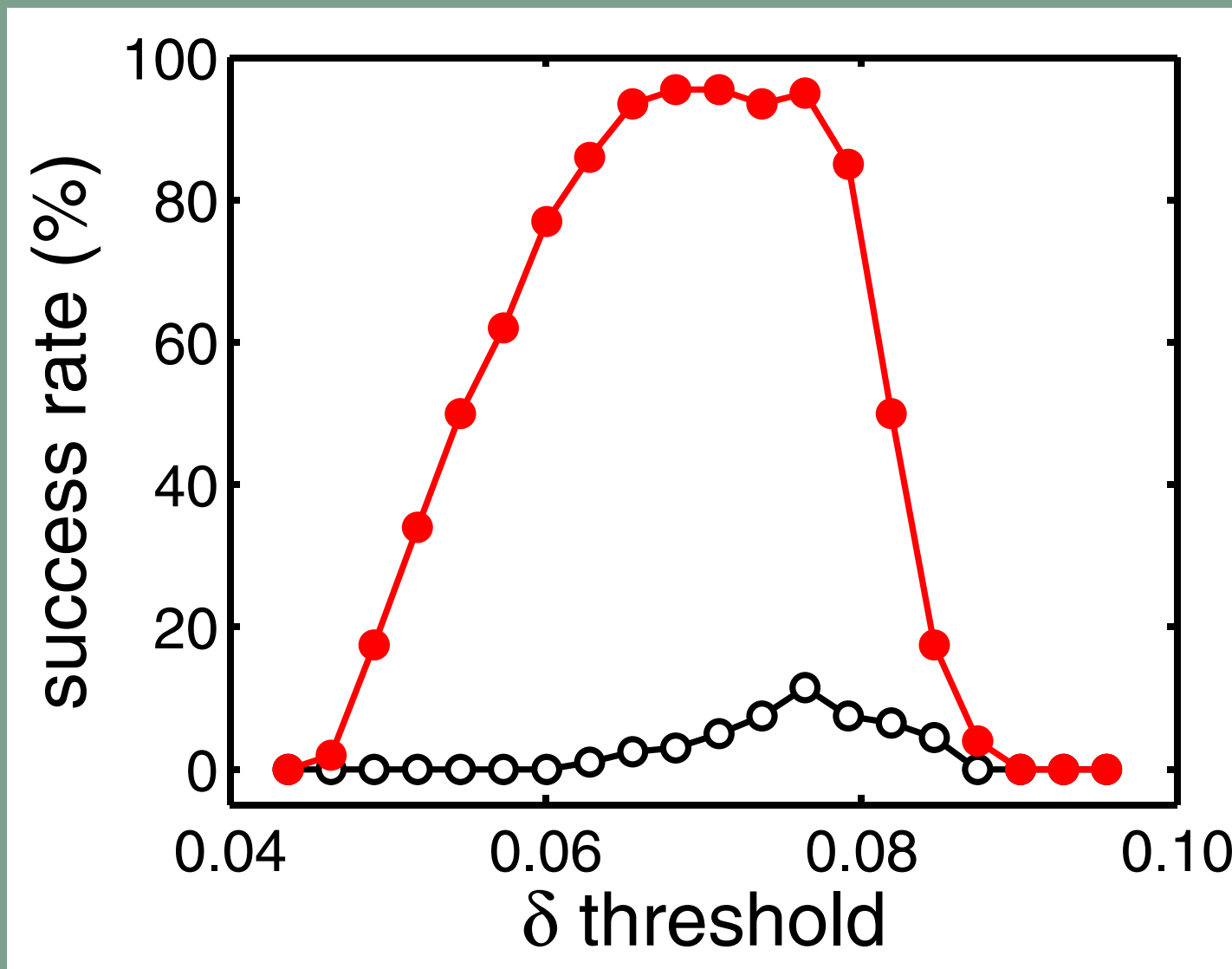
1. Sort reflections based on F_{obs} and mark them as weak and strong.
2. In the reciprocal half cycle
the moduli of weak reflections are allowed to change freely and their phases are shifted by $\Delta\varphi$.



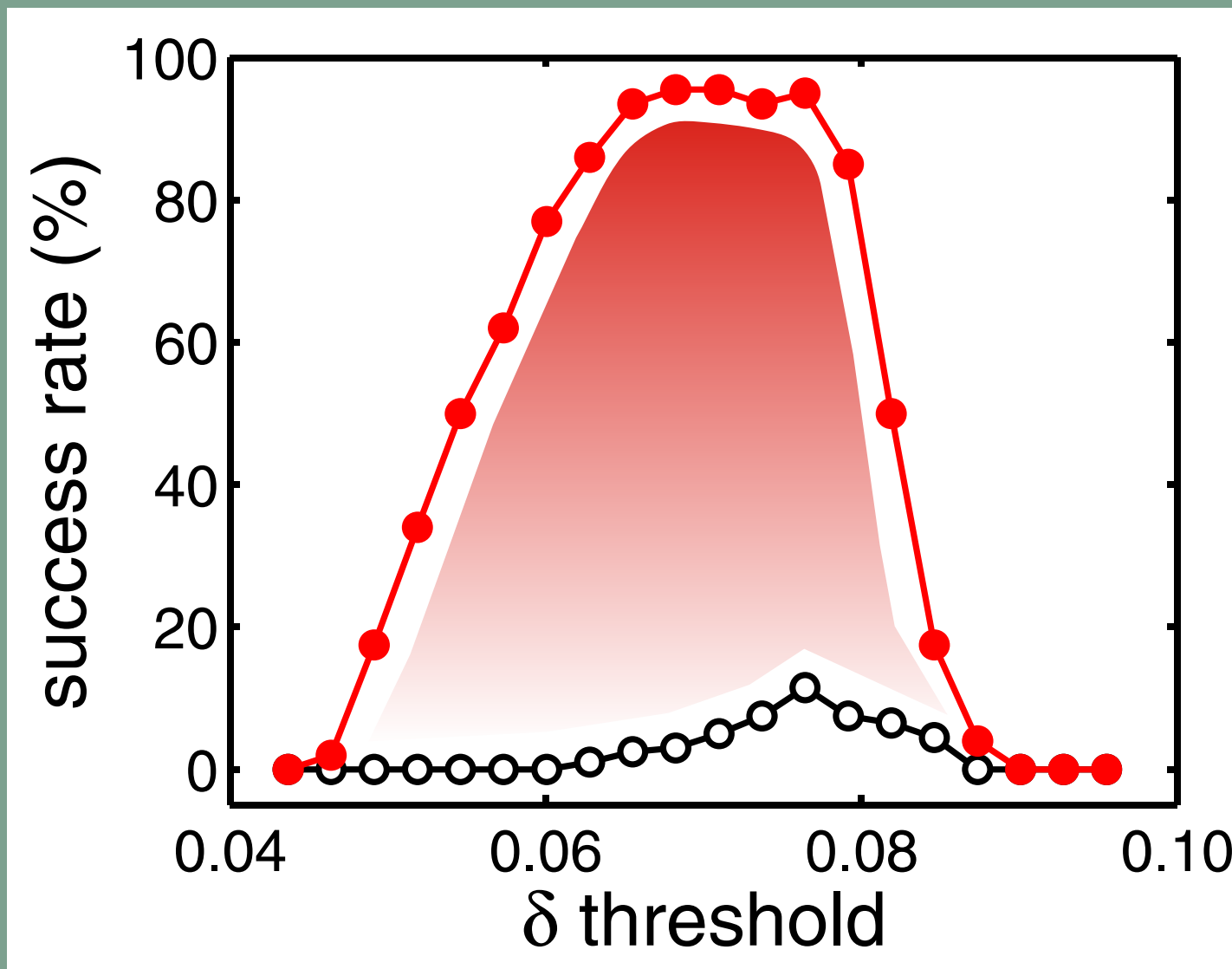
($\delta = \text{const.}$)



($\delta = \text{const.}$)



($\Delta\varphi = 90^\circ$)



($\Delta\varphi = 90^\circ$)

Table 1

Test structures.

Columns: CSD/PDB code and original reference, number of non-H atoms, success rate of the original and modified algorithms (%)

Code and reference	No. of atoms	Original	Modified
gofmod (<i>a</i>)	188	100	100
xeqtui (<i>b</i>)	264	100	100
hegxum (<i>c</i>)	209	0	75
agazud (<i>d</i>)	219	0	51
1a7y (<i>e</i>)	314	0	24

(*a*) Biradha *et al.* (1998); (*b*) Witt *et al.* (2000); (*c*) Rontoyianni *et al.* (1994); (*d*) Alexander *et al.* (2002); (*e*) Schaefer *et al.* (1998)

100 runs, 100000 iterations

Applications of charge-flipping:

L. Palatinus:

- Charge flipping in superspace
- Experimental data of modulated structures

Acta Cryst. A **60**, 604 (2004)

included in BAYMEM & JANA2000

J.S. Wu, J.C.H. Spence *et al.*:

- Experimental data of normal crystals
- CF+HIO for non-periodic objects
- Complex non-periodic objects

Acta Cryst. A **60**, 326 (2004)

Optics Lett. **29**, 2737 (2004)

Acta Cryst. A **61**, 194 (2005)

Future directions:

- use of known information
- increase size
- lower resolution
- handle incomplete data
- applications
- proof of convergence