A Topological Data Analysis Perspective on Non-Covalent Interactions in Relativistic Calculations - supplementary information

Małgorzata Olejniczak[a], André Severo Pereira Gomes[b] and Julien Tierny[c]

[a] *Centre of New Technologies, University of Warsaw, S. Banacha 2c 02-097 Warsaw, Poland*
[b] *Université de Lille, CNRS, UMR 8523 – PhLAM – Physique des Lasers, Atomes et Molécules, F-59000 Lille, France*
[c] *Sorbonne Université, CNRS, Laboratoire d'Informatique de Paris 6, LIP6, F-75005 Paris, France*

August 2, 2019

List of tables:

- Table 13: The values of $log(\rho)$ in the location of extra critical points of this scalar field between Au and H atoms in **g1** molecule. ADF calculations with a selected QM model.

List of plots:

- Figure 1 An example of ED with more complex topology in the interatomic Au-H area.

Additional information:

- The supplementary data also includes the **esi.tgz** file, which contains a collection of inputs, outputs and ED data from QM calculations, as well as the description of the analysis pipeline. The detailed information on the content of this repository is in the **README.md** file (after extracting the esi.tgz).
- TDA of scalar fields is well-described on the TTK website (link) and can be done for each scalar field using TTK-GUI.
- The automated analysis of many electron density files was done with the set of scripts (link) - an example analysis workflow is described in **esi.tgz**.

mol	interactions	R_e (this work) [Å]	R_e (Ref. [1]) [Å]
g1	Au4-H1	2.807	2.819
	Au4-C2	3.446	-
	C2-H1	1.092	1.090
	Au8-H2	2.822	2.830
	Au8-C3	3.480	-
	C3-H2	1.093	1.090
g2	Au4-H1	2.798	2.825
	Au4-C2	3.438	-
	C2-H1	1.092	1.090
	Au8-H2	2.822	2.804
	Au8-C3	3.481	-
	C3-H2	1.093	1.090
g3	Au4-H1	2.820	-
	Au4-C2	3.444	-
	C2-H1	1.090	1.090
	Au8-H2	2.850	-
	Au8-C3	3.483	-
	C3-H2	1.091	1.091

Table 1: Selected interatomic distances (atom numbering as in Ref. [1]) for **g1**, **g2** and **g3** molecules - optimized in this work and compared with the geometrical parameters reported in Ref. [1] (when available).

atom	x	y	z
H	1.447129	-3.218916	0.443356
C	0.891218	-2.282030	0.513704
C	-0.488085	-2.292899	0.482397
H	-1.025116	-3.238994	0.391156
C	-1.231052	-1.081540	0.574520
S	-2.957115	-1.200669	0.552737
C	-0.515616	0.140932	0.691914
H	-1.077478	1.074420	0.768003
C	0.863439	0.152115	0.721561
H	1.406100	1.096468	0.813571
C	1.597343	-1.057583	0.641735
S	3.338453	-1.120221	0.735160
Au	-3.877913	0.894515	0.726014
Au	4.284613	-1.219358	-1.562293
Au	-4.414556	2.043917	3.213722
Au	-5.058650	3.315975	0.973362
Au	-4.596259	2.428347	-1.486199
Au	4.217251	1.068153	0.564033
Au	5.507891	3.266987	-0.151806
Au	5.423294	1.188213	-1.899938

Table 2: Optimized xyz-coordinates of **g1** molecule [Å]. Geometry optimization with scalar ZORA, PBE functional, TZP basis set and $\Delta E = 1.0e-4$ tolerance on the convergence of the energy gradient; singlet (minimum confirmed by frequency calculations). ADF software. Input, output and xyz files available in esi.tgz.

atom	x	y	z
H	1.445543	-3.228520	0.467639
C	0.891585	-2.289730	0.526716
C	-0.491708	-2.300111	0.496800
H	-1.027760	-3.247819	0.417458
C	-1.230387	-1.089980	0.573772
S	-2.969057	-1.214692	0.547851
C	-0.517263	0.130157	0.674760
H	-1.076000	1.066538	0.734930
C	0.866155	0.140807	0.705464
H	1.407948	1.086537	0.785942
C	1.594584	-1.067185	0.637831
S	3.350096	-1.136226	0.748306
Au	-3.868699	0.893830	0.726644
Au	4.270429	-1.187408	-1.541928
Au	-4.446213	2.026757	3.210992
Au	-5.027572	3.339367	0.981216
Au	-4.526540	2.468274	-1.473689
Au	4.220646	1.061036	0.561745
Au	5.475904	3.279692	-0.147066
Au	5.393201	1.226509	-1.928674

Table 3: Optimized xyz-coordinates of **g2** molecule [Å]. Geometry optimization with scalar ZORA, PBE functional, TZP basis set and $\Delta E = 1.0e-4$ tolerance on the convergence of the energy gradient; triplet (minimum confirmed by frequency calculations). ADF software. Input, output and xyz files available in esi.tgz.

atom	x	y	z
H	1.459756	-3.182355	0.461869
C	0.903988	-2.247269	0.530118
C	-0.476221	-2.256657	0.462371
H	-1.009443	-3.199787	0.344118
C	-1.216320	-1.048812	0.545927
S	-2.942748	-1.176034	0.450860
C	-0.508436	0.166999	0.702885
H	-1.068184	1.099653	0.774824
C	0.872705	0.176958	0.766838
H	1.410970	1.118464	0.885680
C	1.602369	-1.027917	0.682554
S	3.347944	-1.094758	0.814537
Au	-3.878050	0.879765	0.690327
Au	4.268177	-1.259067	-1.423403
Au	-4.549077	1.859681	3.184034
Au	-5.089136	3.261072	1.035560
Au	-4.499984	2.544068	-1.416046
Au	4.234028	1.049117	0.502335
Au	5.483517	3.203170	-0.315025
Au	5.389036	1.091540	-1.973655

Table 4: Optimized xyz-coordinates of **g3** molecule [Å]. Geometry optimization with scalar ZORA, PBE functional, QZ4P basis set and $\Delta E = 1.0e-6$ tolerance on the convergence of the energy gradient; triplet (frequency calculations not performed due to large computational cost). ADF software. Input, output and xyz files available in esi.tgz.

atom	x	y	z
H	-0.488085	-2.292899	0.482397
C	-1.231052	-1.081540	0.574520
S	-2.957115	-1.200669	0.552737
C	-0.515616	0.140932	0.691914
H	-1.077478	1.074420	0.768003
H	0.863439	0.152115	0.721561
Au	-3.877913	0.894515	0.726014

Table 5: The xyz-coordinates in **m-a-g1** molecule [Å]. The xyz file available in esi.tgz.

atom	x	y	z
H	0.891218	-2.282030	0.513704
H	-0.515616	0.140932	0.691914
C	0.863439	0.152115	0.721561
H	1.406100	1.096468	0.813571
C	1.597343	-1.057583	0.641735
S	3.338453	-1.120221	0.735160
Au	4.217251	1.068153	0.564033

Table 6: The xyz-coordinates in **m-b-g1** molecule [Å]. The xyz file available in esi.tgz.

Hamiltonian	XC functional	basis set	p_{full}	$p_{BCP-RCP}$ (Au4-H1)	$p_{BCP-RCP}$ (Au8-H2)	$p_{BCP-RCP}$ (2^{nd})
sr-ZORA	PBE	DZ	1.769451e+01	1.125930e-02	1.224516e-02	-
sr-ZORA	B3LYP	DZ	1.769064e+01	1.166529e-02	1.298286e-02	-
sr-ZORA	SAOP	DZ	1.771703e+01	1.226280e-02	1.453581e-02	-
sr-ZORA	M06-2X	DZ	1.763837e+01	3.978651e-03	4.677878e-03	-
sr-ZORA	PBE	TZP	1.642941e+01	5.110330e-03	4.153433e-03	4.817177e-04
sr-ZORA	B3LYP	TZP	1.638242e+01	5.406346e-03	3.624376e-03	3.977777e-04
sr-ZORA	SAOP	TZP	1.660280e+01	6.874537e-03	5.794189e-03	-
sr-ZORA	M06-2X	TZP	1.635400e+01	1.122817e-03	-	-
sr-ZORA	PBE	QZ4P	1.521122e+01	1.525617e-04	1.519517e-03	-
sr-ZORA	B3LYP	QZ4P	1.523449e+01	1.019242e-03	1.016382e-03	5.151300e-04
sr-ZORA	SAOP	QZ4P	1.526692e+01	8.397415e-04	8.749194e-04	-
sr-ZORA	M06-2X	QZ4P	1.503546e+01	-	-	-
so-ZORA	PBE	DZ	1.770511e+01	1.196422e-02	1.263567e-02	-
so-ZORA	B3LYP	DZ	1.770213e+01	1.272368e-02	1.326464e-02	-
so-ZORA	SAOP	DZ	1.772945e+01	1.324461e-02	1.492975e-02	-
so-ZORA	M06-2X	DZ	1.765091e+01	4.419973e-03	5.437300e-03	-
so-ZORA	PBE	TZP	1.643886e+01	5.453016e-03	4.973991e-03	-
so-ZORA	B3LYP	TZP	1.639362e+01	5.761828e-03	4.038796e-03	6.564660e-04
so-ZORA	SAOP	TZP	1.661120e+01	7.168729e-03	6.162753e-03	-
so-ZORA	M06-2X	TZP	1.635670e+01	1.546018e-03	3.733271e-04	-
so-ZORA	PBE	QZ4P	1.521225e+01	4.770581e-04	2.216330e-03	-
so-ZORA	B3LYP	QZ4P	1.524024e+01	1.240513e-03	1.287909e-03	6.496557e-04
so-ZORA	SAOP	QZ4P	1.526583e+01	1.032044e-03	1.023866e-03	-
so-ZORA	M06-2X	QZ4P	1.503793e+01	-	-	-

Table 7: Persistence values of extra saddle-saddle pairs of $log(\rho)$ between Au and H atoms ($p_{BCP-RCP}$ (Au4-H1) and $p_{BCP-RCP}$ (Au8-H2)) and the full persistence range (p_{full}) of $log(\rho)$ in **g1** molecule. In some cases, there are two pairs of saddle-saddle points in the same interatomic area, in which case the second pair exhibits even smaller persistence value ($p_{BCP-RCP}$ (2^{nd})), as also demonstrated in Figure 1. Empty persistence value field means that the corresponding saddle-saddle pair is absent. Nonrelativistic electron densities do not exhibit extra saddle-saddle pairs in these interatomic areas, hence the results are not included in the table, yet the corresponding outputs are attached in esi.tgz. ADF calculations (`data/raw_data/g1/ED_calcs_ADF` directory in esi.tgz). These values were used to prepare the plot in Figure 3 (top) in the main publication.

Hamiltonian	XC functional	basis set	p_{full}	$p_{BCP-RCP}$ (Au4-H1)	$p_{BCP-RCP}$ (Au8-H2)	$p_{BCP-RCP}$ (2^{nd})
sr-ZORA	PBE	DZ	1.717114e+01	1.435171e-02	1.397782e-02	
sr-ZORA	B3LYP	DZ	1.716389e+01	1.495156e-02	1.474009e-02	
sr-ZORA	SAOP	DZ	1.719425e+01	1.592493e-02	1.651262e-02	
sr-ZORA	M06-2X	DZ	1.711547e+01	5.865562e-03	5.235502e-03	
sr-ZORA	PBE	TZP	1.591613e+01	7.602445e-03	5.443757e-03	
sr-ZORA	B3LYP	TZP	1.587128e+01	8.005509e-03	5.035625e-03	
sr-ZORA	SAOP	TZP	1.608863e+01	9.626236e-03	7.196483e-03	
sr-ZORA	M06-2X	TZP	1.585316e+01	3.599969e-03	3.857565e-04	
sr-ZORA	PBE	QZ4P	1.471760e+01	2.000082e-03	1.520771e-03	
sr-ZORA	B3LYP	QZ4P	1.475556e+01	3.396760e-03	1.978182e-03	
sr-ZORA	SAOP	QZ4P	1.488288e+01	4.277207e-03	2.930192e-03	
sr-ZORA	M06-2X	QZ4P	1.458157e+01	8.094562e-04	-	
so-ZORA	PBE	DZ	1.717679e+01	1.644953e-02	1.574424e-02	
so-ZORA	B3LYP	DZ$^{(a)}$	1.718075e+01	1.634773e-02	1.592183e-02	
so-ZORA	SAOP	DZ	1.719425e+01	1.592493e-02	1.651262e-02	
so-ZORA	M06-2X	DZ	1.711381e+01	6.137765e-03	6.322581e-03	
so-ZORA	PBE	TZP	1.588848e+01	8.553137e-03	6.347091e-03	
so-ZORA	B3LYP	TZP	1.586315e+01	8.190917e-03	5.498912e-03	
so-ZORA	SAOP	TZP	1.599783e+01	8.482935e-03	6.617830e-03	
so-ZORA	M06-2X	TZP$^{(b)}$	1.587124e+01	3.872325e-03	6.231982e-04	
so-ZORA	PBE	QZ4P	1.468633e+01	2.316956e-03	2.212547e-03	7.394137e-04
so-ZORA	B3LYP	QZ4P$^{(c,d)}$	1.474735e+01	2.327404e-03	3.987820e-03	
so-ZORA	SAOP	QZ4P	1.471088e+01	2.690176e-03	2.709691e-03	6.570162e-04
so-ZORA	M06-2X	QZ4P$^{(e)}$	1.459987e+01	1.037826e-03	-	

Table 8: Persistence values of extra saddle-saddle pairs of $log(\rho)$ between Au and H atoms ($p_{BCP-RCP}$ (Au4-H1) and $p_{BCP-RCP}$ (Au8-H2)) and the full persistence range (p_{full}) of $log(\rho)$ in **g2** molecule. In some cases, there are two pairs of saddle-saddle points in the same interatomic area, in which case the second pair exhibits even smaller persistence value ($p_{BCP-RCP}$ (2^{nd})), as also demonstrated in Figure 1. Empty persistence value field means that the corresponding saddle-saddle pair is absent. Nonrelativistic electron densities do not exhibit extra saddle-saddle pairs in these interatomic areas, hence the results are not included in the table, yet the corresponding outputs are attached in esi.tgz. ADF calculations. These values were used to prepare the plot in Figure 3 (top) in the main publication.
Issues in ADF calculations (also see `data/raw_data/g2/ED_calcs_ADF/ADF_issues` file in esi.tgz):
$^{(a)}$ Lower convergence criteria in SCF procedure in ED single-point calculations were used: SCFcnv=2e-05 (instead of 1e-06, applied in other cases).$^{(*)}$
$^{(b)}$ Lower convergence criteria in SCF procedure in ED single-point calculations were used: SCFcnv=3e-05 (instead of 1e-06, applied in other cases).$^{(*)}$
$^{(c)}$ Lower convergence criteria in SCF procedure in ED single-point calculations were used: SCFcnv=1e-05 (instead of 1e-06, applied in other cases).$^{(*)}$
$^{(d)}$ Lower integration accuracy in SCF procedure (ED calculations) was used: 1e-04 (instead of 1e-08, applied in other cases).$^{(**)}$
$^{(e)}$ Lower convergence criteria in SCF procedure in ED single-point calculations were used: SCFcnv=8e-06 (instead of 1e-06, applied in other cases).$^{(*)}$
$^{(*)}$ SCFcnv is explained in `https://www.scm.com/doc/ADF/Input/SCF.html`
$^{(**)}$ accint is explained in `https://www.scm.com/doc/ADF/Input/Numerical_integration.html`

Hamiltonian	XC functional	basis set	p_{full}	$p_{BCP-RCP}$ (Au4-H1)	$p_{BCP-RCP}$ (Au8-H2)	$p_{BCP-RCP}$ (2^{nd})
sr-ZORA	PBE	DZ	1.801864e+01	8.709746e-03	5.789720e-03	
sr-ZORA	B3LYP	DZ	1.801225e+01	9.163789e-03	6.593143e-03	
sr-ZORA	SAOP	DZ	1.804687e+01	9.594903e-03	7.400598e-03	
sr-ZORA	M06-2X	DZ	1.796336e+01	1.339880e-03	5.694157e-04	4.944822e-04
sr-ZORA	PBE	TZP	1.658976e+01	1.694424e-03	-	
sr-ZORA	B3LYP	TZP	1.653246e+01	2.039347e-03	-	
sr-ZORA	SAOP	TZP	1.680598e+01	3.201481e-03	6.805312e-04	
sr-ZORA	M06-2X	TZP	1.649374e+01	-	-	
sr-ZORA	PBE	QZ4P	1.537412e+01	-	-	
sr-ZORA	B3LYP	QZ4P	1.549474e+01	-	-	
sr-ZORA	SAOP	QZ4P	1.565850e+01	-	-	
sr-ZORA	M06-2X	QZ4P	1.529012e+01	-	-	
so-ZORA	PBE	DZ	1.802720e+01	1.063200e-02	7.152668e-03	
so-ZORA	B3LYP	DZ	1.802282e+01	1.084425e-02	7.563135e-03	
so-ZORA	SAOP	DZ	1.804031e+01	1.094759e-02	7.291676e-03	
so-ZORA	M06-2X	DZ	1.796916e+01	2.596635e-03	-	
so-ZORA	PBE	TZP	1.656615e+01	2.471294e-03	6.121454e-04	
so-ZORA	B3LYP	TZP	1.652044e+01	2.645973e-03	4.187489e-04	
so-ZORA	SAOP	TZP	1.668164e+01	2.586178e-03	6.677462e-04	
so-ZORA	M06-2X	TZP	1.655847e+01	-	-	
so-ZORA	PBE	QZ4P	1.544652e+01	-	-	
so-ZORA	B3LYP	QZ4P$^{(a,b)}$	1.547454e+01	-	-	
so-ZORA	SAOP	QZ4P	1.547503e+01	-	-	
so-ZORA	M06-2X	QZ4P$^{(c)}$	1.532595e+01	-	-	

Table 9: Persistence values of extra saddle-saddle pairs of $log(\rho)$ between Au and H atoms ($p_{BCP-RCP}$ (Au4-H1) and $p_{BCP-RCP}$ (Au8-H2)) and the full persistence range (p_{full}) of $log(\rho)$ in **g3** molecule. In some cases, there are two pairs of saddle-saddle points in the same interatomic area, in which case the second pair exhibits even smaller persistence value ($p_{BCP-RCP}$ (2^{nd})), as also demonstrated in Figure 1. Empty persistence value field means that the corresponding saddle-saddle pair is absent. Nonrelativistic electron densities do not exhibit extra saddle-saddle pairs in these interatomic areas, hence the results are not included in the table, yet the corresponding outputs are attached in esi.tgz. ADF calculations. These values were used to prepare the plot in Figure 3 (top) in the main publication.

Issues in ADF calculations (also see `data/raw_data/g3/ED_calcs_ADF/ADF_issues` file in esi.tgz):

$^{(a)}$ Lower convergence criteria in SCF procedure in ED single-point calculations were used: SCFcnv=2e-05 (instead of 1e-06, applied in other cases).$^{(*)}$

$^{(b)}$ Lower integration accuracy in SCF procedure (ED calculations) was used: accint=1e-04 (instead of 1e-08, applied in other cases).$^{(**)}$

$^{(c)}$ Lower convergence criteria in SCF procedure in ED single-point calculations were used: SCFcnv=2e-05 (instead of 1e-06, applied in other cases).$^{(*)}$

$^{(*)}$ SCFcnv is explained in `https://www.scm.com/doc/ADF/Input/SCF.html`

$^{(**)}$ accint is explained in `https://www.scm.com/doc/ADF/Input/Numerical_integration.html`

software	Hamiltonian	method	basis set	p_{full}	$p_{BCP-RCP}$ (Au-H)
ADF	NR	PBE	QZ4P	1.305694e+01	-
ADF	sr-ZORA	PBE	QZ4P	1.335749e+01	3.872066e-03
ADF	so-ZORA	PBE	QZ4P	1.335972e+01	4.176261e-03
DIRAC	LL	HF	TZ	1.324935e+01	-
DIRAC	LL	PBE	TZ	1.324776e+01	-
DIRAC	SFDC	HF	TZ	1.359010e+01	-
DIRAC	SFDC	PBE	TZ	1.352066e+01	7.112031e-03
DIRAC	DC	HF	TZ	1.359544e+01	-
DIRAC	DC	PBE	TZ	1.350644e+01	7.252288e-03

Table 10: Persistence values of extra saddle-saddle pairs of $log(\rho)$ between Au and H atoms ($p_{BCP-RCP}$ (Au-H)) and the full persistence range (p_{full}) of $log(\rho)$ in **m-a-g1** molecule. Empty persistence value field means that the corresponding saddle-saddle pair is absent. DIRAC and ADF calculations. These values were used to prepare the plot in Figure 3 (bottom) in the main publication.

software	Hamiltonian	method	basis set	p_{full}	$p_{BCP-RCP}$ (Au-H)
ADF	NR	PBE	QZ4P	1.327969e+01	-
ADF	sr-ZORA	PBE	QZ4P	1.355098e+01	3.954927e-03
ADF	so-ZORA	PBE	QZ4P	1.355417e+01	4.173114e-03
DIRAC	LL	HF	TZ	1.339789e+01	-
DIRAC	LL	PBE	TZ	1.335818e+01	-
DIRAC	SFDC	HF	TZ	1.364721e+01	-
DIRAC	SFDC	PBE	TZ	1.360986e+01	6.706207e-03
DIRAC	DC	HF	TZ	1.365221e+01	-
DIRAC	DC	PBE	TZ	1.359180e+01	6.851428e-03

Table 11: Persistence values of extra saddle-saddle pairs of $log(\rho)$ between Au and H atoms ($p_{BCP-RCP}$ (Au-H)) and the full persistence range (p_{full}) of $log(\rho)$ in **m-b-g1** molecule. Empty persistence value field means that the corresponding saddle-saddle pair is absent. DIRAC and ADF calculations. These values were used to prepare the plot in Figure 3 (bottom) in the main publication.

grid size [^{3}]	basis set	p_{full}	$p_{BCP-RCP}$ (Au-H)	$d_{BCP-RCP}$ (Au-H)
100	DZ	1.195127e+01	1.869950e-02	3.671269e-01
120	DZ	1.309020e+01	2.236385e-02	3.781513e-01
140	DZ	1.248961e+01	1.994952e-02	3.938479e-01
160	DZ	1.208379e+01	1.826069e-02	3.396226e-01
180	DZ	1.241236e+01	2.064556e-02	3.563615e-01
200	DZ	1.239989e+01	2.017480e-02	3.680712e-01
220	DZ	1.225804e+01	1.893280e-02	3.749301e-01
240	DZ	1.231507e+01	1.978607e-02	3.771497e-01
260	DZ	1.261110e+01	2.010359e-02	3.843008e-01
280	DZ	1.276228e+01	1.960953e-02	3.921415e-01
300	DZ	1.251713e+01	1.945282e-02	3.956538e-01
320	DZ	1.331789e+01	1.970133e-02	3.708479e-01
100	TZP	1.221650e+01	1.321338e-02	2.773642e-01
120	TZP	1.335541e+01	1.242765e-02	3.146496e-01
140	TZP	1.275482e+01	1.105273e-02	3.237410e-01
160	TZP	1.234902e+01	1.291310e-02	3.396226e-01
180	TZP	1.267758e+01	1.164339e-02	3.598911e-01
200	TZP	1.266510e+01	1.135396e-02	3.205463e-01
220	TZP	1.252326e+01	1.257816e-02	3.319230e-01
240	TZP	1.258029e+01	1.144852e-02	3.043196e-01
260	TZP	1.287632e+01	1.135001e-02	2.786618e-01
280	TZP	1.302749e+01	1.244543e-02	2.908751e-01
300	TZP	1.278235e+01	1.160138e-02	3.029665e-01
320	TZP	1.358311e+01	1.154929e-02	2.825667e-01
100	QZ4P	1.166440e+01	5.851856e-03	2.773642e-01
120	QZ4P	1.278673e+01	5.696846e-03	2.428267e-01
140	QZ4P	1.220642e+01	3.577124e-03	1.942446e-01
160	QZ4P	1.179808e+01	5.121765e-03	2.830188e-01
180	QZ4P	1.212905e+01	4.983849e-03	2.563753e-01
200	QZ4P	1.211652e+01	4.115400e-03	2.316469e-01
220	QZ4P	1.197374e+01	4.998110e-03	2.507677e-01
240	QZ4P	1.203120e+01	4.605919e-03	2.328481e-01
260	QZ4P	1.232757e+01	4.009358e-03	2.462884e-01
280	QZ4P	1.247791e+01	4.883752e-03	2.286334e-01
300	QZ4P	1.223392e+01	4.408231e-03	2.128415e-01
320	QZ4P	1.303013e+01	4.116861e-03	2.262489e-01

Table 12: The full persistence range (p_{full}) of $log(\rho)$, persistence values of extra saddle-saddle pairs of $log(\rho)$ between Au and H atoms ($p_{BCP-RCP}$ (Au-H)) and the Euclidean distance between the critical points forming these pairs ($d_{BCP-RCP}$ (Au-H)) calculated for **m-a-g1** molecule on grids of various dimensions. ADF calculations with so-ZORA Hamiltonian and PBE functional. These values were used to prepare plots in Figure 4 in the main publication.

critical point	interatomic area	$r^{so-ZORA}$			$log(\rho^{so-ZORA}(r^{so-ZORA}))$	$log(\rho^{NR}(r^{so-ZORA}))$
"BCP"	Au4-H1	-2.101960e+00	7.294119e-01	7.450982e-01	-1.930624e+00	-1.948988e+00
"RCP"	Au4-H1	-2.101960e+00	6.352943e-01	7.450982e-01	-1.931102e+00	-1.947044e+00
"BCP"	Au8-H2	2.415687e+00	8.235295e-01	7.058825e-01	-1.936628e+00	-1.954695e+00
"RCP"	Au8-H2	2.415687e+00	6.352943e-01	7.450982e-01	-1.938844e+00	-1.951012e+00

Table 13: The values of $log(\rho)$ in the location of extra critical points of this scalar field between Au and H atoms in **g1** molecule - an example with the PBE functional and QZ4P basis set (ADF calculations), for which the topology of $log(\rho)$ is visualized in Figure 2 in the main publication. The additional critical points appear only for the electron density calculated with the relativistic so-ZORA Hamiltonian (what is emphasized by the superscript $so-ZORA$ in $r^{so-ZORA}$). The values of $log(\rho)$ within both, the nonrelativistic and the relativistic formalisms ($log(\rho^{NR}(r^{so-ZORA}))$ and $log(\rho^{so-ZORA}(r^{so-ZORA}))$, respectively), were probed in these locations in order to illustrate the total order of the $log(\rho)$ values in these two cases. This analysis justifies the emergence of the additional critical points in the relativistic case and their absence in the nonrelativistic framework (discussion in the main publication).

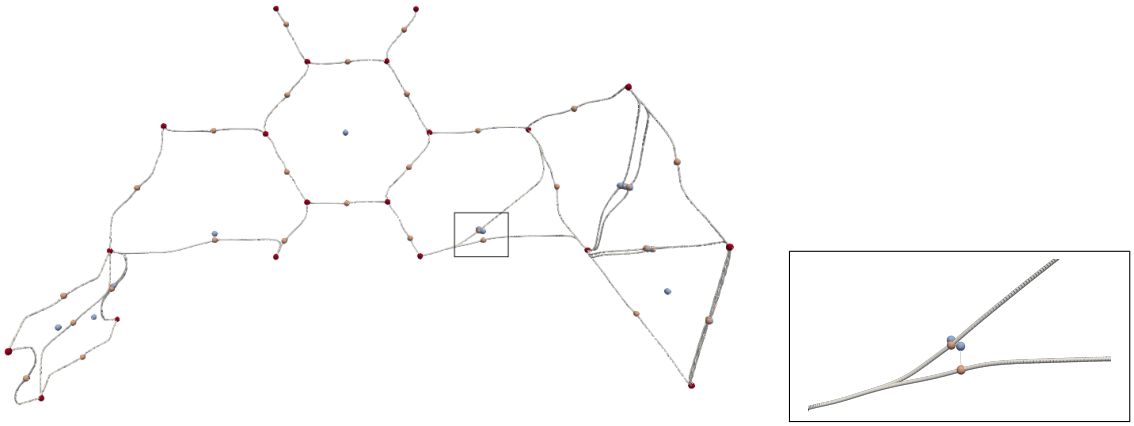

Figure 1: An example of ED with more complex topology of ED in the interatomic Au-H area - ED exhibiting 2 extra pairs of saddle-saddle points in the same interatomic area (here: between Au8-H2 nuclei). ADF calculations on **g1** with so-ZORA/B3LYP/QZ4P setup.

References

[1] Anderson, J.S.M., *et al.*, Chem. Eur. J. **2019**, 25, 2538–2544, doi:10.1002/chem.201804464