Demo in 3 parts:

- Part 1: calculation of Mn(5-crown ether)2+. Ground state configuration Mn 3d^5, and LFDFT without and with spin-orbit coupling.
- Part 2: calculation of Mn L2,3-edge XAS of Mn(5-crown ether)2+. XAS excited state configuration Mn 2p^5 3d^6 and electric-dipole transitions 3d^5 -> 2p^5 3d^6.
- Part 3: calculation of Mn L2,3-edge XMCD of Mn(5-crown ether)2+. XAS with magnetic field

## Part 1. Calculation of Mn(5-crown ether)2+. Ground state configuration Mn 3d^5 (without spin-orbit coupling)

- 1. Open AMSinput (SCM  $\rightarrow$  New Input)
- 2. Click Structure Tool (select Ligands/Multidedantes/5-crown ether)

Ś	AMSinput	SCM	File	Edit	Select	Atoms	Bonds	View	Help								G 0	)
• •	•						AN	/Sinput	2021.202+ (	r94818	;)							
										ADF	Main	Model Pro	perties	Details	MultiLevel		a	L
																	6	5
																	0	
										Task:			Single	Point		•	Ø	)
										Freau	encies:		Yes					
										•								
										Total	charge:			0.0				
										Spin p	olarizat	tion:		0.0				
										Unres	tricted:		TYes					
										XC fur	nctional	ŀ				-		
Str	ucture Tool:											-				_		
Sel	Select a structure from the pull-down menu,								Relativ	/ity:		Scalar			•	$\diamond$	1	
pas	te it with a lef	t-click			-	Alleyl Ober												
Dra	g anywhere o	utside the	e select	tion to:		Anino Ac	ins ide	``````````````````````````````````````		Basis	set:		DZ			•	Ð	)
Lef	t: Rotate as	s trackball	1			Aromatic >		Ś		Frozen core:			Large	Large 🔻		•		
Ctr Mic	l-left: Rotate ii Idle: Transla	n-plane te in-plan	ne			Cyclic Hy	drocarbons	>		Nume	rical qu	ality	Norma			_		
Rig	ht: Zoom					DNA		>		Hume	icai qu	unty.	Norma	1		·		1
						Ligands		>	Bidentates	>	-							
Dra	g inside the s	election to	0:			Metal Cor	nplexes	>	Multidentates	s >	3-Di	iethylene triar	mine					
Lef	t: Rotate as	trackball	I			Polyhedra	1	~	CN		3-Terpyridine							
Ctr Mic	I-left: Rotate II Idle: Transla	n-plane te in-plan	ie			Solvents		· ·	CO3		4-C	htalocvanine						
Rig	ht: Translat	e out-of-p	plane			Manage S	tructures		NC		4-P	orphyrin Ring						
_					_	Save As S	tructure		NH2		4-Tı	riethylene tetr	ramine					
		C 0	N	нс	I X.	0	* ٩	0	NH2CH3		5-C	rown ether						
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	q								00		5-Te	etraethylene p	pentamine					
	and the second		3	-		Care -	-				6-C	enzene						
			1	~	32	22 a	and a second	20	PH3		6-EI	DTA			0			ALLN.
		2	-			3-3	200		Pyridine		6-Pe	entaethylene	hexamine					
	and the second				100	and the second								2-	-			

- 3. Select the central atom (formally dummy atom Xx) and replace it to Mn (go to Atoms/Change Atom Type)
- (optional but for the sake of symmetry) Edit the structure: symmetry to D5h (go to Edit/Symmetry/Dnh/D5h); run pre-optimization; and check bond distances (Mn-O should be about 2 Å)
- 5. Export cartesian coordinates (go to File/Export Coordinates/.xyz)
- 6. Edit the coordinates (it is important that Mn is the first atom in the coordinates list)

Before					After					
	•	💐 zmat.xyz — Edi	ited				zmat.xyz			
36					36					
					Mn	-0.00000000	-0.00000000	0.00000000		
0	1.65102385	-1.19953904	0.0000000		0	1.65102385	-1.19953904	0.0000000		
0	1.65102385	1.19953904	0.0000000		0	1.65102385	1.19953904	0.0000000		
0	-0.63063499	-1.94089494	0.0000000		0	-0.63063499	-1.94089494	0.0000000		
0	-0.63063499	1.94089494	0.0000000		0	-0.63063499	1.94089494	0.0000000		
0	-2.04077771	-0.00000000	0.0000000		0	-2.04077771	-0.00000000	0.0000000		
C	1.61908748	2.59903148	0.00000000		C	1.61908748	2.59903148	0.0000000		
C	0.21780309	-3.05433638	0.0000000		C	0.21780309	-3.05433638	0.0000000		
C	0.21780309	3.05433638	0.00000000		C	0.21780309	3.05433638	0.0000000		
C	2.97215137	-0.73669880	0.0000000		C	2.97215137	-0.73669880	0.0000000		
C	2.97215137	0.73669880	0.00000000		C	2.97215137	0.73669880	0.0000000		
C	-1.97150028	-2.34298859	0.0000000		C	-1.97150028	-2.34298859	0.0000000		
C	-1.97150028	2.34298859	0.0000000		C	-1.97150028	2.34298859	0.0000000		
C	-2.83754166	-1.15098490	0.00000000		C	-2.83754166	-1.15098490	0.0000000		
C	-2.83754166	1.15098490	0.0000000		C	-2.83754166	1.15098490	0.0000000		
C	1.61908748	-2.59903148	0.00000000		C	1.61908748	-2.59903148	0.0000000		
Mn	-0.00000000	-0.00000000	0.0000000		н	2.13478017	3.00053481	-0.90399590		
H	2.13478017	3.00053481	-0.90399590		H	2.13478017	3.00053481	0.90399590		
н	2.13478017	3.00053481	0.90399590		н	0.03659667	-3.68227596	-0.90399590		
H	0.03659667	-3.68227596	-0.90399590		н	0.03659667	-3.68227596	0.90399590		
н	0.03659667	-3.68227596	0.90399590		н	0.03659667	3.68227596	0.90399590		
H	0.03659667	3.68227596	0.90399590		H	0.03659667	3.68227596	-0.90399590		

zmat.xyz

36

Mn	-0.0000000	-0.00000000	0.0000000
0	1.65102385	-1.19953904	0.0000000
0	1.65102385	1.19953904	0.0000000
0	-0.63063499	-1.94089494	0.0000000
0	-0.63063499	1.94089494	0.0000000
0	-2.04077771	-0.00000000	0.0000000
С	1.61908748	2.59903148	0.0000000
С	0.21780309	-3.05433638	0.0000000
С	0.21780309	3.05433638	0.0000000
С	2.97215137	-0.73669880	0.0000000
С	2.97215137	0.73669880	0.0000000
С	-1.97150028	-2.34298859	0.0000000
С	-1.97150028	2.34298859	0.0000000
С	-2.83754166	-1.15098490	0.0000000
С	-2.83754166	1.15098490	0.0000000
С	1.61908748	-2.59903148	0.0000000
Н	2.13478017	3.00053481	-0.90399590
Н	2.13478017	3.00053481	0.90399590
Н	0.03659667	-3.68227596	-0.90399590
Н	0.03659667	-3.68227596	0.90399590
Н	0.03659667	3.68227596	0.90399590
Н	0.03659667	3.68227596	-0.90399590
Н	3.51336154	-1.10308034	-0.90399590
Н	3.51336154	-1.10308034	0.90399590
Н	3.51336154	1.10308034	0.90399590
Н	3.51336154	1.10308034	-0.90399590
Н	-2.19399483	-2.95751284	0.90399590
Н	-2.19399483	-2.95751284	-0.90399590
Н	-2.19399483	2.95751284	-0.90399590
Н	-2.19399483	2.95751284	0.90399590
Н	-3.49074355	-1.17269135	-0.90399590

Н	-3.49074355	-1.17269135	0.90399590
Н	-3.49074355	1.17269135	0.90399590
Н	-3.49074355	1.17269135	-0.90399590
Н	2.13478017	-3.00053481	-0.90399590
Н	2.13478017	-3.00053481	0.90399590

- 7. Open AMSinput (SCM  $\rightarrow$  New Input)
- 8. File → Import Coordinates ..., import the earlier xyz file (with Mn atom on top the coordinate list)
- 9. Define the calculation details in the Main panel:

Task  $\rightarrow$  Single Point Total charge  $\rightarrow$  +2 XC functional  $\rightarrow$  LDA Relativity  $\rightarrow$  Scalar Basis set  $\rightarrow$  DZ Frozen Core  $\rightarrow$  None Numerical Quality  $\rightarrow$  Normal



- 10. In the panel bar select **Details** → **Symmetry** In the Symmetry panel, choose **NOSYM**
- 11. Before we set occupation number and LFDFT, we have to do a preliminary run. To get is quicker, we can set Maximum number of SCF cycles to 0 (go to Details/SCF/).
  File → Save
  File → Run

12. This is a preliminary check for occupation number. The calculation may not converge (or no SCF at all), but the output can be used to set fractional occupation or molecular orbitals. When the calculation is done.

In the panel bar select  $Model \rightarrow Spin$  and Occupation

In **Spin and Occupation**, upload the adf.rkf file from the previous calculation, and revise the occupation number insofar as 138 electrons are restricted to closed shell, and 5 valence electrons are evenly distributed over the 5 molecular orbitals that are identified with large atomic Mn 3d characters:



13. To enable LFDFT calculation:
In the panel bar select Properties → Ligand Field DFT
In the Shell 1 panel, set MO indices → 70 71 72 73 74
In the Shell 1 panel, set n → 3
In the Shell 1 panel, set l → 2
In the Shell 1 panel, set Spin-Orbit scaling factor → 0.0
Set the Degeneracy Threshold to set 10E-06 eV (go to Degeneracy Threshold)

	ADF Main Model Properties	Details MultiLevel Q
	Liga	nd Field DFT 📄 🔞
	Ligar Shell 1 MO indices: n: I: Spin-Orbit type: Spin-Orbit scaling factor: Shell 2 MO indices: n: I: Spin-Orbit type: Spin-Orbit type: Spin-Orbit type: Spin-Orbit type: Spin-Orbit scaling factor: Excitations from:	70 71 72 73 74 3 2 ZORA 0.0 ZORA 2 2 0.0 2 0.0
C'	Excitations from:	0.000001 eV •
D5h	B⊢ield:	0.0 0.0 0.0 Tesla
► С О N H CI X, О ★ ९ Ф		

- 14. Do not forget to set Maximum number of SCF cycles to different than 0 ((go to **Details/SCF/Maximum number of SCF cycles**).
- 15. File  $\rightarrow$  Save
- 16. File  $\rightarrow$  Run

## Results

In the .out file, we can see the MO occupations and orbitals that are involved in the LFDFT calculation, which should look like the following:

List of all MOs, ordered by energy, with the most significant SFO gross populations Each percentage contribution in the table below corres ponds to the indicated SFO. In general, a SFO may be a linear combination of several Fragment Orbitals on the same, or on symmetry-related Fragments. Only the first 'member' of such a combination is specified here. A full definition of all SFOs is given in an earlier part of the output. The numbering of the SFOs in this table does NOT include the Core Orbitals, and starts from one for each symmetry representation, as in the SFO definition list earlier. E(eV) Occ MO % SFO (first member) E(eV) Occ Fragment

-12.366	1.00	70	A	87.12%	1	D:z2	-7.057	1.00	1	Mn
				11.43%	4	S	-5.299	2.00	1	Mn
-11.864	1.00	71	A	87.34%	1	D:yz	-7.057	1.00	1	Mn
				3.55%	1	P:z	-9.267	1.33	5	0
				3.55%	1	P:z	-9.267	1.33	4	0
				1.35%	1	P:z	-9.267	1.33	2	0
				1.35%	1	P:z	-9.267	1.33	3	0
-11.860	1.00	72	A	87.36%	1	D:xz	-7.057	1.00	1	Mn
				3.92%	1	P:z	-9.267	1.33	6	0
				2.56%	1	P:z	-9.267	1.33	3	0
				2.56%	1	P:z	-9.267	1.33	2	0
-10.752	1.00	73	A	84.90%	1	D:x2-y2	-7.057	1.00	1	Mn
				3.21%	1	P:x	-9.267	1.33	6	0
				1.94%	1	P:y	-9.267	1.33	5	0
				1.94%	1	P:y	-9.267	1.33	4	0
				1.44%	2	S	-23.977	2.00	6	0
-10.747	1.00	74	A	84.92%	1	D:xy	-7.057	1.00	1	Mn
				1.85%	1	P:x	-9.267	1.33	2	0
				1.85%	1	P:x	-9.267	1.33	3	0
				1.30%	2	S	-23.977	2.00	2	0
				1.30%	2	S	-23.977	2.00	3	0
				1.05%	1	P:y	-9.267	1.33	2	0
				1.05%	1	P:y	-9.267	1.33	3	0

MO A 70, 71, 72, 73, 74 that are predominant Mn 3d orbitals are occupied with fractional electrons (5/5 = 1.00).

In the .out file, the LFDFT results are listed: (Note that spin-orbit coupling was earlier set to 0)

If a level is degenerate <S2>, <L2>, and <J2> is calculated as the maximum value for one Electron configuration: d05  $\,$ 

level	mul	Energy [eV]	<\$^2>	<l^2></l^2>	<j^2></j^2>
1	6	0.00000005	8.7500	0.0000	8.7500
2	4	1.80851658	3.7500	0.0000	3.7500
3	4	1.81336835	3.7500	0.0000	3.7500
4	4	2.03694672	3.7500	0.0000	3.7523
5	4	2.03708988	3.7500	0.0000	3.7563
6	4	2.16378377	3.7500	0.0000	3.7502
7	4	2.16423099	3.7500	0.0000	3.7502
8	4	2.37622595	3.7500	0.0000	3.7500
9	4	2.37931281	3.7500	0.0000	3.7500
10	4	2.57486331	3.7500	0.0001	3.7585
11	8	2.57493386	3.7500	0.0001	3.7574
12	4	2.90579636	3.7500	0.0000	3.7503
13	4	2.90617549	3.7500	0.0000	3.7507
14	4	2.96384366	3.7500	0.0000	3.7500
15	2	3.10957297	0.7500	0.0002	0.7462
16	2	3.10959841	0.7500	0.0002	0.7641
17	2	3.15873856	0.7500	0.0000	0.7500
18	2	3.16083312	0.7500	0.0000	0.7500
19	2	3.17869524	0.7500	0.0000	0.7500
20	4	3.21611281	3.7500	0.0000	3.7500
21	2	3,27833352	0.7500	0.0000	0.7511

Term	level 1	2	3	4	5	6	7	
	100 0000							
40	100.0000	52 1202	52 2717	80.9677	91 0493	0.0000	0.0000	79.67
40	0.0000	0 0000	0.0000	0.0443	0 0011	39 1655	39 2590	12 69
41	0.0000	20 6059	20 5428	0.0443	0.0011	43 7652	13 8409	2 35
40	0.0000	20.0059	20.5428	0.0485	0.0013	43.7052	43.8409	2.35
21	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
20	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
21	0.0000	27.2640	27 1055	10.0000	10.0000	0.0000	0.0000	0.00 E 20
41	0.0000	2/.2049	2/.1855	10.9390	10.9403	0.4111	0.3053	5.28
20	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
26	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
21	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
25	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
20	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
ZG	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
22	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
	level							
rerm	11	12	13	14	15	16	17	
6S	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
4G	100.0000	38.2395	38.1263	0.0505	0.0000	0.0000	0.0000	0.00
4P	0.0000	0.0452	0.0382	99.8994	0.0000	0.0000	0.0000	0.00
4D	0.0000	57.9863	58.0835	0.0473	0.0000	0.0000	0.0000	0.00
21	0.0000	0.0000	0.0000	0.0000	42.4355	42.4183	62.4114	62.68
2D	0.0000	0.0000	0.0000	0.0000	0.0040	0.0006	3.3182	3.36
2F	0.0000	0.0000	0.0000	0.0000	0.0007	0.0014	2.0379	1.93
4F	0.0000	3.7290	3.7520	0.0028	0.0000	0.0000	0.0000	0.00
2H	0.0000	0.0000	0.0000	0.0000	27.6656	27.6789	2.6569	2.61
2G	0.0000	0.0000	0.0000	0.0000	23.9171	23.9266	6.0725	6.05
2F	0.0000	0.0000	0.0000	0.0000	0.0002	0.0024	5.8905	5.78
25	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.00
2D	0.0000	0.0000	0.0000	0.0000	0.0004	0.0004	0.8475	0.83
2G	0.0000	0.0000	0.0000	0.0000	5.9759	5.9712	13.7343	13.73
	A AAAA	0 0000	0 0000	0 0000	0 0000	0 0002	1 2000	1 20
2P	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	1.3009	1.20

Part 2. Calculation of Mn L2,3-edge XAS of Mn(5-crown ether)2+. Ground state configuration Mn 3d^5, XAS excited state configuration Mn 2p^5 3d^6 (with spin-orbit coupling), and electric-dipole transitions  $3d^5 -> 2p^5 3d^6$ 

- 1. Redo Part 1 by including spin-orbit coupling in LFDFT. This is the calculation for the ground state (go to **Properties/Ligand Field DFT**/ and set **Spin-Orbit scaling factor** to 1.0)
- 2. File  $\rightarrow$  Save
- File → Run Results the LFDFT results are listed:

level	mu1]								
	mar	Energy	[eV]	<\$^2>	<l^2></l^2>	<j^2></j^2>			
1	2	0.000	00002	6.2454	0.0000	6.2500			
2	2	0.000	04781	2.2486	0.0000	2.2503			
3	2	0.0000	07147	4.7470	0.0000	4.7502			
4	2	1.7778	81383	2.2302	3.9503	0.2442			
5	2	1.7968	81127	0.3490	3.8018	2.2398			
6	2	1.8185	53496	0.3440	3.8247	6.1383			
7	2	1.8413	31788	2.2239	4.0115	12.2091			
8	2	2.0236	64534	2.2260	8.9428	2.2454			
9	2	2.033	73952	0.2407	8.9292	6.2406			
10	2	2.0428	85846	0.2575	8.9411	12.2304			
11	2	2.0511	16499	2.2430	8.9749	20.1914			
12	2	2.1144	40386	2.2425	0.9812	0.2592			
13	2	2.1496	66196	0.2571	1.0055	0.2485			
14	2	2.1825	58427	0.2443	1.0106	2.2478			
15	2	2.2140	01406	2.2318	1.0112	6.2476			
16	2	2.3648	84426	2.2420	0.9163	0.3659			
17	2	2.371	77286	0.5360	0.8509	0.6635			
18	2	2.3808	89427	0.4724	0.8915	2.3274			
19	2	2.3908	86735	2.2416	0.9913	6.2141			
20	2	2.5731	14144	2.2381	15.9345	6.2290			
21	2	2.5740	62113	2.2429	0.0248	2.7136			
Spectr	al term	analveie	in perce	ntage (s	11m=100)				
	ar corm	anarysis							
	le	vel							
Term	le	vel 1	2	3	4	5	6		
Term	le	vel 1	2	3	4	5	6	7	
Term 6S	le  99.9	vel 1 080 99.9	2	3	4 0.0002	5	6 6 0.0004	7	0.000
Term 6S 4G	le  99.9 0.0	vel 1 080 99.9 001 0.0	2 129 99 0000 0	3 .9154 .0000	4 0.0002 50.8598	5 0.0004 51.4017	6 0.0004 52.2060	7 0.0000 53.1576	0.0000
Term 6S 4G 4P	1 corm le 99.9 0.0 0.0	vel 1 080 99.9 001 0.0 866 0.0	2 129 99 0000 0 0833 0	3 .9154 .0000 .0817	4 0.0002 50.8598 0.2566	5 0.0004 51.4017 0.2975	6 0.0004 52.2060 0.2002	7 0.0000 53.1576 0.0004	0.0000
Term 6S 4G 4P 4D	99.9 0.0 0.0 0.0	080 99.9 001 0.0 866 0.0	2 129 99 0000 0 0833 0 0036 0	3 .9154 .0000 .0817 .0028	4 0.0002 50.8598 0.2566 21.1478	5 0.0004 51.4017 0.2975 20.8964	6 0.0004 52.2060 0.2002 20.5159	7 0.0000 53.1576 0.0004 20.0700	0.0000 80.568 0.0230 0.066
Term 6S 4G 4P 4D 2I	 99.9 0.0 0.0 0.0 0.0	vel 1 080 99.9 001 0.0 866 0.0 051 0.0 000 0.0	2 129 99 0000 0 0833 0 0036 0 0000 0	3 .9154 .0000 .0817 .0028 .0000	4 0.0002 50.8598 0.2566 21.1478 0.0010	5 0.0004 51.4017 0.2975 20.8964 0.0007	6 0.0004 52.2060 0.2002 20.5159 0.0011	7 0.0000 53.1576 0.0004 20.0700 0.0018	0.0000 80.5683 0.0230 0.0664 0.0012
Term 6S 4G 4P 4D 21 2D	 99.9 0.0 0.0 0.0 0.0 0.0 0.0	vel 1 080 99.9 001 0.0 866 0.0 051 0.0 000 0.0 000 0.0	2 129 99 0000 0 0833 0 0036 0 0000 0	3 .9154 .0000 .0817 .0028 .0000 .0000	4 0.0002 50.8598 0.2566 21.1478 0.0010 0.0093	5 0.0004 51.4017 0.2975 20.8964 0.0007 0.0070	6 0.0004 52.2060 0.2002 20.5159 0.0011 0.0032	7 0.0000 53.1576 0.0004 20.0700 0.0018 0.0000	0.0000 80.568 0.0230 0.066 0.0012 0.016
Term 6S 4G 4P 4D 21 2D 2F	1e 99.9 0.0 0.0 0.0 0.0 0.0 0.0 0.0	vel 1 080 99.9 001 0.0 866 0.0 051 0.0 000 0.0 000 0.0	2 129 99 0000 0 0833 0 0036 0 0000 0 0000 0	3 .9154 .0000 .0817 .0028 .0000 .0000 .0000	4 0.0002 50.8598 0.2566 21.1478 0.0010 0.0093 0.0577	5 0.0004 51.4017 0.2975 20.8964 0.0007 0.0070 0.0252	6 0.0004 52.2060 0.2002 20.5159 0.0011 0.0032 0.0108	7 0.0000 53.1576 0.0004 20.0700 0.0018 0.0000 0.0173	0.0000 80.568 0.0230 0.0664 0.0012 0.016 0.016
Term 6S 4G 4P 4D 2I 2D 2F 4F	1e 99.9 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	vel 1 080 99.9 001 0.0 866 0.0 051 0.0 000 0.0 000 0.0 000 0.0 000 0.0	2 129 99 0000 0 0833 0 0036 0 0000 0 0000 0 0000 0 0000 0	3 .9154 .0000 .0817 .0028 .0000 .0000 .0000 .0000	4 0.0002 50.8598 0.2566 21.1478 0.0010 0.0093 0.0577 27.6071	5 0.0004 51.4017 0.2975 20.8964 0.0007 0.0070 0.0252 27.2925	6 0.0004 52.2060 0.2002 20.5159 0.0011 0.0032 0.0108 26.9848	7 0.0000 53.1576 0.0004 20.0700 0.0018 0.0000 0.0173 26.6917	0.000 80.568 0.023 0.066 0.001 0.016 0.016 0.098 19.212
Term 6S 4G 4P 4D 2I 2D 2F 4F 2H	1e 99.9 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.	vel 1 080 99.9 001 0.0 866 0.0 051 0.0 000 0.0 000 0.0 000 0.0 001 0.0	2 129 99 0000 0 0833 0 0036 0 0000 0 0000 0 0000 0 0001 0 0000 0	3 .9154 .0000 .0817 .0028 .0000 .0000 .0000 .0000 .0001 .0000	4 0.0002 50.8598 0.2566 21.1478 0.0010 0.0093 0.0577 27.6071 0.0128	5 0.0004 51.4017 0.2975 20.8964 0.0007 0.0070 0.0252 27.2925 0.0279	6 0.0004 52.2060 0.2002 20.5159 0.0011 0.0032 0.0108 26.9848 0.0364	7 0.0000 53.1576 0.0004 20.0700 0.0018 0.0000 0.0173 26.6917 0.0353	0.000 80.568 0.023 0.066 0.001 0.016 0.098 19.212 0.003
Term 6S 4G 4D 2I 2D 2F 4F 2H 2H 2G	1e 99.9 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.	vel 1 080 99.9 001 0.0 866 0.0 051 0.0 000 0.0 000 0.0 000 0.0 000 0.0 000 0.0	2 129 99 0000 0 0833 0 0036 0 0000 0 0000 0 0000 0 0001 0 0000 0 0000 0	3 .9154 .0000 .0817 .0028 .0000 .0000 .0000 .0001 .0000 .0000	4 0.0002 50.8598 0.2566 21.1478 0.0010 0.0093 0.0577 27.6071 0.0128 0.0066	5 0.0004 51.4017 0.2975 20.8964 0.0007 0.0070 0.0252 27.2925 0.0279 0.0155	6 0.0004 52.2060 0.2002 20.5159 0.0011 0.0032 0.0108 26.9848 0.0364 0.0203	7 0.0000 53.1576 0.0004 20.0700 0.0018 0.0000 0.0173 26.6917 0.0353 0.0209	0.000 80.568 0.023 0.066 0.001 0.016 0.098 19.212 0.003 0.000
Term 6S 4G 4P 2I 2D 2F 4F 2H 2G 2F	1e 99.9 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.	vel 1 080 99.9 001 0.0 866 0.0 051 0.0 000 0.0 000 0.0 000 0.0 000 0.0 000 0.0 000 0.0	2 129 99 0000 0 0833 0 0036 0 0000 0 0000 0 0000 0 0001 0 0000 0 0000 0 0000 0 0000 0	3 .9154 .0000 .0817 .0028 .0000 .0000 .0000 .0000 .0000 .0000 .0000	4 0.0002 50.8598 0.2566 21.1478 0.0010 0.0093 0.0577 27.6071 0.0128 0.0066 0.0241	5 0.0004 51.4017 0.2975 20.8964 0.0007 0.0070 0.0252 27.2925 0.0279 0.0155 0.0185	6 0.0004 52.2060 0.2002 20.5159 0.0011 0.0032 0.0108 26.9848 0.0364 0.0203 0.0106	7 0.0000 53.1576 0.0004 20.0700 0.0018 0.0000 0.0173 26.6917 0.0353 0.0209 0.0036	0.0000 80.568 0.0230 0.066 0.0012 0.016 0.098 19.212 0.003 0.000 0.003
Term 6S 4G 4P 4D 2I 2D 2F 4F 2H 2G 2F 2S	le 99.9 0.0 0.0 0.0 0.0 0.0 0.0 0.	vel 1 080 99.9 001 0.0 866 0.0 000 0.0 000 0.0 000 0.0 000 0.0 000 0.0 000 0.0 000 0.0 000 0.0	2 129 99 0000 0 0833 0 0036 0 0000 0 0000 0 0000 0 0000 0 0000 0 0000 0 0000 0 0000 0	3 .9154 .0000 .0817 .0028 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000	4 0.0002 50.8598 0.2566 21.1478 0.0010 0.0093 0.0577 27.6071 0.0128 0.0066 0.0241 0.0001	5 0.0004 51.4017 0.2975 20.8964 0.0007 0.0070 0.0252 27.2925 0.0279 0.0155 0.0185 0.0000	6 0.0004 52.2060 0.2002 20.5159 0.0011 0.0032 0.0108 26.9848 0.0364 0.0203 0.0106 0.0000	7 0.0000 53.1576 0.0004 20.0700 0.0018 0.0000 0.0173 26.6917 0.0353 0.0209 0.0036 0.0000	0.0000 80.568 0.023 0.066 0.0016 0.016 0.098 19.212 0.003 0.000 0.000 0.000
Term 6S 4G 4P 4D 2I 2F 4F 2H 2G 2F 2S 2D	le 99.9 0.0 0.0 0.0 0.0 0.0 0.0 0.	0         0	2 129 99 0000 0 0833 0 0036 0 0000 0 000	3 .9154 .0000 .0817 .0028 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000	4 0.0002 50.8598 0.2566 21.1478 0.0010 0.0093 0.0577 27.6071 0.0128 0.0066 0.0241 0.0001 0.0079	5 0.0004 51.4017 0.2975 20.8964 0.0007 0.0070 0.0252 27.2925 0.0279 0.0155 0.0185 0.0000 0.0118	6 0.0004 52.2060 0.2002 20.5159 0.0011 0.0032 0.0108 26.9848 0.0364 0.0203 0.0106 0.0000 0.0081	7 0.0000 53.1576 0.0004 20.0700 0.0018 0.0000 0.0173 26.6917 0.0353 0.0209 0.0036 0.0000 0.0000	0.0000 80.568 0.023 0.066 0.0012 0.016 0.098 19.212 0.003 0.000 0.000 0.000 0.000
Term 6S 4G 4P 4D 2I 2F 2F 2F 2G 2F 2S 2D 2G	le 99.9 0.0 0.0 0.0 0.0 0.0 0.0 0.	unifysis           1           080         99.9           001         0.0           866         0.0           051         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0	2 129 99 0000 0 0833 0 0036 0 0000 0 000	3 .9154 .0000 .0817 .0028 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000	4 0.0002 50.8598 0.2566 21.1478 0.0010 0.0093 0.0577 27.6071 0.0128 0.0066 0.0241 0.0001 0.0079 0.0034	5 0.0004 51.4017 0.2975 20.8964 0.0007 0.0070 0.0252 27.2925 0.0279 0.0155 0.0185 0.0000 0.0118 0.0024	6 0.0004 52.2060 0.2002 20.5159 0.0011 0.0032 0.0108 26.9848 0.0364 0.0203 0.0106 0.0000 0.0081 0.0016	7 0.0000 53.1576 0.0004 20.0700 0.0018 0.0000 0.0173 26.6917 0.0353 0.0209 0.0036 0.0000 0.0000 0.0000	0.0000 80.568 0.023 0.0664 0.0012 0.0098 19.2122 0.003 0.0005 0.0005 0.0005 0.0005 0.0005 0.0005 0.0005 0.0005
Term 6S 4G 4P 4D 2I 2D 2F 4F 2G 2F 2S 2D 2G 2G 2C 2G	le 99.9 0.0 0.0 0.0 0.0 0.0 0.0 0.	unifysis           1           080         99.9           001         0.0           866         0.0           051         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0           000         0.0	2 129 99 0000 0 0833 0 0036 0 0000 0 000	3 .9154 .0000 .0817 .0028 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000	4 0.0002 50.8598 0.2566 21.1478 0.0010 0.0093 0.0577 27.6071 0.0128 0.0066 0.0241 0.0001 0.0079 0.0034 0.0017	5 0.0004 51.4017 0.2975 20.8964 0.0007 0.0070 0.0252 27.2925 0.0279 0.0155 0.0185 0.0000 0.0118 0.0024 0.0006	6 0.0004 52.2060 0.2002 20.5159 0.0011 0.0032 0.0108 26.9848 0.0364 0.0203 0.0106 0.0000 0.0081 0.0016 0.0000	7 0.0000 53.1576 0.0004 20.0700 0.0018 0.0000 0.0173 26.6917 0.0353 0.0209 0.0036 0.0000 0.0000 0.0000 0.0015 0.0000	0.0000 80.568 0.023 0.0664 0.0012 0.0012 0.008 19.2124 0.003 0.0000 0.0030 0.0030 0.0000 0.0000 0.0000 0.0000

If a level is degenerate <S2>, <L2>, and <J2> is calculated as the maximum value for one Electron configuration: d05  $\,$ 

4. Run the calculation for the X-ray excited states (two open-shell configuration 2p^5 3d^6)

First, we set the occupation number of the molecular orbitals. For that, we go to Model

## $\rightarrow$ Spin and Occupation

In **Spin and Occupation**, upload the adf.rkf file from the previous calculation, and revise the occupation number as follows:

MO A 1 and 2 are closed shell (they correspond to Mn 1s and 2s)

MO A 3, 4 and 5 are occupied with 5/3 electrons (they correspond to Mn 2p)

MO A 6, ... 69 are closed shell

MO A 70, 71, 72, 73, 74 are occupied with 6/5 electrons (they correspond to Mn 3d)



To enable LFDFT calculation:

In the panel bar select **Properties**  $\rightarrow$  Ligand Field DFT

In the Shell 1panel, set MO indices  $\rightarrow 3\ 4\ 5$ In the Shell 1 panel, set  $n \rightarrow 2$ In the Shell 1 panel, set  $l \rightarrow 1$ In the Shell 1 panel, set Spin-Orbit scaling factor  $\rightarrow 1.0$  In the Shell 2 panel, set MO indices  $\rightarrow$  70 71 72 73 74 In the Shell 2 panel, set  $n \rightarrow 3$ In the Shell 2 panel, set  $l \rightarrow 2$ In the Shell 2 panel, set Spin-Orbit scaling factor  $\rightarrow 1.0$ 

In the panel Excitations from, upload adf.rkf that was generated in point 3.

- 5. File  $\rightarrow$  Save



------adf\_ES

Part 3. Calculation of Mn L2,3-edge XMCD of Mn(5-crown ether)2+. Ground state configuration Mn 3d^5, XAS excited state configuration Mn 2p^5 3d^6 (with spin-orbit coupling and magnetic field), and electric-dipole transitions 3d^5 -> 2p^5 3d^6

- Redo Part 2 by including Magnetic Field in LFDFT for both the ground and XAS excited state configurations (go to Properties/Ligand Field DFT/ and set Bfield to 0.0 0.0 1.0)
- 2. File  $\rightarrow$  Save
- 3. File  $\rightarrow$  Run

## Results

For the ground configuration, the output looks as follows (No degeneracy because of the Zeeman interaction).

If a level is degenerate <S2>, <L2>, and <J2> is calculated as the maximum value Electron configuration: d05  $\,$ 

1	level	mul	Energy	[eV]	<s^2></s^2>	<l^2></l^2>	<j^2></j^2>
	1 2	1 1	0.0000	00000	6.2454 2.2483	0.0000	6.2500 2.2500
	3 4	1	0.0003	30320 1909	0.2498 0.2498	0.0000	0.2500
	5 6	1 1	0.0005	51132 57938	2.2483 6.2454	0.0000	2.2500 6.2500
	7 8	1 1	1.7780	04544 16151	2.2302 2.2302	3.9502 3.9505	0.2441 0.2442
	9 10	1	1.7970	4598	0.2496	3.8026	2.1038
	11	1	1.8186	5420	0.2446	3.8172	5.9943
	13	1	1.8413	81876	2.2239	4.0113	12.2088
	15	2	2.0239	3523	2.2259	8.9429	2.2454
	16	1	2.0339	1303 L4537	0.2402	8.9293	6.2404
	18 19	1 1	2.0429	91626 37985	0.2570	8.9410 8.9411	12.2299
	20 21	1	2.0511	L0761 30164	2.2430	8.9752 8.9747	20.1918 20.1910
	22 23	1 1	2.1145	57749 30959	2.2380 2.2380	0.9813 0.9811	0.2554

For the XAS excited configuration, open AMSspectra, go to Spectra/Ligand Field DFT/LF MCD

