

(continued from previous page)

```

OrbWin 6,8,0,2000
DoPNO true
TCutPNO 1e-11
XASelems 0
rel
  DoSOC true
end
DoHigherMult true
DoLowerMult true
DoRI true
Decomposefosc true
end

*xyz -2 5
Fe    -0.009575    0.000087    0.011550
Cl    -1.774578   -1.558533   -0.219791
Cl    -0.681385    1.874633    1.289404
Cl     0.666770    0.847828   -2.091305
Cl     1.756927   -1.164015    1.071196
end

```

After all CI calculations are finished, the program gives a list of all calculated roots with their excitation energies and their multiplicities. It is this number that will be referred to as label I in the decomposition of spin-orbit coupled states in the basis $|\Psi_I^{SM}\rangle$. It is very important to note, that when states with different multiplicities are calculated this number might deviate from the number that appears in the respective CI part of the output. If one gets confused about the numbering of the states, the state energies might act as a guideline through the output of the program.

```

-----
Excitation energies
-----

```

ROOT	Mult	Excitation energy [Eh]	[cm ⁻¹]	[eV]
0	5	0.00000000	0.00	0.000
1	5	26.41778649	5798033.94	718.865
2	5	26.42452401	5799512.66	719.048
3	5	26.42621555	5799883.91	719.094
4	5	26.44615744	5804260.65	719.637
5	5	26.45323131	5805813.18	719.829
6	5	26.47192609	5809916.21	720.338
7	5	26.47357807	5810278.78	720.383
8	5	26.48177016	5812076.74	720.606
9	5	26.49063895	5814023.21	720.847
10	5	26.50722706	5817663.88	721.298
11	5	26.50759779	5817745.25	721.308
12	5	26.50982238	5818233.49	721.369
13	3	26.55037043	5827132.76	722.472
14	3	26.58407940	5834531.02	723.390
15	3	26.58587963	5834926.12	723.439
16	3	26.58857702	5835518.13	723.512
17	3	26.59674863	5837311.59	723.734
18	3	26.59825865	5837643.00	723.775
19	3	26.61152227	5840554.03	724.136
20	3	26.61806435	5841989.85	724.314
21	3	26.62812795	5844198.56	724.588
22	3	26.63079807	5844784.58	724.661
23	3	26.63345218	5845367.09	724.733
24	3	26.64337021	5847543.85	725.003
25	3	26.65680719	5850492.92	725.369

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26	3	26.66486245	5852260.85	725.588
27	3	26.66512507	5852318.49	725.595
28	3	26.66741755	5852821.63	725.657
29	3	26.68096811	5855795.63	726.026
30	3	26.68291870	5856223.74	726.079
31	3	26.68410859	5856484.89	726.112
32	3	26.68502036	5856685.00	726.136
33	3	26.68625712	5856956.44	726.170
34	3	26.68835097	5857415.98	726.227
35	3	26.69951161	5859865.46	726.531
36	3	26.70277202	5860581.04	726.619
37	3	26.71055426	5862289.04	726.831
38	3	26.71604333	5863493.75	726.980
39	3	26.71631714	5863553.85	726.988
40	3	26.71801283	5863926.01	727.034
41	3	26.71869535	5864075.80	727.053
42	3	26.71953590	5864260.28	727.076
43	3	26.72200411	5864801.99	727.143
44	3	26.72811146	5866142.40	727.309
45	3	26.73591005	5867853.99	727.521
46	3	26.73675062	5868038.48	727.544
47	3	26.75216877	5871422.37	727.964
48	3	26.78204828	5877980.17	728.777
49	7	27.21891306	5973860.90	740.664
50	7	27.21926225	5973937.54	740.674
51	7	27.21931555	5973949.24	740.675
52	5	27.26974929	5985018.16	742.048
53	5	27.26978849	5985026.77	742.049
54	5	27.27023065	5985123.81	742.061
55	5	27.29466376	5990486.26	742.726
56	5	27.29677691	5990950.04	742.783
57	5	27.31333680	5994584.52	743.234
58	7	27.31641173	5995259.39	743.317
59	5	27.31967798	5995976.24	743.406
60	7	27.32002169	5996051.68	743.416
...				

Without SOC the spin exclusion rule applies which means that only excited states with a total spin equal to the ground state spin ($S' = S$) give rise to non-vanishing intensities. Hence, only these transitions are listed in the spectra before SOC.

----- ROCIS-EXCITATION SPECTRA -----

Center of mass = (-0.0160, 0.0000, 0.0229)

Reading integrals

...

Reading the Dipole integrals

... done

Reading the Linear Momentum integrals

... done

Reading the Angular momentum integrals

... done

Reading the Quadrupole integrals

... done

Reading the Higher Moment integrals

... done

Using One-Photon Spectroscopy Tool

↪-----

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS

↪-----

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Transition		Energy	Energy	Wavelength	fosc(D2)	D2	DX	
↪ DY	DZ	(eV)	(cm-1)	(nm)		(au**2)	(au)	↪
↪ (au)	(au)							↪

0-5A ->	1-5A	718.864517	5798034.0	1.7	0.007967331	0.00045	0.00001	↪
↪ -0.02035	0.00619							
0-5A ->	2-5A	719.047854	5799512.7	1.7	0.000032204	0.00000	0.00123	↪
↪ -0.00019	-0.00052							
0-5A ->	3-5A	719.093883	5799883.9	1.7	0.000038607	0.00000	-0.00060	↪
↪ -0.00039	-0.00130							
0-5A ->	4-5A	719.636530	5804260.7	1.7	0.000000074	0.00000	-0.00004	↪
↪ -0.00001	-0.00005							
0-5A ->	5-5A	719.829019	5805813.2	1.7	0.000257559	0.00001	-0.00007	↪
↪ -0.00364	0.00116							
0-5A ->	6-5A	720.337730	5809916.2	1.7	0.045609938	0.00258	-0.04638	↪
↪ 0.00619	0.01987							
0-5A ->	7-5A	720.382683	5810278.8	1.7	0.043374431	0.00246	0.02031	↪
↪ 0.01315	0.04327							
0-5A ->	8-5A	720.605601	5812076.7	1.7	0.000000543	0.00000	0.00005	↪
↪ 0.00005	0.00016							
0-5A ->	9-5A	720.846933	5814023.2	1.7	0.180244898	0.01021	0.00031	↪
↪ 0.09663	-0.02948							
0-5A ->	10-5A	721.298318	5817663.9	1.7	0.084488140	0.00478	-0.02823	↪
↪ -0.01833	-0.06040							
0-5A ->	11-5A	721.308407	5817745.3	1.7	0.085964316	0.00486	0.06366	↪
↪ -0.00850	-0.02719							
0-5A ->	12-5A	721.368941	5818233.5	1.7	0.000000007	0.00000	-0.00000	↪
↪ 0.00002	0.00001							
0-5A ->	13-5A	742.047603	5985018.2	1.7	0.002287503	0.00013	0.00507	↪
↪ 0.00276	0.00962							
0-5A ->	14-5A	742.048670	5985026.8	1.7	0.002278095	0.00013	0.00999	↪
↪ -0.00164	-0.00477							
0-5A ->	15-5A	742.060702	5985123.8	1.7	0.001342355	0.00007	0.00019	↪
↪ 0.00823	-0.00246							
0-5A ->	16-5A	742.725560	5990486.3	1.7	0.000418059	0.00002	0.00197	↪
↪ 0.00126	0.00419							
0-5A ->	17-5A	742.783062	5990950.1	1.7	0.000464555	0.00003	0.00461	↪
↪ -0.00063	-0.00197							
0-5A ->	18-5A	743.233680	5994584.5	1.7	0.000000003	0.00000	-0.00001	↪
↪ -0.00000	-0.00001							
0-5A ->	19-5A	743.406232	5995976.3	1.7	0.000000000	0.00000	-0.00000	↪
↪ -0.00000	-0.00000							
0-5A ->	20-5A	743.562910	5997239.9	1.7	0.000577479	0.00003	0.00001	↪
↪ 0.00538	-0.00165							
0-5A ->	21-5A	743.597306	5997517.4	1.7	0.000009265	0.00000	-0.00029	↪
↪ -0.00017	-0.00063							
0-5A ->	22-5A	743.658216	5998008.6	1.7	0.000010720	0.00000	-0.00070	↪
↪ 0.00011	0.00029							
0-5A ->	23-5A	744.043391	6001115.3	1.7	0.000081920	0.00000	-0.00088	↪
↪ -0.00059	-0.00184							
0-5A ->	24-5A	744.092953	6001515.0	1.7	0.000301862	0.00002	-0.00017	↪
↪ -0.00389	0.00119							
...								

After calculation of SOC in the basis of all calculated ROCIS roots, the program prints out the composition of the spin-orbit coupled states (if PrintLevel >2) and the corresponding absorption spectrum.

Eigenvectors of SOC calculation:
the threshold for printing is: 0.010000

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	weight	real	image	:	Root	Block	Spin	Ms
State 0:	0.00	cm** ⁻¹	0.00000	eV				
	0.135363	-0.028407	0.366819	:	0	0	2	2
	0.181749	0.224125	0.362653	:	0	0	2	1
	0.367330	-0.135925	-0.590639	:	0	0	2	0
	0.180828	0.039792	-0.423372	:	0	0	2	-1
	0.134728	0.185875	0.316510	:	0	0	2	-2
State 1:	0.00	cm** ⁻¹	0.00000	eV				
	0.078367	-0.271364	0.068762	:	0	0	2	2
	0.306783	0.460606	0.307612	:	0	0	2	1
	0.228162	0.440545	0.184613	:	0	0	2	0
	0.307656	-0.543907	-0.108722	:	0	0	2	-1
	0.079031	-0.142362	-0.242414	:	0	0	2	-2
State 2:	0.02	cm** ⁻¹	0.00000	eV				
	0.416636	0.252581	0.594003	:	0	0	2	2
	0.072004	-0.082420	0.255363	:	0	0	2	1
	0.022669	-0.134504	0.067662	:	0	0	2	0
	0.071994	0.254211	0.085850	:	0	0	2	-1
	0.416695	-0.326890	-0.556631	:	0	0	2	-2
State 3:	0.02	cm** ⁻¹	0.00000	eV				
	0.080023	-0.256741	0.118772	:	0	0	2	2
	0.319001	0.556244	0.097947	:	0	0	2	1
	0.201858	-0.134225	0.428768	:	0	0	2	0
	0.319074	0.512787	0.236903	:	0	0	2	-1
	0.080042	0.143270	0.243959	:	0	0	2	-2
State 4:	0.03	cm** ⁻¹	0.00000	eV				
	0.289609	-0.315623	-0.435879	:	0	0	2	2
	0.120461	0.303600	-0.168190	:	0	0	2	1
	0.179979	-0.232115	-0.355108	:	0	0	2	0
	0.120448	0.275975	-0.210441	:	0	0	2	-1
	0.289502	-0.272469	-0.463963	:	0	0	2	-2
State 5:	5767447.63	cm** ⁻¹	715.07230	eV				
	0.191190	-0.086278	0.428656	:	1	0	2	2
	0.061035	-0.247045	-0.001820	:	1	0	2	1
	0.055460	-0.038920	0.232262	:	1	0	2	0
	0.061035	-0.234143	-0.078813	:	1	0	2	-1
	0.191190	-0.058171	0.433366	:	1	0	2	-2
	0.109587	-0.316206	-0.097982	:	2	0	2	2
	0.026192	-0.108605	-0.119987	:	2	0	2	1
	0.010968	0.017308	-0.103287	:	2	0	2	0
	0.026192	-0.141786	0.078029	:	2	0	2	-1
	0.109587	0.330874	0.010450	:	2	0	2	-2
	0.015452	0.114128	-0.049265	:	3	0	2	2
	0.041882	-0.204634	-0.002607	:	3	0	2	1
	0.027697	0.027504	-0.164135	:	3	0	2	0
	0.041882	-0.194305	-0.064244	:	3	0	2	-1
	0.015452	-0.091834	-0.083778	:	3	0	2	-2
State 6:	5767588.34	cm** ⁻¹	715.08974	eV				
	0.198585	-0.131642	0.425741	:	1	0	2	2
	0.047453	-0.161434	0.146261	:	1	0	2	1
	0.019867	-0.139025	-0.023213	:	1	0	2	0
	0.047453	0.105160	0.190773	:	1	0	2	-1
	0.198585	0.013812	-0.445415	:	1	0	2	-2
	0.160559	-0.388214	-0.099243	:	2	0	2	2
	0.044707	-0.072788	-0.198517	:	2	0	2	1

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0.014352	-0.118163	-0.019729	:	2	0	2	0
0.044707	0.133333	-0.164102	:	2	0	2	-1
0.160559	-0.399398	-0.032262	:	2	0	2	-2
0.012669	-0.111020	-0.018537	:	3	0	2	0
...							

Energy levels:		cm-1	eV	Boltzmann populations for T = 300.00 K			
0 :		0.000	0.0000	2.00e-01			
1 :		0.000	0.0000	2.00e-01			
2 :		0.018	0.0000	2.00e-01			
3 :		0.021	0.0000	2.00e-01			
4 :		0.026	0.0000	2.00e-01			

SOC CORRECTED ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS							

Transition	Energy		Energy	Wavelength	fosc(D2)	D2	DX
DY	DZ						
(au)	(au)	(eV)	(cm-1)	(nm)	(*population)	(au**2)	(au)

0-5.0A -> 1-5.0A	0.000000	0.000000	0.0	0.0	0.0000000000	0.000000	0.
000000 0.000000	0.000000	0.000000					
2-5.0A -> 3-5.0A	0.000000	0.000000	0.0	2927278012.6	0.0000000000	0.000000	
0.000000 0.000000	0.000000	0.000000					
3-5.0A -> 4-5.0A	0.000001	0.000001	0.0	2013441147.3	0.0000000000	0.000000	
0.000000 0.000000	0.000000	0.000000					
2-5.0A -> 4-5.0A	0.000001	0.000001	0.0	1192923906.3	0.0000000000	0.000000	
0.000000 0.000000	0.000000	0.000000					
1-5.0A -> 2-5.0A	0.000002	0.000002	0.0	559585326.1	0.0000000000	0.000000	
0.000000 0.000000	0.000000	0.000000					
0-5.0A -> 2-5.0A	0.000002	0.000002	0.0	554991701.4	0.0000000000	0.000000	
0.000000 0.000000	0.000000	0.000000					
1-5.0A -> 3-5.0A	0.000003	0.000003	0.0	469780906.9	0.0000000000	0.000000	
0.000000 0.000000	0.000000	0.000000					
0-5.0A -> 3-5.0A	0.000003	0.000003	0.0	466539107.5	0.0000000000	0.000000	
0.000000 0.000000	0.000000	0.000000					
1-5.0A -> 4-5.0A	0.000003	0.000003	0.0	380906816.8	0.0000000000	0.000000	
0.000000 0.000000	0.000000	0.000000					
0-5.0A -> 4-5.0A	0.000003	0.000003	0.0	378772788.3	0.0000000000	0.000000	
0.000000 0.000000	0.000000	0.000000					
4-5.0A -> 5-5.0A	715.072294	5767447.6	1.7	0.000853852	0.00024	0.	
000000 0.01494	0.00454						
3-5.0A -> 5-5.0A	715.072294	5767447.6	1.7	0.000001143	0.000000	0.	
000021 0.00018	0.00050						
2-5.0A -> 5-5.0A	715.072295	5767447.6	1.7	0.000001245	0.000000	0.	
000024 0.00053	0.00012						
1-5.0A -> 5-5.0A	715.072297	5767447.6	1.7	0.000000330	0.000000	0.	
000000 0.00029	0.00010						
0-5.0A -> 5-5.0A	715.072297	5767447.6	1.7	0.000024144	0.000001	0.	
000000 0.00251	0.00076						
4-5.0A -> 6-5.0A	715.089740	5767588.3	1.7	0.000002661	0.000000	0.	
000067 0.00036	0.00042						
3-5.0A -> 6-5.0A	715.089741	5767588.3	1.7	0.000008083	0.000000	0.	
000000 0.00145	0.00045						
2-5.0A -> 6-5.0A	715.089742	5767588.3	1.7	0.000775076	0.00022	0.	
000001 0.01423	0.00432						

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1-5.0A	->	6-5.0A	715.089744	5767588.4	1.7	0.000000497	0.00000	0.
→00002		0.00015	0.00035					
0-5.0A	->	6-5.0A	715.089744	5767588.4	1.7	0.000001537	0.00000	0.
→00056		0.00035	0.00007					
4-5.0A	->	7-5.0A	715.115140	5767793.2	1.7	0.000001500	0.00000	0.
→00027		0.00020	0.00056					
3-5.0A	->	7-5.0A	715.115141	5767793.2	1.7	0.000834113	0.00024	0.
→00001		0.01476	0.00449					
2-5.0A	->	7-5.0A	715.115141	5767793.2	1.7	0.000008694	0.00000	0.
→00002		0.00150	0.00050					
1-5.0A	->	7-5.0A	715.115143	5767793.2	1.7	0.000000562	0.00000	0.
→00026		0.00025	0.00018					
0-5.0A	->	7-5.0A	715.115143	5767793.2	1.7	0.000003341	0.00000	0.
→00036		0.00031	0.00085					
4-5.0A	->	8-5.0A	715.184940	5768356.2	1.7	0.000000146	0.00000	0.
→00004		0.00020	0.00001					
3-5.0A	->	8-5.0A	715.184940	5768356.2	1.7	0.000019943	0.00001	0.
→00206		0.00012	0.00120					
2-5.0A	->	8-5.0A	715.184941	5768356.2	1.7	0.000019954	0.00001	0.
→00119		0.00064	0.00197					
1-5.0A	->	8-5.0A	715.184943	5768356.2	1.7	0.000507851	0.00014	0.
→00004		0.01152	0.00348					
0-5.0A	->	8-5.0A	715.184943	5768356.2	1.7	0.000022305	0.00001	0.
→00003		0.00240	0.00077					
4-5.0A	->	9-5.0A	715.206052	5768526.4	1.7	0.000049980	0.00001	0.
→00006		0.00360	0.00113					
3-5.0A	->	9-5.0A	715.206053	5768526.4	1.7	0.000007590	0.00000	0.
→00077		0.00040	0.00119					
...								

The obtained spectra can be prepared for plotting with the use of `orca_mapspc`. Check section [orca_mapspc](#) for details.

5.7.4 Resonant Inelastic Scattering Spectroscopy

General

Starting from ORCA version 4.0 ROCIS module can be used to calculate RIXS spectra

The present implementation is directly based on the Kramers Heisener Dirac (KDH) expression formula for near resonant and resonant conditions

$$|\alpha_{\rho\lambda}(E_{ex}, E_{sc})|_{Total}^2 = \sum_F \left| \sum_V \frac{\langle F | m_\rho | V \rangle \langle V | m_\lambda | I \rangle}{E_{VI} - E_{ex} - i\frac{1}{2}\Gamma_V} \right|^2 \left\{ \frac{\Gamma_F}{(E_{FV} - E_{ex} + E_{sc})^2 + \frac{1}{4}\Gamma_F^2} \right\}$$

$$|\alpha_{\rho\lambda}(E_{ex}, E_{sc}, V)|_{resonant}^2 = \sum_F |\langle F | m_\rho | V \rangle|^2 |\langle V | m_\lambda | I \rangle|^2 f(E_{VI}, E_{FV}, E_{ex}, E_{sc}, \Gamma_V, \Gamma_F)$$

$$|\alpha_{\rho\lambda}(E_{VI}, E_{sc})|_{Direct}^2 = \sum_V |\alpha_{\rho\lambda}(E_{VI}, E_{sc}, V)|_{resonant}^2$$

The resonance scattering cross section for total and direct cases, averaged over all orientations of the molecule and integrated over all directions and polarizations of scattered radiation is given in equations:

$$\sigma_{RXES}^{Total}(E_{ex}, E_{sc}) = \frac{8\pi E_{sc}^3 E_{ex}}{9c^4} \sum_{\rho, \lambda=x,y,z} |\alpha_{\rho\lambda}(E_{ex}, E_{sc})|_{Total}^2$$

$$\sigma_{RXES}^{Direct}(E_{ex}, E_{sc}) = \frac{8\pi E_{sc}^3 E_{ex}}{9c^4} \sum_{\rho, \lambda=x,y,z} |\alpha_{\rho\lambda}(E_{ex}, E_{sc})|_{Direct}^2$$

Interference effects can be then derived in a straightforward way from equation:

$$\sigma_{RXES}^{interference}(E_{ex}, E_{sc}) = \sigma_{RXES}^{Total}(E_{ex}, E_{sc}) - \sigma_{RXES}^{Direct}(E_{ex}, E_{sc})$$

In order to access RIXS spectroscopy in the ROCIS module one needs in addition to specify a 2nd donor space. This is specified by defining an OrbWin array with 6 elements: The first four elements define the ranges of the two donor spaces while the last two elements the respective acceptor space range.

```
OrbWin = 0,0,2,4,45,60
```

An important difference with respect to the conventional ROCIS or DFT/ROCIS calculations is the fact that two donor spaces of very different energy ranges are involved (e.g. K-edge, L-edge) which requires to restrict somewhat the acceptor space and saturate it with as many states as possible.

The main calling commands in order to perform a RIXS calculation within both ROCIS and CASSCF blocks are the following:

- RIXS true. Similar to absorption spectroscopy, this requests the RIXS calculation to be performed based on the calculated non-relativistic ground state multiplicity States
- RIXSSOC true. By turning-on this flag the RIXS is calculated by taking in account the relativistically corrected Ms States.
- Elastic true. This flag indicates whether the resonant condition in which the initial and Final states coincide should be taken into account. Note that the intensity of this spectral feature might be overestimated as presently the non resonant terms are not treated

The respective ROCIS input reads then as follows:

```
!B3LYP def2-TZVP SlowConv

%Basis
  AuxC "def2/J"
end

%ROCIS
  NRoots 200
  PrintLevel 3
  MaxCore 4000
  DoRI true
  DoHigherMult true
  SOC true
  RIXS true # Request RIXS calculation (NoSOC)
  RIXSSOC true # Request RIXS calculation (with SOC)
  Elastic true # Request RIXS calculation (Elastic)
  DoDFTCIS true
  DFTCIS_c = 0.18,0.20,0.40
  OrbWin = 2,4,25,33,0,100
end
* xyzfile 2 2 test.xyz
```

When running the calculation one can monitor if the requested NRoots were sufficient enough to select the states dominated by both the donor orbital spaces

ROOT	Mult	Excitation energy[Eh]	[cm-1]	[eV]
0	2	0.00000000	0.00	0.000
1	2	0.06611737	14511.08	1.799
2	2	0.07728471	16962.03	2.103
3	2	0.07732428	16970.72	2.104
...				
84	2	33.75471831	7408304.35	918.513

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85	2	33.77073325	7411819.22	918.948
86	2	33.77076955	7411827.19	918.949
87	4	34.06882971	7477243.83	927.060
88	2	34.07021441	7477547.74	927.098
...				

If that is not the case the respective RIXS calculations will not be performed and a Warning Message will be generated:

```
Making the RIXS files ...
WARNING!: Flag for RIXS property calculation was identified but
there is zero number of Intermediate and/or Final states:
No Cross-Section properties will be evaluated ...Skipping this part
TIP: Increase the number of NRoots and/or decrease or increase
the acceptor orbital space
...Done
```

A successful run on the other hand will generate the following messages for RIXS and RIXSSOC calculations.

```
-----
ROCIS RIXS SPECTRUM
-----
```

```
Making the RIXS data files for Inelastic and Elastic Scattering
Ground State:          1
Intermediate States:    21
Final States:           59
The RIXS cross section will be generated from:
60 Ground-Final State Pairs and 21 Intermediate States/Pair
Calculating Intensities...
10% done
20% done
30% done
40% done
50% done
60% done
70% done
80% done
90% done
100% done
Storing the files...All Done
-----
```

```
-----
ROCIS RIXSSOC SPECTRUM
-----
```

```
Making the RIXS-SOC data files for Inelastic and Elastic Scattering
Ms States:              2
Intermediate States:     78
Final States:            214
The RIXS cross section will be generated from:
432 Ground-Final State Pairs and 78 Intermediate States/Pair

Calculating Intensities...
10% done
20% done
30% done
40% done
50% done
60% done
70% done
```

(continues on next page)

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```
80% done
90% done
100% done
```

```
Storing the files...All Done
-----
```

In both cases the number of involved Initial, Final and Intermediate states is specified explicitly.

For example in the case of RIXSSOC 2 Ms Ground states, 78 Intermediate states and 214 Final states are involved. Then the RIXS cross section for elastic and inelastic scattering will be generated by 432 ($2 \times (2+214)$) Ground-Final State-Pairs and 78 Intermediate States per Ground-Final state pair.

Processing the spectra with `orca_mapspc`

By calling `orca_mapspc` with the following keywords:

```
orca_mapspc test.el_inel.rocis.rixssoc RIXS -x0871 -x1876 -x2-1 -x34 -w0.4 -g0.4
-l -n125 -m125 -dx20 -eaxis1
```

The program will process the `test.el_inel.rocis.rixssoc` file with the following parameters:

Energy range along x : 871-876 eV

Energy range along y: -1-34 eV

-l indicates Lorentzian broadening

Width along x (gamma): 0.4 eV

Width along y (gamma): 0.4 eV

Points along x: 125

Points along y:125

Shift to be applied along Incident energy/Emission axis: 20 eV

The y axis will be Energy Transfer axis. If -eaxis2 is the y axis will be then Emission Energy axis

All this information is printed during the data processing:

```
Mode is RIXS
Using Lorentzian shape
Cannot read the paras.inp file ...
taking the line width parameter from the command line
Cannot read the udex.inp file ...
taking the excitation energy ranges from the command line
Cannot read the udem.inp file ...
taking the emission energy ranges from the command line
Cannot read the gfsp.inp file ...
No Ground-Final State Pairs will be evaluated
-----
PLOTTING RIXS SPECTRA
-----
Input File : test.el_inel.rocis.rixssoc
Incident Energy Excitation axis : 871.000 ... 876.000 eV 125 points
Energy transfer axis : -1.000 ... 4.000 eV 125 points
Incident Energy Shift : 20.000 eV
Lorentzian Linewidth along Incident Axis : 0.400 eV
Lorentzian Linewidth along Energy Transfer/Emission Axis : 0.400 eV
y axis : 1 -> Energy transfer
Number of user defined cuts at constant Excitation Energy axis: 0
Number of user defined cuts at constant Emission/Energy Transfer Energy axis : 0
```

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```
Making checks...Done

Processing data...
10% done
20% done
...
100% done

RIXS-plotting done
Incident Energy range:      845.800 ...   869.249
Emission/Energy-transfer range:  0.000 ...   4.853

Now storing the 2D file...
Done

Making the Integrated spectra along Energy Transfer/Emission axis... Done

Making the Integrated spectra along Incident axis... Done

All Done
-----
```

Successful run will generate the following files: The RIXS planes of the Total, Direct and Interference RIXS intensity as indicated in the above equations:

```
test.el_inel.rocis.rixsoc.total_rixs.dat
test.el_inel.rocis.rixsoc.direct_rixs.dat
test.el_inel.rocis.rixsoc.interference_rixs.dat
```

In addition one obtains the integrated spectra at constant Incident energies (CIE):

```
test.el_inel.rocis.rixsoc.dw.dat
```

as well as at constant Emission/Energy Transfer energies (CEE/CET):

```
test.el_inel.rocis.rixsoc.wex.dat
```

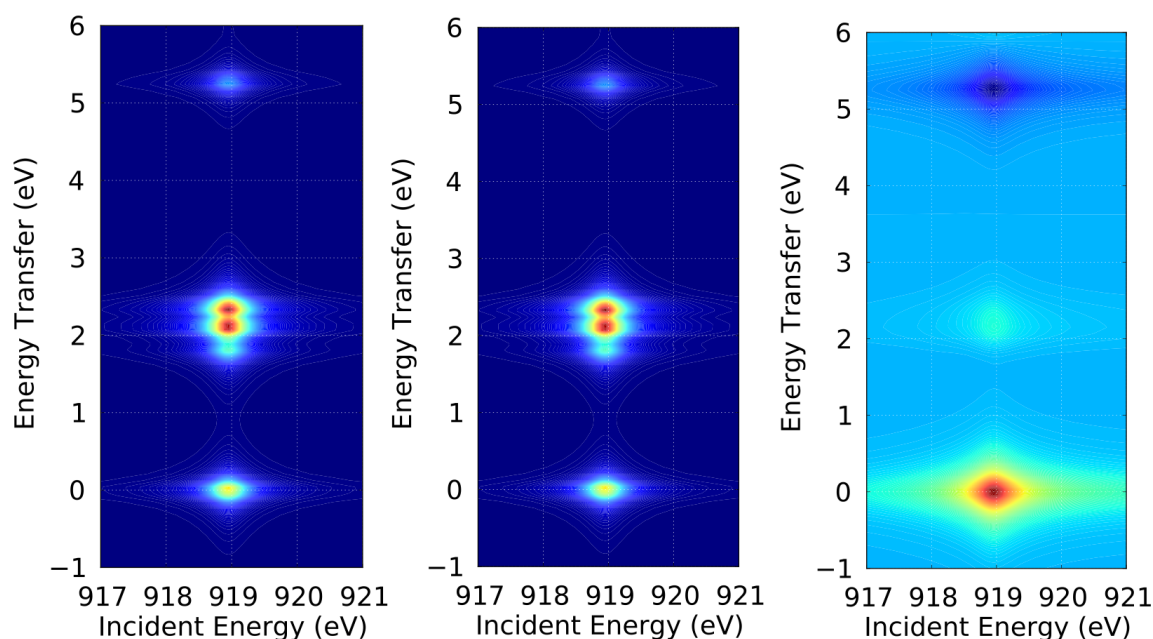


Fig. 5.25: DFT/ROCIS calculated RIXS planes for $[Cu(NH_3)_4]^{2-}$. Left: Total RIXS Intensity, Middle: Direct RIXS intensity and Right: Interference RIXS intensity. Lorentzian lineshape broadening with constant widths along Incident and Energy Transfer axis (0.5 and 0.2 eV respectively) were used throughout.

Generating Cuts

Cuts along x and y axis can be generated with two ways:

- 1) At first, this action can be performed by adding the following keywords: `uex` and `udw` accounting for generating cuts at constant Incident Energies (CIE) and at constant Emission (CEE)/or at constant Energy Transfer (CET) respectively, together with the desired number of cuts.
- 2) Alternatively, the energies of the desired cuts can be specified as lists in the files `udex.inp` (user defined excitations) `udem.inp` (user defined emissions)

For example if in `udex.inp` one specifies:

```
872.5
874.2
```

and for the cuts along Energy Transfer axis one just specify `-udw3`

```
orca_mapspc test.el_inel.rocis.rixssoc RIXS -x0871 -x1876 -x2-1 -x34 -w0.4 -g0.4
-l -n125 -m125 -dx20 -eaxis1 -udw3
```

Then at the end one gets:

```
Making the specified cuts (2) at constant Excitation Energy...
Writing file: test.el_inel.rocis.rixssoc_872.50.rxes_vs.dat ...Done
Writing file: test.el_inel.rocis.rixssoc_872.50.rxes_fs.dat ...Done
```

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```

Writing file: test.el_inel.rocis.rixssoc_874.20.rxes_vs.dat ...Done
Writing file: test.el_inel.rocis.rixssoc_874.20.rxes_fs.dat ...Done
Done

Making the specified cuts (3) at constant Emission/Energy Transfer axis...
Writing file: test.el_inel.rocis.rixssoc_-1.00.xas_vs.dat ...Done
Writing file: test.el_inel.rocis.rixssoc_-1.00.xas_fs.dat ...Done
Writing file: test.el_inel.rocis.rixssoc_1.50.xas_vs.dat ...Done
Writing file: test.el_inel.rocis.rixssoc_1.50.xas_fs.dat ...Done
Writing file: test.el_inel.rocis.rixssoc_4.00.xas_vs.dat ...Done
Writing file: test.el_inel.rocis.rixssoc_4.00.xas_fs.dat ...Done
Done
All Done
-----

```

The files *_rxes_fs.dat are RXES spectra containing all individual contributions from all Final states together with the Direct, the Total and the Interference contributions at the given constant Incident Energy.

Similarly, the *_rxes_vs.dat are RXES spectra containing individual contributions of the Intermediate states, together with the Direct the Total and the Interference contributions at the given constant Incident Energy

Likewise, the respective *_xas_fs.dat and *_xas_vs.dat are XAS type spectra with individual contributions at a given constant Emission or Energy transfer Energy

These files are Energy vs Intensity files and read like:

1) for *_fs.dat

X	S- 1(0- 0)	S- 2(0- 1)	DIRECT	TOT	INTERFERENCE
---	-------------	-------------	--------	-----	--------------

2) for *_vs.dat

X	S- 1(45)	S- 2(47)	DIRECT	TOT	INTERFERENCE
---	-----------	-----------	--------	-----	--------------

In the first case S -1(0-0) represents the individual contribution of a given Ground-Final state pair. The numbering follows the numbering of the output file e.g.:

Eigenvalues:	cm-1	eV	Boltzmann populations at T = 300.000 K
0:	0.0000	0.0000	3.44e-01
1:	8.3818	0.0010	3.31e-01

Hence, in this case S -1 represents the elastic scattering intensity.

In the second case S -1(45) represents the individual contribution of a given Intermediate state.

44:	66918.6071	8.2968	1.43e-140
45:	6996678.8061	867.4775	0.00e+00
46:	6996693.0276	867.4793	0.00e+00

In this case S -1 represents the intensity contribution of the first Intermediate state.

Starting from ORCA 4.2 in every RIXS requested calculation the Off resonant XES spectrum is automatically generated in every RIXS requested calculation.

```

-----
ROCIS RIXS SPECTRUM
-----

```

```

Making the RIXS data files for Inelastic and Elastic Scattering
Ground State:                1
Intermediate States:         28
Final States:                 588

```

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```
The RIXS cross section will be generated from:
589 Ground-Final State Pairs and 28 Intermediate States/Pair
The Off-Resonance XES spectrum will be printed
```

```
Calculating Intensities...
```

```
10% done
20% done
30% done
40% done
50% done
60% done
70% done
80% done
90% done
100% done
```

```
Printing the XES spectrum and Storing the files...
```

```
-----
--
X-RAY EMISSION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS
-----
--
Transition      Energy      INT      TX      TY      TZ
(eV)            (fosc)      (au)      (au)      (au)
-----
--
1  589 -> 0      6403.377    0.000000000721    0.00000    0.00000    0.00000
2  590 -> 0      6403.380    0.000000000083   -0.00000    0.00000    0.00000
3  591 -> 0      6403.685    0.000873238810    0.00236    0.00000    0.00000
4  592 -> 0      6404.766    0.000000000154    0.00000    0.00000    0.00000
5  593 -> 0      6408.288    0.000000006850   -0.00001    0.00000    0.00000
6  594 -> 0      6408.295    0.000034710300   -0.00047    0.00000    0.00000
...
16490 614 -> 588    6387.989    0.000000000000    0.00000    0.00000    0.00000
16491 615 -> 588    6388.222    0.000000000000    0.00000    0.00000    0.00000
16492 616 -> 588    6388.881    0.000000000000    0.00000    0.00000    0.00000
All Done
-----
```

Hence also the myfile-rixs.out file can also be processed with the `orca_mapspc` to generate the respective XES spectra:

```
orca_mapspc myfile_rixs.out XES/XESSOC -x06000 -x16500 -w2.0 -eV -n10000
```

5.7.5 ROCIS Magnetic Properties

Several magnetic properties are available in the ROCIS method Including g-tensors (G-Matrix), zero field splittings (ZFS), hyperfine couplings (HFCs) and electric field gradients (EFGs).

The g-tensors as well as the zfs are calculated on the basis of the Effective Hamiltonian as well in the sum over states (SOS) framework. HFCs are calculated in the SOS framework while EFGs are calculated as expectation values. Please consult also the respective discussion in the MRCI chapter (section *Multireference Configuration Interaction and Perturbation Theory (uncontracted)*)

```
...
DoHeff true      # Requests calculation of G-tensors and ZFS
                  # in the effective Hamiltonian framework
DoEPR true       # Requests calculation of G-tensors, ZFS and HFCs
                  # in the Sum over states (SOS) framework
```

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```

AtensorNuc 0    # Nuclei to account for the HFCs calculation
NAtensors 1     # How many Nuclei are included in the HFCs calculation
ATensor 0       # Nucleus to calculate HFCs and EFGs
NDoubGtensor 1 # Kramers doublets to account for the g tensor calculations
...

```

This will enter the calculation in the ROCIS Spin Hamiltonian section

```

-----
ROCIS SPIN HAMILTONIAN PROPERTIES
-----

```

5.7.6 Natural Transition Orbitals/ Natural Difference Orbitals

Likewise to CIS and TD-DFT (section *Natural Transition Orbitals*) The nature of the calculated excited states in ROCIS and DFT/ROCIS can be analyzed by using the Natural Transition Orbitals (NTO) or Natural Difference Orbitals (NDO) machineries.[658]

Note

- The NTO analysis is based on the transition density between ground and excited states. Hence is valid for singly excited states and for states of the same multiplicity.
- The NDO analysis on the otherhand is somewhat more flexible in this respect as it is based on the difference density between ground and excited states.
- Presently, only one analysis (NTO or NDO) can be performed at a time while when both flags are on the NTO analysis switches off.

To request for NTOs or NDOs the user needs to provide which states are to be calculated:

```

DoNTO true
NTOSTates = 1,2,3,4,5,6,7,8,9,10,13,14,15

```

```

DoNDO true
NDOSTates = 1,2,3,4,5,6,7,8,9,10,13,14,15

```

Which gives:

```

-----
NATURAL TRANSITION ORBITALS FOR STATE    14
-----

done
Solving eigenvalue problem for the Occupied space ... done
Solving eigenvalue problem for the Acceptor space ... done
Natural Transition Orbitals were saved in nto.14.nton
Threshold for printing occupation numbers 1.0e-04

E= 25.447756 au      692.469 eV  5585137.0 cm**--1
49[0] -> 46[1]      : n=  0.39056909
48[0] -> 47[1]      : n=  0.08619374
47[0] -> 48[1]      : n=  0.00441125

```

```

-----
NATURAL DIFFERENCE ORBITALS FOR STATE    14
-----

```

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```

done
Solving eigenvalue problem for the Occupied space ... done
Solving eigenvalue problem for the Acceptor space ... done
Natural Difference Orbitals were saved in ndo.14.ndo
Threshold for printing occupation numbers 1.0e-04

E= 25.447756 au      692.469 eV  5585137.0 cm**-1
49[0] -> 46[1] : n= 0.81173217
48[0] -> 47[1] : n= 0.17903699
47[0] -> 48[1] : n= 0.01165859
46[0] -> 49[1] : n= 0.00922738
45[0] -> 50[1] : n= 0.00112567

```

For closed shell cases the orbitals are save in similar way to TDDFT and CIS (section *Natural Transition Orbitals*). In the case of open shell cases for convenience donor orbitals are saved with orbital operator 0 while acceptor orbitals with orbital operator 1. This needs to be specified in the `orca_plot` program and should not be confused with the spin-up and spin-down orbitals in the UHF and UKS cases.

5.7.7 Keyword List

Table 5.9: %rocis block input keywords.

Keyword	Option / Value	Description
DoGenROCIS	true	Requests the GS-ROCIS method (default: false).
ReferenceMult	1	Sets the multiplicity for the reference CSF for the GS-ROCIS method.
NRroots	5	The number of desired roots.
MaxDim	25	Davidson expansion space = MaxDim * NRroots.
MaxIter	100	Maximum CI Iterations.
NGuessMat	512	The dimension of the guess CI matrix.
ETol	1e-6	Energy convergence tolerance.
RTol	1e-6	Residual Convergence tolerance.
MaxCore	4096	Maximum memory used by the ROCIS module during the calculation in MB.
EWin =	-5,5-5,5	Energy Window that defines orbital excitation space.
OrbWin =	6,8,0,2000	Orbital Window that defines orbital excitation space (overrides EWin).
DoLoc	true	Switch for localization of Donor orbital space (default: false).
LocOrbWin =	6,11	Obital window for the localization scheme.
LocMet	PipekMezey PM	Chooses the Pipek Mezey localization method.
	FosterBoys FB	Chooses the Foster Boys localization method.
DoPNO	true	Performs the calculation in the PNO-ROCIS framework (default: false).
TCutPNO	1e-16	Threshold for PNO selection.
XASelems	0,2	Selects from which atoms are the core MOs going to be used in the PNO procedure.
LocMet	PipekMezey PM	Chooses the Pipek Mezey localization method.
	FosterBoys FB	Chooses the Foster Boys localization method.
DoNTO	true	Request Natural Transition Orbital Analysis (default: false)
NTOTresh	1e-4	Threshold for printing occupation numbers.
NTOSTates =	1,2	Array input for states to be taken into account.
DoNDO	true	Request Natural Difference Orbital Analysis (default: false) (if true it switches off the NTO analysis)
NDOTresh	1e-4	Threshold for printing occupation numbers.
NDOSTates =	1,2	Array input for states to be taken into account.
PrintLevel	3	Controls the amount of output produced during the calculation.
Do_is	true	Include DOMO->SOMO excitations.
Do_sa	true	Include SOMO->Virtual excitation.
Do_ia	true	Include DOMO->Virtual excitations.
Do_ista	true	Include DOMO->SOMO excitations coupled to SOMO->Virtual excitations with s≠ t.
Do_isa	true	Include DOMO->SOMO excitations coupled to SOMO->Virtual excitations with s= t. (only used in the original ROCIS implementation)
DoLowerMult	true	Switch for excitation with S'=S-1.
Do_LM_is	true	Include DOMO->SOMO excitations with S'=S-1.
Do_LM_sa	true	Include SOMO->Virtual excitations with S'=S-1.
Do_LM_ia	true	Include DOMO->Virtual excitations with S'=S-1.
Do_LM_ss	true	Include SOMO->SOMO excitations with S'=S-1.
DoHigherMult	true	Switch for excitations with S'=S+1.
Do_HM_is	true	Include DOMO->SOMO excitations with S'=S+1.

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Table 5.9 – continued from previous page

Keyword	Option / Value	Description
Do_HM_sa	true	Include SOMO->Virtual excitations with $S'=S+1$.
Do_HM_ia	true	Include DOMO->Virtual excitations with $S'=S+1$.
DoCD	true	Request circular dichroism calculation.
DoDipoleLength	true	Request the use of electric moments in a length formulation (default: false).
DoDipoleVelocity	true	Request the use of electric moments in a velocity formulation (default: false).
DoFullSemiclassical	true	Request the calculation of complete semiclassical multipolar moments (default: false).
DecomposeFosc	true	Request the decomposition of the oscillator strengths in a multipolar expansion. (default: false)
RIXS	true	Requests a RIXS calculation (default: false).
RIXSSOC	true	Perform a RIXS calculation on the basis of relativistically corrected states (default: false).
Elastic	true	Include the elastic line in the generation of the RIXS or RIXSSOC spectra (default: false).
PlotDiffDens =	1,2	Array input for plotting difference densities of CI roots to the ground state.
PlotSOCDiffDens =	1,2	Array input for plotting difference densities of SOC states to the ground state.
TPrint	0.01	Threshold for contributions to CI and SOC states to be printed.
rel		Signals the beginning of the relativistic block.
DoSOC	true	Requests the inclusion of spin-orbit coupling (part of the rel block).
DoMCD	true	Requests the calculation of MCD spectra (part of the rel block).
B	30000	Sets external magnetic field (part of the rel block).
Temperature	5	Sets the temperature for the SOC spectra (part of the rel block).

5.8 Excited States via MCRPA

The MCRPA method is a synonym for *CASSCF* linear response theory. Having converged *CASSCF* calculations for the electronic ground state, you can employ ORCA's MCRPA implementation to compute

- excitation energies
- oscillator strengths (intensities of the UV/Vis spectrum)
- rotatory strengths (intensities of the ECD spectrum)
- core excitation energies to simulate XAS spectra primarily for open-shell and strongly correlated systems.

Before running these calculations make sure you are familiar with *CASSCF* calculations in general.

5.8.1 General Description

MCRPA excitation energies and transition moments are computed from the poles and residues of the linear response function of CASSCF a wave function.[592, 593, 594] Those are determined from the generalized eigenvalue equations

$$\mathbf{E}^{(2)} \boldsymbol{\lambda} = \mathbf{S}^{(2)} \boldsymbol{\lambda} \omega,$$

that involve the second-derivative matrices $\mathbf{E}^{(2)}$ and $\mathbf{S}^{(2)}$. The eigenvalues ω correspond to the electronic excitation energies. The second-derivative matrices $\mathbf{E}^{(2)}$ and $\mathbf{S}^{(2)}$ have a paired structure as both kind of operators that express electronic excitation and de-excitations are involved:

$$\left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} - \omega \begin{pmatrix} \boldsymbol{\Sigma} & \boldsymbol{\Delta} \\ -\boldsymbol{\Delta}^* & -\boldsymbol{\Sigma}^* \end{pmatrix} \right] \begin{pmatrix} \mathbf{X} \\ \mathbf{Y}^* \end{pmatrix} = \begin{pmatrix} \mathbf{0} \\ \mathbf{0} \end{pmatrix}$$

The eigenvalue equations above are valid for all variational wave functions methods, e.g. *DFT*, *HF*, *CASSCF* etc. The only difference is the

operator manifold and the time-independent Hamiltonian \hat{H} that is used. For the CASSCF linear response and eigenvalue equations, the super matrices \mathbf{A} , \mathbf{B} , $\boldsymbol{\Sigma}$, and $\boldsymbol{\Delta}$ have the following structure:

$$\mathbf{A} = \begin{pmatrix} \langle 0 | [q_i, [\hat{H}, q_j^\dagger]] | 0 \rangle & \langle 0 | [[q_i, \hat{H}], R_j^\dagger] | 0 \rangle \\ \langle 0 | [R_i, [\hat{H}, q_j^\dagger]] | 0 \rangle & \langle 0 | [R_i, [\hat{H}, R_j^\dagger]] | 0 \rangle \end{pmatrix} \quad \boldsymbol{\Sigma} = \begin{pmatrix} \langle 0 | [q_i, q_j^\dagger] | 0 \rangle & \langle 0 | [q_i, R_j^\dagger] | 0 \rangle \\ \langle 0 | [R_i, q_j^\dagger] | 0 \rangle & \langle 0 | [R_i, R_j^\dagger] | 0 \rangle \end{pmatrix}$$

$$\mathbf{B} = \begin{pmatrix} \langle 0 | [q_i, [\hat{H}, q_j]] | 0 \rangle & \langle 0 | [[q_i, \hat{H}], R_j] | 0 \rangle \\ \langle 0 | [R_i, [\hat{H}, q_j]] | 0 \rangle & \langle 0 | [R_i, [\hat{H}, R_j]] | 0 \rangle \end{pmatrix} \quad \boldsymbol{\Delta} = \begin{pmatrix} \langle 0 | [q_i, q_j] | 0 \rangle & \langle 0 | [q_i, R_j] | 0 \rangle \\ \langle 0 | [R_i, q_j] | 0 \rangle & \langle 0 | [R_i, R_j] | 0 \rangle \end{pmatrix}$$

There are two types of operators for describing electronic excitations, i.e. orbital excitation q_i^\dagger and de-excitation operators q_i ,

$$q_i^\dagger = E_{pq} = a_{p\alpha}^\dagger a_{q\alpha} + a_{p\beta}^\dagger a_{q\beta}, \quad q_i = E_{qp}, \quad \text{with } p > q$$

as well as so called state-transfer operators

$$R_i^\dagger = |i\rangle \langle 0|, \quad R_i = |0\rangle \langle i|, \quad \text{with } i \neq 0$$

Intensities of the (UV/Vis) absorption and electronic circular dichroism (ECD) spectra are obtained from the transition moments. Transition moments are easily computed as dot product

$$\langle 0 | \hat{V} | f \rangle = \begin{pmatrix} \mathbf{X}^f \\ (\mathbf{Y}^f)^* \end{pmatrix}^\dagger \begin{pmatrix} \mathbf{C} \\ \mathbf{D}^* \end{pmatrix}$$

from the eigenvectors \mathbf{X} and \mathbf{Y} of root f and the electronic gradients \mathbf{C} and \mathbf{D} of the dipole operators \hat{V} .

$$\mathbf{C} = \begin{pmatrix} \langle 0 | [q_i, \hat{V}] | 0 \rangle \\ \langle 0 | [R_i, \hat{V}] | 0 \rangle \end{pmatrix} \quad \mathbf{D} = \begin{pmatrix} \langle 0 | [q_i^\dagger, \hat{V}] | 0 \rangle \\ \langle 0 | [R_i^\dagger, \hat{V}] | 0 \rangle \end{pmatrix}$$

The eigenvalue equations are solved iteratively by a customized version of the Davidson algorithm that simultaneously determines the N lowest lying roots. The most time of the calculation is spent on the transformation of trial vectors that contain an orbital and CI coefficient part with the electronic Hessian matrix $\mathbf{E}^{(2)}$. The working equations are very similar to those of the CASSCF electronic gradient that is computed when minimizing the CASSCF ground state energy. Further technical aspects are described in subsection *Computational Aspects*.

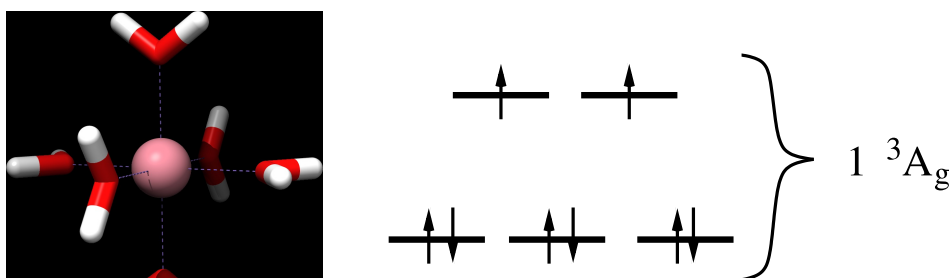
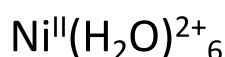


Fig. 5.26: Structure and frontier orbitals of Ni(II) hexaquo complex.

As a show case example, the lowest valence excitation energies of the octahedrally coordinated Ni(II) hexaquo complex are computed with MCRPA (for structure and frontier orbitals see Fig. Fig. 5.26). We include the 3d and 4d Ni orbitals in the active space and converge the CASSCF triplet ground state, first. Then, the MCRPA calculation is launched. It is only necessary to specify the number of desired roots `NRoots`.

```
%casscf
nel      10  # number of active electrons
norb     10  # number of active orbitals
nroots   1   # only the ground state
mult     3   # triplet multiplicity
end

%mcrpa
NRoots 15   # number of roots / excited states
end
```

Note that in contrast to state-averaged CASSCF, the MCRPA excitation energies do not depend on `NRoots` as for *TDDFT* or *EOM-CC* calculations.

It is also possible to omit the orbital part of MCTDA or MCRPA calculations by toggling the `DoOrbResp false` flag. For such calculation, the *CASCI* excitation energies are obtained. Note that for such MCRPA calculations the orbitals were optimized for the CASSCF ground state.

5.8.2 Analyzing Transitions

After convergence, the most significant contributions of the excitation / eigen vector is given for each state. When comparing with the ground state CI coefficients

```
-----
CAS-SCF STATES FOR BLOCK 0 MULT= 3 NROOTS= 1
-----
ROOT   0:  E=   -1962.8698444660 Eh
        0.98088 [      0]: 2221100000
```

we see that the lowest excited state is dominated by a transition from active orbital 3 (dyz) to active orbitals 4 and 5 (mixture of dz2 and dx2-y2).

```
STATE    1 3A  :  E=    0.033027 au      0.899 eV      7248.5 cm**-1

(+) CI                                0.72808 [    21]: 2212100000
(+) CI                                0.25245 [    27]: 2211200000
```

The (+) denotes the upper component of the eigenvectors.

By default the largest elements of the CI eigenvector are printed in the configuration basis. By changing `PrintWF` to `DET` or `CSF` you can also print that in the determinant or configuration state function (CSF) basis, respectively.

Note that the analysis of CI coefficient depends also on the choice of active orbitals which are chosen to be natural orbitals (default option).

There are also transitions dominated by single-electron excitations represented by the orbital part of the eigenvector. In case of the Ni(II) hexaquo complex those are primarily Rydberg states. Below find the most significant orbital pairs (upper (+) and lower (-) component) for the 24th excited state.

```
STATE    24 3A  :  E=    0.469596 au      12.778 eV     103064.3 cm**-1

(+) I    24 ( 35) -> V    0 ( 49) :      0.01744 (c=  0.13206324)
(+) I    26 ( 37) -> V    2 ( 51) :      0.02398 (c= -0.15485895)
(+) I    24 ( 35) -> V    4 ( 53) :      0.02513 (c=  0.15853501)
(+) A     0 ( 39) -> V    0 ( 49) :      0.26647 (c= -0.51620412)
(+) A     7 ( 46) -> V    0 ( 49) :      1.55291 (c=  1.24615978)
(+) A     0 ( 39) -> V   16 ( 65) :      0.11782 (c= -0.34324922)
(+) A     7 ( 46) -> V   16 ( 65) :      0.73241 (c=  0.85580859)

(-) I     0 ( 11) -> A     0 ( 39) :      0.05738 (c=  0.23954155)
```

5.8.3 Natural Transition Orbitals

Rather than analyzing the sections of the excitation vectors directly, visualizing natural transition orbitals[594, 595] (NTO) can be very insightful. Since NTOs are obtained from a singular value decomposition of the MCRPA ground-to-excited state (f) transition density matrices $\rho_{pq}^{0 \rightarrow f}$, they are independent of any unitary transformation of the molecular orbital (inactive, active, and virtual) sections and, thus, independent of type of orbitals (canonical, localized, natural, etc.).

As for *TDDFT* and *ROCIS* one obtains two sets of orbitals for each state that describe the donation (occupied and active) and acceptance (active and virtual) of an electron in the electronic transition. The orbital structure of $\rho_{pq}^{0 \rightarrow f}$ for CASSCF wave functions is illustrated in Fig. 5.27.

	I	A	V
I			
A	ρ_{ti}	ρ_{tu}	
V	ρ_{ai}	ρ_{at}	

Fig. 5.27: Structure of MCRPA transition density matrix $\rho_{pq}^{0 \rightarrow f}$

Note that the configuration part of the excitation vector contributes to the active-active block of $\rho_{pq}^{0 \rightarrow f}$ and is thus respected.

To compute NTOs, only the `DoNTO` flag in the input has to be switched on (`DoNTO true`):

```
%mcrpa
nroots      20      # number of roots
DoNTO       true    # generate NTOs for converged roots
NTOThresh   5e-5    # NTO selection threshold
end
```

This will compute all NTOs with a singular value larger than the NTOThresh threshold for ALL roots.

```
-----
NATURAL TRANSITION ORBITALS FOR STATE      1 3A
-----

STATE      1 3A  :  E=    0.033027 au        0.899 eV        7248.5 cm**=-1

Threshold for printing occupation numbers 1.0000e-03

      0  : n=   0.99567919
      1  : n=   0.02731085
      2  : n=   0.02231787
      ...

=> Natural Transition Orbitals (donor    ) were saved in ni-II-h2o-6-cas-8-10-mcrpa.
    ↳mcrpa.1-3A_nto-donor.gbwn
=> Natural Transition Orbitals (acceptor) were saved in ni-II-h2o-6-cas-8-10-mcrpa.
    ↳mcrpa.1-3A_nto-acceptor.gbwn
```

For the above example, the most important (controlled by NTOThresh) donating and accepting NTOs of state 1 are written to the gbwn-type files. The NTOs can be visualized with the `orca_plot` program (see Sec. [orca_plot](#)), for the donating NTOs

```
orca_plot ni-II-h2o-6-cas-8-10-mcrpa.mcrpa.1-3A_nto-donor.gbwn -i
```

and for the accepting NTOs

```
orca_plot ni-II-h2o-6-cas-8-10-mcrpa.mcrpa.1-3A_nto-acceptor.gbwn -i
```

The NTOs are ordered according to their singular value in descending order as given in the output, starting with index 0 for the most significant NTO pair.

The most dominant NTO pairs (index 0) for the three lowest valence 3Tg transitions of Ni(H₂O)₆²⁺ are given in Fig. [Fig. 5.28](#).