

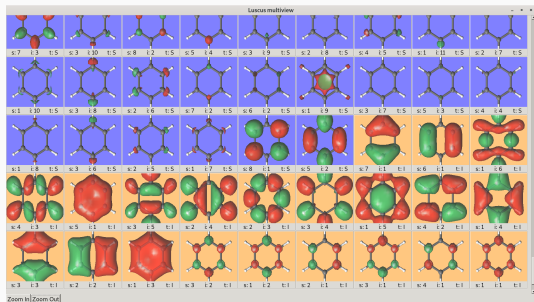
OpenMolcas: Labeling Specific Orbitals for Inclusion in MR Active Space

Benjamin William Kaufold

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Northeastern University

Summary



It is possible to flag specific orbitals for inclusion in the active space for multireference calculations in OpenMolcas. The method presented in the workshop offers finer control than simply specifying the number of active electrons and orbitals and does not require the use of symmetry (but is compatible with it).

Potential Benefits and Caveats

- Useful if one wants to study an excitation with a specific character, e.g. to compare to literature
- Allows for smaller active spaces to capture excitations that normally require large active spaces
- Can be used to determine the importance of specific orbitals for describing a system
- Eschews the use of the "Alter" keyword and does not require a test CASSCF calculation, only a preceding SCF
- **Is not guaranteed to make calculations more accurate** (and isn't meant to); just gives users more options
- **Is not useful for mass/automated calculations** since the user must visualize and choose the desired orbitals

Basic Procedure

#INDEX

* 1234567890

0 iiii iiiiii

1 iiii ii2ii2

2 222ssssssss

3 sssssssssss

4 ssss2ssssss

5 sssssssssss

6 sssssssssss

7 sssssssssss

8 sssssssssss

9 sssssssssss

0 sssssssssss

1 sssssssssss

2 sssssssssss

3 sssssssssss

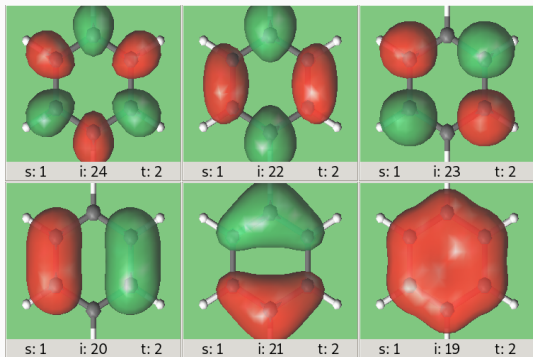
4 sssssssssss

5 sssssssssss

...

1. Generate starting orbitals in OpenMolcas using the SCF module as normal, making sure to produce a Luscus file as well
2. Create a copy of the .ScfOrb file produced by Step 1
3. View the orbitals in Luscus and determine the indices of the orbitals to include in the active space
4. At the very bottom of the new .ScfOrb file from Step 2, replace “i” or “s” with “2” for orbitals that should be included in the active space
5. Run a CASSCF calculation, using the keyword FileOrb to use your custom active space; specify nActEl but not Ras2

Detailed Procedure



The benzene molecule has a simple “intuitive” active space consisting of all valence π system orbitals. This set obeys the correlating orbital principle, and moreover, π -type orbitals are considered useful in active spaces (while σ -type orbitals are usually not except when lone pairs or strain are involved). The example shown will force OpenMolcas to use these orbitals in a set of MR[6,6] calculations without taking advantage of symmetry.

The starting geometry was optimized with B3LYP/aug-cc-pVTZ in Gaussian. Assume all files are in the same folder.

Starting Structure (optimized.xyz)

12

H	0.00000000000000	2.472664049111	0.00000000000000
H	2.141703184311	1.235977868265	0.00000000000000
C	0.00000000000000	1.390832830975	0.00000000000000
H	-2.141703184311	1.235977868265	0.00000000000000
C	1.204662535154	0.695342547527	0.00000000000000
C	-1.204662535154	0.695342547528	0.00000000000000
C	1.204662535154	-0.695342547528	0.00000000000000
C	-1.204662535154	-0.695342547527	0.00000000000000
H	2.141703184311	-1.235977868265	0.00000000000000
C	0.00000000000000	-1.390832830975	0.00000000000000
H	-2.141703184311	-1.235977868265	0.00000000000000
H	0.00000000000000	-2.472664049111	0.00000000000000

OpenMolcas Input for Orbital Generation (orbitals-C1.inp)

&GATEWAY

Title = Benzene Orbitals with Symmetry

Coord = optimized.xyz

Basis = aug-cc-pVTZ

Group = NoSym

&SEWARD

grid input

grid=ultrafine

end of grid input

&SCF

KSDFT = B3LYP

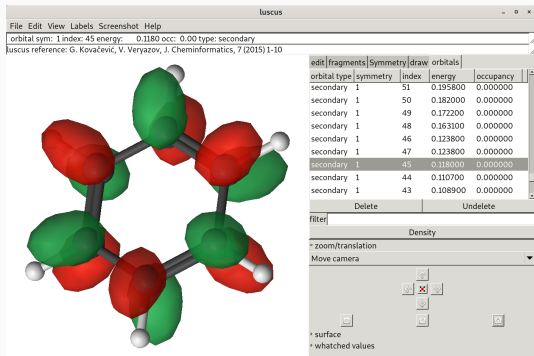
&GRID_IT

Sparse; Pack

All

- Ultrafine grid used in &SEWARD to generate more accurate starting orbitals for MR (recommended by OpenMolcas)
- “Sparse, Pack” keywords in &GRID_IT reduce the size of the Luscus file without affecting the orbitals in .ScfOrb; usually still good enough for visualization (but not for printing)

Analyzing Orbitals (orbitals-C1.lus)



The orbitals belonging to the π system are:

17, 20, 21, 22, 23, 45

17, 20 and 21 have label “i” meaning fully occupied; 22, 23 and 45 have label “s” meaning empty. There is an empty correlating orbital for every occupied valence orbital.

Labeling Orbitals for Active Space (Copy of orbitals-C1.ScfOrb)

Before Editing

#INDEX

* 1234567890

0 iiiiiiiiiii

1 iiiiiiiiiii

2 issssssssss

3 sssssssssss

4 sssssssssss

5 sssssssssss

...

After Editing

#INDEX

* 1234567890

0 iiiiiiiiiii

1 iiiiii2ii2

2 222ssssssss

3 sssssssssss

4 ssss2sssss

5 sssssssssss

...

The orbital label is 10 times the row label plus the column label.

Multireference Calculation (mr-C1.inp)

&GATEWAY

Title = Benzene MR with Symmetry

Coord = optimized.xyz

Basis = aug-cc-pVTZ

Group = NoSym

&SEWARD

grid input

grid=ultrafine

end of grid input

&RASSCF

FileOrb = labeled-C1.ScfOrb

nActEl = 6

Charge = 0

Spin = 1

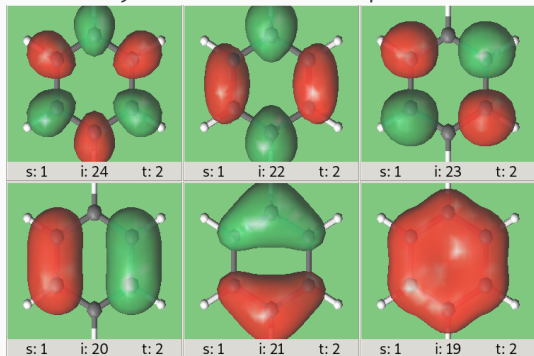
CIRoot = 6 6 1

OutOrbital = Natural; 6

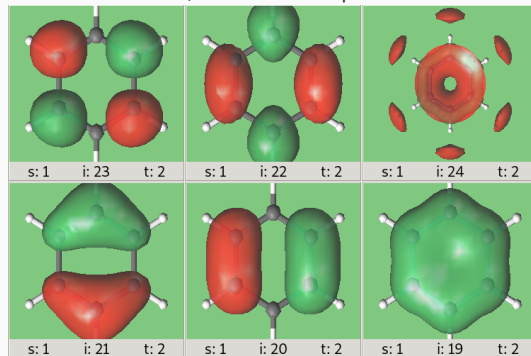
- In &RASSCF, use FileOrb = " to give the name of your manually flagged SCF orbitals
- Still specify the number of active electrons, not no need to specify the number of active orbitals
- No need to make changes to any of the following modules, e.g. &CASPT2 and &MCPDFT; the active space is “decided” in the &RASSCF module

Differences in Active Spaces

Manually Chosen Active Space



Automatic [6,6] Active Space



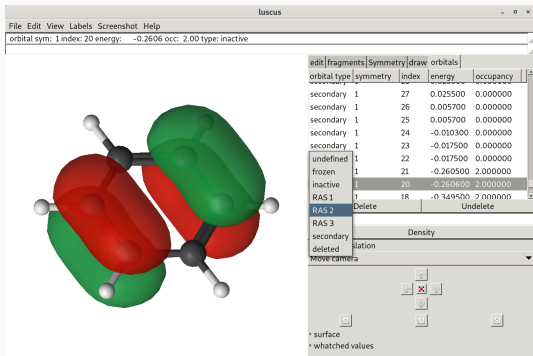
When the active space is not manually chosen, the completely in-phase π orbital does not have a correlating orbital; instead a σ -type Rydberg orbital is chosen (altered zoom and isovalue for clarity).

Excitation Energies (eV)

Calculation					S ₁	S ₂	S ₃	S ₄	S ₅
CASPT2[6,6]/aug-cc-pVTZ (Manual)					5.19	5.88	6.15	8.12	8.14
CASPT2[6,6]/aug-cc-pVTZ (Automatic)					4.72	6.21	6.78	6.78	9.84
51	Benzene	$^1B_{2u}(\pi \rightarrow \pi^*)$	V	86	5.06	CCSDT/AVTZ			
52		$^1B_{1u}(\pi \rightarrow \pi^*)$	V	92	6.45	CCSDT/AVTZ			
53		$^1E_{1g}(\pi \rightarrow 3s)$	R	92	6.52	CCSDT/AVTZ			
54		$^1A_{2u}(\pi \rightarrow 3p)$	R	93	0.066	7.08	CCSDT/AVTZ		
55		$^1E_{2u}(\pi \rightarrow 3p)$	R	92	7.15	CCSDT/AVTZ			
56		$^1E_{2g}(\pi \rightarrow \pi^*)$	V	73	8.28	FCI/6-31+G(d) + [CC3/AVTZ – CC3/6-31+G(d)]			
57		$^1A_{1g}(\text{double})$	V	n.d.	10.55	XMS-CASPT2/AVTZ			

Manually choosing the active space allows us to capture certain excitations that cannot normally be accessed with [6,6] such as $^1E_{2g}(\pi \rightarrow \pi^*)$. But low-lying excitation energies are not necessarily more accurate.

Note: A Graphical Alternative



Luscus can also be used to select the active space without the need to manually edit the text file.

1. Open the Luscus file for the SCF calculation
2. Use a drop-down to change the orbital type to RAS2 as desired
3. File > Save As... a .GvOrb file in a known location
4. Use this as your starting orbitals in &RASSCF with FileOrb = "

Additional Notes

- Make sure the orbitals you choose is consistent with the number of electrons (i.e. for a [6,6] calculation, choose three occupied and three empty orbitals)
 - OpenMolcas will automatically adjust the active space otherwise
- If your calculation uses symmetry, there will be multiple tables with “i” and “s” labels for orbitals, in order of symmetry index; edit them separately
 - For complicated cases it is probably easier to just use Luscus to do this
- Orbitals may change during the optimization procedure if the choice of active space is completely unreasonable (core orbitals, broken degeneracy, etc.)
 - Always check afterwards that the orbitals you wanted to include in the active space are actually there!