

Quick Tutorial on Natural Bond Order 3 Calculations Within Gaussian 09

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Note: The files associated with this tutorial are available at
Dropbox/Tutorials/NaturalBondOrbital

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1. What are Natural Bond Orbitals (NBOs)?

The nboguide.pdf document in the Dropbox (or at <http://www.ncl.ac.uk/chemistry/internal/research/qc/docs/nboguide.pdf>) explains NBOs more. It is good to look at the first 5 pages at least. Essentially they are a different way of reporting the molecular orbitals. They are more localized, like in valence bond theory, and are thus more chemically intuitive.

2. Running a calculation

We will be looking at the following example molecule, propiolamide, saved in **allBonds.gjf**, because it has single (1-3), double (1-2), and triple bonds (6-7). Keep in mind that it is not relaxed, which is why the presumed ~1.5 bond order of C(1)-N(3) is not reflected in this calculation.

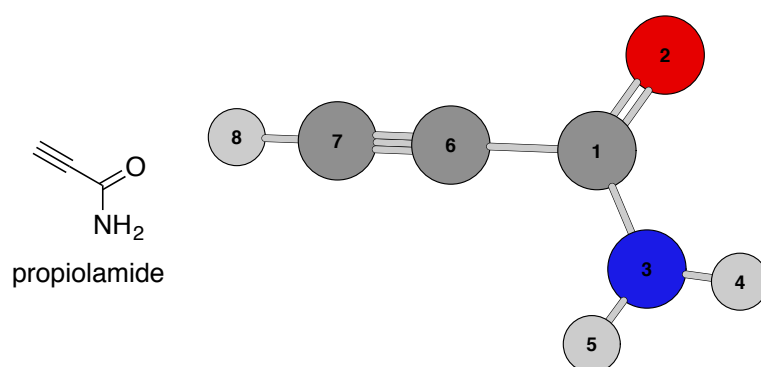


Figure 1. Chemical structure and numbering scheme for propiolamide, the example molecule.

The important part of the input file is the **pop=(nbo,savenbo)** keyword. Running this calculation produces the following section with more stars and without carriage returns.

```
*****Gaussian NBO Version 3.1*****  
      NATURAL ATOMIC ORBITAL AND  
      NATURAL BOND ORBITAL ANALYSIS  
*****Gaussian NBO Version 3.1*****
```

3. Looking at the NBO Summary

It looks like the most relevant section is **Natural Bond Orbitals (Summary)**:, which for the example molecule is as follows (at least part of it):

Natural Bond Orbitals (Summary):

NBO	Occupancy	Energy	Principal Delocalizations (geminal,vicinal,remote)
Molecular unit 1 (C3H3NO)			
1. BD (1) C 1 - O 2	1.99643	-1.36783	19(g),47(v),48(v),45(g)
2. BD (2) C 1 - O 2	1.98886	-0.50458	50(v),43(g),28(v)
3. BD (1) C 1 - N 3	1.99601	-1.11736	48(v),46(g),47(g),49(v) 34(v),20(g)
4. BD (1) C 1 - C 6	1.97991	-0.90335	48(g),37(v),51(v),46(v) 27(v),23(v)
5. BD (1) N 3 - H 4	1.99085	-0.90131	45(v),19(v),42(v),21(v) 44(g),49(r)
6. BD (1) N 3 - H 5	1.99171	-0.90982	42(v),20(v)
7. BD (1) C 6 - C 7	1.98013	-1.18082	45(g),51(g),20(v),21(v) 37(g),33(g),19(v),41(v)
8. BD (2) C 6 - C 7	1.98930	-0.43082	42(v),44(v)
9. BD (3) C 6 - C 7	1.96591	-0.42674	43(v),22(v)
10. BD (1) C 7 - H 8	1.98283	-0.80291	48(g),45(v),33(v)
11. CR (1) C 1	1.99922	-11.21561	48(v),34(v),47(v),46(v) 19(g),35(v)
12. CR (1) O 2	1.99964	-20.10232	19(v),25(g)
13. CR (1) N 3	1.99912	-15.32102	20(v),21(v),32(v),31(v)
14. CR (1) C 6	1.99856	-11.04985	37(v),51(v),48(g),20(v) 45(g),19(v),21(v)
15. CR (1) C 7	1.99826	-11.04139	33(v),45(v),48(g),41(v) 51(g)
16. LP (1) O 2	1.97992	-0.96348	19(v),44(v),45(v),46(r)
17. LP (2) O 2	1.88536	-0.41966	45(v),44(v),20(v),49(r)
18. LP (1) N 3	1.79661	-0.40134	43(v),22(v)
19. RY*(1) C 1	0.01673	1.02275	
20. RY*(2) C 1	0.01036	1.06837	
21. RY*(3) C 1	0.00191	1.57493	
22. RY*(4) C 1	0.00063	1.00103	
23. RY*(1) O 2	0.00082	2.07371	
24. RY*(2) O 2	0.00028	1.92761	

24.	RY*(2)	O	2		0.00028	1.92761	
25.	RY*(3)	O	2		0.00011	1.92619	
26.	RY*(4)	O	2		0.00002	3.54601	
27.	RY*(1)	N	3		0.00110	1.91737	
28.	RY*(2)	N	3		0.00079	1.39151	
29.	RY*(3)	N	3		0.00020	1.86598	
30.	RY*(4)	N	3		0.00005	2.25737	
31.	RY*(1)	H	4		0.00120	0.93554	
32.	RY*(1)	H	5		0.00063	0.90169	
33.	RY*(1)	C	6		0.00532	1.44794	
34.	RY*(2)	C	6		0.00220	1.40611	
35.	RY*(3)	C	6		0.00059	1.23137	
36.	RY*(4)	C	6		0.00014	1.04846	
37.	RY*(1)	C	7		0.00542	1.59529	
38.	RY*(2)	C	7		0.00005	1.04951	
39.	RY*(3)	C	7		0.00004	0.98069	
40.	RY*(4)	C	7		0.00001	1.22901	
41.	RY*(1)	H	8		0.00135	0.76119	
42.	BD*(1)	C	1 - O	2	0.01123	0.76784	
43.	BD*(2)	C	1 - O	2	0.23409	0.14122	50(v),24(g)
44.	BD*(1)	C	1 - N	3	0.05358	0.67053	
45.	BD*(1)	C	1 - C	6	0.06689	0.56971	
46.	BD*(1)	N	3 - H	4	0.00639	0.69930	
47.	BD*(1)	N	3 - H	5	0.00619	0.70308	
48.	BD*(1)	C	6 - C	7	0.02307	1.40075	
49.	BD*(2)	C	6 - C	7	0.00921	0.28023	
50.	BD*(3)	C	6 - C	7	0.01266	0.27445	
51.	BD*(1)	C	7 - H	8	0.00810	0.71519	

	Total Lewis					35.51863	(98.6629%)	
	Valence non-Lewis					0.43142	(1.1984%)	
	Rydberg non-Lewis					0.04995	(0.1387%)	

	Total unit	1				36.00000	(100.0000%)	
	Charge unit	1				0.00000		

The columns give you the NBO (specifically, the number of the orbital, the number of appearance, the element symbol, its own label, the atom it is bonded to (if applicable), and its label (if applicable)) Occupancy (number of electrons in the orbital; recall that 2 electrons = 1 bond, Energy (NOT IN NUMERICAL ORDER), and the Principal Delocalizations (geminal,vicinal,remote). The manual explains the types of orbitals i.e. standard NBO classification of orbitals:

1. "CR is an atomic core state: the atom to which this state is associated is printed alongside".
2. "BD is a bonding orbital: the pair of atoms which are associated with this orbital are printed alongside".
3. "LP is a lone pair: the associated atom is printed alongside"
4. "RY* is a 'Rydberg state' — essentially a high-lying unoccupied core atomic state: the associated atom is printed alongside;
5. "BD* is an anti-bonding orbital: the pair of atoms which are associated with this orbital are printed alongside."

We can use these to calculate the bond order:

$$\text{Bond Order} = 0.5 * (\text{Number of Bonding Electrons} + \text{Number of Antibonding Electrons})$$

as we do in Table 1. So the NBO bond orders correspond to the formal bond orders given in the Bond column.

Table 1. Calculated NBO bond order for the nonhydrogen atom bonds in the molecule in Figure 1 using just the BD and BD* occupancies.

Bond	Bond Order
C(1)=O(2)	$0.5 * (1.99643 + 1.98886 - 0.01123 - 0.23409) = 1.87$
C(1)-N(3)	$0.5 * (1.99601 - 0.05358) = 0.97$
C(1)-C(6)	$0.5 * (1.97991 - 0.06689) = 0.96$
C(6)≡C(7)	$0.5 * (1.98013 + 1.98930 + 1.96591 - 0.02307 - 0.00921 - 0.01266) = 2.95$

4. Visualizing NBOs

This is best done within Gaussview 5.0 with the .chk or .fchk file. Gaussview properly orders the orbitals and they are generated in the usual way. The HOMO and LUMO end up being the orbitals in Table 2. They are visualized in Figure 2. They make intuitive sense since the HOMO is a p-orbital with a lone-pair on the N, since it is nucleophilic and the LUMO is a π^* orbital on the C=O bond, which is electrophilic.

Table 2. The orbitals from the output for HOMO and LUMO with the energy in Hartrees italicized.

Orbital	Entry in Output File
LUMO	43. BD*(2) C 1 - O 2 0.23409 <i>0.14122</i> 50(v),24(g)
HOMO	18. LP (1) N 3 1.79661 <i>-0.40134</i> 43(v),22(v)

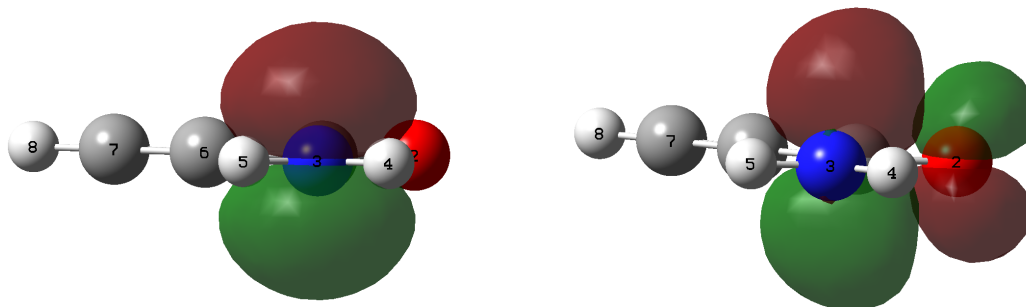


Figure 2. HOMO (left) and LUMO (right) for the example molecule visualized with an isovalue of 0.04.

5. Warnings

- NBO is a part of the regular Gaussian module so no special module is needed.
- NBO can require a lot of memory so use it on Grace, use the example script in the Gaussian folder. Then if you use ~50 GB in the script (5120MB), use 49GB in the actual Gaussian input file, to leave 1 GB for the cluster itself to use.
- Since NBO does valence bond analysis, it may have trouble with bonds involving metals that are a bit complicated to describe with Lewis structures. Therefore your NBO analysis may get split up into molecular groups or fragments that you did not intend for (thanks Adam Matula @ Batista Group for letting me know).