

# NPA/NBO-Analysis

## Examples

**POP =**

### **NBO**

Requests a full Natural Bond Orbital analysis, using NBO version 3

### **NPA**

Requests just the Natural Population Analysis phase of NBO.

### **NBORead**

Requests a full NBO analysis, with input controlling the analysis read from the input stream. Use this option to specify keywords for NBO versions 4 and 5. Refer to the NBO documentation for details on this input.

### *KEYWORD OPTION DESCRIPTION*

**NBOSUM** Request printing of the NBO summary table. This combines elements of the NBO table and 2nd-order perturbation theory analysis table (see below) in a convenient form for recognizing the principal delocalization patterns.

**RESONANCE** Request search for highly delocalized structures. The NBO search normally aborts when one or more Lewis NBOs has less than the default occupancy threshold of 1.90 electrons for a 'good' electron pair. When the **RESONANCE** keyword is activated, this threshold is successively lowered in 0.10 decrements to 1.50, and the NBO search repeated to find the best Lewis structure within each occupancy threshold. The program returns with the best overall Lewis structure (lowest total non-Lewis occupancy) found in these searches. (Useful for benzene and other highly delocalized molecules.)

**NOBOND** Request that no bonds (2-center NBOs) are to be formed in the NBO procedure. The resulting NBOs will then simply be 1-center atomic hybrids. (Useful for highly ionic species.)

**3CBOND** Request search for 3-center bonds. The normal default is to search for only 1- and 2-center NBOs. (Useful for diborane and other electron-deficient 'bridged' species.)

**NLMO** Compute and print out the summary table of Natural Localized Molecular Orbitals. NLMOs are similar to Boys or Edmiston-Ruedenberg LMOs, but more efficiently calculated. (Useful for 'semi-localized' description of an SCF or correlated wavefunction.) Activated automatically by all keywords that pertain to NLMOs (e.g., AONLMO, SPNLMO, DIPOLE).

The following example displays a HF/STO-3G NBO job of formaldehyde (CH<sub>2</sub>O, C<sub>2v</sub> point group):

### INPUT

```
#P HF/STO-3G scf=tight pop=nbo
```

```
HF/STO-3G//HF/STO-3G sp formaldehyde
```

```
0 1
```

```
C1
```

```
O2 1 r2
```

```
H3 1 r3 2 a3
```

```
H4 1 r3 2 a3 3 180.0
```

```
r2=1.21672286
```

```
r3=1.10137241
```

```
a3=122.73666566
```

NBO keyword requests calculation of NBOs and printing of the main NBO table

## OUTPUT

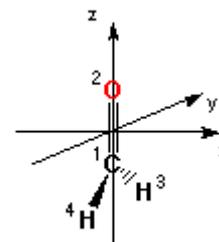
Full point group            C2V    NOp 4  
Largest Abelian subgroup    C2V    NOp 4  
Largest concise Abelian subgroup C2    NOp 2

Standard orientation:

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Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.000000	0.000000	-0.533912
2	8	0	0.000000	0.000000	0.682811
3	1	0	0.000000	0.926436	-1.129510
4	1	0	0.000000	-0.926436	-1.129510

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\*\*\*\*\*Gaussian NBO Version 3.1\*\*\*\*\*

### NATURAL ATOMIC ORBITAL AND NATURAL BOND ORBITAL ANALYSIS

\*\*\*\*\*Gaussian NBO Version 3.1\*\*\*\*\*

/RESON / : Allow strongly delocalized NBO set

Analyzing the SCF density

Job title: HF/STO-3G//HF/STO-3G sp formaldehyde

Storage needed: 510 in NPA, 633 in NBO ( 6291389 available)

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Note that all NBO output is formatted to a maximum 80-character width for convenient display on a computer terminal. The NBO heading echoes any requested keywords (none for the present default case) and shows an estimate of the memory requirements (in double precision words) for the separate steps of the NBO process, compared to the total allocated memory available through your ESS process. Increase the memory allocated to your ESS process if the estimated NBO requests exceed the available storage.

The next four NBO output segments summarize the results of natural population analysis (NPA). The first segment is the main NAO table, as shown below:

---

## NATURAL POPULATIONS: Natural atomic orbital occupancies

NAO	Atom	No	lang	Type(AO)	Occupancy	Energy
1	C	1	S	Cor( 1s)	2.00000	-11.05946
2	C	1	S	Val( 2s)	1.08460	-0.26144
3	C	1	px	Val( 2p)	0.90166	-0.04494
4	C	1	py	Val( 2p)	0.99304	0.07032
5	C	1	pz	Val( 2p)	0.85379	0.14739
6	O	2	S	Cor( 1s)	1.99999	-20.15602
7	O	2	S	Val( 2s)	1.79982	-1.09031
8	O	2	px	Val( 2p)	1.09834	-0.11626
9	O	2	py	Val( 2p)	1.91857	-0.38126
10	O	2	pz	Val( 2p)	1.37055	-0.15404
11	H	3	S	Val( 1s)	0.98982	0.02250
12	H	4	S	Val( 1s)	0.98982	0.02250

For each of the 12 NAO functions, this table lists the atom to which NAO is attached, the angular momentum type 'lang' (s,  $p_x$ , etc.), the orbital type (whether core, valence, or Rydberg, and a conventional hydrogenic-type label), the orbital occupancy (number of electrons, or 'natural population' of the orbital), and the orbital energy (in atomic units: 1 a.u. = 627.5 kcal/mol). [For example, NAO 5 (the highest energy C orbital of the set) is the valence shell  $2p_z$  orbital on carbon, occupied by 0.85379 electrons.

The principal quantum numbers for the NAO labels (1s, 2s, 3s, etc.) are assigned on the basis of the energy order if a Fock matrix is available, or on the basis of occupancy otherwise. A message is printed warning of a 'population inversion' if the occupancy and energy ordering do not coincide.

The next segment is an atomic summary showing the natural atomic charges (nuclear charge minus summed natural populations of NAOs on the atom) and total core, valence, and Rydberg populations on each atom:

### Summary of Natural Population Analysis:

Atom	No	Natural Charge	Core	Valence	Rydberg	Total
C	1	0.16692	2.00000	3.83308	0.00000	5.83308
O	2	-0.18728	1.99999	6.18729	0.00000	8.18728
H	3	0.01018	0.00000	0.98982	0.00000	0.98982
H	4	0.01018	0.00000	0.98982	0.00000	0.98982

=====

\* Total \* 0.00000 3.99999 12.00001 0.00000 16.00000

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This table succinctly describes the molecular charge distribution in terms of NPA charges. [For example, the carbon atom of formaldehyde is assigned a net NPA charge of 0.16692 e at this level; note also the slightly less positive charge on H(3 and 4)]

Next follows a summary of the NMB and NRB populations for the composite system, summed over atoms:

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### Natural Population

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Core	3.99999 ( 99.9997% of 4)
Valence	12.00001 (100.0001% of 12)
Natural Minimal Basis	16.00000 (100.0000% of 16)
Natural Rydberg Basis	0.00000 ( 0.0000% of 16)

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### Atom No Natural Electron Configuration

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C	1	[core]2s( 1.08)2p( 2.75)	<b>total hybridisation on C on O</b>
O	2	[core]2s( 1.80)2p( 4.39)	
H	3	1s( 0.99)	
H	4	1s( 0.99)	

---

The natural populations are summarized as an effective valence electron configuration ("natural electron configuration") for each atom.

Although the occupancies of the atomic orbitals are non-integer in the molecular environment, the effective atomic configurations can be related to idealized atomic states in 'promoted' configurations. [For example, the carbon atom in the above table is most nearly described by an  $1s^2 2s^1 2p^{2.54}$  (or idealized  $sp^2$ ) electron configuration.]

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The next segments of the output summarize the results of NBO analysis. The first segment reports on details of the search for an NBO natural Lewis structure:

---

## NATURAL BOND ORBITAL ANALYSIS:

Cycle	Occ. Thresh.	Occupancies		Lewis Structure				Low	High	occ Dev
		Lewis	Non-Lewis	CR	BD	3C	LP	(L)	(NL)	
1(1)	1.90	15.90533	0.09467	2	4	0	2	0	0	0.04

Structure accepted: No low occupancy Lewis orbitals

Normally, there is but one cycle of the NBO search. The table summarizes a variety of information for each cycle: the occupancy threshold for a 'good' pair in the NBO search; the total populations of Lewis and non-Lewis NBOs; the number of core (CR), 2-center bond (BD), 3-center bond (3C), and lone pair (LP) NBOs in the natural Lewis structure; the number of low-occupancy Lewis (L) and 'high-occupancy' (> 0.1e) non-Lewis (NL) orbitals; and the maximum deviation ('Dev') of any formal bond order from a nominal estimate (NAO Wiberg bond index) for the structure. [If the latter exceeds 0.1, additional NBO searches are initiated (indicated by the parenthesized number under 'Cycle') for alternative Lewis structures.] The Lewis structure is accepted if all orbitals of the formal Lewis structure exceed the occupancy threshold (default, 1.90 electrons).

Next follows a more detailed breakdown of the Lewis and non-Lewis occupancies into core, valence, and Rydberg shell contributions

Core	3.99999 (100.000% of 4)
Valence Lewis	11.90534 ( 99.211% of 12)
=====	
Total Lewis	15.90533 ( 99.408% of 16)
=====	
Valence non-Lewis	0.09467 ( 0.592% of 16)
Rydberg non-Lewis	0.00000 ( 0.000% of 16)
=====	
<b>Total non-Lewis</b>	<b>0.09467</b> ( 0.592% of 16)

This shows the general quality of the natural Lewis structure description in terms of the percentage of the total electron density (e.g., in the above case, about 99.2%). The table also exhibits the relatively important role of the valence non-Lewis orbitals relative to the extra-valence orbitals (e.g. Rydberg NBOs which occur when using a non minimal basis set) in the slight departures from a localized Lewis structure model.

Next follows the main listing of NBOs, displaying the form and occupancy of the complete set of NBOs that span the input AO space:

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**(Occupancy) Bond orbital/ Coefficients/ Hybrids**

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1. (1.99777) BD ( 1) C 1 - O 2  
( 41.41%) 0.6435\* C 1 s( 34.36%)p 1.91( 65.64%)  
0.0000 0.5862 0.0000 0.0000 0.8102  
**1s 2s 2p<sub>x</sub> 2p<sub>y</sub> 2p<sub>z</sub>**  
  
( 58.59%) 0.7654\* O 2 s( 24.04%)p 3.16( 75.96%)  
0.0000 0.4903 0.0000 0.0000 -0.8716

---

**corresponds to  $s(\text{C-O}) = 0.6435 sp^{1.91} + 0.7654 sp^{3.16}$  bond**

**$(0.6435)^2 = 0.4141$  corresponds to  $c^2$  means this NBO is localized with 41.41 % on carbon;  $(0.5859)^2 = 0.7654$  means 58.59 % localization on oxygen, summary: polar C-O sigma bond**

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2. (2.00000) BD ( 2) C 1 - O 2  
( 45.08%) 0.6714\* C 1 s( 0.00%)p 1.00(100.00%)  
0.0000 0.0000 1.0000 0.0000 0.0000  
( 54.92%) 0.7411\* O 2 s( 0.00%)p 1.00(100.00%)  
0.0000 0.0000 1.0000 0.0000 0.0000

3. (1.99522) BD ( 1) C 1 - H 3  
( 51.57%) 0.7181\* C 1 s( 32.82%)p 2.05( 67.18%)  
0.0000 0.5729 0.0000 0.7071 -0.4145  
( 48.43%) 0.6959\* H 3 s(100.00%)  
1.0000

4. (1.99522) BD ( 1) C 1 - H 4  
( 51.57%) 0.7181\* C 1 s( 32.82%)p 2.05( 67.18%)  
0.0000 0.5729 0.0000 -0.7071 -0.4145  
( 48.43%) 0.6959\* H 4 s(100.00%)  
1.0000

5. (2.00000) CR ( 1) C 1 s(100.00%)  
1.0000 0.0000 0.0000 0.0000 0.0000

6. (1.99999) CR ( 1) O 2 s(100.00%)  
1.0000 0.0000 0.0000 0.0000 0.0000

7. (1.99857) LP ( 1) O 2 s( 75.96%)p 0.32( 24.04%)  
0.0000 0.8716 0.0000 0.0000 0.4903

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**corresponds to a  $sp^{0.32}$  lone pair on oxygen**

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8. (1.91857) LP ( 2) O 2 s( 0.00%)p 1.00(100.00%)

0.0000 0.0000 0.0000 1.0000 0.0000

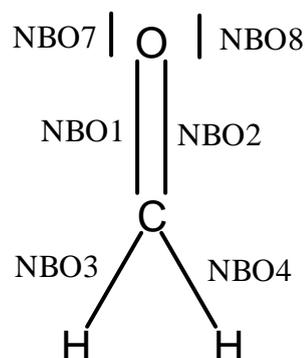
---

corresponds to a  $p_y$  lone pair on oxygen

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9. (0.00338) BD\*( 1) C 1 - O 2  
( 58.59%) 0.7654\* C 1 s( 34.36%)p 1.91( 65.64%)  
0.0000 0.5862 0.0000 0.0000 0.8102  
( 41.41%) -0.6435\* O 2 s( 24.04%)p 3.16( 75.96%)  
0.0000 0.4903 0.0000 0.0000 -0.8716
10. (0.00000) BD\*( 2) C 1 - O 2  
( 54.92%) 0.7411\* C 1 s( 0.00%)p 1.00(100.00%)  
( 45.08%) -0.6714\* O 2 s( 0.00%)p 1.00(100.00%)
11. (0.04564) BD\*( 1) C 1 - H 3  
( 48.43%) 0.6959\* C 1 s( 32.82%)p 2.05( 67.18%)  
0.0000 -0.5729 0.0000 -0.7071 0.4145  
( 51.57%) -0.7181\* H 3 s(100.00%)  
-1.0000
12. (0.04564) BD\*( 1) C 1 - H 4  
( 48.43%) 0.6959\* C 1 s( 32.82%)p 2.05( 67.18%)  
0.0000 -0.5729 0.0000 0.7071 0.4145  
( 51.57%) -0.7181\* H 4 s(100.00%)  
-1.0000
- 

According to NBO, the following Lewis representation was found:



For each NBO (1-12), the first line of printout shows the occupancy (between 0 and 2.0000 electrons) and unique label of the NBO. This label gives the type ("BD" for 2-center bond, "CR" for 1-center core pair, "LP" for 1-center valence lone pair, "RY\*" for 1-center Rydberg, and "BD\*" for 2-center antibond, the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively), a serial number (1, 2,... if there is a single, double,... bond between the pair of atoms), and the atom(s) to which the NBO is affixed. The next lines summarize the natural atomic hybrids  $h_A$  of which the NBO is composed, giving the percentage ( $100|c_A|^2$ ) of the NBO on each hybrid (in parentheses), the polarization coefficient  $c_A$ , the atom label, and a hybrid label showing the  $sp^l$  composition (percentage s-character, p-character, etc.) of each  $h_A$ .

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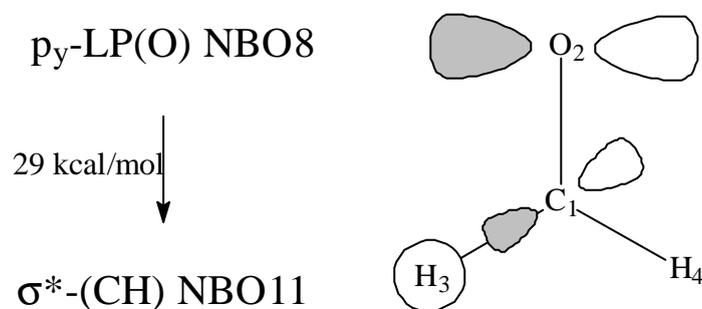
The next segment summarizes the second-order perturbative estimates of 'donor-acceptor' (bond-antibond) interactions in the NBO basis:

### Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis

Threshold for printing: 0.50 kcal/mol

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j) a.u.	-E(i) F(i,j) a.u.
=====				
within unit 1				
1. BD ( 1) C 1 - O 2	/ 11. BD*( 1) C 1 - H 3	0.92	1.76	0.036
1. BD ( 1) C 1 - O 2	/ 12. BD*( 1) C 1 - H 4	0.92	1.76	0.036
3. BD ( 1) C 1 - H 3	/ 9. BD*( 1) C 1 - O 2	1.85	1.59	0.048
3. BD ( 1) C 1 - H 3	/ 12. BD*( 1) C 1 - H 4	1.71	1.36	0.043
4. BD ( 1) C 1 - H 4	/ 9. BD*( 1) C 1 - O 2	1.85	1.59	0.048
4. BD ( 1) C 1 - H 4	/ 11. BD*( 1) C 1 - H 3	1.71	1.36	0.043
<b>8. LP ( 2) O 2</b>	<b>/ 11. BD*( 1) C 1 - H 3</b>	<b>29.85</b>	<b>1.04</b>	<b>0.159</b>
<b>8. LP ( 2) O 2</b>	<b>/ 12. BD*( 1) C 1 - H 4</b>	<b>29.85</b>	<b>1.04</b>	<b>0.159</b>

corresponds to the following non-covalent interaction



### Resonance with $H^- \ ^+O^{\ominus}C-H$

This analysis is carried out by examining all possible interactions between 'filled' (donor) Lewis-type NBOs and 'empty' (acceptor) non-Lewis NBOs, and estimating their energetic importance by 2nd-order perturbation theory. Since these interactions lead to loss of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals (and thus, to departures from the idealized Lewis structure description), they are referred to as 'delocalization' corrections to the zeroth-order natural Lewis structure. For each donor NBO ( $i$ ) and acceptor NBO ( $j$ ), the stabilization energy  $E(2)$  associated with delocalization ("2e-stabilization") is estimated. As the heading indicates, entries are included in this table only when the interaction energy exceeds a default threshold of 0.5 kcal/mol.

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Next appears a condensed summary of the principal NBOs, showing the occupancy, orbital energy, and the qualitative pattern of delocalization interactions associated with each:

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### Natural Bond Orbitals (Summary):

NBO	Principal Delocalizations	
	Occupancy	Energy (geminal,vicinal,remote)
=====		
Molecular unit 1 (CH2O)		
1. BD ( 1) C 1 - O 2	1.99777	-1.09402 11(g),12(g)
2. BD ( 2) C 1 - O 2	2.00000	-0.44319
3. BD ( 1) C 1 - H 3	1.99522	-0.69465 9(g),12(g)
4. BD ( 1) C 1 - H 4	1.99522	-0.69465 9(g),11(g)
5. CR ( 1) C 1	2.00000	-11.05946
6. CR ( 1) O 2	1.99999	-20.15611
7. LP ( 1) O 2	1.99857	-0.98034
8. LP ( 2) O 2	1.91857	-0.38126 11(v),12(v)
9. BD*( 1) C 1 - O 2	0.00338	0.89756
10. BD*( 2) C 1 - O 2	0.00000	0.28199
11. BD*( 1) C 1 - H 3	0.04564	0.66156
12. BD*( 1) C 1 - H 4	0.04564	0.66156
-----		
Total Lewis	15.90533	( 99.4083%)
Valence non-Lewis	<b>0.09467</b>	( 0.5917%)
Rydberg non-Lewis	0.00000	( 0.0000%)
-----		
Total unit 1	16.00000	(100.0000%)
Charge unit 1	0.00000	
Leave Link 607 at Wed Jan 21 12:09:41 2004, MaxMem= 6291456 cpu: 1.0		
(Enter C:\G03W\l9999.exe)		
1 1 UNPC-UNK SP RHF STO-3G C1H2O1 PCUSER 21-Jan-2004 0 #P HF/STO-3G S		
CF=TIGHT POP=NBO  HF/STO-3G//HF/STO-3G sp formaldehyde  0,1 C O,1,1.21		
672286 H,1,1.10137241,2,122.73666566 H,1,1.10137241,2,122.73666566,3,1		
80.,0  Version=x86- Win32-G03RevB.03 State=1-A1 HF=- 112.3543471 RMSD=8.		
544e-009 Dipole=0.,0.,-0.6046575 PG=C02V [C2(C1O1),SGV(H2)]  @		

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The following examples shows the use of the NBOREAD INPUT at the HF/STO-3G level (again formaldehyde, CH<sub>2</sub>O, C<sub>2v</sub> point group):

**POP=NBOREAD**

**INPUT**

#P HF/STO-3G scf=tight **pop=nboread**

HF/STO-3G//HF/STO-3G sp formaldehyde

0 1

C1

O2 1 r2

H3 1 r3 2 a3

H4 1 r3 2 a3 3 180.0

r2=1.21672286

r3=1.10137241

a3=122.73666566

**\$NBO NLMO BNDIDX RESONANCE \$END**

## OUTPUT

When the NLMO keyword is activated, the program computes the NLMOs and prints out three tables summarizing their form. For the RHF/STO-G formaldehyde example, the principal NLMO table is shown below:

...

### NATURAL LOCALIZED MOLECULAR ORBITAL (NLMO) ANALYSIS:

Maximum off-diagonal element of DM in NLMO basis: 0.75221E-10

Hybridization/Polarization Analysis of NLMOs in NAO Basis:

NLMO/Occupancy/Percent from Parent NBO/ Atomic Hybrid Contributions

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1. (2.00000)	99.8882%	BD ( 1) C 1 O 2
	41.418%	C 1 s( 37.69%)p 1.65( 62.31%)
	58.520%	O 2 s( 24.04%)p 3.16( 75.96%)
	0.031%	H 3 s(100.00%)
	0.031%	H 4 s(100.00%)
2. (2.00000)	100.0000%	BD ( 2) C 1 O 2
	45.083%	C 1 s( 0.00%)p 1.00(100.00%)
	54.917%	O 2 s( 0.00%)p 1.00(100.00%)
3. (2.00000)	99.7606%	BD ( 1) C 1 H 3
	51.573%	C 1 s( 37.42%)p 1.67( 62.58%)
	0.038%	O 2 s( 22.04%)p 3.54( 77.96%)
	48.309%	H 3 s(100.00%)
	0.080%	H 4 s(100.00%)
4. (2.00000)	99.7606%	BD ( 1) C 1 H 4
	51.573%	C 1 s( 37.42%)p 1.67( 62.58%)
	0.038%	O 2 s( 22.04%)p 3.54( 77.96%)
	0.080%	H 3 s(100.00%)
	48.309%	H 4 s(100.00%)
5. (2.00000)	99.9999%	CR ( 1) C 1
	100.000%	C 1 s(100.00%)p 0.00( 0.00%)
6. (2.00000)	99.9995%	CR ( 1) O 2
	99.999%	O 2 s(100.00%)p 0.00( 0.00%)
7. (2.00000)	99.9286%	LP ( 1) O 2
	0.032%	C 1 s( 58.11%)p 0.72( 41.89%)
	99.929%	O 2 s( 75.96%)p 0.32( 24.04%)
	0.020%	H 3 s(100.00%)
	0.020%	H 4 s(100.00%)
8. (2.00000)	95.9223%	LP ( 2) O 2
	1.975%	C 1 s( 0.00%)p 1.00(100.00%)
	95.922%	O 2 s( 0.00%)p 1.00(100.00%)
	1.052%	H 3 s(100.00%)
	1.052%	H 4 s(100.00%)

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For each of the nine occupied NLMOs, the table shows first the NLMO occupancy (necessarily 2.0000 at SCF level, as in the present example), the percentage of the total NLMO composition represented by this parent NBO (usually > 99%), and the label of the 'parent' NBO. Below this, there follows an NAO decomposition of the NLMO, showing the percentage of the NLMO on each atom and the hybrid composition ratios (effective  $sp^{\lambda}$  character and percentage  $s$ - and  $p$ -character) of the NAOs. For example, NLMO 8 is the most delocalized NLMO of the table, having only about a 95.9% contribution from the localized O(2) parent lone pair NBO, with 'delocalization tails' composed primarily of contributions (~1.98%) from C(1), and smaller contributions (~1.05%) from H(3) and H(4). This corresponds to what we have been anticipated from the NBO summary table or perturbation theory energy analysis table, which showed that the O(2) lone pair, NBO 8, is principally delocalized onto NBO 11 and 12, the vicinal C(1)-H(3) and C(1)-H(4) antibonds

**NLMO 8 displays the LP(2) O2® BD\*(1) C1 – H3 (4) interaction, see above**

Another type of BNDIDX output appears if the NLMO keyword is included, summarizing a formal "NLMO/NPA bond order" that can be associated with each NLMO:

**Individual LMO bond orders** greater than 0.002 in magnitude, with the overlap between the hybrids in the NLMO given:

Atom I /	Atom J /	NLMO /	Bond Order /	Hybrid Overlap /	
1	2	1	<b>0.8283590</b>	0.6567866	CO <b>s</b> -bond
1	2	2	<b>0.9016559</b>	0.2086851	CO <b>p</b> -bond
1	2	8	<b>0.0394936</b>	0.2086851	CO „triple bond character“
1	3	3	0.9661755	0.6606570	
1	3	8	-0.0210302	-0.3897472	
1	4	4	0.9661755	0.6606570	
1	4	8	<b>-0.0210302</b>	-0.3897472	
2	3	8	<b>-0.0210302</b>	-0.0358680	
2	4	8	<b>-0.0210302</b>	-0.0358680	
3	4	8	<b>-0.0210302</b>	-0.1510551	

This NLMO bond order is calculated by the method described by A. E. Reed and P. v.R. Schleyer [*Inorg. Chem.* **27**, 3969-3987 (1988); *J. Am. Chem. Soc.* (to be published)], based on the shared occupancies and hybrid overlaps (last column) of NAOs composing the NLMO. In the above table, for example, NLMO 1 occurs only in the first line, contributing a bond of formal order 0.828 between C(1) and O(2), whereas NLMO 8 (the oxygen lone pair) contributes a slight strengthening (+0.039) of the C(1)-O(2) bond, a weakening (-0.021) of the vicinal C(1)-H(3) and C(1)-H(4) bonds, **The last four negative bond orders correspond to the the LP(2) O2® BD\*(1) C1 - H3 interaction of the NBO phase, see above**

The NLMO bond order contributions are then summed for each atom pair to give the net NLMO/NPA bond orders shown below:

### Atom-Atom Net Linear NLMO/NPA Bond Orders:

Atom	1	2	3	4
1. C	0.0000	<b>1.7686</b>	<b>0.9425</b>	0.9425
2. O	1.7686	0.0000	-0.0213	-0.0213
3. H	0.9425	-0.0213	0.0000	<b>-0.0232</b>
4. H	0.9425	-0.0213	-0.0232	0.0000

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Since the CO bond is somewhat polar, the CO bond order is „only“ **1.7686** (= **0.828 + 0.901 + 0.039**)

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### Linear NLMO/NPA Bond Orders, Totals by Atom:

Atom	1
1. C	<b>3.6537</b>
2. O	1.7261
3. H	0.8981
4. H	0.8981

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According to the Lewis-representation the total bond order (valency) of C should be 4 but is found **3.6537** (**1.7686 + 0.9425 + 0.9425**) due to some polar character of its bonds. The same holds for the hydrogen atoms which possess a valency of **0.8981**. In addition, small amounts of negative bond orders are found for the H atoms.

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Leave Link 607 at Wed Jan 21 13:33:26 2004, MaxMem= 6291456 cpu: 2.0  
(Enter C:\G03W\19999.exe)  
1|1|UNPC-UNK|SP|RHF|STO-3G|C1H2O1|PCUSER|21-Jan-2004|0|#P HF/STO-3G S  
CF=TIGHT POP=NBOREAD||HF/STO-3G//HF/STO-3G sp formaldehyde||0,1|C|O,1,  
1.21672286|H,1,1.10137241,2,122.73666566|H,1,1.10137241,2,122.73666566  
,3,180.,0||Version=x86-Win32-G03RevB.03|State=1-A1|HF=-112.3543471|RMS  
D=8.544e-009|Dipole=0.,0.,-0.6046575|PG=C02V [C2(C1O1),SGV(H2)]||@