Natural Bond Critical Point (NBCP) Analysis

Reference

F. Weinhold, "Natural Bond Critical Point Analysis: Quantitative Relationships between NBO-based and QTAIM-based Topological Descriptors of Chemical Bonding," *J. Comp. Chem.* **33**, 2440-2449 (2012).

NBCP Sample Input and Output

The NBCP keyword is implemented for all ESS host programs and stand-alone GenNBO configurations.

Basic NBCP analysis is requested by simply including the "NBCP" keyword in the $NBO keylist. A sample Gaussian input deck to request default NBCP analysis for formamide (B3LYP/6-311++G** level) is shown below:

```
#b3lyp/6-311++g** pop=nboread

H2NCHO, E=-169.9548513

0 1
7    1.084401   -0.157302   -0.000171
6   -0.162865    0.386721   -0.000029
8   -1.196169   -0.246396    0.000027
1    1.187639   -1.161267    0.000459
1    1.908579    0.420705    0.000529
1   -0.140489    1.492514    0.000162

$nbo file=h2ncho nbcp $end
```

This produces the basic table comparing conventional BCP and localized NBCP topological descriptors, as well as a second table showing individual NBO contributions to each BCP. The NAIM description makes no provision for spatial dissection of $\rho(\mathbf{r})$ into the virial-based "atomic basins" of QTAIM theory, nor is it restricted to equilibrium geometries in which the virial theorem is satisfied.

The first table of default NBCP output is shown below for the formamide input file of the previous section:

```
NATURAL BOND CRITICAL POINT (NBCP) ANALYSIS

[Topological (3,-1) bond critical points:
   BCP (total density); NBCP (NAO atomic densities)]

  Atoms          Rho    Lapl.   Laplacian curvatures       Coordinates
```

```
   ----------          ------- ------- ----------------------  ----------------------
N  1- C  2  BCP   0.3161 -0.8805  0.4240 -0.6221 -0.6824  0.2969  0.1851  0.0000
            NBCP  0.3175 -0.6776  0.4672 -0.5329 -0.6118  0.3227  0.1764 -0.0001
                                                 [|R(BCP)-R(NBCP)|=  0.0272]
N  1- H  4  BCP   0.3372 -1.6445  0.8714 -1.2256 -1.2903  1.1615 -0.8970  0.0003
            NBCP  0.3374 -1.5771  0.8786 -1.2182 -1.2374  1.1598 -0.8956  0.0003
                                                 [|R(BCP)-R(NBCP)|=  0.0022]
N  1- H  5  BCP   0.3397 -1.6392  0.8779 -1.2240 -1.2931  1.6892  0.2683  0.0003
            NBCP  0.3399 -1.5960  0.8719 -1.2213 -1.2466  1.6890  0.2694  0.0003
                                                 [|R(BCP)-R(NBCP)|=  0.0011]
C  2- O  3  BCP   0.4122 -0.2203  1.8546 -1.0044 -1.0705 -0.5137  0.1637  0.0000
            NBCP  0.4203 -0.1661  1.7268 -0.8540 -1.0390 -0.5226  0.1553  0.0000
                                                 [|R(BCP)-R(NBCP)|=  0.0123]
C  2- H  6  BCP   0.2772 -0.9466  0.5480 -0.7382 -0.7564 -0.1431  1.1029  0.0001
            NBCP  0.2746 -0.8296  0.6229 -0.7220 -0.7305 -0.1426  1.1107  0.0001
                                                 [|R(BCP)-R(NBCP)|=  0.0078]
```

For each listed pair of atoms in the first column, the successive columns describe the density ("Rho"), Laplacian density ("Lapl."), the three Hessian eigenvalues ("Laplacian curvatures"), and the Cartesian position vector ("Coordinates") for the listed BCP and/or NBCP, with the spatial separation ("|R(BCP)-R(NBCP)|", in Å) listed below. As seen in the table, the five atom pairs exhibit BCP features that are generally in close proximity to an idealized NBCP (within 0.01-0.03Å in all cases). The BCP and NBCP are also found to have similar density (within 2% in all cases), and the corresponding Laplacian densities are also of similar magnitude and sign (but with significantly larger differences, ranging up to ca. 35%). Such close agreement of total $\rho(\mathbf{r}_{BCP})$ and idealized $\rho(\mathbf{r}_{NBCP})$ densities is rather typical, suggesting why NAO/NBO descriptors are often highly correlated with measures of chemical bonding interactions inferred from topological BCP densities (although corresponding correlations with Lagrangian densities are significantly weaker).

In the second portion of default NBCP output, the five BCP features are analyzed in terms of individual NBO contributions, as shown below:

```
NBO-based contributions to   5 bond critical points

BCP  1.  N  1- C  2: (  0.2969,  0.1851,  0.0000)
------------------------------------------------
  NBO   1.  N 1- C 2 : Rho = 0.3032 ( 95.9%), LaplRho = -1.6879
  NBO   2.  N 1- H 4 : Rho = 0.0038 (  1.2%), LaplRho = -0.0312
  NBO   3.  N 1- H 5 : Rho = 0.0042 (  1.3%), LaplRho = -0.0344
  NBO   6.  C 2- H 6 : Rho = 0.0005 (  0.2%), LaplRho =  0.1338
  NBO   7.  N 1(cr)  : Rho = 0.0006 (  0.2%), LaplRho = -0.0026
  NBO   8.  C 2(cr)  : Rho = 0.0007 (  0.2%), LaplRho =  0.2435
  NBO  12.  O 3(lp)  : Rho = 0.0027 (  0.8%), LaplRho = -0.0220
  NBO  30.  C 2(ry*) : Rho = 0.0004 (  0.1%), LaplRho = -0.0009
  NBO  31.  C 2(ry*) : Rho = 0.0014 (  0.4%), LaplRho = -0.0226
  NBO  82.  N 1- C 2*: Rho = 0.0084 (  2.7%), LaplRho = -0.0184
              [others =-0.0098 ( -3.1%)           0.5622]
                 Total 0.3161                    -0.8805

BCP  2.  N  1- H  4: (  1.1615, -0.8970,  0.0003)
------------------------------------------------
  NBO   2.  N 1- H 4 : Rho = 0.3352 ( 99.4%), LaplRho = -1.8259
  NBO   3.  N 1- H 5 : Rho = 0.0005 (  0.1%), LaplRho =  0.0301
  NBO   6.  C 2- H 6 : Rho = 0.0002 (  0.1%), LaplRho =  0.0030
  NBO   7.  N 1(cr)  : Rho = 0.0006 (  0.2%), LaplRho = -0.0041
```

```
  NBO   64.  H 4(ry*) : Rho = 0.0001 (   0.0%), LaplRho =   0.0005
  NBO   83.  N 1- H 4*: Rho = 0.0006 (   0.2%), LaplRho =   0.0218
                   [others = 0.0000 (   0.0%)              0.1301]
                       Total 0.3372                       -1.6445

 BCP   3.  N  1- H   5: (   1.6892,  0.2683,  0.0003)
 ------------------------------------------------------
   NBO    2.  N 1- H 4 : Rho = 0.0004 (   0.1%), LaplRho =   0.0334
   NBO    3.  N 1- H 5 : Rho = 0.3378 (  99.4%), LaplRho =  -1.8298
   NBO    5.  C 2- O 3 : Rho = 0.0001 (   0.0%), LaplRho =   0.0005
   NBO    6.  C 2- H 6 : Rho = 0.0002 (   0.1%), LaplRho =   0.0003
   NBO    7.  N 1(cr)  : Rho = 0.0006 (   0.2%), LaplRho =  -0.0043
   NBO   84.  N 1- H 5*: Rho = 0.0004 (   0.1%), LaplRho =   0.0152
                   [others = 0.0003 (   0.1%)              0.1454]
                       Total 0.3397                       -1.6392

 BCP   4.  C  2- O   3: (  -0.5137,  0.1637,  0.0000)
 ------------------------------------------------------
   NBO    1.  N 1- C 2 : Rho = 0.0002 (   0.0%), LaplRho =   0.1604
   NBO    2.  N 1- H 4 : Rho = 0.0010 (   0.2%), LaplRho =  -0.0036
   NBO    3.  N 1- H 5 : Rho = 0.0012 (   0.3%), LaplRho =  -0.0121
   NBO    5.  C 2- O 3 : Rho = 0.3676 (  89.2%), LaplRho =  -2.7691
   NBO    6.  C 2- H 6 : Rho = 0.0017 (   0.4%), LaplRho =   0.2275
   NBO    8.  C 2(cr)  : Rho = 0.0107 (   2.6%), LaplRho =   1.6365
   NBO    9.  O 3(cr)  : Rho = 0.0006 (   0.2%), LaplRho =  -0.0011
   NBO   11.  O 3(lp)  : Rho = 0.0175 (   4.3%), LaplRho =  -0.2191
   NBO   30.  C 2(ry*) : Rho = 0.0017 (   0.4%), LaplRho =   0.0020
   NBO   31.  C 2(ry*) : Rho = 0.0002 (   0.0%), LaplRho =   0.0006
   NBO   82.  N 1- C 2*: Rho = 0.0003 (   0.1%), LaplRho =   0.0282
   NBO   86.  C 2- O 3*: Rho = 0.0012 (   0.3%), LaplRho =  -0.0123
   NBO   87.  C 2- H 6*: Rho = 0.0003 (   0.1%), LaplRho =   0.0225
                   [others = 0.0081 (   2.0%)              0.7192]
                       Total 0.4122                       -0.2203

  BCP   5.  C  2- H   6: (  -0.1431,  1.1029,  0.0001)
 ------------------------------------------------------
   NBO    2.  N 1- H 4 : Rho = 0.0001 (   0.0%), LaplRho =   0.0019
   NBO    3.  N 1- H 5 : Rho = 0.0003 (   0.1%), LaplRho =   0.0005
   NBO    6.  C 2- H 6 : Rho = 0.2735 (  98.6%), LaplRho =  -1.0297
   NBO    8.  C 2(cr)  : Rho = 0.0003 (   0.1%), LaplRho =  -0.0036
   NBO   12.  O 3(lp)  : Rho = 0.0009 (   0.3%), LaplRho =  -0.0016
                   [others = 0.0021 (   0.8%)              0.0859]
                       Total 0.2772                       -0.9466
```

For each BCP, the table displays an exhaustive list of all orbitals contributing at least 0.0001e to $\rho(\mathbf{r}_{NBCP})$. Nevertheless, the table shows that the hydride BCP densities derive ca. 99% from the *single* NBO that is "expected" to link the atoms in elementary Lewis structure representation. The resonance-delocalized C-N (BCP 1) and C-O (BCP 4) BCP densities exhibit somewhat weaker contributions from the dominant "parent" NBOs (96% and 89%, respectively). However, both the reduced percentages and the unusually large NBO contributions from off-diagonal couplings (included in "others") are characteristic signatures of the important *resonance* delocalization in these bonds, as expected on chemical grounds.