Q C P E

QUANTUM CHEMISTRY PROGRAM EXCHANGE
QCPE PROGRAM No. QCPE0802/LNUX101

AIMDELOC 01: Program to Calculate the Localization and Delocalization Indices According to the Quantum Theory of Atoms-In-Molecules (AIM)

by

Chérif F. Matta

Chemistry Department, McMaster University,

1280 Main St. W., Hamilton, Ontario, Canada L8S 4M1.

email: mattacf@mcmaster.ca

R

QCPE Program Number:

QCPE0802

Program Title:

AIMDELOC01: Program for Calculating
Localization and Delocalization Indeces
according to the Quantum Theory of
Atoms-In-Molecules (AIM).

Author:

Chérif F. Matta

Lines of Code:

350

Platform/Language:

Linux bash shell script with some awk commands.

Recommended Citation:

Matta, C.F. and Hernandez-Trujillo, J.
"Aromaticity in Polycyclic Arenes as a Manifestation of
the Delocalization of the Fermi Hole: Benzene,
Naphthalene, Anthracene, Phenanthrene, and
Chrysene." To be submitted to J. Am. Chem. Soc. in August
2001.

Description:

This package contains executable program plus documentation
and sample data files.

PURPOSE

This program is a UNIX shell script designed to calculate the localization and delocalization indices according to the Quantum Theory of Atoms-In-Molecules (QT-AIM) developed by Bader and coworkers.[1]   The input of AIMDELOC consists of the atomic basin integrations files (.int) obtained from the program PROAIM, which is part of the AIMPAC suite of programs,[2-4].   The integration files must contain the atomic overlap matrices, an option which can be turned on within the input of PROAIM.

The output of AIMDELOC is the lower (or upper) triangular matrix elements giving the localization indeces of each atom (diagonal elements), and the delocalization indeces between each possible pair of atoms (off diagonal elements). Only half of the matrix is given in the output since it is a symmetric matrix (because delocalization between atom A and B is the same as the delocalization between atom B and A). The result is written into a file, and the sum of the indeces is given at the bottom of this file, a sum which should be equal to the number of electrons in the molecule. Thus, deviations of this sum from the closest integer number of electrons constitutes a measure of the total integration error over all of the atomic basins.

Language and Platforms

UNIX shell script.   AIMDELOC consists of approximately 250 lines of code (without counting commented lines). It is tested extensively under Linux Red Hat, but may require minor editing for other flavors of UNIX.

Hardware

Any hardware supporting a version of UNIX, e.g. IBM workstations, SGI workstations, or PCs with a version of Linux.

Running time

Typically a few minutes, depending on the number and type of atoms and the size of the basis set.

THEORETICAL BACKGROUND

(I) The Quantum Theory of Atoms-In-Molecules (QT-AIM)

The quantum theory of Atoms-In-Molecules (QT-AIM)[1] extracts chemically-relevant information from the topology of the electron density, whether experimental or theoretically calculated. QT-AIM is a model-free generalization of quantum mechanics from those of a whole isolated (closed) systems to those of open sub-systems. The theory provides a stringent condition to partition a whole quantum system (e.g. a molecule) into a unique set of sub-systems (its constituent atoms) the properties of which add-up to recover those of the whole system. It is shown within this theory that one cannot partition the total system arbitrarily but rather the surfaces of partitioning (the interatomic surfaces) must satisfy the condition of local zero-flux in the gradient vector field of the electron density, mathematically this is written:[1]

$$\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})=0 , \quad \text{for all points } \mathbf{r}_s \text{ on the surface } S(\mathbf{r}_s,\Omega). \tag{1}$$

As a consequence of partitioning the molecule at these zero-flux surfaces, the same theorems that apply for the whole molecule (e.g. the virial theorem) apply to each of the constituent atoms. Every property is represented by a real space "dressed" density that describes the average interaction of a single electron with all the remaining particle in the whole system (e.g. the virial density). In this way, the contribution to property A from atom S is given by the integration of its corresponding density $D_A(\mathbf{r})$ over the atomic basin:

$$A(\Omega)=\int_{\Omega}\rho_A(r)\,dr. \tag{2}$$

It follows from Eq.(2) that the atomic properties are additive, i.e. the average value of property A for the whole system (the molecule) is obtained by summing the atomic contributions, this is expressed:

$$\langle A\rangle=\sum_{\Omega}A(\Omega). \tag{3}$$

Thus, atomic properties such as populations/partial charges, atomic energies, atomic multipoles, atomic volumes can be readily calculated using software implementing QT-AIM such as the AIMPAC suite of programs.[2-4]

The way the density of an electron is spread in space from a given point in space is quantitatively described by it's Fermi hole density. When used in conjunction with QT-AIM, the Fermi whole density provides a consistent conceptual framework within which the localization of electrons within the basin of an atom and their delocalization between two atoms (or two groups of atoms) acquire a precise physical meaning within the Hartree-Fock (HF) or the Configuration Interaction (CI) schemes.[5]

(II) Localization, Delocalization and the Fermi Hole and QT-AIM

A Hartree-Fock (HF) density does not take correlation between electrons of different spin (Coulomb correlation) into account, it only include spin (Fermi)-correlation. Therefore, in the HF scheme the pair density is the simple product of densities of the α - and the β-spin densities multiplied by ½ not to count the same pair twice:[6]

$$\rho^{\alpha\beta}(\mathbf{r_1},\mathbf{r_2})=\frac{1}{2}\rho^{\alpha}(\mathbf{r_1})\rho^{\beta}(\mathbf{r_2}). \tag{4}$$

In Eq.(4), the pair density $D^{\alpha\beta}(\mathbf{r_1},\mathbf{r_2})$ is the conditional probability of finding simultaneously an α-electron at $\mathbf{r_1}$ and a β-electron at $\mathbf{r_2}$. For same-spin electrons, however, the density at $\mathbf{r_2}$, $D^{\alpha}(\mathbf{r_2})$ is less than the one for an opposite-spin electron D^{β} due to the operation of Pauli exclusion principle. The amount by which the same-spin density is reduced (with respect to the opposite-spin density) at $\mathbf{r_2}$ is known as the Fermi hole density $h^{\alpha}(\mathbf{r_1},\mathbf{r_2})$. The same spin density is thus:[6]

$$\rho^{\alpha\alpha}(\mathbf{r_1},\mathbf{r_2})=\frac{1}{2}\rho^{\alpha}(\mathbf{r_1})[\rho^{\alpha}(\mathbf{r_2})-h^{\alpha}(\mathbf{r_1},\mathbf{r_2})], \tag{5}$$

where the Fermi hole density (henceforth referred as Fermi density) for an α-spin electron is expressed in terms of spin orbitals N_i as:

$$h^{\alpha}(r_1, r_2) = -\frac{\sum\limits_{i}^{\alpha}\sum\limits_{j}^{\alpha}[\phi_i^*(\mathbf{r_1})\phi_i(\mathbf{r_2})\phi_j^*(\mathbf{r_2})\phi_j(\mathbf{r_1})]}{\rho^{\alpha}(\mathbf{r_1})} \ . \tag{6}$$

The Fermi density of each electron integrates over the whole molecule to −1, which corresponds to the removal of the density of one electron. The total Fermi correlation (F), defined as the integral of the Fermi density over all space for each electron in the system equals to the negative of the total number of "- and $-electrons in the system (-N). The Fermi correlation for a subsystem (e.g. for an atom A in a molecule, as defined above) denoted F(A,A) is related to the pair density $D^{''}(\mathbf{r_1,r_2})$ by the expression:[7]

$$\text{Total number of pairs in atom } A = D_2(A,A)$$

$$= \int_A d\mathbf{r_1} \int_A d\mathbf{r_2}\, \rho(\mathbf{r_1},\mathbf{r_2})$$

$$= \frac{N(A)^2 + F(A,A)}{2}, \tag{7}$$

where N(A) is the population of atom A. If T is the total space of the quantum system (the whole molecule), then F(T,T)=-N, and the double integral will reduce to ½ N(N-1), which is the total number of pairs formed between a set of same-spin electrons without counting self pairing (N self-pairs). Similarly, the unattainable limit of F(A,A) over the atomic basin of atom A in a molecule is – N(A). In this case, the self-pairing correction would be completely contained within basin A and the N(A) electrons would be totally localized within this basin with no probability of finding them anywhere else in the molecule. It follows that the magnitude of F(A,A) is a measure of the degree of localization of the electrons of atom A within its basin and is termed the *atomic localization index* and is denoted by 8(A).

If instead of a double integral over the basin of one and the same atom, one integral is performed over the basin of atom A and the other over the basin of another atom B then Eq.(7) becomes:[7]

Total number of pairs shared between atoms A and $B = D_2(A,B)$

$$= \int_A d\mathbf{r_1} \int_B d\mathbf{r_2} \, \rho(\mathbf{r_1},\mathbf{r_2})$$

$$= \frac{N(A)\,N(B)+F(A,B)}{2}, \qquad (8)$$

in which the quantity *F(A,B)* is now a measure of the delocalization of the electrons referenced to *A* into the basin of another atom *B*, i.e. it is a measure of how much the Fermi density of a reference electron in *A* is spread into basin *B*. Integration of the coordinates of one electron of the pair density over *A* and of the second over *A+B* yields:

Total number of pairs in atom A

+ the number shared between atoms A and $B =$

$$= \int_A d\mathbf{r_1} \int_{A+B} d\mathbf{r_2} \, \rho(\mathbf{r_1},\mathbf{r_2})$$

$$= \frac{N(A)^2 + N(A)\,N(B)+F(A,A)+F(A,B)}{2},$$

(9)

From Eq.7-9 it can be shown that:[7]

$$F(A,A)+\sum_B F(A,B)=-N(A). \qquad (10)$$

Eq.10 shows that the Fermi density of *N(A)* electrons referenced in atom *A* is delocalized over the remaining atoms in the molecule and that the amount delocalized over atom *B* is given by *F(A,B)*. The sum of the magnitudes of *F(A,B)* and *F(B,A)* is called the *delocalization index* [*(A,B)*].

Within HF theory, the atomic localization index and the delocalization index are:[5]

$$F(A,A)= -\sum_i \sum_j S_{ij}(A)^2,$$

and

$$F(A,B)= F(B,A)= -\sum_i \sum_j S_{ij}(A)S_{ij}(B), \qquad (11)$$

respectively, where S_{ij} denotes the overlap of a pair of spin orbitals over an atom.

HOW TO USE AIMDELOC

(a) Installing AIMDELOC

1. Save a copy of AIMDELOC in a directory declared in the user's $PATH variable of UNIX.

2. Make AIMDELOC executable by invoking a command such as:

    chmod a+x aimdeloc

    (Remember UNIX is <u>case-sensitive</u>)

(b) Using AIMDELOC

1. Put all the integration files (.int) corresponding to the atoms of the molecule of interest (only) in **one** directory.

2. Run AIMDELOC by invoking the command:

    aimdeloc

A screen such as the following will appear:

```
-------------------------------------------------------
ATOMS-IN-MOLECULES DELOCALIZATION INDECES (AIMDELOC)
-------------------------------------------------------


Copywright owner:
            Cherif F. Matta
Chemistry Department, McMaster University,
      Hamiton, Ontario, Canada L8S 4M1


WARNING!
========
File names: *tmp*, *temp*, *table*, *delete*, *trunc*, *.*.joint
will be lost in this directory.
If you wish to exit use 'Cntrl+c' key combination

    The integration files were generated using:
    ----------------------------------------------
    [1]  PROAIMV - Version 94 - Revision B
    [2]  PAIM96 - Version 96, Revision C

    Choose ONE option  1  or  2 :
```

Choose the option referring to the version of the program PROAIM that was used to generate the integration files (Option 1 or 2) and hit enter. The version of PROAIM used is given in the first line of the integrations (.int) files. For the water example provided choose the first option (Enter 1). A sequence of screens similar to the following indicate the execution of different parts of the program:

```
        AIMDELOC  RUNNING
           Please wait

Append/transpose row 1 of the overlap matrix of H1.int to the column
Append/transpose row 2 of the overlap matrix of H1.int to the column
Append/transpose row 3 of the overlap matrix of H1.int to the column
Append/transpose row 4 of the overlap matrix of H1.int to the column
Append/transpose row 5 of the overlap matrix of H1.int to the column

        Column rep. of the matrix H1.int done!

Append/transpose row 1 of the overlap matrix of H3.int to the column
Append/transpose row 2 of the overlap matrix of H3.int to the column
Append/transpose row 3 of the overlap matrix of H3.int to the column
Append/transpose row 4 of the overlap matrix of H3.int to the column
Append/transpose row 5 of the overlap matrix of H3.int to the column

        Column rep. of the matrix H3.int done!
```

....

....

```
Append/transpose row 4 of the overlap matrix of O2.int to the column
Append/transpose row 5 of the overlap matrix of O2.int to the column

        Column rep. of the matrix O2.int done!


        First part done!
        Overlap matrices converted into single column representation.

         AIMDELOC RUNNING
           Please wait

        Overlap matrix indeces done!

         AIMDELOC RUNNING
           Please wait

joining  H1.int.table  and  H1.int.table, cycle 1,0
joining  H1.int.table  and  H3.int.table, cycle 1,1
joining  H1.int.table  and  O2.int.table, cycle 1,2
joining  H3.int.table  and  H3.int.table, cycle 2,0
joining  H3.int.table  and  O2.int.table, cycle 2,1
joining  O2.int.table  and  O2.int.table, cycle 3,0
```

....

....

```
    H1 H1 delta(A,A) = !F(A,A)!         =    0.06555036
    H1 H3 delta(A,B) = !F(A,B)+!F(B,A)! =    0.00674664
    H1 O2 delta(A,B) = !F(A,B)+!F(B,A)! =    0.62319164
    H3 H3 delta(A,A) = !F(A,A)!         =    0.06555036
    H3 O2 delta(A,B) = !F(A,B)+!F(B,A)! =    0.62319164
    O2 O2 delta(A,A) = !F(A,A)!         =    8.61573320
    ----------------------------------------------
      SUM [ ! F(AB) ! ]   =      9.99996384
    ----------------------------------------------
    Normal termination of AIMDELOC.


        All atom-atom permutations done and bond orders computed

        YOUR RESULTS ARE SUMMARIZED IN THE FILE:  deloc.dlc
                                                  =========
        AIMDELOC DONE
        *************


Normal termination of AIMDELOC on:
Tue Mar 13 10:29:07 EST 2001

[cherif@einstein water]$
```

Example I (Complete example): Water

(1)   INPUT

(three atomic integration files, all in ONE directory)

(1.1) Integration File of the first hydrogen atom

(atom number 1): H1

PROAIMV - Version 94 - Revision B

 water
 -V/T FOR THIS WAVEFUNCTION =   2.00209431000
 MOLECULAR SCF ENERGY (AU) =   -76.02361501636

water
PROAIM SURFACE ALGORITHM USED
Critical Points in Atomic Surface:
  1 Bond   2.66545799E-33   1.14377116E+00 -6.58378537E-01
Optional Parameters Read From Input
 INTEGRATION IS OVER ATOM   H   1
 DYNAMIC CUTOFFS USED THROUGHOUT
 CUTOFF VALUE USED IS 1.00E-09
 PRE-INTEGRATION PRIMITIVE CUTOFF ALGORITHM USED
 TOTAL NUMBER OF PRIMITIVES =   42
 NUMBER OF PRIMITIVES USED OUTSIDE BETA SPHERE=   31
 NUMBER OF PRIMITIVES USED INSIDE BETA SPHERE=   31
   72 OF THE   155 PRIM COEFFS ZEROED OUTSIDE BETA SPHERE
   62 OF THE   155 PRIM COEFFS ZEROED INSIDE BETA SPHERE
 RADIUS OF BETA SPHERE: 0.3433 WITH   120 POINTS PER RAY
Default number of theta and phi planes used for Beta Sphere
    6 PHI AND   4 THETA PLANES IN BETA SPHERE
   96 PHI AND   96 THETA PLANES OUTSIDE BETA SPHERE
Integrate Out to 9.00E+00 For Rays Intersecting Surface at Infinity
 VOL1 RHO CONTOUR THRESHOLD=   0.0010
 VOL2 RHO CONTOUR THRESHOLD=   0.0020
Doing Beta Sphere Integration ...
Beta Sphere Integration is done ...
Doing Proaim Surface Routine ...
    80 Initial GradRho Trajectories Per Interatomic Surface
   140 Points per GradRho Surface Trajectory
Max. Dist. Between Ends of Adjacent GradRho Surface Trajectories = 6.00E-01
Maximum Length of GradRho Surface Trajectories = 8.00E+00
 INSERTION LIMIT USED   =   6
 INSERTION LIMIT REACHED   0 TIMES FOR SURFACE   1
 FOR SURFACE # 1 NUMBER OF INSERTED PATHS =   22
 TOTAL NUMBER OF INSERTED PATHS=   22
Surface is done ...
Doing Integration Outside of Beta Sphere ...
Default number of radial points used
Integration Outside of Beta Sphere is Done ...

RESULTS OF THE INTEGRATION

N	3.80523824580906E-01	NET CHARGE	6.19476175419094E-01
G	3.43781061866452E-01		
K	3.43825961717165E-01	E(ATOM)	-3.44546039867049E-01
L	4.48998507128778E-05		
I	1.99366116370111E-01		
R(-1)	6.65056983129070E-01		
R1	3.38417385735130E-01		
R2	4.24162302187338E-01		
R4	1.39330788629000E+00		
GR(-1)	-8.70144552792430E-01		
GR0	-8.29872304627924E-01		
GR1	-1.08572784712492E+00		
GR2	-1.82141367758687E+00		
VNEO	-6.65056983129070E-01	VNEO(COR)	-6.65752672379761E-01
VNET	-2.16802632413046E+00	VNET(COR)	-2.17029420890902E+00
VEET	7.59490452063890E-01	VEET(COR)	7.60284924352592E-01
EHF	-1.06470991034941E+00		
		VREP(COR)	1.48044879483495E+00
		V(ATOM)	-6.89845414074069E-01
EL DX	-5.29906825404073E-08		
EL DY	-1.23188275138175E-01		
EL DZ	9.22990371426744E-02		
EL DIPOLE MAG	1.53930060056463E-01		

ATOMIC QUADRUPOLE MOMENT TENSOR

QXX	3.56542427294804E-02
QXY	-1.12527445418110E-06
QXZ	-9.20699374589318E-07
QYY	-2.67653535263872E-02
QYZ	3.82247680663275E-02
QZZ	-8.88888920309337E-03

EIGENVALUES OF QUADRUPOLE MOMENT TENSOR:
3.56542428723813E-02   2.14287683431968E-02   -5.70830112155783E-02

EIGENVECTORS OF QUADRUPOLE MOMENT TENSOR:
9.99999995008022E-01   -9.98639942859400E-05   -3.33737338434179E-06
-6.46715708731764E-05   -6.21413106844865E-01   -7.83483086262237E-01
-7.61678628861575E-05   -7.83483082566940E-01   6.21413110201146E-01

FAXA	-3.32339744170401E-07
FAYA	4.31489549779392E-02
FAZA	-3.65118792164569E-02
FBXA	-7.73705333240136E-08
FBYA	5.40668964024877E-01
FBZA	-3.81776199128877E-01
RHO*L	5.52293655437397E-02
VOL1	1.89526643556288E+01
VOL2	1.41119716889730E+01
N(VOL1)	3.71195833728326E-01
N(VOL2)	3.64360932274851E-01

MAXIMUM DISTANCE REACHED FROM NUCLEUS = 8.9969919944E+00

The Atomic Overlap Matrix

Restricted Closed-Shell Wavefunction

```
 0.000000
 0.000032  0.037845
 0.000063  0.061862  0.105520
-0.000037 -0.037840 -0.062811  0.042168
 0.000000  0.000000  0.000000  0.000000  0.004727
```

ALPHA ELECTRONS (NA)	1.90260305870185E-01
BETA ELECTRONS (NB)	1.90260305870185E-01
TOTAL ELECTRONS (N)	3.80520611740371E-01
ALPHA FERMI CORRELATION (FOOA)	-3.27753659179714E-02
BETA FERMI CORRELATION (FOOB)	-3.27753659179714E-02
ALPHA LOCALIZATION (ALOC)	1.72265916256511E-01
BETA LOCALIZATION (BLOC)	1.72265916256511E-01
ALPHA FLUCTUATION (FLA)	1.57484939952214E-01
BETA FLUCTUATION (FLB)	1.57484939952214E-01

NORMAL TERMINATION OF PROAIMV

(1.2) Integration File of the oxygen atom

(atom number 2): O2

PROAIMV - Version 94 - Revision B

 water
 -V/T FOR THIS WAVEFUNCTION =   2.00209431000
 MOLECULAR SCF ENERGY (AU) =   -76.02361501636

water
PROAIM SURFACE ALGORITHM USED
Critical Points in Atomic Surface:
 1 Bond   2.66545799E-33   1.14377116E+00 -6.58378537E-01
 2 Bond -1.46307207E-32 -1.14377116E+00 -6.58378537E-01
Optional Parameters Read From Input
 INTEGRATION IS OVER ATOM   O   2
 DYNAMIC CUTOFFS USED THROUGHOUT
 CUTOFF VALUE USED IS 1.00E-09
 PRE-INTEGRATION PRIMITIVE CUTOFF ALGORITHM USED
 TOTAL NUMBER OF PRIMITIVES =   42
 NUMBER OF PRIMITIVES USED OUTSIDE BETA SPHERE=   32
 NUMBER OF PRIMITIVES USED INSIDE BETA SPHERE=   42
   72 OF THE   160 PRIM COEFFS ZEROED OUTSIDE BETA SPHERE
   20 OF THE   210 PRIM COEFFS ZEROED INSIDE BETA SPHERE
 RADIUS OF BETA SPHERE: 1.4388 WITH   120 POINTS PER RAY
Default number of theta and phi planes used for Beta Sphere
   36 PHI AND   24 THETA PLANES IN BETA SPHERE
   96 PHI AND   96 THETA PLANES OUTSIDE BETA SPHERE
Integrate Out to 9.00E+00 For Rays Intersecting Surface at Infinity

VOL1 RHO CONTOUR THRESHOLD=   0.0010
VOL2 RHO CONTOUR THRESHOLD=   0.0020
Doing Beta Sphere Integration ...
Beta Sphere Integration is done ...
Doing Proaim Surface Routine ...
    80 Initial GradRho Trajectories Per Interatomic Surface
    140 Points per GradRho Surface Trajectory
Max. Dist. Between Ends of Adjacent GradRho Surface Trajectories = 6.00E-01
Maximum Length of GradRho Surface Trajectories = 8.00E+00
 INSERTION LIMIT USED   =   6
 INSERTION LIMIT REACHED   0 TIMES FOR SURFACE   1
 INSERTION LIMIT REACHED   0 TIMES FOR SURFACE   2
 FOR SURFACE # 1 NUMBER OF INSERTED PATHS =   22
 FOR SURFACE # 2 NUMBER OF INSERTED PATHS =   22
 TOTAL NUMBER OF INSERTED PATHS=   44
Surface is done ...
Doing Integration Outside of Beta Sphere ...
Default number of radial points used
Integration Outside of Beta Sphere is Done ...

 RESULTS OF THE INTEGRATION
        N 9.23894845269983E+00   NET CHARGE -1.23894845269983E+00
        G 7.51771179991016E+01
        K 7.51770932454561E+01   E(ATOM) -7.53345373836110E+01
        L -2.47536455323028E-05
        I 2.64066976325279E+00
     R(-1) 2.30913366405568E+01
       R1 9.52656118366460E+00
       R2 1.44130811752547E+01
       R4 5.84019155333234E+01
    GR(-1) -4.52603597497707E+01
      GR0 -2.60555287861953E+01
      GR1 -3.49957202684679E+01
      GR2 -6.59530952165873E+01
     VNEO -1.84730693124454E+02   VNEO(COR) -1.84923932441895E+02
     VNET -1.94868502090833E+02   VNET(COR) -1.95072346160803E+02
     VEET 3.64673708425503E+01   VEET(COR) 3.65055178863973E+01
      EHF -8.32240380028266E+01
                         VREP(COR) 4.43950185056128E+01
                          V(ATOM) -1.50677327655190E+02
     EL DX -2.38745257134657E-08
     EL DY 2.46759755776491E-16
     EL DZ 2.99622824080028E-01
  EL DIPOLE MAG 2.99622824080029E-01

   ATOMIC QUADRUPOLE MOMENT TENSOR
        QXX -7.21591526366375E-01
        QXY 1.18361419434001E-16
        QXZ 1.92079410882619E-06
        QYY 7.83761083144845E-01
        QYZ -1.76868023273884E-17
        QZZ -6.21695567784710E-02

   EIGENVALUES OF QUADRUPOLE MOMENT TENSOR:
     7.83761083144845E-01 -7.21591526371970E-01 -6.21695567728761E-02

EIGENVECTORS OF QUADRUPOLE MOMENT TENSOR:

```
 8.61790927000061E-17   9.99999999995758E-01   2.91284518470337E-06
 1.00000000000000E+00   1.96648301880415E-18   2.09080225039835E-17
-2.09080167758342E-17  -2.91284518470337E-06   9.99999999995758E-01
```

```
    FAXA    3.01917884651128E-07
    FAYA    1.97878609885474E-14
    FAZA   -1.27850448867748E+00
    FBXA    1.17086485705721E-06
    FBYA   -1.57512502512934E-15
    FBZA    3.10921409007521E+00
    RHO*L   4.65133862473618E+03
    VOL1    1.35947421436461E+02
    VOL2    1.10756236606682E+02
   N(VOL1)  9.19840139692710E+00
   N(VOL2)  9.16259863458802E+00
```

MAXIMUM DISTANCE REACHED FROM NUCLEUS = 8.9973726517E+00

The Atomic Overlap Matrix

Restricted Closed-Shell Wavefunction

```
 0.999999
-0.000086  0.924310
 0.000000  0.000000  0.788965
 0.000091  0.075685  0.000000  0.915656
 0.000000  0.000000  0.000000  0.000000  0.990541
```

```
    ALPHA ELECTRONS (NA)           4.61947043296209E+00
    BETA ELECTRONS (NB)            4.61947043296209E+00
    TOTAL ELECTRONS (N)            9.23894086592418E+00
    ALPHA FERMI CORRELATION (FOOA)   -4.30786550270746E+00
    BETA FERMI CORRELATION (FOOB)    -4.30786550270746E+00
    ALPHA LOCALIZATION (ALOC)        9.32545313412726E-01
    BETA LOCALIZATION (BLOC)         9.32545313412726E-01
    ALPHA FLUCTUATION (FLA)          3.11604930254635E-01
    BETA FLUCTUATION (FLB)           3.11604930254635E-01
```

NORMAL TERMINATION OF PROAIMV

(1.3) Integration File of the second hydrogen atom

(atom number 3): H3

PROAIMV - Version 94 - Revision B

water
-V/T FOR THIS WAVEFUNCTION =   2.00209431000
MOLECULAR SCF ENERGY (AU) =   -76.02361501636

water

PROAIM SURFACE ALGORITHM USED
Critical Points in Atomic Surface:
  1 Bond -1.46307207E-32 -1.14377116E+00 -6.58378537E-01
Optional Parameters Read From Input
 INTEGRATION IS OVER ATOM   H   3
 DYNAMIC CUTOFFS USED THROUGHOUT
 CUTOFF VALUE USED IS 1.00E-09
 PRE-INTEGRATION PRIMITIVE CUTOFF ALGORITHM USED
 TOTAL NUMBER OF PRIMITIVES =   42
 NUMBER OF PRIMITIVES USED OUTSIDE BETA SPHERE=   31
 NUMBER OF PRIMITIVES USED INSIDE BETA SPHERE=   31
   72 OF THE   155 PRIM COEFFS ZEROED OUTSIDE BETA SPHERE
   62 OF THE   155 PRIM COEFFS ZEROED INSIDE BETA SPHERE
 RADIUS OF BETA SPHERE: 0.3433 WITH   120 POINTS PER RAY
Default number of theta and phi planes used for Beta Sphere
    6 PHI AND   4 THETA PLANES IN BETA SPHERE
   96 PHI AND   96 THETA PLANES OUTSIDE BETA SPHERE
Integrate Out to 9.00E+00 For Rays Intersecting Surface at Infinity
 VOL1 RHO CONTOUR THRESHOLD=   0.0010
 VOL2 RHO CONTOUR THRESHOLD=   0.0020
Doing Beta Sphere Integration ...
Beta Sphere Integration is done ...
Doing Proaim Surface Routine ...
   80 Initial GradRho Trajectories Per Interatomic Surface
  140 Points per GradRho Surface Trajectory
Max. Dist. Between Ends of Adjacent GradRho Surface Trajectories = 6.00E-01
Maximum Length of GradRho Surface Trajectories = 8.00E+00
 INSERTION LIMIT USED   =   6
 INSERTION LIMIT REACHED   0 TIMES FOR SURFACE   1
 FOR SURFACE # 1 NUMBER OF INSERTED PATHS =   22
 TOTAL NUMBER OF INSERTED PATHS=   22
Surface is done ...
Doing Integration Outside of Beta Sphere ...
Default number of radial points used
Integration Outside of Beta Sphere is Done ...

 RESULTS OF THE INTEGRATION
        N   3.80523824580906E-01   NET CHARGE   6.19476175419094E-01
        G   3.43781061866452E-01
        K   3.43825961717165E-01   E(ATOM) -3.44546039867049E-01
        L   4.48998507128897E-05
        I   1.99366116370112E-01
      R(-1)   6.65056983129070E-01
       R1   3.38417385735130E-01
       R2   4.24162302187338E-01
       R4   1.39330788629000E+00
     GR(-1) -8.70144552792430E-01
      GR0 -8.29872304627924E-01
      GR1 -1.08572784712492E+00
      GR2 -1.82141367758687E+00
     VNEO -6.65056983129070E-01   VNEO(COR) -6.65752672379761E-01
     VNET -2.16802632413046E+00   VNET(COR) -2.17029420890902E+00
     VEET   7.59490452063890E-01   VEET(COR)   7.60284924352592E-01
      EHF -1.06470991034941E+00
                        VREP(COR)   1.48044879483495E+00
                        V(ATOM) -6.89845414074070E-01

EL DX -5.29906825334461E-08
EL DY   1.23188275138175E-01
EL DZ   9.22990371426744E-02
EL DIPOLE MAG   1.53930060056463E-01

ATOMIC QUADRUPOLE MOMENT TENSOR
QXX   3.56542427294803E-02
QXY   1.12527445418166E-06
QXZ -9.20699374582753E-07
QYY -2.67653535263872E-02
QYZ -3.82247680663275E-02
QZZ -8.88888920309330E-03

EIGENVALUES OF QUADRUPOLE MOMENT TENSOR:
3.56542428723812E-02   2.14287683431968E-02   -5.70830112155783E-02

EIGENVECTORS OF QUADRUPOLE MOMENT TENSOR:
9.99999995008022E-01   9.98639942856036E-05   -3.33737338439052E-06
6.46715708730056E-05   -6.21413106844865E-01   7.83483086262237E-01
-7.61678628858637E-05   7.83483082566940E-01   6.21413110201146E-01

FAXA -3.32339744200725E-07
FAYA -4.31489549779394E-02
FAZA -3.65118792164569E-02
FBXA -7.73705333336139E-08
FBYA -5.40668964024877E-01
FBZA -3.81776199128877E-01
RHO*L   5.52293655437397E-02
VOL1   1.89526643556288E+01
VOL2   1.41119716889730E+01
N(VOL1)   3.71195833728326E-01
N(VOL2)   3.64360932274851E-01

MAXIMUM DISTANCE REACHED FROM NUCLEUS = 8.9969919944E+00

The Atomic Overlap Matrix

Restricted Closed-Shell Wavefunction

 0.000000
 0.000032 0.037845
-0.000063 -0.061862 0.105520
-0.000037 -0.037840 0.062811 0.042168
 0.000000 0.000000 0.000000 0.000000 0.004727

ALPHA ELECTRONS (NA)   1.90260305870185E-01
BETA ELECTRONS (NB)   1.90260305870185E-01
TOTAL ELECTRONS (N)   3.80520611740371E-01
ALPHA FERMI CORRELATION (FOOA)   -3.27753659179715E-02
BETA FERMI CORRELATION (FOOB)   -3.27753659179715E-02
ALPHA LOCALIZATION (ALOC)   1.72265916256511E-01
BETA LOCALIZATION (BLOC)   1.72265916256511E-01
ALPHA FLUCTUATION (FLA)   1.57484939952214E-01
BETA FLUCTUATION (FLB)   1.57484939952214E-01

NORMAL TERMINATION OF PROAIMV

(2) OUTPUT

(water_deloc.dlc file in the same directory which contains the .int files)

H1 H1 delta(A,A) = |F(A,A)| = 0.06555036
H1 H3 delta(A,B) = |F(A,B)+|F(B,A)| = 0.00674664
H1 O2 delta(A,B) = |F(A,B)+|F(B,A)| = 0.62319164
H3 H3 delta(A,A) = |F(A,A)| = 0.06555036
H3 O2 delta(A,B) = |F(A,B)+|F(B,A)| = 0.62319164
O2 O2 delta(A,A) = |F(A,A)| = 8.61573320
```
-----------------------------------
```
 SUM [| F(AB) |] =   9.99996384
```
-----------------------------------
```
 Normal termination of AIMDELOC.

These results can be cast into a tabular form:

|	H1	O2	H3
H1	0.06555		
O2	0.62319	8.61573	
H3	0.00675	0.62319	0.06555

Note the very low delocalization found between the two hydrogens and each other (since they do not share a bond path, and are not bonded). The sum of |F(AB)| is very close to the total number of electrons in the water molecule (10 e) indicating accurate integration results.

Example II (Output only): Butadiene

The integration files and the output file for butadiene are also provided and can serve as another trial case for the program. Choose option 2 when prompted by AIMDELOC since the integration files were obtained using PROAIM96.

Numbering scheme:
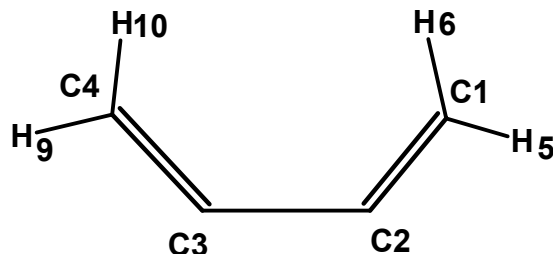
OUTPUT (butadiene_deloc.dlc):

```
but_c1 but_c1 delta(A,A) = |F(A,A)|        =  4.04682014
but_c1 but_c2 delta(A,B) = |F(A,B)+|F(B,A)| =  1.83067872
but_c1 but_c3 delta(A,B) = |F(A,B)+|F(B,A)| =  0.06779112
but_c1 but_c4 delta(A,B) = |F(A,B)+|F(B,A)| =  0.07304244
but_c1 but_h10 delta(A,B) = |F(A,B)+|F(B,A)| =  0.01007284
but_c1 but_h5 delta(A,B) = |F(A,B)+|F(B,A)| =  0.97352040
but_c1 but_h6 delta(A,B) = |F(A,B)+|F(B,A)| =  0.96538396
but_c1 but_h7 delta(A,B) = |F(A,B)+|F(B,A)| =  0.06018320
but_c1 but_h8 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00664744
but_c1 but_h9 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00393928
but_c2 but_c2 delta(A,A) = |F(A,A)|        =  3.96759196
but_c2 but_c3 delta(A,B) = |F(A,B)+|F(B,A)| =  1.07184888
but_c2 but_c4 delta(A,B) = |F(A,B)+|F(B,A)| =  0.06779112
but_c2 but_h10 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00650228
but_c2 but_h5 delta(A,B) = |F(A,B)+|F(B,A)| =  0.05845332
but_c2 but_h6 delta(A,B) = |F(A,B)+|F(B,A)| =  0.05610036
but_c2 but_h7 delta(A,B) = |F(A,B)+|F(B,A)| =  0.96103124
but_c2 but_h8 delta(A,B) = |F(A,B)+|F(B,A)| =  0.03821084
but_c2 but_h9 delta(A,B) = |F(A,B)+|F(B,A)| =  0.01002788
but_c3 but_c3 delta(A,A) = |F(A,A)|        =  3.96759196
but_c3 but_c4 delta(A,B) = |F(A,B)+|F(B,A)| =  1.83067872
but_c3 but_h10 delta(A,B) = |F(A,B)+|F(B,A)| =  0.05610036
but_c3 but_h5 delta(A,B) = |F(A,B)+|F(B,A)| =  0.01002788
but_c3 but_h6 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00650228
but_c3 but_h7 delta(A,B) = |F(A,B)+|F(B,A)| =  0.03821084
but_c3 but_h8 delta(A,B) = |F(A,B)+|F(B,A)| =  0.96103124
but_c3 but_h9 delta(A,B) = |F(A,B)+|F(B,A)| =  0.05845332
but_c4 but_c4 delta(A,A) = |F(A,A)|        =  4.04682014
but_c4 but_h10 delta(A,B) = |F(A,B)+|F(B,A)| =  0.96538396
but_c4 but_h5 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00393928
but_c4 but_h6 delta(A,B) = |F(A,B)+|F(B,A)| =  0.01007284
but_c4 but_h7 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00664744
but_c4 but_h8 delta(A,B) = |F(A,B)+|F(B,A)| =  0.06018320
but_c4 but_h9 delta(A,B) = |F(A,B)+|F(B,A)| =  0.97352040
but_h10 but_h10 delta(A,A) = |F(A,A)|        =  0.43149056
but_h10 but_h5 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00110884
but_h10 but_h6 delta(A,B) = |F(A,B)+|F(B,A)| =  0.01209544
but_h10 but_h7 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00038356
but_h10 but_h8 delta(A,B) = |F(A,B)+|F(B,A)| =  0.01164332
but_h10 but_h9 delta(A,B) = |F(A,B)+|F(B,A)| =  0.03281372
but_h5 but_h5 delta(A,A) = |F(A,A)|        =  0.42815414
but_h5 but_h6 delta(A,B) = |F(A,B)+|F(B,A)| =  0.03281372
```

```
but_h5 but_h7 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00735824
but_h5 but_h8 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00115144
but_h5 but_h9 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00021732
but_h6 but_h6 delta(A,A) = |F(A,A)|         =  0.43149056
but_h6 but_h7 delta(A,B) = |F(A,B)+|F(B,A)| =  0.01164332
but_h6 but_h8 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00038356
but_h6 but_h9 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00110884
but_h7 but_h7 delta(A,A) = |F(A,A)|         =  0.44089452
but_h7 but_h8 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00545744
but_h7 but_h9 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00115144
but_h8 but_h8 delta(A,A) = |F(A,A)|         =  0.44089452
but_h8 but_h9 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00735824
but_h9 but_h9 delta(A,A) = |F(A,A)|         =  0.42815414
 ------------------------------------
 SUM [ | F(AB) | ]  =   29.99856816
 ------------------------------------
 Normal termination of AIMDELOC.
```

The sum is close to the total number of electrons in the molecule (30 e), indicating good integrations. The AIMDELOC results can again be cast in a tabular format:

	C1	C2	C3	C4	H5	H6	H7	H8	H9	H10
C1	4.0468									
C2	1.8307	3.9676								
C3	0.0678	1.0718	3.9676							
C4	0.0730	0.0678	1.8307	4.0468						
H5	0.9735	0.0585	0.0100	0.0039	0.4282					
H6	0.9654	0.0561	0.0065	0.0101	0.0328	0.4315				
H7	0.0602	0.9610	0.0382	0.0066	0.0074	0.0116	0.4409			
H8	0.0066	0.0382	0.9610	0.0602	0.0012	0.0004	0.0055	0.4409		
H9	0.0039	0.0100	0.0585	0.9735	0.0002	0.0011	0.0012	0.0074	0.4282	
H10	0.0101	0.0065	0.0561	0.9654	0.0011	0.0121	0.0004	0.0116	0.0328	0.4315

Note the delocalization indeces of 1.83, indicating a little less than two pairs shared between atoms that are bonded by a "formal" double bond (respectively C1=C2, and C3=C4). In contrast, only 1.07 pair of electrons are delocalized between the basins of the two atoms bonded by a single bond (C2-C3), as can be expected.

Example III (Output only): Benzene

The integration files and the output file for benzene are provided as a further test case. Choose option 2 when prompted by AIMDELOC since the integration files were obtained using PROAIM96.

Numbering scheme:
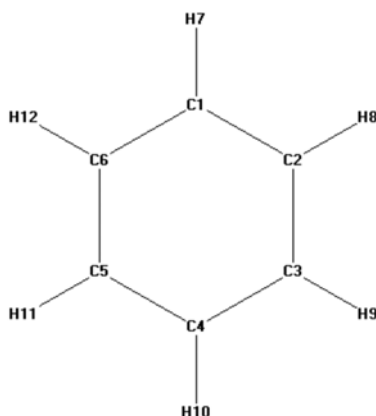
OUTPUT (benzene_deloc.dlc):

```
benz_c1 benz_c1 delta(A,A) = |F(A,A)|     =  3.89738664
benz_c1 benz_c2 delta(A,B) = |F(A,B)+|F(B,A)| =  1.38777164
benz_c1 benz_c3 delta(A,B) = |F(A,B)+|F(B,A)| =  0.07131884
benz_c1 benz_c4 delta(A,B) = |F(A,B)+|F(B,A)| =  0.09885448
benz_c1 benz_c5 delta(A,B) = |F(A,B)+|F(B,A)| =  0.07131884
benz_c1 benz_c6 delta(A,B) = |F(A,B)+|F(B,A)| =  1.38777164
benz_c1 benz_h10 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00501324
benz_c1 benz_h11 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00823908
benz_c1 benz_h12 delta(A,B) = |F(A,B)+|F(B,A)| =  0.04900140
benz_c1 benz_h7 delta(A,B) = |F(A,B)+|F(B,A)| =  0.97442636
benz_c1 benz_h8 delta(A,B) = |F(A,B)+|F(B,A)| =  0.04900140
benz_c1 benz_h9 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00823908
benz_c2 benz_c2 delta(A,A) = |F(A,A)|     =  3.89738994
benz_c2 benz_c3 delta(A,B) = |F(A,B)+|F(B,A)| =  1.38777540
benz_c2 benz_c4 delta(A,B) = |F(A,B)+|F(B,A)| =  0.07131884
benz_c2 benz_c5 delta(A,B) = |F(A,B)+|F(B,A)| =  0.09885076
benz_c2 benz_c6 delta(A,B) = |F(A,B)+|F(B,A)| =  0.07131972
benz_c2 benz_h10 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00823920
benz_c2 benz_h11 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00501640
benz_c2 benz_h12 delta(A,B) = |F(A,B)+|F(B,A)| =  0.00824152
benz_c2 benz_h7 delta(A,B) = |F(A,B)+|F(B,A)| =  0.04900048
benz_c2 benz_h8 delta(A,B) = |F(A,B)+|F(B,A)| =  0.97443272
benz_c2 benz_h9 delta(A,B) = |F(A,B)+|F(B,A)| =  0.04899560
benz_c3 benz_c3 delta(A,A) = |F(A,A)|     =  3.89738994
benz_c3 benz_c4 delta(A,B) = |F(A,B)+|F(B,A)| =  1.38777164
benz_c3 benz_c5 delta(A,B) = |F(A,B)+|F(B,A)| =  0.07131972
benz_c3 benz_c6 delta(A,B) = |F(A,B)+|F(B,A)| =  0.09885076
```

benz_c3 benz_h10 delta(A,B) = |F(A,B)+|F(B,A)| =   0.04900048
benz_c3 benz_h11 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00824152
benz_c3 benz_h12 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00501640
benz_c3 benz_h7 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00823920
benz_c3 benz_h8 delta(A,B) = |F(A,B)+|F(B,A)| =   0.04899560
benz_c3 benz_h9 delta(A,B) = |F(A,B)+|F(B,A)| =   0.97443272
benz_c4 benz_c4 delta(A,A) = |F(A,A)| = 3.89738664
benz_c4 benz_c5 delta(A,B) = |F(A,B)+|F(B,A)| =   1.38777164
benz_c4 benz_c6 delta(A,B) = |F(A,B)+|F(B,A)| =   0.07131884
benz_c4 benz_h10 delta(A,B) = |F(A,B)+|F(B,A)| =   0.97442636
benz_c4 benz_h11 delta(A,B) = |F(A,B)+|F(B,A)| =   0.04900140
benz_c4 benz_h12 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00823908
benz_c4 benz_h7 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00501324
benz_c4 benz_h8 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00823908
benz_c4 benz_h9 delta(A,B) = |F(A,B)+|F(B,A)| =   0.04900140
benz_c5 benz_c5 delta(A,A) = |F(A,A)| = 3.89738994
benz_c5 benz_c6 delta(A,B) = |F(A,B)+|F(B,A)| =   1.38777540
benz_c5 benz_h10 delta(A,B) = |F(A,B)+|F(B,A)| =   0.04900048
benz_c5 benz_h11 delta(A,B) = |F(A,B)+|F(B,A)| =   0.97443272
benz_c5 benz_h12 delta(A,B) = |F(A,B)+|F(B,A)| =   0.04899560
benz_c5 benz_h7 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00823920
benz_c5 benz_h8 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00501640
benz_c5 benz_h9 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00824152
benz_c6 benz_c6 delta(A,A) = |F(A,A)| = 3.89738994
benz_c6 benz_h10 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00823920
benz_c6 benz_h11 delta(A,B) = |F(A,B)+|F(B,A)| =   0.04899560
benz_c6 benz_h12 delta(A,B) = |F(A,B)+|F(B,A)| =   0.97443272
benz_c6 benz_h7 delta(A,B) = |F(A,B)+|F(B,A)| =   0.04900048
benz_c6 benz_h8 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00824152
benz_c6 benz_h9 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00501640
benz_h10 benz_h10 delta(A,A) = |F(A,A)| = 0.49042540
benz_h10 benz_h11 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00584796
benz_h10 benz_h12 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00139340
benz_h10 benz_h7 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00030120
benz_h10 benz_h8 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00139340
benz_h10 benz_h9 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00584796
benz_h11 benz_h11 delta(A,A) = |F(A,A)| = 0.49043192
benz_h11 benz_h12 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00584864
benz_h11 benz_h7 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00139340
benz_h11 benz_h8 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00030136
benz_h11 benz_h9 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00139592
benz_h12 benz_h12 delta(A,A) = |F(A,A)| = 0.49043192
benz_h12 benz_h7 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00584796
benz_h12 benz_h8 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00139592
benz_h12 benz_h9 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00030136
benz_h7 benz_h7 delta(A,A) = |F(A,A)| = 0.49042540
benz_h7 benz_h8 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00584796
benz_h7 benz_h9 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00139340
benz_h8 benz_h8 delta(A,A) = |F(A,A)| = 0.49043192
benz_h8 benz_h9 delta(A,B) = |F(A,B)+|F(B,A)| =   0.00584864
benz_h9 benz_h9 delta(A,A) = |F(A,A)| = 0.49043192

 SUM [| F(AB) |] =   41.98592296

 Normal termination of AIMDELOC.

These results can be cast into a tabular form:

	C1	C2	C3	C4	C5	C6	H7	H8	H9	H10	H11	H12
C1	3.8974											
C2	1.3878	3.8974										
C3	0.0713	1.3878	3.8974									
C4	0.0989	0.0713	1.3878	3.8974								
C5	0.0713	0.0989	0.0713	1.3878	3.8974							
C6	1.3878	0.0713	0.0989	0.0713	1.3878	3.8974						
H7	0.9744	0.0490	0.0082	0.0050	0.0082	0.0490	0.4904					
H8	0.0490	0.9744	0.0490	0.0082	0.0050	0.0082	0.0058	0.4904				
H9	0.0082	0.0490	0.9744	0.0490	0.0082	0.0050	0.0014	0.0058	0.4904			
H10	0.0050	0.0082	0.0490	0.9744	0.0490	0.0082	0.0003	0.0014	0.0058	0.4904		
H11	0.0082	0.0050	0.0082	0.0490	0.9744	0.0490	0.0014	0.0003	0.0014	0.0058	0.4904	
H12	0.0490	0.0082	0.0050	0.0082	0.0490	0.9744	0.0058	0.0014	0.0003	0.0014	0.0058	0.4904

Note the delocalization index between two adjacent carbon atoms (1.39) indicating an intermediate more than one pair but less than two pairs are delocalized between their respective basins. Each hydrogen atom shares almost one (0.97) pairwith its bonded carbon atom.

References

[1] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory* (Oxford University Press, Oxford, U.K., 1990).

[2] F. W. Biegler-König *et al.*, J. Phys. B: At. Mol. Phys. **14**, 2739 (1981).

[3] F. W. Biegler-König, R. F. W. Bader, and T.-H. Tang, J. Computational Chem. **13**, 317 (1982).

[4] Web Page, *AIMPAC program suite can be downloaded free of charge from Internet at http://www.chemistry.mcmaster.ca/aimpac/* .

[5] R. F. W. Bader *et al.*, J. Am. Chem. Soc. **118**, 4959 (1996).

[6] R. F. W. Bader, S. Johnson, T.-H. Tang, and P. L. A. Popelier, J. Phys. Chem. **100**, 15398 (1996).

[7] X. Fradera, M. A. Austen, and R. F. W. Bader, J. Phys. Chem. A **103**, 304 (1999).

APPENDIX: AIMDDELOC PROGRAM LISTING

```bash
#!/bin/bash

# ABOUT THIS SCRIPT:
#===================
# This shell script produces a file containing the bond orders calculated
# according to the AIM theory. To operate properly, move all the integration
# files corresponding to ONE molecule or system into a separate directory
# and copy and run this script.

clear
 echo
 echo "    --------------------------------------------------- "
 echo "    ATOMS-IN-MOLECULES DELOCALIZATION INDECES (AIMDELOC)  "
 echo "    --------------------------------------------------- "
 echo
 echo "    Copywright owner:"
 echo "        Cherif F. Matta"
 echo "    Chemistry Department, McMaster University,"
 echo "     Hamiton, Ontario, Canada L8S 4M1 "
 echo
 echo
 echo "   WARNING!"
 echo "   ========"
 echo " File names: *tmp*, *temp*, *table*, *delete*, *trunc*, *.*.joint "
 echo " will be lost in this directory."
 echo " If you wish to exit use 'Cntrl+c' key combination"
 echo

echo "    The integration files were generated using:"
echo "    ----------------------------------------"
echo "    [1] PROAIMV - Version 94 - Revision B "
echo "    [2] PAIM96 - Version 96, Revision C"
echo
echo "    Choose ONE option 1 or 2 :"
read option
echo

# SELECT THE VERSION OF PROAIM (DIFFERENT OVERLAP MATRIX IDENTIFYING TEXT)

case $option
 in
  1) string="Restricted Closed-Shell Wavefunction";;
```

```
  2) string="Restricted, SCF, closed-shell orbital wavefunction";;
  *) echo You entered an invalid number, please enter 1 or 2
    exit 1;;
 esac

echo
echo Ovelap matrix identifying string is:
echo
echo "     $string"
echo

# CLEANUP WORK PLACE
 rm -f *table*
 rm -f *deleteme*
 rm -f *temp*
 rm -f *tmp*
 rm -f *trunc*
 rm -f *.*.joint
 rm -f *fileslist*
 rm -f *j*
 rm -f *prd*
 rm -f *fileinfo*
 rm -f *fileslist*
 rm -f MatrixIndeces
 rm -f DelocIndeces
clear

echo
echo "   AIMDELOC RUNNING "
echo "    Please wait"
echo

# Loop extracting the overlap matrix from the integration files of the
# atoms in the molecule (the output files of PROAIM)
# The end-result of this loop is a one-column sequential file listing
# the elements of the lower triangle of the overlap matrix. One file is
# produced for each integration file. The output of this loop has the form
# atom.int.table .


 for i in $(ls *.int)
 do

# GET THE OVERLAP MATRIX OF EACH ATOM FROM ITS INTEGRATION FILE INTO A
# A SEPARATE FILE (i.e. EXTRACTING THE OVERLAP MATRIX PORTION FROM THE .int
# FILES BY REMOVING ALL LINES BEFORE AND AFTER IT USING THE HEAD AND TAIL
# COMMANDS)

  grep -A 20000 "$string" < $i > $i.truncated

  wc $i.truncated > truncinfo
  read x1 x2 x3 x4 < truncinfo
  y=`expr $x1 - 2`
  tail -$y $i.truncated > $i.temp

  z=`expr $x1 - 14`
```

```
  head -$z $i.temp > $i.temp2

  rm -f $i.truncated
  rm -f $i.temp
  rm -f truncinfo

# TRANSFORMING THE LINES OF THE OVERLAP MATRIX INTO ONE COLUMN OF
NUMBERS
# EACH (LOWER TRIANGLULAR OVERLAP MATRIX IS CONVERTED INTO A ONE-COLUM
# LIST OF NUMBERS (CREATION OF atom.int.table)

  mv $i.temp2 $i.OvrlpMtrx
  cp $i.OvrlpMtrx $i.OM
  wc $i.OvrlpMtrx > truncinfo
  read xx1 xx2 xx3 xx4 < truncinfo

# xx1 = number of LINES (NOT ROWS) in the overlap matrix, the maximum number
# of entries per line is 8 numbers: a1 ... a8, which are transposed in the
# following loop

 xxx1=`expr $xx1 + 1`
 j=1
 until [ $j -eq $xxx1 ]
  do

  echo "Append/transpose row $j of the overlap matrix of $i to the column"

  read a1 a2 a3 a4 a5 a6 a7 a8 < $i.OM

  echo $a1 >> $i.table
  echo $a2 >> $i.table
  echo $a3 >> $i.table
  echo $a4 >> $i.table
  echo $a5 >> $i.table
  echo $a6 >> $i.table
  echo $a7 >> $i.table
  echo $a8 >> $i.table

  tail -$(($xx1-$j)) $i.OM > $i.temp.$j

  rm -f $i.OM
  mv $i.temp.$j $i.OM

  j=$(($j+1))

 done

# REMOVING EMPTY LINES FROM atom.int.table

  sed -e '/^$/d' < $i.table > $i.temp
  rm -f $i.table
  mv $i.temp $i.table
  echo
  echo "   Column rep. of the matrix $i done!"
  echo
 done
```

```
echo
echo "   First part done!"
echo "   Overlap matrices converted into single column representation."
echo
echo "    AIMDELOC RUNNING"
echo "    Please wait"
echo

# COUNTING THE NUMBER OF LINES IN THE TABULAR FORM OF THE ATOMIC
# OVERLAP MATRIX

  wc *.table > deleteme
  read MatrixSize y z s < deleteme
  rm -f deleteme

# CREATING A FILE WITH SERIAL NUMBERING AND MATRIX ELEMENTS LABELS FOR
THE
# TABULAR FORM OF THE ATOMIC OVERLAP MATRIX. (file: MatrixIndeces)

 k=1
 i=1
 while test $i -gt 0
  do
   j=0
   ii=`expr $i - 1 `
     while test $j -le $ii
      do
       if test $k -eq $(($MatrixSize+1))
        then break 2
       fi
       j=$((j+1))
       echo $k $i $j >> MatrixIndeces
       k=$((k+1))
      done
    i=$((i+1))
  done

echo "   Overlap matrix indeces done!"
echo
echo "    AIMDELOC RUNNING"
echo "    Please wait"
echo

# NUMBERING THE LINES OF atom.int.table
# ....................................

 for k in $(ls *.int.table)
 do
  cp $k $k.temp
  rm -f $k
  cat -n $k.temp > $k
 done

rm -f *.int.temp*
rm -f *.int.O*
```

```
# PREPARE A LIST OF atom.int.table FILES & COUNTING THEM:
#===========================================================
# X1= the number of .int files

    ls *.int.table > fileslist
    wc fileslist > fileslist.info
    read X1 X2 X3 X4 < fileslist.info
    rm -f fileslist.info
    cp fileslist fileslist.tmp1
    cp fileslist fileslist.tmp11

# PEPARE ALL POSSIBLE PERMUTATIONS OF atom.int.table FILES AND
# MULTIPLYING THE ATOMIC OVERLAP MATRIX ELEMENTS OF TWO ATOMS. (DIAGONAL
# ELEMENTS ARE TAKEN ONCE AND OFF DIAGONAL ELEMENTS ARE TAKEN TWICE TO
ACCOUNT
# FOR THE MISSING UPPER TRIANGULAR PART OF THE MATRIX, AS PROAIM GIVES THE
# LOWER TRIANGLE OF THIS SYMMETRIC MATRIX.

l=0
  while test $X1 -gt $l
  do
  tail -$(($X1-$l)) fileslist.tmp11 > fileslist.tmp22
  rm -f fileslist.tmp11
  mv fileslist.tmp22 fileslist.tmp11
  wc fileslist.tmp11 > fileslist.tmp11.info
  read XX1 XX2 XX3 XX4 < fileslist.tmp11.info
  rm -f fileslist.tmp11.info
  l=$(($l+1))

   k=0
   while test $XX1 -gt $k
    do
     read filenameA < fileslist.tmp11
     tail -$(($XX1-$k)) fileslist.tmp1 > fileslist.tmp2
     read filenameB < fileslist.tmp2
     echo $filenameA $filenameB >> jointname.$k.$l
     echo "joining $filenameA and $filenameB, cycle $l,$k"
     sed -e 's/.int.table//g' <jointname.$k.$l> $l.$k.jointname
     rm -f jointname.$k.$l
     sed -e 's/ /__/g' <$l.$k.jointname> jointname.$k.$l
     read jointfilename < jointname.$k.$l
     rm -f jointname.$k.$l
     join $filenameA $filenameB >> $jointfilename.tmp
     join MatrixIndeces $jointfilename.tmp > $jointfilename.jnt
     rm -f *.tmpm
     rm -f joint.$k.$l

#   READING THE JOINT-FILE ELEMENTS AND TESTING IF THEY ARE LOWER
#   TRIANGULAR MATRIX ELEMENTS (IN WHICH CASE THEY ARE MULTIPLIED BY
#   2 TO COMPENSATE FOR THE MISSING UPPER TRIANGULAR MATRIX ELEMENTS)
#   OR IF THEY ARE DIAGONAL ELEMENTS IN WHICH CASE THEIR PRODUCT IS
#   OUTPUTED AS SUCH.

    l=0
```

```
    J=0
    awk '{ I=I+1
      J=J+1
        if ( $2 == $3 ) w[I,J] = $4*$5
        else     w[I,J] = 2*$4*$5
      ++num
   printf("%d %d %d %11.7f %11.7f %11.8f\n", $1, $2, $3, $4, $5, w[I,J])
      }' $jointfilename.jnt > $jointfilename.prd
    rm -f *.jnt
```

```
#   SUMMING THE COLUMN OF THE PRODUCTS OF THE CORRESPONDING MATRIX
#   ELEMENTS BELONGING TO TWO ATOMS. (SUMMING LOOP).
#   THE SUM IS MULTIPLIED BY TWO TO ACCOUNT FOR TWO ELECTRONS
#   (CLOSED SHELL), THEN BY 2 TO INCLUDE F(A,B) AND F(B,A).
#   THE DELOCALIZATION INDEX IS GIVEN BY:
#     delta(A,B) = |F(A,B)| + |F(B,A)| ,
#   where F(A,B) = F(B,A). DELTA IS THE DELOCALIZATION INDEX.
```

```
    K=0

    awk '  {
        K=K+1
        sum += 2*2*$6
        ++num
        }
      END {
        printf("%s %11.8f\n", "The bond order is: ", sum)
        } ' $jointfilename.prd >> $jointfilename.prd
```

```
    k=$(($k+1))
    done
  done
```

```
 grep "The bond order is: " *.prd > DelocIndeces.tmp
 sed -e 's/.prd//g' <DelocIndeces.tmp> DelocIndeces.tmp2
 sed -e 's/:/__/g' <DelocIndeces.tmp2> DelocIndeces.tmp3
```

```
awk ' BEGIN{ FS = "__" }
 {
  if ( $1 == $2 )
   { printf ("%s %s %s %11.8f\n", $1, $2, "delta(A,A) = |F(A,A)|     = ", 0.5*$4 ) }
   else printf ("%s %s %s %11.8f\n", $1, $2, "delta(A,B) = |F(A,B)+|F(B,A)| = ", $4 )
 }' DelocIndeces.tmp3  > DelocIndeces
```

```
# SUMMING THE DELTAS OVER ALL THE MOLECULE, THE SUM = THE TOTAL NUMBER
OF
# ELECTRONS IN THE MOLECULES.
```

```
    K=0
    sum=0
    awk ' BEGIN { FS = "=" }
        {
         sum += $3
         ++num
        }
```

```
        END {
     printf("%s\n", " ------------------------------------")
   printf("%s %11.8f\n", " SUM [ | F(AB) | ]  =  ", sum)
     printf("%s\n", " ------------------------------------")
     printf("%s\n", " Normal termination of AIMDELOC.")
         } ' DelocIndeces >> DelocIndeces

echo
cat DelocIndeces
echo

rm -f *table*
rm -f *deleteme*
rm -f *temp*
rm -f *tmp*
rm -f *trunc*
rm -f *.*.joint
rm -f *fileslist*
rm -f *j*
rm -f *fileinfo*
rm -f *fileslist*
rm -f MatrixIndeces

mv DelocIndeces deloc.dlc

echo
echo "   All atom-atom permutations done and bond orders computed"
echo
echo "   YOUR RESULTS ARE SUMMARIZED IN THE FILE: deloc.dlc "
echo "             ========="
echo "   AIMDELOC DONE"
echo "   *************"
echo
echo
echo "Normal termination of AIMDELOC on:"
date
echo
```