

# QCPE

## QUANTUM CHEMISTRY PROGRAM EXCHANGE

QCPE PROGRAM No. QCPE0801

**FRAGDIP 01: A Program to Calculate the Functional  
Group Contributions to the Molecular Dipole Moment  
According to the Quantum Theory of Atoms-In-  
Molecules (AIM)**

by

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**QCPE Program Number:**

**QCPE0801**

**Program Title:**

**FRAGDIP01: Program for Calculating  
Functional Group Contributions to the Molecular  
Dipole Moment according to the Quantum  
Theory of Atoms-In-Molecules (AIM)**

**Author:**

**Chérif F. Matta**

**Lines of Code:**

**390**

**Platform/Language:**

**Windows (95, 98, 2000) / Turbo Pascal**

**Recommended Citation:**

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Atoms in Crystals: Dielectric Polarization." Int. J.  
Quantum Chem.: Proceedings of the 41st  
Sanibel Quantum Chemistry Symposium (In  
press, to appear in 2001).**

**Description:**

**This package contains executable and source  
code in Pascal plus documentation and sample  
data files.**

## PURPOSE

FRAGDIP is a Windows-based program that computes the contributions of individual atoms or groupings of atoms, fragments, or functional groups to the total dipole moment of a whole molecule. The atoms in the molecule are bounded by zero-flux surfaces in the gradient vector field of the electron density, a quantum condition imposed on the density of a proper open system in the Quantum Theory of Atoms-In-Molecules (QT-AIM).[1] The contribution of an atom or a grouping of atoms to the molecular dipole is the result of two contributions: an internal dipolar polarization term (due to the polarization of charge within the atom or the group), and a charge transfer term due to the transfer of charge between an atom or a group and its bonded neighbours.[2] FRAGDIP provides the vector components of each type of group polarization (in addition to the group volume, group energy, and net group charge). The vector sum of the group dipoles is provided at the end of the output which equals to the molecular dipole. A comparison with the molecular dipole obtained from the direct calculation provides a measure of the overall integration accuracy.

### Language and Platforms

FRAGDIP is written in Turbo Pascal and compiled using the Borland Turbo Pascal compiler ver.1.5 (1992) on Windows98. FRAGDIP consists of approximately 390 lines of code. The program was extensively tested on Windows98. It also runs on all other versions of the Windows operating system, but has not been tried on Windows NT on which it is expected to run without problems.

### Hardware

PC with Windows as operating system.

### Running time

Interactive.

## 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]

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

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 measurable 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:

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

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:

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

Thus, the integrated atomic properties such as populations/partial charges, atomic dipoles and higher multipoles, atomic volumes, atomic energies can be

readily calculated using software implementing QT-AIM such as the AIMPAC suite of programs.[3-5]

## (II) Group contributions to dielectric polarization [2]

The molecular dipole moment is obtained from eqn 4:

$$\boldsymbol{\mu} = - \int d\mathbf{r} \mathbf{r} \rho(\mathbf{r}) + \sum_A \mathbf{X}_A Z_A. \quad (4)$$

To define group (fragment) contributions, set  $\mathbf{r} = \mathbf{r}_A + \mathbf{X}_A$ , where  $\mathbf{r}_A$  is referenced to the nucleus of A with position coordinate  $\mathbf{X}_A$  and charge  $Z_A$ , to obtain eqn (5)

$$\boldsymbol{\mu} = \sum_A \left[ - \int d\mathbf{r} \mathbf{r}_A \rho(\mathbf{r}) + \mathbf{X}_A \left( Z_A - \int d\mathbf{r} \rho(\mathbf{r}) \right) \right] = \sum_A [\mathbf{M}(A) + \mathbf{X}_A q(A)], \quad (5)$$

where the net charge on atom A is given by  $q(A) = Z_A - N(A)$ ,  $N(A)$  being the average electron population of A. The dipole moment is expressed as a sum of atomic polarizations  $\mathbf{M}(A)$  plus a term resulting from the transfer of electronic charge between the atoms. Each charge transfer term  $\mathbf{X}_A q(A)$  depends upon the choice of origin, a dependence removed by introducing terms that take into account the explicit transfer of charge from an atom to each of its bonded neighbours, that is to each group with which it shares an interatomic surface. As a result, the molecular dipole moment is expressible as a sum of atomic contributions,  $\boldsymbol{\mu}(A)$ , as indicated in eqn (6).

$$\boldsymbol{\mu} = \sum_A \boldsymbol{\mu}(A) = \sum_A \left\{ \mathbf{M}(A) + \sum_{B \neq A} [\mathbf{X}^c(A|B) - \mathbf{X}_A] q(B) \right\}. \quad (6)$$

$\mathbf{X}^c(A|B)$  is the coordinate of the bond critical point (bcp) whose associated trajectories of  $\nabla D(\mathbf{r})$  define the interatomic surface  $S(A|B)$ , where  $B$  runs over all of the atoms or groups linked to and sharing a surface with atom A. Since  $q(A) = - \sum_{B \neq A} q(B)$  and the contributions to the sum describes the manner in which the electronic charge lost or gained by A is shared between its bonded neighbours B. The dependence of  $\boldsymbol{\mu}(A)$  on the charges of neighbouring groups can be removed

and replaced by corresponding interatomic surface integrals of the flux in the electrostatic field  $\mathbf{E}(\mathbf{r})$  using Poisson's equation, as in eqn (7)

$$\boldsymbol{\mu} = \sum_A \boldsymbol{\mu}(A) = \sum_A \left\{ \mathbf{M}(A) - \frac{1}{4\pi} \sum_{B \neq A} [\mathbf{X}^c(A|B) - \mathbf{X}_A] \int dS(A|B; \mathbf{r}_s) \mathbf{E}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) \right\}. \quad (7)$$

The contribution of each atom to the dipole moment  $\boldsymbol{\mu}$  is given by  $\mathbf{M}(A)$ , the polarization of its density relative to its nucleus, together with the dipoles resulting from the flux in the electric field through each of its interatomic surfaces, measured relative to its nuclear position, that is, as a result of the corresponding charge transfers. The surface integral of eqn (7), including the factor of  $-1/4B$ , determining the charge transferred across  $S(A|B)$ , is denoted by  $Q(A|B)$  - the surface transfer charge - with the surface normal directed from B to A.

## FRAGDIP INPUT FILES

### (I) First input file:

A file containing 10 fields (separated by one or more blank spaces) and  $n$  records, where  $n$  is the total number of atoms in the molecules.

- Filed 1: serial number labeling the atoms (integer)
- Fields 2,3,4: the x, y, and z coordinates of the atom
- Fields 5,6,7: the x, y, and z components of the atomic dipole moments
- Field 8: the net atomic charge
- Field 9: the atomic energy
- Field 10: the atomic volume

Any number of decimal places is acceptable, the more the better. Overflowing lines do not constitute a problem as far as there is no line breaks (carriage returns) within a record. A line break is necessary however at the end of an atom's record. The file should be saved in the "text only with line breaks" format. The entries of this file are generated by the PROAIM program of the AIMPAC series.[3-5] A shell script can be written to extract the necessary entries from the AIMPAC atomic integration files and arranging them into the required tabular form.

**Example of the first input file for methanol (The file MeOHinp.txt):**

```

1 2.038323320 1.844054640 0.000000000 -0.101960670 -0.037340148 -0.000001918 -
0.043563311 -0.658805213 49.414741800
2 0.086636170 1.234716500 0.000000000 -0.000744828 -0.598768379 0.000003949
0.850001548 -37.291462500 53.553775400
3 0.086636170 -1.408103000 0.000000000 0.228426673 -0.134270549 0.000000160 -
1.262296800 -75.402099300 116.455826000
4 -1.590285860 -2.006882040 0.000000000 0.143716040 0.055301805 0.000000627
0.613669328 -0.352518777 18.727875600
5 -0.830471950 2.009676200 1.669548280 0.054500437 -0.040552212 -0.091839982 -
0.077939593 -0.671203603 52.073887900
6 -0.830471950 2.009676200 -1.669548280 0.054500437 -0.040552212 0.091839982 -
0.077939593 -0.671203603 52.073887900

```

**(II) Second input file:**

This file contains a listing of the bond critical points (bcp) coordinates. The file has at least 4 fields and as many records as there is bcp in the molecule. Each record consist of the following fields:

Field 1: a serial number (integer) to identify the bcp (no relation to the serial number of the first file)

Fields 2,3,4: x, y, and z coordinates of the bond critical point identified by the serial number

The entries of this file are generated by the EXTREME program of the AIMPAC series.[3-5] The output of EXTREME provides a list of the critical points and their coordinates at the end of the critical point file (.crt).

**Example of the second input file for methanol (The file MeOHbcp.txt):**

```

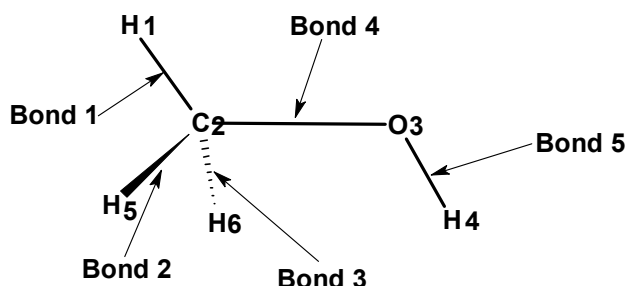
1 1.29435356E+00 1.60931408E+00 -5.34521673E-18 H 1 C 2
2 -4.79636675E-01 1.70261232E+00 1.02198082E+00 C 2 H 5
3 -4.79636675E-01 1.70261232E+00 -1.02198082E+00 C 2 H 6
4 5.77779745E-02 3.93252513E-01 -4.43743300E-18 C 2 O 3
5 -1.26827111E+00 -1.88076518E+00 -8.27553522E-19 O 3 H 4

```

**(iii) Third input file (Depends on how the fragments are chosen)**

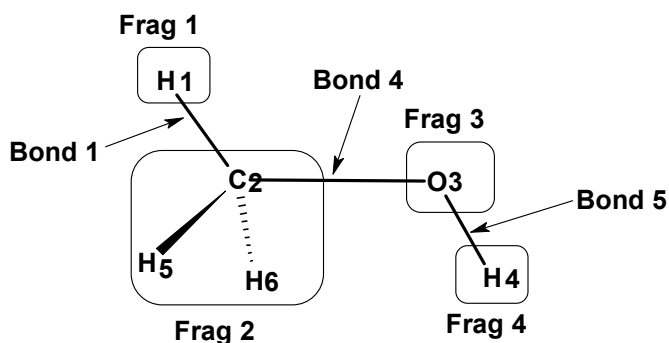
The first two input files are independent of the way the fragments making up the molecule are chosen method. The third input file depends on how the fragments are chosen, and serves to define what residues are connected to each chosen

fragment. This input file consists of a single column listing the atom numbers (labels) of the atoms of the residual groups (groups attached to the fragment in question). The list is in the order that will be entered in the interactive run of the program. The dependence of this list on how the molecule is broken down into contributing fragments will be illustrated by two different choices of fragments that make up the methanol molecule (Choice A and Choice B). The numbering scheme of the atoms and bonds of the methanol molecule used in the following examples is as in the following figure:

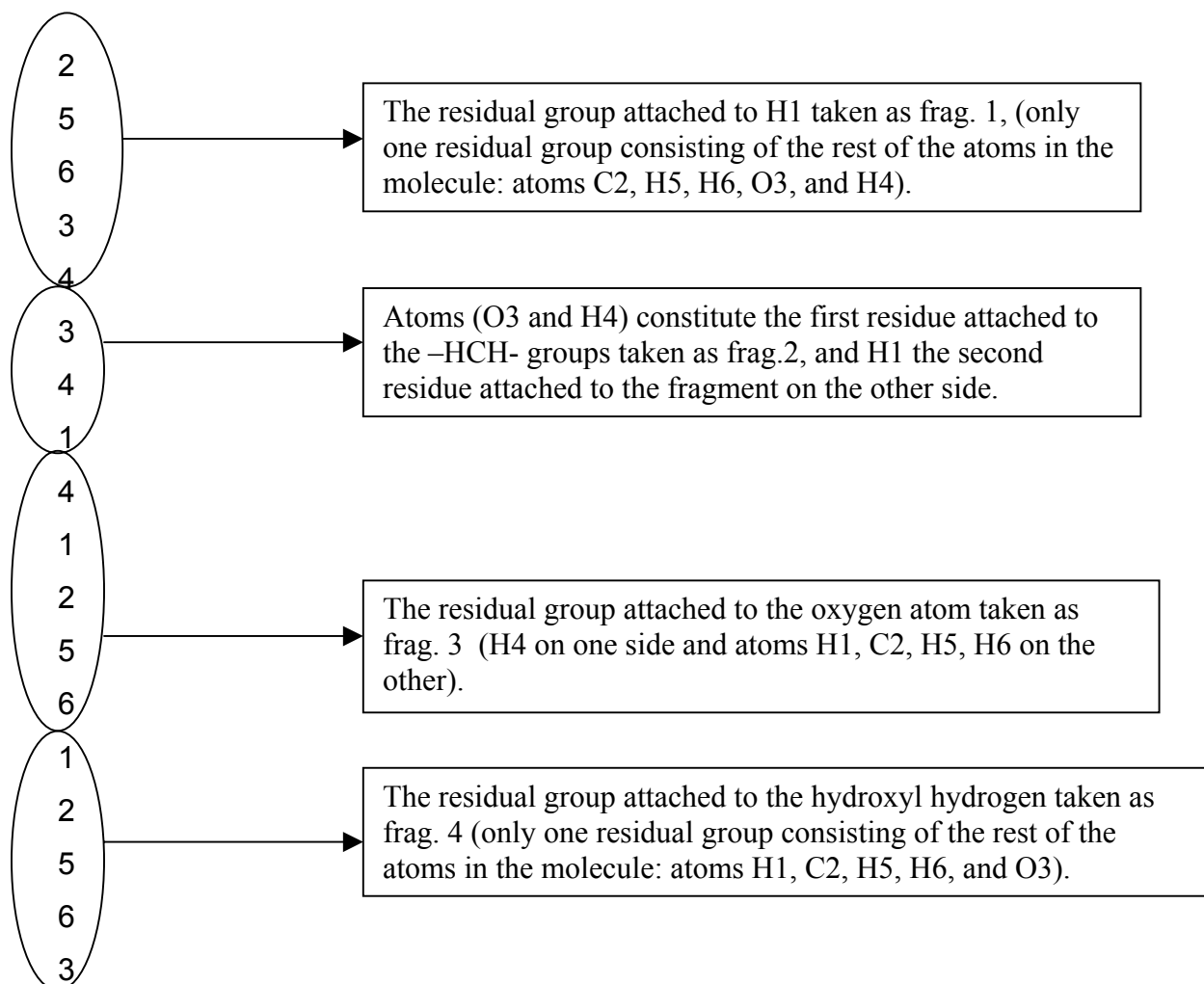


**(iii-a) Choice A of Fragments contributions to the dipole moment of methanol:**

Say you wish to find the contribution of the following four fragments to the total dipole moment of methanol: (Frag.1= H1), (Frag.2 = C2 H5 H6), (Frag.3 = O3), and (Frag.4 = H4). Choice A is illustrated in the following figure:



In the case of Choice A, the third input file (MeOHresA.txt) is:



### INVOKING FRAGDIP

The program is invoked by copying the executable FRAGDIP.EXE together with the three input files in the same directory and double clicking the mouse on the executable file FRAGDIP.EXE from Windows explorer. Once started, the program is interactive. In the following table we will list FRAGDIP prompts and the user response corresponding to the example of fragmentation Choice A of methanol.

#### Interactive session A

FRAGDIP Prompts:	User response/input
INFO FILE NAME WITH EXTENSION: -->	MeOHinf.txt

BCP FILE NAME WITH EXTENSION: -->	MeOHbcp.txt
RESIDUES FILE NAME WITH EXTENSION: -->	MeOHresA.txt
Output file name with extension: -->	MeOHoutA.txt
How many ATOMS are in FRAGMENT1 ? -->	1
How many R GROUPS are connected to FRAGMENT1 ? -->	1
Enter an atom number:	
Atom[ 1]--->	1
Enter the bcp between atom 1 of fragment 1 and R[1] :	1
R[1] consists of how many atoms? -->	5
Do you want more calculations (y/n):	y
How many ATOMS are in FRAGMENT2 ? -->	3
How many R GROUPS are connected to FRAGMENT2 ? -->	2
Enter an atom number:	
Atom[ 1]--->	2
Enter an atom number:	
Atom[ 2]--->	5
Enter an atom number:	
Atom[ 3]--->	6
Enter the bcp between atom 2 of fragment 2 and R[1] :	4
R[1] consists of how many atoms? -->	2
Enter the bcp between atom 2 of fragment 2 and R[2] :	1
R[2] consists of how many atoms? -->	1
Do you want more calculations (y/n):	y
How many ATOMS are in FRAGMENT3 ? -->	1
How many R GROUPS are connected to FRAGMENT3 ? -->	2
Enter an atom number:	
Atom[ 1]--->	3
Enter the bcp between atom 3 of fragment 3 and R[1] :	5
R[1] consists of how many atoms? -->	1
Enter the bcp between atom 3 of fragment 3 and R[2] :	4
R[2] consists of how many atoms? -->	4
Do you want more calculations (y/n):	y
How many ATOMS are in FRAGMENT4 ? -->	1
How many R GROUPS are connected to FRAGMENT4 ? -->	1
Enter an atom number:	
Atom[ 1]--->	4
Enter the bcp between atom 4 of fragment 4 and R[1] :	5
R[1] consists of how many atoms? -->	5
Do you want more calculations (y/n):	n

### **Output A: MeOHoutA.txt**

```
=====
FRAGMENTS DIPOLE MOMENTS COMPUTATION (FRAGDIP)
=====
```

Input atomic info file: MeOHinf.txt  
Input bond critical point (bcp) info file: MeOHbcp.txt  
Residues information from info file: MeOHresA.txt

```
FRAGMENT 1
=====
```

There are 1 atom(s) in FRAGMENT1 connected to 1 residual group(s)

FRAGMENT1 consist of the following atoms: 1

Volume of the Fragment = 49.4147

Energy of the Fragment = -0.658805

Charge of the Fragment = -0.043563

Total charge on residue R[1] = 0.045495

Fragment group dipole components:

x	y	z	dipole magnitude
-0.135807	-0.048020	-0.000002	0.144047

Fragment group dipole components (Normalized):

x	y	z	dipole magnitude
-0.942799	-0.333361	-0.000013	1.000000

---

#### FRAGMENT 2

=====

There are 3 atom(s) in FRAGMENT2 connected to 2 residual group(s)

FRAGMENT2 consist of the following atoms: 2 5 6

Volume of the Fragment = 157.7016

Energy of the Fragment = -38.633870

Charge of the Fragment = 0.694122

Total charge on residue R[1] = -0.648627

Total charge on residue R[2] = -0.043563

Fragment group dipole components:

x	y	z	dipole magnitude
0.217320	-0.271195	0.000004	0.347527

Fragment group dipole components (Normalized):

x	y	z	dipole magnitude
0.625334	-0.780357	0.000011	1.000000

---

#### FRAGMENT 3

=====

There are 1 atom(s) in FRAGMENT3 connected to 2 residual group(s)

FRAGMENT3 consist of the following atoms: 3

Volume of the Fragment = 116.4558

Energy of the Fragment = -75.402099

Charge of the Fragment = -1.262297

Total charge on residue R[1] = 0.613669

Total charge on residue R[2] = 0.650559

Fragment group dipole components:

x	y	z	dipole magnitude
-0.621812	0.747559	0.000000	0.972366

Fragment group dipole components (Normalized):

x	y	z	dipole magnitude
-0.639484	0.768805	0.000000	1.000000

---

#### FRAGMENT 4

=====

There are 1 atom(s) in FRAGMENT4 connected to 1 residual group(s)

FRAGMENT4 consist of the following atoms: 4

Volume of the Fragment = 18.7279

Energy of the Fragment = -0.352519

Charge of the Fragment = 0.613669

Total charge on residue R[1] = -0.611738

Fragment group dipole components:

x	y	z	dipole magnitude
-0.053273	-0.021849	0.000001	0.057579

Fragment group dipole components (Normalized):

x	y	z	dipole magnitude
-0.925210	-0.379456	0.000011	1.000000

=====  
Sums of fragments dipole components contributions\* :

x	y	z	dipole magnitude
-0.593572	0.406496	0.000003	0.719421

\* These sums equal to the molecular values only if all the fragments are included in the calculation.  
=====

#### SUMMARY

=====

	x	y	z	dipole magnitude
FRAGMENT1	-0.135807	-0.048020	-0.000002	0.144047
FRAGMENT2	0.217320	-0.271195	0.000004	0.347527
FRAGMENT3	-0.621812	0.747559	0.000000	0.972366
FRAGMENT4	-0.053273	-0.021849	0.000001	0.057579

Molecule (a.u.) -0.593572 0.406496 0.000003 0.719421

Molecule (D) -1.508861 1.033313 0.000007 1.828769

TOTAL CHARGE = 0.001932

TOTAL ENERGY = -115.047293

TOTAL VOLUME = 342.299995

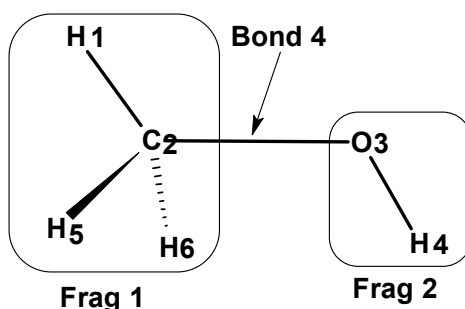
Normalized fragments dipoles

	x	y	z	dipole magnitude
FRAGMENT1	-0.942799	-0.333361	-0.000013	1.000000
FRAGMENT2	0.625334	-0.780357	0.000011	1.000000
FRAGMENT3	-0.639484	0.768805	0.000000	1.000000
FRAGMENT4	-0.925210	-0.379456	0.000011	1.000000

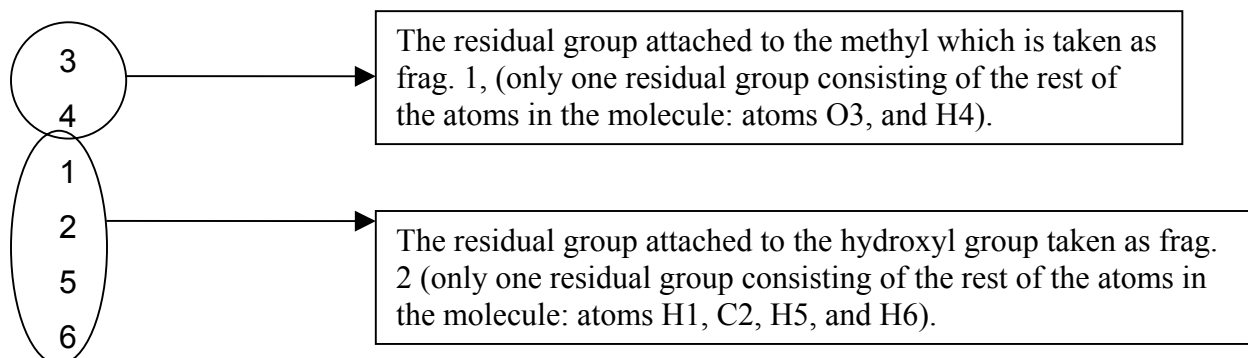
Normal termination of FRAGDIP.

**(iii-b) Choice B of Fragments contributions to the dipole moment of methanol:**

Now let's consider another choice of fragments contributing to the molecular dipole of methanol. Consider the methanol molecule as consisting of a methyl group (atoms C2, H1, H5, H5) and a hydroxyl group (atoms O3 and H4), the two functional groups being bonded by bond 4. In other words, the contributions of the following groups (fragments) to the molecular dipole is to be calculated (Fragmentation B):



The first two input files are the same as in the previous example since they are independent of the choice of fragments. The third file will be different, though, as it reflects the choice of the fragments and serves to define what residues are connected to each fragment. In the case of fragments Choice B, the third input file (MeOHresB.txt) is:



**Interactive session B**

FragDip Prompts:	User response/input
INFO FILE NAME WITH EXTENSION: -->	MeOHinf.txt
BCP FILE NAME WITH EXTENSION: -->	MeOHbcp.txt

RESIDUES FILE NAME WITH EXTENSION: -->	MeOHresB.txt
Output file name with extension: -->	MeOHoutB.txt
How many ATOMS are in FRAGMENT1 ? -->	4
How many R GROUPS are connected to FRAGMENT1 ? -->	1
Enter an atom number:	
Atom[ 1]--->	2
Enter an atom number:	
Atom[ 1]--->	1
Enter an atom number:	
Atom[ 1]--->	5
Enter an atom number:	
Atom[ 1]--->	6
Enter the bcp between atom 2 of fragment 1 and R[1] :	4
R[1] consists of how many atoms? -->	2
Do you want more calculations (y/n):	y
How many ATOMS are in FRAGMENT2 ? -->	2
How many R GROUPS are connected to FRAGMENT2 ? -->	1
Enter an atom number:	
Atom[ 1]--->	3
Enter an atom number:	
Atom[ 2]--->	4
Enter the bcp between atom 2 of fragment 2 and R[1] :	4
R[1] consists of how many atoms? -->	4
Do you want more calculations (y/n):	n

### **Output B: MeOHoutB.txt**

```
=====
FRAGMENTS DIPOLE MOMENTS COMPUTATION (FRAGDIP)
=====
```

Input atomic info file: MeOHinf.txt  
 Input bond critical point (bcp) info file: MeOHbcp.txt  
 Residues information from info file: MeOHresB.txt

```
FRAGMENT 1
=====
```

There are 4 atom(s) in FRAGMENT1 connected to 1 residual group(s)

FRAGMENT1 consist of the following atoms: 2 1 5 6

Volume of the Fragment = 207.1163

Energy of the Fragment = -39.292675

Charge of the Fragment = 0.650559

Total charge on residue R[1] = -0.648627

Fragment group dipole components:

x	y	z	dipole magnitude
0.082950	-0.318761	0.000002	0.329377

Fragment group dipole components (Normalized):

x	y	z	dipole magnitude
0.251838	-0.967769	0.000006	1.000000

```
-----
FRAGMENT 2
```

=====

There are 2 atom(s) in FRAGMENT2 connected to 1 residual group(s)

FRAGMENT2 consist of the following atoms: 3 4

Volume of the Fragment = 135.1837

Energy of the Fragment = -75.754618

Charge of the Fragment = -0.648627

Total charge on residue R[1] = 0.650559

Fragment group dipole components:

x	y	z	dipole magnitude
-0.675707	0.725467	0.000001	0.991404

Fragment group dipole components (Normalized):

x	y	z	dipole magnitude
-0.681565	0.731757	0.000001	1.000000

=====

Sums of fragments dipole components contributions\* :

x	y	z	dipole magnitude
-0.592757	0.406706	0.000003	0.718868

\* These sums equal to the molecular values only if all the fragments are included in the calculation.

=====

#### SUMMARY

=====

	x	y	z	dipole magnitude
FRAGMENT1	0.082950	-0.318761	0.000002	0.329377
FRAGMENT2	-0.675707	0.725467	0.000001	0.991404

Molecule (a.u.) -0.592757 0.406706 0.000003 0.718868

Molecule (D) -1.506789 1.033846 0.000007 1.827362

TOTAL CHARGE = 0.001932

TOTAL ENERGY = -115.047293

TOTAL VOLUME = 342.299995

Normalized fragments dipoles

	x	y	z	dipole magnitude
FRAGMENT1	0.251838	-0.967769	0.000006	1.000000
FRAGMENT2	-0.681565	0.731757	0.000001	1.000000

Normal termination of FRAGDIP.

### DESCRIPTION OF THE OUTPUT

The output file starts by listing the names of input files used in the calculations. Then it provides a list of the chosen fragments giving the sums of some integrated scalar quantities as well as the dipole components (all in the same units as in the input file: in atomic units if the user used the output of AIMPAC

without modifying the units). The scalar quantities summed by FRAGDIP for each fragment are: the volume, the energy, and the total charge of the fragment. Then the total charge on the residues attached to the fragment of interest are given. The sum of the charge of the fragment and all of its residue must be equal to the molecular charge, i.e. should be zero. Deviation from zero is a measure of the total integration error.

The fragment dipole moment component is given in atomic units. This dipole moment includes both the charge polarization contribution as well as the charge transfer contribution from the fragment to its bonded neighbours: the residues [ : (A), or the term in the braces in eqn (6), which represent the contribution of an atom or grouping of atoms to the molecular dipole moment]. The normalized (magnitude = unity) dipole contribution is also given for each fragment.

After the above information is given for all the fragments in the molecule, a summary is provided. The summary starts by listing the group contribution to the molecular dipole of each fragment, giving the DX, DY, and DZ components as well as the magnitude of the fragment dipole contribution. The vector sum of the fragments dipoles is then given, a sum which yields the molecular dipole [up to a numerical integration error, which one can estimate by comparing the molecular dipole obtained through this sum and the molecular dipole obtained directly from the self-consistent-field (SCF) or density functional theory (DFT) calculation]. The molecular dipole obtained through this vector sum is given in atomic units as well as in Debyes.

FRAGDIP also provides the sum of the fragments charges, energies and volumes, sums which must yield the corresponding molecular property within an integration error.

### **COMPARISON OF OUTPUTS FROM CHOICE A AND CHOICE B**

One can see that of course that the molecular dipole does not depend on the choice of fragments. Choice A and Choice B give identical dipole to within a small numerical error. Both of the Choice A and Choice B molecular dipole obtained in this fashion reproduce closely the dipole obtained from a direct SCF

calculation.

	DX	DY	DZ	D
Choice A: Molecule (D)	-1.508861	1.033313	0.000007	1.828769
Choice B: Molecule (D)	-1.506789	1.033846	0.000007	1.827362
SCF :	-1.5185	1.0279	0.0000	1.8337

The self-consistent-field (SCF) results were obtained from a restricted Hartree-Fock SCF implemented in the GAUSSIAN94[6] program calculation using a 6-31g\*\* basis set. Note that the basis set is not important in this illustrative example, what is important is the agreement between the dipole moment calculated as the vector sum of fragments contributions and the direct SCF dipole moment.

## REFERENCES

- [1] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory* (Oxford University Press, Oxford, U.K., 1990).
- [2] R. F. W. Bader and C. F. Matta, *Int. J. Quantum. Chem: Quantum Chem. Symp.* **41**, [Submitted] (2001).
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- [5] F. W. Biegler-König, R. F. W. Bader, and T.-H. Tang, *J. Computational Chem.* **13**, 317 (1982).
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## APPENDIX: PROGRAM LISTING

```
program dipole_from_fragments;
```

```
{N+}
```

```
uses
```

```
  winCRT;
```

```
const
```

```
  MaxNum=50;
```

```

type
  IntArray=array [1..MaxNum] of Integer;
  IntArray2D=array [1..Maxnum,1..MaxNum] of integer;
  ExtendedArray=array [1..MaxNum] of Extended;

var
  SumQ,SumE,SumVol,molecX,molecY,molecZ,molecMag:Extended;
  SumQrunning,SumErunning,SumVolrunning:Extended;
  Atom,AtomR,n,ncp,BondNumber,R,NR:IntArray;
  counter, counter1, counter11,counter111: Integer;
  counter2, counter6,MaxCounter: Integer;
  ii,NumAtoms,NumBonds,NumResiduals,i,j,k,newindex: integer;
  x,y,z,dx,dy,dz,q,E,Vol:ExtendedArray;
  n1,x1,y1,z1,dx1,dy1,dz1,q1:ExtendedArray;
  cpx,cpy,cpz,qR:ExtendedArray;
  xContrib,yContrib,zContrib:ExtendedArray;
  xRContrib,yRContrib,zRContrib:ExtendedArray;
  yesORno:char;
  InFileName1, InFileName2, InFileName3, OutFileName, Title: String;
  InFile1, InFile2, InFile3, OutFile: Text;
  bol6: boolean;
  xContribTotal,yContribTotal,zContribTotal,xmu,ymu,zmu:Extended;
  xRContribTotal,yRContribTotal,zRContribTotal:Extended;
  Xtotal,Ytotal,Ztotal,magnitude:ExtendedArray;

begin {Start the program}
  Writeln;
  Writeln ('=====');
  Writeln (' FRAGMENTS DIPOLE MOMENTS COMPUTATION (FRAGDIP)');
  Writeln ('=====');
  Writeln;

  counter6:=0;

{Input section}

  Writeln (' Info file contains the following field:');
  Writeln (' serial numbers, atomic coordinates, dipoles components, and charge:');
  Write (' INFO FILE NAME WITH EXTENSION: --> ');
  Readln (InFileName1);
  Assign(InFile1, InFileName1);

  Writeln;
  Writeln (' Bond critical points file contains the following field:');
  Writeln (' serial numbers, critical points coordinates:');
  Write (' BCP FILE NAME WITH EXTENSION: --> ');
  Readln (InFileName2);
  Assign(InFile2, InFileName2);

  Writeln;
  Write (' RESIDUES FILE NAME WITH EXTENSION: --> ');
  Readln (InFileName3);
  Assign(InFile3, InFileName3);
  Reset (InFile3);

  Writeln;

```

```

Write (' Output file name with extension: --> ');
Readln (OutFileName);
Writeln;
Writeln ('*****');

{Prepare output file}

Assign (OutFile,OutFileName);
Rewrite (OutFile);
Writeln (OutFile);
Writeln (OutFile,'=====');
Writeln (OutFile,' FRAGMENTS DIPOLE MOMENTS COMPUTATION (FRAGDIP)');
Writeln (OutFile,'=====');
Writeln (OutFile);
Writeln (OutFile,'Input atomic info file: ',InFileName1);
Writeln (OutFile,'Input bond critical point (bcp) info file: ',InFileName2);
Writeln (OutFile,'Residues information from info file: ', InFileName3);
Writeln (OutFile);

{MAIN LOOP: computes the dipole of a FRAGMENT in a molecule}
{=====}

counter:=1;
molecX:=0.0;
molecY:=0.0;
molecZ:=0.0;
molecMag:=0.0;
SumQrunning:=0.0;
SumErunning:=0.0;
SumVolrunning:=0.0;

repeat

Xtotal[counter]:=0.0;
Ytotal[counter]:=0.0;
Ztotal[counter]:=0.0;

{Reading the atoms composing the fragment}
Writeln (OutFile,'FRAGMENT ',counter);
Writeln (OutFile,'=====');
Writeln (OutFile);
NumAtoms:=0;
Writeln;
Write (' How many ATOMS are in FRAGMENT',counter,' ? --> ');
Readln (NumAtoms);
Writeln;

NumResiduals:=0;
Write (' How many R GROUPS are connected to FRAGMENT',counter,' ? --> ');
Readln (NumResiduals);
Writeln;
Writeln ('-----');
Writeln (OutFile,'There are ',NumAtoms,' atom(s) in FRAGMENT',counter,' connected to
',NumResiduals,' residual group(s)');

```

```

i:=0;
for i:=1 to NumAtoms do
begin
  Writeln;
  Writeln (' Enter an atom number:');
  if i=1 then
    Writeln (' (IMPORTANT:First atom is the one connected to the rest of the molecule)');
  Writeln;
  Write (' Atom[',i,']---> ');
  Readln (Atom[i]);
  Writeln;
  Writeln ('-----');
end;

```

{Displaying+printing the atom numbers of atoms in the FRAGMENT and calculating}  
 {the fragment total charge, energy and volume}

```

Write ('FRAGMENT', counter,' consist of the following atoms: ');
Write (OutFile,'FRAGMENT', counter,' consist of the following atoms: ');

```

```

i:=0;

```

```

SumQ:=0;

```

```

SumE:=0;

```

```

SumVol:=0;

```

```

for i:=1 to NumAtoms do

```

```

begin

```

```

  Write (' ');

```

```

  Write (Atom[i]);

```

```

  Write (' ');

```

```

  Write (OutFile,' ');

```

```

  Write (OutFile,Atom[i]);

```

```

  Write (OutFile,' ');

```

```

  Reset (InFile1);

```

```

  counter111:=0;

```

```

  While counter111<(Atom[i]-1) do

```

```

  begin

```

```

    Readln (InFile1);

```

```

    counter111:=counter111+1;

```

```

  end;

```

```

  Readln (InFile1,n[i],x[i],y[i],z[i],dx[i],dy[i],dz[i],q[i],E[i],Vol[i]);

```

```

  SumQ:=SumQ+q[i];

```

```

  SumE:=SumE+E[i];

```

```

  SumVol:=SumVol+Vol[i];

```

```

end;

```

```

  SumQrunning:= SumQrunning+SumQ;

```

```

  SumErunning:= SumErunning+SumE;

```

```

  SumVolrunning:= SumVolrunning+SumVol;

```

```

Writeln;

```

```

Writeln ('Charge of the Fragment = ',SumQ:12:6);

```

```

Writeln ('Energy of the Fragment = ',SumE:12:6);

```

```

Writeln ('Volume of the Fragment = ',SumVol:12:4);

```

```

Writeln (OutFile);

```

```

Writeln (OutFile,'Volume of the Fragment = ',SumVol:12:4);

```

```

Writeln (OutFile,'Energy of the Fragment = ',SumE:12:6);

```

```

Writeln (OutFile,'Charge of the Fragment = ',SumQ:12:6);

```

```

Writeln;

{Input information about the residuals attached to the fragment}
j:=0;
for j:=1 to NumResiduals do
begin
  Write (' Enter the bcp between atom ', Atom[1],' of fragment',counter,' and R['',j,'] : ');
  Read (ncp[j]);
  Writeln;
  Write (' R['',j,'] consists of how many atoms? --> ');
  Readln (NR[j]);
  Writeln;
  Writeln ('.....');
{Reset (InFile3);}
{Reading atoms in residual and summing up their charges to obtain
the total charge on the residue}

```

```

k:=0;
qR[j]:=0.0;
for k:=1 to NR[j] do
begin
  Writeln (' Enter the atoms of R['',j,']);
  Write (' AtomR['',j,k,']--> ');
  Readln (InFile3, AtomR[k]);
  Write (AtomR[k]);
  {Charge on residue Rj}
  Reset (InFile1);
  counter11:=0;
  While counter11<(AtomR[k]-1) do
  begin
    Readln (InFile1);
    counter11:=counter11+1;
  end;
  Readln (InFile1,n1[k],x1[k],y1[k],z1[k],dx1[k],dy1[k],dz1[k],q1[k]);
  qR[j]:=qR[j]+q1[k];
  Writeln;
  Writeln ('Total charge on residue R['',j,'] = ',qR[j]:12:6);
  Writeln;
  Writeln ('.....');
end;

Writeln (OutFile,'Total charge on residue R['',j,'] = ',qR[j]:12:6);
Writeln;
end;

```

```

{Reading the coords.(x,y,z), dipole components (dx, dy, dz) and
atomic charges of i atoms from the inf file}

```

```

i:=0;
for i:=1 to NumAtoms do
begin
  Reset (InFile1);
  counter1:=0;
  While counter1<(Atom[i]-1) do
  begin

```

```

        Readln (InFile1);
        counter1:=counter1+1;
    end;
    Readln (InFile1,n[i],x[i],y[i],z[i],dx[i],dy[i],dz[i],q[i]);
    {Writeln (n[i],x[i],y[i],z[i],dx[i],dy[i],dz[i],q[i]);}
end;

{Reading the coords.(cpx,cpy,cpz) of the bond critical points
from the bcp file}
j:=0;
for j:=1 to NumResiduals do
begin
    Reset (InFile2);
    counter2:=0;
    While counter2<(ncp[j]-1) do
    begin
        Readln (InFile2);
        counter2:=counter2+1;
    end;
    Readln (InFile2,ncp[j],cpx[j],cpy[j],cpz[j]);
    { Writeln (ncp[j], cpx[j], cpy[j], cpz[j])}
end;

{Calculating the contribution of FRAGMENT's atoms DIPOLES}
xmu:=0.0;
ymu:=0.0;
zmu:=0.0;
i:=0;
for i:=1 to NumAtoms do
begin
    xmu:=xmu+dx[i];
    ymu:=ymu+dy[i];
    zmu:=zmu+dz[i];
    Writeln (xmu:10:5, ymu:10:5, zmu:10:5);
end;
Writeln ('TOTALS mu',xmu:10:5, ymu:10:5, zmu:10:5);

{Calculating the contribution of FRAGMENT's atoms}
xContribTotal:=0.0;
yContribTotal:=0.0;
zContribTotal:=0.0;
i:=0;
if NumAtoms >=2 then
for i:=2 to NumAtoms do
begin
    xContrib[i]:=x[i]-x[1])*q[i];
    yContrib[i]:=y[i]-y[1])*q[i];
    zContrib[i]:=z[i]-z[1])*q[i];
    xContribTotal:=xContribTotal+xContrib[i];
    yContribTotal:=yContribTotal+yContrib[i];
    zContribTotal:=zContribTotal+zContrib[i];
    Writeln (xContrib[i]:10:5, yContrib[i]:10:5, zContrib[i]:10:5);
end;
Writeln ('TOTALS',xContribTotal:10:5,yContribTotal:10:5,zContribTotal:10:5);

{Calculating the contribution of FRAGMENT-to-Rs contributions}

```

```

xRContribTotal:=0.0;
yRContribTotal:=0.0;
zRContribTotal:=0.0;
j:=0;
for j:=1 to NumResiduals do
  begin
    xRContrib[j]:=(cpX[j]-x[1])*qR[j];
    yRContrib[j]:=(cpY[j]-y[1])*qR[j];
    zRContrib[j]:=(cpZ[j]-z[1])*qR[j];
    xRContribTotal:=xRContribTotal+xRContrib[j];
    yRContribTotal:=yRContribTotal+yRContrib[j];
    zRContribTotal:=zRContribTotal+zRContrib[j];
    Writeln (xRContrib[j]:10:5, yRContrib[j]:10:5, zRContrib[j]:10:5);
  end;
Xtotal[counter]:= xContribTotal+xRContribTotal+xmu;
Ytotal[counter]:= yContribTotal+yRContribTotal+ymu;
Ztotal[counter]:= zContribTotal+zRContribTotal+zmu;
magnitude[counter]:=SQRT(sqr(Xtotal[counter])+sqr(Ytotal[counter])+sqr(Ztotal[counter]));
Writeln ('Fragment group dipole components:');
Writeln (Xtotal[counter]:12:6,' ',Ytotal[counter]:12:6,' ',Ztotal[counter]:12:6,'
',magnitude[counter]:12:6);
Writeln (OutFile,'Fragment group dipole components:');
Writeln (OutFile,' x      y      z      dipole magnitude');
Writeln (OutFile,Xtotal[counter]:12:6,' ',Ytotal[counter]:12:6,' ',Ztotal[counter]:12:6,'
',magnitude[counter]:12:6);
Writeln (OutFile);
Writeln (OutFile,'Fragment group dipole components (Normalized):');
Writeln (OutFile,' x      y      z      dipole magnitude');
Writeln (OutFile,Xtotal[counter]/magnitude[counter]:12:6,
' ',Ytotal[counter]/magnitude[counter]:12:6,' ',
Ztotal[counter]/magnitude[counter]:12:6,' ',magnitude[counter]/magnitude[counter]:12:6);
Writeln (OutFile,'-----');
Writeln (OutFile);

{Calculate the molecular dipole}

molecX:=molecX+Xtotal[counter];
molecY:=molecY+Ytotal[counter];
molecZ:=molecZ+Ztotal[counter];
molecMag:=SQRT(sqr(molecX)+sqr(molecY)+sqr(molecZ));

{Update the counter after the MAIN LOOP}
counter:=counter+1;

write ('Do you want more calculations (y/n):');
readln (yesORno);
bol6:=yesORno='n';

until bol6;
  MaxCounter:=counter;
  Writeln (OutFile,'=====');
  Writeln (OutFile);
  Writeln (OutFile,'Sums of fragments dipole components contributions* :');
  Writeln (OutFile,'      x      y      z      dipole magnitude');
  Writeln (OutFile,molecX:12:6,' ',molecY:12:6,' ',molecZ:12:6,' ',molecMag:12:6);
  Writeln (OutFile);

```

```

Writeln (OutFile,'* These sums equal to the molecular values only if all the fragments');
Writeln (OutFile,' are included in the calculation. ');
Writeln (OutFile,'=====');
Writeln (OutFile);
Writeln (OutFile,'SUMMARY');
Writeln (OutFile,'=====');
Writeln (OutFile,'      x      y      z      dipole magnitude');
for counter:=1 to (MaxCounter-1) do
begin
  Write (OutFile,'FRAGMENT',counter,' ');
  Writeln (OutFile,Xtotal[counter]:12:6,' ',Ytotal[counter]:12:6,' ',Ztotal[counter]:12:6,'
,magnitude[counter]:12:6);
end;
Writeln (OutFile);
Write (OutFile,'Molecule (a.u.) ');
Writeln (OutFile,molecX:12:6,' ',molecY:12:6,' ',molecZ:12:6,' ',molecMag:12:6);
Write (OutFile,'Molecule (D) ');
Writeln (OutFile,2.542*molecX:12:6,' ',2.542*molecY:12:6,' ',2.542*molecZ:12:6,'
,2.542*molecMag:12:6);

Writeln ('TOTAL CHARGE = ',SumQrunning:12:6);
Writeln ('TOTAL ENERGY = ',SumErunning:12:6);
Writeln ('TOTAL VOLUME = ',SumVolrunning:12:6);
Writeln (OutFile);
Writeln (OutFile,'TOTAL CHARGE = ',SumQrunning:12:6);
Writeln (OutFile,'TOTAL ENERGY = ',SumErunning:12:6);
Writeln (OutFile,'TOTAL VOLUME = ',SumVolrunning:12:6);
Writeln (OutFile);

Writeln (OutFile,'Noramilzed fragments dipoles');
Writeln (OutFile,'      x      y      z      dipole magnitude');
for counter:=1 to (MaxCounter-1) do
begin
  Write (OutFile,'FRAGMENT',counter,' ');
  Writeln (OutFile,Xtotal[counter]/magnitude[counter]:12:6,
' ',Ytotal[counter]/magnitude[counter]:12:6,' ',
Ztotal[counter]/magnitude[counter]:12:6,' ',magnitude[counter]/magnitude[counter]:12:6);
end;
Writeln (OutFile);

Writeln (OutFile, 'Normal termination of FRAGDIP. ');

Close (InFile1);
Close (InFile2);
Close (OutFile);
DoneWinCrt
end.

```