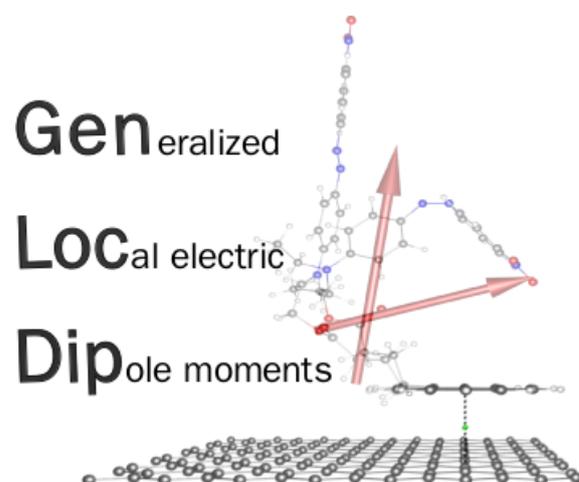


GENLOC DIP

A program to calculate local electric dipole moments
via Atoms-In-Molecules (AIM) analysis

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1 Introduction

GENLOCDIP is a program for calculating and visualizing local dipole moments of molecular subsystems according to the Atoms-In-Molecules (AIM) partitioning scheme [1]. It employs a modified version of Bader’s and Laidig’s approach [2,3] for achieving origin-independence of local dipoles by referring to internal reference points such as bond critical points. The programs’ main new feature is the possibility to interface grid-based AIM codes where the critical point search is bypassed in order to improve the computational efficiency. In particular, this offers the advantage of investigating extended non-covalently bonded systems on surfaces using plane-wave based electronic structure packages.

2 Theory

The implementation of the local dipole moments in the Atoms-In-Molecules (AIM) approach shall only be briefly summarized. When defining local dipole moments, an additional difficulty arises, as fragments of molecular or supramolecular systems are usually (partially) charged, and dipole moments of charged systems depend on the choice of origin,

$$\boldsymbol{\mu} = \sum_A \left[\underbrace{- \int_A \mathbf{r}_A \rho(\mathbf{r}) d\mathbf{r}}_{\boldsymbol{\mu}_A^p} + \underbrace{q_A \mathbf{X}_A}_{\boldsymbol{\mu}_A^c} \right], \quad (1)$$

where origin-dependent terms have been underlined. \mathbf{r}_A denotes a point in space relative to a nuclear coordinate \mathbf{X}_A , $\mathbf{r}_A = \mathbf{r} - \mathbf{X}_A$, q_A the partial charge of atom A , and ρ the electron density. The first part of the local dipole moment refers to a polarization term, the second to a charge transfer term.

In order to overcome the origin-independence, the charge transfer contribution is divided into fragment F and n residual group R_i contributions (with $i = 1, 2, \dots, n$),

$$\boldsymbol{\mu}^c = \sum_A \mathbf{X}_A q_A = \sum_{A \in F} \mathbf{X}_A q_A + \sum_{i=1}^n \sum_{A \in R_i} \mathbf{X}_A q_A. \quad (2)$$

All nuclear coordinates \mathbf{X}_A are now reformulated with respect to internal reference points (IRPs) \mathbf{X}^r between fragment F and residual groups R_i ,

$$\begin{aligned} \boldsymbol{\mu}^c &= \sum_{A \in F} [\mathbf{X}_A - \mathbf{X}^r(F|R_n)] q_A + \mathbf{X}^r(F|R_n) q_F + \sum_{i=1}^n \mathbf{X}^r(F|R_i) q_{R_i} \\ &+ \sum_{i=1}^n \sum_{A \in R_i} [\mathbf{X}_A - \mathbf{X}^r(F|R_i)] q_A, \end{aligned} \quad (3)$$

where it has been exploited that the fragment partial charge is $q_F = \sum_{A \in F} q_A$. In order to demonstrate that $\boldsymbol{\mu}^c$ does not depend on the choice of the origin, we exploit

that for neutral systems $q_F = -\sum_{i=1}^n q_{R_i}$,

$$\begin{aligned} \boldsymbol{\mu}^c = & \sum_{A \in F} [\mathbf{X}_A - \mathbf{X}^r(F|R_n)] q_A + \sum_{i=1}^{n-1} [\mathbf{X}^r(F|R_i) - \mathbf{X}^r(F|R_n)] q_{R_i} \\ & + \sum_{i=1}^n \sum_{A \in R_i} [\mathbf{X}_A - \mathbf{X}^r(F|R_i)] q_A. \end{aligned} \quad (4)$$

In Eq. (4), the second term is a difference between IRPs (Note that it vanishes if $i = n$) and, thus, origin-independent. If we define local dipole moments, this term either needs to be assigned to the fragment or to the residual contribution. Here, the former is done to get the following expression for the dipole moment of a fragment F ,

$$\boldsymbol{\mu}_F = \sum_{A \in F} \boldsymbol{\mu}_A^p + \sum_{A \in F} [\mathbf{X}_A - \mathbf{X}^r(F|R_n)] q_A + \sum_{i=1}^{n-1} [\mathbf{X}^r(F|R_i) - \mathbf{X}^r(F|R_n)] q_{R_i}. \quad (5)$$

The first term of the charge transfer contribution represents the intrafragment charge transfer and both final terms represent the interfragment charge transfer.

3 Installation

GENLOCDIP is written in FORTRAN90 and was compiled using the gfortran 4.8.2 compiler on an Ubuntu 14.4 operating system with eight 64-bit Intel Xeon CPUs. Furthermore, it has been successfully installed from source code on a 64-bit Mac OS X 10.7.5 system with a 2.0 GHz Intel Core i7 processor using gfortran 4.6.2. In principle, it can be installed on any machine with a FORTRAN compiler installed (and POVRAY if a graphical representation is desired). A stable and tested version of the code is distributed as a zipped archive file. You can test the installation by checking the examples in `examples/`. To install the code, unzip and unpack the zipped tar directory,

```
tar -jxvf genlocdip.tar.bz2
```

To compile the code,

```
make
```

This will create the binary `$GENLOCDIP_HOME/bin/genlocdip`.
If necessary edit the Makefile in `src/` (`tools/`) and compile again.

Please set the following environment variables (e.g. in your BASHRC).

```
GENLOCDIP_HOME=<path-to-your-genlocdip-directory>/genlocdip
PATH=$GENLOCDIP_HOME/bin:$GENLOCDIP_HOME/scripts:$PATH
```

AIMAll by Todd A. Keith

Available from: <http://aim.tkgristmill.com> (Standard mode).
Note that you have to register first.

Multiwfn by Tian Lu

Available from: <https://multiwfn.codeplex.com/>.

Bader by Graeme Henkelman's group

The `bader` code (with some modifications by the BigDFT developers [4, 5] and LG) is provided in `tools/`. It is essential to use the modified version otherwise the atomic polarizations cannot be read.

4 How to run a local dipole calculation

In general, the following steps are necessary:

1. Perform an electronic structure calculation using software such as GAUSSIAN, TURBOMOLE or QUANTUM ESPRESSO.
2. Generate a wavefunction (`.wfn/.wfx`), a formatted checkpoint (`.fchk`) or a density-on-a-grid (`.cube`) file using, e.g. the `molden2aim` [6], `formchk` [7] or the `cubegen` [7] tool.
3. Run the local dipole calculation by typing `genlocdip` and choose an AIM program which will be started automatically (`GENLOCDIP` currently interfaces `AIMALL` [8], `MULTIWFN` [9] and `BADER` [10])
4. The relevant information from the AIM analysis is extracted: Cartesian atomic coordinates \mathbf{X}_A , partial charges $q(A)$ and atomic polarizations $\boldsymbol{\mu}^p(A)$.
If a wavefunction based AIM program is selected, coordinates of the bond critical points (BCPs), ring critical points (RCPs) and cage critical points (CCP) are read as well and the bond charges $q(A|B)$ are calculated numerically. Furthermore, the atomic dipole moments $\boldsymbol{\mu}_A$ are calculated.
5. The molecular system is partitioned into subsystems based on the user input. Examples of `GENLOCDIP` prompts and user response is provided in Section 8.
6. Choose an option to define the BCP(s) between the fragment and the residual group(s). Available options are shown in Table 1.
7. A fragment dipole moment is calculated using Eq. (5).

Table 1: Different options to choose an IRP between a fragment and a residual group.

<code>man X Y Z atomF atomR</code>	<p><code>man</code>: manually type in IRP coordinates between fragment and residual group <code>X,Y,Z</code>: coordinates of the IRP (in Bohr) <code>atomF,atomR</code>: fragment and residual atom number</p>
<code>sel BCPnum</code>	<p><code>sel</code>: select a BCP from a previous BCP search <code>BCPnum</code>: number of the BCP</p>
<code>bond atomF atomR fac</code>	<p><code>bond</code>: guess an IRP between fragment and residual group along the bond of atom pairs <code>atomF,atomR</code>: fragment and residual atom number <code>fac</code>: shifting factor ($0 < \text{fac} < 1$), e.g. <code>fac = 0.5</code> corresponds to the midpoint of atom pairs</p>
<code>aprx atomF atomR</code>	<p><code>aprx</code>: check which grid point of the Bader volume of the fragment is closest to <code>atomR</code>, and drop a perpendicular from this point to the straight line connecting <code>atomF</code> and <code>atomR</code>. <code>atomF,atomR</code>: fragment and residual atom number</p>

- An output file containing a summary of the calculation and a POV-Ray input file illustrating the coordinates of the studied system, BCPs/IRPs between the fragment and residual groups, as well as the fragment dipole moment are written.

Figure 1 shows the main steps in a calculation of the fragment dipole moment as implemented in the GENLOCDIP code [11].

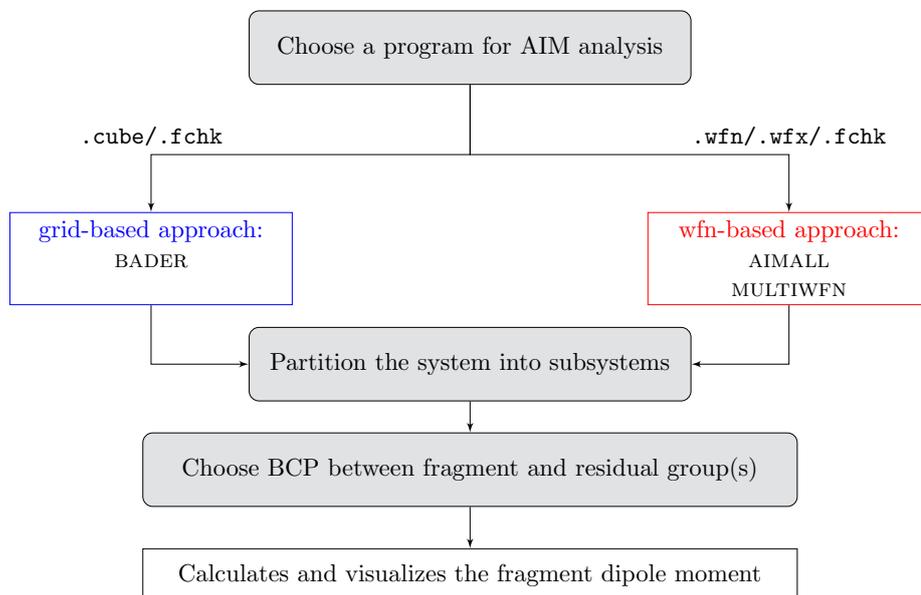


Figure 1: Schematic picture of the main steps in a calculation of the fragment dipole moment using the program GENLOCDIP.

5 More details on how to get the necessary input files from electronic structure calculations

5.1 TURBOMOLE

Wavefunction files

First, generate a MOLDEN file with `tm2molden`. By using the `molden2aim` tool written by W. Zou [6], MOLDEN input files can be converted to `.wfn` format. For details, see <http://people.smu.edu/wzou/program/index.html>

It should be noted that wavefunction files generated by TURBOMOLE sometimes contain molecular orbitals that are not sufficiently orthonormal [8]. Hence it is recommended to instead generate density-on-a-grid files using TURBOMOLE.

Cube files

For generating a grid-based file, add the following keywords to the control file.

```
$pointval fmt=cub
  grid1 vector 1 0 0  range -7.4,7.4 points 75
  grid2 vector 0 1 0  range -6.0,6.0 points 61
  grid3 vector 0 0 1  range -6.0,7.1 points 66
```

and run `ridft -proper`.

The density is written to the resulting `td.cub` file. Note that the range and grid (point per Bohr) values must be adapted according to the molecular system size.

5.2 GAUSSIAN

Wavefunction files

Set up a structure optimization or a single-point calculation with GAUSSIAN using the PYTHON script `makeg09input.py` (located in `scripts`),

```
python $GENLOCDIP_HOME/scripts/makeg09input.py <filename>.xyz
```

In order to generate an extended wavefunction (`.wfx`) file, the GAUSSIAN input file may look like the following.

```
%chk=water.chk
%NProcShared=1
#P bp86/tzvp output=wfx force nosymm
```

Generate extended wavefunction file, single point calculation (with forces)

```
0 1
O 0.018731 -0.289011 0.227189
H 0.804898 0.281119 0.249723
H -0.726202 0.334232 0.241724
```

water.wfx

Cube files

First, generate a formatted checkpoint file, `formchk <filename>.chk`. Gaussian includes a standalone utility for generating cubes from the data in a formatted checkpoint file, named `cubegen` [7].

```
cubegen 1 density <fchkfile> <cubefile> <npts> h
```

where `npts` indicates the number of points per side in the cube. A value of 0 selects the default value of 80^3 points distributed evenly over a rectangular grid generated automatically by the program (not necessarily a cube).

5.3 QUANTUM ESPRESSO

When using Quantum Espresso (QE), please note that (1) the molecule or adsorbate must be placed in the center of the unit cell and (2) the Bravais-lattice index must be set to `ibrav=0` (in the PWscf calculation).

For generating a density-on-a-grid file, set up a `<filename>.pp.in` input file as shown below,

```
&INPUTPP
      prefix = 'H2O' ,
      outdir = 'ESPRESSO_TMPDIR'
      plot_num = 0,
/
&PLOT
      nfile = 1 ,
      weight(1) = 1.0,
      fileout = 'h2o.cube' ,
      iflag = 3 ,
```

```
output_format = 6 ,
```

```
/
```

and run `pp.x < <filename>.pp.in`.

This will start a QUNATUM ESPRESSO post-processing calculation for data analysis and plotting.

6 Output files

Regardless of the AIM method used, the following output files will be written.

- `genlocdip_AIMPROG_DATE_TIME.out`: GENLOCDIP output
- `dipole_AIMPROG_DATE_TIME_FRAGNR.pov`: POVRAY input file for visualizing the local dipole moment of a fragment

In case of a wfn-based AIM method, additional output files will be provided.

- `allcp_AIMPROG_DATE_TIME_FRAGNR.pov`: POVRAY input for visualizing all CPs
- `sumatm_AIMPROG_DATE_TIME_FRAGNR.pov`: POVRAY input file for visualizing the summed atomic dipole moments for the fragment

7 Plotting local dipole moments

1. Create a file `pov.dat` in your working directory.

```
0 0 5           # camera position
0 0 6           # position of the light source
0 0 0           # orientation of the molecule
0 0 0           # position of the molecule
1              # color code (0 = b/w, 1 = color)
allbcp_AIMPROG_DATE_TIME_FRAGNR # names of povray input files
sumatm_AIMPROG_DATE_TIME_FRAGNR # (without the .pov ending)
dipole_AIMPROG_DATE_TIME_FRAGNR
```

If you do not get the orientation or position you like with the default settings, try changing numbers in the third line from 0 to 90 for a quarter rotation or to 180 for a full rotation etc. and in the fourth line from -1 to 1 for a slight displacement in x , y , and z direction, respectively.

2. Postprocess the POVRAY files with the tool `pov_edit` (provided in the `tools/` directory): `pov_edit < pov.dat`
3. Process the modified files (ending with `_new.pov`) with POVRAY.

```
povray +Q20 +H640 +W840 +A0.2 <povray-input-filename>_new.pov
```

8 Examples of GenLocDip prompts and user response

Example 1: Choose wfn-based AIM program

```
=====
=          GENLOCDIP V0.4          =
=   calculates local dipole moments   =
=   written by LG, Nov. 2014, Uni Hamburg =
=====
-----
>> Choose Bader AIM program (default=aimall)
-----
multiwfn (m) : needs .wfn/.wfx/.fchk input file
aimall   (a) : needs .wfn/.wfx/.fchk input file
bader    (b) : needs .cube/.fchk input file
-----
a
-----
>> Name of input file (.wfn|.wfx|.fchk|.cube):
-----
waterdimer.wfn
-----
>> List of atoms in fragment      1
      (i.e. 1-5,12,34-55) ?
-----
1-3
-----
>> How many residual groups are connected to fragment 1? default=1
-----
1
-----
>> BCP b/w fragment 1 and residual 1 (default= sel Bcpnum)
-----
man <X Y Z> <atomF> <atomR>   - type in BCP coordinates manually
sel <Bcpnum>                  - select a BCP from a previous BCP search

   1  2.1476832246893700E-008  0.25979566099244700  3.0054016182053100  01  H5

bond <atomF> <atomR> <fac>   - guess a BCP along the bond of atom pairs
                              (0 < fac < 1)
aprx <atomF> <atomR>        - approximate a BCP from summed Bader volumes
                              of the fragment
-----
sel 1
-----
>> Do you want to continue (y/n)? default: n
-----
n
```

Example 2: Choose grid-based AIM program

```
=====
=          GENLOCDIP V0.4          =
=   calculates local dipole moments   =
=   written by LG, Nov. 2014, Uni Hamburg =
=====

-----
>> Choose Bader AIM program (default=aimall)
-----

multiwfn (m) : needs .wfn/.wfx/.fchk input file
aimall   (a) : needs .wfn/.wfx/.fchk input file
bader    (b) : needs .cube/.fchk input file
-----

bader
-----
>> Name of input file (.wfn|.wfx|.fchk|.cube):
-----

waterdimer.cube
-----

>> List of atoms in fragment      1
    (i.e. 1-5,12,34-55) ?
-----

1-3
-----

>> How many residual groups are connected to fragment 1? default=1
-----

1
-----

>> BCP b/w fragment 1 and residual 1 (default= sel Bcpnum)
-----

man <X Y Z> <atomF> <atomR> - type in BCP coordinates manually
sel <Bcpnum>                - select a BCP from a previous BCP search
bond <atomF> <atomR> <fac>  - guess a BCP along the bond of atom pairs
                             (0 < fac < 1)
aprx <atomF> <atomR>        - approximate a BCP from summed Bader volumes
                             of the fragment
-----

aprx 1 4
-----

>> Do you want to continue (y/n)? default: n
-----

n
```

References

- [1] Bader, R. F. W., *Atoms in Molecules: A Quantum Theory*, Oxford University Press: Oxford, U.K., 1990.
- [2] Laidig, K. E. and Bader, R. F. W., *J. Chem. Phys.*, 1990, **93**(10), 7213–7224.
- [3] Bader, R. F. W.; Keith, T. A.; Gough, K. M. and Laidig, K. E., *Mol. Phys.*, 1992, **75**(5), 1167–1189.
- [4] Genovese, L.; Neelov, A.; Goedecker, S.; Deutsch, T.; Ghasemi, S. A.; Willand, A.; Caliste, D.; Zilberberg, O.; Rayson, M.; Bergman, A. and Schneider, R., *J. Chem. Phys.*, 2008, **129**, 014109.
- [5] Mohr, S.; Ratcliff, L. E.; Boulanger, P.; Genovese, L.; Caliste, D.; Deutsch, T. and Goedecker, S., *J. Chem. Phys.*, 2014, **140**, 204110.
- [6] Zou, W., molder2aim; <http://people.smu.edu/wzou/program/index.html>.
- [7] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J. and Fox, D. J., Gaussian 09 Revision A.1, gaussian inc. wallingford ct 2009.
- [8] Keith, T. A., AIMAll (Version 14.11.23), TK Gristmill Software, Overland Park KS, USA, 2014; available from aim.tkgristmill.com.
- [9] Lu, T. and Chen, F., *J. Comp. Chem.*, 2011, **33**(5), 580–592.
- [10] Henkelman, G.; Arnaldsson, A. and Jónsson, H., *Comp. Mater. Sci.*, 2006, **36**(3), 354–360.
- [11] Groß, L., GENLOCDIP – A program to calculate and visualize local electric dipole moments via Atoms-In-Molecules analysis, university of hamburg, 2014-2015.