Xaim-1.0

Users Guide

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X a i m - 1 . 0

Scope and Availability

Xaim is a X11 graphical user interface to several programs based on some aspects of the Theory of Atoms in Molecules[1] developed by Prof. R.F.W. Bader and coworkers. The two programs currently interfaced are:

- EXTREME [2], the program that locates critical points in the electronic charge density distribution $\rho(r)$ (i.e. points where $\nabla\rho(r) = 0$) and determines various properties at that points.

- FLOPO [3], the program that makes plots of molecular distribution functions such as molecular orbitals, electronic density, Laplacian, kinetic energy density, fermi hole density and density difference maps.

In many cases, specially for large systems, the topological analysis of the charge density is focused in only some critical points that may exist in the system rather than in the whole set. For this reason and to make our life easier, we decided to build an interface to search only those critical points that may be relevant in some case and to store the results. These are the two tasks that are easily accomplished by the Xaim-EXTREME interface.

Xaim-FLOPO interface generates the information required to make contour plots, i.e. 2D plots of several molecular distribution functions (a 3D module is planned). Plot parameters are easily specified: the plot plane may be defined in different ways, default contour values may be fully override, etc. Three output formats are currently generated: on a X-Window screen and GIF and Postscript files.

Gaussian and Slater basis sets are supported. For Gaussian basis sets, s,p,d and f functions are available. For Slater basis sets the following functions are coded:
1s, 2s, 3s, 4s, 5s, 6s and 7s; 2p, 3p, 4p, 5p, 6p and 7p; 3d, 4d, 5d and 6d and 4f and 5f.

Xaim is available from the WWW site distribution http://www.quimica.urv.es/XAIM for the following systems:

- IBM RS/6000 AIX, SGI Irix, HP HP-UX, Sun Solaris

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[1] Bader, R.F.W., "Atoms in Molecules: A Quantum Theory", Oxford University Press, 1990.
[2] EXTREME was written by F.W. Biegler-Koenig

[3] FLOPO was written by S.G.Anderson, Clement Lau, Preston Mac Dougall and Carles Bo

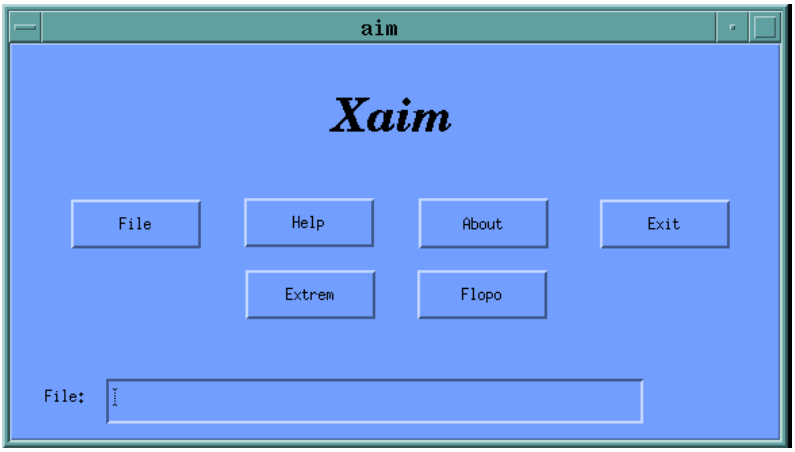
Installing Xaim

Once you have downloaded the distribution file corresponding to your hardware environment, uncompress it (*gzip -d file_name.tar.gz*) and untar it (*tar -xf file_name.tar*). This procedure will build a XAIM/bin directory containing the binaries and some PGPLOT files. Move the XAIM tree to your preferred location, include in your environment variable PATH the absolute path to XAIM/bin and define a new environment variable PGPLOT_DIR that should contain the absolute path to XAIM/bin.

Getting Started

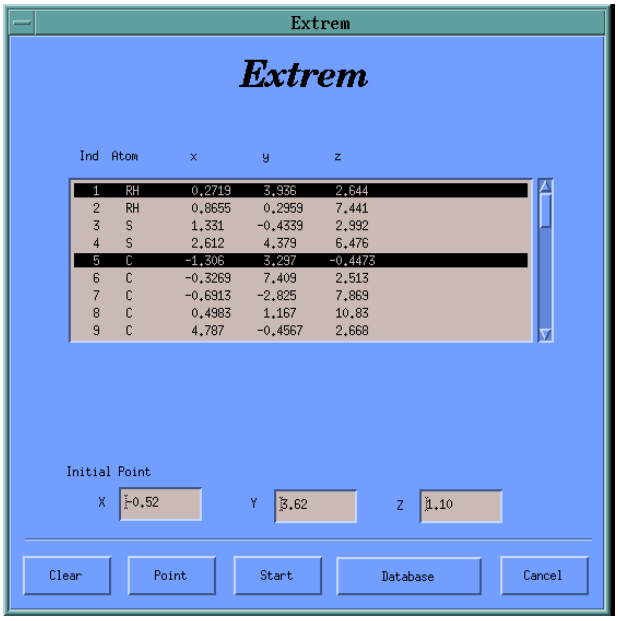
Xaim uses a single file as input (the WFN file). This file contains the molecular geometry, basis set functions description and molecular orbitals. It can be directly obtained from an ADF or GAUSSIAN run or easily generated from other packages (see Appendix I for a detailed description of the WFN file format).

To invoke the program simply type *Xaim*. This step will also determine the working directory where several files will be written, either result files or scratch ones. The main window will be created (see below). Before using EXTREME or FLOPO, the user has to select a WFN file. Push the FILE button and select a file from the file selection window. Once a valid file has been chosen, you are allowed to choose either EXTREME or FLOPO.
The HELP button provide a brief description. The ABOUT button give information about the authors and how to contact them.



Xaim-EXTREME

Extreme Window

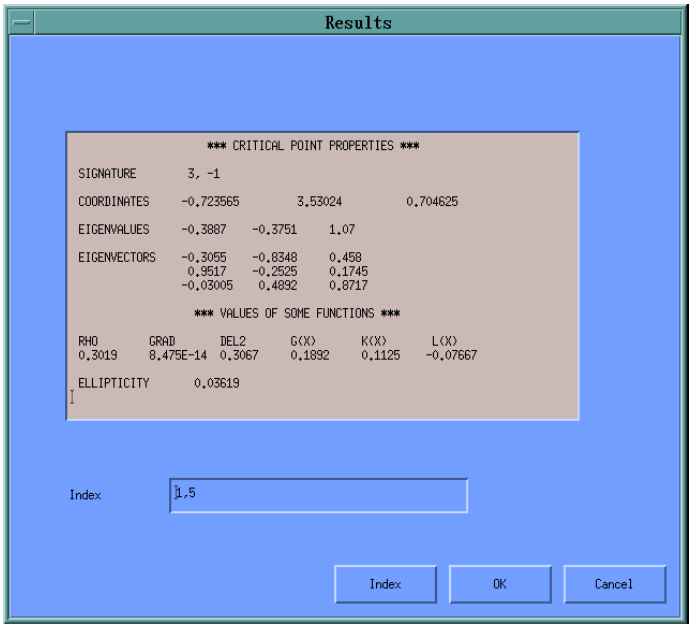


If you have selected Extreme from the main window a new one, the Extreme Window, will show the atoms list and some action buttons.

Click on those atoms you think are near the critical point you would like to find (at least one atom). Push the POINT button to determine the initial search point. This point is always computed as the midpoint of the nuclear coordinates that have been selected. If you are satisfied with this guess, push SEARCH to start a critical point search. Otherwise, you may change x, y and z values by typing directly on the corresponding box. A new search is always started with the coordinates that are currently displayed.

Browsing results

A new window will monitor EXTREME execution. If the critical point is found this window will be merely informative, but in some cases input will be required in it (see below Difficult Cases). The results will be displayed in the Results Window.



The Index box contains the atoms index corresponding to that point. If the critical point is a bond critical point, two atoms index will be displayed and the INDEX button is inactive in this case. Sometimes, for ring or cage critical points is not easy to deduce Index values. In these cases, the INDEX button allow

the user to select those atoms near the critical point. This task is easily done because a new window, the Index Selection Window, showing a critical point-atom distance ordered list will be opened and the user only has to select the last atom to be included in Index. Push OK to close the Index Selection Window.

Push OK, again, on the Results Window to keep the results in the database file or CANCEL to forget this point and return to the Extreme Window.

Xaim-EXTREME Database

Xaim stores the critical points properties in a database file (an ASCII file named *WFN_filename*.cp). The program will prevent you from finding the same point again by verifying the atoms index you are selecting with those stored in the database. The contents of this file can be browsed by pushing the DATABASE button on the Extreme Window. Select a critical point and push PROPERTIES to view them.

Difficult Cases

In some cases, standard critical point search procedure fails. It can be due to various reasons:

- there is not any critical point in that space zone
- there is a point but the density is very flat and the search procedure is too slow
- the WFN file has the right format but the contents are meaningless

It may also occur you find a critical point that you had not been looking for. Or, in other words, that you cannot find the critical point you desire.

In such case, after some iterations the program asks what you would like to do. You can finish EXTREME execution or you can continue searching by modifying manually the following default values (you will be asked for them):

NITER : number of iterations you would like to do

DUMP: gradient scale factor (Xnew=Xold-DUMP*GRAD) (default=0.1)

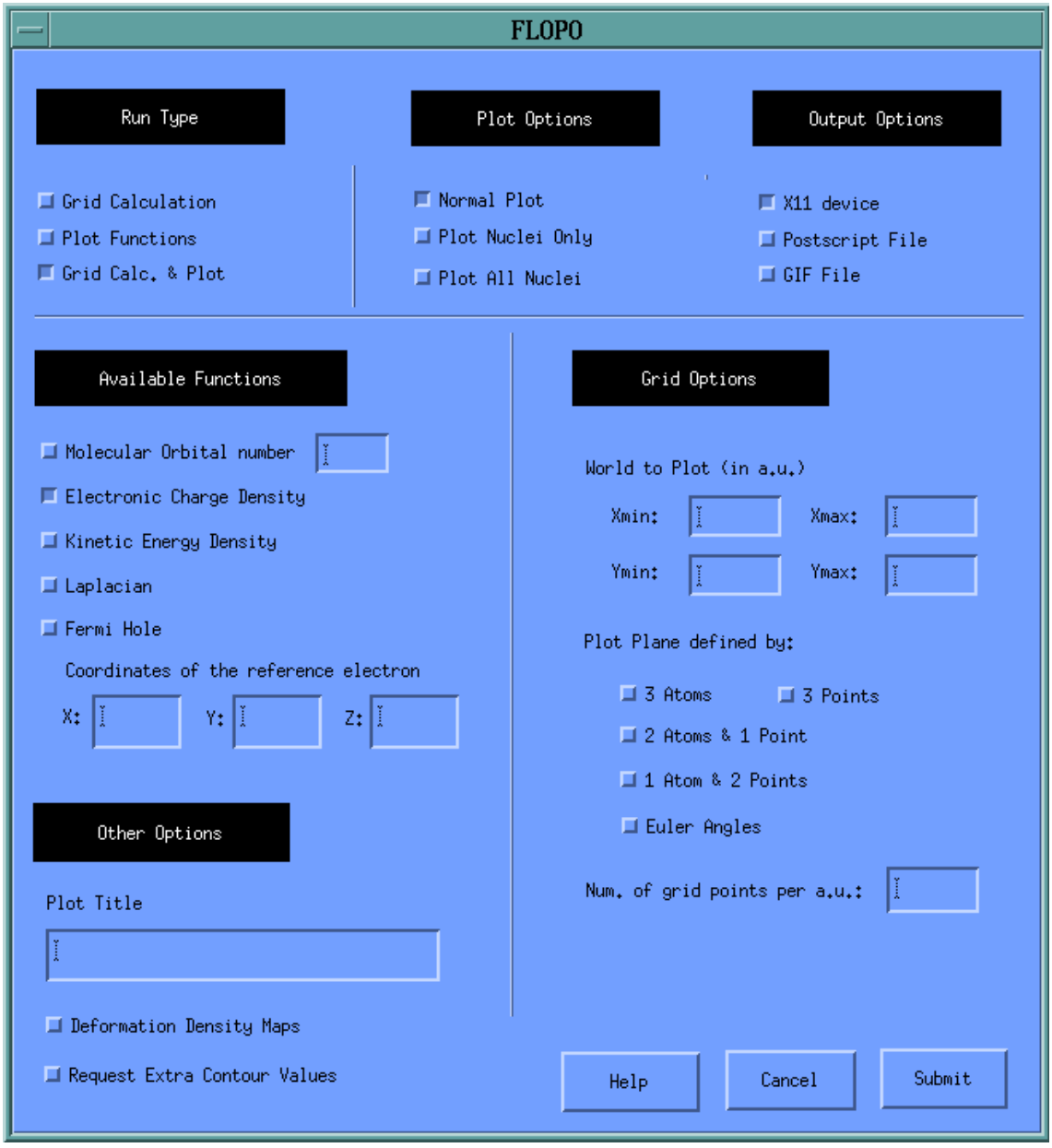
Some hints:

Begin with 2 or 3 iterations with 2.0 < DUMP < 0.5, followed by iterations at 0.1 .

If you have not yet found a critical point, verify the initial point: **it is the most important guess** in the search procedure.

Xaim-FLOPO

FLOPO WINDOW



AVAILABLE FUNCTIONS

- Molecular Orbitals $\psi_i(r) = \sum_j c_{ji}\phi_j(r)$
- Electronic charge density $\rho(r) = \sum_i^{NMO} \eta_i |\psi_i(r)|^2$
- Kinetic energy density $K(r) = -\frac{1}{2}\sum_i^{NMO} \eta_i \psi_i(r)\nabla^2\psi_i(r)$
- Laplacian of the charge density $\nabla^2\rho(r) = \frac{\partial^2\rho(r)}{\partial x^2} + \frac{\partial^2\rho(r)}{\partial y^2} + \frac{\partial^2\rho(r)}{\partial z^2}$
- Fermi Hole density

$$h^\alpha(r_1, r_2) = -\sum_i^\alpha \sum_j^\alpha \psi_i(r_1)\psi_j^*(r_1)\psi_i(r_2)\psi_j^*(r_2) \Big/ \sum_i^\alpha \psi_i(r_1)\psi_i^*(r_1)$$

(For this function, the position of the reference electron, r_1, has to be specified . If its location lies on the plot plane, a star will be plotted on it.)

- Density Difference Maps $\rho_{dif}(r) = \rho_1(r) - \sum_i \rho_i(r)$

GRAPHICAL OUTPUT OPTIONS

- X11 DEVICE ***(Default)***

  It plots on a new X11 window

- Postscript FILE

  It plots on a file postscript file named ***pgplot.ps***

- Gif FILE

  It plots on a file named ***pgplot.gif***

RUN TYPES

- GRID CALCULATION

  No plot will be produced. This part of the program is always the most time consuming and it may take some minutes (some minutes may be half an hour or more in some cases). A new file named ***GRID*** will be created in the working directory.

- PLOT

  Read the ***GRID*** file and plot requested functions. In this version the program assumes that the ***GRID*** file exists and that the plot parameters (see below) are the same that those used to create the ***GRID*** file.

- GRID CALCULATION & PLOT ***(Default)***

PLOT OPTIONS

- NORMAL PLOT ***(Default)***

- PLOT NUCLEI ONLY

  Use this option to verify that the plot will look nice (zoom, orientation).

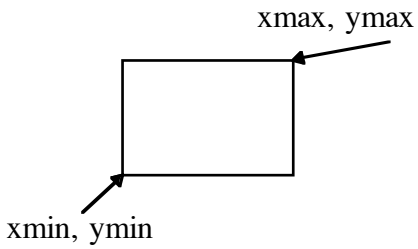
- PLOT ALL NUCLEI

  By default, only those atoms lying on the plane plot are drawn. If this option is activated, it also plots the other nuclei projected on the map.

PLOT PARAMETERS

- WORLD TO PLOT

  (xmin, ymin) define the low left corner of the plot plane and (xmax,ymax) the high right one in atomic units.



- PLANE TO PLOT

  There are two procedures implemented in order to define the plot plane:

  - Specifying three space points, that may be:
    - 3 atoms
    - 2 atoms & 1 point
    - 1 atom & 2 points
    - 3 points

In these cases the first point will determine the center of the plot plane, the second one the horizontal X axis and the third one the plane.

- Specifying:
  - x0, y0 and z0 that are the coordinates of the center of the plot plane and
  - the Euler Angles (alpha, theta, phi). These are the three angles required to rotate the plot plane (X'Y') into the molecular coordinate system (XYZ). They correspond to the following.

    Rotation alpha degree around the Z axis
    Rotation theta degree around the X' axis
    Rotation phi degree around the Z' axis

  (A positive rotation is defined as a counterclockwise rotation while looking down the positive axis toward the origin)

- NUMBER OF GRID POINTS PER A.U.

Keep in mind that this value and the length of each direction determine the grid size, i.e., the number of points in each direction where the functions will be evaluated. Take care because the time required to compute the grid will hardly depend on it (from 60x60 points to 120x120 there is a factor of 4 in the CPU time).

Use low values (4 or 5) to test plots and higher values to produce print quality plots. Excellent print quality is usually obtained with a grid of about 150x150 on a A4 paper page.

OTHER OPTIONS

- PLOT TITLE

Any string of characters that will be printed on the plot (max. 25 chars)

- DENSITY DIFFERENCE MAPS

This option allows the calculation of density difference functions. This program version can compute density differences up to four functions:

$$\rho_{dif} = \rho_1 - \rho_2 - \rho_3 - \rho_4$$

The first function corresponds to the actual molecule and the other ones should correspond to the same molecule but with a distinct ρ or to some constituent fragments of it. The program does not check the geometry between different functions, so be sure that all data are consistent, otherwise meaningless results will be obtained **without errors**.

A new window will be shown up when this option is activated. The user can select the WFN filenames for functions 2,3 and 4. At least the filename for function 2 has to be defined.

- EXTRA CONTOURS TO PLOT

  This option gives the possibility to override the default contour values that are used to plot each function. A new window will be created where the user can specify to use or not the default values and to add up to 25 new contour values.

PROGRAM OUTPUT

After each run, a file named ***Flopo.out*** is written on the working directory. This file contains information about the WFN file and about the plot , i.e., plot values, grid size, the contour values drawn, etc.

Appendix

WFN file format

The WFN file is read by the following Fortran code:

```
      READ(KR,101) (TITLE(I),I=1,80)
      READ(KR,102) MODE,NMO,NPRIMS,NCENT
     DO 2 I=1,NCENT
      READ(KR,103) KATOM(I),X(I),Y(I),Z(I),CHARGE(I)
   2 CONTINUE
      READ(KR,104) (ICENT(I),I=1,NPRIMS)
      READ(KR,104) (ITYPE(I),I=1,NPRIMS)
      READ(KR,105) (E(I),I=1,NPRIMS)
     DO 7 I=1,NMO
      READ(KR,106) (MOLAB(J),J=1,2),P(I),EORB(I)
      READ(KR,107) (CO(I,J),J=1,NPRIMS)
   7 CONTINUE
 101 FORMAT (80A1)
 102 FORMAT (4X,A4,11X,I4,16X,I4,17X,I3)
 103 FORMAT (A4,20X,3F12.8,10X,F5.1)
 104 FORMAT (20X,20I3)
 105 FORMAT (10X,5E14.7)
 106 FORMAT (10X,2A5,15X,F12.8,15X,F12.8)
 107 FORMAT (5E16.8)


    TITLE   - A TITLE FOR THE WAVE FUNCTION
    MODE    - WAVE FUNCTION TYPE (SLATER OR GAUSSIAN)
    NMO     - NO. OF MOLECULAR ORBITALS
    NPRIMS  - NO. OF (PRIMITIVE) BASIS FUNCTIONS
    NCENT   - NO. OF NUCLEI

 THEN FOR EACH NUCLEUS

    KATOM   -  NAME
    X/Y/Z   -  COORDINATES
    CHARGE  -  ATOMIC NUMBER

 AND FOR EACH BASIS FUNCTION

    ICENT   -  THE NO. OF THE NUCLEUS ON WHICH IT'S CENTERED
    ITYPE   -  FUNCTION TYPE
    E       -  EXPONENT

 AND FOR EACH MOLECULAR ORBITAL

    MOLAB   -  A LABEL
    P       -  OCCUPATION NUMBER
    EORB    -  ORBITAL ENERGY
    CO      -  COEFFICIENTS OF PRIMITIVE BASIS FUNCTIONS.
               THESE INCLUDE ALL NORMALIZATION AND
               CONTRACTION COEFFICIENTS.
```

How can I get the WFN file from ADF or Gaussian ?

• ADF

It's possible to transform the data contained in TAPE21 into a WFN file. The next release of ADF will contain an utility program called rdt21 that do this job. Meanwhile, rdt21 is available upon request to the following e.mail address: bo@quimica.urv.es.

• GAUSSIAN

Gaussian94 generates the WFN file at the end of the run (I hope Gaussian98 will do the same) simply specifying the keyword *Output=WFN* .

Ordering of the Orbitals

Xaim-Flopo can be used to generate 2D maps of the molecular orbitals, but its worth to say that the WFN file only contain the occupied molecular orbitals.

The ordering of the orbitals in the WFN file depends on the origin of that file:

from ADF:

- core orbitals
- for each symmetry
  alpha orbitals in increasing energy
  beta orbitals in increasing energy

from GAUSSIAN:

The orbitals are ordered by increasing energy: the HOMO is the last orbital in the file.

Acknowledgments

Xaim has been programmed with the aid of VXP (Visual X-windows Programming Interface) written by Yong Chen (http://www.shsu.edu/~stdyxc05/VXP)

FLOPO uses PGPLOT graphical routines. This is a standard package that is available for a large variety of operating systems (http://astro.caltech.edu/~tjp/pgplot/).

We thank the members of the "Grup de Química Quàntica" (Department of Physical and Inorganic Chemistry - Universitat Rovira i Virgili - Tarragona - Spain) for their suggestions, for their patience and friendly support.

Part of the Slater functions code was generated by of our students Carles Agut and Engelbert Sans.

Credits

If the results obtained with this software are used for publishing purposes, please refer to it in the following manner:

> " The results published were generated using Xaim. This program was developed by Jose Carlos Ortiz and Carles Bo. Universitat Rovira i Virgili. Tarragona. Spain"

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Questions concerning this software should be directed to:

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