

*Wavefunction and density analysis:
DOS/Bader/Angular momentum*

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Outline

- Electronic density of states (DOS)
 - Smearing technique
 - Tetrahedron method
 - Angular momentum decomposition
- Charge density analysis
 - Hirshfeld surface
 - Bader analysis
- Wavefunction analysis

Density of states

Abinit input parameter:

prtdos

- 0: (default value) No DOS computed
- 1: DOS computed using a smearing technique
- 2: DOS computed using a tetrahedron method
- 3: DOS and angular-momentum projected DOS are computed using a tetrahedron method

DOS: smearing technique (prtdos=1)

$$D(\varepsilon) = \frac{V}{(2\pi)^3} \int_{BZ} d^3k \delta(\varepsilon - \varepsilon_{\vec{k}}) \quad \# \text{ states per unit cell per spin per energy}$$

As a first approximation, for a finite sampling of k-points (as always!), we can replace the Delta function by a Gaussian:

$$D(\varepsilon) \approx \sum_{\text{bands}} \sum_{\text{k-points}} \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-(\varepsilon - \varepsilon_{n\vec{k}})^2 / 2\sigma^2\right]$$

The actual function which is used to replace the Delta function is determined by the value of **ocopt** input parameter

DOS: smearing technique *(prtdos=1)*

Caution!

If you are doing a calculation on an insulating material using **occopt**=1 or 2, in order to do a DOS calculation using **prtdos**=1, you will have to do a non-SCF calculation where the **occopt** parameter is set between 3 and 7.

Preferably use **occopt**=7 and **tsmear**<0.25 eV

DOS: smearing technique (prtdos=1)

```
ndtset 2

#Dataset 1 : usual self-consistent calculation
kptopt1 1      # Option for the automatic generation of k points,
              # taking into account the symmetry

...
ngkpt1 4 4 4
prtden1 1      # Print the density, for use by dataset 2
toldfe1 1.0d-6

#Dataset 2 : the DOS calculation using a smearing technique
iscf2 -3 # a non-SCF calculation
tolwfr2 1.0d-10
getden2 -1
kptopt2 1

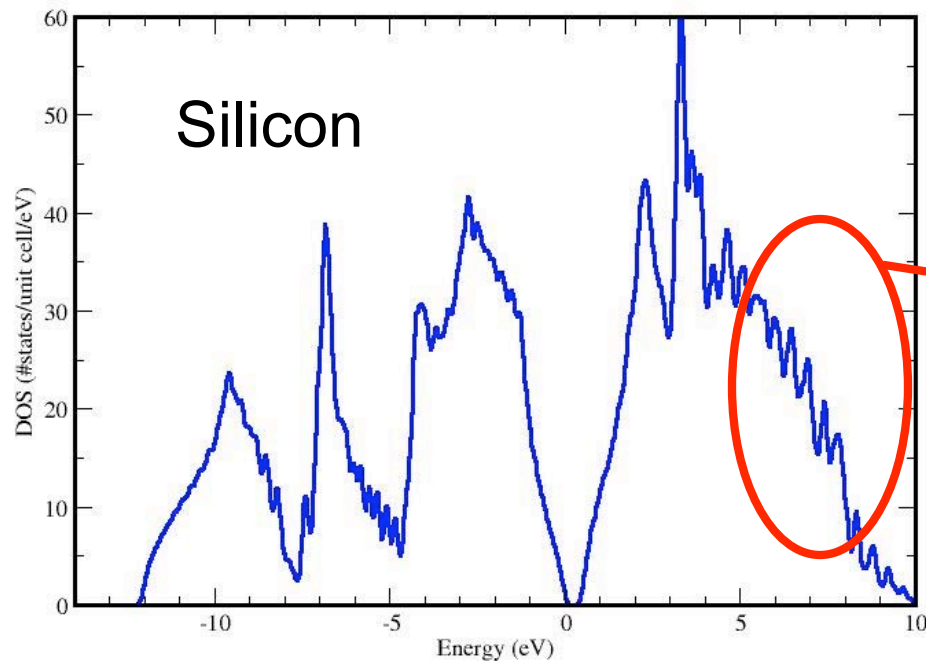
...
ngkpt2 20 20 20 # need a lot of k-points!
nband2 8 # ask for more bands to get unoccupied states
prtdos2 1
occopt2 7
tsmear2 0.1 eV # choose an appropriate smearing

...
```

DOS: smearing technique (*prtdos=1*)

Edit the file “file”_DOS and use your favorite graphic program

Note the value of the Fermi energy to appropriately shift the energy axis.



Not physical!

We ask for only 8 bands!

DOS: tetrahedron method (prtdos=2)

$$D(\varepsilon) = \frac{V}{(2\pi)^3} \int_{BZ} d^3k \delta(\varepsilon - \varepsilon_{\vec{k}}) = \frac{V}{(2\pi)^3} \int_{S_\varepsilon} \frac{dS}{|\nabla \varepsilon_{\vec{k}}|}$$

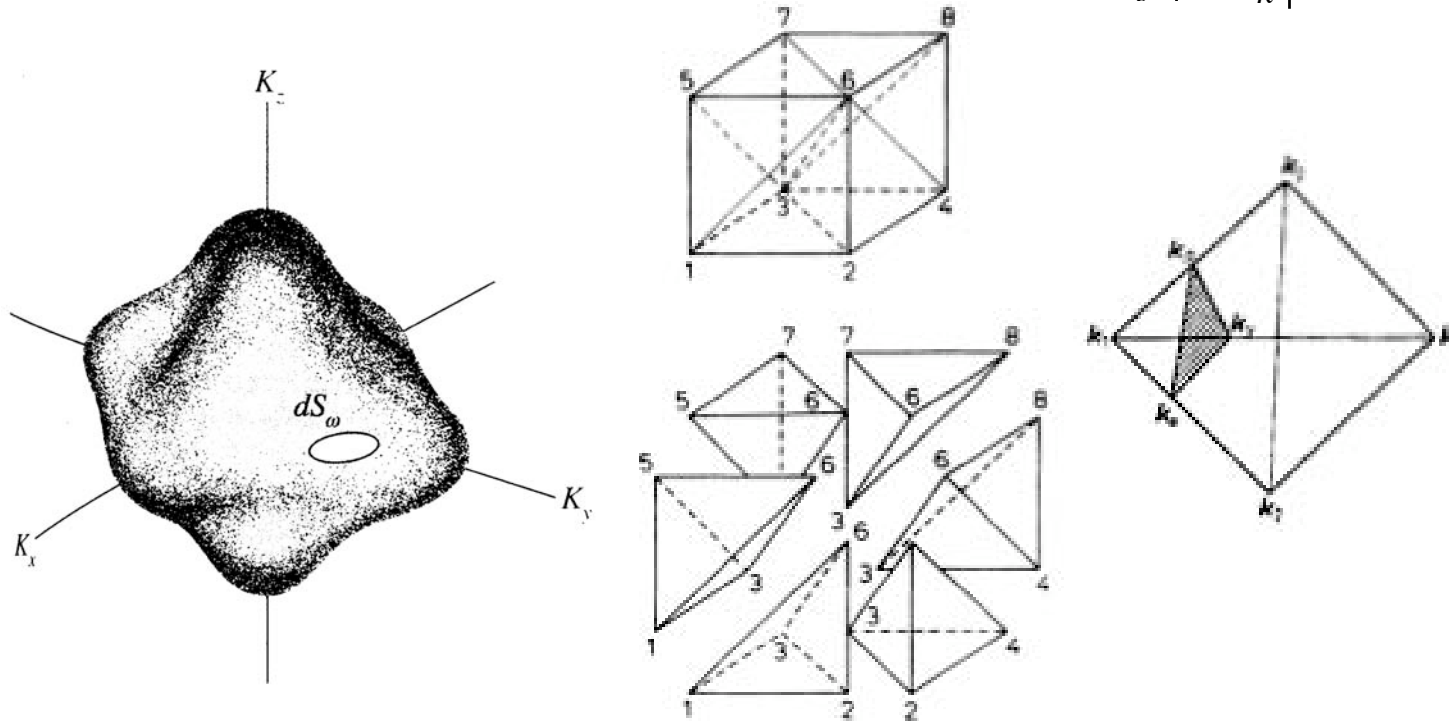


FIG. 5. Breakup of a submesh cell into six tetrahedra.

Ref: P.E. Blöchl, O. Jepsen and O.K. Andersen, "Improved tetrahedron method for Brillouin-zone integrations", PRB 49(23) 16 223 (1994).

DOS: tetrahedron method (prtdos=2)

ndtset 2

#Dataset 1 : usual self-consistent calculation

kptopt1 1 # Option for the automatic generation of k points,
taking into account the symmetry

...

ngkpt1 4 4 4

nband1 8

prtden1 1 # Print the density, for use by dataset 2

toldfe1 1.0d-6

prtdos1 2 # print the DOS with this shifted grid

#Dataset 2 : the DOS calculation using a non-shifted grid

iscf2 -3 # a non-SCF calculation

tolwfr2 1.0d-10

getden2 -1

kptopt2 1

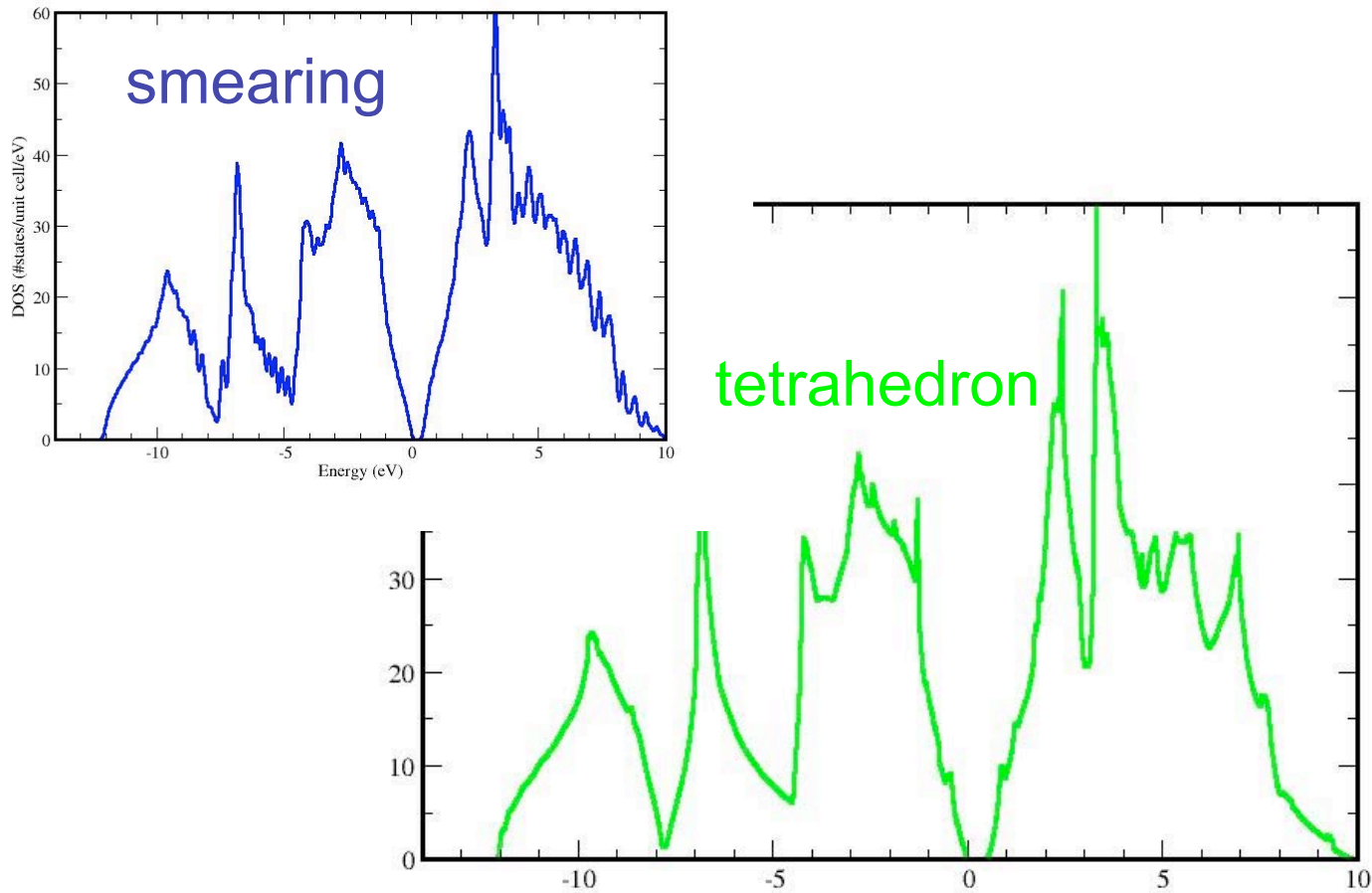
...

ngkpt2 8 8 8

nband2 8

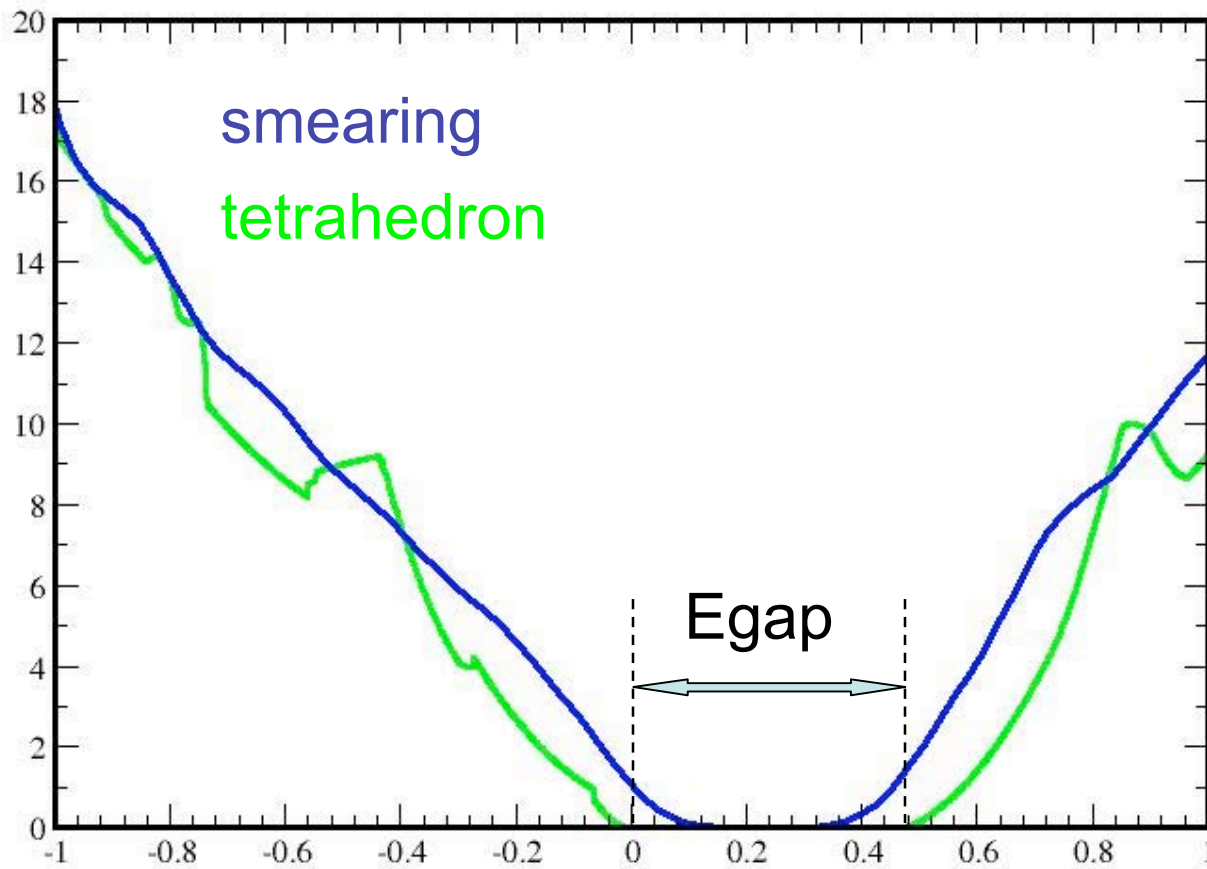
prtdos2 2

DOS: tetrahedron method (*prtdos=2*)



With the tetrahedron method we obtain a much better resolution with fewer k-points!

Comparison : *smearing vs tetrahedron*



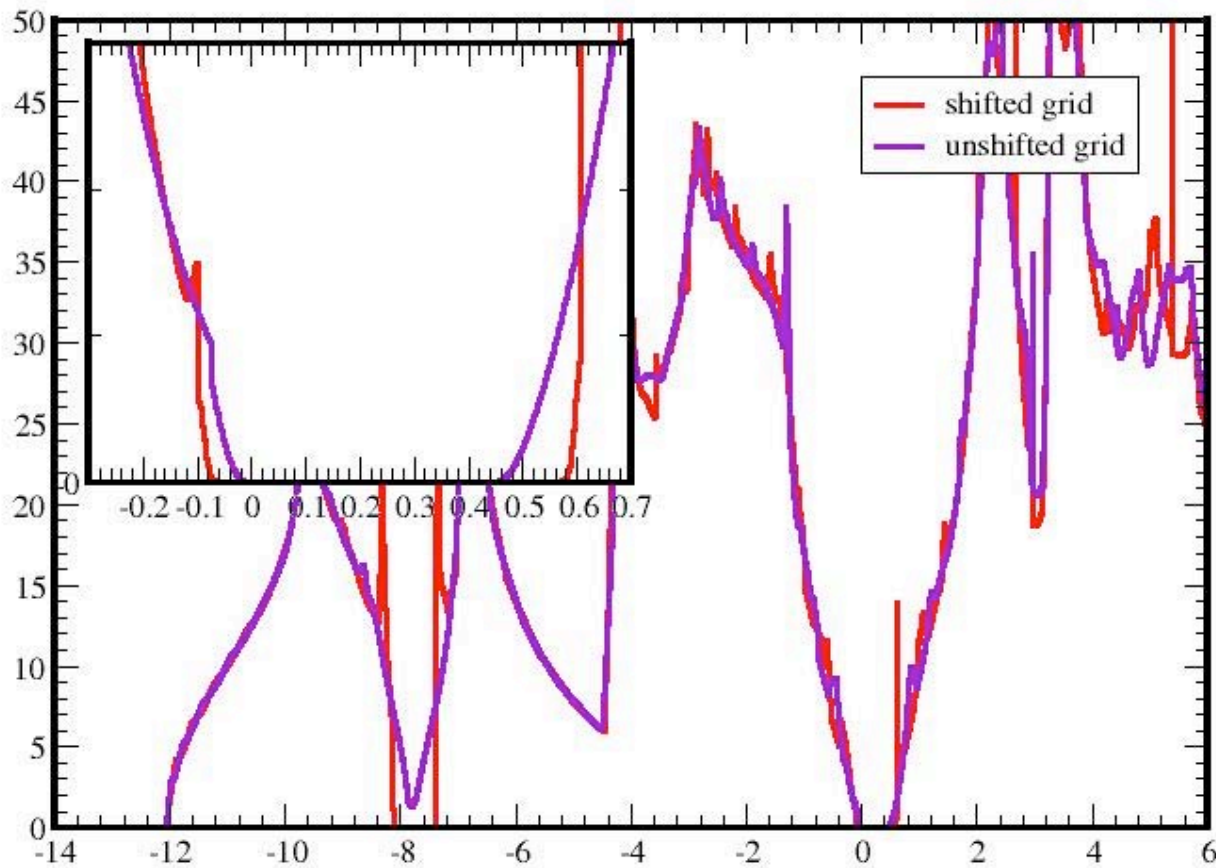
K-points: shifted vs not shifted

```
#Dataset 1 : usual self-consistent calculation
kptopt1 1      # Option for the automatic generation of k points,
              # taking into account the symmetry
nshiftk1 4
shiftk1 0.5 0.5 0.5 # These shifts will be the same for all grids
        0.5 0.0 0.0
        0.0 0.5 0.0
        0.0 0.0 0.5
ngkpt1 8 8 8
nband1 8
prtden1 1      # Print the density, for use by dataset 2
toldfe1 1.0d-6
prtdos1 2      # print the DOS with this shifted grid

#Dataset 2 : the DOS calculation using a non-shifted grid
iscf2 -3 # a non-SCF calculation
tolwfr2 1.0d-10
getden2 -1
kptopt2 1
nshiftk2 4
shiftk2 0.0 0.0 0.0 # Gamma is included!
        0.0 0.5 0.5
        0.5 0.0 0.5
        0.5 0.5 0.0
ngkpt2 8 8 8
nband2 8
prtdos2 2
```

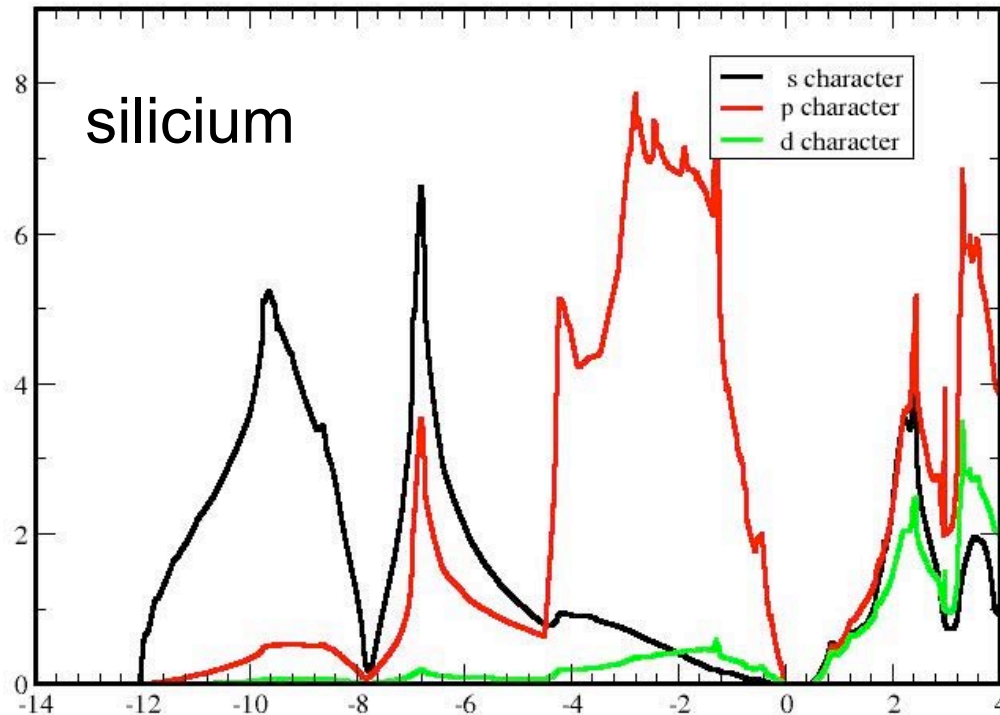
K-points: shifted vs not shifted

Caution: Your sampling grid should include critical k-points.



DOS: angular momentum projection (prtdos=3)

Arbitrary scale:
Depends on
ratsph



Also consider the input parameters: **natsph**,
iatsph and **ratsph** (radius of analysis).

Charge density analysis

There are two methods of charge density analysis provided with the Abinit package:

- Hirshfeld method: with **cut3d** code
- Bader analysis: with **aim** code

No unique definition of charge. Hirshfeld gives small charge transfer where as Bader gives large charge transfer.

Hirshfeld method

In **cut3d**, when using a density, option: 11

$$w(\mathbf{r}) = \frac{\sum_{A \in \text{molecule}} \rho_A(\mathbf{r})}{\sum_{A \in \text{crystal}} \rho_A(\mathbf{r})}$$

$$= \rho_{\text{promolecule}}(\mathbf{r}) / \rho_{\text{procrystal}}(\mathbf{r}) .$$

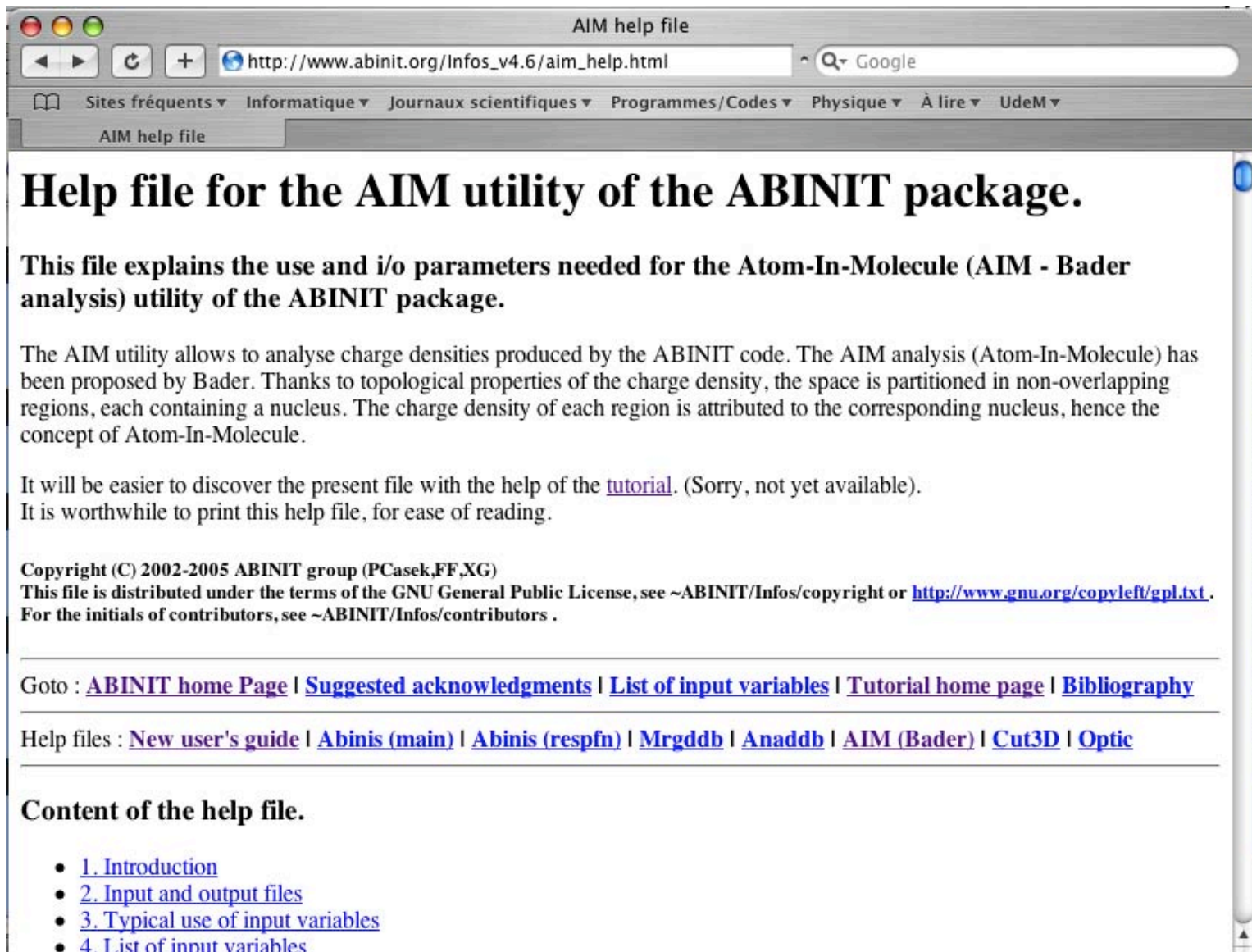
$$\rho^{\text{Hirshfeld}}(\mathbf{r}) = \rho_{\text{valence}}(\mathbf{r}) \times w(\mathbf{r})$$

$$\text{charge} = \int_{\text{cell}} \rho^{\text{Hirshfeld}}(\mathbf{r}) d\mathbf{r}$$

References:

- Hirshfeld, F.L., *Theoretica Chimica Acta*, **44**: p. 129-138 (1977)
- <http://www.une.edu.au/chemistry/research/spackman/index.shtml>

Bader analysis (AIM)



The screenshot shows a web browser window titled "AIM help file" with the URL http://www.abinit.org/Infos_v4.6/aim_help.html. The browser's address bar includes a search engine icon and the text "Google". Below the address bar is a navigation menu with items: "Sites fréquents", "Informatique", "Journaux scientifiques", "Programmes/Codes", "Physique", "À lire", and "UdeM". The main content area of the browser displays the following text:

Help file for the AIM utility of the ABINIT package.

This file explains the use and i/o parameters needed for the Atom-In-Molecule (AIM - Bader analysis) utility of the ABINIT package.

The AIM utility allows to analyse charge densities produced by the ABINIT code. The AIM analysis (Atom-In-Molecule) has been proposed by Bader. Thanks to topological properties of the charge density, the space is partitioned in non-overlapping regions, each containing a nucleus. The charge density of each region is attributed to the corresponding nucleus, hence the concept of Atom-In-Molecule.

It will be easier to discover the present file with the help of the [tutorial](#). (Sorry, not yet available).
It is worthwhile to print this help file, for ease of reading.

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Goto : [ABINIT home Page](#) | [Suggested acknowledgments](#) | [List of input variables](#) | [Tutorial home page](#) | [Bibliography](#)

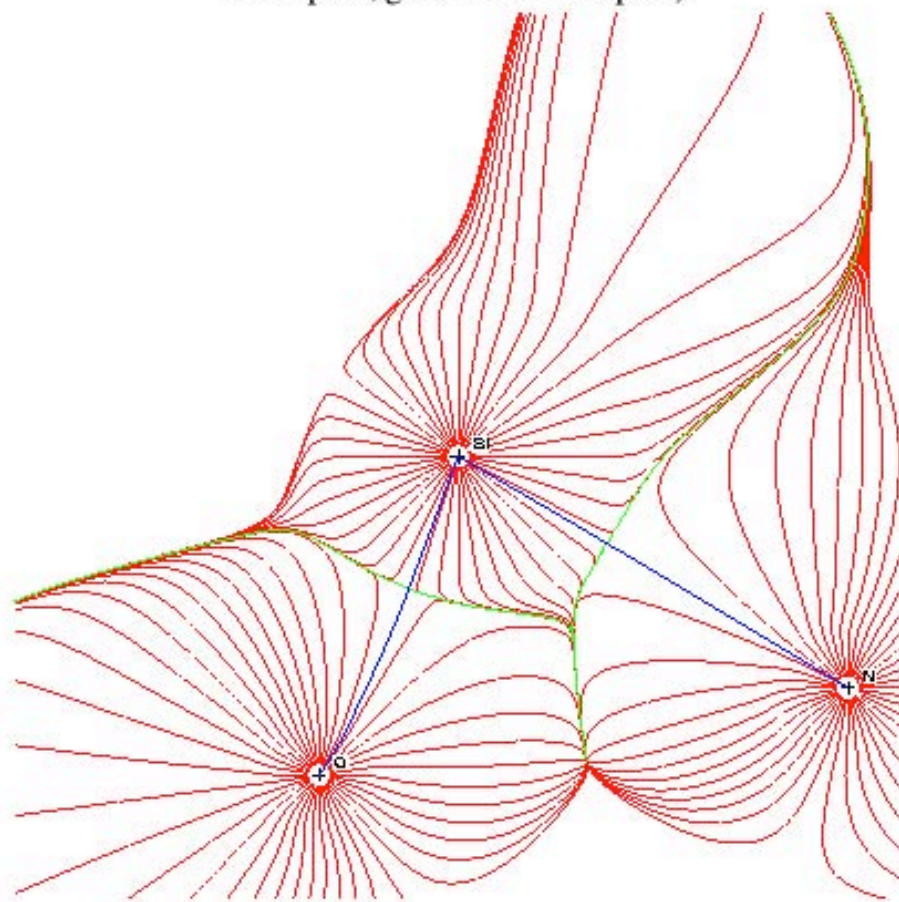
Help files : [New user's guide](#) | [Abinis \(main\)](#) | [Abinis \(respfn\)](#) | [Mrgddb](#) | [Anaddb](#) | [AIM \(Bader\)](#) | [Cut3D](#) | [Optic](#)

Content of the help file.

- [1. Introduction](#)
- [2. Input and output files](#)
- [3. Typical use of input variables](#)
- [4. List of input variables](#)

Bader analysis (AIM)

Figure 4: Gradient field of the core of our chiral silatrane in a plane defined by Si(1), O(2) and N(5) (red: gradient paths, blue: bond path, green: zero-flux path)



<http://www.ch.ic.ac.uk/ectoc/echet98/pub/048/node7.htm>

Bader analysis (AIM)

<http://www.chemistry.mcmaster.ca/faculty/bader/aim/>

Atoms and Molecules

Richard F.W. Bader
Department of Chemistry
McMaster University

An Introduction to the Electronic Structure of Atoms and Molecules

Theory of Atoms in Molecules

Matthieu Verstraete and Michel Côté
First Principles Calculations for Condensed Matter and Nanoscience
International Center for Materials Research, UCSB, August 2005

Atomic densities

Because Abinit uses pseudopotentials, the core charge needs to be added to the valence charge.

Atomic Densities

http://www.abinit.org/Psps/?text=atomicDEN

Sites fréquents ▾ Informatique ▾ Journaux scientifiques ▾ Programmes/Codes ▾ Physique ▾ À lire ▾ UdeM ▾

Atomic Densities

abinit.org

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ABINIT Package

- Sources, help files...
- Binaries (summary)
- Browse latest sources

Extra Packages

- Pseudopotentials
- PAW Atomic Data
- Atomic Densities
- Input Files

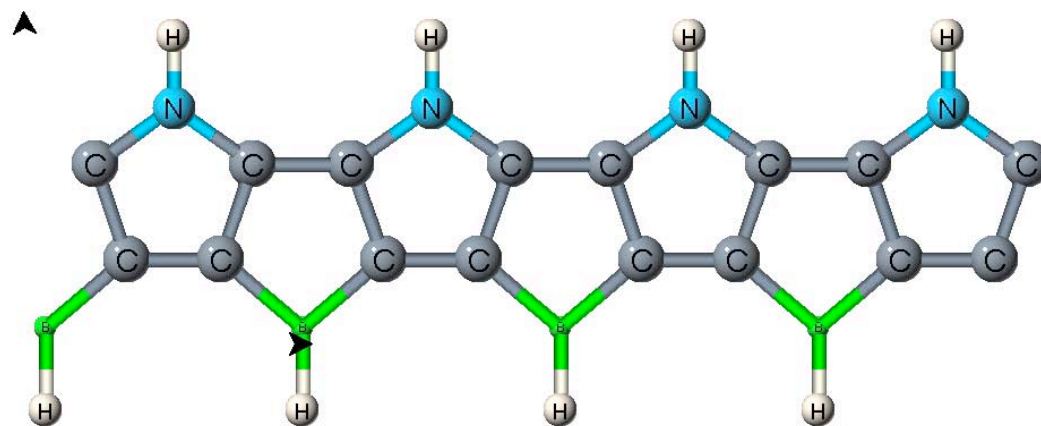
Documentation

- Help files

Atomic Densities

- [All-electron density files](#) (for use with Hirschfeld atomic charge analysis)
- [Core-electron density files](#) (for use with Bader atomic charge analysis)

Examples



Δ Charge	N	B	H _N	H _B	C _N	C _B
Hirshfeld	-0.046	0.027	0.162	-0.048	0.033	-0.085
Bader	-0.61	1.60	0.05	-0.55	0.28	-0.57

May need larger E_{cut} for Bader...

Wavefunction analysis

The goal is to plot the wavefunction.

The **cut3d** program can produce output that can be read by several other programs. At present, the supported programs are:

- OpenDX (www.opendx.org)
- XCrySDen (www.xcrysden.org)
- Molekel (www.cscs.ch/molekel/)

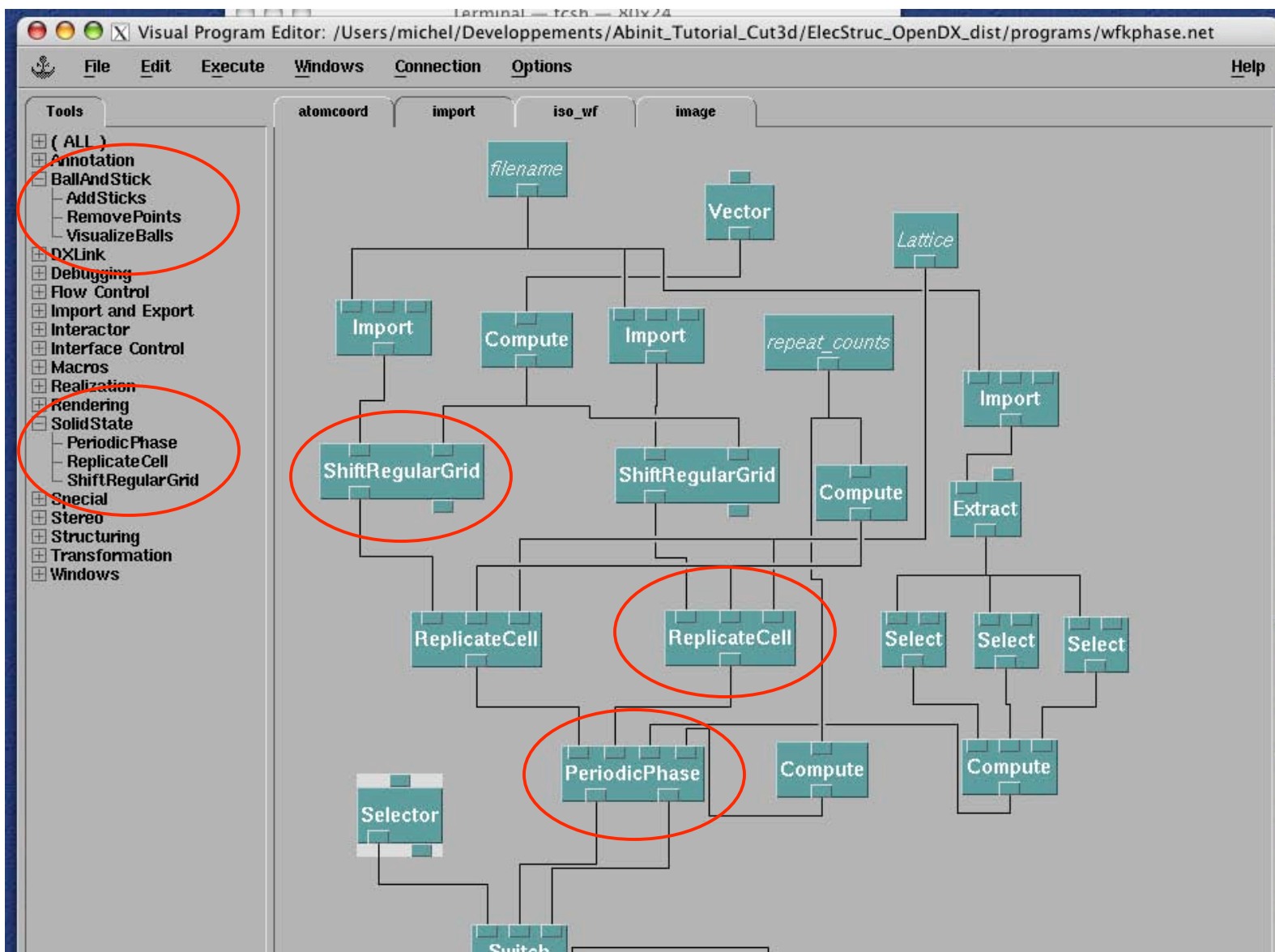
OpenDX

OpenDX is a general tool to visualize data. It is object oriented and let you "code" the image you want to display. It is a bit harder to master but once you know how to use it, it is a powerful tool. Over the years, we have developed a series of macros and modules to treat electronic structure data.

OpenDX is open source and freely distributed.

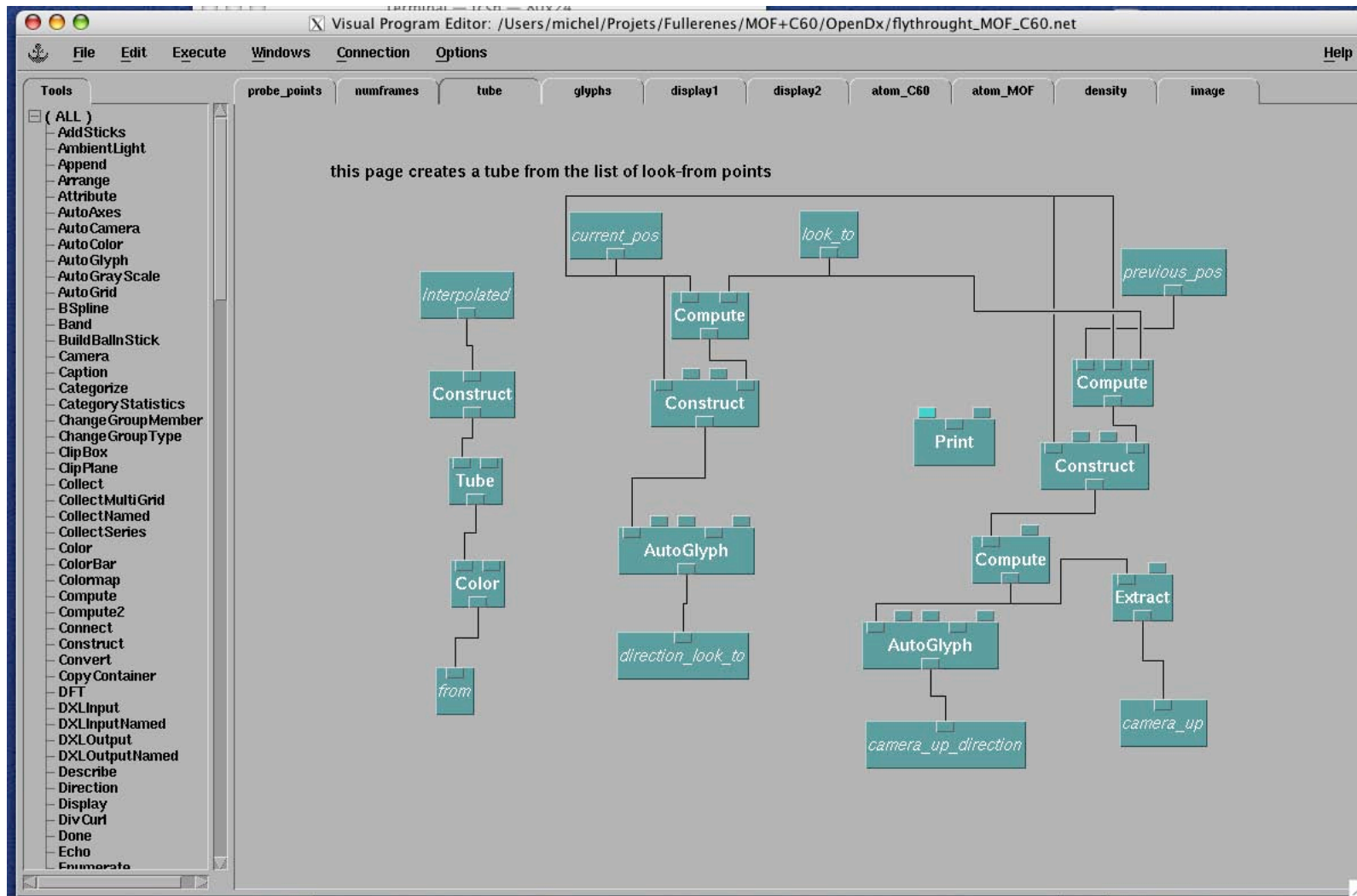
Best way to learn OpenDX is by example!

OpenDX: macros and modules



Matthieu Verstraete and Michel Côté
First Principles Calculations for Condensed Matter and Nanoscience
International Center for Materials Research, UCSB, August 2005

MOF + C60: more on Friday



Matthieu Verstraete and Michel Côté
First Principles Calculations for Condensed Matter and Nanoscience
International Center for Materials Research, UCSB, August 2005

Summary

- Look at **cut3d** for more options and possibilities
- For wavefunction and density, evaluate your needs; choose between a ready made solution (XCrySDEN) or a more malleable program (OpenDX).