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)

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

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:

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

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

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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
...
```

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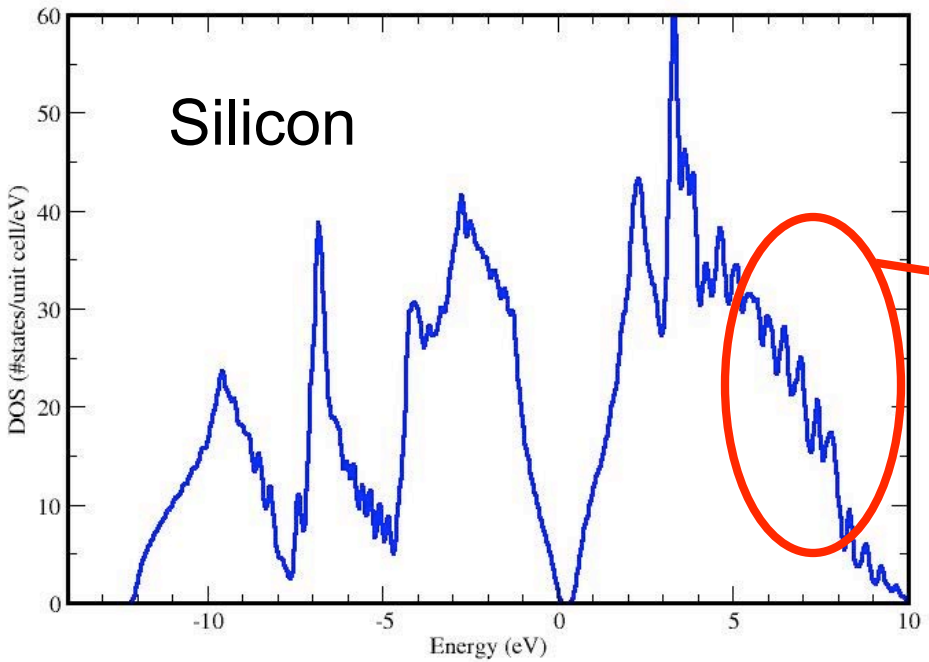
DOS: smearing technique (prtdos=1)

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!

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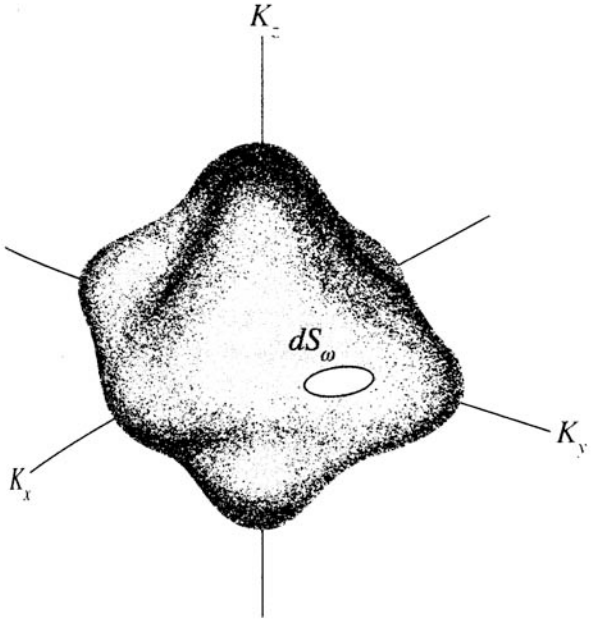
DOS: tetrahedron method (prtdos=2)

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



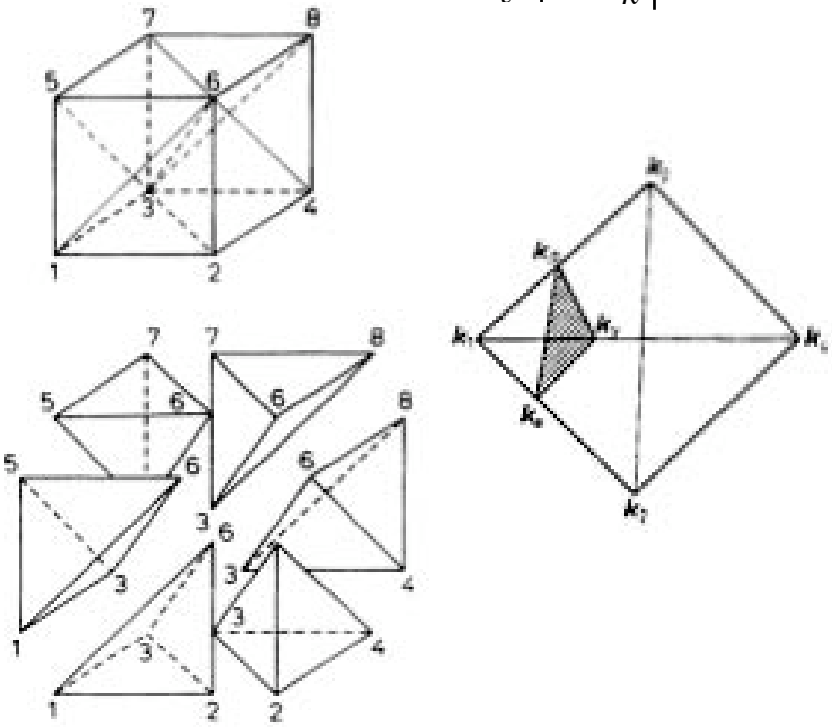


FIG. 5. Breakup of a submesh cell into six tetrahedra.

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

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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
```

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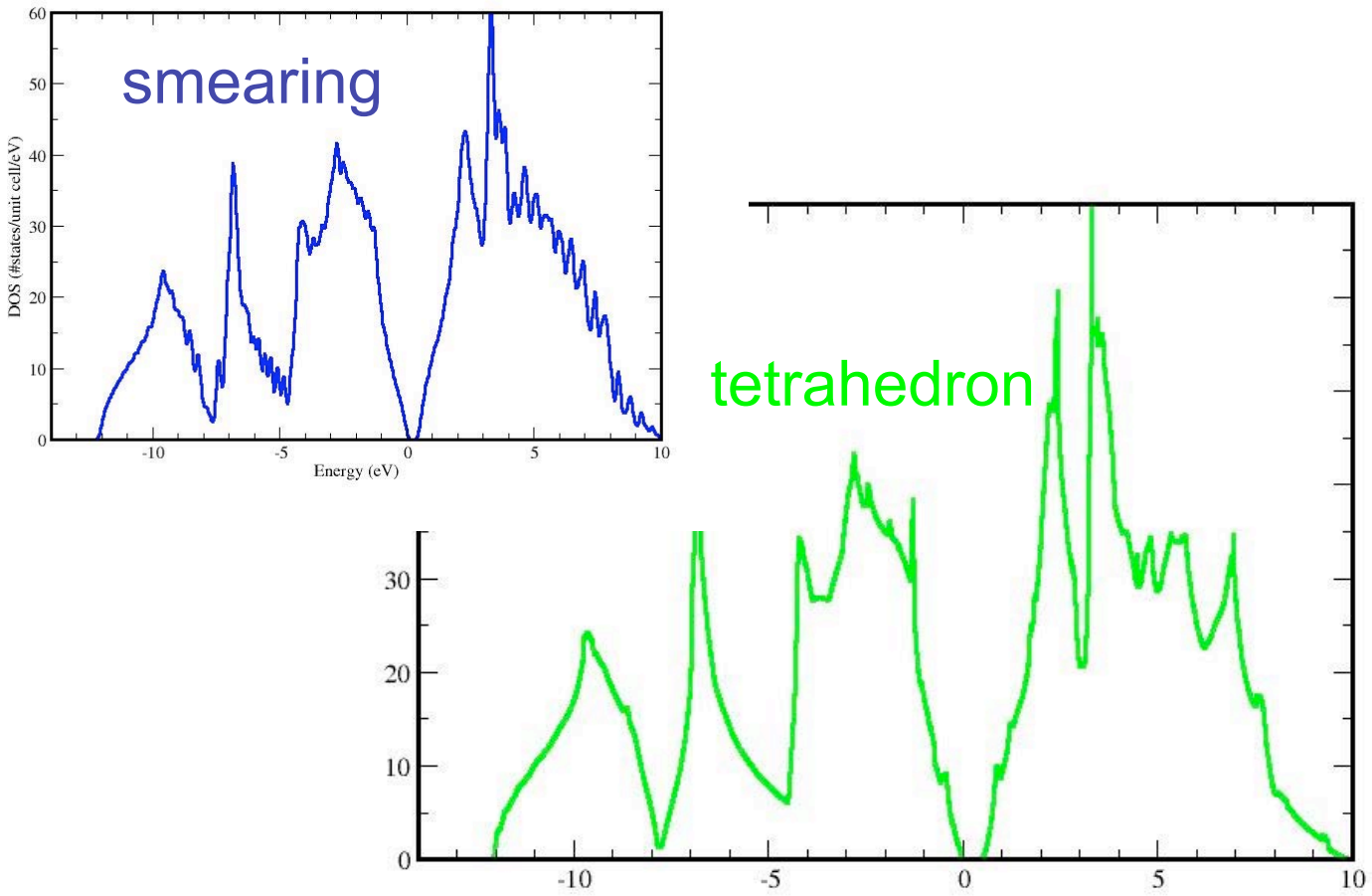
DOS: tetrahedron method (prtdos=2)



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

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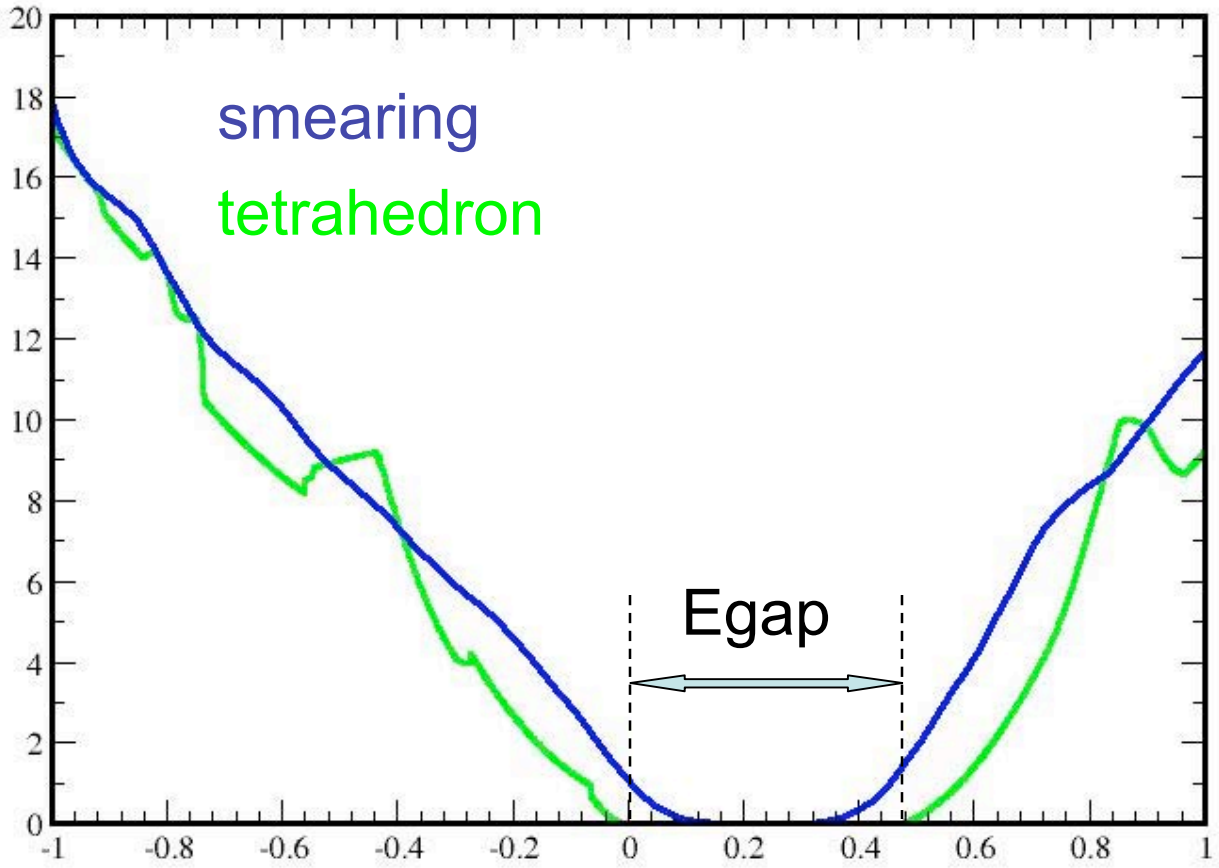
Comparison : smearing vs tetrahedron



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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
```

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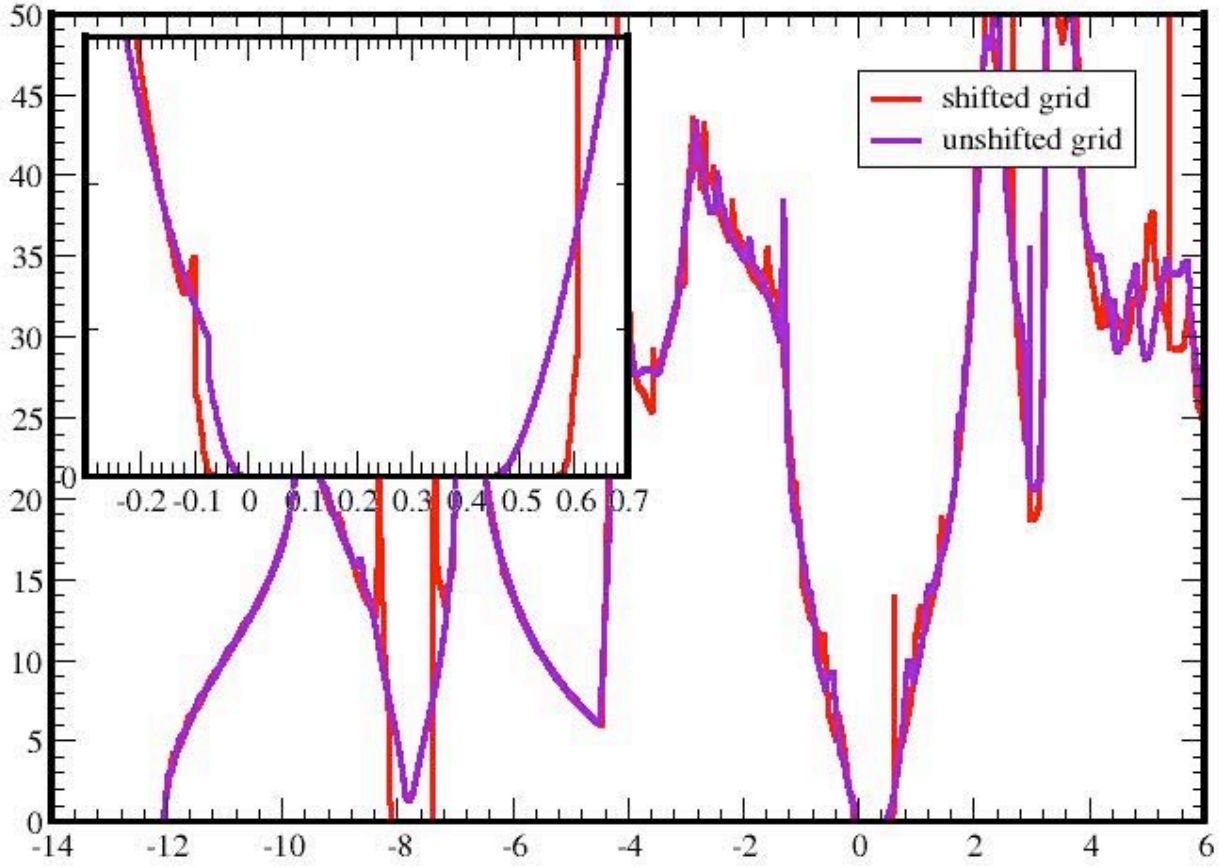
K-points: shifted vs not shifted

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



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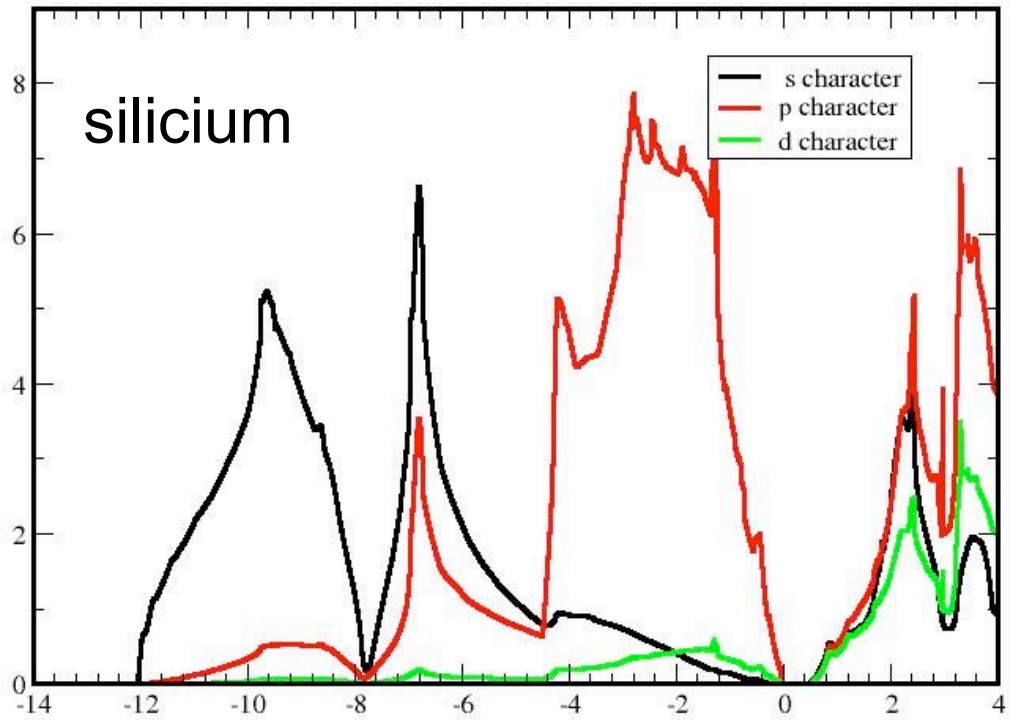
DOS: angular momentum projection (prtdos=3)

Arbitrary scale:
Depends on
ratsph



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

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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.

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Hirshfeld method

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

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

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

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

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

References:

•Hirshfeld, F.L., Theoretica Chimica Acta, **44**: p. 129-138 (1977)

•http://www.une.edu.au/chemistry/research/spackman/index.shtml

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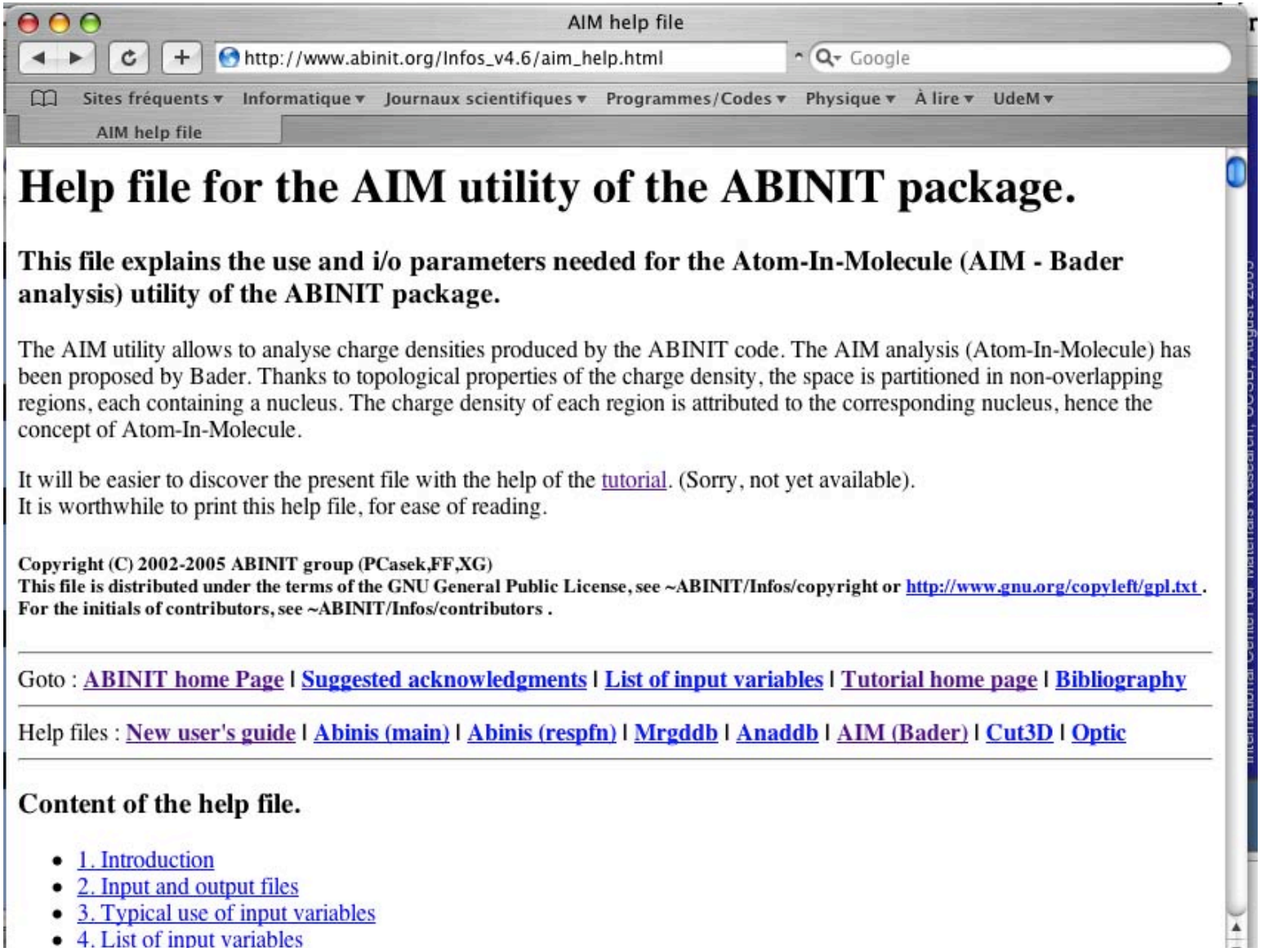
Bader analysis (AIM)



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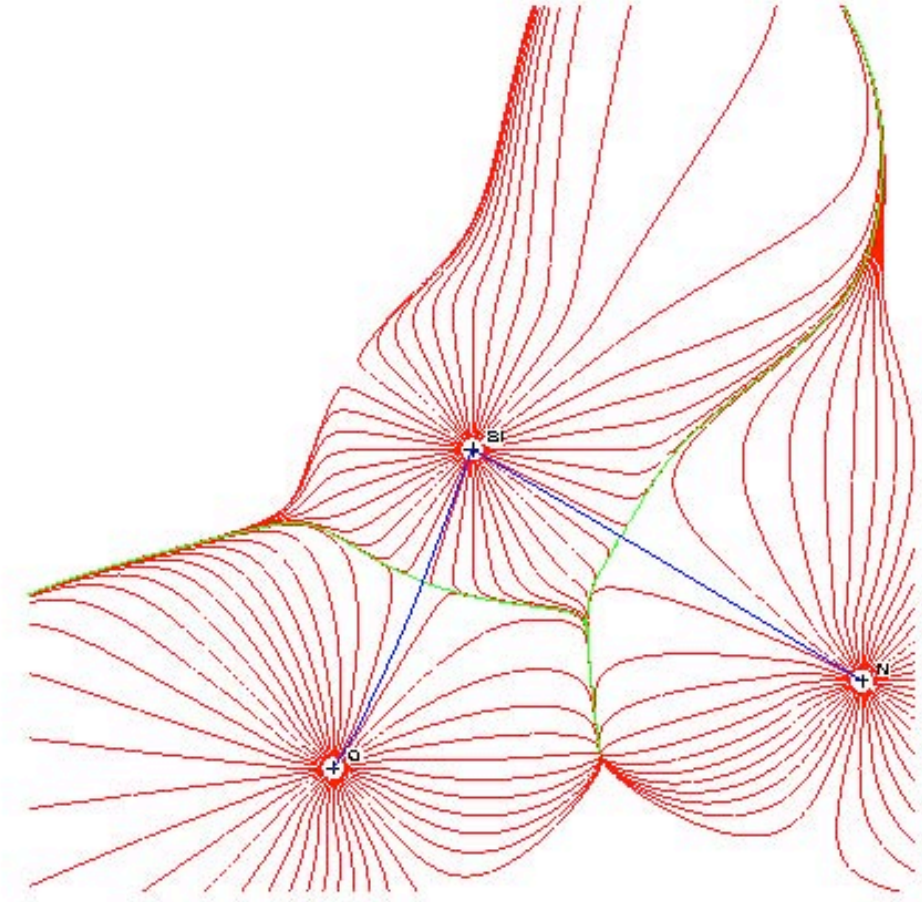
Bader analysis (AIM)

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

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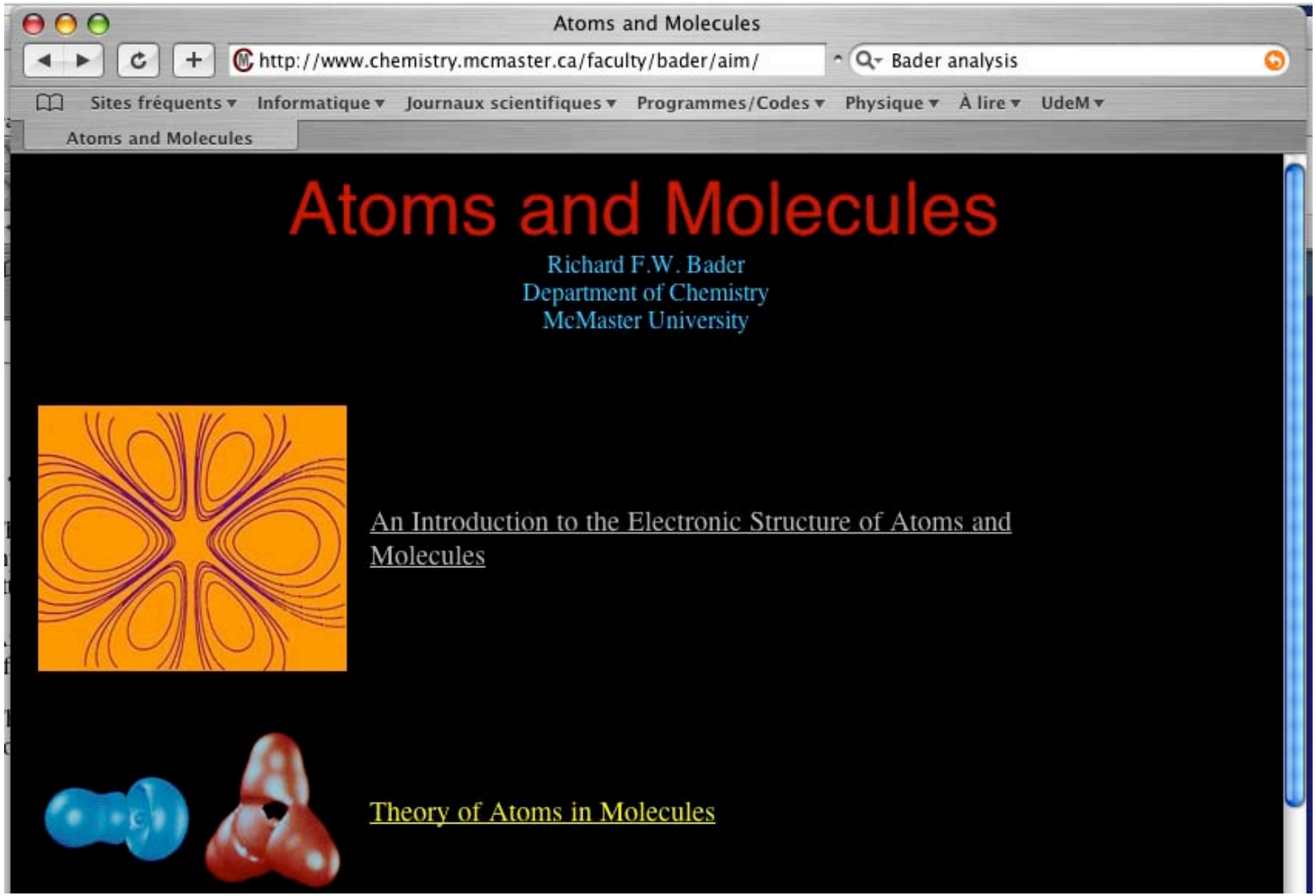
Bader analysis (AIM)

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



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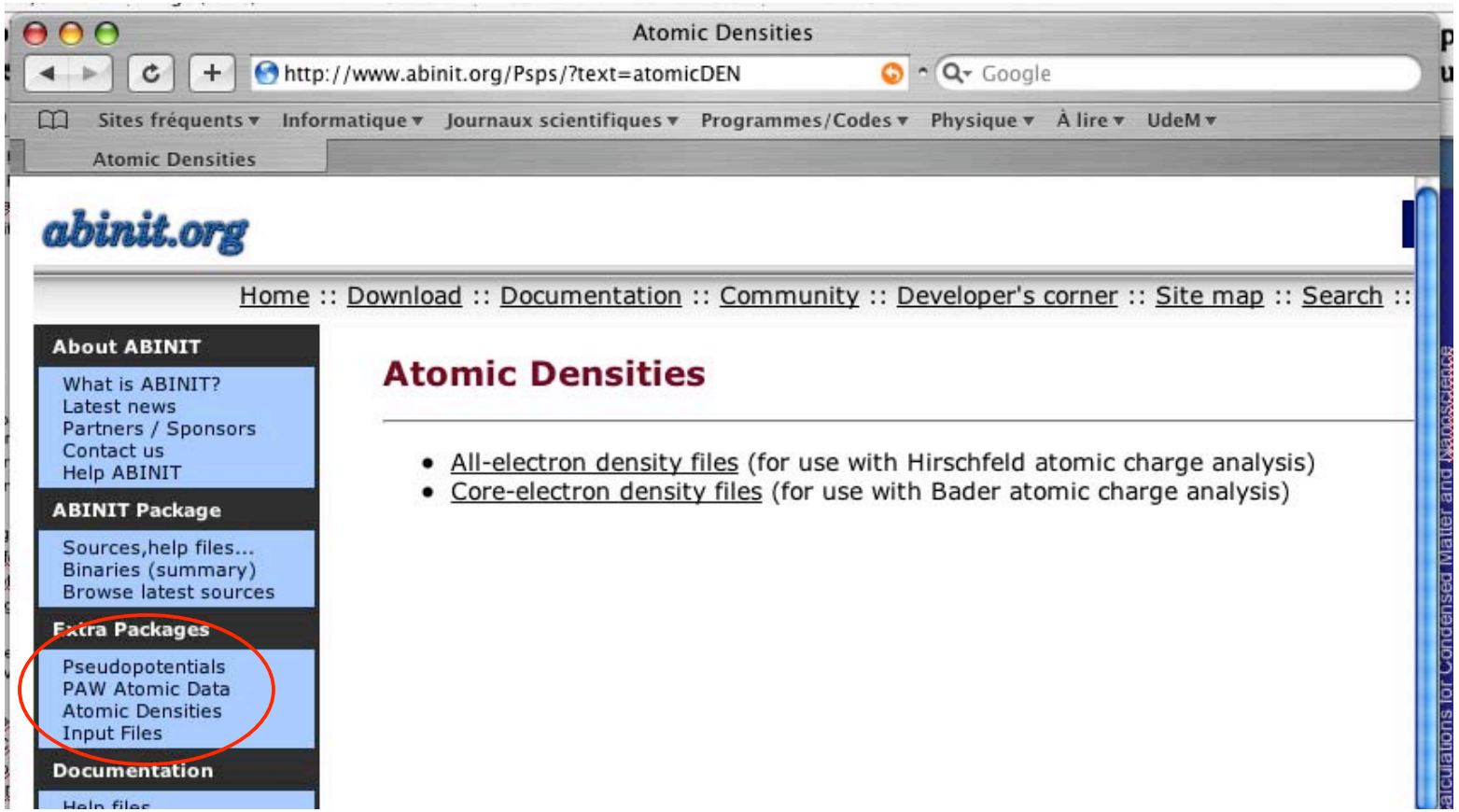
Atomic densities

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



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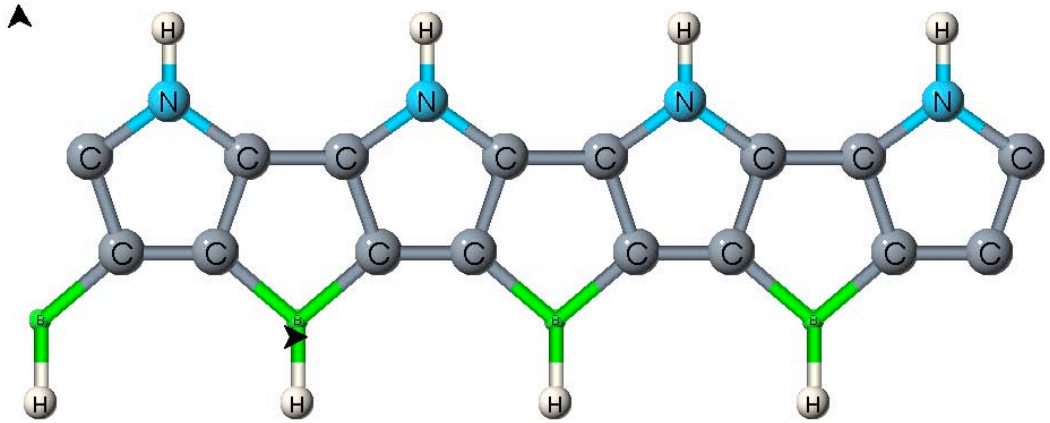
Examples



ΔCharge	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…

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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/)

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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!

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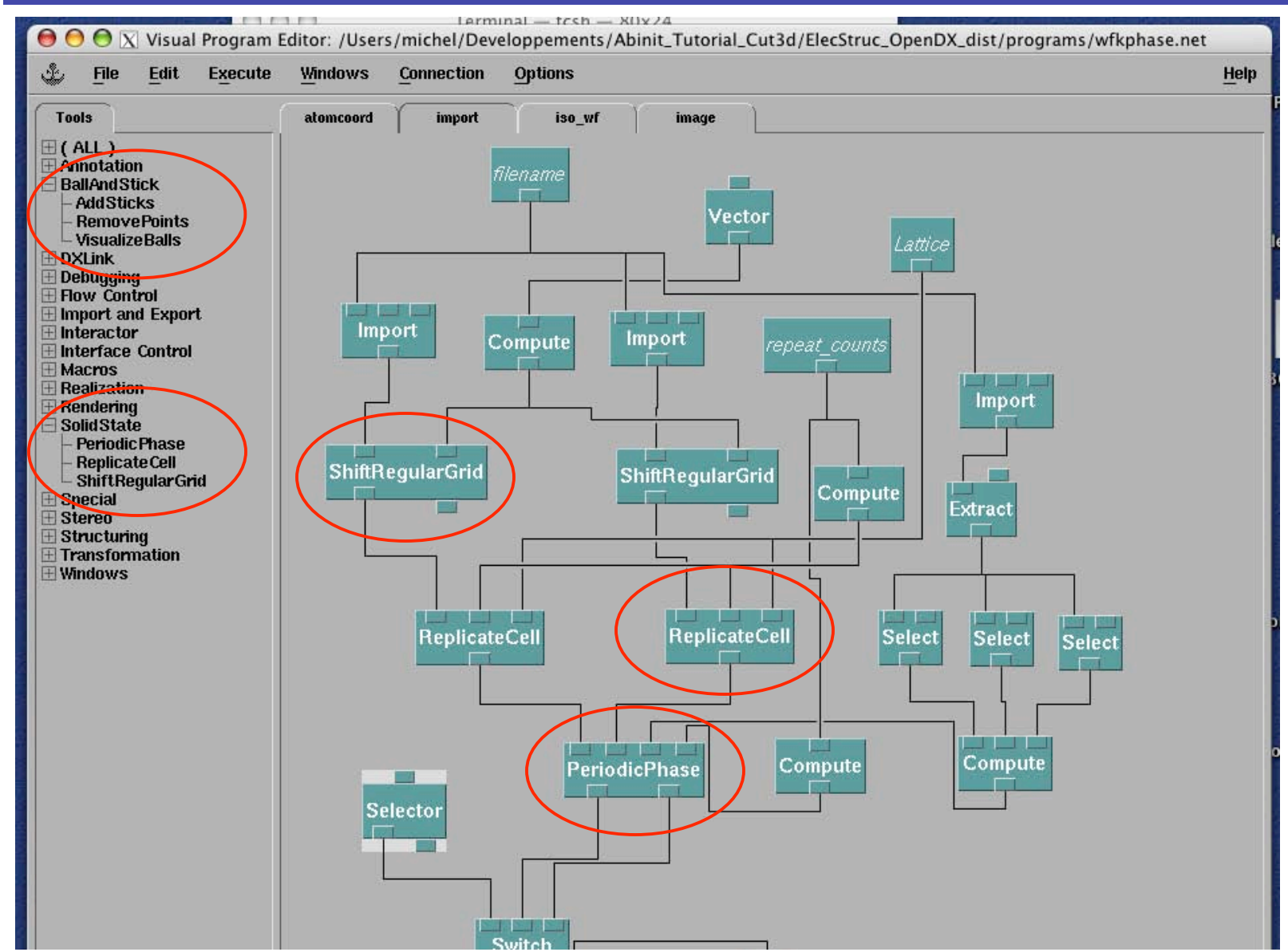
OpenDX: macros and modules



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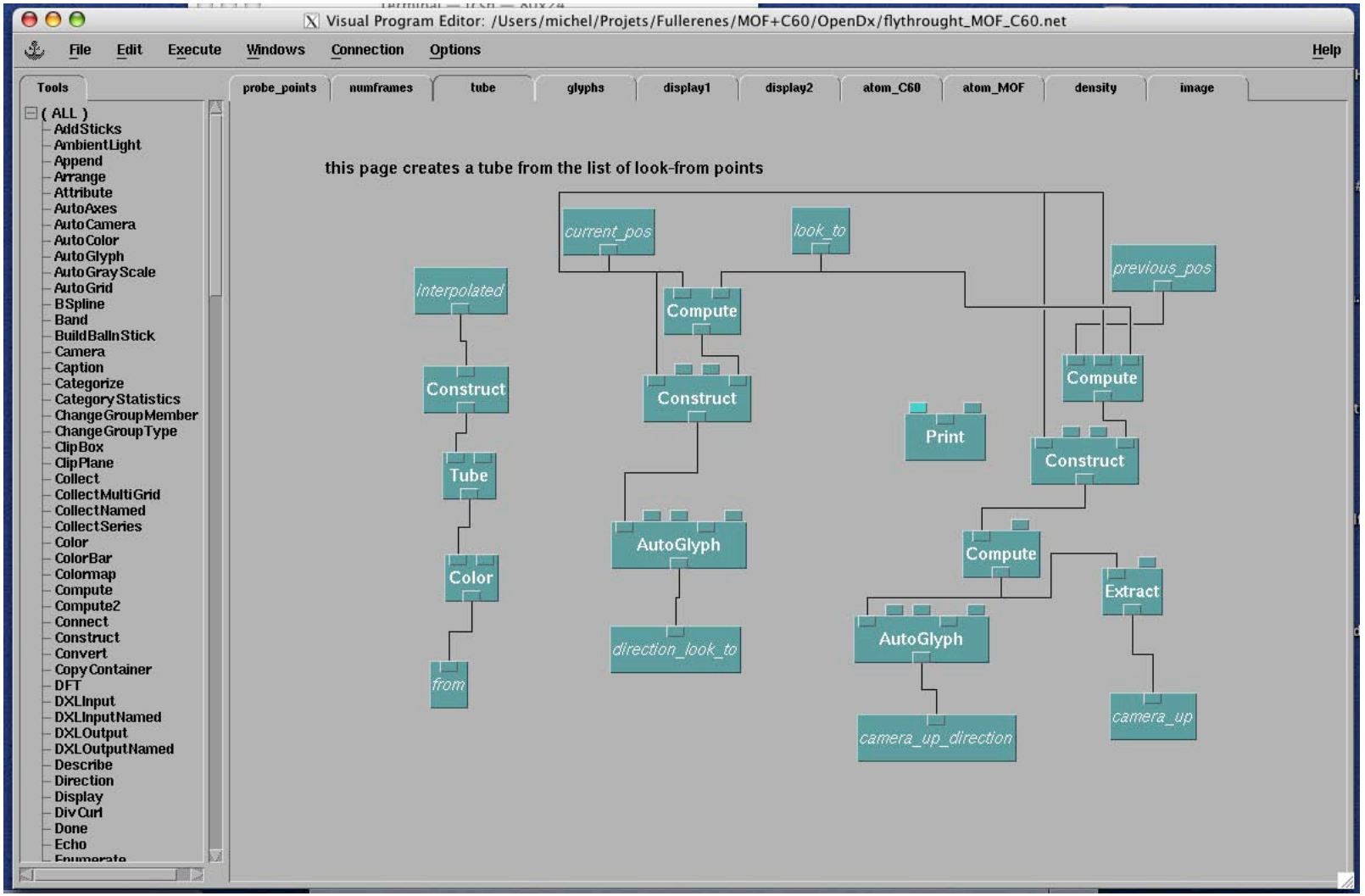
MOF + C60: more on Friday



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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).