```
-------------------------------------------------------------------------

  #####   #####   ####   #    #   ####    #       #####   ######  #     #
  #    #  #    #  #    #  #    #  ##  ##   #       #    #  #    #  ##    #
  #    #  #    #  #    #  #  # #  # ## #   #       #    #  #####   # #   #
  #####   #####   #    #  #    #  #    #   #       #    #  #       #  #  #
  #       #    #  #    #  #    #  #    #   #       #    #  #       #   # #
  #       #    #   ####   #    #  #    #   ######  #####   ######  #    #
```

                         A. Martin Pendas
                         University of Oviedo
                         Version 1.00 (c) 2001

2002-03-25: Victor Lua~na (VLC)
             Added topological analysis of the electron density laplacian.

This code analyzes first order real space and momentum molecular densities.
Wavefunctions are necessarily gaussian in nature and in WFN (a la Bader)
format.

CAPABILITIES:

.. S C A L A R S ...
A list of scalar densities computed follows:
Momentum densities:
  -3D first order momentum density (pi)
  -3D form factors (form)
* -3D and 1D compton profiles in a near future....
  -1D spherical average of the 3D momentum density (spi)
  -Expectation values of <p^n> operators (expect)

Real space densities
  -3D first order real density (rho)
  -3D laplacian of the real electron density (lap)
  -3D B functions (bfun)
  -3D ELF localization function (elf)
.....

.. T O P O L O G I E S...
For all the 3D and 1D scalars, not only their magnitudes, but also their
first and second derivatives (gradients and hessians) are computed
analytically. This allows us to make automatic topological analyses
of of them. A Morse consistency check is done on all topologies, and
paths connecting (3,-1) to (3,-3) points are traced and studied.
......

.. G R I D S ....
0D, 1D, 2D and 3D grids are allowed for all the scalars separately, in
general format. 3D cube (gaussianXX format) multigrids are also allowed,
so isosurfaces of the scalars are easily displayed by standard
molecular graphics programs like molekel.
......

.. A S S O C I A T E D   S C A L A R S .....
A number of interesting associated scalars related to the real space
density are also obtained. These include:
  -kinetic energy densities: K (positive definite)
                             G (Schrodinger density)
                             P (Pauli repulsion kinetic energy density)
  -kinetic stress tensor
  -Potential stress tensor (Maxwell selfinteraction-less form)
  -Ehrenfest Force densities (~ eigenvalues of the kinetic stress tensor)
  -Potential energy densities:
                               nn (nucleus-nucleus)
                               ne (electron-nucleus)
                               ee (electron-electron) !Monodeterminantal
                               (Beware that it is also computed in non-
                                determinantal, meaningless cases)
```

```
    -nuclear and electronic total force densities (f+(r), f-(r))
.......


.. B A S I N   I N T E G R A T I O N
As of version 1.00, promolden includes a variety of methods to integrate
the above real density associated scalars within Bader atomic basins.
In the near future, elf integration will also be available. The user
is warned about the computational efficiency of these integrations.
It is extremely expensive to integrate maxwell densities numerically.

Both search-of-basin-boundary and Biegler-Konig's natural-coordinate
methods have been implemented. Several adaptive and non-adaptive
integration quadratures are also allowed.
.....

----------------------------------------------------------------------
----------------------------------------------------------------------
INPUT

The code is invoked: promolden input.file [output.file]
The input is keyword oriented, freeformat, and the output is meant to
be selfcontained.

-The first line must contain the name of the wavefunction file in
 the AIMPAC WFN format. We have finally not included other wavefunction
 formats, but they are easily added if needed. Notice that the precision
 of the primitive coefficients on building molecular orbitals may be
 smaller than that needed for very, very accurate momentum density properties
 The latter are known to be extremely dependent on the former.

-The following lines are not mandatory. Each of them is an order for
 promolden, and the user may concatenate as many as he/she desires.
 All of them will be executed in the order given. They consist of a
 keyword name and numeric/character options. There are 4 general types
 of keywords:
     -informative keywords : Activate general options of the program.
     -scalar keywords      : Obtain scalars (sometimes on grids).
     -topology keywords    : Demand the topology of a scalar field.
     -basin integ. keywords: Integrate rho associated scalars in atomic basins

-A description of each keyword and its options follows:

     INFORMATIVE KEYWORDS:
     -----------
     NOMAXWELL: By default, all maxwellian stress tensors are computed
                on spatial density calculations. As their computation is
                time consuming, the user may force NOT to obtain them.
     NOBFUNC  : Similar arguments apply to the calculation of B functions
                in cube grids. (see below).

                None of these keywords admit additional parameters.

     SCALAR KEYWORDS:
     ----------------
     PI, RHO, ELF, FORM, BFUN: Demand the computation of the scalars
                in 0D,1D,2D,or 3D grids. On output, a record per point
                is printed in a format suitable for most graphing codes,
                like Gnuplot. This record has the following form:

                x,y,z,scalar,(grad(i),i=1,3),((hess(i,j),j=1,3),i=1,3),
                laplacian.     i runs over x,y,z. Keyword=Pi,Elf,Form,Bfun

                In the case of the spatial density rho, the number of
                properties per record is greater:

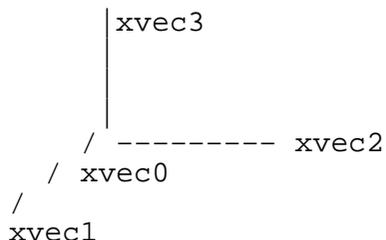                x,y,z,scalar,(grad(i),i=1,3),((hess(i,j),j=1,3),i=1,3),
```

```
(fieldn(1),f+(1),3),eii)(f+(1),f-1,3),(f+(1),f-1,3)]
```

Here, g,k,p are the kinetic energy densities; nn,ne,ee the
maxwellian potential energy densities; fielde/n the
electronic/nuclear components of the electric field;
f+/- the nuclear/electronic force densities. All magnitudes
within brackets [] are not computed if the NOMAXWELL
flag is turned on.

PIP, RHOP, ELFP, FORMP, BFUNP: Demand the computation of the scalars
in 0D,1D,2D,or 3D grids. On output, a set of records is produced
at each point of the grid, including diagonalization of the
hessian matrix. These kind of output is intended to be more
easily read by humans. All the previous properties are
computed and displayed in a common way.

Usage: Each of these keyword is followed by the following
parameters.

KEYWORD ndim xvec0 [xvec1 [xvec2 [xvec3]] npoints]

A ndim-dimensional GRID will be computed. 0<=ndim<=3.
xvecn, 0<=n<=2, are points in real or momentum space
defining a ndim-dimensional parallelepiped.

```
                    |xvec3
                    |
                    |
                    |
                    |
                   / ---------- xvec2
                  / xvec0
                 /
                xvec1
```

```
      ndim=0    properties at a point xvec0
      ndim=1    properties along a line defined by the
                xvec0 and xvec1 points. Npoints will be
                computed.
      ndim=2    properties in the rectangle defined by
                the xvec0, xvec1, xvec2 points.
                Npoints X Npoints in the grid
      ndim=3    properties in the box defined by
                the xvec0, xvec1, xvec2, xvec3 points.
                Npoints X Npoints X Npoints in the grid
```

EXPECTATION: Obtain the expectation values of the $<p>^n$ operators
for the molecule under study. $-2<=n<=4$

SPI   : Obtain the spherically averaged momentum density.

Usage:

SPI pmax, npoints

This order construct a curve of the spherically
averaged momentum density from p=0 to p=pmax
using npoints.

CUBE   : Obtain a "cube" file (to be used by molecular
graphics programs) for a set of relevant scalars.
A file named as the wavefunction filename plus
an informative suffix will be written for each
scalar. These files are immediately read by MOLEKEL.
If NOMAXWELL or NOBFUNC flags are active, no maxwellian
nor B function files will be written.

```
                        CUBE x, y, z, nx, ny, nz

                        This order will generate cube files centered in the
                        box  -x/2<=x<=x/2,  -y/2<=y<=y/2,  -z/2<=z<=z/2 using
                        nx, ny, and nz points in each direction.
                        At the moment k,g,nn,ne,ee,vt,et,elf,rho,lap,grad,b,
                        blap,bgrad files will be written. All of them
                        have their common meaning. vt is the total potential
                        energy density; et is the total energy (HF) density;
                        grad is the  gradient module; b,blap, bgrad are
                        the B function, and its laplacian and gradient module.


        SQUARE    :Obtain a proaim "grid" file to be used directly by
                        the proaim codes "contor" and "relief" to make isoline
                        and surface plots of a set of relevant scalars in a plane.
                        A file named as the wavefunction filename plus
                        an informative suffix will be written for each
                        scalar.  If NOMAXWELL or NOBFUNC flags are active,
                        no maxwellian nor B function files will be written.

                        Usage:

                        SQUARE xvec0, xvec1, xvec2, nx, ny

                        This order will generate grid files on a plane described
                        using the same notation as in the scalar keywords examples
                        given above. xvec0, xvec1, and xvec2 are 3D vectors.
                        nx X ny grid points will be used.
                        At the moment k,g,nn,ne,ee,vt,et,elf,rho,lap,grad,b,
                        blap,bgrad files will be written. See the CUBE keyword
                        for more information.


   TOPOLOGY KEYWORDS:
   ------------------

 TPI,TRHO,TLAP,TELF,TBFUN: Obtain automatically the topology of the 3D
                        scalars PI, RHO, LAP, ELF, and BFUN, respectively.
                        It has been demonstrated over the years that a simple
                        Newton-Raphson (NR) search of the zeros of the equation:

                                       ->              ->
                                       Grad(Scalar)=0,

                        is, probably, the simplest and quickest way of obtaining
                        the complete topology of these scalar densities.
                        For each scalar, a full search is made by starting NR
                        steps at points uniformly distributed over a sphere of
                        a given maximum radius and given number of points along
                        the r, theta, and phi directions. A judicious value of
                        the maximum radius of the sphere and the number of trial
                        points gives almost invariably the complete topology of
                        the scalar. A wealth of information is given at each
                        critical point found. A Morse analysis is done on the
                        final topology, and the (3,-1) to (3,-3) gradient paths
                        are computed.

                        Usage:

                        KEYWORD rmax, np, epsilon

                        Obtain the topology within a sphere of radius rmax,
                        using  np X np X np radial,theta, and phi points, and
                        accepting a critical point when |Grad(scalar)|<epilon.
```

spherically averaged momentum density). A 1D NR search
is used.

Usage:

TSPI pmax, np, epsilon

Start np NR searches for 0<=p<=rmax. Accept a CP if
d(tspi)/dp< epsilon

BASIN INTEGRATION KEYWORDS

BASINT : Numerically integrate the real density associated scalars
         within a given AIM atomic basin. A rather large number of
         integration procedures have been implemented. It is
         desirable to introduce some terms before giving a detailed
         account of them. A spherical coordinate system is attached
         to the (3,-3) Critical Point that defines the atomic basin
         under study. Notice that frequently the position of this
         CP does not coincide exactly with the nuclear coordinate.
         This effect is particularly strong for hydrogens.
         A ray is a given (theta,phi) pair in this coordinate system.
         The surface of the basin is the union of all the 2D
         attraction basins of all the bond points linked to the
         nucleus studied. The scalar densities integrated are
         numbered. The order is:

         L, Q, mux, muy, muz, qxx, qxy, qxz, qyy, qyz, qzz
         1 2   3   4   5   6   7   8   9   10   11

         V, [nn, ne, ee, vtot], K, G, [HF], P, Fx, Fy, Fz
         12 13 14 15   16   17 18 19   20 21 22 23
         12   13 14   15 16 17 18

         virb
          24
          19

          where the new symbols are L (laplacian integral),
          Q (charge) mu (dipolar moments), q (quadrupolar
          moments), F (Ehrenfest forces), and virb (basin
          virial)

         Our methods can be divided in two large classes:
             (S) Algorithms that determine the position of the
                 basin's surface at each ray by a bipartition
                 process. The gradient field is integrated at
                 several values along a ray, and the omega-limit
                 at each of this points us used as a logic gate
                 for a bipartition algorithm. The subsequent
                 techniques of integration of the Theta and Phi
                 variables define the (S) class.

             (N) Algorithms that use a Biegler-Konig natural
                 coordinate system and integrate the radial coordinate
                 in these coordinates by solving the BK radial
                 differential equations. The basin's surface is
                 never determined.

          We have classified the algorithms according to a triplet
          (doublet) of letters that code the integration algorithm
          in theta, phi, and r, respectively. In this way, the
          LPN algorithm refers to the usage of a gauss-laguerre
          quadrature in theta, a periodic quadrature in phi and a
          natural coordinate method in r. All (S) algorithms use

Integration. This quadrature is also used to integrate
the beta sphere in the (N) algorithms. A brief description
of the methods follow:

    TJN, TTN, JTS, TTS: combination of Perez-Jorda's (J)
            quadratures and trapezoidal romberg (T) in theta
            and phi. The integration is followed until a chosen
            density converges to a given precision. The J algorithm
            was unsuccessfully tried for Phi integrations, but
            its asymmetry precludes good convergence of multipolar
            moments when other densities control the stop criterion

            Usage:

            BASINT [TJN,TTN,JTS,TTS] nint, nuc, eps, maxp

            Integration around nuclues nuc. Convergence equals
            eps in density number nint. No more than maxp points
            will be used.

    DDN: A complete 3D BK differential equation is solved by
            means of the VODE package. All equations are
            considered stiff.

            Usage:

            BASINT DDN nint, nuc, eps

    LPN,LPS: Fixed number of points Gauss-Lengendre quadrature
             for theta and periodic for phi.

            Usage:

            BASINT [LPN,LPS] nint, nuc, eps, ntheta, nphi

            ntheta X nphi points used.

     BN,BS : Adaptive bidimensional quadrature in theta and phi (B)
            using 15 point Gauss-Kronrod rules (package dcuhre)

            Usage:

            BASINT [BN,BS] nint, nuc, eps, maxp

            No more than maxp points will be used.

    AAN,AAS: Adaptive 1D quadratures for each theta and phi.
             The phi quadrature uses simple 15-point Gauss-Kronrod
             rules (qag package), while the theta one includes
             the epsilon-extrapolation algorithm to manage
             the isolated singularities associated with bond
             critical points (qags package).
             In this case both a 15-point GK
             rule as well as a 21-point rule have been implemented

            Usage:

            BASINT [AAN,AAS] nint, nuc, eps, nkey

            If nkey=0 a 15 point rule is used in theta
            If nkey=1 a 21 point rule is used in theta

  Warning!!! Integrating properties within atomic basins is
  far from a solved problem. Sometimes (actually much more

of 'running until convergence' algorithms use a number of
points to achieve the given convergence intolerably large.
This is particularly so when natural coordinates are used.
The stiff nature of the differential equations to be solved
requires quite sophisticated integration procedures. Following a
gradient path accurately is a solved problem, but the number
of points needed may vary greatly from one case to another.
This means that the (N) algorithms are not very suitable to
integrate Maxwell stress tensor densities, and that in these
cases, simpler, brute force bipartitions may be much more
efficient. Also notice that the crudest LPN, LPS methods, with
a pre-fixed number of rays may give very good results in some
cases using a fraction of the time of other methods.
Finally, recall that all (N) methods give laplacian integrals
of extremely good quality due to their nature. DO NOT use the
laplacian as the convergence criterion.