

# ATOM User Manual

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# 1 PREFACE

ATOM is the name of a program originally written (circa 1982) by Sverre Froyen at the University of California at Berkeley, modified starting in 1990 by Norman Troullier and Jose Luis Martins at the University of Minnesota, and currently maintained by Alberto Garcia (wdp-gaara@lg.ehu.es), who added some features and made substantial structural changes to the April 1990 (5.0) Minnesota version while at Berkeley and elsewhere.

Jose Luis Martins is maintaining his own version of the code:

`{\tt http://bohr.inesc.pt/~jlm/pseudo.html}`

The program's basic capabilities are:

- All-electron DFT atomic calculations for arbitrary electronic configurations.
- Generation of ab-initio pseudopotentials (several flavors).
- Atomic calculations in which the effect of the core is represented by a previously generated pseudopotential. These are useful to make sure that the pseudopotential correctly reproduces the all-electron results for the valence complex.

## 2 A PRIMER ON AB-INITIO PSEUDOPOTENTIALS

Time constraints prevent the inclusion of this section in this first release of the ATOM manual. But, in this case more than ever, there is a lot to be gained from reading the original literature... Here are some basic references:

- Original idea of the ab-initio pseudopotential:  
Kerker, J. Phys. C 13, L189-94 (1980)  
Hamann, Schluter, Chiang, Phys. Rev. Lett. 43, 1494 (1979)
- More on HSC scheme:  
Bachelet, Schluter, Phys. Rev. B 25, 2103 (1982)  
Bachelet, Hamann, Schluter, Phys. Rev. B 26, 4199 (1982)
- Troullier-Martins elaboration of Kerker method:  
Troullier, Martins, Phys. Rev. B 43, 1993 (1991)  
Troullier, Martins, Phys. Rev. B 43, 8861 (1991)
- Core corrections:  
Louie, Froyen, Cohen, Phys. Rev. B 26, 1738 (1982)
- The full picture of plane-wave pseudopotential ab-initio calculations:  
W. E. Pickett, "Pseudopotential Methods in Condensed Matter Applications", Computer Physics Reports 9, 115 (1989)  
M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias and J. D. Joannopoulos, "Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients", Rev. Mod. Phys. 64, 1045, (1992)  
Also, the book by Richard Martin "Electronic Structure: Basic Theory and Practical Methods" (Cambridge University Press) has a chapter on pseudopotentials.

- Use in SIESTA:

J.M. Soler, E. Artacho, J.D. Gale, A. Garcia, J. Junquera, P. Ordejon, D. Sanchez-Portal, "The SIESTA method for ab initio O(N) materials simulation", Jour. Phys.: Condens. Matter, 14, 2745-2779 (2002).

### 3 COMPILING THE PROGRAM

Edit `makefile` in the main source directory, and modify, if needed, the defaults for Fortran compiler and auxiliary file containing date and time routines (not standard in `Fortran77`).

Type `make`. After a short while you will have the executable (called `atm`) in that same directory. The program should work for any atom without recompilation.

Directory `Tutorial` in the source distribution contains a set of scripts to automate the process of running `ATOM` and to analyze the results. The file-manipulation details involved in each of the basic functions of all-electron calculations, generation of pseudopotentials, and testing of the pseudopotentials, are taken care of by `ae.sh`, `pg.sh`, and `pt.sh`, respectively. These scripts need to know where the `ATOM` executable `atm` is. If you have moved the `Tutorial` directory around, or you do not have the source, the default location might not be right for you. The easiest way to fix it is to define an environmental variable `ATOM_PROGRAM`. Assuming `atm` is in `/somedir/somewhere`, you would do:

```
ATOM_PROGRAM=/somedir/somewhere/atm ; export ATOM_PROGRAM # sh-derived shells
setenv ATOM_PROGRAM /somedir/somewhere/atm                # csh-derived shells
```

Due to the shortcomings of the basic (GNUplot) plotting package used in the Tutorial section, it is also necessary to copy some scripts from a central repository. Again, if the default does not work for you, define the `ATOM_UTILS_DIR` variable:

```
ATOM_UTILS_DIR=/somewhere ; export ATOM_UTILS_DIR # sh-derived shells
setenv ATOM_UTILS_DIR /somewhere                  # csh-derived shells
```

### 4 USING THE ATOM PROGRAM

#### 4.1 All-electron calculations

Assume we want to find the orbital eigenvalues, total energy, and/or charge density of Si in its ground state. (You should now go to the `Tutorial/All_electron` directory and try the following.) Our input file is named `si.ae.inp` and contains the lines (see Sect. 5 for more details):

```
ae Si ground state all-electron
Si  ca
    0.0
    3   2
    3   0   2.00   0.00
    3   1   2.00   0.00
```

```
#2345678901234567890123456789012345678901234567890 Ruler
```

We can run the calculation by using the `ae.sh` script. Following the layout of the **Tutorial** directory, we will assume that the script is in the directory directly above the current one. We run the script and go into the directory created for the calculation (named as the input file without the extension `.inp`):

```
$ sh ../ae.sh si.ae.inp
==> Output data in directory si.ae
$ cd si.ae
$ ls
AECHARGE  CHARGE  RHO      charge.gplot  vcharge.gps
AEWFNR0   INP      ae.gplot  charge.gps    vspin.gplot
AEWFNR1   OUT      ae.gps    vcharge.gplot vspin.gps
$
```

We see some data files (those in all caps) and a few GNUPLOT plotting scripts<sup>1</sup>.

The files are:

- **INP**: A copy of the input file for the calculation.
- **OUT**: Contains detailed information about the run.
- **AECHARGE**: Contains in four columns values of  $r$ , the “up” and “down” parts of the *total* charge density, and the total core charge density (the charges multiplied by  $4\pi r^2$ ). **CHARGE** is exactly identical and is generated for backwards compatibility.
- **RHO**: Like **CHARGE**, but without the  $4\pi r^2$  factor.
- **AEWFNR0...AEWFNR3**: All-electron valence wavefunctions as function of radius, for  $s$ ,  $p$ ,  $d$ , and  $f$  valence orbitals (0, 1, 2, 3, respectively — some channels might not be available). They include a factor of  $r$ , the  $s$  orbitals also going to zero at the origin.

It is interesting to peruse the **OUT** file. In particular, it lists the orbital eigenvalues (in Rydbergs, as every other energy in the program):

nl	s	occ	eigenvalue	kinetic energy	pot energy
1s	0.0	2.0000	-130.36911241	183.01377616	-378.73491463
2s	0.0	2.0000	-10.14892694	25.89954259	-71.62102169
2p	0.0	6.0000	-7.02876268	24.42537874	-68.74331203
3s	0.0	2.0000	-0.79662742	3.23745215	-17.68692611
3p	0.0	2.0000	-0.30705179	2.06135782	-13.62572515

(For a relativistic or spin-polarized calculation, there would be “up” and “down” flags in the **s** column above.)

The **plotting** scripts come in two flavors: `.gplot` for terminal use (default X11, use `gnuplot -persist`), and `.gps` for postscript output.

For all-electron calculations, the relevant scripts (without `.gplot` or `.gps` extensions) are:

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<sup>1</sup>GNUPLOT is not a publication-quality package, and suffers from serious shortcomings, but it is free, and installed almost everywhere. Hence we have chosen it as the lowest-common denominator for basic plotting

- **charge**: Charge density (separated core and valence contributions, multiplied by  $4\pi r^2$ ).
- **vcharge**: Valence charge density (same normalization).
- **ae**: Orbital valence wavefunctions (radial part multiplied by  $r$ )

## 4.2 Pseudopotential generation

(You should now go to the **Tutorial/Si** directory and try the following.) We are going to generate a pseudopotential for Si, using the Troullier-Martins scheme. The calculation is relativistic and we use the LDA (Ceperley-Alder flavor). The input file is named **Si.tm2.inp** and contains the lines (see Sect. 5 for more details):

```
#
# Pseudopotential generation for Silicon
# pg: simple generation
#
pg      Silicon
      tm2      3.0      # PS flavor, logder R
n=Si c=car      # Symbol, XC flavor,{ |r|s}
      0.0      0.0      0.0      0.0      0.0      0.0
      3      4      # norbs_core, norbs_valence
      3      0      2.00      0.00      # 3s2
      3      1      2.00      0.00      # 3p2
      3      2      0.00      0.00      # 3d0
      4      3      0.00      0.00      # 4f0
      1.90      1.90      1.90      1.90      0.00      0.00
#
# Last line (above):
# rc(s)      rc(p)      rc(d)      rc(f)      rcore_flag      rcore
#
#23456789012345678901234567890123456789012345678901234567890
```

Note the two extra lines with respect to an all-electron calculation. The pseudopotential core radii for all channels are 1.90 bohrs. Even though they are nominally empty in the ground state, we include the  $3d$  and  $4f$  states in order to generate the corresponding pseudopotentials.

We can run the calculation by using the **pg.sh** script. Following the layout of the **Tutorial** directory, we will assume that the script is in the directory directly above the current one. We run the script and go into the directory created for the calculation (named as the input file without the extension **.inp**):

```
$ sh ../pg.sh Si.tm2.inp
==> Output data in directory Si.tm2
==> Pseudopotential in Si.tm2.vps and Si.tm2.psf
$ cd Si.tm2
$ ls [A-Z]*      # show only the data filesAE
CHARGE AEWFNR3  PSLOGD3  PSPOTR3  PSWFNR3
AELOGD0  CHARGE  PSPOTQ0  PSWFNQ0  RHO
AELOGD1  INP      PSPOTQ1  PSWFNQ1  SCRSPOTR0
AELOGD2  OUT      PSPOTQ2  PSWFNQ2  SCRSPOTR1
```

AELOGD3	PSCHARGE	PSPOTQ3	PSWFNQ3	SCRPSPTR2
AEWFNR0	PSLOGD0	PSPOTR0	PSWFNR0	SCRPSPTR3
AEWFNR1	PSLOGD1	PSPOTR1	PSWFNR1	VPSFMT
AEWFNR2	PSLOGD2	PSPOTR2	PSWFNR2	VPSOUT

There are quite a few data files now. The new ones are:

- **PSCHARGE**: Contains in four columns values of  $r$ , the “up” and “down” parts of the *pseudo valence* charge density, and the pseudo core charge density (see Sect. 4.2.1) (the charges multiplied by  $4\pi r^2$ ).
- **PSWFNR0...PSWFNR3**: Valence pseudowavefunctions as function of radius, for  $s$ ,  $p$ ,  $d$ , and  $f$  valence orbitals (0, 1, 2, 3, respectively — some channels might not be available). They include a factor of  $r$ , the  $s$  orbitals also going to zero at the origin.
- **PSPOTR0...PSPOTR3**: Ionic pseudopotentials (i.e. unscreened) as a function of  $r$ , for  $s$ ,  $p$ ,  $d$ , and  $f$  channels (0, 1, 2, 3, respectively — some channels might not be available). The last column is  $-2Z_{ps}/r$ , that is, the Coulomb potential of the pseudo atom. All the ionic pseudopotentials tend to this Coulomb tail for  $r$  beyond the range of the core electrons.
- **SCRPSPTR0...SCRPSPTR3**: Screened pseudopotentials as a function of  $r$ , for  $s$ ,  $p$ ,  $d$ , and  $f$  channels (0, 1, 2, 3, respectively — some channels might not be available). They tend to  $-2Z_{ion}/r$  for large  $r$ , where  $Z_{ion}$  is the global charge of the reference configuration used in pseudopotential generation.
- **PSPOTQ0...PSPOTQ3**: Fourier transform  $V(q)$  (times  $q^2/Z_{ps}$ ) of the ionic pseudopotentials as a function of  $q$  (in bohr $^{-1}$ ), for  $s$ ,  $p$ ,  $d$ , and  $f$  channels (0, 1, 2, 3, respectively — some channels might not be available).
- **PSWFNQ0...PSWFNQ3**: Fourier transform  $\Psi(q)$  of the valence pseudowavefunctions as a function of  $q$  (in bohr $^{-1}$ ), for  $s$ ,  $p$ ,  $d$ , and  $f$  channels (0, 1, 2, 3, respectively — some channels might not be available).
- **VPSOUT**, **VPSFMT**: Files (formatted and unformatted) containing pseudopotential information. They are used for *ab-initio* codes such as SIESTA and PW. Copies of these files are deposited in the top directory after the run.

The OUT file has two sections, one for the all-electron (AE) run, and another for the pseudopotential (PS) generation itself. It is instructive to compare the AE and PS eigenvalues. Simply do

\$ grep '&v' OUT

ATM3		12-JUL-02	Silicon		
3s	0.5	2.0000	-0.79937161	0.00000000	-17.74263363
3p	-0.5	0.6667	-0.30807129	0.00000000	-13.66178958
3p	0.5	1.3333	-0.30567134	0.00000000	-13.60785822
3d	-0.5	0.0000	0.00000000	0.00000000	-0.27407047
3d	0.5	0.0000	0.00000000	0.00000000	-0.27407047
4f	-0.5	0.0000	0.00000000	0.00000000	-0.26482365
4f	0.5	0.0000	0.00000000	0.00000000	-0.26482365
----- &v					
3s	0.5	2.0000	-0.79936061	0.50555315	-3.74113059

3p	-0.5	0.6667	-0.30804995	0.77243805	-3.26356669
3p	0.5	1.3333	-0.30565760	0.76702460	-3.25197500
3d	-0.5	0.0000	0.00000000	0.00140505	-0.07847269
3d	0.5	0.0000	0.00000000	0.00140505	-0.07847269
4f	-0.5	0.0000	0.00000000	0.00243411	-0.07586534
4f	0.5	0.0000	0.00000000	0.00243411	-0.07586534
----- &v					

(The AE and PS eigenvalues are not *exactly* identical because the pseudopotentials are changed slightly to make them approach their limit tails faster).

The relevant plotting scripts (without `.gplot` or `.gps` extensions) are:

- **charge**: It compares the AE and PS charge densities.
- **pseudo**: A multi-page plot showing, on one page/window per channel:
  - The AE and PS wavefunctions
  - The AE and PS logarithmic derivatives.
  - The real-space pseudopotential
  - The Fourier-transformed pseudopotential (times  $q^2/Z_{ps}$ )
- **pots**: All the real-space pseudopotentials.
- **scrpots**: Comparison of the screened and unscreened pseudopotentials.

#### 4.2.1 Core Corrections

The program can generate pseudopotentials with the non-linear exchange-correlation correction proposed in S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B 26, 1738 (1982).

In the traditional approach (which is the default for LDA calculations), the pseudocore charge density equals the charge density outside a given radius  $r_{pc}$ , and has the smooth form

$$\rho_{pc}(r) = Ar \sin(br)$$

inside that radius. A smooth matching is provided with suitable  $A$  and  $b$  parameters calculated by the program.

A new scheme has been implemented to fix some problems in the generation of GGA pseudopotentials. The smooth function is now

$$\rho_{pc}(r) = r^2 \exp(a + br^2 + cr^4)$$

and derivatives up to the second are continuous at  $r_{pc}$ .

To use core corrections in the pseudopotential generation the jobcode in the first line should be **pe** instead of **pg**.

The radius  $r_{pc}$  should be given in the sixth slot in the last input line (see above). If it is negative or zero (or blank), the radius is then computed using the fifth number in that line (**rcore\_flag**, see the example input file above) and the following criterion: at  $r_{pc}$  the core charge density equals **rcore\_flag**\*(valence charge density). It is *highly recommended* to set an explicit value for the pseudocore radius  $r_{pc}$ , rather than letting the program provide a default.



If `rcore_flag` is input as negative, the full core charge is used. If `rcore_flag` is input as zero, it is set equal to one, which will be thus the default if `pe` is given but no numbers are given for these two variables.

The output file contains the radius used and the  $A$  ( $a$ ) and  $b$  (and  $c$ ) parameters used for the matching. The `VPSOUT` and `VPSFMT` files will contain the pseudocore charge in addition to the pseudopotential.

It is possible to override the default (new scheme for GGA calculations, old scheme for LDA calculations) by using the directives

```
%define NEW_CC
%define OLD_CC
```

The program will issue the appropriate warnings. (See Sect. 5)

Relevant files:

- **PSCHARGE**: Contains the pseudocore charge in column four. (multiplied by  $4\pi r^2$ ).
- **COREQ**: Fourier transform of the pseudocore charge density  $\rho_{pc}(q)$  in units of electrons, with  $q$  in bohr $^{-1}$ .

Useful plotting scripts (without `.gplot` or `.gps` extensions) are:

- **charge**: Shows also the pseudocore charge.
- **coreq**: Shows the Fourier transform of the pseudocore charge.

### 4.3 Pseudopotential test

While it is helpful to “have a look” at the plots of the pseudopotential generation to get a feeling for its quality, there is no substitute for a proper **transferability testing**. A pseudopotential with good transferability will reproduce the all-electron energy levels and wavefunctions in arbitrary environments, (i.e., in the presence of charge transfer, which always takes place when forming solids and molecules). We know that norm conservation guarantees a certain degree of transferability (usually seen clearly in the plot of the logarithmic derivative), but we can get a better assessment by performing all-electron and “pseudo” calculations on the same series of atomic configurations, and comparing the eigenvalues and excitation energies.

In the same `Tutorial/Si` directory we can find file `Si.test.inp`, containing the concatenation of ten jobs. The first five are all-electron (**ae**) calculations, and the last five, pseudopotential test (**pt**) runs for the same configurations:

```
#
# All-electron calculations for a series of Si configurations
#
ae Si Test -- GS 3s2 3p2
Si   ca
    0.0
    3   2
    3   0      2.00
```

```

3      1      2.00
ae Si Test -- 3s2 3p1 3d1
Si      ca
      0.0
3      3
3      0      2.00
3      1      1.00
3      2      1.00
ae Si Test -- 3s1 3p3
Si      ca
      0.0
3      2
3      0      1.00
3      1      3.00
ae Si Test -- 3s1 3p2 3d1
Si      ca
      0.0
3      3
3      0      1.00
3      1      2.00
3      2      1.00
ae Si Test -- 3s0 3p3 3d1
Si      ca
      0.0
3      3
3      0      0.00
3      1      3.00
3      2      1.00
#
# Pseudopotential test calculations
#
pt Si Test -- GS 3s2 3p2
Si      ca
      0.0
3      2
3      0      2.00
3      1      2.00
pt Si Test -- 3s2 3p1 3d1
Si      ca
      0.0
3      3
3      0      2.00
3      1      1.00
3      2      1.00
pt Si Test -- 3s1 3p3
Si      ca
      0.0
3      2
3      0      1.00
3      1      3.00

```

```

pt Si Test -- 3s1 3p2 3d1
Si   ca
    0.0
  3   3
  3   0      1.00
  3   1      2.00
  3   2      1.00
pt Si Test -- 3s0 3p3 3d1
Si   ca
    0.0
  3   3
  3   0      0.00
  3   1      3.00
  3   2      1.00

```

The configurations differ in the promotion of electrons from one level to another (it is also possible to transfer *fractions* of an electron).

We can run the file by using the `pt.sh` script. Following the layout of the `Tutorial` directory, we will assume that the script is in the directory directly above the current one. We need to give it **two** arguments: the calculation input file, and the file containing the pseudopotential we want to test. Let's make the latter `Si.tm2.vps`:

```

$ sh ../pt.sh Si.test.inp Si.tm2.vps
$ sh ../pt.sh Si.test.inp Si.tm2.vps
==> Output data in directory Si.test-Si.tm2
$ cd Si.test-Si.tm2/
$ ls [A-Z]*
AECHARGE  AEWFN1R0  CHARGE  OUT          PTWFNR0  PTWFNR2  VPSIN
AEWFNR0   AEWFN2R0  INP     PTCHARGE    PTWFNR1  RHO

```

The working directory is named after *both* the test and pseudopotential files. It contains several new files:

- **VPSIN**: A copy of the pseudopotential file to be tested.
- **PTCHARGE**: Contains in four columns values of  $r$ , the “up” and “down” parts of the *pseudo valence* charge density, and the pseudo core charge density (see Sect. 4.2.1) (the charges multiplied by  $4\pi r^2$ ).
- **PTWFNR0...PTWFNR3**: Valence pseudowavefunctions as function of radius, for  $s$ ,  $p$ ,  $d$ , and  $f$  valence orbitals (0, 1, 2, 3, respectively — some channels might not be available). They include a factor of  $r$ , the  $s$  orbitals also going to zero at the origin.

The `OUT` file has two sections, one for the all-electron (AE) runs, and another for the pseudopotential tests (PT). At the end of each series of runs there is a table showing the excitation energies. A handy way to compare the AE and PT energies is:

```

$ grep '&d' OUT
[...elided...]
&d total energy differences in series

```

```

&d      1      2      3      4      5
&d  1      0.0000
&d  2      0.4308      0.0000
&d  3      0.4961      0.0653      0.0000
&d  4      0.9613      0.5305      0.4652      0.0000
&d  5      1.4997      1.0689      1.0036      0.5384      0.0000
*----- End of series -----* spdfg &d&v
ATM3      12-JUL-02      Si Test -- GS 3s2 3p2
ATM3      12-JUL-02      Si Test -- 3s2 3p1 3d1
ATM3      12-JUL-02      Si Test -- 3s1 3p3
ATM3      12-JUL-02      Si Test -- 3s1 3p2 3d1
ATM3      12-JUL-02      Si Test -- 3s0 3p3 3d1
&d total energy differences in series
&d      1      2      3      4      5
&d  1      0.0000
&d  2      0.4299      0.0000
&d  3      0.4993      0.0694      0.0000
&d  4      0.9635      0.5336      0.4642      0.0000
&d  5      1.5044      1.0745      1.0051      0.5409      0.0000
*----- End of series -----* spdfg &d&v

```

The tables (top AE, bottom PT) give the cross-excitations among all configurations. Typically, one should be all right if the AE-PT differences are not much larger than 1 mRy.

You can also compare the AE and PT eigenvalues. Simply do

```

$ grep '&v' OUT | grep s
ATM3      12-JUL-02      Si Test -- GS 3s2 3p2
3s  0.0      2.0000      -0.79662742      3.23745215      -17.68692611
ATM3      12-JUL-02      Si Test -- 3s2 3p1 3d1
3s  0.0      2.0000      -1.08185979      3.53885995      -18.40569836
ATM3      12-JUL-02      Si Test -- 3s1 3p3
3s  0.0      1.0000      -0.85138783      3.35438895      -17.96219240
ATM3      12-JUL-02      Si Test -- 3s1 3p2 3d1
3s  0.0      1.0000      -1.11431855      3.62997498      -18.60814708
ATM3      12-JUL-02      Si Test -- 3s0 3p3 3d1
3s  0.0      0.0000      -1.14358268      3.71462770      -18.79448684
*----- End of series -----* spdfg &d&v
ATM3      12-JUL-02      Si Test -- GS 3s2 3p2
1s  0.0      2.0000      -0.79938037      0.50556261      -3.74114712
ATM3      12-JUL-02      Si Test -- 3s2 3p1 3d1
1s  0.0      2.0000      -1.08384468      0.55070398      -3.81988817
ATM3      12-JUL-02      Si Test -- 3s1 3p3
1s  0.0      1.0000      -0.85392666      0.52020429      -3.76852577
ATM3      12-JUL-02      Si Test -- 3s1 3p2 3d1
1s  0.0      1.0000      -1.11546463      0.56048425      -3.83646615
ATM3      12-JUL-02      Si Test -- 3s0 3p3 3d1
1s  0.0      0.0000      -1.14353959      0.56945741      -3.85106049
*----- End of series -----* spdfg &d&v

```

(and similarly for  $p$ ,  $d$ , and  $f$ , if desired). Again, the typical difference should be of around

1 mRyd for a “good” pseudopotential. (The *real* proof of good transferability, remember, can only come from a molecular or solid-state calculation). Note that the PT levels are labeled starting from principal quantum number 1.

The relevant plotting scripts (without `.gplot` or `.gps` extensions) are:

- **charge**: It compares the AE and PT charge densities.
- **pt**: Compares the valence all-electron and pseudo-wavefunctions.

## 5 APPENDIX: THE INPUT FILE

For historical reasons, the input file is in a rigid column format. Fortunately, most of the column fields line up, so the possibility of errors is reduced. We will begin by describing in detail a very simple input file for an **all-electron calculation** for the ground state of Si. More examples can be found in the `Tutorial` directory.

The file itself is:

```
#
# Comments allowed here
#
  ae Si ground state all-electron
Si   car
    0.0
    3   2
    3   0      2.00      0.00
    3   1      2.00      0.00
#
# Comments allowed here
#
#234567890123456789012345678901234567890      Ruler
```

- The first line specifies:
  - The calculation code (**ae** here stands for “all-electron”).
  - A title for the job (here **Si ground state all-electron**).
 (format 3x,a2,a50)
- Second line:
  - Chemical symbol of the nucleus (here **Si**, obviously)
  - Exchange-correlation type. Here, **ca** stands for Ceperley-Alder. Other options are **wi** (Wigner), **hl** (Hedin-Lundqvist), **gl** (Gunnarson-Lundqvist), and **bh** (von Barth-Hedin). The “best” LDA choice should be **ca**. It is also possible to use a gradient-corrected functional: **pb** indicates use of the PBE scheme by Perdew, Burke, and Ernzerhof (PRL 77, 3865 (1996)), **rp** indicates the RPBE scheme by Hammer, Hansen, and Norskov, (PRB 59, 7413 (1999)), **rv** indicates the revPBE scheme by Zhang and Yang, (PRL 80,890(1998)), and **bl** selects the BLYP (Becke-Lee-Yang-Parr) scheme (see source file `xc.f` for more details). By default, the exchange-correlation energy and potential are computed using the Soler-Balbás package, except for the **wi**, **hl**, **gl**, and **bh** flavors.

- The character **r** next to **ca** is a flag to perform the calculation relativistically, that is, solving the Dirac equation instead of the Schrodinger equation. The full range of options is:

- \* **s** : Spin-polarized calculation, non-relativistic.
- \* **r**: Relativistic calculation, obviously polarized.
- \* (blank) : Non-polarized (spin ignored), non-relativistic calculation.

(format 3x,a2,3x,a2,a1,2x)

- Third line. Its use is somewhat esoteric and for most calculations it should contain just a 0.0 in the position shown.

The rest of the file is devoted to the specification of the electronic configuration:

- Fourth line:  
Number of core and valence orbitals. For example, for Si, we have *1s*, *2s*, and *2p* in the core (a total of 3 orbitals), and *3s* and *3p* in the valence complex (2 orbitals).

(format 2i5)

- Fifth, sixth... lines: (there is one line for each valence orbital)

- **n** (principal quantum number)
- **l** (angular momentum quantum number)
- Occupation of the orbital in electrons.

(format 2i5,2f10.3)

(There are two f input descriptors to allow the input of “up” and “down” occupations in spin-polarized calculations (see example below))

Comments or blank lines may appear in the file at the beginning and at the end. It is possible to perform two or more calculations in succession by simply concatenating blocks as the one described above. For example, the following file is used to study the ground state of N and an excited state with one electron promoted from the *2s* to the *2p* orbital taking into account the spin polarization:

```
#
ae N ground state all-electron
N      cas
      0.0
      1      2
      2      0      2.00      0.00
      2      1      3.00      0.00
#
# Second calculation starts here
#
ae N 1s2 2s1 2p4 all-electron
N      cas
      0.0
      1      2
```

2	0	1.00	0.00
2	1	3.00	1.00

```
#234567890123456789012345678901234567890      Ruler
```

The different treatment of core and valence orbitals in the input for an all-electron calculation is purely cosmetic. The program “knows” how to fill the internal orbitals in the right order, so it is only necessary to give their number. That is handy for heavy atoms... Overzealous users might want to check the output to make sure that the core orbitals are indeed correctly treated.

For a **pseudopotential test calculation**, the format is exactly the same, except that the job code is **pt** instead of **ae**.

For a **pseudopotential generation run**, in addition to the electronic configuration chosen for the generation of the pseudopotentials (which is input in the same manner as above), one has to specify the “flavor” (generation scheme) and the set of core radii  $r_c$  for the construction of the pseudowavefunction. Here is an example for Si using the Hamann-Schluter-Chiang scheme:

```
#
pg Si Pseudopotential
      hsc      2.00
Si   ca
      0
      3      3
      3      0      2.00
      3      1      0.50
      3      2      0.50
      1.12      1.35      1.17      0.0      0.0      0.0
#
#2345678901234567890123456789012345678901234567890      Ruler
-----
```

Apart from the **pg** (pseudopotential generation) job code in the first line, there are two extra lines:

- Second line:

Flavor and radius at which to compute logarithmic derivatives for test purposes.

hsc    Hamann-Schluter-Chiang

The flavor can be one of :    ker    Kerker

tm2    Improved Troullier-Martins

The **ker** and **tm2** schemes can get away with larger  $r_c$ , due to their wavefunction matching conditions.

(format 8x, a3, f9.3)

- The last line (before the blank line) specifies:

- The values of the  $r_c$  in atomic units (bohrs) for the  $s$ ,  $p$ ,  $d$ , and  $f$  orbitals (it is a good practice to input the valence orbitals in the order of increasing angular momentum, so that there is no possible confusion).

(format 4f10.5)

- Two extra fields (2f10.5) which are relevant only if non-local core corrections are used (see Sect 4.2.1).

In the `hsc` example above, only  $s$ ,  $p$ , and  $d$   $r_c$ 's are given. Here is an example for Silicon in which we are only interested in the  $s$  and  $p$  channels for our pseudopotential, and use the Kerker scheme:

```
#
pg Si Kerker generation
   ker      2.00
Si   ca
   0
3    2
3    0      2.00
3    1      2.00
   1.80     1.80     0.00     0.0     0.0     0.0

#2345678901234567890123456789012345678901234567890 Ruler
```

This completes the discussion of the more common features of the input file. See the Appendix 6 for more advanced options.

## 6 APPENDIX: INPUT FILE DIRECTIVES

The fixed format can be a source of desperation for the beginner, and its rigidity means that it is not easy to add new items to the input. For this purpose, the program takes another route: several variables can be entered in a specially flexible format by means of *directives* at the top of the file. For example

```
%define NEW_CC
.... rest of the input file
```

would signal that we want to use a new core-correction scheme.

There are two kinds of directives, with syntax:

```
%VARIABLE=value
%define NAME
```

In the first case we assign the value `value` to the variable `VARIABLE`. The program can look at the value via a special subroutine call.

The second form is a bit more abstract, but can be understood as assigning a special “existence” value of 1 to the variable `NAME`. Again, the program can check for the existence of the variable via a special subroutine call.

Currently, the program understands the following `NAMES`:

- **COMPAT\_UCB**: Revert to the standard circa 1990 UCB values. Note that these correspond to the first released version of Jose Luis Martins code, not to the old Froyen version. (The defaults are: use a denser grid up to larger radii. Use a larger value for the pseudopotential cutoff point. Use the Soler-Balbas XC package.)



- **NEW\_CC**: New core-correction scheme
- **OLD\_CC**: Old core-correction scheme (see Sect. 4.2.1)
- **USE\_OLD\_EXCORR**: Use the old exchange-correlation package.
- **NO\_PS\_CUTOFFS**: Avoid cutting off the tails of the pseudopotentials. Currently, a simple exponential tapering function is used, which introduces a discontinuity in the first derivative of the ionic pseudopotential.