

Notes for 4.2.0.0 version of atompaw code.

N. A. W. Holzwarth, Wake Forest University, Winston-Salem, NC.

March 23, 2022

In the ATOMPAW Release 4.2.0.0, several changes from earlier versions have been introduced.

- Marc Torrent constructed a new module `input_dataset_mod.F90` which now takes care of all of the input and stores the relevant parameters in a datastructure.
- Natalie Holzwarth implemented the capability for graphatom to self-consistently solve the Dirac equation. At the moment, this capability is not yet integrated into the atompaw and PAW formalism.
- Natalie Holzwarth, Marc Torrent, and Michel Côté completed a reasonable version of the code to converge the generalized Kohn-Sham equations for meta-GGA functionals including the kinetic energy density. This came with a “splinesolver” algorithm for the self-consistent radial equations that replaces the inward and outward integrations to find bound state radial wavefunctions. The splinesolver is used by default for meta-GGA functionals, but can be requested for other functionals. Some of the pseudoization schemes have been adopted for developing self-consistent PAW datasets appropriate for meta-GGA functionals within the generalized Kohn-Sham approach. Details of this implementation are published – PRB (2022).

With these changes come new options for the input files for GRAPHATOM and ATOMPAW.

Some examples input data for GRAPHATOM and their corresponding summary output [Atom].GA and input data for ATOMPAW and the corresponding summary output [Atom] are as follows.

Example 1: GRAPHATOM input for Si – LDA, non-relativistic

```
Si 14
LDA-PW loggrid      2001
3 3 0 0 0 0
3 1 2
0 0 0
END

####Si.GA####
Completed calculations for Si
Perdew-Wang LDA -- PRB 45, 13244 (1992)
Radial integration grid is logarithmic
r0 = 4.3309254E-04 h = 6.0632956E-03 n = 2001 rmax = 8.0000000E+01
Non-relativistic calculation
AEatom converged in 28 iterations
for nz = 14
delta = 4.0395229093591495E-017

Orbital energies
n l occupancy energy
```

```

1 0      2.0000000E+00 -1.3036860E+02
2 0      2.0000000E+00 -1.0149628E+01
3 0      2.0000000E+00 -7.9623458E-01
2 1      6.0000000E+00 -7.0293986E+00
3 1      2.0000000E+00 -3.0661972E-01

```

Total energy

Total : -576.38746219636232

#####

Example 2: GRAPHATOM input for Si – LDA, non-relativistic, using splinesolver

```

Si 14
LDA-PW splineinterp splr00.1d0 splns600 loggrid 2001
3 3 0 0 0 0
3 1 2
0 0 0
END

```

###Si.GA###

```

Completed calculations for Si
Perdew-Wang LDA -- PRB 45, 13244 (1992)
Radial integration grid is logarithmic
r0 = 4.3309254E-04 h = 6.0632956E-03 n = 2001 rmax = 8.0000000E+01
Splinesolver used for bound states
Splinesolver method used for bound states
Splinesolver grid parameters r0 and ns:
0.10000 600
Non-relativistic calculation
AEatom converged in 23 iterations
for nz = 14
delta = 2.2774037112883901E-016

```

Orbital energies

```

n l      occupancy      energy
1 0      2.0000000E+00 -1.3037233E+02
2 0      2.0000000E+00 -1.0149191E+01
3 0      2.0000000E+00 -7.9616715E-01
2 1      6.0000000E+00 -7.0296405E+00
3 1      2.0000000E+00 -3.0664292E-01

```

Total energy

Total : -576.38791341463855

#####

Example 3: GRAPHATOM input for Si – r2SCAN01, non-relativistic, using generalized Kohn-Sham

Si 14

```

WTAU XC_MGGA_X_R2SCAN01+XC_MGGA_C_R2SCAN01 splr00.1d0 splns600 loggrid 2001
3 3 0 0 0 0
3 1 2
0 0 0
END

```

```

###Si.GA###

```

```

Completed calculations for Si
Using Libxc -- XC_MGGA_X_R2SCAN01+XC_MGGA_C_R2SCAN01
Radial integration grid is logarithmic
r0 = 4.3309254E-04 h = 6.0632956E-03 n = 2001 rmax = 8.0000000E+01
Splinesolver used for bound states
Splinesolver method used for bound states
Splinesolver grid parameters r0 and ns:
0.10000 600
Non-relativistic calculation
AEatom converged in 19 iterations
for nz = 14
delta = 3.9767450008378184E-017

```

```

Orbital energies

```

| n | l | occupancy | energy |
|---|---|---------------|----------------|
| 1 | 0 | 2.0000000E+00 | -1.3175185E+02 |
| 2 | 0 | 2.0000000E+00 | -1.0501811E+01 |
| 3 | 0 | 2.0000000E+00 | -8.1811500E-01 |
| 2 | 1 | 6.0000000E+00 | -7.1862608E+00 |
| 3 | 1 | 2.0000000E+00 | -3.0245126E-01 |

```

Total energy

```

```

Total : -578.62529162965529
#####

```

Example 4: GRAPHATOM input for Si – Dirac equation

```

Si 14
LDA-PW diracrelativistic loggrid 2001
3 3 0 0 0 0
3 1 -2 0.d0
3 1 1 2.d0
0 0 0 0
END

```

```

###Si.GA

```

```

Completed calculations for Si
Perdew-Wang LDA -- PRB 45, 13244 (1992)
Radial integration grid is logarithmic
r0 = 4.3309254E-04 h = 6.0632956E-03 n = 2001 rmax = 8.0000000E+01
Dirac-relativistic calculation
AEatom converged in 31 iterations

```

```
for nz = 14
delta = 8.7051691277235455E-017
```

Orbital energies

| n | kappa | l | occupancy | energy |
|---|-------|---|---------------|----------------|
| 1 | -1 | 0 | 2.0000000E+00 | -1.3070214E+02 |
| 2 | -1 | 0 | 2.0000000E+00 | -1.0194340E+01 |
| 3 | -1 | 0 | 2.0000000E+00 | -7.9837677E-01 |
| 2 | 1 | 1 | 2.0000000E+00 | -7.0556273E+00 |
| 3 | 1 | 1 | 2.0000000E+00 | -3.0662229E-01 |
| 2 | -2 | 1 | 4.0000000E+00 | -7.0081090E+00 |
| 3 | -2 | 1 | 0.0000000E+00 | -3.0422316E-01 |

Total energy

```
Total : -578.91322954391410
#####
```

Example 5: ATOMPAW input for Si – r2SCAN01, non-relativistic, using generalized Kohn-Sham

```
Si 14
WTAU XC_MGGA_X_R2SCAN01+XC_MGGA_C_R2SCAN01 splr00.1d0 splns600 loggrid 2001
3 3 0 0 0 0
3 1 2
0 0 0
c
c
v
c
v
2
1.7 1.5 1.7 1.7
y
14
n
y
14
n
y
2
y
12
n
MODRRKJ VANDERBILTORTHO Besselshape
3 0 VPSMATCHNC
1.7
1.7
1.7
1.7
1.7
```

```

1.7
ABINITOUT
default
XMLOUT
default
PWSCFOUT
UPFDX 0.0125d0  UPFXMIN -7.d0  UPFZMESH 14.d0
PWPAWOUT
END

```

```
###Si####
```

```

Completed calculations for Si
Exchange-correlation type:
Exchange functional (LibXC):
  J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, J. Phys. Chem. Lett. 11, 8208
  J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, J. Phys. Chem. Lett. 11, 9248
Correlation functional (LibXC):
  J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, J. Phys. Chem. Lett. 11, 8208
  J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, J. Phys. Chem. Lett. 11, 9248
Full generalized Kohn-Sham equations solved
Radial integration grid is logarithmic
r0 = 4.3309254E-04 h = 6.0632956E-03 n = 2001 rmax = 8.0000000E+01
Splinesolver method used for bound states
Splinesolver grid parameters r0 and ns:
  0.10000 600
Non-relativistic calculation
AEatom converged in 19 iterations
  for nz = 14.00
  delta = 3.9767450008378184E-017
All Electron Orbital energies:
n l occupancy energy
1 0 2.0000000E+00 -1.3175185E+02
2 0 2.0000000E+00 -1.0501811E+01
3 0 2.0000000E+00 -8.1811500E-01
2 1 6.0000000E+00 -7.1862608E+00
3 1 2.0000000E+00 -3.0245126E-01

```

```
Total energy
```

```
Total : -578.62529162965529
```

```

Completed calculations for Si
Exchange-correlation type:
Exchange functional (LibXC):
  J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, J. Phys. Chem. Lett. 11, 8208
  J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, J. Phys. Chem. Lett. 11, 9248
Correlation functional (LibXC):
  J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, J. Phys. Chem. Lett. 11, 8208
  J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, J. Phys. Chem. Lett. 11, 9248
Full generalized Kohn-Sham equations solved
Radial integration grid is logarithmic
r0 = 4.3309254E-04 h = 6.0632956E-03 n = 2001 rmax = 8.0000000E+01

```

Splinesolver method used for bound states

Splinesolver grid parameters r0 and ns:

0.10000 600

Non-relativistic calculation

SCatom converged in 8 iterations

for nz = 14.00

delta = 9.9941022151552512E-017

Valence Electron Orbital energies:

| n | l | occupancy | energy |
|---|---|---------------|----------------|
| 3 | 0 | 2.0000000E+00 | -8.1811472E-01 |
| 3 | 1 | 2.0000000E+00 | -3.0245141E-01 |

Total energy

Total : -578.62527041729822

Valence : -46.479751073168650

paw parameters:

lmax = 2

rc = 1.7016270216702749

irc = 1366

rc_shape = 1.5072490061787436

rc_vloc = 1.7016270216702749

rc_core = 1.7016270216702749

Sequence of dataset construction steps modified for mGGA

Only projectors from Vanderbilt scheme available

Vloc: VPS match (norm-conservation) with l= 3;e= 0.0000E+00

Projector type: modified RKKJ projectors + Vanderbilt ortho.

Bessel compensation charge shape zeroed at 1.5072E+00

Number of basis functions 6

| No. | n | l | Energy | Cp coeff | Occ |
|-----|-----|---|----------------|----------------|---------------|
| 1 | 3 | 0 | -8.1811472E-01 | 3.4456771E+00 | 2.0000000E+00 |
| 2 | 999 | 0 | 1.4000000E+01 | 1.0928984E-01 | 0.0000000E+00 |
| 3 | 3 | 1 | -3.0245141E-01 | 7.7138408E+00 | 2.0000000E+00 |
| 4 | 999 | 1 | 1.4000000E+01 | 2.3344063E-01 | 0.0000000E+00 |
| 5 | 999 | 2 | 2.0000000E+00 | -4.9695966E-01 | 0.0000000E+00 |
| 6 | 999 | 2 | 1.2000000E+01 | -2.2394019E-01 | 0.0000000E+00 |

Completed diagonalization of ovlp with info = 0

Eigenvalues of overlap operator (in the basis of projectors):

| | |
|---|----------------|
| 1 | 1.70014131E-01 |
| 2 | 1.05637034E+00 |
| 3 | 1.68670242E+00 |
| 4 | 1.10551313E+01 |
| 5 | 2.25209551E+01 |
| 6 | 2.73898074E+01 |

Summary of PAW energies

Total valence energy -46.479751063306111

Smooth energy 11.559261831969753

One center -58.039012895275860

| | |
|------------------|----------------------|
| Smooth kinetic | 2.4995956007877114 |
| Vloc energy | -0.91305325877548571 |
| Smooth exch-corr | -2.2202015931524510 |
| One-center xc | -39.215909951163795 |

#####

Some details of input file options

Line 1 This line contains two inputs only, separated with space(s): [Atomic symbol (a2)] [Atomic number (i3)]

Line 2 This line is very complicated, starting with the exchange-correlation functional and followed by formalism and grid information. The input is not case sensitive.

The exchange-correlation functional can be one of several in-house routines or can reference libxc subroutines.

The following keywords reference in-house routines:

- LDA-PW
- GGA-PBE
- GGA-PBESOL
- HF
- MGGA-R2SCAN-001 – Original r2SCAN (generalized Kohn-Sham equations)
- MGGA-R2SCAN-01 – Modified r2SCAN (generalized Kohn-Sham equations)

The following examples illustrate the syntax used to access the libxc routines using the names assigned on the libxc webpage <https://www.tddft.org/programs/libxc/functionals/>, each optionally prepended with “XC_”.

- PBESOL: GGA_X_PBE_SOL+GGA_C_PBE_SOL
- r2SCAN01 (partial): XC_MGGA_X_R2SCAN01+XC_MGGA_C_R2SCAN01
Note that in this case, only $V_{xc}(r)$ will be used in the Kohn-Sham formulation.
- r2SCAN01 (complete): WTAU XC_MGGA_X_R2SCAN01+XC_MGGA_C_R2SCAN01
Note that in this case, the keyword “WTAU” means that the kinetic energy density will be used and the generalized Kohn-Sham equations will be solved self-consistently.

The remainder of line 2 controls the formalism (if not Kohn-Sham or generalized Kohn-Sham), the discretization grid, splinesolver parameters, and additional features. The order of these entries are not important. Some of these are as follows:

- SCALARRELATIVISTIC – Solve Harmon and Koelling scalar relativistic equations (does not work with generalized Kohn-Sham (meta-GGA))
- DIRACRELATIVISTIC – Solve Dirac equations for upper and lower radial wavefunctions (does not work with generalized Kohn-Sham (meta-GGA) and only implemented for graphatom)
- SPLINEINTERP SPLR0xxxx SPLNSnnnn – Use splinesolver algorithm to solve self-consistent Kohn-Sham or generalized Kohn-Sham equations. This is the default for meta-GGA calculations, but the SPLINEINTERP keyword enables the splinesolver algorithm for other exchange-correlation functionals. SPLR0xxxx, where xxxx is a real number

(with or without a space) allows for the adjustment of the $r0$ parameter of the spline grid for values other than the default of $0.1d0$. SPLNSnnnn, where nnnn is an integer (with or without a space) allows for the adjustment of the ns parameter of the spline grid for values other than the default of 400. Note that setting $ns > 400$ typically increases the computation time because in the current version of the code, all of the eigenvalues/eigenvectors of the $n_s \times n_s$ matrix \mathbf{A} are calculated in each self-consistent cycle to find the all-electron radial functions of the bound states.

- LOGGRID nnnn – Set the main discretization grid for the calculation. For example, LOGGRID 2001 seems to work well in most cases.

Line 3 $n_0 n_1 n_2 n_3 n_4 n_5$

Here n_l represents the maximum principal quantum for each occupied or partially occupied shell l or 0 if the shell l is not relevant. For example,

4 4 3 0 0 0

represents the configuration $1s^2 2s^2 3s^2 4s^2 2p^6 3p^6 4p^6 3d^{10}$, or the ground state of Kr.

Line 4 The following information concerns line 4 and possibly several lines following.

- For non-relativistic or scalar relativistic calculations, the following lines list

$n l occ$

for each partially occupied shell, ending with the line 0 0 0

For example, for Kr, line 4 reads

0 0 0

For Cu in the configuration $1s^2 2s^2 3s^2 4s^1 2p^6 3p^6 4p^0 3d^{10}$, lines 4, 5, and 6 read

4 0 1

4 1 0

0 0 0

- For Dirac equation calculations, the following lines list

$n l \kappa occ$

for each partially occupied shell, ending with the line 0 0 0 0

For example, for Kr, line 4 reads

0 0 0 0

For Cu in the configuration $1s^2 2s^2 3s^2 4s^1 2p^6 3p^6 4p^0 3d^{10}$, lines 4, 5, 6, and 7 read

4 0 -1 1.d0

4 1 1 0.d0

4 1 -2 0.d0

0 0 0 0

Note that for each shell $l\kappa$, the maximum occupancy is $2|\kappa|$. Also note that κ is related to the total angular momentum quantum number j according to $\kappa = \pm (j + \frac{1}{2})$.

The remaining lines of the input file are very similar to older versions of the code.