Notes for 4.2.0.0 version of atompaw code.

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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, 820
  J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, J. Phys. Chem. Lett. 11, 924
Correlation functional (LibXC):
  J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, J. Phys. Chem. Lett. 11, 820
  J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, J. Phys. Chem. Lett. 11, 924
 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, 820
  J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, J. Phys. Chem. Lett. 11, 924
Correlation functional (LibXC):
  J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, J. Phys. Chem. Lett. 11, 820
  J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, J. Phys. Chem. Lett. 11, 924
 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.

- 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 κ 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 $\kappa = \pm\left(j + \frac{1}{2}\right)$.

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