Status

Oct. 2015: The G2 data base has been changed substantially again on Oct. 14, 2015. Now the species files are in the nodeless construction and the comparison with Paier were good except for Na. A number of new tools have been added.

Aug 2014: The G2 data base has been changed substantially on Aug. 17, 2014 in order to concentrate the required shell scripts into few and to exploit the new paw scripts such as paw_resolve.

Overview

1. `src/g2_makedo` scans the directory `src/Strcfiles`. For each molecule in this directory it creates the directories in the directory "Cases", if necessary, and it creates a shellscript `g2_do_sample`,

2. `g2_do_sample` performs PAW on all molecules. It can be added to exclude certain molecules.

3. `src/g2_analyse` compiles and runs the fortran program `src/analyze.f90`, which extracts atomization energies and compares them with internal tables of experiment and other numbers. It creates a list `readpaw.in` of the latest energies for all molecules, from which it computes the results which are printed in in `readpaw.out` in humnan readable form. Some results are written to `g2results.dat` to be viewed with a viewer such as `xmgrace`.

Files required

```
src/Strcfiles
src/Speciesfiles
src/g2_makedo
src/g2_analyse
src/g2_analyse.f90
src/sample.cntl_relax
src/sample.cntl_start
src/g2_tar
src/splitspecieslist.f90
src/modify
doc/readme.tex
```

- **doc/readme.tex, doc/Figs, doc/Bib, doc/Sources**: documentation of the G2-directory.

- **Samples/*.strc_sample**: containes the structure files for all molecules without the specific setup information. This information will be incorporated into the structure files of all calculations.
- **specieslist**: contains the setup information for all elements, which will be included into the structure files.
- **src/g2_makedo:** Basic installation and update script:
  - Constructs the sample runscript `g2_do_sample`.
  - sets up the directory Cases holding the run directories for all substances in the `src/Strcfiles` directory.
  - updates the .strc files for all substances
- **src/sample.cntl_start, src/sample.cntl_relax:** contains the examples for the control input file.
- **src/g2_analyse** shell script to compile and execute `src/g2_analyse`. It reads readpaw.in and produces readpaw.out.
- **src/g2_analyse.f90** fortran code, extracts atomization energies and comparison with benchmark tests
- **src/splitspecies.f90** fortran code, used by `src/g2_makedo` to expand the specieslist into separate files.
- **src/modify** is a small helper script which is not required. It may be useful for an administrator to construct scripts that perform global changes on a large set of files in one shot.
- **src/cleanup** is a small helper script which removes some of the files in the directory `Cases`, which need not be stored permanently.
- **src/g2_tar** creates a tar file `bare_g2.tgz` containing only the essential files of the database without any results.

Adapt and run G1 tests

1. enter the main directory of the database. Check if you are in the correct place:
   - execute `ls`. You should obtain "`src doc`.
   - execute `ls src`. You should obtain "Strcfiles, specieslist, g2_makedo, sample.cntl_start, sample.cntl_relax, g2_analyse, g2_analyse.f90, splitspecies, modify, g2_cleanup g2_tar"
2. compile this documentation file readme.pdf as follows:

```
cd doc
cat Bib/* > all.bib
pdflatex readme
bibtex readme
pdflatex readme
cd ..
```

3. execute `src/g2_makedo`. When done, there should be a directory "`Cases`" and a shell script "`g2_do_sample`"

4. Adjust the variable NNODES in "`g2_do_sample`" to the maximum number of paw-related jobs you want to allow on your computer.

5. make a copy of the shell script `g2_do_sample` with name `g2_do` and adhjust "LIST" in `g2_do` by removing lines with those substances that shall be excluded from the calculation.

6. create a file `sample.cntl`. One can copy a one of the files `src/sample.cntl_start`, `src/sample.cntl_relax`. Into the current directory and modify it. This is the control file used for all calculations.

7. execute `g2_do`

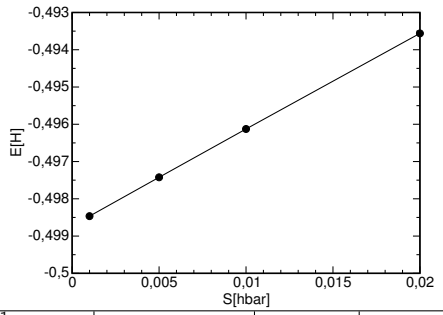
Construct documentation

```
cd doc
cat Bib/* > all.bib
pdflatex readme
bibtex readme
pdflatex readme
```

Problems

- Some of the atoms cannot be converged with Safeortho=F because of its energy-level structure

- The hydrogen atom has problems probably because there is no spin density in the minority spin direction. NO! it seems to be also safeortho. Again YES: I get problems also with SAFEORTHO=T. It helps to make a calculation with spin[hbar]=0.499 and then multiply the energy level difference with 0.001.



$\frac{1}{2}\hbar - S$	$E_{tot}[H]$	$\epsilon_\uparrow$[eV]	$\epsilon_\downarrow$[eV]
0.001	-0.4984656	-7.621	-0.388
0.005	-0.4974234	-7.646	-0.627
0.010	-0.4961265	-7.686	-0.831
0.020	-0.4935614	-7.766	-1.091

$$E_{tot}[H] = -0.49872 + 0.258(\frac{1}{2} - S/hbar)$$

If we perform calculations with a spin of $0.4990\hbar$, the total energy is too high by 0.2544×10^3 H.

The unit cell for hydrogen has been fixed to a lattice constant of 10 Åto avoid instabilitis.

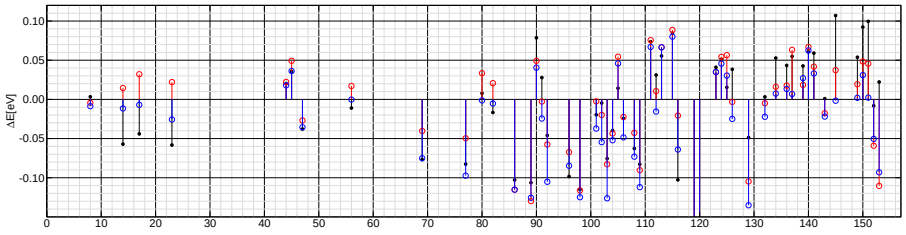
- Be2 may need a larger cell!
- take care of zero point vibration energy
- in DFT some of the atoms are non-psherical
- The G2 database contains some open shell systems besides atoms: BeH (spin=$0.5\hbar$), CH,...
  - C_2 is has a band crossing of a σ-state and a doublet of π states right at the energy minimum
- for Li I had to reduce the projectors with the nodeless setups to npro=1 0 0 to avoid an instability. This is probably the well-known overcompleteness problem.

Results

Benchmark Oct.17, 2015

Look up the paw_setups report for a systematic study of constructing a set of species.

- O-cutoff: $r_{c,\ell} = 0.75\ r_{cov}$. Oxygen is the most critical element with one of the slowest plane wave convergence. It is the smallest first row element (following Ne and F) which in addition forms strong bonds. Furthermore it is a ubiquitous element. With this cutoff the O_2 bondlength deviates by less than 1 %. The result can be improved with a cutoff of $r_{c,\ell} = 0.75\ r_{cov}$ at the cost of a slower plane wave convergence.
- H-cutoff: $r_{c,\ell} = 1.2\ r_{cov}$. Hydrogen is a frequent element. It does not have any core states so that the partial waves turn into all-electron wave functions if the cutoff is reduced.
- C-cutoff: $r_{c,\ell} = 0.75\ r_{cov}$. Compounds with oxygen, CO and CO_2 gave results that vary a lot with $r_{c,\ell}$. At the chosen value the energies go through a minimum so that the results are maximally independent of the cutoff.
- N-cutoff: $r_{c,\ell} = 0.75\ r_{cov}$. Nitrogen forms very strong bonds and is intermediate of oxygen and carbon. Therefore it is treated similarly.
- Other first-row elements with p-electrons $r_{c,\ell} = 0.75\ r_{cov}$. We choose the other first-row elements with p-electrons similar to C,N and O.
- first-row elements with s-electrons $r_{c,\ell} = 0.85\ r_{cov}$. Lithium and beryllium obtain a somwhat larger radius. (No special reason)
- second-row elements with p-electrons $r_{c,\ell} = 0.9\ r_{cov}$.



Benchmark Oct.10, 2015

Test nodeless setups using the PBE functional[1]. The comparison has been done on the basis of the G2 database. The comparison has been done with the calculations using VASP and Gaussian by Paier et al.[2]

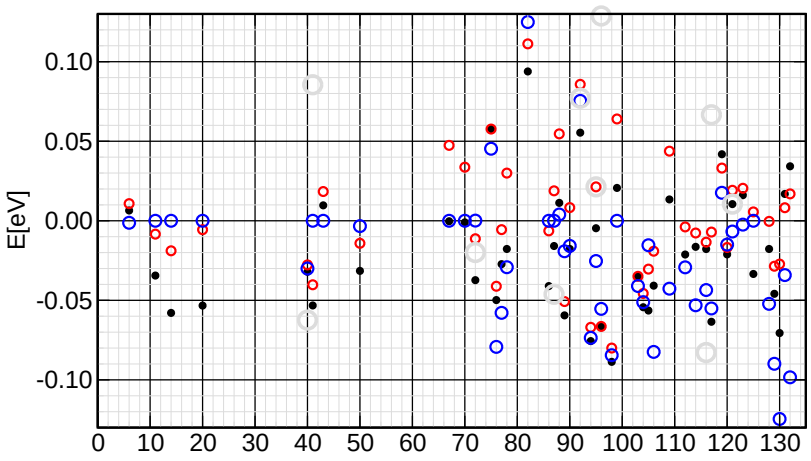


Figure 1: Deviations of atomization energies calculated by VASP (black dots), Gaussian (red spheres) and GPAW (blue spheres) from CPPAW and obtained from experiment. The largest consisten deviations are for F_2 (82), HF (92),Li_2 (94), LiH (96) and N_2 (98).

```
!CONTROL
 !GENERIC NSTEP=200 DT=10.0 NWRITE=100 START=F  !END
 !FOURIER EPWPSI=80. CDUAL=4.0 !END
 !DFT     TYPE=10 !END
 !PSIDYN STOP=T  FRIC=0.05
   !AUTO FRIC(-)=0.05 FACT(-)=0.97  FRIC(+)=0.3 FACT(+)=1. minfric=0.01 !END
 !END
!END
!EOB
```

Below, the setup parameters are provided. Note, that the NTBO construction is not used.

```
  !SPECIES   NAME='Al'  M=40. NPRO=2 2 1 LRHOX=4 RAD/RCOV=1.0
    !NTBO    NOFL=1 1 0 CV=T LHFWEIGHT=0.100
             TAILLAMBDA=4.0 2.0 RAUG/RCOV=1.2 RTAIL/RCOV=1.4
    !END
    !AUGMENT ID='MY_NDLSS_AL' EL='AL' ZV= 3.
             TYPE='NDLSS' RBOX/RCOV=1.2 RCSM/RCOV=.25
             RCL/RCOV=.919 .919 .919 .919
      !GRID  DMIN=1.E-6 DMAX=.15 RMAX=9. !END
      !POT   POW=3. RC/RCOV=.919 VALO_X= -1.5 !END
      !CORE  POW=2. RC/RCOV=.919 !END
    !END
  !END
  !SPECIES   NAME='B_'  M=40. NPRO=1 1 1 LRHOX=4 RAD/RCOV=1.4
    !NTBO    NOFL=1 1 0 CV=T LHFWEIGHT=0.100
             TAILLAMBDA=4.0 2.0 RAUG/RCOV=1.2 RTAIL/RCOV=1.4
    !END
    !AUGMENT ID='MY_NDLSS_B' EL='B' ZV= 3.
             TYPE='NDLSS' RBOX/RCOV=1.2 RCSM/RCOV=.25
             RCL/RCOV=.75 .75 .75 .75
      !GRID  DMIN=1.E-6 DMAX=.15 RMAX=9. !END
      !POT   POW=3. RC/RCOV=.774 VALO_X= -3.9 !END
      !CORE  POW=2. RC/RCOV=.774 !END
    !END
  !END
  !SPECIES   NAME='BE'  M=40. NPRO=1 1 0 LRHOX=2 RAD/RCOV=1.4
```

```
  !NTBO    NOFL=1 1 0 CV=T LHFWEIGHT=0.100
           TAILLAMBDA=4.0 2.0 RAUG/RCOV=1.2 RTAIL/RCOV=1.4
  !END
  !AUGMENT ID='MY_NDLSS_BE' EL='BE' ZV= 2.
           TYPE='NDLSS' RBOX/RCOV=1.2 RCSM/RCOV=.25
           RCL/RCOV=.882 .882 .882 .882
    !GRID  DMIN=1.E-6 DMAX=.15 RMAX=9. !END
    !POT   POW=3. RC/RCOV=.882 VALO_X= -1.6 !END
    !CORE  POW=2. RC/RCOV=.882 !END
  !END
!END
!SPECIES   NAME='Br'  M=40. NPRO=1 1 1 LRHOX=2 RAD/RCOV=1.4
  !NTBO    NOFL=1 1 0 CV=T LHFWEIGHT=0.100
           TAILLAMBDA=4.0 2.0 RAUG/RCOV=1.2 RTAIL/RCOV=1.4
  !END
  !AUGMENT ID='MY_NDLSS_BR' EL='BR' ZV= 7.
           TYPE='NDLSS' RBOX/RCOV=1.2 RCSM/RCOV=.25
           RCL/RCOV=.975 .975 .975 .975
    !GRID  DMIN=1.E-6 DMAX=.15 RMAX=9. !END
    !POT   POW=3. RC/RCOV=.975 VALO_X= -2.0 !END
    !CORE  POW=2. RC/RCOV=.975 !END
  !END
!END
!SPECIES   NAME='C_'  M=40. NPRO=1 1 1 LRHOX=4 RAD/RCOV=1.4
  !NTBO    NOFL=1 1 0 CV=T LHFWEIGHT=0.100
           TAILLAMBDA=4.0 2.0 RAUG/RCOV=1.2 RTAIL/RCOV=1.4
  !END
  !AUGMENT ID='MY_NDLSS_C' EL='C' ZV= 4.
           TYPE='NDLSS' RBOX/RCOV=1.2 RCSM/RCOV=.25
           RCL/RCOV=0.85 0.85 0.85 0.85
    !GRID  DMIN=1.E-6 DMAX=.15 RMAX=9. !END
    !POT   POW=3. RC/RCOV=0.75  VALO_X=-2.7 !END
    !CORE  POW=2. RC/RCOV=0.75  !END
  !END
!END
!SPECIES   NAME='CL'  M=40. NPRO=2 2 1 LRHOX=2 RAD/RCOV=1.4
  !NTBO    NOFL=1 1 0 CV=T LHFWEIGHT=0.100
           TAILLAMBDA=4.0 2.0 RAUG/RCOV=1.2 RTAIL/RCOV=1.4
  !END
  !AUGMENT ID='MY_NDLSS_CL' EL='CL' ZV= 7.
           TYPE='NDLSS' RBOX/RCOV=1.2 RCSM/RCOV=.25
           RCL/RCOV=0.802 0.802 0.802 0.802
    !GRID  DMIN=1.E-6 DMAX=.15 RMAX=9. !END
    !POT   POW=3. RC/RCOV=0.802 VALO_X=-3.5 !END
    !CORE  POW=2. RC/RCOV=0.802  !END
  !END
!END
!SPECIES   NAME='F_'  M=80. NPRO=1 1 1 LRHOX=2 RAD/RCOV=1.4
  !NTBO    NOFL=1 1 0 CV=T LHFWEIGHT=0.100
           TAILLAMBDA=4.0 2.0 RAUG/RCOV=1.2 RTAIL/RCOV=1.4
  !END
  !AUGMENT ID='MY_NDLSS_F' EL='F_' ZV= 7.
           TYPE='NDLSS' RBOX/RCOV=1.2 RCSM/RCOV=.25
           RCL/RCOV=0.8 0.8 0.8  0.8
    !GRID  DMIN=1.E-6 DMAX=.15 RMAX=9. !END
    !POT   POW=3. RC/RCOV=0.75 VALO_X=-3.5 !END
    !CORE  POW=2. RC/RCOV=0.75  !END
  !END
!END
!SPECIES   NAME='H_'  M=2. NPRO=1 1 LRHOX=2 RAD/RCOV=1.2
  !NTBO    NOFL=1 0 CV=T LHFWEIGHT=0.100
           TAILLAMBDA=4.0 2.0 RAUG/RCOV=1.2 RTAIL/RCOV=1.4
  !END
  !AUGMENT ID='MY_NDLSS_H' EL='H' ZV= 1.
           TYPE='NDLSS' RBOX/RCOV=1.2 RCSM/RCOV=.25
           RCL/RCOV=1.2 1.2  1.2  1.2
    !GRID  DMIN=1.E-6 DMAX=.15 RMAX=9. !END
    !POT   POW=3. RC/RCOV=1.2 VALO_X=-1.6 !END
    !CORE  POW=2. RC/RCOV=1.2 !END
  !END
!END
!SPECIES   NAME='LI'  M=40. NPRO=1 0  LRHOX=4 RAD/RCOV=1.0
  !NTBO    NOFL=1 0 0 CV=T LHFWEIGHT=0.100
           TAILLAMBDA=4.0 2.0 RAUG/RCOV=1.2 RTAIL/RCOV=1.4
  !END
  !AUGMENT ID='MY_NDLSS_LI' EL='LI' ZV= 1.
           TYPE='NDLSS' RBOX/RCOV=1.2 RCSM/RCOV=.25
           RCL/RCOV=.861 .861 .861  .861
    !GRID  DMIN=1.E-6 DMAX=.15 RMAX=9. !END
    !POT   POW=3. RC/RCOV=.861 VALO_X=-0.8 !END
    !CORE  POW=2. RC/RCOV=.861  !END
  !END
!END
!SPECIES   NAME='N_'  M=40. NPRO=1 1 1 LRHOX=4 RAD/RCOV=1.4
  !NTBO    NOFL=1 1 0 CV=T LHFWEIGHT=0.100
           TAILLAMBDA=4.0 2.0 RAUG/RCOV=1.2 RTAIL/RCOV=1.4
  !END
  !AUGMENT ID='MY_NDLSS_N' EL='N' ZV= 5.
           TYPE='NDLSS' RBOX/RCOV=1.2 RCSM/RCOV=.25
           RCL/RCOV=0.75 0.75 0.75  0.75
    !GRID  DMIN=1.E-6 DMAX=.15 RMAX=9. !END
```

```
    !POT   POW=3. RC/RCOV=0.75 VALO_X=-4.3 !END
    !CORE  POW=2. RC/RCOV=0.75  !END
  !END
!END
!SPECIES   NAME='Na'  M=40. NPRO=2 2 1 LRHOX=4 RAD/RCOV=1.0
  !NTBO    NOFL=1 1 0 CV=T LHFWEIGHT=0.100
           TAILLAMBDA=4.0 2.0 RAUG/RCOV=1.2 RTAIL/RCOV=1.4
  !END
  !AUGMENT ID='MY_NDLSS_NA' EL='NA' ZV= 9.
           TYPE='NDLSS' RBOX/RCOV=1.2 RCSM/RCOV=.25
           RCL/RCOV=0.780 0.790 0.804
    !GRID  DMIN=1.E-6 DMAX=.15 RMAX=9. !END
    !POT   POW=3. RC/RCOV=0.766 VALO_X=-1.1  !END
    !CORE  POW=2. RC/RCOV=0.766  !END
  !END
!END
!SPECIES   NAME='O_'  M=80. NPRO=1 1 1 LRHOX=4 RAD/RCOV=1.4
  !NTBO    NOFL=1 1 0 CV=T LHFWEIGHT=0.100
           TAILLAMBDA=4.0 2.0 RAUG/RCOV=1.2 RTAIL/RCOV=1.4
  !END
  !AUGMENT ID='MY_NDLSS_O' EL='O' ZV= 6.
           TYPE='NDLSS' RBOX/RCOV=1.2 RCSM/RCOV=.25
           RCL/RCOV=.65 0.65 0.65 0.65
    !GRID  DMIN=1.E-6 DMAX=.15 RMAX=9. !END
    !POT   POW=3. RC/RCOV=0.65 VALO_X=-3.8 !END
    !CORE  POW=2. RC/RCOV=.65 !END
  !END
!END
!SPECIES   NAME='P_'  M=40. NPRO=2 2 1 LRHOX=2 RAD/RCOV=1.4
  !NTBO    NOFL=1 1 0 CV=T LHFWEIGHT=0.100
           TAILLAMBDA=4.0 2.0 RAUG/RCOV=1.2 RTAIL/RCOV=1.4
  !END
  !AUGMENT ID='MY_NDLSS_P' EL='P_' ZV= 5.
           TYPE='NDLSS' RBOX/RCOV=1.2 RCSM/RCOV=.25
           RCL/RCOV=0.899 0.899 0.899  0.899
    !GRID  DMIN=1.E-6 DMAX=.15 RMAX=9. !END
    !POT   POW=3. RC/RCOV=.899 VALO_X=-2.4 !END
    !CORE  POW=2. RC/RCOV=.899 !END
  !END
!END
!SPECIES   NAME='S_'  M=40. NPRO=2 2 1 LRHOX=4 RAD/RCOV=1.4
  !NTBO    NOFL=1 1 0 CV=T LHFWEIGHT=0.100
           TAILLAMBDA=4.0 2.0 RAUG/RCOV=1.2 RTAIL/RCOV=1.4
  !END
  !AUGMENT ID='MY_NDLSS_S' EL='S_' ZV= 6.
           TYPE='NDLSS' RBOX/RCOV=1.2 RCSM/RCOV=.25
           RCL/RCOV=0.954 0.960  0.882  0.882
    !GRID  DMIN=1.E-6 DMAX=.15 RMAX=9. !END
    !POT   POW=3. RC/RCOV=0.742 VALO_X=-3.3 !END
    !CORE  POW=2. RC/RCOV=0.742 !END
  !END
!END
!SPECIES   NAME='Si'  M=40. NPRO=2 2 1 LRHOX=4 RAD/RCOV=1.4
  !NTBO    NOFL=1 1 0 CV=T LHFWEIGHT=0.100
           TAILLAMBDA=4.0 2.0 RAUG/RCOV=1.2 RTAIL/RCOV=1.4
  !END
  !AUGMENT ID='MY_NDLSS_SI' EL='SI' ZV= 4.
           TYPE='NDLSS' RBOX/RCOV=1.2 RCSM/RCOV=.25
           RCL/RCOV=0.953 0.953 0.953 0.953
    !GRID  DMIN=1.E-6 DMAX=.15 RMAX=9. !END
    !POT   POW=3. RC/RCOV=0.953  VALO_X= -1.8 !END
    !CORE  POW=2. RC/RCOV=0.953  !END
  !END
!END
```

Bibliography

[1] John P. Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. *Phys. Rev. Lett*, 77:3865, 1996.

[2] J. Paier, R. Hirschl, M. Marsman, and G. Kresse. The perdew-burke-ernzerhof exchange-correlation functional applied to the g2-1 test set using a plane-wave basis set. *J. Chem. Phys.*, 122:234102, 2005.