Optimisation of GPAW setups and basis functions

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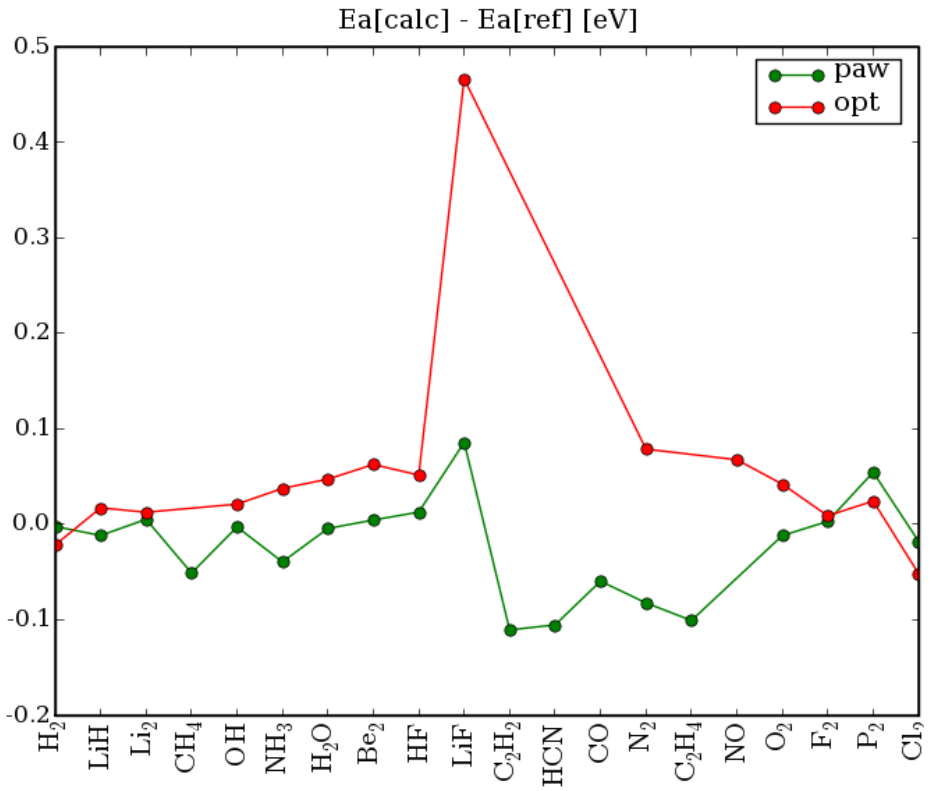
Optimisation scheme

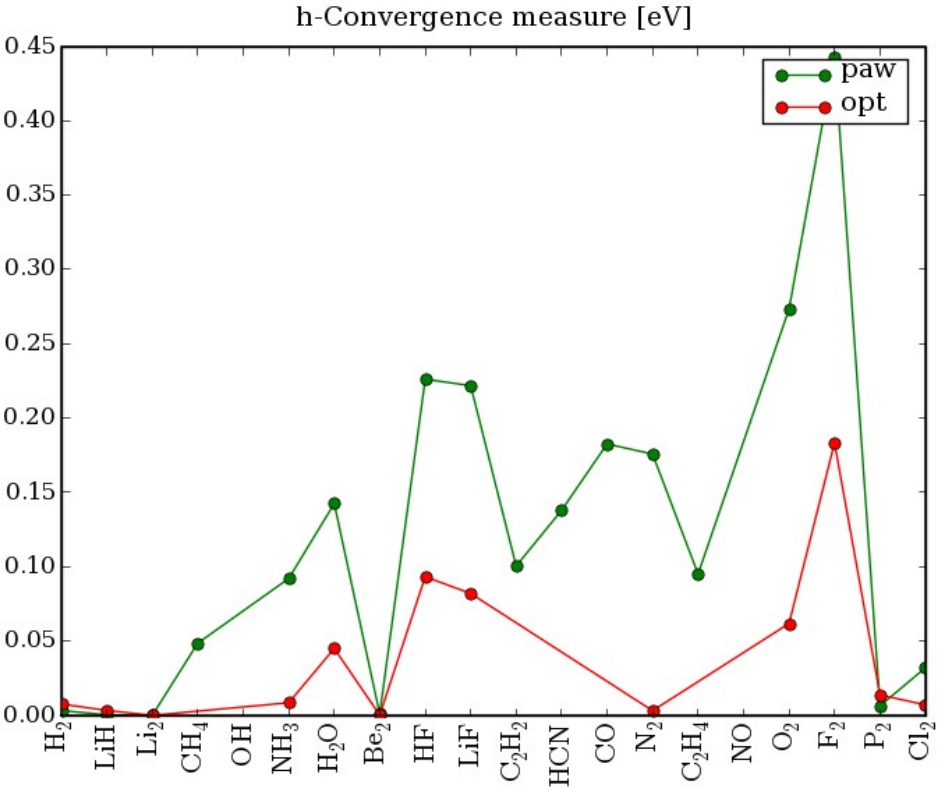
- Select a set of setup or basis parameters such as cutoff radii that can be optimised.
- Find a way to calculate some measure of quality of the setup or basis.
- Use the “Downhill simplex method” to find optimal set of parameters.
  - This is a optimisation algorithm which evaluates function values on a number of points (a *simplex*), then moves the “worse” points in the direction of the “better” ones until things are good.

Setup optimisation

- Setup quality is evaluated for dimer-forming atoms as follows:
  - Compare dimer atomisation energy and bond length to reference values.
  - Calculate “egg-box” amplitude.
  - Calculate deviation of energies with varying grid spacings under 0.2 Å.
  - Add squares of the above numbers, multiply by the iteration count during the calculations. This number is referred to as the *badness.* This is what we want to minimize.

Results





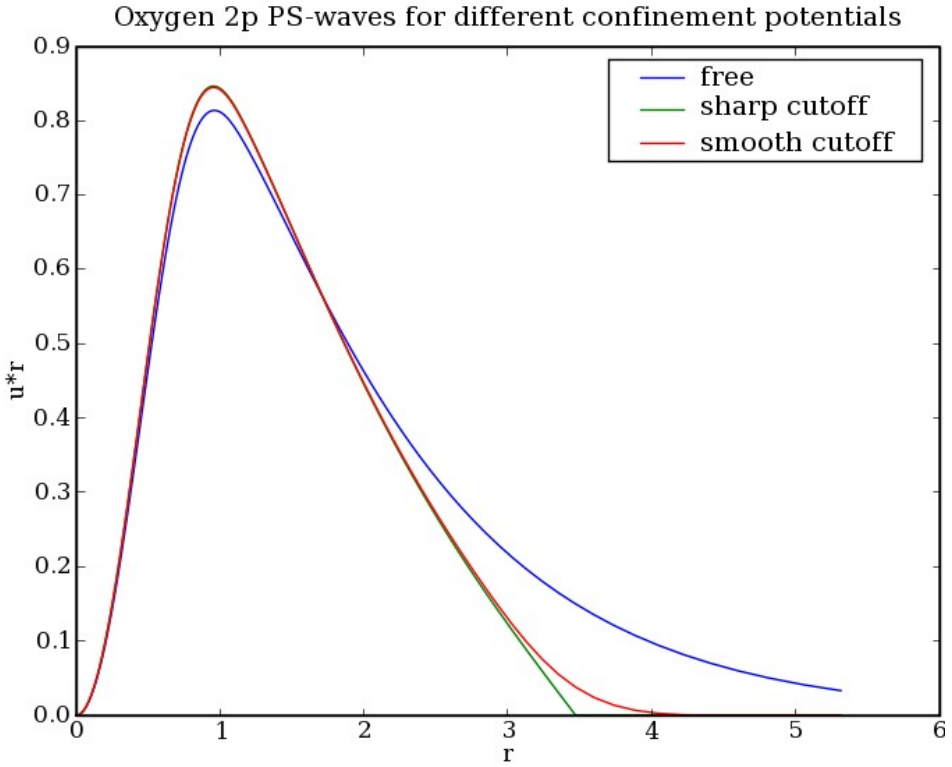
- New setups perform better in some tests, but this depends on the test weights during optimisation.
- There are some systematic deviations, probably due to cell sizes and similar settings.
- There are many local minima in the parameter space, unfortunately.

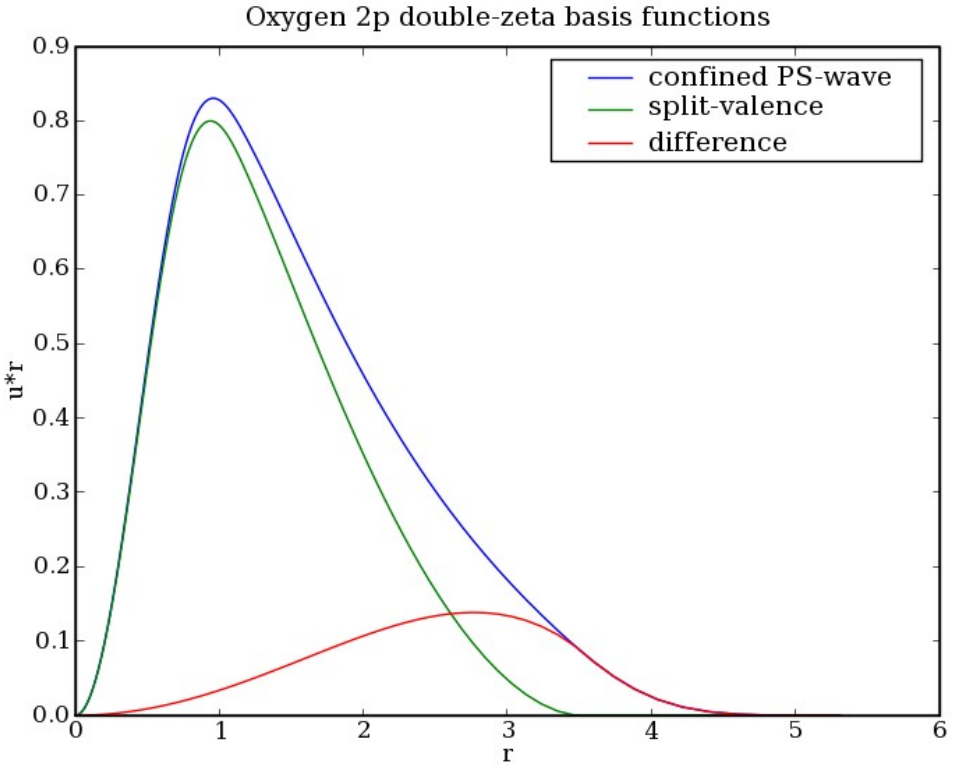
LCAO Basis vectors

- “Double-zeta polarised” (DZP) basis set:
  - Two basis functions for each valence state (hence “double”) plus two for the first unoccupied state with higher *l*-quantum number (hence “polarised”).
  - The first basis function is the atomic orbital, confined with some infinite potential well.
  - Obtain second basis function by subtracting a polynomial φ which joins the orbital smoothly within some cutoff:

$$\phi(r) = r^l(a - br^2)$$

LCAO Basis vectors





- [Fig1] Orbitals with different confinement potentials: None, ordinary infinite well and smooth infinite well.
- [Fig2] The atomic orbital, the secondary (“split-valence”) basis vector and the difference, plotted for the smooth infinite well.

The immediate future

- Apply optimiser to basis functions to find good cutoffs and confinement potentials.
- Find better setup test weights for the optimiser.
- Improve setup tests: parameter tweaking - cell sizes, grid spacings, etc.