



NGWF Setup in ONETEP:

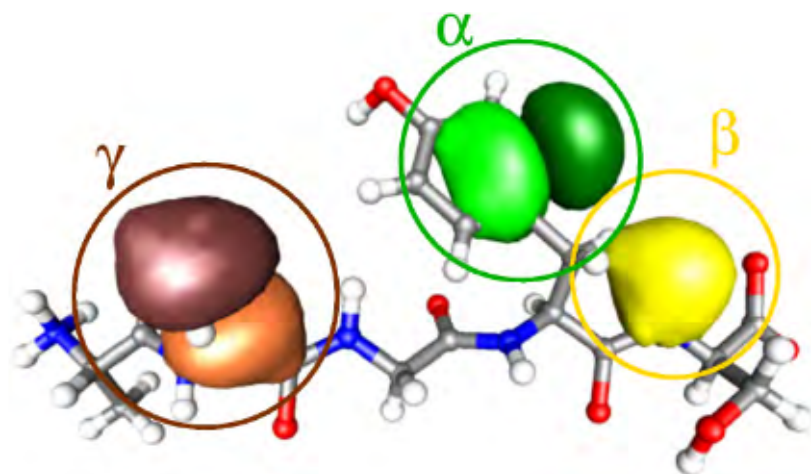
Tips and Tricks

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The ONETEP linear-scaling approach

- Use a minimal number of $\{\phi_\alpha\}$
- Optimise both \mathbf{K} and $\{\phi_\alpha\}$
- Aim is to have linear-scaling DFT with large basis set accuracy



$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{\alpha\beta} \phi_\alpha(\mathbf{r}) K^{\alpha\beta} \phi_\beta(\mathbf{r}')$$

Non-orthogonal
Generalised
Wannier Functions
(NGWFs)

Density
kernel

- NGWFs confined to spherical regions
- Density kernel \mathbf{K} sparse by truncation

How many NGWFs do I need?

- In theory, given perfect optimisation, $N_\phi = \frac{1}{2} N_e$ would be enough... but in practice this is very rarely optimal, partly because the algorithms used for NGWF optimisation do not easily break symmetries.
- Check what semicore states are left in the valence by your chosen pseudopotential
- Always use complete m-subshells
- Generally speaking if you have a given s-subshell you usually also want the corresponding p-subshell, or there is no angular freedom at all.

Examples

- Hydrogen: $1s^1$... 1 s-like NGWF: $N=1$
- Carbon: $[\text{He}] 2s^2 2p^2$... 1 s, 3 p NGWFs $N=4$
- Magnesium: $[\text{Ne}] 3s^2 3p^0$... 1 s, 3 p NGWFs: $N=4$
- Sodium: $[\text{He}] 2s^2 2p^6 3s^2 3p^0$... 2 s, 6 p NGWFs: $N=8$
- Iron: $[\text{Ar}] 3d^6 4s^2 4p^0$... 5 d-like, 1 s, 3 p NGWFs: $N=9$
- Molybdenum: $[\text{Ar} 3d^{10}] 4s^2 4p^6 4d^5 5s^1 5p^0$, 2 s, 2 p, 1d NGWFs: $N=13$
- If this does not make sense: stick to $N=-1$ (auto-set-up)!

Initial NGWFs are determined by the atom solver

- Solves the Kohn-Sham equations self-consistently for a “guessed” configuration (by default, the neutral atom config)
- Orbitals are filled by aufbau principle based on a built-in table (can be overridden, but usually not necessary)
- Unused subshells are automatically “knocked out” by setting their occupation to “X” eg 4f not included until 5s, 5p filled.

The pseudoatomic orbitals we are looking for solve the Kohn-Sham equation:

$$\hat{H}_{\text{KS}}\psi_n(\mathbf{r}) = \epsilon_n\psi_n(\mathbf{r})$$

where

$$\hat{H}_{\text{KS}} = -\frac{1}{2}\nabla^2 + V_{\text{loc}}(r) + \sum_i |p_i\rangle D_{ij} \langle p_j|$$

Atom Solver Choices

The atomic solver is the default approach to NGWF initialisation, so if you do not need to change any settings for any species, simply omit the `%block species_atomic_set`

If there are any tweaks to be made to the default, this block is required, and for each element symbol the string “SOLVE” should appear in the entry

To use automatic initialisation of the number of NGWFs, then specify -1 in the third column of species block. The code will attempt to determine how many orbitals to use, which orbitals constitute the valence, and what their default occupancies should be.

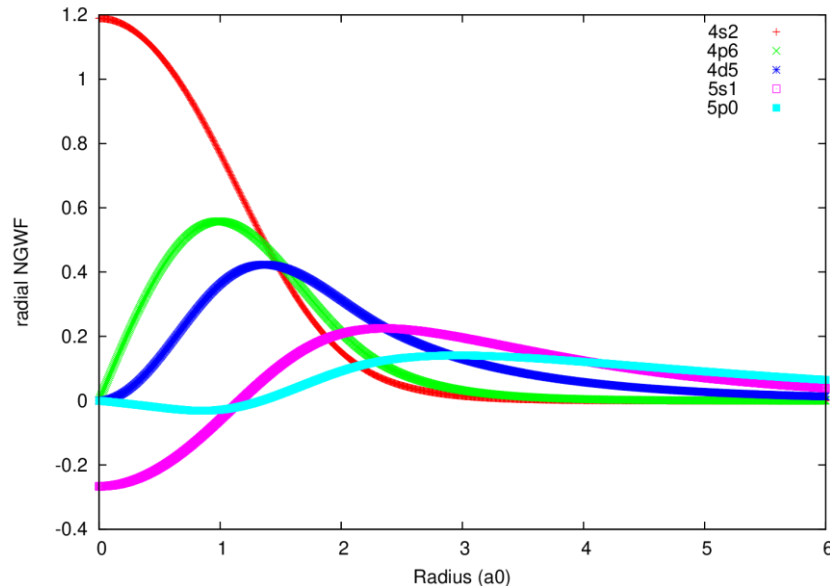
Confining Potentials

- NGWF radii: $R_c=8.0a_0$ for organic materials is a good starting point
- For anything ionic you need to be careful as some systems need quite large NGWFs: needing $R_c=10a_0$ or more is not unusual for heavier elements eg Mo, W
- If you have d-electrons present with large NGWFs, it is almost always preferable to confine them more than the default values
- By default, a confining potential is applied during NGWF generation, of the form:

$$V_{\text{conf}}(r) = S \exp[-w_l/(r - R_c + w_l)]/(r - R_c)^2$$

Confining Potentials

- Can inspect initial NGWFs with `write_initial_radial_ngwfs : TRUE`
- Example for Molybdenum: 4s2 4p6 4d5 5s1 5p0



Confining Potentials

- Confining potential added: “Mo SOLVE w=10 S=20000”
- Tails of NGWFs are faster decaying towards large R - much better convergence

