Jun. 2025 - Scalar and Fully relativistic pseudopotential theory - Exercise 1

In this exercise we analyze the Zn pseudopotential (PP) `Zn.pbe-spn-kjpaw_psl.1.0.0.UPF` of `pslibrary`. Our goal will be to plot the main quantities that characterize the PP and to test its transferability and the absence of ghost states. We will also try to improve it. After unpacking the file `pslibray.1.0.0.tar.gz` that you find at the web page `https://dalcorso.github.io/pslibrary`, generate the Zn PP by editing the file `make.ps` and choosing as element `Zn`.

1. The PP is generated by running the `ld1.x` code with the input that can be found in the directory `WORK`. Identify the parameters given in the input by reading the documentation of the `ld1.x` code and describe the PP.

2. Using the code `ld1.x`, plot the all-electron and pseudo wavefunctions for the Zn atom. In this plot mark the cut-off radii used for each orbital angular momentum l.

3. Using the code `ld1.x`, plot the all-electron and pseudo logarithmic derivatives for the s, p, and d angular momenta at $R = 1.4$ a.u.. Compare these logarithmic derivatives and identify the range of energies in which the two are similar.

4. Perform a few transferability tests using `iswitch=2` in the `ld1.x` input by considering electronic configurations different from the one used for the PP generation: $[Ar]3s^2 3p^6 3d^{10} 4s^2$. Consider only configurations whose energy differ less than 1 Ry from that of the reference configuration. For instance you can consider $3s^2 3p^6 3d^{10} 4s^1 4p^1$ or the ionized configuration $3s^2 3p^6 3d^9 4s^2 4p^0$. Compare the all-electron and pseudo eigenvalues on these configurations. Discuss the transferability of the PP.

5. Identify the main functions contained in the PP file: radial mesh, all-electron wavefunctions, pseudo wavefunctions, projector functions, augmentation functions. Plot them as a function of the radial mesh.

6. The Zn PP is characterized by the following parameters: $r_{core} = 1.1$ a.u., $r_s = 1.25$ a.u., $r_p = 1.15$ a.u., $r_d = 1.35$ a.u. $\epsilon_{4p} = 6.3$ Ry, $\epsilon_{3d} = -0.3$ Ry. Determine the allowed range of variation of each parameter, by keeping all the others constant. Check if it is possible to improve the PP so that the transferability tests made at point 4 improve by changing only one parameter of the PP.

7. Now using the three best PPs determined at previous point determine in a plane wave calculation the a and c/a of hcp- Zn using the `thermo_pw.x` code. Check the convergence of the results with the kinetic energy cut-off of the wavefunctions and of the charge density. Determine the cut-offs necessary to converge the lattice constant within 0.005 Å. Discuss also the convergence with **k**-points and smearing. Determine the phonon frequencies at $\mathbf{\Gamma}$, **K**, **M** and **A** with the new PPs and compare the results of the different PPs.