Analysis of atompaw "problem" cases for Abinit and quantum-espresso

Notes by N. A. W. Holzwarth – 09/19/2018

The atompaw software package has for many years generated atomic datasets that work well with both Abinit and quantum-espresso, in most cases giving very equivalent answers. However we recently noticed more than two cases, where the datasets behaved very differently with the two codes. In the first case, we generated a dataset for Cs which gave a reasonable binding energy curve for CsBr, but failed at the scf step for quantum espresso.
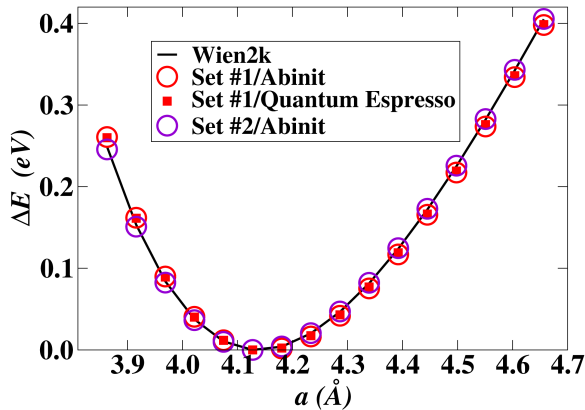

Figure 1: Binding energy plot for CsBr, comparing results from Abinit and quantum-espresso (using atompaw datasets) with those of WIEN2k. Set #1 refers to the datasets generated from the JTH parameters while set #2 refers to datasets generated using different parameters which give reasonable results for Abinit, but fail to converge at the scf level for quantum espresso.

In the second case, we generated a dataset for Cl which gives a reasonable binding energy curve for NaCl using both Abinit and quantum espresso, but the density functional perturbation theory results are quite different. The Abinit phonon density of states curves agree well with previous literature, but the quantum espresso phonon density of states curves deviate considerably.

We now have traced these two behaviors back to an old problem concerning the difference in how Abinit and quantum espresso evaluate the exchange-correlation functional within the PAW formalism. In 2010 we wrote a paper on this subject – *Computer Physics Communications* **181**, 1862-1867 (2010) (`http://dx.doi.org/10.1016/j.cpc.2010.07.036`), arguing that for logical reasons, the compensation charge should not be included within the exchange-correlation functional, and can cause numerical difficulties. In the 2010 paper, the numerical difficulties were identified for terms involving the gradient of the electron density. However, in the present case, the numerical difficulties are caused by the compensation charge having negative values which can occur for some choices of the PAW parameters. For atompaw code, this comes into the evaluation of the local pseudopotential $v_{loc}(r)$. This is calculated by unscreening the constructed pseudopotential used in generating the PAW basis and projector functions including subtracting the appropriate exchange-correlations potential $- v_{xc}(\tilde{\rho}_c + \tilde{\rho}_v)$ in the case of Abinit and $v_{xc}(\tilde{\rho}_c + \tilde{\rho}_v + \hat{\rho}_v)$ in the case of quantum espresso.
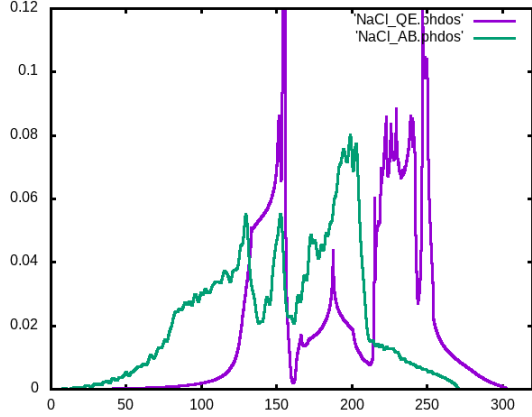
Figure 2: Phonon density of states for NaCl, comparing Abinit and quantum espresso results. The horizontal axis represents the phonon frequencies in units of $(\text{cm})^{-1}$.

Within atompaw, the subroutine calculating the exchange-correlation functional returns 0 when the density is negative, resulting in a discontinuous $v_{loc}(r)$ curve for both Cs and Cl. It can be conjectured that, in addition to having a discontinuous local potential, these cases would also suffer from having a negative density in the exchange-correlation contributions in the scf and/or dfpt steps. One could perhaps blame atompaw for allowing the compensation charge to be negative. However, the purpose of the compensation charge is to make sure that the Coulombic energies are correctly calculated and negative values are not precluded. The compensation charge has no logical role in the exchange-correlation functional and can cause numerical problems. As a practical matter, one could adjust $\tilde{\rho}_c$ to make sure that $\tilde{\rho}_c + \hat{\rho}_v > 0$ within the atom, although this may not be sufficient in the solid.
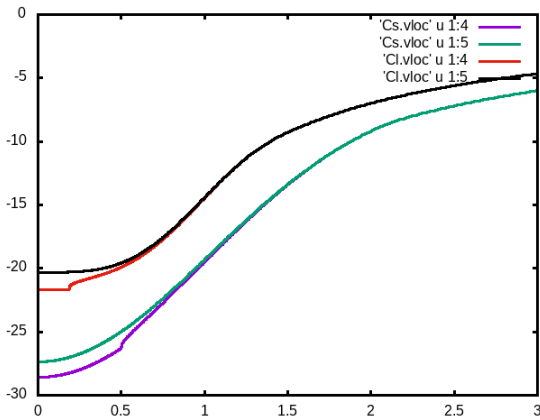

Figure 3: Plot of $v_{loc}(r)$ generated by atompaw code for Cs (lower two lines) and Cl (upper two lines), comparing the Abinit versions (black and green curves) and the quantum espresso versions (red and purple curves). The two versions differ by the assumed form of the exchange-correlation functional which for Abinit is $v_{xc}(\tilde{\rho}_c + \tilde{\rho}_v)$ and for quantum-espresso is $v_{xc}(\tilde{\rho}_c + \tilde{\rho}_v + \hat{\rho}_v)$.

In order to check whether it might be effective to adjust $\tilde{\rho}_c$ in order to ensure that $\tilde{\rho}_c + \tilde{\rho}_v + \hat{\rho}_v) > 0$, we adjusted the parameter `rc_core` in the atompaw code. The results for CsBr are encouraging as

seen in the binding energy plot, where Quantum Espresso and Abinit now give essentially the same result, very similar to the Abinit result using the original dataset. We also similarly changed the datasets for Cl and S and now the phonons of NaCl and Na_2S given nearly identical results using both Abinit and Quantum Espresso. While this solves the big mystery, we still think it would be better to remove $\hat{\rho}_v$ from the exchange-correlation evaluations if possible.
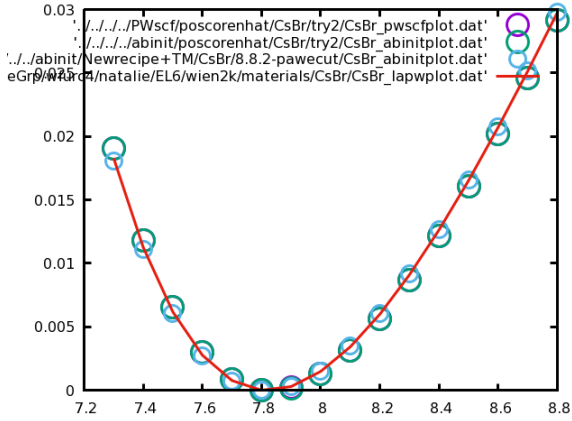

Figure 4: Binding energy plot for CsBr, where $\tilde{\rho}_c$ has been increased to ensure that $\tilde{\rho}_c + \tilde{\rho}_v + \hat{\rho}_v > 0$.
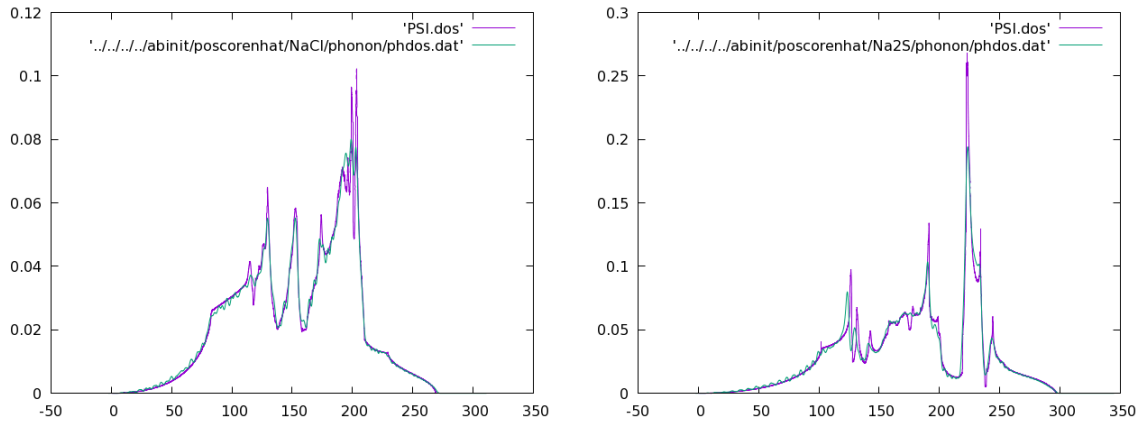

Figure 5: Phonon density of states for NaCl (left) and Na_2S (right) comparing Quanum Espresso (purple) and Abinit (green) results for datasets with adjusted values of $\tilde{\rho}_c$.