Assessment of Accuracy and Efficiency of PAW Datasets in Materials Simulations

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Outline

- Goal -- Reliable and efficient simulations of materials
- Enumeration and testing of factors contributing to the goal
- Example -- cubic and hexagonal boron nitride
- A cautionary tale

Conclusions

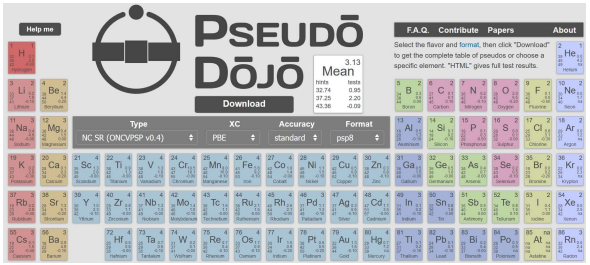
- Science is well served by having several independent and public code collaborations
- Big thanks to developers of ABINIT, QUANTUM ESPRESSO, …..

Acknowledgements: Supported by NSF grant DMR-1507942; computations performed on WFU's DEAC Cluster; thanks to Marc Torrent and Francois Jollet for discussions and advice

Factors contributing to the goal of reliable and efficient materials simulations within the context of density functional theory

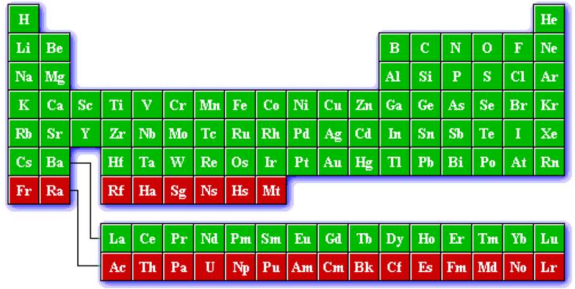
- **Formalism**
  - **Optimized norm-conserving pseudopotentials (ONC), D. R. Hamann, PRB 88, 085117 (2013)**
  - **Projector augmented wave (PAW), P. E. Blöchl, PRB 50, 17953 (1994)**
- **Atomic datasets**
- **Details of code implementations**

Many sources for atomic datasets



PROJECTOR AUGMENTED-WAVE (PAW) DATASETS

http://www.pseudo-dojo.org/



https://www.abinit.org/psp-tables

Current version of the library: **JTH - v1.1**

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ATOMPAW

Download source code and example files:

- atompaw-4.1.0.5.tar.gz (5.5mb) 12/2018 Marc Torrent modified abinitinterface.F90 so that (case).abinit file correctly handles the case of pbesol, compatable with abinit using libxc. Note that the (case).abinit datasets are superceded by the (case).xml files.
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http://pwpaw.wfu.edu

Several sources of public code collaborations

https://www.abinit.org/

http://www.quantumespresso.org/

Specific datasets for this study –

ONC – Optimized Norm-Conserving Vanderbilt Pseudopotentials -- Hamann, PRB 88, 085117 (2013) as obtained from PseudoDojo

JTH -- Projector Augmented Wave (PAW) datasets generated by Jollet *et al.* CPC 185, 1246 (2014) as obtained from abinit.org

WFU – PAW datasets as obtained from pwpaw.wfu.edu

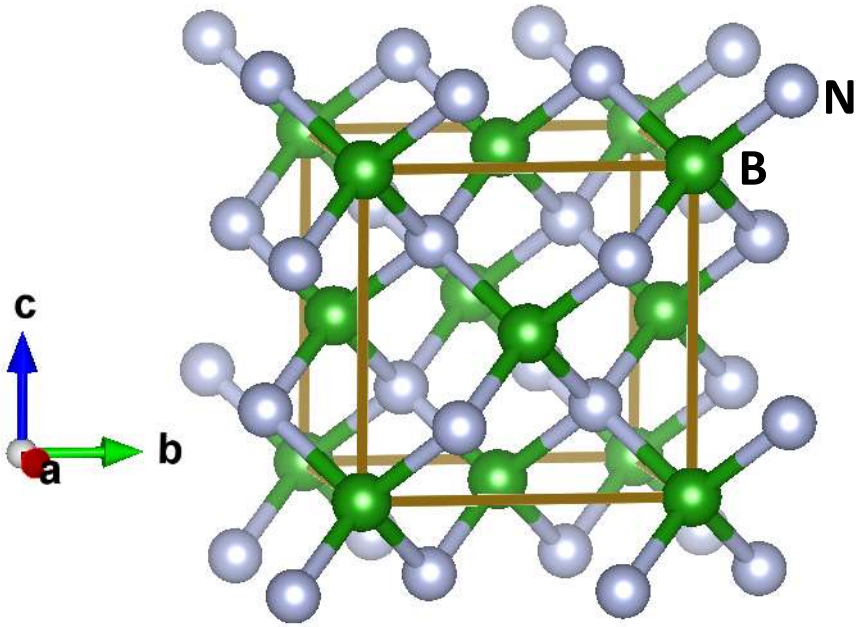
Specific codes for this study –

AB – Abinit -- https://www.abinit.org/

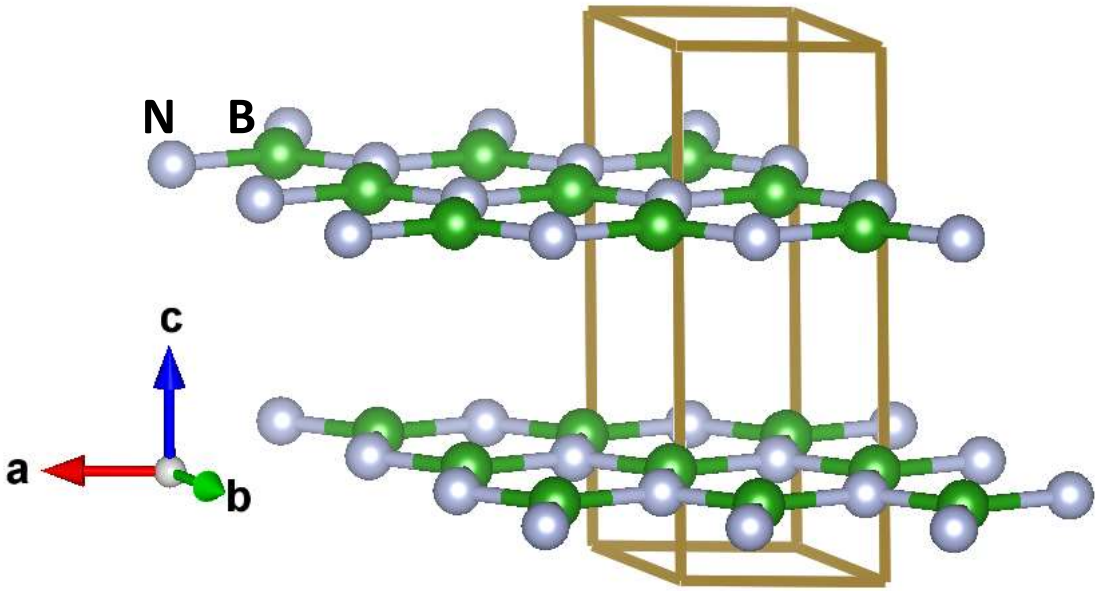
QE – Quantum Espresso -- http://www.quantum-espresso.org/

All calculations were performed using the local density approximation (LDA)
Perdew and Wang, PRB 45, 13244 (1992)

Example – cubic and hexagonal boron nitride



c-BN *F-43m* (#216)



h-BN *P6$_3$/mmc* (#194)

Most experiments and simulations agree that c-BN is the ground state structure at RTP, however there are a few dissenters

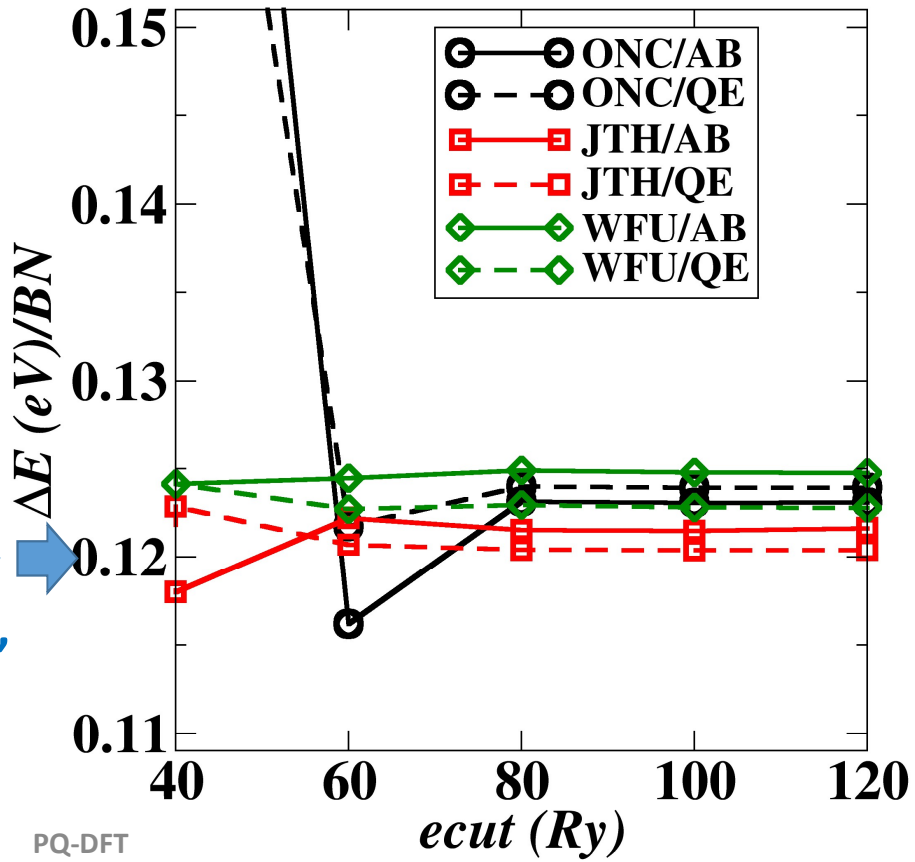
Convergence wrt planewave cutoff "*ecut*" of static lattice energy difference $\Delta E \equiv E_{\text{h-BN}} - E_{\text{c-BN}}$ where wavefunction planewave expansion includes all reciprocal lattice vectors $\mathbf{G}$ such that

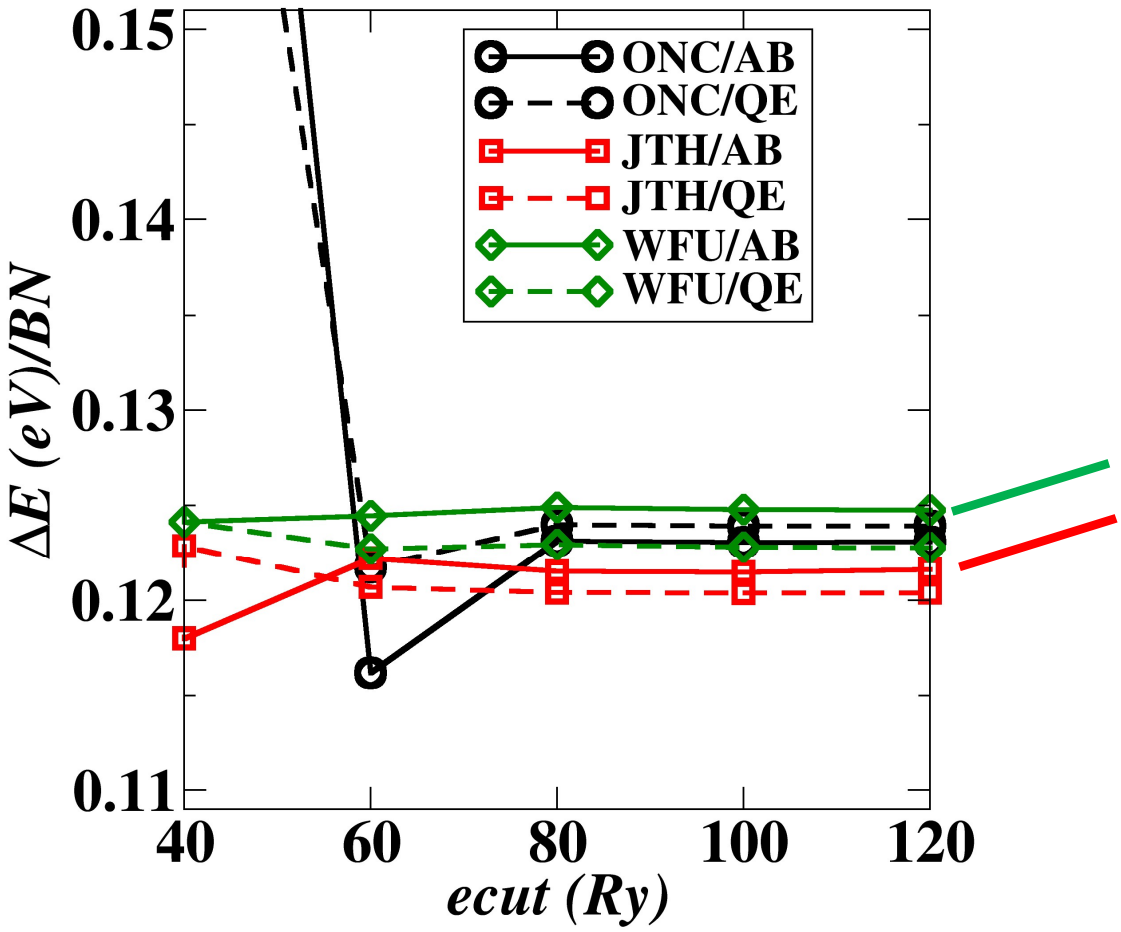
$$|\mathbf{k}+\mathbf{G}|^2 \le \frac{2m}{\hbar^2}(ecut)$$

AB → Abinit
QE → Quantum Espresso

ONC → Optimized Norm-Conserving
JTH → PAW (Jollet et al.)
WFU → PAW (WFU)

Value reported by Kern et al. PRB 59, 8553 (1999) with *ecut*=25.7 Ry (USSP+VASP)





Note that some of the differences between WFU and JTH are due to the fact that WFU used a Schrödinger solver while JTH used a scalar relativistic solver

AB → Abinit
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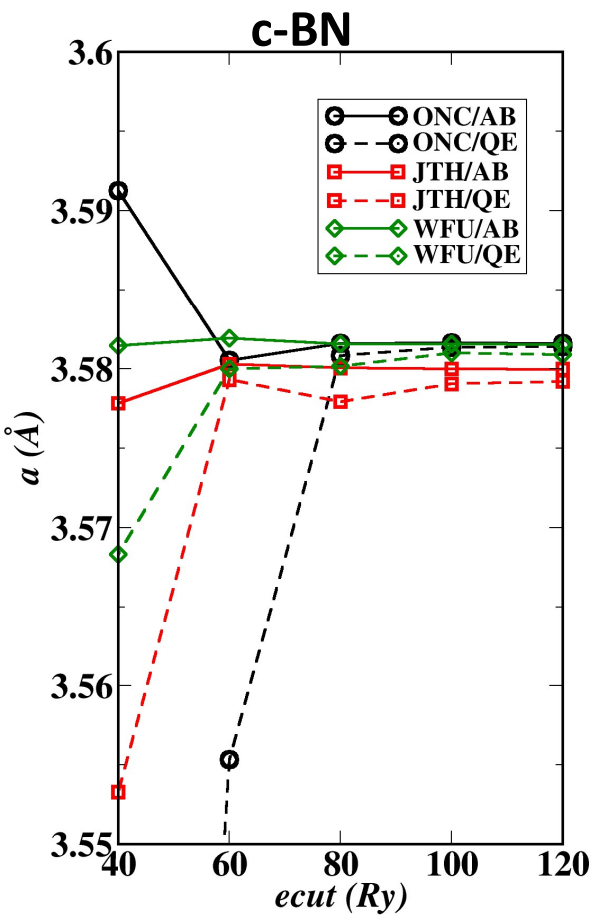
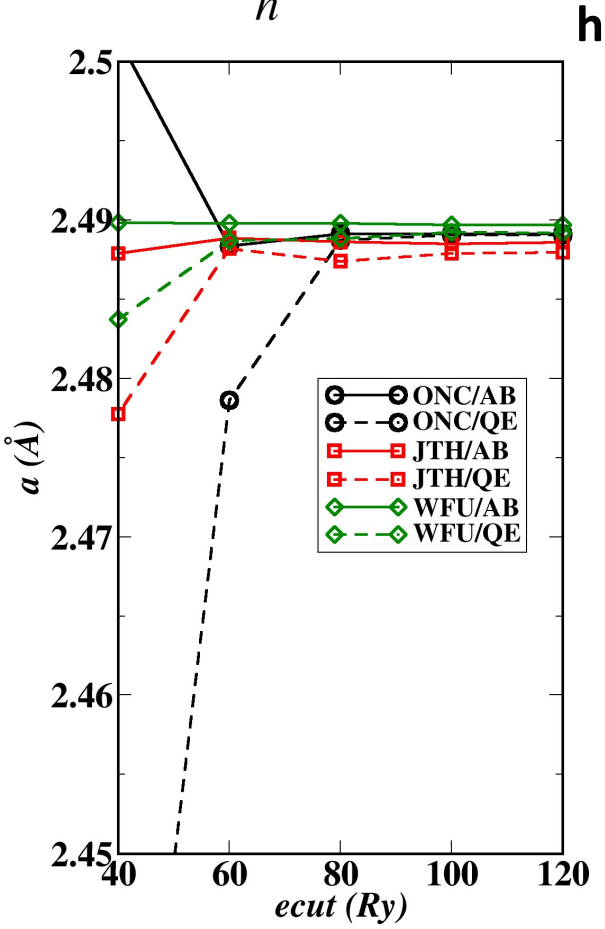
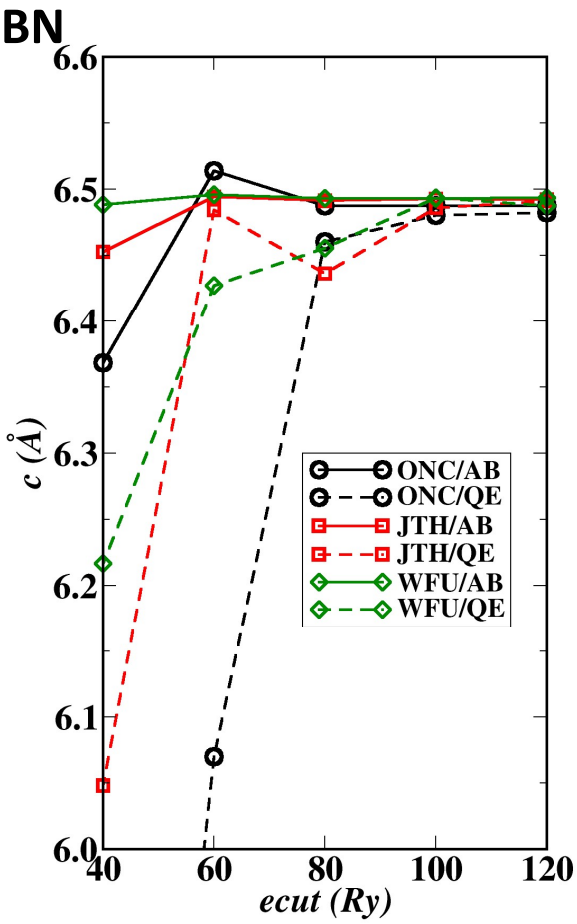
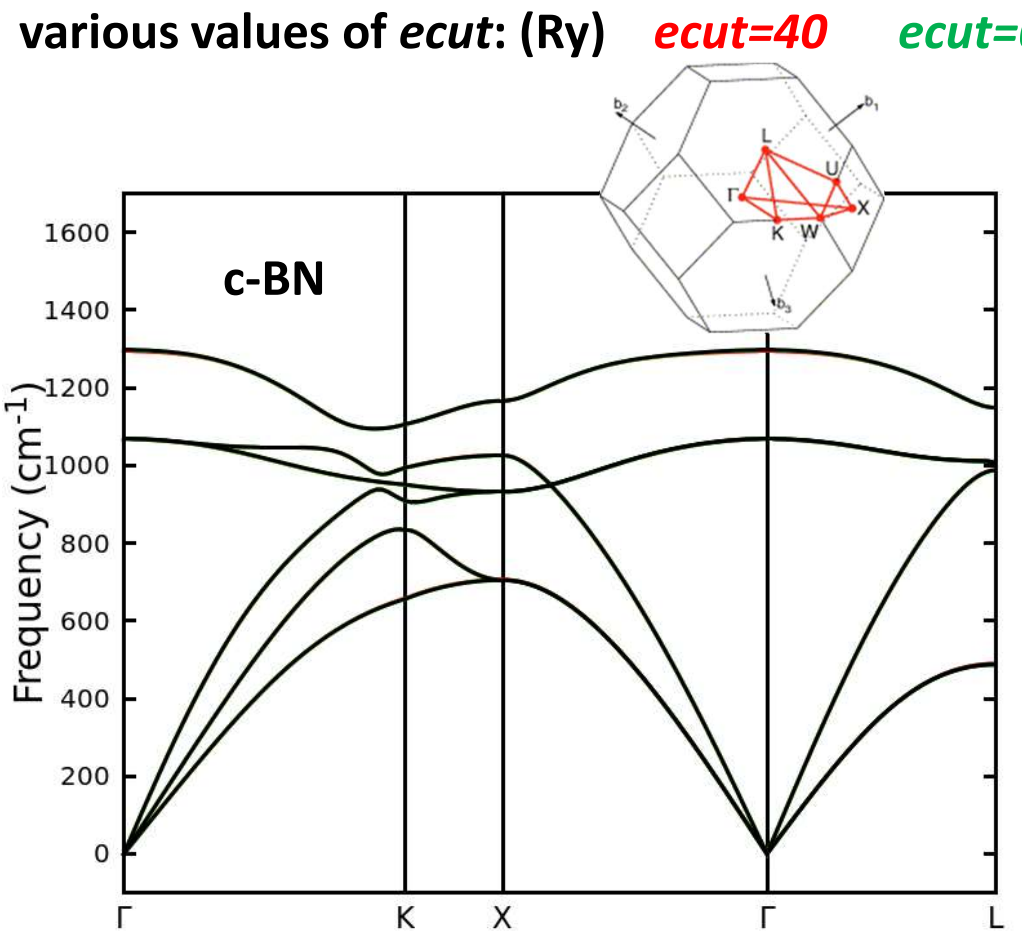
Convergence wrt planewave cutoff "*ecut*" of lattice constants of wavefunction planewave expansion including all $|\mathbf{k}+\mathbf{G}|^2 \le \frac{2m}{\hbar^2}(ecut)$.

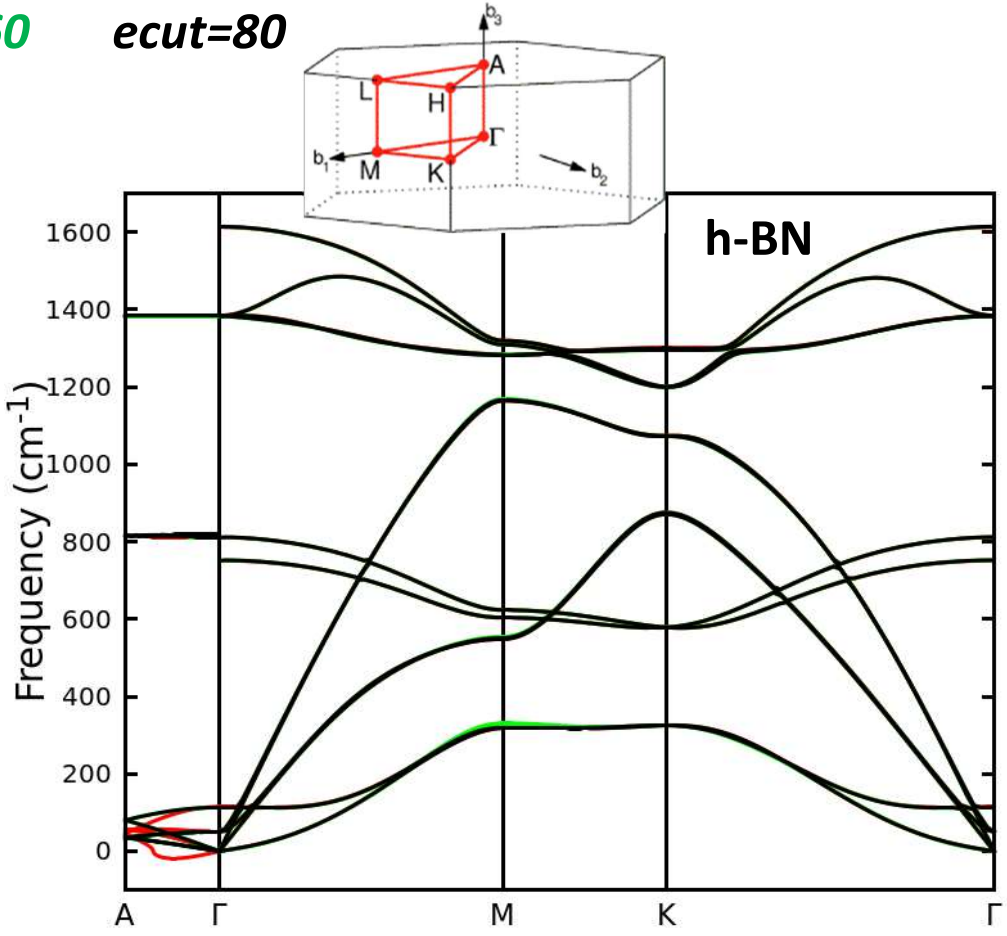






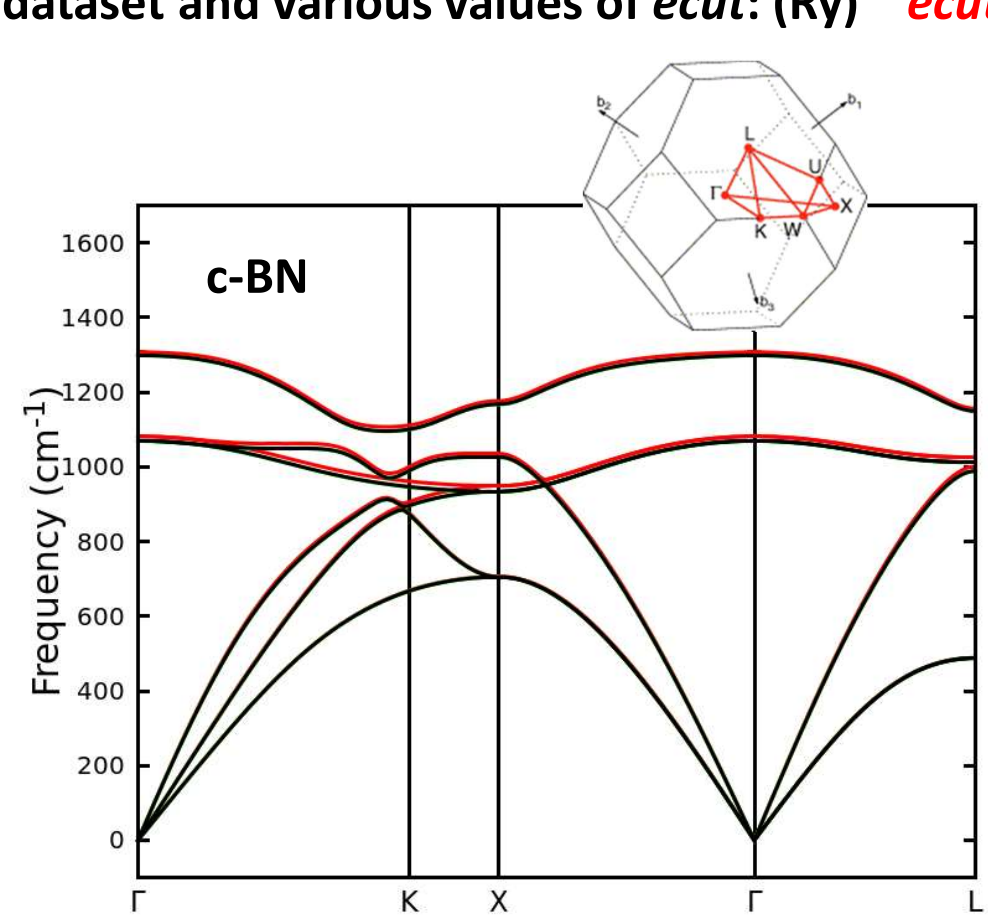
Phonon band dispersions calculated using Abinit with WFU dataset and various values of *ecut*: (Ry) ***ecut=40*** ***ecut=60*** ***ecut=80***

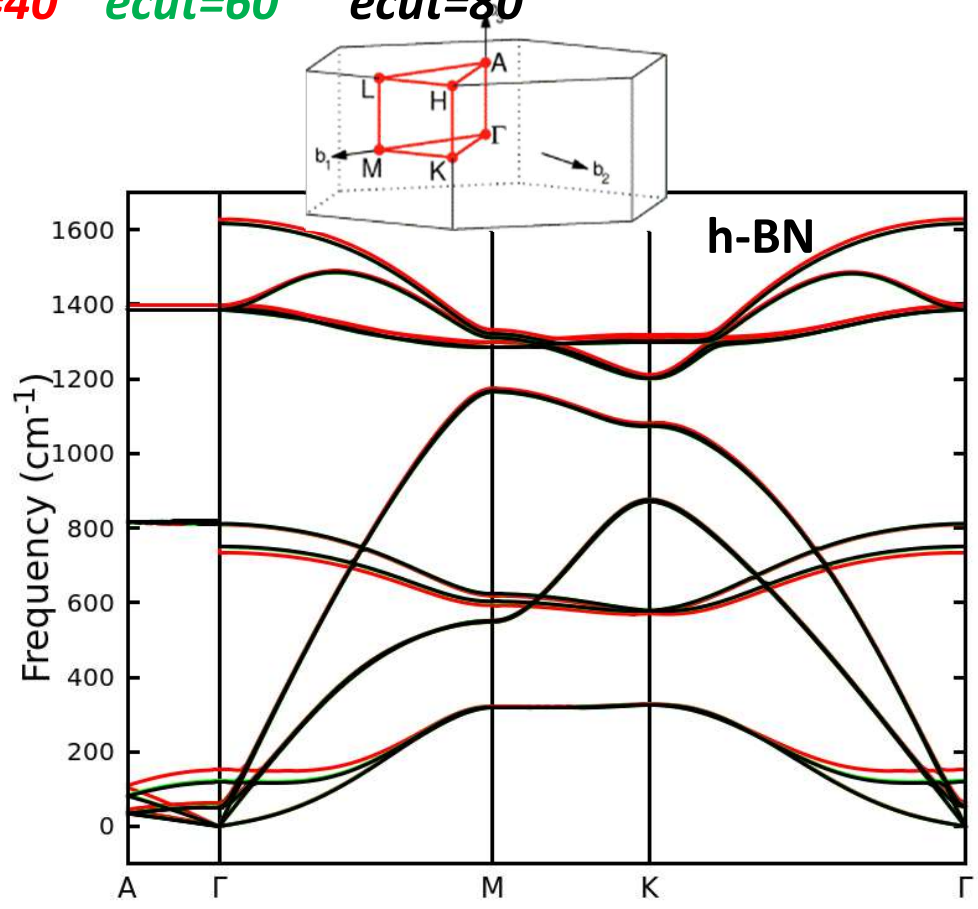




(Brillouin zone diagrams from Setyawan & Curtarolo, CPC 49, 299 (2010))

Phonon band dispersions calculated using Quantum Espresso with WFU dataset and various values of *ecut*: (Ry) ***ecut=40*** ***ecut=60*** ***ecut=80***





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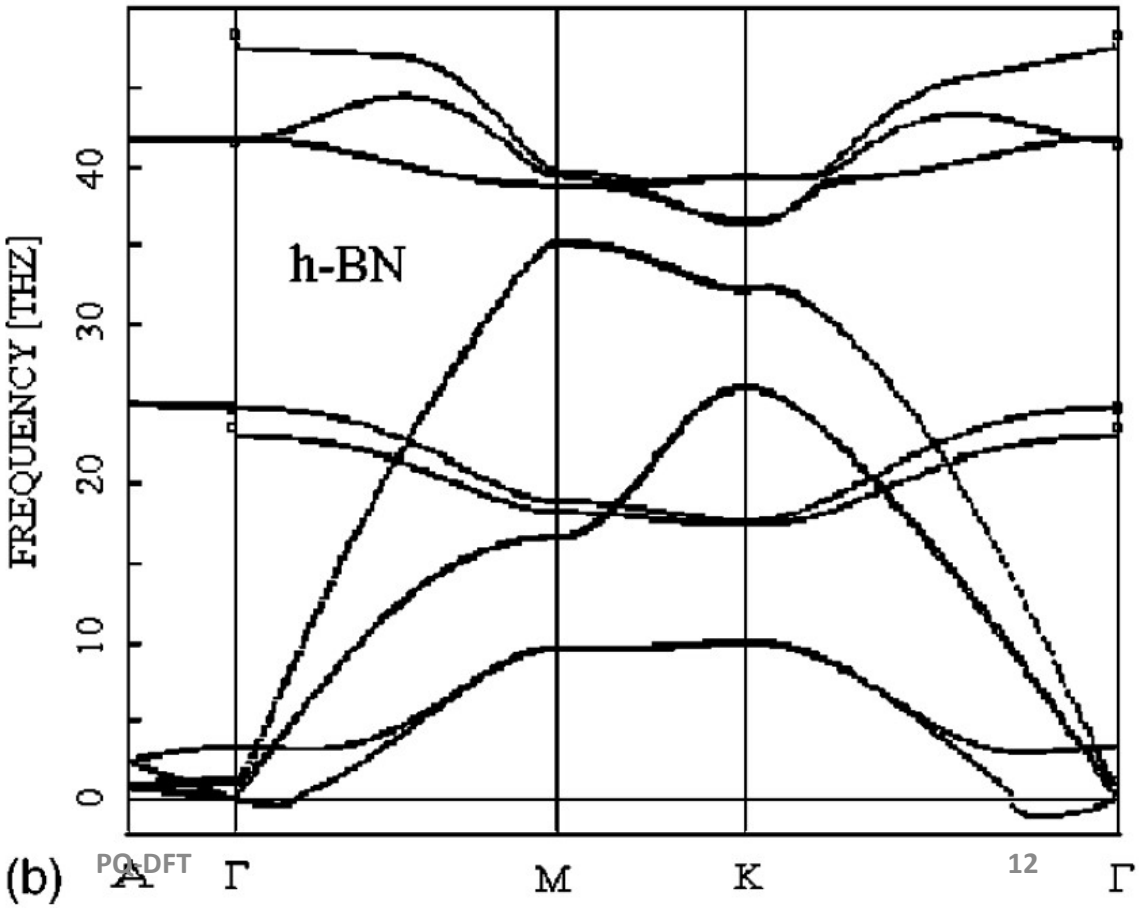
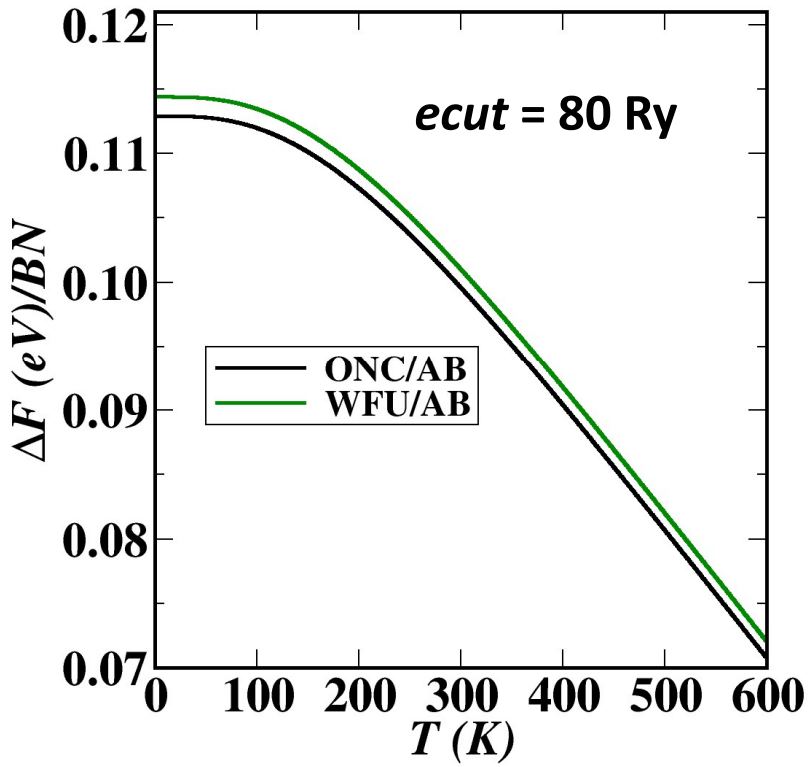
Summary of our results for phonon dispersions:

- **All calculations are well converged for *ecut*=80 Ry and nearly identical for the three datasets**
- **The phonon dispersions of more complicated lattice structures are harder to converge than lattices of high symmetry and are often susceptible to spurious imaginary frequencies.**

Example of imaginary phonon modes for h-BN found in literature -- Yu et al. PRB 67, 014108 (2003)



Estimation of free energy difference $\Delta F(T) = F_{c\text{-}BN}(T) - F_{h\text{-}BN}(T)$



Note that $F(T) = F^{SL}(T) + F^{vib}(T)$

$F^{SL}(T) \approx F^{SL}(0) \equiv E$ (DFT total energy)

$$F^{vib}(T) = k_B T \int d\omega \; g(\omega) \; \ln\left(2\sinh\left(\frac{\hbar\omega}{2k_B T}\right)\right)$$

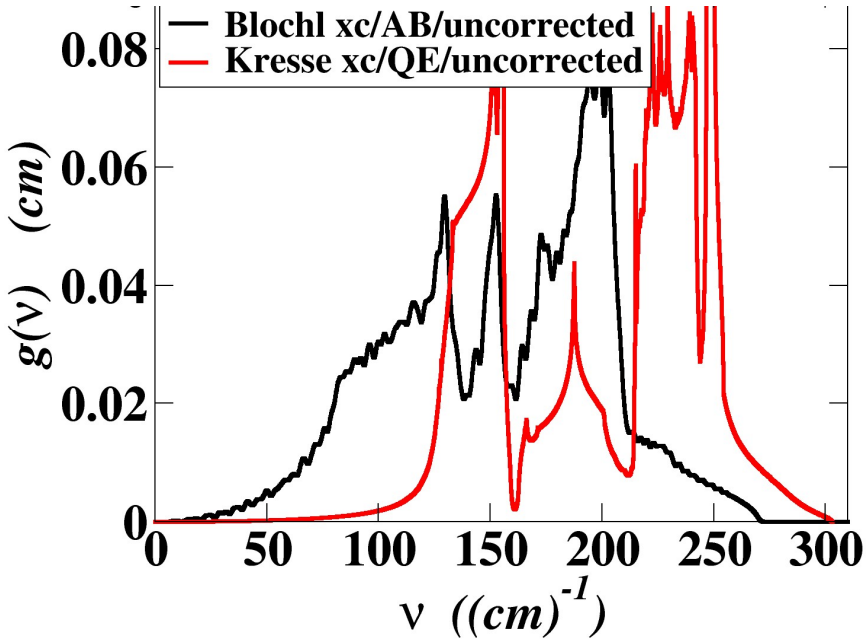
Phonon DOS

	0 K	300K
$\Delta F_{ONC}(T)$	0.113	0.100 eV/BN
$\Delta F_{WFU}(T)$	0.114	0.101

Note that the 0.001 eV difference may be largely due to the different solvers. WFU used a Schrödinger solver and ONC used a scalar relativistic solver.

Cautionary tale about code implementations

For many years we have shared atomic datasets on our ATOMPAW webpage: http://pwpaw.wfu.edu for use with both ABINIT and QUANTUM ESPRESSO
Last summer we obtained a surprising result for the phonon densities of states of NaCl



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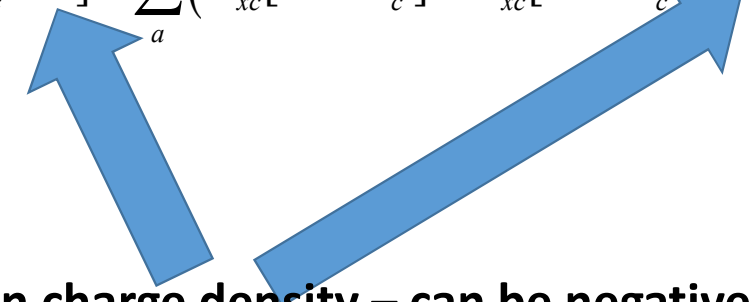
The explanation comes in the different implementations of the exchange-correlation functionals in the two codes.

Blochl's formulation: **Used by default in ABINIT**

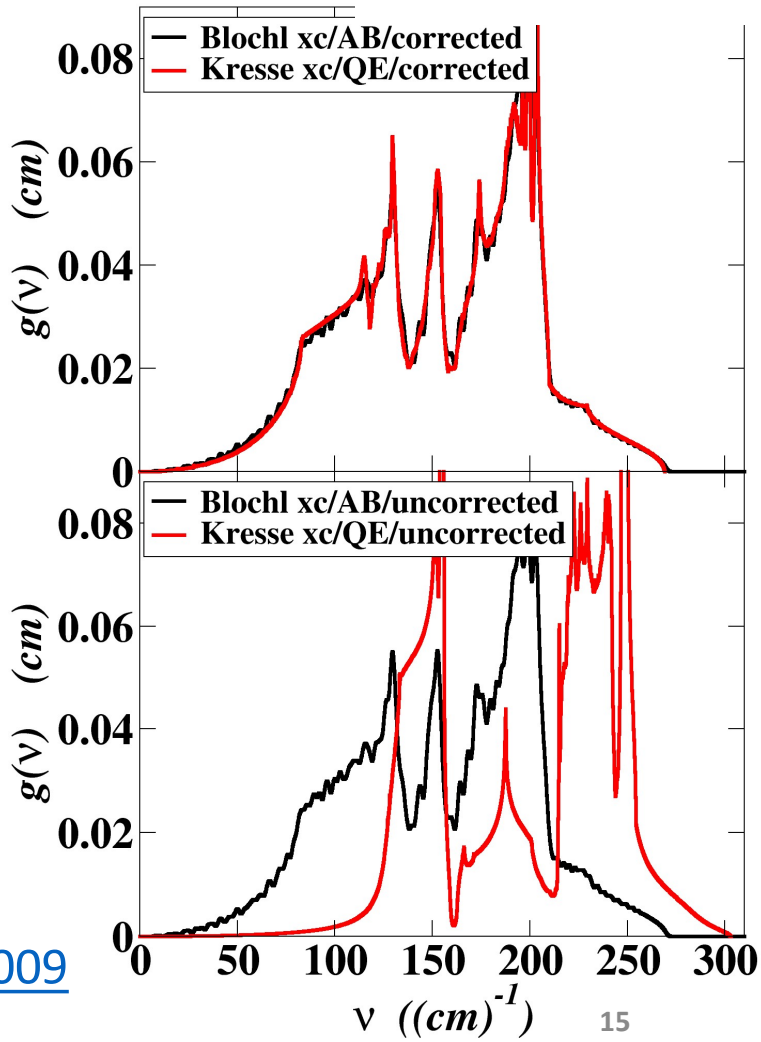
$$E_{xc}^{\mathrm{B}} = E_{xc}[\tilde{n} + \tilde{n}_c] + \sum_a \left(E_{xc}[n^a + n_c^a] - E_{xc}[\tilde{n}^a + \tilde{n}_c^a] \right).$$

Kresse's formulation: **Used by QUANTUM ESPRESSO**

$$E_{xc}^{\mathrm{K}} = E_{xc}[\tilde{n} + \tilde{n}_c + \hat{n}] + \sum_a \left(E_{xc}[n^a + n_c^a] - E_{xc}[\tilde{n}^a + \tilde{n}_c^a + \hat{n}^a] \right).$$



Compensation charge density – can be negative and does not logically belong in evaluation of the exchange-correlation terms. "Correction" ensures that compensation charge is positive.



Comp. Phys. Comm. https://doi.org/10.1016/j.cpc.2019.05.009

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Conclusions –

- **These comments are meant to be the start of a conversation**
- **It is important to quantify the numerical accuracy of the calculations and to recognize the sometimes hidden factors that contribute**
- **In the BN example, the converged differences have the values +/- 0.001 eV**
- **It is not useful to insistent on numerical tolerance smaller than the accuracy of the level of the theory.**
- **It is useful to share atomic datasets between codes, but apparently the convergence properties are quite code-dependent**
- **It is important to train users to be vigilant and skeptical**