Phonons and elastic constants including vdW interactions

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fnrs
FREEDOM TO RESEARCH

Introduction

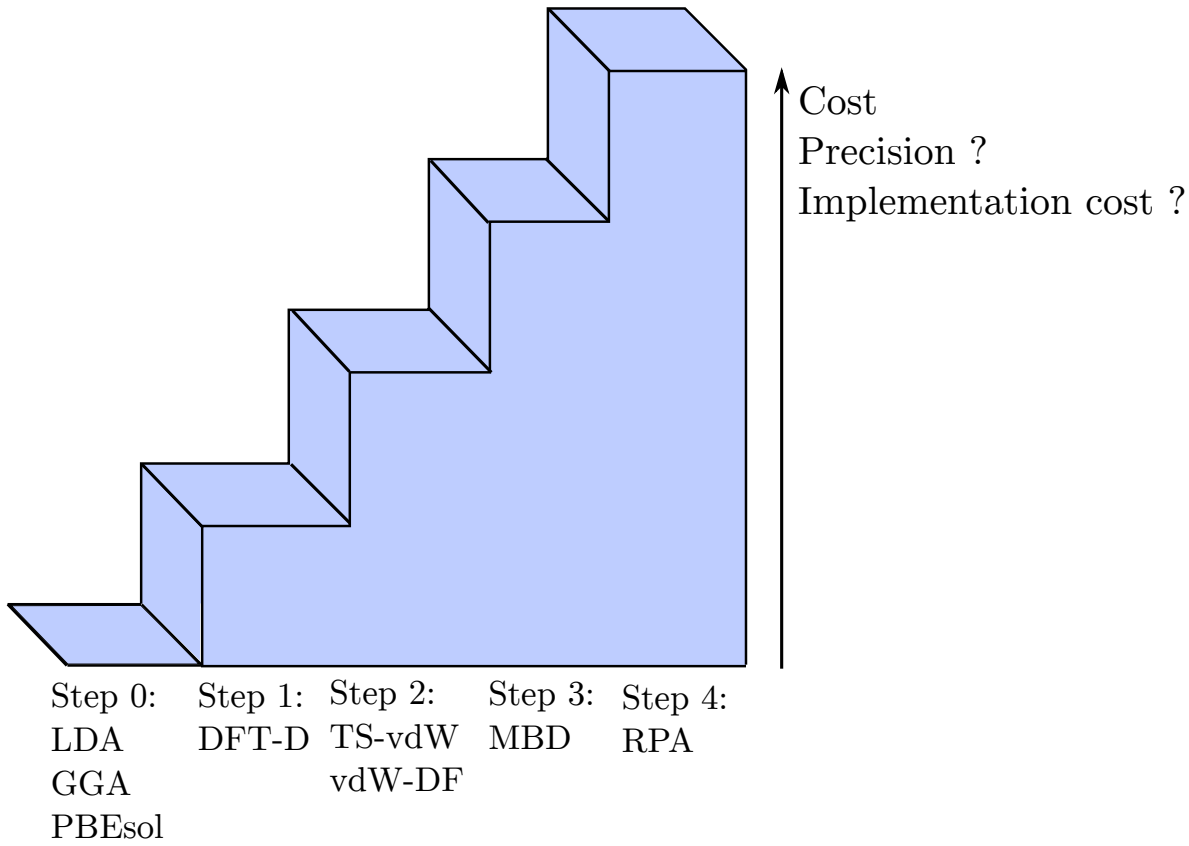
vdW interactions are everywhere...

- Layered materials (graphite, h-BN, ...)
- Molecular crystals (benzene, naphthalene, ...)
- Hydrogen-bonds
- Crystals with heavy chemical species

Jacob's ladder

Exactly known through the Fluctuation-Dissipation Theorem...

... but costly, generally approximated.



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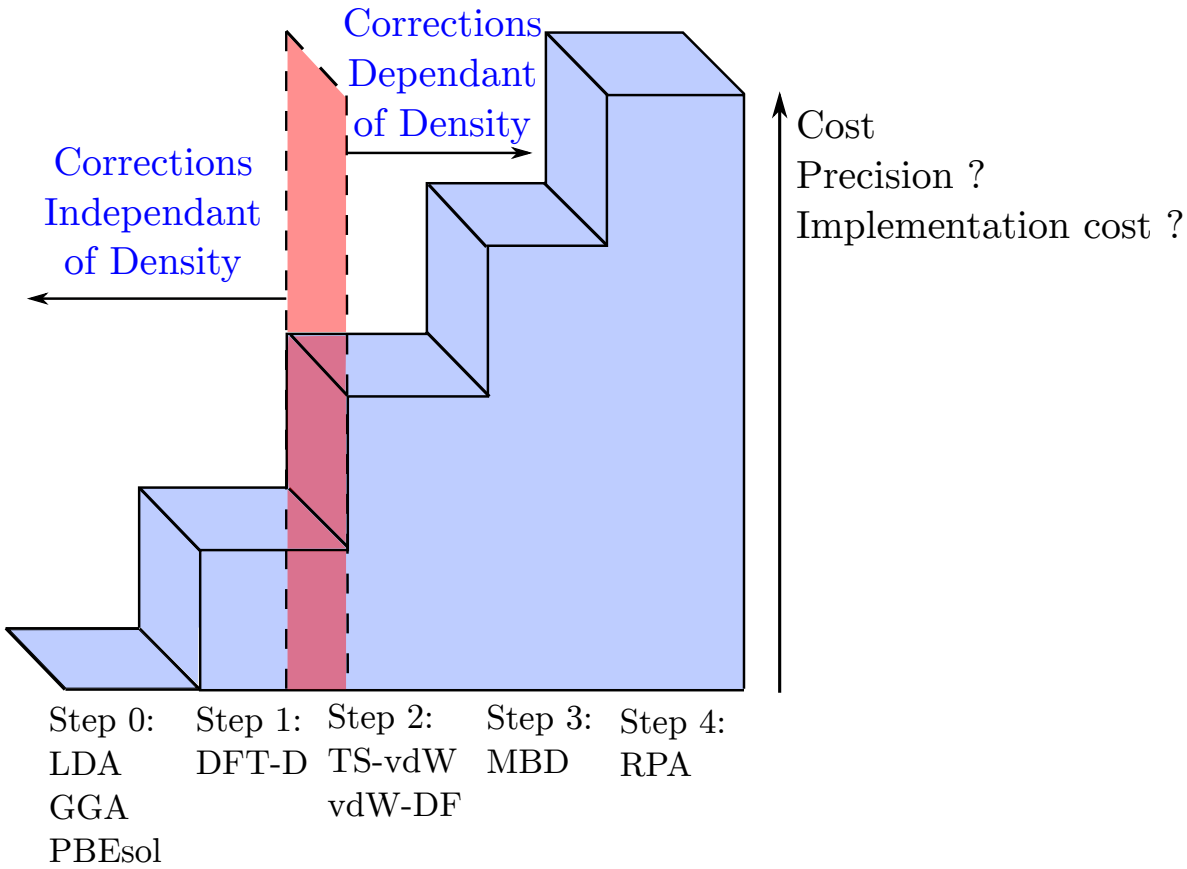
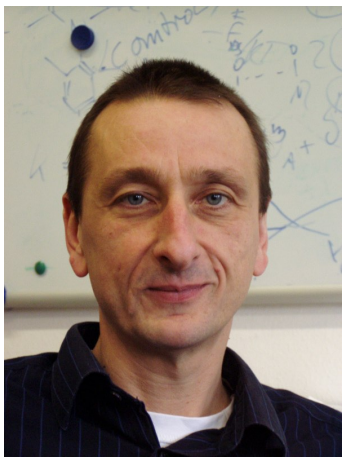


Independance on density $\Rightarrow \nearrow$ compatibility, $\searrow$ complexity

Grimme's DFT-D

$$E^{disp} = \frac{-1}{2} \sum_{n} \sum_{I,J} \frac{C_{n,IJ}}{R_{IJ}^{n}} f_{dmp}^{n}(R_{IJ})$$

$C_{n,IJ}$ dispersion coefficient, f_{dmp}^{n} damping function



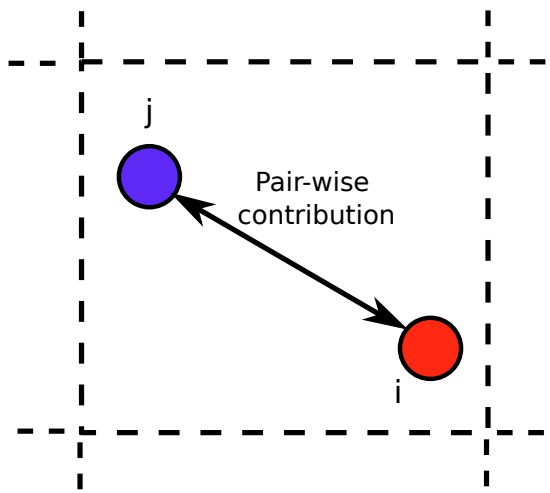
S. Grimme

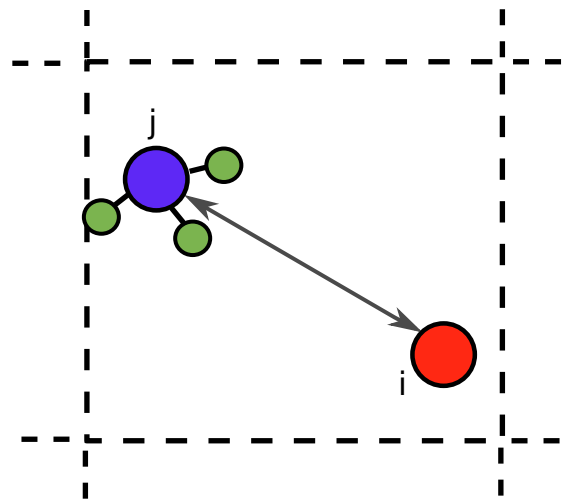
- DFT-D2 (2006): n=6, $C_{n,IJ}$
- DFT-D3 (2010): n=6,8, $C_{n,IJ}(\{\mathbf{R}\})$
- DFT-D3(BJ) (2010): same
- (TS-vdW (2010): n=6, $C_{n,IJ}(\rho(\mathbf{r}))$

Dispersion coefficient

$$C_{6,IJ} = \frac{3}{\pi} \int_0^\infty \alpha_I(j\omega)\alpha_J(j\omega)d\omega$$

α_I is the polarizability of the atom I

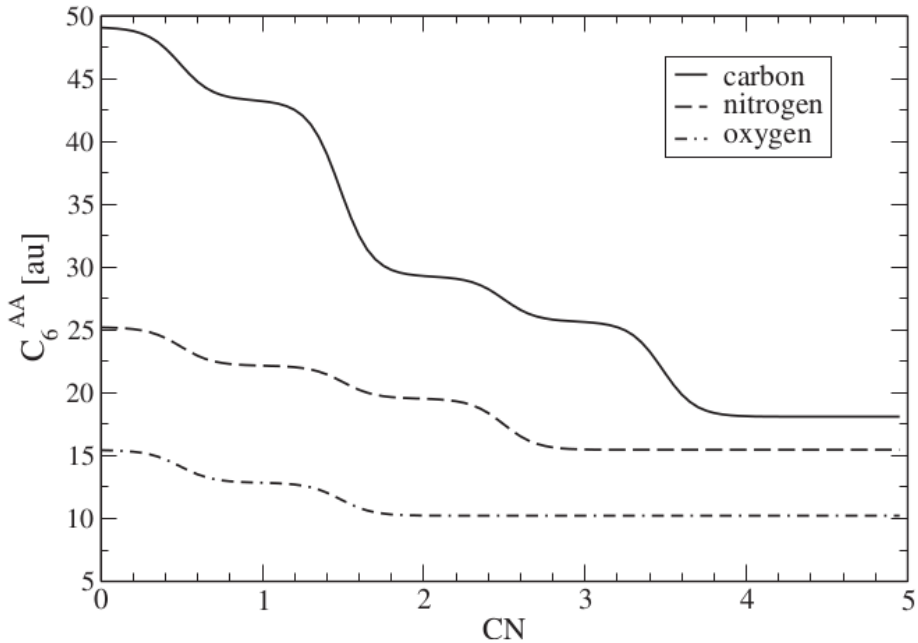




The contribution of $i - j$ pair should be $\neq$ ($\neq$ polarizability)!

Dispersion coefficient

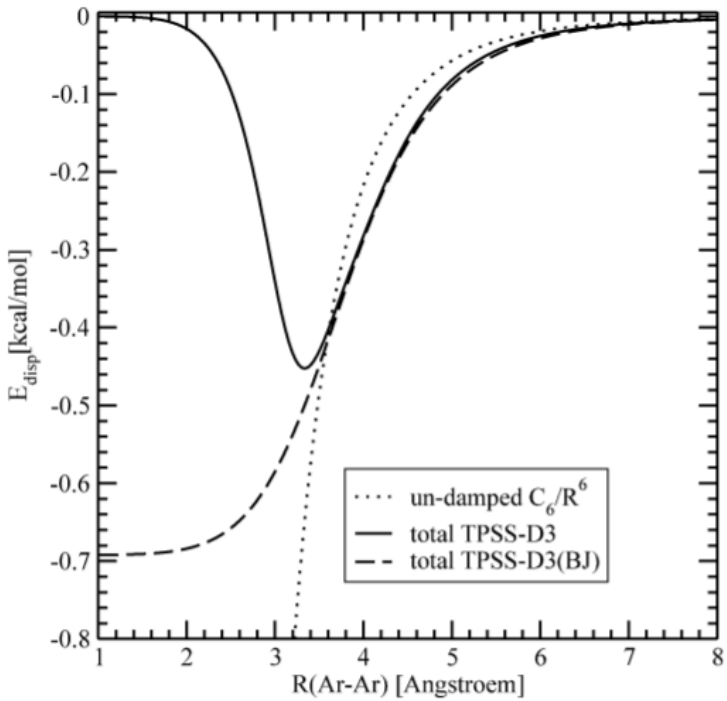
In DFT-D3, $C_{n,IJ}$ depends on the Coordination Number (number of neighbors); interpolated between tabulated values



- $\oplus$ depends on the chemical environment (graphite $\neq$ diamond)
- $\ominus$ does not depend on the oxidation state

Damping function

$\frac{1}{R_{IJ}^6}$ is a diverging function $\Rightarrow$ introduction of a damping function

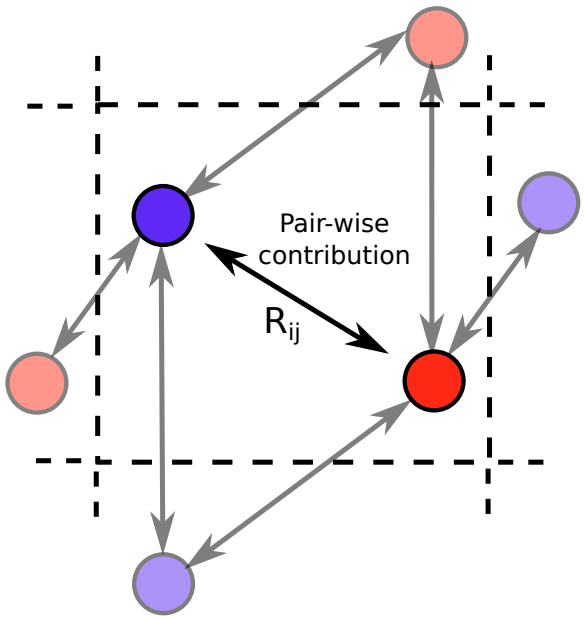


$\Rightarrow$ Only difference between DFT-D3 and DFT-D3(BJ)

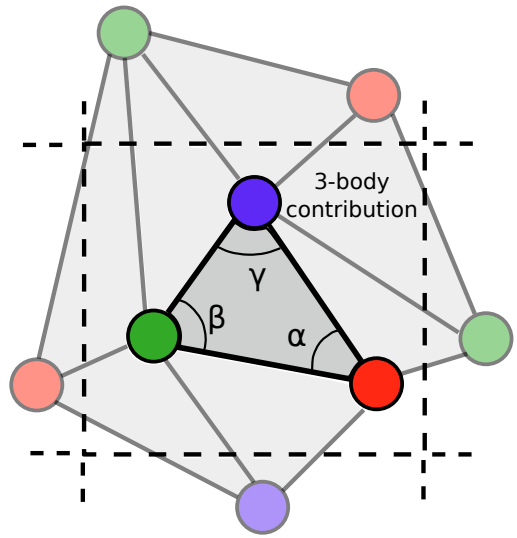
Three-body term

DFT+D3: $E_{tot} = E_{DFT} + E^{(2)}_{disp} + E^{(3)}_{disp}$

$E^{(2)}_{disp}(C_{6,ij}/R^6_{ij}, C_{8,ij}/R^8_{ij})$



$E^{(3)}_{disp}(R^{-3}_{ij}, R^{-3}_{jk}, R^{-3}_{ki}, \alpha, \beta, \gamma)$



Only in DFT-D3

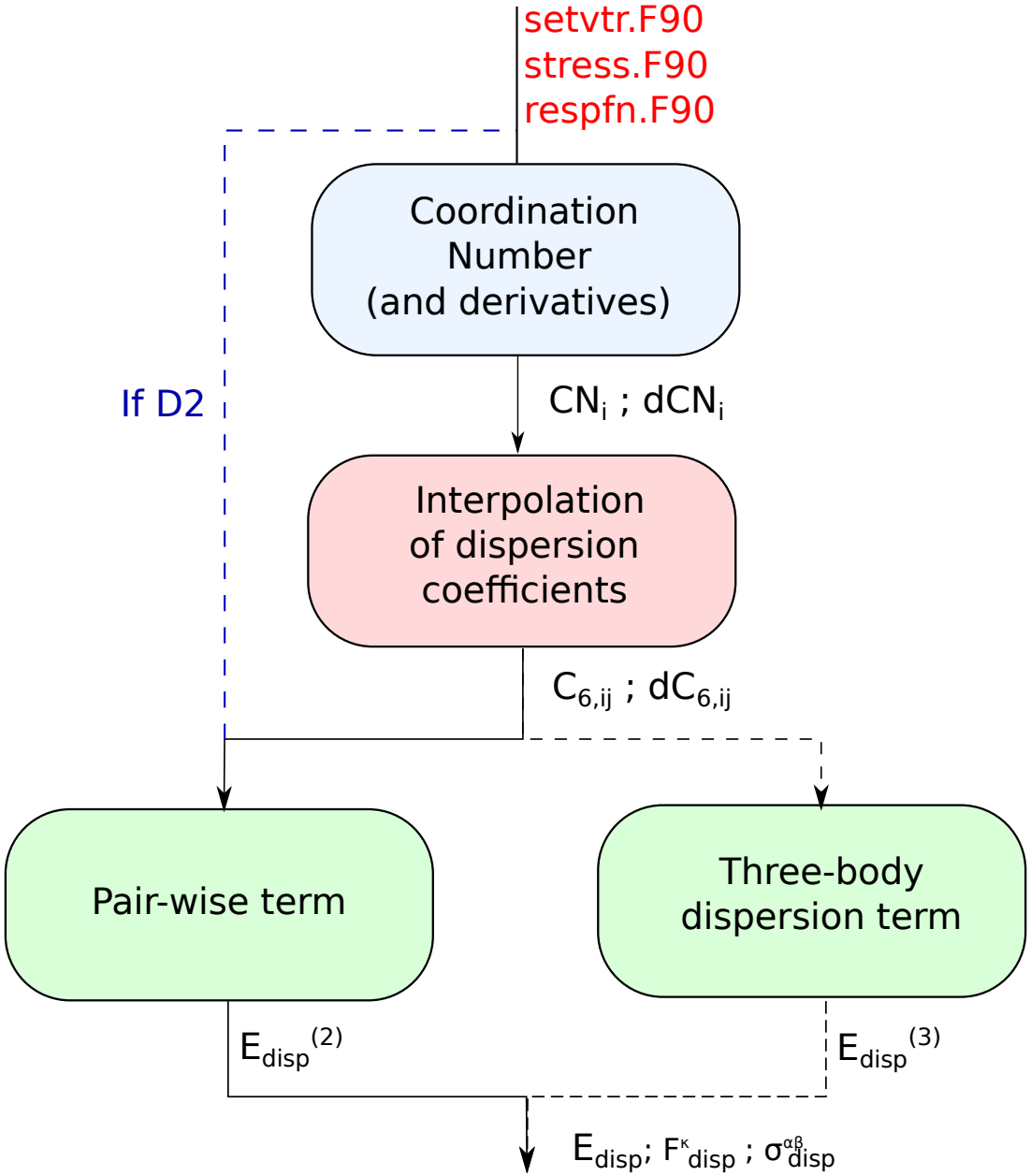
Cost a lot for a few percent of the vdW energy

Response functions

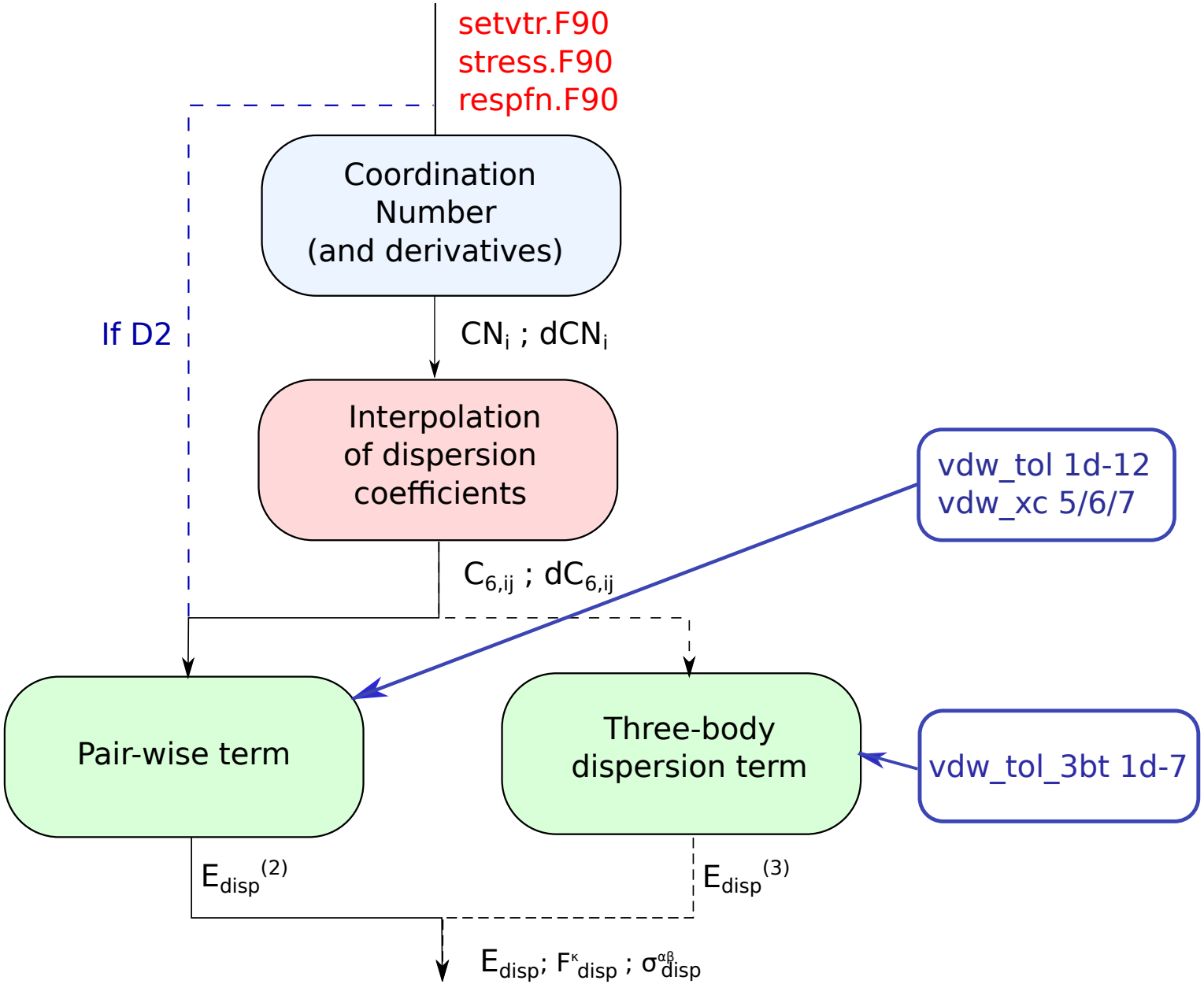
	$\partial R_{\kappa\alpha}$	$\partial \mathcal{E}_{\alpha}$	$\partial \eta_{\alpha\beta}$
	$F_{\kappa\alpha}$	P_{α}	$\sigma_{\alpha\beta}$
$\partial R_{\kappa'\gamma}$	$\tilde{C}_{\kappa\alpha\kappa'\gamma}(\mathbf{q})$	$Z^{*}_{\kappa'\gamma\alpha}$	$\Lambda_{\kappa'\gamma\alpha\beta}$
$\partial \mathcal{E}_{\gamma}$	$Z^{*}_{\kappa\alpha\gamma}$	$\varepsilon^{\infty}_{\alpha\gamma}$	$\bar{e}_{\gamma\alpha\beta}$
$\partial \eta_{\gamma\delta}$	$\Lambda_{\kappa\alpha\gamma\delta}$	$\bar{e}_{\alpha\gamma\delta}$	$C^{*}_{\alpha\beta\gamma\delta}$

Impacted by the DFT-D methods and implemented inside Abinit

In Practice

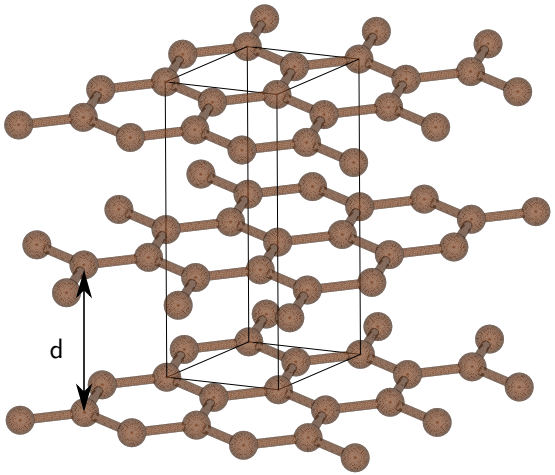

setvtr.F90
stress.F90
respfn.F90
Coordination Number (and derivatives)
If D2
CN_i ; dCN_i
Interpolation of dispersion coefficients
$C_{6,ij}$; $dC_{6,ij}$
Pair-wise term
Three-body dispersion term
$E_{disp}^{(2)}$
$E_{disp}^{(3)}$
E_{disp}; F^{κ}_{disp} ; $\sigma^{\alpha\beta}_{disp}$

In Practice


setvtr.F90
stress.F90
respfn.F90
Coordination Number (and derivatives)
If D2
CN_i ; dCN_i
Interpolation of dispersion coefficients
vdw_tol 1d-12
vdw_xc 5/6/7
$C_{6,ij}$; $dC_{6,ij}$
Pair-wise term
Three-body dispersion term
vdw_tol_3bt 1d-7
$E_{disp}^{(2)}$
$E_{disp}^{(3)}$
E_{disp}; F^{κ}_{disp} ; $\sigma^{\alpha\beta}_{disp}$

Ground-state

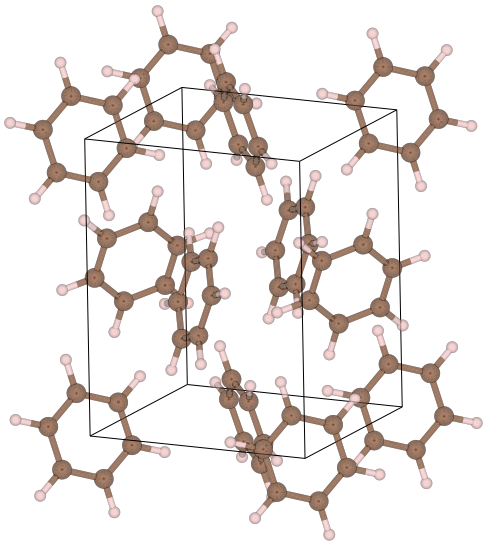
Graphite



	d [Å]	E_{coh} [meV/C]
DFT	4.4	-1.3
DFT-D2	3.21	-57.8
DFT-D3	3.48	-48.9
DFT-D3(BJ)	3.37	-53.9
OptB88-vdW	3.38	-69.5
TS-vdW	3.34	-82
Exp.	3.35	-52 $\pm$ 5

Benzene

Benzene



	Vol [Å^3]	E_{coh} [kJ/mol]
DFT	615.3	-9.3
DFT-D2	416.5	-56.3
DFT-D3	481.8	-47.4
DFT-D3(BJ)	465.5	-55.0
TS-vdW	456.6	-66.4
Exp.	462.5	-55.3

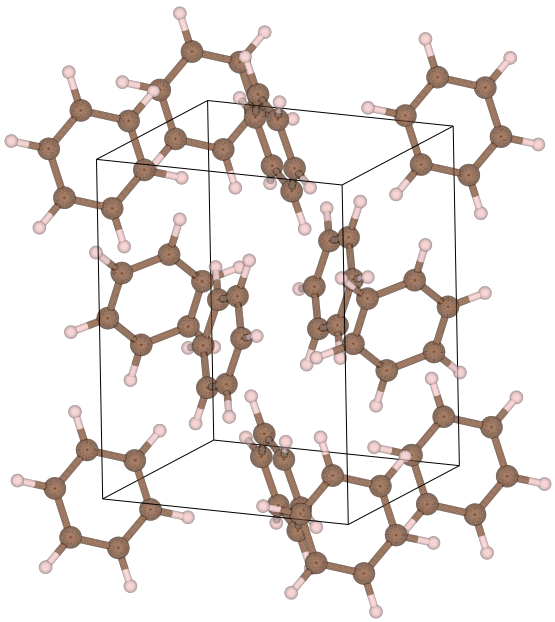
In general, same precision TS-vdW, vdW-DF and DFT-D

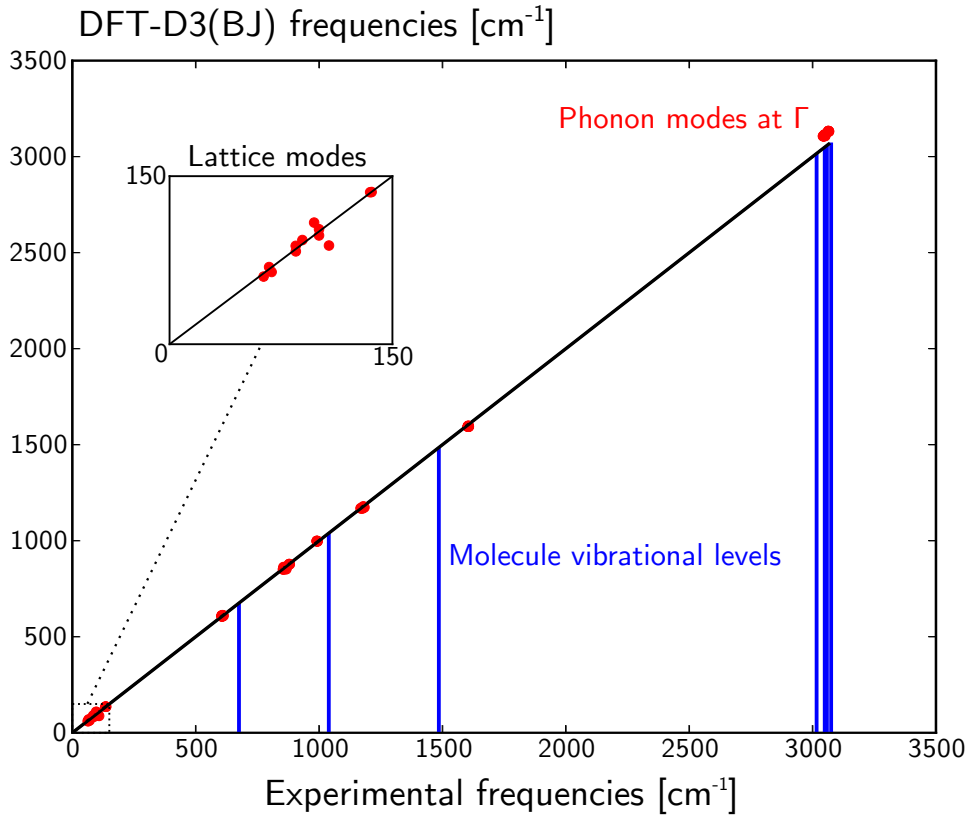
Best method is system dependant !

Phonons and vdW

Lattice modes = intermolecular phonon modes

For benzene molecular crystal:

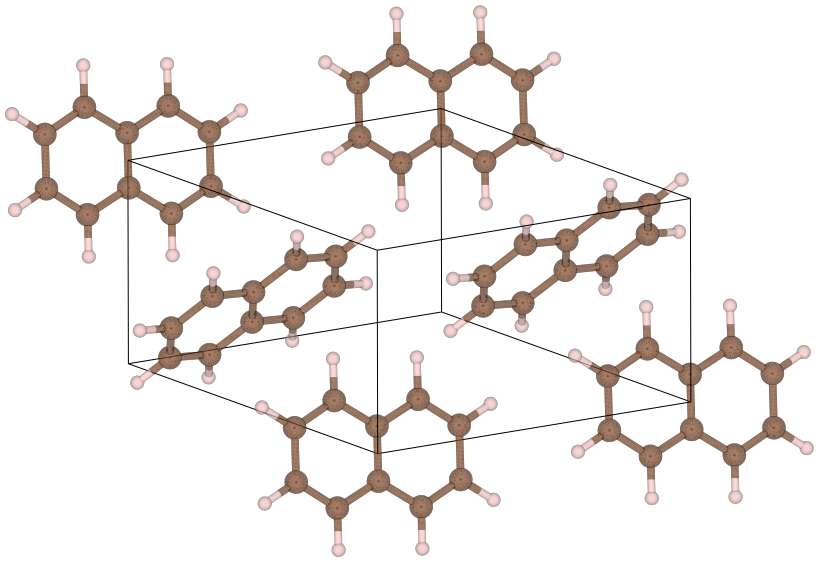


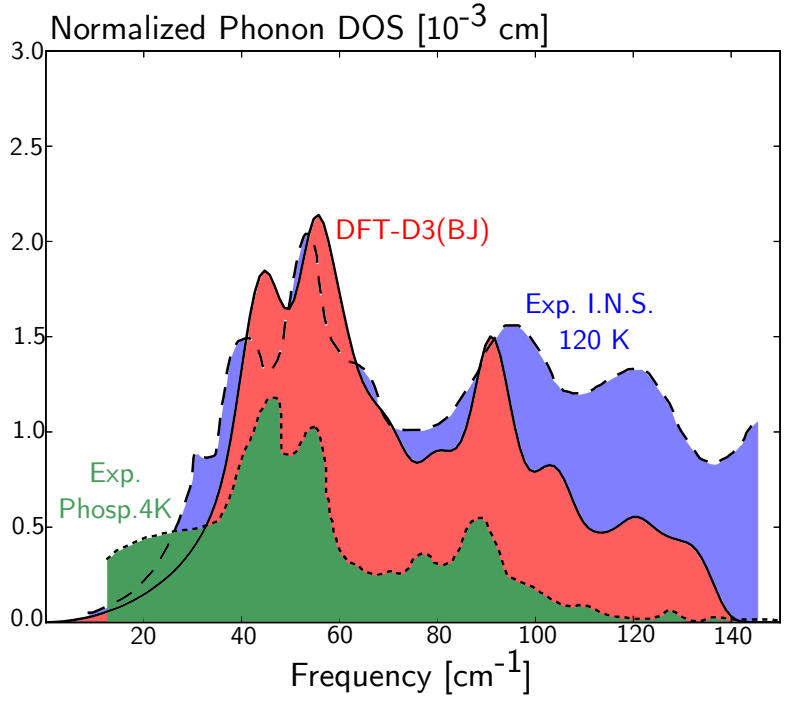


Small errors, very satisfactory

Phonons and vdW

For naphthalene molecular crystal:



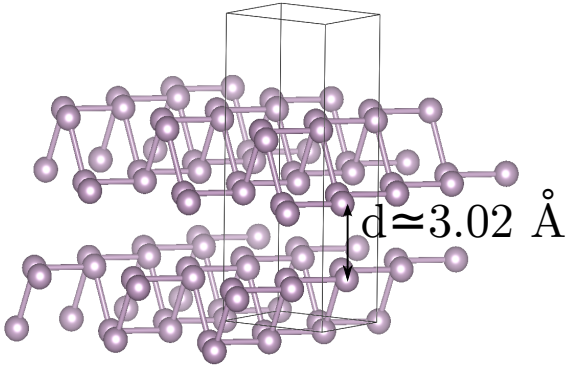


Convenient agreement with the experiments

But impact of temperature effects on phonons (anharmonicities) ?

Elastic constants and vdW

For black phosphorus (layered material):



	Elastic constants [GPa]		
	c_{33}	c_{22}	c_{55}
PBE	13.0	40.7	2.6
DFT-D2	73.0	52.3	8.8
DFT-D3	43.1	40.4	4.6
TS-vdW	30.6	36.8	23.4
Exp.	53.6	55.1	5.5

Elastic constants with vdW are...

Elastic constants and vdW

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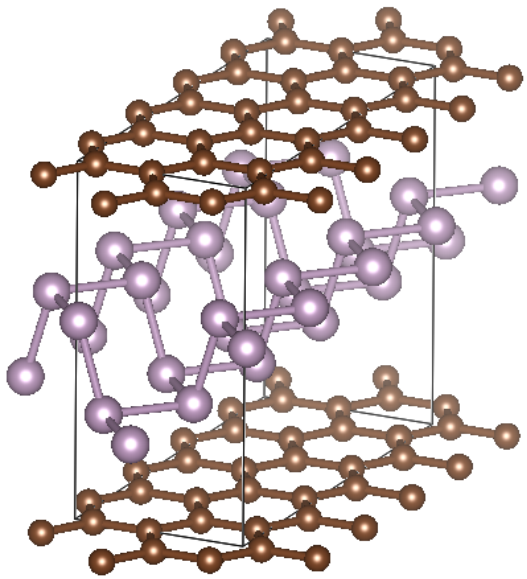
Exp.	53.6	55.1	5.5

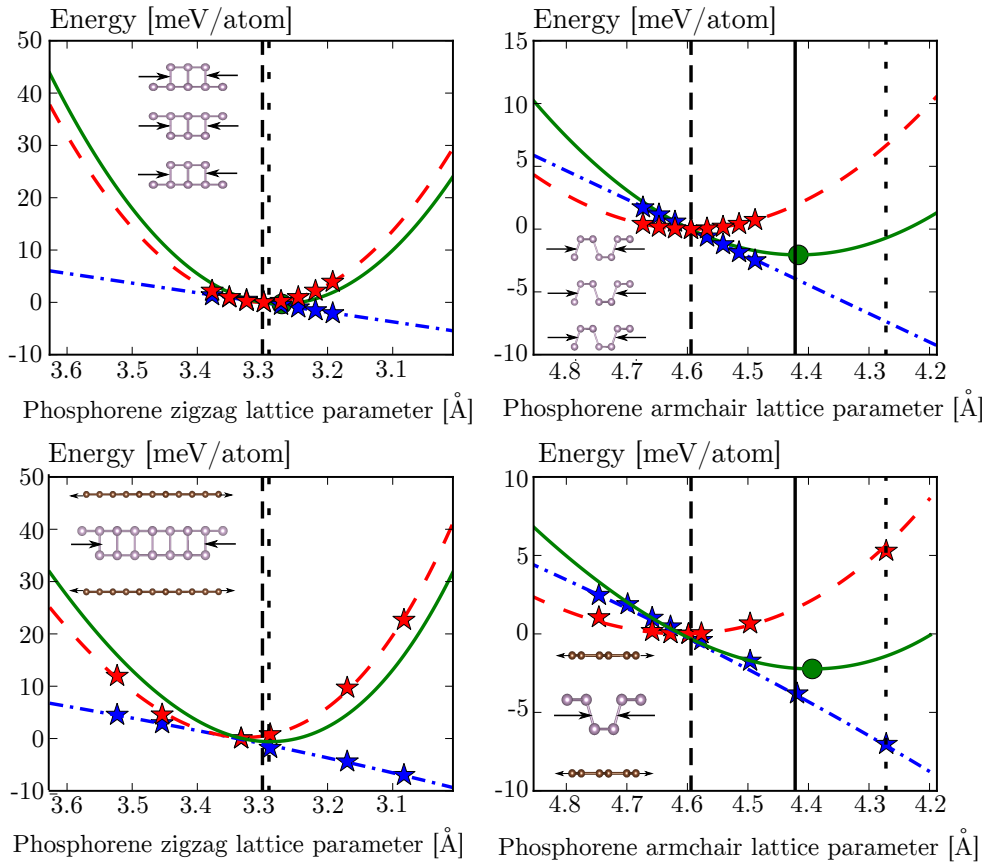
Elastic constants with vdW are... cat-astrophic !

Can we still do something with it ?

Elastic constants and vdW

Graphene-phosphorene vdW-heterostructure





Independance w.r. to density $\Rightarrow$ large systems (>1000 atoms)

What's next ?

Hottest theoretical method a.t.m.:

- Many Body Dispersion...
- ... based on self-consistent TS-vdW

$$E^{disp} = -\sum_{I,J} \frac{C_{6,IJ}[\rho(\mathbf{r})]}{R_{IJ}^6} f_{dmp}[\rho(\mathbf{r}), R_{IJ}]$$

Difficultie(s):

- Density must be interpolated, integrated + Hirshfeld each step
- Stress theorem becomes horrible

$\Rightarrow$ Some "clever" thinking before implementing

Conclusion

- DFT-D methods implemented in Abinit
- Fully-consistent with all parts of the code
- Accuracy in all crystals is a challenging issue
- Phonons look fine in general...
- ... but be Cautious with elastic constants !