Role of the vdWs interaction in DFPT and the Dynamic Charges in the TMDs

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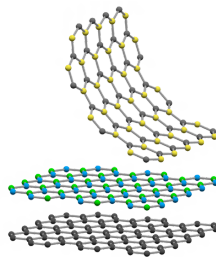1-CESAM and ETSF, Universite de Liege, Liege, 4000 Belgium
2-NAPS and ETSF, Universite catholique de Louvain, 1348 Louvain-la-Neuve, Belgium
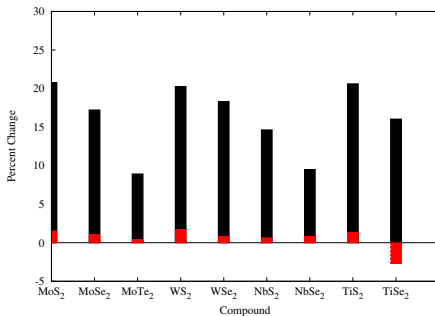
Abinit Developers Meeting 2017

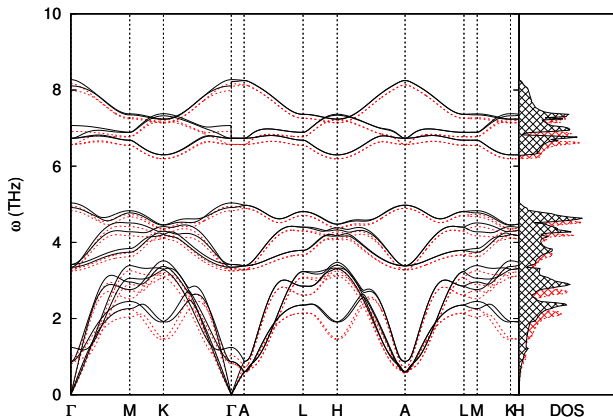Individual layers are semiconductors, metals, semi-metals...

Accurate calculations of two dimensional materials beyond Graphene requires better understanding of the bonding and charge transfer within these materials.

Structural Effects on the vdWs Functional

Percent change in the a and c lattice parameters with and without the vdWs functional during the relaxation calculation with GGA fhi98 NC pseudopotentials.

DFPT Effects of the vdWs Functional

Calculated phonon band structure with the vdWs functional during the DFPT calculation (in red) and with no vdWs functional during the DFPT calculation.

Accuracy of Phonon Mode Frequencies

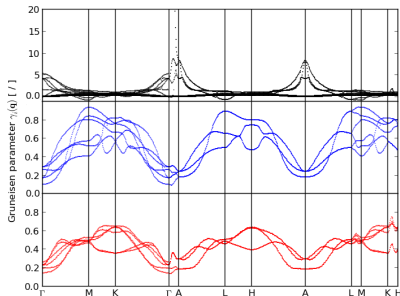|	Phonon Mode		vdW-D3 (THz)	vdW-D3(BJ) (THz)	Exp. (THz)
	E_{2g}	R	0.98	1.06	0.99
	E_{1g}	R	8.14	8.34	8.57
MoS_2	E_{2g}	R	10.89	11.16	11.31
	E_{1u}	IR	10.90	11.17	11.51
	A_{1g}	R	11.90	11.87	12.16
	A_{2u}	IR	13.46	13.67	14.08
	E_{2g}	R	0.71	0.94	0.72
	E_{1g}	R	5.17	5.16	5.32
WSe_2	E_{2g}	R	7.28	7.35	7.43
	E_{1u}	IR	7.28	7.35	7.34
	A_{1g}	R	7.48	7.52	7.52
	A_{2u}	IR	9.09	9.16	9.14
MAE[THz]			0.21	0.19	
MAPE [%]			2.90	4.93	

With two similar vdWs functionals we find slightly different phonon frequencies, D3 more accurate at low frequencies and D3(BJ) more accurate at high frequencies.

Phonon Mode Frequency Changes

The phonon mode frequencies can change due to:

1. the change in the lattice parameters during the structural relaxation, or

2. the introduction of the vdWs functional during the DFPT calculation.

To distinguish the two cases $\rightarrow$ use the (mode dependent) Grüneisen parameter ($MoTe_2$ shown here).

This, and other checks, indicate that inclusion of the vdWs functional during the DFPT calculation is critical for obtaining accurate phonon frequencies.

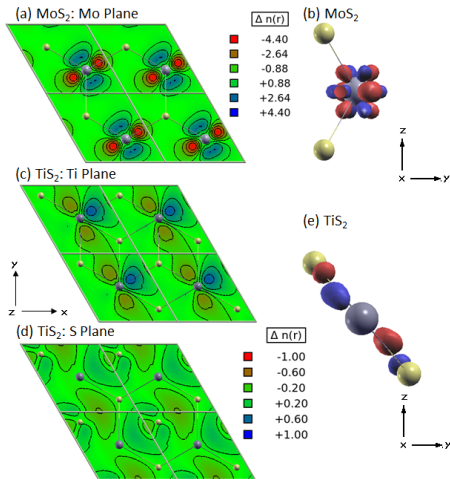# Interatomic Force Constants and Vibrational Properties

- As part of our Phonon and Raman calculations we also have access to various vibrational properties

- While agreement between these vibrational properties an experiment is rather good we found some interesting results...

Born Effective Charge

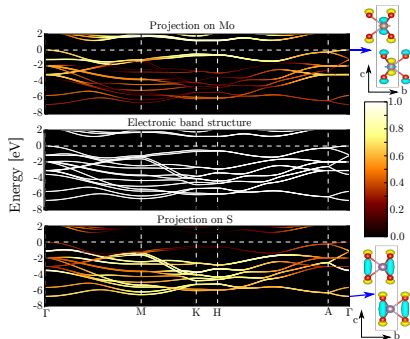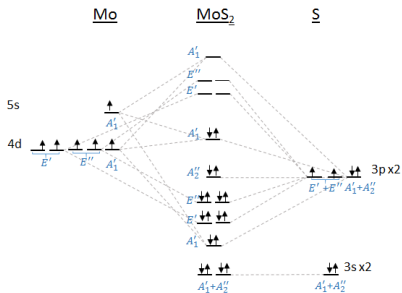|	Born effective charge [e]				Bader [e]	BPDC [e]
	This work		Exp.			
	$Z^*_{M,xx}$	$Z^*_{M,zz}$	$|Z^*_{M,xx}|$	$|Z^*_{M,zz}|$	$Z^B_{M,z}$	$Z^{B,*}_{M,z}$
MoS_2	-1.090	-0.628	1.1	0.4	1.155	0.635
$MoSe_2$	-1.906	-0.955	2.1	0.5	0.910	0.652
$MoTe_2$	-3.095	-1.544	3.4		0.575	0.752
WS_2	-0.491	-0.426	0.4	0.2	1.400	
WSe_2	-1.243	-0.776	1.7	0.5	1.081	
TiS_2	6.323	1.208	6.0	2.2	1.764	1.330
$TiSe_2$	6.122	0.855	9.2	2.1	1.599	

- Experimental measurements can only determine the magnitude of the BEC
- The Bader Partitioned Dynamic Charge (BPDC) is our finite-differences calculation of the Bader charge
- Electronegativity indicates charge should move from Mo to S (or Se, Te)

Localization of the Molecular Orbitals

(a) MoS₂: Mo Plane

(b) MoS₂

(c) TiS₂: Ti Plane

(e) TiS₂

(d) TiS₂: S Plane

Comparisons between hexagonal and trigonal TMDs indicate that a localized effect on the transition metal for MoS₂.

Molecular Orbital diagram

Conclusions

- The decrease in the phonon frequencies due to the inclusion of a vdWs functional indicates that the vdWs interaction softens the lattice.
  - Therefore, the vdWs interaction will modify other vibrational properties through the ifcs.
- We present the BEC for several compounds in which the sign of the BEC is opposite what one would expect based on the electronegativity of the individual atoms.
  - This sign change stems from the presence of an occupied antibonding orbital at the Fermi energy.
- We have also found small differences in the ifcs (via the phonon mode frequencies) for two related vdWs functionals (vdW-D3 and vdWs-D3(BJ))

Thank you for our attention!

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Reference:

Pike *et al.* "Origins of the Counterintuitive Effective Charges in the Transition Metal Dichalcogenides". PRB Rapid Comm. ACCEPTED (2017).

Pike *et al.* "Dynamic Properties of the Transition Metal Dichalcogenides: Part I" *In Preparation*

Pike *et al.* "Dynamic Properties of the Transition Metal Dichalcogenides: Part II" *In Preparation*