GRAPHENE FLAGSHIP

Full relativistic calculations on 2D materials

Ricardo Mendes Ribeiro

Workshop on correlations, criticality, and coherence in quantum systems
Évora 6-10 October 2014

European Commission

Universidade do Minho

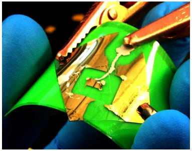
Summary

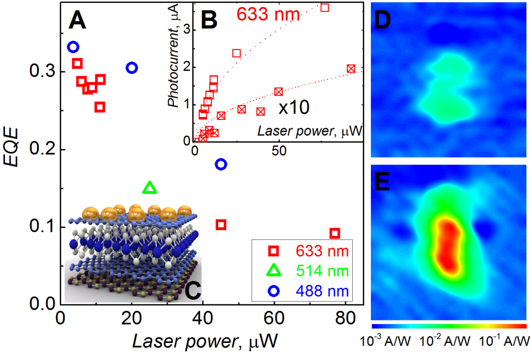
- Introduction and motivation
- Relativistic calculations
- The Transition Metal Dichalcogenides
- Optical conductivity: band nesting
- Conclusions and future developments

Photoelectric devices with TMDC

Heterostructure of 2D materials

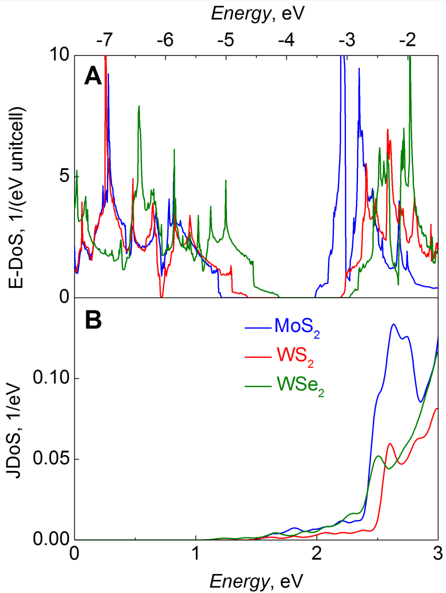
BN / Gr / TMDC / Gr / BN TMDC= MoS_2, WS_2, WSe_2





L. Britnell *et al.*, Science **340** (2013) 1311

- External quantum efficiency $\sim$ 30% (A)
- Larger quantum efficiency for lower intensities (B)
- Photocurrent increases 10x with gold nanoparticles (D, E)



L. Britnell *et al.*, Science **340** (2013) 1311

Full Relativistic Calculations

Basically, use Dirac KS equation instead of Schrödinger equation.

$$\left\{-i\hbar c\,\boldsymbol{\alpha}.\boldsymbol{\nabla} + (\beta - 1)\,mc^2 + v_s(\boldsymbol{r}) + \mu_B\beta\boldsymbol{\Sigma}\cdot\boldsymbol{B}_s(\boldsymbol{r})\right\}\phi_i(\boldsymbol{r}) = \varepsilon_i\phi_i(\boldsymbol{r})$$

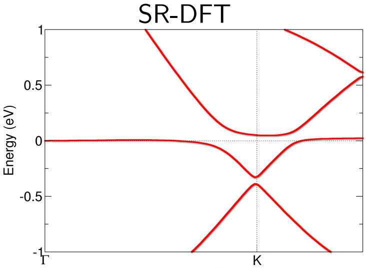
with the 4-component spinors:

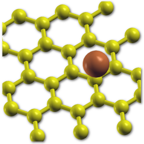
$$\phi_i(\boldsymbol{r}) = \begin{bmatrix} \phi_i^0(\boldsymbol{r}) \\ \phi_i^1(\boldsymbol{r}) \\ \phi_i^2(\boldsymbol{r}) \\ \phi_i^3(\boldsymbol{r}) \end{bmatrix}$$

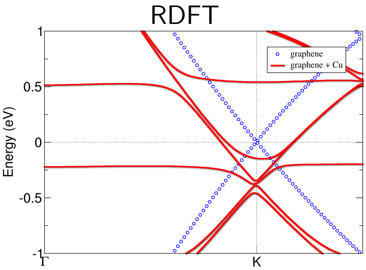
Atomic energy levels: Non-Relativistic, Scalar-Relativistic, Full-Relativistic

	nl	NR-DFT (eV)	SR-DFT (eV)	j	RDFT (eV)
C	2p	-5.2887	-5.2855	0.5	-5.2876
C	2p			1.5	-5.2789
Cu	3d	-5.2137	-5.0378	1.5	-5.2024
Cu	3d			2.5	-4.9324
Mo	4d	-3.9908	-3.7529	1.5	-3.8112
Mo	4d			2.5	-3.6085
W	5d	-5.8050	-4.4802	1.5	-4.6458
W	5d			2.5	-3.9348

Copper on graphene

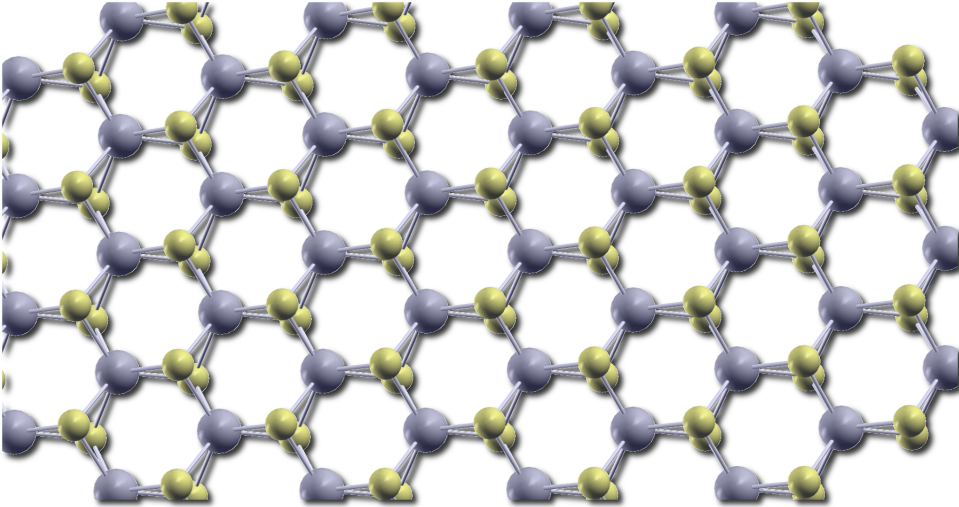






The differences are clear: even for a *light* system there is a notable Rashba-Dresselhaus effect.

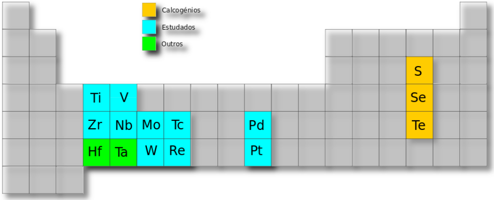
Transition Metal Dichalcogenides (TMDC)

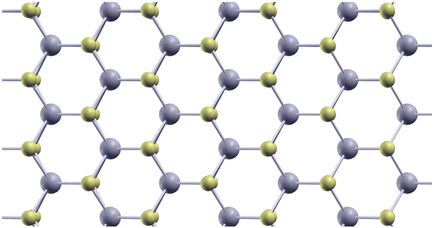


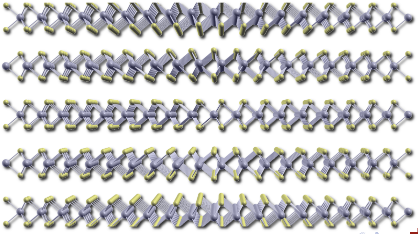
Transition Metal Dichalcogenides (TMDC)

Materials like: MX_2

M=transition metal; X=chalcogen







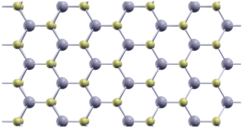
Easy to esfoliate

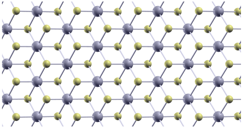
Transition Metal Dichalcogenides

Hexagonal structures

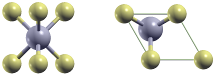
Materials of type: MX_2

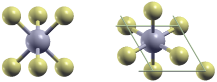
M= Ti, V, Zr, Nb, Mo, Tc, Pd, Hf, Ta, W, Re, Pt; X= S, Se, Te





Two types of structures:

Trigonal prismatic  No inversion

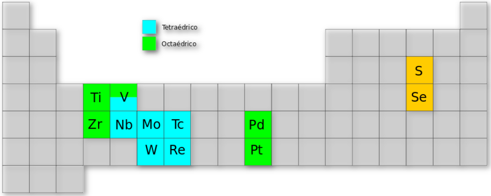
Octaedric  Has inversion

(side) (top)

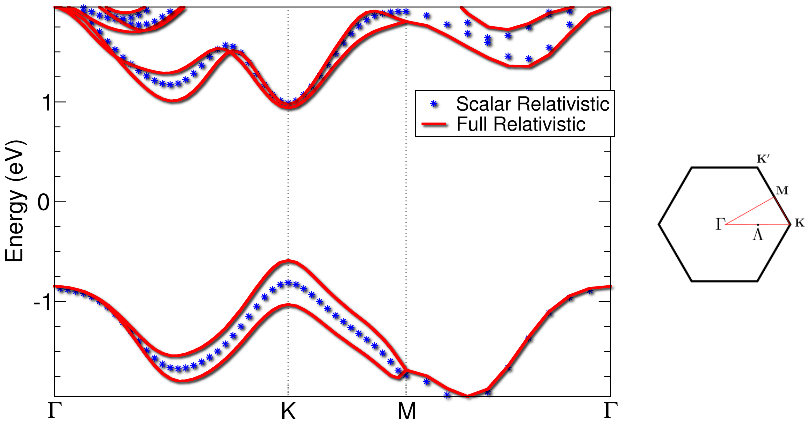
Trigonal prismatic (T-) or octaedric (O-)?

Which is the prefered structure? (Lattice parameters (Å) and relative energy $\Delta E = E_O - E_T$ (eV))

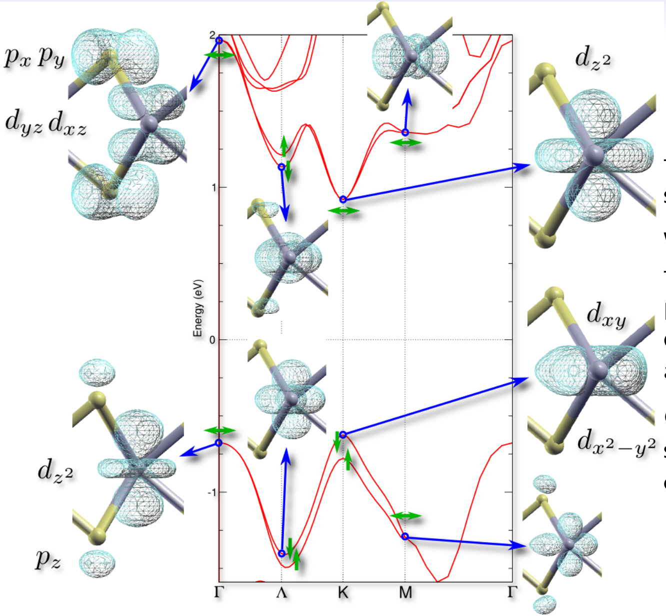
M	O-MS_2	T-MS_2	ΔE	O-MSe_2	T-MSe_2	ΔE
Ti	3.48	3.41	−0.40	3.40	3.38	−0.33
V	3.25	3.23	0.03	3.34	3.35	−0.01
Zr	3.74	3.64	−0.50	3.60	3.56	−0.39
Nb	3.42	3.40	0.12	3.52	3.52	0.10
Mo	3.22	3.23	0.81	3.33	3.37	0.68
Tc	3.13	3.32	0.35	3.24	3.48	0.31
Pd	3.61	–		3.76	–	
W	3.23	3.21	0.86	3.84	3.76	0.74
Re	3.15	3.33	0.24	3.23	3.48	0.26
Pt	3.61	3.54	−1.67	3.78	3.70	−1.28



Description of TMDC



Band diagram of WS_2, NR-DFT e RDFT calculations. On the right, the high symmetry points in the reciprocal space are shown.



MoS_2 monolayer, trigonal prismatic structure.

Wavefunctions in the signaled points of the band diagram (blue arrows).

Green arrows show the nature of the spin.

Electronic and optical properties

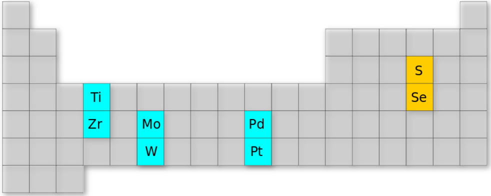
Among the TMDC single layers, we will take a look at the ones that are semiconductors.

These are, in trigonal form:

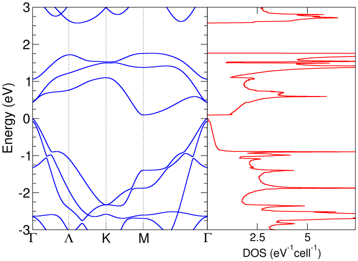
TiS_2, ZrS_2, MoS_2, WS_2, $TiSe_2$, $ZrSe_2$, $MoSe_2$, WSe_2.

And in octahedral form:

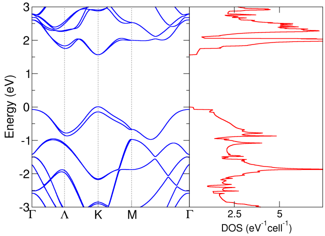
TiS_2, ZrS_2, PdS_2, PtS_2, $ZrSe_2$, $PdSe_2$, $PtSe_2$.



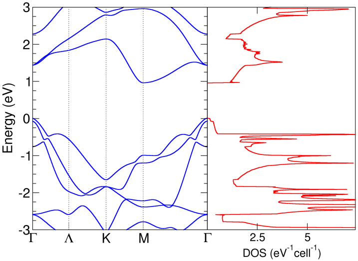
O-TiS_2



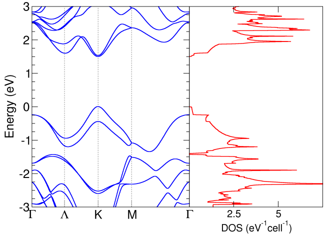
T-MoS_2



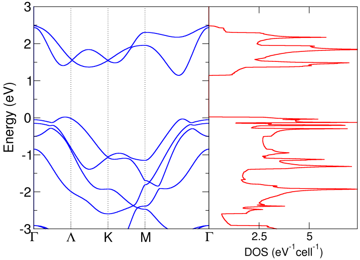
O-ZrS_2



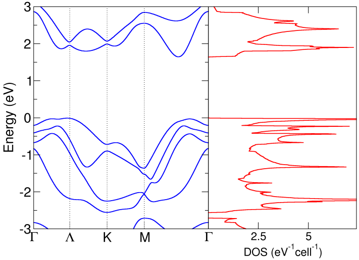
T-WS_2



O-PdS_2


3
2
1
0
-1
-2
-3
Energy (eV)
Γ
Λ
K
M
Γ
2.5
5
DOS (eV-1cell-1)

O-PtS_2


3
2
1
0
-1
-2
-3
Energy (eV)
Γ
Λ
K
M
Γ
2.5
5
DOS (eV-1cell-1)

Optical conductivity: *band nesting*

Critical points: $\nabla_k (E_c - E_v) = 0$.

$$\nabla_k E_c = \nabla_k E_v = 0 \Rightarrow \begin{cases} \text{maximum} \\ \text{minimum} \\ \text{saddle point} \end{cases}$$

on each band. These are the van Hove (VHS) singularities; give origin to peaks in the DOS. This, in general, can only occur in high symmetry points.

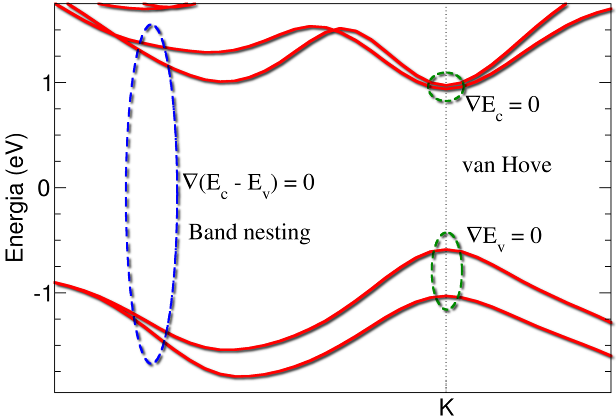
$$\nabla_k (E_c - E_v) = 0, \text{ com } |\nabla_k E_c| \approx |\nabla_k E_v| > 0, \equiv \textit{band nesting}$$

Phys. Rev. B 88 (2013) 115205

Can happen anywhere in the BZ.

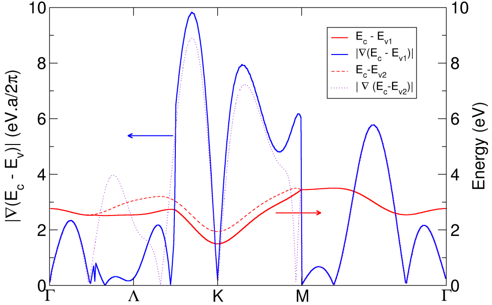
Band nesting × van Hove singularities

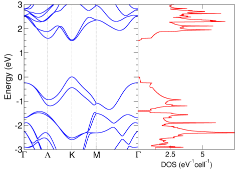
Critical points: $\nabla_k (E_c - E_v) = 0$

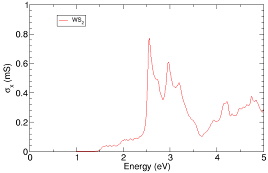


Charges move in opposite directions!

T-WS_2



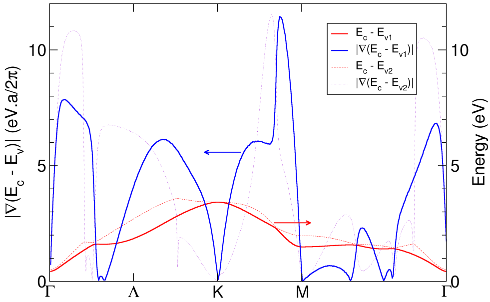


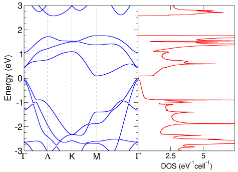


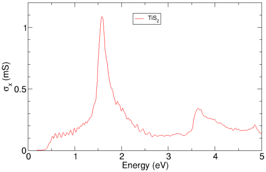
Criterium: $$\left|\nabla_k\left(E_c - E_v\right)\right| < 1 \text{ eV.a}/2\pi.$$

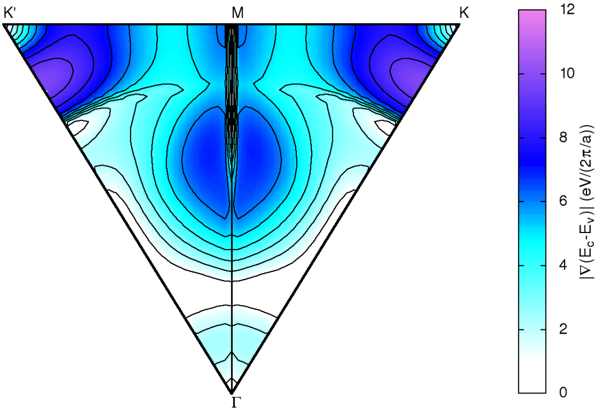
a is the lattice constant.

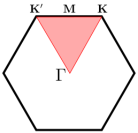
O-TiS_2


$|\nabla(E_c - E_v)|$ (eV.a/2π)
Energy (eV)
$E_c - E_{v1}$
$|\nabla(E_c - E_{v1})|$
$E_c - E_{v2}$
$|\nabla(E_c - E_{v2})|$
Γ
Λ
K
M
Γ
0
5
10

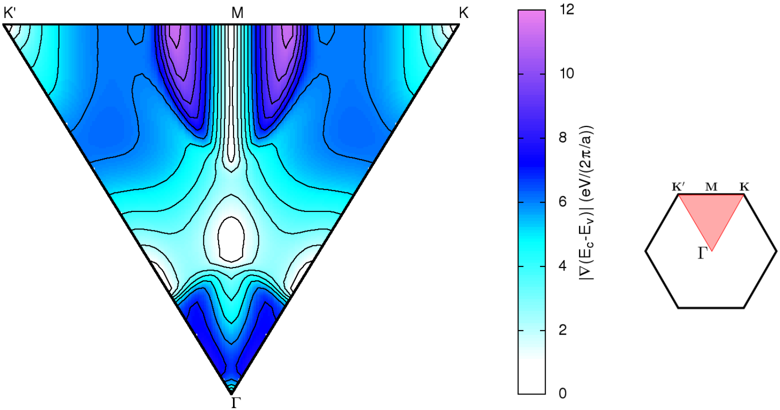

Energy (eV)
Γ
Λ
K
M
Γ
DOS ($eV^{-1}cell^{-1}$)
2.5
5


σ_x (mS)
Energy (eV)
TiS_2



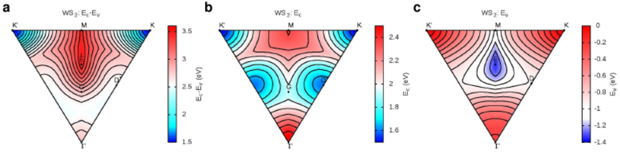


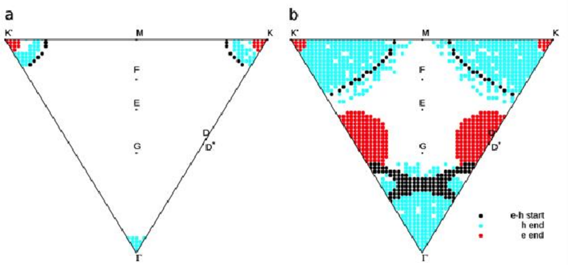
Map in BZ of $|\nabla_k (E_c - E_v)|$ for T-WS_2. a is the lattice constant.



Mapa na BZ de $|\nabla_k (E_c - E_v)|$ para o O-TiS_2. a is the lattice constant.

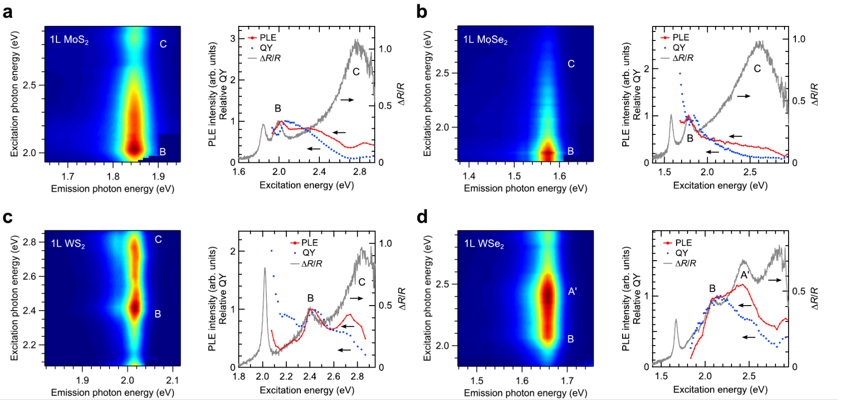
Monte-Carlo





Nat. Commun. 5:4543 doi: 10.1038/ncomms5543 (2014)

Experimental



PLE intensity map, PLE spectra, relative quantum yield (QE) of emission for band gap emission, and differential reflectance spectra.

Nat. Commun. 5:4543 doi: 10.1038/ncomms5543 (2014)

Conclusions and future developments

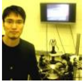
- Bi-dimensional materials will continue to surprise us with interesting properties;
- It is necessary to be alert to eventual relativistic phenomena;
- A simple criterion to find high optical absorption in materials has been established, for less obvious regions in the reciprocal space.

Collaborations / Sponsors

From NUS
Graphene Research Centre

António H. Castro Neto

Alexandra Carvalho



Goki Eda group (experiment)

From Manchester

Kostya Novoselov group (experiment)

GRAPHENE FLAGSHIP

European Commission

FCT Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR Portugal

QREN QUADRO DE REFERÊNCIA ESTRATÉGICO NACIONAL PORTUGAL 2007.2013

COMPETE

Governo da República Portuguesa

União Europeia - Fundos Estruturais

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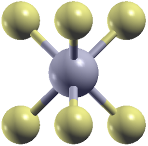
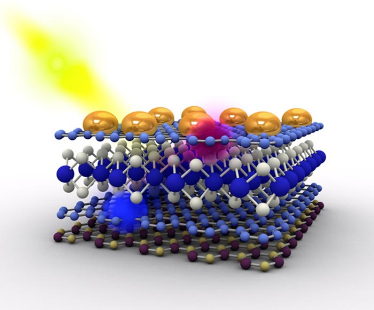
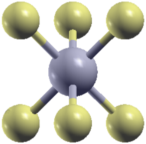
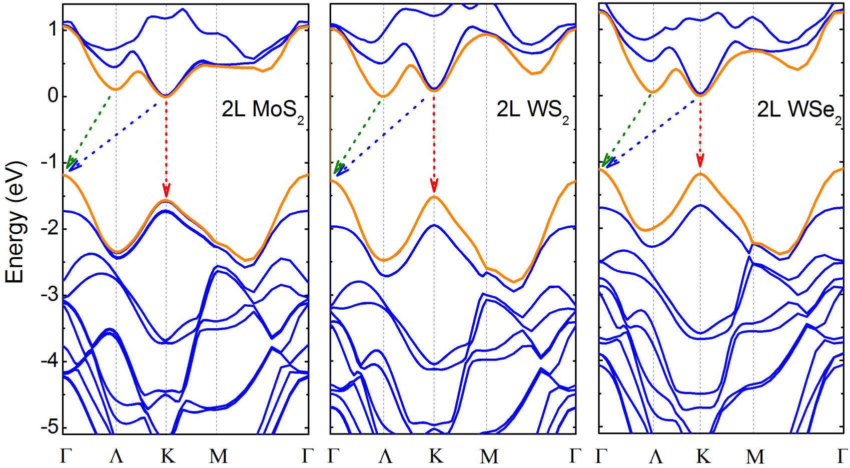
Thank you!





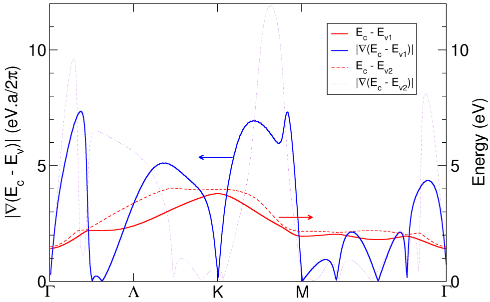


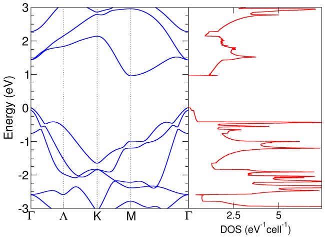
Bi-layers: observed transitions

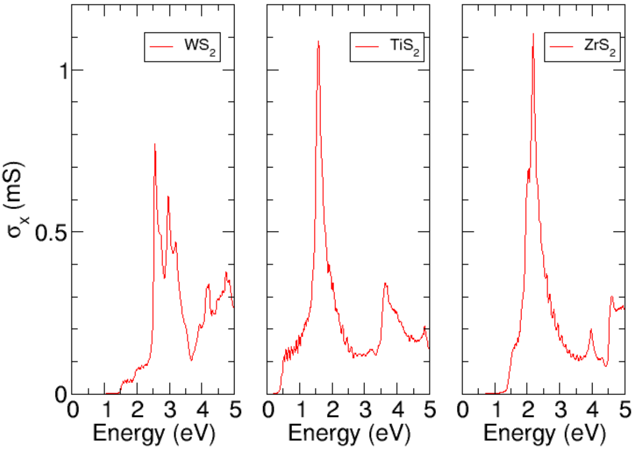


W. Zhao *et al.*, Nano Lett. 13 (2013) 5627

O-ZrS_2


E_c - E_v1
|∇(E_c - E_v1)|
E_c - E_v2
|∇(E_c - E_v2)|
|∇(E_c - E_v)| (eV.a/2π)
Energy (eV)
Γ
Λ
K
M
Γ


Energy (eV)
Γ
Λ
K
M
Γ
DOS (eV^-1cell^-1)



Real part of the optical conductivity of WS_2, TiS_2, e ZrS_2 single layers.