Electronic and Catalytic properties of MoS_2 Nanoplatelets: An *ab initio* study

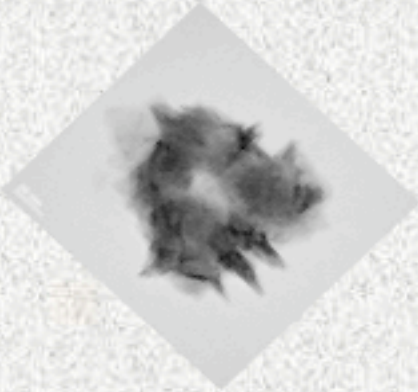
X. López-Lozano[1], S. Botti[1, 2],
M. A. L.Marques[3], M. Jose Yacaman[3], A. Rubio[4]

1. Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-DSM, F-91128 Palaiseau, France.
2. European Theoretical Spectroscopy Facility (ETSF)
3. LPMCN, Université Lyon 1, CNRS, Villeurbanne, France
4. Department of Chemical Engineering and Texas Materials Institute, University of Texas at Austin, USA.
5. Departamento de Física de Materiales, Facultad de Químicas, Universidad del País Vasco, Unidad de Física de Materiales Centro Mixto CSIC-UPV/EHU, and Donostia International Physics Center (DIPC), Apdo. 1072, 20018 San Sebastian, Spain.

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Nanoquanta Network of Excellence

Abstract



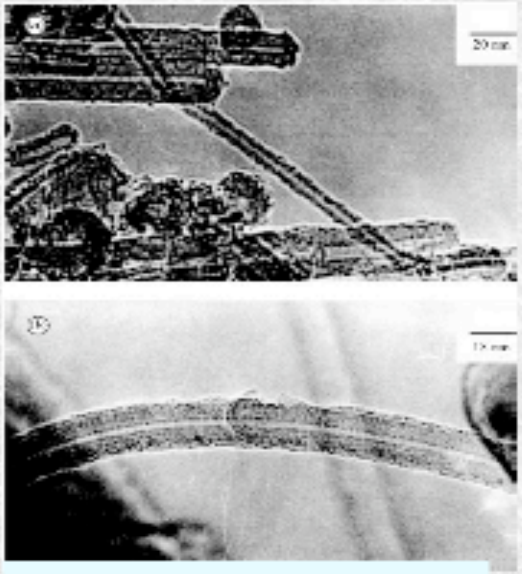
Catalysts based on MoS_2 are the most commonly used layered transition-metals-sulfides catalysts in petroleum refining. The study of the local active sites of these systems are of fundamental interest to understand and enhance their catalytic activity. MoS_2 nanostructures consisting on single/double-layer-structure are under experimental study because of their potential applications as nanocatalysts [1]. In this work we have performed *ab initio* density functional theory calculations using the ABINIT code [2] to determine the structural, electronic and catalytically active sites of **MoS_2 Nanoplatelets.** The calculated total energy of the optimized atomic structures reveals that the double-sheet models is more stable than the single-sheet model. The electronic band structures show the existence one-dimensional metallic states located at the nanoplatelet edges. Our results provide theoretical support to employ such nanostructures as a novel nanocatalyst.

Motivation

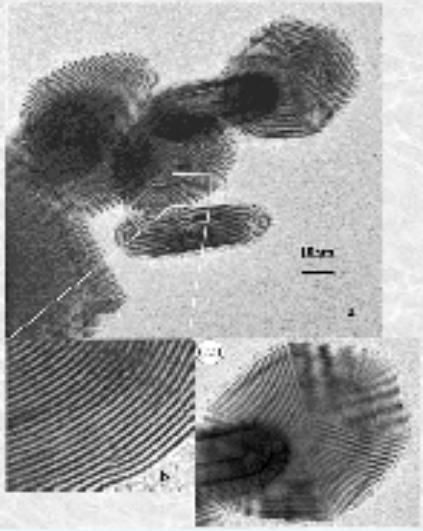
Why MoS_2 ?

A remarkable material !

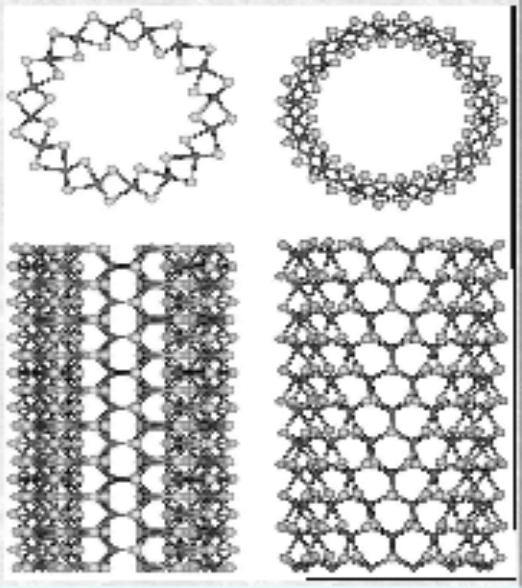
- **The ability to form nanotubes.**
  Like graphene, a single layer of MoS_2 can be warped into nanotubes.
- **Can work as a catalyst.**
  Catalysts based on MoS_2 particles are used on carbon-upgrading reactions like hydrodesulfurization (HDS).
- **It Is an effective solid lubricant.**
  MoS_2 fullerenelike particles have very low friction. Potential applications in space technology and ultrahigh-vacuum.
- **Can generate one-dimensional (1D) conducting-electron states.**
  Triangular single-layer MoS_2 nanocrystals/nanoclusters.



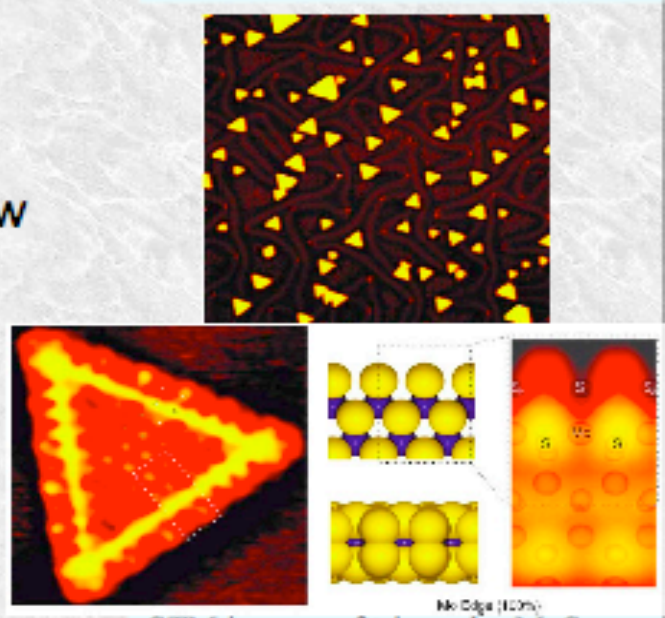
(a)Low-resolution TEM and (b) HREM images of MoS_2 Nanotubes [3]



MoS_2 nanoparticles [5]

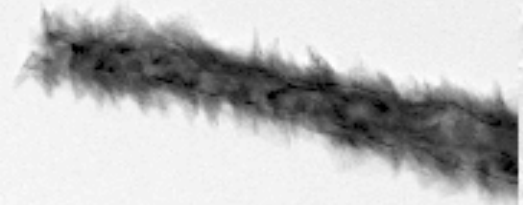


Armchair (8,8) (left) and zigzag (14,0) MoS_2 nanotubes. Light atoms are S, dark Mo.[4]

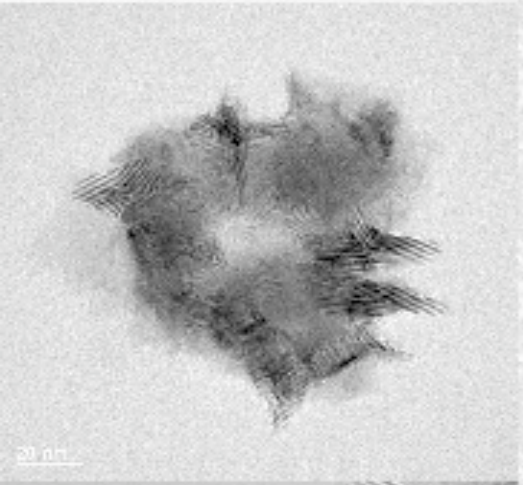


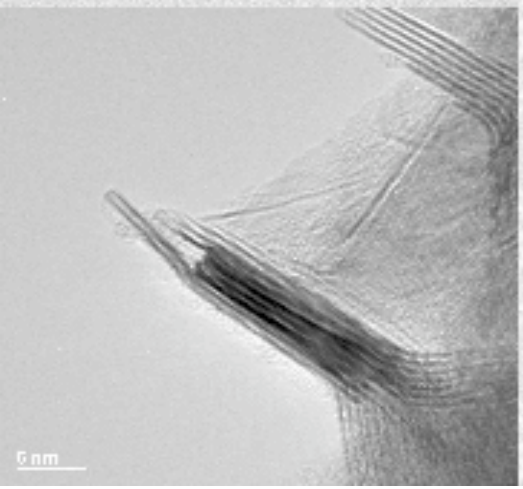
STM images of triangular MoS_2 nanoclusters on Au(111) [6]

MoS_2 Nanoplatelets



Core rode is MoO_2



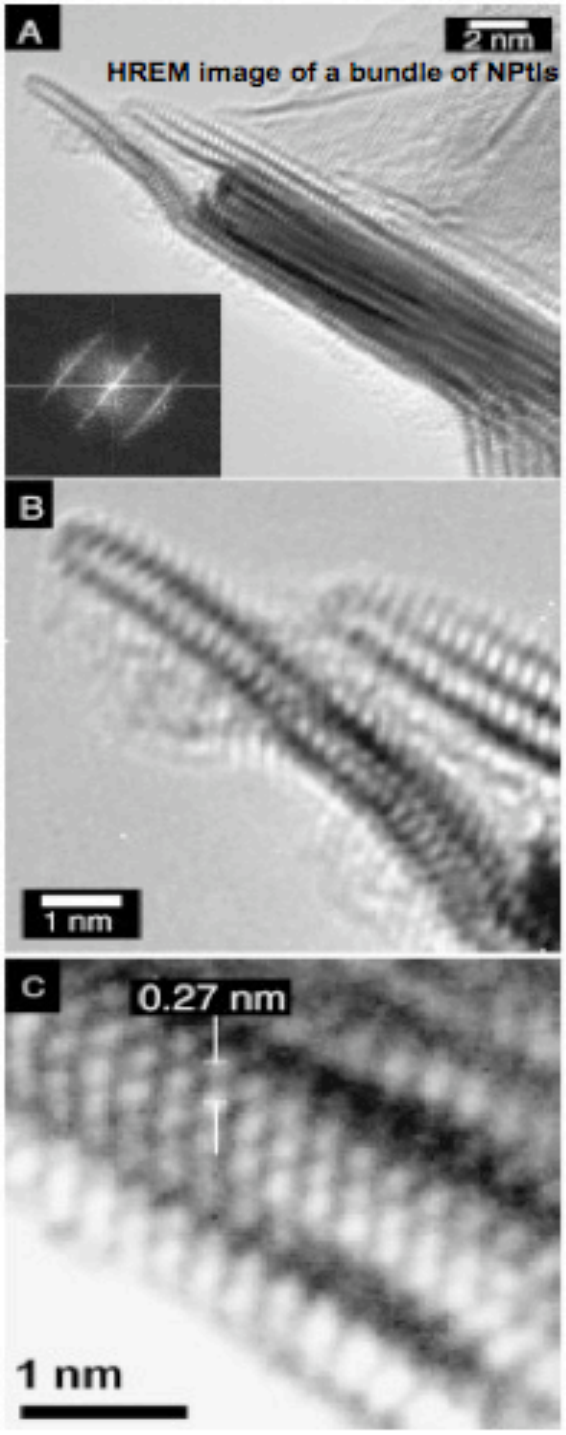


Nanostructures of MoS2 are of great interest for experimetalists

- Motivated by the need to develop better fuels and, as a consequence, better HDS catalysts, experimentalists synthesize nanostructures to study their catalytic properties.
- Single-layer transition metals like MoS_2 are of particular interest because their peculiar properties at nanometric size.
- Recently, pseudo-1D-structures of MoS_2 were proposed as potential nanocatalysts, they were named **nanoplatelets** [1].

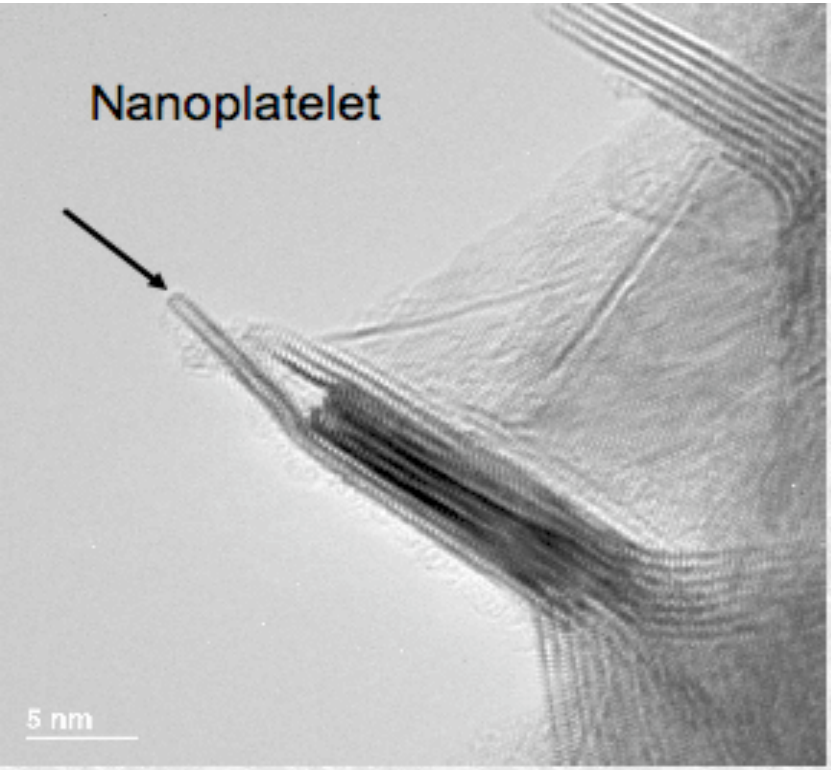
- MoS_2 nanoplatelets (NPtls) are composed of a solid MoO_2 core with MoS_2 crystallites nucleating on its surface.
- Most of the NPtls are 14 to 30 nm long and are about one MoS_2 unit cell.
- These pictures show different HREM (High-Resolution Electron Microscopy) images at different scales of the NPtls.

HREM images were provided by J. Yacaman from the Department of Chemical Engineering and Texas Materials Institute, University of Texas at Austin, USA.



A closer look to MoS_2 NPtls

- NPtls look like needles that grow well off the core surface and can be seen as single entities (A), a NPtl.
- NPtls can be also regarded as nanowires with a thickness of a half of the regular MoS_2-2H unit cell (B).
- A resolved HREM image of a NPtls shows that the atoms are configured in an hexagonal array (C), similar to the bulk.
- In analogy with MoS_2 triangular clusters, NPtls might be used as new nanocatalyst due to the properties of their edge states (like metallic brim-sites) [1].
- Preliminar results of the electronic structure suggested a metallic behavior [1]. However, a complete and detailed theoretical study was still missing.

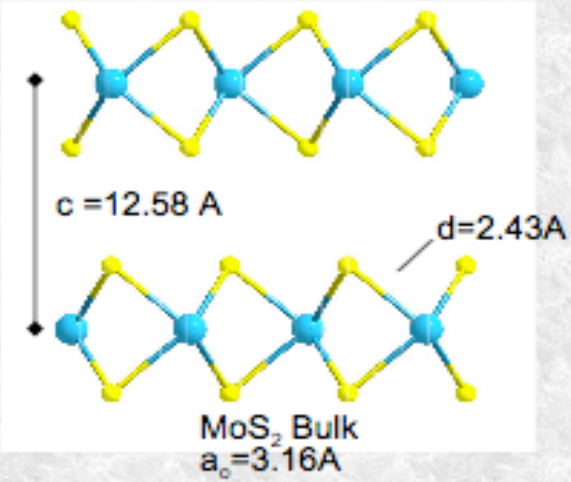


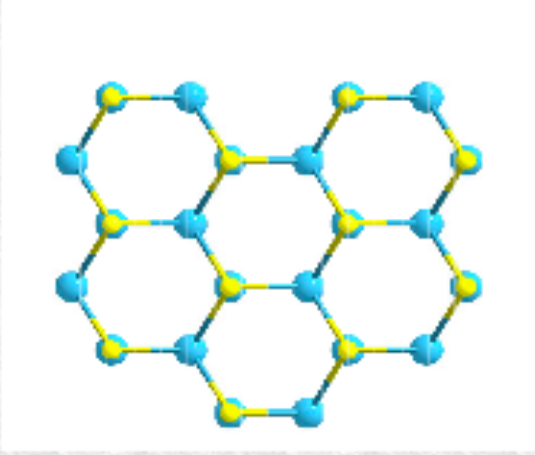
Modeling MoS_2 nanoplatelets

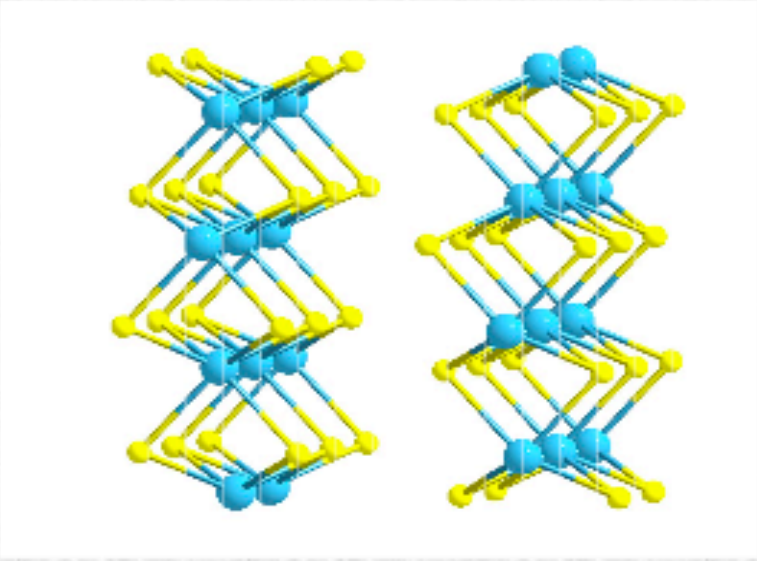
- Bulk MoS_2 is a layered material and a single layer consist of a S-Mo-S sandwich.
- In each layer the Mo atoms are arranged in an hexagonal lattice.
- Each Mo atom is six-fold coordinated by S atoms.
- A single layer can be terminated by two different low-Miller index edges:

the sulfur-terminated $(\bar{1}010)$ edge (S edge)

the molybdenum-terminated $(10\bar{1}0)$ edge (Mo edge)







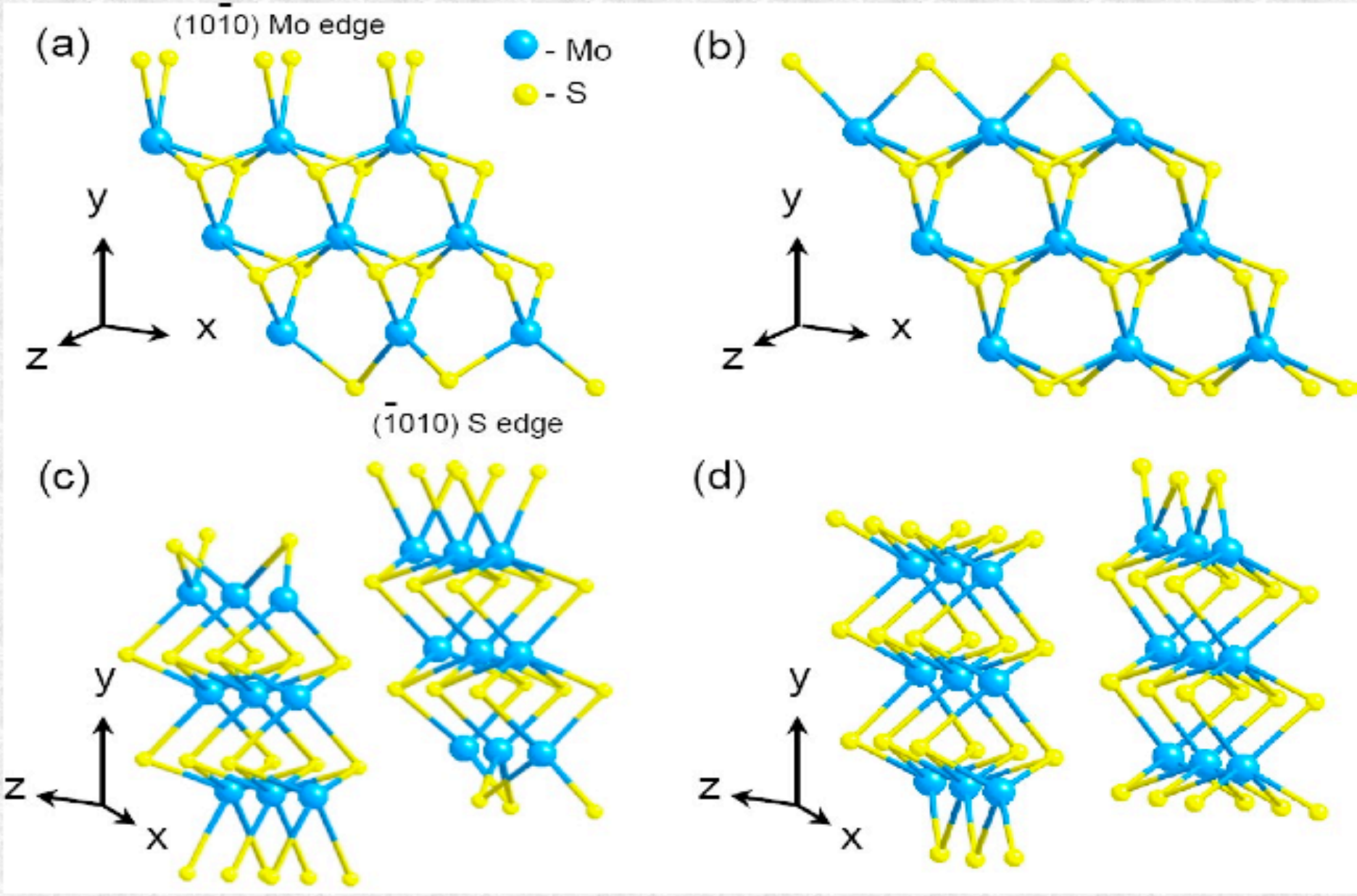
Modeling MoS_2 nanoplatelets

Calculational Method

- The *ab initio* calculations are performed within density functional theory (DFT) using the code ABINIT [2].
- We use norm-conserving Troullier-Martin pseudopotentials and the generalized gradient approximation (GGA) from Perdew-Burke-Ernzerhof to describe the exchange and correlation potential.
- A Monhorst-Pack type mesh (4 k points) is used to sample the Brillouin zone, and a cut off energy of E_{cut}= 20 Ha is set for the plane waves.
- To model the Nptls we employ a supercell. The supercell consists of two S-Mo-S trilayers. Each S-Mo-S sandwich consists of three rows of MoS_6 stacked in the y direction. The neighboring units are separated by a vacuum layer of 12 A. Two different sulfur coverages are taken into account.
- A supercell consisting of 60 atoms (18-Mo,42-S) for 50% sulfur-coverage and one of 66 atoms (18-Mo, 48-S) for 100% sulfur-coverage are used.
- In our calculations all the atomic positions are allowed to relax until the Hellmann-Feynman forces are less than 0.1 mH/bohr.

Supercells

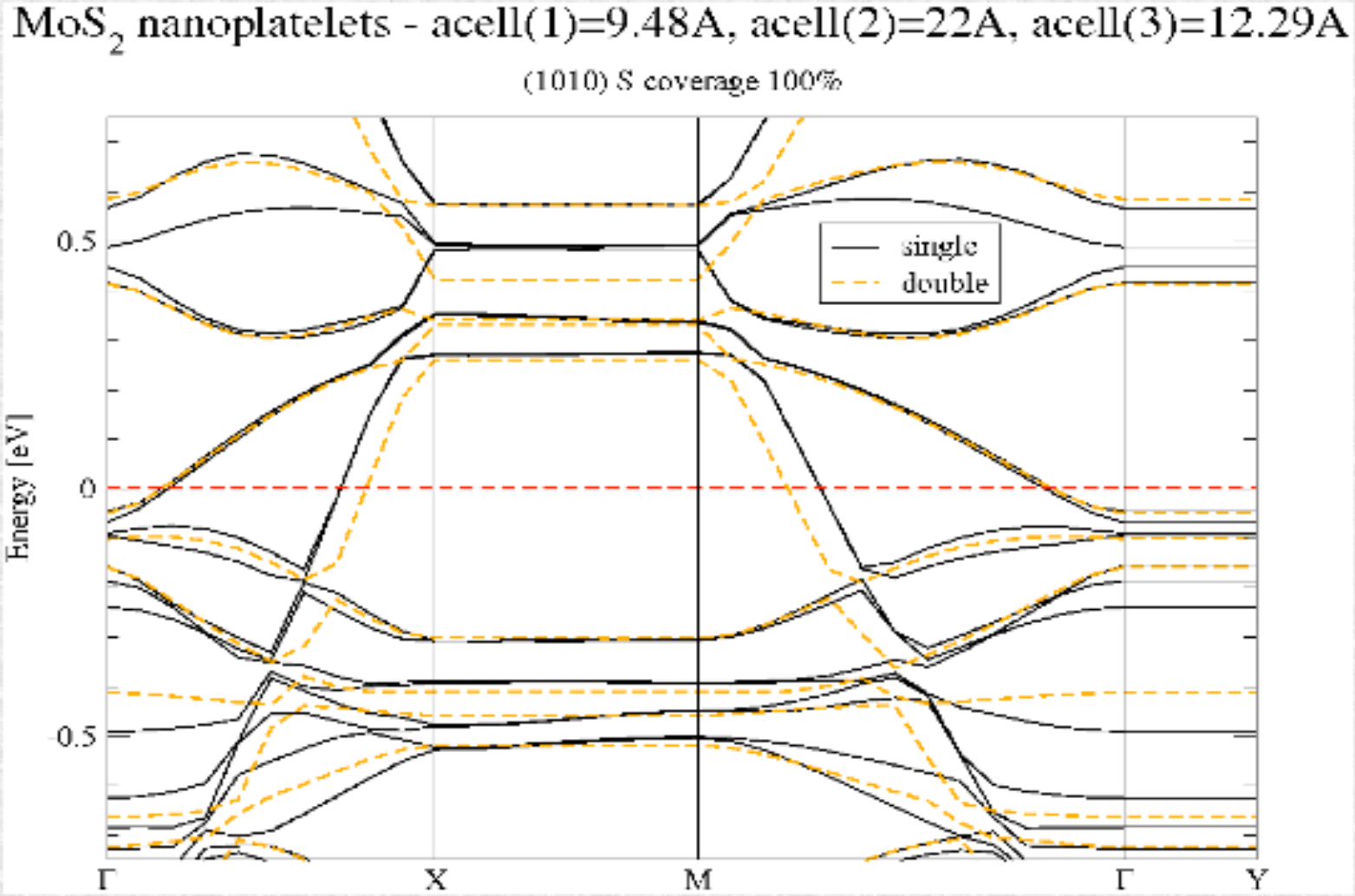
The atomic model of MoS_2 NPtls



Comments and Objetives

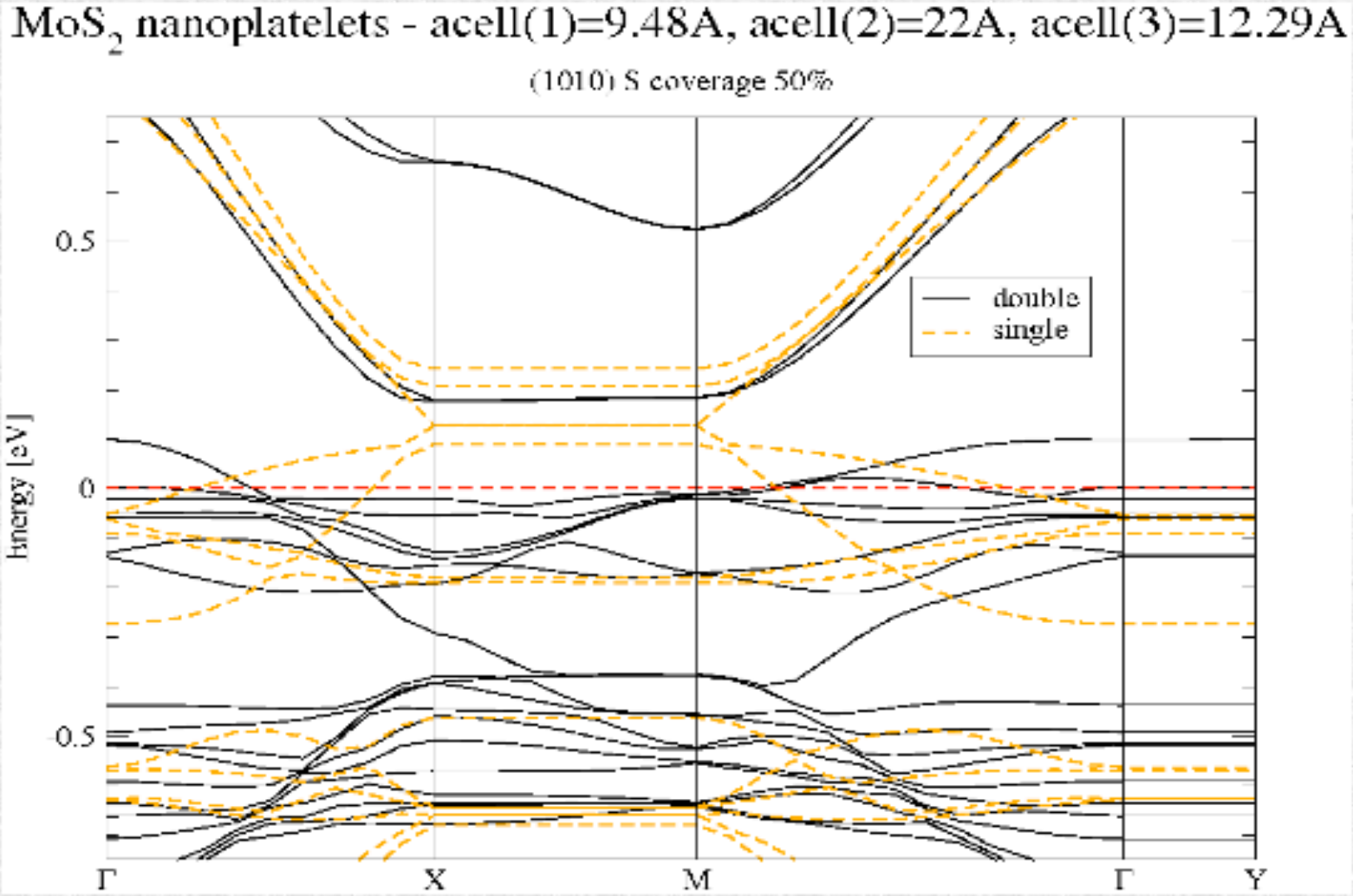
- The transition-metal oxides and sulfides are two important classes of catalytically active materials. A lot of effort is employed on the synthesis of new nanostructured MoS_2- based materials like nanoclusters [6] and nanoplatelets[1].
- The chemical catalytic activity is often explained in terms of the geometric coordination of the surface-edge atoms.
- Low-coordinated point defects with a high affinity towards bond formation are the key ingredient of catalytic reactions (like sulfur vacancies).
- Anion vacancies play an important role on the catalytic activity of MoS_2-based catalysts used in HDS processes [6].
- Motivated by the new kind of chemical activity associated with fully sulfur-saturated active sites on two-dimensional MoS_2 nanoclusters [7], we decided to investigate the electronic and catalytical properties of MoS_2 nanoplatelets.

Nanoplatelet band structure: 100% S-coverage



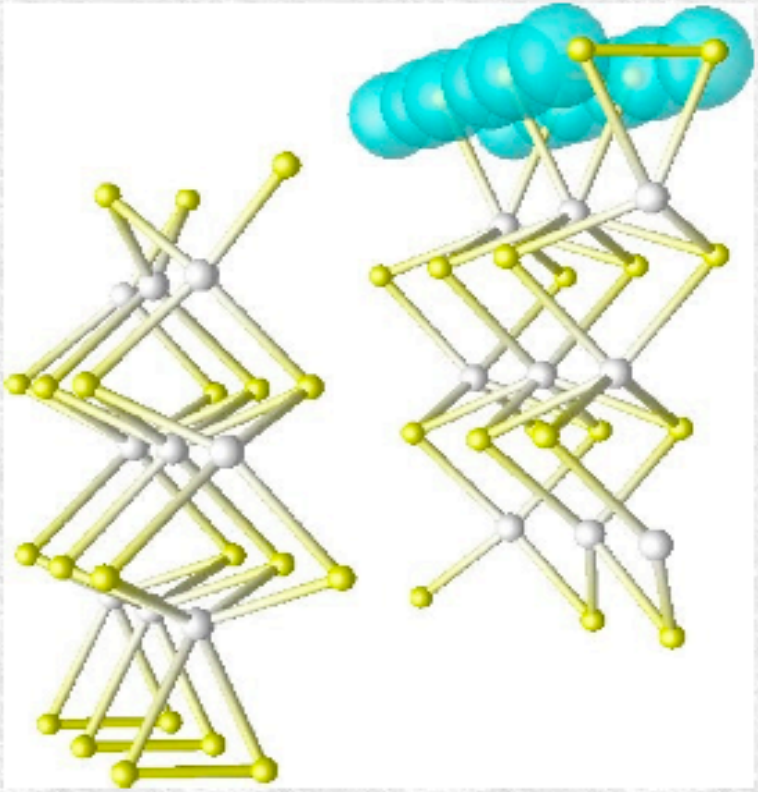
Comparison between single- and double-sheet geometries

Nanoplatelet band structure: 50% S-coverage

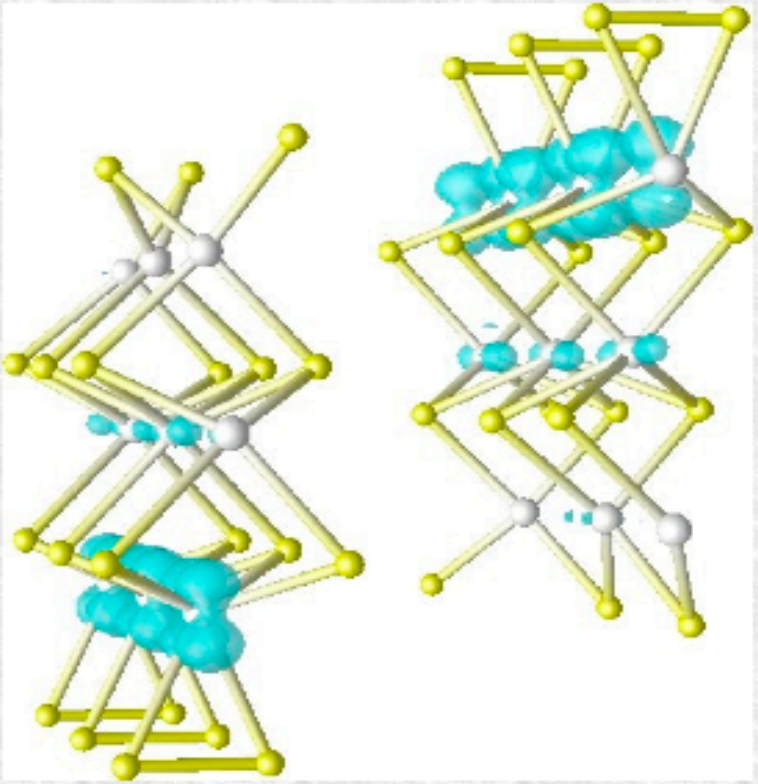


Comparison between single- and double-sheet geometries

Wavefunctions at E_F : 100% S-coverage

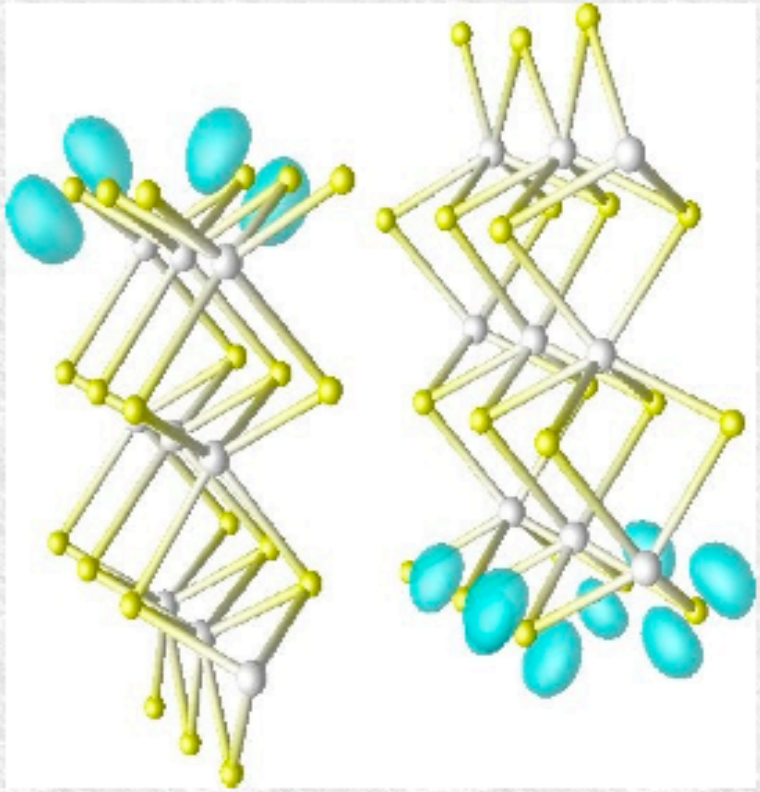


1D-metallic states localized at the sulfur dimers

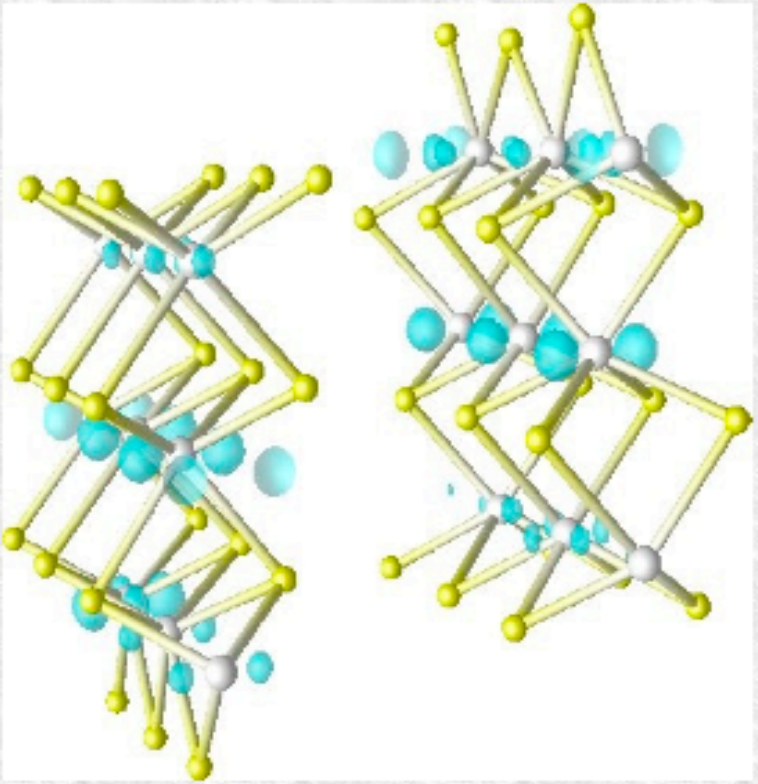


Metallic surface-resonance states localized at Mo atoms

Wavefunctions at E_F : 50% S-coverage



1D-metallic states localized at the S-edge



Metallic surface-resonance states localized at Mo atoms

Results

- The search of catalytic active sites or coordinatively unsaturated sites are our initial objetives. We chose two different models with different sulfur saturation (100%-S and 50%-S) for both single and double-sheet MoS_2. In the case of double-sheets we explored the effect of different separation distances.
- In analogy with nanoclusters, we found localized low dimensional-metallic electron-states at the NPtl edges, which can be considered as the actives catalytic sites (brim sites [7]).
- Our results show clearly a metallic character for both sulfur coverages. Sulfur dimers (disulfide bonds) and monomers at bridge sites relax like in the case of the MoS2 $(\bar{1}010)$ edge-surface.
- The double-sheet structure also remains similar to the bulk, though the bond lengths decreased slightly (0.1A).
- Double-sheet nanoplatelets are always more stable than single-sheet counterparts.

References

[1] G. A. Camacho-Bragado *et al.*, J. Catal. 234 (2005) 182-190 and references in there.

[2] http://www.abinit.org

[3] M. Nath *et al.*, Adv. Mat. 13, 283 (2001).

[4] Gotthard Seifert *et al.*, Physical Review Letters **85**, 146 (2000).

[5] Zak *et al.*, J. Am Chem. Soc. **124**, 4747 (2002).

[6] Jeppe V. Lauritsen *et al.*, Catalysis Today **111** (2006) 34-43.

[7] Jeppe V. Lauritsen *et al.*, Nature Nanotechnology 2, 53-58 (2007).

[8] M. V. Bollinger *et al.*, Phys. Rev. B **67**, 085410 (2003).

[9] X. Lopez-Lozano, S. Botti, M. A. L. Marques, M. J. Yacaman, and A. Rubio, in preparation (2008).