Chalcogenides: From Nanoflakes to 2D Solids

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Acknowledgments:

Center for Innovation on New Energies
Division 4: Computational Material Science and Chemistry

CINE
CENTER FOR INNOVATION ON NEW ENERGIES

CINE HUB (Executive Committee, Executive Manager, …..)

UFABC · unesp UNIVERSIDADE ESTADUAL PAULISTA JÚLIO DE MESQUITA FILHO" · USP · UNIFESP · ufscar

Juarez L. F. Da Silva
+
Co-PI

1. Project Management Office – IQSC (FAPESP)
2. USP Foundation– FUSP (SHELL)
3. CMSC Coordination Assistant – IQSC
4. IQSC Computational Analist (8 hours/week)
5. IQSC staff (events, secretary, ….)

~50 pesquisadores

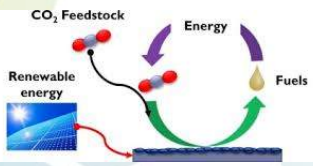
Project 16
PI, Co-PI, AI, Students

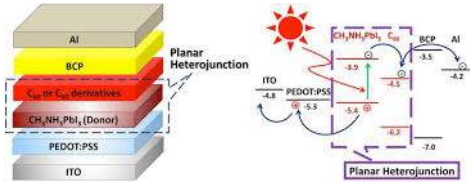
Project 17
PI, Co-PI, AI, Students

Project 18
PI, Co-PI, AI, Students

Project 19
PI, Co-PI, AI, Students

Project 20
PI, Co-PI, AI, Students





QTNano: Projects of Interest

– H_2 production: ethanol, methanol, glycerol, etc.

– Solar cells based materials: Chalcogenides, perovskites, transparent conducting oxides, etc.

– CO_2 reduction on nanocatalysts: unsupported and supported transition-metal particles (oxides, chalcogenides), etc.

– CH_4 conversion to high-value products, e.g., methanol, carbon-nanostructures, etc.

– Global optimization algorithms: BHMC and genetic algorithms, etc.

– Machine learning techniques applied in the investigation of material science properties.

QTNano Members and Structure

-Posdocs

Dr. Augusto C. R. Da Silva
Dra. Karla F. Andriani
XXX (01.01.2019)
XXX (01.01.2019)

-PhD students – Supervisor

Larissa Z. Besse.
Rafael C. Amaral.
Naidel A. M. S. Cuturello.
Rafael Besse
Paulo de C. D. Mendes
Vivianne K. O. Restrepo
Priscilla F. Sousa
Mailde da Silva Ozório
Johnatan Mucelini

QTNano physical space: ~80 m²
18 L-shaped + 2 linear tables; no-break system

- IC students – Supervisor

Ahmad Fort (**Rafael C. Amaral**), sem bolsa.
Victor M. P. Da Silva (**Larissa**), bolsa PUB USP
Matheus N. Collacique (**Vivianne**), bolsa PUB USP.
Henrique A. B. Fonseca (**Dr. Augusto**), FAPESP.
Leonardo S. Delacqua (**Naidel**), bolsa FAPESP.
Mariana C. Galego (**Johnatan/Mailde**), bolsa PET
Guilherme K. Inui (**Rafael Besse**), bolsa FAPAESP.
Vinicius L. Capucin (**Dra. Karla**), bolsa PUB USP.
Eduardo O. Bartaquim (**Paulo Mendes**), bolsa CNPq.
Guilherme S. Marcon (**Juarez**), bolsa XXX.

Open Positions: Postdocs

-PhD students – Co-Supervisor

Carlos M. O. Bastos (Prof. Guilherme M. Sipahi - USP)
Krys E. A. Batista (Prof. Maurício J. Piotrowski - UFPel)

THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

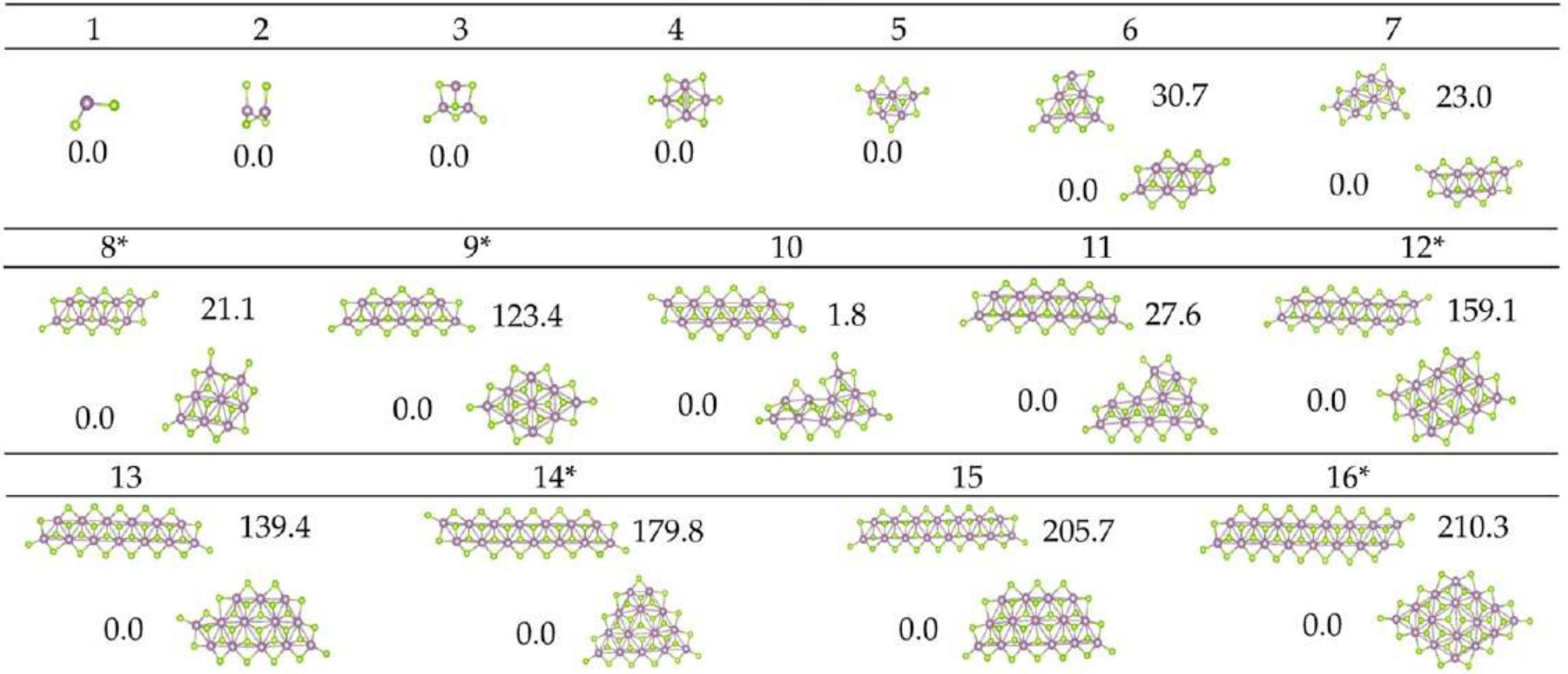
Cite This: J. Phys. Chem. C 2018, 122, 20483−20488

pubs.acs.org/JPCC

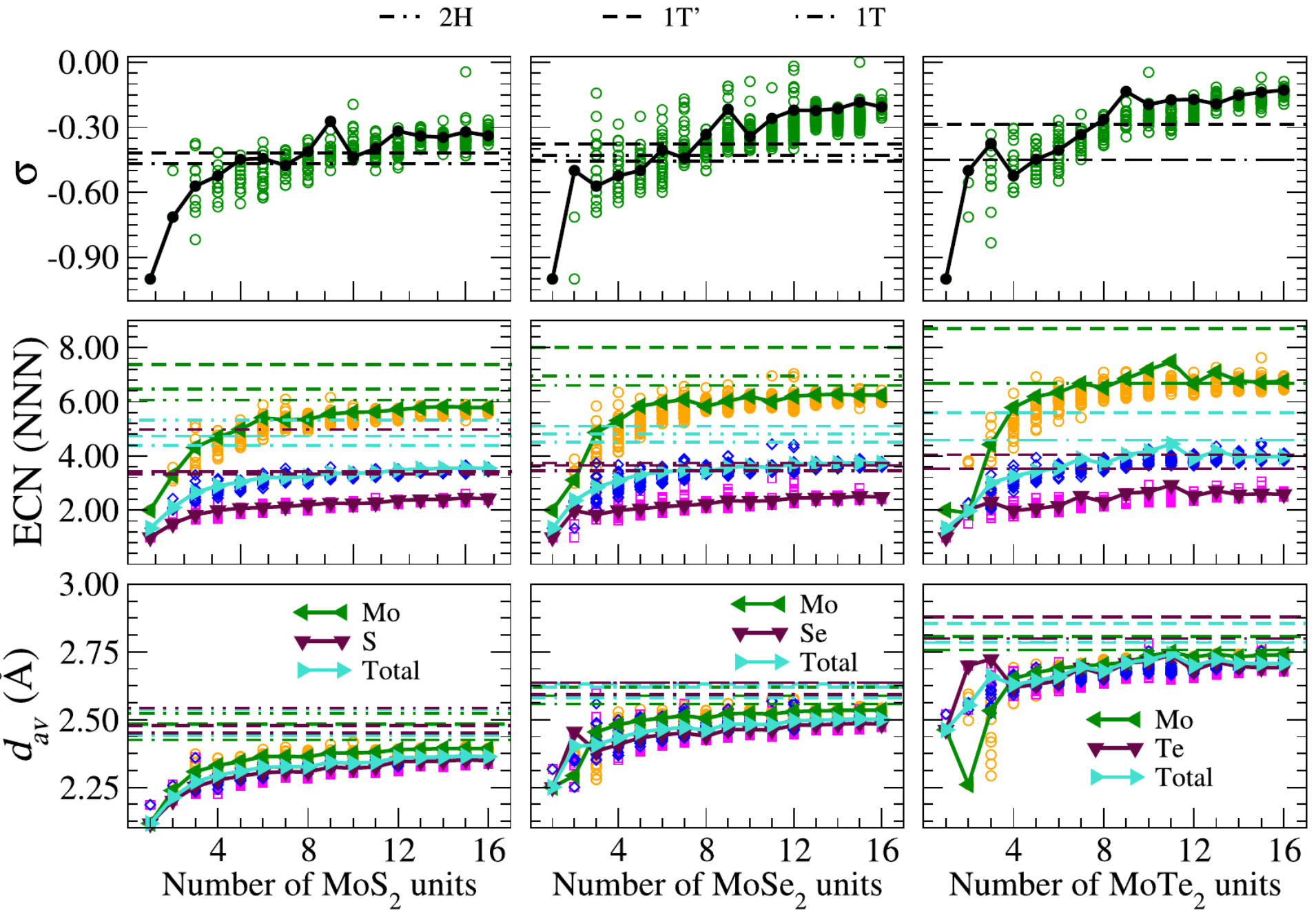
Ab initio Investigation of Atomistic Insights into the Nanoflake Formation of Transition-Metal Dichalcogenides: The Examples of MoS_2, $MoSe_2$, and $MoTe_2$

Naidel A. M. S. Caturello,[†] Rafael Besse,[‡] Augusto C. H. Da Silva,[†] Diego Guedes-Sobrinho,[§,†] Matheus P. Lima,[∥] and Juarez L. F. Da Silva*[,†]

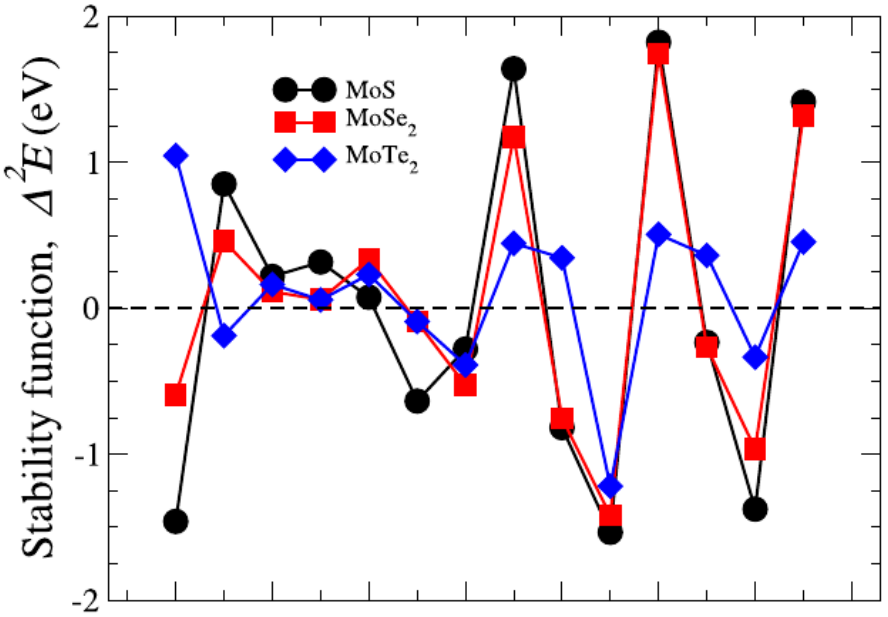
Size Evolution of the $MoSe_2$ Nanoflakes

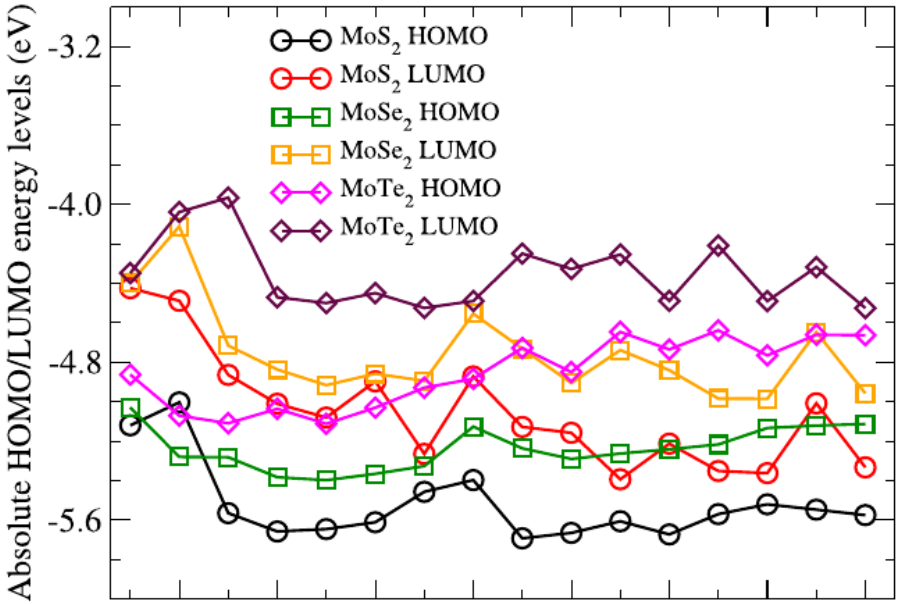


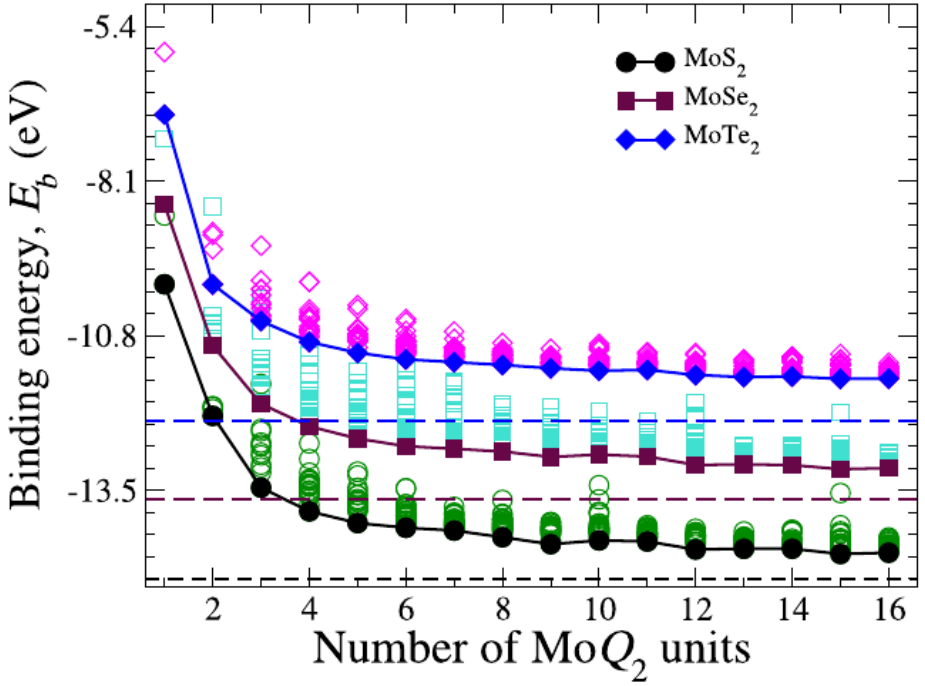
Size Evolution: Structural Properties

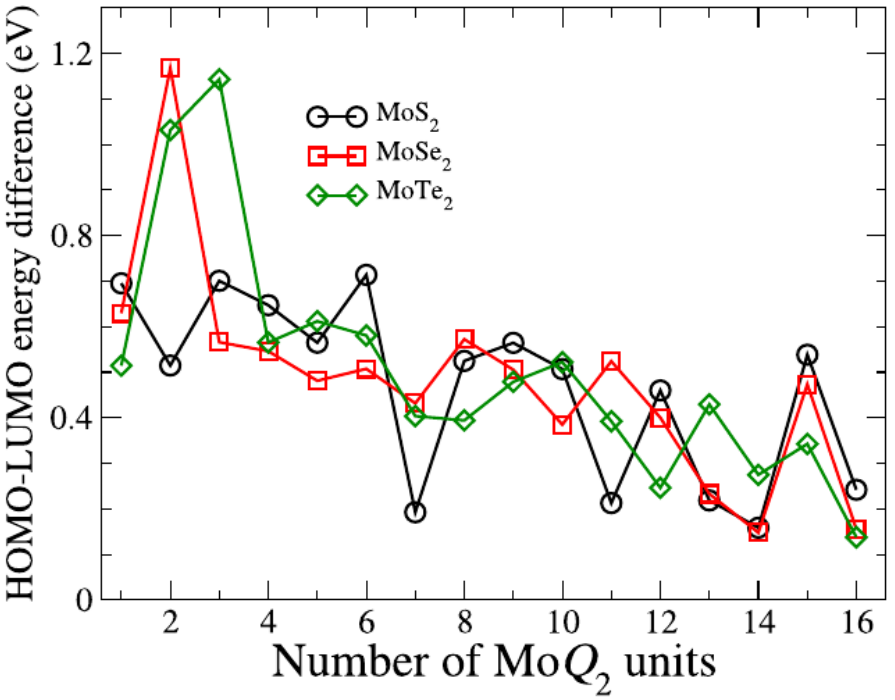


Size Evolution of the $MoSe_2$ Nanoflakes

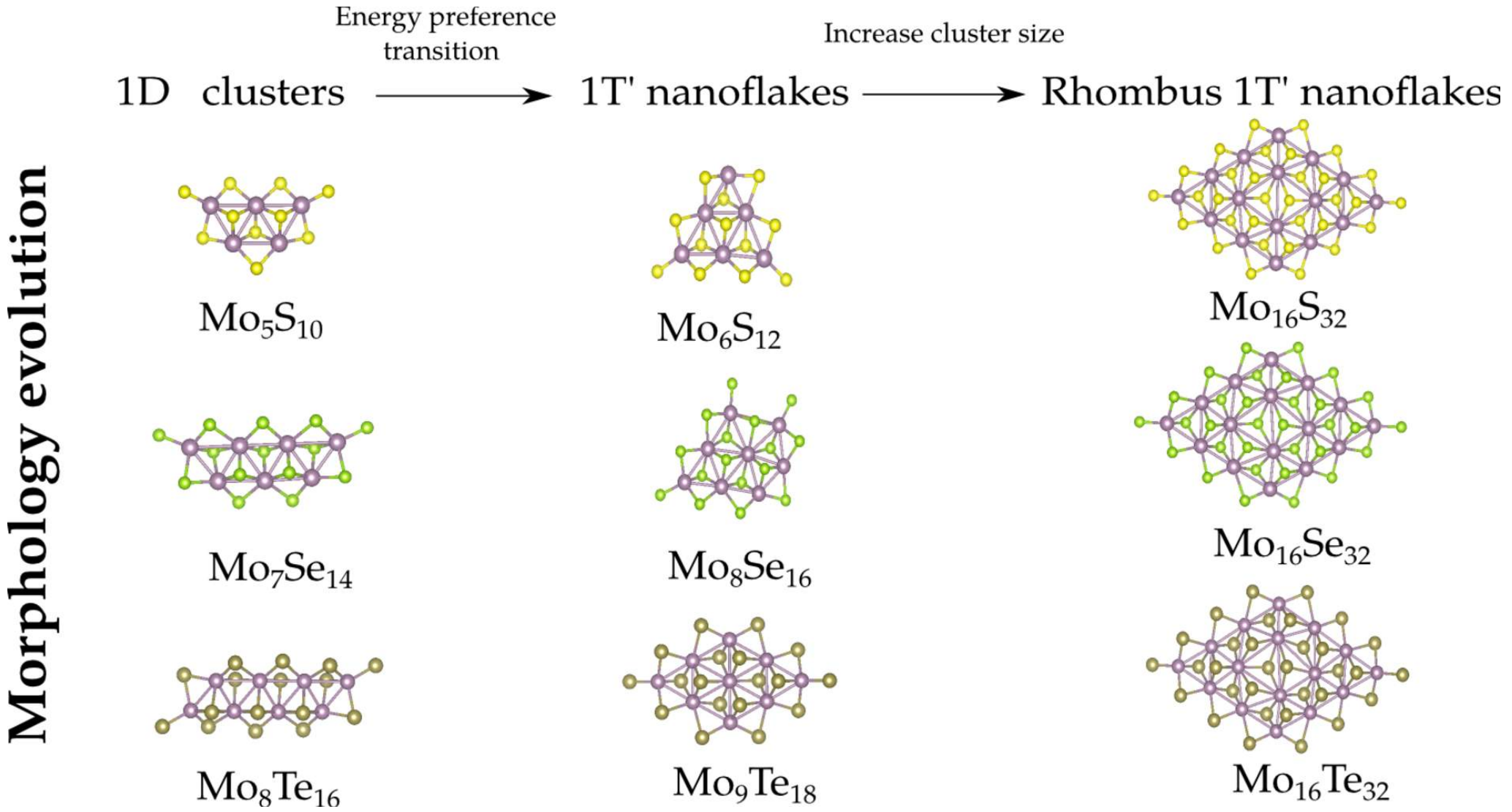








Size Evolution and Transitions



There is a transition from 1D structures to 2D structures at n = 6, 9, and 9 for MoS_2, $MoSe_2$, and $MoTe_2$, respectively.

THE JOURNAL OF PHYSICAL CHEMISTRY C

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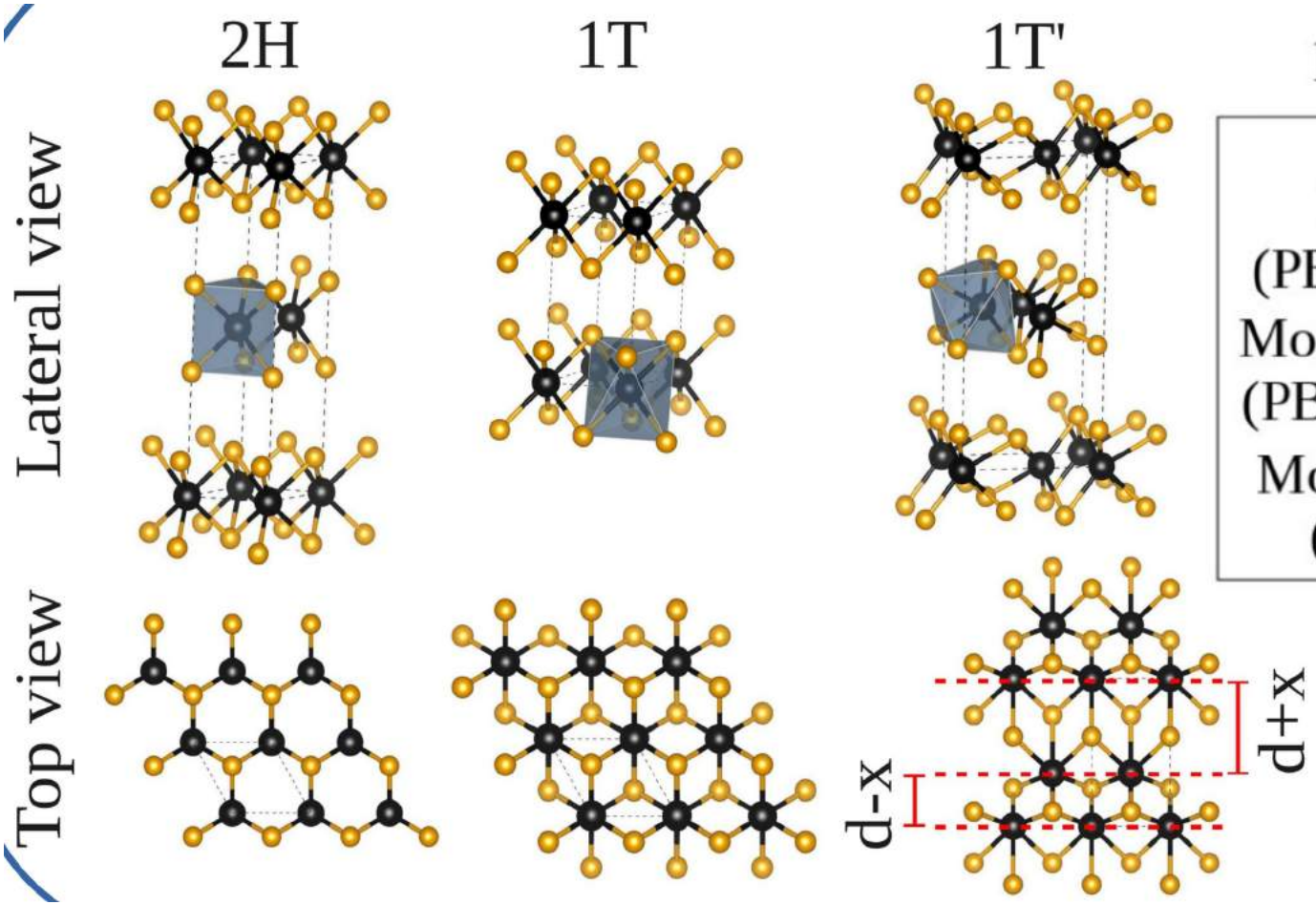
Size-Induced Phase Evolution of $MoSe_2$ Nanoflakes Revealed by Density Functional Theory

Rafael Besse,[†] Naidel A. M. S. Caturello,[‡] Carlos M. O. Bastos,[†] Diego Guedes-Sobrinho,[§,‡] Matheus P. Lima,[∥] Guilherme M. Sipahi,[†] and Juarez L. F. Da Silva*[,‡]

Bulks $MoSe_2$ and Relative Stability



Relative energy (eV/f.u.)

	2H	1T	1T'
Bulk (PBE+D3)	0.00	0.68	0.34
Monolayer (PBE+D3)	0.00	0.70	0.33
Monolayer (PBE)	0.00	0.71	0.32

Intralayer binding is dominated by covalent and ionic bonding.
PBE calculations for nanoflakes.

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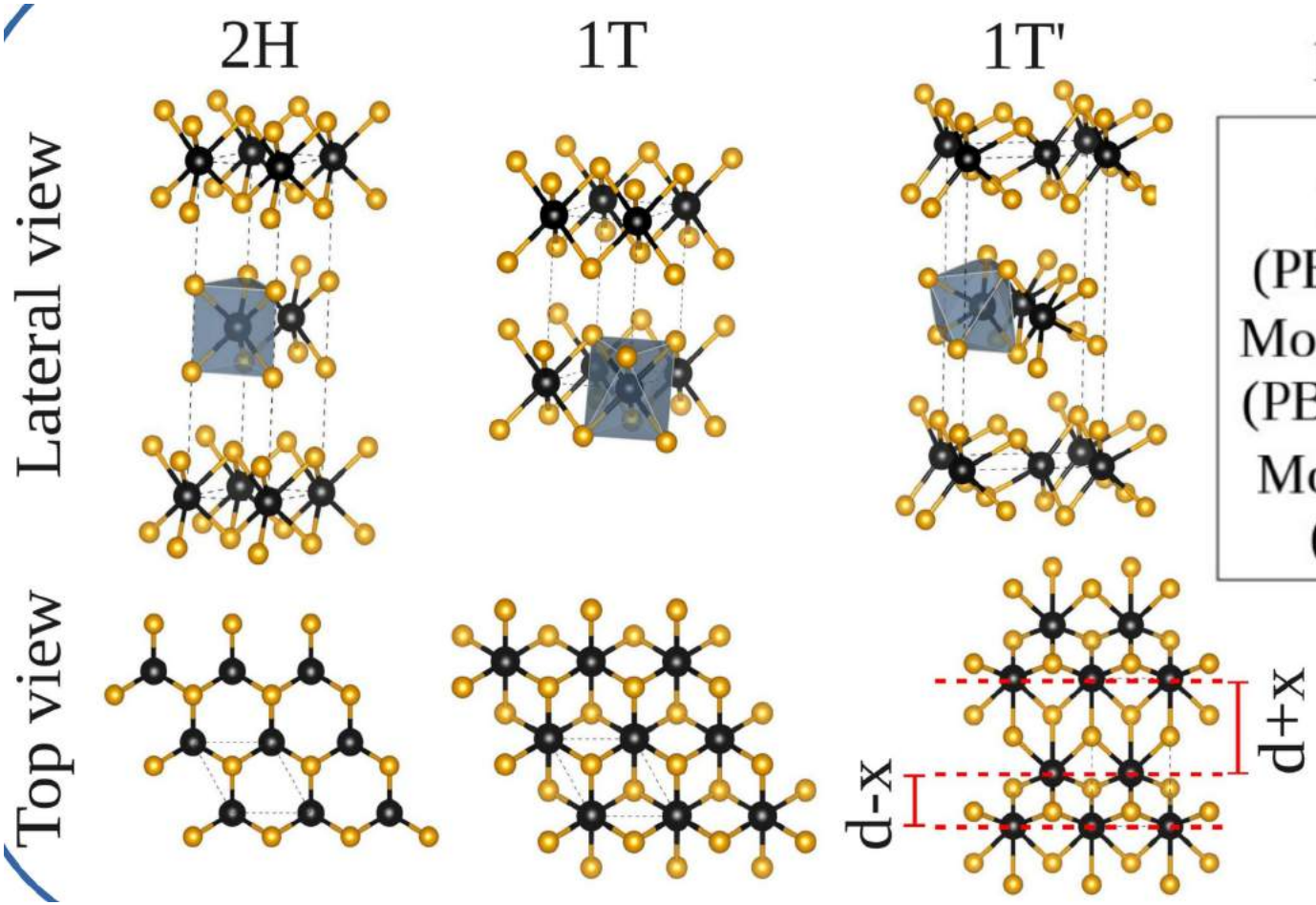
Bulks $MoSe_2$ and Relative Stability



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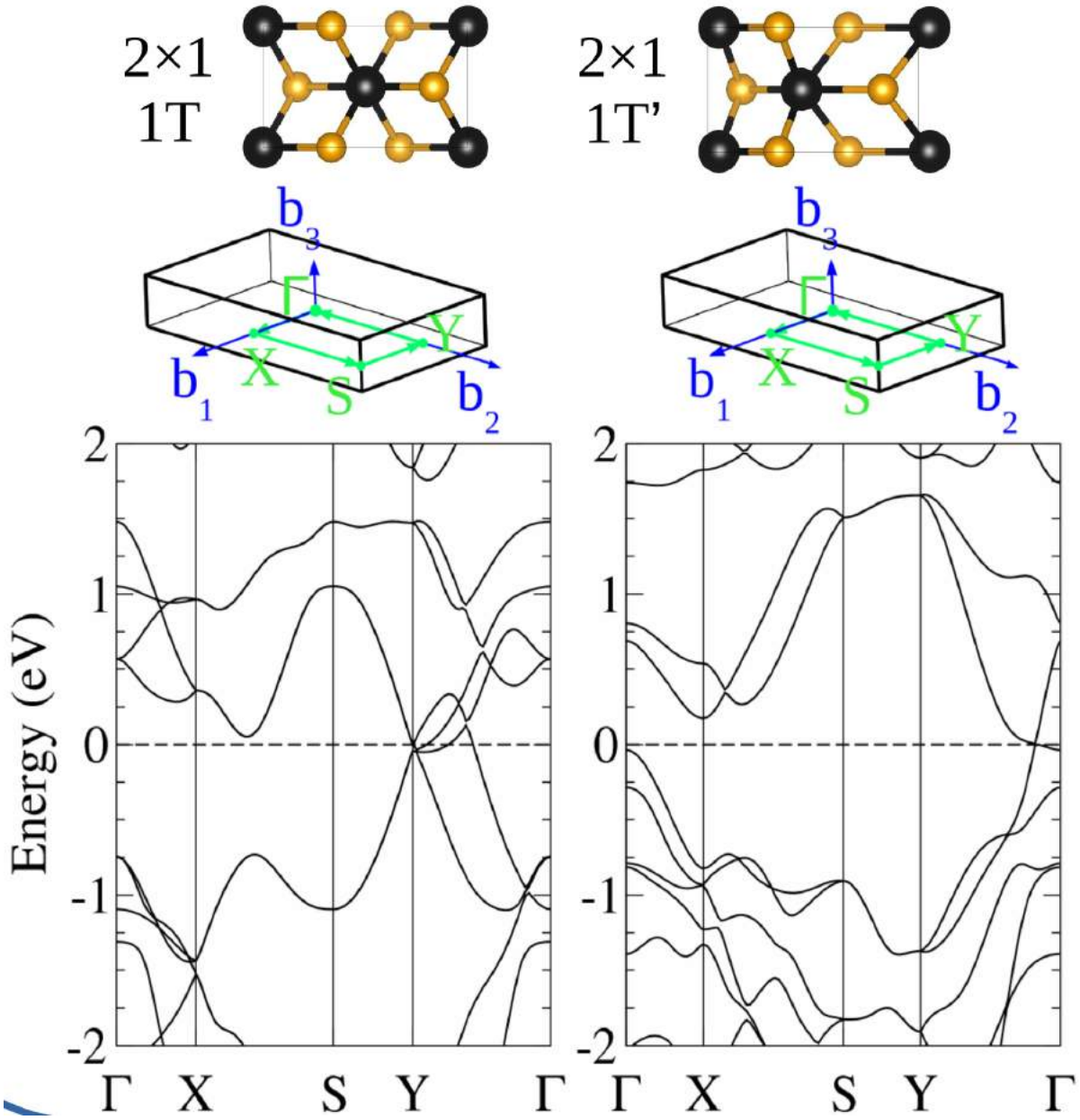
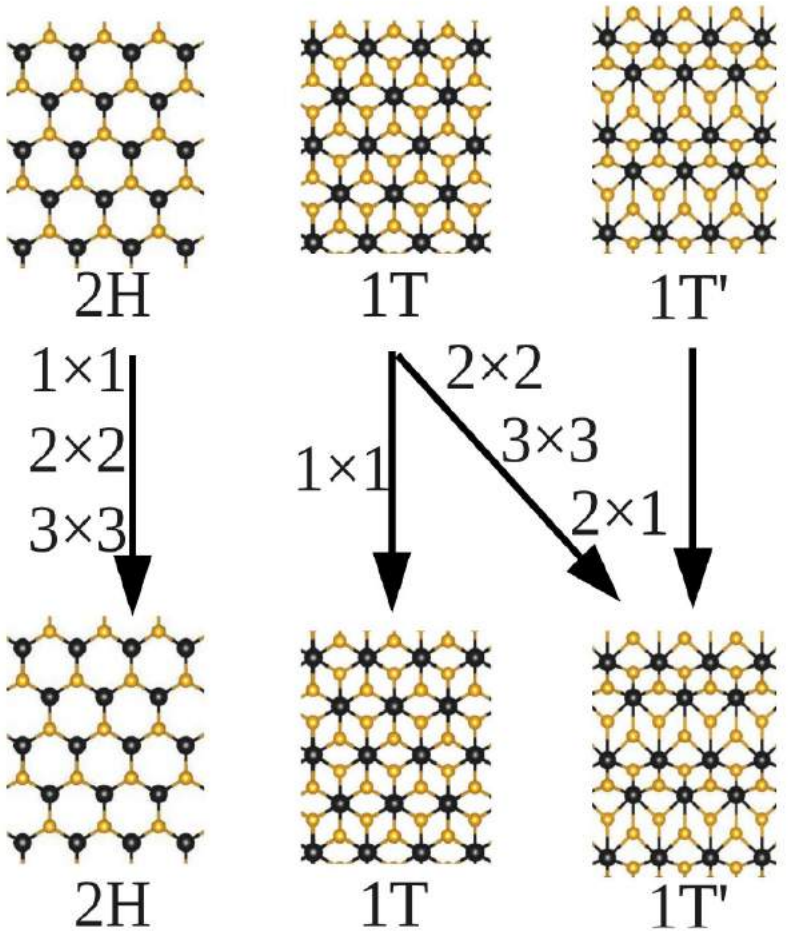
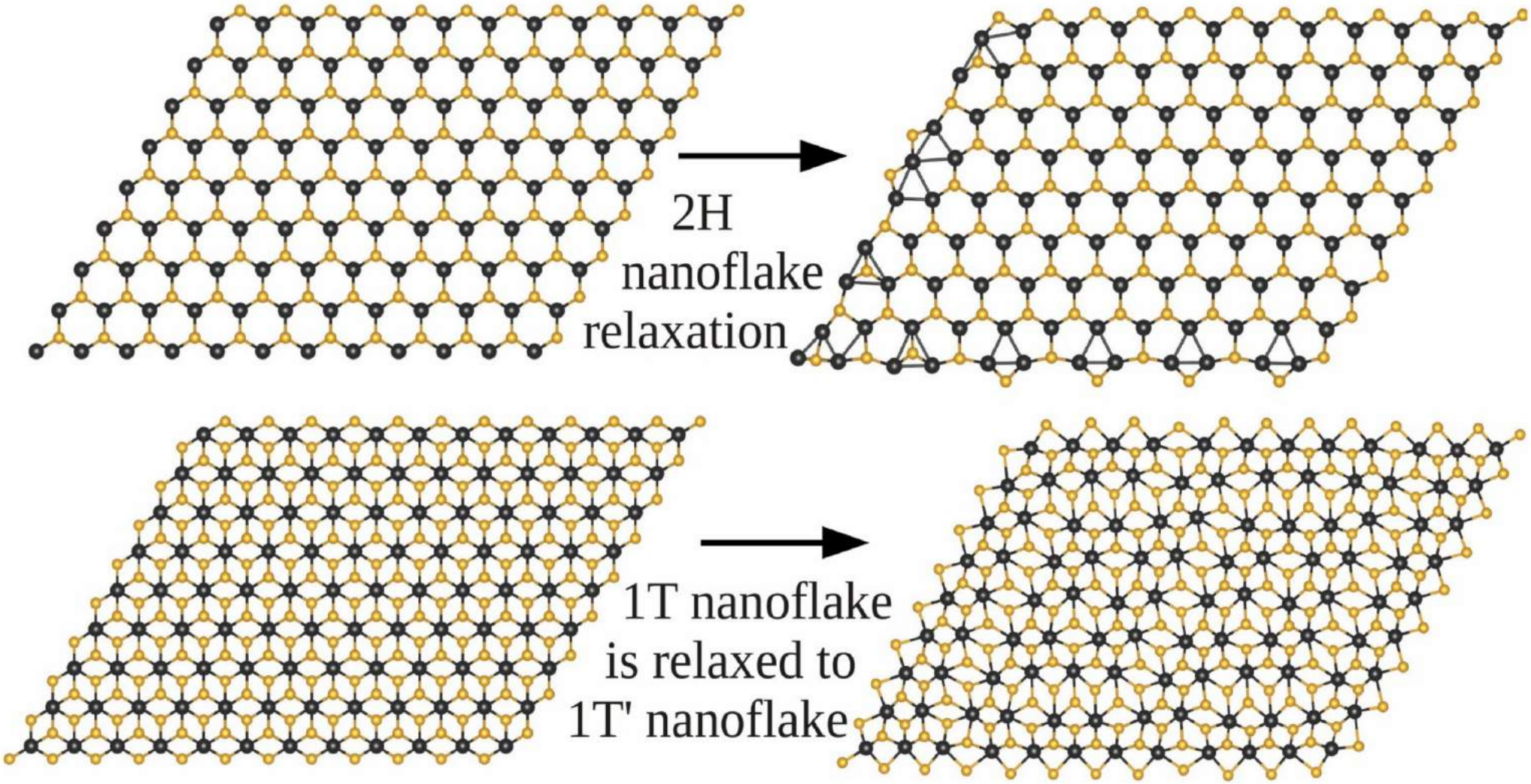
Intralayer binding is dominated by covalent and ionic bonding.
PBE calculations for nanoflakes.

Bulks $MoSe_2$ and Peierls Distortions



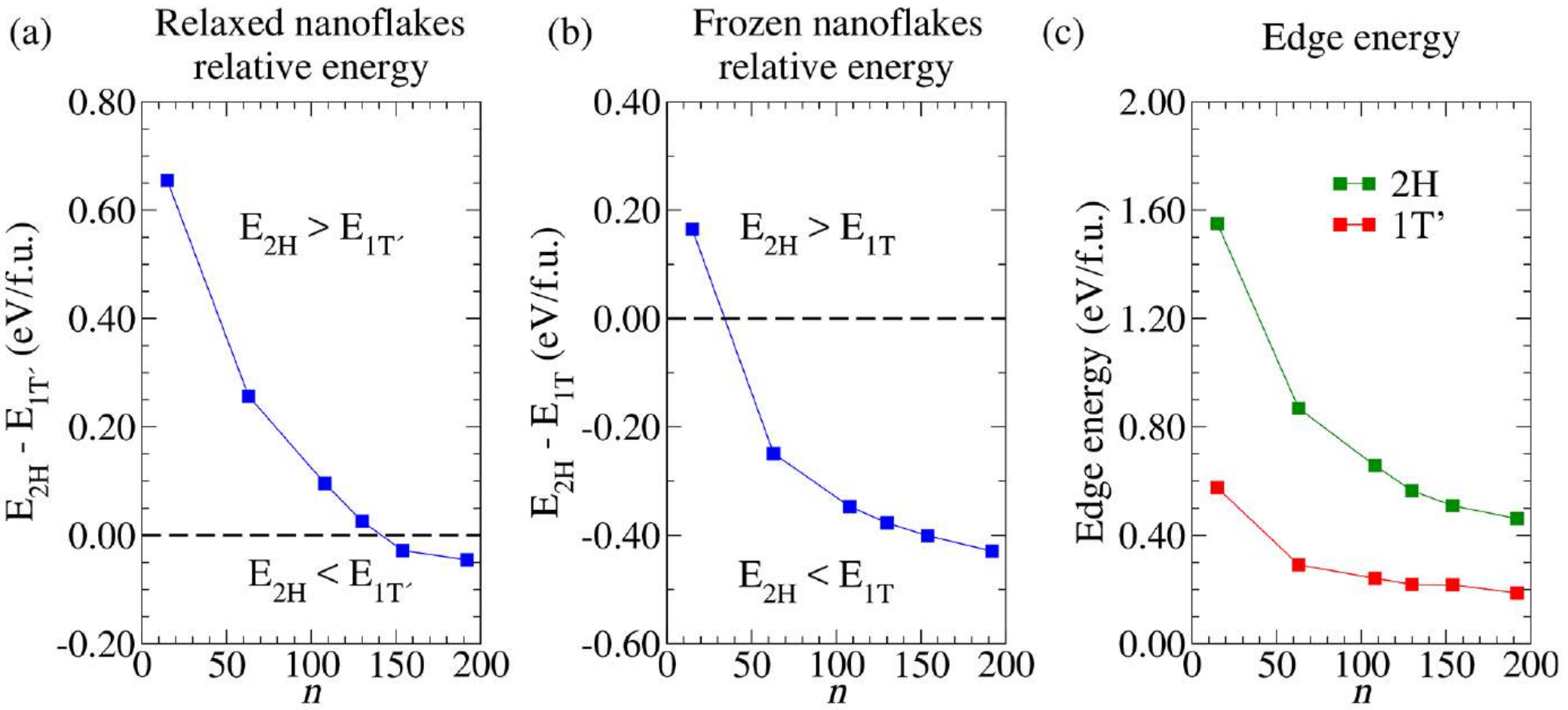


$MoSe_2$ Nanoflakes Relaxation



- There is a strong reconstruction of the nanoflake edges.
- The 1T nanoflake relaxes to the 1T‘ structure upon geometric optimization, i.e., Peierls mechanism drive the reconstruction.

Size-Induced Phase Evolution of $MoSe_2$ Nanoflakes



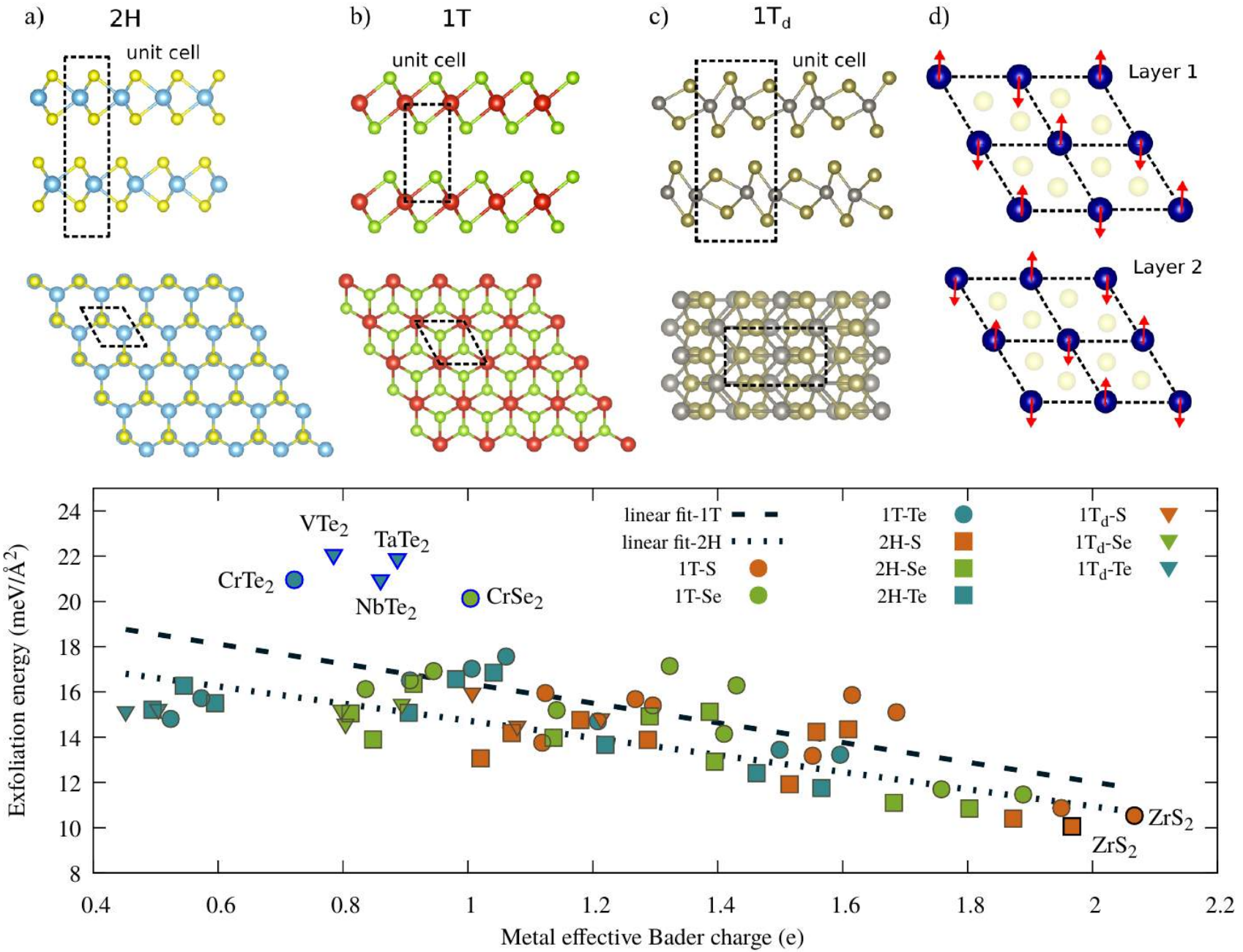
At small size, the relative stability of the nanoflakes change from 2H to 1T‘ structures, in which the relaxation effects play a crucial role, in particular de edge energy.

Further studies are in progress to improve our atomistic understanding.

Ab-initio Investigation of Structural Stability and Exfoliation Energies in Transition Metal Dichalcogenides based on Ti-, V-, and Mo-Group Elements

Carlos M. O. Bastos,[1] Rafael Besse,[1] Juarez L. F. Da Silva,[2] and Guilherme M. Sipahi[1]

Submitted: Phys. Rev. B



Electronic structure of layered quaternary chalcogenide materials for band-gap engineering: The example of $Cs_2M^{II}M_3^{IV}Q_8$

PHYSICAL REVIEW B **93**, 165205 (2016)

Rafael Besse and Fernando P. Sabino

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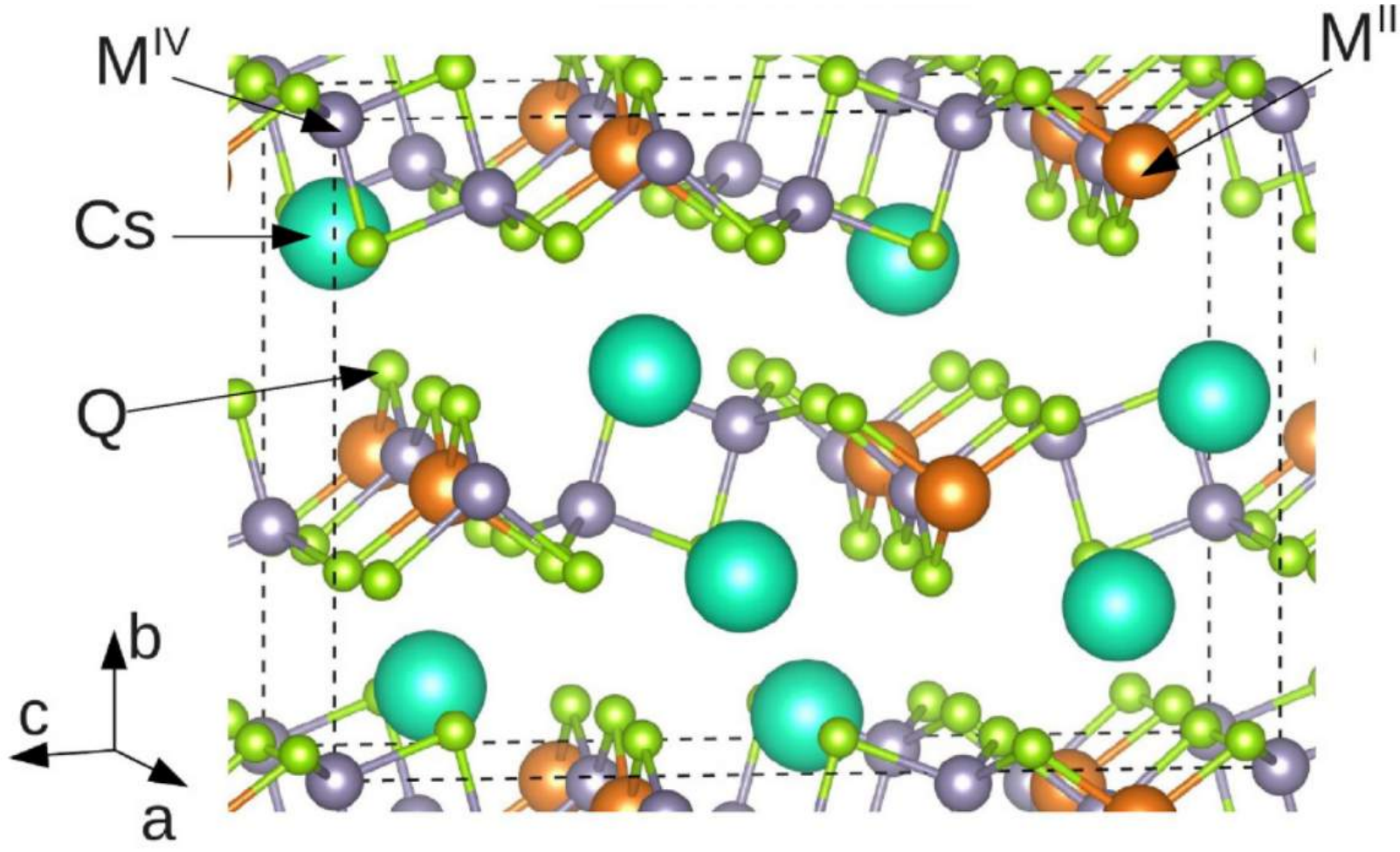
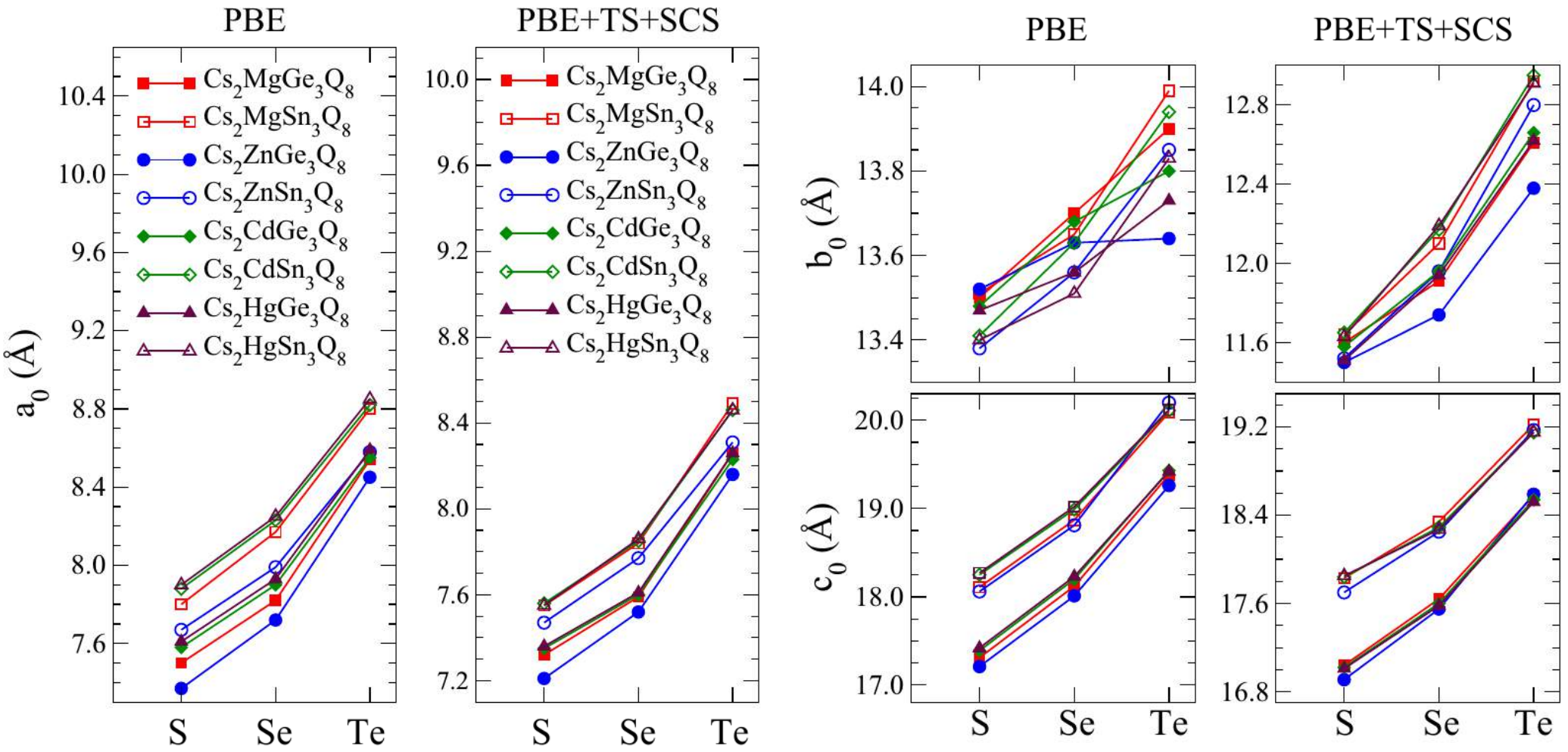
(Received 9 February 2016; revised manuscript received 20 March 2016; published 22 April 2016)



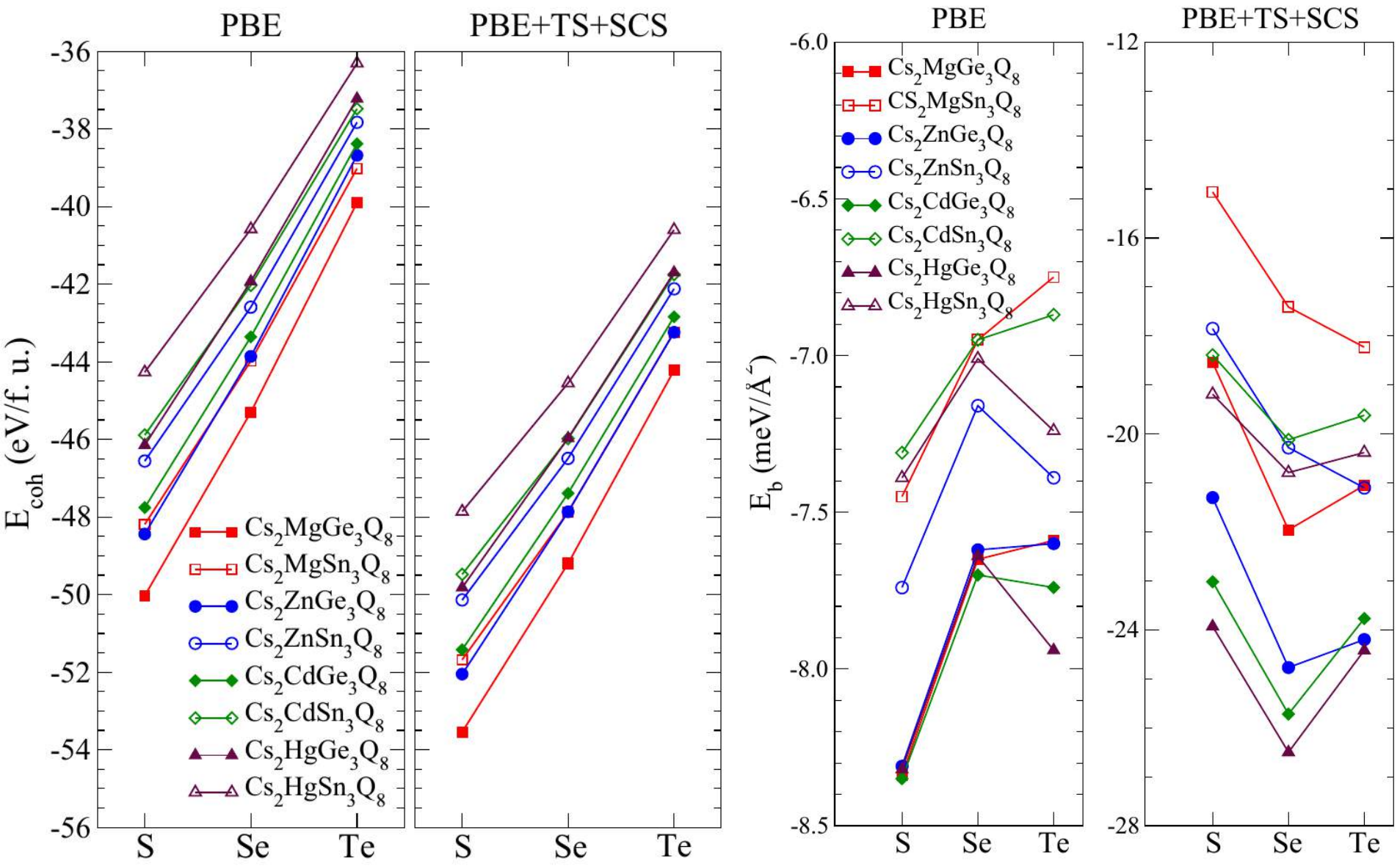
$Cs_2M^{II}M_3^{IV}Q_8$ family ($M^{II} = Mg, Zn, Cd, Hg$, $M^{IV} = Ge, Sn$ and $Q = S, Se, Te$).

Lattice Parameters



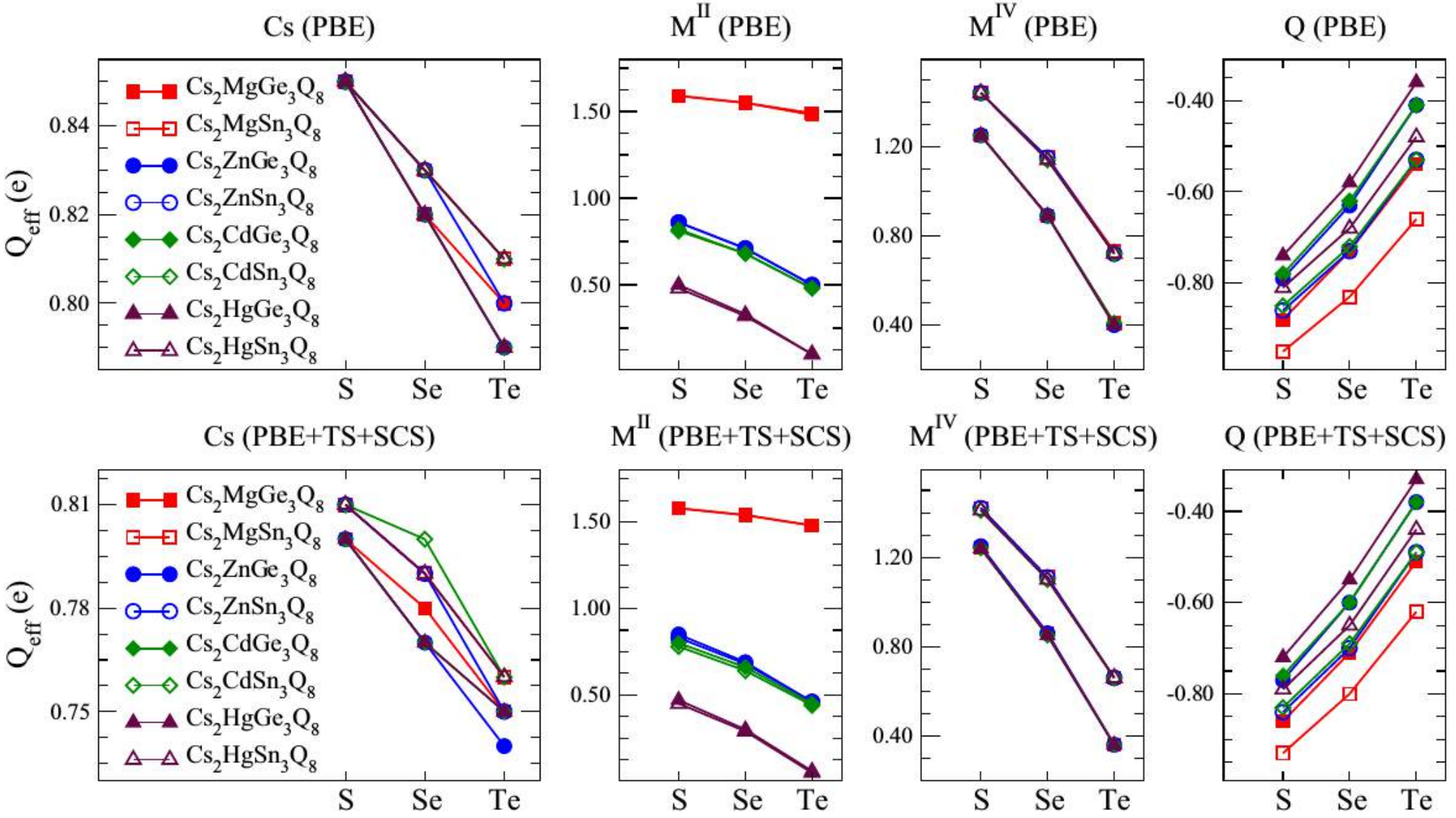
The atomic radius of the chalcogen atoms (S, Se, Te) plays a crucial role in the equilibrium volume, and hence, lattice parameters. The employed van der Waals Correction improve only slightly the lattice parameters.

Cohesive Energy and Exfoliation Energy



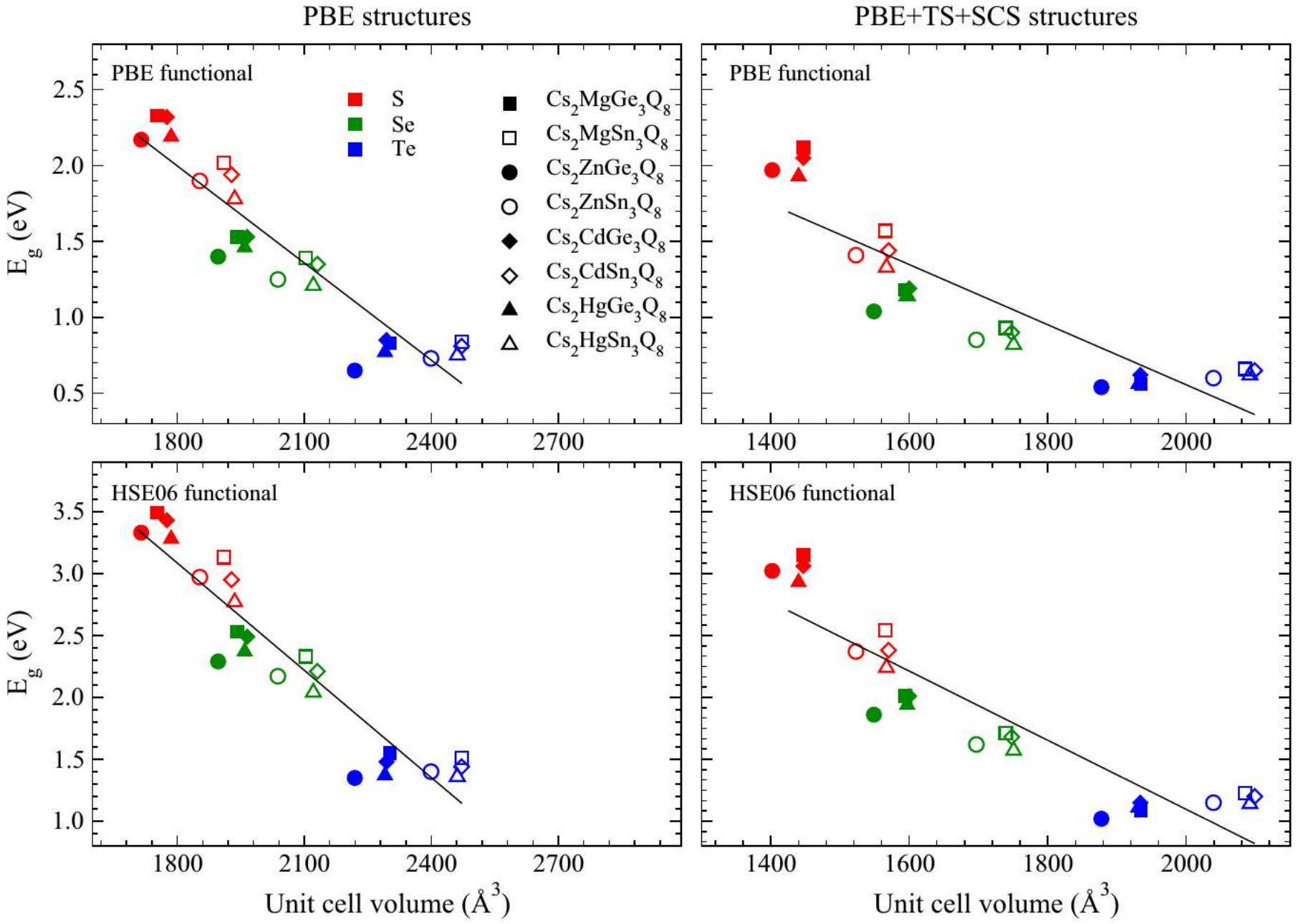
The cohesive energy descreases in absolute value from S → Se → Te.
The exfoliation energy per unit area is nearly the same for all systems.

Ion-Ion Interations and Cohesive Energy



The effective ionic charge (Bader) increases in absolute value from Te → Se → S, Which explains the behavior of the cohesive energy.

Fundamental Band Gap: PBE and HSE06



Conclusions

- For the study of the nanoflakes size-evolution, we employed our Implementation of the tree-growth scheme combined with the Euclidean Similarity distance algorithm – it works better than our initial expectations.

- We studied the size-evolution of nanoflakes of the most studied chalcogenides, and several trends were obtained, which includes a transition from 1D to 2D at small size.

- We identified the energy difference between the 2H, 1T, and 1T‘ structures depend on the nanoflake size, and there is a size in which 1T‘ is the lowest energy configuration.

- For particular chalcogenide systems, there is a correlation between the exfoliation energy and the ionic changes on the cations and anions.