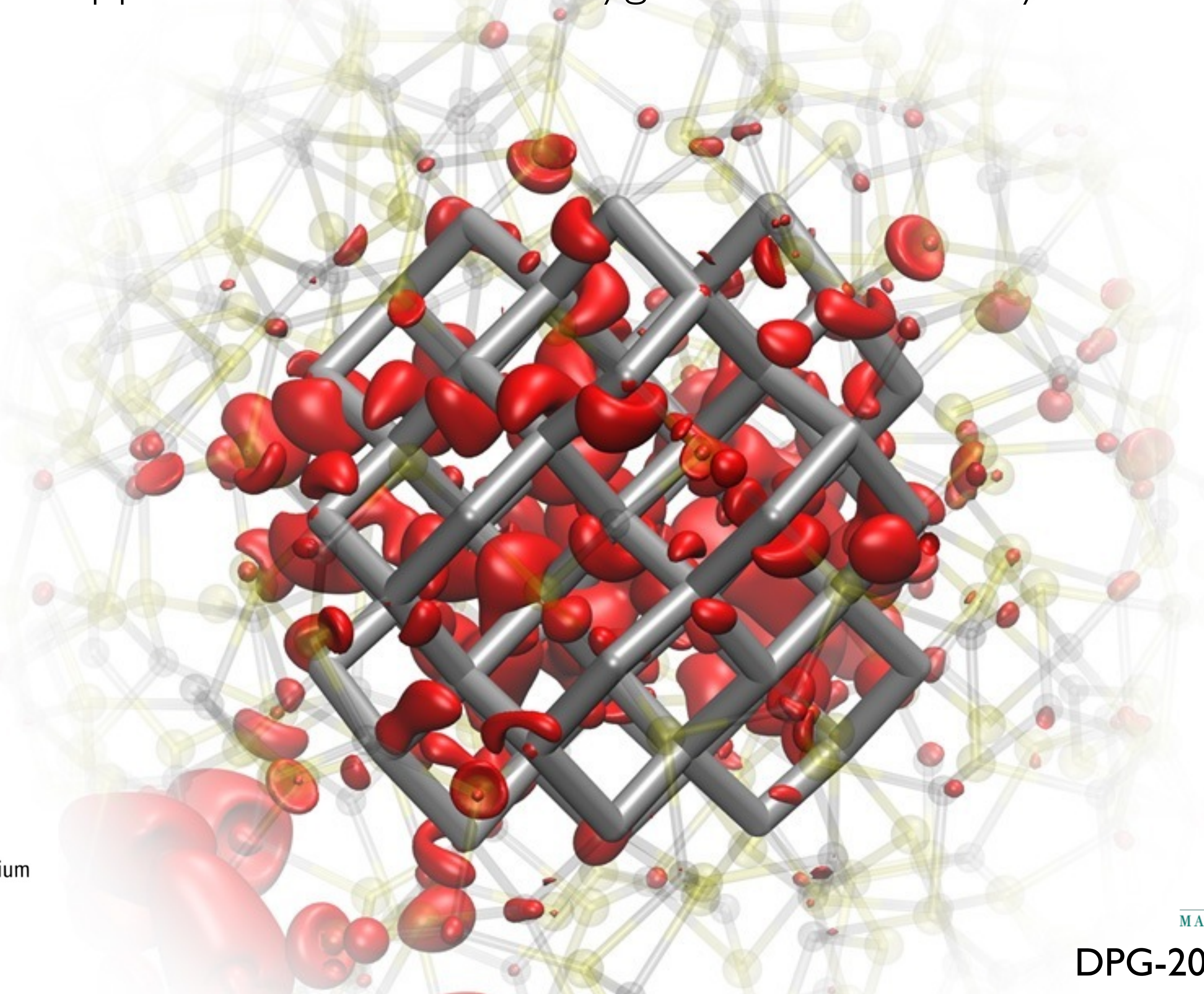
Solar nanocomposites with complementary charge extraction pathways for electrons and holes: Si embedded in ZnS

S. Wippermann, M. Vörös, F. Gygi, A. Gali, G. Zimanyi, G. Galli



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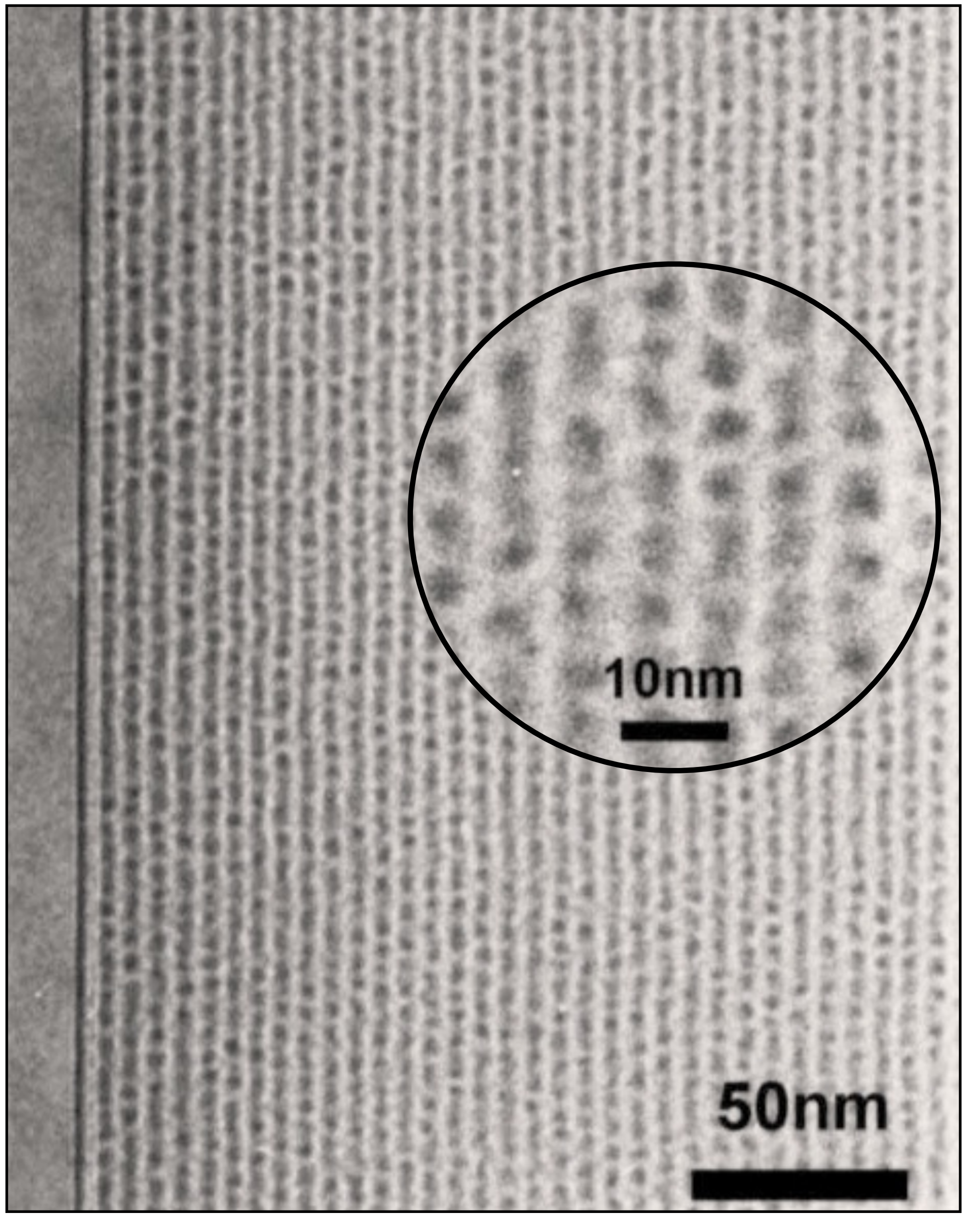
DPG-2014, 04/03/2014

Search for materials to harvest light

- Nanocomposites based on **Si nanocrystals embedded in a charge transport matrix** are promising candidates for light absorbers in quantum dot based 3rd generation photovoltaics architectures

d = 3.3nm Si nanocrystals in SiO_2



[M. Zacharias *et al.*, Appl. Phys. Lett. **80**, 661 (2002)]

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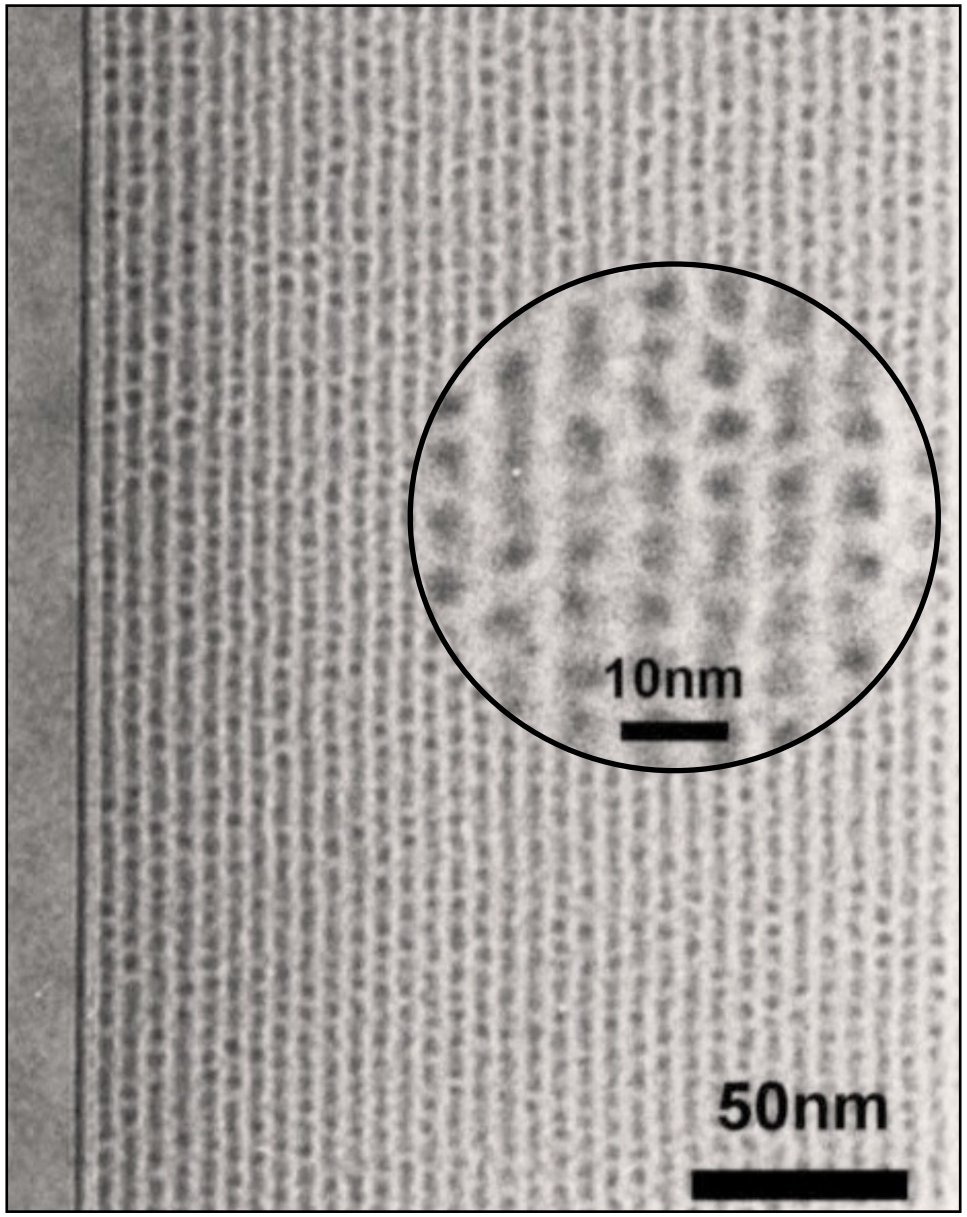

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Si nanocrystals in ZnS:

- ZnS is earth-abundant, non-toxic and features a favourable band-alignment with Si at least for planar heterointerfaces
- Investigate Si-ZnS nanocomposites from *first principles*

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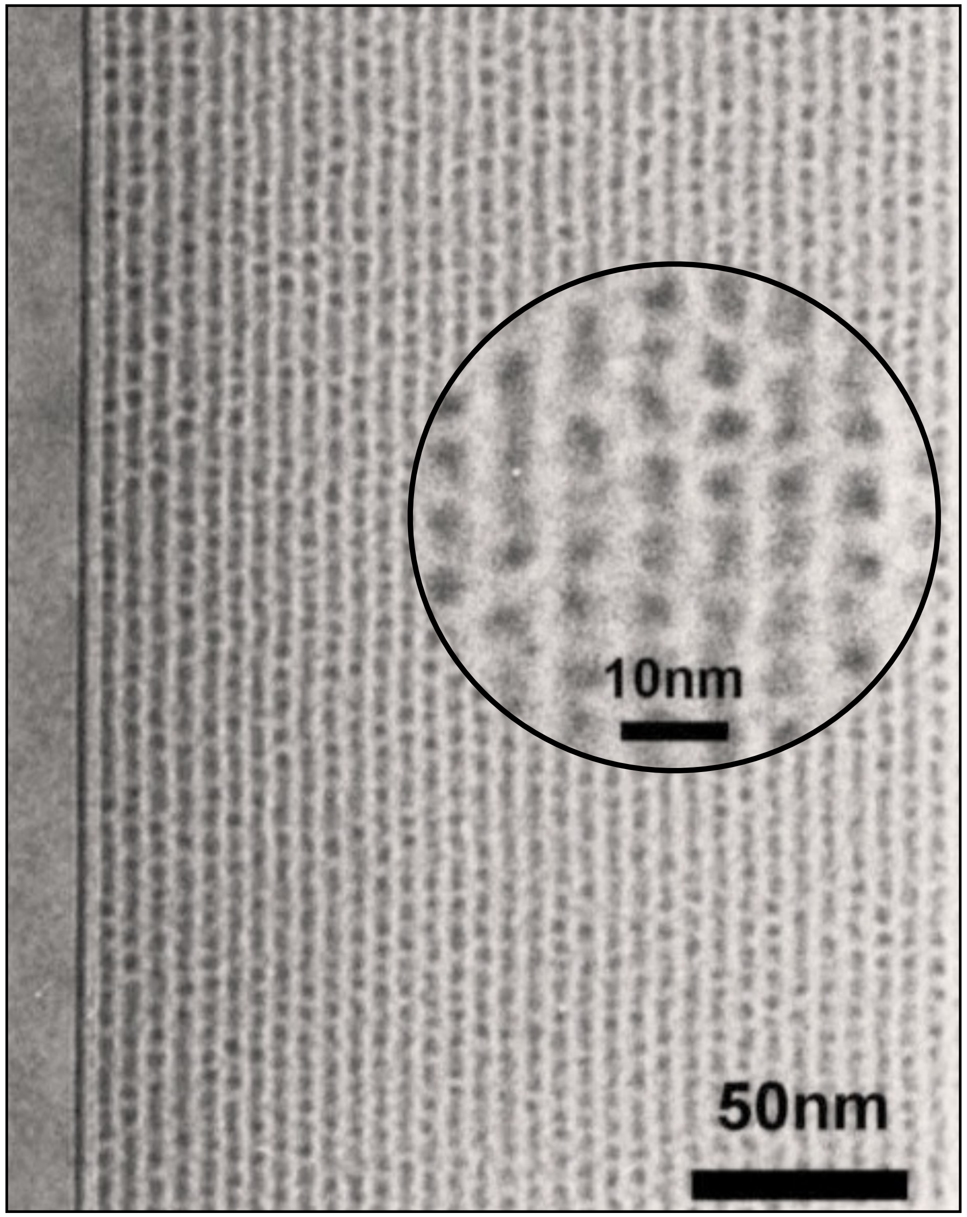

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Embedding Si nanocrystals in a-ZnS

- Create structural models for a-ZnS embedded **Si_{35}, Si_{66}, Si_{123}, Si_{172}** nanoparticles (NPs): **replace spherical region (1.1 - 1.9 nm) in 4x4x4 ZnS unit cell and amorphize ZnS matrix using *ab initio* molecular dynamics (MD)**
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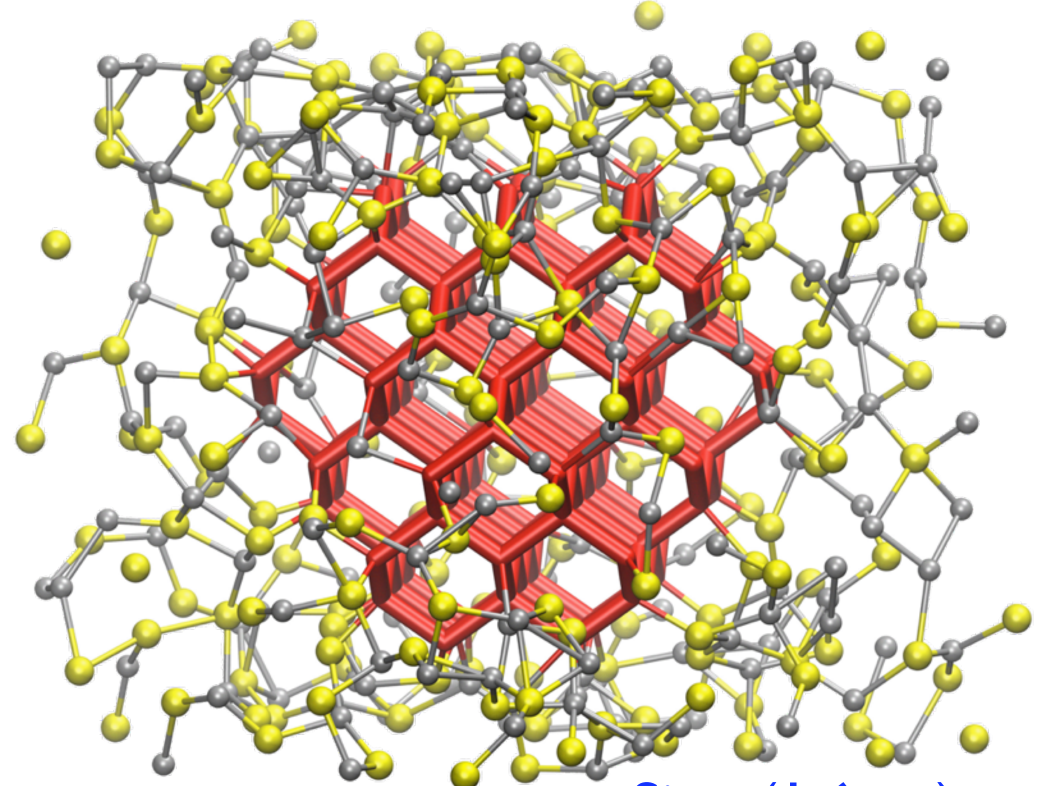

Si_{123} (1.6nm)

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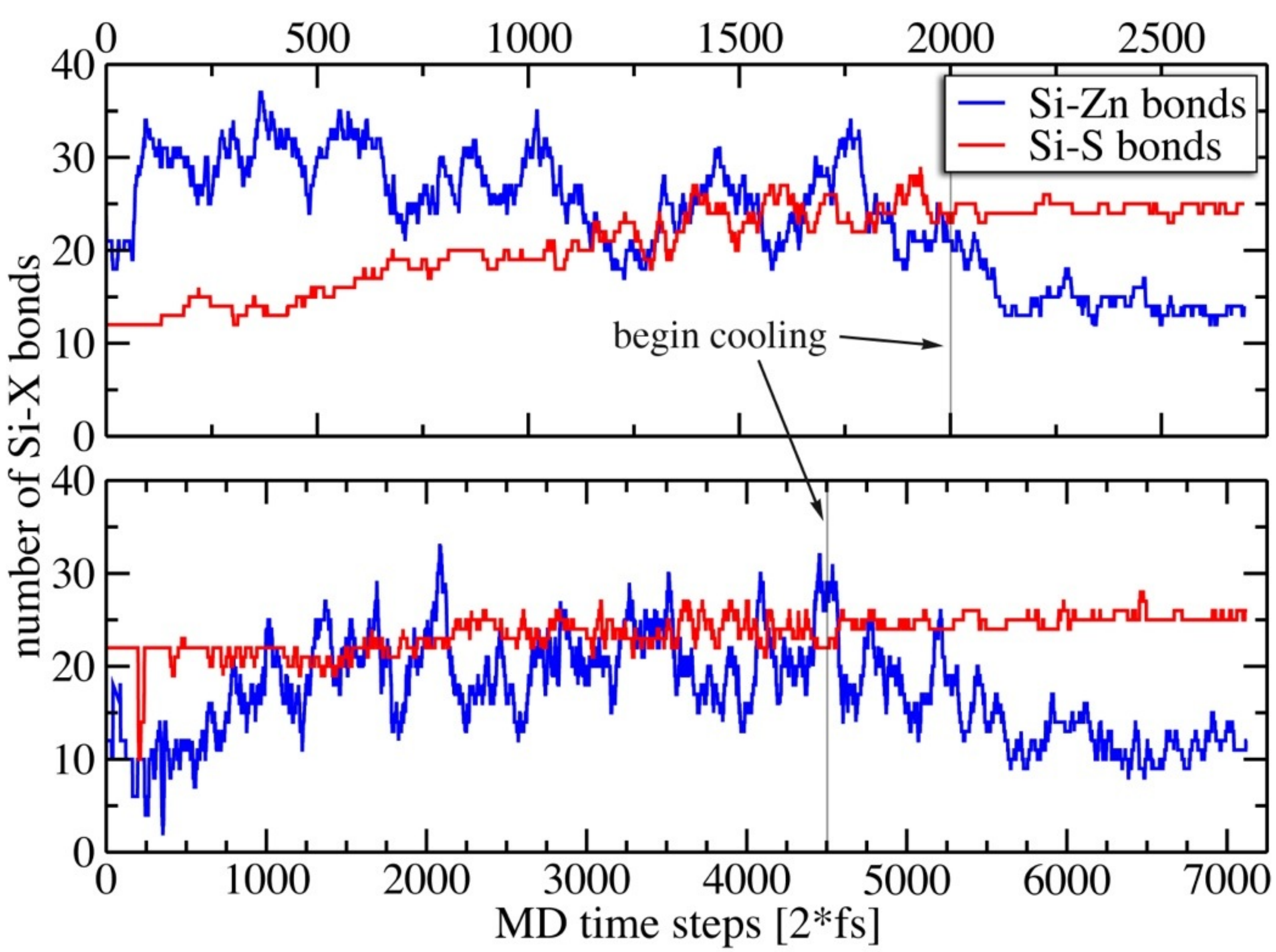
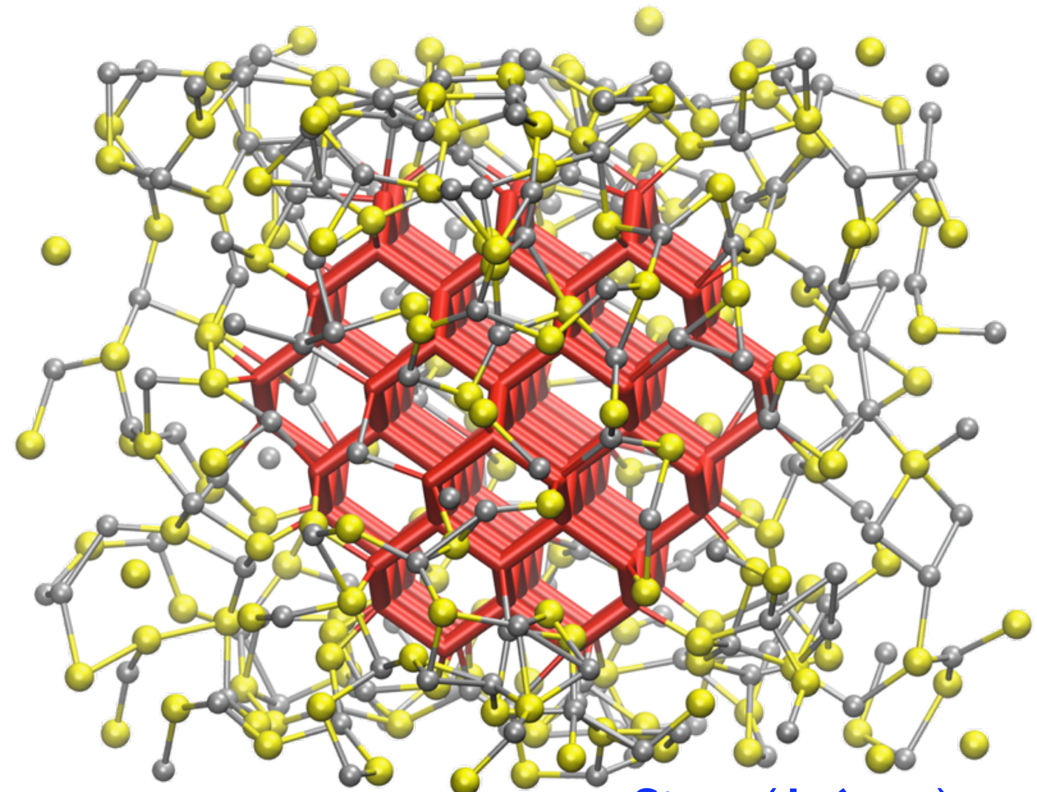




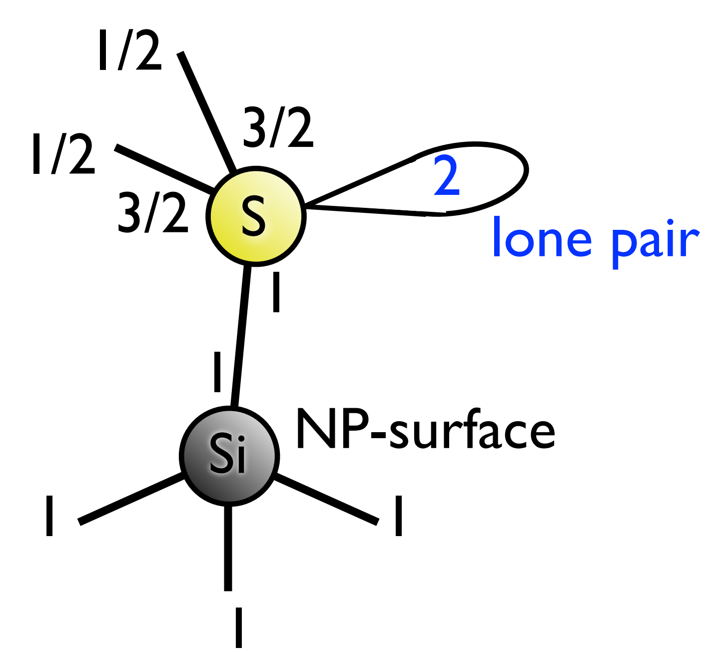
Si_{123} (1.6nm)

- Different starting geometries, equilibration & cooling times lead to very similar structures
- Formation of sulfur-shell on Si-NP surface observed

=> Examine interface structure

Sulfur shell formation introduces new mid-gap states

- 3-fold coordinated interfacial sulfur: achieves noble gas state with 1 S-Si, 2 S-Zn bonds and 1 lone pair



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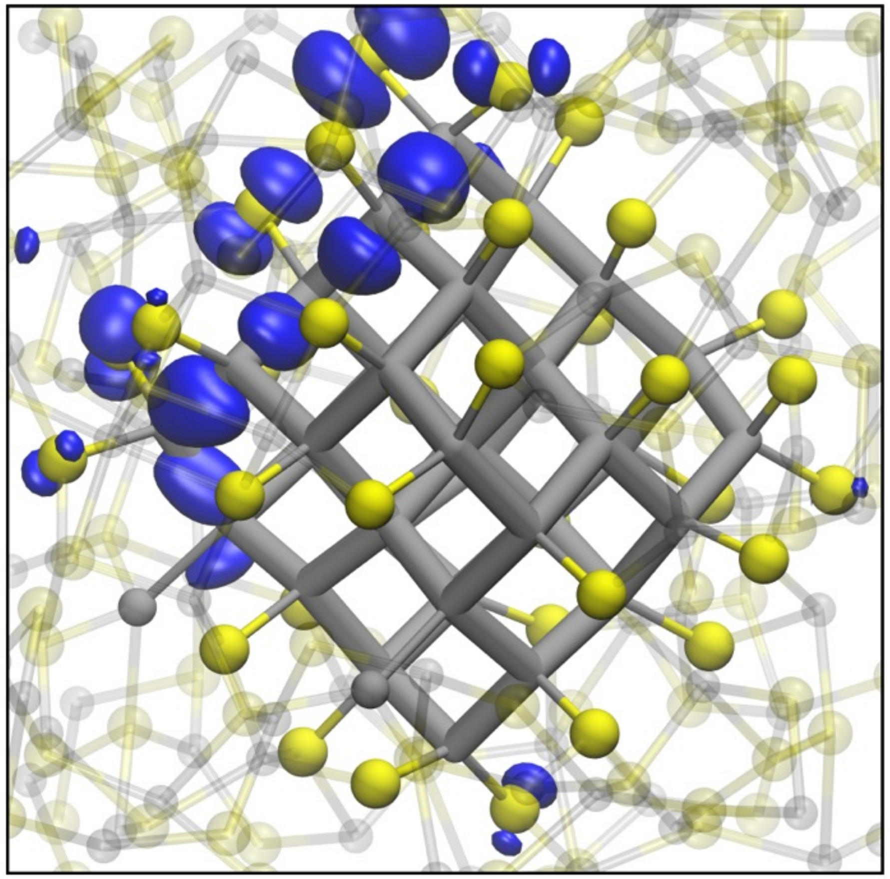
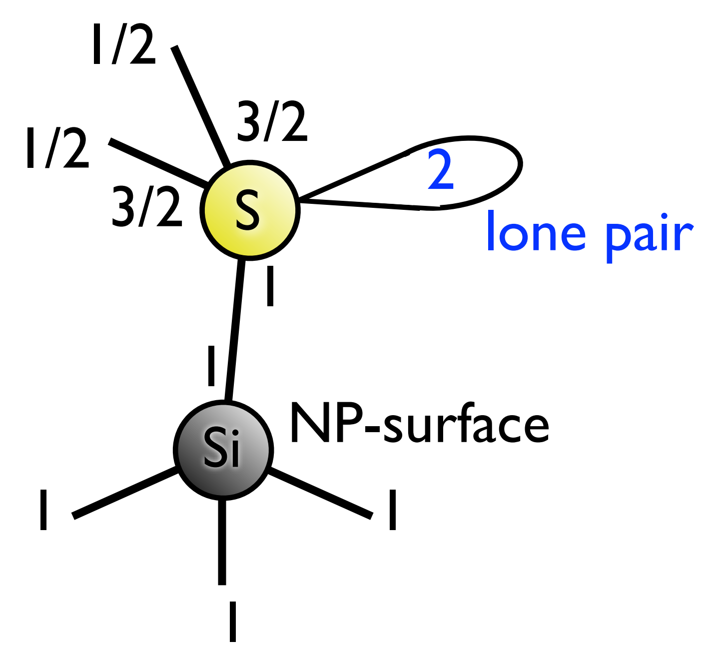


Si_{35} NP HOMO



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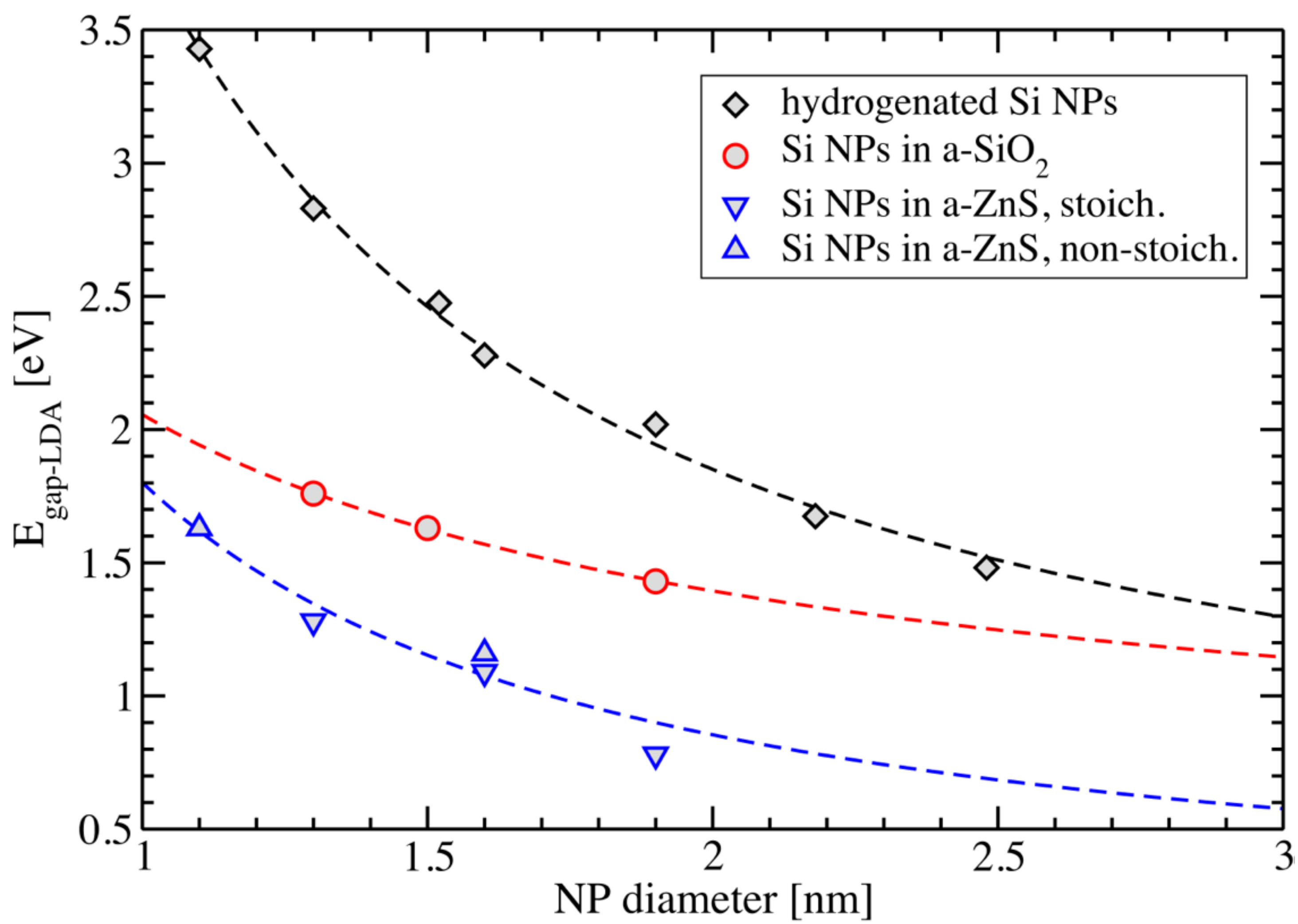
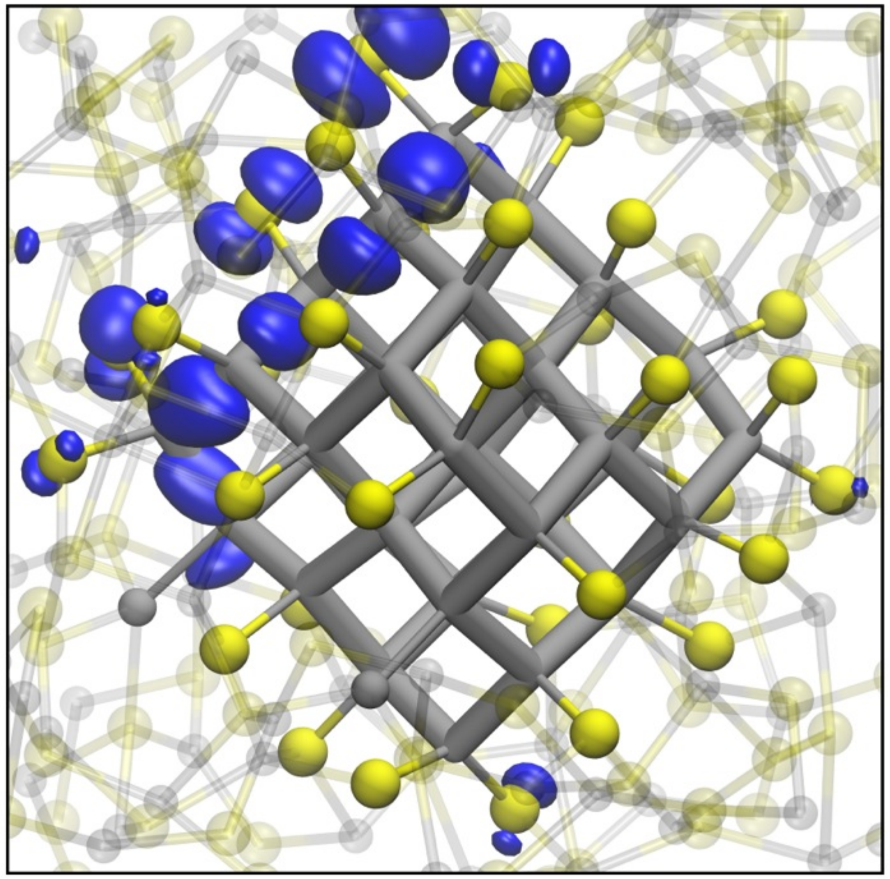
=> pronounced gap-reduction of embedded NPs





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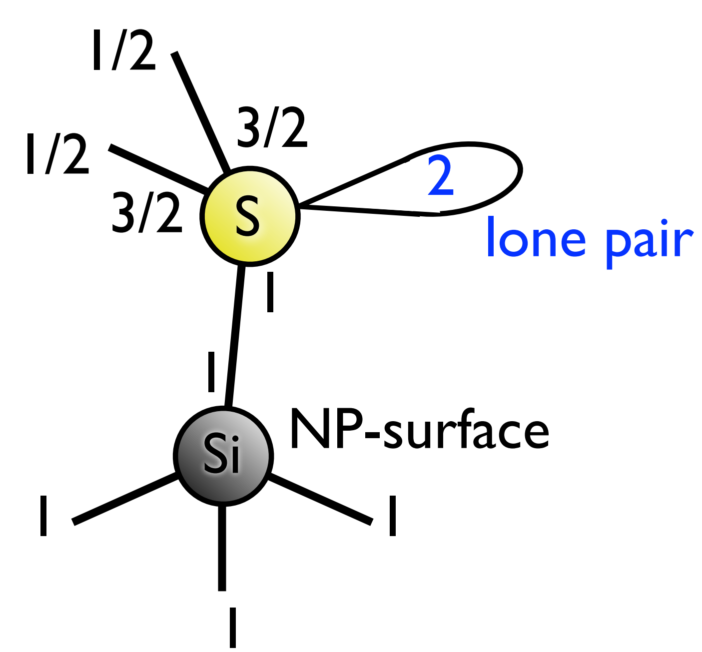
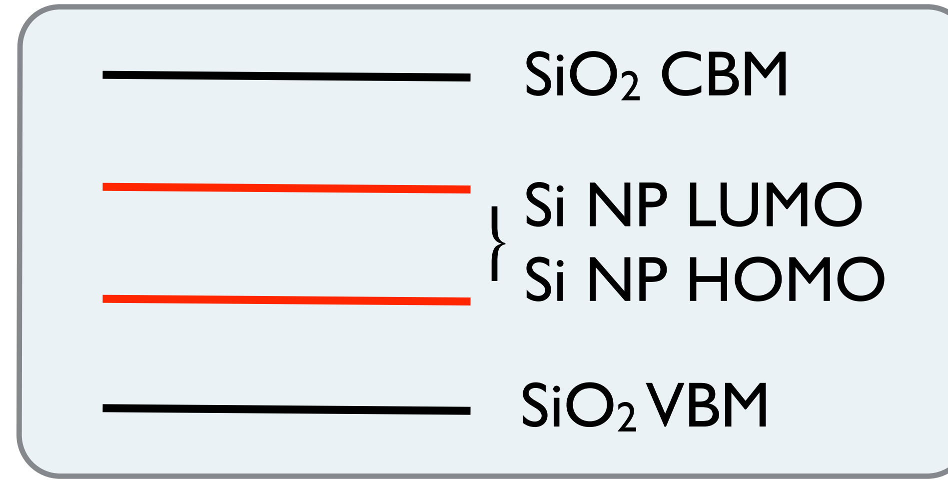
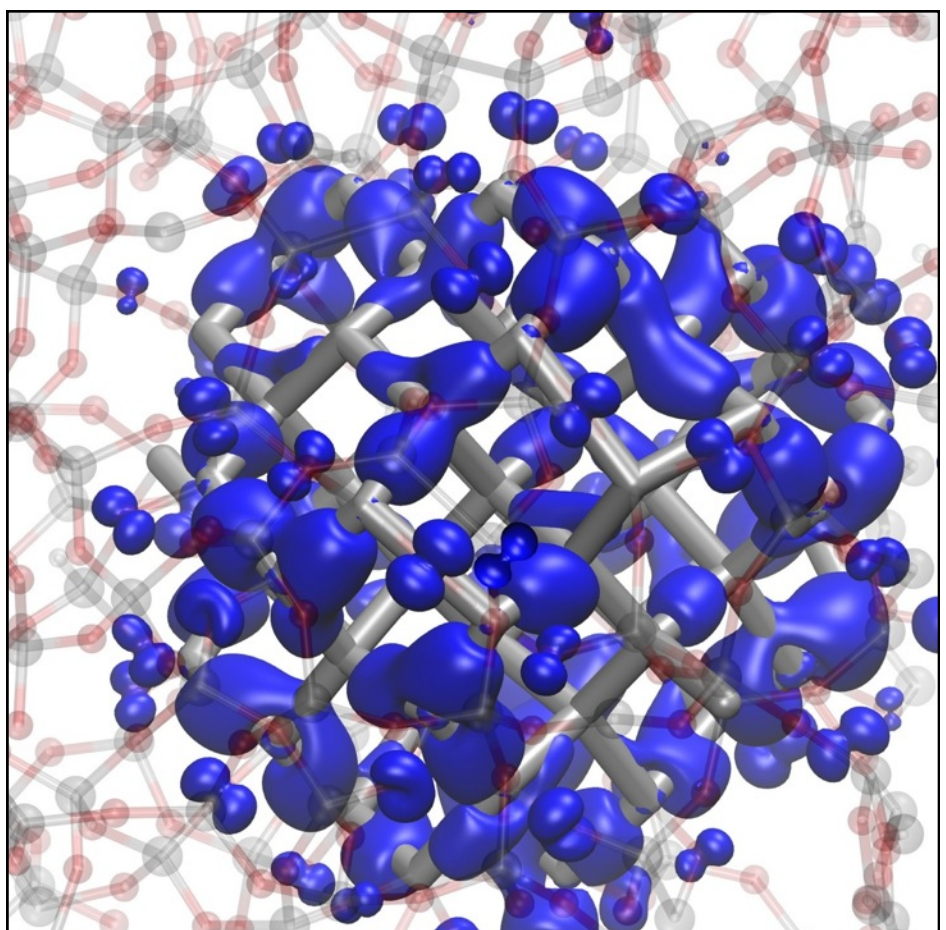


Si nanoparticles (NPs) in SiO_2: *type I junction*

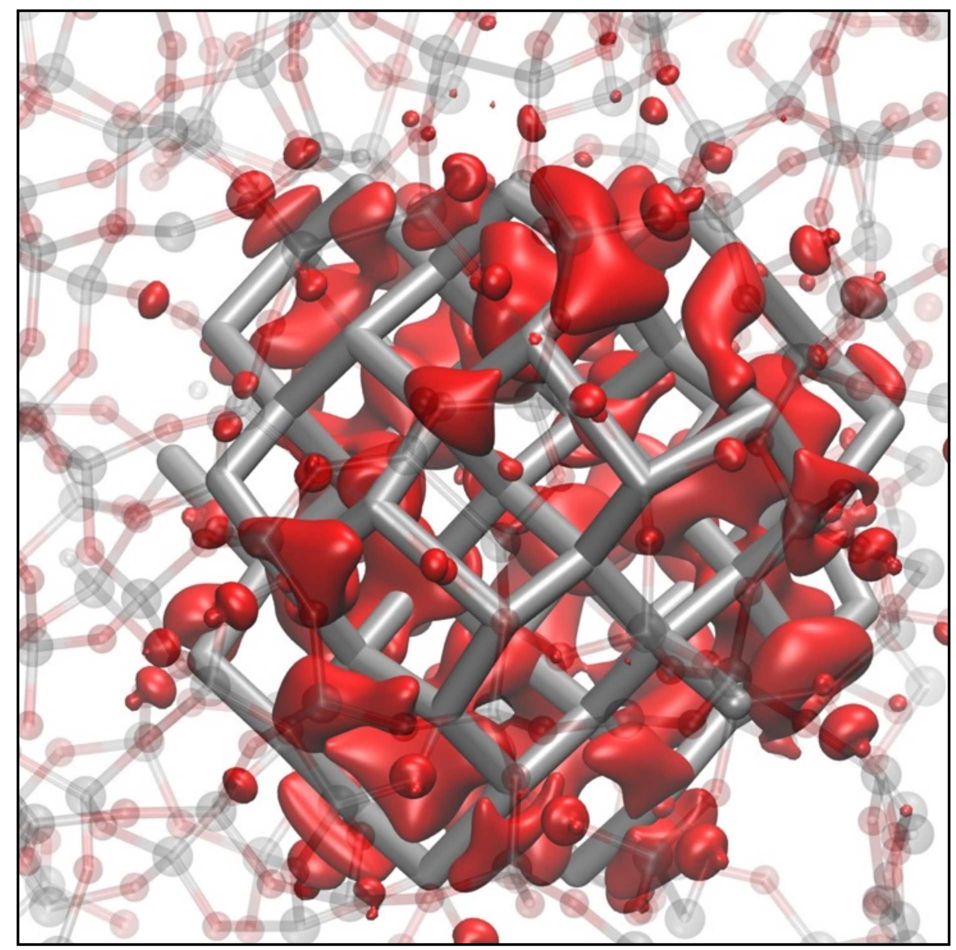
- Si NPs embedded in SiO_2 form a type I junction with their silica host
- Valence and conduction band edges localized inside Si NP => no charge transport
- NP LUMO may be pushed above SiO_2 CBM by compressive strain [T. Li, F. Gygi, G. Galli, PRL 2011]



valence band edge

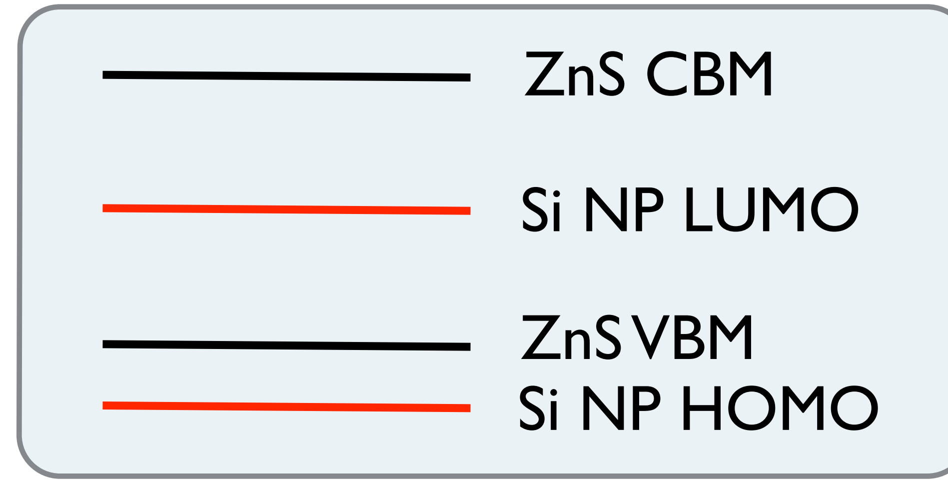


conduction band edge



Si nanoparticles (NPs) in ZnS: *type II junction*

- Si NPs in ZnS form a type II junction at equilibrium density
- Charge-separated transport channels for electrons and holes may facilitate charge extraction and suppress recombination
- Hole transport through host matrix, highly desirable for solar cells



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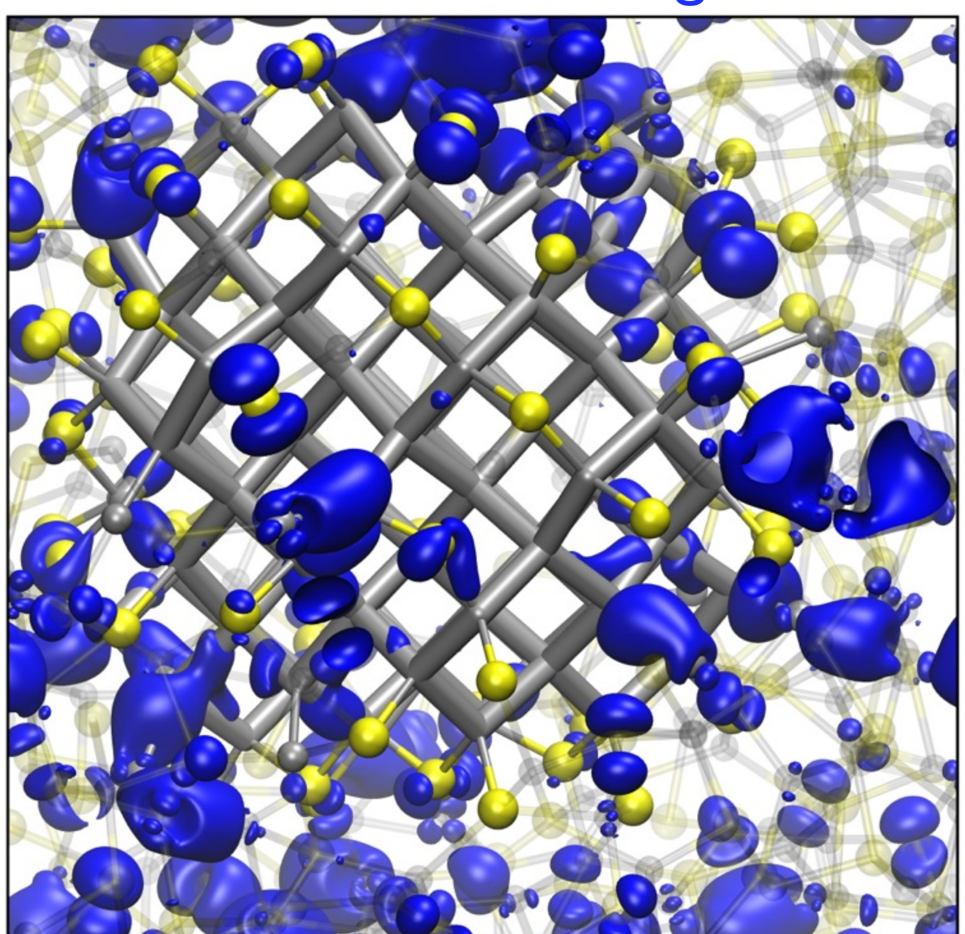

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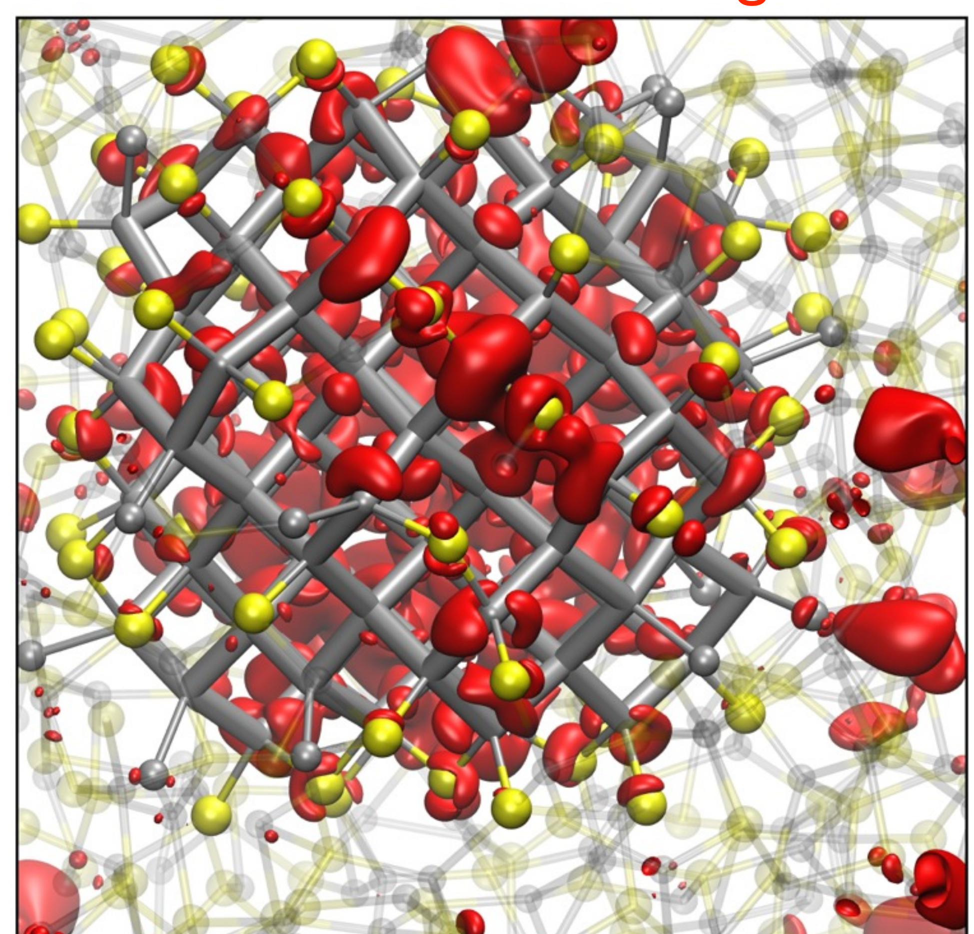
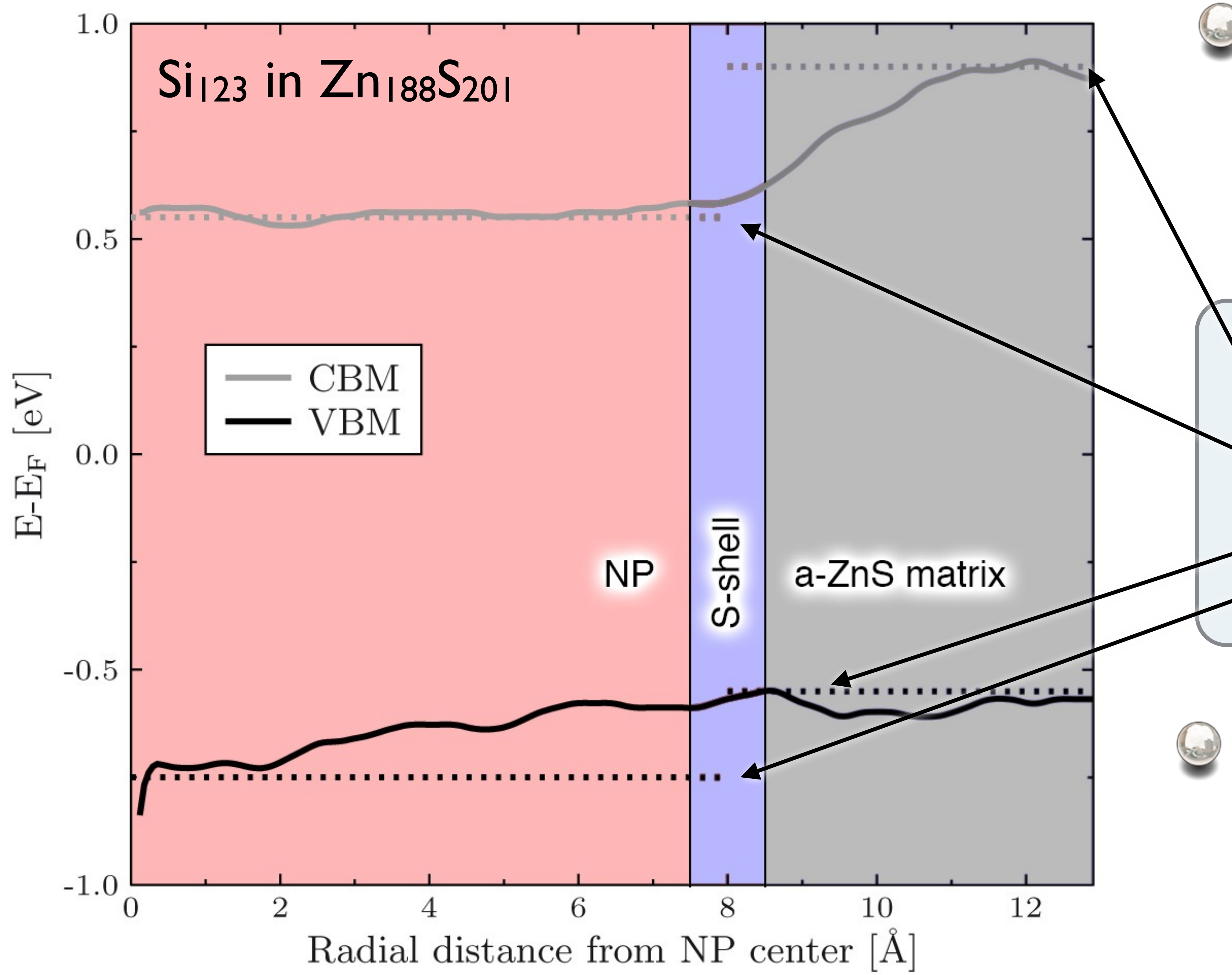
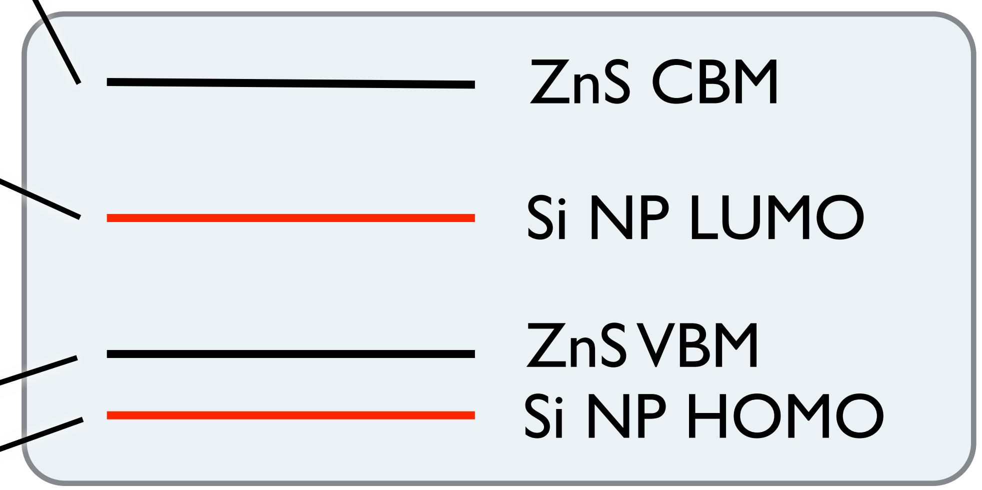


Si nanoparticles in ZnS: *band alignment*



- Calculate band edge energies as a function of the radial distance from the center of the NP



- Formation of type II interface between Si NP and a-ZnS matrix, if, and only if, sulfur content is above a certain threshold

- DFT-LDA band offsets reliable?

  => calculate band offsets in GW approximation

GW for large systems

- Calculation, storage & inversion of dielectric matrix **ε** is major computational bottleneck **=> spectral representation of ε (RPA)**

$$\tilde{\epsilon} = \sum_{i=1}^{N} \tilde{\mathbf{v}}_i \lambda_i \tilde{\mathbf{v}}_i^H = \sum_{i=1}^{N} \tilde{\mathbf{v}}_i (\lambda_i - 1) \tilde{\mathbf{v}}_i^H + I$$

[4] H.-V. Nguyen, T. A. Pham, D. Rocca, G. Galli, PRB **85** 081101 (2012), PRB **87**, 155148 (2013)

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- Calculating eigenvectors/-values does <u>NOT</u> require explicit knowledge of the matrix itself; knowing the **action of ε on an arbitrary vector** is sufficient
- In linear response: $(\epsilon - I)\Delta V_{SCF} = -v_c \Delta n$
- **Charge density response Δn to perturbation of self-consistent field ΔV_{SCF} can be evaluated from density functional perturbation theory**

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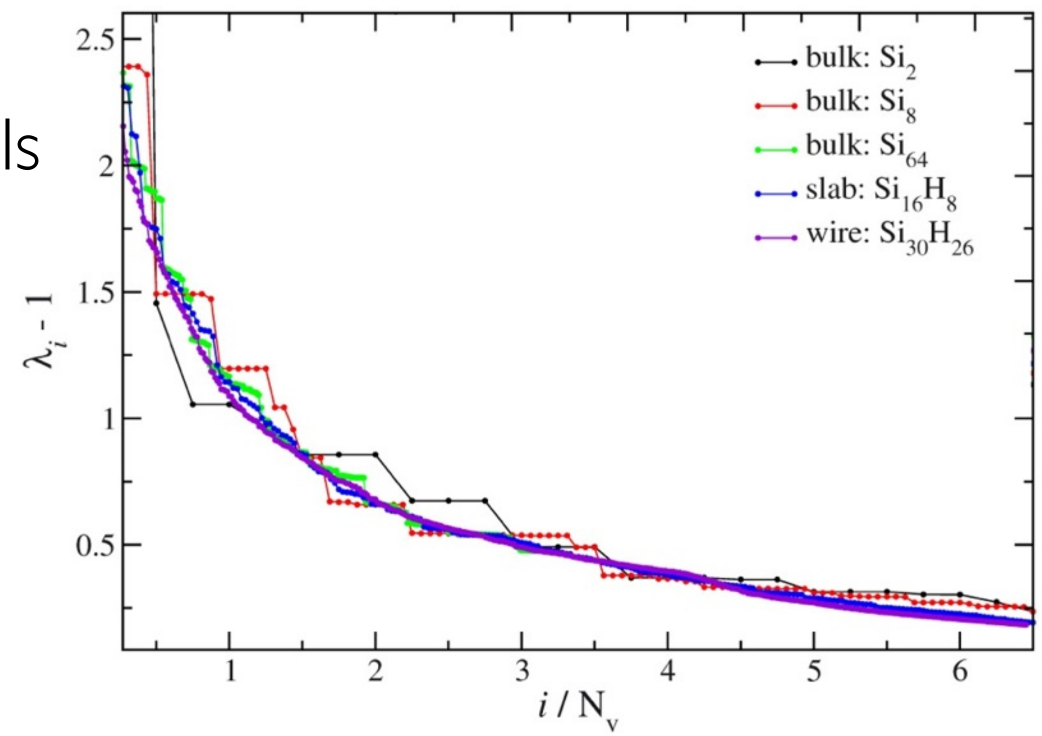
- Single parameter ***N*$_{eig}$** to control numerical accuracy
- **No summation over empty states, no inversion**



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D. Rocca, H.-V. Nguyen, T.A. Pham (UCD)

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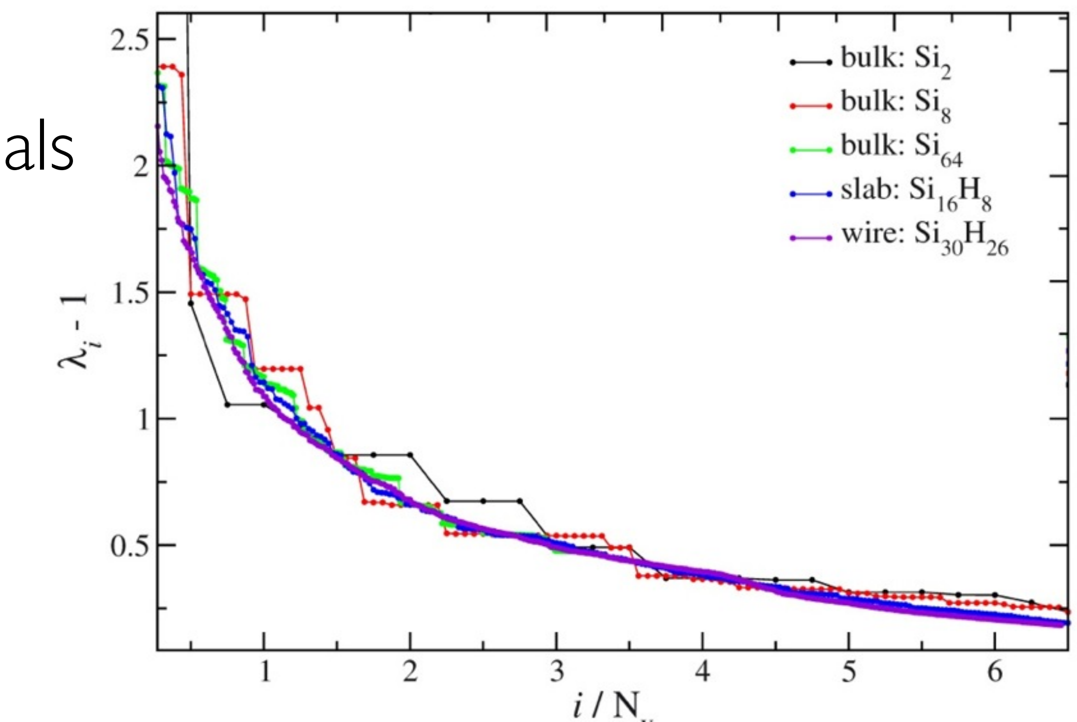

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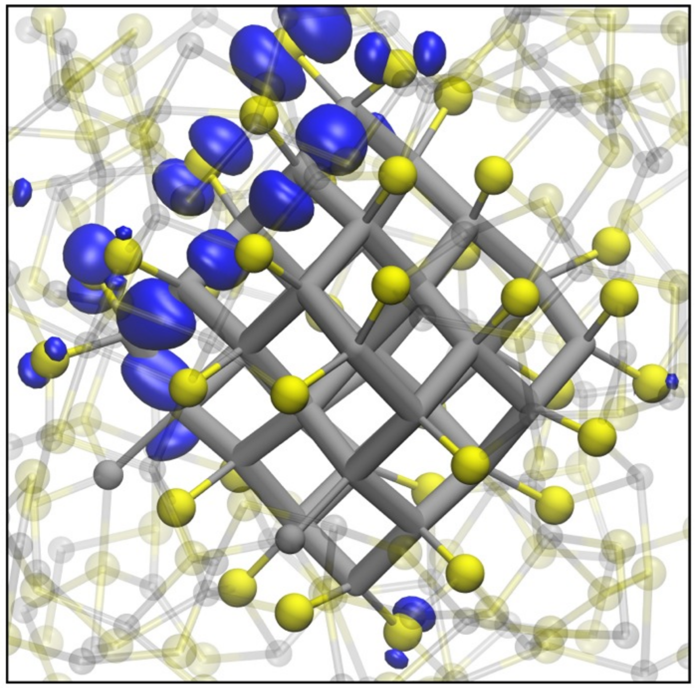
Band alignment from many body perturbation theory (GW)



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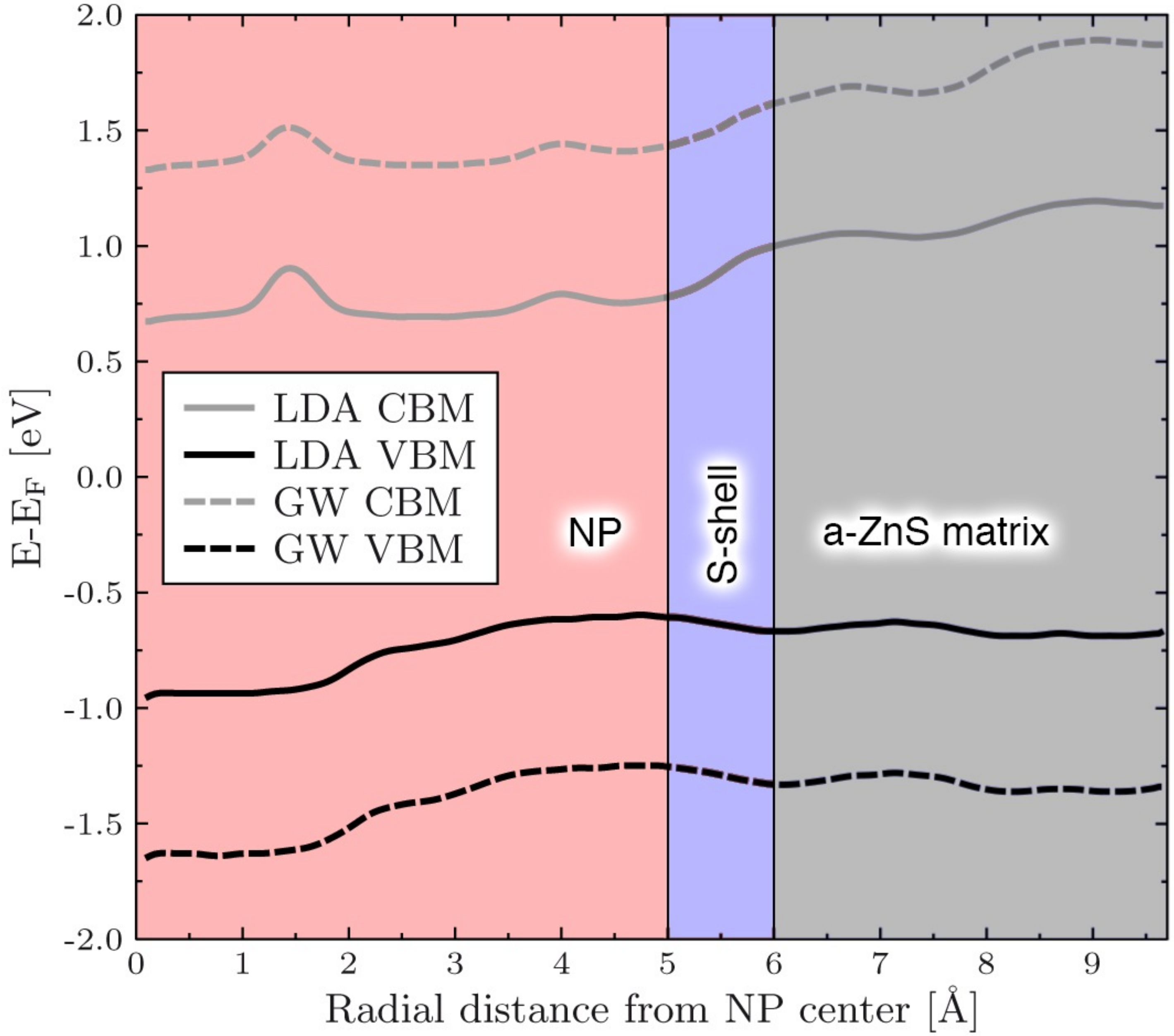

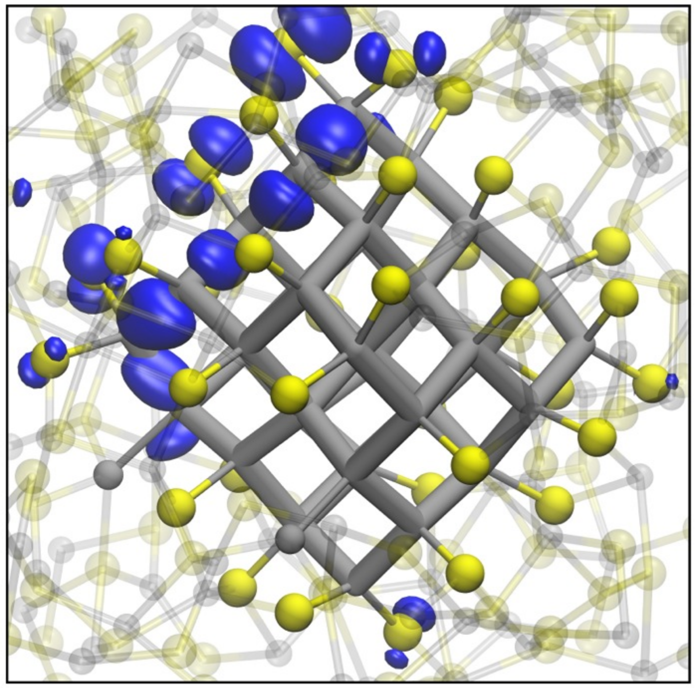

- GW calculations possible for a system as large as $Si_{35}Zn_{81}S_{100}$

- Many body corrections in GW approximation introduce mainly a rigid shift
  => confirms type II alignment

Summary

- Investigated 1.1 - 1.9 nm Si nanocrystals embedded in a-ZnS using ab initio MD and quasiparticle calculations in GW approximation
- ZnS-embedded Si nanocrystals form a type II junction with the ZnS host in sulfur-rich conditions
- Band edges localized in different portions of nanocomposite => charge-separated transport channels for electrons and holes

PRL **112,** 106801 (2014) PHYSICAL REVIEW LETTERS week ending 14 MARCH 2014

Solar Nanocomposites with Complementary Charge Extraction Pathways for Electrons and Holes: Si Embedded in ZnS

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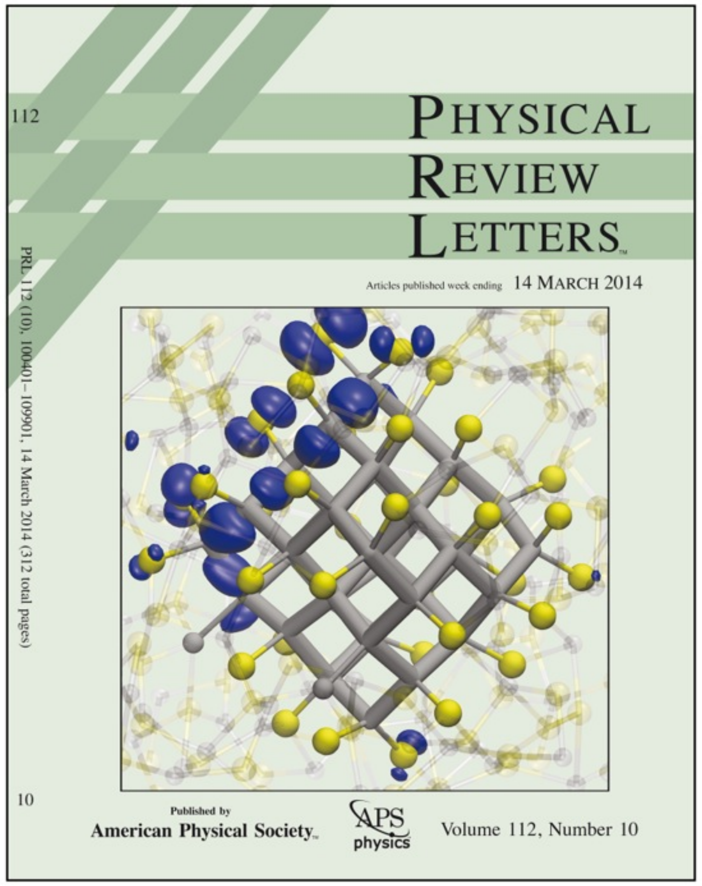

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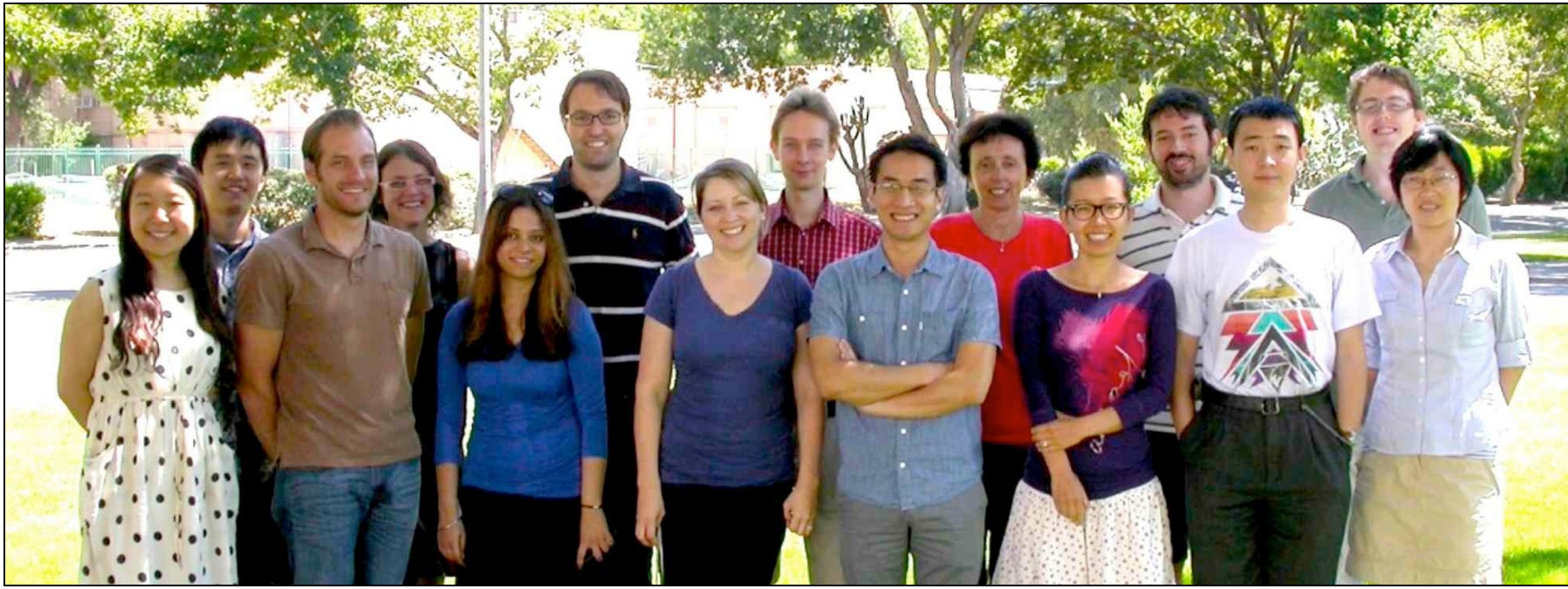

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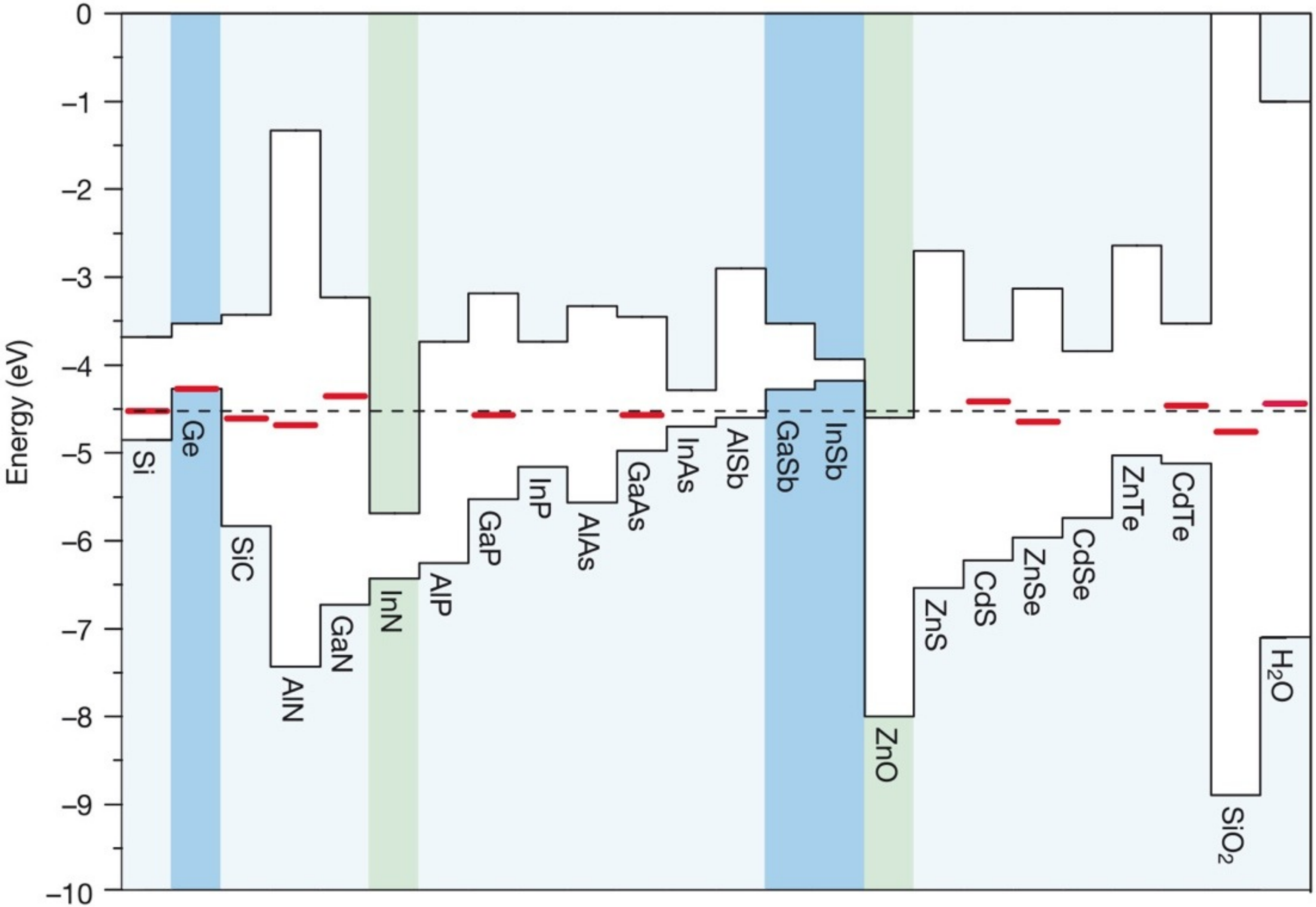
Band alignments of semiconductors



C. Van de Walle, J. Neugebauer, Nature **423**, 626 (2003)

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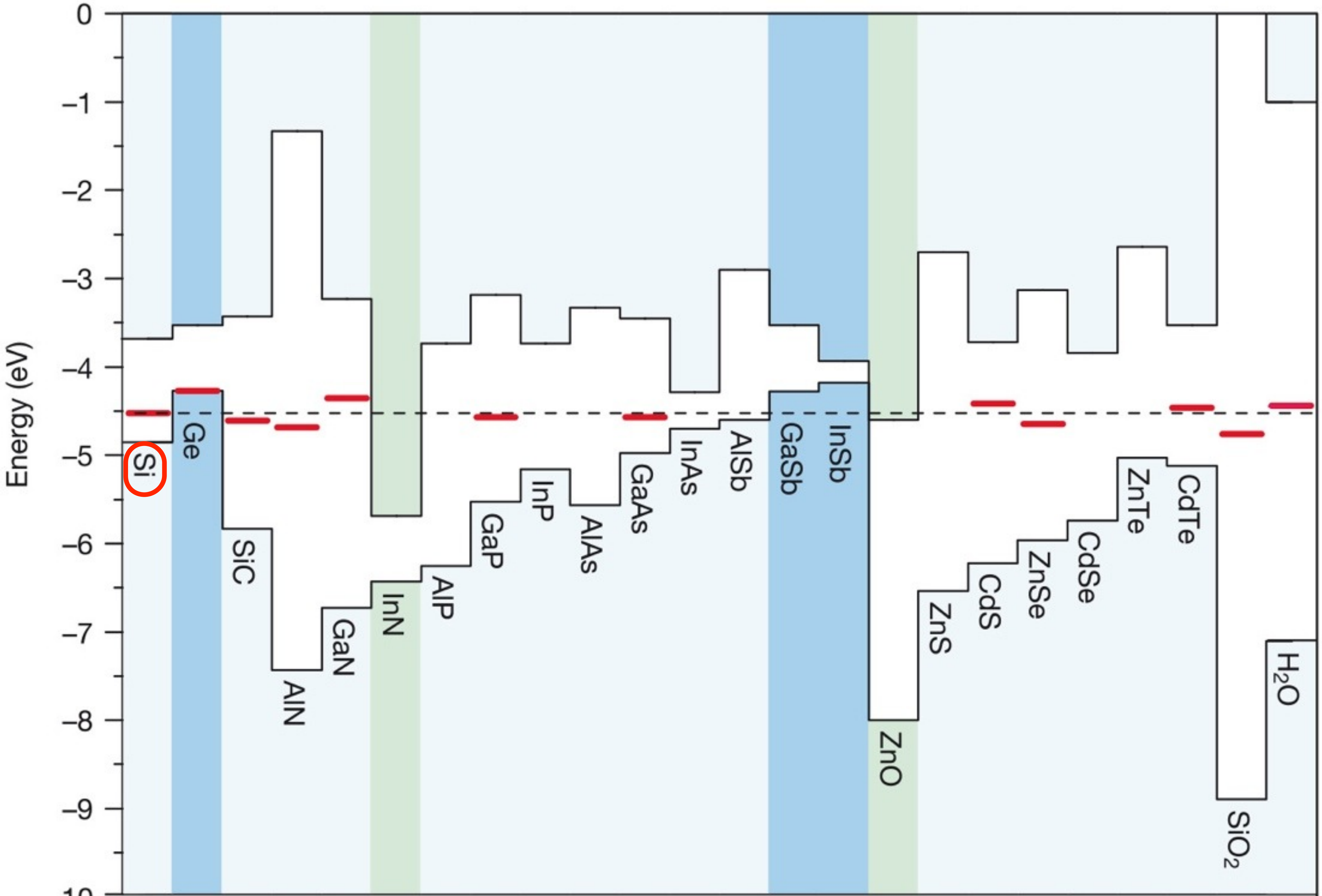

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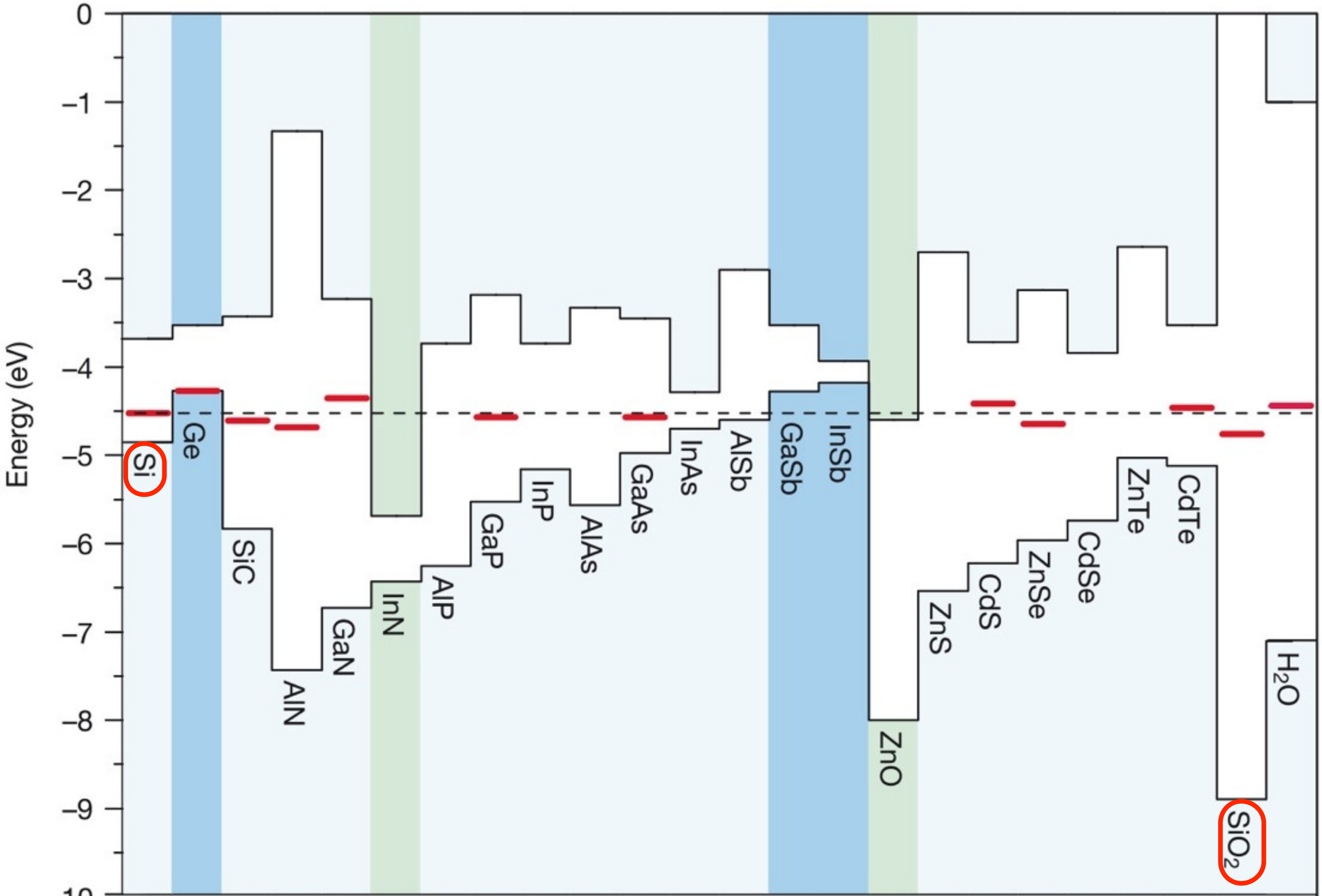

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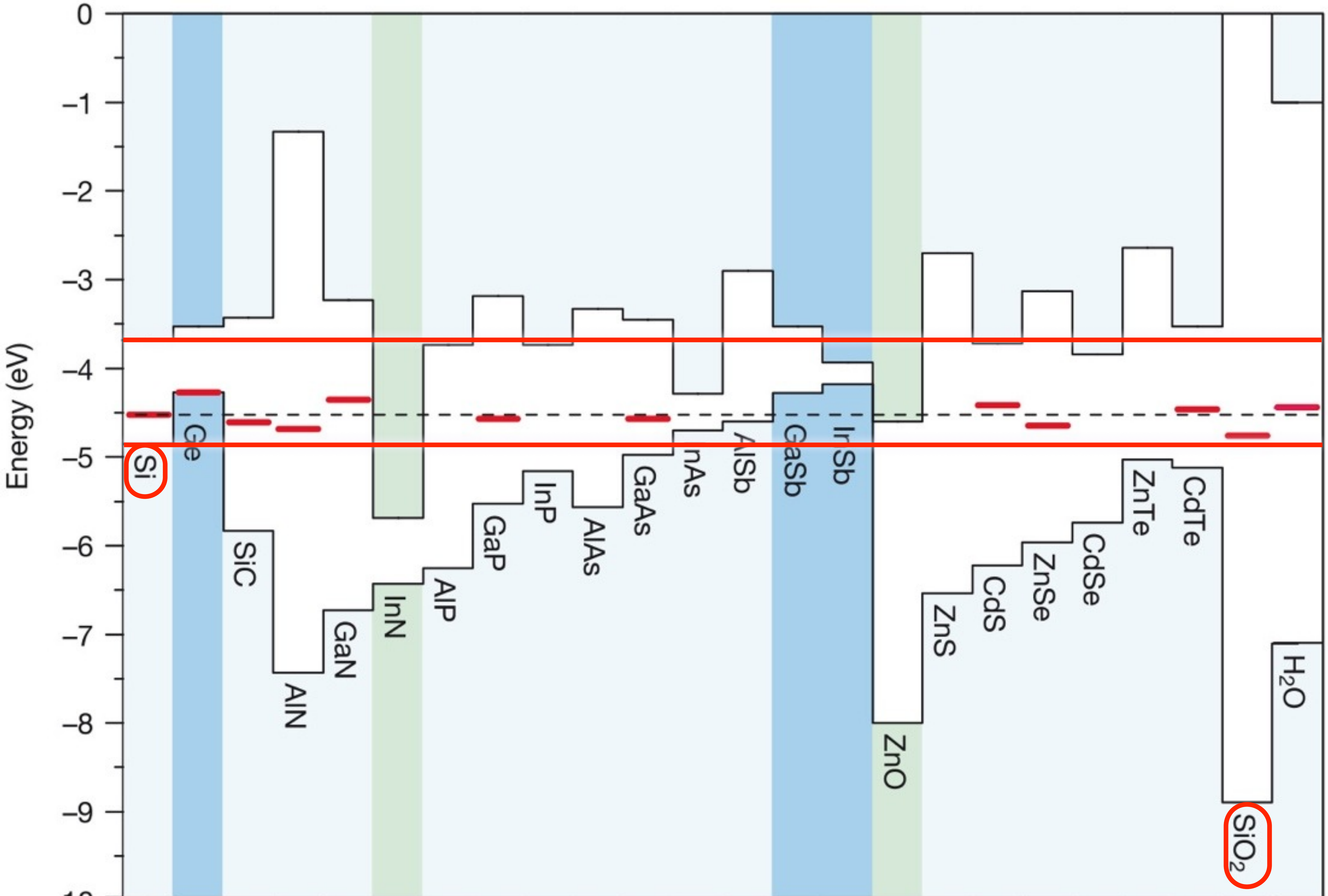

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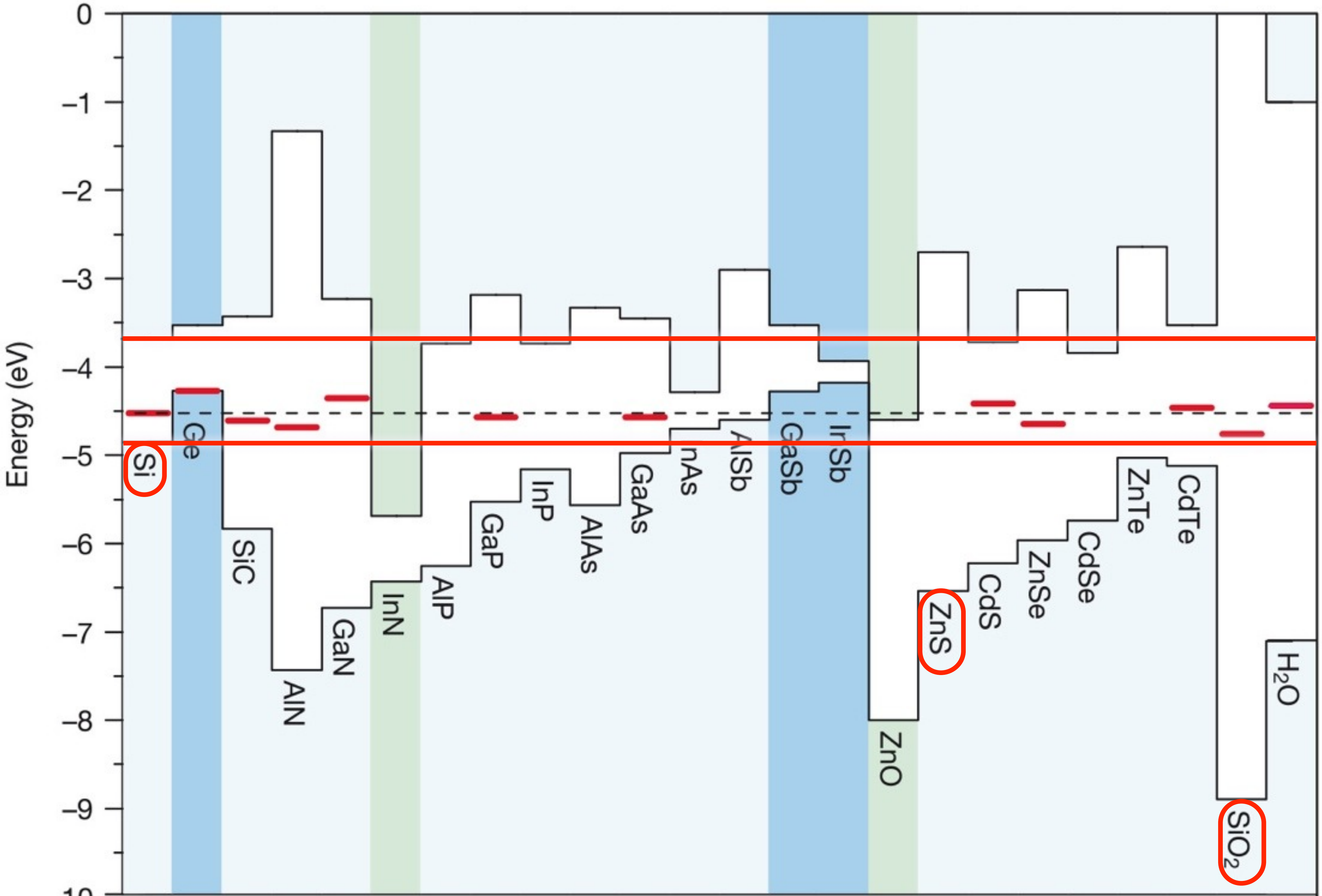

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