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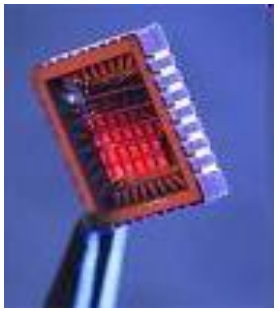
Large-scale DFT calculations on H-passivated Si nanorods using the ONETEP code

Outline

- Introduction
  - Applications of Si nanocrystals
  - Categories of Si nanoparticles
  - Reconstructions
- Validation Tests
  - $Si_{242}H_{140}$ nanoplate
  - $Si_{29}H_{36}$ nanoparticle
- Methodology
- Results
  - Formation Energies
  - Energy Band Gaps
  - Density of States
  - Orbital Densities
- Summary

Applications of Si nanocrystals

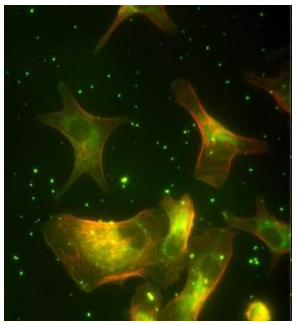


Computer Chips:

Field-effect nanotransistor.

Bio-sensors:

Biological Fluorescent Imaging.

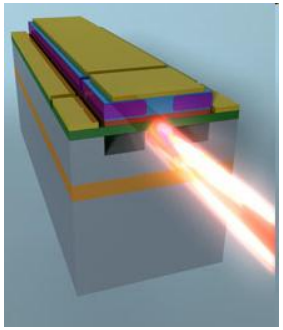


Solar Cells:

Ultrathin films of luminescent Si

Nano-Lasers:

Optical data processing



Categories of Si nanoparticles

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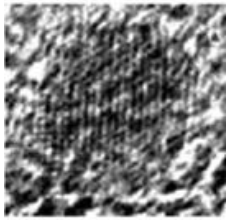
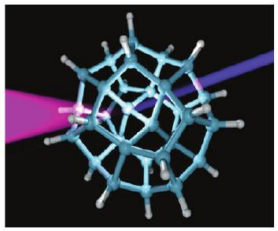
- **Quantum Dots**



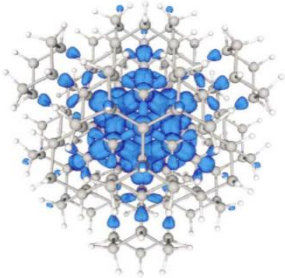
Belomoin et al.

Ultra-small →

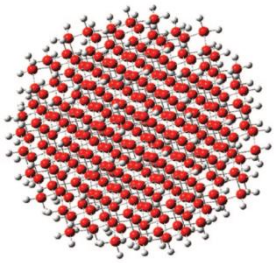


Draeger et al.

Small →

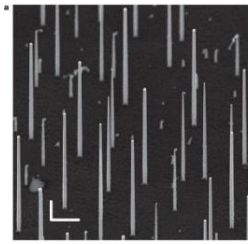


Puzder et al.



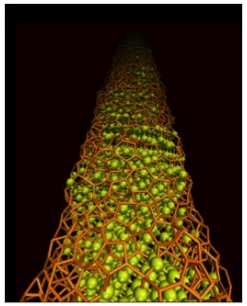
Wang et al.

- **Nanowires**



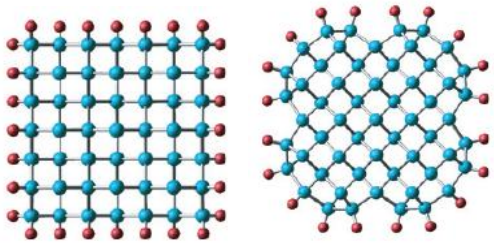
Hannon et al.

Infinite nanocrystal →



Galli et al.

Periodic Images →

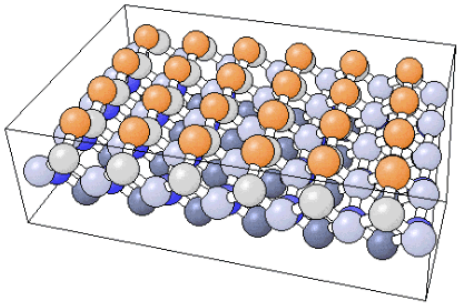


Singh et al.

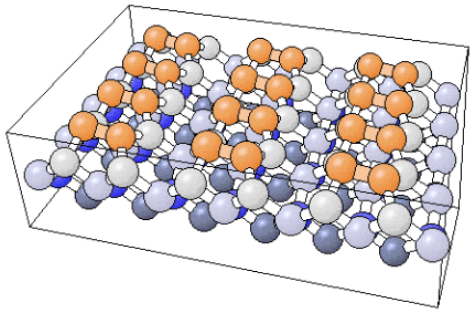
Reconstructions

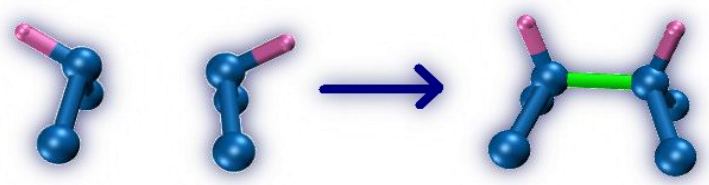
- **Surface Reconstructions of Si:**

Unreconstructed Si(100)-(1x1) surface.



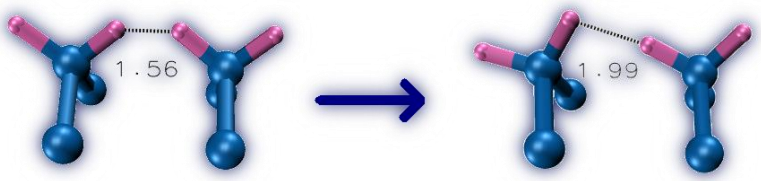
Reconstructed Si(100)-(2x1) surface.





- **Dimerisation** of a pair of surface Si atoms on a **(2x1)** surface **enlarges** their near neighbouring distances.

- **SiH_2 dimers** located on **(1x1)** surface can adopt a **"canted"** conformation allowing neighbour **H** atoms to **minimise** their **repulsive** interactions.

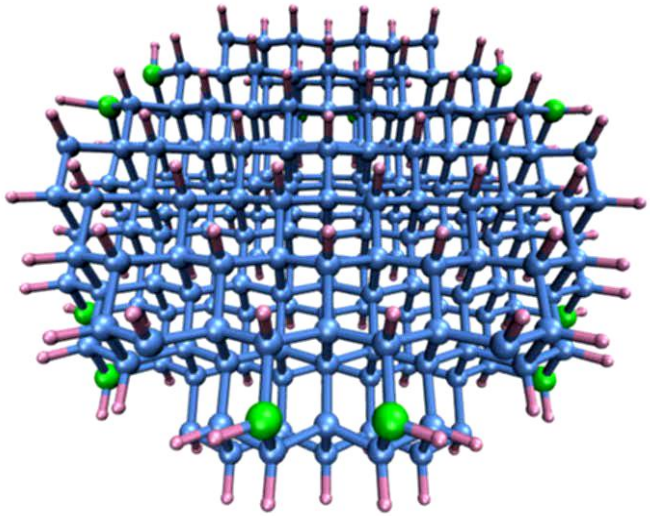


The $Si_{242}H_{140}$ nanoplate

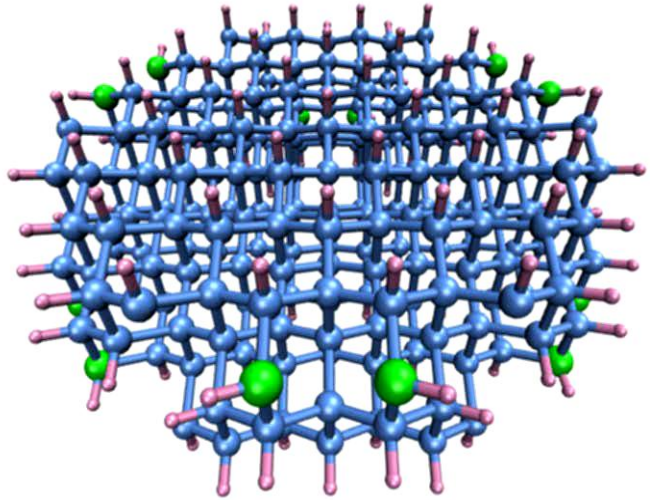
Test surface reconstruction:

- **Geometry optimisations** on a **2.0 nm** thick nanoplate ($Si_{242}H_{140}$) by using:

Classical Molecular Dynamics



- Classical Force Field:
  Stillinger-Weber potential [1]
- Force tolerance of ~$1x10^{-9}$ eV/Å

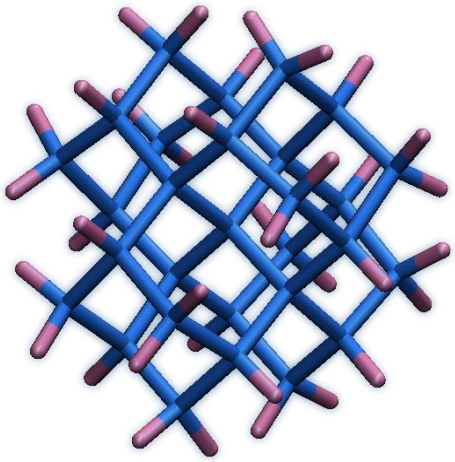


- Kinetic energy cut-off = 650 eV
- Density kernel cut-off = 25.0 a_0
- Force tolerance of 0.05 eV/Å

Density Functional Theory

[1] F. H Stillinger and T. A. Weber; *Phys. Rev. B*, **31,** 8, 5262–5271 (1985)

The $Si_{29}H_{36}$ nanoparticle

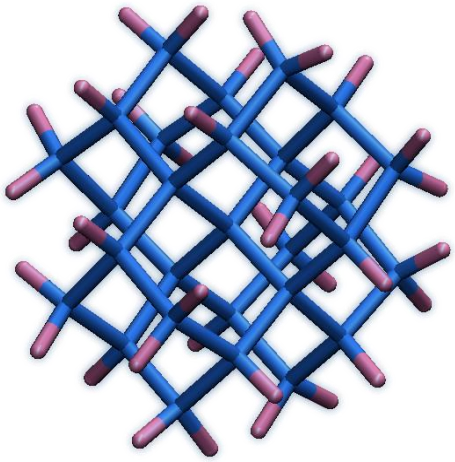


- **Variation of Bond Lengths:**

Atomic Interaction	Bond Lengths			
	ONETEP	CASTEP	NWCHEM	DFTB+
Si-Si (inner shell)	2.326	2.335	2.343	2.363
Si-Si (outer shell)	2.319	2.325	2.337	2.339
Si-H (monomers)	1.503	1.487	1.509	1.503
Si-H (dimers)	1.498	1.480	1.503	1.498

- Energy tolerance = 0.2 meV
- Force tolerance = 0.05 eV/Å (CASTEP, ONETEP and DFTB+)
- 6-31+G* basis set for Si and H atoms (NWCHEM)
- PBE exchange-correlation functional
- 9 NGWFs/6 NGWFs for Si atoms

The $Si_{29}H_{36}$ nanoparticle



- **Energy Band Gaps:**

ONETEP:

- **LDA** [2] = 3.75 eV

{Ref. [4] 3.6 eV, Ref [5] 3.67 eV}

- **B3LYP** [3] = 5.3 eV

{Ref. [4] 5.3 eV (QMC), Ref. [5] 5.32 eV (B3LYP/6-31G(d))}

Experiment = 3.7 eV ($Si_{29}H_{24}$)

[2] J. P. Perdew, A. Zunger; *Phys. Rev. B,* **23**, 5048–5079 (1981)

[3] A. D. Becke. *J. Chem. Phys.,* **98,** 7, 5648–5652 (1993)

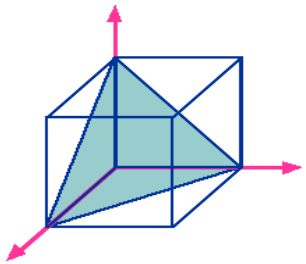
[4] A. Puzder, A. J. Williamson, J. C. Grossman, and G. Galli; *J. Am. Chem. Soc.*, **125,** 9, 2786–2791 (2003)

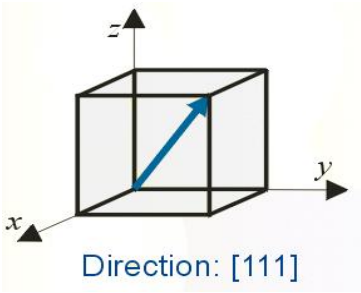
[5] Bo-Cheng Wang, Yu-Ma Chou, Jin-Pei Deng and Yu-Tsai Dung; *J. Phys. Chem. A* **112,** 28, 6351-6357 (2008)

Methodology

- **Construction** of H-passivated Si nanorods with diameters **0.8, 1.1** and **1.3 nm**, length ~**5 nm** and **(1x1)** or **(2x1)** surface reconstruction.

- All the nanorods were elongated along the **[111] growth direction.**





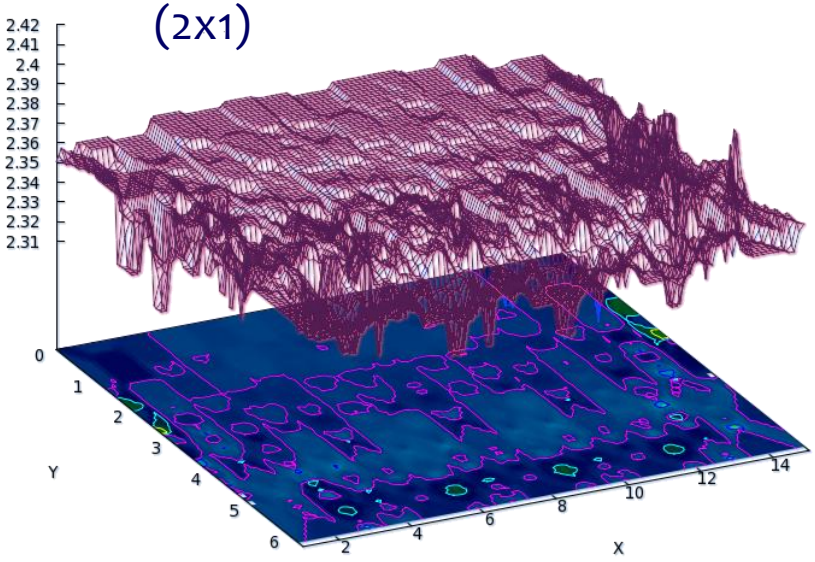
- **Geometry optimisations** using **tight-binding DFT** [6] on all the constructed nanorods within the **PBE** exchange –correlation functional [7].

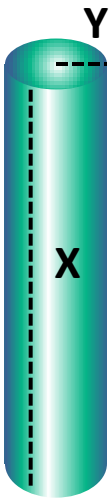
- **Structural properties** (surface reconstruction, geometry distortion) and **electronic properties** (stabilities, energy band gaps, density of states, HOMO - LUMO orbital densities).

[6] B. Aradi, B. Hourahine, and Th. Frauenheim. *J. Phys. Chem. A*, **111**, 26 5678–5684 (2007)

[7] J. P. Perdew, K. Burke, and M. Ernzerhof. *Phys. Rev. Lett.*, **77**, 18, 3865–3868 (1996)

Structural Properties



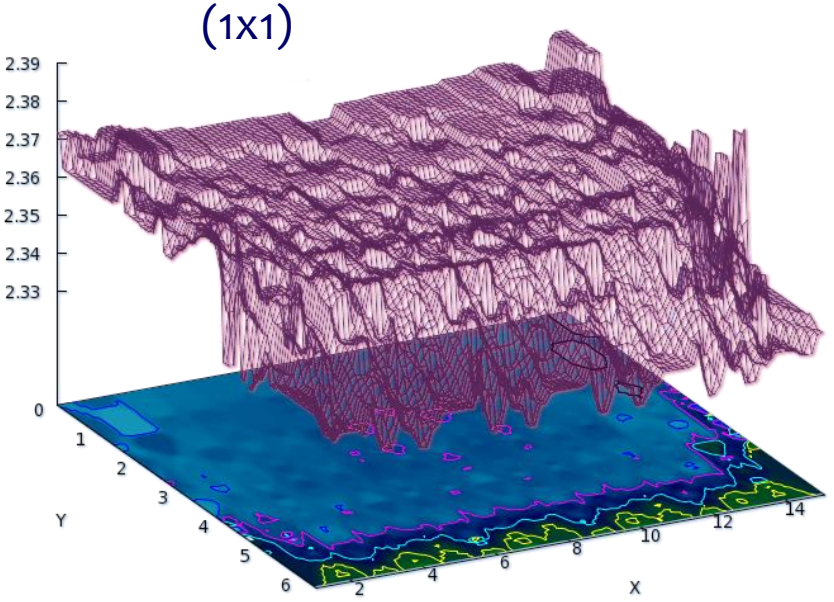


- Nanorod **volume** with **bulk crystalline silicon** properties from diameters 0.8 -1.3 nm:

  (1x1) reconstruction : 60% - 75%

  (2x1) reconstruction: 25% - 45%

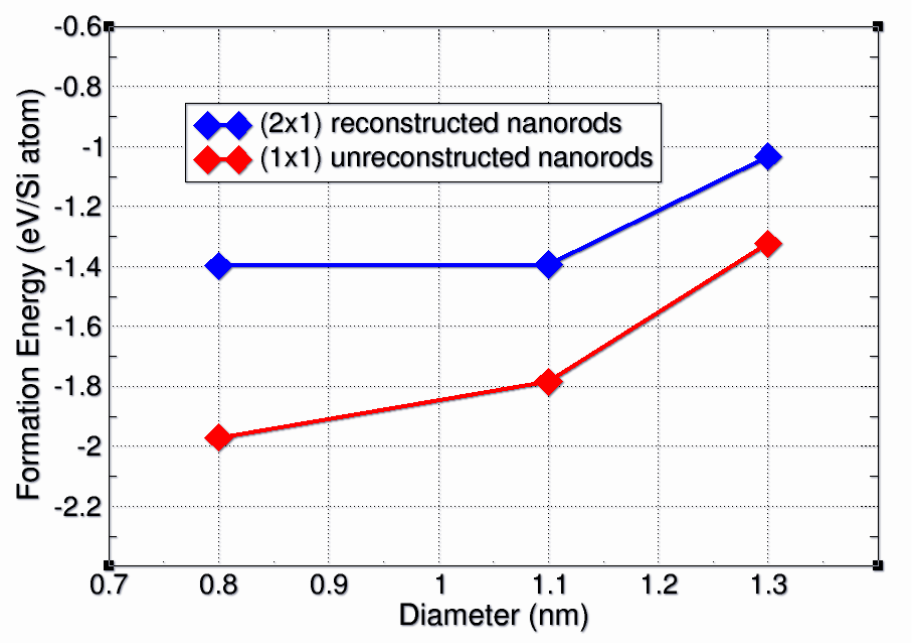
- **Structural stability** in the "**core**".
- **(1x1):** Si-Si bond lengths become **shorter** from the "**core**" to the **surface.**



Formation Energies

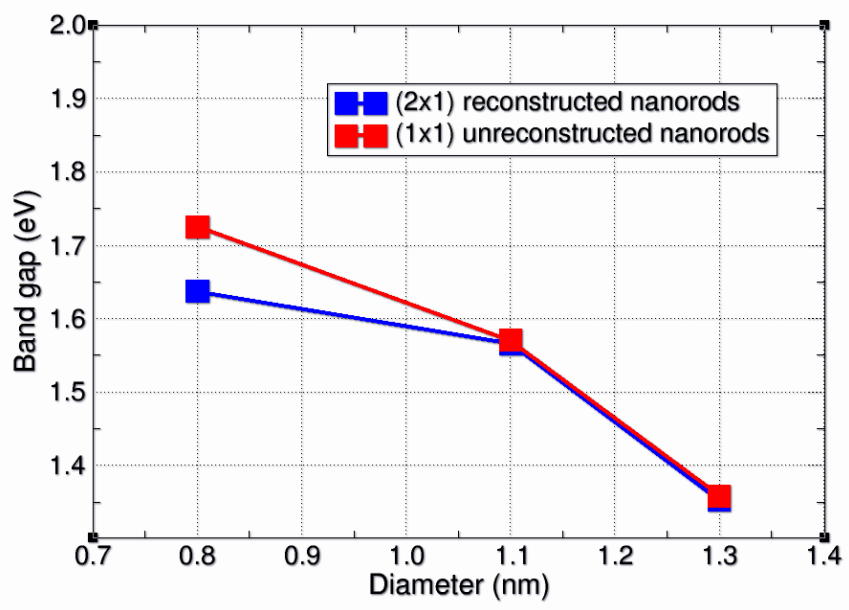
$$E_f = \frac{(E^{tot} - (n_H E_H))}{n_{Si}} - E_{Si} \quad [8]$$

- E_{Si} and E_H: Energies of a **single** atom in **bulk silicon** and **H_2** respectively .
- n_H and n_{Si}: number of **H** and **Si** atoms in the nanorod .
- E^{tot} = **Total energy** of the nanorod.
- As the system **size increases** the **stability decreases.**



[8] T-L Chan, C. V. Ciobanu, F-C Chuang, N. Lu, C-Z Wang, K-M Ho; *Nano Letters*, **6**, 2, 277–281 (2006)

Energy Band Gaps



- **Reduction** as the diameter **increases .**
- **Reconstructed** surfaces - **smaller** band gaps from **unreconstructed.**
- **Surface reconstruction** does **not** affect band gaps from diameters **larger** than 1.1 nm.
- **Underestimated** values - still provide **reliable** trends for optical gaps [9].
- **No post-processing** correction:
  e.g. GW approach [10] = n^5 time scale

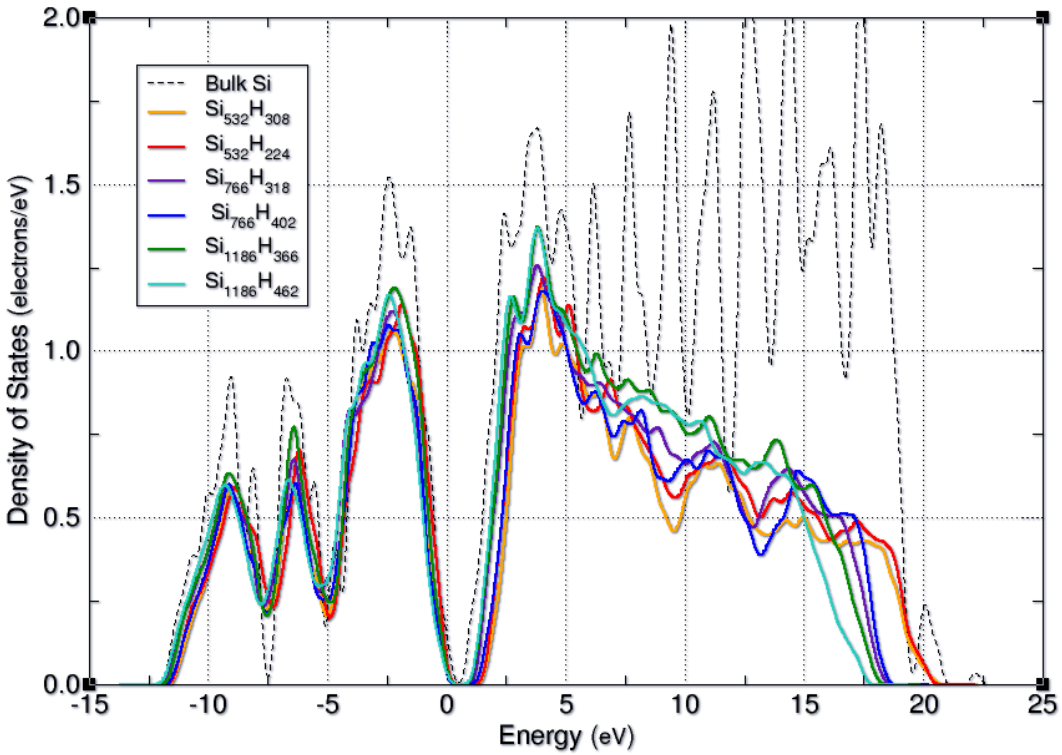
[9] R. Rurali, B. Aradi, Th. Frauenheim, G. Galli; *Phys. Rev. B*, **76** , 11, 1133303 (2007)
[10] M. S. Hybertsen and S. G. Louie. *Phys. Rev. Lett.*, **55,** 13, 1418–1421 (1985)

Density of States

- **Reduction** of the band gap as the diameter **increases.**
- **Valence band :**

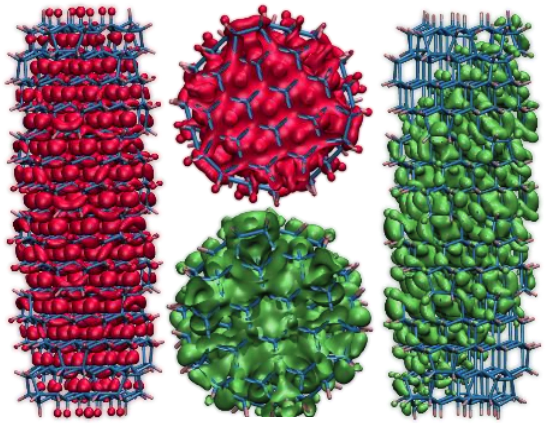
  good agreement between DOS of **nanorods** (ONETEP) and **bulk Si** (CASTEP).
- **Conduction band:**

  Localised orbital approaches only reliable for **low-lying conduction bands** [11].

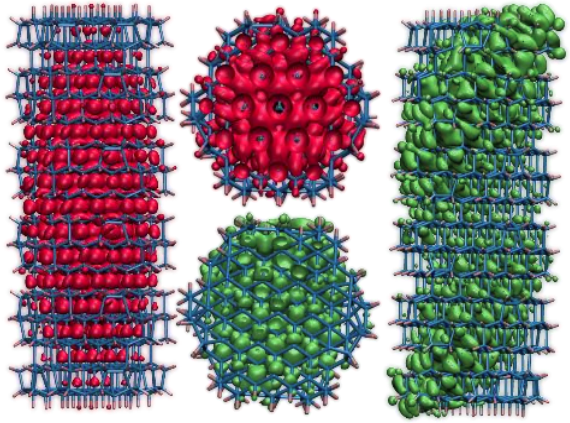


[11] C-K. Skylaris, P. D. Haynes; *J. Chem. Phys.*, **127,** 16, 164712 (2007)

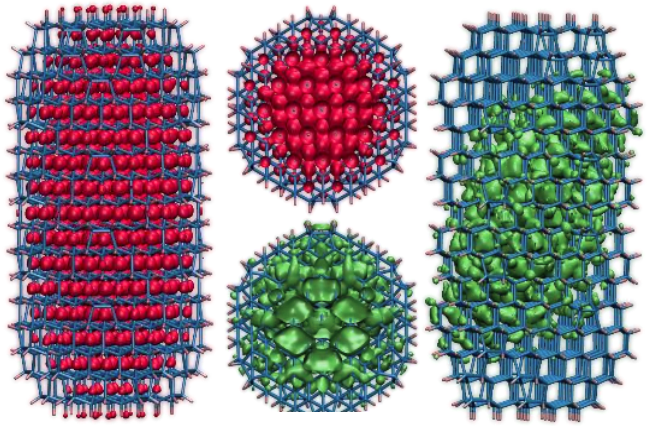
Orbital Densities



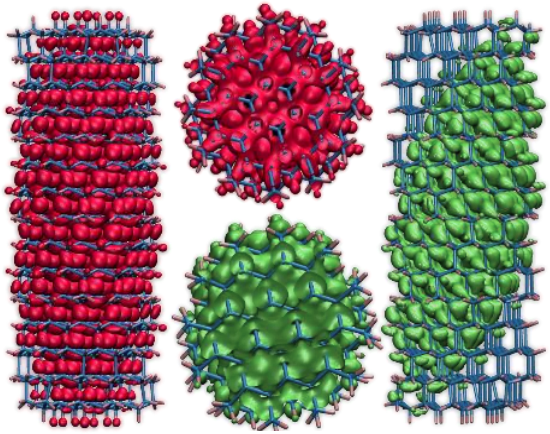
$Si_{532}H_{224}$



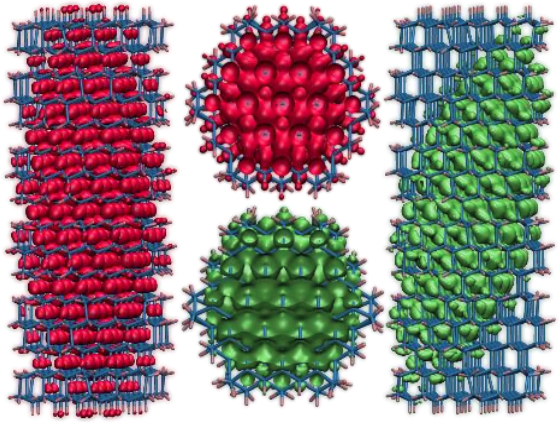
$Si_{766}H_{318}$



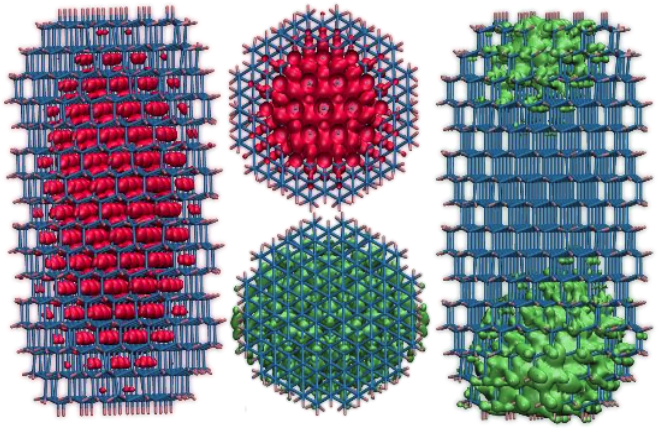
$Si_{1186}H_{366}$



$Si_{532}H_{308}$



$Si_{766}H_{402}$



$Si_{1186}H_{462}$

Summary

- Computational study by **DFT**, using the **ONETEP** code of Si nanorods containing more than 1000 atoms with varying **aspect ratios** and **surface passivation** by H, **without** the use of **symmetry** or **periodicity.**
- **(2x1)** reconstructed nanorods have **larger structural distortions** and **lower stabilities** than **(1x1)** as the **diameter** of the nanorod **increases.**
- **Reduction** of ~ 0.5 eV for the **(1x1)** surfaces and of ~ 0.3 eV for the **(2x1)** nanorods of the **HOMO-LUMO band gap** when the **diameter** is **increased** from 8 Å to 13 Å.
- **Benchmark results** of experimental interest with possible applications in **optical** and **photonic devices.**
- This work has been published:

  N. Zonias, C.-K. Skylaris, P. Lagoudakis; J. Phys.: Condens. Matter, **22**, 025303 (2010)

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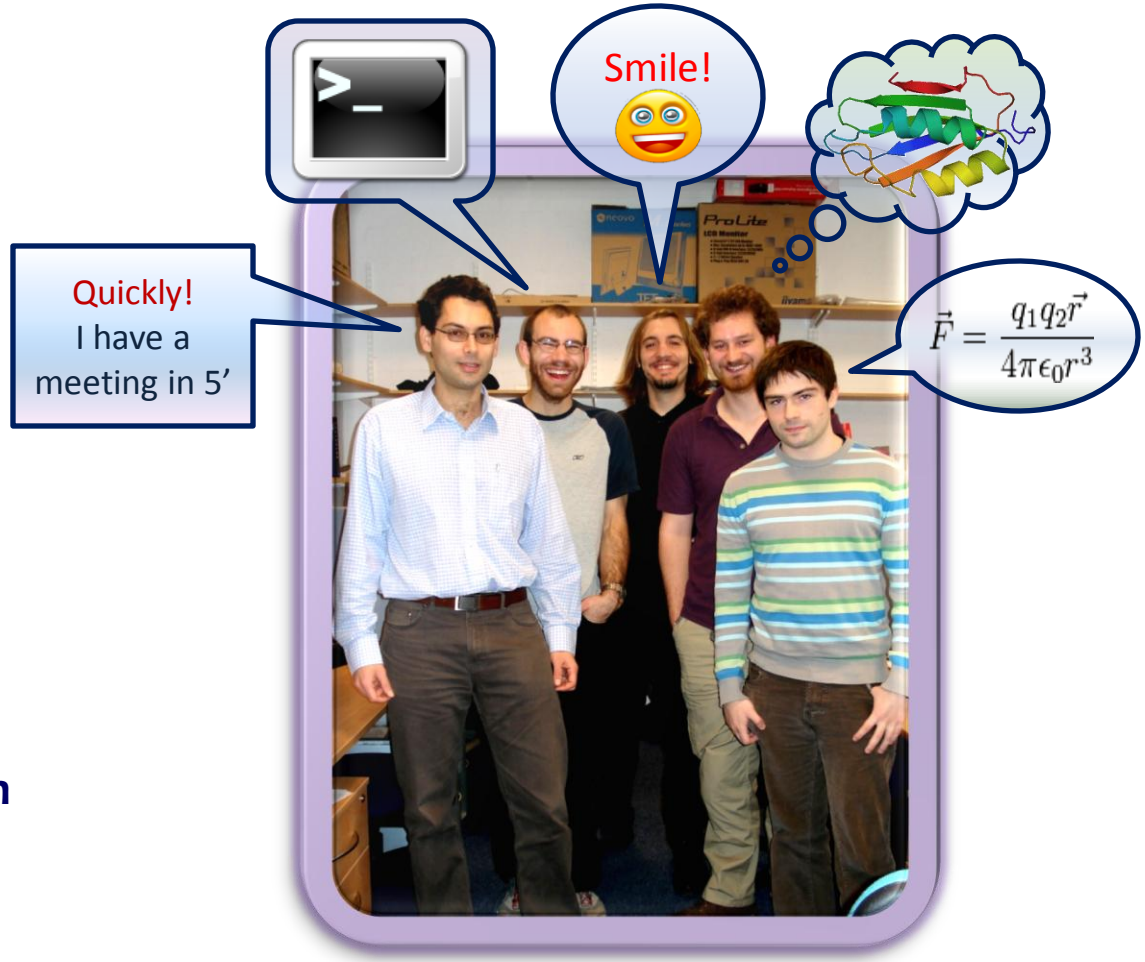
  iSolutions
  HECToR



Thank you for your attention!