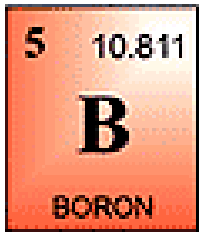

Predicting Materials and Material Properties by Density Functional Theory:

The Case Study of Boron

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Outline

- Motivation
- Boron Sheets
- Boron Nanotubes
- Structure Control
- Nanotubular Junctions
- Layered Bulk Phases of Boron
- Enatom Method
- Summary

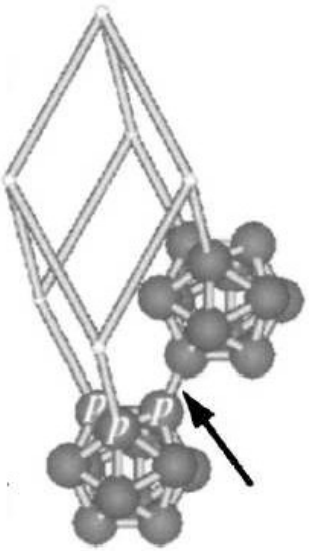
Motivation

Why is elemental boron interesting?

- little studied
- many fundamental properties are unknown (phase diagram, ground state structure, etc.)
- very complex chemistry and bonding

Bulk Phases

- 3D frameworks of B_{12} icosahedra
- different bulk phases
  → α-rhombohedral (12 at./cell)
  → β-rhombohedral (106.7 at./cell)
  → β-tetragonal (189.9 at./cell)
- semiconducting
- **superconducting** at high pressure
  Eremets *et al.*, Science **293**, 272 (2001)



α-rhomb. boron

Motivation

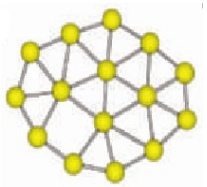
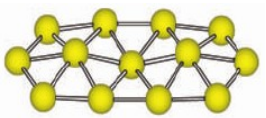
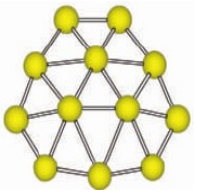
Clusters

- Aufbau principle: Boustani, Phys. Rev. B **55** (1997)

  → prediction of boron **nanostructures**:
  nanotubes, fullerenes, sheets

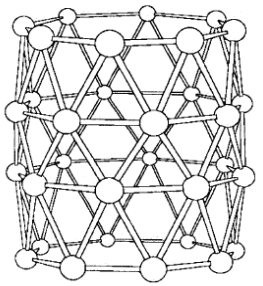
- small boron clusters are quasiplanar

  → theory: I. Boustani, Surf. Sci. **370** (1997)
  → experiments: H.J. Zhai, et al. Nat. Mater. **2** (2003)

- boron nanotubes

  → theory: Boustani *et al.*, Europhys. Lett. **39** (1997)
  → experiments: Ciuparu *et al.*, J. Phys. Chem. B **108** (2004)



Motivation

Many open questions:

- What is the **detailed** atomic structure of the boron nanostructures?
- What are the properties of these nanostructures?
- How can we understand the chemical bonding in the different phases?
- What is the ground state structure/phases diagram?
- What bulk phase is responsible for the high-pressure superconductivity?
- ....

Methods

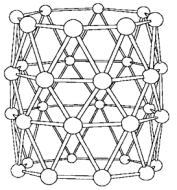
Density Functional Theory (DFT)

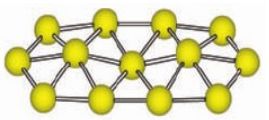
- calculate electronic structure
  (charge density, DOS, band structure, Fermi surface)
- structural simulations and optimizations
- Codes:
  → TB-LMTO-ASA: tight-binding LMTO in
  atomic sphere approximation
  → LmtART: all-electron full-potential LMTO
  → VASP: plane waves and pseudopotentials

Boron Sheet

Experiment:

- nanotubes
  Ciuparu *et al.*, J. Phys. Chem. B **108** (2004)
- small quasiplanar clusters
  H.J. Zhai, et al. Nat. Mater. **2** (2003)





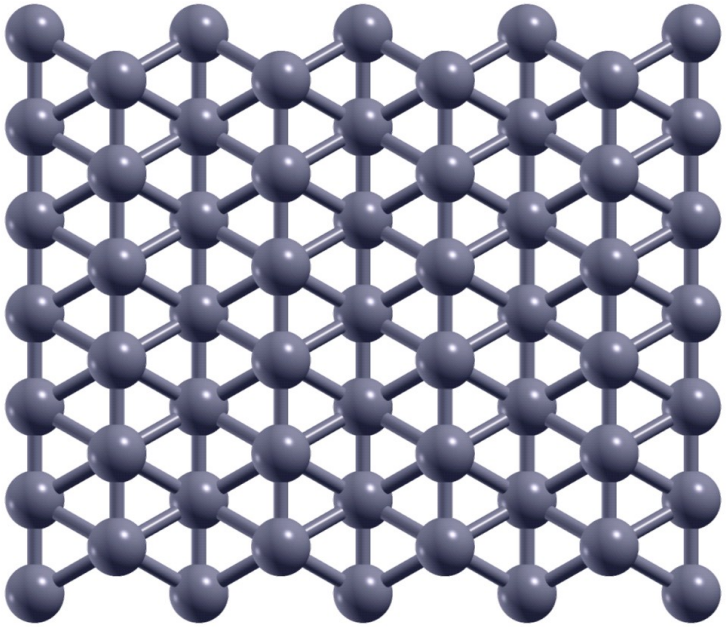
Broad Boron Sheet:

- the precursor of boron nanotubes
- the boron analogue of a single graphite sheet

What does a broad boron sheet look like?

Boron Sheet

top view



triangular lattice

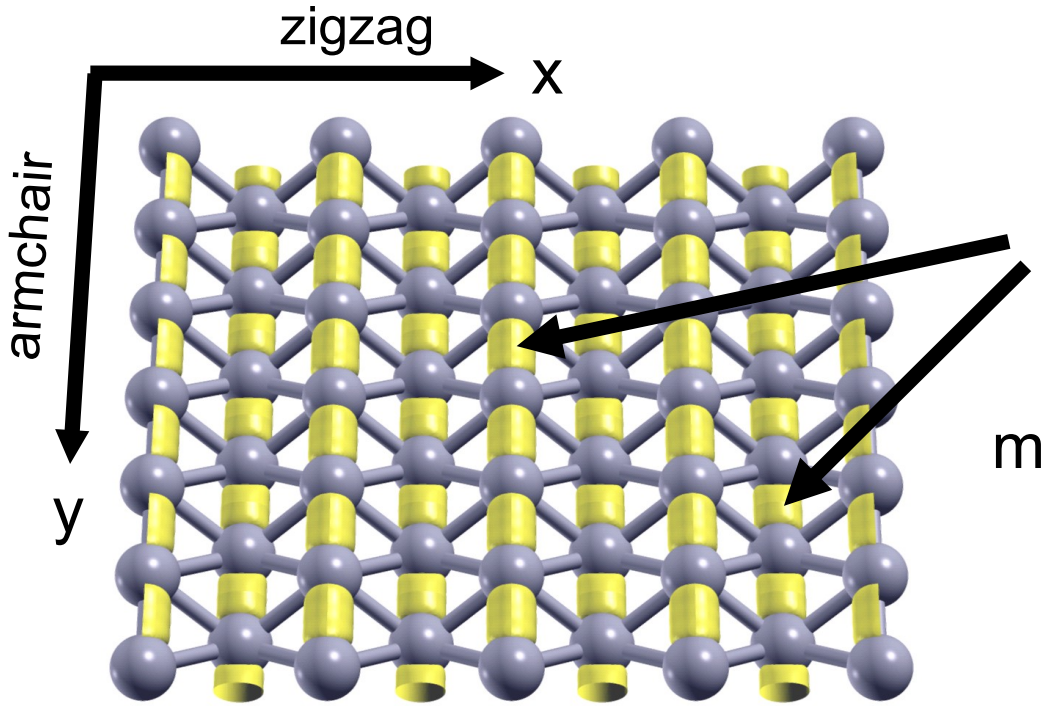
side view

simple up-and-down structure

- structure found by DFT simulations
- structure independently found also by
  Evans *et al.*, Phys. Rev. B **72**, 45434 (2005).
  Cabria *et al.*, Nanotechnology **17**, 778 (2006).

JK *et al.*, Phys. Rev. B **74** (2006)

Boron Sheet



sp σ bonds
along armchair
direction
+
multi center bonds
=
anisotropy

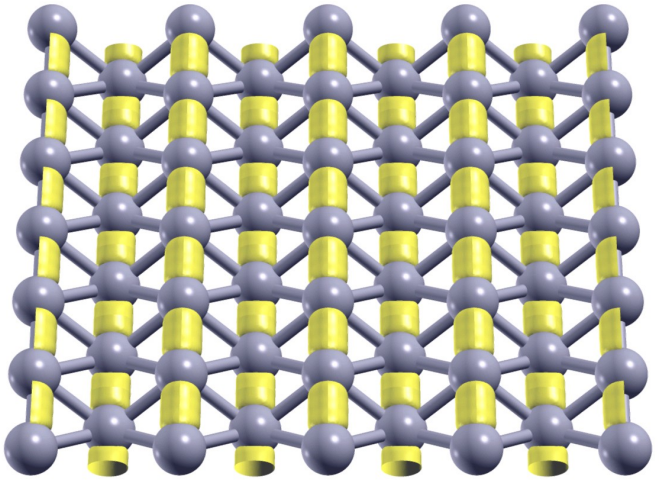
yellow: charge density contour at 0.9 e/Å^3

- **anisotropic in-plane mechanical properties**
- **metallic properties**

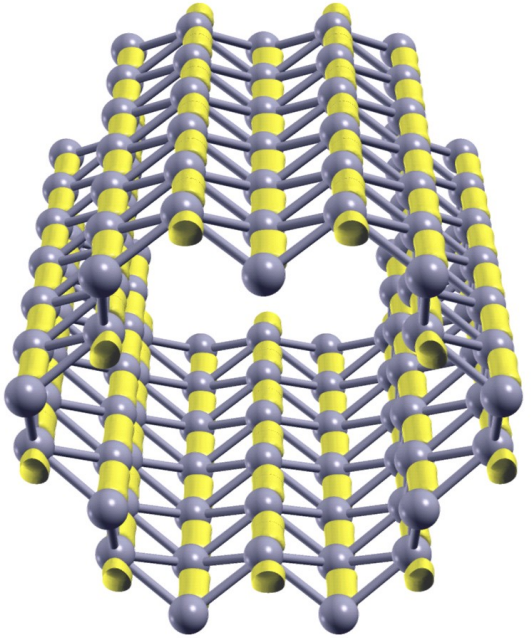
Boron Nanotubes:

- **All boron nanotubes are metallic!**

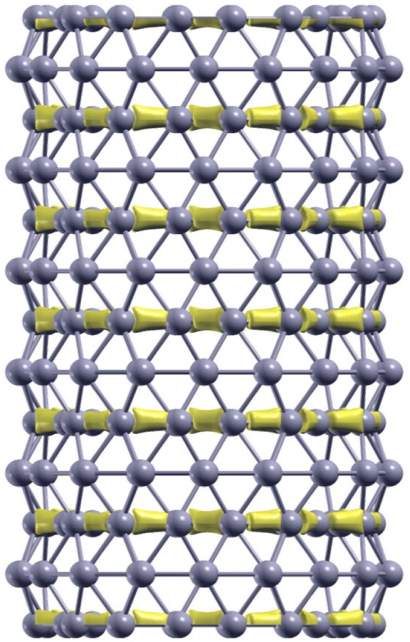
Boron Nanotubes



zigzag



armchair



armchair BNT:

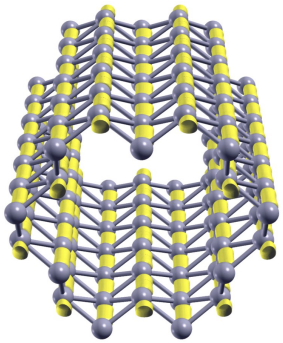
- **bent** circumferential σ bonds

zigzag BNT:

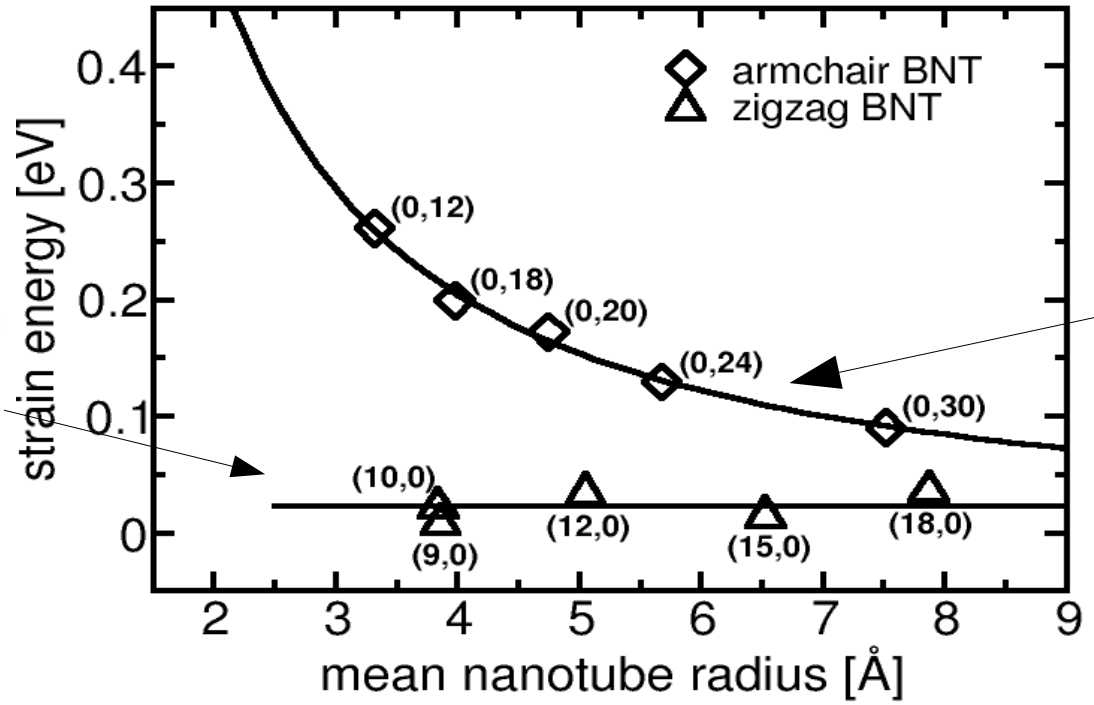
- **straight** axial σ bonds
- NO circumferential σ bonds

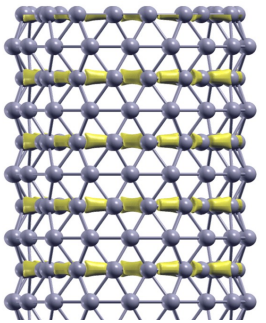
Boron Nanotubes

- strain energy (curvature energy):
  $E_{strain}(tube) = E_{coh}(sheet) - E_{coh}(tube)$



zigzag



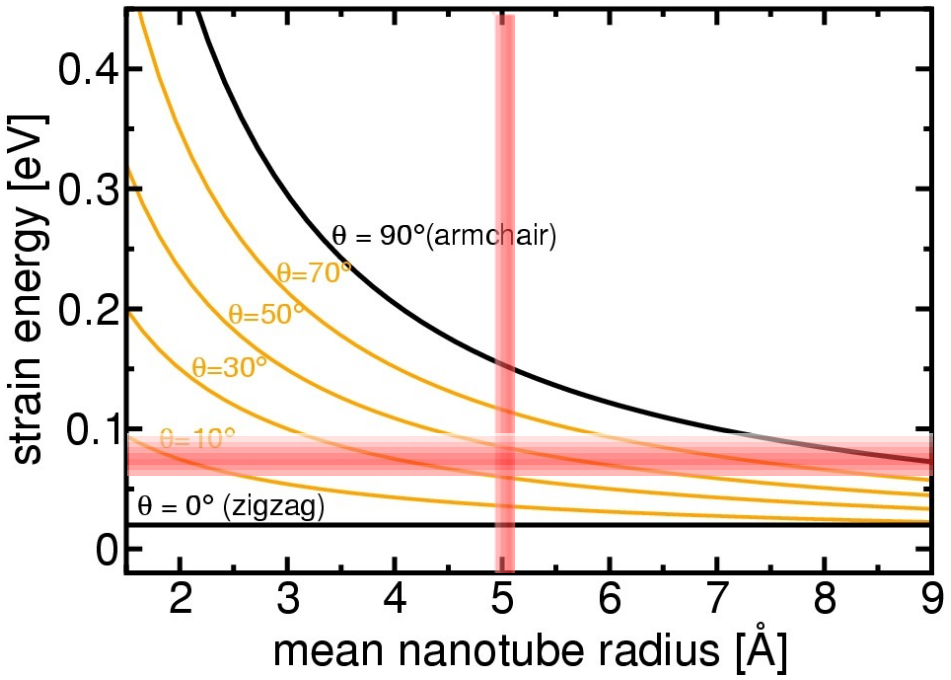


armchair

$E_{strain} = E_{strain}(R,\theta)$

- unique property among nanotubular materials
  usually $E_{strain} = E_{strain}(R)$ only

Structure Control



JK *et al.*, Nanotechnology **18**, 155703 (2007).

suggestion:

- control radius R by growing nanotubes out of porous catalysts with well defined pores sizes (e.g. Mg-MCM-41)
- control chiral angle θ by tuning the reaction conditions

synthesis of a specific (R,θ) nanotube

Anisotropic in-plane mechanical properties of sheets allow for more structure control of the tubes!

Boron Nanotubes

Summary:

- theory of boron nanotubes (BNTs): unifying and generalizing former studies in the field

  JK *et al.*, Chem Phys. Lett. **402** (2005).
  JK *et al.*, Phys. Rev. B **74** (2006).

- all BNTs are metallic
- the strain energy of a BNT is a function of the tube's radius and chiral angle: $E_{strain} = E_{strain}(R,\theta)$
- new approach to the long standing problem of structure control in nanoscience

  JK *et al.*, Nanotechnology **18**, 155703 (2007).

further developments:

- revised version of our theory:

  Tang *et al.*, Phys. Rev. Lett. **99** (2007).
  Yang *et al.*, Phys. Rev. B **77** (2008).

Nanotubular Junctions

- There are many *different* nanotubular materials:
  existing: BN, MoS_2, VO_x, …
  predicted: MB_2, B_2O, $CaSi_2$, …

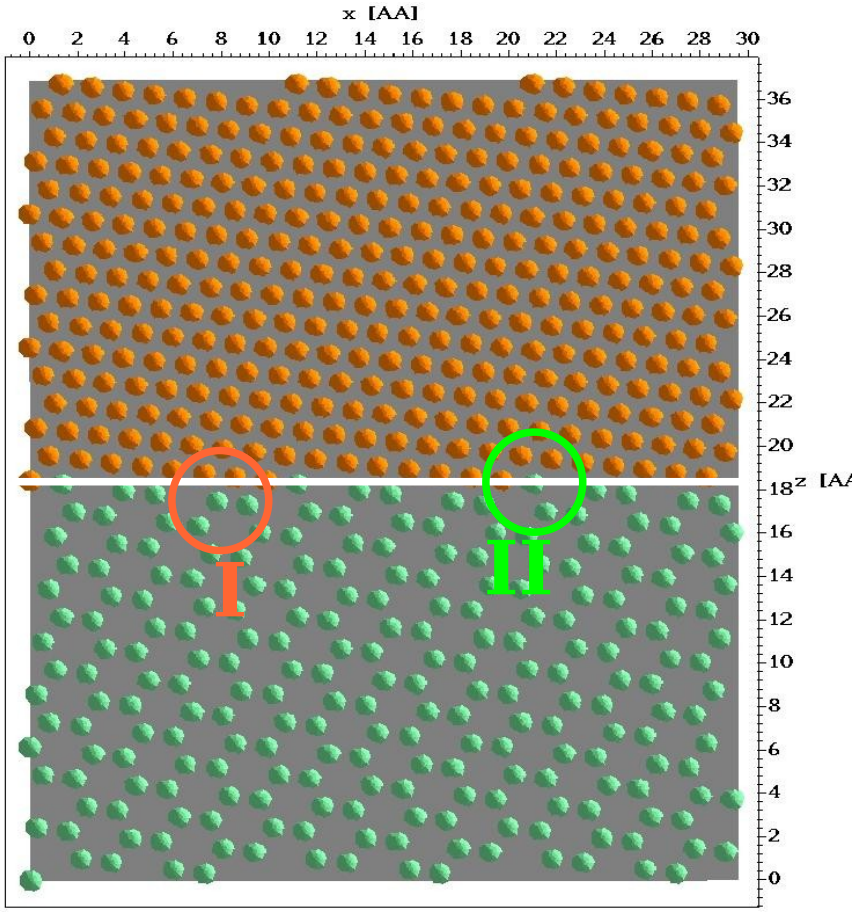
- **Idea**:
  Heterogeneous Nanotubular Networks

- **Basic question:**
  Is it possible to *connect* different nanotubular materials?

- **Structural paradigm:**
  intamoledular junctions between
  boron and carbon nanotubes

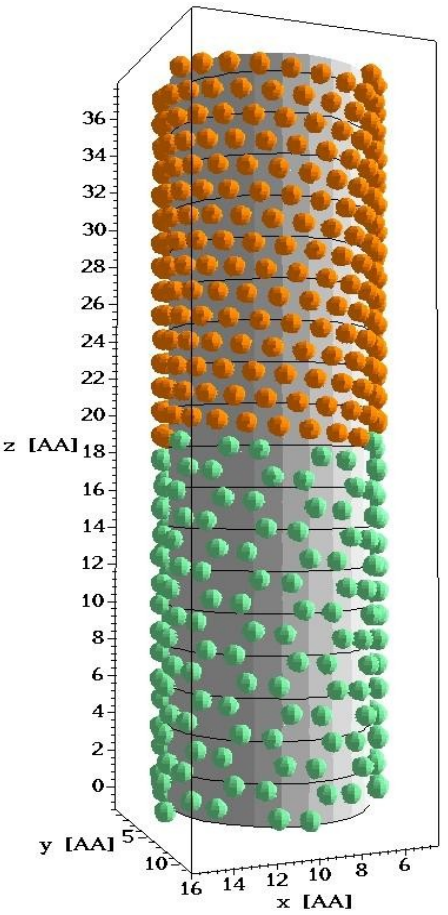
Nanotubular Junctions

Model System: linear BC-heterojunction of arbitrary radius and chirality from a single sheet



boron part

carbon part



?

- Only structure elements I and II can appear at the interface

Nanotubular Junctions

Results:

DFT simulations of different model junctions that only contain structure element

I

- serious structural problems
- formation energy from isolated boron and carbon nanotubes: 0.13 eV/at.

or

II

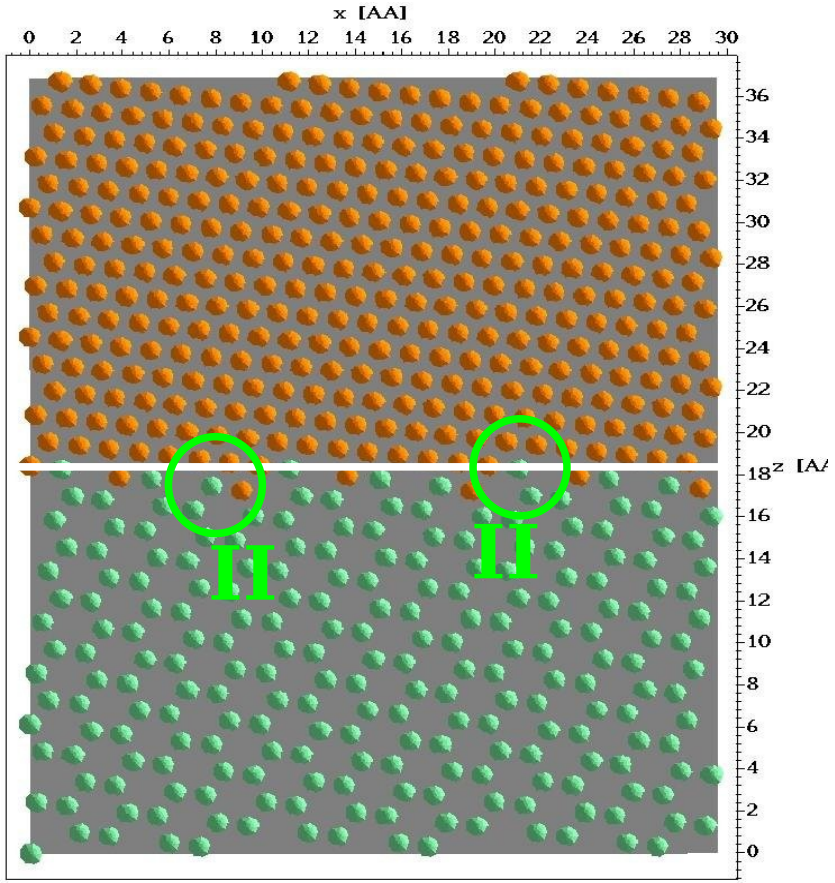
- optimal structure
- formation energy from isolated boron and carbon nanotubes: **only 0.07 eV/atom**

JK *et al.*, J. Chem. Phys. **121** (2004)

Nanotubular Junctions

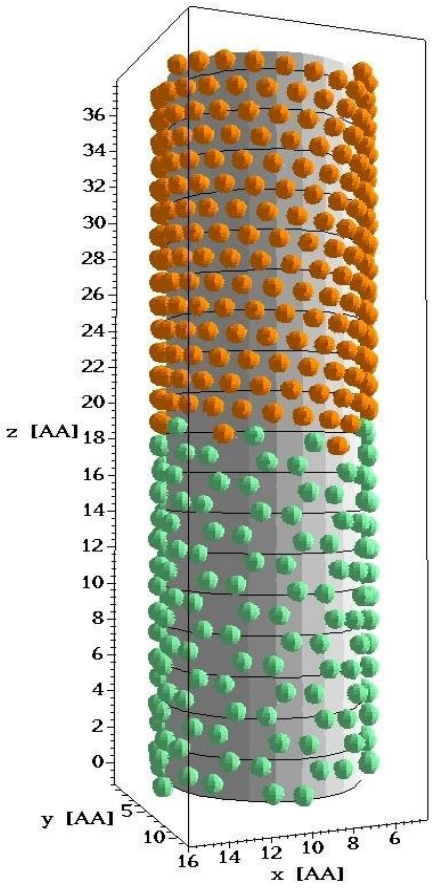
Solution:

- Linear BC-heterojunctions of any type can be formed by incorporating structure element **II** at the interface.



boron part

carbon part



!

Heterogeneous Nanotubular Networks are possible!

Enatom-Method

Theory:

- electrons, phonons, and EP interaction are described in reciprocal space
- we want a real-space desription of
  → solids
  → vibrational properties
  → electron-phonon interactions

Enatom:

- introduced by M. A. Ball as *generalized pseudoatom*
  J. Phys. C **8**, 3328 (1975)
- from greek:
  en = inside
  atom = the indivisible part
  enatom = an atom inside a solid

JK *et al.*, Phys. Rev. B **75** (2007)

Enatom-Method

Definition:

- atomic displacement: $\delta \boldsymbol{R}_j = \boldsymbol{R}_j - \boldsymbol{R}_j^o$
- definition via Helmholz decomposition of first order change in charge density:

$$\frac{\partial n(\boldsymbol{r})}{\partial \boldsymbol{R}_j} = -\nabla \rho_j(\boldsymbol{r} - \boldsymbol{R}_j^o) + \nabla \times \boldsymbol{B}_j(\boldsymbol{r} - \boldsymbol{R}_j^o)$$

$n(\boldsymbol{r})$ ... total charge density

$\rho_j(\boldsymbol{r})$ ... **rigid density** (scalar field); describes the charge density that moves rigidly with the atom upon a displacement

$\nabla \times \boldsymbol{B}_j(\boldsymbol{r})$ ... **deformation density** (vector field); describes how the charge density deforms due to a nuclear displacement

Enatom-Method

Properties:

- $\sum_j \rho_j(\boldsymbol{r} - \boldsymbol{R}_j^o) = n(\boldsymbol{r})$

  The enatom is a unique decomposition of the total charge density into a sum of atomic-like contributions.

- charge density of displaced atoms:

$$n(\boldsymbol{r}; \{\boldsymbol{R}_j\}) = \sum_j [\rho_j(\boldsymbol{r} - \boldsymbol{R}_j^o - \delta\boldsymbol{R}_j) + \delta\boldsymbol{R}_j \cdot \nabla \times \boldsymbol{B}_j(\boldsymbol{r} - \boldsymbol{R}_j^o)]$$

This holds for a first order displacement of the atoms from their equilibrium position.

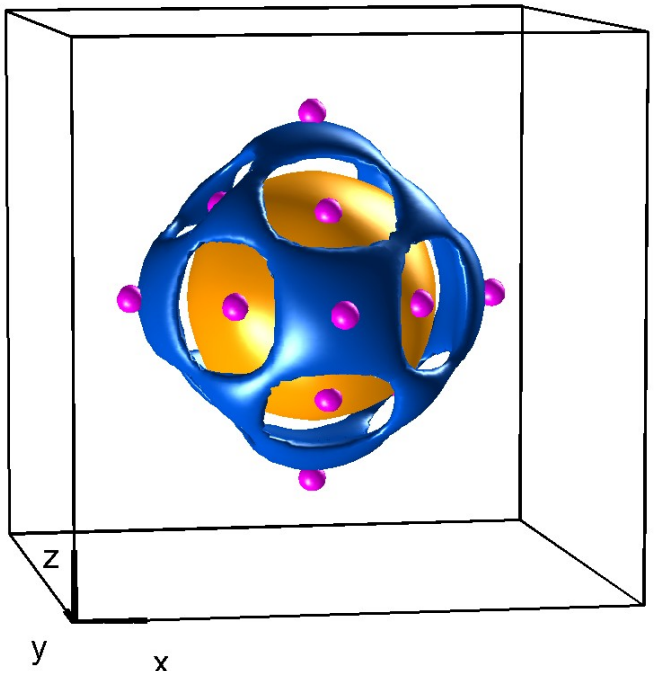
→ The same construction can also be applied to the total **potential**

$$\begin{aligned} n(\boldsymbol{r}) &\rightarrow v(\boldsymbol{r}) \\ \rho_j(\boldsymbol{r}) &\rightarrow V_j(\boldsymbol{r}) \\ \nabla \times \boldsymbol{B}_j(\boldsymbol{r}) &\rightarrow \nabla \times \boldsymbol{W}_j(\boldsymbol{r}) \end{aligned}$$

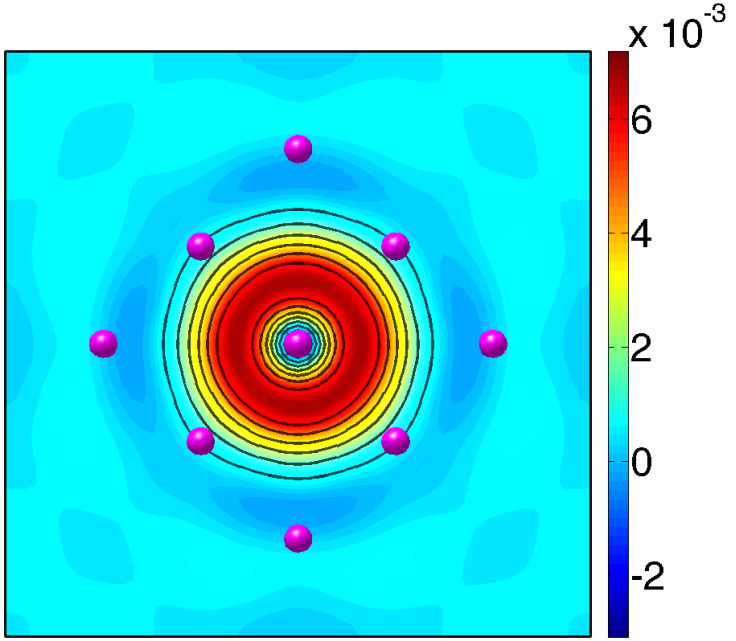
Enatom-Method

Example: enatom density of fcc Li at P=35 GPa

rigid density ρ



isocountour plot at
$\rho = \pm 4.8 \times 10^{-4}\ a_B^{-3}$

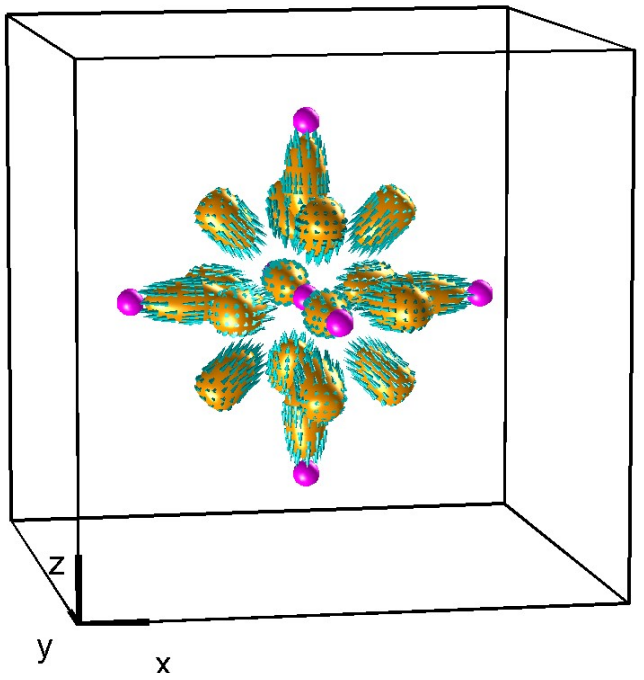


countour plot of ρ in xy plane

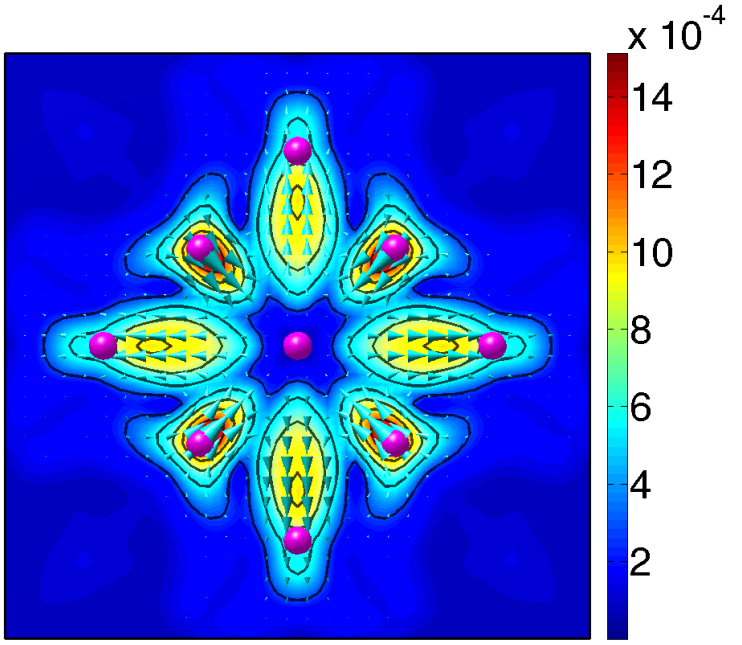
Enatom-Method

Example: enatom density of fcc Li at P=35 GPa

deformation density $\nabla \times \mathbf{B}$



isocountour plot at
$|\nabla \times \mathbf{B}| = 8 \times 10^{-4}$



countour plot of $|\nabla \times \mathbf{B}|$ in xy plane

Enatom-Method

Results:

- first realization of the enatom method
- studied pressure evolution of enatom quantities for fcc Li and fcc Al

Outlook:

- generalization of the enatom code for more complex systems
- study of non-metals
- calculation of phonon frequencies
- calculation of electron-phonon matrix elements
- study boron

Summary

- generalized theory for boron nanotubes

  JK *et al.*, Chem Phys. Lett. **402** (2005).
  JK *et al.*, Phys. Rev. B **74** (2006).

- new route for structure control of nanotubes during synthesis

  JK *et al.*, Nanotechnology **18**, 155703 (2007).

- intramolecular junctions of nanotubes

  JK *et al.*, J. Chem. Phys. **121** (2004)

- proposed layered bulk phases of boron

  JK *et al.*, (to be published)

- first realization of entaom method

  JK *et al.*, Phys. Rev. B **75** (2007)

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