Solid State Theory: Band Structure Methods

Lilia Boeri

Wed., 11:00-12:30

HS P3 (PH02112)

http://itp.tugraz.at/LV/boeri/ELE/

Who am I?

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Who am I?

- Assistant Professor, Institute for Theoretical and Computational Physics, TU Graz, since March 2013.

- Before this:

  Universita' la Sapienza (Rome, Italy) - Master and PhD studies;

  Max Planck Institute for Solid State Physics, Stuttgart, Germany - postdoc and head of a Junior Research Group on Computational Superconductivity.

- My research (keywords):

  Superconductivity, ab-initio, density-functional theory (DFT), Phonons, Electron-Phonon Interaction, Model Hamiltonians.

What About you?

What is this lecture about?

Modern Band Structure methods are applied in many fields of condensed matter physics, to understand and guide experiments.

In contrast to other theoretical approaches, they are ab-initio, i.e. they only require the knowledge of the number, position and species of atoms in a given system.

Most modern band structure methods employ Density Functional Theory to solve the full many-mody Schroedinger equation for electrons in a solid/molecule.

Density Functional Theory (DFT):

Density Functional Theory was proposed by Walter Kohn, who received the Nobel prize in Chemistry in 1985.

DFT is based on two fundamental papers:

1) Hohenberg and Kohn, Phys. Rev. 136 B 864 (1964) : the ground-state property of a system of N interacting electrons depend only on its ground-state density, which is much easier to handle than the N-particles wave-function. (Density is the basic variable).

$$\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) \rightarrow \rho(\mathbf{r})$$

2) Kohn and Sham (Phys. Rev. 140, A1133 1965): The ground-state density of a system of interacting electrons can be obtained solving a set of equations for effective non-interacting quasi-particles (Kohn-Sham quasi-particles).

DFT:

Traditional Applications of DFT-based methods are calculations of electronic structures and total energies of complex solids and molecules (interpretation of experimental spectra: photoemission, optics, inelastic neutron scattering, specific heat ...), including the effect of spin-polarisation. This often allows a microscopic understanding of many phenomenological and empirical trends.

More Recent Developments:

- Effect of small perturbations (linear-response theory): calculations of phonons, electric polarizabilities, ...
- Wannier functions: Real-space wave functions for solids, real-space effective Hamiltonians, a.s.o.
- Use of accurate DFT total-energies to search for desired properties of known materials (high-throughput methods), or to explore/predict new structures/phases (metadynamics and genetic algorithms).

Charge Densities:

DFT charge densities can be used to visualise different types of chemical bonds. One of the first applications was that of tetrahedral semiconductors.

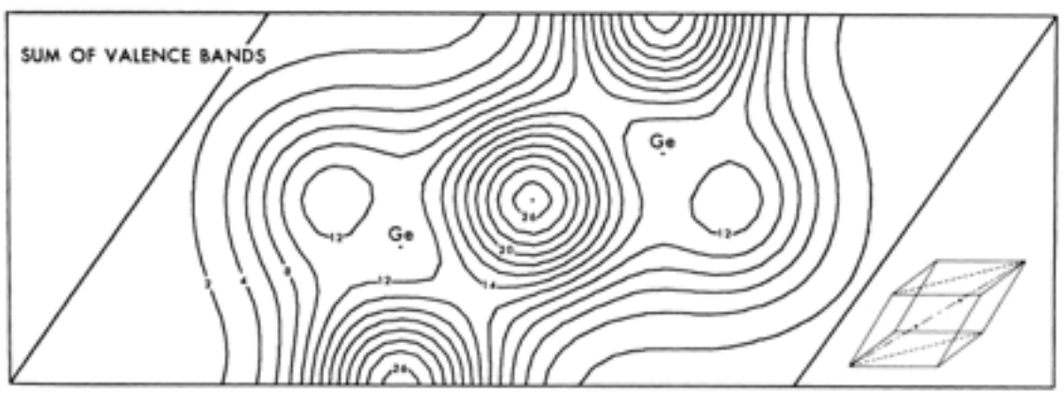


FIG. 1. Valence-electron-density contour map (in units of e per primitive cell) for Ge in the (1,−1,0) plane. The orientation of the plane (dashed lines) with respect to the primitive cell is shown in the inset. The radii of the cores for Ge is 0.20 of the Ge-Ge distance. This radius is that of a sphere containing 80 % of the outermost shell of core electrons.

Ge

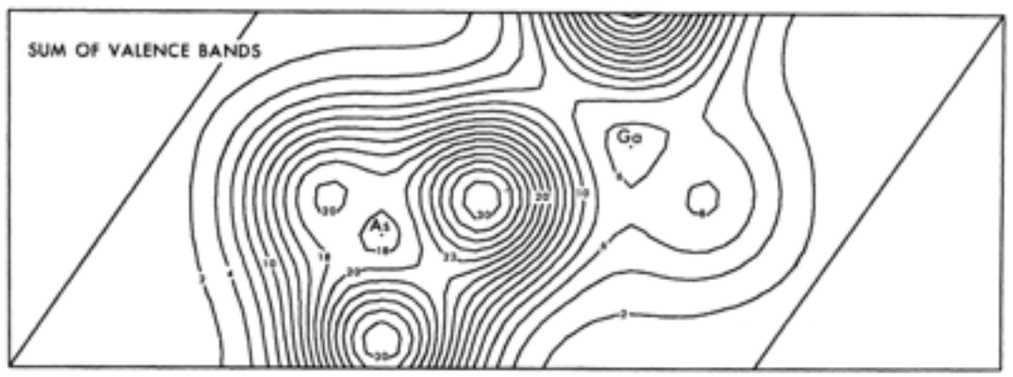


FIG. 2. Valence-electron-density contour map (in units of e per primitive cell) for GaAs in the (1,−1,0) plane. See inset of Fig. 1. The core radii for Ga and As are 0.23 and 0.18 of the Ga-As distance. The radii are those of spheres containing 80 % of the outermost shell of core electrons.

GaAs

Electronic Structures:

Kohn-Sham quasi-particles often approximate quite well the "real" electronic structure of solids (as measured by photoemission, optics, positron annihilation, de-Haas-van-Alphen). One of the first successes of DFT was the calculation of Fermi surfaces for complicated (non-free-electron) metals.

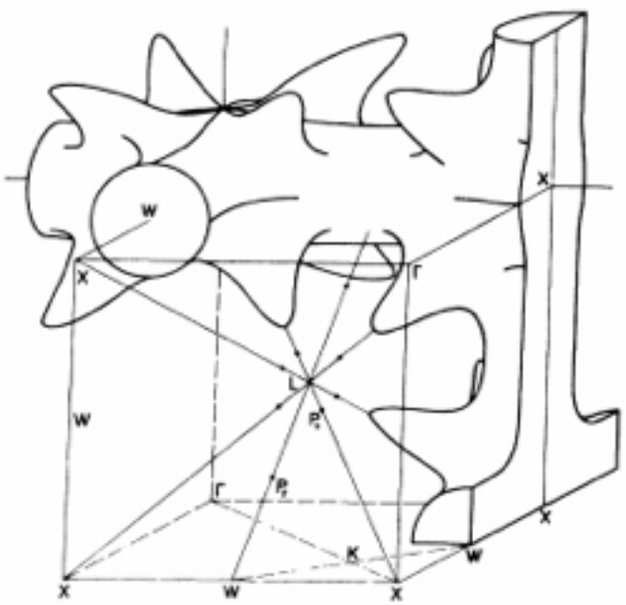
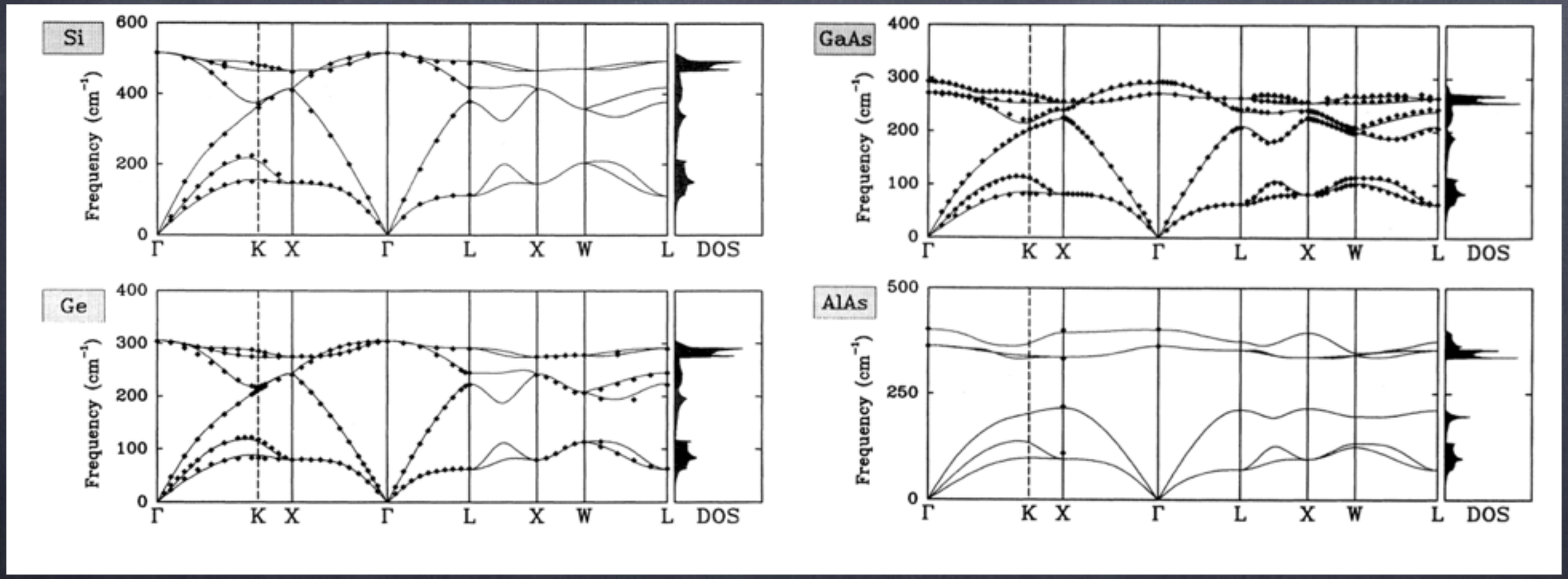


FIG. 6. Sketch of the open hole surface $XW5$ of the Pd or Pt Fermi surface in the periodic zone scheme. The part of reciprocal space shown, and its connection with the Brillouin zone, may be found in Fig. 9. The critical points P_1 and P_2 have also been indicated (Sec. III C).

O. K. Andersen, Phys. Rev. B (1975).

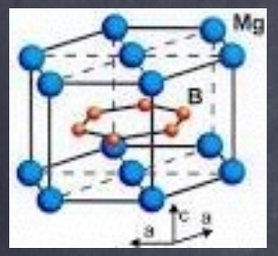
Lattice Dynamics:

Density functional perturbation theory (1986) permits to compute the linear response of the electronic system to a small external perturbation. If the perturbation is the displacement of an atom from its equilibrium position, DFPT can be used to calculate phonon frequencies.

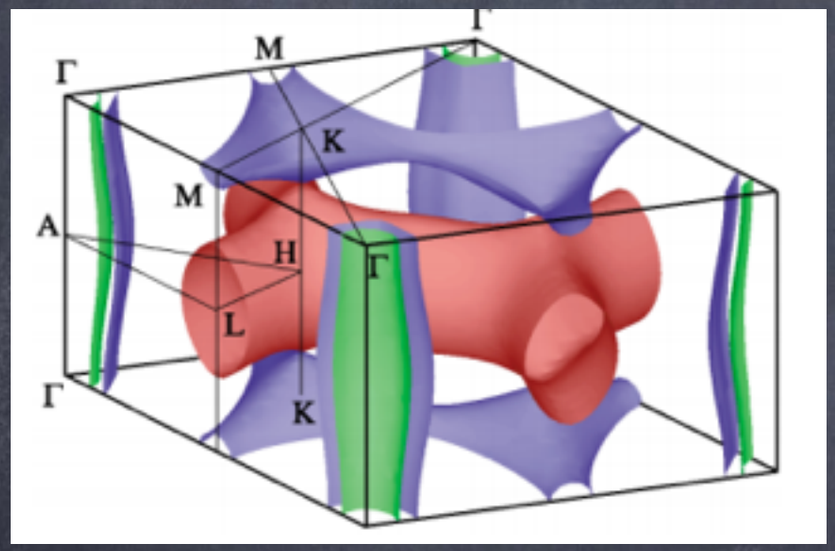


P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B 43, 7231 (1991).

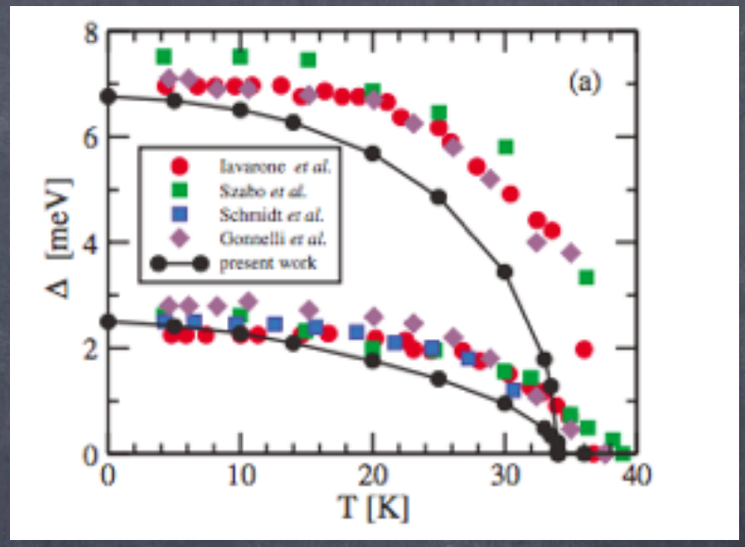
Two-gap Superconductivity:



Two-gap superconductivity was predicted theoretically in 1959 by Suhl, Matthias, Walker, but never observed experimentally, until 2001 (Magnesium diboride, Tc=39 K). First-Principles calculations clarified that the two-gap nature and the high-Tc descend from the peculiar electronic structure of MgB2 (hole-doped graphite).



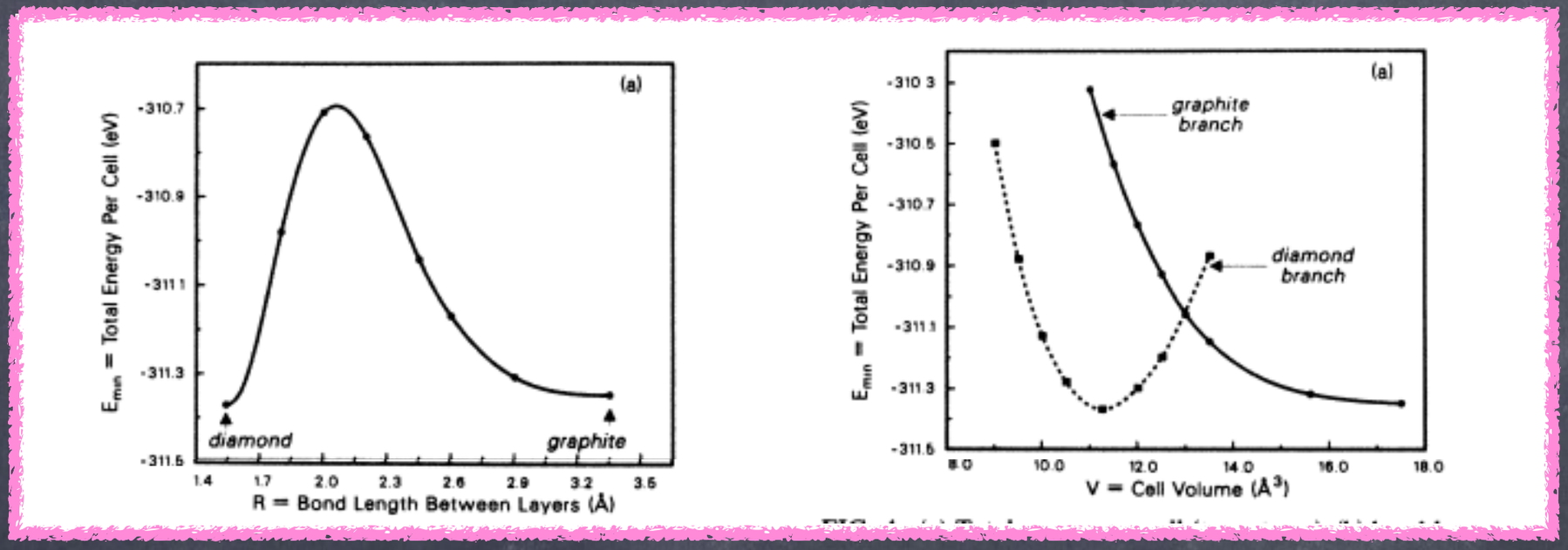
Superconductivity of Metallic Boron in MgB2, J. Kortus, I. I. Mazin, K. D. Belashchenko, V. P. Antropov, and L. L. Boyer, Phys. Rev. Lett. 86, 4656 (2001).



Superconducting Properties of MgB2 from First Principles, A. Floris, G. Profeta, N. N. Lathiotakis, M. Lüders, M. A. L. Marques, C. Franchini, E. K. U. Gross, A. Continenza, and S. Massidda (2005).

Total Energies:

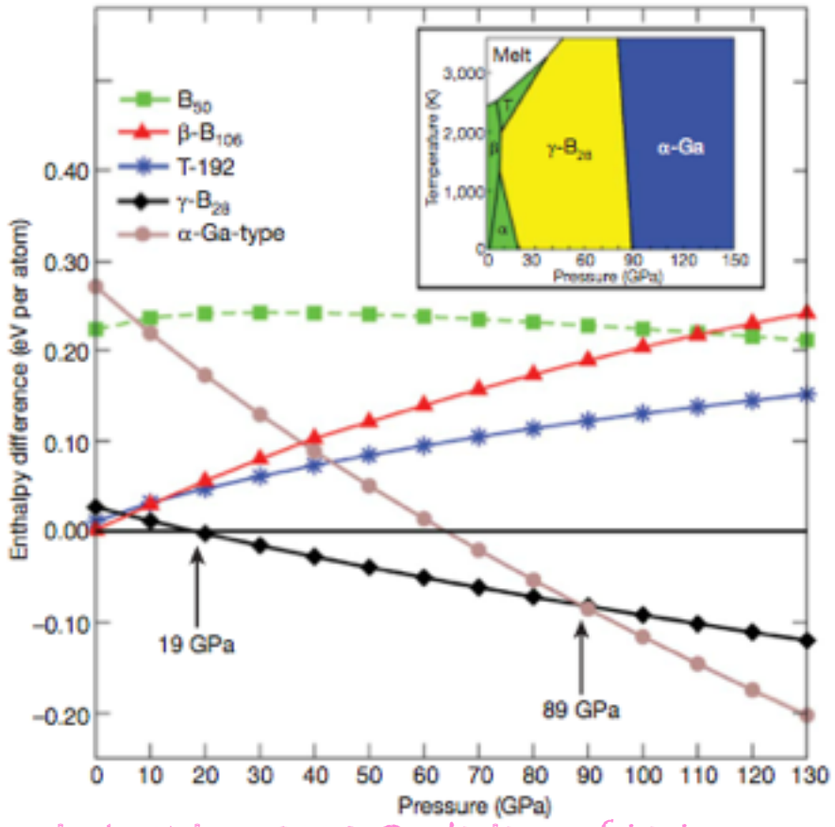
Knowing accurate total energies allows to predict/understand transformations between different phases of the same material as a function of external parameters. One of the most famous examples is the reaction barrier between diamond and graphite for carbon.

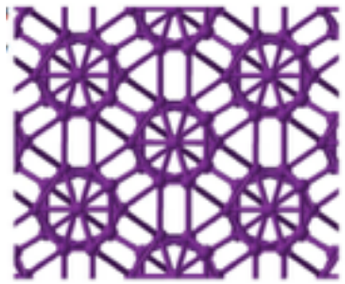


Pseudopotential total-energy study of the transition from rhombohedral graphite to diamond, S. Fahy, Steven G. Louie, and Marvin L. Cohen, Phys. Rev. B 34, 1191 (1986).

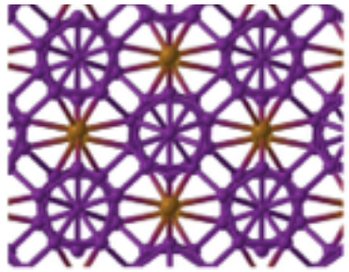
Crystal Structure Prediction:

With high-performance computer, total energy calculations for structures with hundredths of atoms and complicated symmetries are feasible. This permits to construct complicated energy surfaces which can be explored using efficient methods for the search of minima.





P=0: alpha-B (known)



P=90 GPa: gamma-B (new)

Oganov et al., Nature 2005: Prediction of high-pressure phases of elemental boron using genetic algorithms.

This permits to predict, for example, new high-pressure phases of known compounds...

What will you learn exactly?

Band Structure Methods:

Density Functional Theory:

Basics

Practical Problems

Advanced Topics:

Density Functional Perturbation Theory

Methods for Wannier Functions

Applications:

Bulk Silicon (tetrahedral semiconductor): Electronic Structure, Phonon Dispersions, tight-binding model using a state-of-the-art code for electronic structure calculations (quantum espresso).

Density Functional Theory

Basics:

- Density Functional Theory: Hohenberg-Kohn and Kohn-Sham papers.
- Exchange and Correlation: Local Density Approximation and Beyond.

Practical Problems (Solving K-S equations in practice):

- Full vs pseudopotential methods. Basis functions.
- Methods for k-space integration.

Advanced Topics:

Linear Response Theory:

- Density Functional Theory: First-order perturbations (general).
- Linear response for phonons.

Methods for Wannier Function generation:

- Wannier Functions: definition and general properties.
- Generation of Wannier function: maximally localised Wannier functions and N-th order Muffin-Tin method.

Practical Part:

For the practical part, we will employ a state-of-the-art DFT code, distributed under GPL.

The code can be downloaded at the following address: http://www.quantum-espresso.org/

I will install it on our computer cluster for the first exercise session (14/5). You can also download it and install it on your local machine any time.

- Many other (free and commercial) DFT codes are available on the web (CASTEP, ABINIT, VASP, WIEN2k, ELK ...)
- The basic ideas and functionalities of quantum espresso that you will learn in our practical session apply to all codes.
- The idea of the practical session is to give you an overview of how to setup a calculation, control the basic parameters for convergence, and use the code to reproduce known literature results for a particular compound (this year, elemental silicon).

- In the exam, you will be asked to discuss these calculations (convergence, problems, ...)

Topics (Theory):

Basic Topics (DFT):

- DFT 1-2: Hohenberg-Kohn Theorem and Kohn and Sham equations.
- DFT 3-4: Solving K-S in practice; basis functions, augmented methods and psp theory.
- DFT 5: practical problems in DFT (k space integration, convergence etc)

Advanced Topics:

- ADV 1: Linear Response theory (mostly for phonons). (21st-28th May).
- ADV 2: Wannier Functions and TB approximation. (11th June).

Practical Sessions:

- DFT: EOS and band structure of silicon.
- ADV1: Phonons of Si.
- ADV2: Wannier Functions and BOM for silicon.

Dates:

	12/3 Intro	19/3 DFT1	26/3 DFT2	
2/4 DFT3	9/4 DFT4	16/4 BREAK	23/4 BREAK	30/4 BREAK
7/5 DFT5	14/5 P1	21/5 ADV1	28/5 ADV2	
4/6 P2	11/6 ADV3	25/6 P2		

NB: hands-on sessions last 3 hours; we may have to shift time/date according to the availability of the computer room.

Useful Books/Links:

There are many available resources on DFT and applications on the web, but few good books. The most famous is the following:

Richard Martin, Electronic Structure: Basic Theory and Practical Methods, Cambridge University Press.

I have collected a few references on the web page of the course:

http://itp.tugraz.at/LV/boeri/ELE/

Please check it regularly because I will update it and upload relevant material.

If you would like to discuss any specific topic
you can also pass by my office!