

Introduction and Overview

What do we want to understand?

What do we want to calculate?

Why?

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Introduction and Overview

Topics

**** First week -**

Lectures gradually turning into hands-on computing

Lecture Topics

Crystal Structures, Bands, Plane wave methods,

Density Functional Theory, Kohn-Sham calculations,

Forces, Phonons, Magnetic systems

Introduction to Quantum Espresso, visualization, plotting packages

**** Second week -**

Primarily hands-on instruction using the Quantum Espresso codes

Gradually turning into work on projects

**Discussions of projects: motivations, theory, practical calculations
and plans for continuation after the school**

**What aspects of materials
(solids, molecules, liquids, surfaces, . . .)
would we like to understand?**

**What are the topics in a
typical solid state physics textbook?**

Contents of a typical solid state physics text (Kittel, Ashcroft and Mermin,)

- **Structures of crystals**
 - Definitions of structures
 - Typical bonding and structures
 - Structural phase transitions
- **Mechanical Properties**
 - Lattice vibrations – phonons
 - Elastic constants
 - Piezoelectric constants
 - Effective charges
- **Thermal Properties**
 - Heat capacity, heat conduction
- **Electronic properties**
 - Definition of bands
 - Metals vs. insulators
 - Conductivity, dielectric functions
 - Magnetism

Properties that can be described without knowing anything about electrons

So why are they a part of electronic structure?

Properties that can only be understood in terms of the electrons

Electrons and Properties of Materials

All properties of materials are controlled by the electrons interacting with the nuclei

The effects can be divided into two categories

- **Electrons form the bonds that hold the nuclei together**
 - The structures of molecules and solids
 - Strength of materials, elastic constants, vibration frequencies, . . .
 - Thermal properties, melting, liquids, . . .

Determined by the ground state of the electrons

- **Electrons determine**

- Electrical conductivity: Insulators, Metals, Semiconductors, Superconductors
- Optical properties, dielectric constant, colors, . . .
- Magnetism - a purely quantum effect – due to the electrons

Determined by the excited states of the electrons

What can be accomplished by Electronic Structure Theory and Computation?

**Calculate ALL these properties from the
same theoretical methods!**

**Provide quantitative understanding of
relations among different properties and materials**

IMPORTANT!

No theory is perfect – there are approximations

To provide real understanding

We must understand what we are doing!

That is what this school is about!

**Learning methods to make interesting, useful
calculations with real understanding**

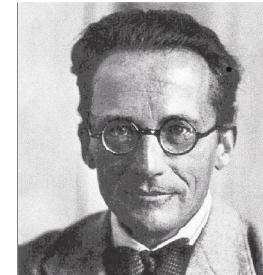
Electronic Structure in Perspective

A brief History

A long way in less than 90 years



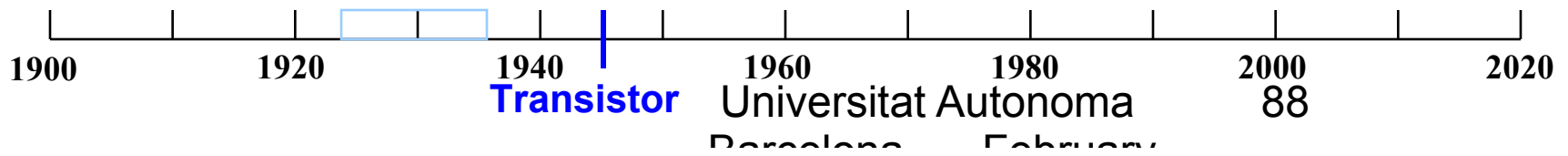
L. de Broglie –
Nature 112, 540 (1923).



E. Schrödinger –
1925,

- Pauli exclusion principle - 1925
- Fermi statistics – 1926
- Thomas-Fermi approximation – first density functional – 1927
- Dirac - Thomas-Fermi + local exchange functional – 1928

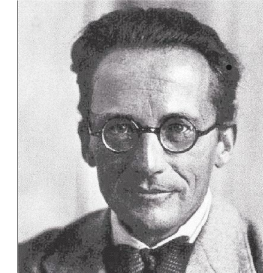
- Bloch theorem – 1928
- Slater (spin) determinant - 1929
- Wilson - Implications of band theory – metals, Insulators, semiconductors –1931
- Wigner- Seitz – Quantitative calculation for Na - 1935
- Shockly - Bands of NaCl - 1934
- Bardeen - Fermi surface of a metal - 1935



A long way in less than 90 years



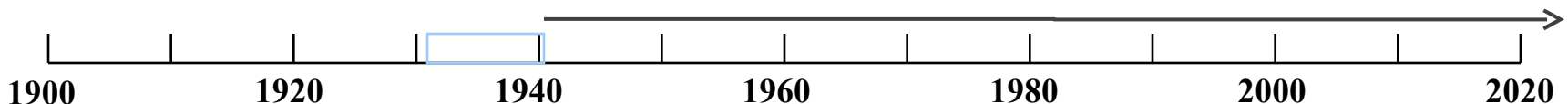
L. de Broglie –
Nature 112, 540 (1923).



E. Schrödinger –
1925,

The basic methods of electronic structure

- Slater – Augmented Plane Waves (APW) - 1937
Not used in practice until 1950's, 1960's – electronic computers
- Herring – Orthogonalized Plane Waves (OPW) – 1940
First realistic bands of a semiconductor – Ge – Herman, Callaway (1953)
(Many of Herman's calculations done by his mother)
- Hellman, Fermi – Pseudopotentials – 1930's
 - Phillips, Kleinman, Antoncik, - 1950's - Hamann, Vanderbilt, others – 1980's
 - Andersen – Linearized Muffin Tin Orbitals (LMTO) – 1975
 - The full potential “L” methods – LMTO, LAPW



Major change ~ 1964-5 ---- ~ 50 years ago

Quantitative Theory and Computational Methods

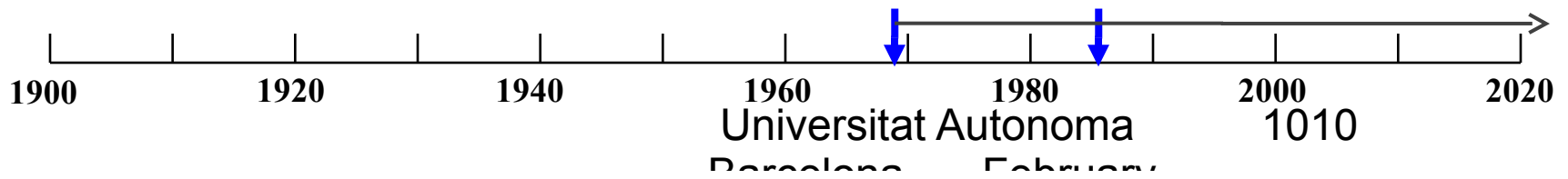
1964-5 **Density Functional Theory** **Hohenberg, Kohn, Sham**
Exact ground state energy as a functional of electron density
Local Density Approx. (LDA)
(Also in 1964-5 –first quantum Monte Carlo calculations, first GW methods)

1970's **Computation established as powerful tools**

1985 **Car-Parrinello** molecular dynamics treating electrons in DFT
(also in 1980s – First QMC Calculations on electrons
– first quantitative GW calculations)

1990's **Many computational developemnts following Car-Parrinello**

2000's **Discoveries and Methods continue**



**How do we know when we are on
the right track?**

Results agree (amazingly) well with experiment for ground state properties in important classes of materials

Different methods agree (when done carefully)

Method	C		Si		CaF ₂		bcc Fe		
	<i>a</i>	<i>B</i>	<i>a</i>	<i>B</i>	<i>a</i>	<i>B</i>	<i>a</i>	<i>B</i>	<i>m</i>
NCP ^a	3.54	460	5.39	98	5.21	90	2.75 ^c	226 ^c	
PAW ^a	3.54	460	5.38	98	5.34	100			
PAW ^b	3.54	460	5.40	95	5.34	101	2.75	247	2.00
USPP ^b	3.54	461	5.40	95	5.34	101	2.72	237	2.08
LAPW ^a	3.54	470	5.41	98	5.33	110	2.72 ^d	245 ^d	2.04 ^d
EXP ^a	3.56	443	5.43	99	5.45	85-90	2.87 ^d	172 ^d	2.12 ^d

- **a** – lattice constant, **B** – bulk modulus, **m** – magnetization
- aHolzwarth , *et al.*; bKresse & Joubert; cCho & Scheffler; dStizrude, *et al.*

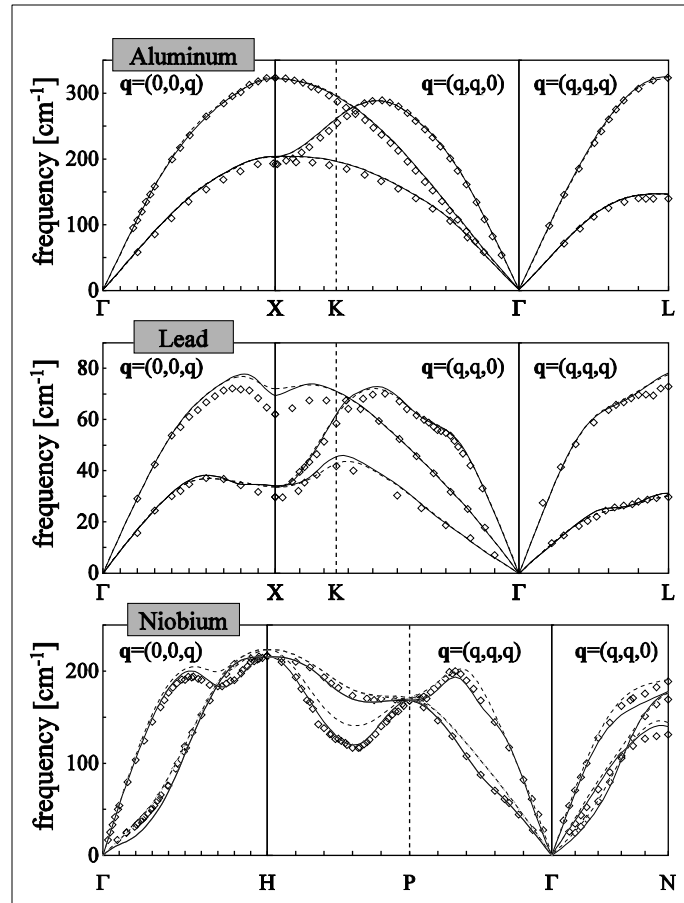
**This is the basic argument that such calculations
also will be accurate for
similar properties of similar systems**

Vibration frequencies – Phonons

Phonons Comparison of theory and experiment

- Calculated from the response function –
“Density functional perturbation theory”
- Now a widely-used tool in **ABINIT**, **ESPRESSO**, . . .

de Gironcoli, et al.



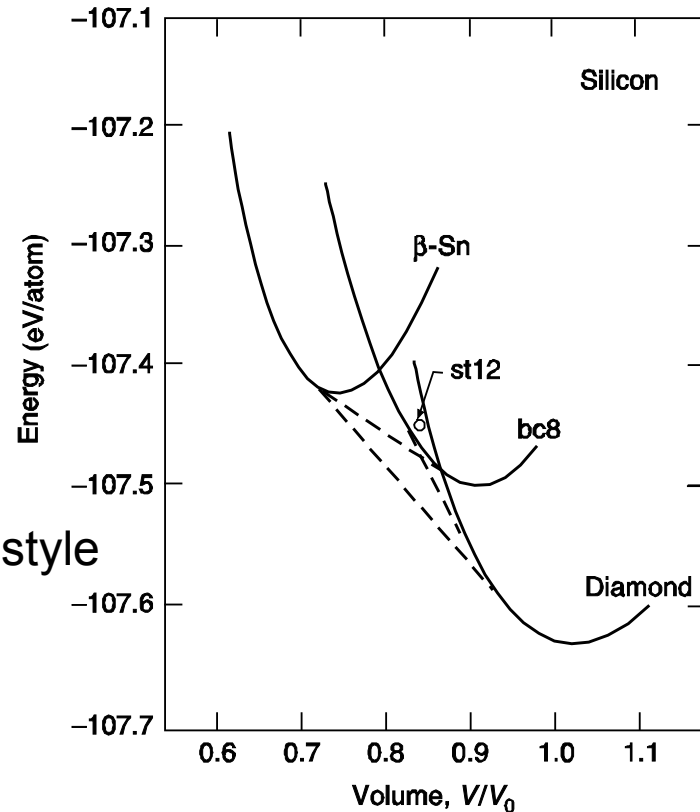
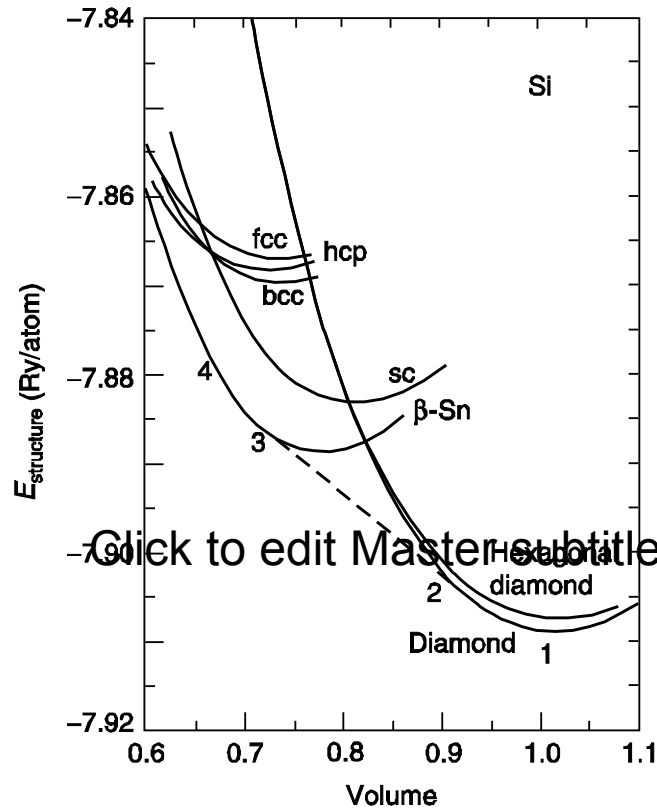
S. de Gironcoli, Phys.Rev B 51, 6773 (1995)

**This is the basic argument that such calculations
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similar properties of similar systems**

Examples: Phase Transitions Under Pressure

Transformation of silicon to metallic structures under pressure

Predictions from LDA – first demonstrations that DFT gives accurate results

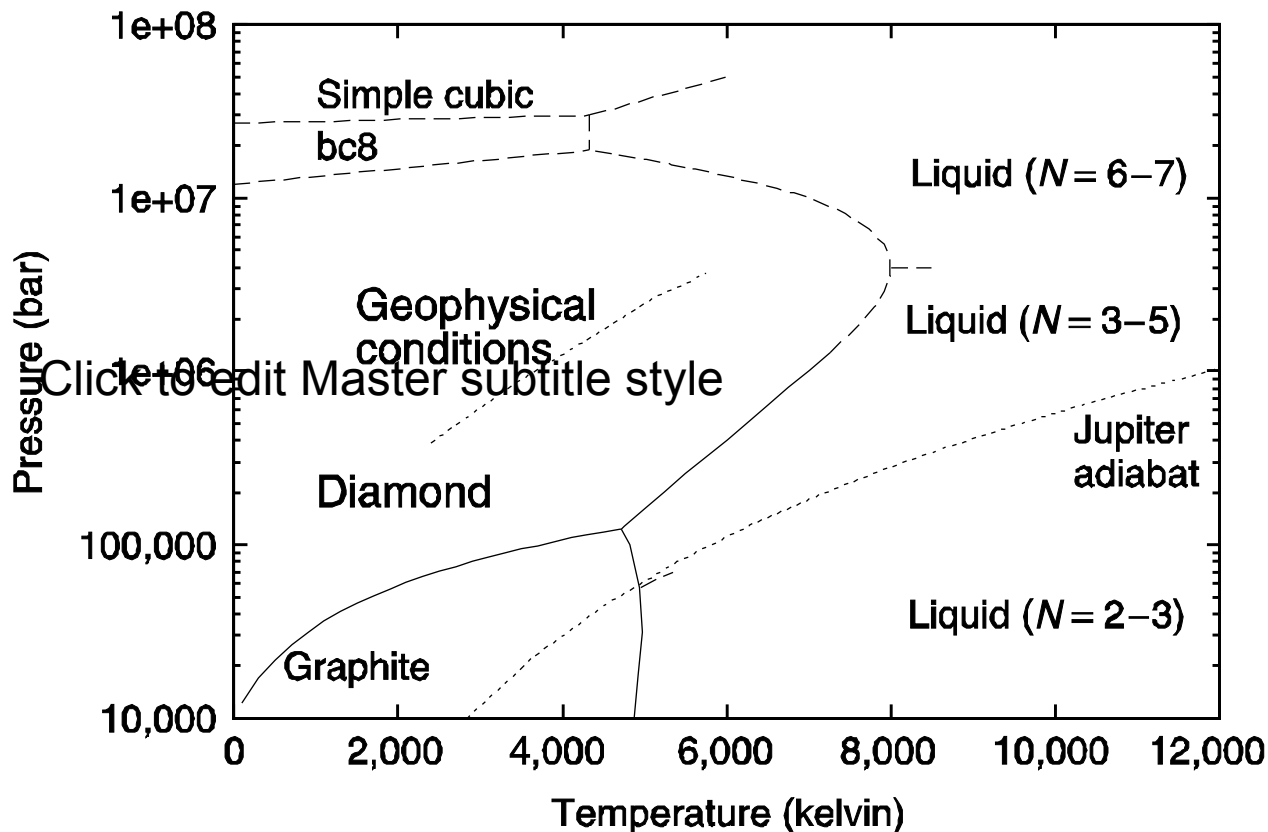


Modern codes (ABINIT, VASP, ESPRESSO, Wein LAPW, FPLO, . . .)
easily reproduce similar curves.

Car-Parrinello Simulation

Carbon at high pressure and temperature

Melting of diamond at high pressure – other phases -
geophysical, planetary physics

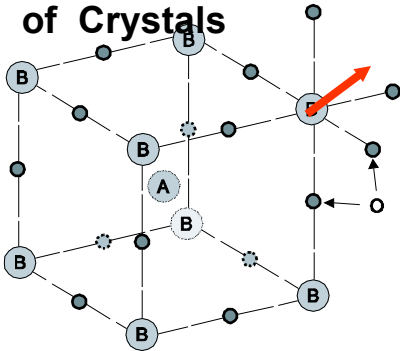


Galli, Martin, Car, Parrinello, Grumbach
1989-1994

A large and growing field!

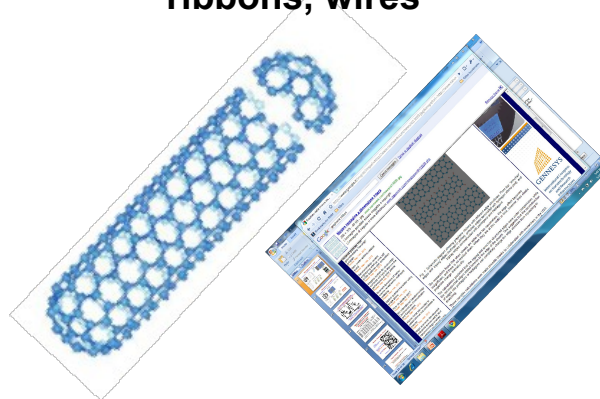
Treat many types of materials in a unified way from the basic equations

Calculate properties of Crystals

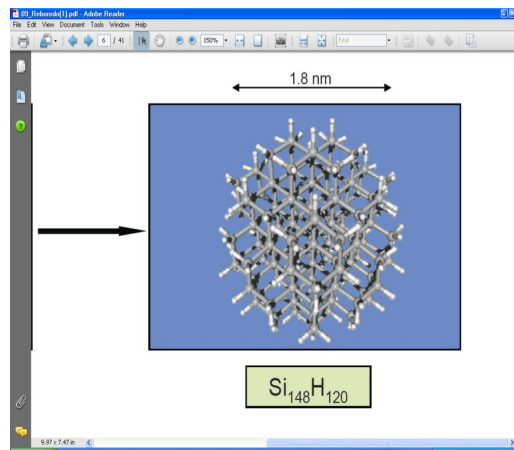


Predict crystal structures
Example – atomic positions in a ferroelectric

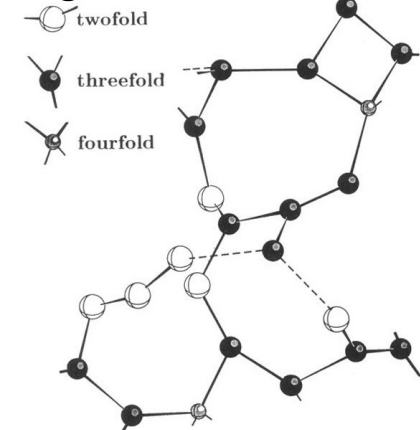
nanotubes, graphene, ribbons, wires



Predict properties of nanostructures



Simulation of Liquids – example Carbon at high T



“snapshot” of liquid

Many other examples!

How does one person make an important contribution in this important field?

**A contribution valued by others
A contribution you are proud of yourself.**

Work on a very specific problem!

**Calculate a definite result using
well-founded theoretical methods!**

Provide understanding of a specific issue

IMPORTANT!

No theory is perfect – there are approximations

To provide real understanding

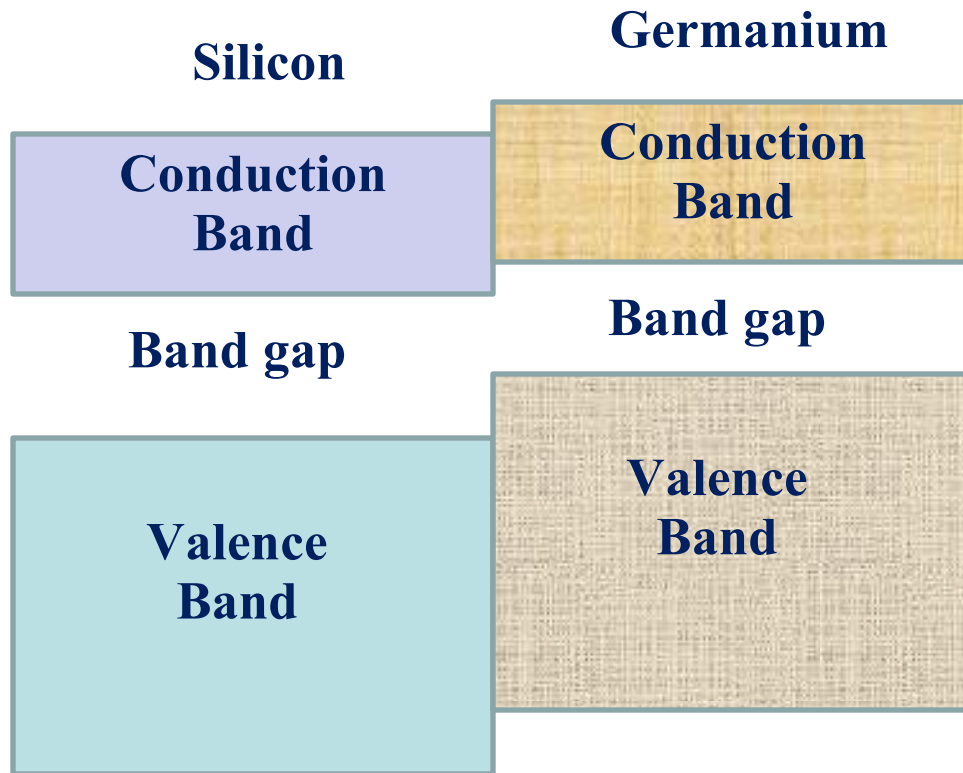
You must be clear on the problem and the issues

That is what this school is about!

We (you) will work on specific exercises and projects
with the goal for each person to have a definite project
to continue after the school

A personal example of very specific problem

The “band offset” for a Si/Ge interface



Density Functional “LDA” approximation

Conclusions

- **Work in an important field with well-founded methods**

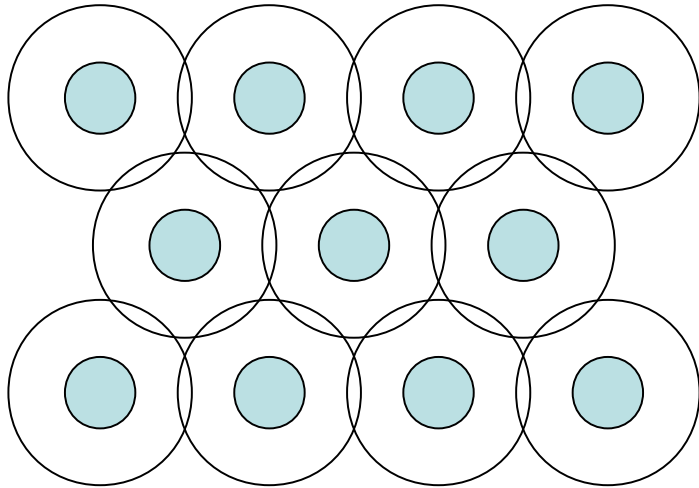
- **Choose a specific problem with a well-founded question**

- **Be careful and know what you are doing**

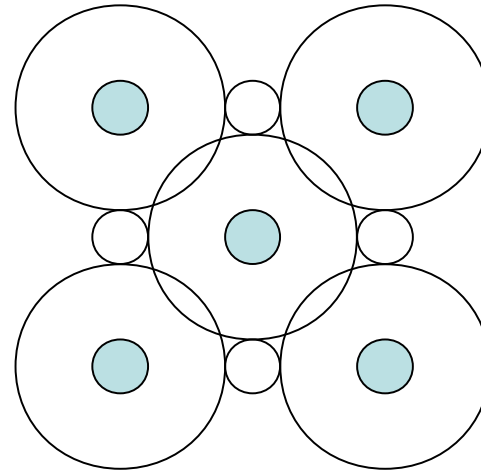
Additional slides

Examples of types of materials

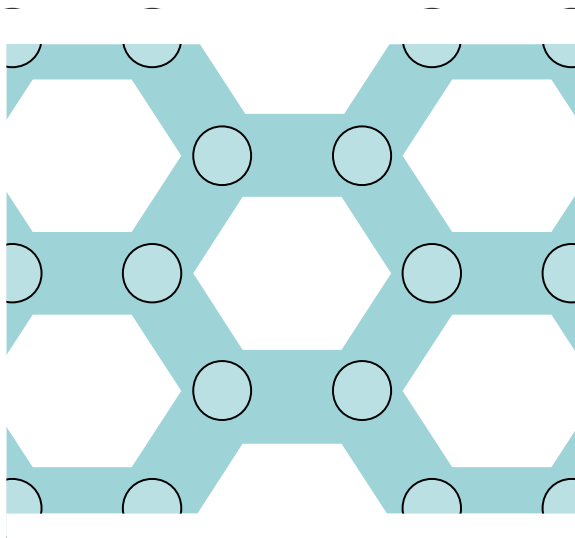
Characteristic types of binding



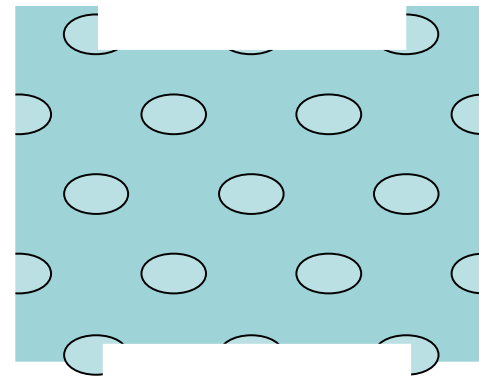
Closed-Shell Binding



Ionic Binding

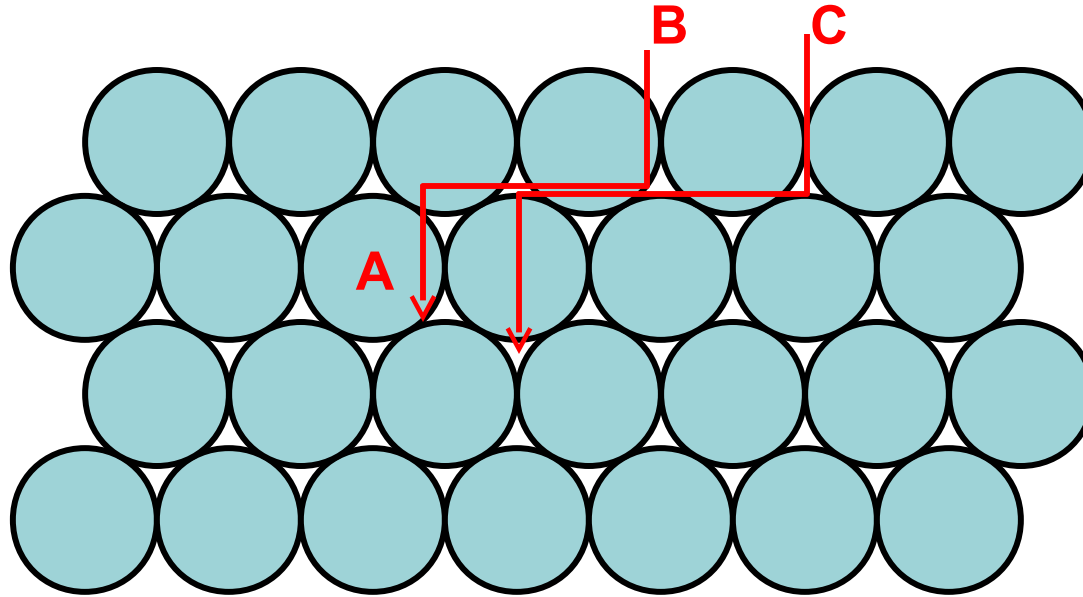


Covalent Binding



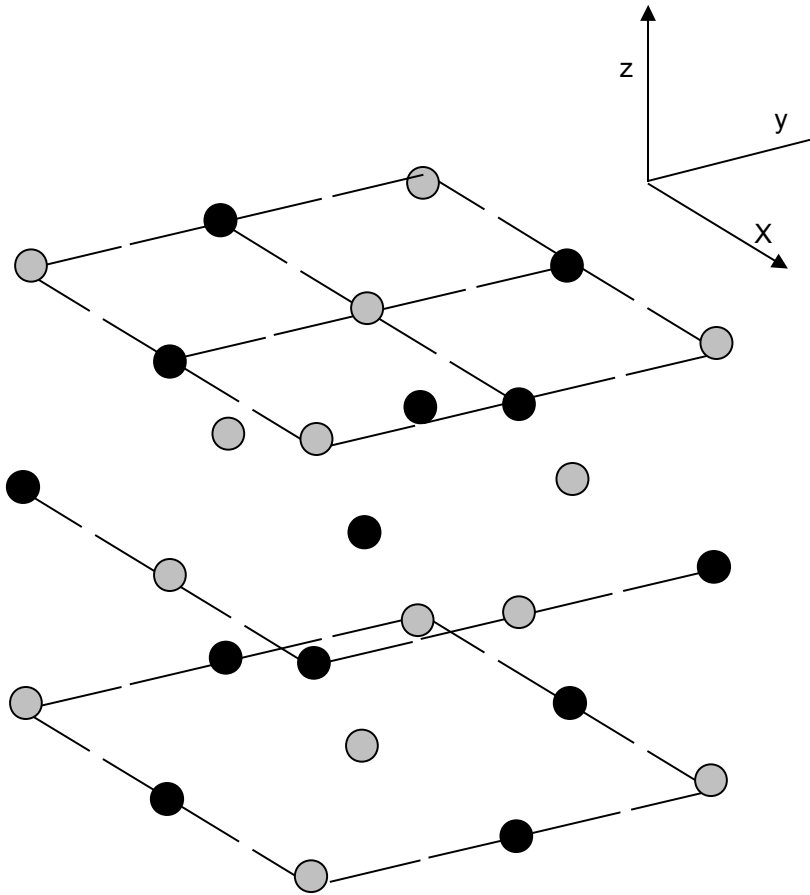
Metallic Binding

Close packed structures

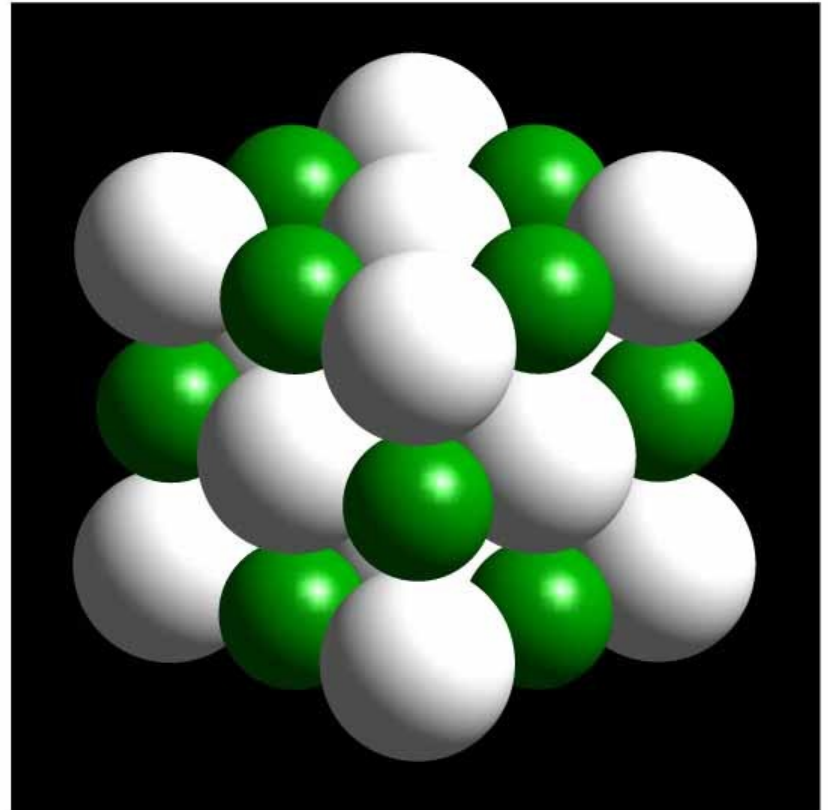


- . Each sphere has 12 equal neighbors
- . 6 in plane, 3 above, 3 below
- . Close packing for spheres
- . Can stack next layer as either B or C

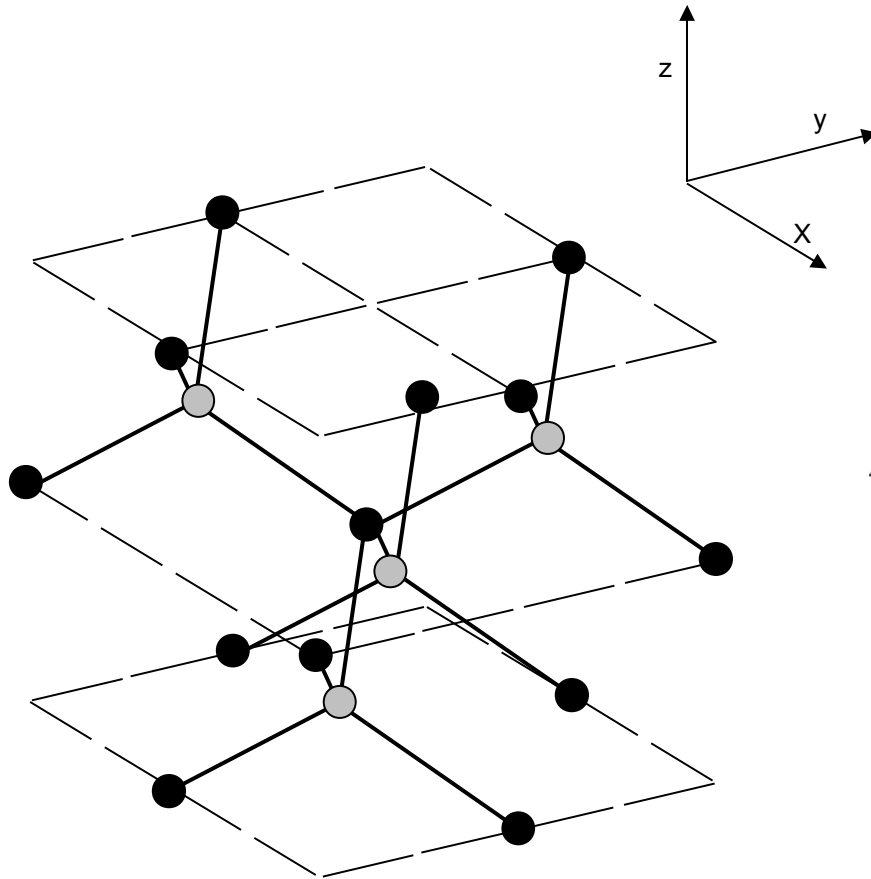
NaCl Structure



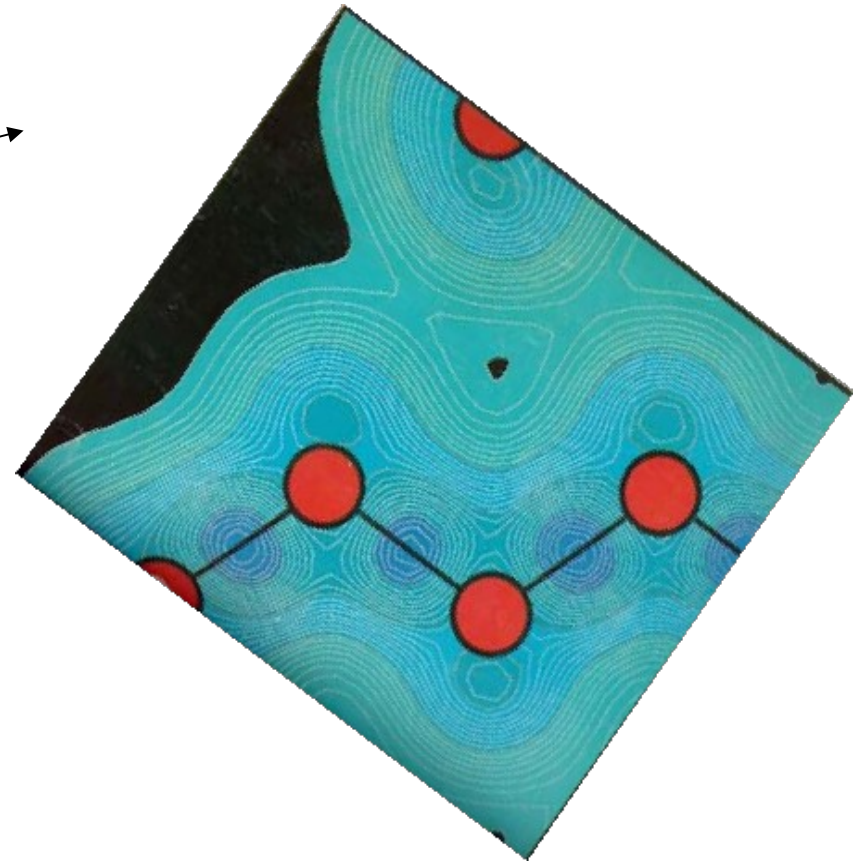
NaCl Structure with
Face Centered Cubic Bravais
Lattice



(110) plane in diamond structure crystal



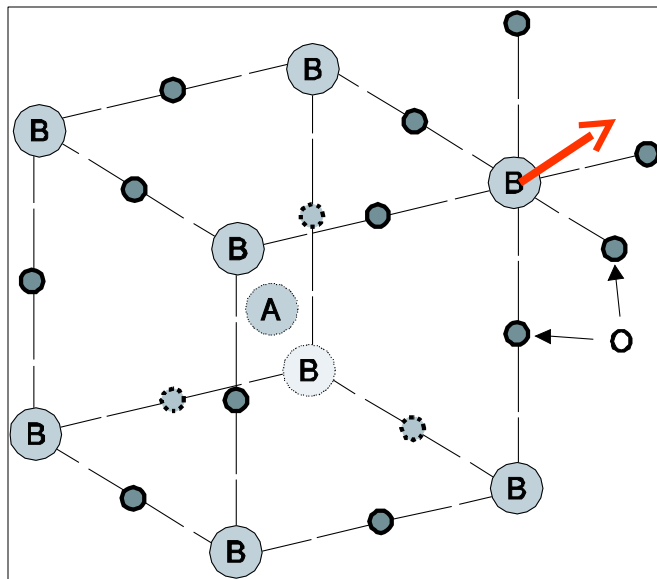
(100) plane in ZnS crystal
zig-zag Zn-S chains of atoms
(diamond if the two atoms are the
same)



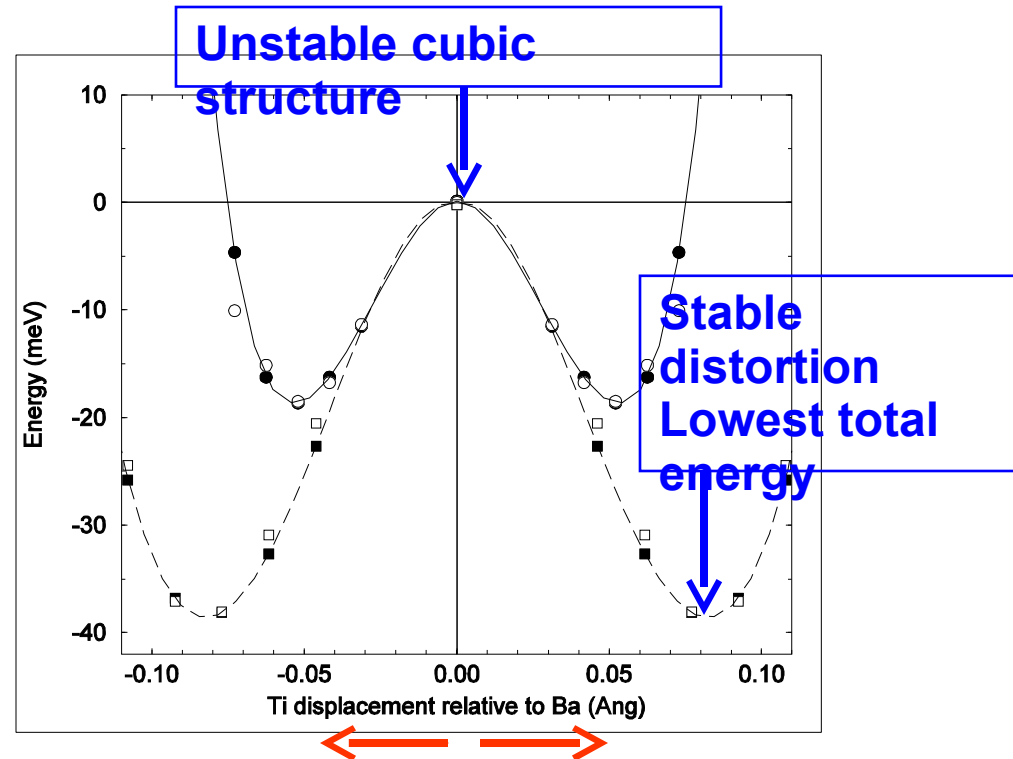
Calculated valence electron
density
in a (110) plane in a Si crystal
(Cover of Physics Today, 1970)

Predictions of Crystal structures, phase transitions

- Perovskite Structure – example
- Instability and predicted ferroelectric displacement in BaTiO₃



Perovskite structure



Equivalent results using plane waves, local orbitals, LAPW, ...

**End of this brief description
of types of materials**