Electronic Structure of Condensed Matter
Fudan University - April 2010

Lecture 1
Introduction and Overview

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Outline for Course

- **Qualitative concepts – electrons in materials**
  - Molecules, solids, liquids, ...
  - Here we emphasize solids - Examples, unique features of solids
- **Basic theory and methods**
  - Calculations for real materials possible only because of the power of computers and development of algorithms
  - But much more important is the fundamental developments that are the basis for all present-day (and future!) methods
- **Calculations of the properties of materials**
  - Theoretical relations that make possible quantitative calculations
  - Working hand-in-hand with experimentalists
  - Important: The most used methods do not always work!
    Crucial to know how to recognize errors and inaccuracies!
- **Developments of many-body methods**
  - Topics of special lectures

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Aspects of course

- **Material on Web site: schedule, links to files**
  - PDF files for lectures posted after the lecture
    (Thursday afternoon or Friday this week)
- **Three sets of homework exercises**
- **Project of your choice – but approved by me in advance**
  - time required approximately equal to 2 sets of exercises)

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?

Electronic Structure Theory and Computation 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

Electronic Structure Theory and Computation Properties of Materials

If all properties of materials are determined by the electrons, What is not "Electronic structure"?

- **Theoretical and experimental methods that are fields in themselves**
  - **Example: Superconductivity**
    - **Electronic Structure has an important role**
      - **Calculation of electron-phonon interactions**
      - **Recent developments actually predict transition temperatures**
      - **In all the recent discoveries (High-Tc, C_{60}, MgB_2, Fe pnictides) the first questions were: What is the electronic structure? What does "LDA" predict?**
    - **Nevertheless, the phenomena are an entire field of research**
  - **Many other examples**
    - **Not included here**

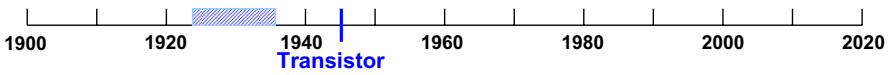
Electronic Structure in Perspective A brief History

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
- **Independent Electron Approximation**
- Thomas-Fermi approximation – 1927 (First density functional – Dirac – 1928
- Dirac equation – relativistic quantum mechanics - 1928
- Bloch theorem – 1928
- Wilson - Implications of band theory - Insulators/metals –1931
- Wigner- Seitz – Quantitative calculation for Na - 1935
- Slater - Bands of Na - 1934 (proposal of APW in 1937)
- Bardeen - Fermi surface of a metal - 1935



A long way in less than 90 years

The basic methods of electronic structure

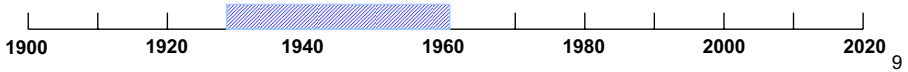
- Slater – Augmented Plane Waves (APW) - 1937
  Not used in practice until 1950's, 1960's – electronic computers
- Herring – Orthogonalized Plane Waves (OPW) – 1940
  First realistic bands of a semiconductor – Ge – Herrman, Callaway (1953)
- Hellman, Fermi – Pseudopotentials – 1930's
  - Phillips, Kleinman,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

Many-body methods to treat electron-electron interactions

- Recognized since the early days of quantum mechanics (Hylleras H_2 – 1929)

The basic advances in many-body theory – 1950's - 60's

- Landau – Feyman – Bohm – Pines – Gell-Mann – Breuckner – Hubbard – . . . .
- Baym – Kadanoff . . . .



Emphasis in this course

Basic Theory and Practical Methods | **Special Lectures (very brief)**

1964-5 **Density Functional Theory** | **Quantum Monte Carlo and "GW"**

- **Hohenberg, Kohn, Sham**
  Exact ground state energy
  a functional of electron density
  Local Density Approx. (LDA)
- **McMillan**
  QMC - Exact ground state for interacting Bosons
- **Hedin " GW ""**

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

- **Methods using DFT**
  Computational power for precise calculations in diverse crystals
- **Fermion QMC (Ceperley, …)**
  Computational power to treat homogeneous electron gas

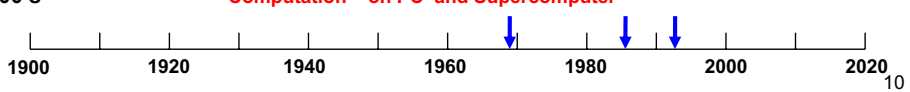
1980's **New Methods and New Discoveries (STM, QHE, C_{60}, Hi-Tc, …)**

- **Car-Parrinello molecular dynamics in electronic calculations**
- **QMC Calculations on solid H**
  Quantitative "GW" for Excited States

1990's **Discoveries and Methods continue (Nanotubes, CMR, MgB_2, …)**

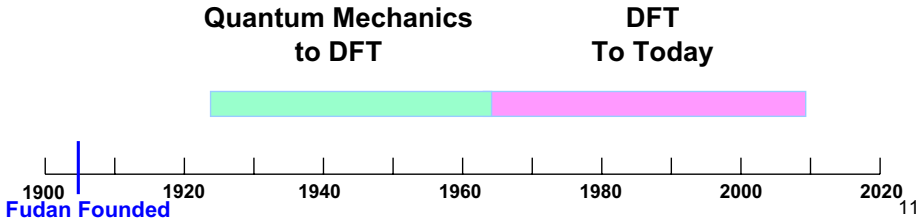
- **Polarization -- "Order N"**
  "Order N"
- **Dynamical Mean Field Theory**

2000's **Computation – on PC and Supercomputer**



A long way in less than 90 years

Electronic Structure in Perspective
A brief History



The Fundamental Hamiltonian

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

- **Only one small term, the kinetic energy of the nuclei**
  - **Very good approximation to neglect in determining the electronic states - Born-Oppenheimer approximation**
- **All other terms are large and of the same order of magnitude**
  - **The difficult part is the electron-electron interaction**
  - **Cannot be neglected in any quantitative calculation**
- **Note – For simplicity, we do not consider magnetic fields, and we neglect spin orbit and other relativistic**

Two types of Goals for Electronic Structure

- **Understanding**
  - Qualitative understanding of electronic properties does NOT require large calculations
  - Understanding also means understanding the behavior of specific materials that are ultimately determined by the electrons

- **Quantitative theoretical and computational methods for properties of materials**
  - Truly predictive methods must start from the fundamental equations
  - This requires:
    1. Ingenious theoretical methods to treat the interactiing electron problem for large classes of materials
    2. Ingenious computational methods to make calculations feasible for real materials

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Lecture 1 - continued
Examples related to Chapter 2

Physical distinction between different materials
Delocalized vs, Localized electronic states
Narrow vs. Wide bands

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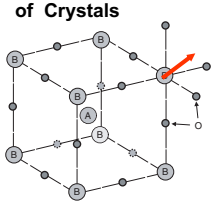
What does one want to do?

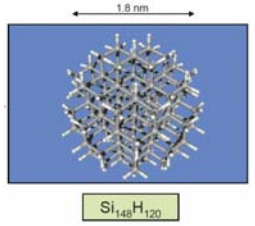
Treat many types of materials in a unified way from the basic equations

Calculate properties of Crystals

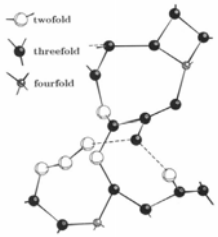


Predict crystal structures
Example – atomic positions in a ferroelectric

Predict properties of nanostrcutures

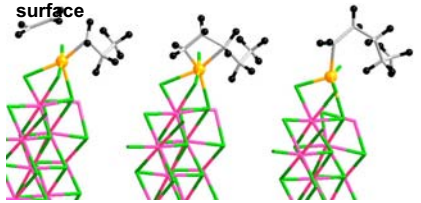


Simulation of Liquids – example Carbon at high T



"snapshot" of liquid

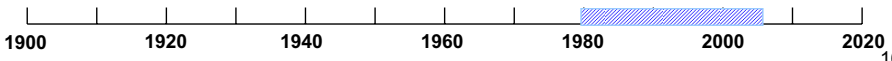
Reactions – example catalysis at a surface



Many other examples!

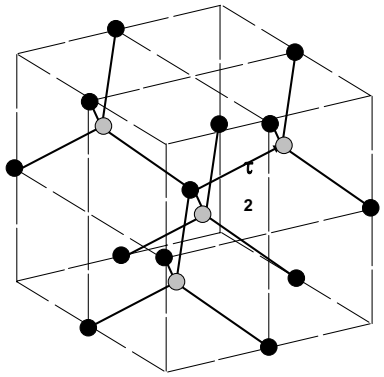
Examples of Modern Calculations

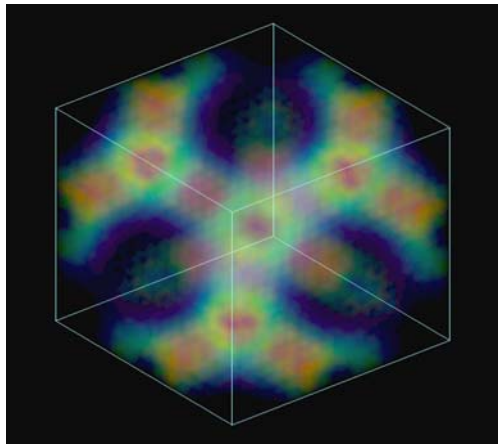
- Properties of crystals – many calculations are now "routine"
  - Definitive tests of the theory – comparisons with experiments
- Calculations for complex systems
  - Theory provides key role along with experiments
  - Understanding
  - Predictions
  - Direct simulation of atomic scale quantum phenomena
- Examples
  - Surfaces, interfaces, defects, ….
  - Thermodynamic phase transitions, Liquids, Melting, …
  - Nanostructures – in real environments, …
  - Large complex molecules – in solution, ….



Examples of Modern Calculations

Electron density in silicon





In Si the black and grey atoms are identical

Measure of methods – density agrees well with experiments

Results agree with experiment

(in important classes of materials)

Different methods agree

(when done carefully)

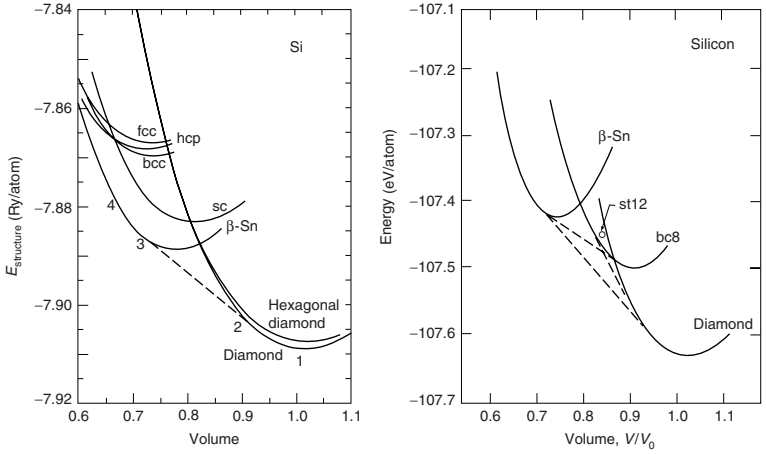
Method	C		Si		CaF_2		bcc Fe		
	a	B	a	B	a	B	a	B	m
NCPP[a]	3.54	460	5.39	98	5.21	90	2.75[c]	226[c]	
PAW[a]	3.54	460	5.38	98	5.34	100			
PAW[b]	3.54	460	5.40	95	5.34	101	2.75	247	2.00
USPP[b]	3.54	461	5.40	95	5.34	101	2.72	237	2.08
LAPW[a]	3.54	470	5.41	98	5.33	110	2.72[d]	245[d]	2.04[d]
EXP[a]	3.56	443	5.43	99	5.45	85-90	2.87[d]	172[d]	2.12[d]

- **a – lattice constant, B – bulk modulus, m – magnetization**
- [a]Holzwarth , *et al.*; [b]Kresse & Joubert; [c]Cho & Scheffler; [d]Stizrude, *et al.*

Phase Transitions Under Pressure

Transformation of silicon to metallic structures under pressure

Predictions from LDA – first demonstrations that DFT gives accurate results



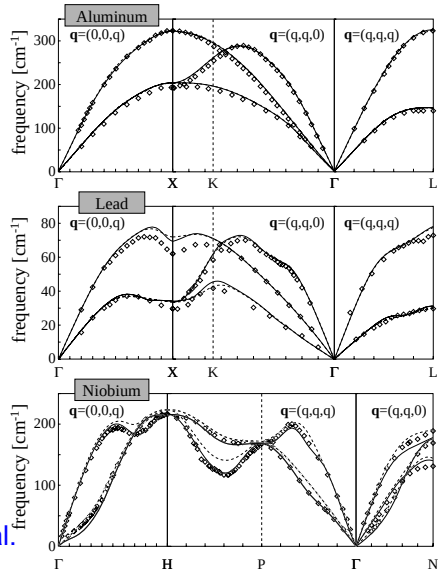
Modern codes ((ABINIT, VASP, ESPRESSO, Wein LAPW, FPLO, Beijing code, . . .) can easily reproduce similar curves.

Possible project: calculations with various functionals.

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, . . .



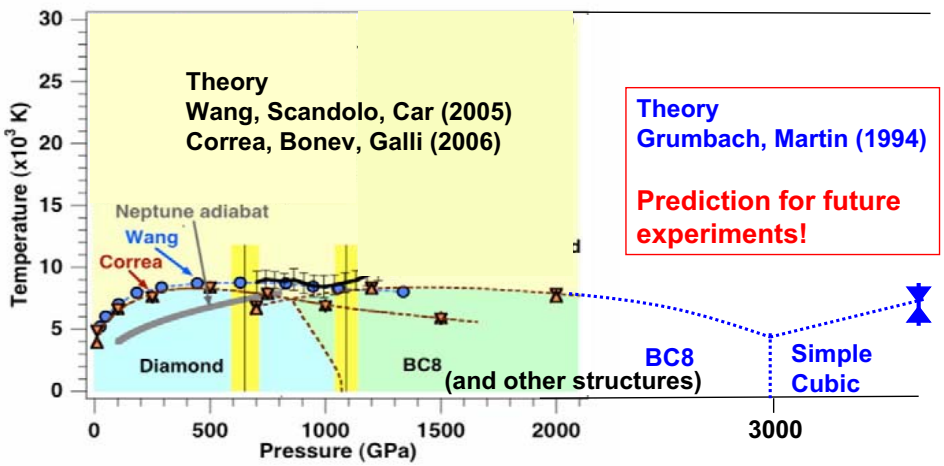
De Gironcoli, et al.

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

The Car-Parrinello Advance

- **Car-Parrinello Method – 1985**
  - Simultaneous solution of Kohn-Sham equations for electrons and Newton's equations for nuclei
- **A revolution in the power of the methods**
  - Relaxation of positions of nuclei to find structures
  - "First principles" molecular dynamics simulations of solids and liquids with nuclei moving thermally
  - Chemical reactions, . . .
- **Stimulated further developments . . . .**

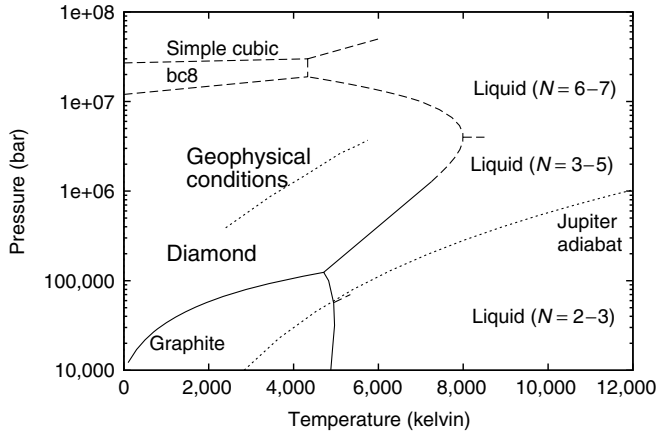
Predicted phase diagram of Carbon
Prediction Before Experiment



Agrees well with earlier calculations
Galli, Grumbach, Martin (1989-1994)

Unified MD – nuclei and electronic states
Example of Carbon

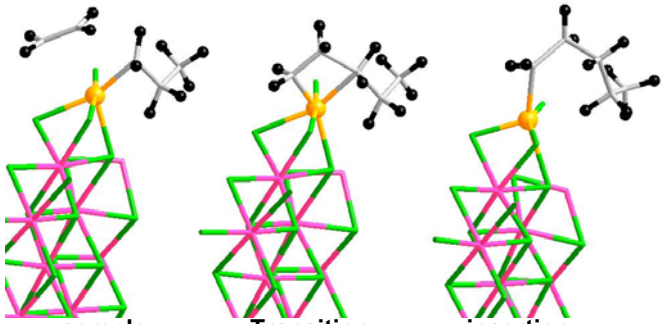
Melting of diamond at high pressure – other phases - geophysical, planetary physics



Grumbach, Galli, Martin, 1989-1994

Simulation of Catalysis for polymerization

- **Unraveling the steps in the Ziegler-Nata reaction**
  - **Industrial process for production of polyethylene**
  - Simulations with Car-Parrinello molecular dynamics – M. Boero, et al.

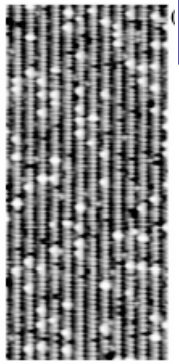


π-complex – Transition – insertion
Adds one ethelyne unit to polymer

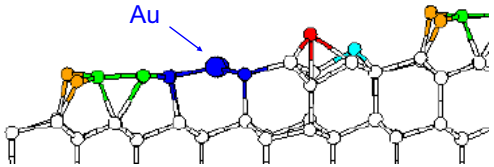
Surfaces – Au on Silicon surfaces

("vicinal" surface at angle to 111)

Atomic scale Au wires on Si (557) surface



STM image of self-assembled atomic "wires" on a Si surface
Crain, et al, Phys Rev B 69, 125401 (2004)



Theoretical prediction of structure in very good agreement with experiment– done later!
Sanchez-Portal and R. M. Martin, Surf. Sci. 532, 655 (2003)

Explains one-dimensional metallic bands observed by photoemission

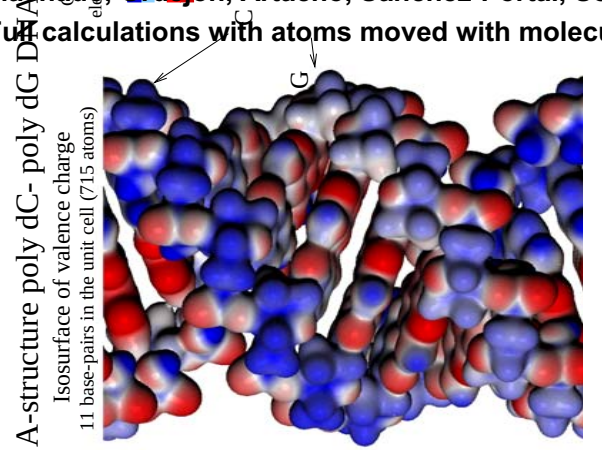
So what is left to do?

- **Failures of present density functional approximations in important cases!**
- **Electronic excitations**
  - **The "band gap problem"**
  - **. . .**
- **Strongly interacting systems**
  - **Magnetic insulators, metal-insulator transitions, . . .**
  - **. . .**
- **Example of "Failure" that has been solved!**
  - **Weak Van der Waals bonds**
  - **Development of non-local functional has the right distance dependence and is accurate enough for real materials**
- **. . .**

Simulations of DNA

(Early calculation – not very accurate)

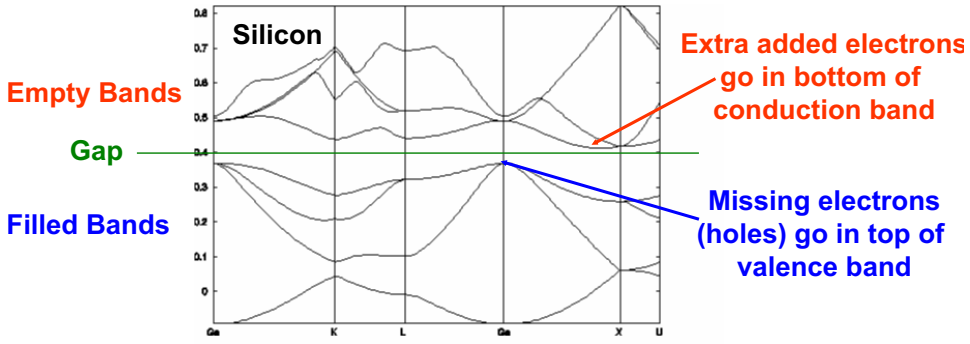
- **Machado, Ordejon, Artacho, Sanchez-Portal, Soler**
- **Full calculations with atoms moved with molecular dynamics**



Iso-density surfaces

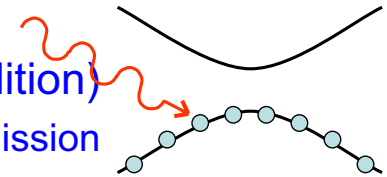
Electron Excitations - Bands

- **Understood since the 1920's - independent electron theories predict that electrons form bands of allowed eigenvalues, with forbidden gaps**
- **Established by experimentally for states near the Fermi energy**



Electron Excitations – Bands

(Description using Many-Body Methods)

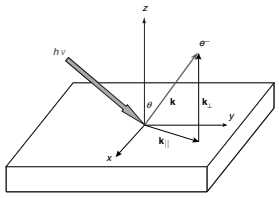


- Excitations
- Electron removal (addition)
  - – Experiment - Photoemission
  - – Theory – Quasiparticles
    "GW" Approximation

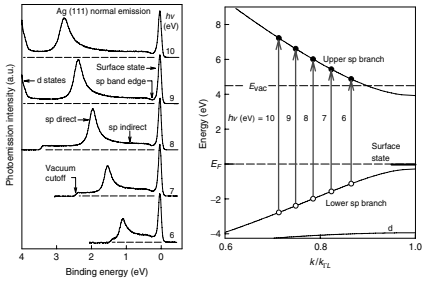
  - – Discussion in Special topics lectures.
    Theoretical concepts and basic methods,
    but not details mathematics or methods.

Experiment

Angle Resolved Photoemission (Inverse Photoemission)
Reveals Electronic Removal (Addition) Spectra

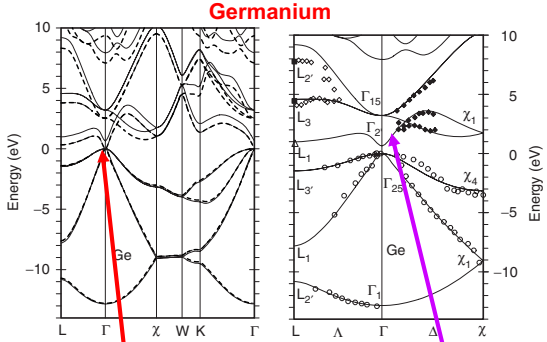


Silver



The Band-Gap Problem
Comparison of theory (lines) and experiment (points)

Germanium



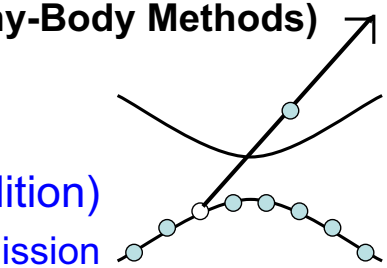
A metal in "LDA" calculations!

Improved many-Body Calculations

Figs. 2.22, 2.23, 2.25

Electron Excitations – Bands

(Description using Many-Body Methods)



- Excitations
- Electron removal (addition)
  - – Experiment - Photoemission
  - – Theory – Quasiparticles
    "GW" Approximation

  - – Discussion in Special topics lectures.
    Theoretical concepts and basic methods,
    but not details mathematics or methods.

Experiment

Angle Resolved Photoemission (Inverse Photoemission)
Reveals Electronic Removal (Addition) Spectra

Recent ARPES experiment on the superconductor MgB_2
Intensity plots show bands very close to those calculated

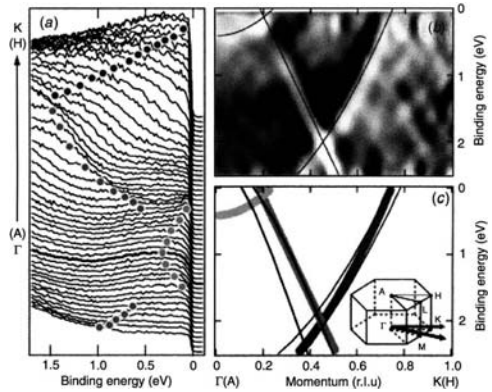


Fig. 2.30 Domasicelli, et al.

Extended band-like vs. Localized atomic-like behavior of electrons in solids

Very delocalized states

Nearly free electron bands
Alkali metals: Na, K, ...

Very localized states

4f states
Rare earths: Pr – Th

Intermediate cases

Semiconductors
"Band Gap Problem"

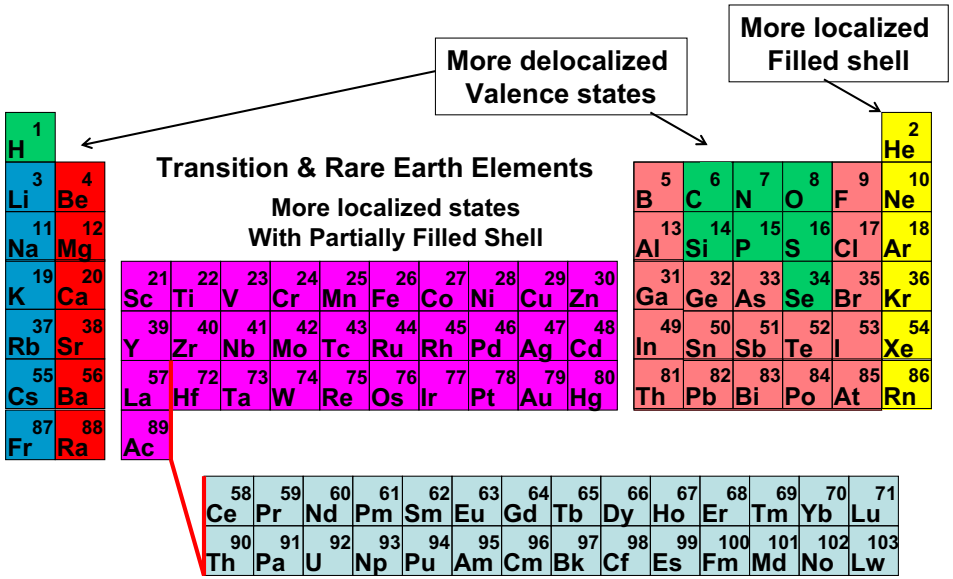
Transition Metals
Magnetism, Met-Ins Trans.

NOT included in text

Mott Metal-Insulator Transitions
Hydrogen under pressure (not reached experimentally)
NiO, CuO (actual Mott transitions)
"Colossal Magneto-Resistance" CMR

Anderson/Kondo/Heavy Fermion Problems
"Anomalous" Rare Earths, e.g., Ce
Transition Metal – Semiconductor alloys – Magnetic semiconductors
Hi-Tc, ….

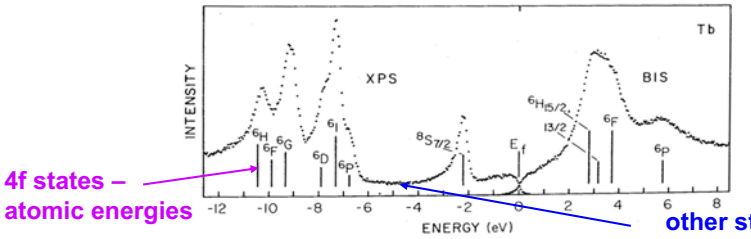
Periodic Table



Examples of Strong Correlations

Review Articles: Imada, et al., Rev. Mod. Phys. 70, 1039 (1998)
Damascelli, et al., Rev. Mod. Phys. 75, 473 (2003)

4f states --- Lanthanide rare earths: Ce – Yb
Example of Tb (half-filled shell with 7 electrons)



4f states – atomic energies

other states – form bands

FIG. 1. 4f final states observed by XPS and BIS.

For the 4f states, the energies to add or remove electrons are essentially the same as in an isolated atom – strong interactions on the atom lead to "multiplets" – different ways the same number of electrons on an atom can be arranged

Examples of Strong Correlations

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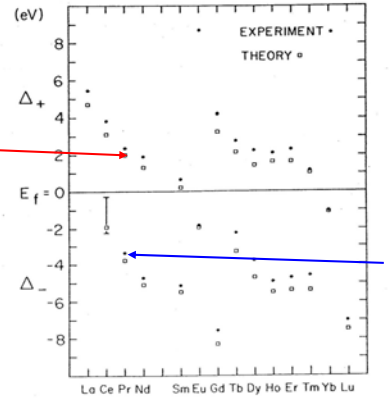
4f states Lanthanide rare earths: Ce – Yb

Lowest energy to add an electron in a 4f state

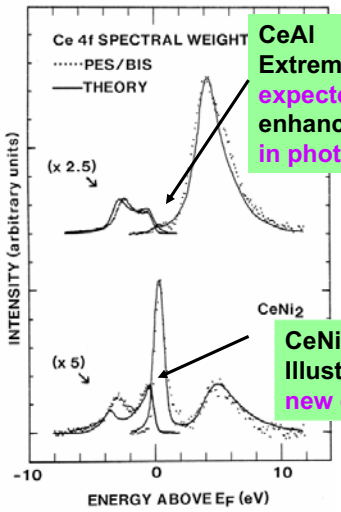


Lowest energy to remove an electron from a 4f state

FIG. 2. Comparison of experimental and theoretical (Refs. 11 and 12) values of Δ_- and Δ_+. The experimental Δ_- value for Ce lies within the error bar.

Example of Extreme Enhancements - Ce

Ce J. W. Allen and Coworkers



CeAl ("heavy fermion material")
Extremely large specific heat (1000 times larger than expected on simple arguments !) shows there is a large enhancement due to correlation – but almost no weight in photoemission at Fermi energy !

$CeNi_2$
Illustrates the "many-body" peak at Fermi energy - new energy scale due to correlation

Goal of Course

Understanding of the role of electrons in condensed matter

- **Practical, useful knowledge** of methods that are working tools of theorists, experimentalists, and researchers in many fields
  Without the burden of heavy math, many-body theory, …..

- **Appreciation** for the real many-body problems presented by electrons in condensed matter
  Understanding when to expect correlation to be important
  The grand challenges of condensed matter physics today

For those who are interested

- **Practical, useful knowledge** of **many-body** methods that are becoming more and more important for quantitative predictions and understanding the grand challenges in condensed matter