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

- 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

Electronic Structure of Condensed Matter
Fudan University - April 2010

Electronic Structure of Condensed Matter
Fudan University - April 2010
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, etc.
  - Thermal properties, melting, liquids, etc.
  Determined by the ground state of the electrons

- Electrons determine
  - Electrical conductivity: Insulators, Metals, Semiconductors, Superconductors
  - Optical properties, dielectric constant, colors, etc.
  - 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

- Pauli exclusion Principle - 1925
- Fermi statistics – 1926
- 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 H₂ – 1929)
- The basic advances in many-body theory – 1950’s - 60’s
  - Baym – Kadanoff . . . .

Basic Theory and Practical Methods

1964-5
- Density Functional Theory
  Hohenberg, Kohn, Sham
  Exact ground state energy
  a functional of electron density
  Local Density Approx. (LDA)

1970’s
- Computation established as powerful tools
  Methods using DFT
  Computational power to treat homogeneous electron gas

1980’s
- New Methods and New Discoveries (STM, QHE, C₆₀, 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, MgB₂, …)
  Polarization – “Order N”
  “Order N”

2000’s
- Computation – on PC and Supercomputer

A long way in less than 90 years

Electronic Structure in Perspective
A brief History

Quantum Mechanics DFT To Today

The Fundamental Hamiltonian

\[ \hat{H} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,j} \frac{Z_i e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \]

- 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 interacting 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

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

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.

Results agree with experiment
(in important classes of materials)

Different methods agree
(when done carefully)

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<th>C</th>
<th>Si</th>
<th>CaF$_2$</th>
<th>bcc Fe</th>
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<tr>
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<td>$a$</td>
<td>$B$</td>
<td>$a$</td>
<td>$B$</td>
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<td>460</td>
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<tr>
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<td>3.56</td>
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</tr>
</tbody>
</table>

- $a$ – lattice constant, $B$ – bulk modulus, $m$ – magnetization

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.

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 . . . .

Unified MD – nuclei and electronic states
Example of Carbon

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

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.
Theoretical prediction of structure in very good agreement with experiment—done later!

Explains one-dimensional metallic bands observed by photoemission

Surface – 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

Simulations of DNA
(Early calculation – not very accurate)
• Machado, Cardona, Artacho, Sanchez-Portal, Soler
• Full calculations with atoms moved with molecular dynamics

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
  – …

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

- Extra added electrons go in bottom of conduction band
- Missing electrons (holes) go in top of valence band
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 MgB₂
Intensity plots show bands very close to those calculated

Fig. 2.22, 2.23, 2.25

Domasicelli, et al.

Electron Excitations – Bands

(Description using Many-Body Methods)

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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
- Transition Metals

- "Band Gap Problem"

- Magnetism, Met-Ins Trans.

- Mott Metal-Insulator Transitions

- Hydrogen under pressure (not reached experimentally)

- NiO, CuO (actual Mott transitions)

- "Colossal Magneto-Resistance" CMR

**Examples of Strong Correlations**


**4f states — Lanthanide rare earths: Ce – Yb**

Example of Tb (half-filled shell with 7 electrons)

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.

**Periodic Table**

More delocalized Valence states

More localized Filled shell

Transition & Rare Earth Elements

More localized states

With Partially Filled Shell

Examples of Strong Correlations


**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
Example of Extreme Enhancements - 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 !

CeNi₂
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