Electronic Structure: Yesterday, Today and Tomorrow

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Electronic structure: 
Yesterday, Today and Tomorrow

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Electronic structure: Yesterday, Today and Tomorrow

First
No one can say what tomorrow will bring!

I do not pretend to be a fortune teller

Nevertheless
we can identify trends and developments
that will bring
new ideas, methods, capabilities, and understanding
Electronic structure: Yesterday, Today and Tomorrow

Next

THINK BIG

ABOUT SMALL THINGS

- The strongest materials known
- Improved catalysts
- The smallest transistors
- Tunable light emitters
- The best conductors
- Between molecules and solids controllable
Electronic structure: Yesterday, Today and Tomorrow

Themes of this talk: I

Although this is a college on computational nanoscience

The understanding should be based upon general theoretical methods that apply broadly to many problems

A long and distinguished history
Electronic structure: Yesterday, Today and Tomorrow

Themes of this talk: II

Electronic Structure has reached the point where it provides quantitative results and understanding in actual materials.

Essentially very topic of a standard solid state text is the subject of electronic structure theory and computation.

Among the most active areas of physics, chemistry and materials science.
Electronic structure: Yesterday, Today and Tomorrow

Themes of this talk: III

Electronic Structure has reached the point where it provides quantitative results and understanding in actual materials

Essentially very topic of a standard solid state text is the subject of electronic structure theory and computation

Every topic in the solid state text is stretched to the breaking point by changes at the nanoscale
Electronic structure: Yesterday, Today and Tomorrow

Themes of this talk: IV

Electrons in materials are the quintessential many-body problem in physics – in depth and breadth.

Density functional theory is a theory of many-body interacting electron systems - but not the theory.

Explicit many-body methods (GW, QMC, DMFT, ….) are needed to go beyond DFT.

With 100% certainty we can say that the future of the field will deal with the many-body problems and many of the great challenges will be quantitative calculations and understanding at the nanoscale.
Electronic structure: Yesterday, Today and Tomorrow

Plan for this talk

• Some of the remarkable history
• THE problem if we want to have a firm foundation
• Comments on the power of density functional theory and pointers to some of the talks in this college
• Explicit many-body methods that build upon DFT
• Some examples of models that provide understanding

With 100% certainty we can say that future work will be methods to deal with the many-body problems and develop simplifications and models to provide quantitative calculations and understanding at the nanoscale
Nanoscience
Experiments, theory and computation

In nanoscience, experiments are very difficult and difficult to interpret

Theory and computation based upon solid foundations can help unravel the puzzles and provide quantitative understanding in actual, (possibly) useful nanosystems and qualitatively new phenomena

With 100% certainty we can say that there will be new opportunities and challenges for experimentalist and theorists working together
Electronic Structure in Perspective
A brief History
A long way in less than 90 years


E. Schrödinger – 1925, ....

- Pauli exclusion principle - 1925

**Independent Electron Approximation**

- Fermi statistics – 1926
- 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, ....

• Pauli exclusion principle - 1925

Interacting Electrons
Recognized since the early days of quantum mechanics

• Hund’s Rules for atomic moments - 1925
• Hartree – Self-consistent field calculations multi-electron for atoms – 1928
  Self-interaction corrected! (Calculations done by his father)
• Hylleraas - Essentially exact numerical solution for the He atom – 1930

The basic advances in many-body theory – 1950’s - 60’s
A long way in less than 90 years

E. Schrödinger – 1925, ....

• Pauli exclusion principle - 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

– 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
  a functional of electron density
  Local Density Approx. (LDA)

* Quantum Monte Carlo and “GW”
  McMillan, Hedin
  QMC - Exact ground state for interacting Bosons
  Hedin “GW”

1970's

Computations 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}, …)

Computational methods, Polarization, --
Dynamical Mean Field Theory

2000’s

Discoveries and Methods continue
Electronic Structure in Perspective
Moving on
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

Ground state properties of the electrons – the “glue” that holds the solid together

Every aspect should be considered again in nanosystems

Explicitly expressed in terms of the electrons – Some are ground state – some require excited states
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
Reminder of what we are dealing with: The Fundamental Hamiltonian

\[
\hat{H} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \\
- \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|}
\]

- 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
- (For simplicity, we do not consider magnetic fields, and we neglect spin orbit and other relativistic effects)
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
What does one want to do?

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

3D -- Crystals

2D -- layers

1D -- tubes, ribbons, wires

0D - nanostructures

Structures and Properties – example ferroelectricity

Minimum thickness for ferroelectricity?

Liquids

“snapshot”

Reactions – catalysis at a surface

Supported clusters

Thermal motion

Mesoscopic (same theory?)

Single molecule transport

Of course many other examples!
Methods for theory and computation
Density Functional Theory

• The ground state energy of the interacting electron problem is a functional of the density – in principle exact - \( E_0[n] \), minimum at \( n = n_0 \)

• Kohn-Sham “auxiliary system” - non-interacting particles

\[
n_0(\mathbf{r}) = \sum_{\sigma} \sum_{i=1}^{\infty} |\psi_i^\sigma(\mathbf{r})|^2,
\]

\[
E_{KS} = \frac{1}{2} \sum_{\sigma} \sum_{i=1}^{\infty} |\nabla \psi_i^\sigma|^2 + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{\text{Hartree}}[n] + E_{\text{II}} + E_{\text{xc}}[n].
\]

Equations for independent particles - soluble

• Required to be the same as the density of the interacting electrons

• Exchange-Correlation Functional – Exact theory but unknown functional

• A new paradigm for the many-body problem:
  Choose only certain properties to calculate
  Find approximate functionals for those properties

• Practical points for our purposes:
  Approximate functionals are very accurate in large classes of problems
  The only way at present for calculation of ground state properties
  Practical methods can treat large classes of nanosystems

Kohn-Sham calculations are not supposed to work for all properties
Kohn-Sham calculations do NOT work for all properties

For a much more pedagogical presentation see talks by Baroni
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.
SIESTA works as well – but is not designed for such problems
It is more effective for nanosystems
Results agree (amazingly) well with experiment for ground state properties in important classes of materials

Different methods agree  (when done carefully)

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</table>

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

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

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

More, better analysis in Baroni’s talks
Exchange and Correlation in an atom

Why should simple approximation work?

• Exchange and correlation around each electron, other electrons tend to be excluded – “x-c hole”
• $E_{xc}$ is the interaction of the electron with the “hole” – which involves only a spherical average

Exchange hole in Ne atom

Is the local density approximation a good approximation?

(Gunnarsson, et. al.)
Exchange and Correlation in an atom

Why should simple approximation work?

- Exchange and correlation → around each electron, other electrons tend to be excluded – “x-c hole”
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which involves only a spherical average

Is the local density approximation a good approximation?
For finding the ground state energy

( Gunnarsson, et. al.)
Example of H$_2$ Molecule

- It seems ridiculous to approximate the correlation of the two electrons by the LDA derived from the homogeneous gas
- How good are the results?

Very Good!
Supports a local approximation – exact is the homogeneous limit and amazingly good for the H$_2$ molecule!

What do the Ne atom and the H$_2$ molecule have in common?
Closed shell systems with large gaps to all excitations

In general NOT so good for open shells that are “more correlated”
A few examples and cases that show the need to go beyond the widely-used DFT methods
Atomic Scale Gold Wires on Silicon Surfaces

"self-assembled" on "vicinal" 557 surface at angle to 111

STM image of self-assembled atomic “wires

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

For the bands of the wires see my next talk

Done using SIESTA (tutorial Wednesday by Ordejon, Torres)
Simulations of DNA
(Early calculation)

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

Iso-potential surfaces

Done using SIESTA (tutorial Wednesday by Ordejon, Torres)
Simulation of Catalysis for Polymerization

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

\[ \pi\text{-complex} \rightarrow \text{Transition} \rightarrow \text{insertion} \]

Adds one ethylene unit to polymer
Failures of present density functional approximations in important classes of problems

• **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

  Langreth and coworkers

• . . .
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

In nanostructures, states are discrete but they retain bulk features except at the smallest sizes where they can be considered as molecules
Electron Excitations

The correct term is Energies for removal and addition of electrons

The real problem approached using Many-Body Methods

- Excitations
- Electron removal (addition)
  - Experiment - Photoemission
  - Theory – Quasiparticles
    “GW” Approximation.

More, better analysis in talks by Galli, Scheffler (others?)
Electron Excitations

The correct term is
Energies for removal and addition of electrons
The real problem approached using Many-Body Methods

- Excitations
- Electron removal (addition)
  - Experiment - Photoemission
  - Theory – Quasiparticles
    “GW” Approximation.

Most actual practical approaches use DFT as the starting point
LDA, GGAs, hybrids, LDA+U, . . .

More, better analysis in talks by Galli, Scheffler (others?)
Example of Germanium

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

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

Germanium

A metal in “LDA” calculations!
Improved many-Body Calculations

What about nanosystems?
Crucial roles of electronic excited states
Gaps in clusters

What about nanosystems? - Silicon clusters

Gaps much larger than the bulk
Decrease in oscillator strength shows approach to the bulk

BS – Bethe-Salpeter – many body calculation
TDDFT – time dependent DFT

Why is TDDFT so good?

My talk this afternoon – talks by Baroni, Galli, . . .
Extended band-like vs. Localized atomic-like states

Transition & Rare Earth Elements
More localized states
With Partially Filled Shell

More delocalized
Valence states

More localized
Filled shell

Transition & Rare Earth Elements

More delocalized
Valence states

More localized
Filled shell

Extended band-like vs. Localized atomic-like states

Magnetism - “Strongly Correlated” States in Solids
What about nanosystems?
Example of important effects of correlation

Kondo resonance in a single-molecule transistor

Wenjie Liang*, Matthew P. Shores†, Marc Bocarath*, Jeffrey R. Long† & Hongkun Park*

Effect vanishes above ~10K.

Note the molecule contains Vanadium

Energies for electrons to move through molecule? Coulomb Blockade? Kondo Effect?

Screening by metal leads? . . .

Figure 1 Fabrication of single-molecule transistors incorporating individual divanadium molecules. Top left, the structure of [(N,N',N"-trimethyl-1,4,7-triazacyclononane)$_2$V$_2$(CN)$_6$(μ-C$_3$N$_4$)] (the V$_2$ molecule) as determined by X-ray crystallography; red, grey and blue spheres represent respectively V, C and N atoms. Top
Electronic structure: Yesterday, Today and Tomorrow

Conclusions

• If we want to have a firm foundation:
  Look back at history
  THE problem is many interacting electrons

• DFT is a powerful theory of the many-body problem
  It is amazingly accurate for some problems

• Explicit many-body methods are needed to go further
  Quantitative methods build upon DFT

• It is also essential to develop simplified (but firmly founded)
  pictures provide understanding

With 100% certainty we can say that future work will be methods to
deal with the many-body problems
and develop simplifications and models to provide quantitative
calculations and understanding at the
nanoscale