Spring College on Computational Nanoscience

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Examples of Electron Properties DFT and TD-DFT calculations. Explicit many-body methods.

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Examples of Electronic Properties
DFT and TD-DFT calculations
Explicit many-body methods

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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!
Electronic excited states
Bands for addition/removal of electrons

A surprise
(at least it was a surprise to me!)
From Previous Lecture

**Atomic Scale Gold Wires on Silicon Surfaces**

(“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!

Explains one-dimensional metallic bands observed by photoemission

Done using SIESTA (tutorial Wednesday by Ordejon, Torres)
Atomic Scale Gold Wires on Silicon Surfaces

What about bands?

The correct question is:
What is the dispersion along the wires for removal or addition of electrons?

What do we expect?
One band – half filled
6s state of Au (role of Si?)

Luttinger Liquid?
Effects only near $E_F$ How near? Scale?

Expect weak (?) correlations
6s state of Au (role of Si?)

What does experiment find?
Si(557)-Au: Photoemission experiments

Two bands observed

Note: the two bands are very similar. Accident?

What does theory predict?

R. Losio et al. PRL 86, 4632 (2001)
Several flat bands (open dots) Not part of the “wire” and very sensitive to surface details, e.g., disorder

We can give good reasons, but in fact it is experiment that shows there are no flat bands at the Fermi energy

Si(557)-Au: Theory II – Perhaps a surprise?

Au wires - 6s states

Does bonding to Si qualitatively change the picture?

Do spin-orbit interactions affect s states?

Au – Si wires --- Au 6s + Si 3p

Net Momentum around each Au atom
Large S-O interaction!

Si(557)-Au: Theory II – Perhaps a surprise?

Electron wavefunction is not symmetric around a Au atom

Au – Si wires --- Au 6s + Si 3p

Net Momentum around each Au atom
Large S-O interaction!

Actually a very general effect – “Rashba Effect” (well known!)
A surface state is never symmetric – relativistic effect due to the electric field perpendicular to the surface: \((\nabla V \times p) \cdot \sigma\)

Si(557)-Au: Experiment + Theory

With S-O interaction

Agrees quantitatively

Electronic excited states
Bands for addition/removal of electrons

How to go beyond DFT eigenvalues?
Electron Excitations – Bands

The real problem approached using Many-Body Methods beyond DFT

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

More, better analysis in talks by Galli, Scheffler (others?)
Electron Excitations – Bands
The real problem approached using Many-Body Methods beyond DFT

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

DFT has a critical role:
The real practical approaches use DFT as the starting point
LDA, GGAs, hybrids, LDA+U, . . .

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

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 nanoclusters of Ge?
Optical absorption in Nanosystems
Electron Excitations – Optical absorption

- Electrons are promoted to excited states
- One Experiment - Optical absorption
- Appears to be even harder than electron removal or addition
- A standard text treats this as the problem of Interaction between the electron and “hole”.
Electron Excitations – Optical absorption

- Electrons are promoted to excited states
- **One Experiment**
  - Optical absorption
- Appears to be even harder than electron removal or addition
- A standard text treats this as the problem of Interaction between the electron and “hole”
- **Always attractive** – lowers energy for absorption.

But there is another way to look at the effect
Simply a oscillation of the electron density!
Optical absorption in a nanoscale system

• In a solid a photon causes “displacement currents”
• Optical properties described by $D(\omega) = \varepsilon(\omega) E(\omega)$
  \[ = E(\omega) + 4\pi P(\omega) \]

In nanoscale system the size is much less than the wavelength of light – optical response is $d(\omega) = \alpha(\omega) E(\omega)$ where $d$ is the dipole moment.
Optical absorption in a nanoscale system

- Electrons are promoted to excited states
- Interaction between the electron and "hole" is increased in a nanosystem because the electron and "hole" are forced to be close
- Appears to make the problem harder.

But it can be considered in a simpler way!

The oscillation of the electron density due to an applied electric field

\[
\text{E}(\omega) \quad \text{d}(\omega)
\]
Time-dependent Density Functional Theory

• The static Kohn-Sham equations for the ground state density have been generalized to a time-dependent potential $V_{\text{ext}}(x,t)$ felt by the electrons.

• For a nanoscale system we have $V_{\text{ext}}(x,t) = E(t)x$.

• Solve time-dependent Kohn-Sham equations for the density in presence of the time-dependent electric field.

• Either in time $E(t)$ or frequency $E(\omega)$.

See talks by Baroni
Optical Absorption in clusters

What about nanosystems? - Silicon clusters

Gaps much larger than the bulk
Can be understood roughly as effect of confinement in a box

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

Decrease in oscillator strength shows approach to the bulk

Why is TDDFT so good?
Excitations in Ge clusters calculated using many-body quantum Monte Carlo methods (DMC)

For nanoscale clusters Si and Ge are not so different!

Optical gaps can be in the visible – tunable by size

Why is TDDFT so good?  
Vincent, et al, 2006
Time-dependent Density Functional Theory

Again

Why is TDDFT so good for these problems?

- Recall the argument for the ground state Kohn-Sham method
- A key point was that the method accounted for the large terms – kinetic energy and all the Coulomb terms (nuclei and electrons)
- This is also the case in TDDFT which includes the Coulomb potential due to the density oscillations

See talks by Baroni
When are the addition and removal energies important in nanosystems?
Conduction through a single molecule

Schematic illustration of system

left metal lead  molecule  right metal lead

Chemistry World web site
Conduction through a single molecule

Schematic illustration of energy levels

No states at the Fermi energy – no conduction through molecule

E_Fermi

states of the molecule
Conduction through a single molecule

Schematic illustration of energy levels

States at the Fermi energy allow conduction

Key Points:
1. Energies of the molecule states relative to the Fermi energies
2. Energy gap in the molecule
3. How are these affected by the coupling to the metal?
4. Here we have ignored Interaction between electrons –

In fact if there is a electron on the molecule, the energy to add a second electron is changed – next slide
Conduction through a single molecule

Simple model with interactions between electrons (Anderson model)

Energy for one electron on molecule (can be up or down)

Coulomb blockade: no current can flow

But see later: there is a quantum effect due to the fact that the electron can have up or down spin
Conduction through a single molecule

Consider a potential (called $V_{\text{gate}}$) that changes the energy of the molecule relative to the Fermi energy.

For simplicity, set Fermi energies equal $V = 0$ between metal leads.

Conduction occurs when a level lines up with the Fermi energy.
Conduction through a single molecule

Results for the Anderson model

Number of electrons on molecule

Conductance as a function of voltage $V$ for different values of $V_{\text{gate}}$

Calculated by the “GW” method – screening due to the metal changes energies from Hartree Fock values

Spartaru, et al 2009
Conduction through a single molecule

The Kondo effect
A simple description that provides the physical picture

The spin of the one electron in the molecule can flip if an electron in the metal also flips with little change in energy ---- causes a strong interaction at the Fermi energy

The states at the Fermi energy extend into molecule – and lead to conduction even if the state are not at the Fermi energy!
Conduction through a single molecule

The Kondo effect
An impurity in a metal leads to the maximum possible resistance for a single impurity

In a junction between metals it leads to the maximum possible conductance for a single channel

Moral of this story
A simple model shows the basic effects that can happen

The task for computational nanoscience is to make quantitative predictions for the levels, the interactions, and the final consequences for transport in the full coupled system
Effect vanishes above ~10K.

Note the molecule contains Vanadium – larger Coulomb interaction

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)₂V₂(CN)₆[μ- C₅N₃]] (the V₂ molecule) as determined by X-ray crystallography; red, grey and blue spheres represent respectively V, C and N atoms. Top
Conclusions

The same as the previous lecture!

• 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