



2145-12

Spring College on Computational Nanoscience

17 - 28 May 2010

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

R.M. MARTIN Univ. of Illinois at Urbana Champaign Urbana, IL U.S.A. Examples of Electronic Properties DFT and TD-DFT calculations Explicit many-body methods

Spring College on Computational Nanoscience ICTP, Trieste, Italy, 17 to 28 May 2010

Richard M. Martin

University of Illinois Stanford University

What does one want to do?

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



Of course many other examples!

Electronic excited states Bands for addition/removal of electrons

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



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?

Electron momentum

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

R. Losio et al. PRL 86, 4632 (2001)

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

Sanchez-Portal, et al. PRL 93, 46803 (2004)]

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

Sanchez-Portal, et al. PRL 93, 46803 (2004)]

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

Electron wavefunction is not symmetric around a Au atom

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: ($\nabla V \ge p$) σ

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?)

From previous lecture – Disaster in Germanium! Metal!

Experiment

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

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 $D(\omega) = \varepsilon(\omega) E(\omega)$

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

Time-dependent Density Functional Theory

- The static Kohn-Sham equations for the ground state density have been generalized to a time-dependent potential $V_{ext}(x,t)$ felt by the electrons
- For a nanoscale system we have $V_{ext}(x,t) = E(t)x$

•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(ω)

Optical Absorption in clusters

What about nanosystems? - Silicon clusters

IGOR VASILIEV, SERDAR ÖGÜT, AND JAMES R. CHELIKOWSKY

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

PHYSICAL REVIEW B 65 115416

Decrease in oscillator strength shows approach to the bulk

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

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

When are the addition and removal energies important in nanosystems?

Conduction through a single molecule Schematic illustration of system

Chemistry World web site 25

Conduction through a single molecule Schematic illustration of energy levels

States at the Fermi energy allow conduction

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_{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

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 impuriy

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

Example of important effects of correlation

Kondo resonance in a single-molecule transistor

Wenjie Liang*, Matthew P. Shores†, Marc Bockrath*, Jeffre & Hongkun Park*

NATURE | VOL 417 | 13 JUNE 2002 | www.nature.com/natur 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 $[(N,N',N'' - trimethyl-1,4,7 - triazacyclononane)_2V_2(CN)_4(\mu-C_4N_4)]$ (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 <u>understanding</u> at the nanoscale 34