The Abdus Salam
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Educational, Scientific and
Cultural Organization

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Spring College on Computational Nanoscience

17 - 28 May 2010

Electronic Structure: Yesterday, Today and Tomorrow

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Electronic structure:
Yesterday, Today and Tomorrow

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

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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, <u>Today</u> 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

Nanocience
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

L. de Broglie –
Nature 112, 540 (1923).

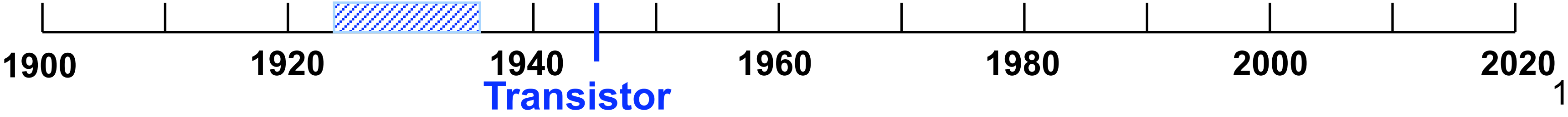
E. Schrödinger –
1925, ….

- Pauli exclusion principle - 1925

Independent Electron Approximation

- Fermi statistics – 1926
- Thomas-Fermi approximation – first density functional – 1927
- 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

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Interacting Electrons

Recognized since the early days of quantum mechanics

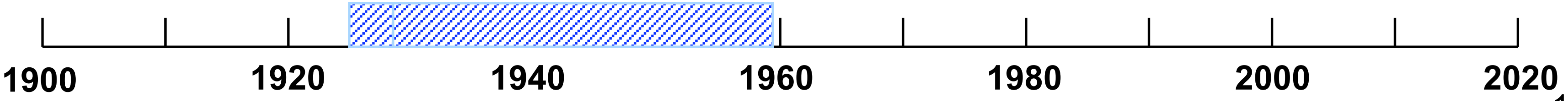
- Hund's Rules for atomic moments - 1925
- Hartree – Self-consistent field calculations multi-electron for atoms – 1928

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

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



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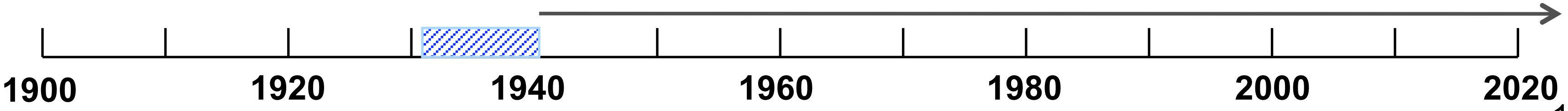
The basic methods of electronic structure

- 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
  - Phillips, Kleinman, Antoncik, - 1950’s - Hamann, Vanderbilt, others – 1980’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

<u>Exact ground state energy</u>
a functional of electron density
Local Density Approx. (LDA)

Quantum Monte Carlo and **“GW”**

* McMillan, Hedin

QMC - <u>Exact ground state</u> 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

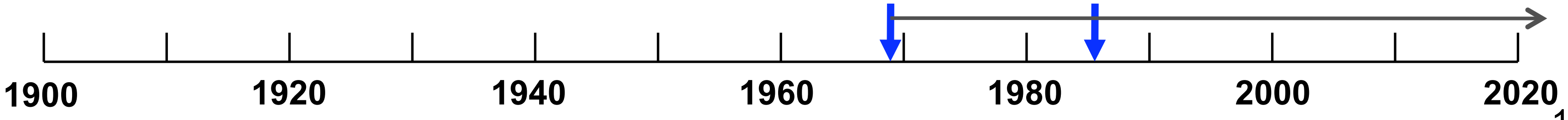
QMC Calculations on solid H
Quantitative “GW” for Excited States

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

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

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

Every aspect should be considered again in nanosystems

- "Electronic properties"
  - Definition of bands
  - Metals vs. insulators
  - Conductivity, dielectric functions
  - Magnetism

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

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

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

- **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**
- **(For simplicity, we do not consider magnetic fields, and we neglect spin orbit and other relativistic effects)**

Two types of Goals for Electronic Structure

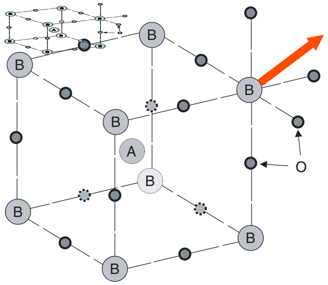
- Understanding
  - Qualitative understanding of electronic properties does NOT require large calculations
  - Understanding also means understanding the behavior of specific materials that are ultimately determined by the electrons

- 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 interactiing electron problem for large classes of materials
    2. Ingenious computational methods to make calculations feasible for real materials

What does one want to do?

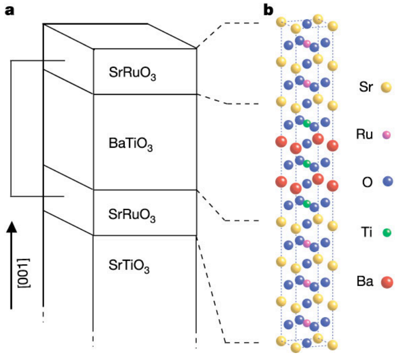
Treat many types of materials in a unified way from the basic equations

3D -- Crystals



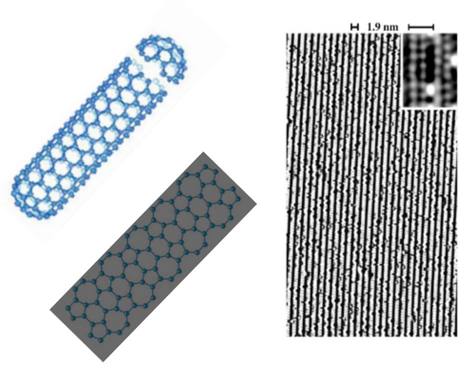
Structures and Properties – example ferroelectricity

2D -- layers

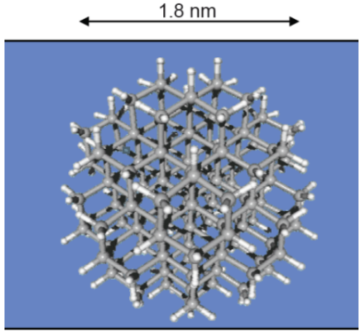


Minimum thickness for ferroelectricity?

1D – tubes, ribbons, wires

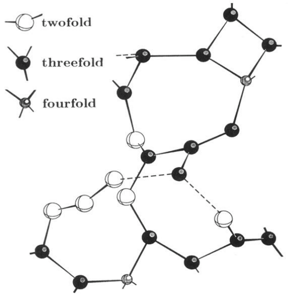


0D - nanostrcutures



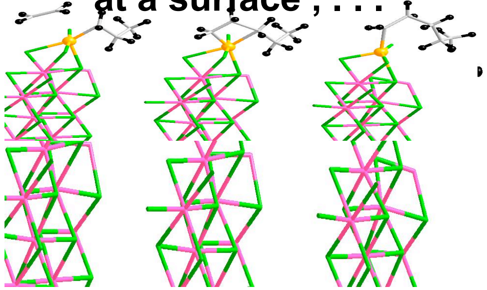
$Si_{148}H_{120}$

Liquids

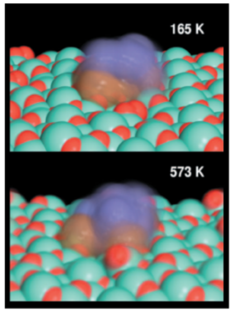


“snapshot”

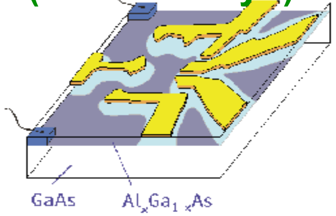
Reactions – catalysis at a surface , . . .



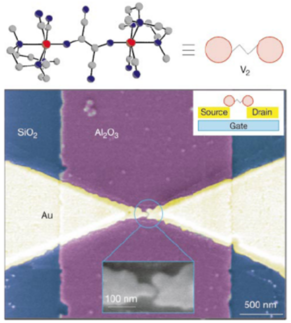
Supported cluster Thermal motion



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

$$n_0(\mathbf{r}) = \sum_\sigma \sum_{i=1} |\psi_i^\sigma(\mathbf{r})|^2, \longleftarrow$$

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

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

Equations for independent particles - **soluble**

Exchange-Correlation Functional – Exact theory but **unknown** functional

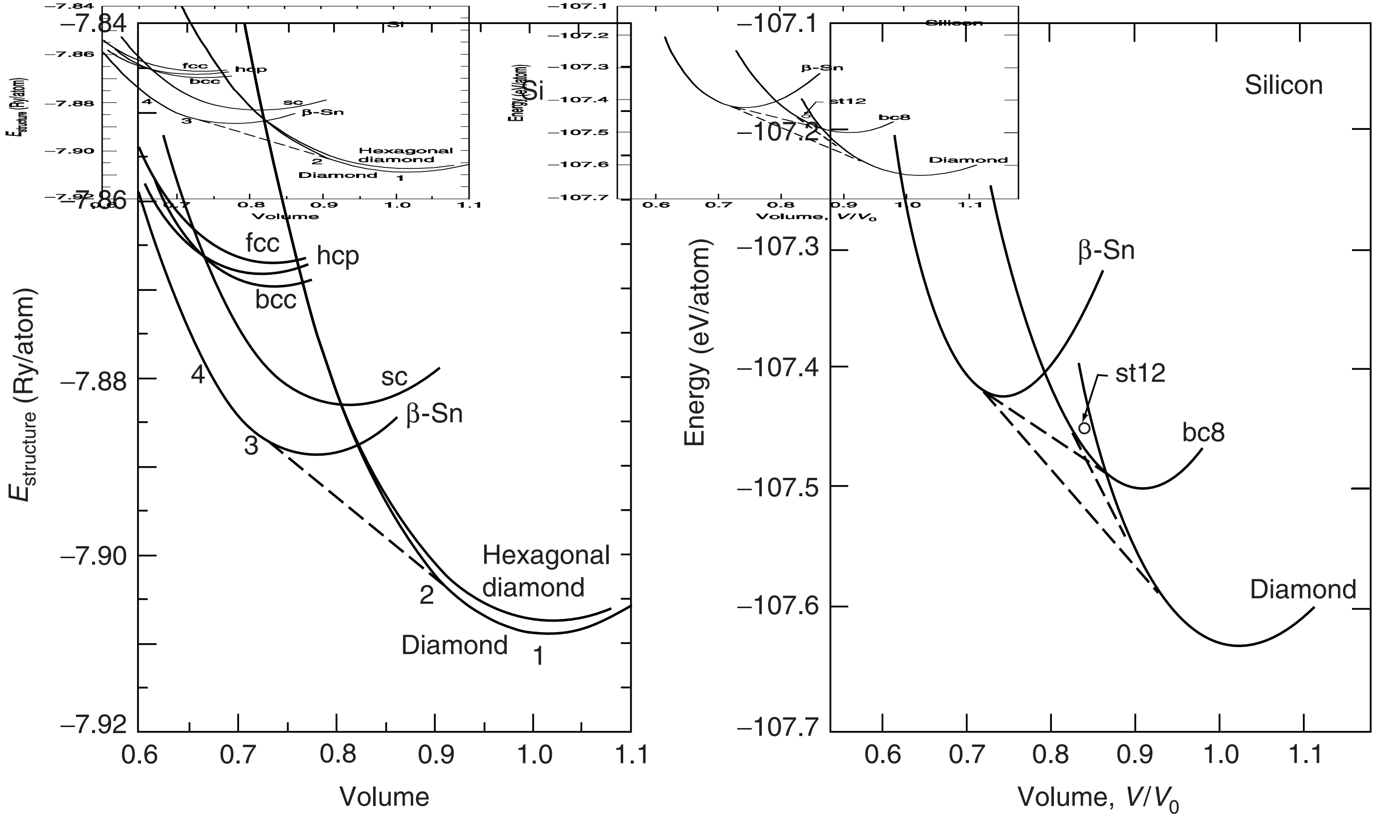
- **A new paradigm for the many-body problem:**
  - Choose only certain properties to calculate
  - Find approximate functionals for those properties
- **Practical points for our purposes:**
  - Approximate functionals are very accurate in large classes of problems
  - The only way at present for calculation 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



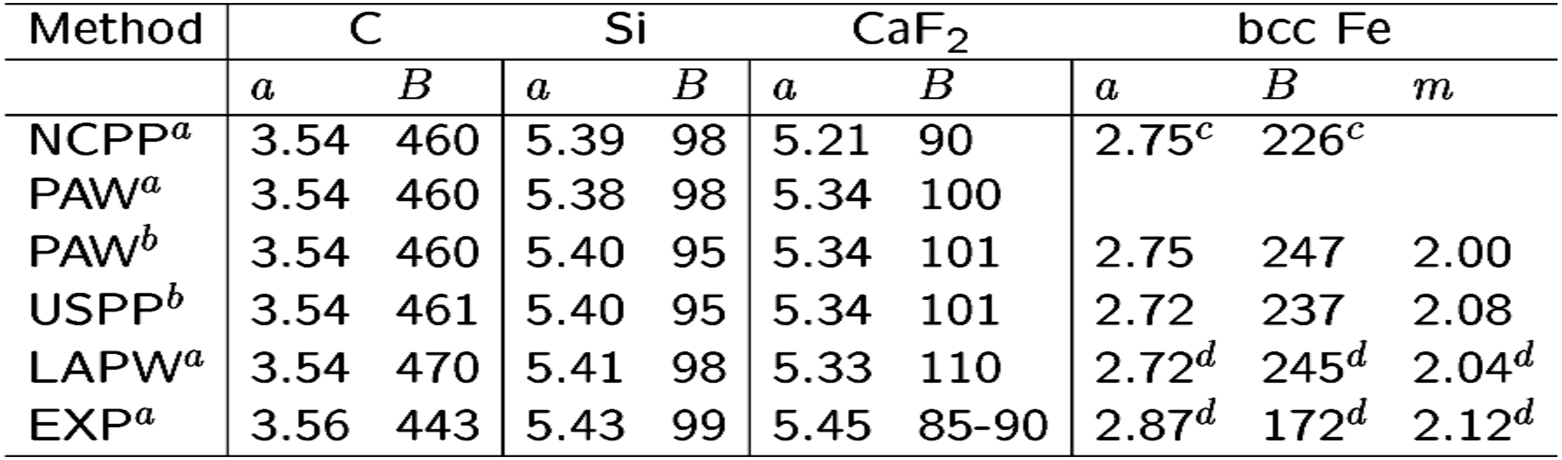
Modern codes (ABINIT, VASP, ESPRESSO, Wein LAPW, FPLO, . . .) easily reproduce similar curves.

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)



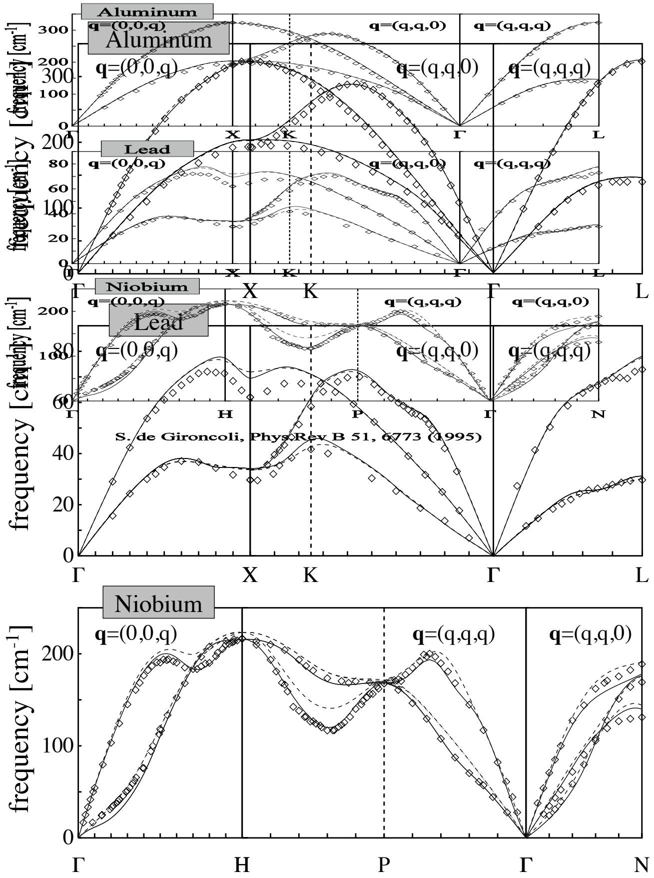
Method	C		Si		CaF_2		bcc Fe		
	a	B	a	B	a	B	a	B	m
NCPP[a]	3.54	460	5.39	98	5.21	90	2.75[c]	226[c]	
PAW[a]	3.54	460	5.38	98	5.34	100			
PAW[b]	3.54	460	5.40	95	5.34	101	2.75	247	2.00
USPP[b]	3.54	461	5.40	95	5.34	101	2.72	237	2.08
LAPW[a]	3.54	470	5.41	98	5.33	110	2.72[d]	245[d]	2.04[d]
EXP[a]	3.56	443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

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

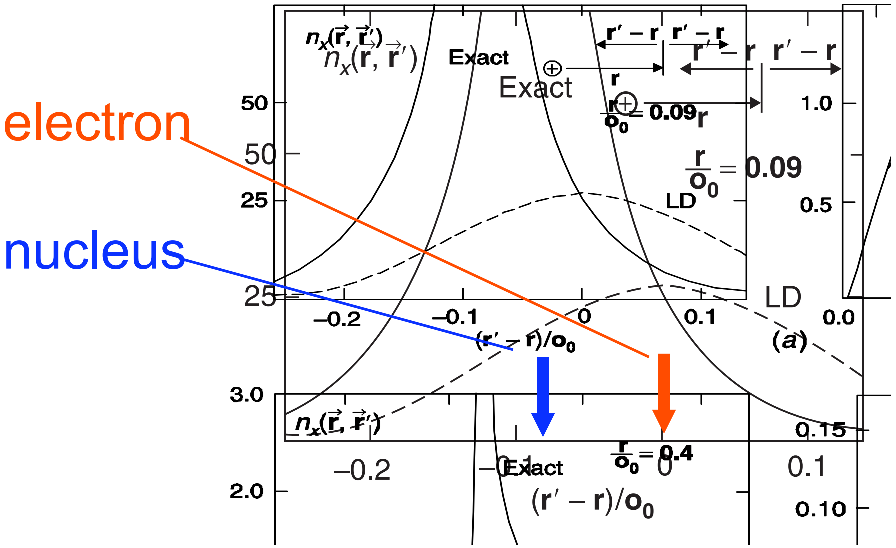
Exchange and Correlation in an atom

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.)

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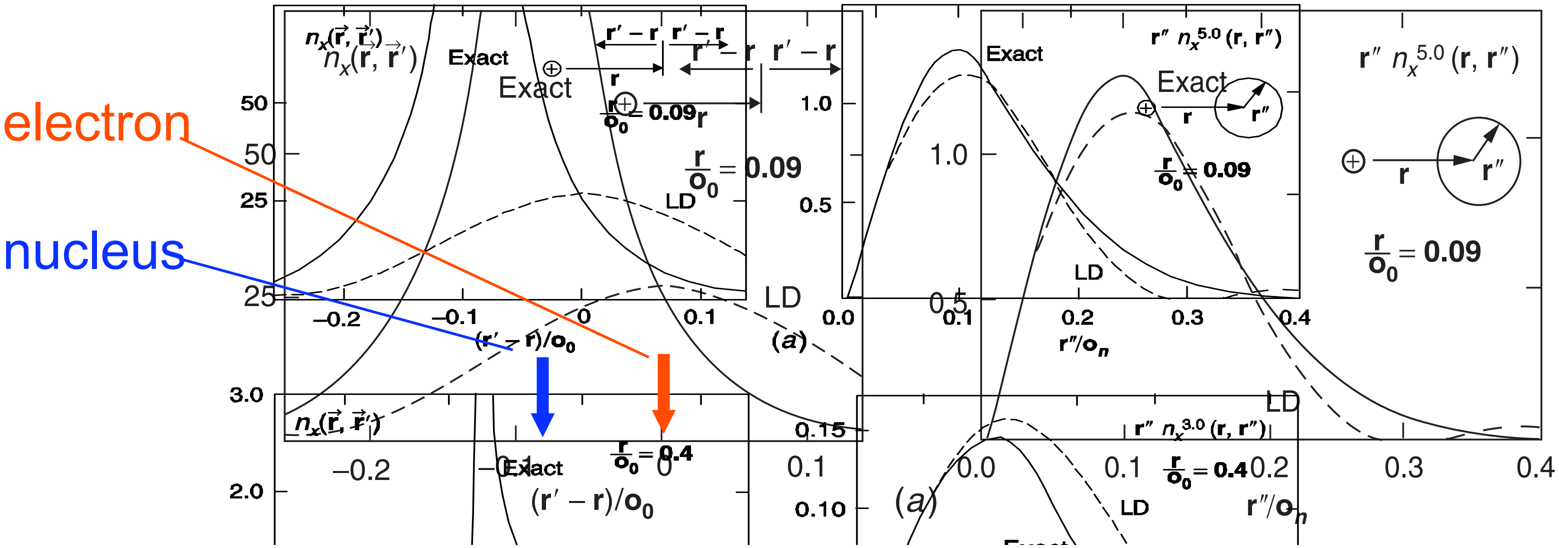


Exchange hole in Ne atom

Spherical average

electron

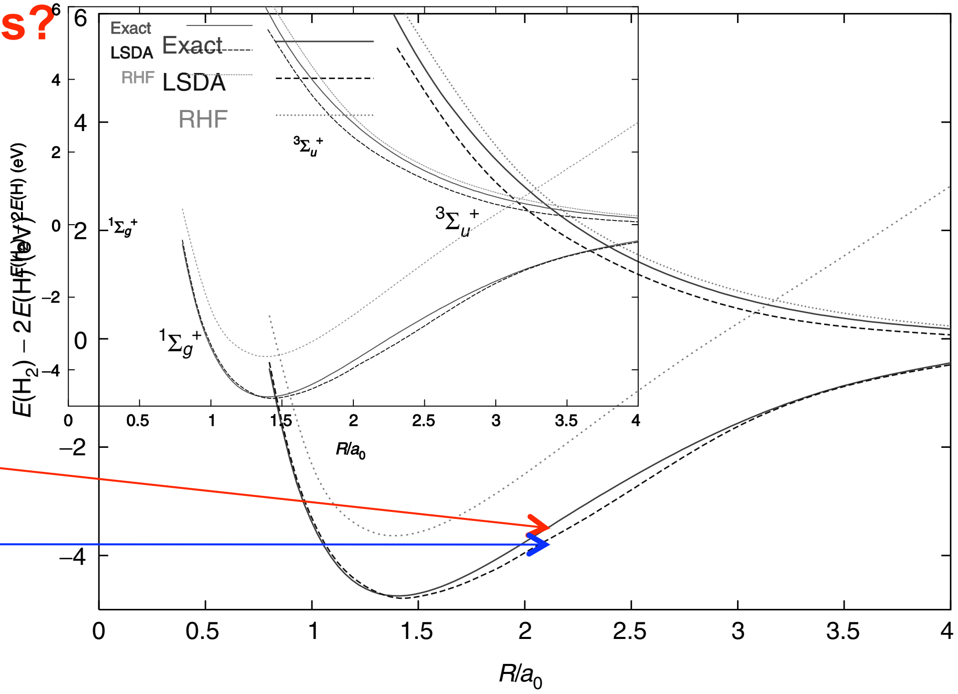
nucleus

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?**



Exact

Local density Approx.

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”

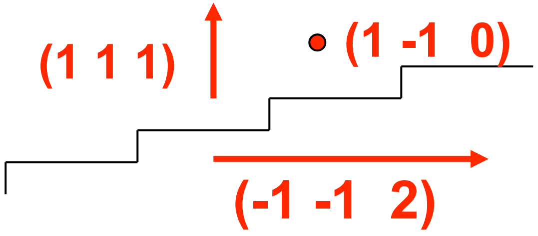
A few examples and cases that show the need to go beyond the widely-used DFT methods

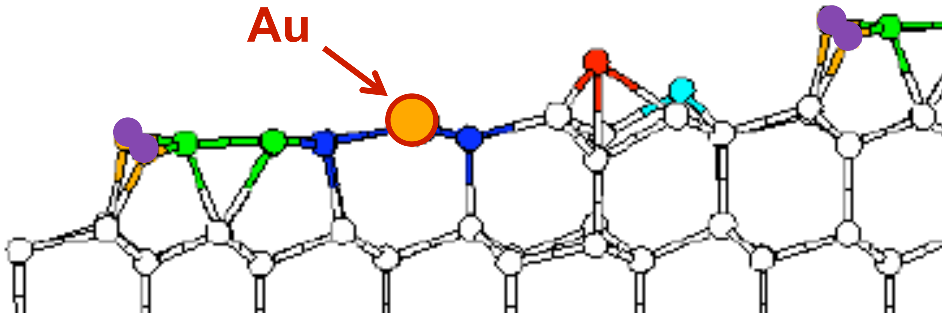
Atomic Scale Gold Wires on Silicon Surfaces

”self-assembled” on “vicinal” 557 surface at angle to 111

STM image of self-assembled atomic “wires

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)

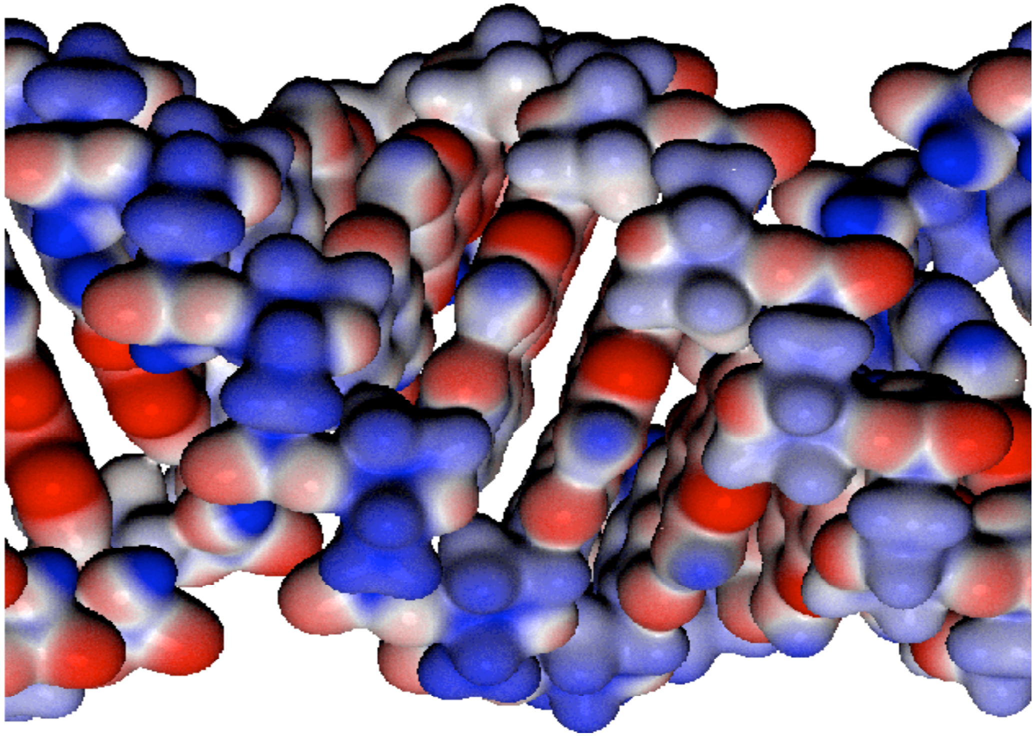
For the bands of the wires see my next talk

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

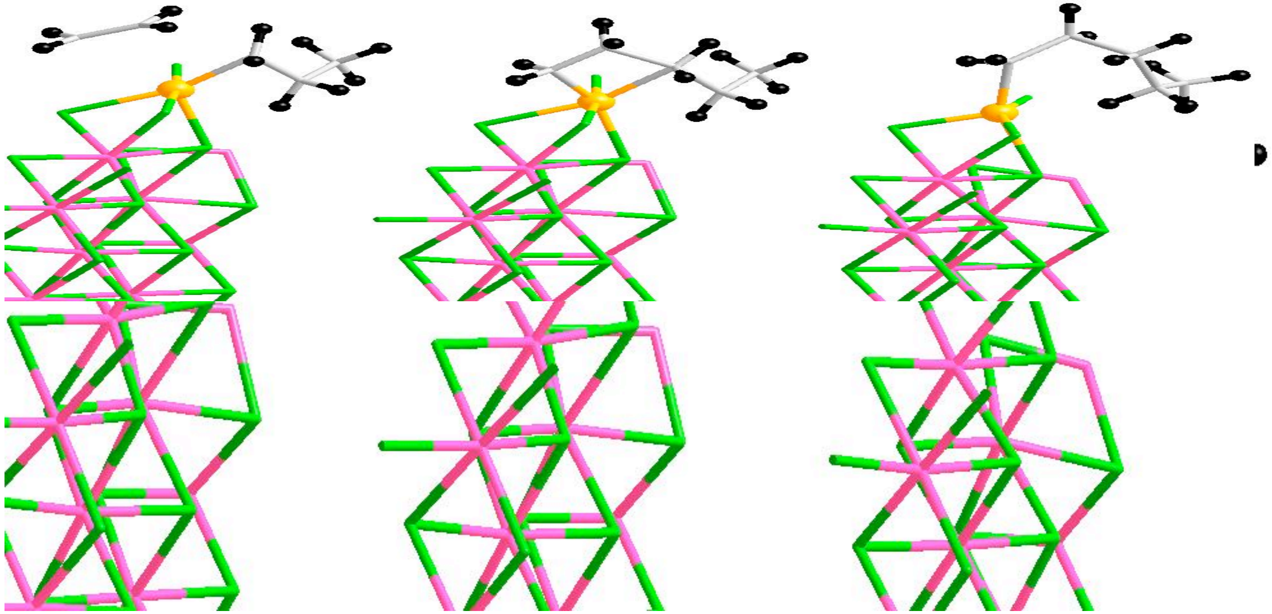


Iso-potential surfaces

Done using SIESTA (tutorial Wednesday by Ordejon, Torres)

Simulation of Catalysis for Polymerization

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



π-complex – Transition – insertion

Adds one ethylene unit to polymer

Failures of present density functional approximations in important classes of problems

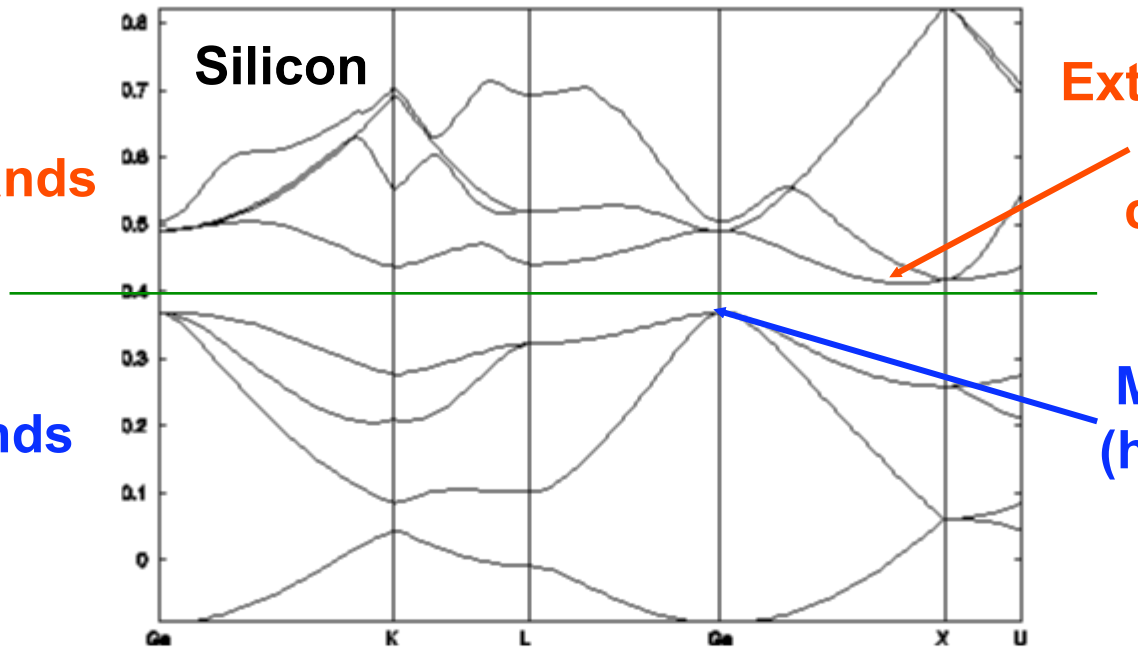
- **Electronic excitations**
  - The “band gap problem”
  - . . .
- **Strongly interacting systems**
  - Magnetic insulators, metal-insulator transitions, . . .
  - . . .
- **Example of “Failure” that has been solved!**
  - Weak Van der Waals bonds
  - Development of non-local functional has the right 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



Empty Bands

Gap

Filled Bands

Extra added electrons go in bottom of conduction band

Missing electrons (holes) go in top of valence band

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

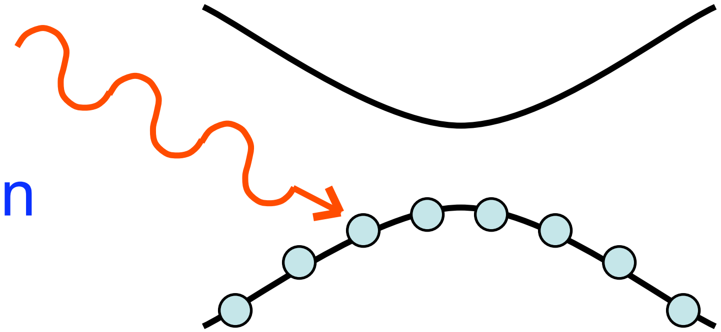
Electron Excitations

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

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The real problem approached using Many-Body Methods

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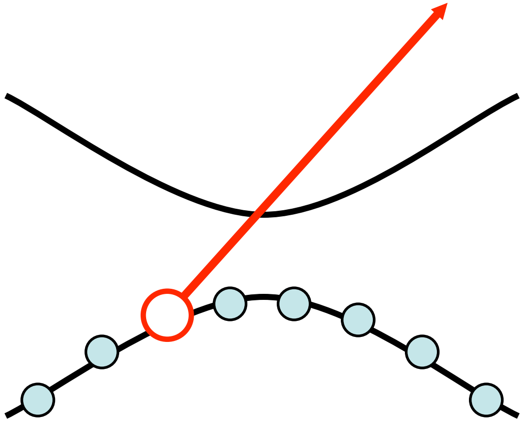


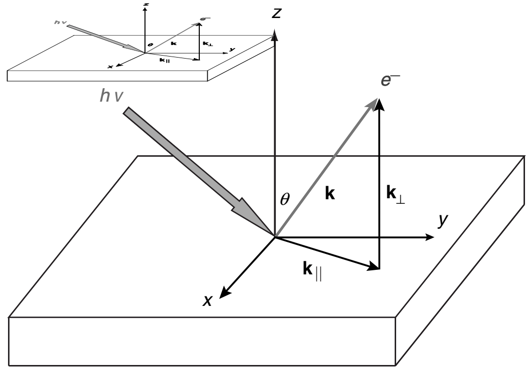
Most actual practical approaches use DFT as the starting point
LDA, GGAs, hybrids, LDA+U, . . .

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

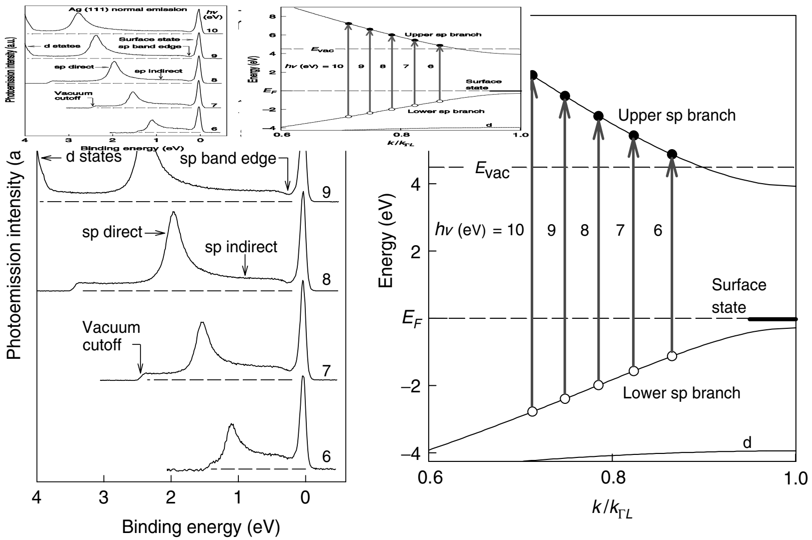
Example of Germanium

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

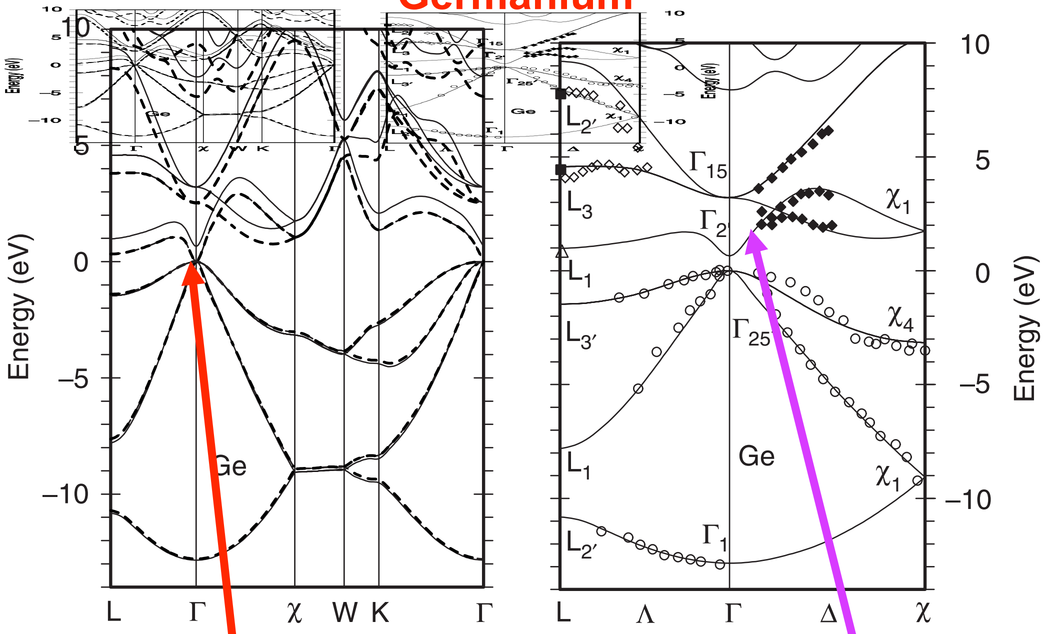
The Band-Gap Problem
Comparison of theory (lines) and experiment (points)



Silver



Germanium



A metal in “LDA” calculations!

Improved many-Body Calculations

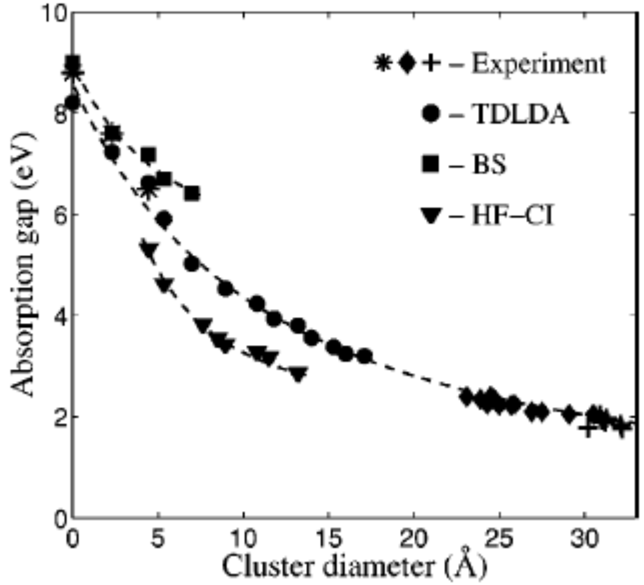
What about nanosystems?

Crucial roles of electronic excited states

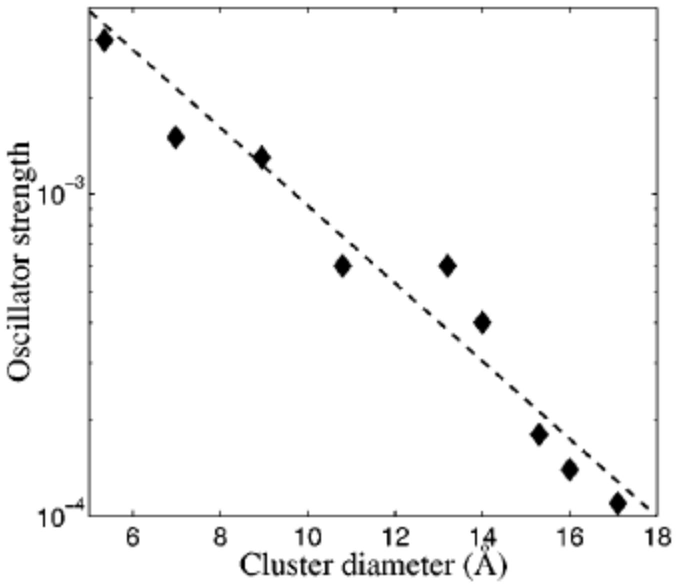
Gaps in clusters

What about nanosystems? - Silicon clusters

IGOR VASILIEV, SERDAR ÖĞÜT, AND JAMES R. CHELIKOWSKY PHYSICAL REVIEW B **65** 115416



Gaps much larger than the bulk



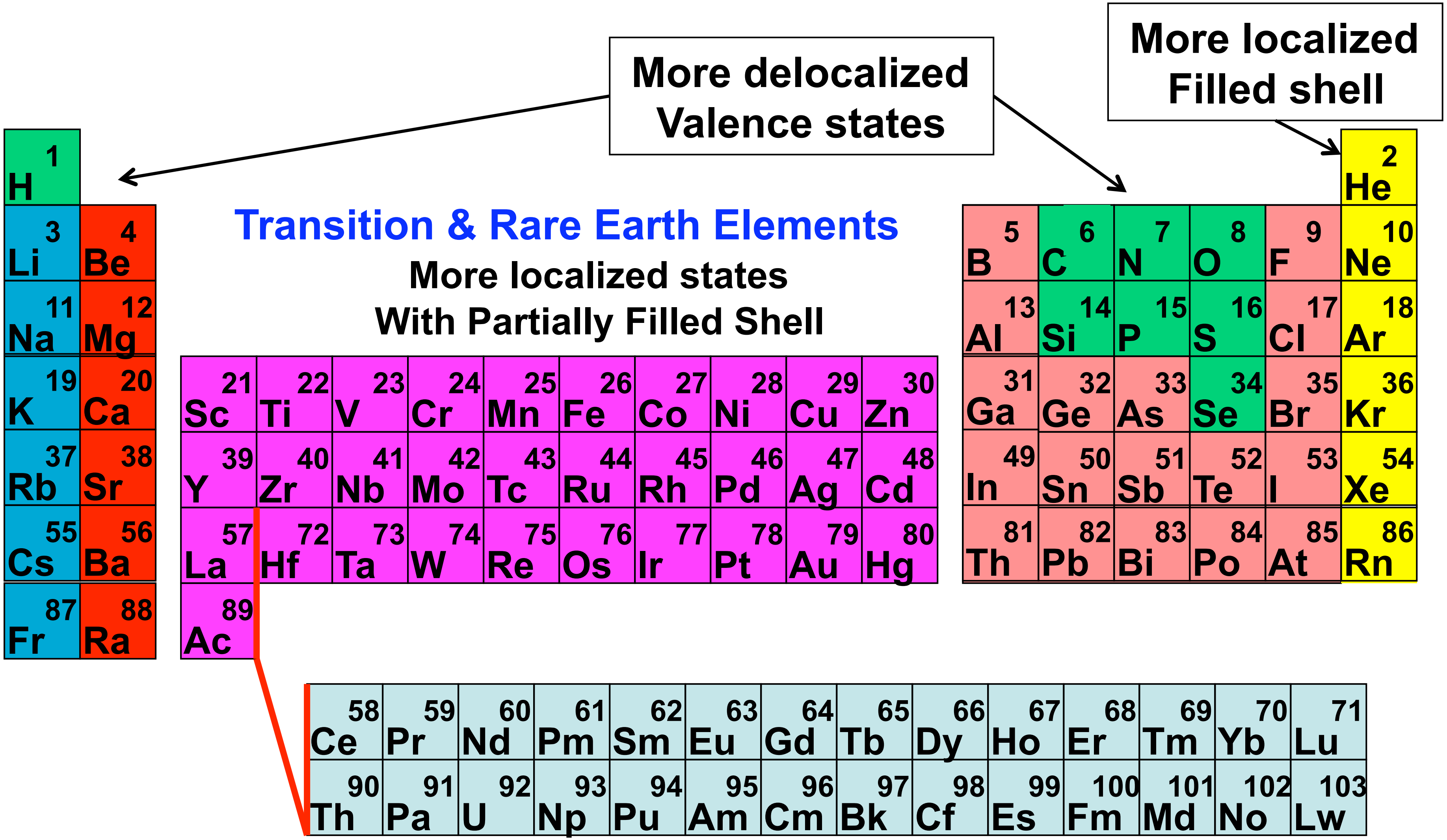
Decrease in oscillator strength shows approach to the bulk

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



More delocalized
Valence states

More localized
Filled shell

Transition & Rare Earth Elements

More localized states
With Partially Filled Shell

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Th	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw

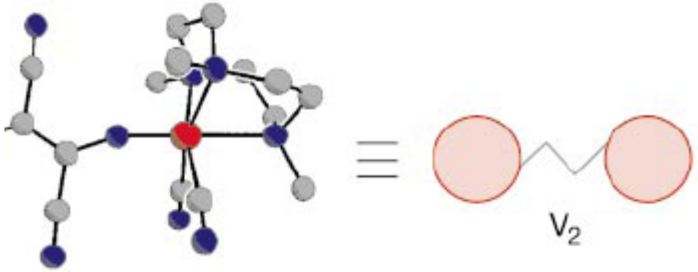
Magnetism - “Strongly Correlated” States in Solids

What about nanosystems?

Example of important effects of correlation

Kondo resonance in a single-molecule transistor

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



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Effect vanishes above ~10K.

Note the molecule contains Vanadium

Energies for electrons to move through molecule?
Coulomb Blockade?
Kondo Effect?
Screening by metal leads?
. . .

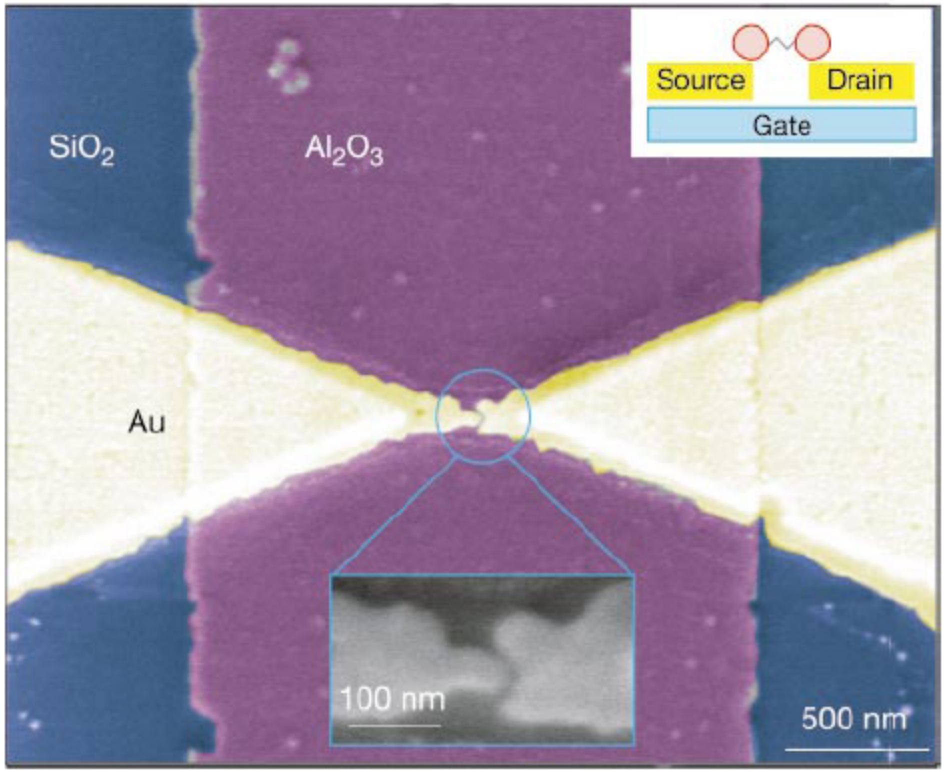

Figure 1 Fabrication of single-molecule transistors incorporating individual divanadium molecules. Top left, the structure of [(*N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane)$_2$V$_2$(CN)$_4$(μ-C$_4$N$_4$)] (the V_2 molecule) as determined by X-ray crystallography; red, grey and blue spheres represent 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