Quantum Mechanical Modeling of Advanced Materials

Biplab Sanyal
Dept. of Physics and Materials Science
UPP MAX
Uppsala University, Sweden
Plan of the talk

• Introduction
• Theoretical methods
• Applications
  (i) Molecule-substrate interaction for molecular electronics
  (ii) Diluted magnetic semiconductor for semiconductor spintronics
• Summary
### Periodic Table - The World of Materials

#### Design of Advanced Materials with Novel Properties

![Periodic Table Image](Periodic_Table_The_World_of_Materials.png)

**Lanthanide Series**
- Ce
- Pr
- Nd
- Pm
- Sm
- Eu
- Gd
- Tb
- Dy
- Ho
- Er
- Tm
- Yb
- Lu

**Actinide Series**
- Th
- Pa
- U
- Np
- Pu
- Am
- Cm
- Bk
- Cf
- Es
- Fm
- Md
- No
- Lr

---

Young Investigators Symposium, ORNL 3
Quantum mechanical modeling
(analysis and prediction)

Materials properties from ground state energy
Density Functional Theory (Walter Kohn, Noble Prize, 1998)

Total energy is a functional of density of electrons, $E[n]$
Explicit dependence of wavefunction avoided

$$\left\{-\frac{1}{2}\nabla^2 + V_{\text{eff}}[n(r)]\right\} \psi_i(r) = \epsilon_i \psi_i(r)$$

$$V_{\text{eff}}[n(r)] = V_{\text{ext}} + \int \frac{2n(r')}{|r - r'|} dr' + \frac{\delta(n(r)\mathcal{E}_{xc}[n(r)])}{\delta n(r)}.$$ 

$$\mathcal{E}[n(r)] = \int V_{\text{ext}}(r)n(r) dr + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r - r'|} dr dr' + \mathcal{T}_s[n(r)] + \mathcal{E}_{xc}[n(r)]$$
1. Plane wave Projector Augmented Wave calculations (VASP): structural relaxations, clusters, total energy calculations of supercells (ordered system)

2. (a) Korringa-Kohn-Rostoker-Coherent Potential Approximation (KKR-CPA) calculations: disorder averaging, calculation of Heisenberg pair-exchange parameters using methodology of Liechtenstein et al.

\[ H = -\sum_{i \neq j} J_{ij} \vec{e}_i \cdot \vec{e}_j \]

- \( J_{ij} > 0 \) (ferromagnetic)
- \( J_{ij} < 0 \) (antiferromagnetic)

(b) Monte-Carlo simulations including disordered spins: magnetic percolation due to disorder

Metropolis algorithm

Determination of Curie temperature by the cumulant-crossing method
Nano-bio-technological applications

- Optical switches
- Information storage
- Molecular electronics
- Spin crossover by thermal, optical and pressure effects

A. Taton, Nat. Mater.
Magneto-optic biosensor for fast detection of Malaria

normal blood

infected blood

S=1 spin state

Haemoglobin,S=5/2

Electronic structure calculations:
Correct geometric and electronic structure, spin state
Molecule-substrate interaction (molecular electronics)

FeP on Cobalt substrate

X-ray Magnetic Circular Dichroism

Fe - Co coupling is ferromagnetic
FeP/Co(001) : 3 Co layers (184 atoms in the unit cell)

Fe↑- Co↑ configuration is stable

Tuning the coupling

FeP/O/Co

Experiment: Antiferromagnetic coupling

Theory: Antiferromagnetic coupling from total energies
180° superexchange through Fe-O-Co network
(Goodenough-Kanamori rule)

Magnetization density demonstrates this.
Semiconductor spintronics
Diluted magnetic semiconductors (DMS)

Magnetic elements (Cr, Mn, Fe, Co) doped in semiconductors

- Simultaneous properties of semiconductors and ferromagnets
- III-V DMS (Mn doped GaAs), II-VI DMS (Co doped ZnO)
- Manipulation of charge carriers by doping, electric field etc.
- Defects are obstacles
- Growth condition is crucial (often inhomogeneous distribution of dopants as well as formation of secondary phases)

Complexities in DMS materials

- How do spins interact?
- How do defects control the properties?
- How can we increase the ordering temperatures ($T_C$)?
- How do the electron-electron correlations affect the electronic and magnetic properties?
Electronic structure and magnetic interaction

- Electronic structure and magnetic interaction are material-specific
- Correctly captured by ab-initio simulations
Magnetic percolation & inhomogeneity (Monte-Carlo Simulations)

Half-Heusler alloy (Mn doped NiTiSn)

No ferromagnetic long range order below 3 %
(magnetic percolation threshold)
Room temperature ferromagnetism at 22 % Mn doping

Time evolution of growth

Simulation of desired nanostructures

Simulations for 3D bulk
CoZnO: microscopic picture

Chemical and magnetic structure

Probability of cluster formation
Inhomogeneties & Magnetism
Co doped ZnO

Young Investigators Symposium, ORNL
Summary

• Quantum mechanical modeling of materials is very important for the understanding of properties in an atomic scale.
• Fe-porphyrin molecule couples ferromagnetically with Co substrate. The coupling mechanism is indirect exchange. One can turn the ferromagnetic coupling to an antiferromagnetic one in presence of oxygen. Theory explains experimental findings.
• Magnetic percolation effects are crucial for establishing long ranged magnetic order in diluted magnetic semiconductors due to short-ranged exchange interactions and chemical disorder. Theory explains the wide variation of ordering temperatures observed in different experiments.

Thanks to:
Coworkers: D. Iusan, P. Panchmatia, O. Eriksson
Funding bodies: Swedish Research Council, STINT, SIDA, Göran Gustafssons Stiftelse
Computation: Swedish National Supercomputing facility (SNIC)