Doping of Nanostructures

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Doping of Nanocrystals

- Introduction
- Computational Methods
- Doping Si nanocrystals with P
- Doping of InP nanowires with Zn
- Doping Semiconductor crystals with Mn
- Conclusions

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Donor ionization energy, $E_d$, is roughly $50$ meV, which is comparable to $kT=25$ meV.

\[ E_d = I_{(extrinsic)} - A_{(intrinsic)} \]

What happens for nanocrystals?
Computational Methods

- Two key ingredients:
  - Pseudopotentials theory
    - Focus on chemically active electronic (valence) states
    - Capture the physical content of the periodic table
  - Density functional theory
    - Map all electron problem to one electron problem:

\[
\begin{bmatrix}
\frac{-\hbar^2 \nabla^2}{2m} + V_T \left[ \rho(r), r \right]
\end{bmatrix} \Psi_n (r) = E_n \Psi_n (r)
\]

\[
V_T = V_{ion}^p + V_H + V_{xc}
\]

\[
\rho(r) = \sum_{n, \text{occup}} |\Psi_n|^2
\]

Pseudopotential model:
“Standard Model”

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Real Space Methods

System of interest (quantum dot)

No supercells: One can readily handle charged systems.
No plane waves: Avoid Fourier transforms of the vacuum.

FLEXIBLE BOUNDARY CONDITIONS.

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Real-space Finite Difference Methods

- Use High-Order Finite Difference Methods [Fornberg & Sloan '94]
- Typical Geometry = Cube – regular structure.
- Laplacian matrix need not even be stored.

Order 4 Finite Difference Approximation:

\[
\left. \frac{\partial^2 \Psi}{\partial x^2} \right|_{x=x_0} = \frac{1}{h^2} \sum_{m=-M}^{m=M} C_m \Psi(x_0 + mh)
\]
Chebyshev Subspace Iteration

Main ingredient: Chebyshev filtering. Given a set of basis vectors filter the basis.

\[ \hat{\psi}_i = P_k(H)\psi_i \]
Iterate to Generate a Self-Consistent Potential

Select initial $V = V_{at}$

Get initial basis $\{\psi_i\}$ (diag)

Calculate new $\rho(r) = \sum_i \rho^{occ}_i |\psi_i|^2$

Find new $V_H$: $-\nabla^2 V_H = 4\pi \rho(r)$

Find new $V_{xc} = f[\rho(r)]$

$V_{new} = V_{ion} + V_H + V_{xc} + \text{‘Mixing’}$

If $|V_{new} - V| < tol$ stop

Filter basis $\{\psi_i\}$ (with $H_{new}$)+orth.

Most of the time is now spent on filtering! Much faster and requires fewer orthogonalization operations than does a full diagonalization.

This method is about an order of magnitude faster than previous ones.
This software is free!

Pseudopotential Algorithm for Real-space Electronic Calculations

http://www.ices.utexas.edu/parsec/
Synthesis of P-doped Si nano clusters

Hyperfine Splitting can be calculated from a knowledge of the wave function at the nucleus:

\[ H = \mu_b g_e B_a \cdot S + A S \cdot I \]

\[ A = \frac{8\pi}{3} g_e g_n \mu_b \mu_n |\psi_e(0)|^2 \]


Model the system with hydrogenated nanocrystals of silicon.
Comparison to Experiment

P assumed to be located in the center of the nanocrystal.

Structural relaxation included for all but the largest.

Expect site energy for smaller nanocrystals may not be at the center of the nanocrystal.
The binding energy is approaching that of shallow donor, but even for nanocrystals at 5 nm the level is not “shallow.”

Lowest unoccupied state
Defect state $E_D$

Highest doubly occupied state $E_{HDO}$
Theoretical Models for Doping Nanowires
(passivate surfaces with fictitious H atoms)
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Bulk Crystal

Nanowire Acceptor States

Nanowire Bulk-like state

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Acceptor state binding energy as a function of impurity separation and the diameter of the wire.

Up triangles are the singly degenerate states. Down triangles are the doubly degenerate states.
Doping with Magnetic Impurities: Spintronics Materials by materials issues

- Efficient spin injection into a semiconductor
- Compatibility with semiconductor technology

A promising route: Dilute magnetic semiconductors

e.g.,
\begin{align*}
Mn_xGa_{1-x}As \\
Mn_xGa_{1-x}N \\
Mn_xGe_{1-x}
\end{align*}

magnetic

dilute magnetic

non-magnetic

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Comparing Mn:Ge, Mn:GaAs and Mn:ZnSe at THE NANO SCALE

• Well-known semiconductors
• Bulk Mn:GaAs and Mn:Ge half-metallic
• Mn:ZnSe nanocrystals successfully synthesized (D. Norris)
• Hardly any theory (notable exception: N. Spaldin, UCSB)
• Same crystalline structure, periodic table row
Mn:Ge Nano-Crystals

- Spherical fragments of bulk material
- Size: 1~2 nm in diameter for Mn-doped dots
- Mn substitutional site takes the cation sites (Ga, Zn)
- Surface passivation: fictitious hydrogens for GaAs and ZnSe; hydrogen for Ge

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Electronic Structure and Magnetic Moments

<table>
<thead>
<tr>
<th>Ge</th>
<th>GaAs</th>
<th>ZnSe</th>
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- Half metallic nature for Mn:Ge and Mn:GaAs
- Semiconducting nature for Mn:ZnSe
- Deep impurity levels (localized states) for nanocrystals in this size regime

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Spin-Spin Interaction:
Two Mn Atoms in a Nanocrystal
Magnetic Interactions in Bulk Crystals

Holes will stabilize ferromagnetic configuration

Explains magnetic properties in the corresponding bulk:
- Mn:Ge - FM (2 holes per Mn)
- Mn:GaAs - FM (1 hole per Mn)
- Mn:ZnSe - AFM (no holes)
Magnetic coupling in Nanocrystals

Mn atoms are bridged through a Ge or anion

- Mn:Ge - FM
  - FM stable by 0.42 eV
- Mn:GaAs - FM
  - FM stable by 0.38 eV
- Mn:ZnSe - AFM
  - AFM stable by 0.14 eV

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Nitrogen dopant adds holes, which give rise to ferromagnetic coupling.

\[\text{Mn:ZnSe} - \text{AFM} \quad \text{AFM stable by 0.14 eV} \]

\[\text{(Mn,N):ZnSe} - \text{FM} \quad \text{FM stable by 0.20 eV} \]
Nature of the magnetic coupling can be changed by nanocrystal size.

Holes in “small” nanocrystals are not shallow.

“Double Exchange” (“GaN-like GaAs”) dominant mechanism, not Zener or free hole mechanism.

Changing the dot size changes the magnetic mechanism.
At the nanoscale it is easy for an impurity to diffuse to the surface.
Energetics of Adding Mn Impurity Atoms to CdSe Nanocrystals

Adding Mn impurities to CdSe nanocrystals becomes energetically unfavorable at small diameters. This implies that it is not only kinetically difficult to keep impurities in nanostructures; it is also thermodynamically difficult.

New Algorithms Make It Possible to Predict Doping Properties Across the Nano Regime

Nanocrystals
• P in Si and Magnetic dopants in Ge, GaAs, ZnSe and CdSe

Nanowires
• Zn in InP