Doping of Nanostructures

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2007 International Conference on the Frontiers of Characterization and Metrology for Nanoelectronics

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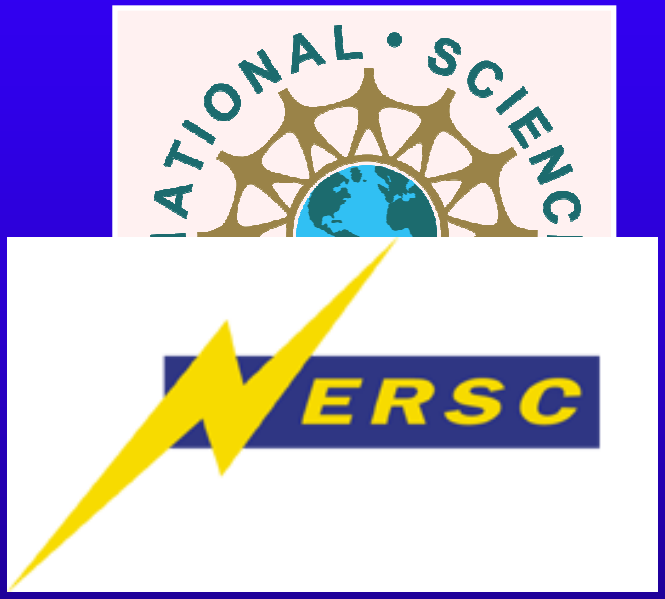

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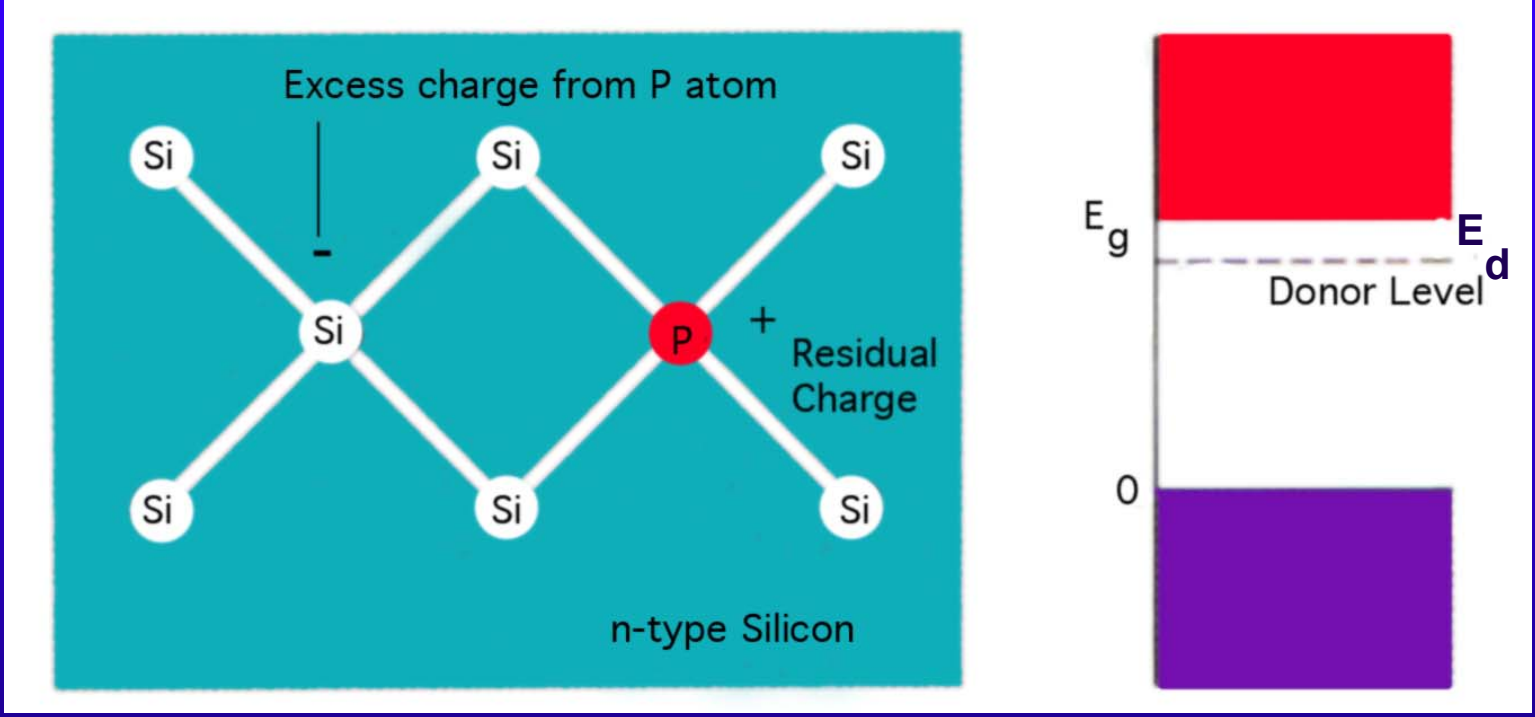
Doping of Nanocrystals

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

Doping Si with P atoms: Crystalline Limi



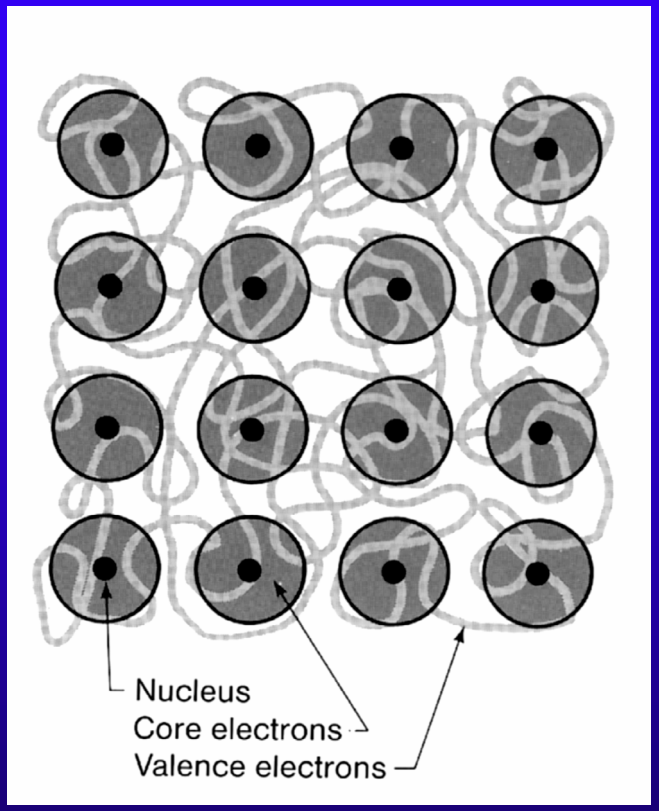
Donor ionization energy, E_d, is roughly 50 meV, which is comparable to kT≈25 meV.

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:



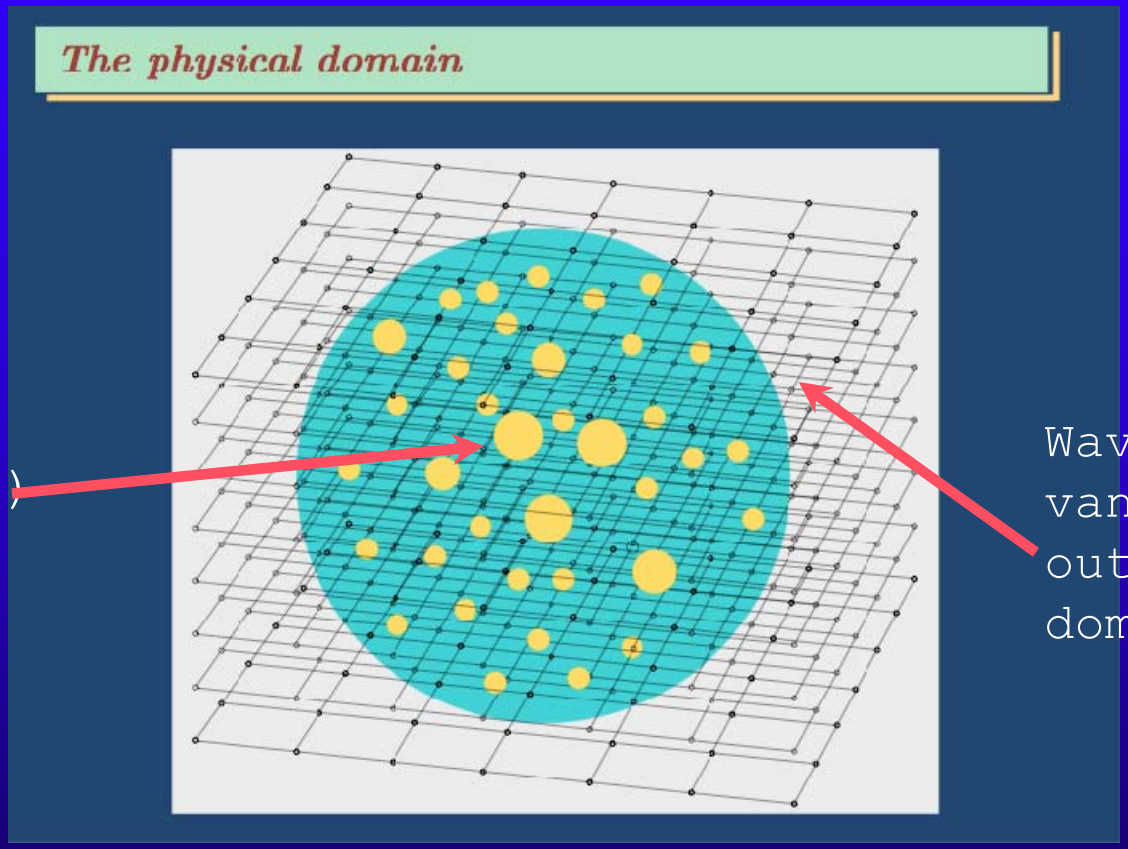
$$\left[\frac{-\hbar^2\nabla^2}{2m} + V_T\left[\rho(r), r\right]\right]\Psi_n(r) = E_n\Psi_n(r)$$

$$V_T = V_{ion}^{p} + V_H + V_{xc}$$

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

Pseudopotential model: "Standard Model"

Real Space Methods



System of interest (quantum dot)

Wave function vanishes outside the domain

No supercells: One can readily handle charged systems.

No plane waves: Avoid Fourier transforms of the vacuum.

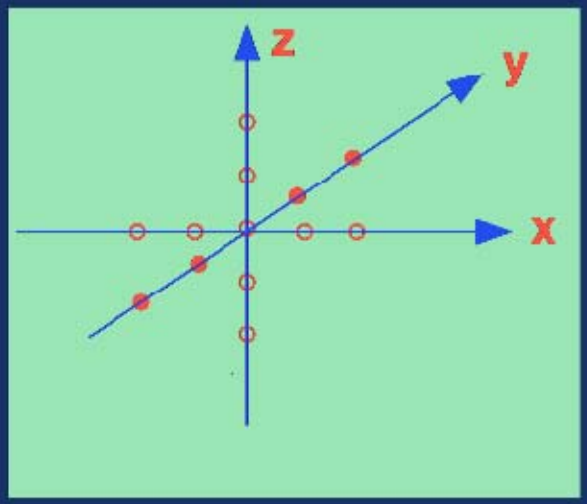
FLEXIBLE BOUNDARY CONDITIONS.

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:

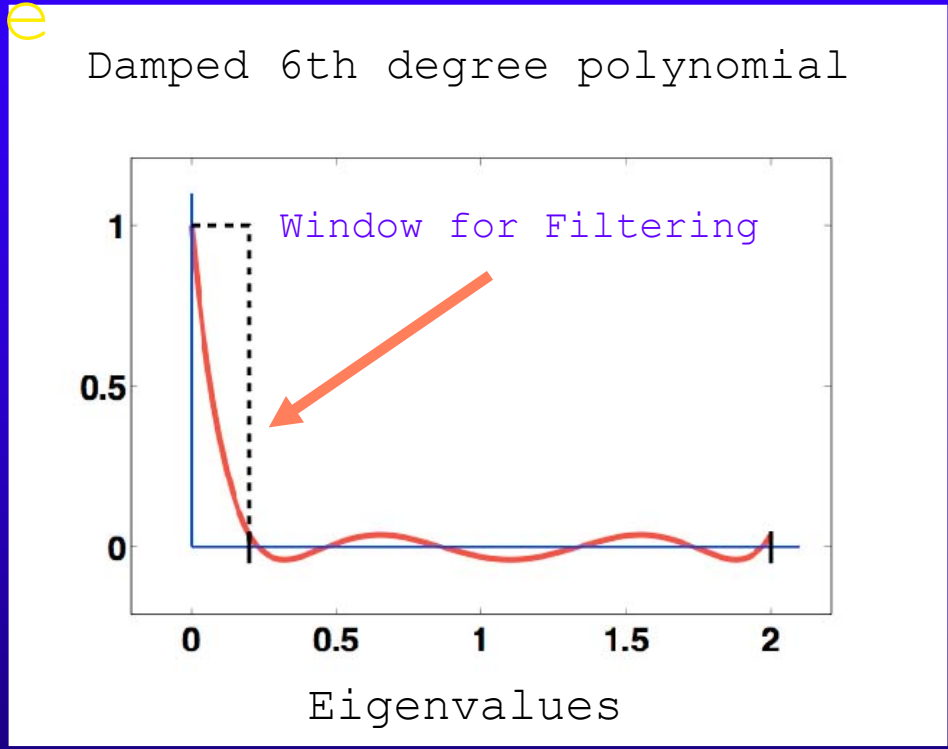
$$\left.\frac{\partial^2 \Psi}{\partial x^2}\right|_{x=x_0} = \frac{1}{h^2} \sum_{m=-M}^{m=M} C_m \Psi(x_0 + mh)$$



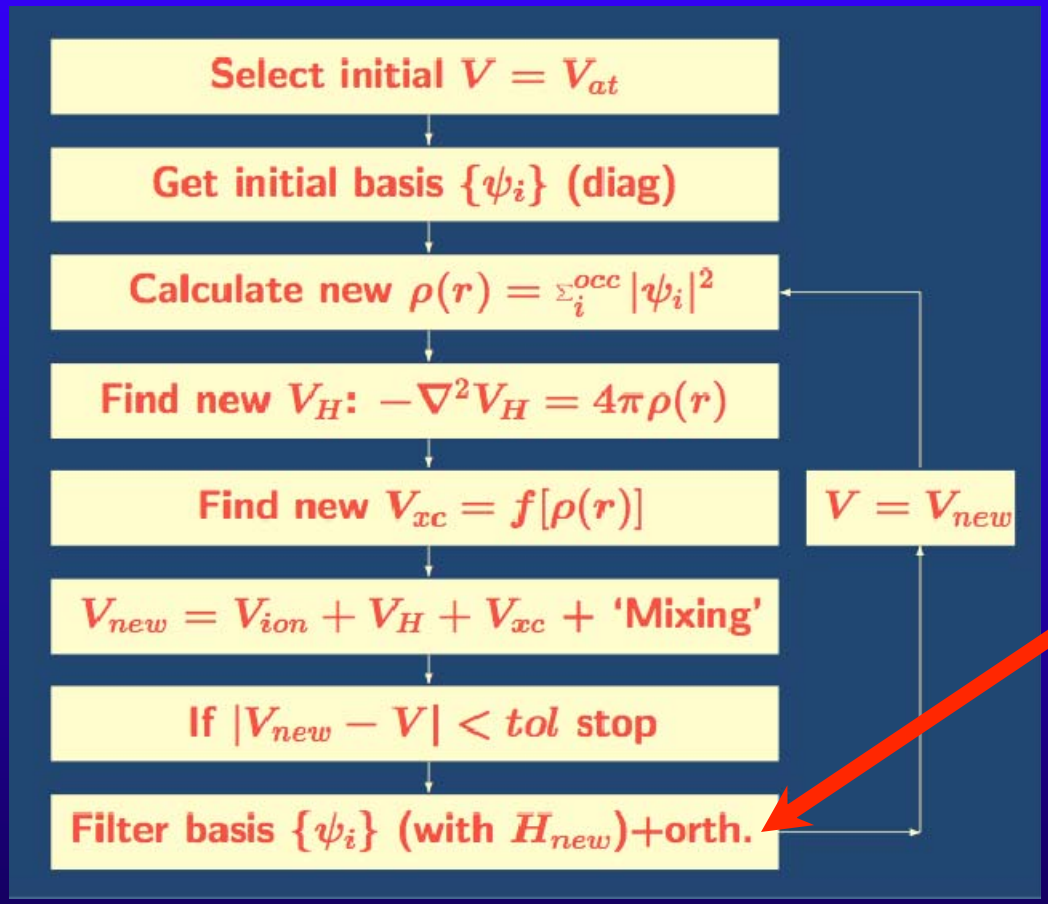
Chebyshev Subspace Iteration

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

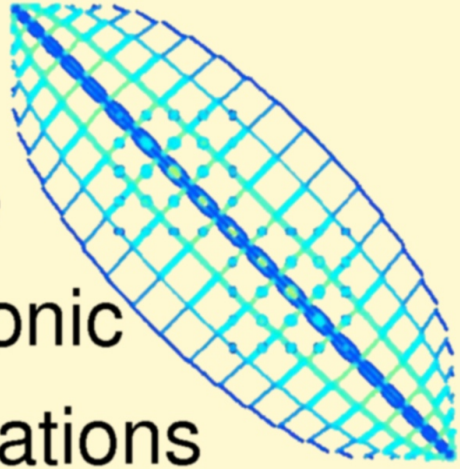


Most of the time is now spent on filtering! Much faster and requires fewer orthogonalization operations than does a full diagonalization.

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

PARSEC

Pseudopotential
Algorithm for
Real–
Space
Electronic
Calculations



This software is free!

http://www.ices.utexas.edu/parsec/

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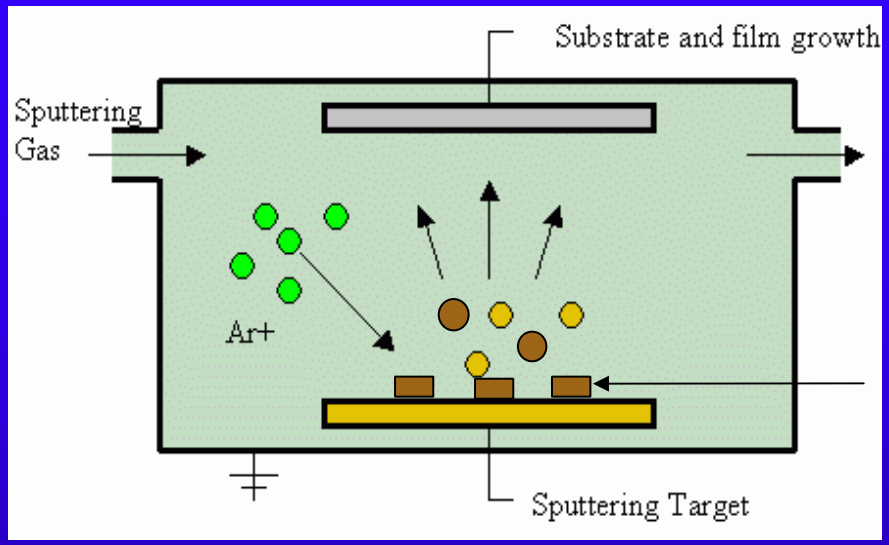
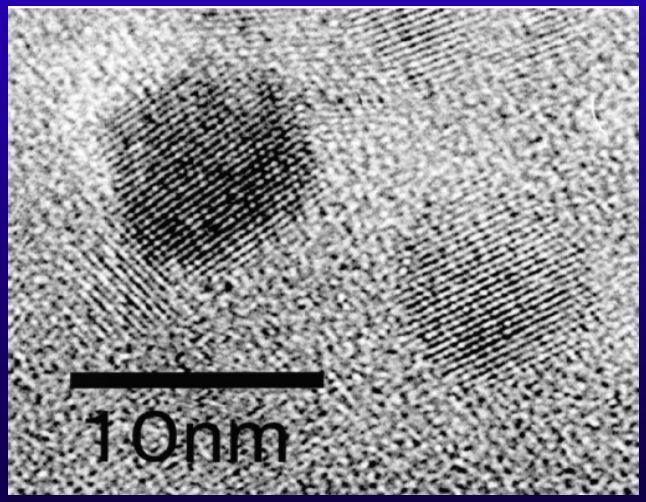
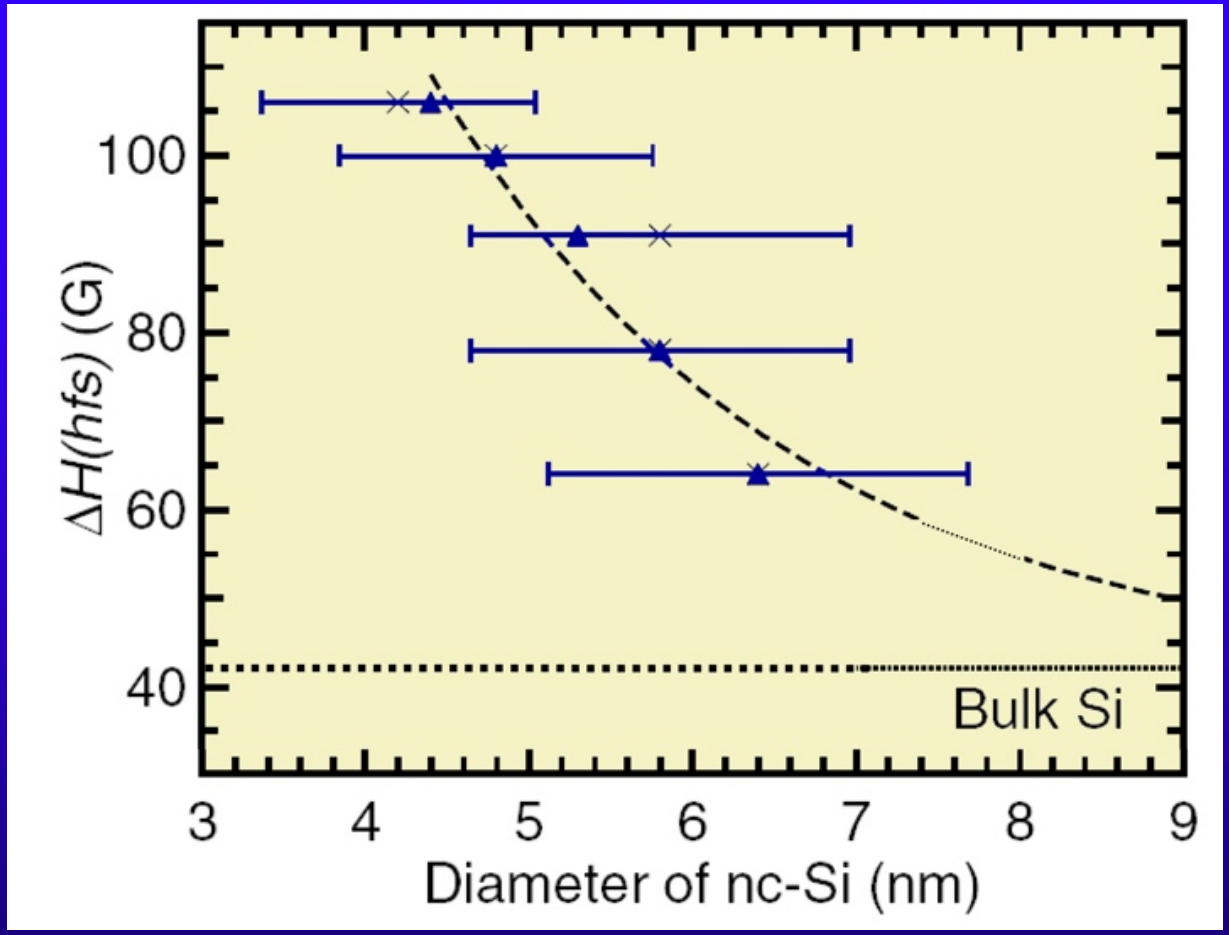
Synthesis of P-doped Si nano clusters





M. Fujii, K. Toshikiyi, Y. Takase, Y. Yamaguchi, S. Hayashi, J. Appl. Phys. 94, 1990 (2003)



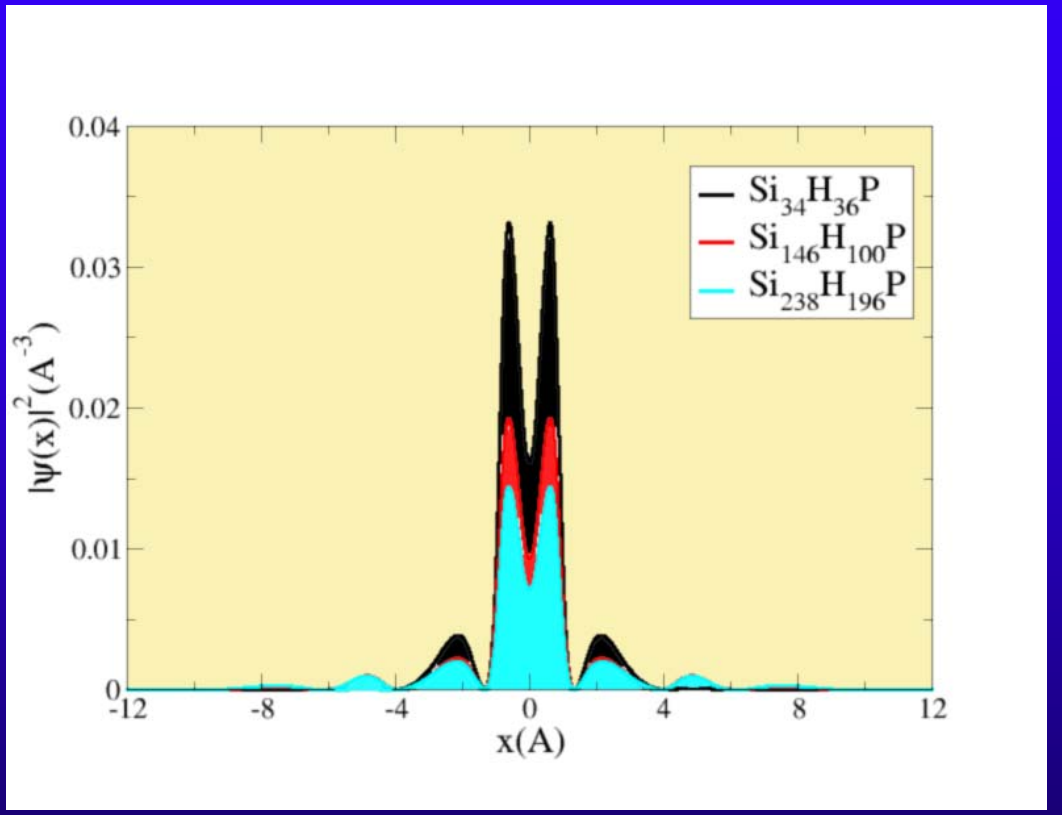
Size estimates from TEM and PL: M. Fujii, A. Mimura, S. Hayashi, Phys. Rev. Lett. 89, 206805(2002)

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

$$\mathrm{H} = \mu_b g_e B_a \cdot S + AS \cdot I$$

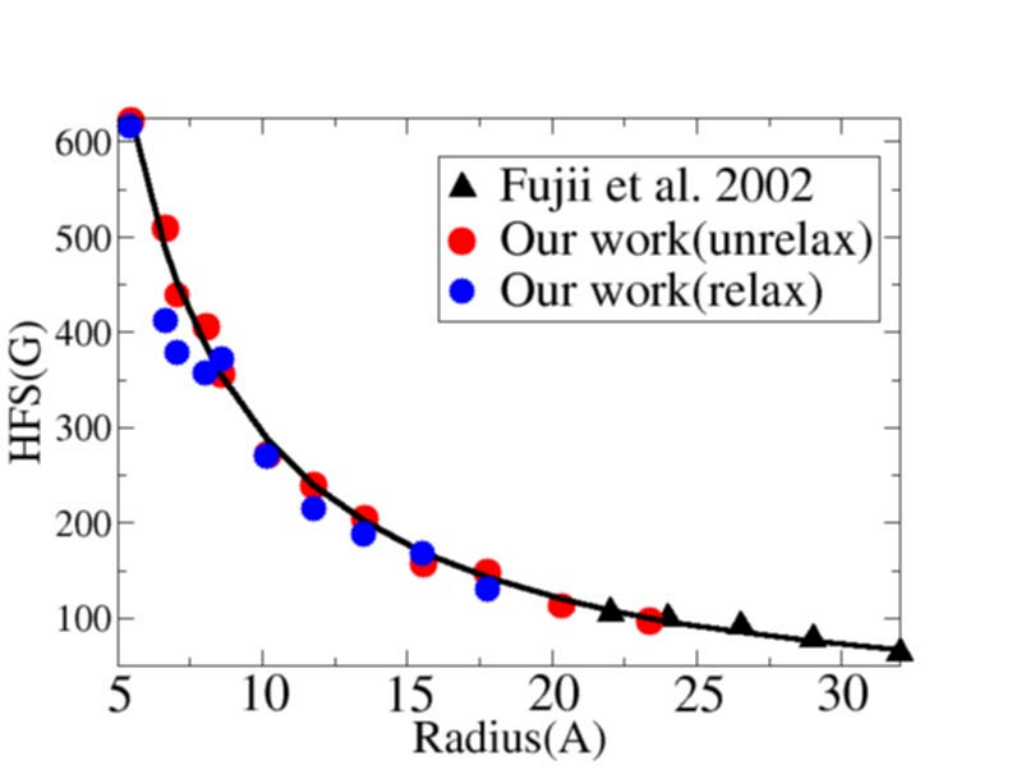
$$A = \frac{8\pi}{3} g_e g_n \mu_b \mu_n |\psi_e(0)|^2$$

C. Van de Walle and P. Blochl: Phys. Rev. B 47, 4244 (1993).



Model the system with hydrogenated nanocrystals of silicon

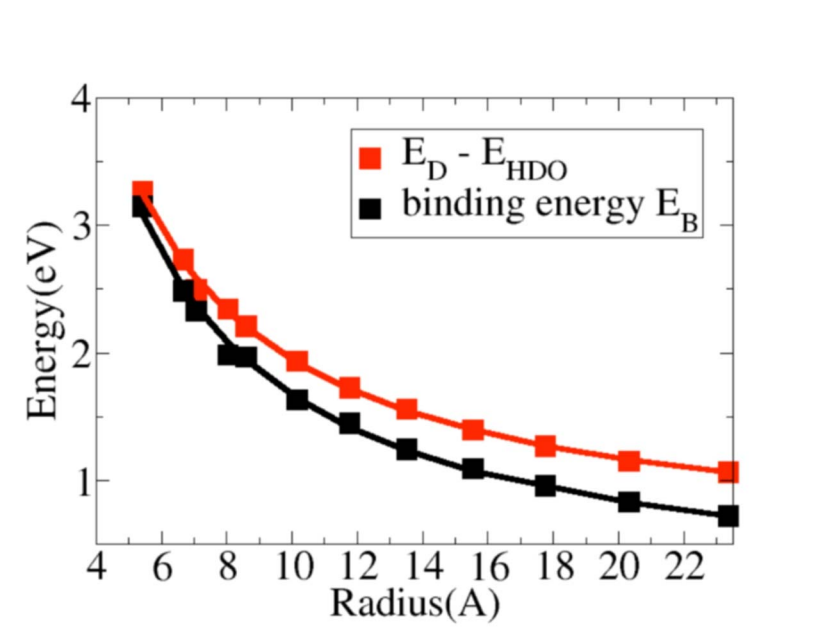
Comparison to Experiment



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.

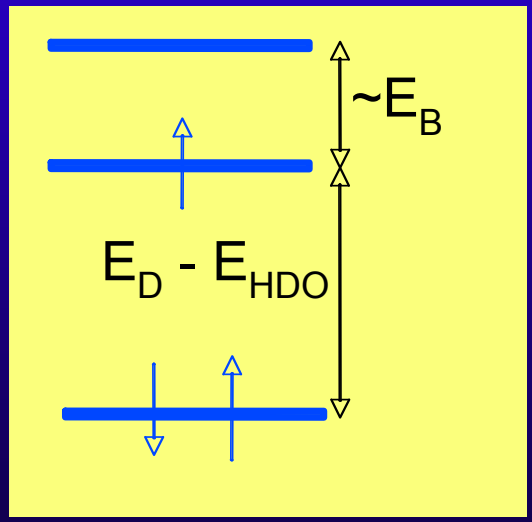


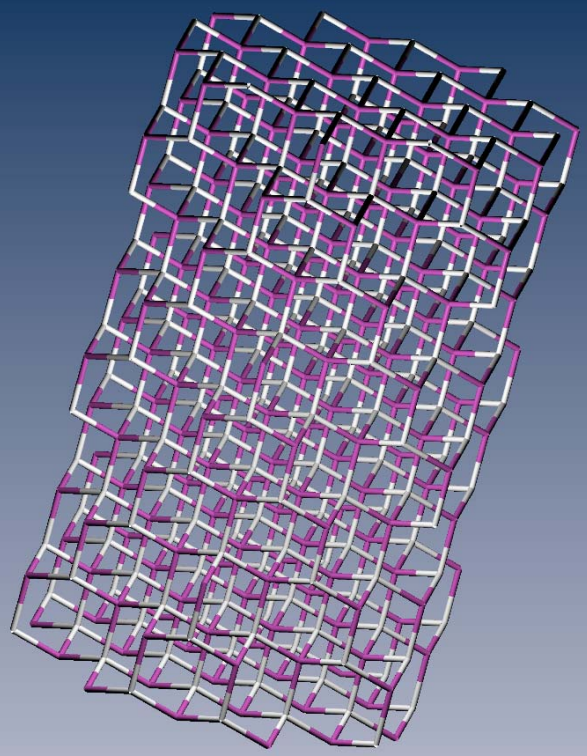
The binding energy is approaching that of shallow donor, but even for nanocrystals at 5 nm the level is not "shallow."

Lowest unoccupied state

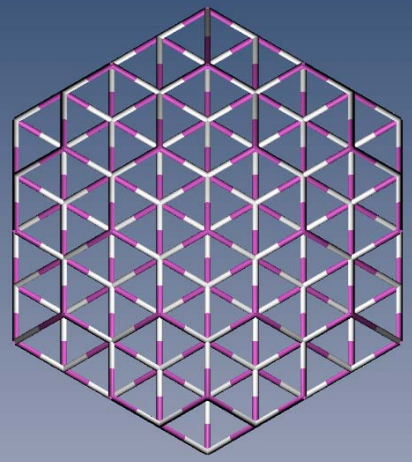
Defect state E_D

Highest doubly occupied state E_{HDO}





Strong anisotropy!



Theoretical Models for Doping Nanowires

(passivate surfaces with fictitious H atoms)

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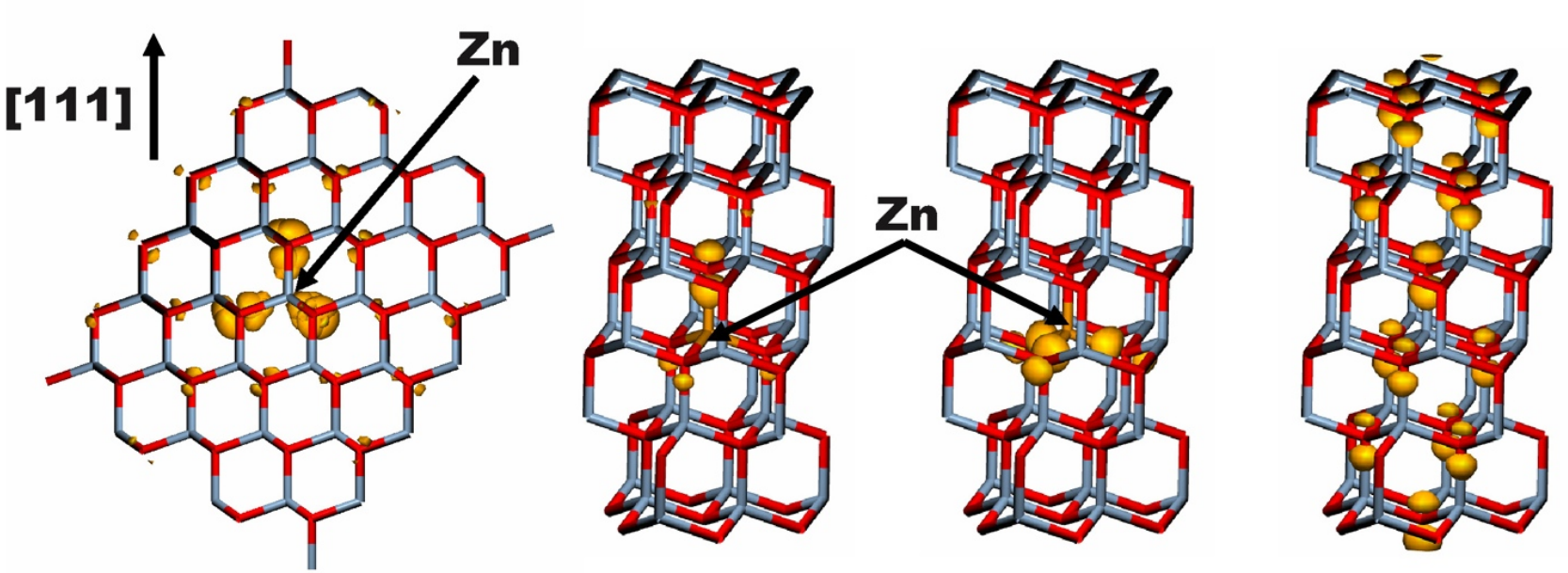
Bulk Crystal

Nanowire Acceptor States

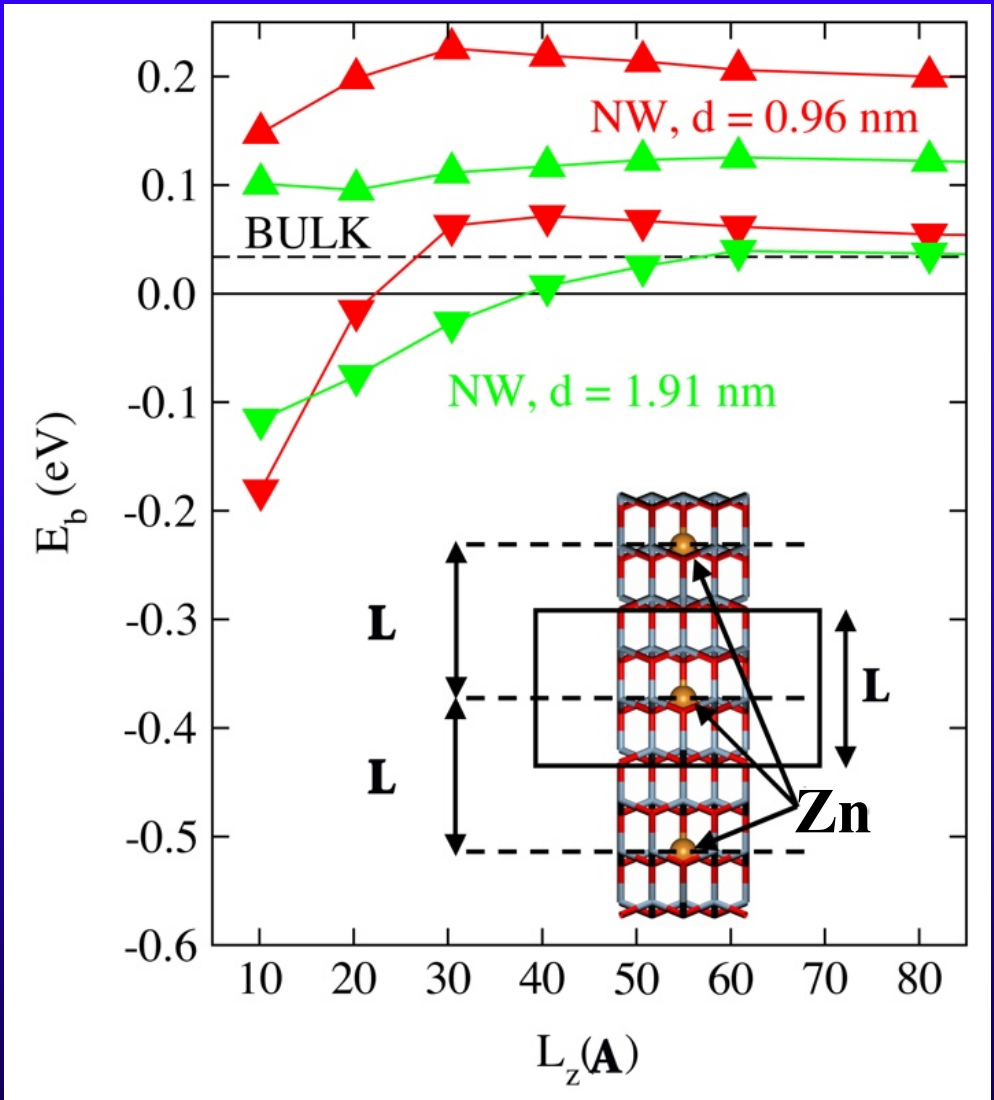
Nanowire Bulk-like state



Singly degenerate state

Doubly degenerate state

Top of the "valence band"



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

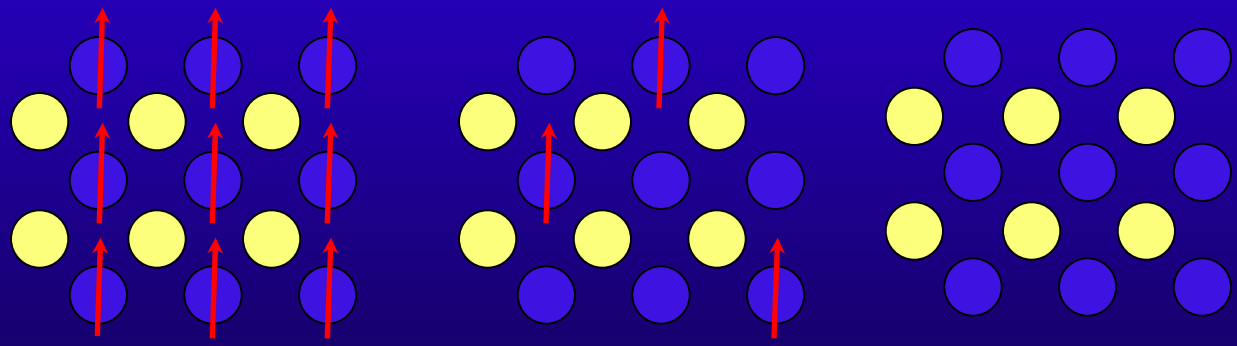
A promising route: Dilute magnetic semiconductors

e.g.,

$Mn_xGa_{1-x}As$

$Mn_xGa_{1-x}N$

Mn_xGe_{1-x}



magnetic **dilute magnetic** **non-magnetic**

Comparing Mn:Ge, Mn:GaAs and Mn:ZnSe at THE NANOSCALE

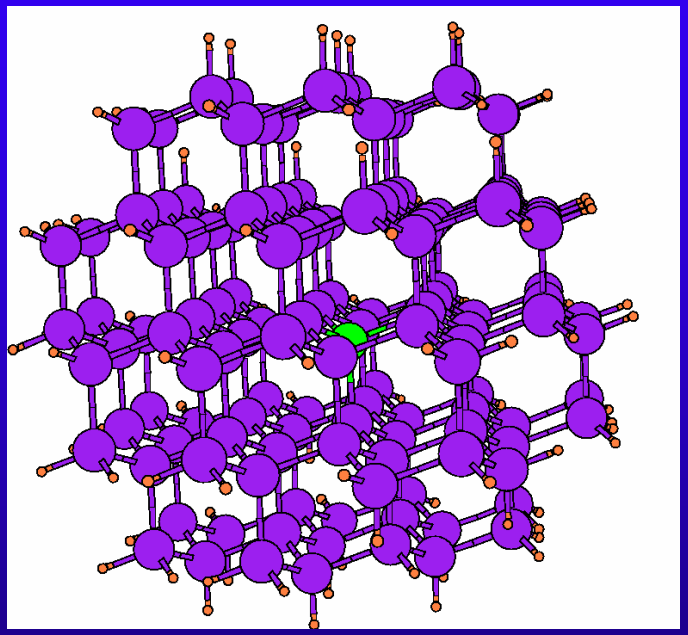
- Well-known semiconductors
- Bulk Mn:GaAs and Mn:Ge half-metallic
- Mn:ZnSe nanocrystals successfully synthesized (D. Norris)
- Hardly any theory (notable exception: N. Spaldin, UCSB)
- Same crystalline structure, periodic table row

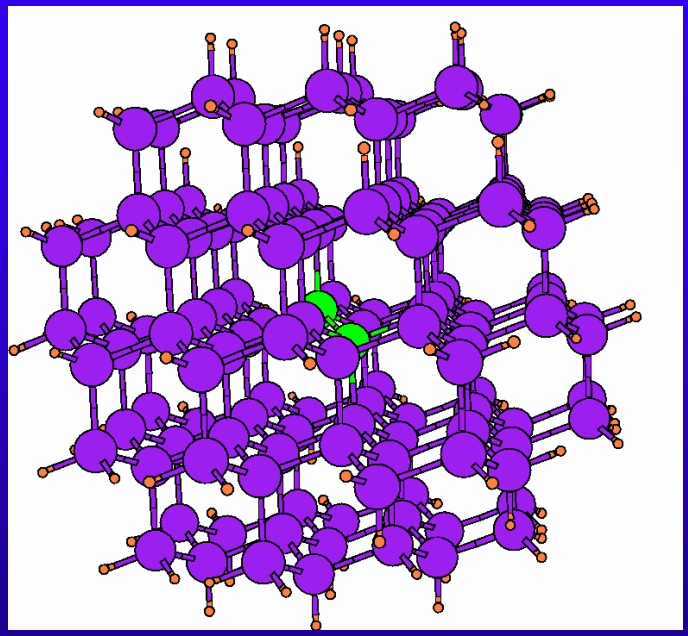
Mn:Ge Nano-Crystals

H (to avoid dangling bonds)

Ge

Mn

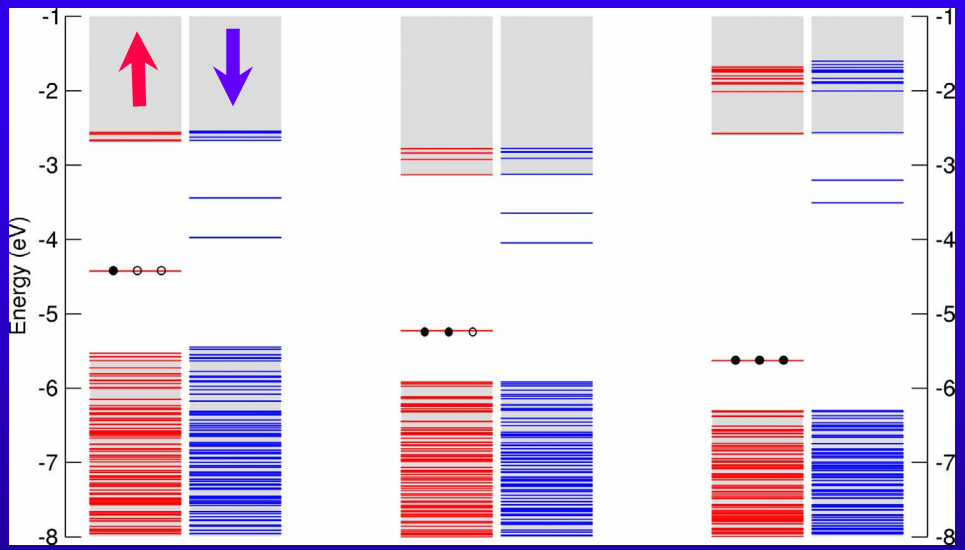




- Spherical fragments of bulk material
- Size: 1~2 nm in diameter for Mn-doped dots
- Mn substitutional site takes the cation sites (Ga, Zn)
- Surface passivation: fictitious hydrogens for GaAs and ZnSe; hydrogen for Ge

Electronic Structure and Magnetic Moments

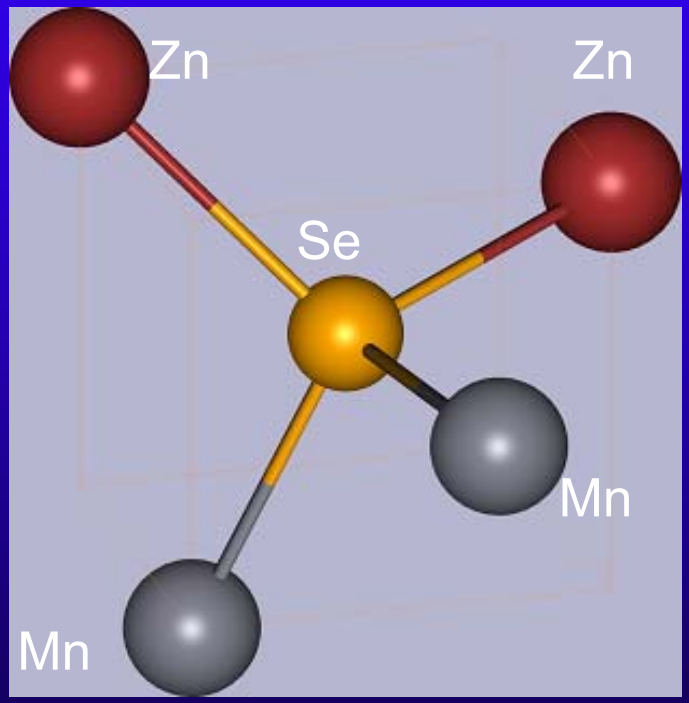
Ge GaAs ZnSe



	Mn:Ge	Mn:GaAs	Mn:ZnSe
"holes"	2	1	0
Magnetic Moment	3	4	5

- 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

Spin-Spin Interaction: Two Mn Atoms in a Nanocrystal



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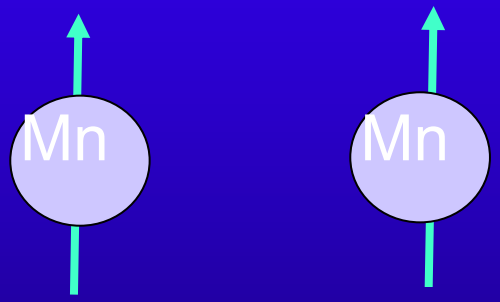
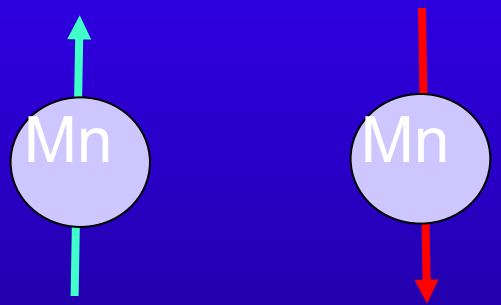
Magnetic Interactions in Bulk Crystals

Ferromagnetic (FM)



Anti-ferromagnetic (AFM)



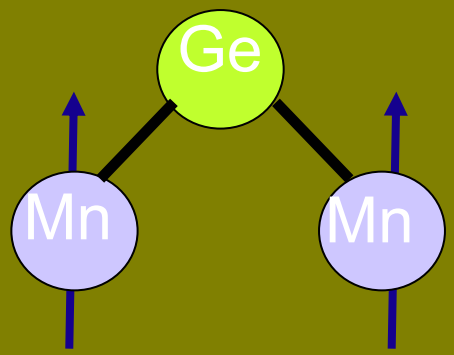
Holes will stabilize ferromagnetic configuration

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)

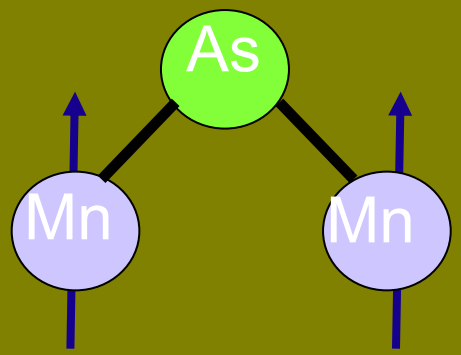
Magnetic coupling in Nanocrystals

Mn atoms are bridged through a Ge or anion



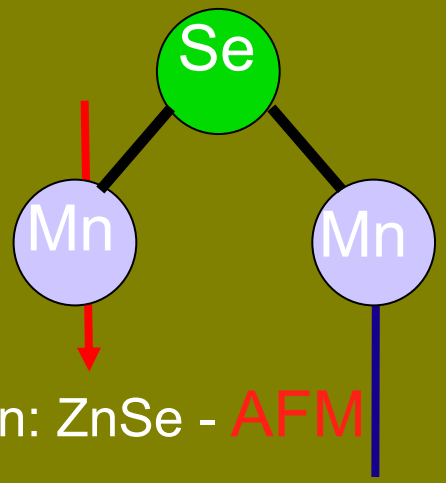
Mn:Ge - FM

FM stable by 0.42 eV



Mn:GaAs - FM

FM stable by 0.38 eV



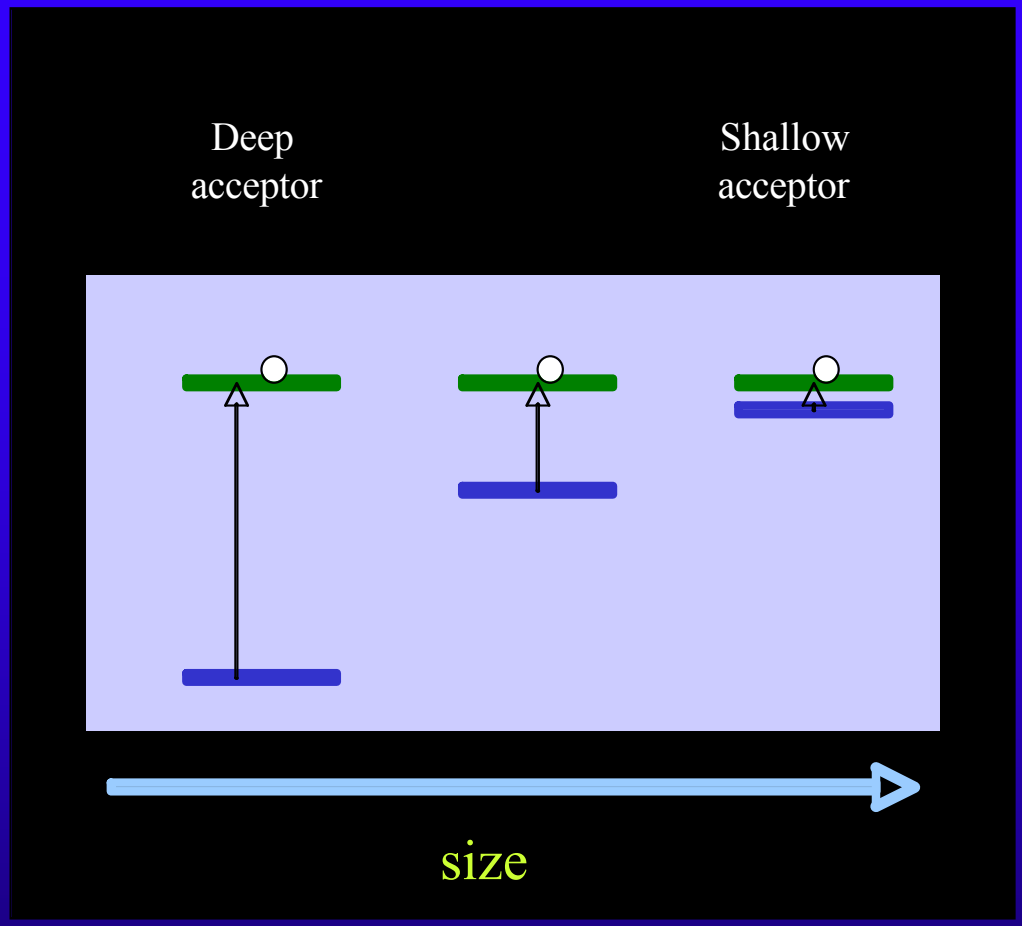
Mn: ZnSe - AFM

AFM stable by 0.14 eV

Ferromagnetism in Mn:ZnSe

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

Nature of the magnetic coupling can be changed by nanocrystal size

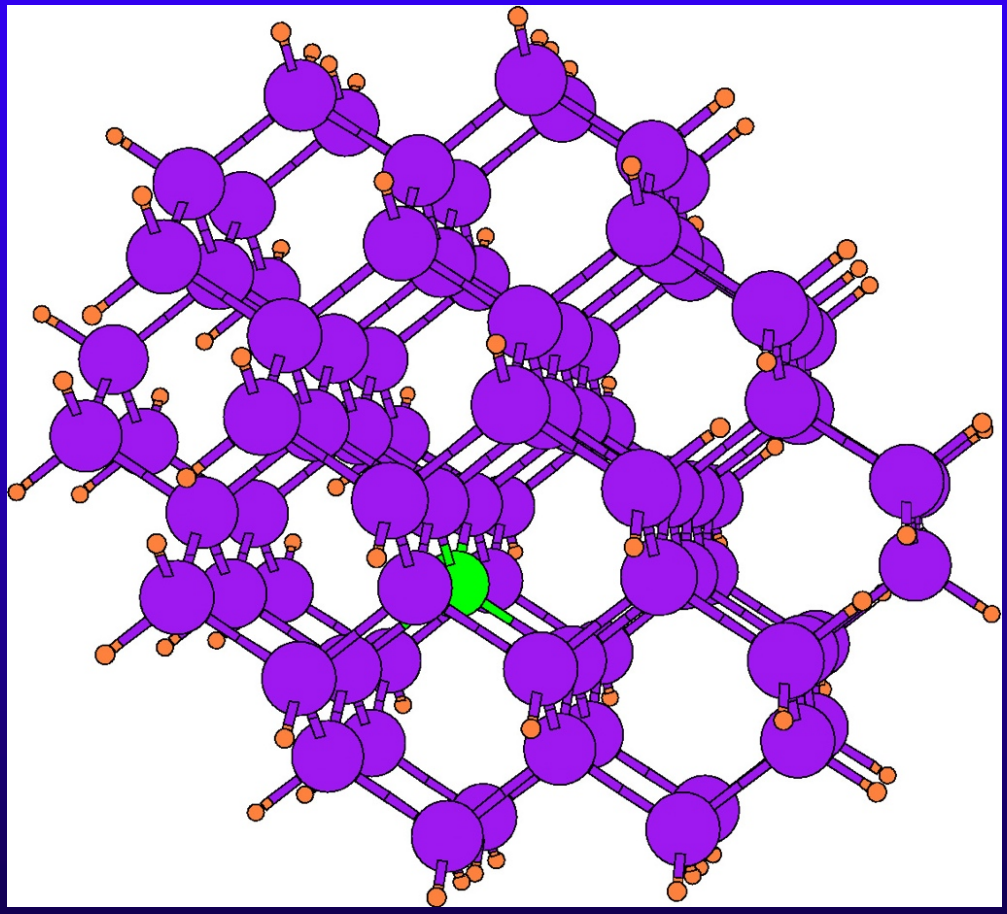


Holes in "small" nanocrystals are not shallow

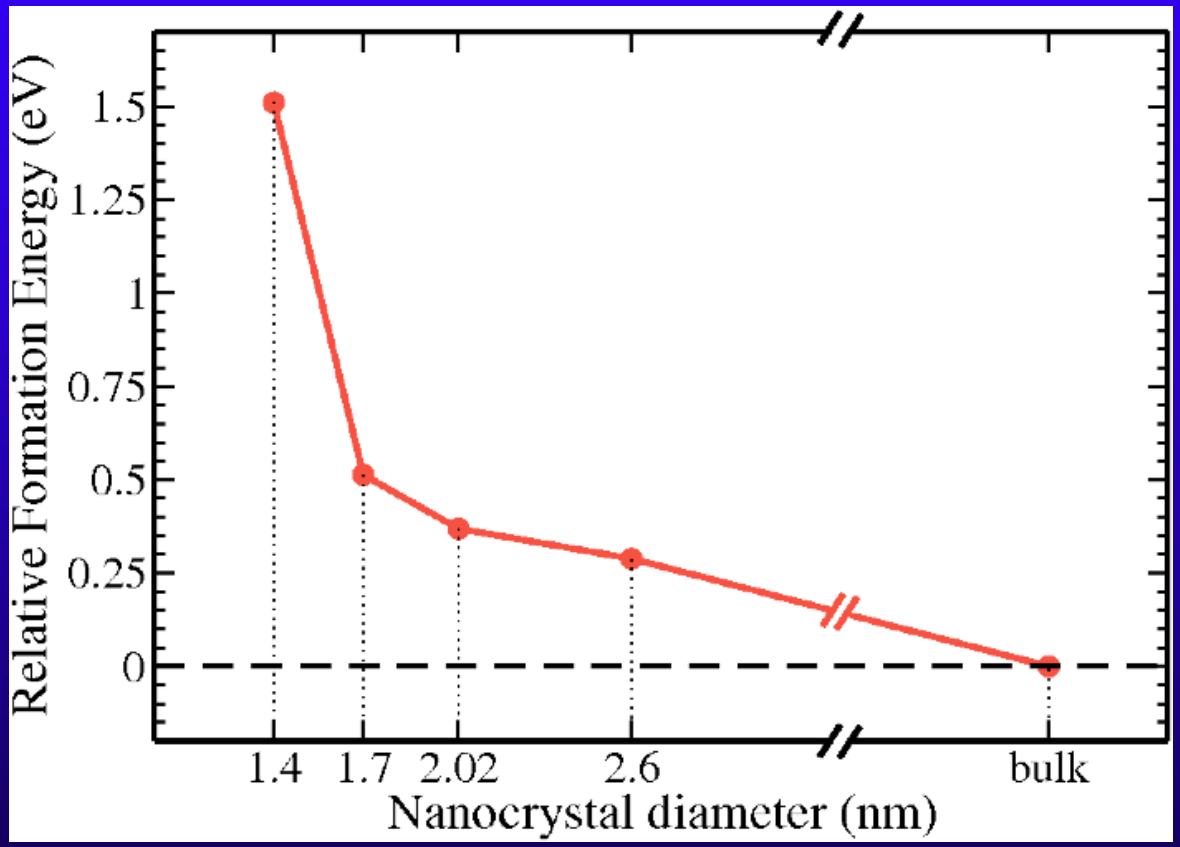
"Double Exchange" ("GaN-like GaAs") dominant mechanism, not Zener or free hole mechanism

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.

G. Dalpian and J.R. Chelikowsky, Phys. Rev. Lett. 96, 226802 (2006).

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**

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