An Introduction to Computational Nanoscience

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US Department of Energy
Office of Science

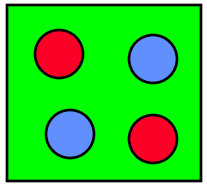
- What can we do ?
- How do we do it ?
- Examples

Contact: linwang wang, lwwang@lbl.gov

Making new solid state materials

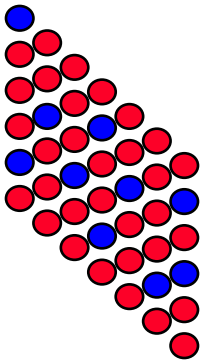
- New crystal compounds

A_2B_2

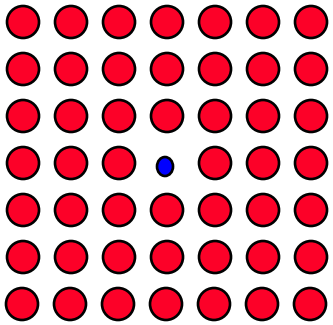


- Alloys

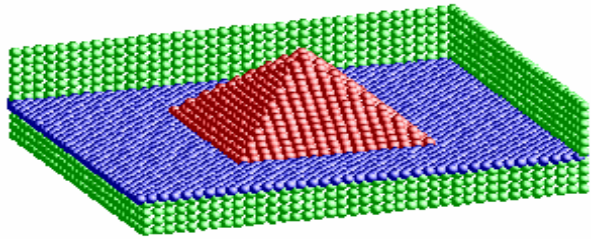
$A_{1-x}B_x$



- Impurity and doping



- Modifying the size and shape of the material



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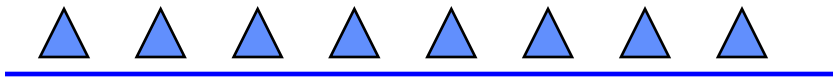
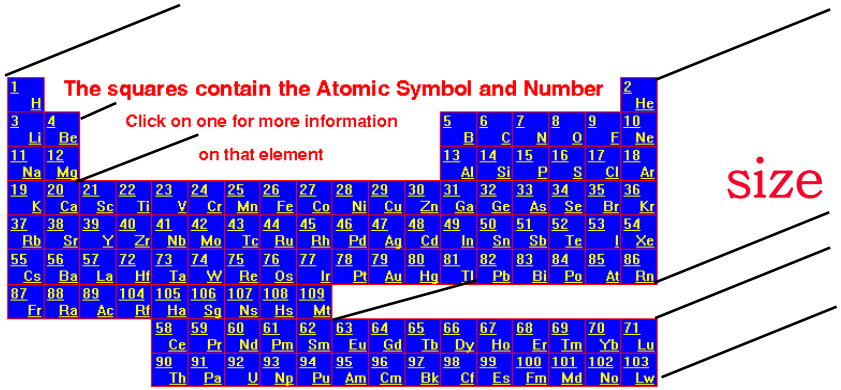
Nanostructure as a new material

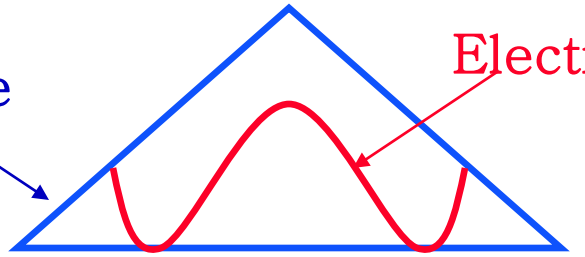
Definition: Nanostructure is an assembly of nanometer scale "building blocks".



Why nanometer scale: This is the scale when the properties of these "building blocks" become different from bulk.



size



Both are in nanometers

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Computational challenge

atoms
molecules → nanostructures → bulk

size { 1-100 atoms | 1000-10^6 atoms | Infinite (1-10 atoms in a unit cell)

⇩ ⇩ ⇩

method { Ab initio method $O(N^3)$ | Challenge for computational nanoscience. | •Ab initio method •Effective mass method

Ab initio elements and reliability

New methodology and algorithm

Even larger Supercomputer (ES!)

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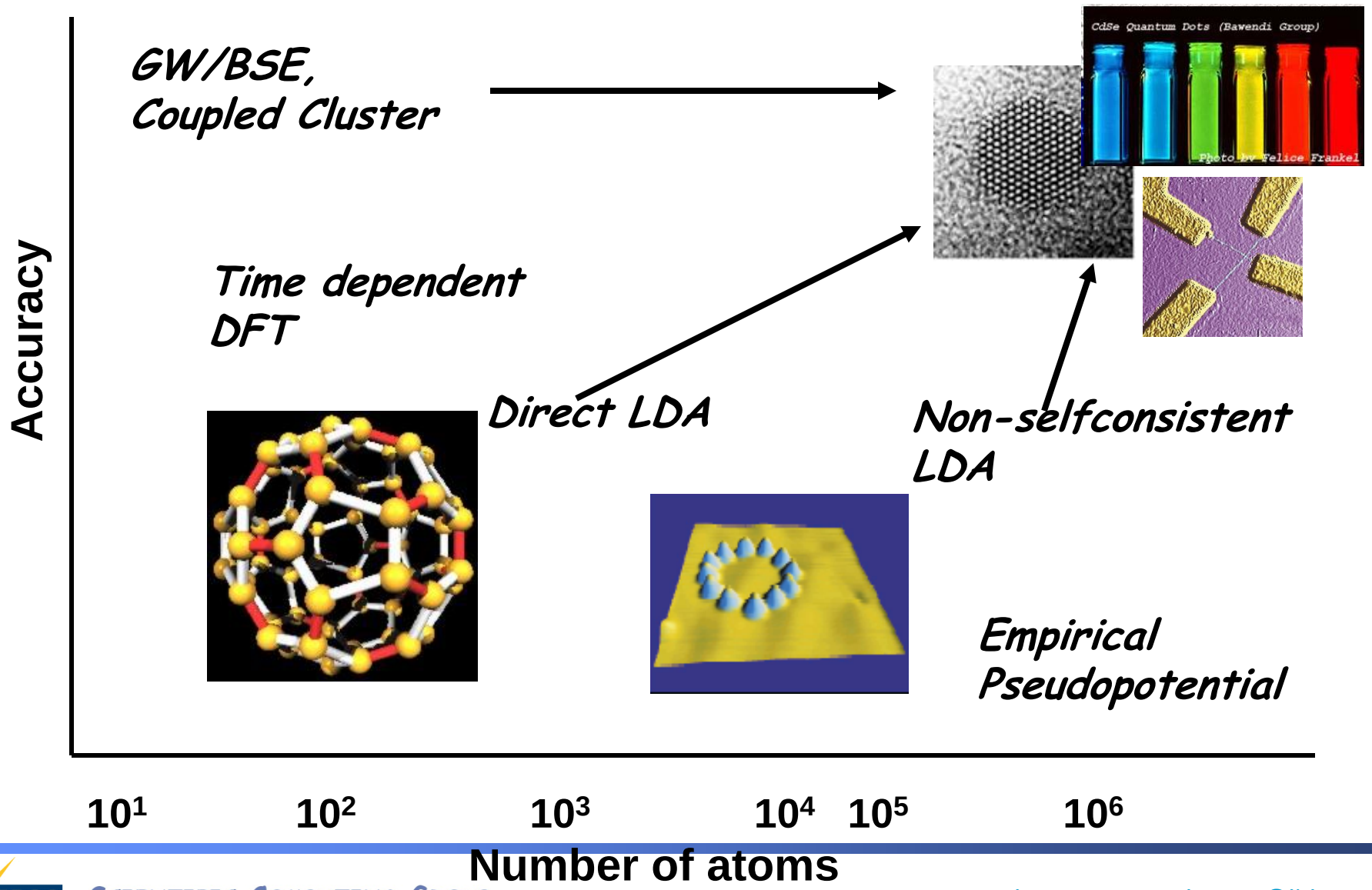
Computational methods: accuracy versus size



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Ab initio density functional calculations

$$\{-\frac{1}{2}\nabla^2 + V(r)\}\psi_i(r) = E_i\psi_i(r)$$

$$\{\psi_i\}_{i=1,..,N}$$

$$\rho(r) = \sum_i^N |\psi_i(r)|^2$$

$$V(r)$$

Selfconsistency

Density Functional

N electron
N wave functions

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Two tasks for a hybrid nano computation method

(1) To get the potential V(r) [or the charge density ρ (r)]

so we will have the Hamiltonian.

(We want ab initio reliability, but not a full ab initio calculation)

(2) To solve the single particle Hamiltonian (Schroedinger's equation), to get the physical properties.

$$\{-\frac{1}{2}\nabla^2 + V(r)\}\psi_i(r) = E_i\psi_i(r)$$

(Not the usual PDE, many eigen states, don't want and need to solve all of them)

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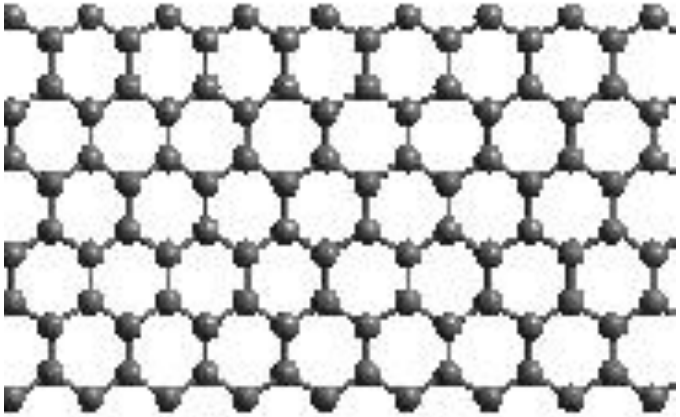
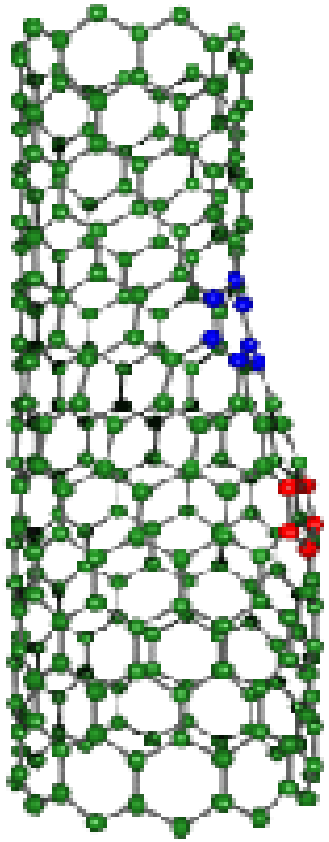
Charge patching method

Selfconsistent LDA calculation of a single graphite sheet

Non-selfconsistent LDA quality potential for nanotube





Get information from small system ab initio calc., then generate the charge densities for large systems

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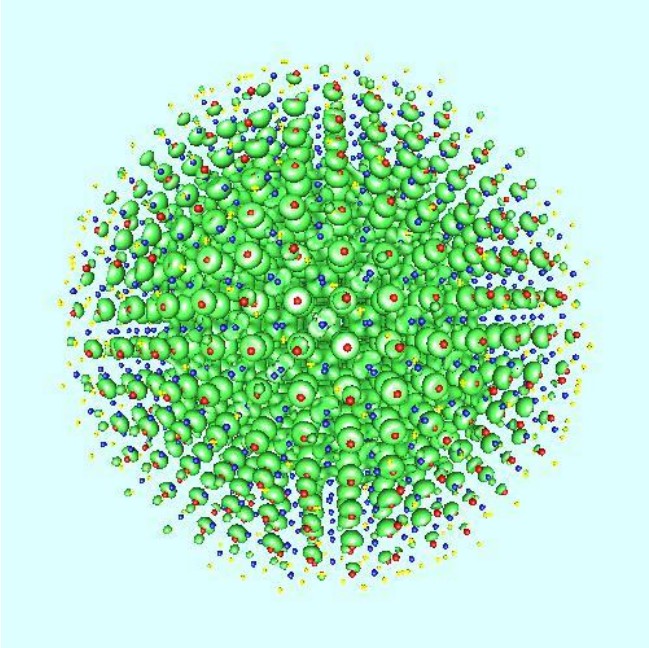
Charge patching: free standing quantum dots

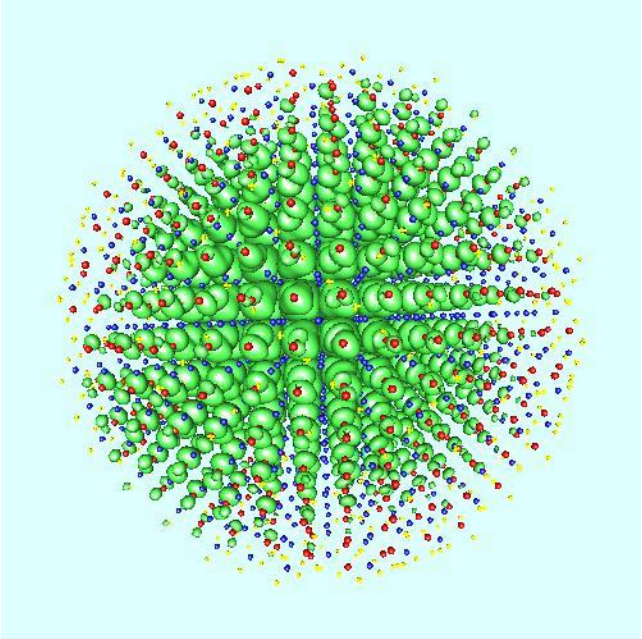
$In_{675}P_{652}$ LDA quality calculations (eigen energy error ~ 20 meV)

64 processors (IBM SP3) for ~ 1 hour

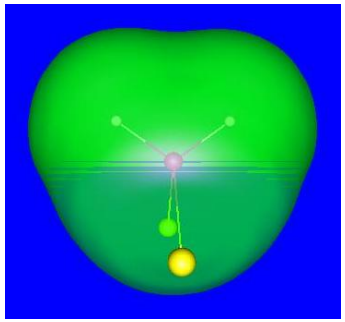
CBM

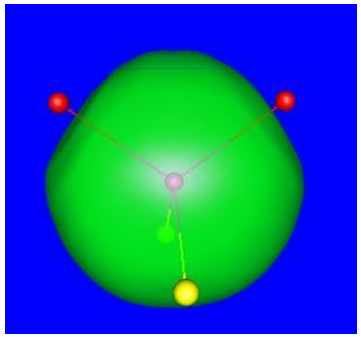


VBM



Total charge density motifs





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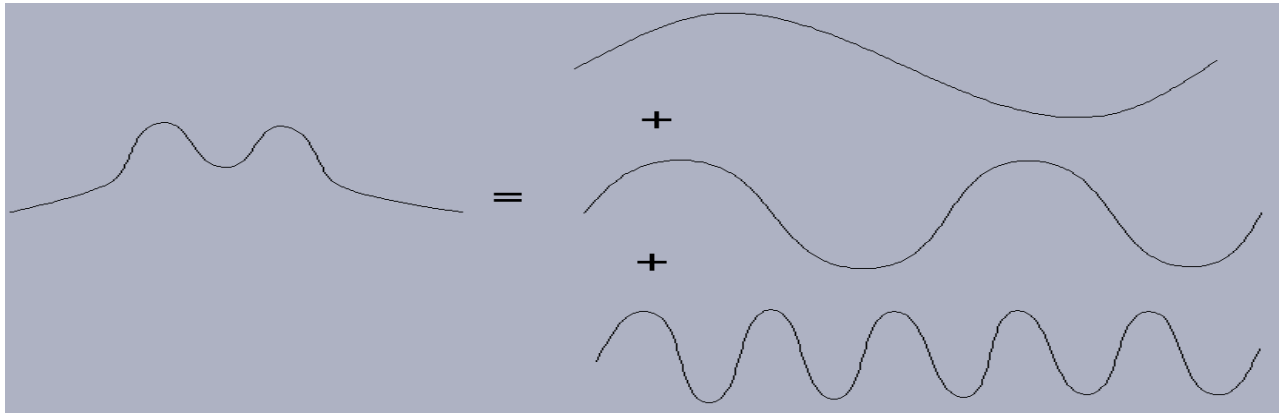
Planewave expansion of the wavefunction

$$\{-\frac{1}{2}\nabla^2 + V(r)\}\psi_i(r) = E_i\psi_i(r)$$

$$\psi(r) = \sum_q C(q)e^{iqr}$$



Fast Fourier Transformation between real space ψ(r) and Fourier space C(q).

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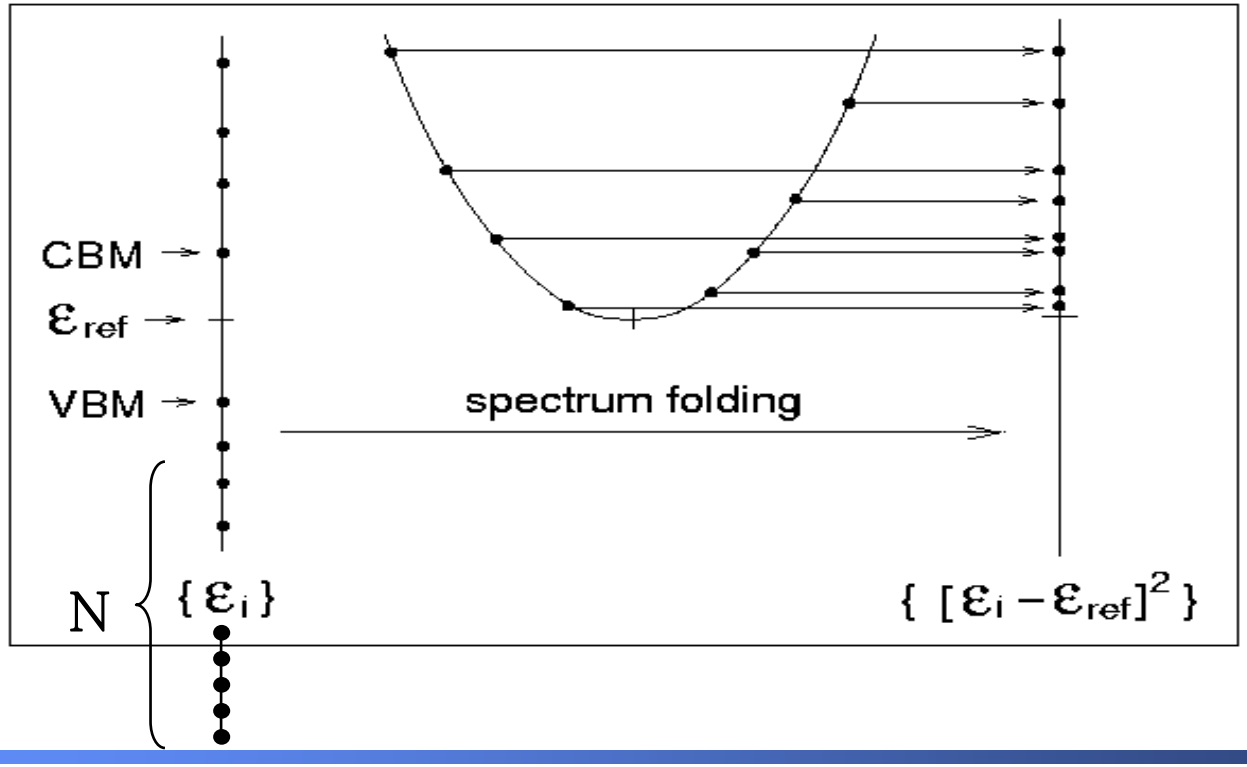
Folded Spectrum Method

$$\{-\frac{1}{2}\nabla^2 + V(r)\}\psi_i(r) = E_i\psi_i(r)$$

$$H\psi_i = \varepsilon_i\psi_i \qquad (H-\varepsilon_{ref})^2\psi_i = (\varepsilon_i - \varepsilon_{ref})^2\psi_i$$



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NERSC: National Energy Research Scientific Computing Center

Hopper, Cray XE6 machine, 150,000 computing cores, 1.3 Petaflops

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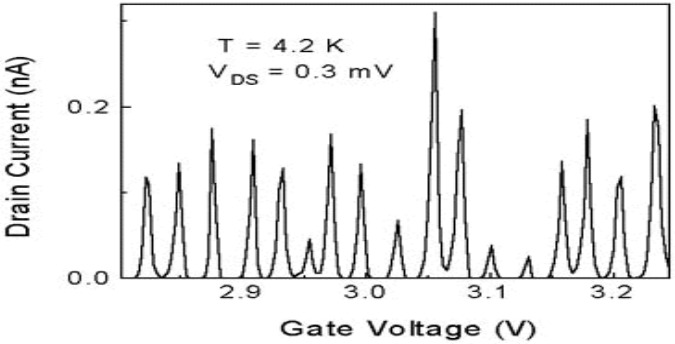
Examples of new properties

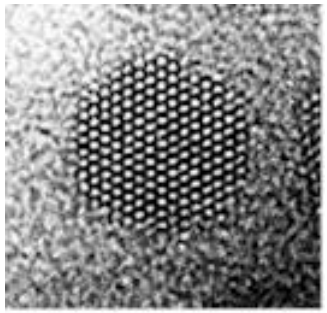
- Band gap increase

CdSe quantum dot

- Single electron effects on transport (Coulomb blockade).



- Mechanical properties, surface effects and no dislocations



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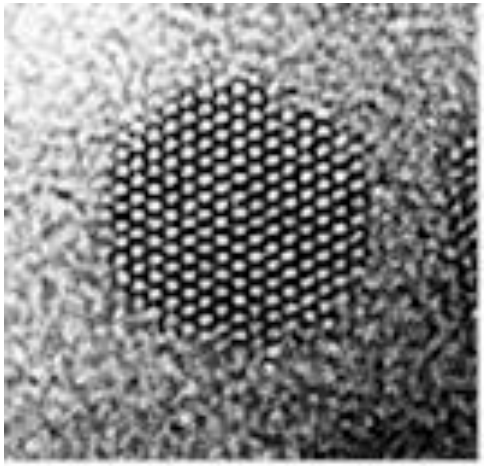
Free standing quantum dots



CdSe
quantum dot
TEM image

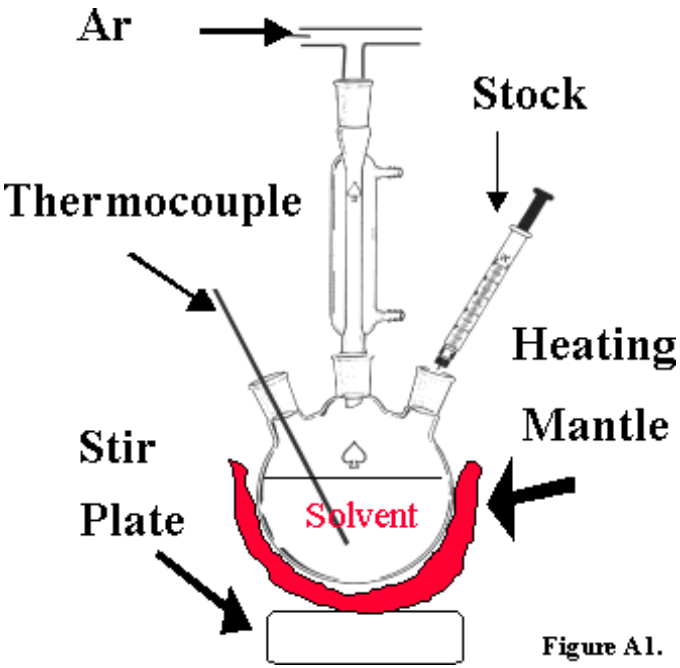


Figure A1.

- Chemically synthesised
- Interior atoms are in bulk crystal structure
- Surface atoms are passivated
- Diameter ~ 20-100 A
- A few thousand atoms, beyond ab initio method

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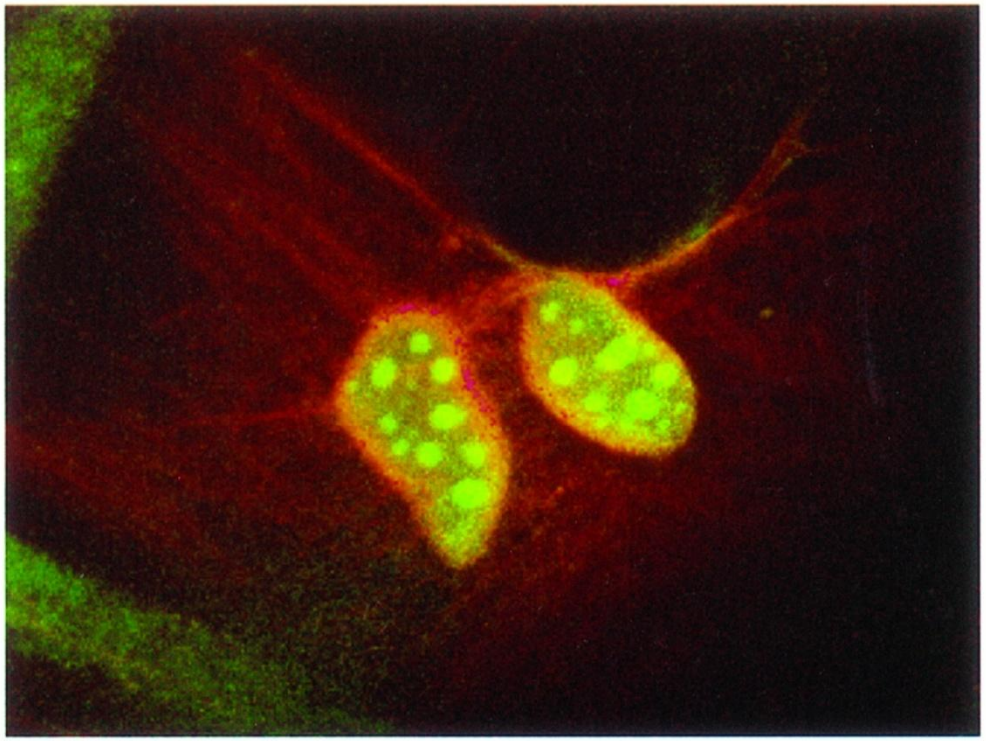
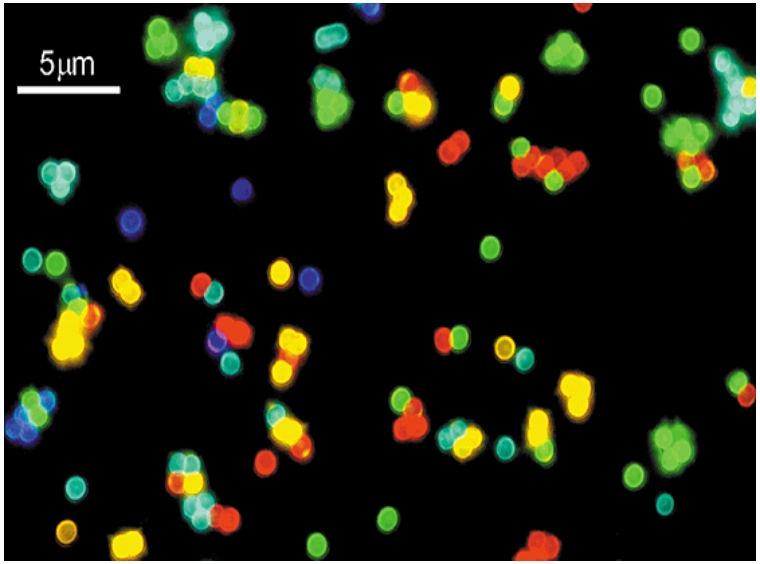
CdSe quantum dots as biological tags





- Optically more stable than dye molecules
- Can have multiple colors

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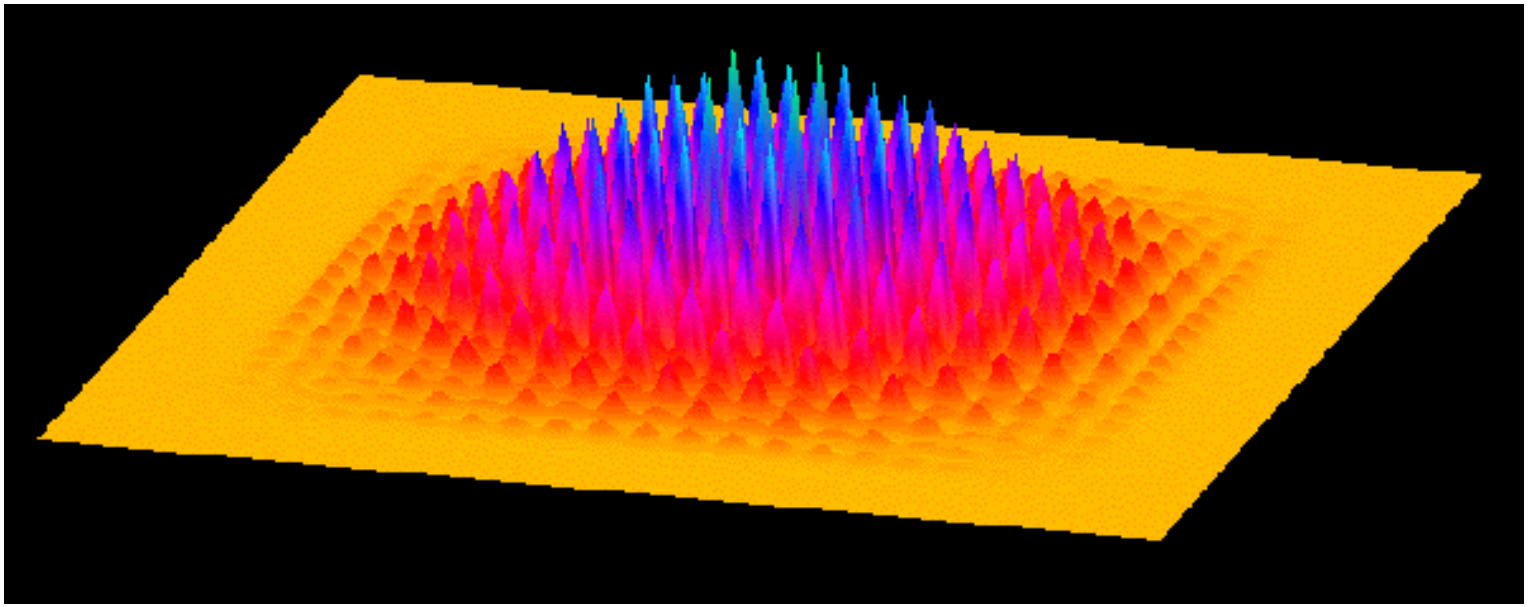
Quantum dot wavefunctions



Cross section electron wavefunctions

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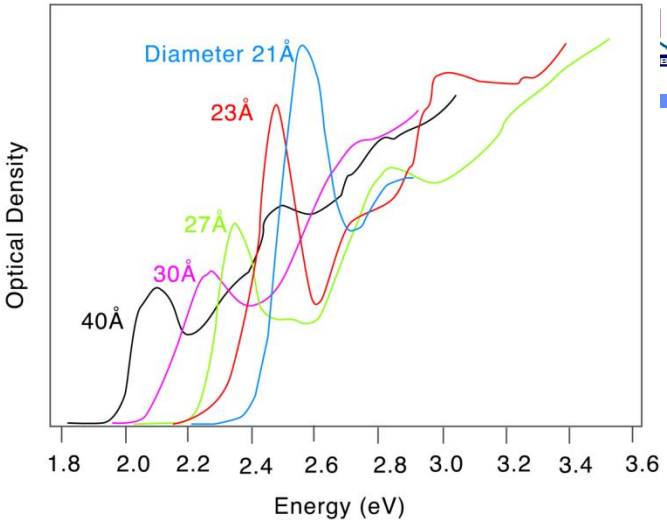
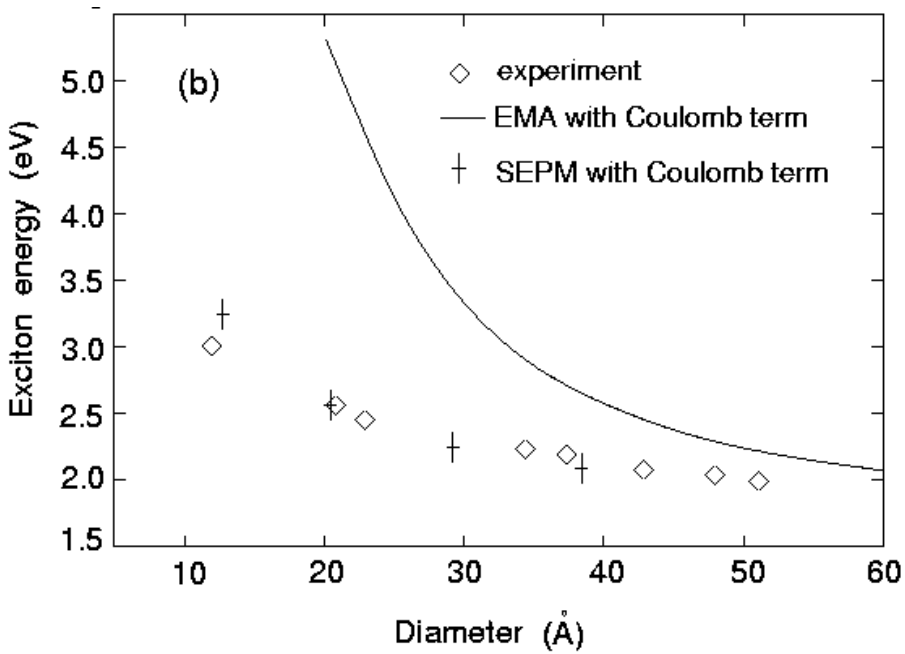
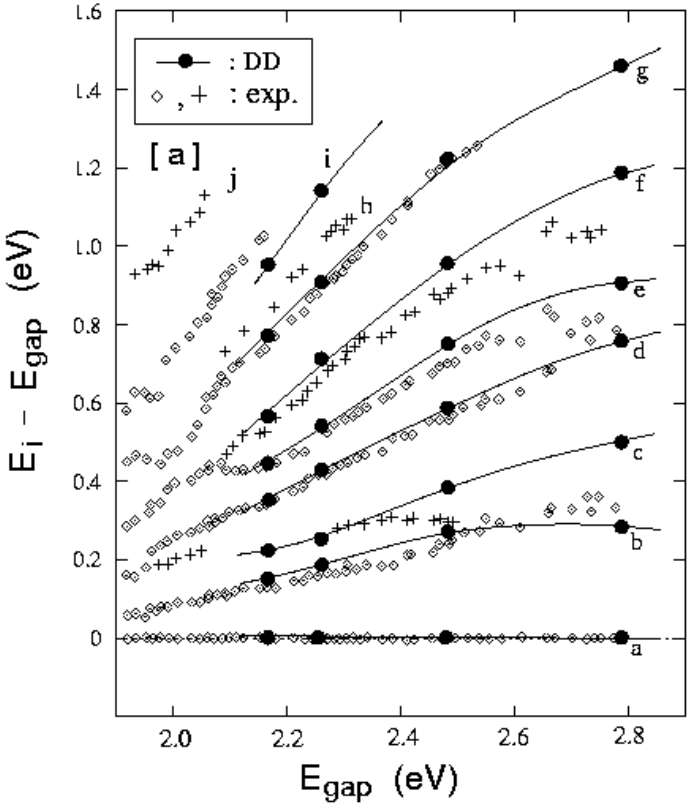
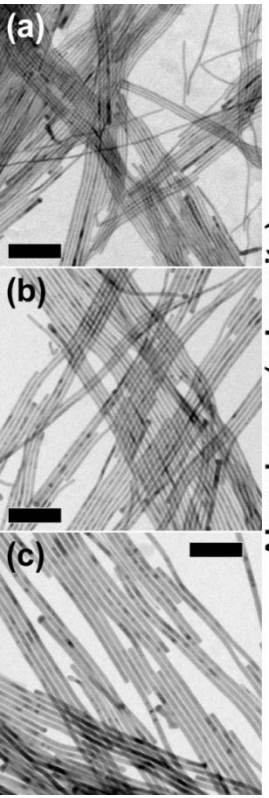
CdSe quantum dot results

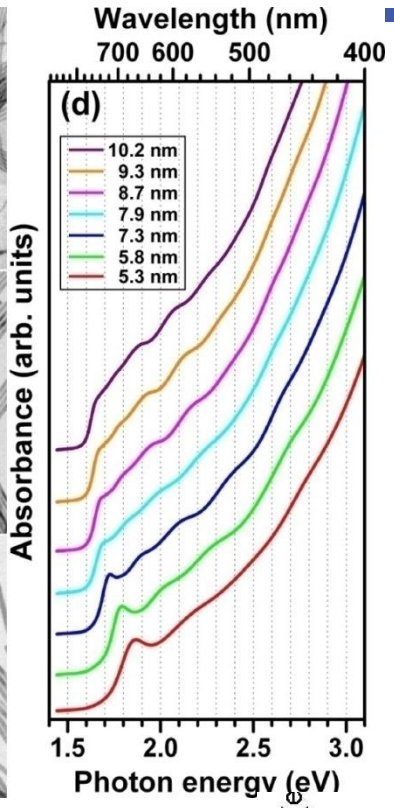






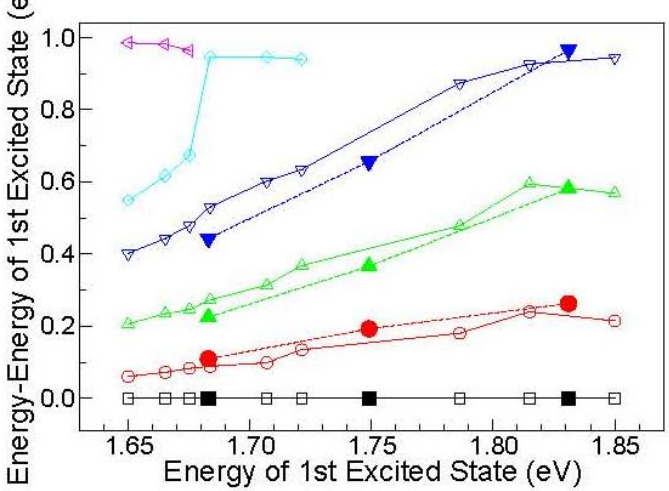
CdTe nanowire

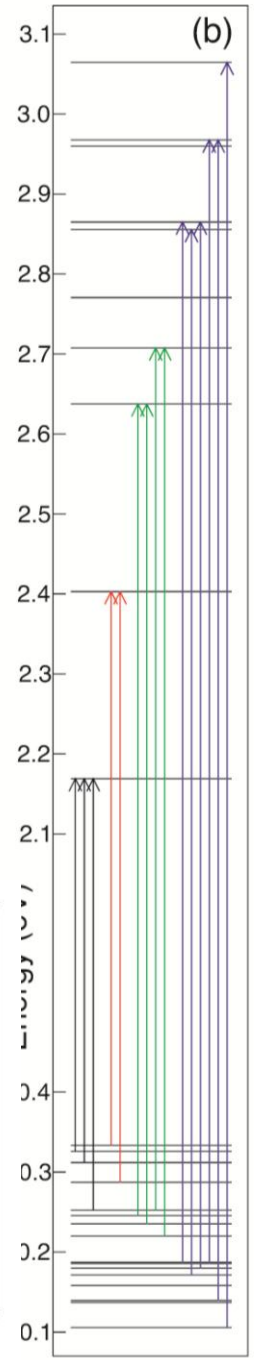


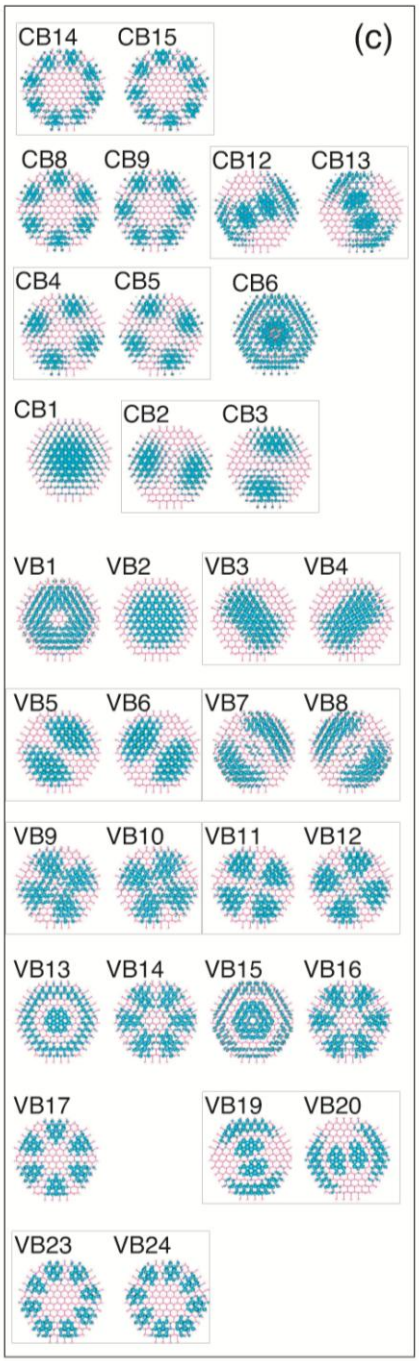


Exp: ———

Calc: - - - - - -





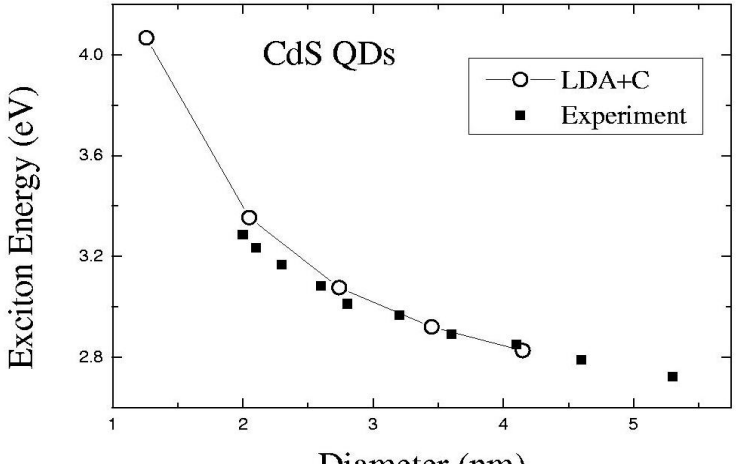


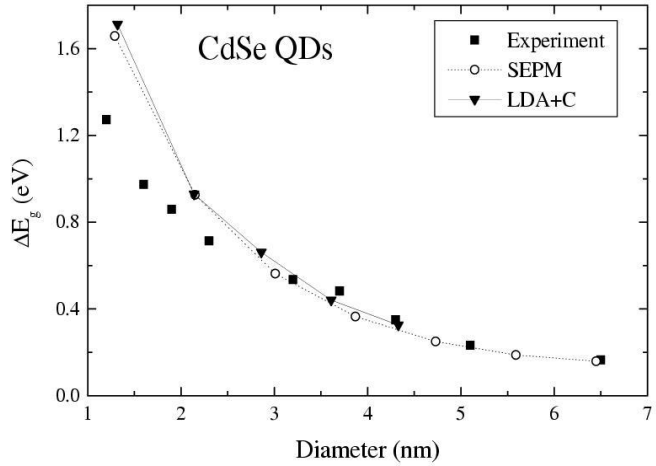
Quantum dot and wire calculations for semiconductor materials

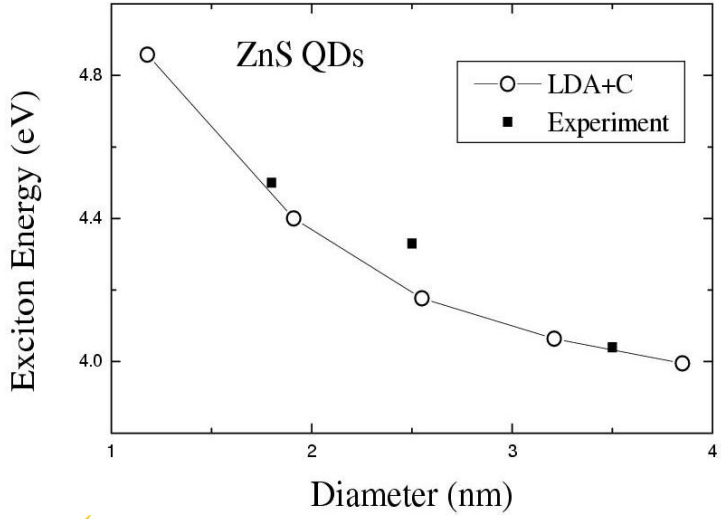
IV-IV: Si

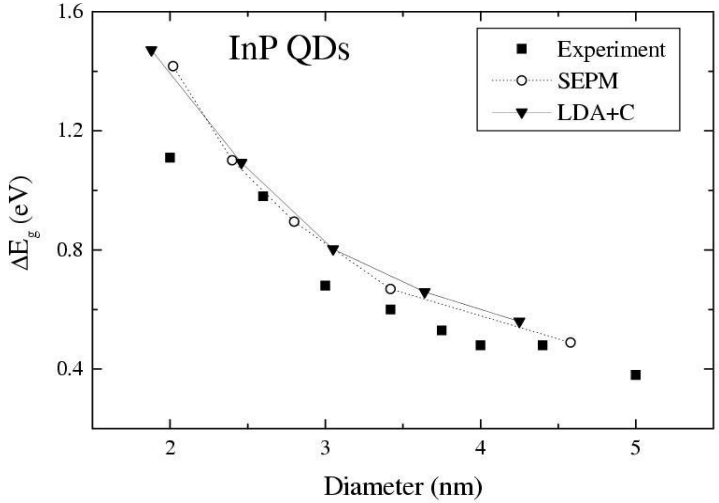
III-V: GaAs, InAs, InP, GaN, AlN, InN

II-VI: CdSe, CdS, CdTe, ZnSe, ZnS, ZnTe, ZnO









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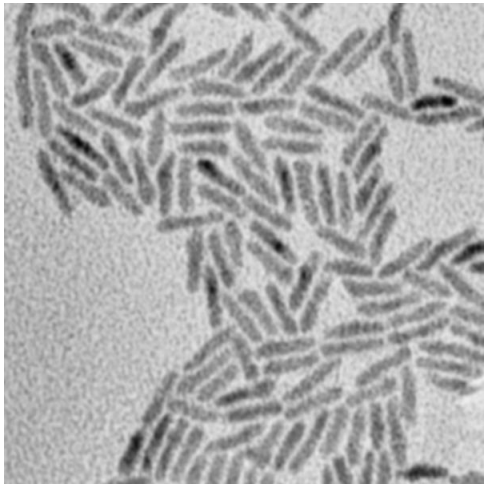
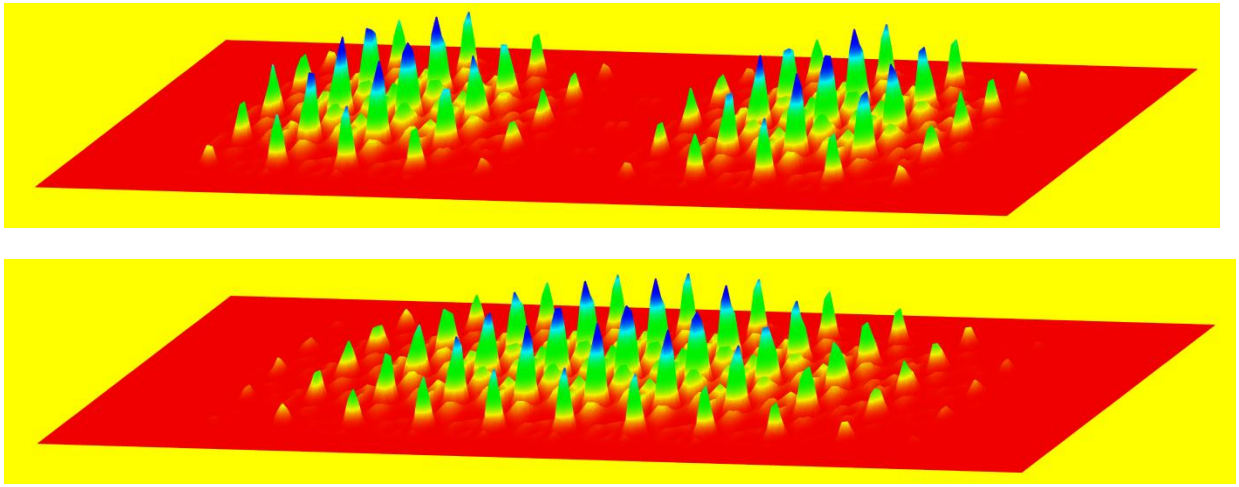
Polarization of CdSe quantum rods



CdSe quantum rods



The electron wavefunctions of a quantum rods

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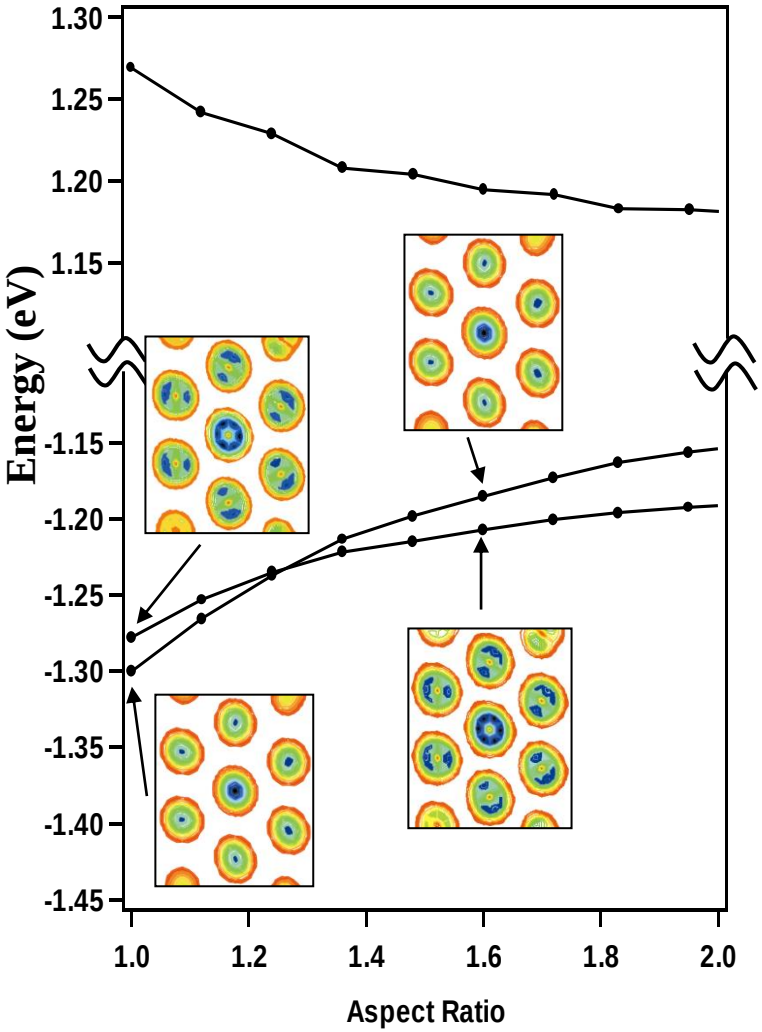
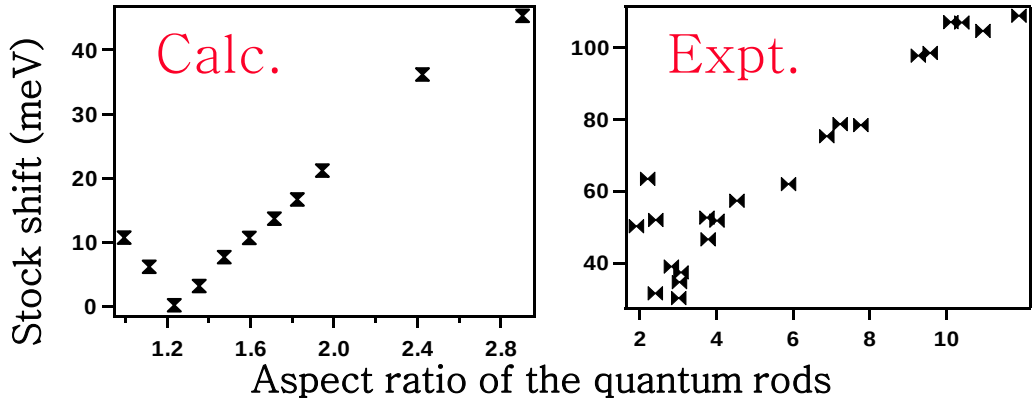
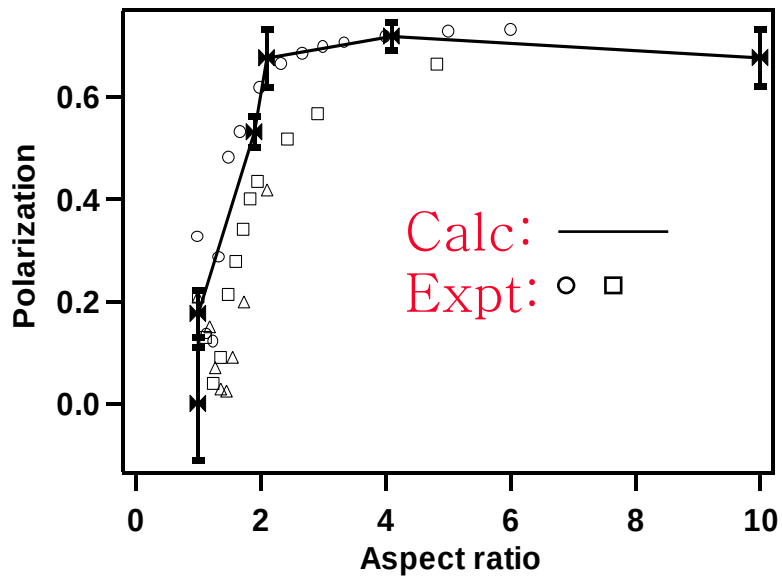
Polarization of quantum rods (continued)







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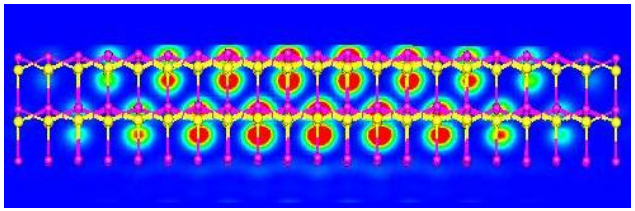
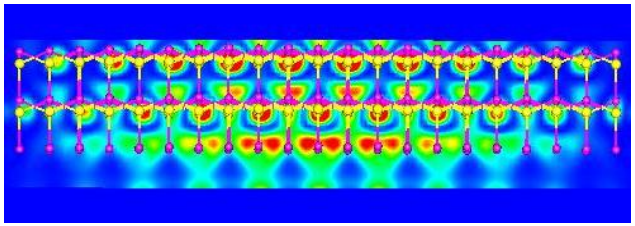
Quantum wire electronic states

[111]

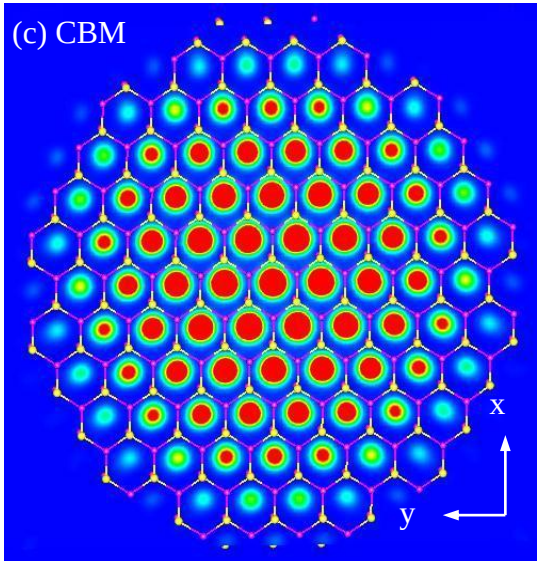
(a) CBM (xz-plane)

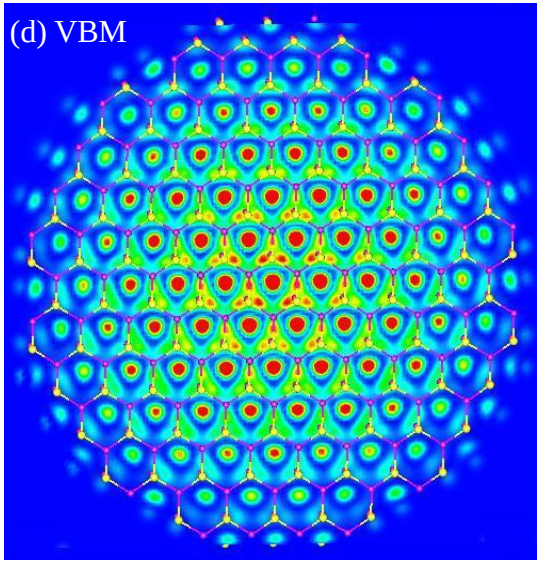


(b) VBM (xz-plane)



d=5.18 nm





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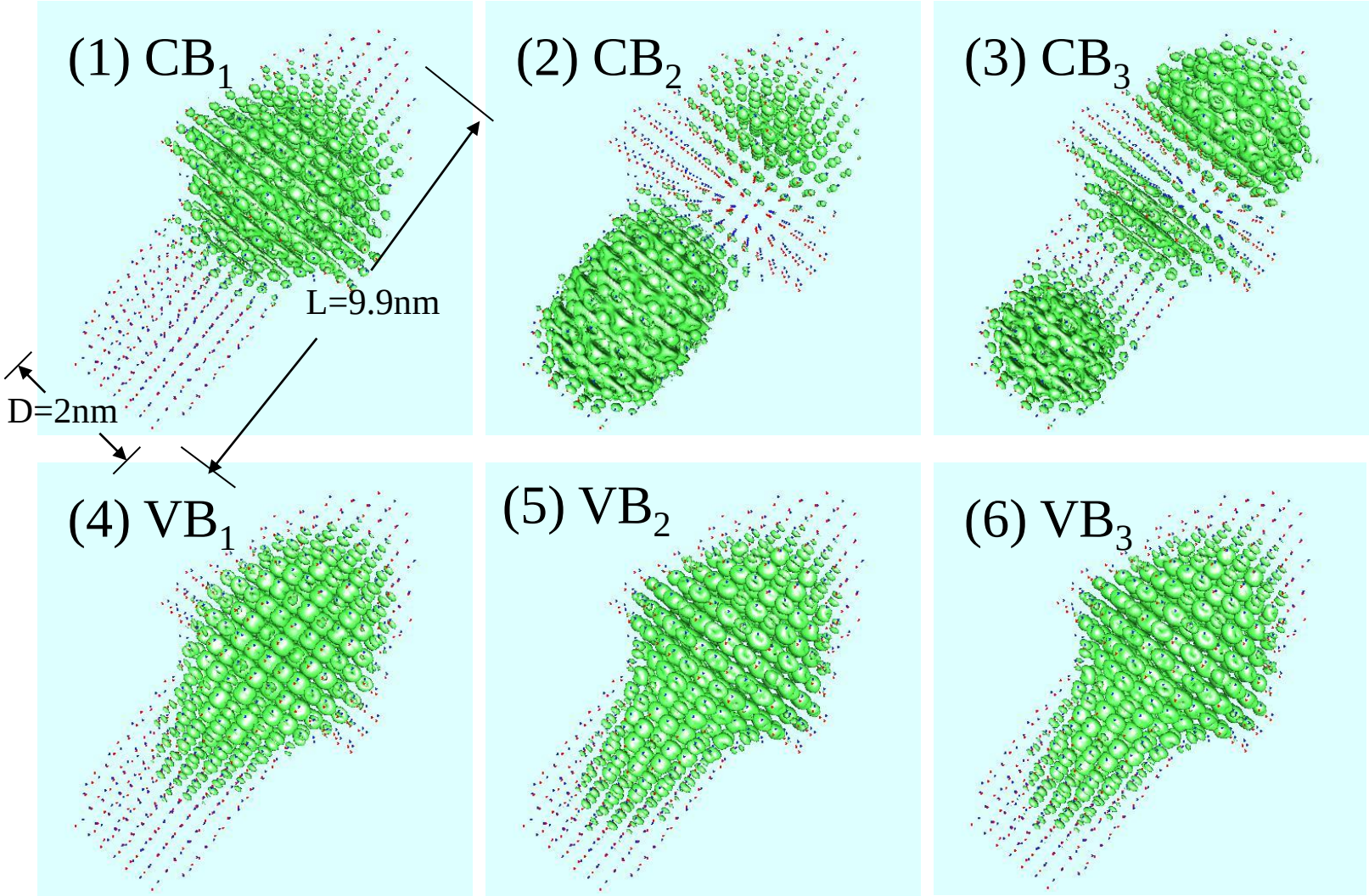
CdSe quantum dot: arrow shape



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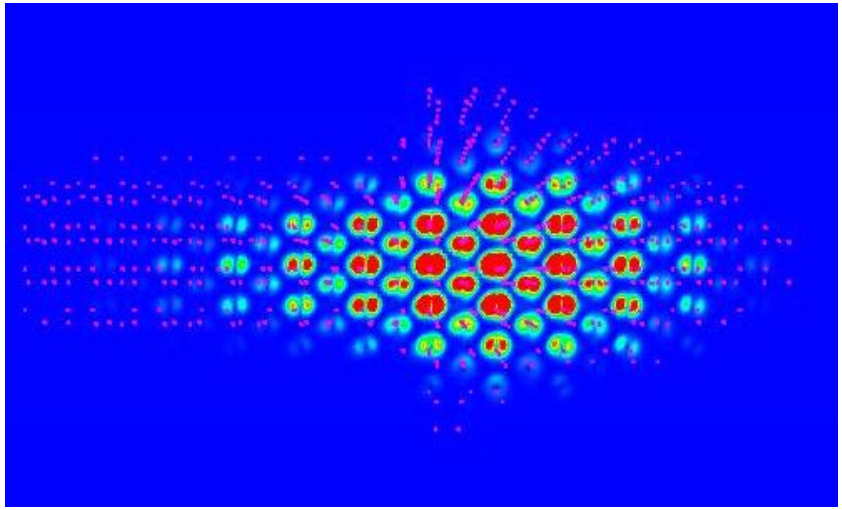
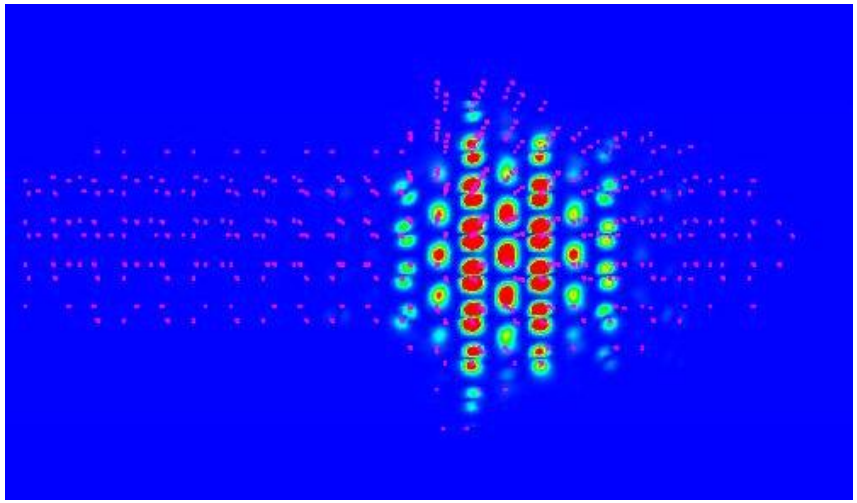
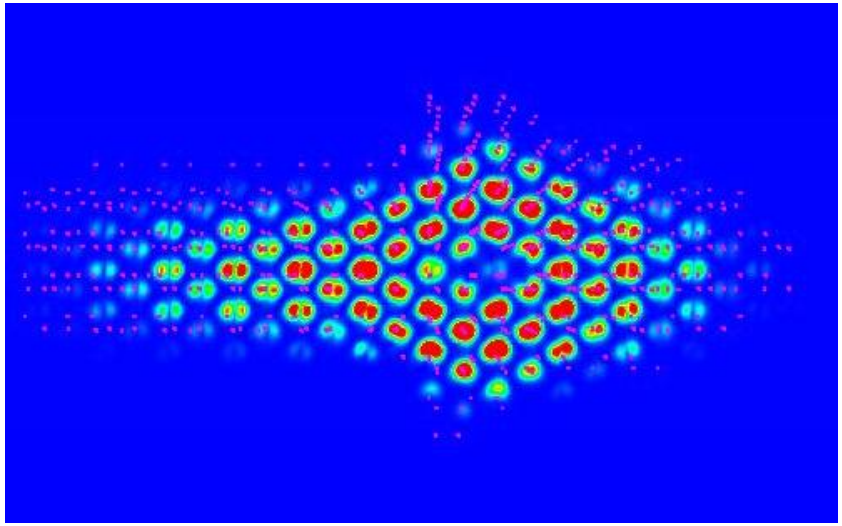
Different Bloch state characters for the VB states

VB-1

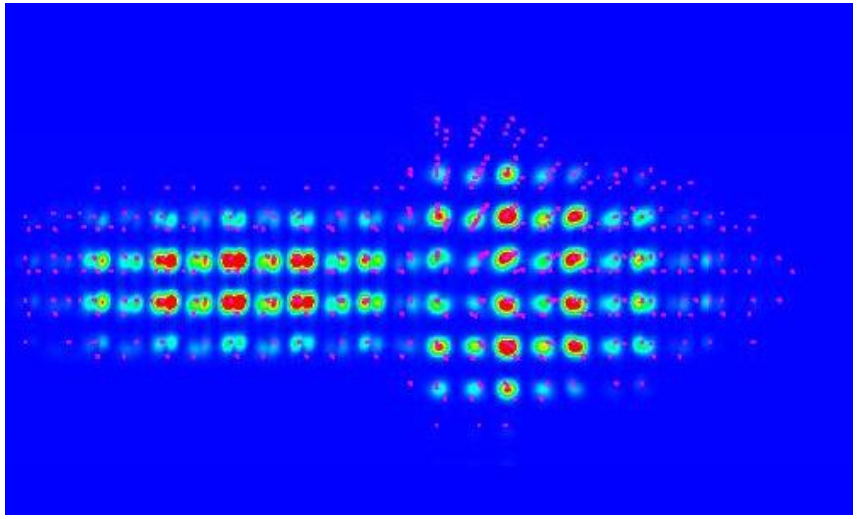


VB-2





VB-3



VB-4

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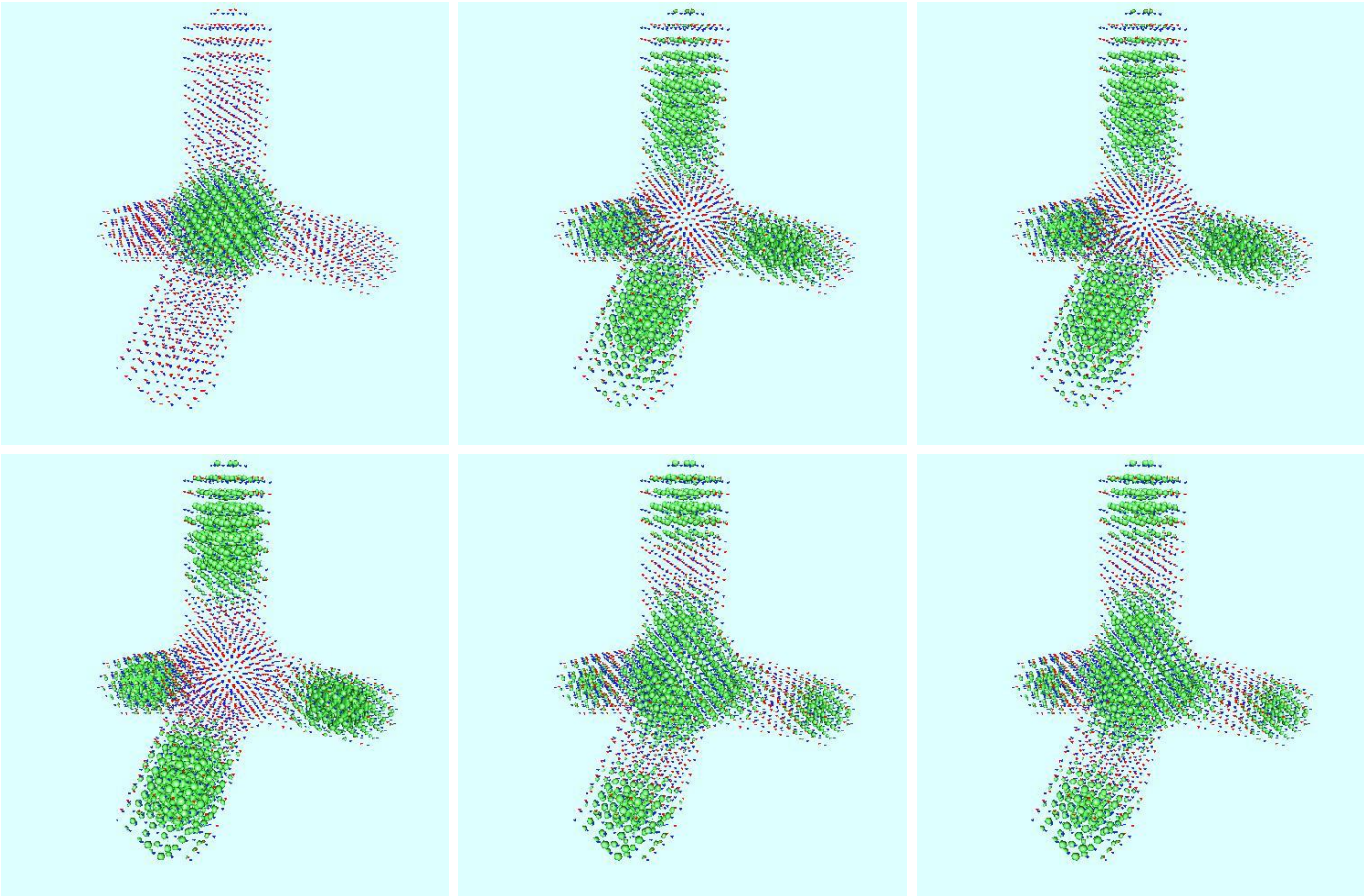
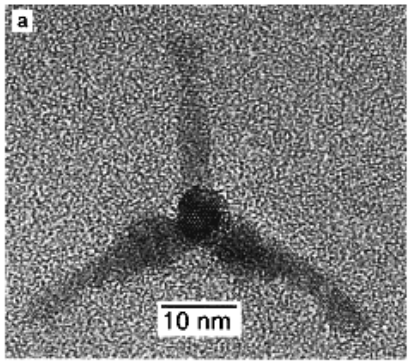
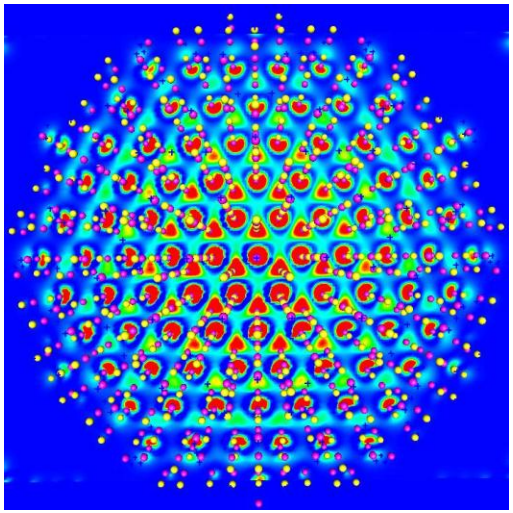
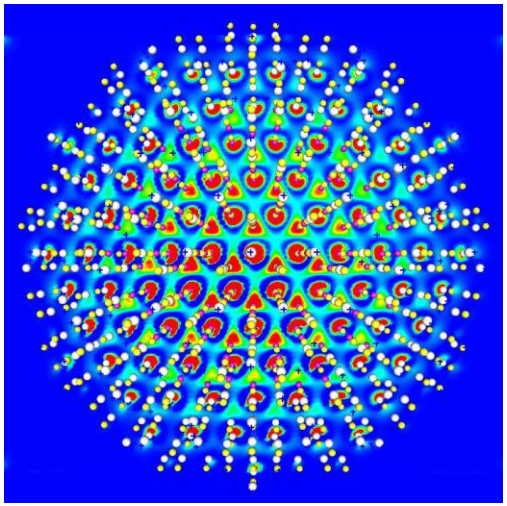
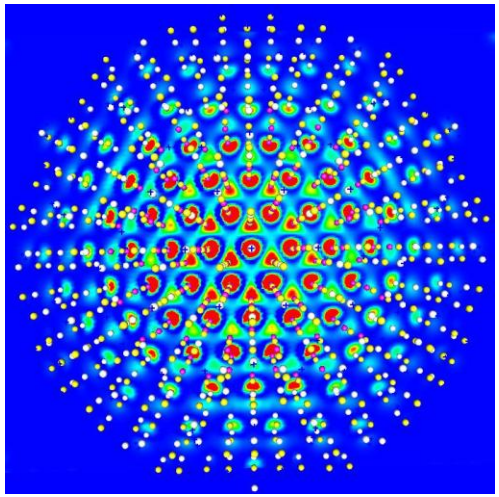
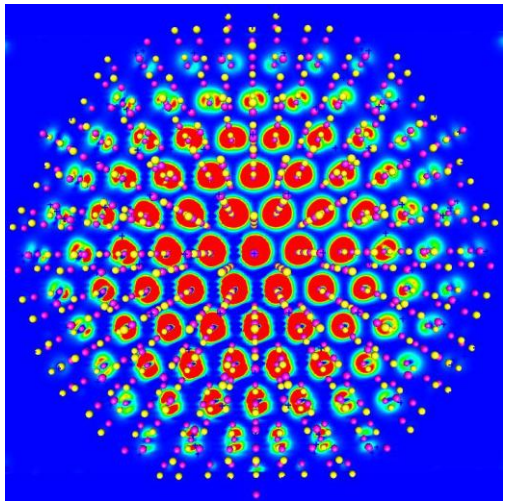
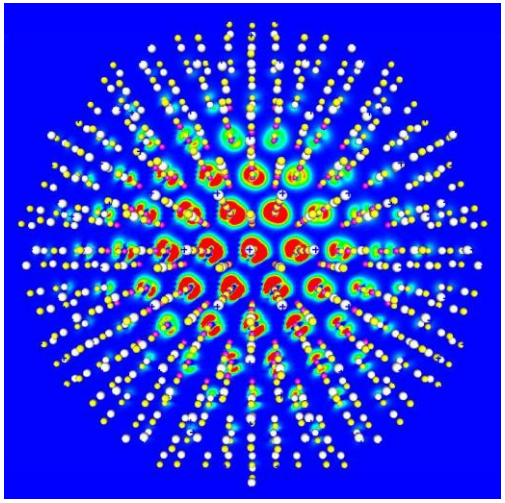
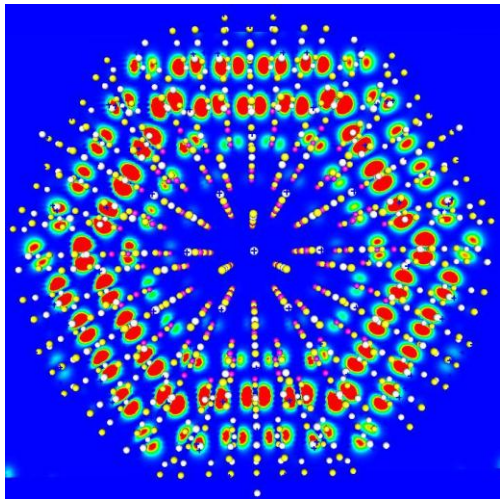
CdSe tetrapod electronic states





Contact: linwang wang, lwwang@lbl.gov

Core/shell quantum dots

	CdSe	CdSe/CdS	CdSe/CdTe
CBM			
VBM			

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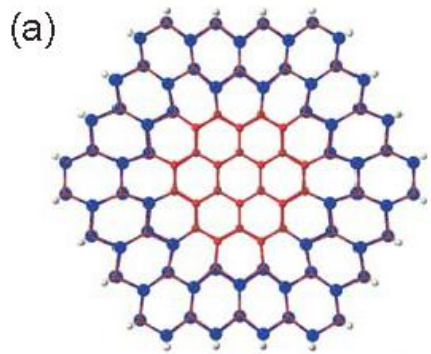
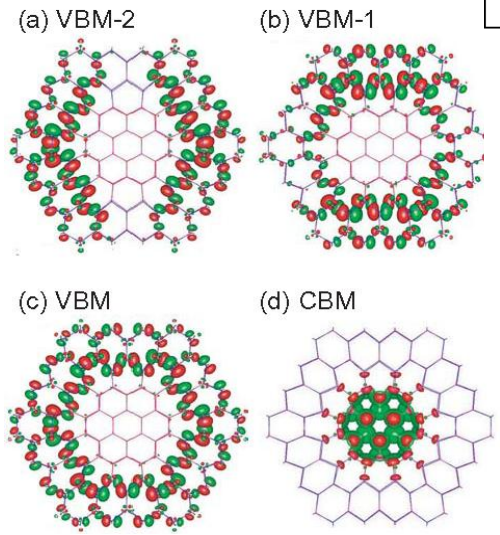
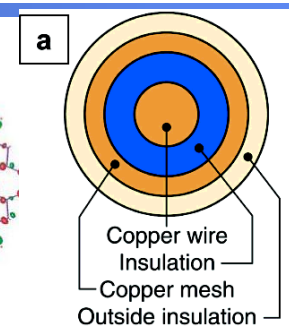
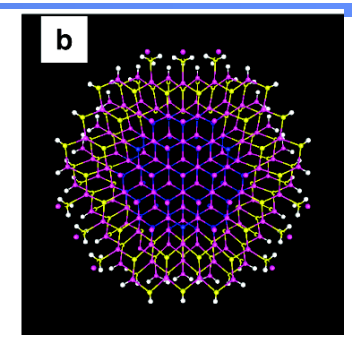
Solar cell using stable, abundant, and env. benign mat

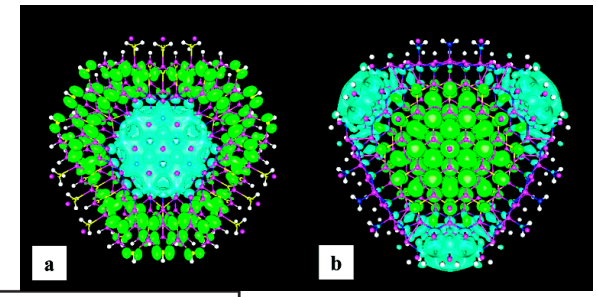
ZnO/ZnS core/shell wire

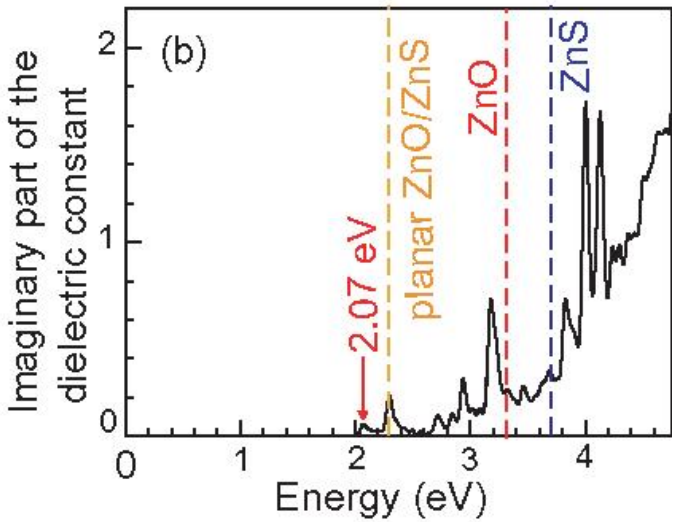


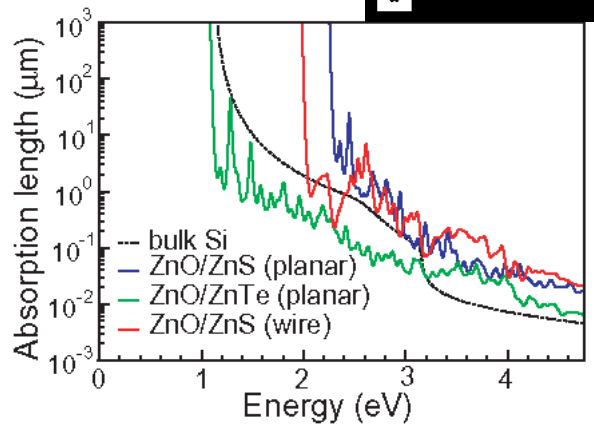












Band gap lowers down further from superlattices.

The absorption length is similar to bulk Si, thus similar among f material for solar cell.

23% theoretical efficiency for solar cell

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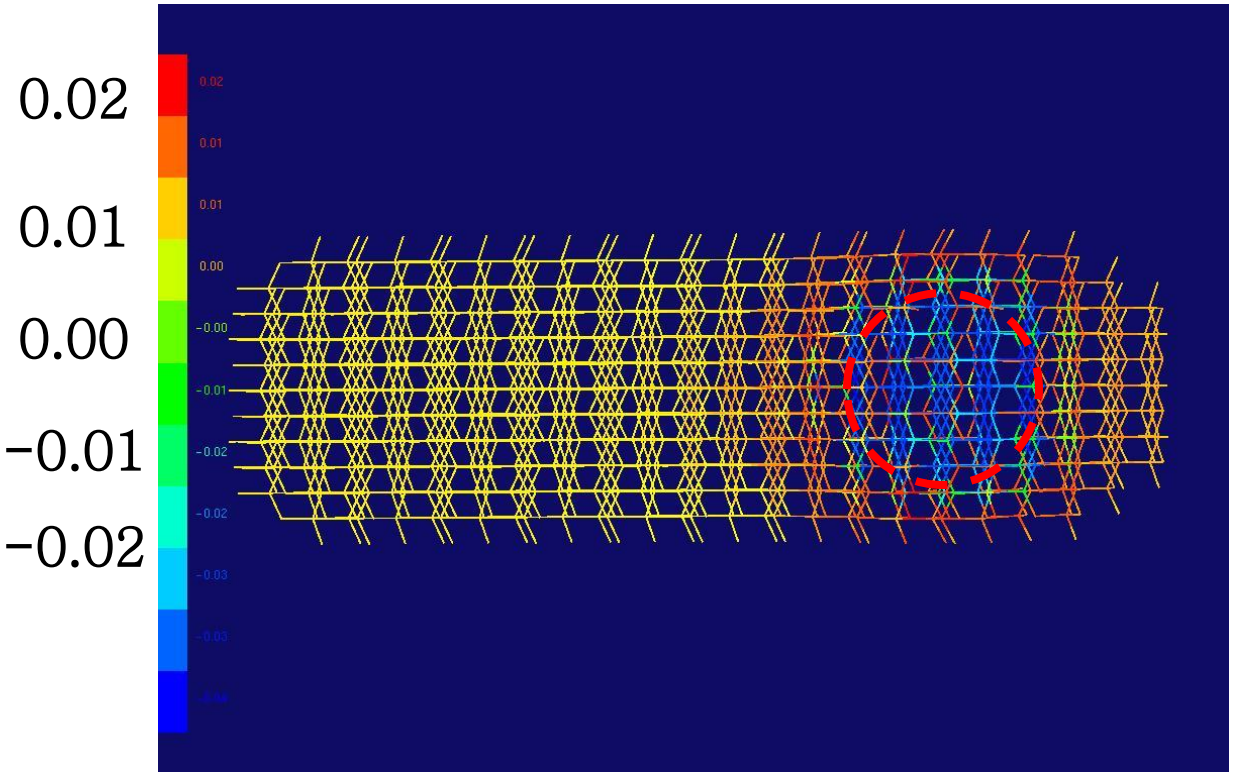
CdSe core inside CdS nanorode

Hydrodynamic strain profile (relaxed using VFF)



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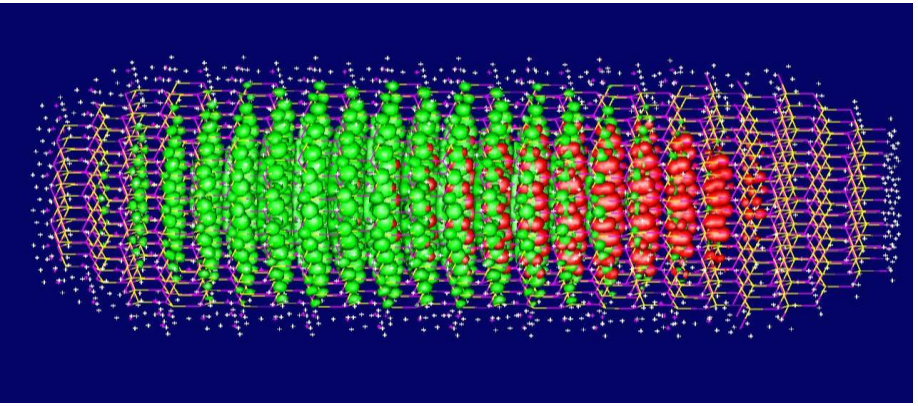
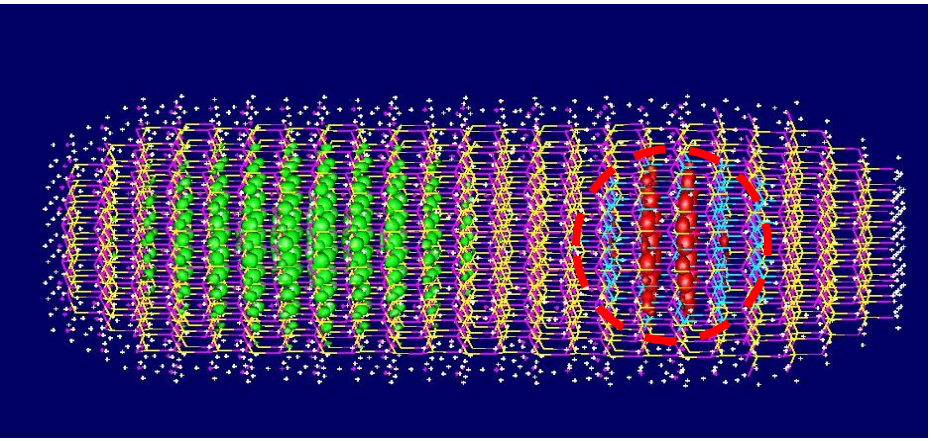
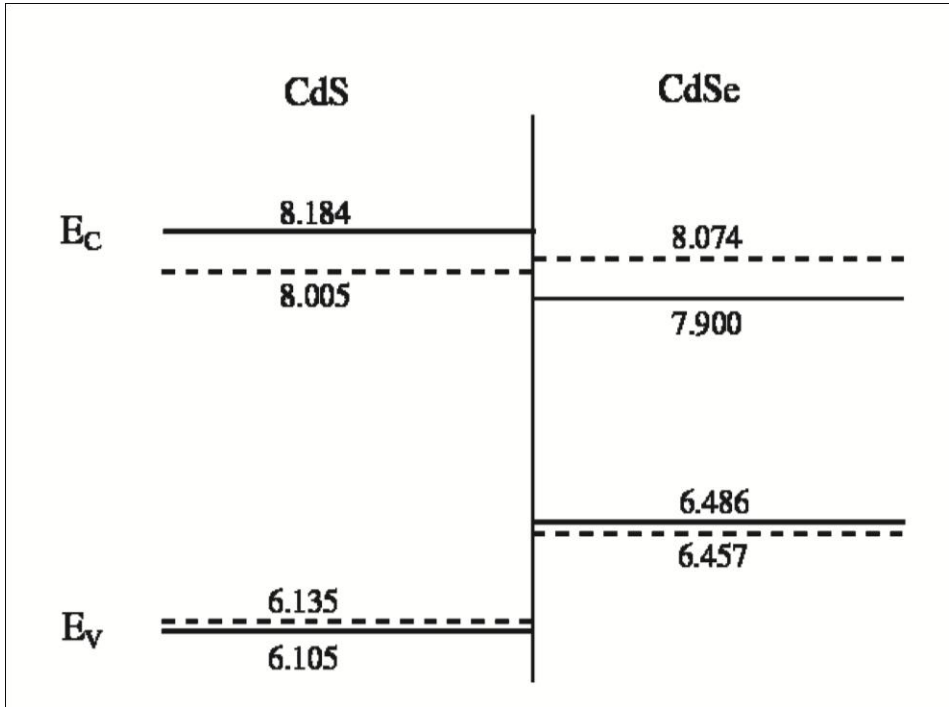
The effect of the CdSe core to electron and hole

Without core



With core





Green: electron, red: hole

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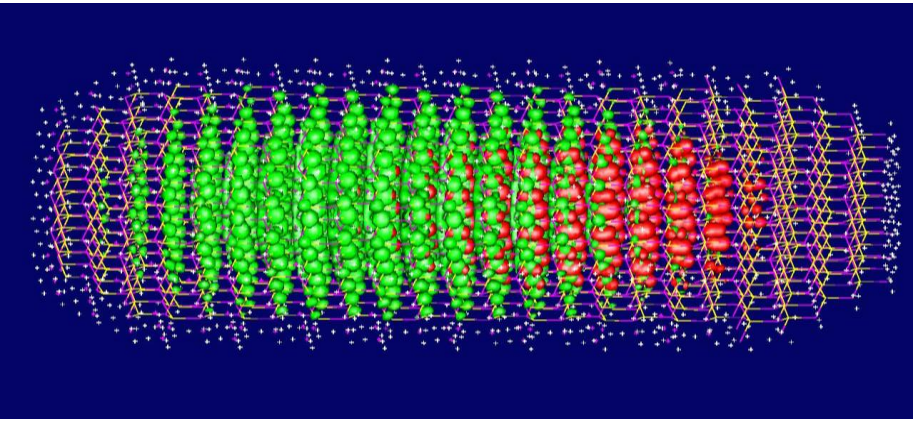
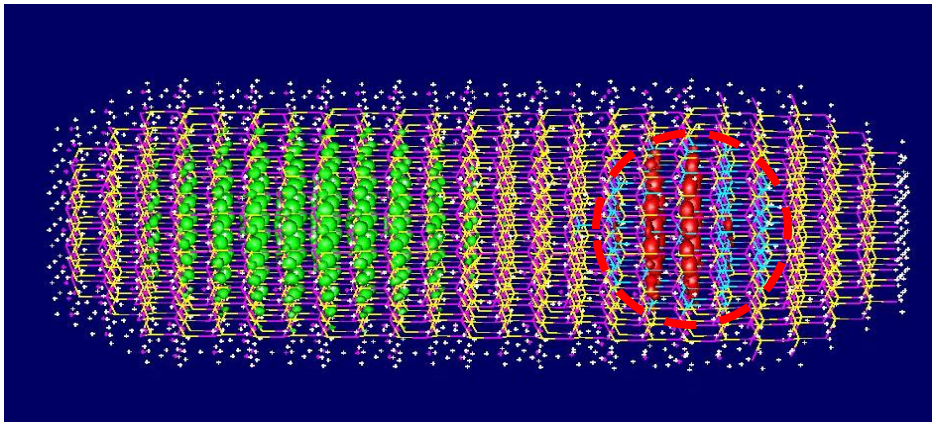
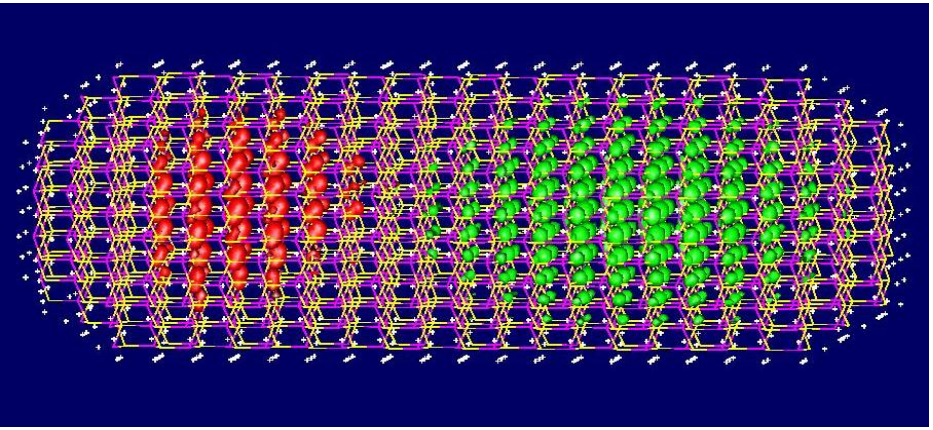
Effect of surface dipole moment

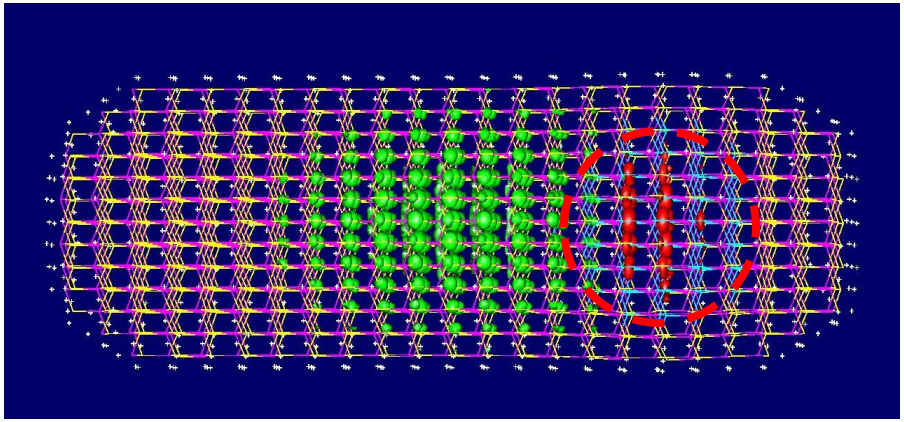
Cd terminated surface





Cd and Se terminated surface





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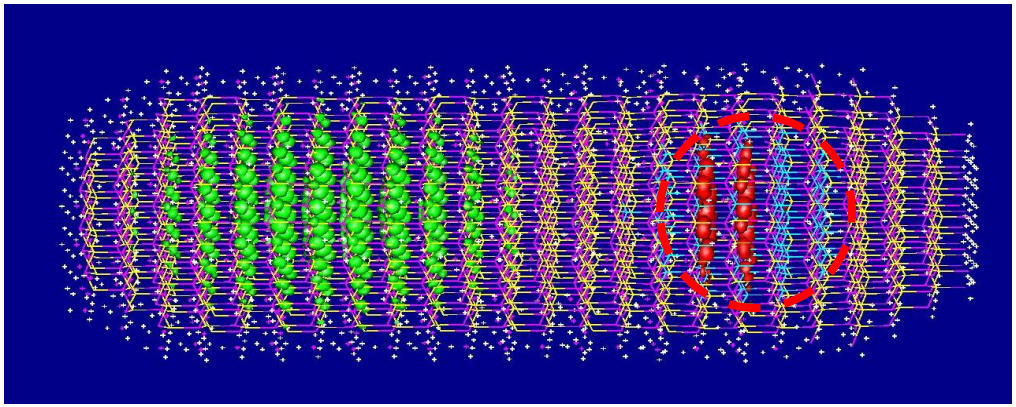
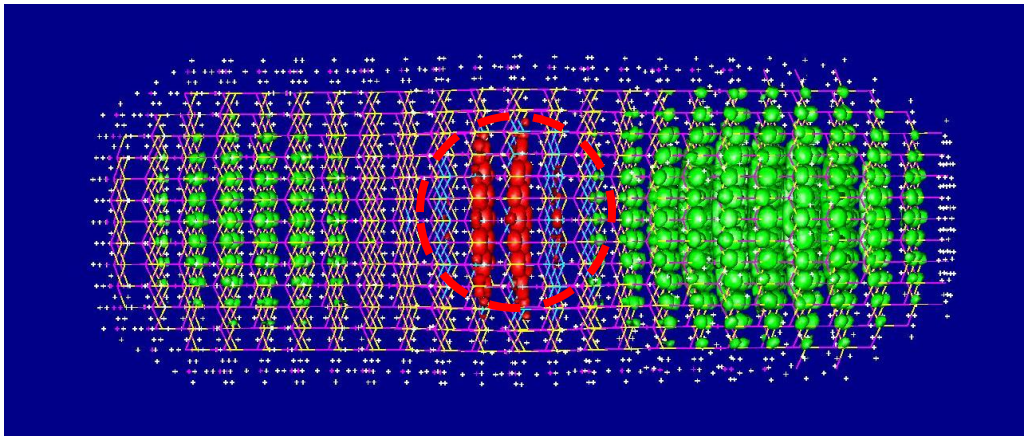
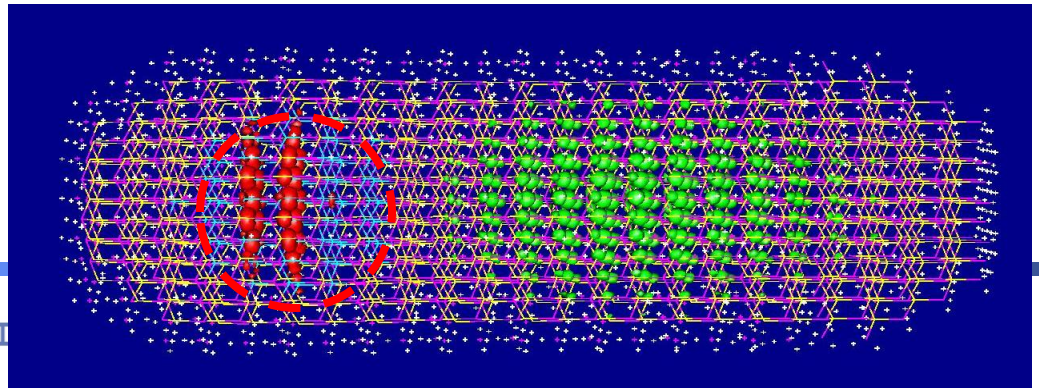
The shift of CdSe core







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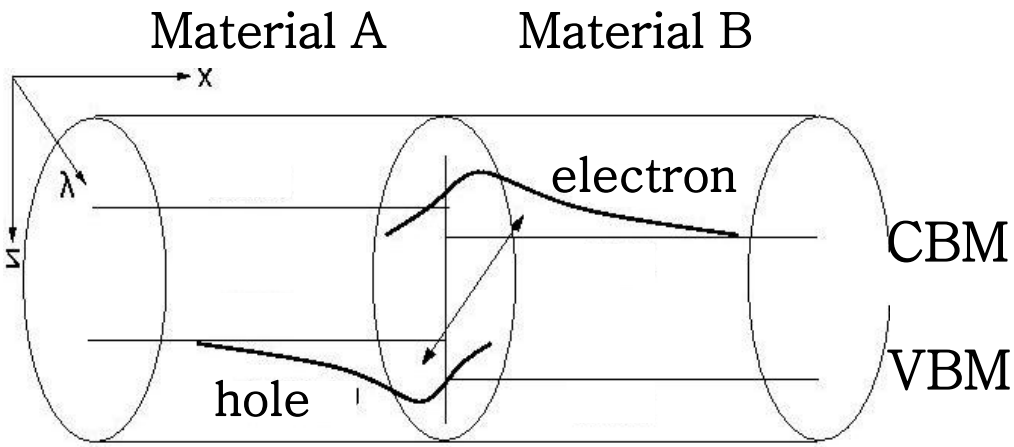
How to calculate an exciton in nanosystem?



What is the binding energy of the interface exciton ?

The approach: GW+ BSE

Approximation: GW → LDA+ C (for bulk short range effect)
P(r) (surface image potential, for long range effe

BSE → CI calculation

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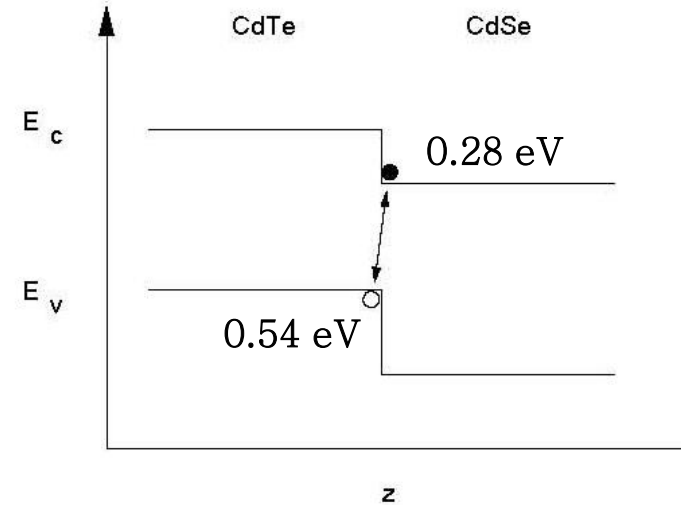
A selfconsistent calculation for a bound exciton

$$\left\{-\frac{1}{2}\nabla^2 + V_{LDA+C}(r) + P(r) - V_v(r)\right\}\psi_c(r) = \varepsilon_c\psi$$

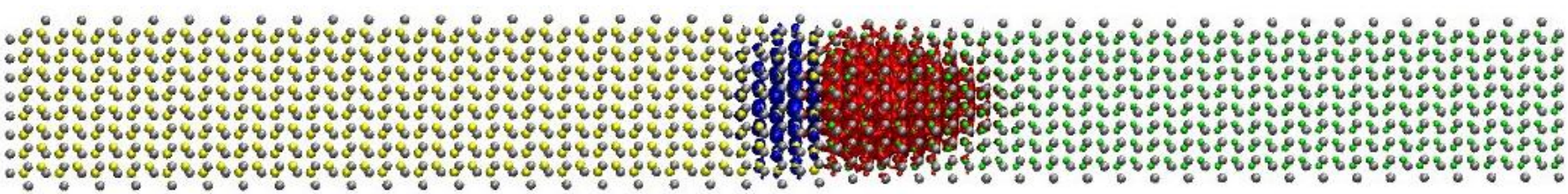
$$\left\{-\frac{1}{2}\nabla^2 + V_{LDA+C}(r) - P(r) + V_c(r)\right\}\psi_v(r) = \varepsilon_v\psi$$

Natural band alignment



$$\nabla[\varepsilon(r)\nabla V_{C(V)}(r)] = 4\pi\psi^2_{V(C)}(r)$$

$$P(r) = \frac{1}{2}\lim_{r'\to r}[W(r,r') - W_{bulk}(r,r')]$$



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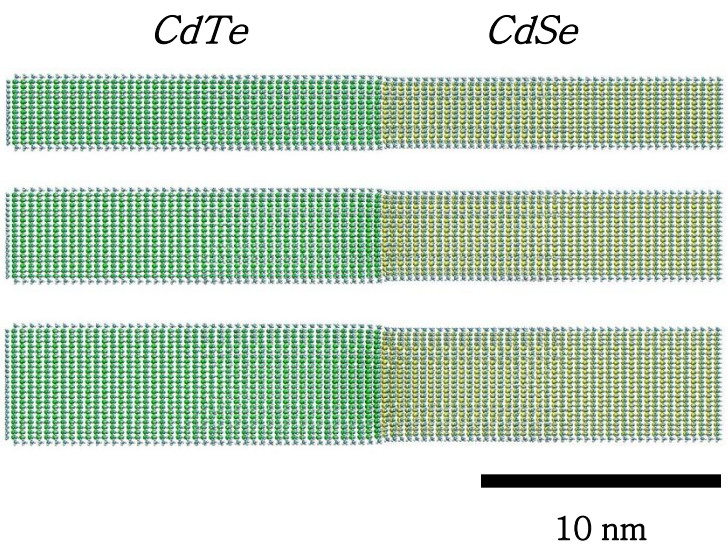
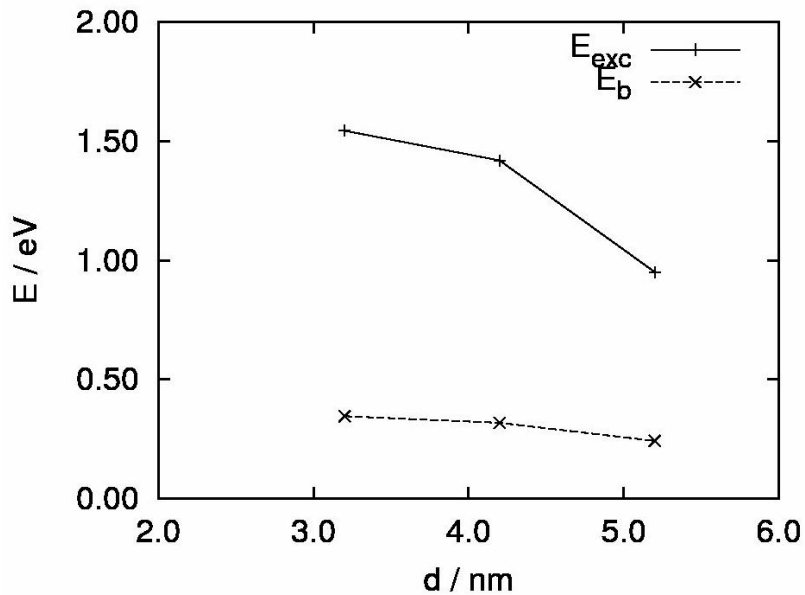
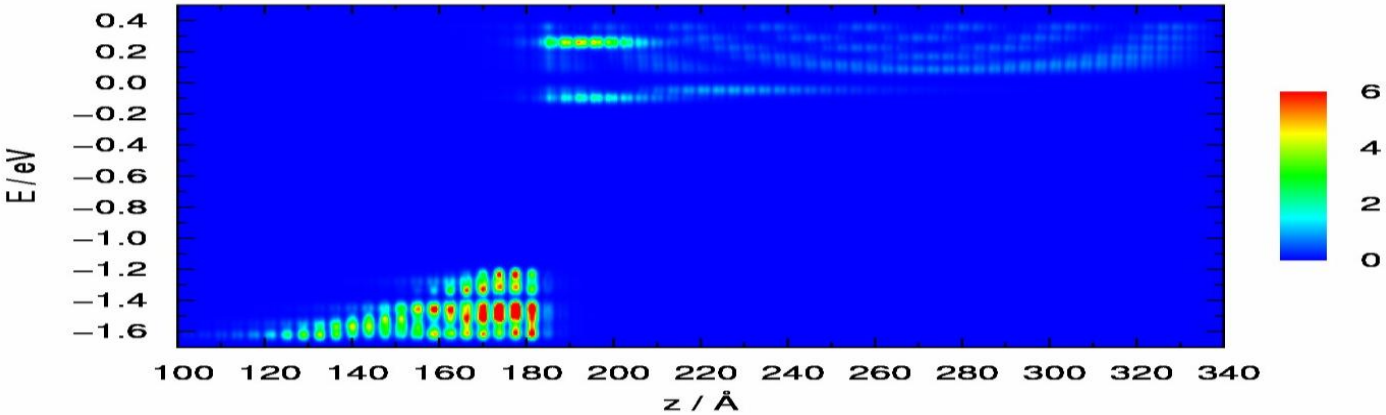
CdSe/CdTe Nanorods





- Exciton binding energy: 0.4 to 0.25 eV
- Exciton radiative recombination life time: ~1 μs
- Correlation effect: < 1 meV for ground exciton state



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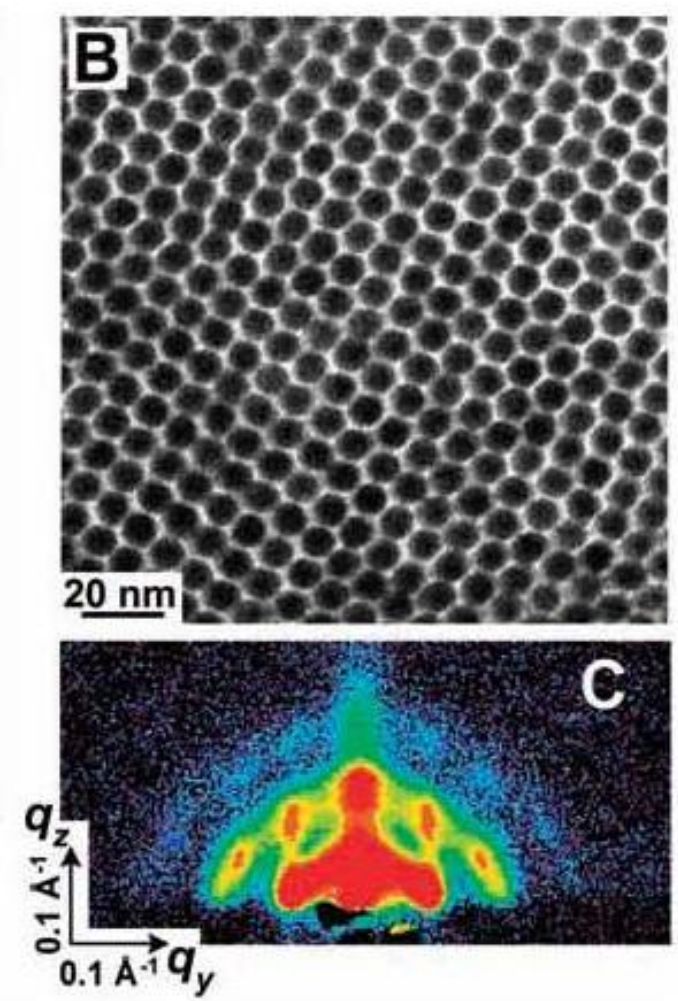
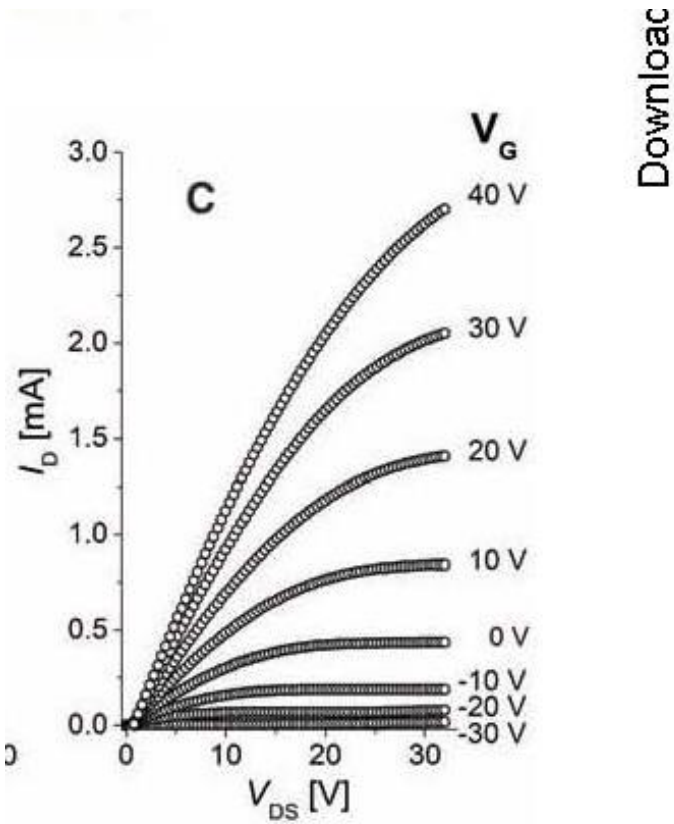
CdSe quantum dot array, connected by Sn_2S_6 molecule



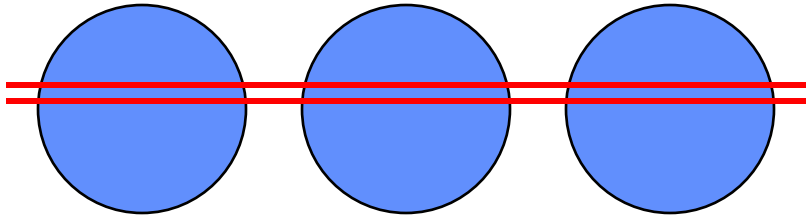


Talapin, et.al, Science (2005);
Kovalenko, et.al, Science (2009).

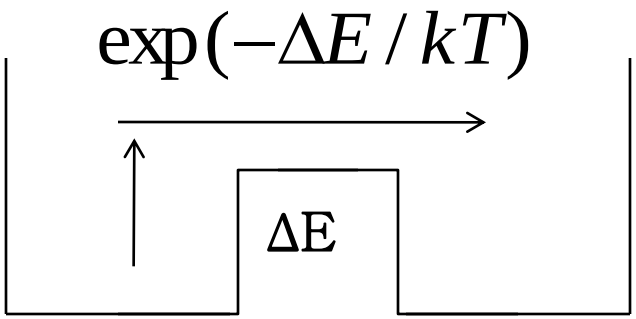
Contact: linwang wang, lwwang@lbl.gov

What cause the electron transport ?

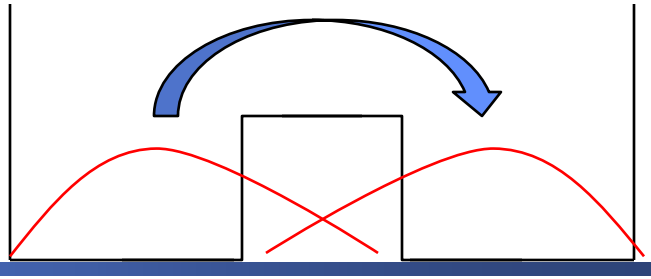
(1) Mini-band bulk like transport:



(2) Thermo activation, over the barrier
(like the Schottky barrier)



(3) Phonon assisted hopping
(e.g., described by Marcus theory)



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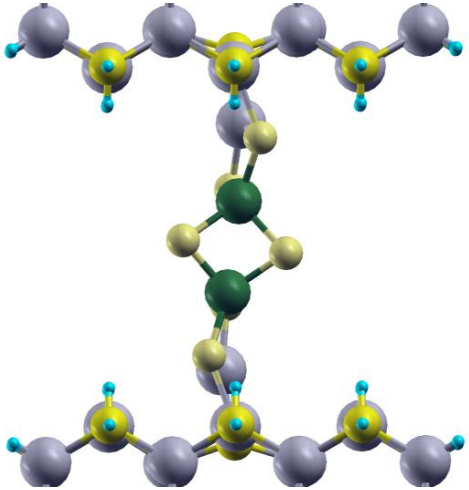
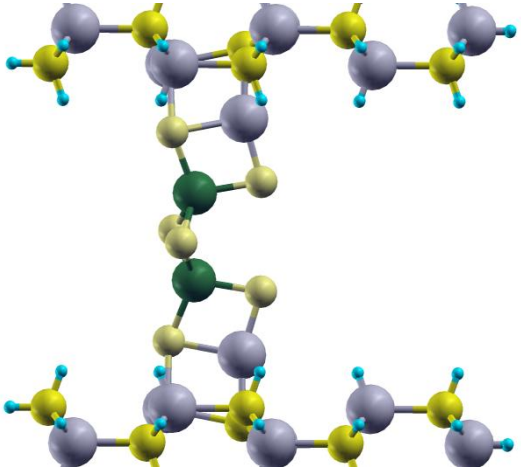
Sn_2S_6 atomic attachment to CdSe surfaces





Flat surface calculation for the molecule attachment

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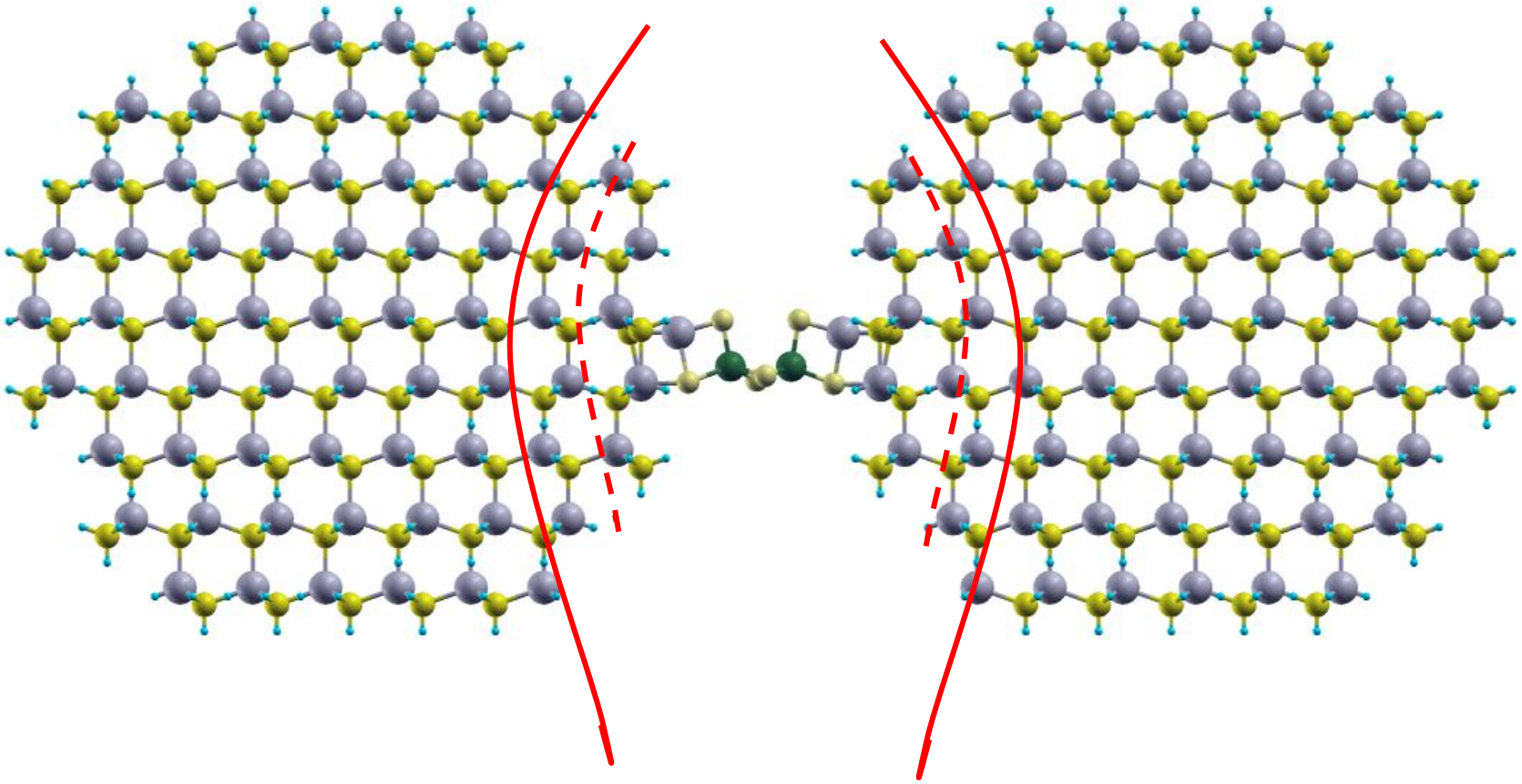
Divide-and-conquer scheme to get the charge density



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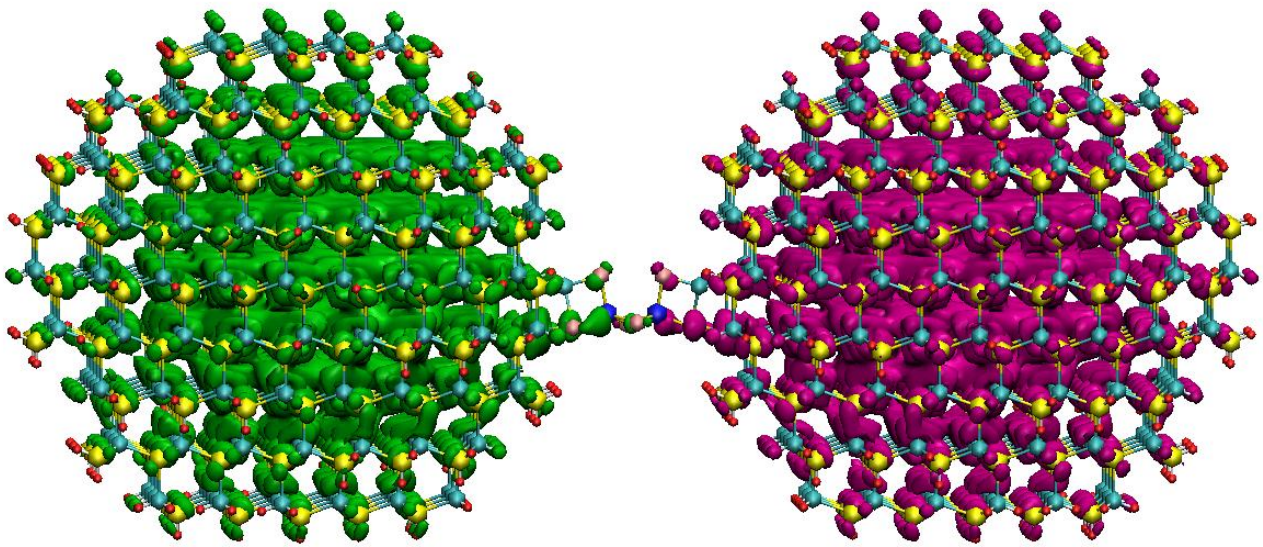
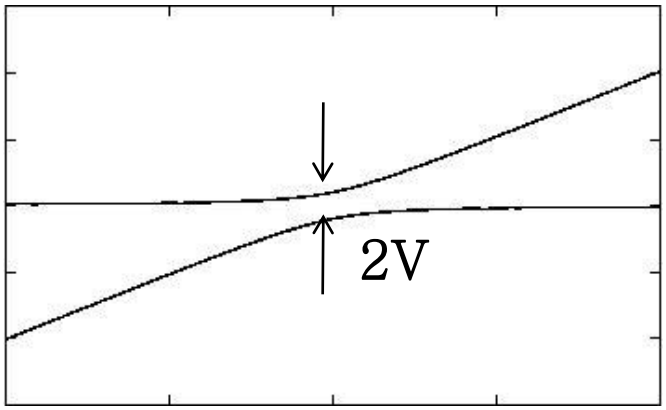
The electron coupling between the two states

CBM



CBM+ 1



Natom	Size D (nm)	V (coupling meV)
468	2.5	4.1
1051	3.4	1.4
1916	4.3	0.37
3193	5.1	0.14

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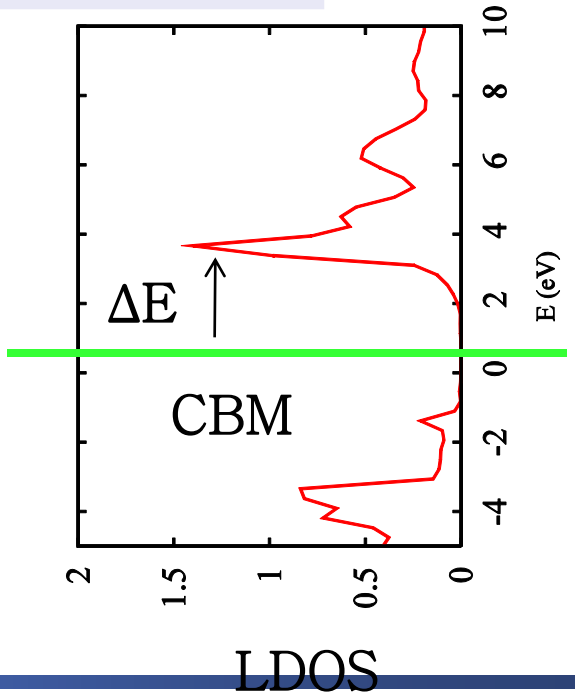
Calculating the re-organization energy

Natom	Size D (nm)	λ (re-org. energy, meV)	V (coupling meV, type I)
468	2.5	145	4.1
1051	3.4	62	1.4
1916	4.3	32	0.37
3193	5.1	23	0.14

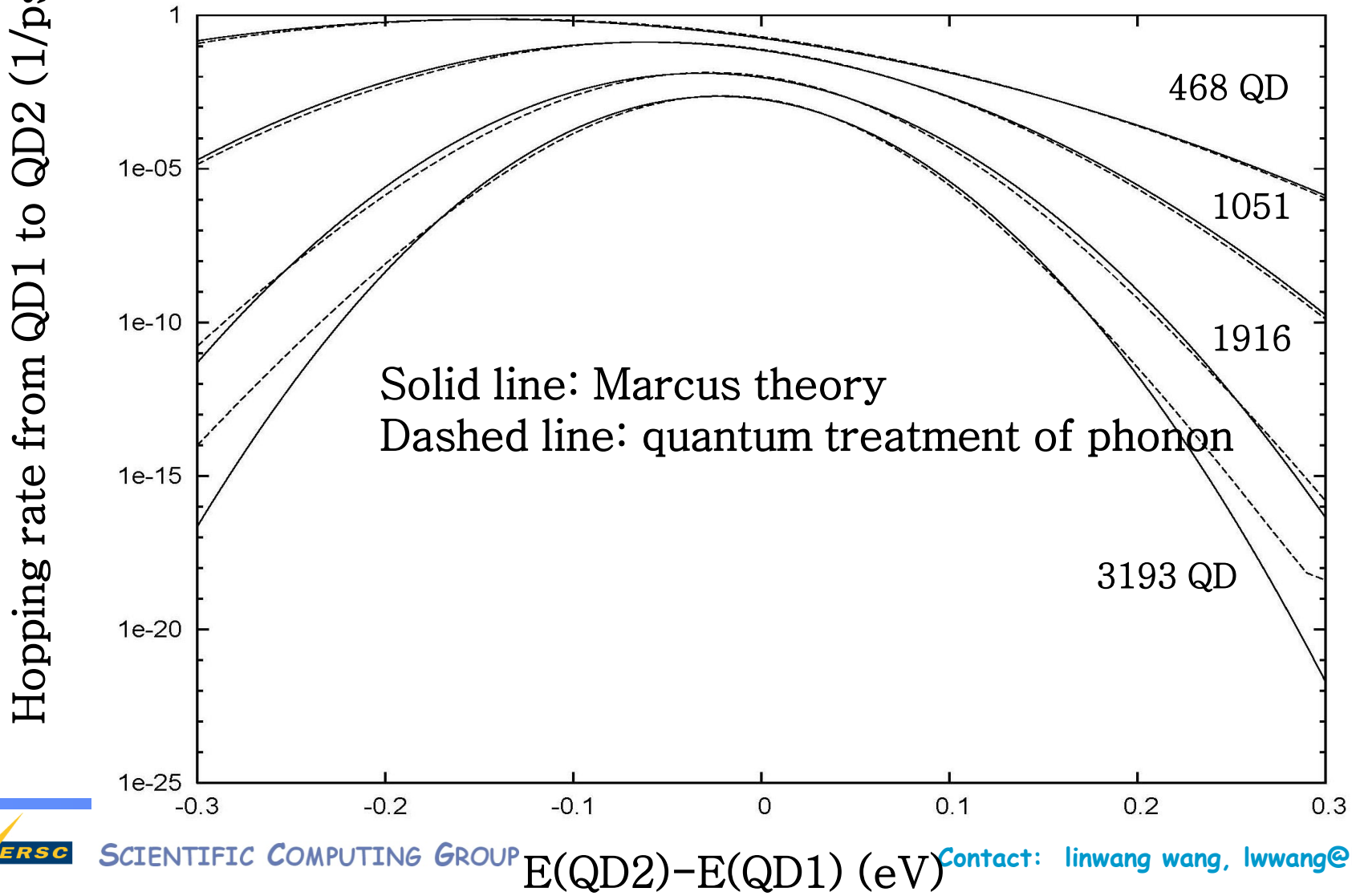
(1) The λ >> V, so the wave function will be localized, it is not mini-band transport

(2) the barrier height ΔE can be ~ 2 eV. It cannot be over-the-barrier thermally excited transport.

(3) Must be phonon-assisted hopping transport



Attachment type I



Contact: linwang wang, lwwang@lbl.gov

Carrier mobility of the QD array in small carrier density limit

Situation (QD cubic array, size=4.3nm)	Type-I attachment Mobility μ ($cm^2/V/S$)
No QD size fluctuation, no connection fluctuation	8.22×10^{-2}
5% QD size fluctuation, no connection fluctuation	4.80×10^{-2}
5% QD size fluctuation, uniform connection fluctuation	1.02×10^{-2}
Experiment, size=4.5nm	3×10^{-2}

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Why are quantum mechanical calculations so expensive?

$$[-\frac{1}{2}\nabla^2 + V_{tot}(r)+]\psi_i(r) = \varepsilon_i \psi_i(r)$$

- If the size of the system is *N*:
- *N* coefficients to describe one wavefunction $\psi_i(r)$
- *i* = 1,…, *M* wavefunctions $\psi_i(r)$, *M* is proportional to *N*.
- Orthogonalization: M^2 wavefunction pairs $\int \psi_i(r)\psi_j^*(r)d^3r$ each with *N* coefficients: $N*M^2$, i.e N^3 scaling.

The repeated calculation of these orthogonal wavefunctions make the computation expensive, $O(N^3)$. For large systems, an $O(N)$ method is critical

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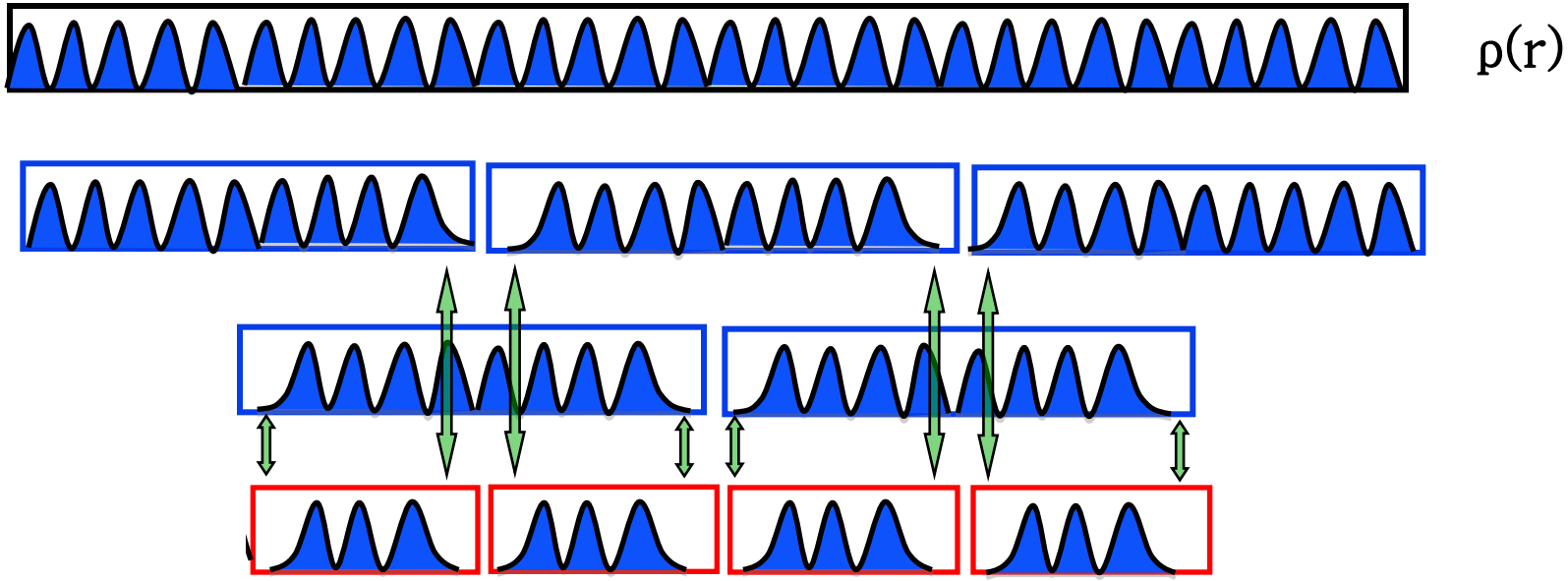
LS3DF: 1D Example



Total = Σ_F { $_F$ − $_F$ }

Phys. Rev. B 77, 165113 (2008); J. Phys: Cond. Matt. 20, 294203 (2008)

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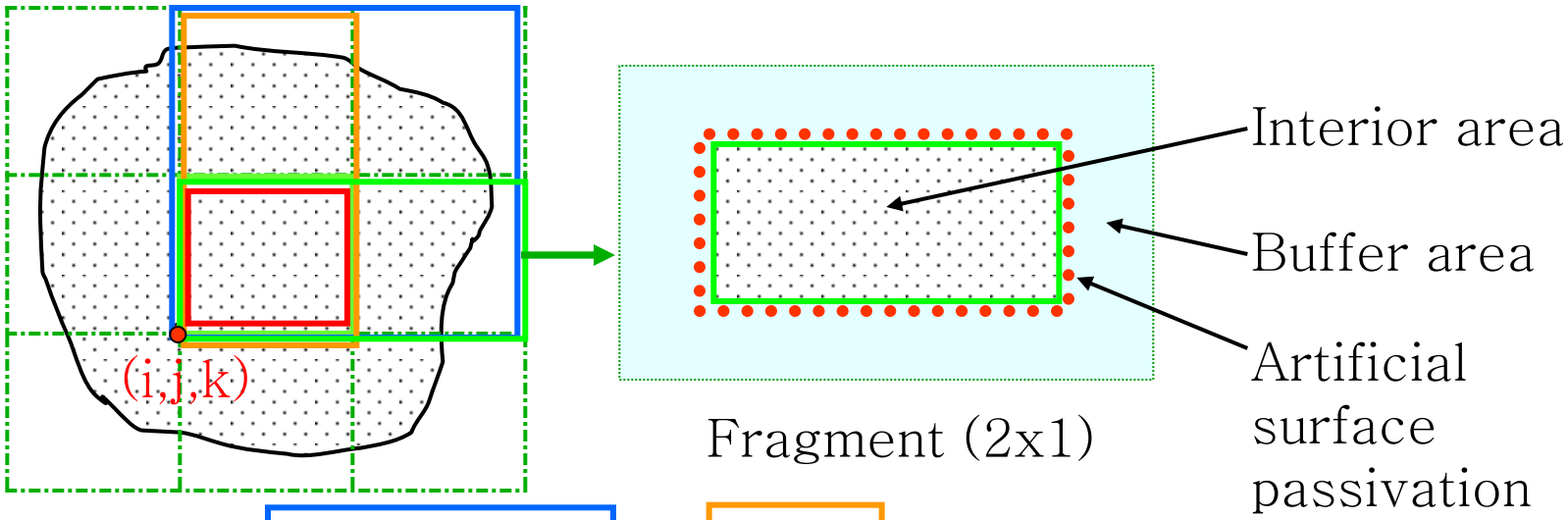
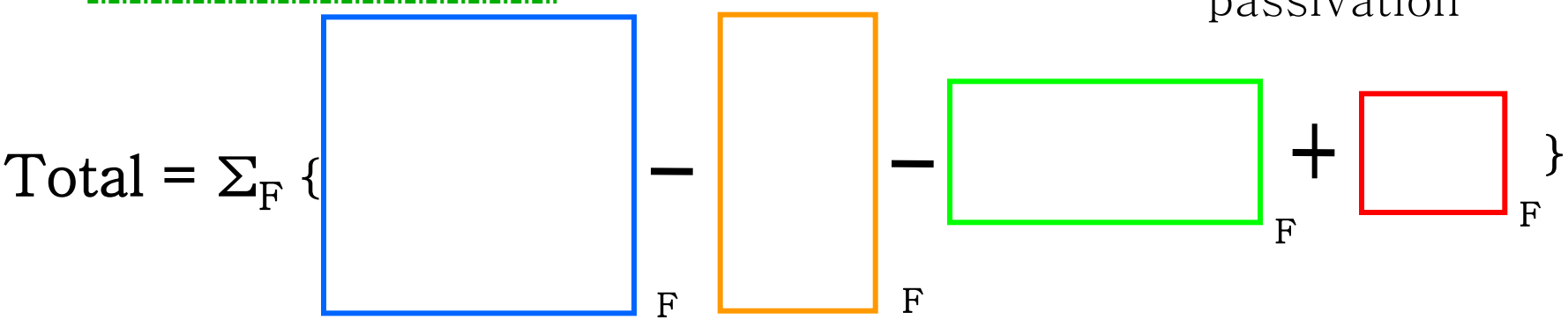
Similar procedure extends to 2 and 3D





Boundary effects are (nearly) cancelled out between the fragments

$$System = \sum_{i,j,k} \{F_{222} + F_{211} + F_{121} + F_{112} - F_{221} - F_{212} - F_{122} - F_{111}\}$$

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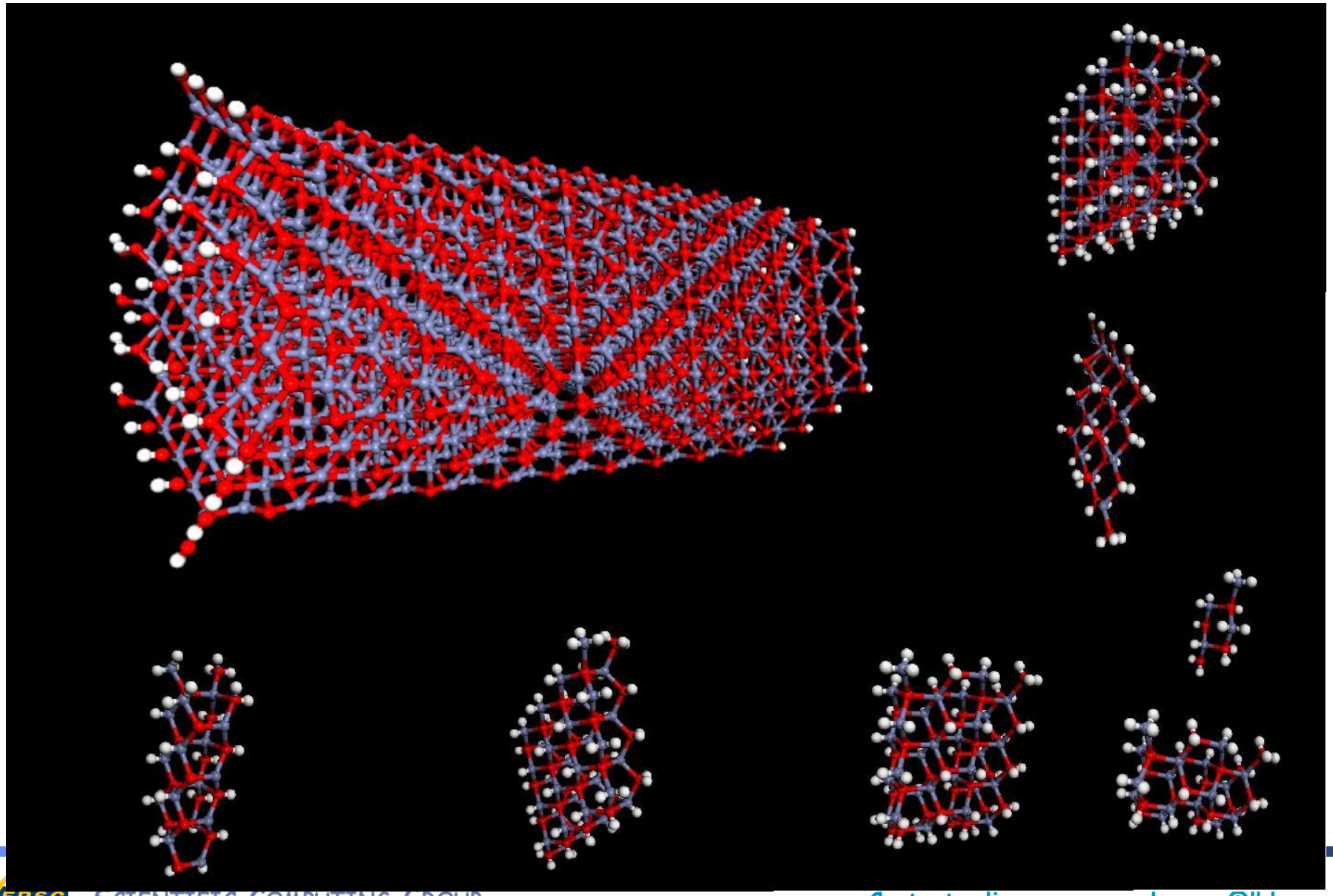
A example of the global system and the fragments



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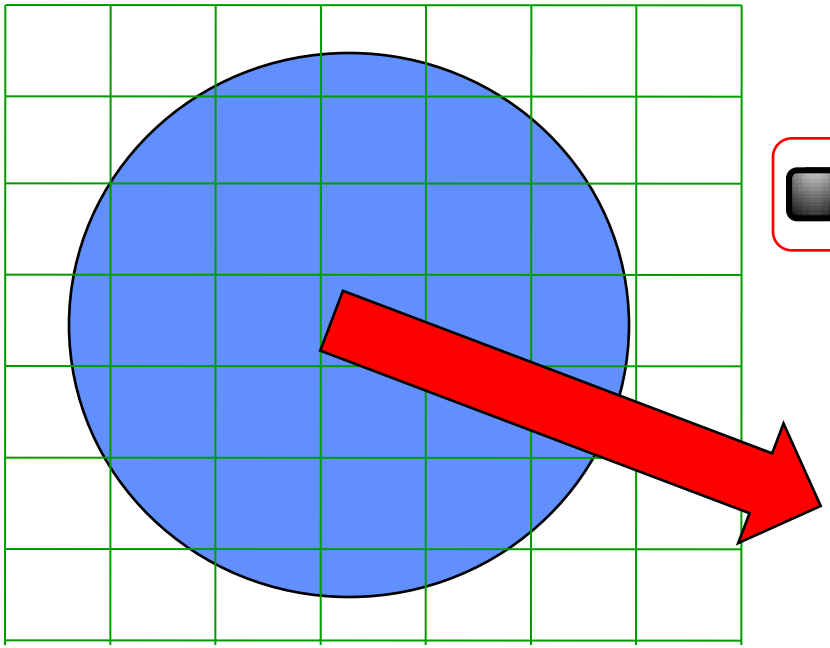
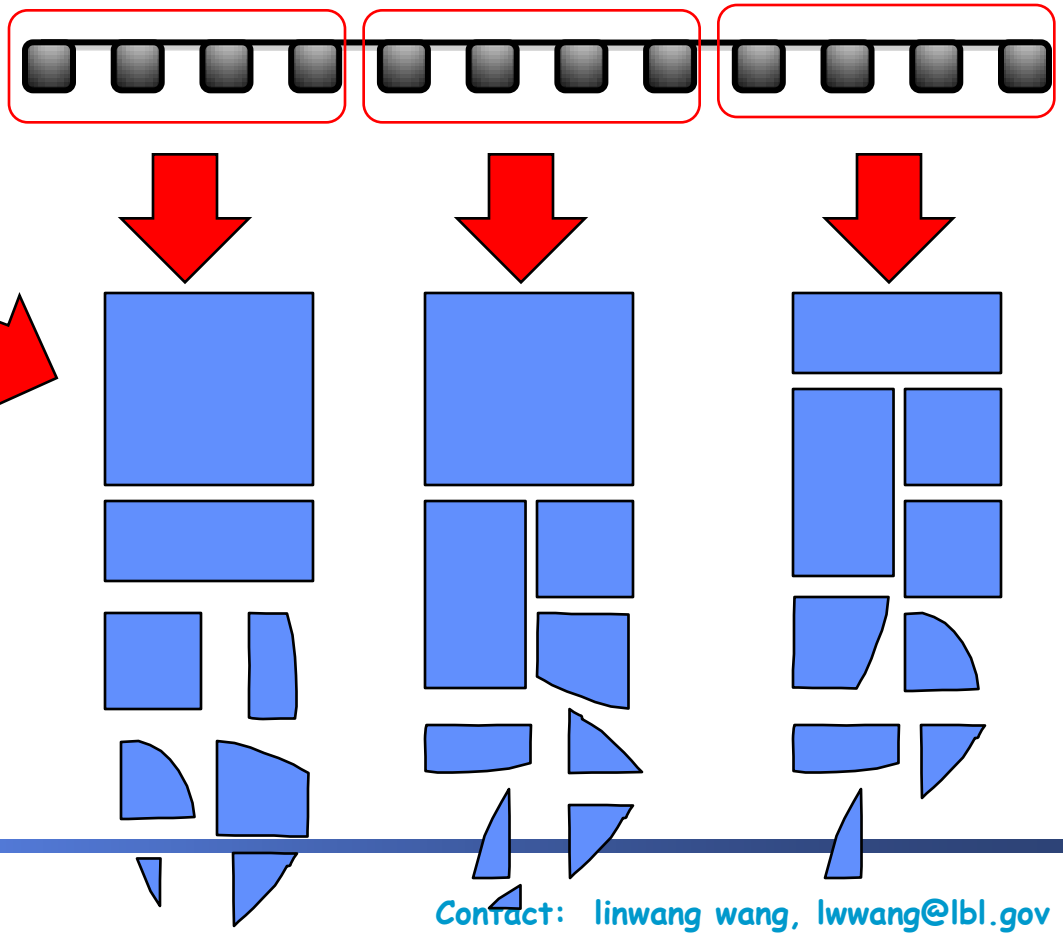
Schematics for LS3DF calculation





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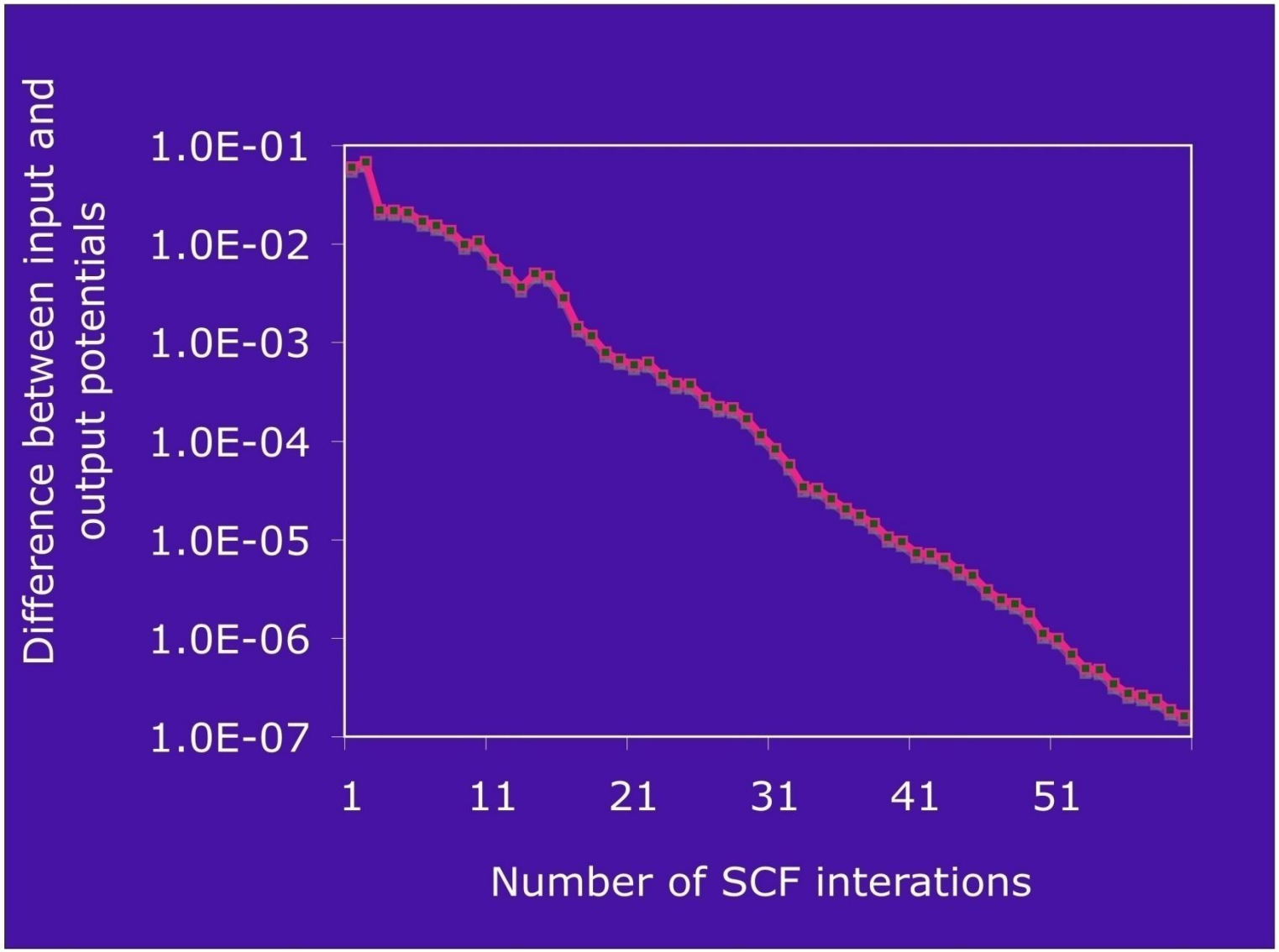
No selfconsistent problem for the global system



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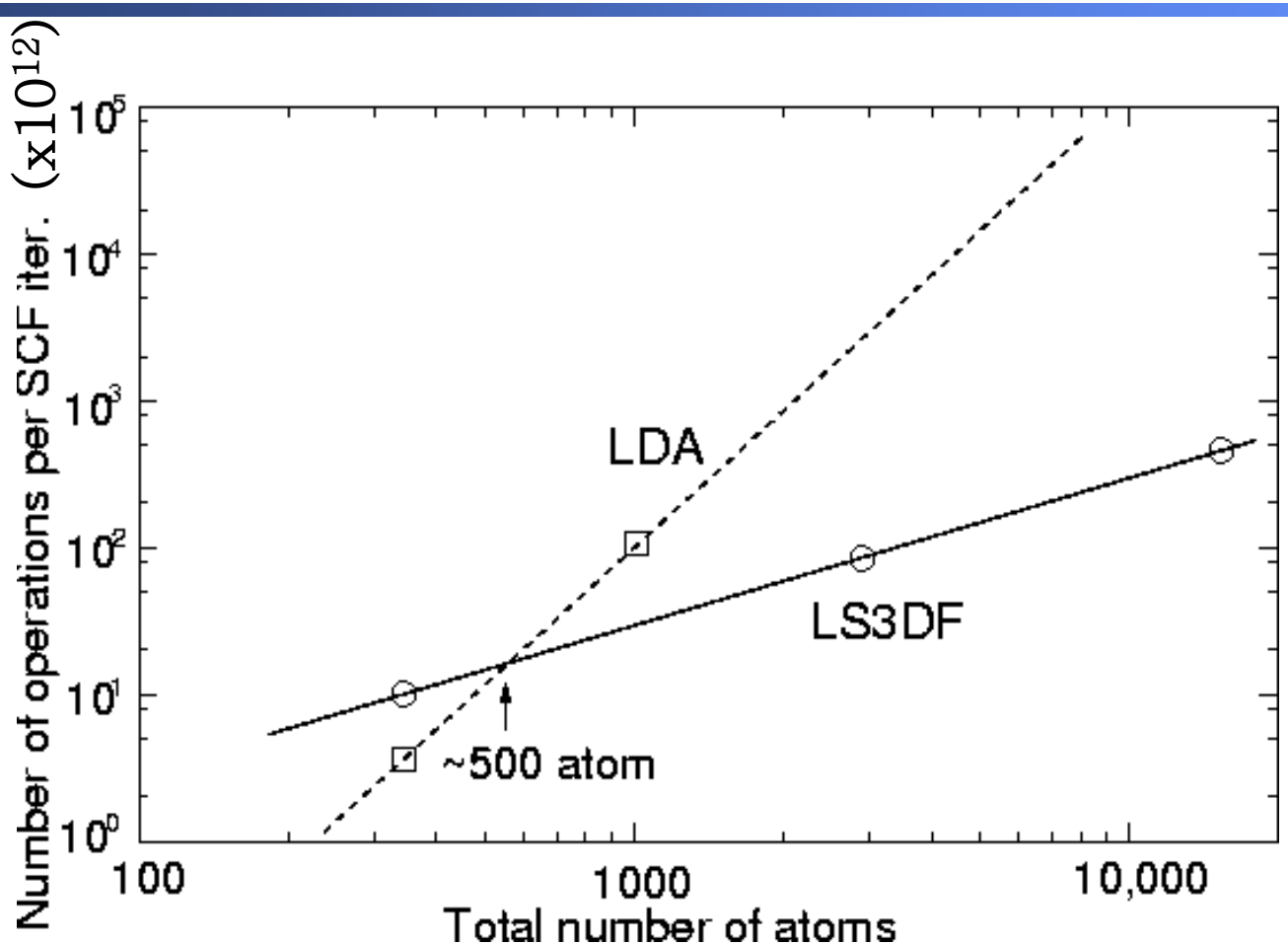
Operation counts



- Cross over with direct LDA method [PEtot] is 500 atoms.
- Similar to other *O(N)* methods.

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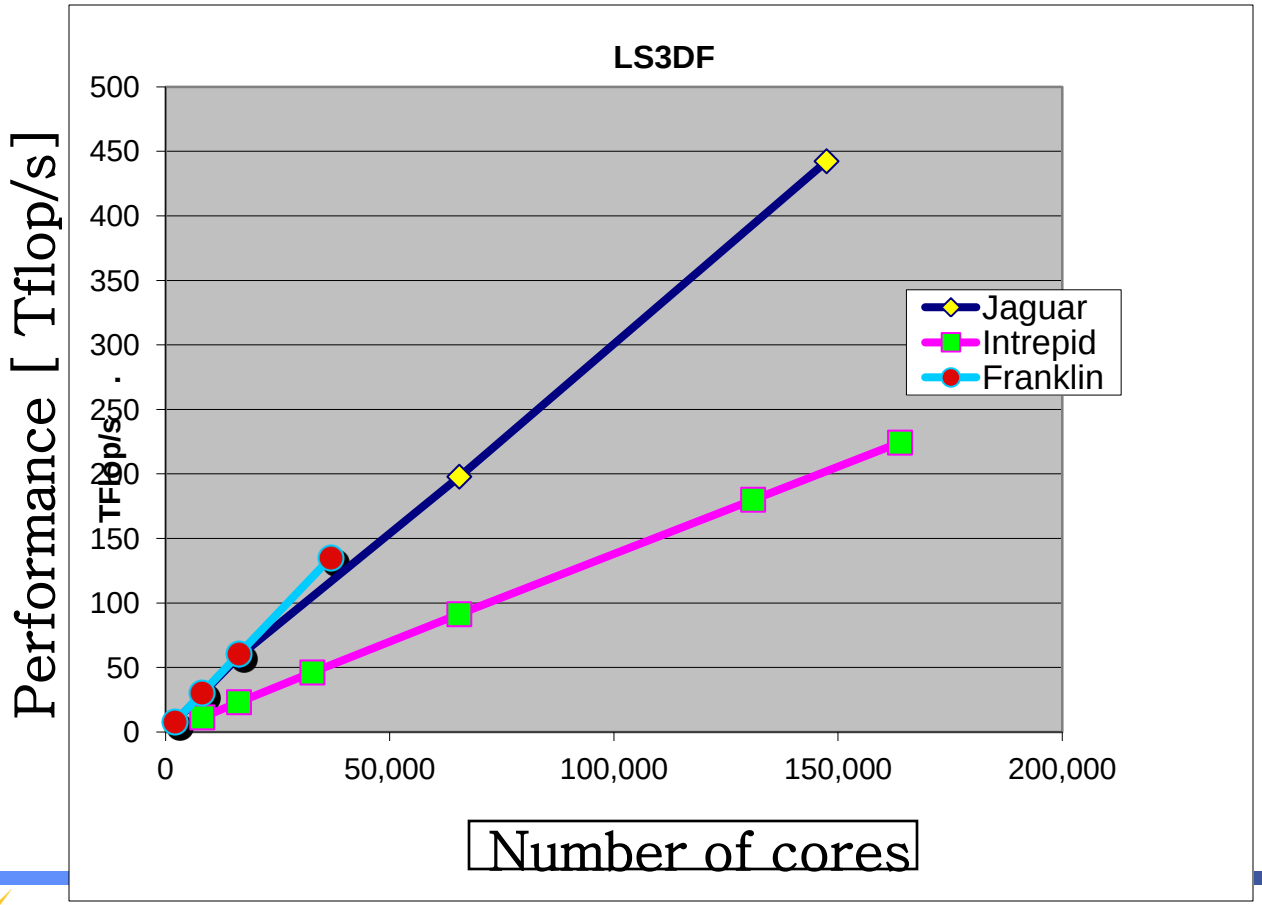
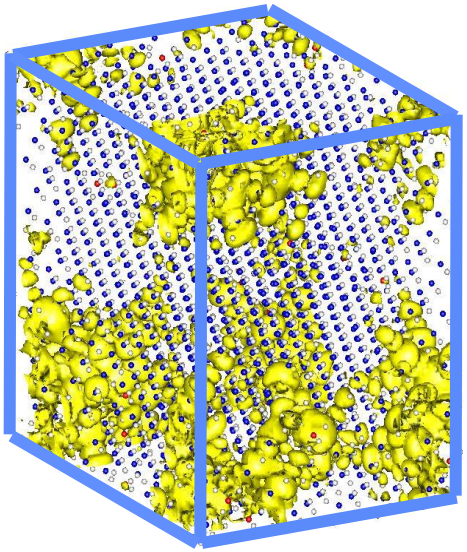
ZnTeO alloy weak scaling calculations

- First large scale run on Franklin at NERSC: 135 Tflops/s, 40% efficiency
- Subsequent runs on Intrepid at ALCF: 224 Tflops/s, 40% efficiency
- Final runs on Jaguar XT5 at NCCS: 442 Tflops/s, 33% efficiency





Note: Ecut = 60Ryd with *d* states, up to 36864 atoms

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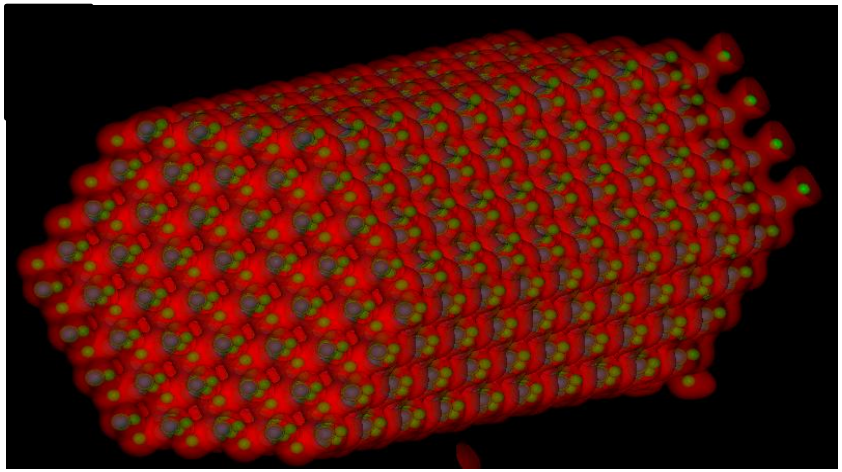
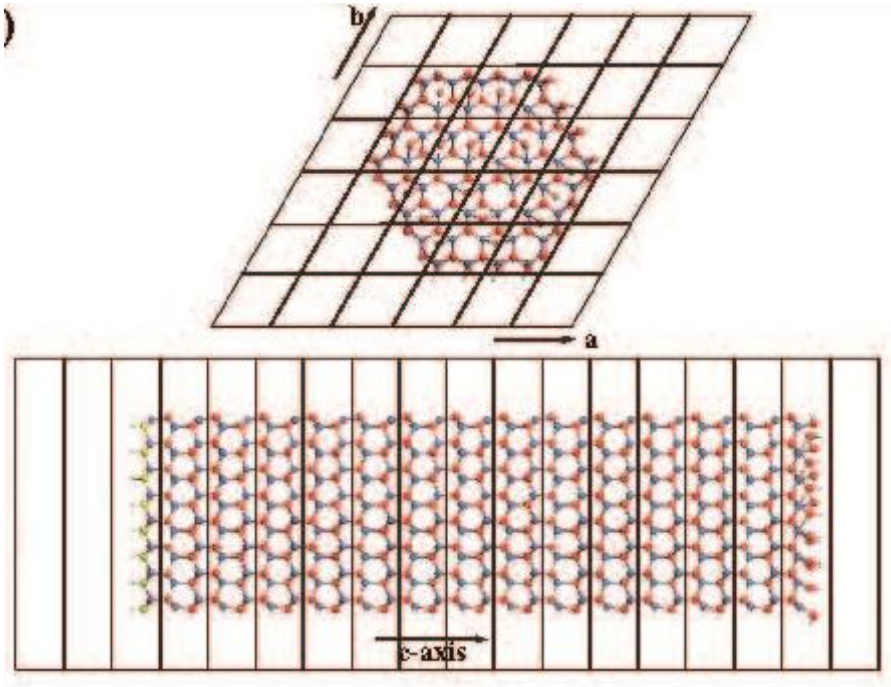
A more detail example of the ZnO nanorod system





Num atom: 2776
Num electron: 24220
Real space grid: 720x300x300
Fragment dividing grid: 18x6x6

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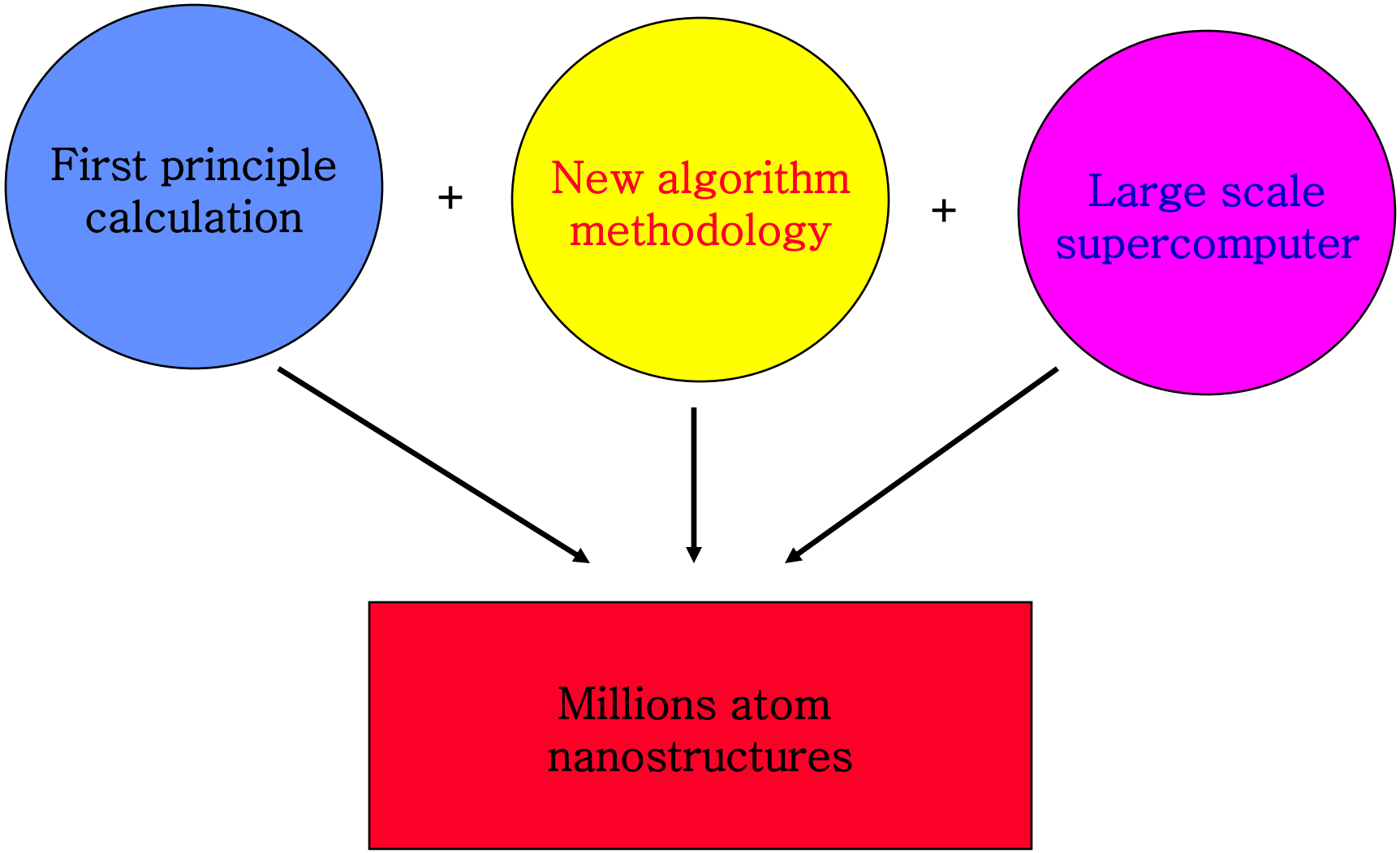
Conclusion



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