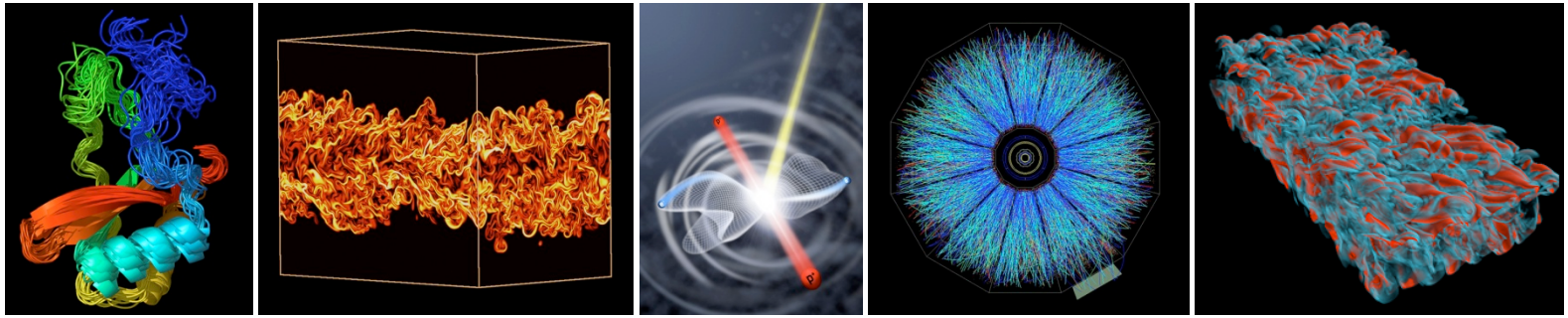

Applications of the LS3DF method in CdSe/CdS core/shell nano structures

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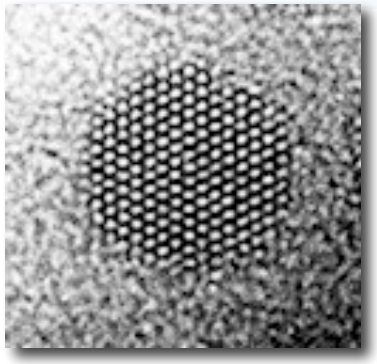
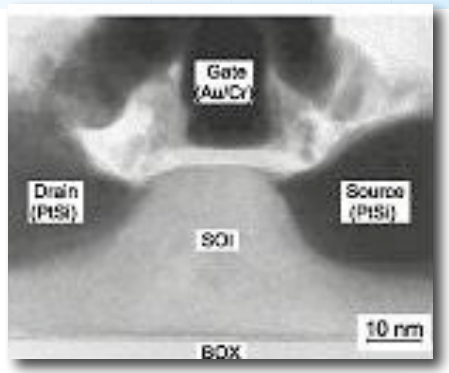
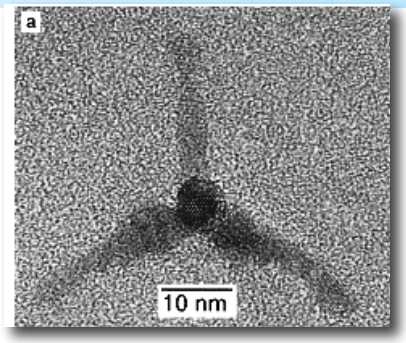
[1]National Energy Research Scientific Computing Center (NERSC)
[2]Computational Research Division
Lawrence Berkeley National Laboratory

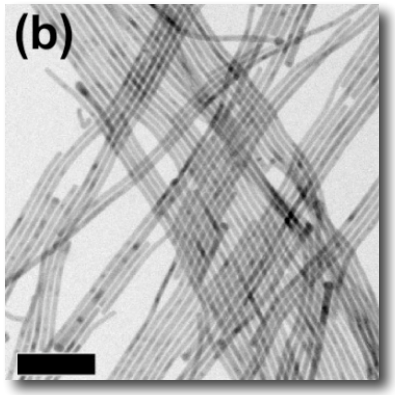
(LS3DF: Linearly Scaling 3 Dimensional Fragment)

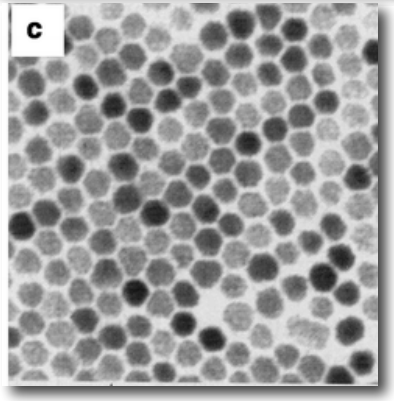
Nanostructures have wide applications including: solar cells, biological tags, electronics devices

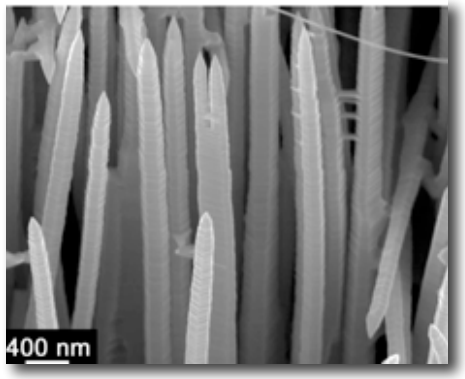












- Different electronic structures than bulk materials
- 1,000 ~ 100,000 atom systems are too large for direct $O(N^3)$ *ab initio* calculations, N is the size of the system
- $O(N)$ computational methods are required
- Parallel supercomputers are critical for solving these systems

Density functional theory (DFT) and local density approximation (LDA)

Kohn-Sham equation

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

Where, $\int \psi_i(r)\psi_j^*(r)d^3r = \delta_{ij}$, $i=1,\ldots,M$

Potential $V_{tot}(r)$ is a functional of $\rho(r)$, $\rho(r) = \sum_{i=1}^{M} |\psi_i(r)|^2\, dr$

- 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 algorithm scales to $N*M^2 \propto O(N^3)$

The repeated calculation of these orthogonal wave functions make the computation expensive, *O(N³)*. For large systems, an *O(N)* method is critical.

Previous Work on Linear Scaling DFT methods

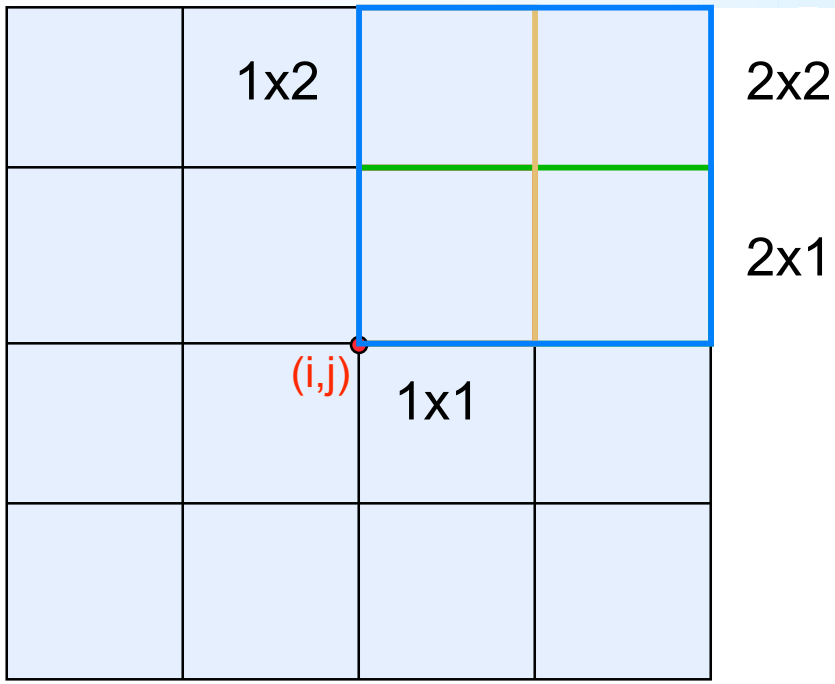
- Three main approaches:
  - Localized orbital method
  - Truncated density matrix method
  - Divide-and-conquer method
- Some widely codes:
  - Parallel SIESTA (atomic orbitals, not for large parallelization)
  - Many quantum chemistry codes (truncated D-matrix, Gaussian basis, not for large parallelization)
  - ONETEP (M. Payne, PW to local orbitals, then truncated D-matrix)
  - CONQUEST (D. Bowler, UCL, localized orbital)
- Most of these use localized orbital or truncated-D matrix
- Challenge: scale to large number of processors (tens of thousand).

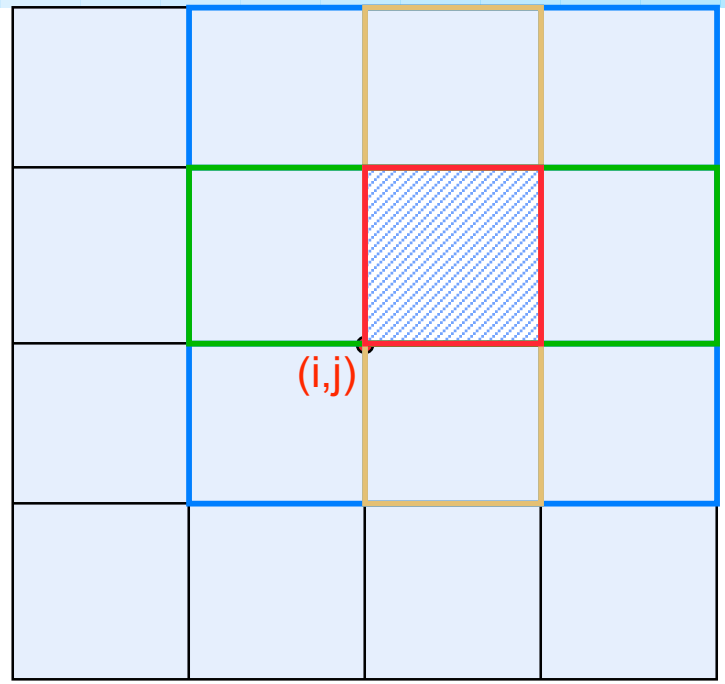
Linearly Scaling 3 Dimensional Fragment method (LS3DF)

- Main idea: divide and conquer
  - Quantum energy is near sighted, it can be solved locally. => Cut the system to small pieces, solve each piece separately, then put them together.
  - Classical energy is long ranged, it has to be solved globally => Solve Poisson equation for the whole system.
- Heart of the method: the novel patching scheme
  - Uses overlapping positive and negative fragments
  - Minimizes artificial boundary effects

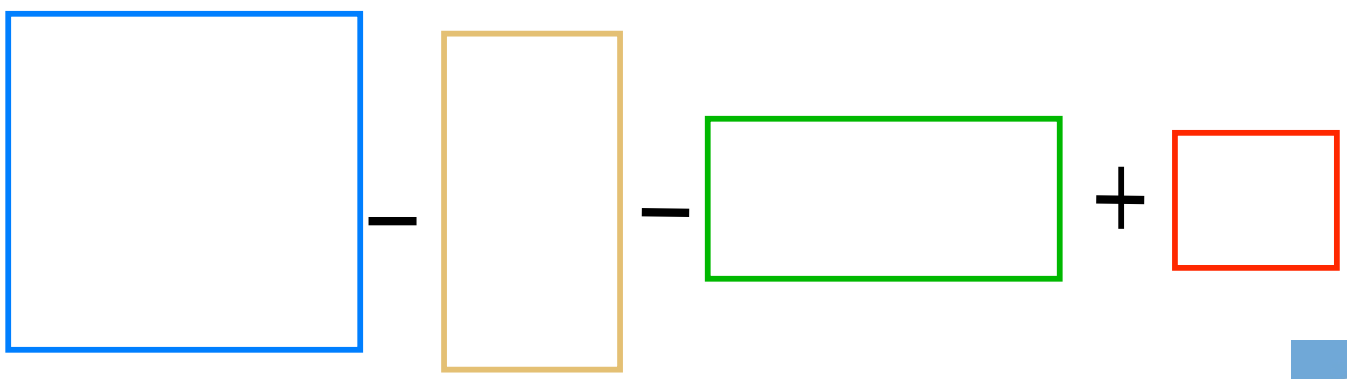
LS3DF method → **O(N) scaling**
Massively parallelizable
Highly accurate

LS3DF patching scheme: 2D Example





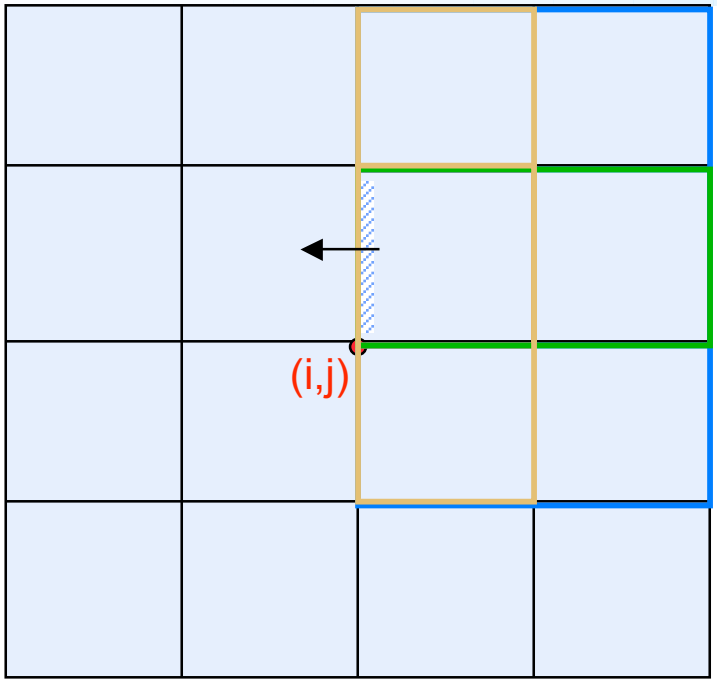
Total = Σ {
(i,j)

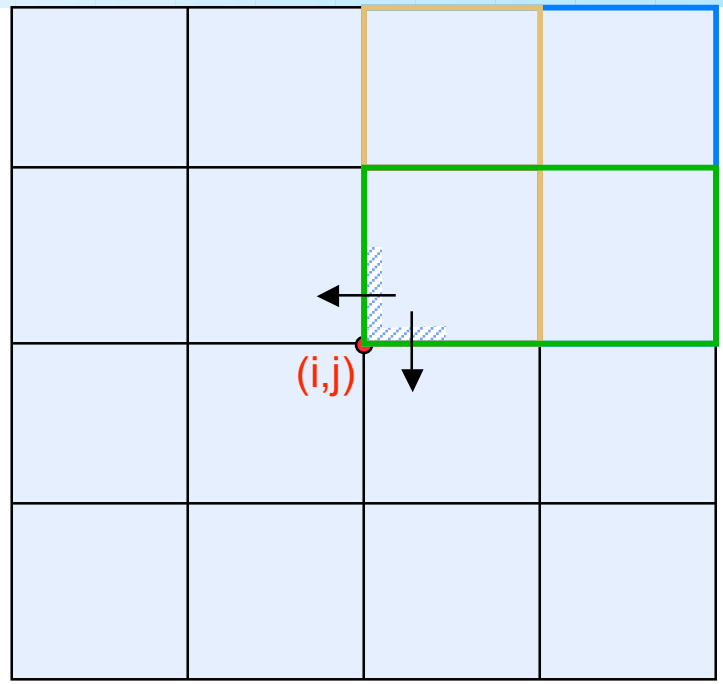


}

Boundary effects are (nearly) cancelled out

LS3DF patching scheme: 2D example



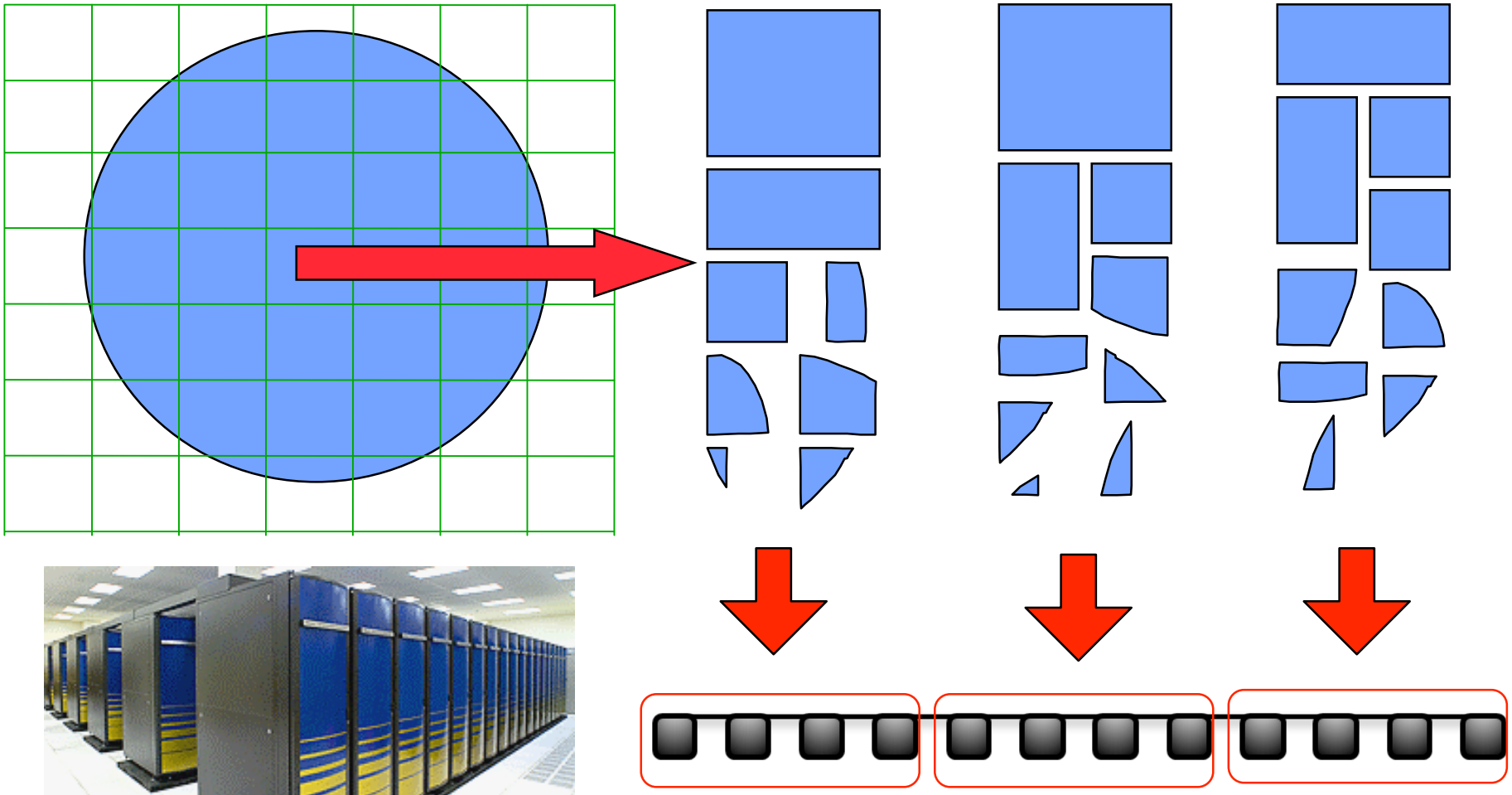


Patching scheme is similar for 3D:

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

Ref. [1] Lin-Wang Wang, Zhengji Zhao, and Juan Meza, Phys. Rev. B 77, 165113 (2008);
Ref. [2] Zhengji Zhao, Juan Meza, Lin-Wang Wang, J. Phys: Cond. Matt. 20, 294203 (2008)

Schematic for LS3DF calculation



Formalism of LS3DF

❖ **Kohn-Sham equation of original DFT (*O(N³)*):**

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

❖ **Kohn-Sham equation of LS3DF :**

$$[-\frac{1}{2}\nabla^2 + V_{tot}(r) + \Delta V_F(r)]\psi_{F,i}(r) = \varepsilon_{F,i}\psi_{F,i}(r) \quad \text{for } r \in \Omega_F$$

Where, $V_{tot}(r)$: **usual LDA total potential calculated from** $\rho_{tot}(r)$

$\Delta V_F(r)$: **surface passivation potential**

Overview of computational effort in LS3DF

- Most time consuming part of LS3DF calculation is for the fragment wavefunctions
  - Modified from the stand alone PEtot code (Ref. [3])
  - Uses planewave pseudopotential (like VASP, Qbox)
  - All-band algorithm takes advantage of BLAS3

- 2-level parallelization:
  - q-space (Fourier space)
  - band index (*i* in $\psi_i(r)$)

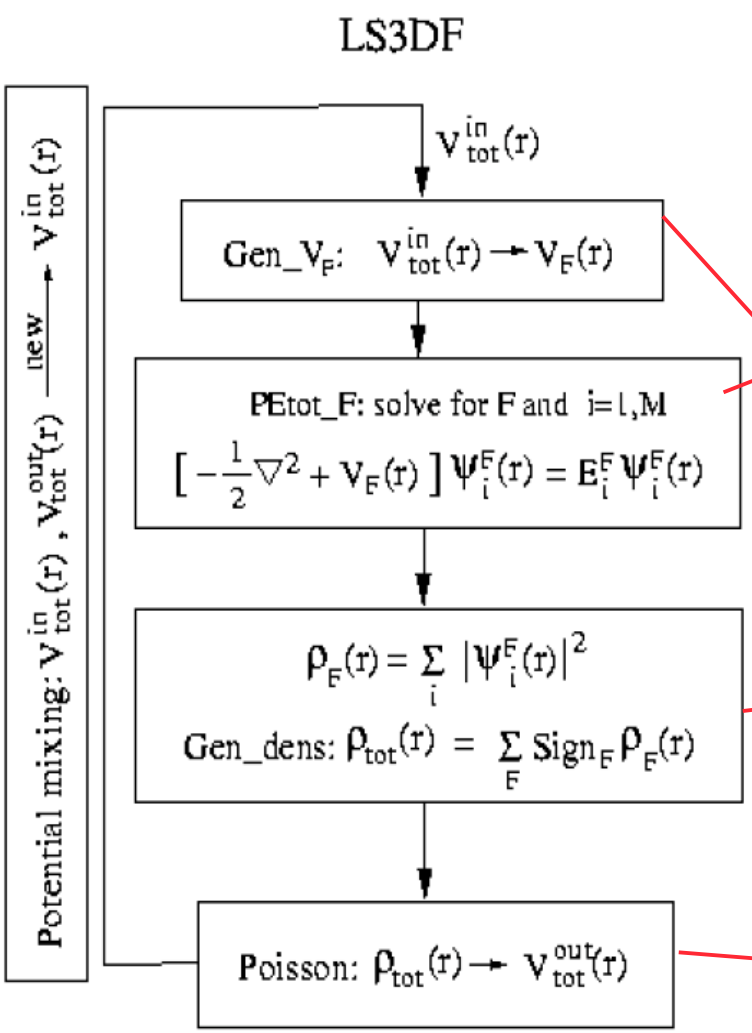
- PEtot efficiency > 50% for large systems (e.g, more than 500 atoms), 30-40% for our fragments.

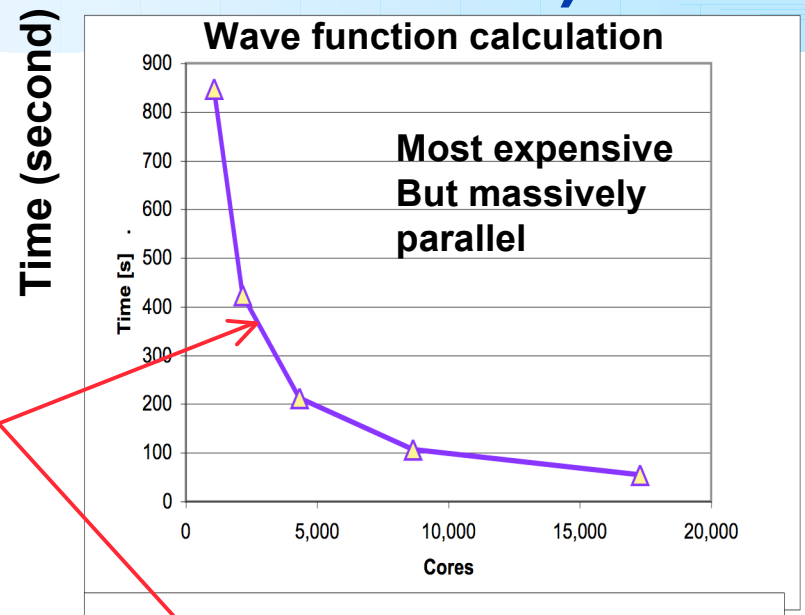
Ref. [3] PEtot code: http://hpcrd.lbl.gov/~linwang/PEtot/PEtot.html

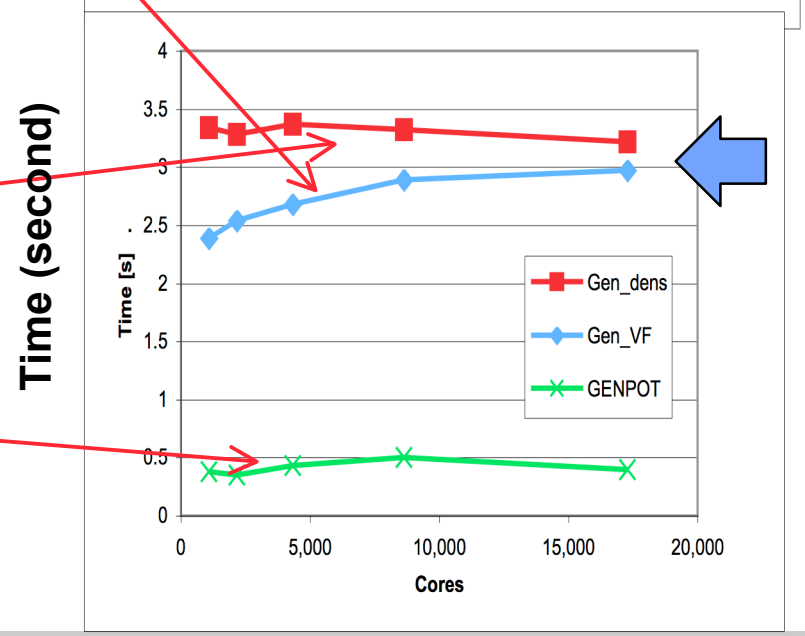
Details on the LS3DF divide and conquer scheme

- Variational formalism, sound mathematics
- The division into fragments is done automatically, based on atom's spatial locations
- Typical large fragments (2x2x2) have ~100 atoms and the small fragments (1x1x1) have ~ 20 atoms
- Processors are divided into N_g groups, each with N_p processors.
  - N_p is usually set to 16 – 128 cores
  - N_g is between 100 and 10,000
- Each processor group is assigned N_f fragments, according to estimated computing times, load balance within 10%.
  - N_f is typically between 8 and 100

The performance of LS3DF method (strong scaling, NERSC Franklin)

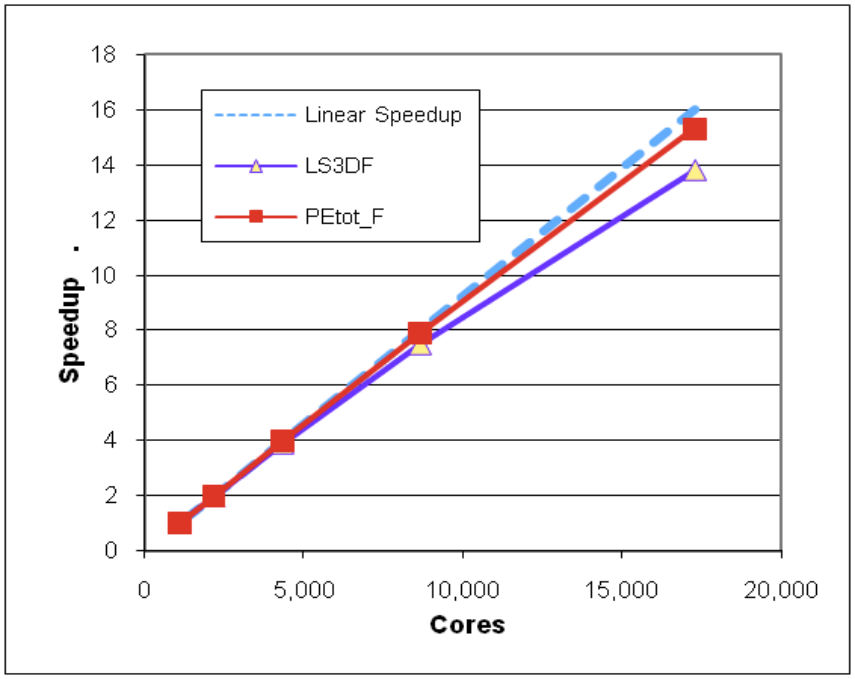


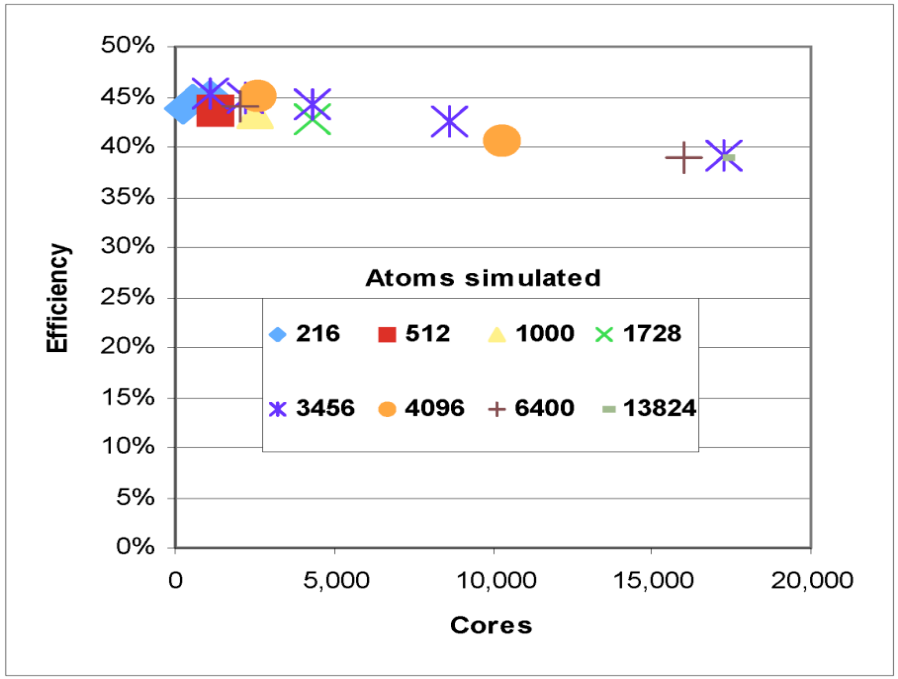




data movement

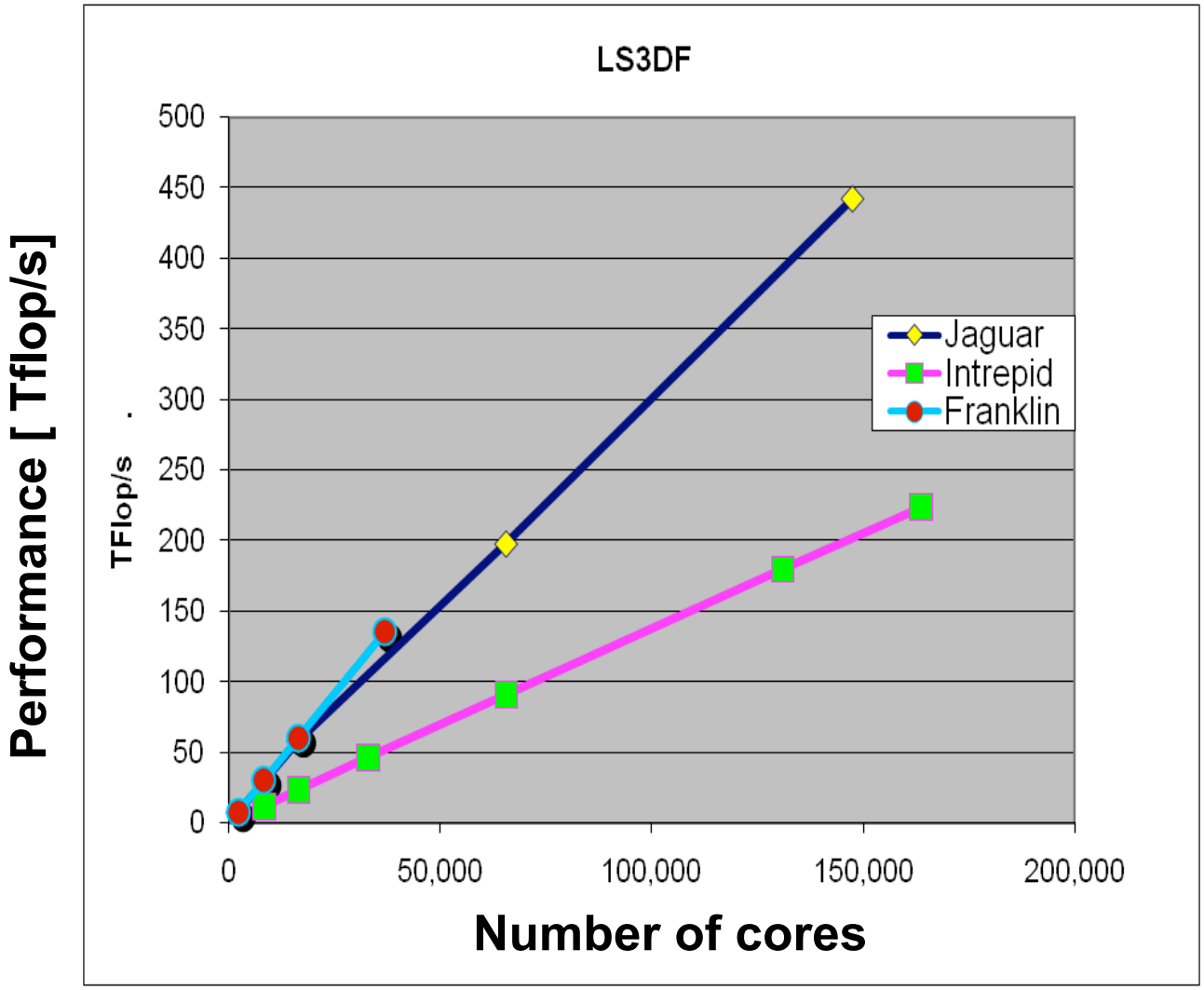
NERSC Franklin (dual core) results





- 3456 atom system, 17280 cores:
  - one min. per SCF iteration, one hour for a converged result
- 13824 atom system, 17280 cores,
  - 3-4 min. per SCF iteration, 3 hours for a converged result

ZnTeO alloy weak scaling calculations



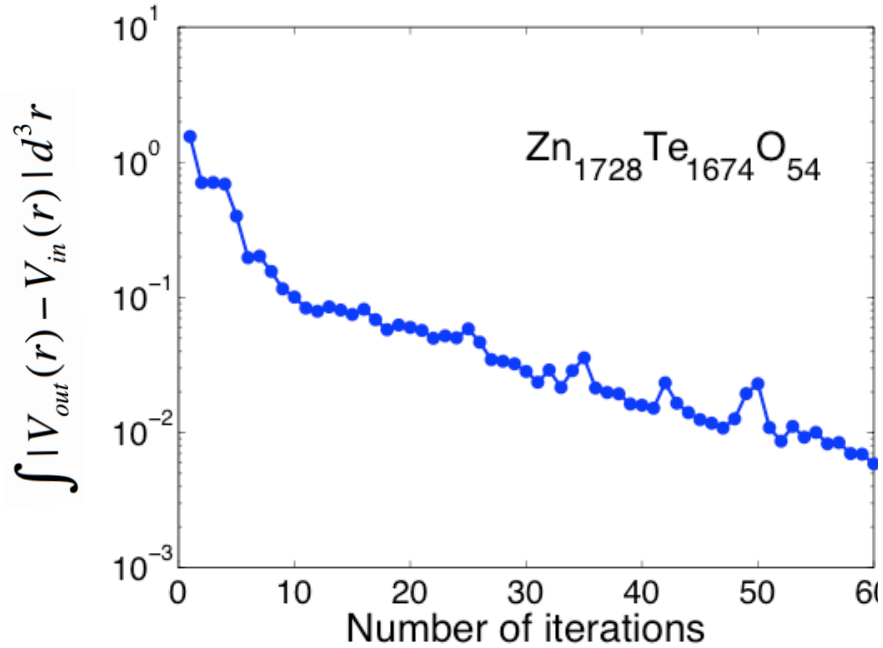
Note: Ecut = 60Ryd with *d* states, up to 36864 atoms

System Performance Summary

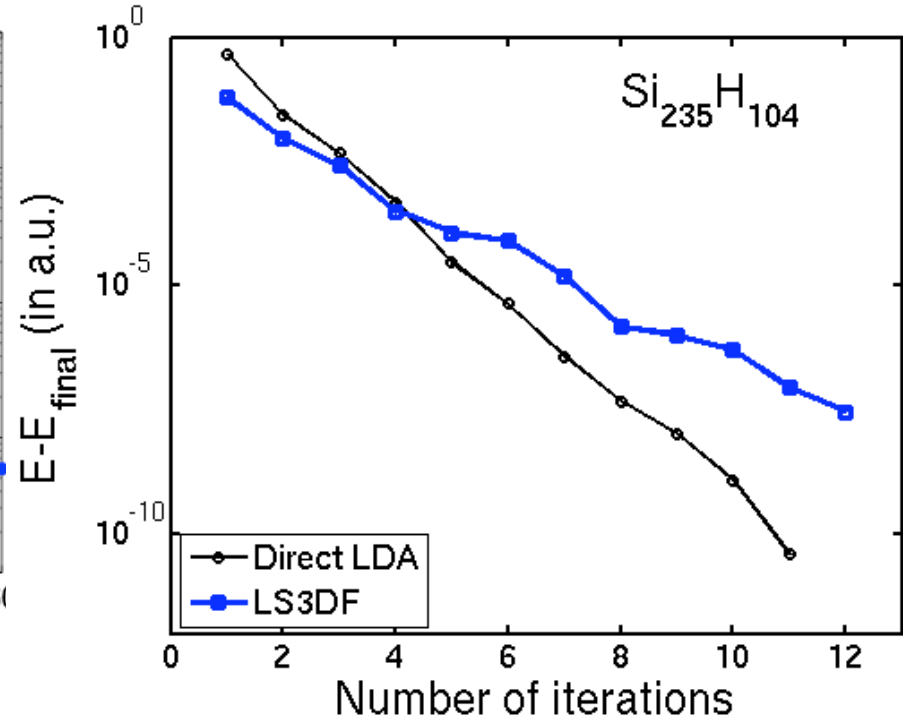
- 135 Tflops/s on 36,864 processors of the quad-core Cray XT4 Franklin at NERSC, 40% efficiency
- 224 Tflops/s on 163,840 processors of the BlueGene/P Intrepid at ALCF, 40% efficiency
- 442 Tflops/s on 147,456 processors of the Cray XT5 Jaguar at NCCS, 33% efficiency

For the largest physical system (36,000 atoms).

Selfconsistent convergence of LS3DF



Measured by potential



Measured by total energy

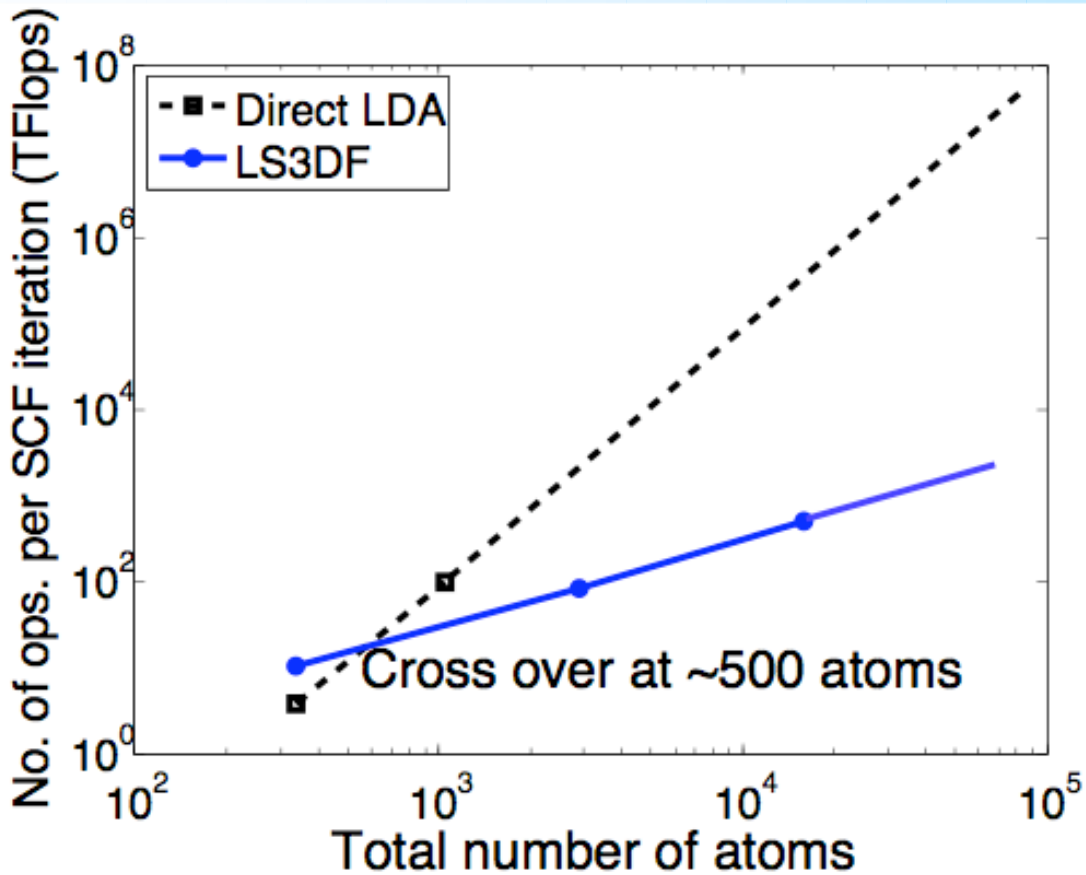
- ❖ **SCF convergence of LS3DF is similar to direct LDA methods**
- ❖ **It doesn't have the SCF problem some other *O(N)* methods have**

LS3DF accuracy is determined by fragment size

- A comparison to direct LDA calculation, with an 8 atom 1x1x1 fragment size division:
  - The total energy error: 3 meV/atom ~ 0.1 kcal/mol
  - Charge density difference: 0.2%
  - Better than other numerical uncertainties (e.g. PW cut off, pseudopotential)
- Atomic force difference: 10^{-5} a.u
  - Smaller than the typical stopping criterion for atomic relaxation
- Other properties:
  - The dipole moment error: 1.3×10^{-3} Debye/atom, 5% smaller than other numerical errors

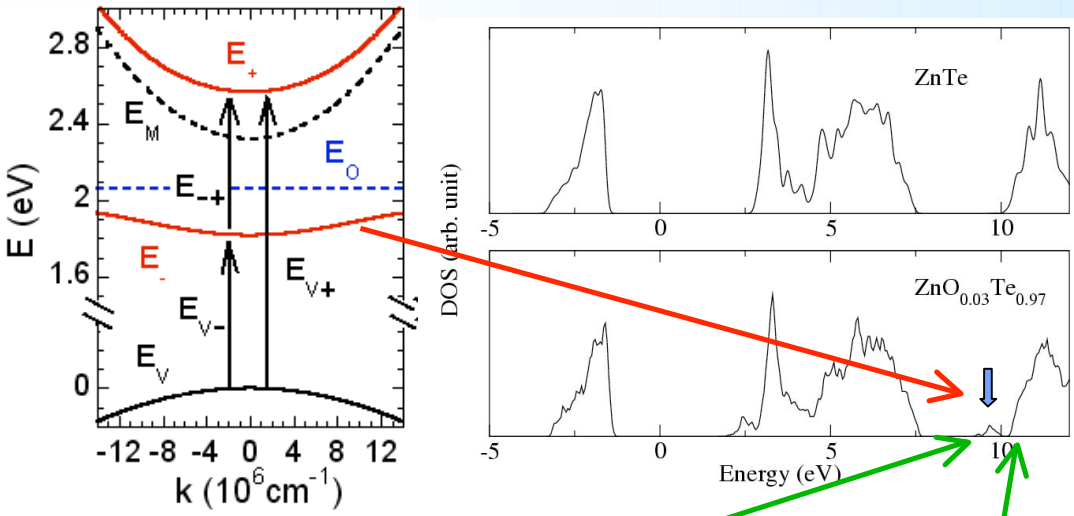
LS3DF yields essentially the same results as direct LDA

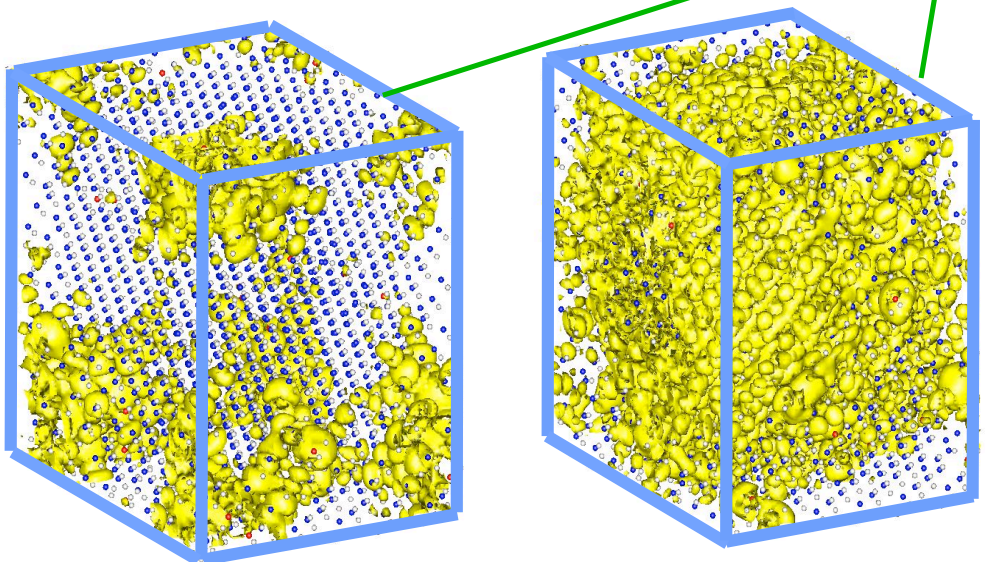
Algorithmic scaling



- Cross over with direct LDA method [PEtot] is 500 atoms, similar to other *O(N)* methods.
- More than 3 order of magnitude faster than the direct LDA method for systems with more than 10,000 atoms.

Can one use an intermediate state to improve solar cell efficiency?





Highest O induced state

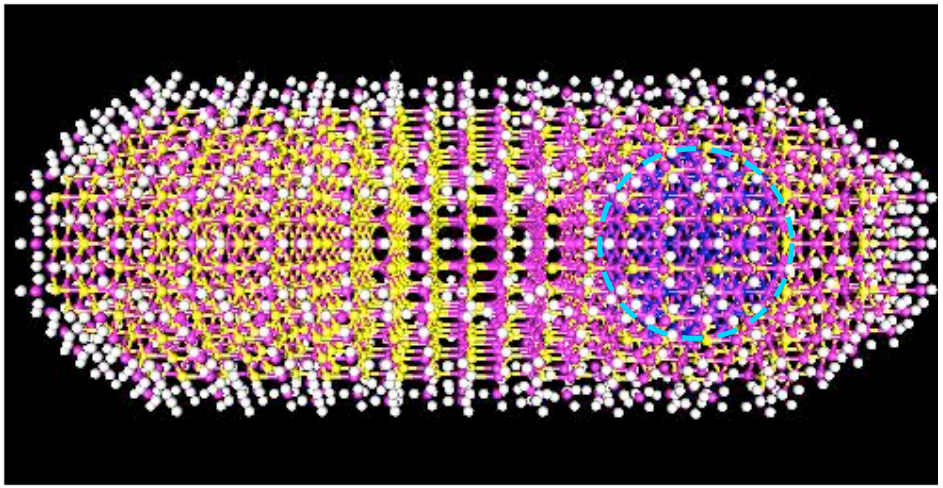
ZnTe bottom of cond. band state

- Single band material theoretical PV efficiency is 30%
- With an intermediate state, the PV efficiency could be 60%
- One proposed material ZnTe:O
  - Is there really a gap?
  - Is it optically forbidden?
- LS3DF calculation for 3500 atom 3% O alloy [one hour on 17,000 cores of Franklin]
- Yes, there is a gap, and O induced states are very localized.

INCITE project, NERSC, NCCS.

Ref. [4]. Lin-Wang Wang, Byounghak Lee, Hongzhang Shan, Zhengji Zhao, Juan Meza, Erich Strohmaier, David Bailey, Gordon Bell submission, (2008).

Asymmetric CdSe/CdS core/shell nanorods



A spherical CdSe core (Se:blue) embedded in a CdS cylindrical shell (Cd:magenta; S:yellow). White dots are pseudo H atoms.

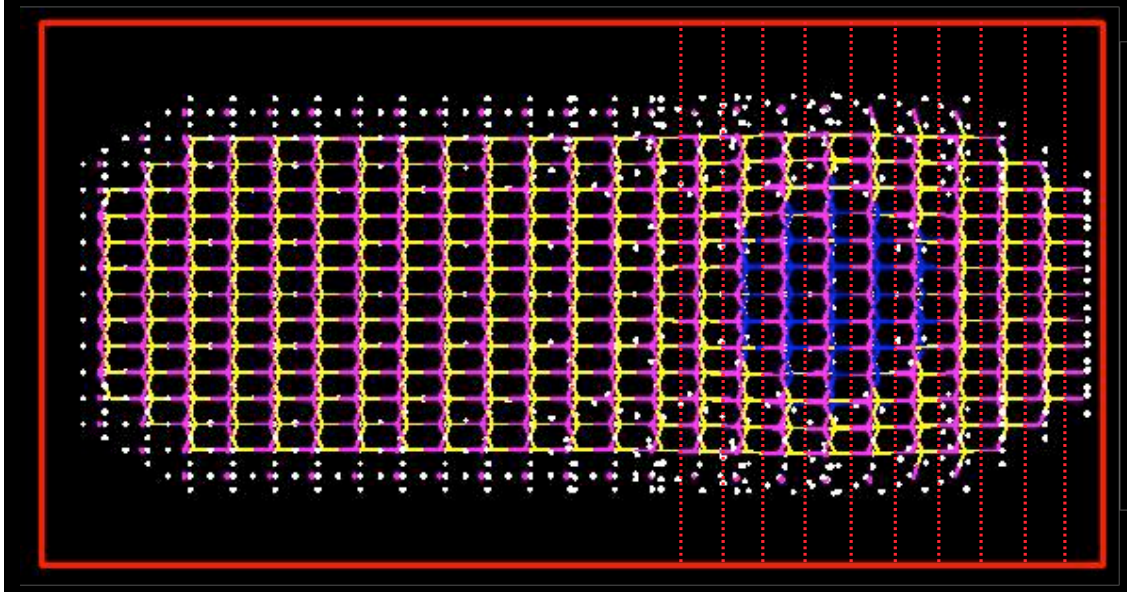
D_rod=2.8nm, D_core=2.1nm, H=8.4nm
3063 atoms: Cd_1113Se_84_S750_H1116.
Wurzite structure.

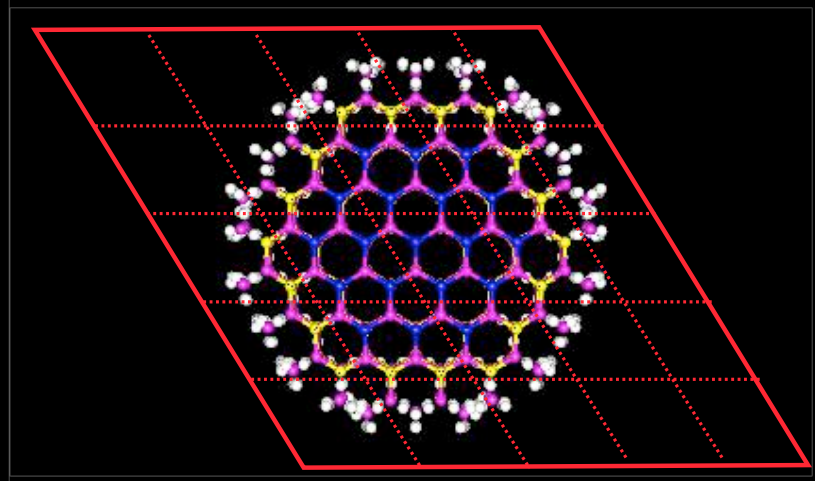
Importance of asymmetric core/shell structures

- Provides a way to manipulate the electronic structure inside nano structure through the band alignment, strain, the surface dipole moment and the quantum confinement effect.
- One proposed solar cell material.

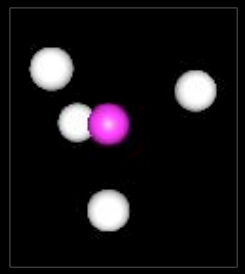
We studied how the CdSe core and the surface affect the electronic structures inside the CdS nanorod. We applied the LS3DF method to four CdS nanorods with/without CdSe core and with different surface passivations (Cd terminated and Cd+S terminated).

Computational details

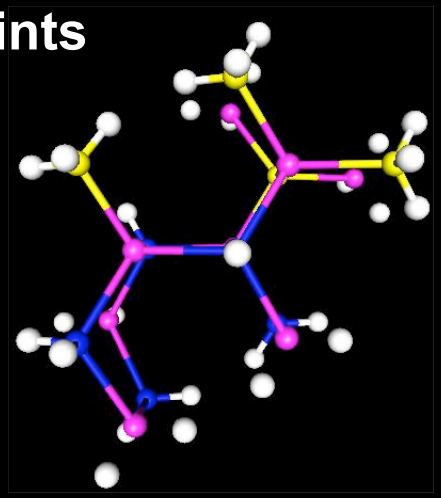




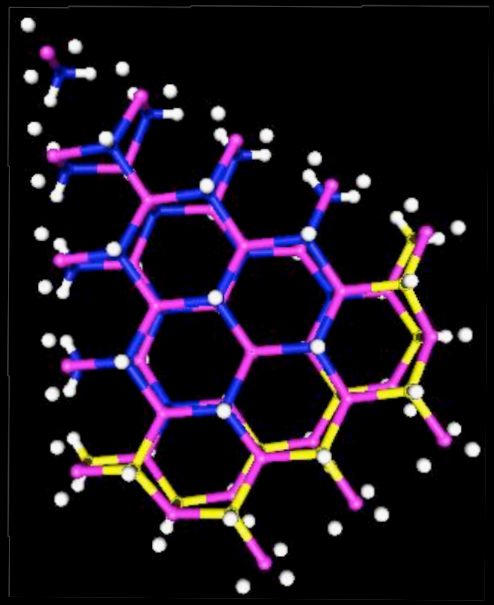
24x5x5 fragments grid points



1x1x1 fragment



2x1x1 fragment



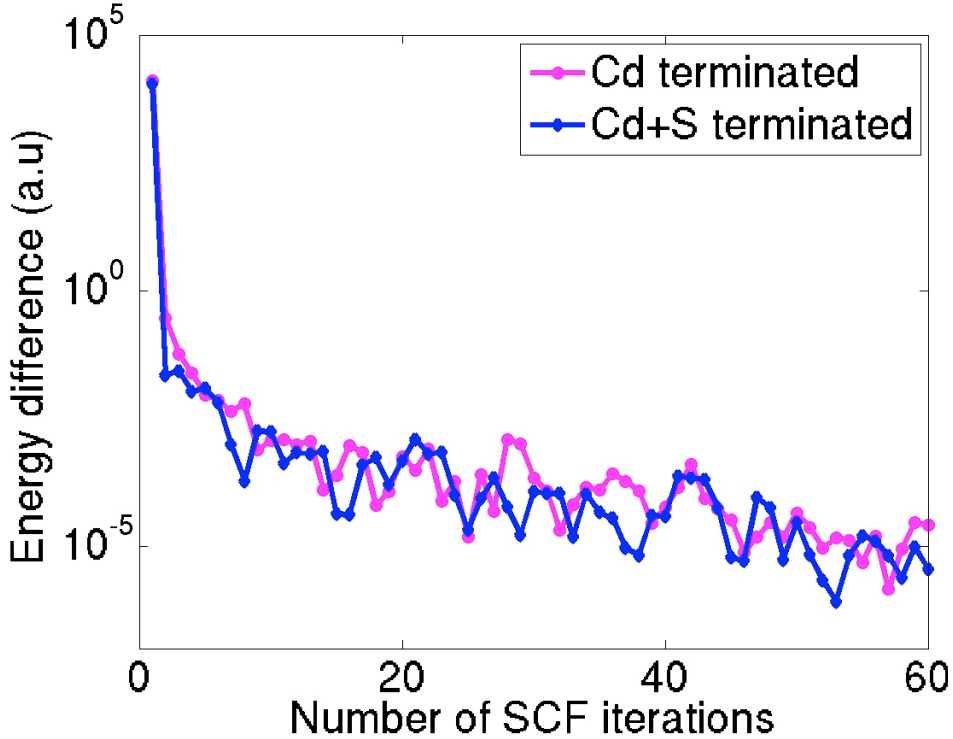
2x2x2 fragment

Computational details

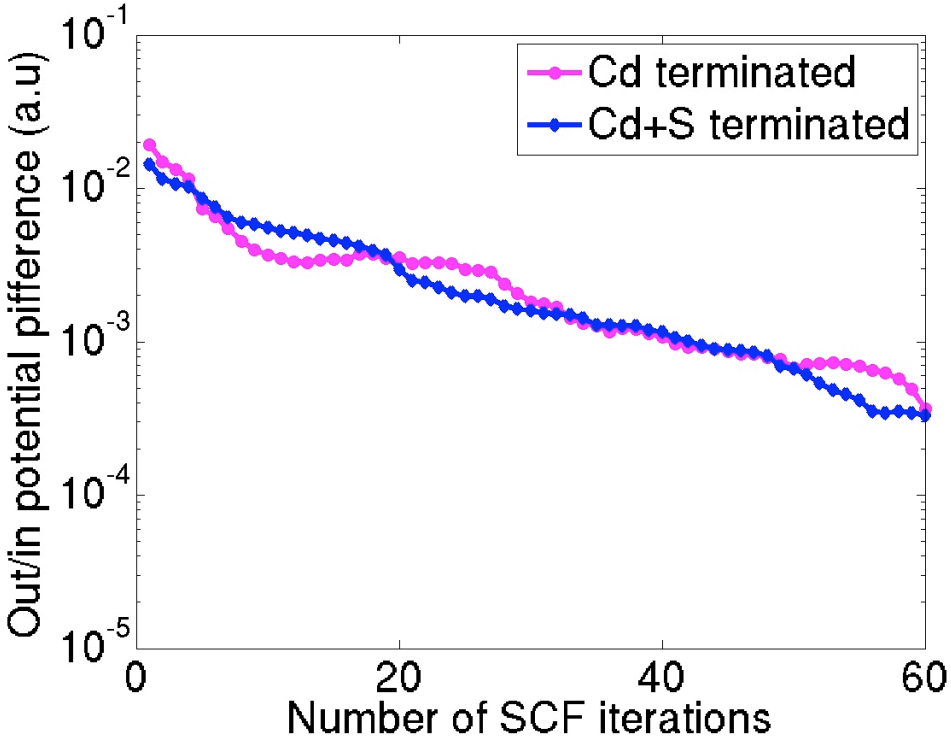
- 4079, 3908 fragments for two CdSe/CdS core/shell nanorods with different surface passivation models.
- 120 processor group, 48 processors per group, 5760 processors in total
  - Load balance, memory issue
- Converges in ~ 3 hours (60 SCF iterations)
  - Surface passivation potential generation
- The direct output from the LS3DF code is total energy, charge density, and total potential.
- Need to run Escan code (folded spectrum method, Ref. [5]) to obtain the near band edge states, conduction band minimum (CBM, electron) and valance band maximum (VBM, hole).

Ref. [5] Folded spectrum method: L.W. Wang, A. Zunger, Comp. Mat. Sci. 2, 326 (1994)].

Results: convergence of SCF iterations for CdSe/CdS core/shell nanorods



Measured by total energy



Measured by potential

SCF converged in 60 iterations for CdSe core/shell nanorod with both surface models.

Results: band gaps $E_{CBM} - E_{VBM}$ (eV)

Surface / nanorod	Cd termin. (eV)	Cd+S termin. (eV)
CdSe/CdS core/shell	2.0534	2.1299
Pure CdS	2.2174	2.2613

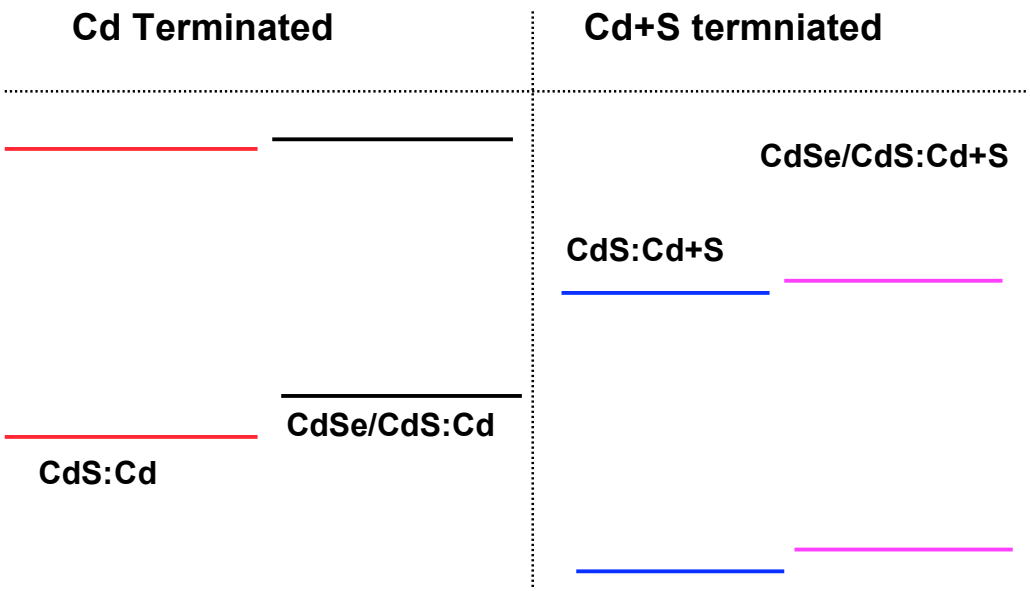


Illustration of the relative CBM and VBM energy levels of the 4 nanorods.

- Due to the quantum confinement the band gaps of nanorods are increased in comparison with the CdSe or CdS bulk band gaps.
- The band gap change due to the different surface passivations (~0.06eV) is smaller than that due to the introduction of the CdSe core (~0.15eV) inside the CdS naorods.
- The band gap difference between CdS nanorods with/without the CdSe core is mainly from the VBM shift, the CBM change is negligible. The different surface passivations make the CBM and VBM shift together.

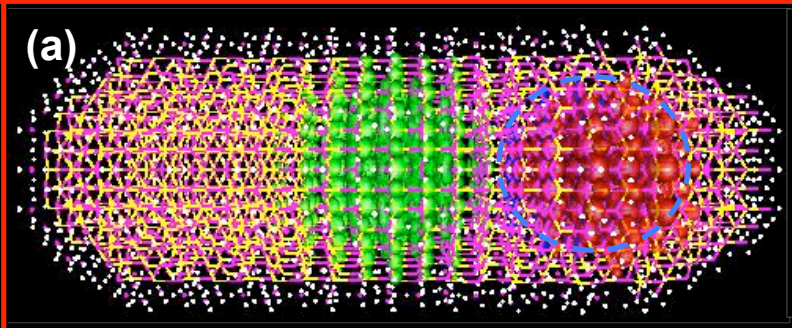
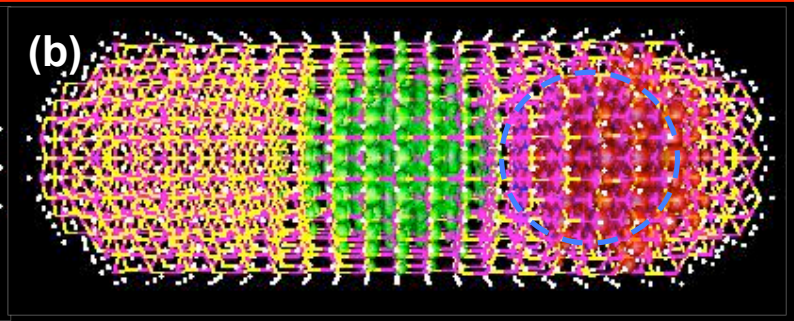
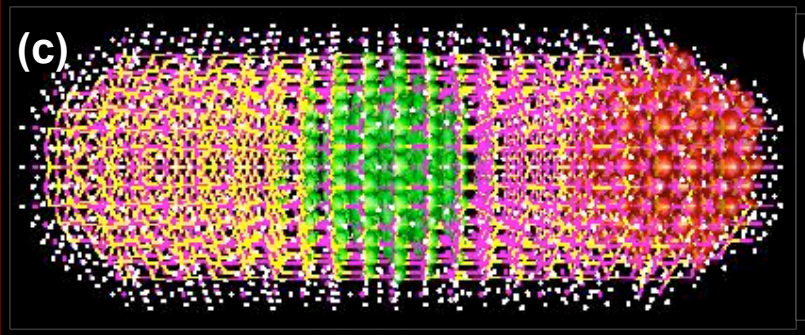
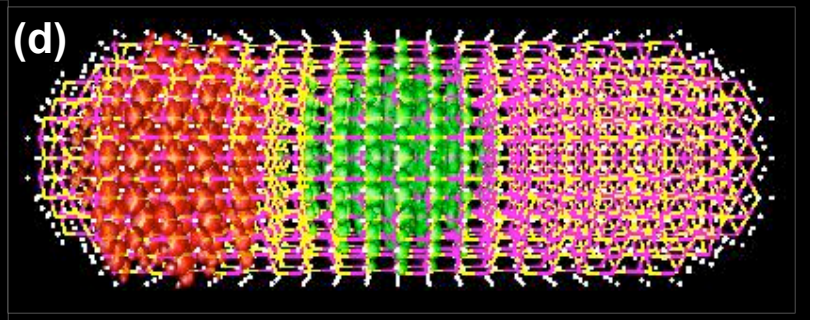
Results: dipole moments and internal electric field

Dipole moments d_x, d_y, d_z (z: c-axis)

Surface / nanorod	Cd terminated (a.u)	Cd+S terminated (a.u)
CdSe/CdS core/shell	-0.0100, 0.1298, **-8.6135**	-0.0064, -0.0456, **-10.6354**
Pure CdS	0.0070, 0.1590, **6.6616**	-0.0364, -0.0586, **-6.0208**

1. None zero dipole moments inside the nano rods indicate that there exist an internal electric filed inside the nano rods.
2. The dipole moment change due to the difference surface passivations is significant in the pure CdS rods, but in the CdSe/CdS core/shell nanorods the change due to the different surface is not as significant.

Results: electron and hole localization in CdSe/CdS core/shell nanorods

	Cd terminated surface	Cd+S terminated surface
CdSe/CdS core/shell nanorod		
CdS nanorod		

Isosurface of the wave function square of the conduction band minimum (CBM, green) and the valance band maximum (VBM, red) states of the four CdS nanorods with/without CdSe core. Where (a) and (b) are for the CdSe/CdS core/shell nanorods with the Cd terminated and the Cd+S terminated surfaces, respectively, while (c) and (d) are for the pure CdS nanorods with the Cd terminated and the Cd+S terminated surfaces, respectively. The isovalue larger than 0.001 e/bhor^3 was shown for both VBM and CMB.

Results: electron and hole localization in core/shell structures

- In both surface passivation models, the electron (CBM) and hole (VBM) states of the CdSe/CdS core/shell nanorods are separated.
  - The electron states are localized in the center of the rod.
  - The hole (VBM) states are localized in core area.
  - In the nanorod with the Cd terminated surface, the hole is localized more in the radial direction of the rod then that in the Cd+S terminated one.
- The surface significantly changes the electronic structure localizations in the pure CdS nanorods.
  - In the Cd terminated CdS rod, the hole state (red) is localized at the right end of the rod, while in Cd+S terminated surface model, the hole state is localized in the left end of the rod.
  - The core inside the asymmetric core/shell rods helps to better control the hole's spatial location, this could be a useful feature for the electronic device design when we don't have much control on the surface passivation.
- Further analysis is under the way to understand some differences between the results from the LS3DF method and the charge patching method Ref [6].

Ref. [6] Luo Ying, Lin-Wang Wang, Electronic structures of the nanorod with CdSe/CdS core-shell structure, to be submitted.

Summary and Conclusions

- LS3DF scales linearly to over 160,000 processors. It reached 442 Tflops/s.
- Yields the same numerical results as an $O(N^3)$ DFT method, but at the $O(N)$ computational cost.
- LS3DF can be used to compute electronic structures for >10,000 atom systems self consistently with total energy.
- Wide applications in the electronic structure calculations for proposed new solar cell materials.
- LS3DF has been used to study the electronic structures of asymmetric CdSe/CdS core/shell nanorods, our preliminary results show that the CdSe core screens the strong surface effect and makes the hole localize in the CdSe core.

Future work on the LS3DF method

- A more features to the code, eg., atomic relaxations.
- More rigorous procedure to generate the surface passivation potentials for fragments
- Molecular dynamics
- A way to calculate electron wave functions.
- Go beyond LDA

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