

Recent Developments in Electronic Structure Calculations

Juan Meza

High Performance Computing Research
Lawrence Berkeley National Laboratory

Advanced Light Source Users' Meeting
Photon-In/Photon-Out Inelastic Soft X-Ray
Spectroscopy in Renewable Energy Science Workshop
Berkeley, CA, October 4-6, 2007



Our Team

- Byoungnak Lee, postdoc, Scientific Computing Group, LBNL
- Lin-Wang Wang, Scientific Computing Group, LBNL
- Chao Yang, Scientific Computing Group, LBNL
- Zhengji Zhao, NERSC
- Also collaborating extensively with S. Louie's and Martin Head-Gordon's groups



Outline

1 Motivation

2 Scalability

- Self-Consistent Field
- Linear Scaling Methods

3 Robustness

- Direct Constrained Minimization

4 Ease of Use

- KSSOLV

5 Summary and Future Work



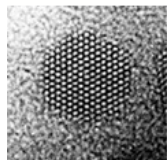
DFT for solar energy

Advances in density functional theory coupled with multinode computational clusters now enable accurate simulation of the behavior of multithousand atom complexes that mediate the electronic and ionic transfers of solar energy conversion. These new and emerging nanoscience capabilities bring a fundamental understanding of the atomic and molecular processes of solar energy utilization within reach.

Basic Research Needs for Solar Energy Utilization
Report of the BES Workshop on Solar Energy Utilization
April 18-21, 2005

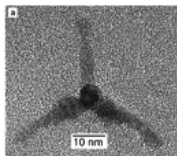


Large-scale electronic structure calculations



CdSe QD

1000-5000



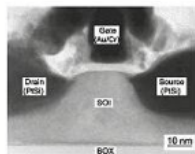
Tetrapod

10,000



Solar Cell

50,000



CMOS

1,000,000 atoms

- Nanosystems often involve 1000-1,000,000 atoms
- Atomic details are still important: surface charge, impurities, dopant, symmetry, passivation
- **Materials by design** could potentially be accelerated through the judicious use of computational and mathematical tools

Kohn-Sham Density Functional

- Kohn-Sham total energy

$$\begin{aligned} E_{total}[\{\psi_i\}] &= \frac{1}{2} \sum_{i=1}^{n_e} \int_{\Omega} |\nabla \psi_i|^2 + \int_{\Omega} V_{ext} \rho \\ &+ \frac{1}{2} \int_{\Omega} \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' + E_{xc}(\rho), \end{aligned}$$

where $\rho = \sum_{i=1}^{n_e} |\psi_i(r)|^2$, $\int_{\Omega} \psi_i \psi_j = \delta_{i,j}$.

Kohn-Sham equations

$$\left[-\frac{1}{2} \nabla^2 + V_{ext}(r) + \int \frac{\rho}{|r-r'|} + V_{xc}(\rho) \right] \psi_i = \epsilon_i \psi_i, \quad i = 1, 2, \dots, n_e$$

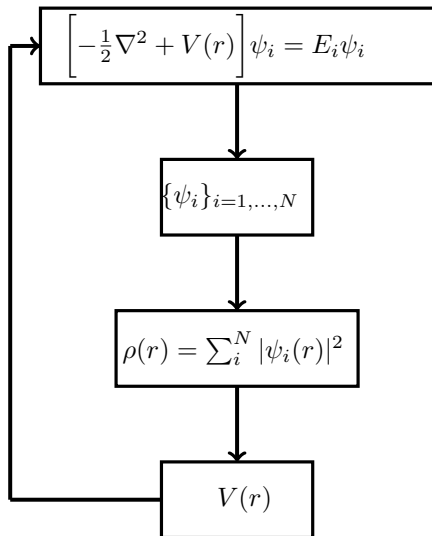


Approaches for solving the Kohn-Sham Equations

- Work with the KS equations directly
 - Self-Consistent Field Iteration
 - Large-scale linear eigenvalue problem
 - Need to precondition
 - Use charge mixing for faster convergence
- Minimize the total energy directly
 - Direct Constrained Minimization
- Many other methods - unfortunately we don't have the time to discuss them today



The SCF Iteration



- Memory $O(N^2)$
- Complexity $O(N^3)$
- Major work load
 - 3D FFT
 - Orthogonalization
 - Nonlocal potential



Scaling of conventional DFT methods

- DFT methods account for 75% of the material science simulations at NERSC, totaling over 5 million hours of computer time last year
- Parallelization can improve performance
 - on plane wave basis can scale to ≈ 1000 processors
 - on plane wave basis and wavefunction index can scale to $\approx 10,000$ processors
- Parallel efficiencies can be quite high

So what's the problem?

Algorithms scale as $O(N^3)$; Would it be more efficient to use a linear scaling method for larger systems?



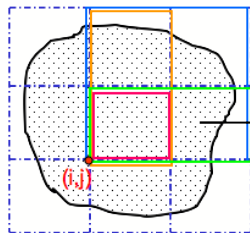
Divide and conquer approach

- Divide a large system into smaller sub-domains that can be solved independently, then stitch the sub-domains back together again
- Why might this work?
 - quantum mechanical effects are near-sighted, i.e. treat the quantum mechanical wavefunctions locally
 - classical electrostatic interactions are long-ranged, i.e. solve one global Poisson equation
- Requires minimal communication between the sub-domains
- Artificial boundary effects due to sub-dividing domains can be cancelled out
- Based on ideas from fragment molecular method
- We call our method Linear Scaling 3D Fragment or LS3DF ¹

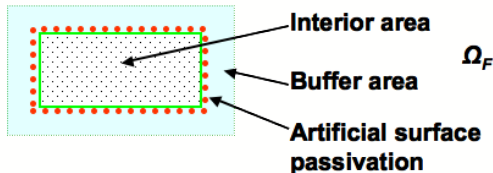
¹L.W. Wang, Z. Zhao, J. Meza, LBNL-61691 (2006)



Divide and conquer (pictorially)



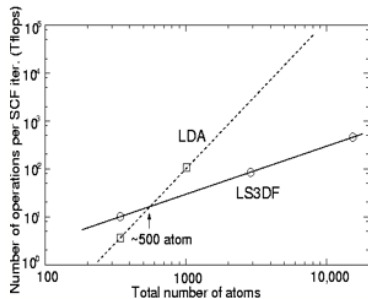
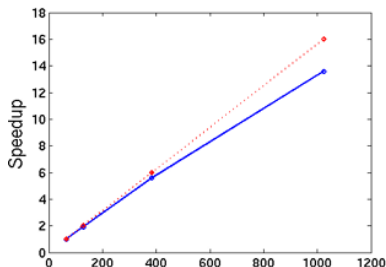
2D: Fragment (2x1)



Total = \sum_F

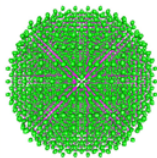
3D:
$$\text{System} = \sum_{i,j,k} \{F_{222} + F_{211} + F_{121} + F_{112} - F_{221} - F_{212} - F_{122} - F_{111}\}$$

Scaling of LS3DF

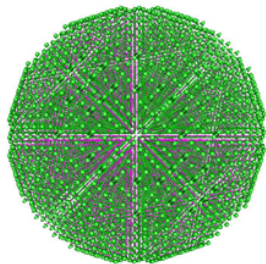


- Almost linear speedup up to 1000 processors
- Cross over between LS3DF and direct LDA happens around 500 atoms
- LS3DF should scale well to petascale machines

Results for Si quantum dot



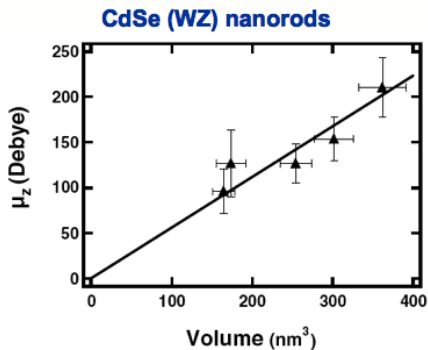
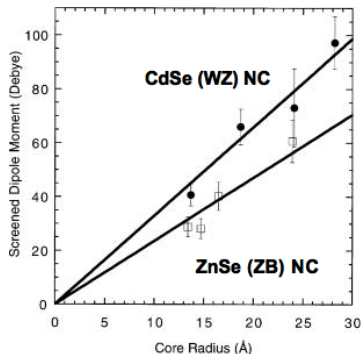
$\text{Si}_{2253}\text{H}_{652}$



$\text{Si}_{13607}\text{H}_{2236}$

- LS3DF on 3000 atom quantum dot using 1024 processors at NERSC took 1 hour
- A similar simulation using direct LDA would take several days
- LS3DF on 15,000 atom quantum dot using 2048 processors at NERSC took 5 hours
- A similar simulation using direct LDA would take a few months

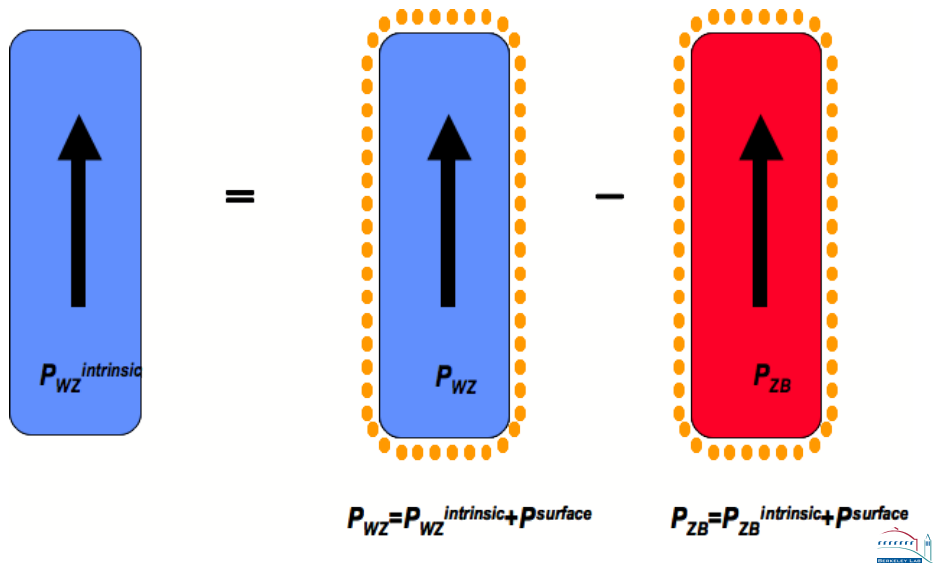
Nanostructure Dipole Moment



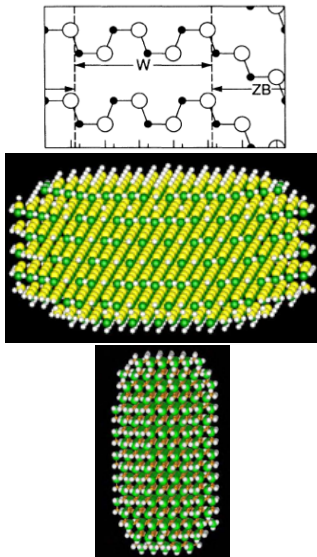
M. Sim, P. Guyot-Sionnet, JCP 111, 6955 (1999) L. Li, A.P. Alivisatos, PRL 90, 097402 (2003)

- What is the net dipole moment of ZnSe (ZB)?
- Is there a volume dependence?

Removing the Surface Contribution

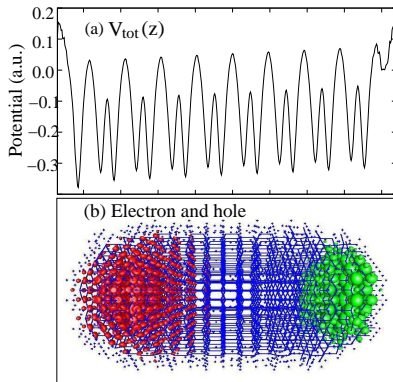


Geometric Effects on Dipole Moment



- Pure bulk contribution = $0.0143 \times (N_{Cd} + N_{Se})$
- $P_0 = 20.5(a.u.) (\approx 2500 \text{ atoms})$
- $R = 7, L = 3 (a.u.), P = 30.3 (a.u.) \rightarrow \text{effective screening}$
- $R = 4.5, L = 9 (a.u.), P = 73.3 (a.u.) \rightarrow \text{weak screening}$
- Dipole moment of this nanostructure has a strong geometry dependence

CdSe wurtzite quantum rods



- $\text{Cd}_{961}\text{Se}_{724}$ wurtzite quantum rods
- Used experimental crystal structures
- Top figure depicts potential along the central axis
- Bottom figure depicts the electron (red) and hole states (green) isosurfaces
- Electrons and holes are localized on opposite ends indicating internal electric field

When can we expect SCF to work?

SCF convergence properties

- SCF does not always converge;

$$\lim_{i \rightarrow \infty} \|H(x^{(i+1)}) - H(x^{(i)})\| \neq 0,$$

or

$$\lim_{i \rightarrow \infty} \|\rho(x^{(i+1)}) - \rho(x^{(i)})\| \neq 0$$

- For some problems, we can show subsequence convergence;

$$\lim_{i \rightarrow \infty} \|\rho(x^{(i+1)}) - \rho(x^{(i-1)})\| = 0$$

- $E(x)$ may not decrease in SCF



Why does SCF fail?

- SCF is attempting to minimize a sequence of surrogate models
- Objective:
 - $E(x) = \frac{1}{2}x^T Lx + \frac{\alpha}{4}\rho(x)^T L^{-1}\rho(x)$
 - $E_{sur}(x) = \frac{1}{2}(x^T H(x^{(i)})x),$
- Gradient:
 - $\nabla E(x) = H(x)x$
 - $\nabla E_{sur}(x) = H(x^{(i)})x$

Gradients match

$$\nabla E(x^{(i)}) = \nabla E_{sur}(x^{(i)})$$



Improving SCF

- Construct better surrogate
 - Cannot afford to use local quadratic approx (Hessian too expensive)
 - **Charge mixing** to minimize lack of self consistency (heuristic)
- Use **Trust Region** to restrict the update of the x in a small neighborhood of the gradient matching point
- TRSCF (Thogersen, Olsen, Yeager & Jorgensen 2004 Yang, Meza & Wang 2007)



Direct Constrained Minimization

- Assume $x^{(i)}$ is the current approximation
- Idea: minimize the energy in a certain subspace
- Update $x^{(i+1)} = \alpha x^{(i)} + \beta p^{(i-1)} + \gamma r^{(i)}$;
 - $p^{(i-1)}$ previous search direction;
 - $r^{(i)} = H^{(i)} x^{(i)} - \theta^{(i)} x^{(i)}$;
 - choose α , β and γ so that
 - $x_{k+1}^T x_{k+1} = 1$;
 - $E(x_{k+1}) < E(x_k)$;



Direct Constrained Minimization ²

Algorithm

Input: Initial guess $X^{(0)} \in \mathbb{C}^{n \times n_e}$, pseudopotential etc;

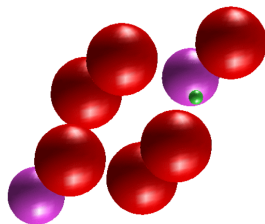
Output: X such that $E_{KS}(X)$ is minimized

- 1 $P^{(0)} = \emptyset, i = 0;$
- 2 while (not converged)
 - 1 $\Theta^{(i)} = X^{(i)*} H^{(i)} X^{(i)};$
 - 2 $R^{(i)} = H^{(i)} X^{(i)} - X^{(i)} \Theta^{(i)};$
 - 3 Set $Y = (X^{(i)}, P^{(i-1)}, K^{-1} R^{(i)});$
 - 4 Solve $\min_{G^* Y^* Y G = I_k} E_{tot}(Y G);$
 - 5 $X^{(i+1)} = Y G(1 : n_e, :); P^{(i+1)} = Y G(n_e + 1 : 3n_e, :);$
 - 6 $i \leftarrow i + 1;$

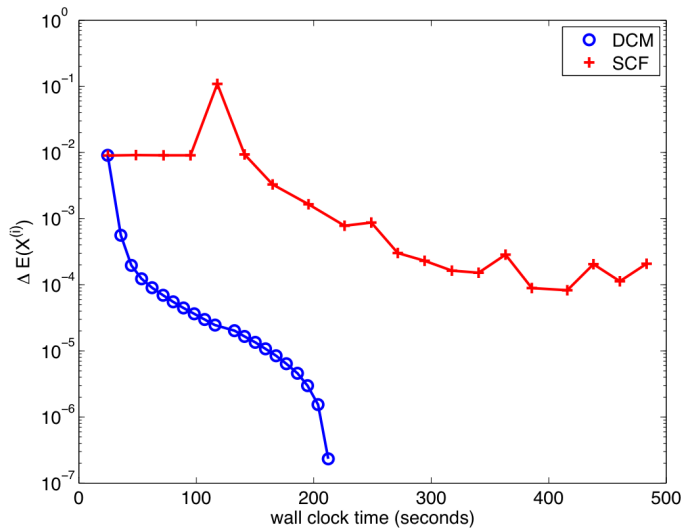
²C. Yang, J. Meza, L. Wang, A Constrained Optimization Algorithm for Total Energy Minimization in Electronic Structure Calculation, J. Comp. Phys., 217 709-721 (2006)

Example: Pt_6Ni_2O

```
cell:
  19.59 0.0 0.0
  ...
sampling size: n1 = 96, n2 = 48, n3 = 48
atoms and coordinates:
  1   Pt   1.3 -0.180 -0.015
  ...
  7   Ni   8.4  0.003  3.069
  8   Ni   8.5  7.998  7.762
  9    O  14.9  2.644  1.511
number of electrons   : 86
spin type              : 1
kinetic energy cutoff: 60.0
```



Comparison of DCM vs. SCF



Ease of use

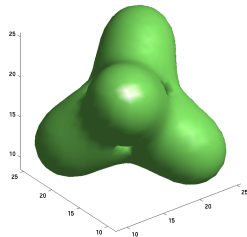
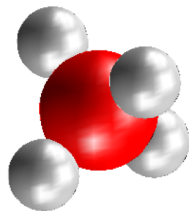
- KSSOLV Matlab code for solving the Kohn-Sham equations
- Open source package
- Handles SCF, DCM, Trust Region
- Example problems to get started with
- Object-oriented design - easy to extend
- Good starting point for students

Beta version of KSSOLV available, ask one of us for more information!



Example: SiH_4

```
a1 = Atom('Si');  
a2 = Atom('H');  
alist = [a1 a2 a2 a2 a2];  
xyzlist= [  
  0.0   0.0   0.0  
  1.61  1.61  1.61  
  ...  ];  
mol = Molecule();  
mol = set(mol,'Blattice',BL);  
mol = set(mol,'atomlist',alist);  
mol = set(mol,'xyzlist',xyzlist);  
mol = set(mol,'ecut', 25);  
mol = set(mol,'name','SiH4');  
...  
isosurface(rho);
```



Other work in our group

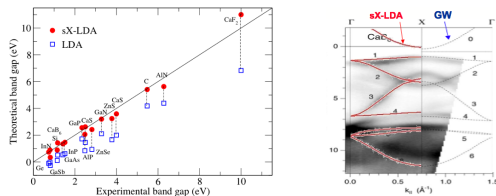


Figure: (left) band gap calculations using screened exchange; (right) band gap for CaB_6

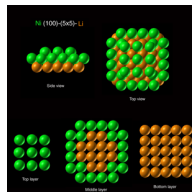


Figure: optimization of structure using LEED

Summary

- New computational tools for modeling and simulation of nanosystems (large and small)
- Codes for large systems that scale linearly
- New algorithms that are potentially more robust than standard methods
- Rapid prototyping of new systems
- Tools can be used to help explain (guide?) experimental results



Invitation

- Invite you to come by and talk with our computational science group
- Discuss computational tools
- We're open to collaborations and partnerships

Let's do it together

Materials properties, transformations, and functionalities by **design** for real world applications, Pat Dehmer

