Mathematical Challenges and Opportunities in Energy and the Environment

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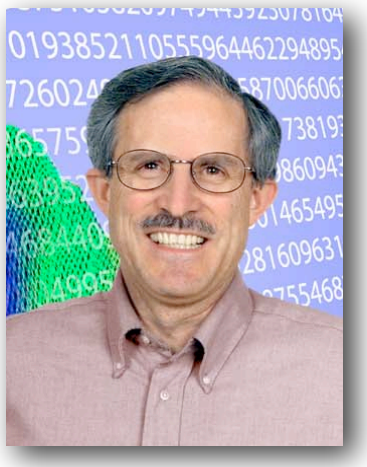
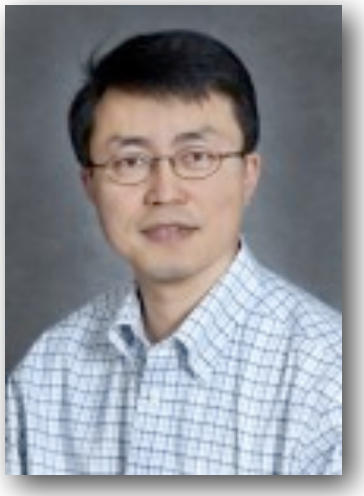
Acknowledgements



David Bailey

Zhengji Zhao



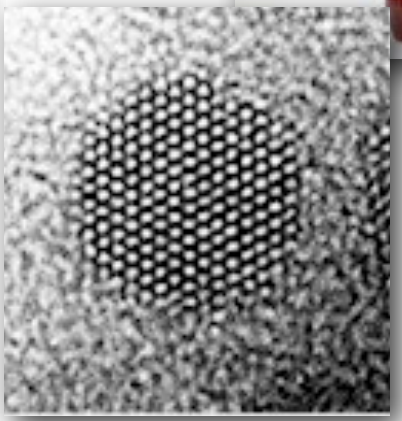
Chao Yang

HongZhang Shan

Erich Strohmaier

Lin-Wang Wang

How are these related?



Combustion

Carbon Capture & Sequestration

Efficiency

Energy Storage

Solar PV

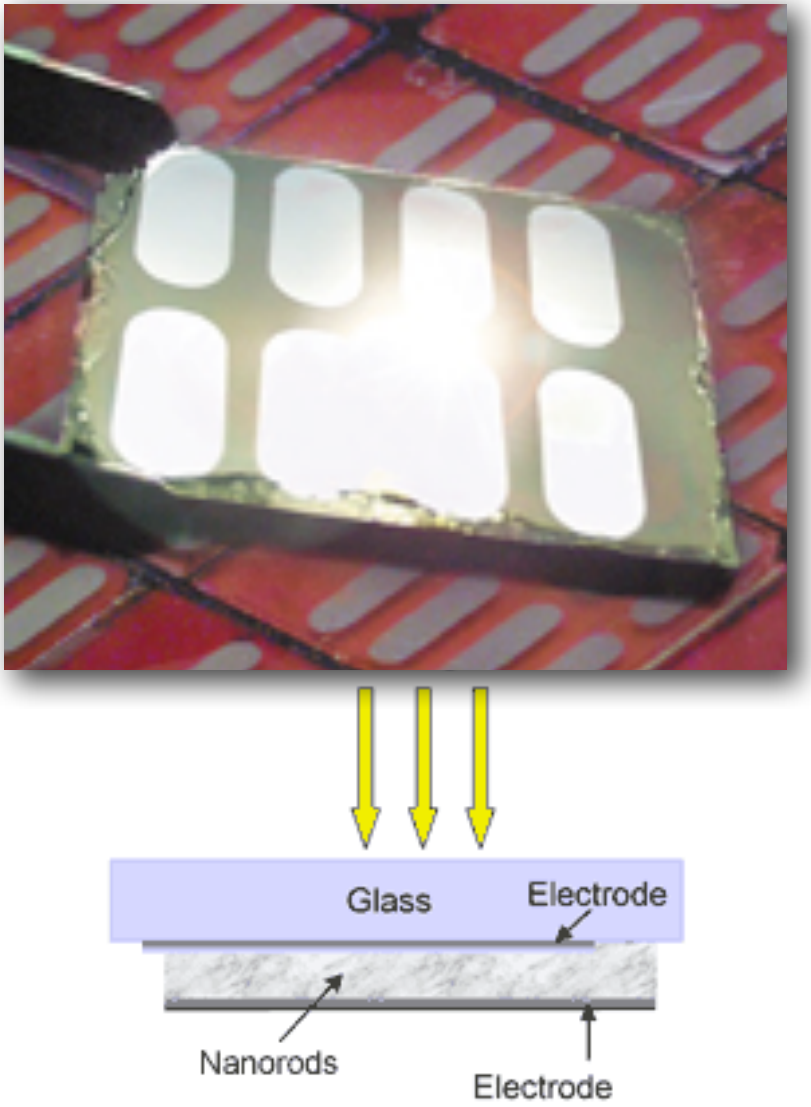
Biofuels

Solar PV Facts

- Cumulative global installed solar PV capacity has topped the 100 GW in 2012
- Global installed PV capacity increased by **30 GW** in 2012.
- Global average PV module prices were $3.65/W in 2008

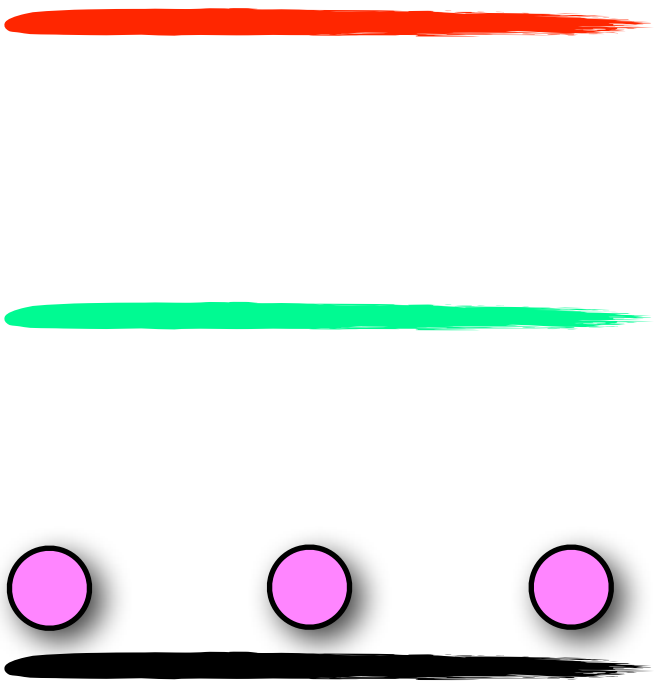
http://www.nrel.gov/analysis/re_market_data_solar.html?print

Photovoltaic Solar Cells



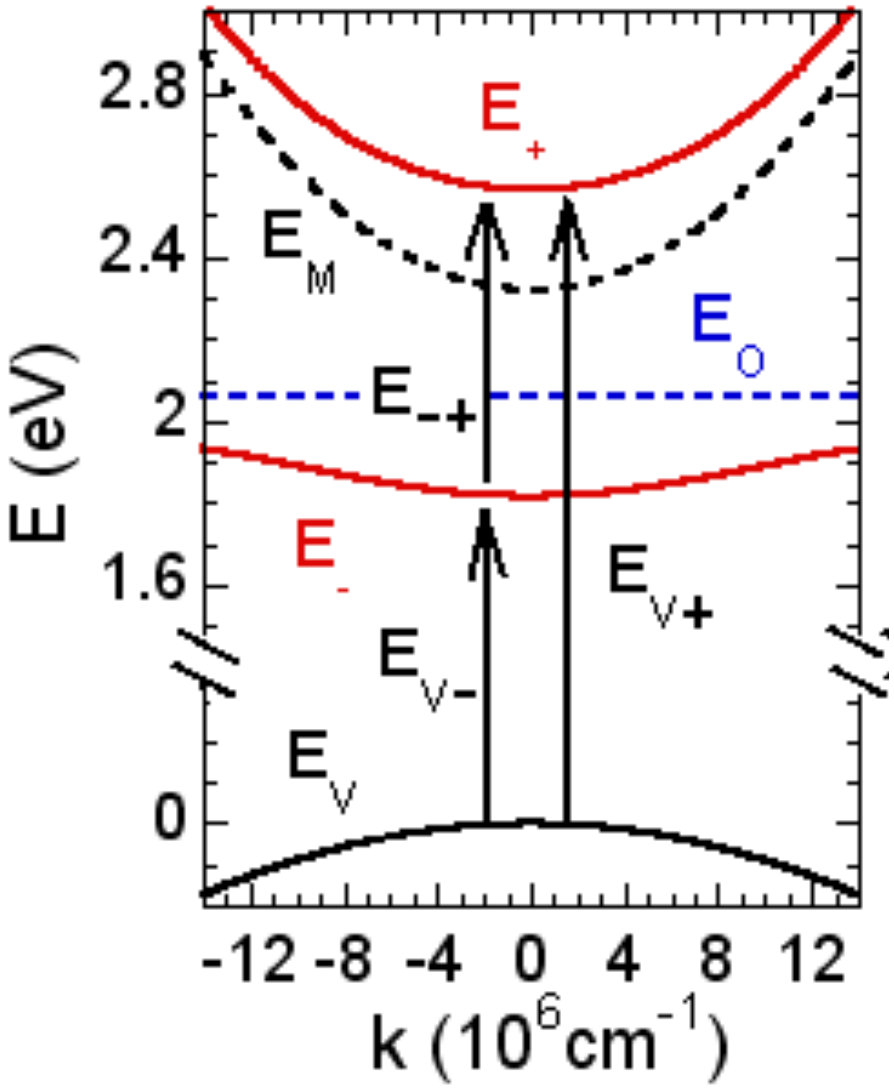
- Solar cells based on inorganic nanorods and semiconducting polymers
- Nanorods can be made of CdSe, a semiconducting material
- Nanorods act like wires, absorbing light and generating hole-electron pairs
- Biggest challenge is cost, ~30 cents/kWh

Solar cell efficiency in a nutshell



- Photons strike electrons with a given energy
- If the energy is sufficient then the electron can "jump" up to a higher state
- Combined effect is to generate electricity

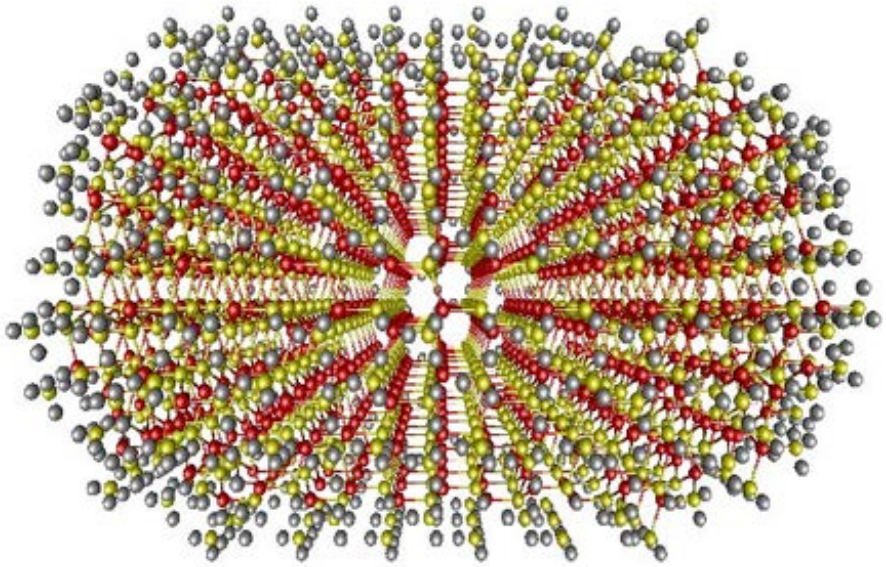
Can one use an intermediate state to improve solar cell efficiency?



- Single band material theoretical PV efficiency is 30%
- One proposed material ZnTe:O
- Is there really a gap?
- What's the right mixture of O to ZnTe?

L-W. Wang, B. Lee, Z. Zhao, H. Shan, J. Meza, D. Bailey, E. Strohmaier. INCITE project, NERSC, NCCS.

Need to simulate realistic nanosystems

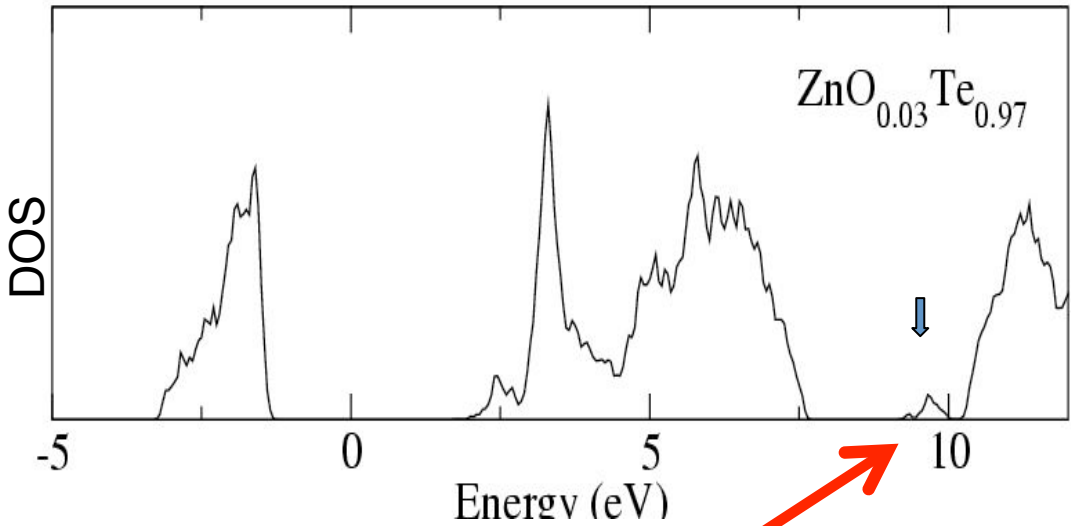


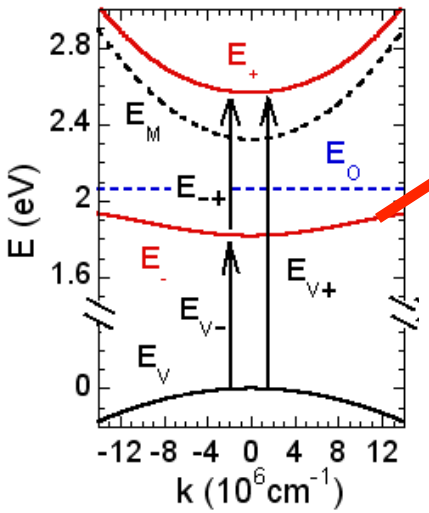
The calculated dipole moment of a 2633 atom CdSe quantum rod, $Cd_{961}Se_{724}H_{948}$. Using 2560 processors at NERSC the calculation took about 30 hours.

Wang, Zhao, Meza, Phys. Rev. B, 77, 165113 (2008)

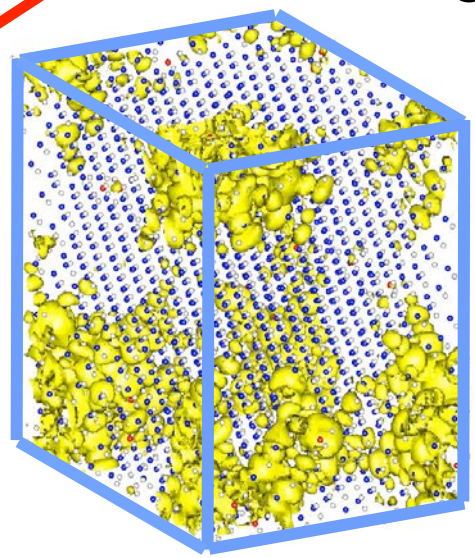
- 1,000 ~ 100,000 atom systems are too large for direct $O(N^3)$ ab initio calculations
- Take advantage of the "near-sighted" principle
- A divide and conquer scheme with a new approach for patching the fragments together

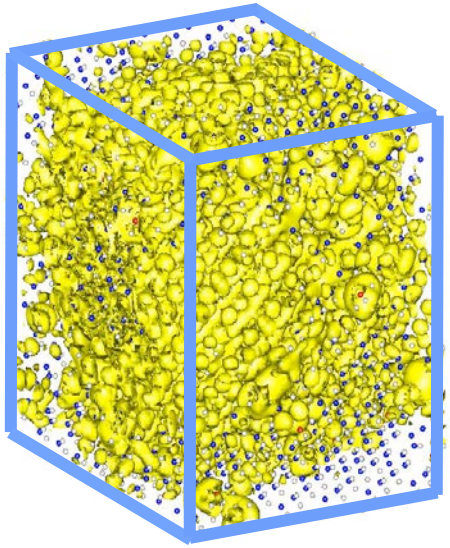
Can one use an intermediate state to improve solar cell efficiency?





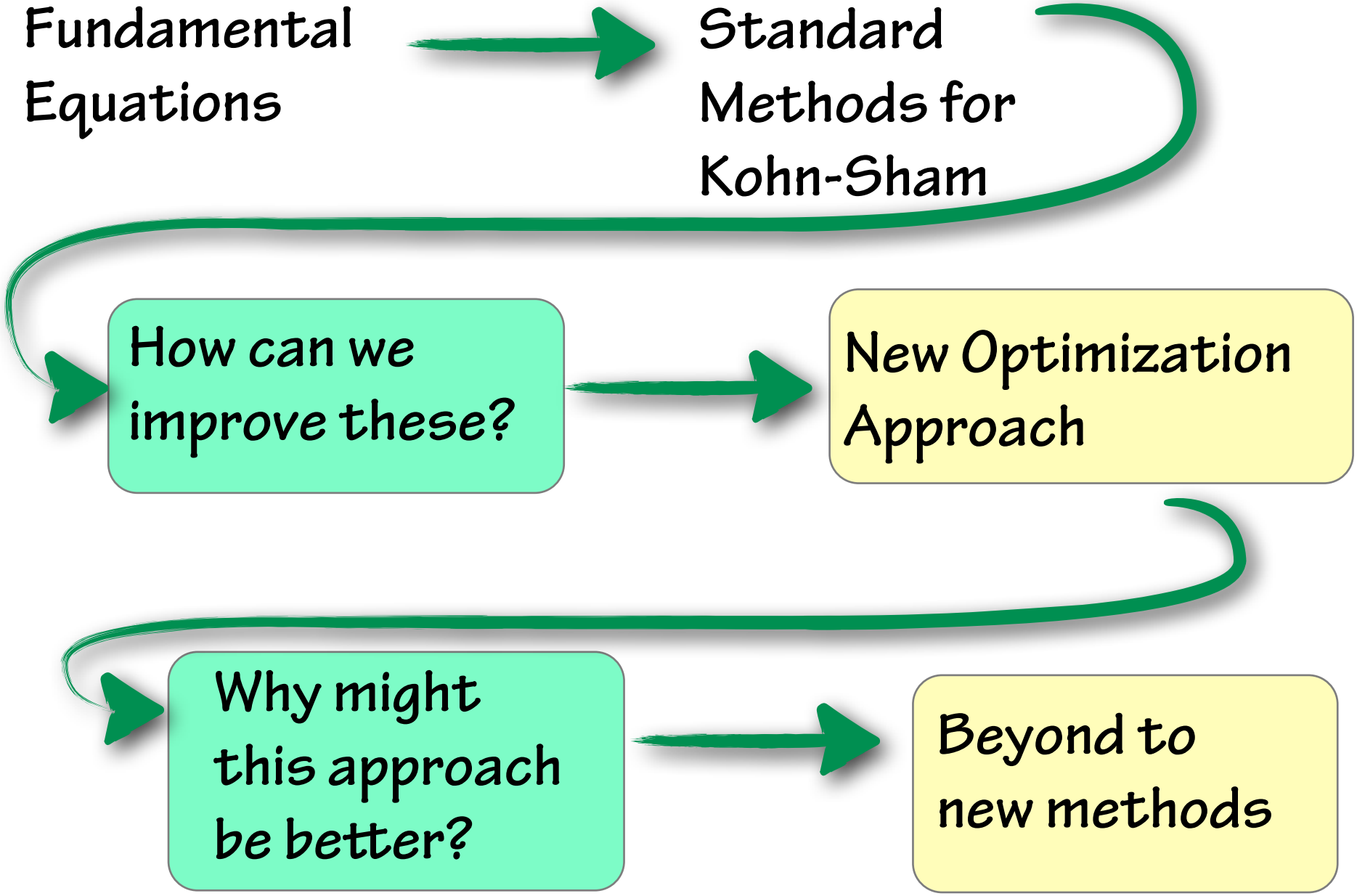
- Yes, there is a gap, and O induced states are very localized
- One calculation for 3500 atom 3% O alloy took 1 hour on 17,000 cores





L-W. Wang, B. Lee, Z. Zhao, H. Shan, J. Meza, D. Bailey, E. Strohmaier. INCITE project, NERSC, NCCS.

Our Roadmap


Fundamental Equations
Standard Methods for Kohn-Sham
How can we improve these?
New Optimization Approach
Why might this approach be better?
Beyond to new methods

Review of Fundamental Equations

Problem Solved

...in the Schrödinger equation we very nearly have the mathematical foundation for the solution of the whole problem of atomic and molecular structure ...

almost

…the problem of the many bodies contained in the atom and the molecule cannot be completely solved without a great further development in mathematical technique.

G.N. Lewis, J. Chem. Phys. 1, 17 (1933)

Many-body Schrödinger equation

$$H\Psi_i(r_1, r_2, ..., r_N) = E_i\Psi(r_1, r_2, ..., r_N)$$

$$H = -\frac{h}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N}v(r_i) + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i - r_j|}$$

- Ψ_i contains all the information needed to study a system
- $|\Psi_i|^2$ probability density of finding electrons at a certain state
- E_i quantized energy
- Computational work goes as 10^{3N}, where N is the number of electrons

Density Functional Theory

- The unknown is simple – the electron density, ρ
- Hohenberg-Kohn Theory (1964)
  - There is a unique mapping between the ground state energy from Schrödinger's equation and the electron density, i.e. $E(\rho)$
  - Exact form of the functional is unknown
- Independent particle model
  - Electrons move independently in an average effective potential field
  - Add correction for correlation
- Good compromise between accuracy and feasibility

Kohn-Sham formulation

- Replace many-particle wavefunctions, Ψ_i, with single-particle wavefunctions, ψ_i
- Write Kohn-Sham total energy as:

$$E_{total}[\{\psi_i\}] = \frac{1}{2}\sum_{i=1}^{n_e}\int_\Omega |\nabla\psi_i|^2 + \int_\Omega V_{ion}\rho$$

$$+\frac{1}{2}\int_\Omega \frac{\rho(r)\rho(r')}{|r-r'|}drdr' + E_{xc}(\rho),$$

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

- Exchange-correlation term, E_{xc}, contains quantum mechanical contributions, plus part of K.E. not covered by first term when using single-particle wavefunctions

Kohn-Sham equations

- Goal is to find the ground state energy by minimizing total energy, E_{total}
- Leads to:

$$
\begin{aligned}
H\psi_i &= \epsilon_i \psi_i, \quad i = 1, 2, ..., n_e \\
H &= \left[-\frac{1}{2}\nabla^2 + V_{ion}(r) + \int \frac{\rho}{|r - r'|} + V_{xc}(\rho) \right]
\end{aligned}
$$

Discretized Kohn-Sham equations

$$
\begin{aligned}
H(X)X &= X\Lambda, \\
X^*X &= I_{n_e}, \\
H(X) &= \frac{1}{2}L + V_{ion} + \mathrm{Diag}\,(L^\dagger \rho(X)) + \mathrm{Diag}\; g_{xc}(\rho(X))
\end{aligned}
$$

- Many different discretization schemes available
- Large nonlinear eigenvalue problem
- Orthogonality constraints

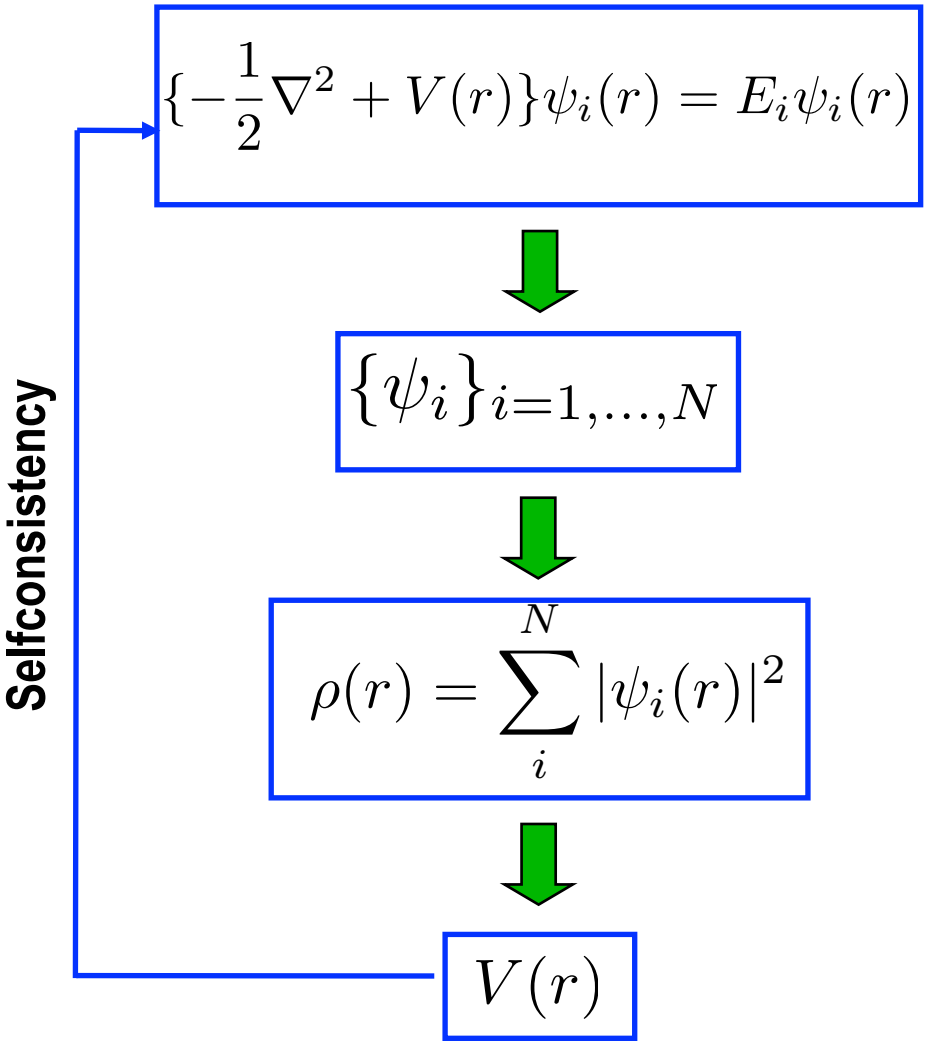
Standard Methods for the Kohn-Sham Equations

Solving the Kohn-Sham equations

- Self-Consistent Field (SCF) iteration
  - view as a linear eigenvalue problem
  - need to precondition
  - usually used with other acceleration techniques to improve convergence
  - no good convergence theory
- Direct Constrained Minimization
  - minimize the total energy directly
  - pose as a constrained optimization problem
  - also requires globalization techniques
- Invariance property

$$\begin{aligned} E(XQ) &= E(X) \\ H(XQ) &= H(X) \end{aligned} \quad \text{for any} \quad Q^*Q = I_{n_e}$$

Basic SCF iteration



- Overall Complexity $O(N^3)$
- Major computational work (for plane wave codes):
  - 3D FFT
  - Orthogonalization
  - Nonlocal potential
- May converge slowly and sometimes doesn't converge at all
- Energy need not decrease monotonically

Improving SCF

- Construct better surrogate – cannot afford to use local quadratic approximations (Hessian too expensive)
- **Charge mixing** to improve convergence; related to Broyden methods
- Use **trust region** to restrict the update to stay within a neighborhood of the gradient matching point
  - Level-Shifting (Saunders & Hillier 1973)
  - Cances & LeBris 2000
  - TRSCF – Thogersen, Olsen, Yeager & Jorgensen 2004; Francisco, Martinez, Martinez 2006; Yang, Meza, Wang (2007)

Many choices for charge mixing

- Simple mixing

$$\rho^{(i+1)} \leftarrow \tau\rho_{in}^{(i)} + (1-\tau)\rho_{out}^{(i)}, \quad 0 < \tau < 1.$$

- Pulay mixing (Direct Inversion of Iterative Subspace)

$$\rho^{(i+1)} = \sum_{j=1}^{i} \alpha_j \rho^{(j)}, \quad \sum_{j=1}^{i} \alpha_j = 1$$

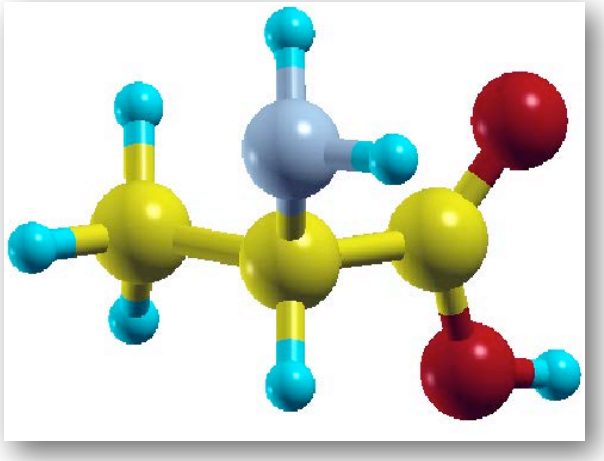
- Broyden mixing

$$\rho^{(i+1)} = \rho^{(i)} + \tau C_{i+1} r_i$$

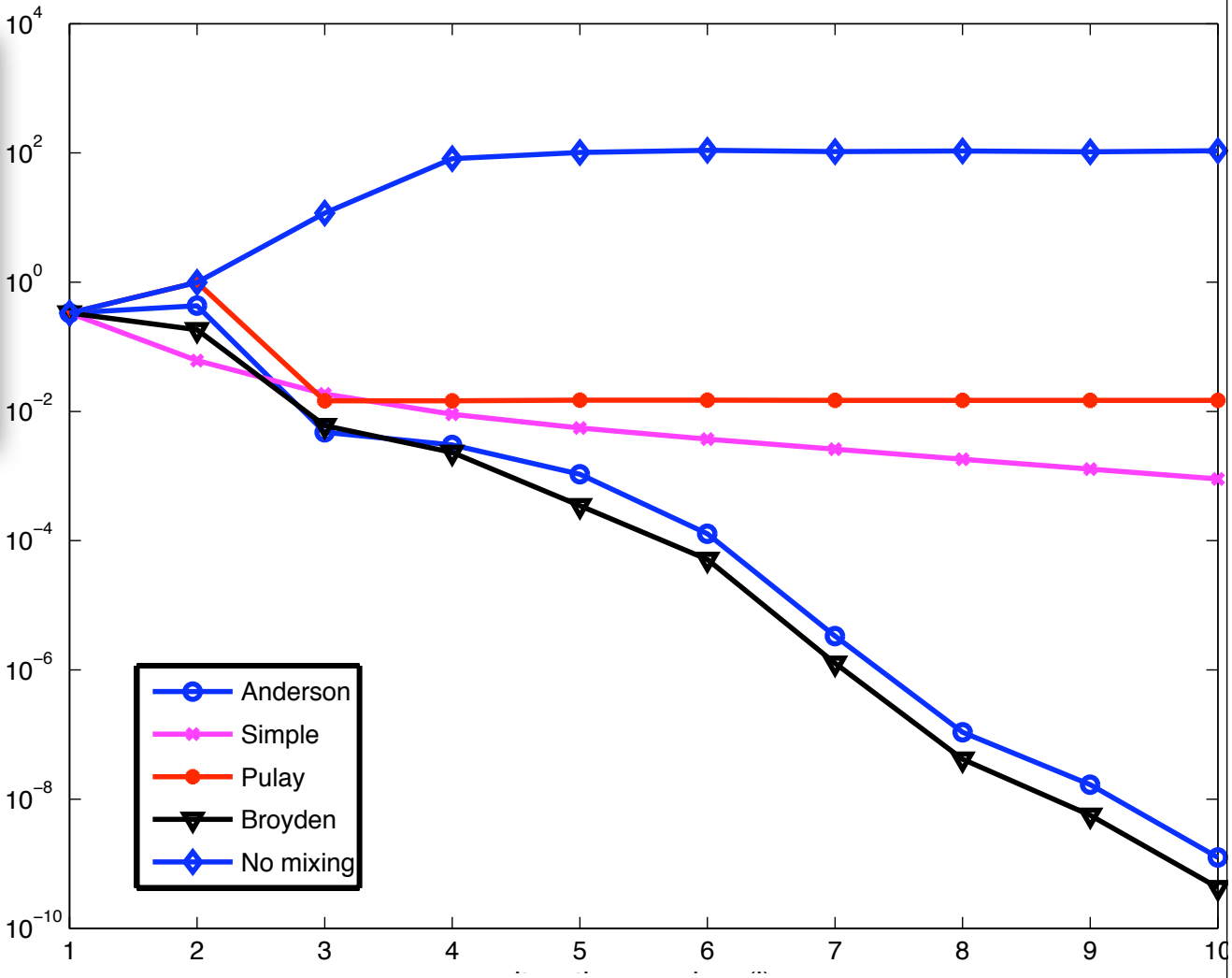
- Anderson mixing

$$\rho^{(i+1)} = \rho^{(i)} + \tau r_i + (S_i - \tau Y_i) Y_i^{\dagger} r_i$$

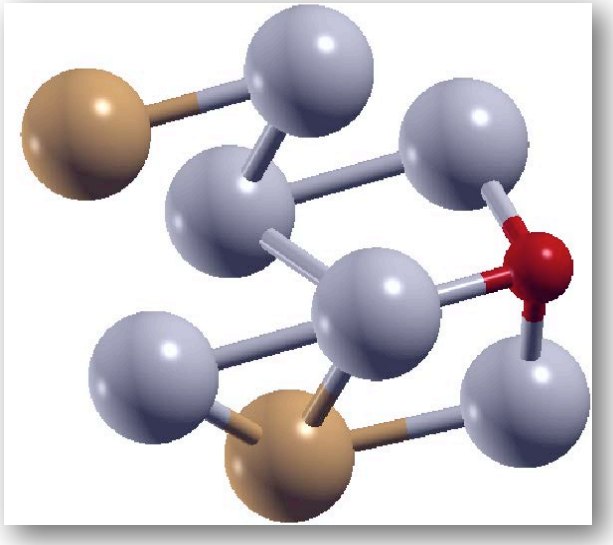
Comparison of charge mixing schemes



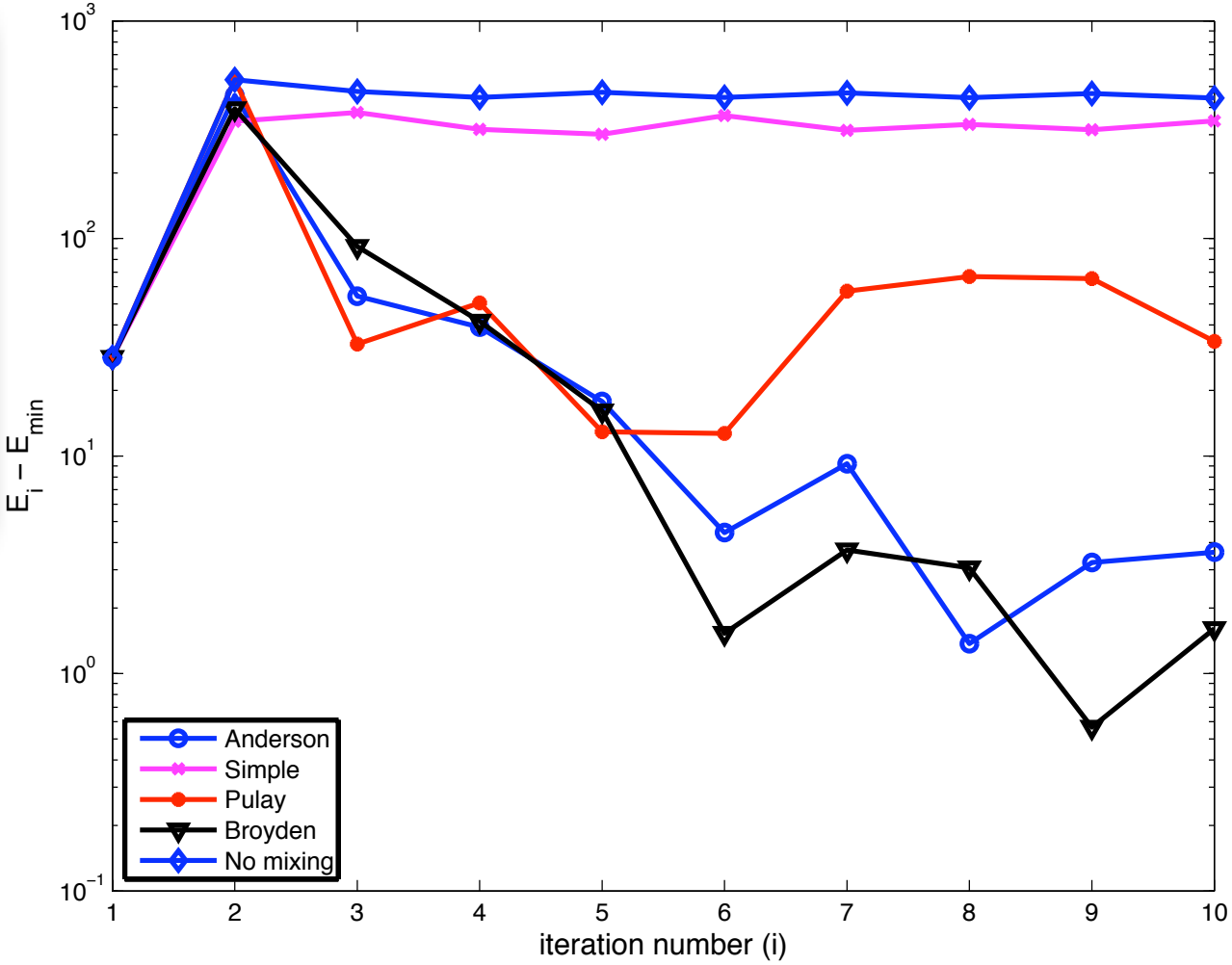
Alanine



Charge mixing can fail



Pt_6Ni_2O



Trust Region subproblem

- Solve

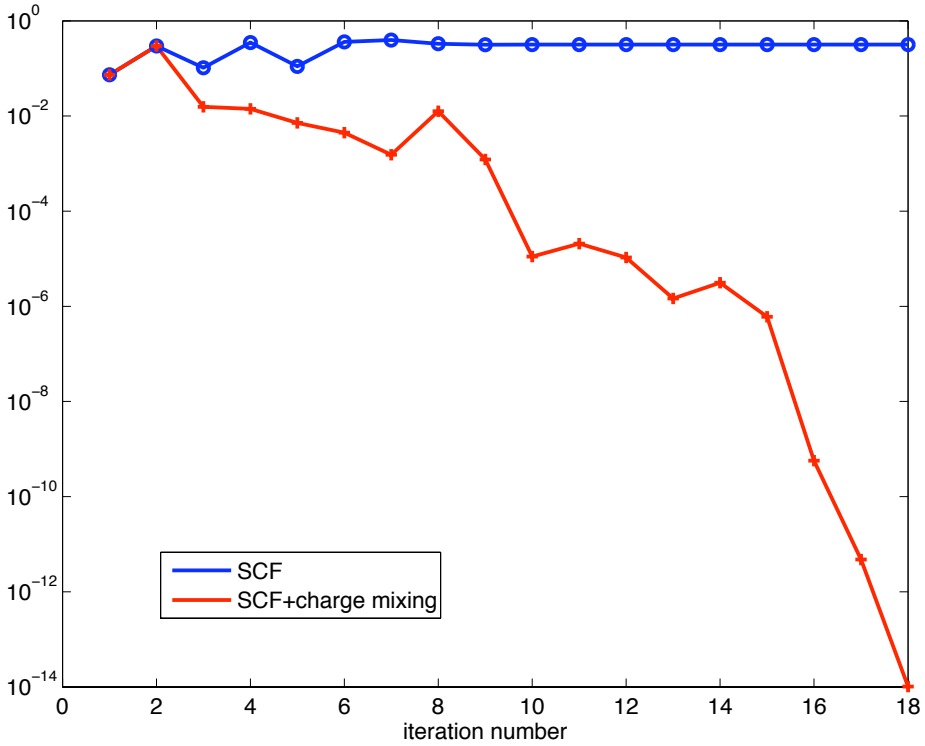
$$\begin{aligned} \min \quad & E_{sur}(x) \\ \text{s.t.} \quad & \\ & x^T x = 1, \\ & \|xx^T - x^{(i)}(x^{(i)})^T\|_F^2 \leq \Delta \qquad \text{trust region constraint} \end{aligned}$$

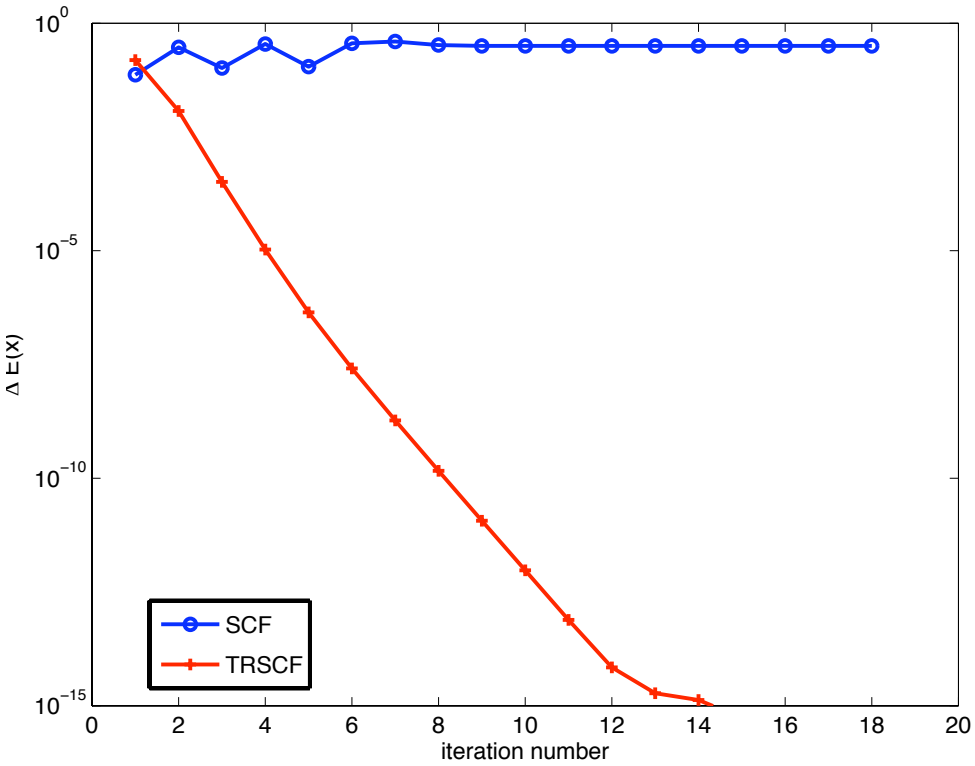
- Equivalent to solving

$$\begin{aligned} \left[H(x^{(i)}) - \sigma x^{(i)}(x^{(i)})^T\right] x &= \lambda x \\ x^T x &= 1 \end{aligned}$$

- σ is a penalty parameter (Lagrange multiplier for TR)

Comparison of TRSCF vs. mixing





Direct Constrained Minimization of the Kohn-Sham Equations

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Direct Constrained Minimization

- Assume $x^{(i)}$ is the current approximation
- Idea: minimize the energy in a certain (smaller) 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
    - $x_{k+1}^T x_{k+1} = 1$;
    - $E(x_{k+1}) < E(x_k)$;

Remark 1: A nonlinear CG-like algorithm

Remark 2: Extension of LOBPCG (Knyazev) to nonlinear EV

Subspace minimization

- Let $V = (x^{(i)}, p^{(i-1)}, r^{(i)})$; $x^{(i+1)} = Vy$, for some y;
- Solve

$$\min_{y^T V^T V y = 1} E(Vy)$$

- Equivalent to solving

$$\begin{aligned} G(y)y &= \lambda By \\ y^T By &= 1 \end{aligned}$$

where $B = V^T V$ and $G(y) = V^T[L + \alpha \mathrm{Diag}(L^{-1}\rho(Vy))]V$

DCM algorithm

- Input: Initial guess
- Output: X such that E_{KS} is minimized

1. $P^{(0)} = [], \mathrm{i} = 0;$
2. while (not converged)
   (a) $\Theta^{(i)} = {X^{(i)}}^* H^{(i)} X^{(i)};$
   (b) $R^{(i)} = H^{(i)} X^{(i)} - X^{(i)} \Theta^{(i)};$
   (c) Set $Y = (X^{(i)}, P^{(i-1)}, K^{-1} R^{(i)});$
   (d) Solve $\min_{G^* Y^* Y G = I_k} E_{tot}(YG);$
   (e) $X^{(i+1)} = YG(1 : n_e, :);\ P^{(i+1)} = YG(n_e + 1 : 3n_e, :);$
   (f) $i \leftarrow i + 1;$

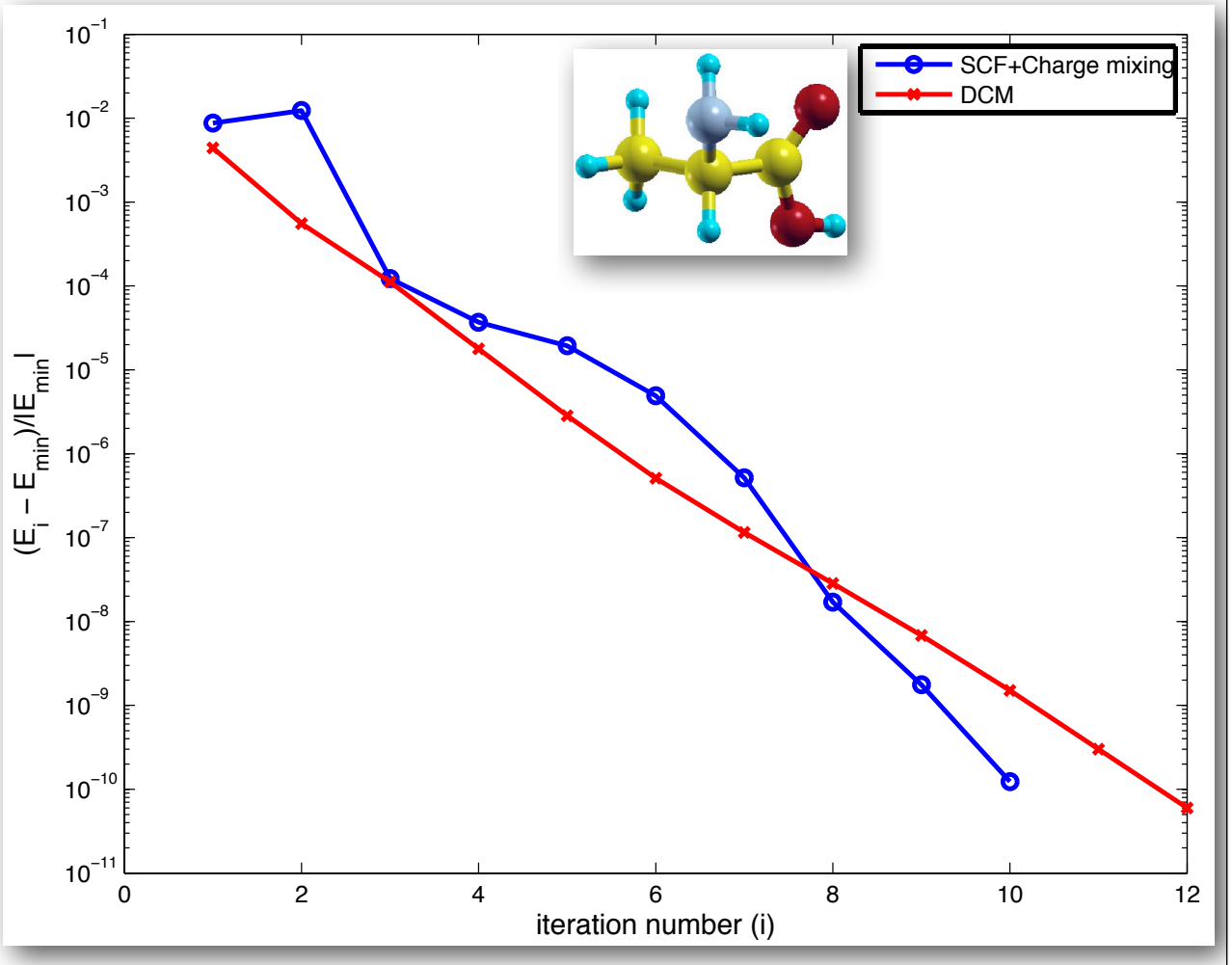
C. Yang, J. Meza, L. Wang, A Constrained Optimization Algorithm for Total Energy Minimization in Electronic Structure Calculation, J. Comp. Phy., 217 709-721 (2006)

Test problems

- KSSOLV Matlab code for solving the Kohn-Sham equations
  - Open source package
  - Handles SCF, DCM, Trust Region
  - Various mixing strategies
- Example problems: alanine and graphene
- Tests run on desktop computer

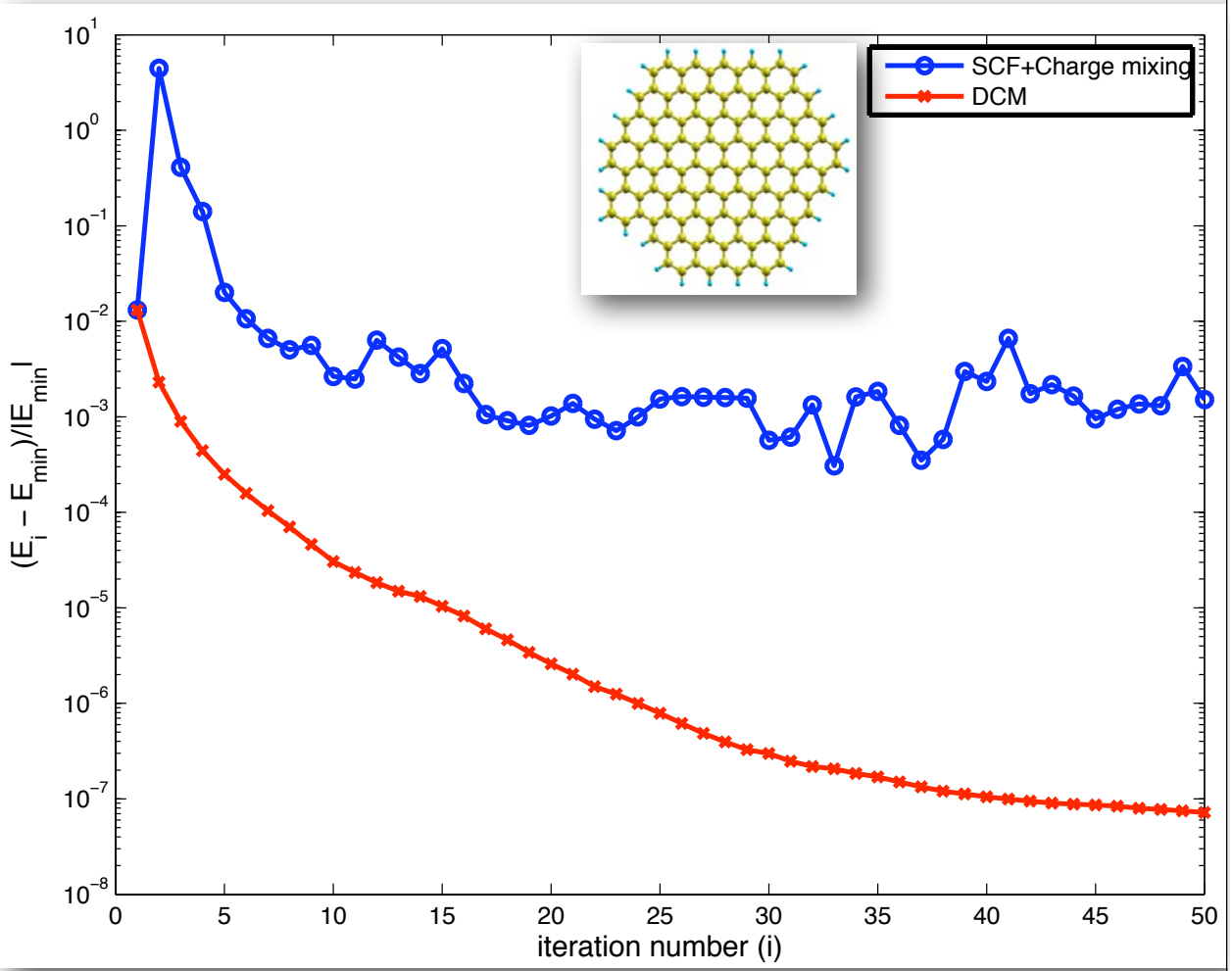
Example: Alanine

- sampling grid:
  - 96 x 48 x 96 (ecut=25 Ryd)
- 10 PCG iterations / SCF outer iteration
- 3 inner SCF iteration / DCM outer iteration
- supercell:
  - 20 x 15 x 20
- DCM: 253 secs
  SCF: 504 secs



Example: Graphene

- sampling grid:
  - 114 x 114 x 15
- 10 PCG iterations / SCF outer iteration
- 5 inner SCF iteration / DCM outer iteration
- supercell:
  - 40 x 40 x 5
- DCM: 2169 sec.
- SCF: 4109 sec.



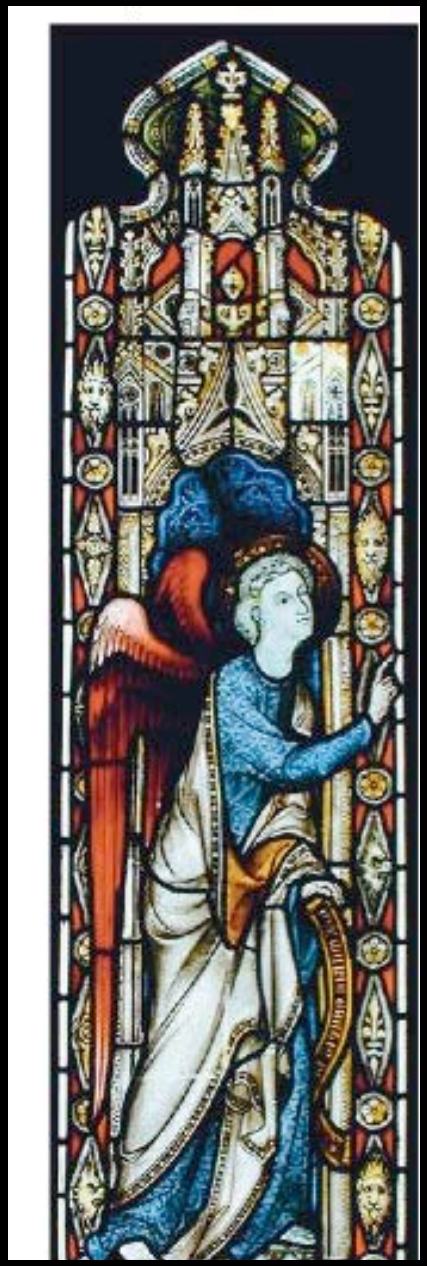
Comparison of DCM vs. SCF

system	SCF time	DCM time	SCF error	DCM error
C_2H_6	26	25	9.4 e-6	3.5 e-6
CO_2	26	23	3.1 e-3	1.1 e-4
H_2O	16	16	5.7 e-5	2.2 e-5
$HNCO$	34	32	7.4 e-3	6.8 e-5
Quantum dot	18	16	5.0 e-3	3.7 e-1
Si_2H_4	25	23	1.8 e-3	2.7 e-4
silicon bulk	15	15	3.0 e-4	9.6 e-6
SiH_4	20	19	9.7 e-6	4.9 e-7
Pt_2Ni_6O	415	281	3.7 e0	4.9 e-2
pentacene	887	493	5.2 e-1	2.5 e-2

Summary

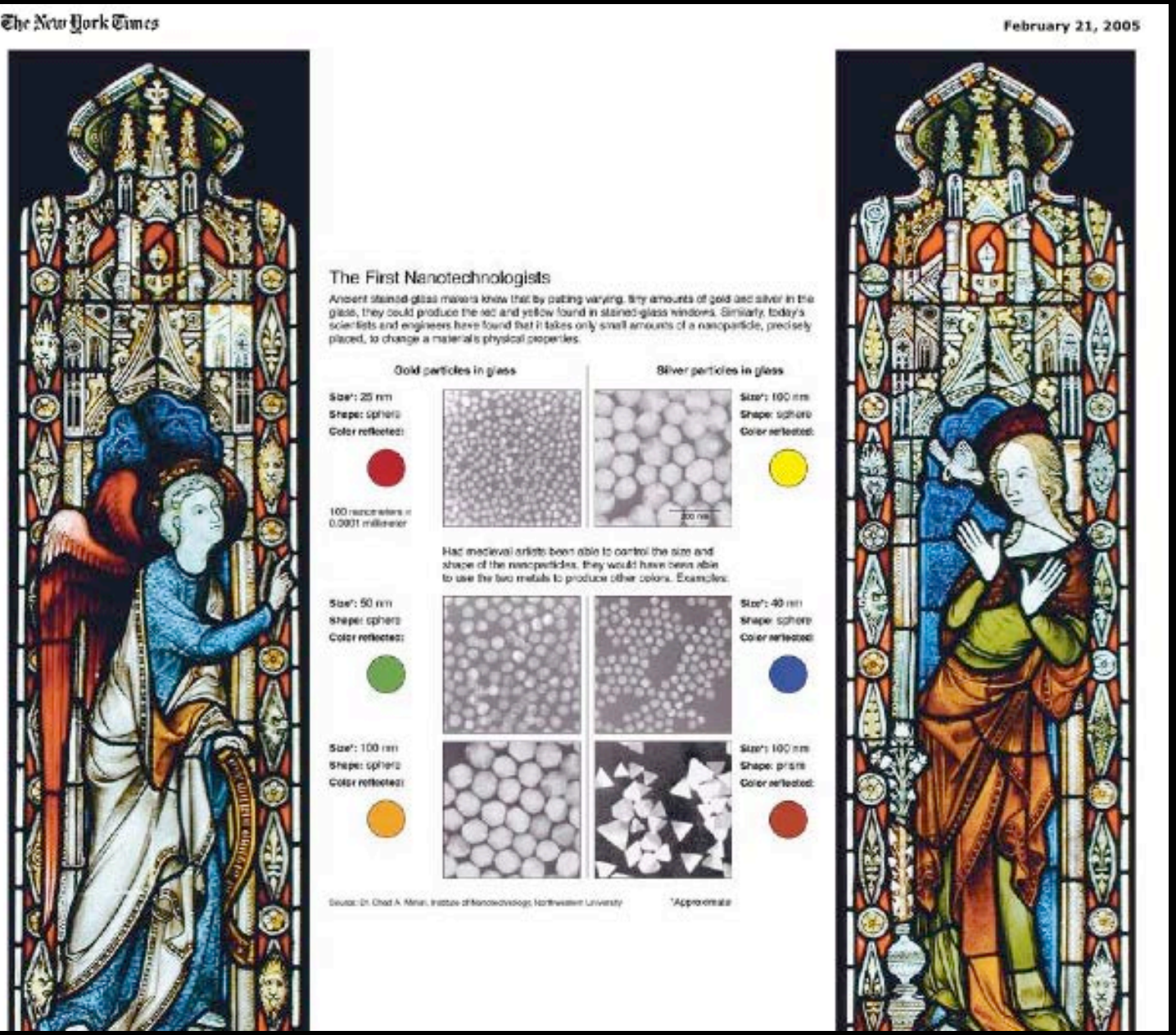
- Numerous opportunities for numerical analysts in energy and environmental applications
- New approach for solving the Kohn-Sham equations for modeling solar photovoltaic materials
- The combination of modeling, algorithms, and computational software is providing unprecedented levels of predictive simulations
- Much more to come ....


Thank you!
University of California, Merced
January 2004



Questions

First Nanoscientists?



The New York Times

February 21, 2005

The First Nanotechnologists

Ancient stained-glass makers knew that by putting varying, tiny amounts of gold and silver in the glass, they could produce the red and yellow found in stained-glass windows. Similarly, today's scientists and engineers have found that it takes only small amounts of a nanoparticle, precisely placed, to change a material's physical properties.

Gold particles in glass

Size*: 25 nm
Shape: sphere
Color reflected:

100 nanometers =
0.0001 millimeter

Silver particles in glass

Size*: 100 nm
Shape: sphere
Color reflected:

200 nm

Had medieval artists been able to control the size and shape of the nanoparticles, they would have been able to use the two metals to produce other colors. Examples:

Size*: 50 nm
Shape: sphere
Color reflected:

Size*: 40 nm
Shape: sphere
Color reflected:

Size*: 100 nm
Shape: sphere
Color reflected:

Size*: 100 nm
Shape: prism
Color reflected:

Source: Dr. Chad A. Mirkin, Institute of Nanotechnology, Northwestern University

*Approximate