

Ab Initio Methods in Materials Science

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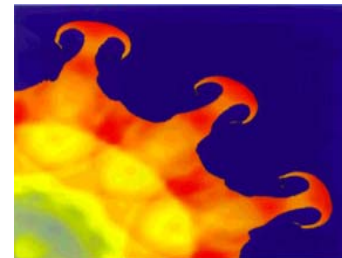
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Application to Fusion and Generation-IV Fission Reactors
Washington DC.
March 30th – April 2nd 2004



*Division of Materials
Sciences and Engineering*



OASCR



*Mathematical, Information, and
Computational Sciences Division*

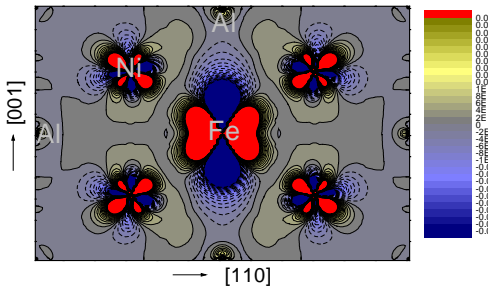
Ab Initio Methods in Materials Science

- Charge: Current state of the art in relevant multiscale computational materials science models, what phenomena can be adequately modeled?
- Try to answer for ab initio quantum mechanical approaches
 - Electronic structure methods
 - “Standard Model” of Condensed Matter
 - Density functional theory (DFT) in local density approximation (LDA)
 - LDA-DFT
 - What can be done
 - Properties. Scaling. “Real world” example.
 - When LDA fails!
 - QMC
 - What can it do?
 - Examples

Materials Simulation

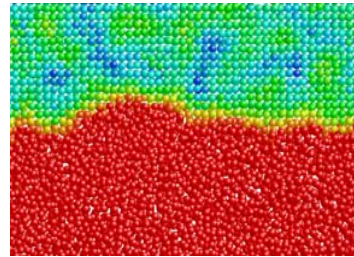
Spanning Length and Time Scales

Scale	Quantum	Nanoscopic	Mesoscopic	Macroscopic
L (m)	10^{-11} — 10^{-8}	10^{-9} — 10^{-6}	10^{-6} — 10^{-3}	$> 10^{-3}$
T (s)	10^{-16} — 10^{-12}	10^{-13} — 10^{-10}	10^{-10} — 10^{-6}	$> 10^{-6}$



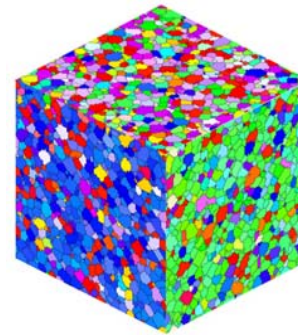
Bonding, Cohesion,
Magnetism

Quantum
Electrons



Interfaces,
Dislocations
Domain walls

Discrete
Effective Interactions



Microstructure,
Domains

Quasi-continuum
Heuristic models



Devices,
Structures

Continuum
Finite Element etc.

Ab Initio Electronic Structure Methods

- Born Oppenheimer approximation: $m_e / M \approx 10^{-3} - 10^{-5}$
- Solve many electron Schrodinger equation

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_\alpha \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} + \frac{1}{2} \sum_i \sum_j \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\Psi(\dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots) = -\Psi(\dots, \mathbf{x}_j, \dots, \mathbf{x}_i, \dots)$$

- “Quantum Chemistry” approaches
 - Hartree-Fock
 - Single Slater determinant variational trial wave function
 - Multiple Slater determinants
 - Couple Cluster method with Single and Double excitations (CCSD)
 - Highly accurate but limited to small molecules
 - Chemical accuracy Error < 0.05eV/atom
 - Scales as N^6
 - Standard implementations
 - NWChem

Density Functional Theory

- Density Functional Theory [DFT] - Walter Kohn (Nobel Prize in Chemistry)
- Formally exact theory of ground state
 - Ground state energy obtained by minimizing energy functional:

$$E[n(\mathbf{r})] = \frac{1}{2} \sum_{i=1}^N \int \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) d\mathbf{r} + \int n(\mathbf{r}) V_{ion} d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{ex}[n(\mathbf{r})]$$
$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2$$

- Get ground state charge density by solving set of self-consistent equations

$$\left(-\frac{1}{2} \nabla^2 + V_{ion}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

$$V_{ex}(\mathbf{r}) = \frac{\delta E[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

- Local density approximation (LDA)

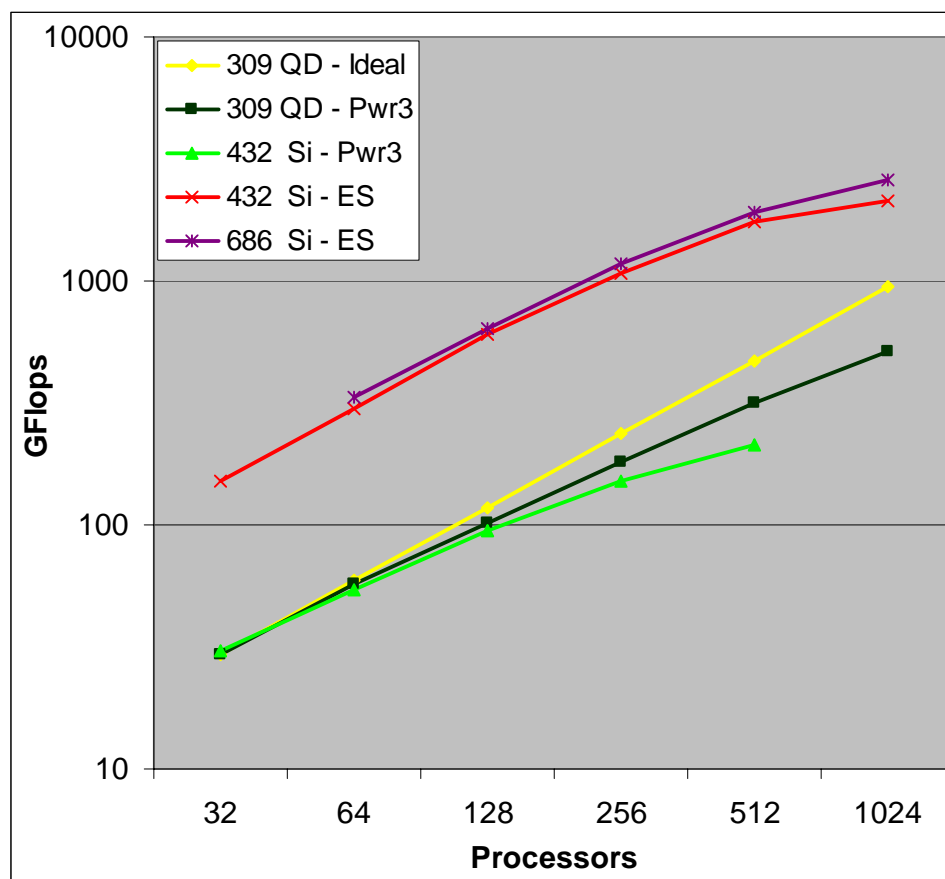
$$E_{xc}^{LDA}[n(\mathbf{r})] = \int \varepsilon_{xc}^{hom}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}$$

What Does LDA-DFT Deliver?

- Unbiased (*ab initio*, first principles, parameter free) models of materials properties
 - Interpretation is in terms of electronic structure (electron “glue”)
- “Standard Model” of materials properties
 - Ground State
 - Global relaxation: 100s of atoms: ~1000 steps
- Dynamics
 - Molecular dynamics, Spin Dynamics
- Accuracy
 - Depends on system and property
 - Metals, semi-conductors,
 - Strongly correlated systems, weakly interacting systems
- System sizes
 - 1-10³ atoms structure
 - Pico seconds
- Implementations
 - Periodic solids, surfaces, interfaces, clusters. molecules, defects
 - Pseudopotential methods: PARATEC, VASP, SIESTA,
 - KKR-Green’s function methods
 - FLAPW

PARATEC (PARAllel Total Energy Code)

- PARATEC - first-principles quantum mechanical total energy calculation using pseudopotentials & plane wave basis set
 - Developed with Louie and Cohen's groups (UCB, LBNL), Raczkowski (Multiple 3d FFTs Peter Haynes and Michel Cote)



- ES can run the same system about 10 times faster than the IBM SP
- Main advantage of ES for these types of codes is the fast communication network
- Fast processors require less fine-grain parallelism in code to get same performance as RISC machines

Andrew Canning (NERSC)

PARATEC: Performance

432
Si-atom
system
with
5CG
steps

P	Power 3		Power4		ES		X1	
	Mflops/P	%peak	Mflops/P	%peak	Mflops/P	%peak	Mflops/P	%peak
32	950	63%	1490	29%	4763	60%	3044	24%
64	848	57%	750	14%	4674	59%	2588	20%
128	739	49%			4742	59%	1907	15%
256	592	39%			4169	52%		
512					3392	42%		
1024					2077	26%		

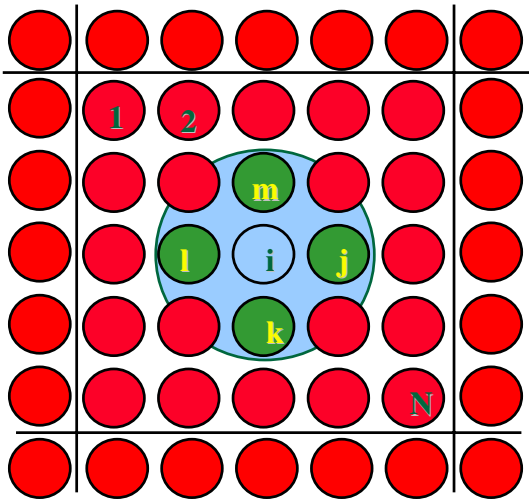
Preliminary x1 results

- Aggregate 2.6 TFlop/s - 686 Si atom simulation
 - Previous ~ 0.7 TFlop on Power3 using 1500 processors

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First Principles Methods for Large Systems

- N^3 problem
 - Solution of LDA Schrodinger equation requires
 - Computational effort $\rightarrow N^3$: Memory $\rightarrow N^2$
- Order-N methods
 - Pseudo-potential methods; Tight-binding molecular dynamics (Density matrix); All electron methods
- Locally Self-consistent Multiple Scattering (LSMS) Method



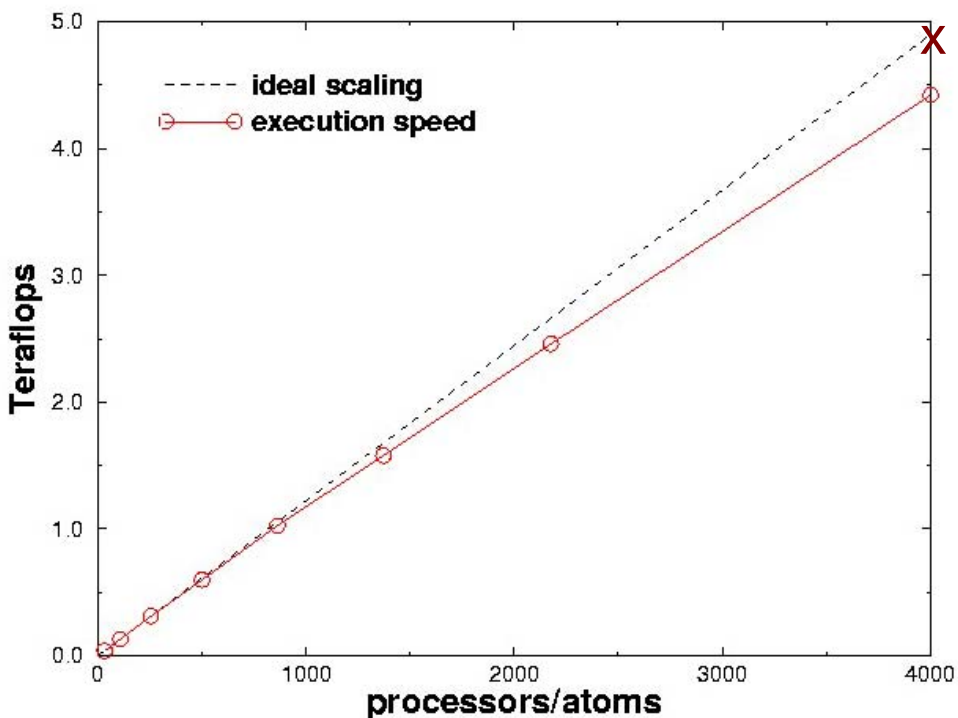
- Approximate total electron density by sum of locally determined fragment densities :

$$\rho_M(\mathbf{r}) = \sum_i \rho_M^i(\mathbf{r}) \sigma(\mathbf{r})$$

- $\rho_M^i(\mathbf{r})$ - on central site of a M cluster
- M : size of the *local interaction zone (LIZ)*

Order-N Scaling Enables Treatment of Large Systems

Iron Manganese (FeMn) 32–4000 atoms



A larger simulation of 4000 atoms of FeMn ran at **4.42 Teraflops** on 250 nodes.

- LSMS: Near ideal $O[N]$ scaling
 - First application code to run >1 Tflop/s

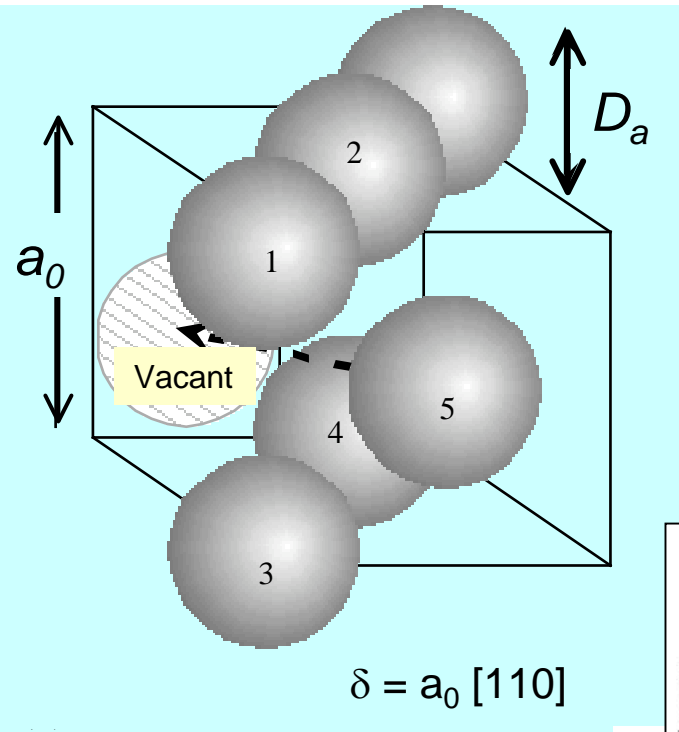
T3E900-LC512	NERSC	267 Gigaflops
T3E1200 -LC512	Cray	329 Gigaflops
T3E1200 -LC1024	Gov. Site	657 Gigaflops
~1500-Node T3E1200	Cray	1.02 Teraflops

- Impact of Massively Parallel Computers
 - 10^4 improvement since 1988
Gordon Bell Prize
 - 1988 - 1 Gflop/s
 - 1999 - 1 Tflop/s (LSMS)
 - 2003 - ~15 Tflop/s (ES)

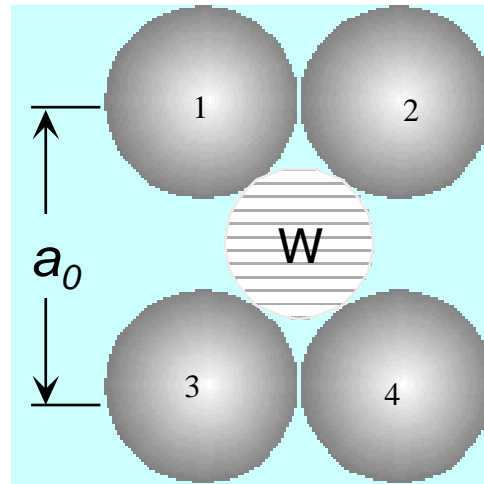
Vacancy-assisted diffusion in fcc structures

Janotti et al. PRL 92, (2004)

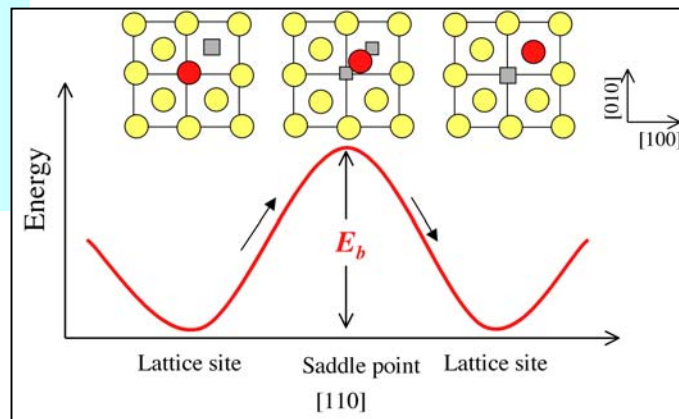
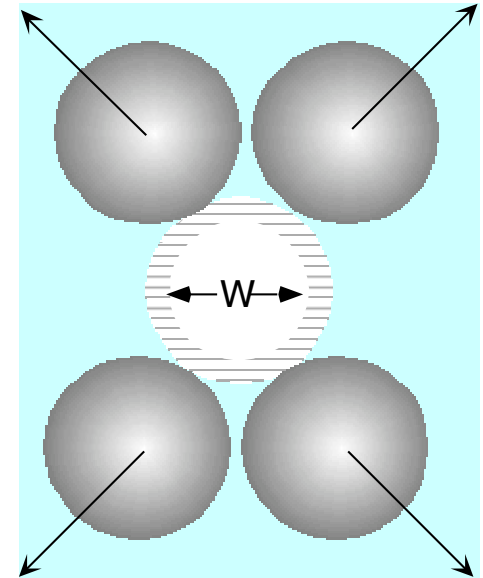
The FCC lattice geometry



plan view



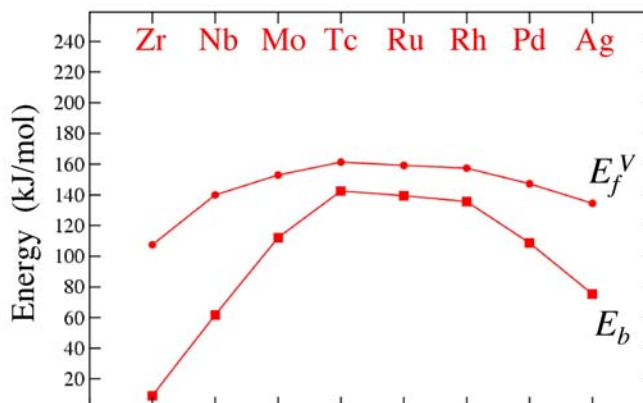
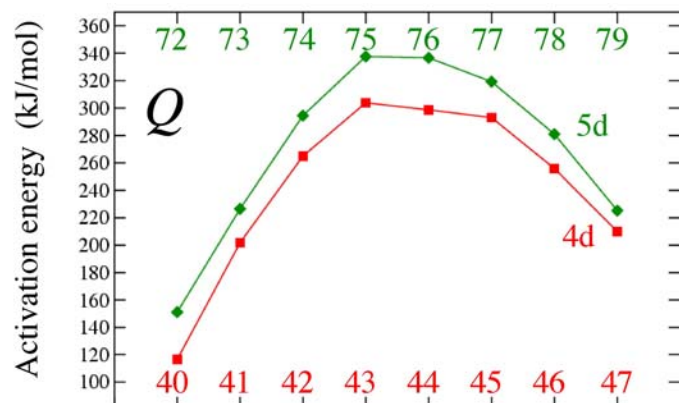
Dilated configuration of a diffusion jump "window" on the $\{110\}$ plane in FCC



$$D = f a_0^2 \exp \left(-\frac{E_f + E_b}{kT} \right)$$

The conventional thought based on strain considerations is that larger solute atoms would have to overcome higher potential energy barriers in order to diffuse.

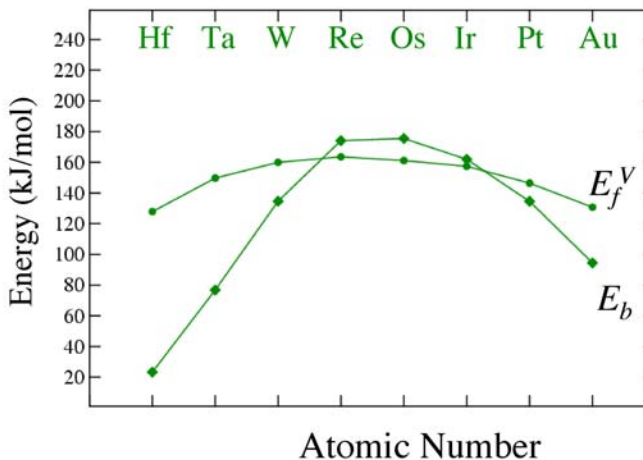
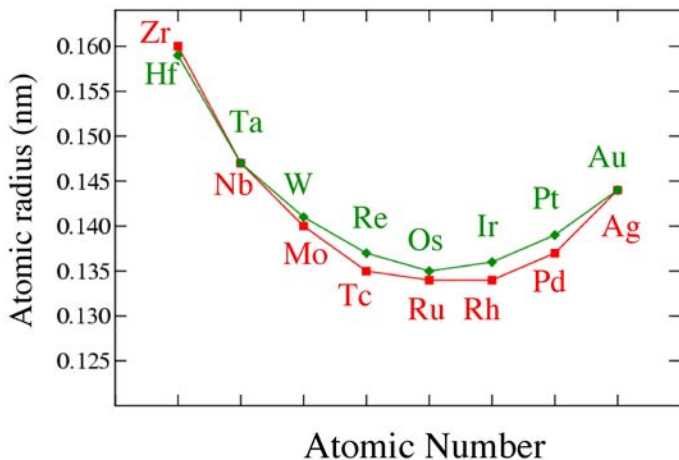
Calculated diffusion activation energy



$$D = f a_0^2 \nu_0 \exp \left(-\frac{Q}{kT} \right),$$

where

$$Q = E_f^V - E_b$$



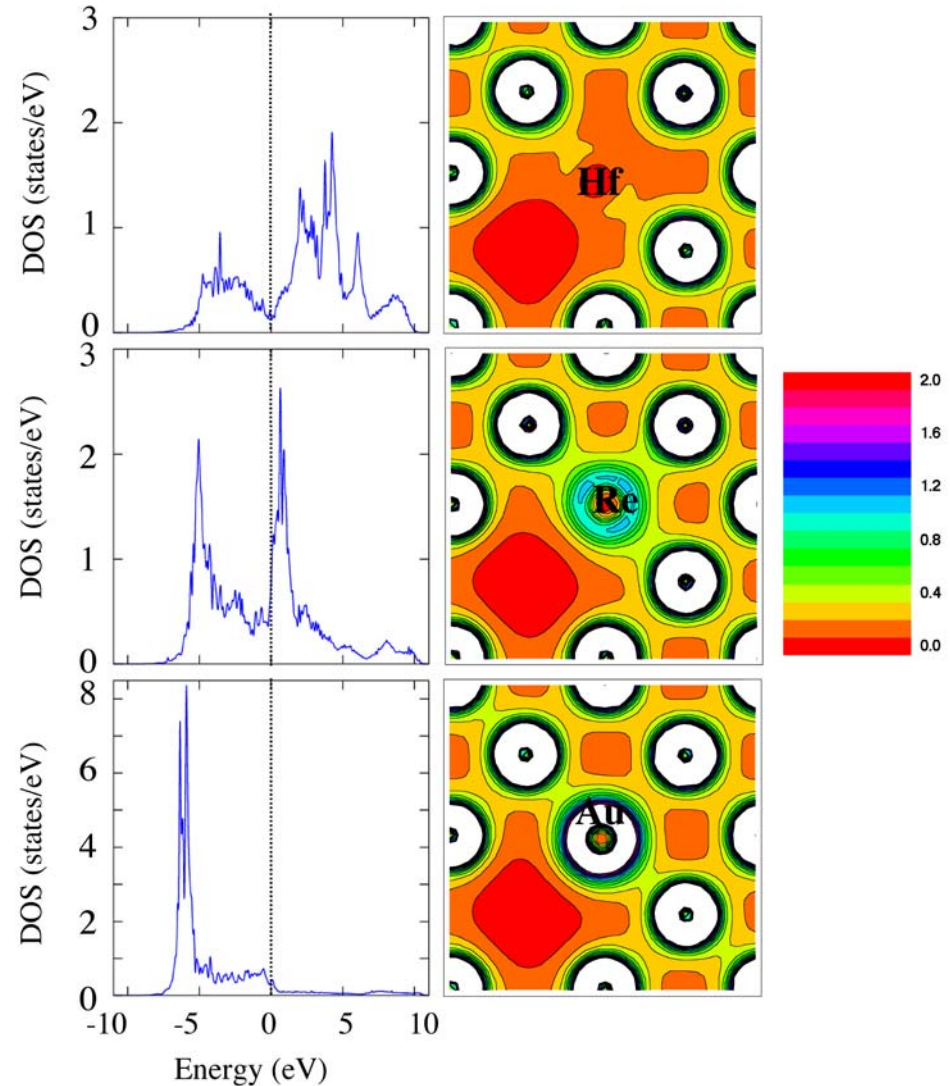
- Larger elements at eastern and western sides display significantly lower activation energy Q than smaller elements at the middle of the period
- Vacancies are easier to form next to larger solutes (as expected)
- But, the energy barrier E_b is the dominant factor in this counterintuitive effect. (that is unexpected)

Density of States and Valence Charge Density

- Hf has almost empty d-states and bonds very weakly to the Ni lattice, and, therefore, is easy to diffuse

- Re has almost half-filled d-states and shows strong directional bonding to its Ni neighbors, and, therefore, it is difficult to move.

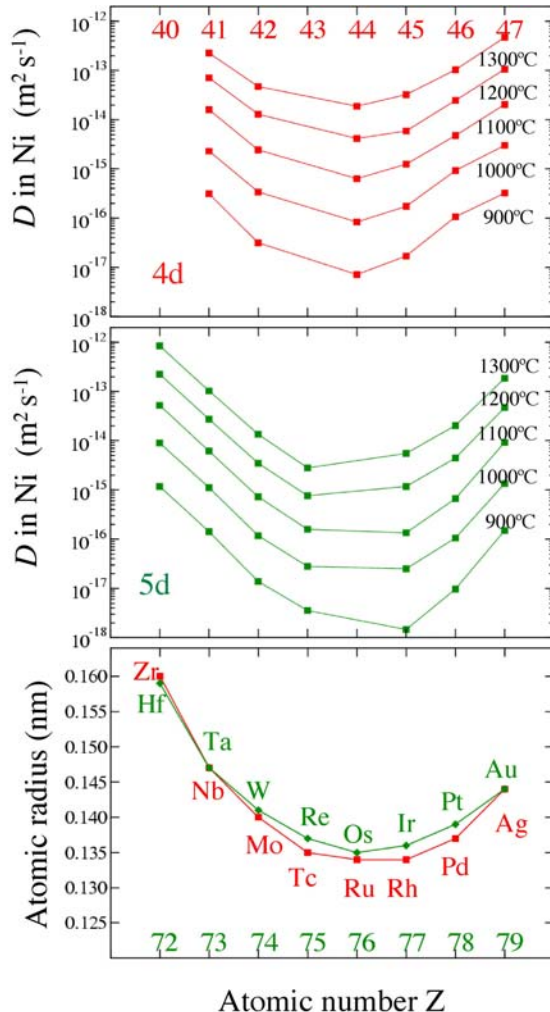
- Au 5d states are completely filled, localized at about 6 eV below the Fermi level, and weakly hybridizes with the host d states, making Au a faster diffuser in Ni.



Diffusion coefficients of transition metal solutes in Ni

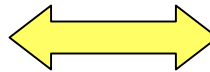
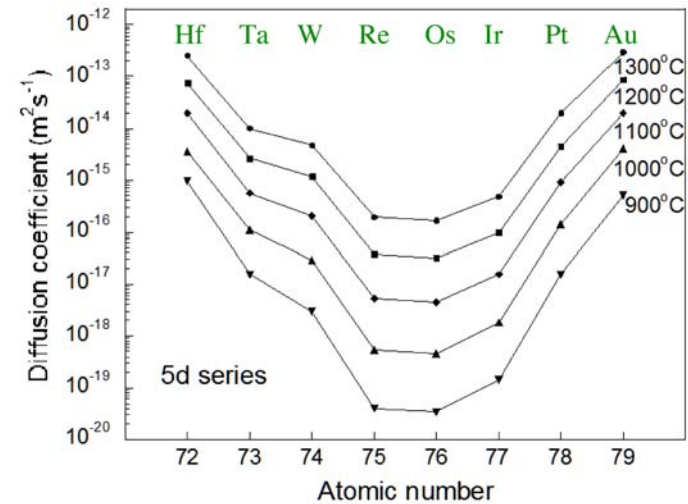
Experiments

Karunaratne and Reed
Acta mater. **51**, 2905 (2003),



Calculations

Janotti, krcmar, Fu and Reed
Phys. Rev Lett. **92**, 85901 (2004)

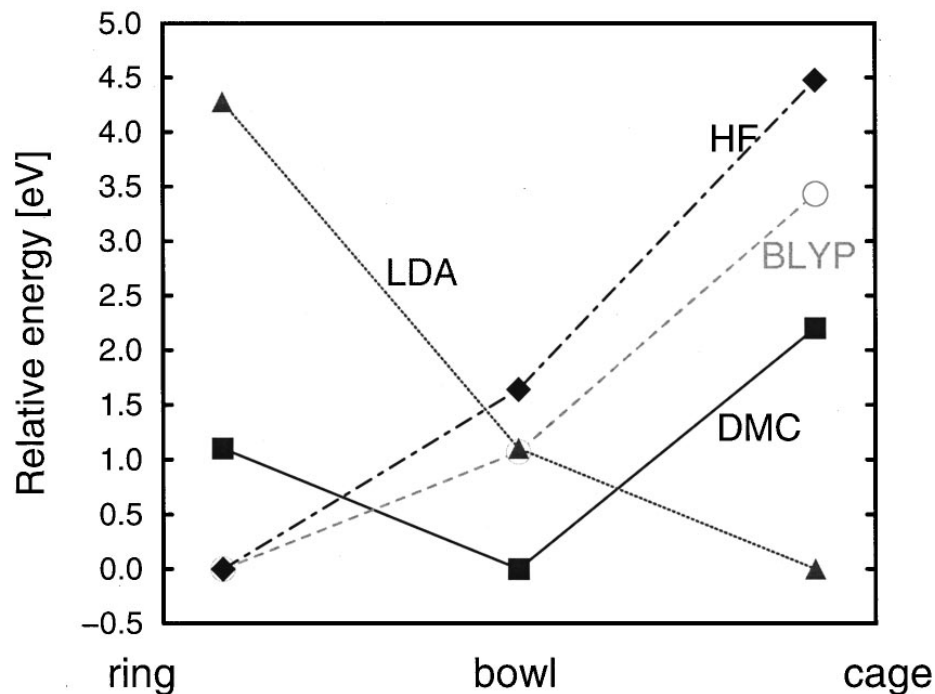
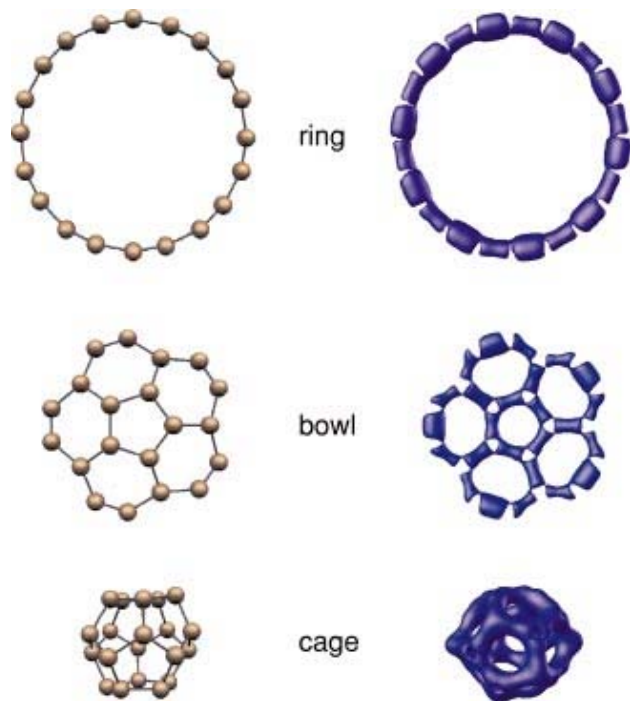


- Larger atoms can diffuse much faster than smaller ones in close-packed transition metals.
- It is a gigantic effect: the difference can be of 3 orders of magnitude

What do we do when LDA-DFT fails?

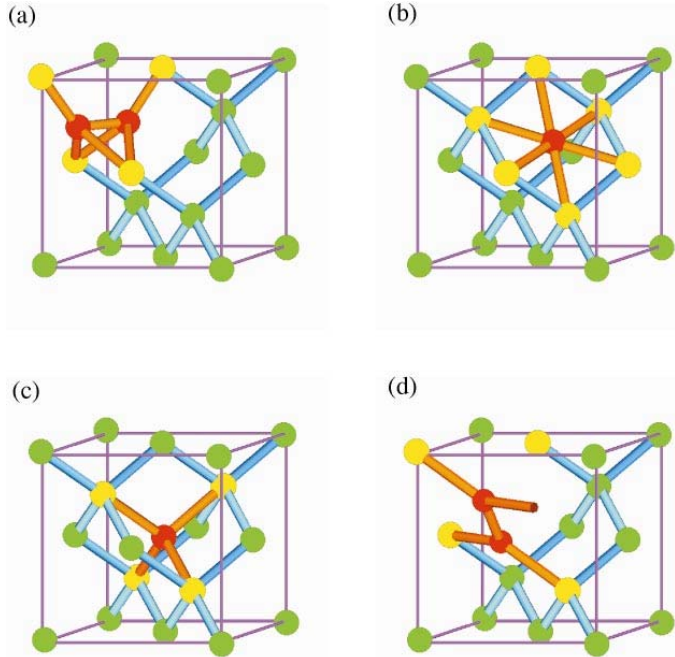
- Where does LDA-DFT fail
 - Strongly correlated systems, weakly interacting, chemical accuracy (0.05 eV/atom)
 - Fusion, fission: He, H interaction with materials
 - LDA fails for He phase diagram
 - Quantum chemistry, Quantum Monte Carlo
- LDA-DFT + correlations
 - LDA-SIC
 - Strongly localized
 - LDA+U, LDA+DMFT
 - Currently needs introduction of adjustable parameter: Hubbard-U
- Quantum Monte Carlo
 - Formally exact approach; rivals quantum chemistry
 - Can deliver chemical accuracy
 - Implementation difficult
 - Fermion sign problem
 - Recent good progress towards use in real systems
 - Variational Monte Carlo (VMC)
 - Diffusion Monte Carlo (DMC)
 - Limits $\sim 10^2$ electrons

QMC: Stability of C_{20} Clusters



- Search for smallest Fullerene
 - Grossman et al. PRL **74**, 1323 (1995); **79**, 4353, (1995)
 - LDA structures of C_{20} clusters
 - Different approximations in DFT lead to “opposite” results
 - LDA: Cage
 - BLYP: Ring
 - DMC: Bowl

QMC: Self-interstitials in Si

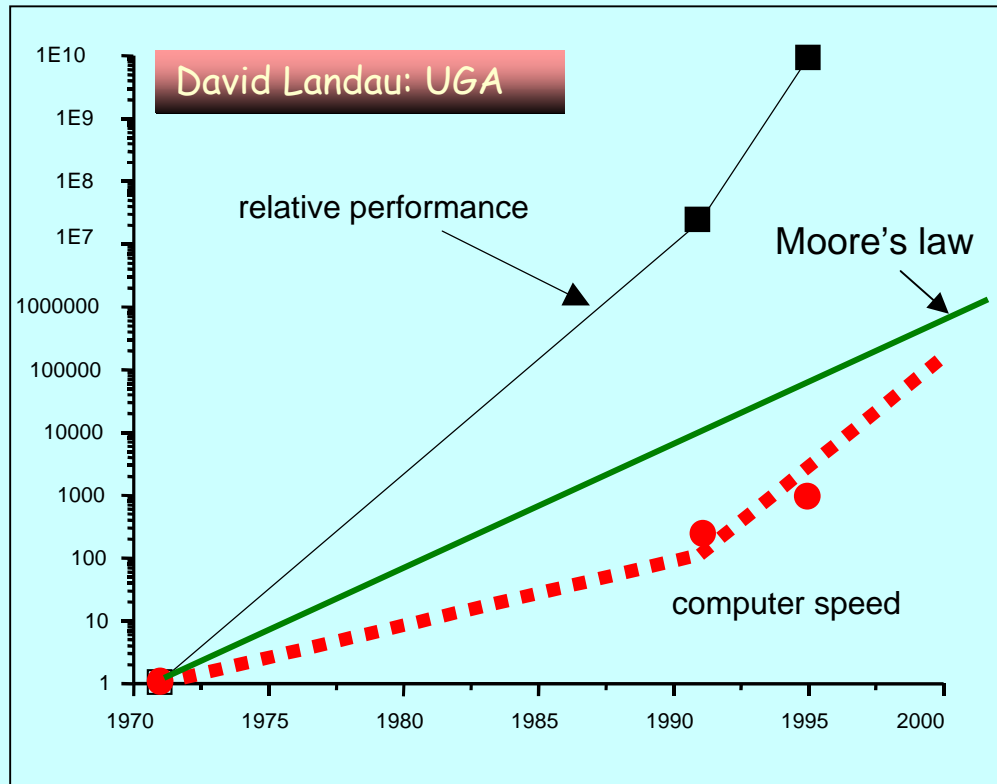
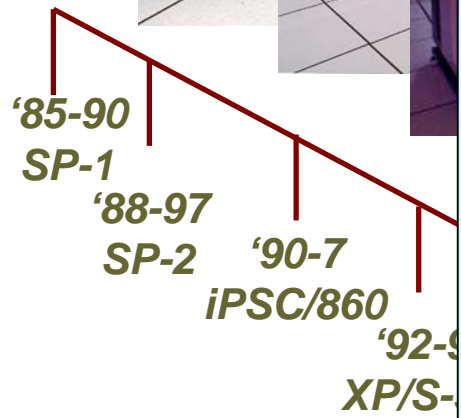
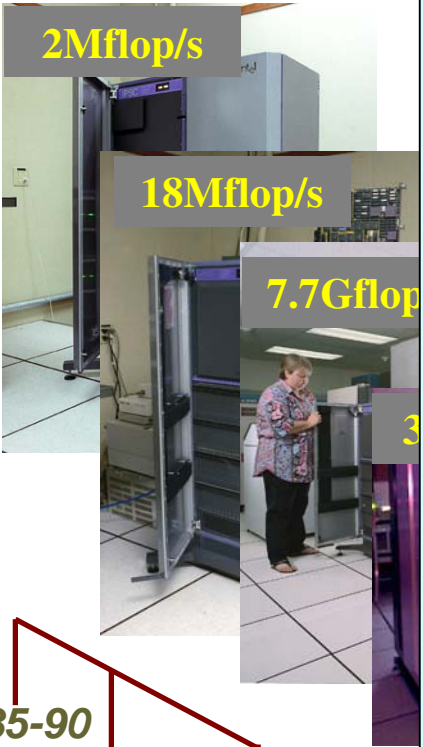


- Controversy regarding mechanism of high temp diffusion
 - Leung, W-K. et al. PRL **83**, 2351 (1999)
 - Fixed node diffusion Monte-Carlo
 - Activation energy
 - DMC 4.84 eV; Expt. ~5.0eV

Defect	LDA	GGA	DMC ^a	DMC ^b
Split-(110)	3.31	3.84	4.96(24)	4.96(28)
Hexagonal	3.31	3.80	4.70(24)	4.82(28)
Tetrahedral	3.43	4.07	5.50(24)	5.40(28)
Concerted exchange	4.45	4.80	5.85(23)	5.78(27)

Challenges in Ab Initio Methods

- Scaling
 - Robust $O[N]$ methods
 - Scaling beyond $\text{few} \times 10^3$
 - Length scales - parallel computers, domain decomposition
 - Time scales ?
- Chemical accuracy
 - Improved functionals
 - Integrating QMC with LDA
 - Parameter free DFT-DMFT
 - Order-N scaling of QMC
- How do we utilize more than a $\text{few} \times 10^3$ CPUs?
- Integration within multiscale modeling
 - Different models at different scales
 - Parameter passing
 - Seamless integration



Relative performance increase of Ising model simulations (■) compared the normalized speed of the computers (●) the simulations were executed on. The dashed line is a schematic of the increase in peak performance of the fastest supercomputers since 1972.

