SAND2014-15172PE

Exceptional service in the national interest

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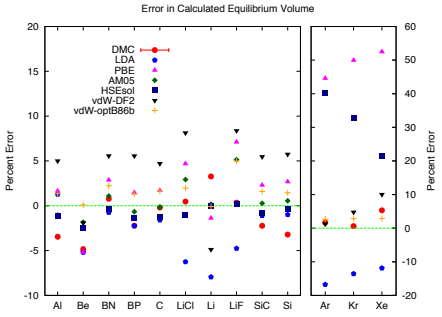

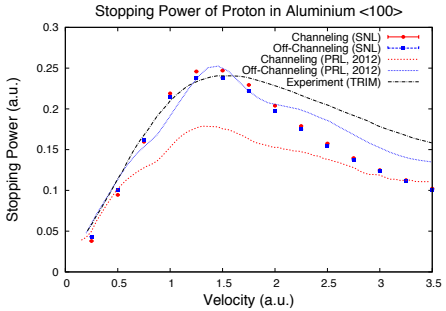

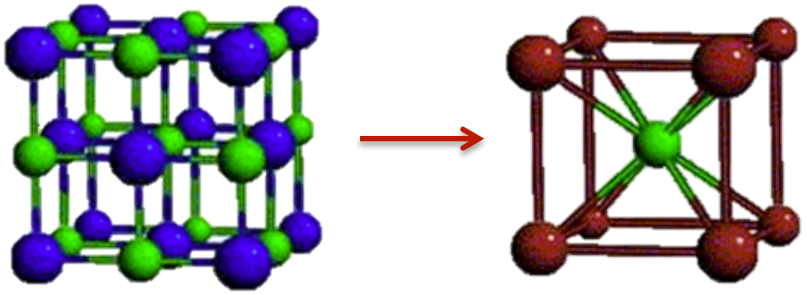

B1 B2

Quantum Mechanical Calculations at High Pressure beyond Kohn-Sham: Opportunities and Challenges

L. Shulenburger

U.S. DEPARTMENT OF ENERGY

National Nuclear Security Administration

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Techniques to probe materials at extreme conditions

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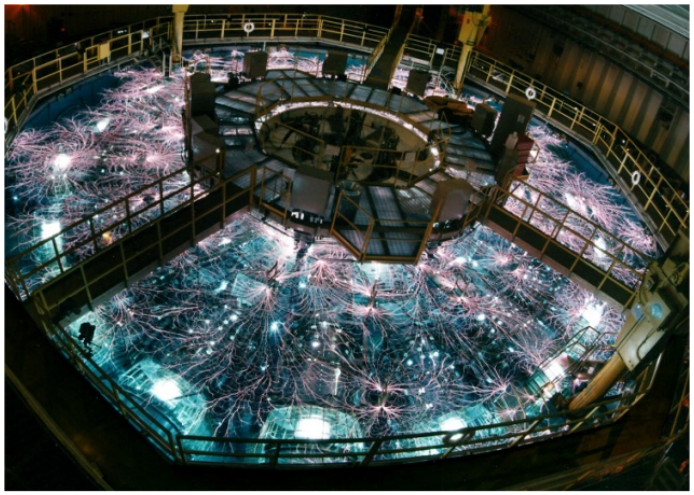

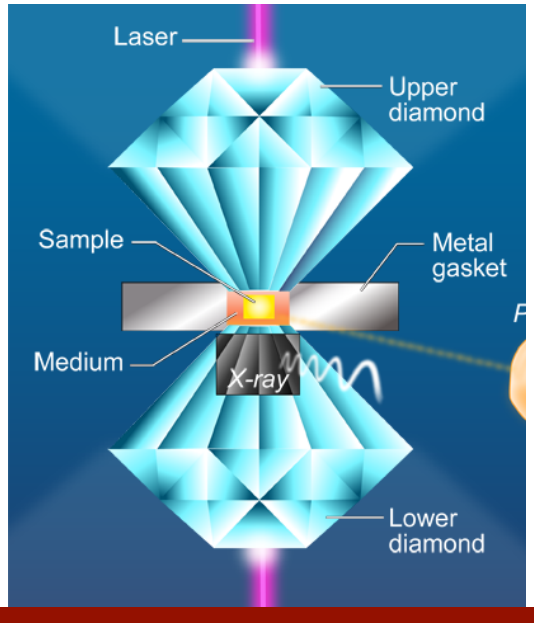

Towards ab initio simulation of materials

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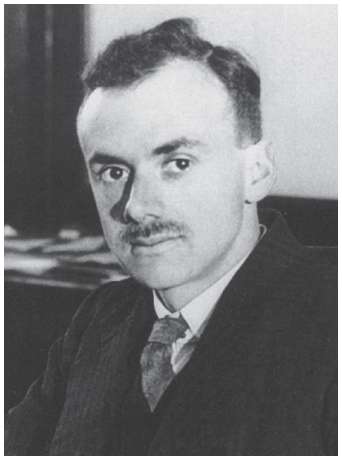
- Goal: Solution of governing equations without approximation
  - Equations are the same for carbon at 50 Mbar and dilute xenon gas
  - Results would be predictive for all materials and environments!

"The underlying physical laws necessary for a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact applications of these laws lead to equations much too complicated to be soluble."

-- Paul Dirac 1929



Are we there yet?

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- Density functional theory (DFT) calculations have become ubiquitous in HED science
  - Fundamental insight: density, not the wavefunction can be used as the basic variable
  - Kohn-Sham ansatz: solve an independent particle problem in the presence of an effective potential (exchange-correlation)
  - Calculations provide precise detail on microstructure of material
  - Response functions are routinely calculated with high precision

Are we there yet? -- No

- Simple forms for the effective potential have proven quite useful, but they are difficult to judge and improve
- Scaling with particle number is not favorable for anything beyond the nanoscale – $O(N^3)$
- Properties other than the energetics are not easily available without relying on Kohn-Sham wavefunction
  - Even relative energetics may be a problem – see the band gap problem
- Lack of time dependence for electrons

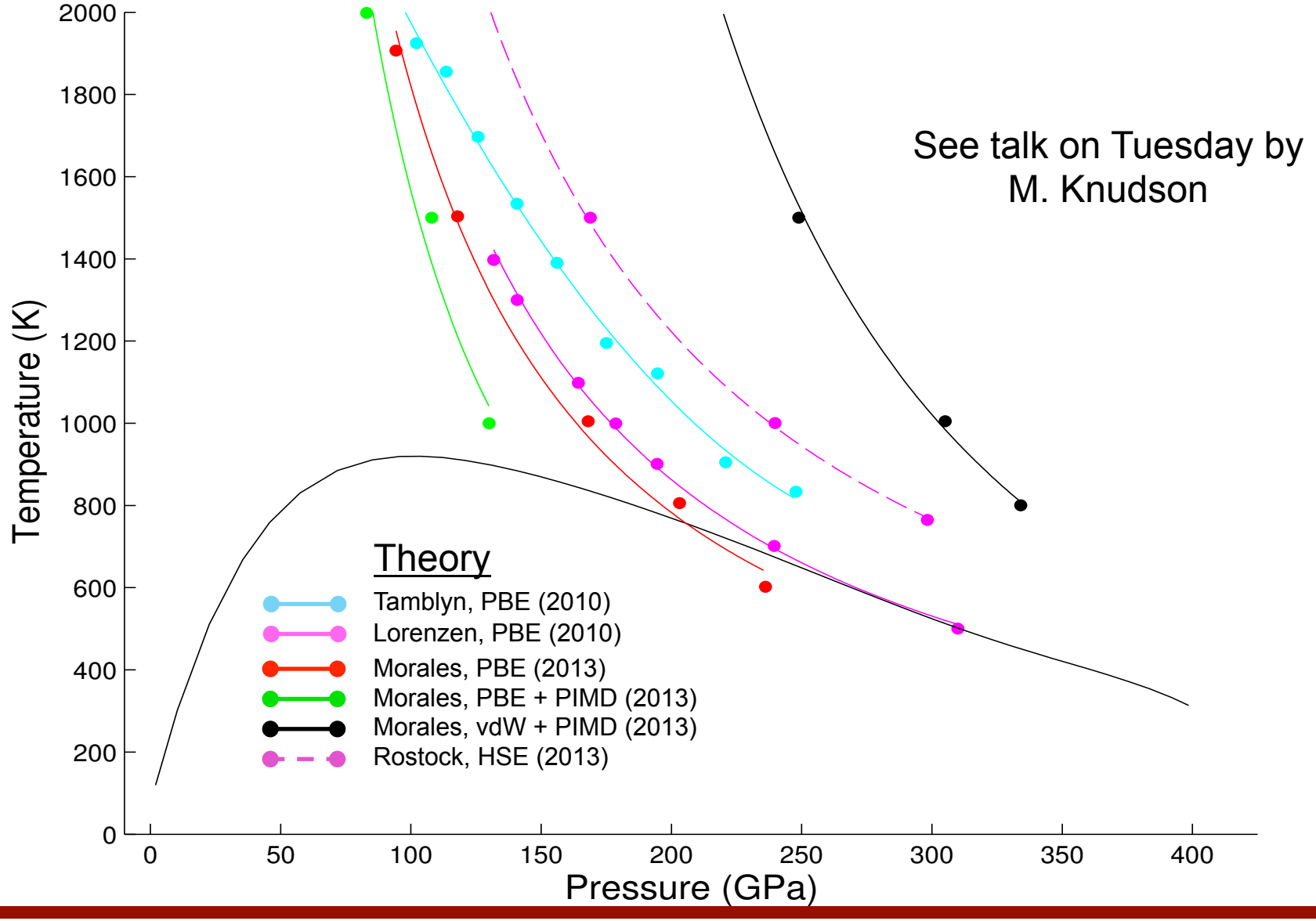
"Jacob's Ladder" of Functionals

Table 1: Overview of selected popular XC functionals. X is the exchange functional, C the correlation functional.

Functional	Authors	Ref.
Local Density Approximation (LDA) (I)		
SVWN[1]	X: Slater	23
	C: Vosko, Wilk, Nusair	24
PW[1]	Perdew, Wang	25
Generalized Gradient Approximation (GGA) (II)		
BP86	X: Becke	15
	C: Perdew	26
BLYP	X: Becke	15
	C: Lee, Yang, Parr	16
PW91	Perdew, Wang	27,28
PBE	Perdew, Burke, Ernzerhof	14
PBEsol	Perdew, Ruzsinszky *et al.*	22
RPBE	Hammer, Hansen, Nørskov	29
SOGGA	Zhao, Truhlar	30
Meta-Generalized Gradient Approximation (meta-GGA) (III)		
TPSS	Tao, Perdew, Staroverov, Scuseria	17
Hybrid Functionals (IV)		
B3LYP	Becke	18,19
PBE0	Perdew, Ernzerhof, Burke	31
HSE	Heyd, Scuseria, Ernzerhof	32
B97	Becke	33
TPSSh	Staroverov, Scuseria, Tao, Perdew	34,35
Fully nonlocal functionals (V)		
RPA	Bohm, Pines	36
B2PLYP	Grimme	37

[a]Both SVWN and PW are different parameterizations for the exchange-correlation energy of uniform electron gas and give almost identical results.

Recent predictions for LL-IMT in H



The path forward

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- More accurate treatment of interaction
  - Quantum Monte Carlo
- Realistic energy transfer between electrons and ions
  - Time dependent density functional theory

Improving electronic approximations:

Quantum Monte Carlo

- Solve Schrodinger equation directly?

$$i\hbar\frac{\partial}{\partial t}\Psi(t,r_1\ldots r_N)=\hat{H}\Psi(t,r_1\ldots r_N)$$

$$\hat{H}=-\sum_i\frac{\nabla_i^2}{2m}+\frac{1}{2}\sum_{i\neq j}\frac{e^2}{\left|\vec{r}_i-\vec{r}_j\right|}+\sum_{i,I}\frac{Z_I e^2}{\left|\vec{R}_I-\vec{r}_i\right|}=\hat{T}+\hat{V}$$

- Ignore scaling problem
  - Green's function approach changes differential equation to integral
- Integral is still evaluated in 3N dimensions!
  - Stochastic sampling vs deterministic

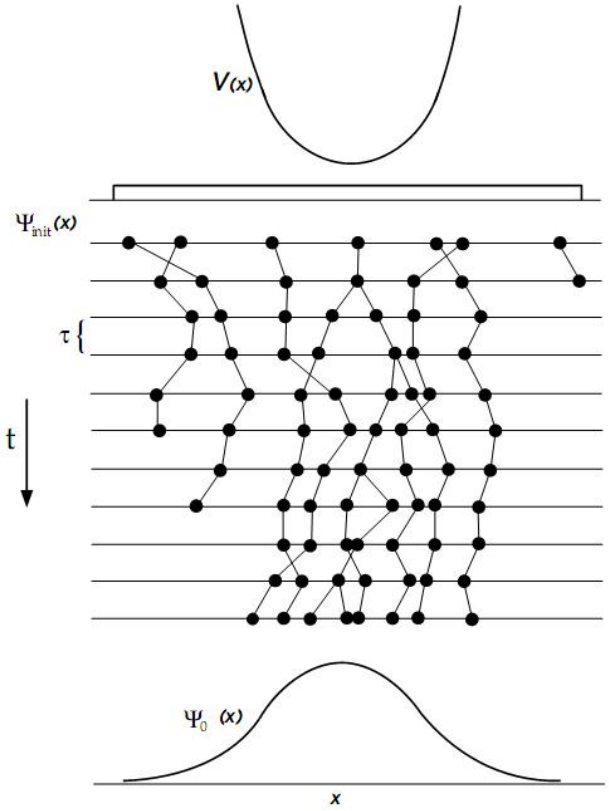
Error ∝ $N^{-1/D}$

Error ∝ $1/\sqrt{N}$

Circle area ~ 6/7 of square

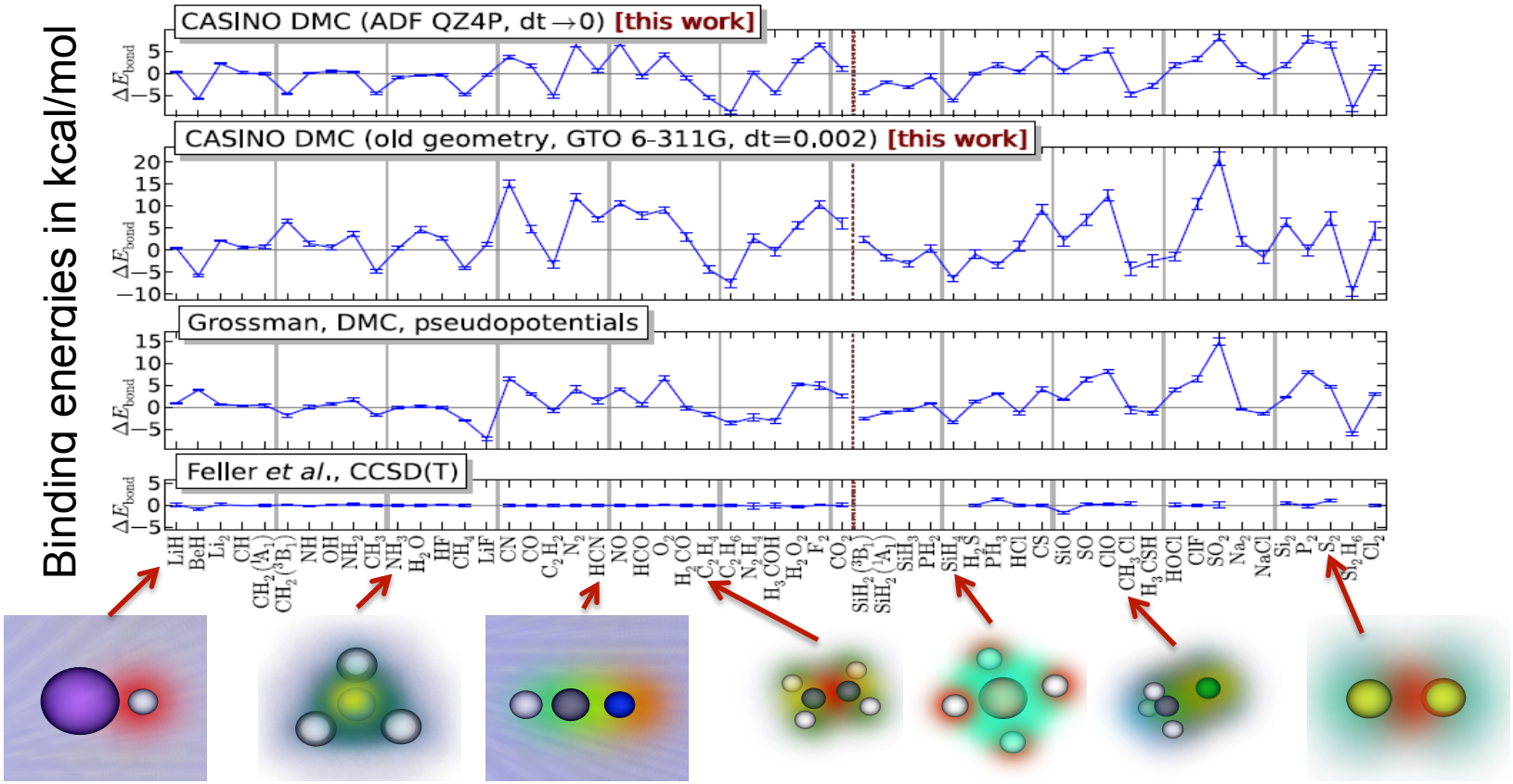
Quantum Monte Carlo uses statistical sampling to solve the Schrödinger equation

- Electron configurations are sampled randomly
  - Natural parallelism over walkers
- Wavefunction we would like to sample from is not positive everywhere (Pauli exclusion principle applies)
- Assume we know where wavefunction changes sign and force walkers to never cross this boundary
  - Fermion sign problem
  - Most fundamental research question in QMC



J. Needs, M. D. Towler, N. D. Drummond, and P. Lopez-Rios,
Casino Version 2.2 User Manual, University of Cambridge , Cambridge (2008)

DMC has been extensively benchmarked for molecular systems



•from Nemec et al, JCP. **132**, 034111 (2010)

QMCPACK – Massively Parallel QMC

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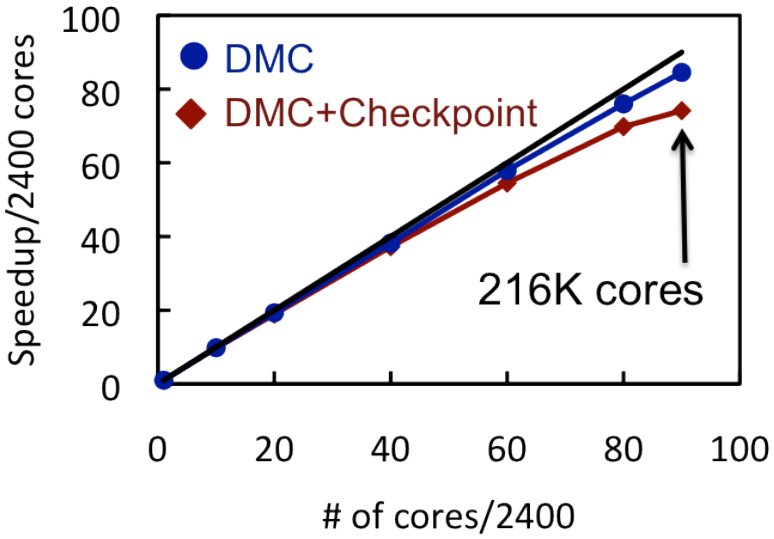
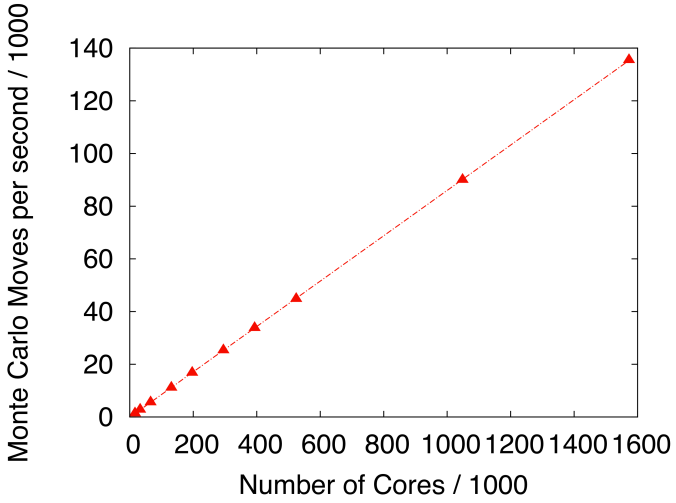
- Quantum Monte Carlo code designed for massive parallelism
- Developed by J. Kim et al.
- Hybrid MPI / OpenMP parallelism
  - Shared Memory on Nodes, Distributed between
- Can efficiently scale to more than 1,000,000 CPU cores
- CUDA port to GPUs with 15X speedup

Scaling on Jaguar_pf

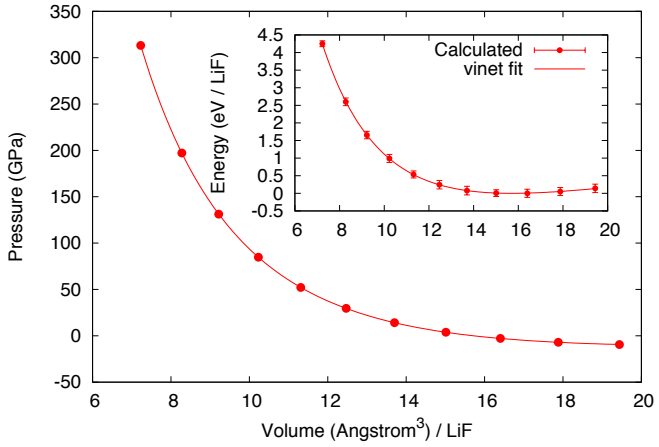


Scaling on Sequoia



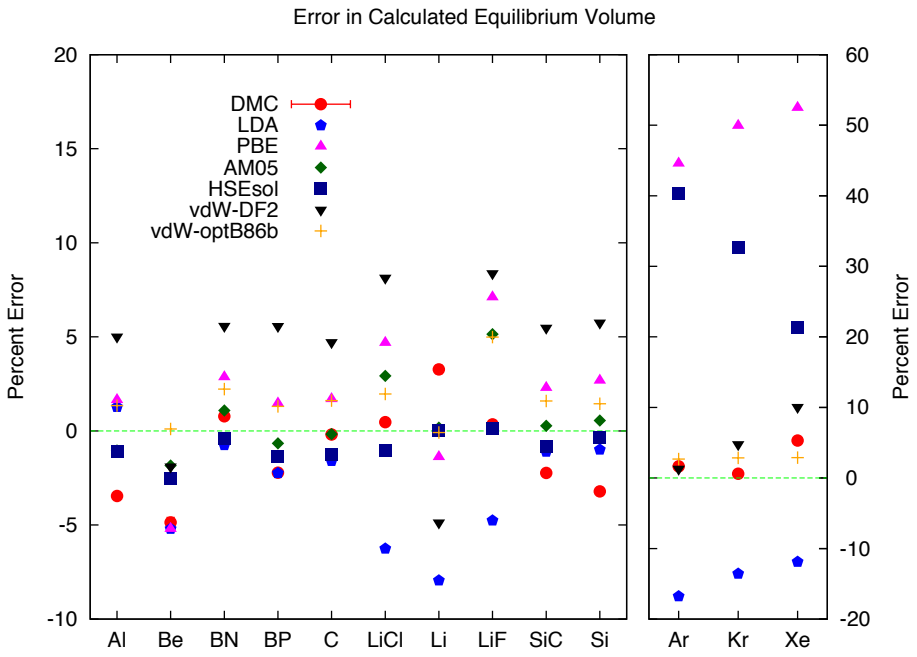
We conducted the first extensive benchmarks of DMC on condensed matter

- Test compares to easily measured experimental data
  - high pressure calculations to derive properties of ambient phase
- Previous calculations have required 1 year of time on NSF machines for a single solid
- Choice of systematic approximations can greatly affect results
- Calculations performed on Cielo



We conducted the first extensive benchmarks of DMC on condensed matter

- **Fit Vinet form to E(V) and compare equilibrium volume (density) and bulk modulus (compressibility) to experiment**

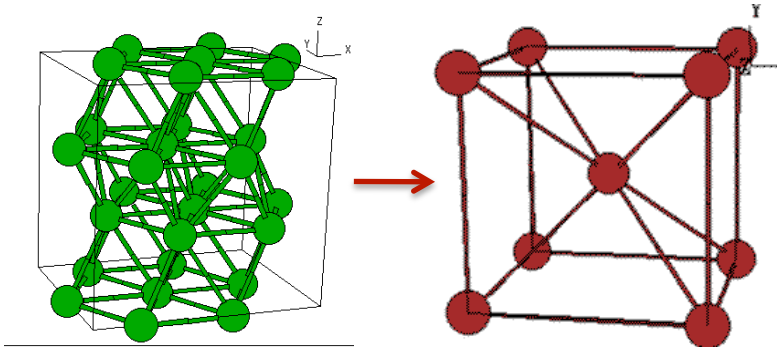


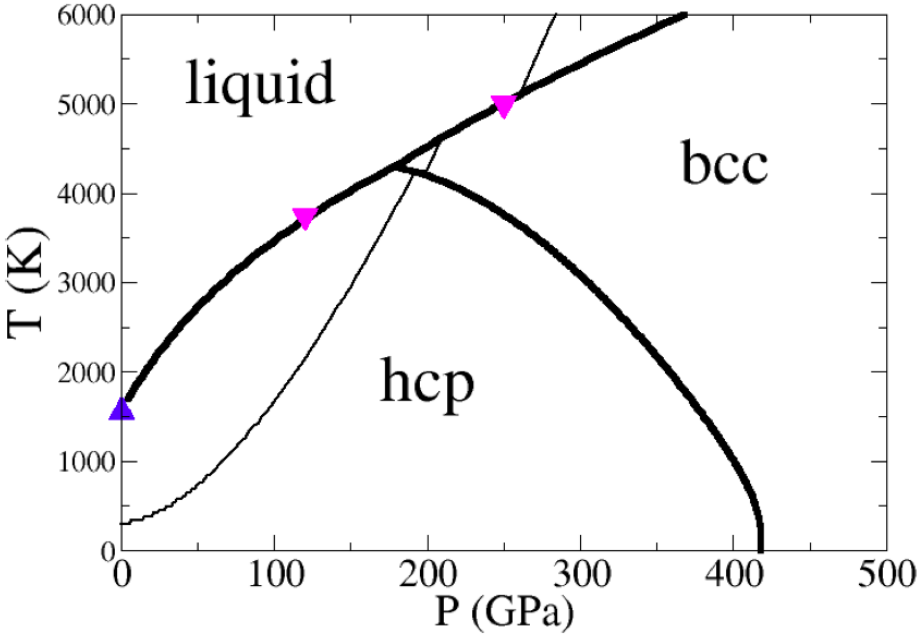
- Materials span a factor of 10 in equilibrium volume
- Four types of bonding are included
  - Ionic
  - Covalent
  - Metallic
  - Van der Waals
- Lattice Constants within ~0.9%
- This provides a new baseline procedure for a QMC calculations
- PRB 88, 245117 (2013)

Mean error: -0.38 +/- 0.15
Mean absolute error: 2.28 +/- 0.15
RMS error: -0.697 +/- 0.066%
Mean absolute relative error: 1.79 +/- 0.07%

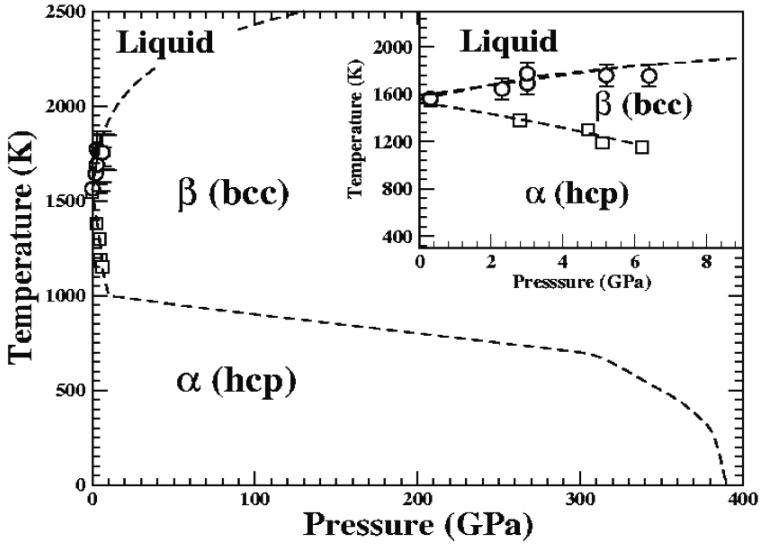
Applying QMC to HED science

- Solid Be used in ICF
  - High strength, low Z material, Low x-ray absorption
- HCP at ambient temperature and pressure
- Phase transition to BCC at high pressure
- Simple but demanding computationally





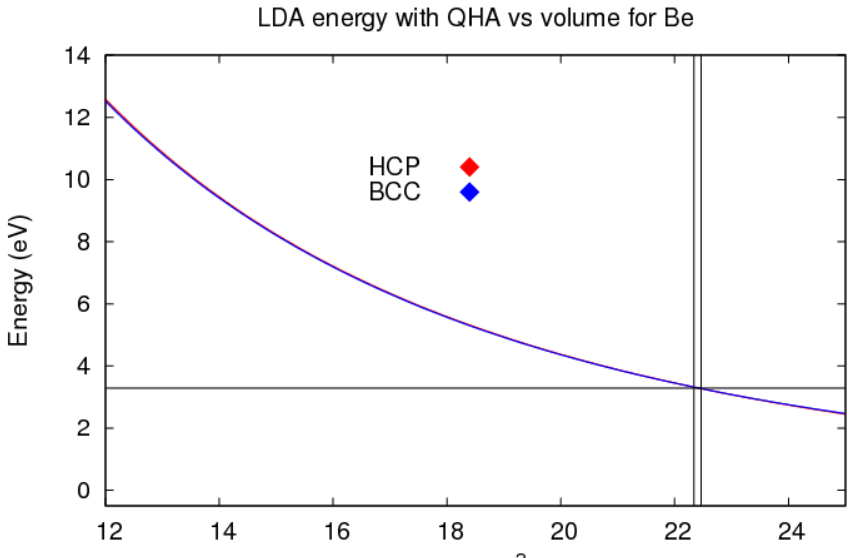
Benedict et al. PRB **79**, 064106 (2009)

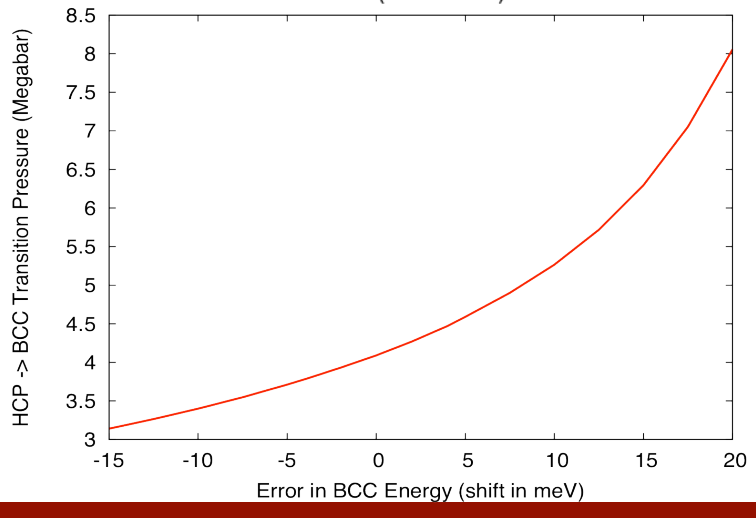


Rober and Sollier. J. Phys. IV France **134**, 257 (2006)

Be Phase transition is exquisitely sensitive to errors!

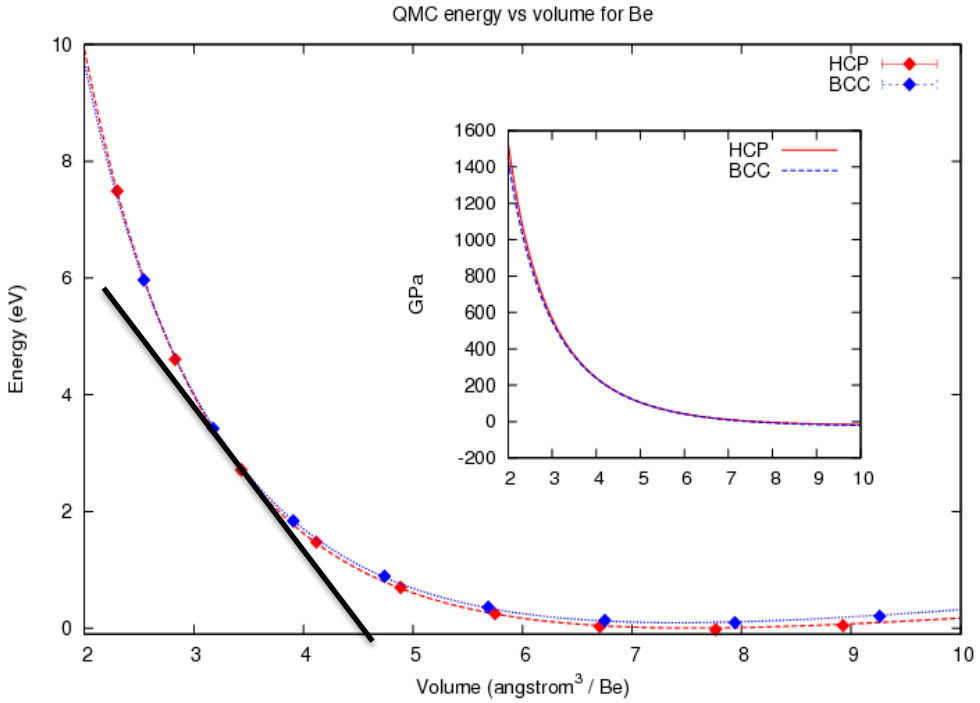
- Calculate Be HCP-> BCC phase transition pressure with LDA+QHA
- What is sensitivity of transition?
  - Make constant shift of $E_{HCP}(V)$
    - Transition pressure changes from 350 GPa to 525 GPa with a 1 kcal/mol shift
    - Zero point energies were an order of magnitude larger
- "Chemical Accuracy" is not good enough!





Early DMC calculations yielded disappointing results

- **Equation of state is fit using Vinet form**
  - More crucial because values have statistical errors
- **Phase transition occurs at > 700 GPa**
  - Significantly higher than DFT result ~ 390 GPa



HCP Equilibrium Parameters		
	QMC	Exp
c/a	1.569 +/- 0.004	1.568
V_0 (angstrom^3)	7.746 +/- 0.078	8.117
Bulk Modulus (Gpa)	124 +/- 2	116.8

Pseudopotential approximation is single largest uncertainty, can we do better?

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- Cost of DMC scales as $Z^{5.5}$ without pseudopotentials
- For light elements, modest supercell sizes are possible
- DFT trial wavefunctions must not be pathological near nucleus
- Use pseudopotential with all electrons in valence in DFT
  - replace with -4/r potential in DMC
  - use one body jastrow to handle cusp at ion
- Must carefully check technical parameters to avoid bias due to issues near core

All electron method significantly improves HCP phase description

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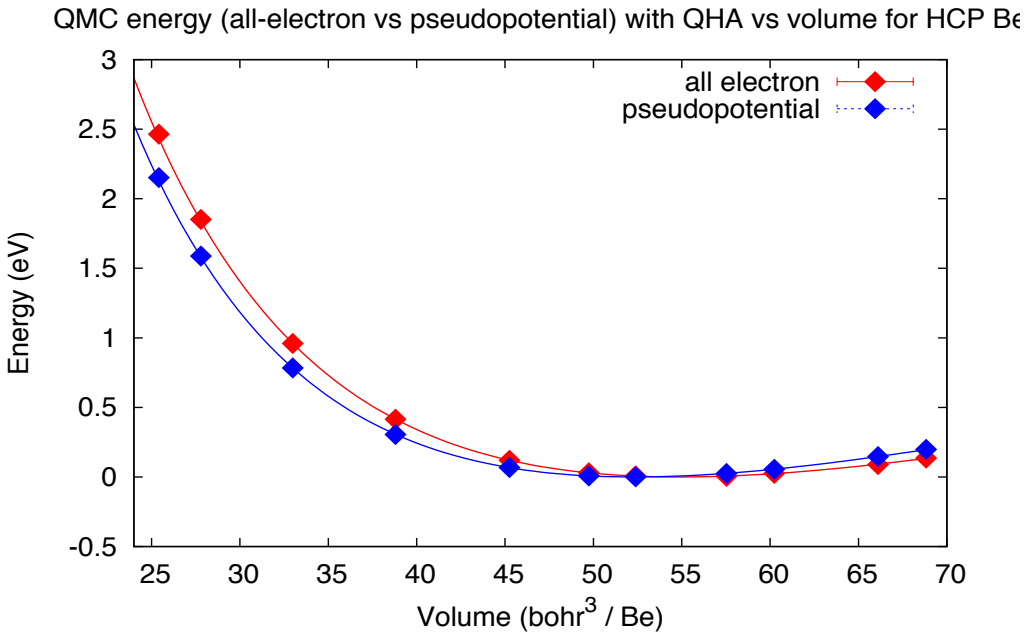
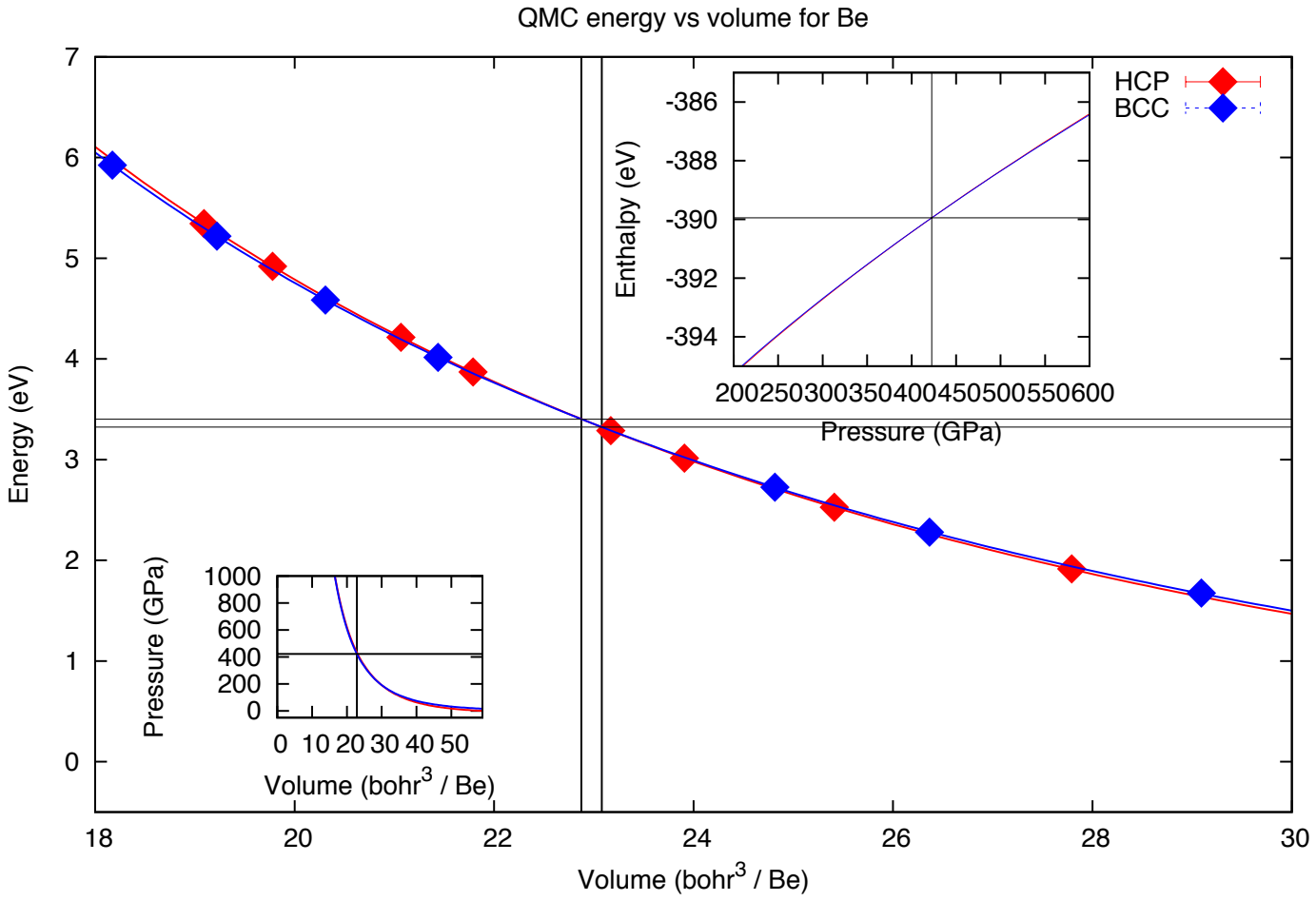


All EOS Properties agree with experiment within small error bars!

HCP Equilibrium Parameters			
	QMC	All Electron QMC	Exp
c/a	1.569 +/- 0.004	1.569 +/- 0.004	1.568
V_0 (angstrom^3)	7.746 +/- 0.078	8.129 +/- 0.012	8.117
Bulk Modulus (Gpa)	124 +/- 2	115.7 +/- 1.5	116.8

Phase transition pressure is brought more in to line with transition inferred from shock experiments

- **Percent volume change upon transition is ~0.9 %**
- **Transition pressure is 422 +/- 5 GPa**



Accuracy of all electron methodology holds for another light nuclei phase transition

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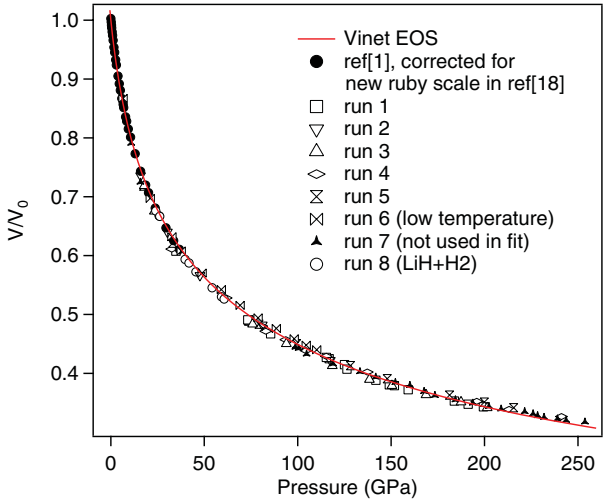
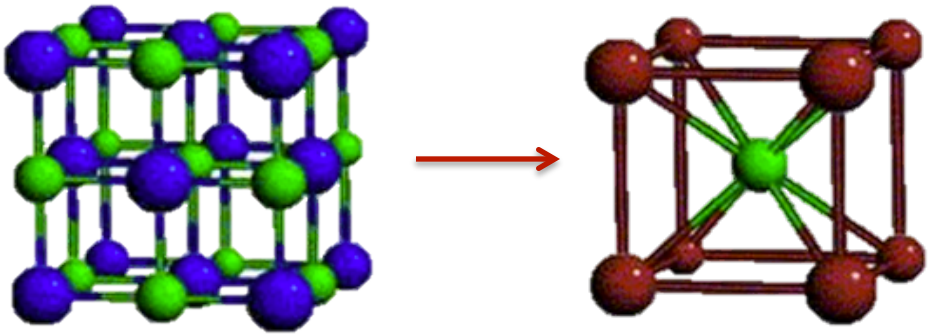
- **Calculate LiH transition from B1 to B2 phase**
- **Ambient (B1) phase in excellent agreement with experiment**
- **Phase transition pressure 337 GPa**
- **DFT (LDA) calculations 308 Gpa**
- **Complements DAC experiments which top out near 250 GPa**

B1 Equilibrium Parameters		
	QMC	Exp
Lattice Constant (angstrom)	4.074 +/- 0.002	4.08
Bulk Modulus (GPa)	32.2 +/- 0.4	33.1 +/- 0.3
B'	3.64 +/- 0.05	3.64 +/- 0.05



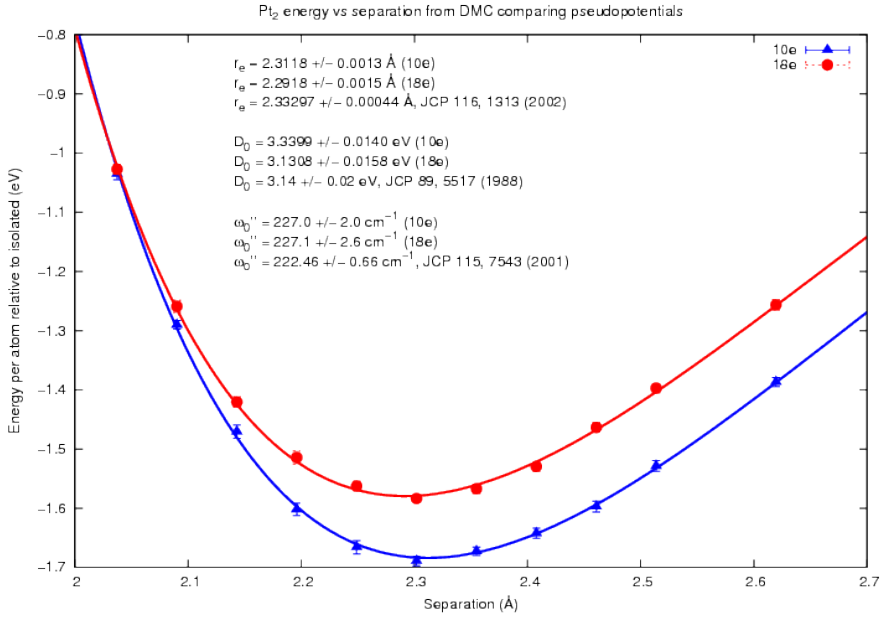


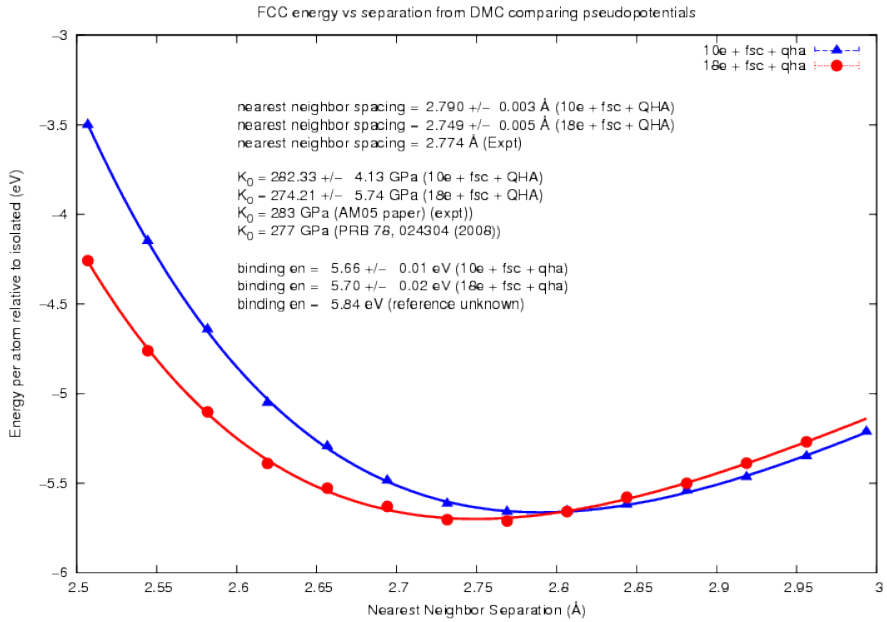
B1 B2

Lazicki et al. PRB, **85**, 054103 (2012)

Towards Heavier Elements

- Actual generation techniques are relatively stagnant
  - Exception is Trail and Needs, JCP **139**, 014101 (2013)
- Testing methodology has improved, allowing for more efficient screening of candidate pseudopotentials
  - Calculations of electron affinities and ionization potentials as well as small molecules
- This has allowed for highly accurate calculations of even heavier elements albeit with significant effort for instance Pt:





QMC Challenges going forward

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- Further construction / validation of pseudopotentials for heavier elements
- Non-parasitic method
  - Improving nodal surfaces
- Finite temperatures
- Reliable and efficient calculations of forces
- Magnetic properties

Beyond the Born-Oppenheimer approximation -TDDFT

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- A variety of problems in HED physics require relaxing the Born-Oppenheimer approximation
  - Electron-ion equilibration in laser shocks
  - Interpreting XRTS spectra
  - Calculating energy transfer with fast ions
- The most mature way to perform these calculations is using the time dependent extension of DFT – TDDFT
- Consider n electrons that obey:

$$\left(\hat{T}+\hat{V}_{ee}+\hat{V}_{ext}(t)\right)\left|\Psi\right\rangle = i\frac{d}{dt}\left|\Psi\right\rangle$$

- Runge-Gross Theorem and Kohn-Sham ansatz pave way for a time dependent DFT whereby single particle orbitals obey

$$i\frac{d}{dt}\left|\psi_m(t)\right\rangle = H_{KS}(t)[n(t)]\left|\psi_m(t)\right\rangle$$

Implementation of TDDFT

Sandia National Laboratories

- We have implemented TDDFT in VASP 5.3.x
  - One of the first TDDFT implementations in periodic boundary conditions
  - Projector Augmented Waves (PAWs) are used to represent core valence partitioning
    - *Simple linear map between 'real' and 'pseudo' orbitals*

$$\left|\psi_n\right\rangle = \mathrm{T}\left|\tilde{\psi}_n\right\rangle + \sum_l \sum_{j_1,j_2} \left|\tilde{p}^l_{j_1}\right\rangle Q^l_{j_1,j_2} \left\langle \tilde{p}^l_{j_2}\right|$$

    - *Transforms Linear algebra from a standard to a generalized eigenproblem*
- Coding was led by A. Baczewski
  - Part of an LDRD including R. J. Magyar and M. P. Desjarlais

Added benefit – Reduced Complexity

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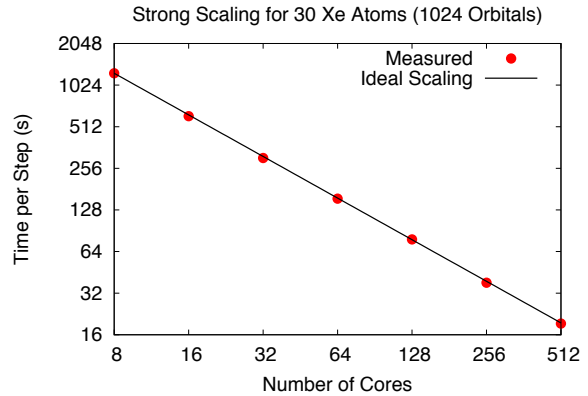
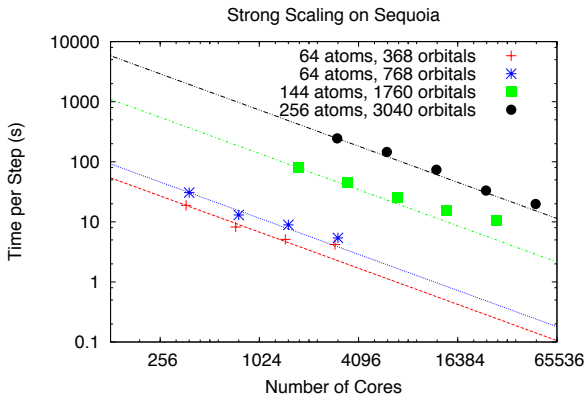
- Starting from an initial wavefunction, we use the Crank-Nicholson scheme to propagate single particle states:

$$\left[S + i\Delta t \frac{H_{KS}(t+\Delta t/2)}{2}\right]\left|\tilde{\psi}_n(t+\Delta t)\right\rangle = \left[S - i\Delta t \frac{H_{KS}(t+\Delta t/2)}{2}\right]\left|\tilde{\psi}_n(t)\right\rangle$$

- This is a very accurate unitary integrator
  - States remain orthogonal upon propagation
  - Particle number is exactly conserved
- Orthogonalization in DFT has the highest complexity $O(N^3)$ and most expensive parallel communication
- Now linear algebra is leading bottleneck: $O(N^2)$
- Also allows a much more efficient route to finite temperatures





Stopping a fast moving ion

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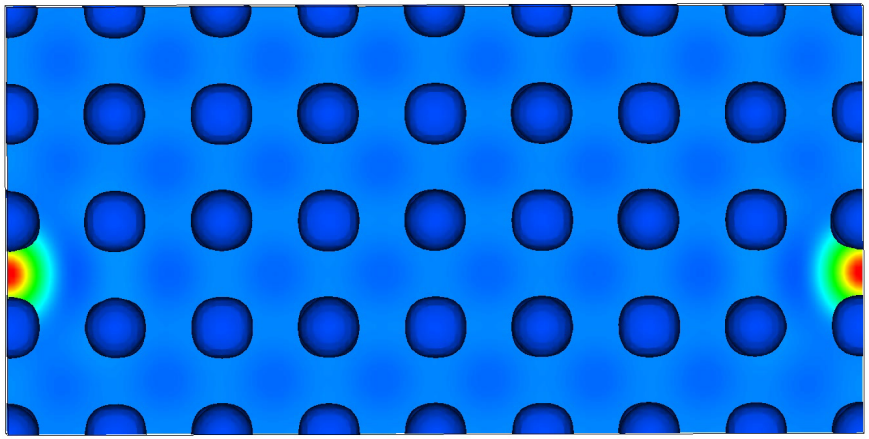
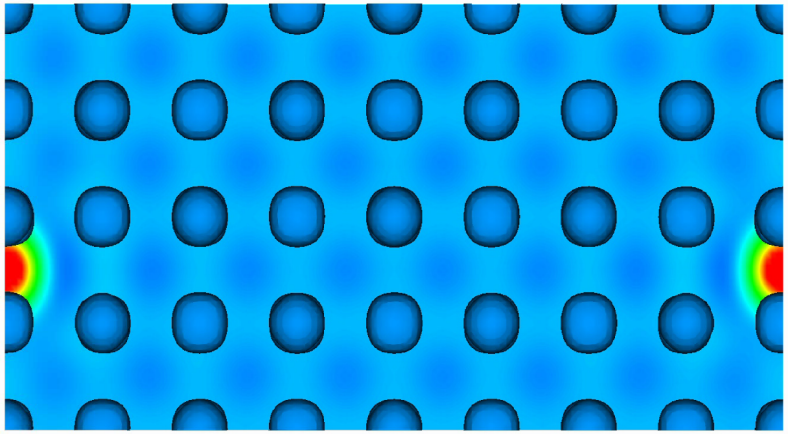
- Understanding how fast moving ions are slowed is essential to understanding the energy balance in inertial confinement fusion
- As a test problem, we drag a hydrogen ion through aluminum at constant velocity and measure the force on the ion
  - Generation of plasmons necessary to capture the proper behavior

Born-Oppenheimer

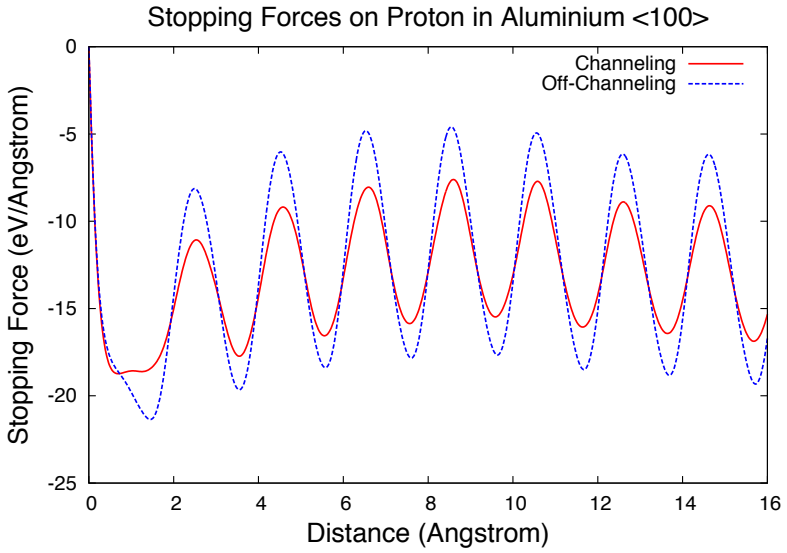


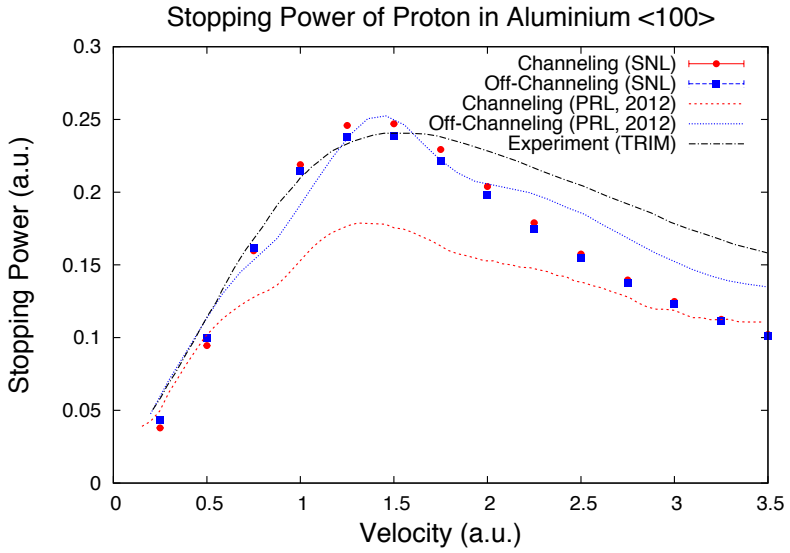
TDDFT



Stopping a fast moving ion

- Stopping in cold aluminum can be compared to an experimental database (TRIM)
  - Also earlier Ehrenfest TDDFT by Correa et al. PRL **108**, 213201 (2012)

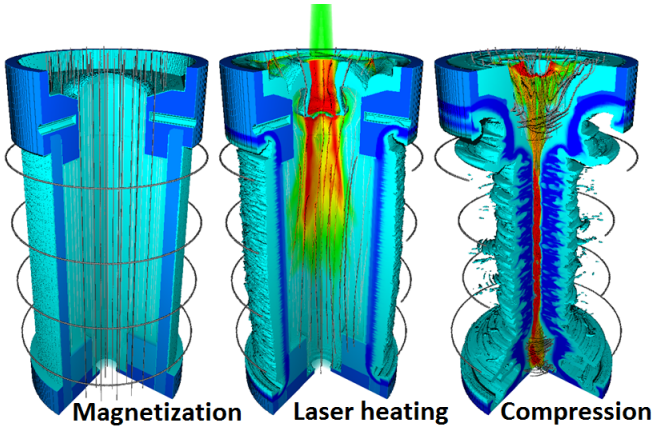


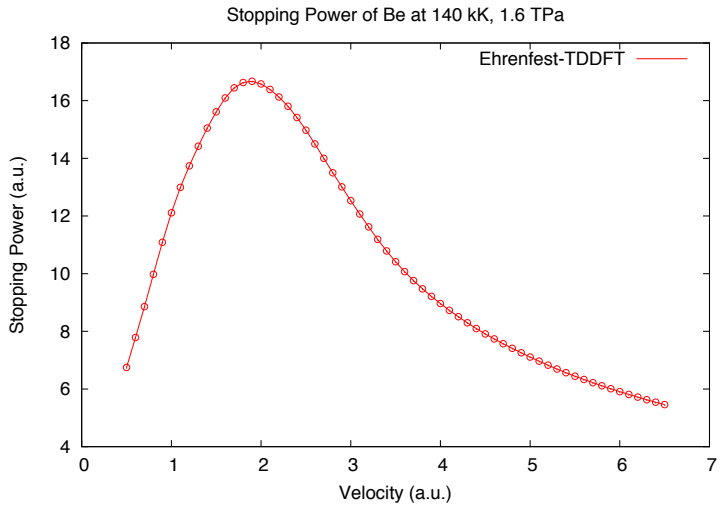


  - Good agreement with experiments through peak
  - Little difference between channeling and off channeling trajectories
  - Core-valence separation is rigorously checked with smaller core PAWs

Stopping at high pressure and temperature

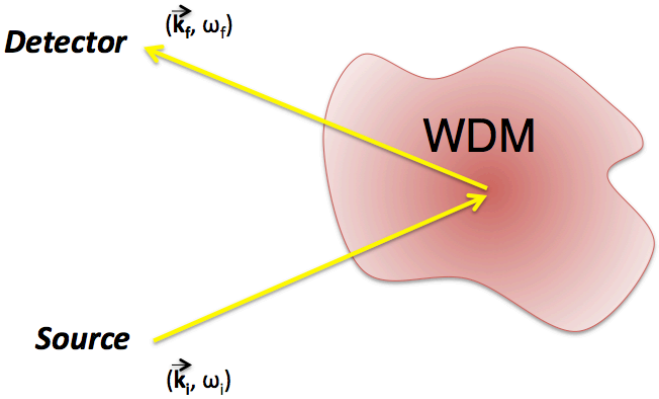
- In order to understand the energy balance in inertial confinement fusion experiments, a quantitative knowledge of stopping power at WDM conditions is required
- For example in magLIF, a beryllium liner is compressed around DT fuel
- We are calculating stopping of fast H ions in highly compressed hot Be
  - This involves propagating a finite temperature electronic state
  - It is unclear how well a Mermin initial state represents this finite temperature state or how well adiabatic functionals handle the propagation

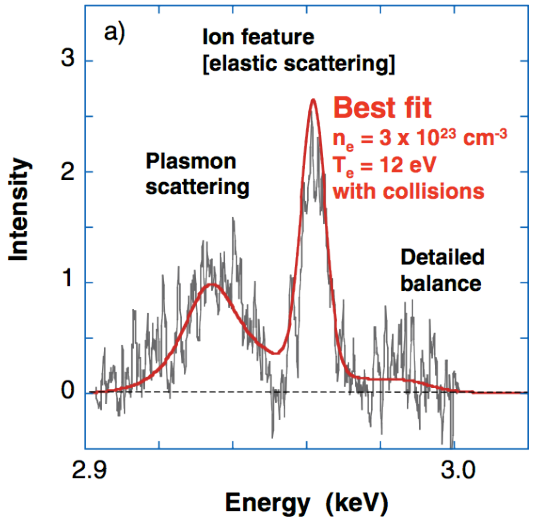




Understanding WDM diagnostics

- X-ray Thomson scattering (XRTS) is a widely used tool for diagnosing the state of warm dense matter
  - Difficult small-K DSF features -> collective regime, plasmons





Glenzer et al. PRL **98**, 065002 (2007)

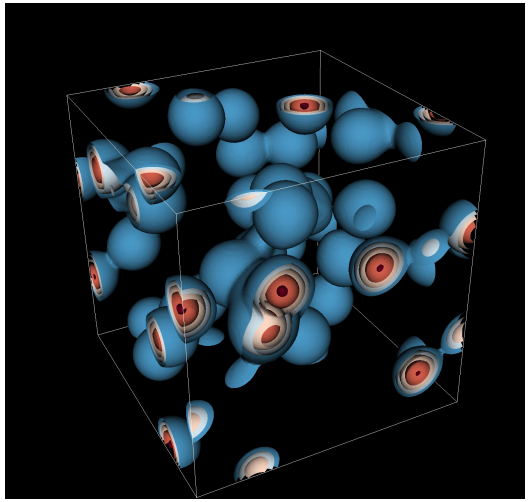
Understanding XRTS

- XRTS spectra are directly related to the dynamic structure factor S(k,ω)

$$S(k,\omega) = \frac{\varepsilon_0 \hbar |k|^2}{\pi e^2 n_e} \frac{1}{1 - e^{\hbar\omega / k_B T_e}} \operatorname{Im} \varepsilon^{-1}(k,\omega)$$

$$S(k,\omega) = \frac{1}{2\pi N_e} \int dr\, dt e^{i\omega t - ik\bullet r} \int dr' \left\langle \hat{n}(r+r',t)\hat{n}(r',0) \right\rangle$$

- S(k,ω) is related to the dielectric function and/or the density-density response
  - To get the dielectric function, need to be able to calculate the response to a vector potential
  - Need a density functional for the density-density correlation function
    - *As a start, try* $\left\langle \hat{n}(r+r',t)\hat{n}(r',0) \right\rangle \approx n(r+r',t)n(r',0)$
    - *Need very long calculations to accumulate statistics*



Advanced electronic structure methods are promising for studies of material at extreme conditions

Sandia National Laboratories

- **Diffusion Monte Carlo**
  - Path forward for improved treatment of electron correlations -> crucial for heavy elements and strong correlations
  - Not as technically mature as DFT
  - Work will continue in becoming less dependent on DFT
- **Time Dependent Density Functional Theory**
  - Promising approach for next generation of supercomputers
  - Capable of treating some electron -> ion energy transfer
  - May greatly aid in interpretation of XRTS
  - Questions remain about usage of adiabatic functionals
  - Can temperature be accurately handled?