



Meaningfully Interpreting ~~Designing Meaningful~~ Density Functional Theory Calculations in Materials Science—A Primer

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Site occupation and migration of hydrogen, helium, and oxygen in β -phase ErH₂

Ryan R. Wixom, JF Browning, CS Snow, DR Jennison, and PA Schultz
Energetics Characterization, 2555 SNL, ABQ



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The quality of density functional theory calculations must be first determined **independent from the comparison between calculated results and experimental observations.**

Dirac (1929)

“ The general theory of quantum mechanics is now almost complete The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. ”

P.A.M. Dirac, Proc. R. Soc. London Ser. A 123, 714 (1929).

Properties of the system

Hard problem to solve

“Easy” problem to solve

Schrödinger view

DFT view

Formally equivalent

● electron
↔ interaction
— external potential

● Kohn-Sham particle
(non-interacting)
- - - effective potential

(1965)

Remember:
Dirac made his statement in 1929.

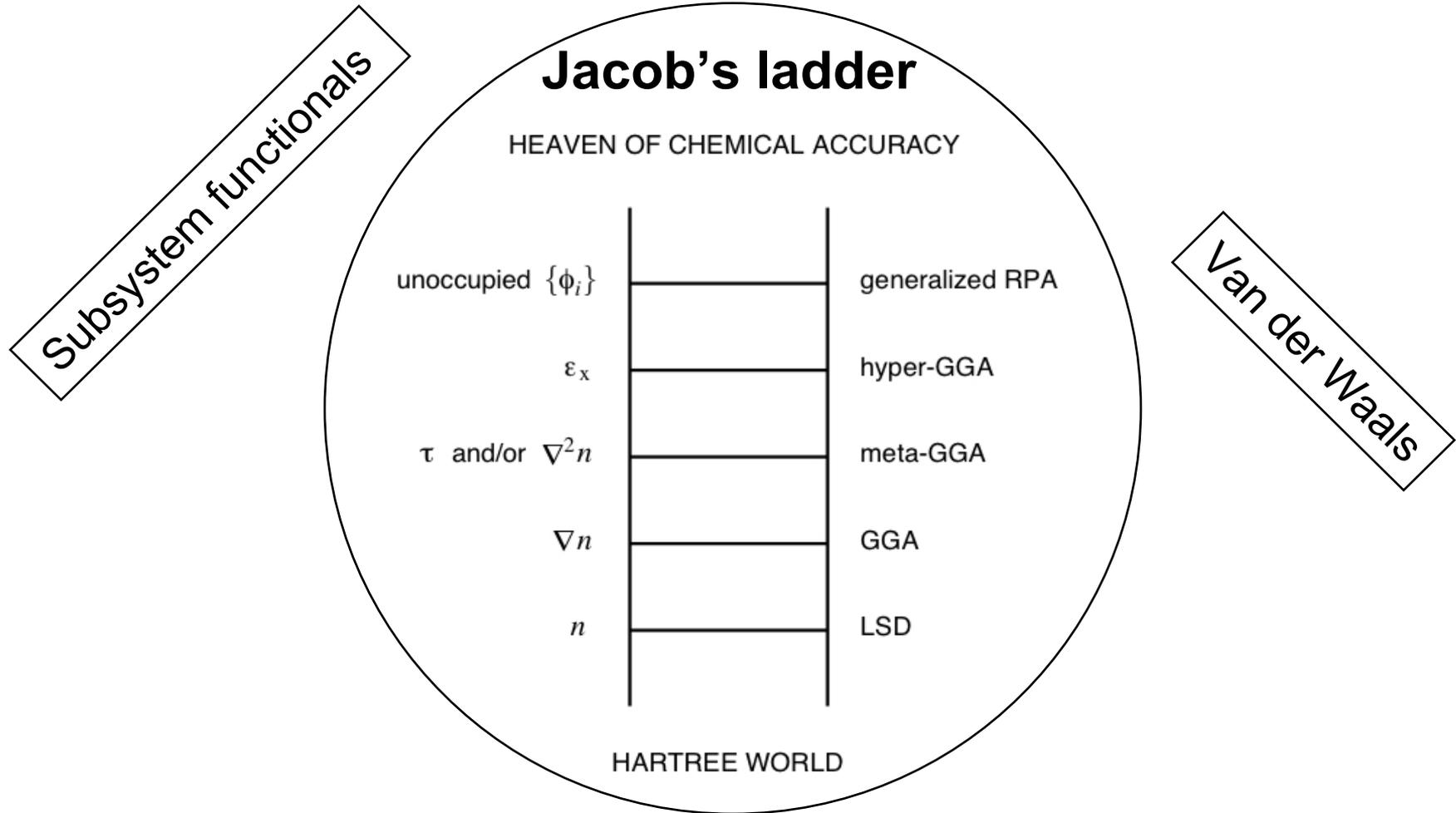
Kohn-Sham equations:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right) \psi_\nu(\mathbf{r}) = \epsilon_\nu \psi_\nu(\mathbf{r}) \quad \nu = 1, 2, \dots, N$$

$$n(\mathbf{r}) = \sum_{\nu=1}^N |\psi_\nu(\mathbf{r})|^2$$

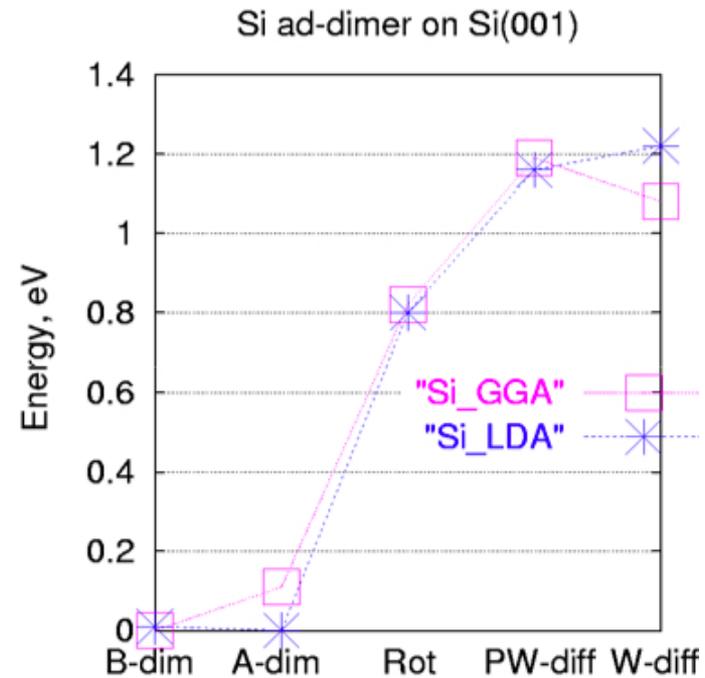
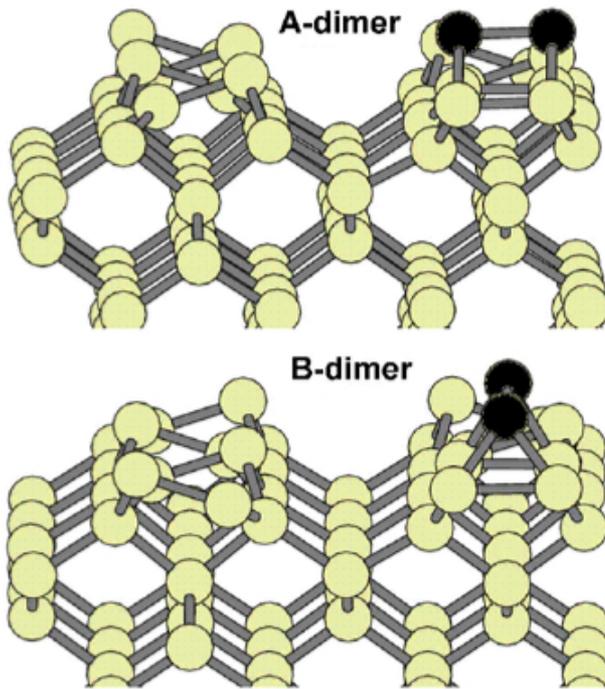
$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

Hierarchy of functionals

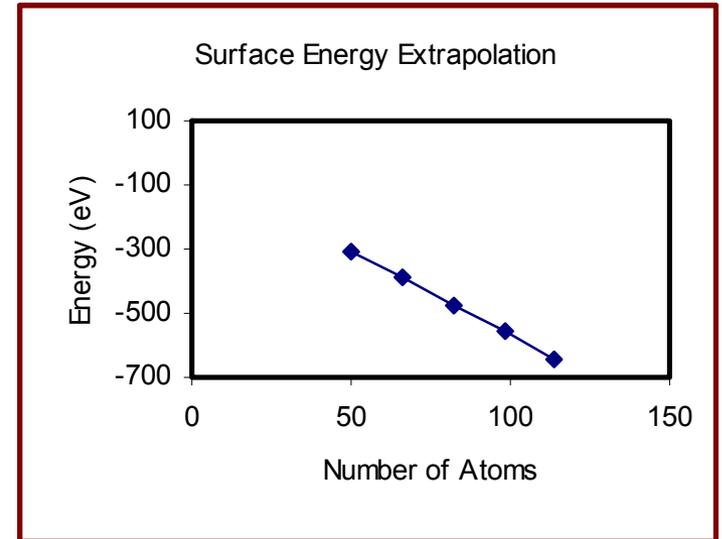
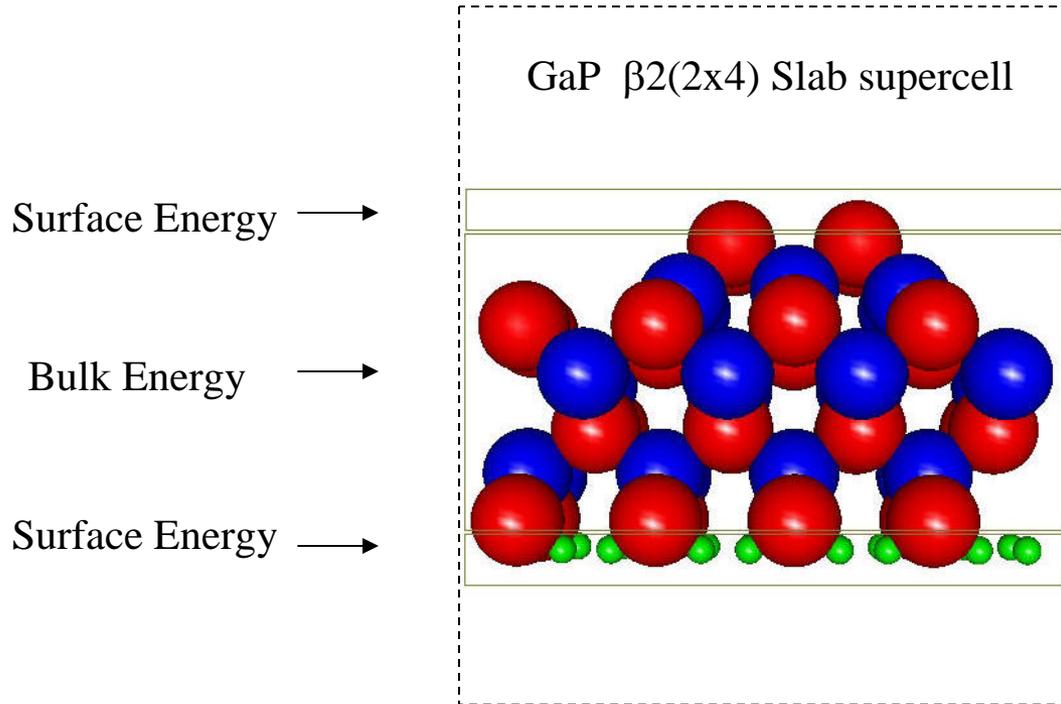


**The choice of XC-functional is the
limiting factor
for the accuracy of DFT**

Silicon ad-dimer diffusion on Si(001)



System size – Relaxation – Boundary conditions



$$E_{slab}^n = \sigma + n E_{bulk}$$

From 6 layers:

0.01 eV difference

0.3 eV Error in surface energy

From 10 layers

0.0005 eV difference

0.023 eV Error in surface energy

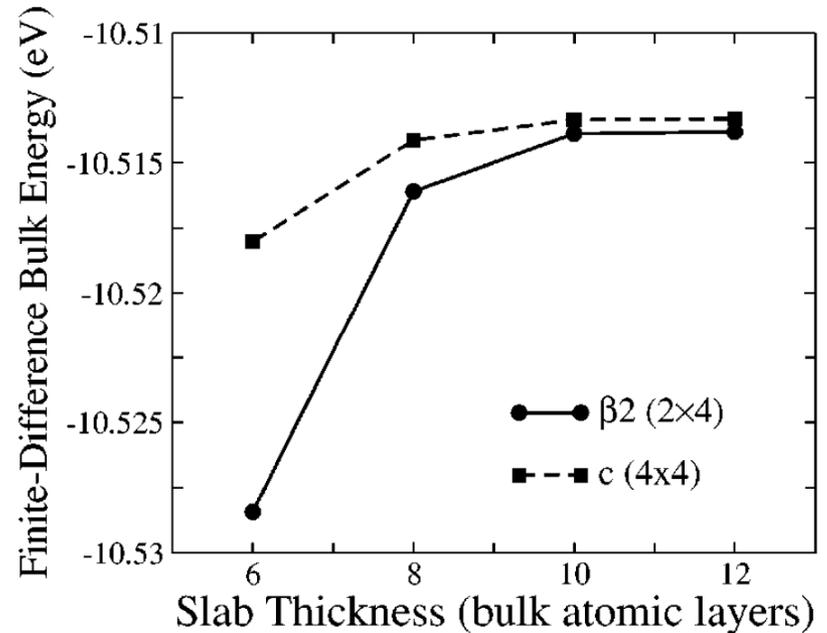


FIG. 1. GaP bulk energy calculated by finite-difference using the total energies of slabs with n and $n + \Delta n$ layers.

$$E_{bulk}(N) = \frac{E_{total}(N + \Delta N) - E_{total}(N)}{\Delta N}$$

System size – Relaxation – Boundary conditions

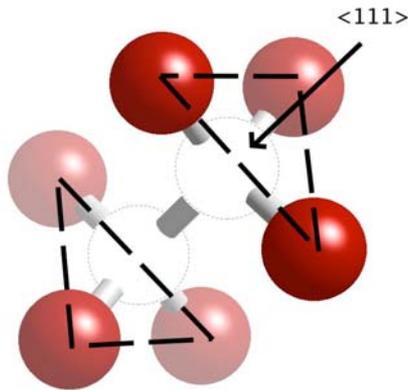
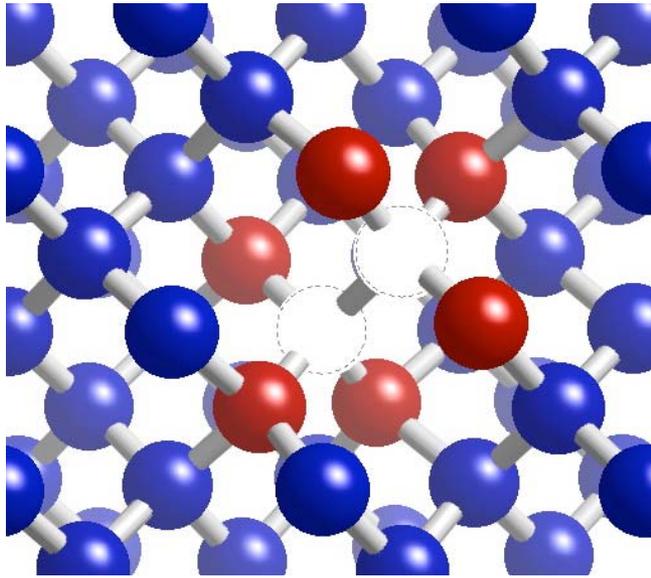


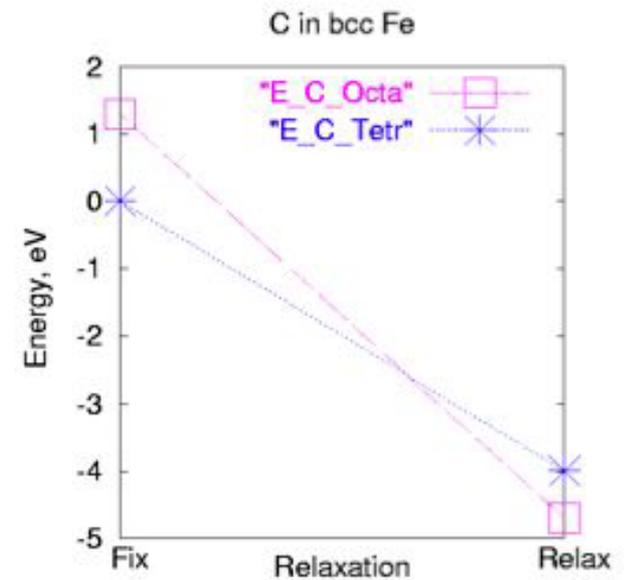
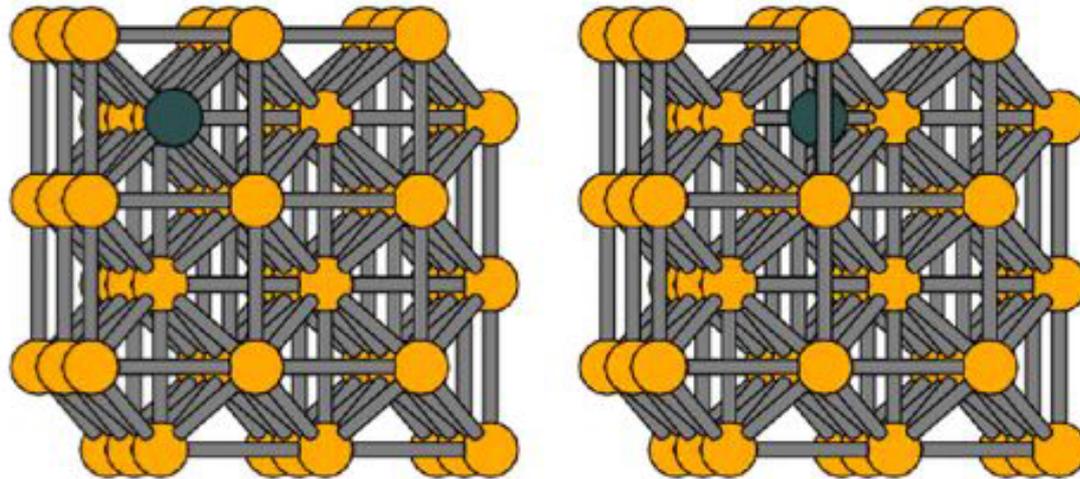
TABLE II. Formation energies for VV_{Si} calculated with the LDA. The Brillouin zone was sampled using $n_{MP}=4$, $n_{MP}=4$, and $n_{MP}=3$ MP parameters for the 214-, 510-, and 998-atom supercells, respectively. The last row contains values extrapolated to an infinite sized supercell.

Cell size	VV_{Si}^+	VV_{Si}^0	VV_{Si}^-	VV_{Si}^{2-}
214	5.481	5.340	5.498	5.627
510	5.368	5.269	5.545	5.777
998	5.316	5.247	5.579	5.861
∞	5.333	5.220	5.649	6.111

TABLE III. Formation energies for VV_{Si} calculated with the PBE. The Brillouin zone was sampled using $n_{MP}=4$, $n_{MP}=4$, and $n_{MP}=3$ MP parameters for the 214-, 510-, and 998-atom cells, respectively. The last row contains values extrapolated to an infinite sized supercell.

Cell size	VV_{Si}^+	VV_{Si}^0	VV_{Si}^-	VV_{Si}^{2-}
214	5.486	5.445	5.618	5.786
510	5.415	5.402	5.691	5.952
998	5.393	5.380	5.721	6.042
∞	5.418	5.363	5.800	6.298

Carbon impurities in bcc iron



The importance of relaxation

K-point sampling

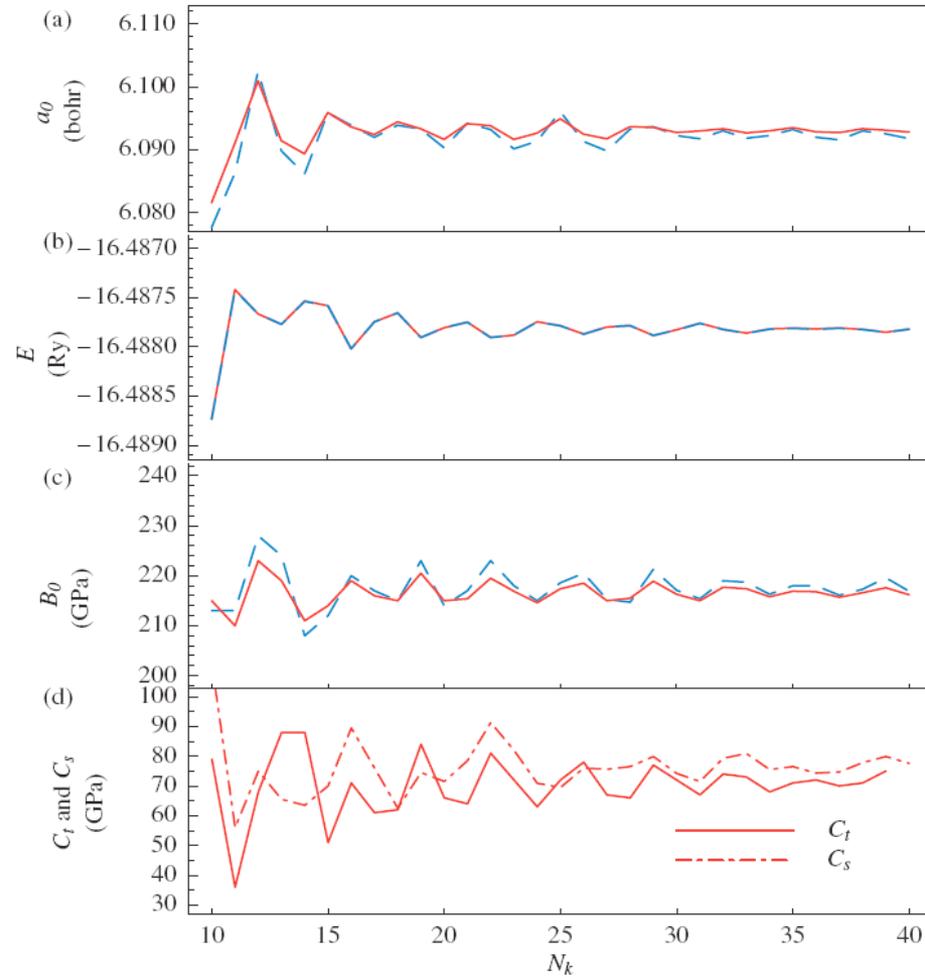


Figure 4. The convergence of computed equilibrium quantities for bcc Ta as a function of the k sample: (a) lattice constant; (b) total energy; (c) bulk modulus; (d) shear moduli. The values extracted using the computed stress tensor are given as solid red lines, and the values obtained using fits to the potential energy surface are dashed blue (the shear moduli in (d) were both obtained from the stress calculation). While the total energy, lattice parameter and bulk modulus appear to converge, if slowly, the computed shear moduli (d) are much more sensitive to the k sample, and are still varying over a range of 5 GPa at a k grid of 40^3 .

K-point sampling

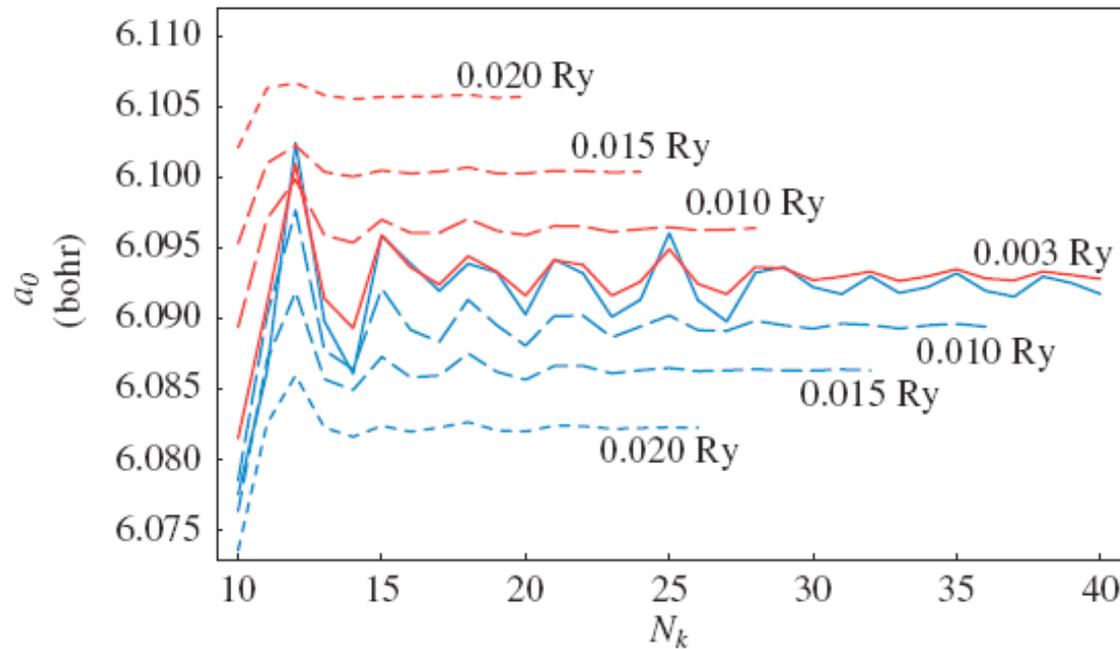
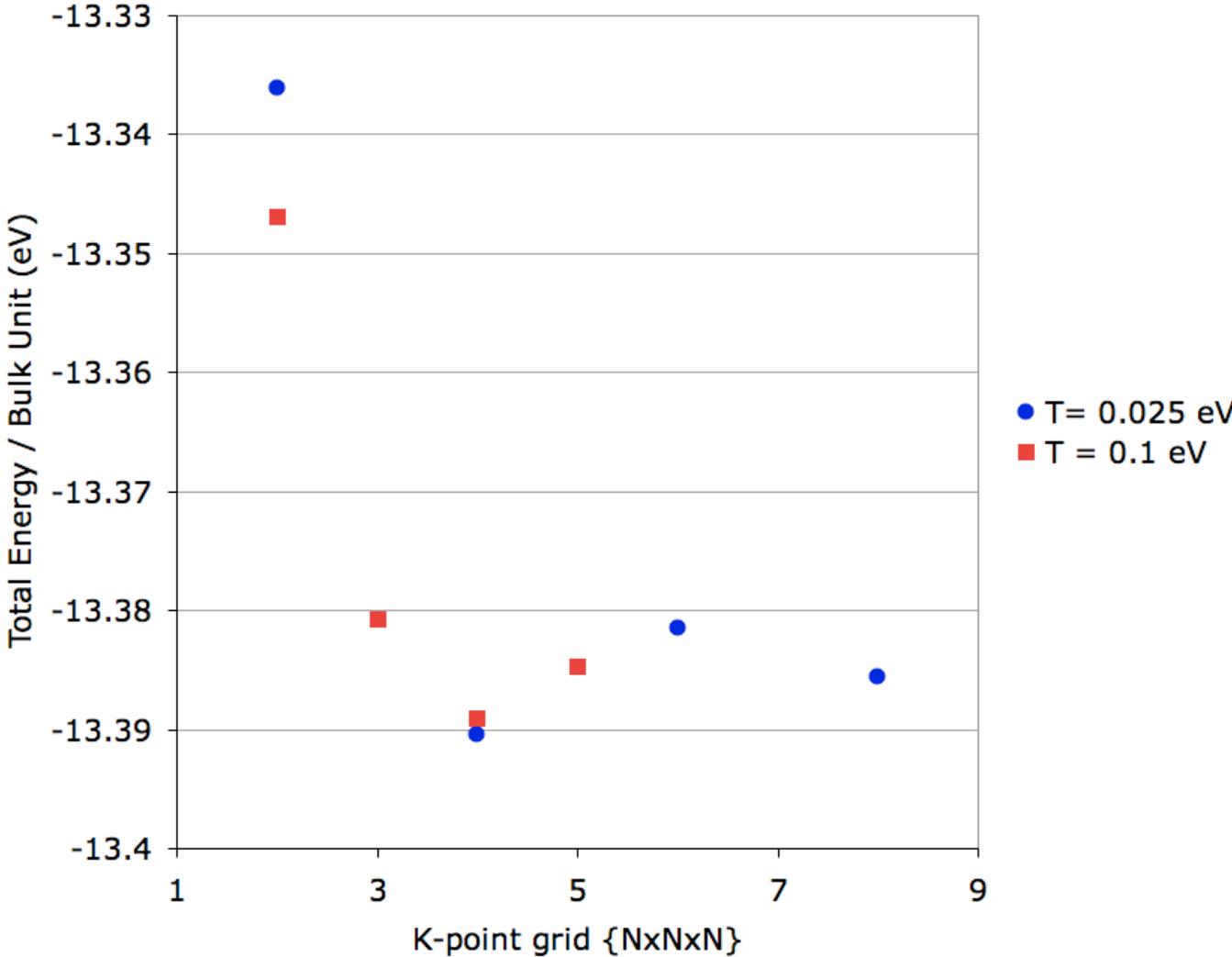
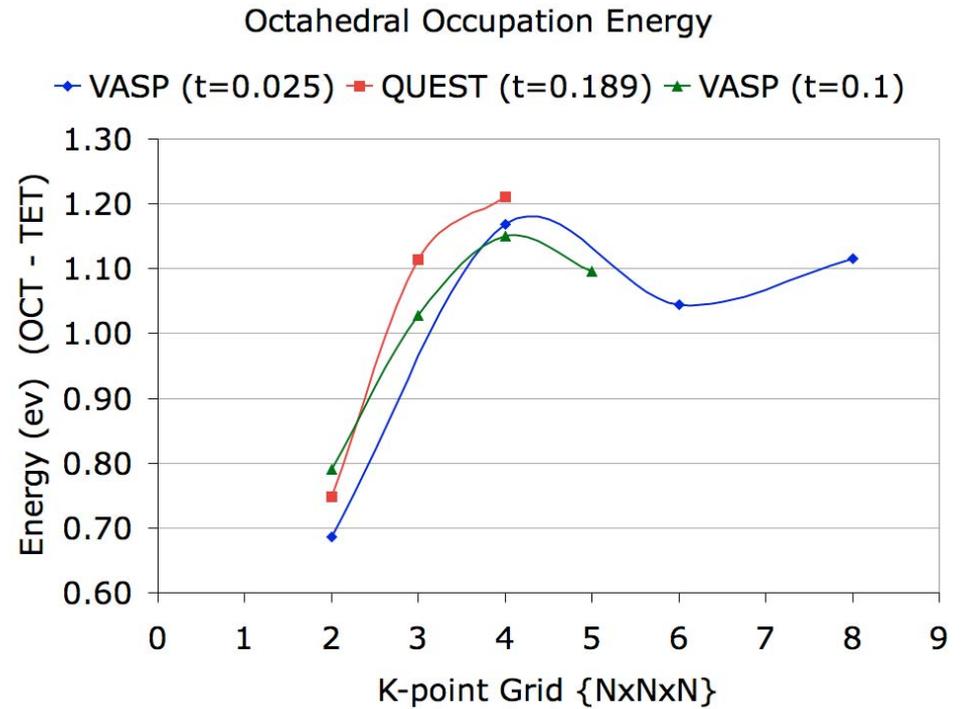
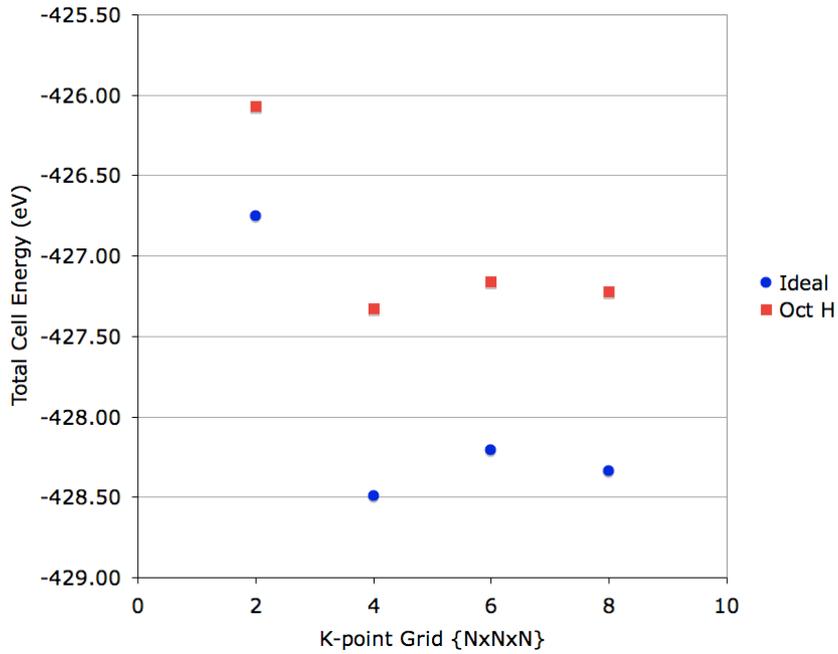


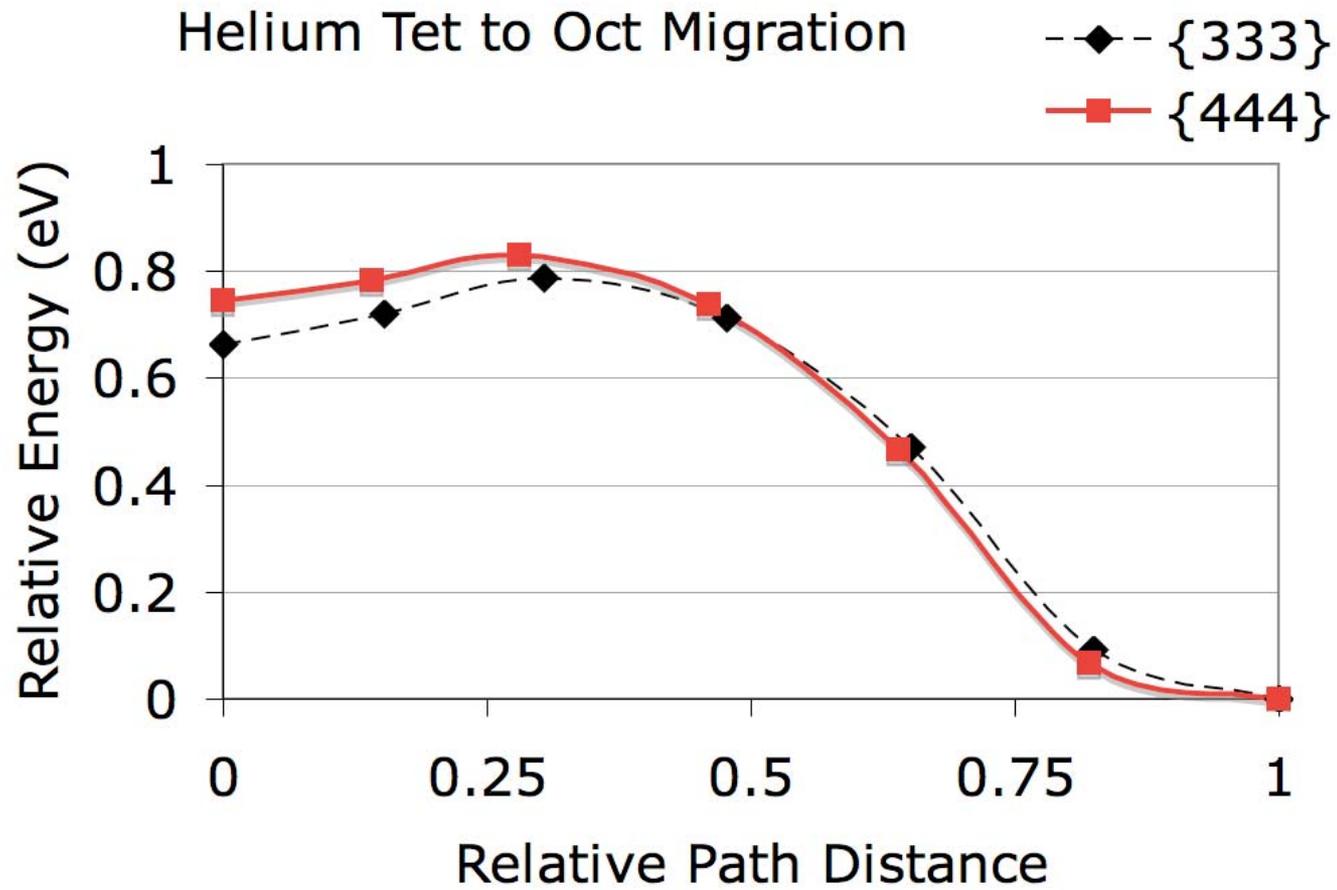
Figure 5. The computed equilibrium lattice constant, a_0 , of Ta as a function of Fermi filling temperature and k point sample. The a_0 computed as the point of zero stress is in red, and a_0 at the minimum of the potential energy curve is in blue. Both these methods converge better versus the k sample with higher Fermi occupation temperatures. However, for both methods the lattice constant drifts as the occupation temperature increases, and the drift is in opposite directions.

K-point sampling: erbium hydride 96 atom cell

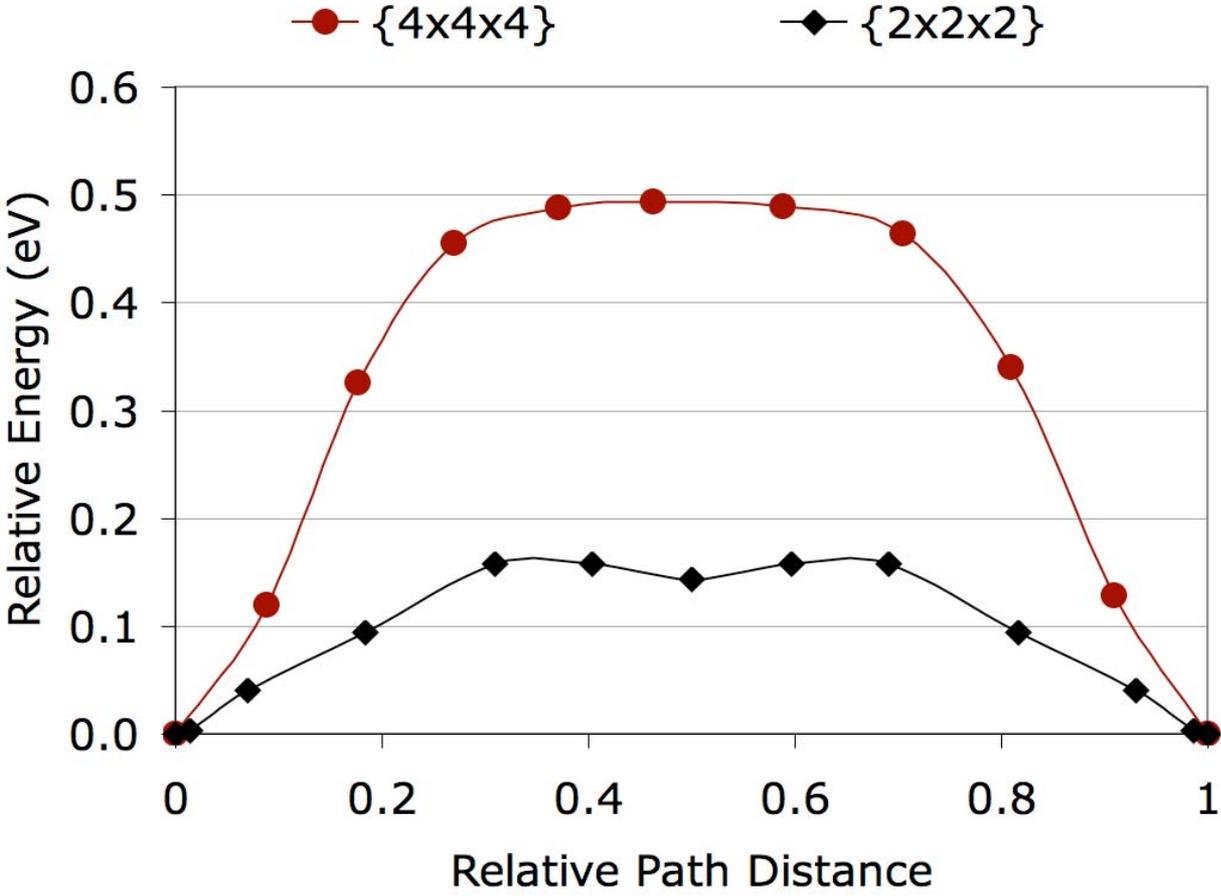


K-point sampling





K-point sampling

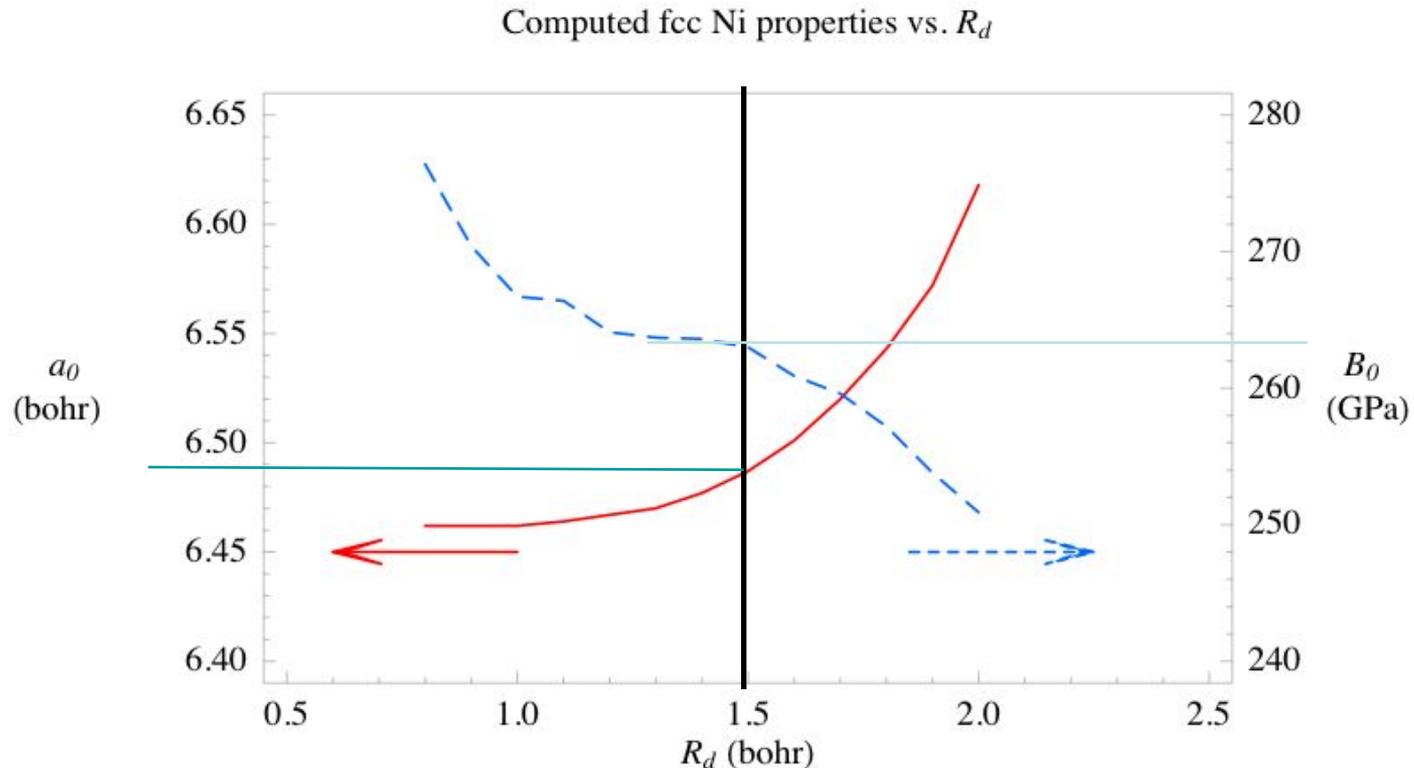


Pseudopotentials: A Black Art

- **Core electrons do not actively participate in chemistry.**
- **They can be replaced with a pseudo core.**
- **Fewer electrons to deal with.**
- **Smoother wave functions.**
- **Larger systems can be studied faster.**

But it is an approximation

Pseudopotentials



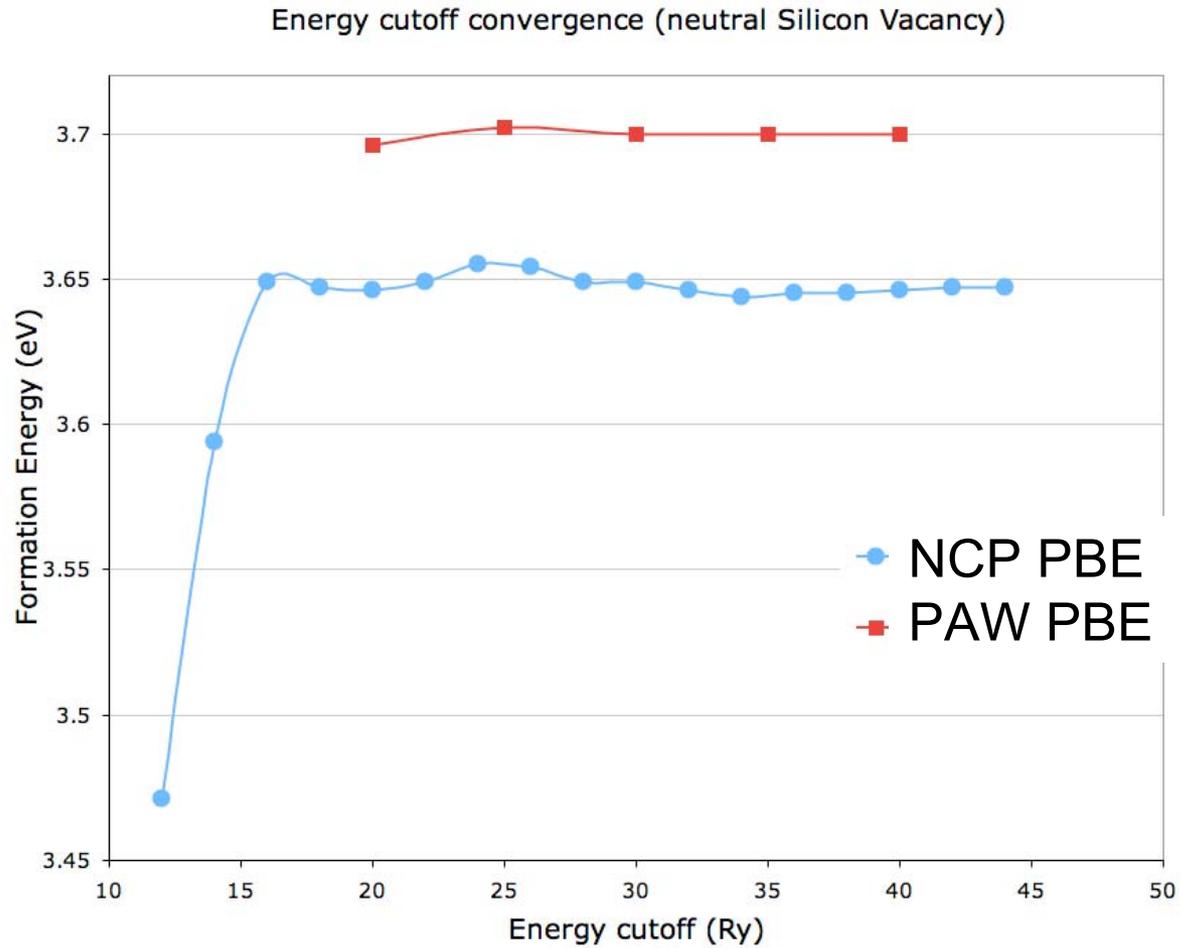
R_d is the ‘core radius parameter’, one of the main parameters to decide when constructing a pseudopotential.

The temptation is to tune these results to match w/ experiment.

Remember: A pseudopotential is an approximation for the full core potential.

The quality of a pseudopotential should be determined by **how well it reproduces the results from all electron calculations.**

Basis Set / Energy cut off: Formation energy of $[V_{Si}]^{+0}$ 216-atom supercell



Basis Set / Energy cut off

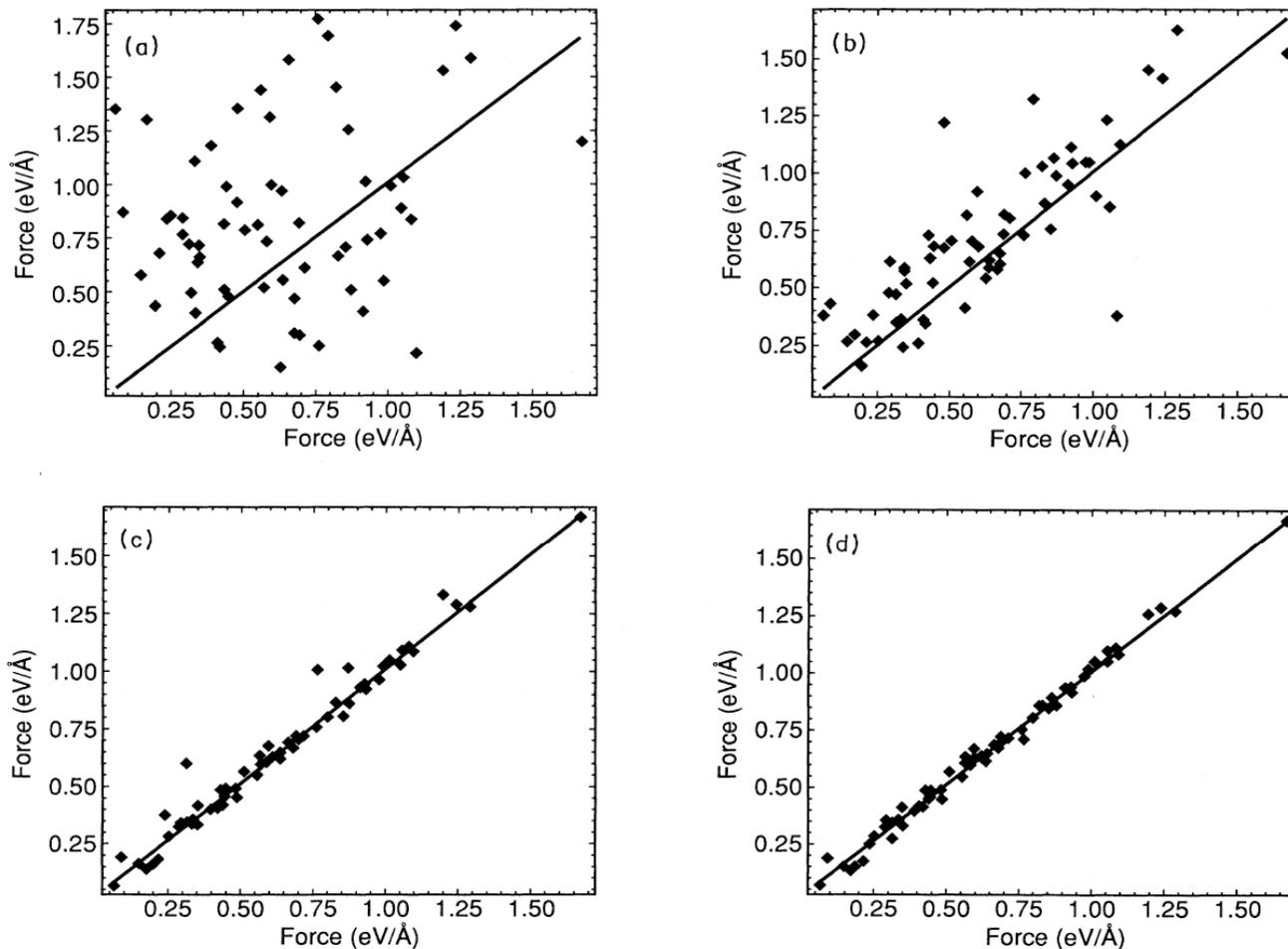


FIG. 6. Correlation of the magnitude of the converged plane-wave forces (120 Ry, Γ point Brillouin zone sampling) and LCAO forces for different basis sets: (a) single zeta; (b) double zeta; (c) double zeta plus polarization; and (d) double zeta plus polarization and triple zeta plus polarization on atoms numbered 21, 32, 39, 52, 61, and 11. The solid-diamond symbols are the LCAO results and the solid line is the plane-wave results.

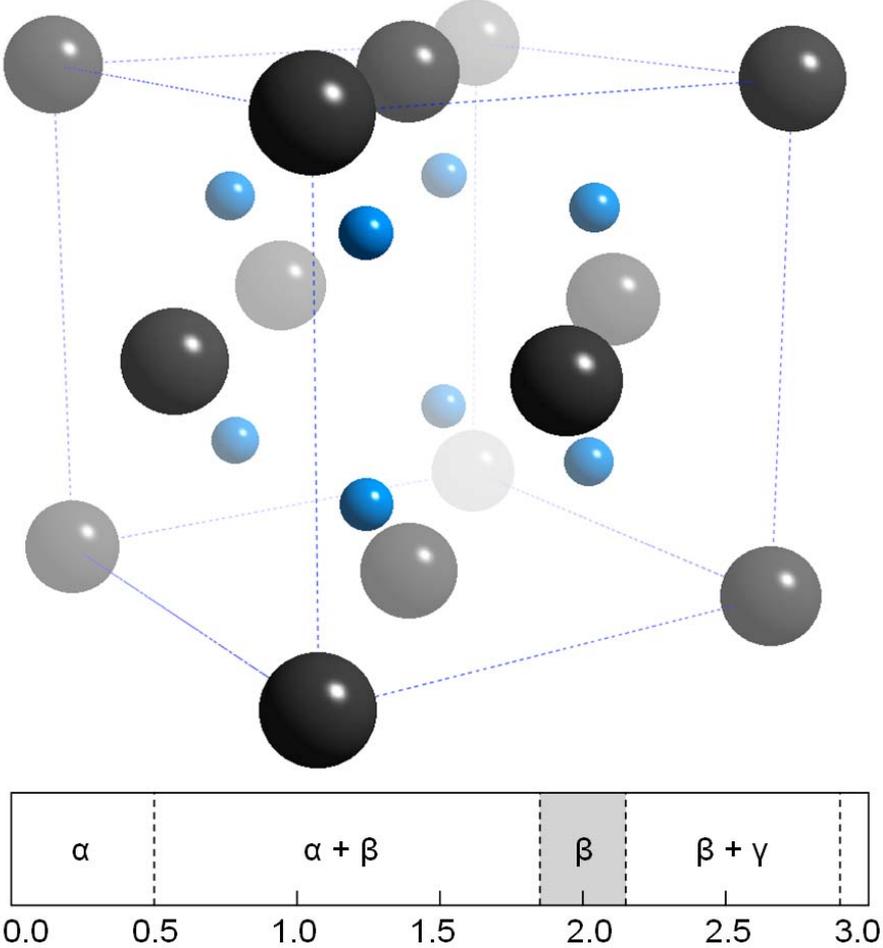
JS Nelson, EB Stechel, AF Wright, SJ Plimpton, PA Schultz, and MP Sears,
Basis-set convergence of highly defected sites in amorphous carbon
PRB 52 9354 (1995)

Summary of factors to consider:

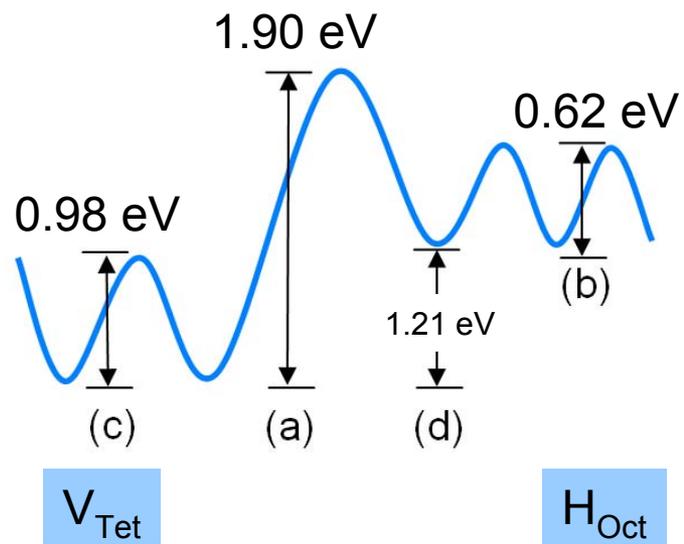
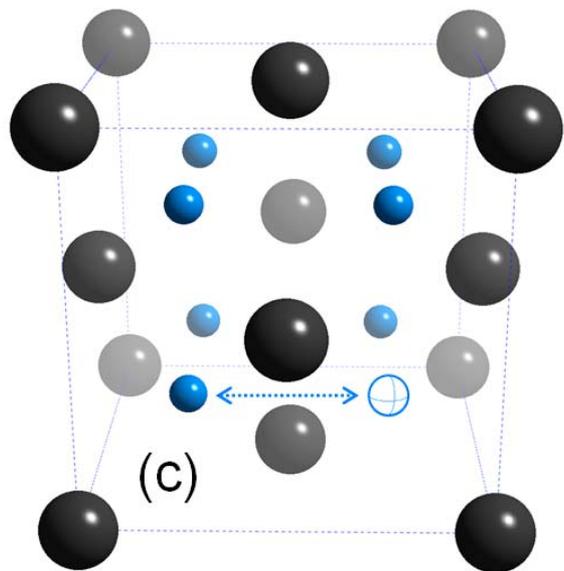
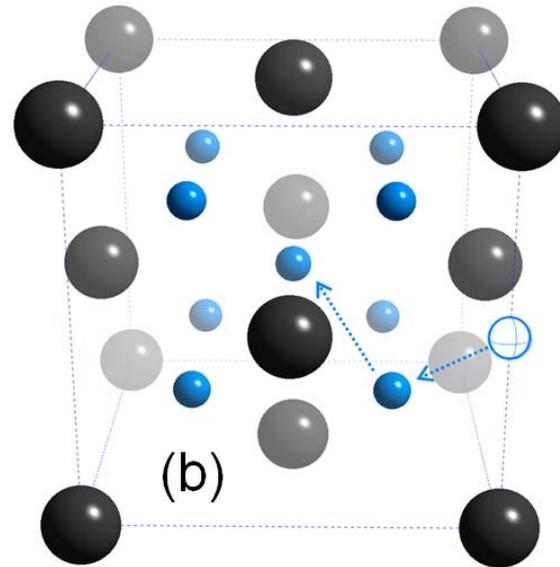
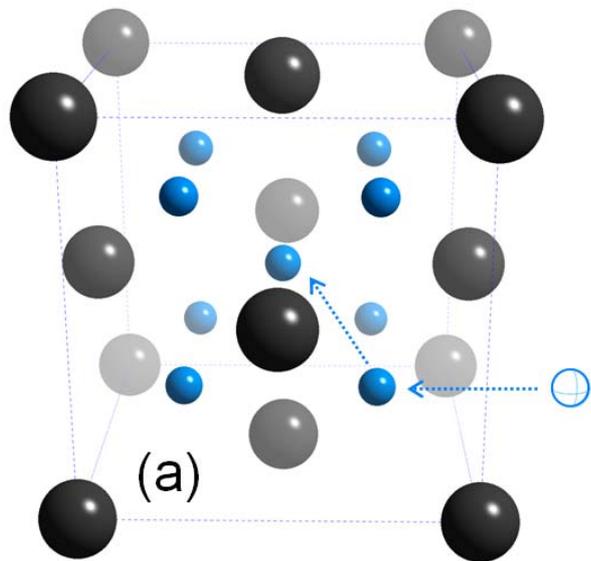
1. **Choice of functional**
2. **System Size**
3. **Relaxation**
4. **Boundary conditions**
5. **Sampling: *k*-points**
6. **Pseudopotentials**
7. **Basis Set / Energy cut off**
8. Trajectory length / time step
9. Equilibration (initial configurations)
10. Fictitious electron mass (CPMD)

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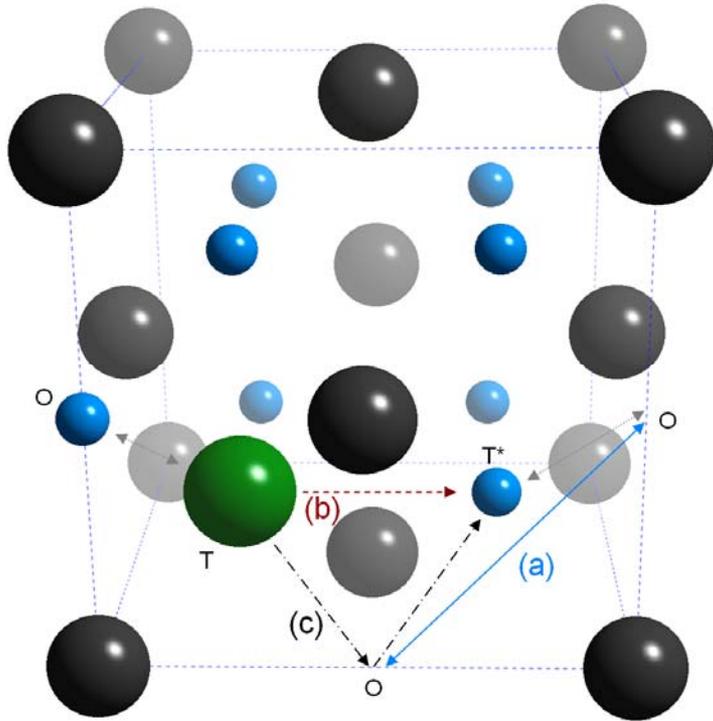
Erbium dihydride



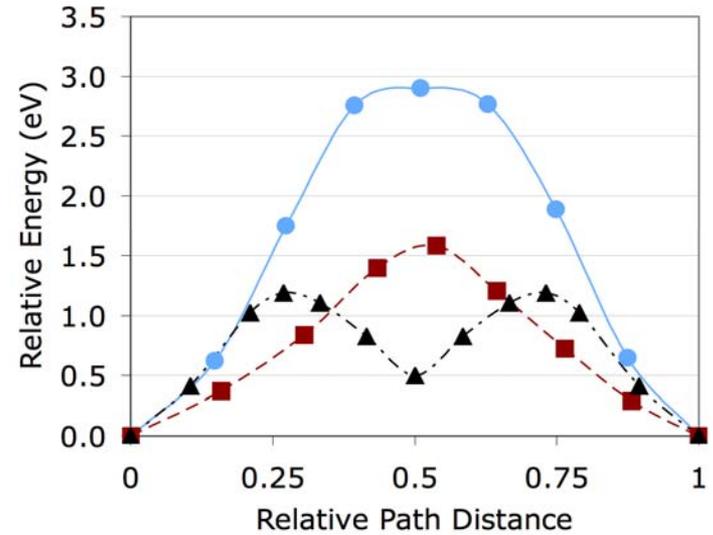
Hydrogen in erbium dihydride



Oxygen in erbium dihydride



—●— (a) Oct-Oct -■- (b) Tet-Tet -▲- (c) Tet-Oct



$$E_a = 1.2 \text{ eV} \quad D_0 = 1 \times 10^{-3}$$

Immobile @ 20 °C for 1 hr
250 nm @ 300 °C for 1 hr
6.5 μm @ 500 °C for 1 hr

Binding Energy for clusters:

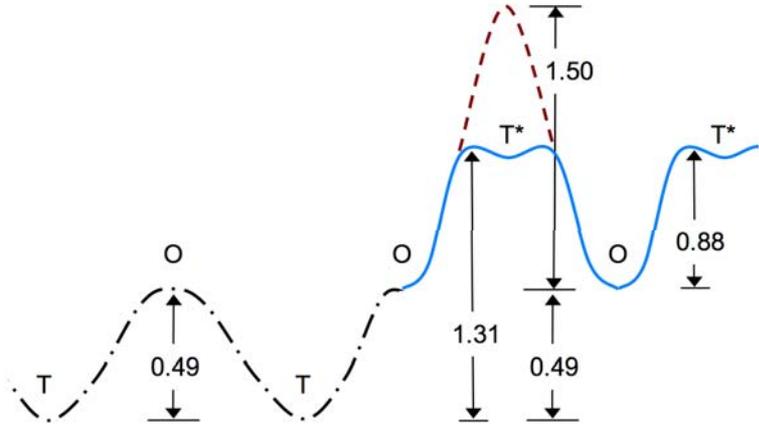
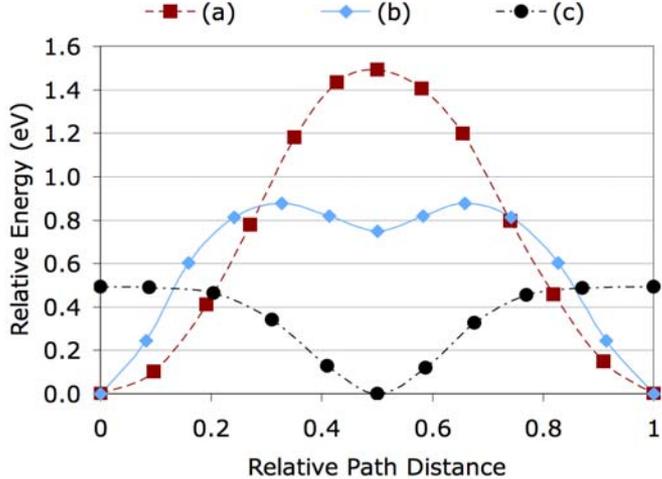
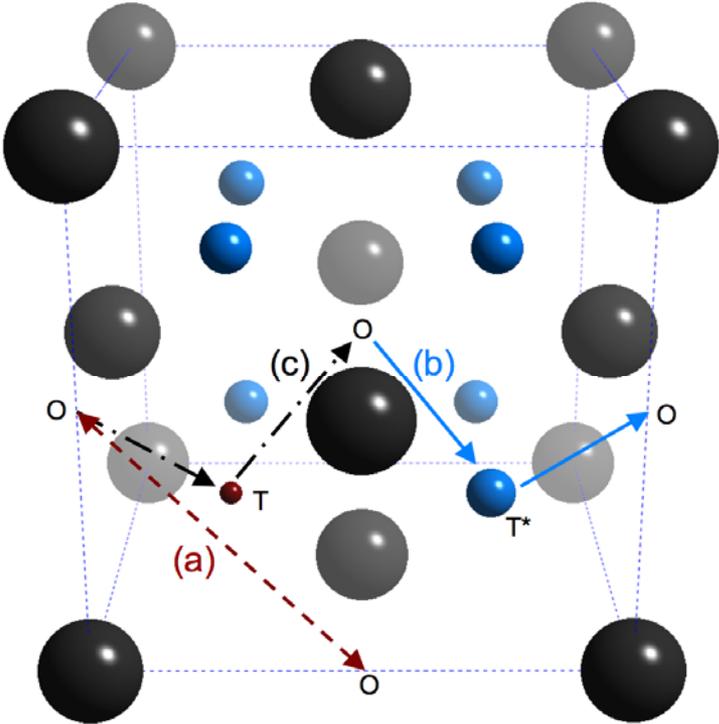
2 atoms = 0.28 eV

3 atoms = 0.34 eV

4 atoms = 0.45 eV

5 atoms = 0.48 eV

Helium in erbium dihydride/tritide

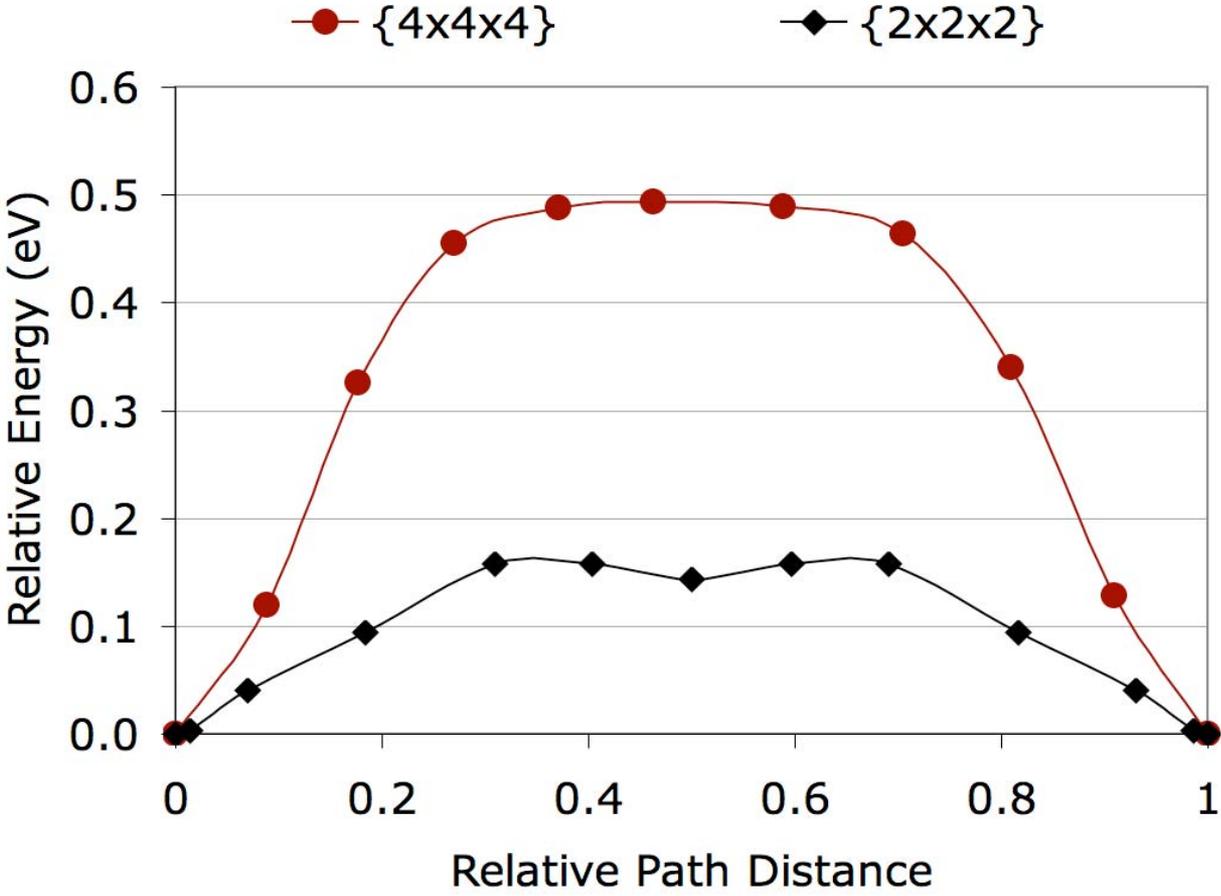


Conclusions:

1. Gas/Metal ratio determines mobility of hydrogen
2. Oxygen resides in tetrahedral sites, increases octahedral hydrogen occupancy.
3. In ideal erbium hydride, helium sits in octahedral site.
4. If $H/Er < 2.0$, helium ground state inside tetrahedral vacancies where it is pretty well trapped.
5. Networks of vacancies possible/probable? Multiple helium atoms trapped together?

Molecular dynamics movie?

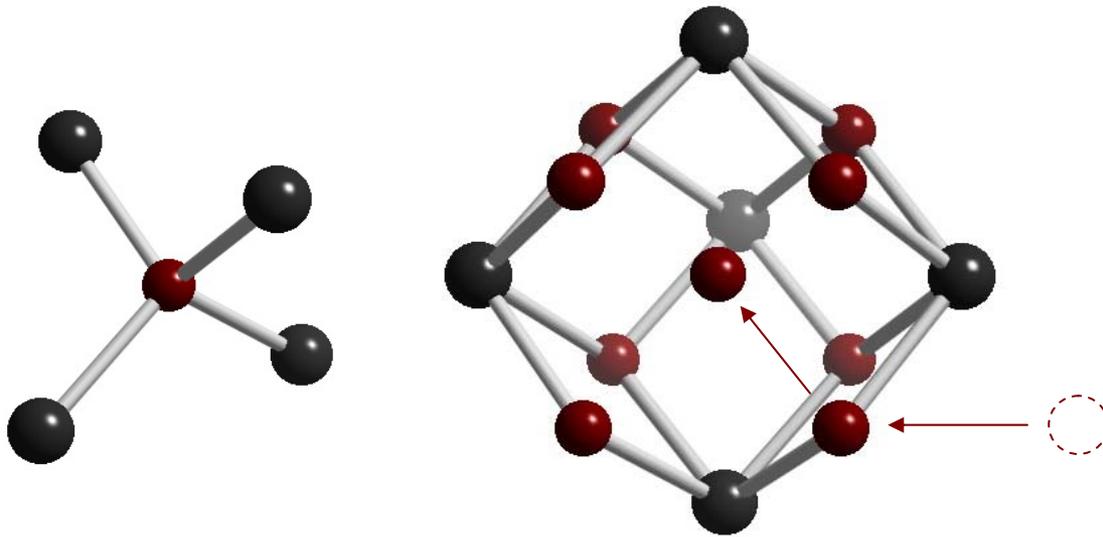
K-point sampling



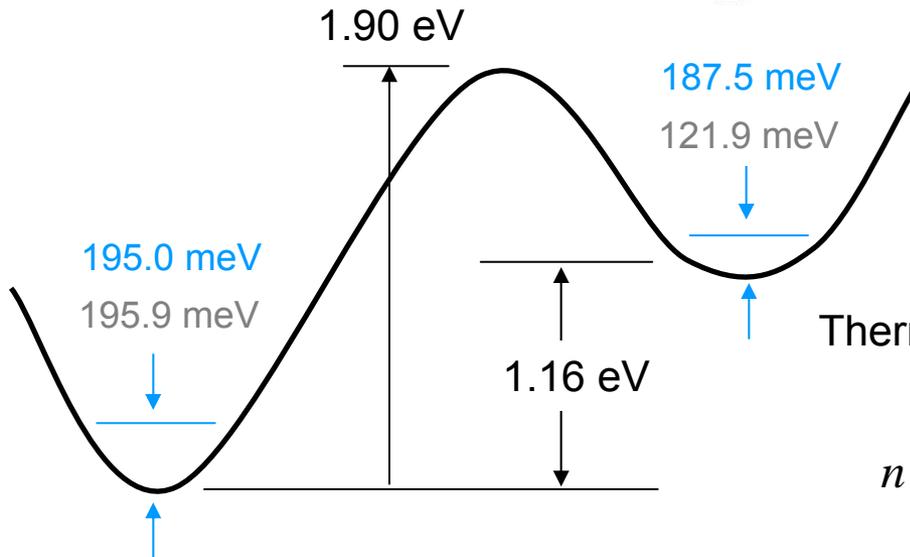
$$n = (NN') \exp(-E_f / kT)$$

$$v = \left(\frac{1}{2\pi} \right) \sqrt{\frac{k}{m}}$$

$$ZPE = \frac{hc}{2} \sum v_i$$



ΔZPE (meV)	
H	(74) 7.5
D	5.3
T	4.3



Thermally generated H_{Oct} & V_{Tet}

@ 500 °C, $n \sim 10^{18}$

$$n = (NN') \exp(-E_f / kT)$$

