Site occupation and migration of hydrogen, helium, and oxygen in β–phase ErH$_2$

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

Properties of the system

Hard problem to solve
Schrödinger view
Formally equivalent
“Easy” problem to solve
DFT view
Kohn-Sham particle (non-interacting) effective potential
(1965)

Remember:
Dirac made his statement in 1929.
Kohn-Sham equations:

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

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

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

Jacob's ladder

HEAVEN OF CHEMICAL ACCURACY

unoccupied \( \{ \phi_i \} \)
generalized RPA

\( \varepsilon_x \)
hyper-GGA

\( \tau \) and/or \( \nabla^2 n \)
meta-GGA

\( \nabla n \)
GGA

\( n \)
LSD

HARTREE WORLD

From preprint by J.P. Perdew et. al. to appear in JCP
The choice of XC-functional is the limiting factor for the accuracy of DFT
Silicon ad-dimer diffusion on Si(001)

Mattsson T R, Swartzentruber B S, Stumpf R and Feibelman P J 2003 Electric field effects on surface dynamics: Si ad-dimer diffusion and rotation on Si(001) Surf. Sci. 536 121
Surface Energy Extrapolation

\[
E_{slab}^n = \sigma + n E_{bulk}
\]
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.

\[
E_{\text{bulk}}(N) = \frac{E_{\text{total}}(N + \Delta N) - E_{\text{total}}(N)}{\Delta N}
\]
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.

<table>
<thead>
<tr>
<th>Cell size</th>
<th>$VV_{Si}^+$</th>
<th>$VV_{Si}^0$</th>
<th>$VV_{Si}^-$</th>
<th>$VV_{Si}^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>214</td>
<td>5.481</td>
<td>5.340</td>
<td>5.498</td>
<td>5.627</td>
</tr>
<tr>
<td>510</td>
<td>5.368</td>
<td>5.269</td>
<td>5.545</td>
<td>5.777</td>
</tr>
<tr>
<td>998</td>
<td>5.316</td>
<td>5.247</td>
<td>5.579</td>
<td>5.861</td>
</tr>
<tr>
<td>$\infty$</td>
<td>5.333</td>
<td>5.220</td>
<td>5.649</td>
<td>6.111</td>
</tr>
</tbody>
</table>

**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.

<table>
<thead>
<tr>
<th>Cell size</th>
<th>$VV_{Si}^+$</th>
<th>$VV_{Si}^0$</th>
<th>$VV_{Si}^-$</th>
<th>$VV_{Si}^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>214</td>
<td>5.486</td>
<td>5.445</td>
<td>5.618</td>
<td>5.786</td>
</tr>
<tr>
<td>510</td>
<td>5.415</td>
<td>5.402</td>
<td>5.691</td>
<td>5.952</td>
</tr>
<tr>
<td>998</td>
<td>5.393</td>
<td>5.380</td>
<td>5.721</td>
<td>6.042</td>
</tr>
<tr>
<td>$\infty$</td>
<td>5.418</td>
<td>5.363</td>
<td>5.800</td>
<td>6.298</td>
</tr>
</tbody>
</table>
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 $40^3$. 
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

![Graph showing total energy per bulk unit for different K-point grids and temperatures.](image-url)
K-point sampling
K-point sampling

Helium Tet to Oct Migration

- {333}
- {444}

Relative Energy (eV) vs. Relative Path Distance
K-point sampling

![Graph showing relative energy versus relative path distance for different k-point sampling settings: {4x4x4} and {2x2x2}.](image-url)
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
$R_d$ 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

Energy cutoff convergence (neutral Silicon Vacancy)

- **NCP PBE**
- **PAW PBE**
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)

AE Mattsson, PA Schultz, MP Desjarlais, TR Mattsson, K Leung
Erbium dihydride

C.S. Snow et al., J. Nuclear Materials (2007) (4.25 yrs old Film)

ErD$_2$ : Brewer et al.
Erbium dihydride
Hydrogen in erbium dihydride

(a) 0.98 eV

(b) 1.90 eV

(c) 0.62 eV

$V_{Tet}$

$H_{Oct}$
Oxygen in erbium dihydride

Ea = 1.2 eV    Do = 1x10^{-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
\[ n = (N N') \exp(-E_f / kT) \]

\[ \nu = \left( \frac{1}{2\pi} \right) \sqrt{\frac{k}{m}} \]

[ \Delta ZPE (meV) ]

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>74</td>
</tr>
<tr>
<td>D</td>
<td>5.3</td>
</tr>
<tr>
<td>T</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Thermally generated \( H_{Oct} \) & \( V_{Tet} \)

@ 500 °C, \( n \sim 10^{18} \)

\[ n = (N N') \exp(-E_f / kT) \]