Defects in materials

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July 8, 2014
Outline

- Motivation.
- Computational methods.
- Defects in oxides.
  - Why are defects challenging?
  - Defects in high-$\kappa$ dielectric – HfO$_2$.
  - Defects in technologically important material – TiO$_2$.
  - Defects for quantum computing.
Motivation.

- Computational methods.
- Defects in oxides.
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  - Defects in high-$\kappa$ dielectrics – HfO$_2$.
  - Defects in technologically important material – TiO$_2$.
  - Defects for quantum computing.
Motivation – High-$\kappa$ dielectric material HfO$_2$

- Moore’s law about size of transistor.
- HfO$_2$ has replaced SiO$_2$ in today’s MOSFET devices.

$\kappa_{\text{SiO}_2} \approx 3.9$

$\kappa_{\text{HfO}_2} \approx 16 - 17$

\[1\text{http://www.intel.com/technology/45nm/index.htm}\]
High-κ dielectric materials – Motivation

- High defect density.

- Charge trapping by defects in the interfacial layer or oxide – threshold voltage instability$^1$.

- Oxygen-related defects – vacancy$^2$ ($\text{V}_\text{O}$) or interstitials ($\text{I}_\text{O}$) major cause.

- Study the stability of point defects – $\text{V}_\text{O}$.

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Motivation – TiO\textsubscript{2}

- Photovoltaic material in solar cells\textsuperscript{1}.
- Photocatalytic material – hydrolysis of water\textsuperscript{2}.
- Memresistive switches for non-volatile memory\textsuperscript{3}.
- Oxygen vacancies are believed to play a very important role in all these applications.

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  ● Why are defects challenging?
  ● Defects in high-\(\kappa\) dielectrics – HfO\(_2\).
  ● Defects in technologically important material – TiO\(_2\).
  ● Defects for quantum computing.
Methods – Ground-state properties

Properties that are intrinsic to a system with all its electrons in equilibrium.

- Density functional theory is the “standard model” for understanding ground-state properties.
- Total energy is a functional of the charge density.
- Kohn-Sham formulation: Map the interacting many-electron problem to non-interacting electrons moving in a self-consistent field.

\[
\left(-\frac{\nabla^2}{2} + V_{\text{ionic}}(r) + V_{\text{Hartree}}(r) + V_{\text{xc}}(r)\right)\psi(r) = \epsilon \psi(r)
\]

- Local density approximation
- Generalized gradient approximation
Methods – Excited-state properties

Spectroscopic properties that involve experiments creating an excited particle above the ground state.

- Concept and formalism of the interacting particle Green’s function \( G \).
- Many-body perturbation theory is the “standard model” for understanding excited-state properties.

\[
G^{-1} = G_0^{-1} + \Sigma
\]

- GW approximation to the self-energy \( \Sigma \).

\[
\Sigma = \bullet \rightarrow \bullet = iGW
\]

\[
W = \varepsilon^{-1} v
\]
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Why are defects challenging?

- Potentially strong electron-electron correlations.
  - Can be open-shell systems.
  - Multiple localized, interacting electrons.

- Lattice relaxation effects.

- Screening from the host.
  - Mimicking the system by isolated cluster may be incorrect.

- Experiments often involve excited-state properties (deep level transient spectroscopy or optical absorption etc.)

- Computational difficulty – isolated defect.
Motivation.

Computational methods.

Defects in oxides.

• Why are defects challenging?
• Defects in high-$\kappa$ dielectric – HfO$_2$.
• Defects in technologically important material – TiO$_2$.
• Defects for quantum computing.
Formation energy of an oxygen-vacancy:

\[ E^f[\vec{R}] = E[\vec{R}] - E_{\text{ref}} + \frac{1}{2}E_{O_2} \]
High-κ dielectric materials – Definitions

Formation energy of an oxygen-vacancy:

\[ E^f_{q}[\vec{R}_q](E_F) = E_q[\vec{R}_q] - E_{\text{ref}} + \frac{1}{2}E_{O_2} + q(E_F + E_V) \]

Example: \( V_o \)

From slides by C. G. Van de Walle
Formation energy of an oxygen-related defect in hafnia:

\[ E_{q}^{f}[\vec{R}_{q}](E_{F}) = E_{q}[\vec{R}_{q}] - E_{HfO_{2}} - n_{O}\mu_{O} + q(E_{F} + E_{V}) \]

where \( \mu_{O} \) is the oxygen chemical potential.
High-$\kappa$ dielectric materials – Definitions

Formation energy of an oxygen-related defect in hafnia:

$$E^f_q[\vec{R}_q](E_F) = E_q[\vec{R}_q] - E_{HfO_2} - n_O\mu_O + q(E_F + E_V)$$

where $\mu_O$ is the oxygen chemical potential.

Charge transition level: $\varepsilon^{q/q-1} = $ Fermi energy where defect $q \rightarrow q - 1$. 

![Diagram of band structure with $E_f$ and $E_v$]
High-$\kappa$ dielectric materials – Definitions

Formation energy of an oxygen-related defect in hafnia:

\[ E^f_q[\vec{R}_q](E_F) = E_{q}[\vec{R}_q] - E_{\text{HfO}_2} - n_O\mu_O + q(E_F + E_v) \]

where $\mu_O$ is the oxygen chemical potential.

Charge transition level: $\varepsilon^{q/q-1} = \text{Fermi energy where defect } q \rightarrow q - 1.$

\[ = E^{f}_{q-1}[\vec{R}_{q-1}](E_F = 0) - E^{f}_q[\vec{R}_q](E_F = 0) \]
High-κ dielectric materials – Methodology

DFT + GW methodology.

Formation energy

$E^f_q(\vec{R}_q)$

$E^f_{q-1}(\vec{R}_{q-1})$

$\varepsilon^{q/q-1}$

Generalized coordinate

High-$\kappa$ dielectric materials – Methodology

DFT + GW methodology.

Formulation of the formation energy:

$$E_{f}^{q}(\vec{R}_{q}) - E_{f}^{q-1}(\vec{R}_{q-1}) = \varepsilon_{q/q-1}$$

Generalized coordinate

Three fold coordinated ($V_{O(3)}$) and four fold coordinated ($V_{O(4)}$) vacancies in charge states \{0, +1, +2\}

96 atom super cells.

Norm conserving pseudopotentials - Hf $5s^25p^65d^26s^2$ and O $2s^22p^4$.

250 Ry energy cutoff for wavefunctions.

PBE functional for structural energies.

‘One shot’ GW done within generalized plasmon pole model done with BerkeleyGW.

Bulk structural parameters and band gap (6.00 eV) in good agreement with experiment.

SIESTA for large supercells to get electrostatic corrections.
Electrostatic corrections - $V_{O(3)}$

GW charge transition levels (eV)

<table>
<thead>
<tr>
<th>$\varepsilon^{+2/+1}$</th>
<th>4.50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon^{+2/+1}$</td>
<td>3.42</td>
</tr>
<tr>
<td>$\varepsilon^{+1/0}$</td>
<td>3.55</td>
</tr>
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<td>$\varepsilon^{+1/0}$</td>
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Generalized coordinate
Electrostatic corrections - $V_{O(3)}$

GW charge transition levels (eV)

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<td>4.33</td>
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Electrostatic corrections - $V_{O(3)}$

Number of atoms in supercell

<table>
<thead>
<tr>
<th>$N$</th>
<th>1500</th>
<th>768</th>
<th>324</th>
<th>96</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{\text{defect}} - \varepsilon_v$ (eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V^+2_{O(3)}$</td>
<td>$V^+1_{O(3)}$</td>
<td>$V^0_{O(3)}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>2.66</td>
<td>3.42</td>
<td>3.55</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>3.40</td>
<td>3.25</td>
<td>3.53</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>4.18</td>
<td>3.95</td>
<td>3.56</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>4.95</td>
<td>4.35</td>
<td>4.33</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>5.72</td>
<td>5.22</td>
<td>4.33</td>
<td></td>
</tr>
</tbody>
</table>

$\varepsilon_{\text{defect}} - \varepsilon_v (eV)$

$PBE$ defect levels.

$GW$ charge transition levels (eV)

| $\varepsilon^{+2/+1}$ | 4.50 |
| $\varepsilon^{+2/+1}$ | 3.42 |
| $\varepsilon^{+1/0}$ | 3.55 |
| $\varepsilon^{+1/0}$ | 4.33 |

Generalized coordinate

$E_{q-1}^f(\vec{R}_{q-1})$ and $E_{q}^f(\vec{R}_{q})$
Electrostatic corrections - $V_{O(3)}$

Number of atoms in supercell
\[ \propto V^{-\frac{1}{3}} \]

PBE defect levels.
High-$\kappa$ dielectric materials – Formation energy of $V_0$

$\text{Relative formation energy (eV)}$

$\text{Fermi energy (eV)}$

$V_{O(3)}$

$V_0^{+1}$

$V_0^{+2}$

$V_0^0$

$V_0$

$V_{BM}$

$CBM$

High-$\kappa$ dielectric materials – Formation energy of $V_0$

![Graph showing formation energy of $V_0$](image)

- $V_0^{(3)}$
- $V_0^{(4)}$
- $V_0^{+1}$
- $V_0^{+2}$

Relative formation energy (eV) vs Fermi energy (eV)

VBM: 2
CBM: 0

High-κ dielectric materials – Formation energy of $V_O$

High-κ dielectric materials – Formation energy of vacancies

![Graph showing formation energy vs. Fermi Energy for oxygen poor and oxygen rich conditions.](image)

Defect charging energy – $U$

$U$, defect charging energy, is defined as the energy of the reaction:

$$2V^+ \rightarrow V^{2+} + V^0$$

$$U = E^f_{+2}(\vec{R}_{+2}) + E^f_0(\vec{R}_0) - 2E^f_{+1}(\vec{R}_{+1})$$

$$= -\varepsilon^{+2/+1} + \varepsilon^{+1/0}$$
## Comparison with previous studies

All values are in eV.

<table>
<thead>
<tr>
<th></th>
<th>$V_{O(3)}$</th>
<th>$V_{O(4)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon^{+2/+1}$</td>
<td>$\varepsilon^{+1/0}$</td>
</tr>
<tr>
<td>GGA</td>
<td>2.74</td>
<td>2.69</td>
</tr>
<tr>
<td>HSE$^1$</td>
<td>3.93</td>
<td>4.42</td>
</tr>
<tr>
<td>PBE0$^2$</td>
<td>3.7</td>
<td>4.1</td>
</tr>
<tr>
<td>GW$^3$ (24 atoms)</td>
<td>4.00</td>
<td>3.10</td>
</tr>
<tr>
<td>GW$^4$ (96 atoms)</td>
<td>2.56</td>
<td>3.46</td>
</tr>
</tbody>
</table>

---

U, defect charging energy, is defined as the energy of the reaction:

\[ 2V^+ \rightarrow V^{2+} + V^0 \]

\[ U = E_{+2}^f (\vec{R}_{+2}) + E_0^f (\vec{R}_0) - 2E_{+1}^f (\vec{R}_{+1}) \]
\[ = -\varepsilon^{+2/+1} + \varepsilon^{+1/0} \]
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$$= -\varepsilon^{+2/+1} + \varepsilon^{+1/0}$$

$$\equiv U_{\text{elec}} + U_{\text{relax}}$$

$$= \{E^f_{+2}(\vec{R}_{+1}) + E^f_0(\vec{R}_{+1}) - 2E^f_{+1}(\vec{R}_{+1})\} +$$

$$\{[E^f_{+2}(\vec{R}_{+2}) - E^f_{+2}(\vec{R}_{+1})] + [E^f_0(\vec{R}_0) - E^f_0(\vec{R}_{+1})]\}$$
Defect charging energy – $U$

$U$, defect charging energy, is defined as the energy of the reaction:

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$$U = E_f^{+2}(\vec{R}_{+2}) + E_f^0(\vec{R}_0) - 2E_f^{+1}(\vec{R}_{+1})$$

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$$\{[E_f^{+2}(\vec{R}_{+2}) - E_f^{+2}(\vec{R}_{+1})] + [E_f^0(\vec{R}_0) - E_f^0(\vec{R}_{+1})]\}$$

$U_{\text{elec}} \geq 0 \text{ and } U_{\text{relax}} \leq 0$
Defect charging energy – U

\[ 2V^+ \rightarrow V^{2+} + V^0 \]

<table>
<thead>
<tr>
<th></th>
<th>( U_{\text{elec}} )</th>
<th>( U_{\text{relax}} )</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_{O(3)} )</td>
<td>2.24</td>
<td>-1.33</td>
<td>0.90</td>
</tr>
<tr>
<td>( V_{O(4)} )</td>
<td>2.13</td>
<td>-1.35</td>
<td>0.81</td>
</tr>
</tbody>
</table>
DFT+GW method for calculating the stability of oxygen vacancies.

Qualitative agreement with previous hybrid functional calculations on the vacancies.

Quantitative disagreement with previous hybrid functional calculations - vacancies near a Si/HfO$_2$ interface.

<table>
<thead>
<tr>
<th>$V_O$</th>
<th>DFT+GW</th>
<th>HSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1,0</td>
<td>+2,+1</td>
<td></td>
</tr>
</tbody>
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Motivation.

Computational methods.

Defects in oxides.

- Why are defects challenging?
- Defects in high-$\kappa$ dielectric – HfO$_2$.
- Defects in technologically important material – TiO$_2$.
- Defects for quantum computing.
Vacancies in TiO$_2$ – Computational details

- Oxygen vacancies (V$_O$) in rutile in charge states {0, +1, +2}
- 72 atom super cells.
- 200 Ry energy cutoff for wavefunctions.
- HSE functional for structural energies.
- ‘One shot’ GW done within generalized plasmon pole model done with BerkeleyGW.
- Bulk structural parameters and band gap (3.13 eV) in good agreement with experiment.
Relaxation of the atoms: Two minima

(a)

(b)

Polaron formation – $V_{O}^{+1}$

Not relevant for charge transition level
Polaron formation – $V_{O}^{+1}$

Relaxation of the atoms: Two minima

- A state in the gap – polaron.
- $V_{O}^{+1} \rightarrow V_{O}^{+2} + \text{polaron}$. Lower in energy by 1.2 eV.
- Not relevant for charge transition level.

- A state in the gap – defect state.
- Charge density on the defect site.
- Local minima.
- Relevant for charge transition level.
TiO$_2$ – Formation energy of vacancies

Oxygen rich

Titanium rich

(a) $V^0_O$  
(b) $V^0_O$
Comparison with previous studies

All values are in eV.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td></td>
<td>( \varepsilon^{+2/+1} )</td>
</tr>
<tr>
<td>GGA(^1)</td>
<td>2.0</td>
</tr>
<tr>
<td>HSE(^2)</td>
<td>3.8</td>
</tr>
<tr>
<td>GW(^3)</td>
<td>3.01</td>
</tr>
</tbody>
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Negative U defect.

---


- DFT+GW method for calculating the stability of oxygen vacancies.
- Negative U defect.
- *Qualitative* agreement with previous hybrid functional calculations.
- *Quantitative* disagreement with previous hybrid functional calculations.

<table>
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</tr>
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<tbody>
<tr>
<td></td>
<td>+2,0</td>
<td>+2</td>
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Motivation.

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- Defects for quantum computing.
Defects for spin-qubit applications

- Room temperature individually addressable spin systems in the solid-state for quantum computing.

**NV**− center in diamond is the leading candidate.

Possible room-temperature qubit with long coherence time (∼1ms) for quantum computing.

High sensitivity, high-spatial resolution magnetometry.
Defects for spin-qubit applications

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Defects for spin-qubit applications

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- Possible room-temperature qubit with long coherence time ($\sim1$ms) for quantum computing.
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NV$^-$ center in diamond – Motivation

Optical initialization at room-temperature provides initial spin pure state for spin-qubit operation.

Notation: $^{2S+1} \Lambda$

$\Lambda$ : Irreducible representation of the orbital symmetry
$S$ : Total Spin
NV$^-$ center in diamond – Motivation

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$\Lambda$: Irreducible representation of the orbital symmetry
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At Room Temperature

Absorption

\[ ^3E \]

Unpolarized

$\hbar \omega = 2.2eV$

\[ ^3A_2 \]

Degenerate mixed ground state

Unentangled spin pure state
• Identification of singlet-level structure.

• Effective optical initialization path between the two triplet levels.
NV$^-$ is a deep level center in a band gap of diamond with multiple localized, interacting electrons.

- Open-shell problem$^1$.
- Correlation due to degenerate ground-states.

**NV⁻ center in diamond – Dangling orbitals**

8 dangling spin-orbitals in and near band-gap of diamond

Good basis for low energy excitations.
\[ \hat{H} = \sum_{i,\sigma} E_i n_{i\sigma} + \sum_{i \neq j,\sigma} t_{i,j} c_{i,\sigma}^{\dagger} c_{j,\sigma} + \sum_i U n_{i,\uparrow} n_{i,\downarrow} + \sum_{i \neq j,\sigma,\sigma'} V n_{i,\sigma} n_{j,\sigma'} \]

- \( i, j \): Atomic sites (C or N)
- \( \sigma, \sigma' \): Spin direction
- \( E_i \): On-site energy
- \( t_{i,j} \): Hopping integral
- \( U \): On-site Coulomb repulsion
- \( V \): Nearest neighbor Coulomb repulsion

- Effective Coulomb interaction parameters
- Geometry dependent parameter sets

Strong electron-electron correlation
Screening from diamond
Large structural relaxation

Hindered by the difficulty in getting physically grounded model parameters.
Use *ab initio* GW to get model parameters, incorporating realistic electron-electron interactions.

\[ E_{qp}^{ab} = E_{qp}^H? \]

---

**Diagram:**

- **Ab initio GW**
  - Defect state quasiparticle energy
  - \[ E_{qp}^{ab} = E_{qp}^H? \]
  - No → Tune model parameters
  - Yes → Done

- **Extended Hubbard model GW**
  - Initial sets of parameters
  - Defect state quasiparticle energy
  - Yes → Done
- $U/t > 3 \rightarrow$ strongly correlated system.
- Reasonable values of parameters.
- Geometry dependent parameters.

All parameters are in eV.

<table>
<thead>
<tr>
<th></th>
<th>$E_C - E_N$</th>
<th>$t_{NC}$</th>
<th>$t_{CC}$</th>
<th>$U$</th>
<th>$V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground-state</td>
<td>2.56</td>
<td>-0.68</td>
<td>-1.03</td>
<td>3.43</td>
<td>0.83</td>
</tr>
<tr>
<td>Excited-state</td>
<td>2.86</td>
<td>-0.75</td>
<td>-0.90</td>
<td>3.45</td>
<td>0.67</td>
</tr>
</tbody>
</table>
Level diagram\(^1\) from exact diagonalization of model Hamiltonian – all many-electron correlation effects within our Hilbert space.

All energies in eV.

\begin{table}
\begin{tabular}{|c|c|c|}
\hline
 & Theory & Exp \\
\hline
1 & 2.1 & 2.2 \\
\hline
2 & 2.0 & 1.945 \\
\hline
3 & 1.8 & 1.8 \\
\hline
\end{tabular}
\end{table}

\[^1\text{S. Choi, M. Jain and S. G. Louie, Phys. Rev. B 86, 041202 (2012)}\]
Spin triplet

$^3E$  \hspace{1cm}  $^3A_2$

$^3E$  \hspace{1cm} $^3A_2$

Spin singlet

$^1E'$  \hspace{1cm} $^1A_1$

$^1E$

$\ell_s = \pm 1$

$\ell_s = 0$

SO coupling

Qualitatively and quantitatively consistent with available experimental data.

---

■ Constructed extended Hubbard Hamiltonian from \textit{ab initio} GW calculations.

■ Through exact diagonalization, many-electron effects strongly affect the energy level diagram qualitatively and quantitatively.

■ Computed ground- and excited-state energy surfaces and transition rates between them provided a consistent picture with experiments.

■ Proposed an optical initialization pathway in which inter-system crossing plays a crucial role.

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Conclusion

- *Ab initio* methods to understand and predict properties of defects in materials.
- Oxygen vacancies in high-$\kappa$ material – HfO$_2$ and photocatalytic material – TiO$_2$.
- NV$^-$ center in diamond for quantum computing application.
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