First-principles simulations of defects in oxides and nitrides

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Why study defects?

- **“Defects”**
  - Extended defects
    » dislocations
  - Point defects:
    » Native defects
    » Impurities

- **Defects often determine the properties of materials**
  - Doping and its limitations
  - Device degradation
  - Diffusion
    » Mediated by point defects
Technological significance

• **Semiconductors**
  – Achieve higher doping levels
    » *p*-type doping of AlN would allow UV lasers
  – Controllably dope materials *p*-type and *n*-type
    » Oxides

• **Photovoltaics**
  – CuIn$_x$Ga$_{1-x}$Se$_2$

• **Hydrogen storage materials**
  – Kinetics of hydrogen release in NaAlH$_4$

• **Embrittlement of structural metals**
Links to experiment

- **Secondary Ion Mass Spectrometry (SIMS)**
  - Impurity concentrations (to within factor of 2)
- **Positron annihilation spectroscopy**
  - Most sensitive to negatively charged vacancy(-like) defects
- **EXAFS (extended x-ray absorption fine structure)**
  - Microscopic structure, atomic relaxations
- **Electron paramagnetic resonance + ENDOR**
  - Hyperfine parameters (wave functions, atomic positions)
- **Vibrational spectroscopy (Raman, FTIR)**
  - Local vibrational modes; sensitive to atomic positions
- **Deep level transient spectroscopy**
  - Electronic transition levels
    - Total-energy differences, not Kohn-Sham levels
- **Photoluminescence (PL), PL excitation**
  - Optical transition levels
Defect calculations: geometry

• Green’s functions
  – Implementation difficult
  – Non-intuitive

• Clusters
  – Surface effects
  – Not “bulk” (quantum confinement)

• Supercells
  – “Molecular unit cell approach (MUCA)"
Defect Formation Energies

Example: $V_O$

oxide: $V_O$  \[ - \]  oxide  \[ + \]  $\frac{1}{2} O_2$
Defect Formation Energies

Example: $V_O$

oxide: $V_O$

oxide

+$\frac{1}{2}O_2$

reservoir

e$^-@\varepsilon_F$

(reservoir)
Formalism

- **$E_{\text{form}}$:** formation energy
  
  Concentration of defects or impurities:
  \[
  C = N_{\text{sites}} \exp \left[ - \frac{E_{\text{form}}}{kT} \right]
  \]

- **Example: oxygen vacancy in ZnO**

  \[
  E_{\text{form}}(V_O^+) = E_{\text{tot}}(V_O^+) - E_{\text{tot}}(\text{bulk}) + \mu_O + E_F
  \]

  $\mu_O$: energy of oxygen in reservoir, i.e., oxygen chemical potential

  $E_F$: energy of electron in its reservoir, i.e., the Fermi level

- **General expression**

  \[
  E_{\text{form}}(D^q) = E_{\text{tot}}(D^q) - E_{\text{tot}}(\text{bulk}) + n_i \mu_i + qE_F
  \]

  $n_i$: number of atoms being exchanged to form the defect
Formation energy

- $V_0$ in ZnO

Zn-rich conditions:

$$\mu_{\text{Zn}} = E_{\text{tot}}(\text{bulk Zn})$$

$$\Rightarrow \mu_{O} = E_{\text{tot}}(O_2) + \Delta H_f(\text{ZnO})$$
Transition levels

• Charge-state transition levels

- $\varepsilon_{+/0}$
- $\varepsilon_{2+/+}$
- $\varepsilon_{2+/0}$

Diagram showing formation energy (eV) vs Fermi level (eV) with transitions at $\varepsilon_{2+/0}$ and $\varepsilon_{2+/+}$.
Issues...

- **Band gap problem**
  - DFT (LDA, GGA)

- **Affects formation energies and transition levels**
  - Even for neutral charge states, if defect-induced Kohn-Sham states are occupied with electrons
Band-gap corrections: Empirical corrections

• **Ad hoc corrections**
  – “Scissors operator”
    » Shift gap levels based on conduction- vs. valence-band character
  – Delta-function(-like) term added to potential, shifts s states
  – “Modified pseudopotentials”
  – Issues
    » Hard to control
    » May have unintended consequences (indirect vs. direct gaps, …)

• **Extrapolations based on calculations that yield different gaps**
  – Different plane-wave cutoffs
  – Different exchange-correlation functionals
  – …
  – Issue: different choices of parameter not only produce different gap, but also different levels of accuracy for description of defect
Band-gap corrections: SIC and LDA+U

• Physically meaningful improvements
• Self-interaction corrections
  – Difficult to implement in self-consistent calculations for solids
  – Incorporate in pseudopotentials

• “LDA+U” approach

• Issues:
  – Determination of $U$
  – Band gap not fully corrected
    » How to extrapolate to the experimental gap?
Oxygen vacancy in ZnO
Band-gap corrections: Hybrid functionals

- **Mixing of Hartree-Fock (exact exchange) and DFT**
- **Functionals mix in ~25% of exact exchange**
- **PBE0**
- **HSE**
  - Exact exchange only for short-range interactions
- **Obtain very good description of many properties**
  - Band gaps close to experiment
- **Details of the physics still to be explored/understood**
Band-gap corrections: Beyond DFT

- **Quasiparticle calculations**
  - Combine DFT and $G_0W_0$
  - DFT: good for structural properties
  - $G_0W_0$: many-body perturbation theory for defects: accurate electron affinities in solids

- **Quantum Monte Carlo**
  - Richard Hennig
“Deep” vs. “shallow” defects

- Note: dispersion
  - Due to finite supercell size
  - Energetics taken care of by special-point sampling
  - Make sure correct occupation of states
“Deep” vs. “shallow” defects

**Deep**
- Localized wave function
- Level (usually) far from band edges

**Shallow**
- Defect-induced state is resonance in VB or CB
- Near VB or CB: only small perturbation
- “Effective mass” state
Alignment of Fermi level

- Charges are exchanged with $E_F$, referenced to $E_v$

$$E_{\text{form}}(D^q) = E_{\text{tot}}(D^q) - E_{\text{tot}}(\text{bulk}) + n_i \mu_i + qE_F$$

- Presence of defect in supercell shifts average electrostatic potential with respect to bulk
Supercell size effects

• Neutral defects:
  – Supercell should be large enough to ensure atomic relaxations are included, and overlap of wave functions is small enough

• Charged defects:
  – Inbalance in electronic and ionic charge would lead to Coulomb divergence
  – Neutralizing background
    » No need to explicitly include; \( G=0 \) term calculated for neutral system
Supercell size effects

• Neutralization leads to unintended terms in total energy
  – Interactions with neutralizing background and between periodic images of defects

• “Makov-Payne” correction

\[ E(L) = E(\infty) - \alpha q^2/\varepsilon L - C_3 q^2/L^3 + O(L^{-5}) \]

  – Correct in vacuum
  – Effect of solid: dielectric constant \( \varepsilon \)
Supercell size effects

- Explicit studies as a function of supercell size have shown complex behavior
  - Fits to $1/L$ and $1/L^3$ terms
  - In some cases, Makov-Payne correction satisfactory
  - In other cases: Makov-Payne correction makes things significantly worse
    » Example: $V^{2+}$ in diamond
Supercell size effects

- Need rigorous analysis of electrostatic interactions in dielectric media
  - Produces rigorous definitions for
    - Coefficient of $1/L^3$ (“quadrupole”) term
    - Alignment term
  - Allows testing whether “point charge” correction (Makov-Payne) suffices or not
    - Fails if defect state decays slowly; point-charge model overcorrects
    - Prescription for addressing this problem
Native point defects in ZnO

- **$V_O$, $V_{Zn}$ dominate**

- **$V_O$: deep donor**
  - Also high formation energy in $n$-type ZnO

- **$V_{Zn}$: deep acceptor**
  - Cause of green luminescence
Native defects vs. impurities

- Native defects cannot explain *n*-type doping
- Impurities: donors?
Hydrogen in ZnO

$H^+$ is the only stable charge state $\Rightarrow$ hydrogen acts as shallow donor

Unexpected! In other semiconductors hydrogen reduces the conductivity


Hydrogen is a likely candidate for unintentional incorporation

• But: highly mobile


$\Rightarrow$ unstable at temperatures where $n$-type conductivity is known to persist (>500°C)

Also cannot explain dependence of conductivity on oxygen partial pressure…
Substitutional hydrogen in ZnO

• Forced to reconsider the role of hydrogen...
  – … and in the process some interesting new physics/chemistry emerged!
• Substitutional hydrogen
  – Hydrogen on a substitutional oxygen site
  – Formation energy: low
  – Ionization energy: small; shallow donor
• Consistently explains dependence of $n$-type conductivity on oxygen partial pressure
**p-type doping of ZnO**

- Nitrogen is often regarded as most suitable hole dopant
  - Shallow acceptor in ZnSe
- Numerous reports of *p*-type ZnO crystals
  - Using N and other group-V impurities (Sb, As, P)
- Reliability? Reproducibility?

<table>
<thead>
<tr>
<th>Group I</th>
<th>$R$ (Å)</th>
<th>$\epsilon_i$ (eV)</th>
<th>Group V</th>
<th>$R$ (Å)</th>
<th>$\epsilon_i$ (eV)</th>
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<tr>
<td>Li</td>
<td>2.03</td>
<td>0.09</td>
<td>N</td>
<td>1.88</td>
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<td>Na</td>
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<td>0.17</td>
<td>P</td>
<td>2.18</td>
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<td>K</td>
<td>2.42</td>
<td>0.32</td>
<td>As</td>
<td>2.23</td>
<td>1.15</td>
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Band-gap corrections: Hybrid functionals

• Mixing of Hartree-Fock (exact exchange) and DFT
• Functionals mix in ~25% of exact exchange
• PBE0
• HSE
  – Exact exchange only for short-range interactions
• Obtain very good description of many properties
  – Band gaps close to experiment
HSE calculations for ZnO

- Hybrid functionals include a portion of exact exchange, correct band gap
  - $\alpha=0.36$
- VASP code (ver. 5.1)

<table>
<thead>
<tr>
<th></th>
<th>PBE</th>
<th>HSE</th>
<th>Exp.</th>
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</thead>
<tbody>
<tr>
<td>ZnO</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$a$ (Å)</td>
<td>3.28</td>
<td>3.23</td>
<td>3.25</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>5.28</td>
<td>5.24</td>
<td>5.21</td>
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<tr>
<td>$E_g$ (eV)</td>
<td>0.73</td>
<td>3.35</td>
<td>3.40</td>
</tr>
<tr>
<td>$\Delta H_f$(eV)</td>
<td>-2.93</td>
<td>-3.66</td>
<td>-3.64</td>
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</table>
Nitrogen acceptor in ZnO

Deep acceptor
Large ionization energy: 1.3 eV
Low formation energy under n-type conditions
Localized wavefunction

Axial bond = 2.12 Å  
Planar bonds = 1.94 Å

Test case: $N_{Se}$ in ZnSe

- Similar semiconductor
- $N_{Se}$ known shallow acceptor in ZnSe
- Effective $p$-type dopant
- Results agrees well with experimental values
  - Theory: $E_A = 150$ meV
  - Exp.: $E_A = 110$-$130$ meV

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<th></th>
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<th>HSE</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>5.73</td>
<td>5.69</td>
<td>5.67</td>
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<tr>
<td>ZnSe $E_g$ (eV)</td>
<td>1.19</td>
<td>2.80</td>
<td>2.82</td>
</tr>
<tr>
<td>$\Delta H_f$ (eV)</td>
<td>-1.43</td>
<td>-1.74</td>
<td>-1.69</td>
</tr>
</tbody>
</table>
**$N_O$ acceptor: Experiment**

Configuration coordinate diagram

**Absorption:** exciting electron from $N_O^0$ to CB
- $2.4 \text{ eV} = 520 \text{ nm}$
- Zero phonon line at $2.1 \text{ eV}$

**Emission:** electron falling from CB to $N_O$ level
- $1.7 \text{ eV} = 730 \text{ nm}$
**N\text{O}** acceptor: experiment

Localization on N atom  
Directed towards axial zinc neighbor  
Agrees with EPR signals


TiO$_2$ in GGA-PBE

Rutile

VBM - O p states
CBM - Ti d states
Hybrid functional calculations for TiO$_2$

- HSE functional
- H-F mixing parameter 0.20;
  - screening parameter $\mu = 0.2$ Å$^{-1}$
- PAW, VASP 5.1
- 72 atom-supercell
- 2 k-points: (0,0,0) (0.5,0.5,0.5); tested for (2x2x2)
- cutoff: tested for up to 400 eV

TiO$_2$ - structural properties

PBE versus HSE

<table>
<thead>
<tr>
<th>functional</th>
<th>$a$ (Å)</th>
<th>$c/a$</th>
<th>$u/a$</th>
<th>$E_g$ (eV)</th>
<th>$\Delta H_f$ (eV)</th>
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</thead>
<tbody>
<tr>
<td>PBE</td>
<td>4.65</td>
<td>0.639</td>
<td>0.305</td>
<td>1.77</td>
<td>-9.33</td>
</tr>
<tr>
<td>HSE</td>
<td>4.59</td>
<td>0.642</td>
<td>0.305</td>
<td>3.05</td>
<td>-9.73</td>
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<tr>
<td>Exp.</td>
<td>4.59</td>
<td>0.644</td>
<td></td>
<td>3.1</td>
<td>-9.74</td>
</tr>
</tbody>
</table>

Rutile
Band structure of TiO$_2$
GGA versus hybrid functional (HSE)

HSE can be tuned to reproduce the exp. band gap value
Effects of HSE on valence band versus conduction band (determined from surface calculations)

HSE lowers the VBM by 0.6 eV and raises the CBM by 0.7 eV
Single-particle states of $V_o$ in TiO$_2$

GGA results for unrelaxed vacancy

Unrelaxed vacancy induced single-particle states are in the gap.
Single-particle states of $V_0$ in TiO$_2$ relaxed versus unrelaxed vacancy

GGA cannot describe relaxed vacancy in 0 and +1 charge states occupied states above the CBM
Single-particle states of $V_0$ in TiO$_2$

GGA versus hybrid functional (HSE)

Relaxed $V_0^0$ and $V_0^+$ can be described in HSE.
Formation energies of $V_O$ in TiO$_2$

- Formation energies of $V_O$ in TiO$_2$ unrelaxed.
- All transition levels in the gap are lowered, consistent with the PBE/HSE band alignment.

Diagram showing formation energy of $V_O$ in TiO$_2$ across different Fermi levels (eV).
Formation energies of $V_O$ in TiO$_2$

unrelaxed

- all transition levels in the gap
- formation energy of +2 and + are lowered, consistent with the PBE/HSE band alignment

relaxed

- relaxation energies for +2 are similar in PBE and HSE
- transition levels (+2/0) and (+/0) are near the CBM
Oxygen vacancy in TiO$_2$ - relaxations and charge densities

+2 (PBE and HSE)

+1 (HSE)

Neutral (HSE) state localized on axial Ti neighbors
Oxygen vacancy in TiO$_2$

- shallow donor - can cause conductivity
- low formation energy in O-poor conditions
Summary and Outlook

• The field of defects in materials is active with direct applications for many technologically important systems
  – Much broader than merely “point defects in semiconductors”

• Significant progress has recently been made on crucial issues:
  – DFT band-gap errors
  – Supercell size corrections

• Still need for deeper physical understanding

• References/Overviews