QMC for point defects in semiconductors and wide band-gap oxides

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QMC@TTI, Vallico Sotto Italy. July 31 2013
Example: F-center Defect in MgO

Electronic Band Structure from DFT-GGA

Experimental Gap: 7.81 eV
DFT Gap: 4.83 eV
A good hint why DFT struggles with point defect calculations: point defects introduce localized states into systems that otherwise have bulk-like (delocalized) states. DFT is unable to treat both types on an even footing – we need a theory that can.
example: Nitrogen impurities in ZnO

Explore the quantum Monte Carlo approach to calculating point defect properties
## Zoo of Techniques

<table>
<thead>
<tr>
<th>Method</th>
<th>Computation al Scaling</th>
<th>Directly based on Schrödinger Equation?</th>
<th>Accurate Band Gap?</th>
<th>Accurate Total Energy?</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>$\sim CN_e^3$</td>
<td>No</td>
<td>No</td>
<td>Sometimes</td>
</tr>
<tr>
<td>Hybrid DFT</td>
<td>$\sim 5*CN_e^{3-4}$</td>
<td>No</td>
<td>Often</td>
<td>Often</td>
</tr>
<tr>
<td>DFT+U</td>
<td>$\sim CN_e^3$</td>
<td>No</td>
<td>When Fitted</td>
<td>Sometimes</td>
</tr>
<tr>
<td>GW</td>
<td>$\sim CN_e^4$</td>
<td>Yes</td>
<td>Often</td>
<td>No</td>
</tr>
<tr>
<td>QMC</td>
<td>$\sim 100*CN_e^3$</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
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</tbody>
</table>
vacancy in diamond:

magnesium oxide:

self-interstitials in silicon:

vacancies, interstitials in aluminium:

insulator-to-metal transition in highly-doped silicon:
Discussion Topics

Thermal and Optical Ionization Energies of Point Defects in Magnesium Oxide

Metal-Insulator Transition in Chalcogen-Hyperdoped Silicon

in Magnesium Oxide

in Zinc Oxide

[1] A. Luque
Defect Formation Energies

\[ \Delta E_f = (E_{D,q} - E_{perf}) + \sum n_i \mu_i + q(E_V + E_F) \]

- Donors have low formation energies when \( E_f \) is low.
- Acceptors have low formation energies when \( E_f \) is high.

Positive charged (donor)

Neutral

Negatively charged (acceptor)
3 Properties of Interest

- Defect Formation Energies
- Thermal Ionization Energies
- Optical Ionization Energies

\[ \Delta E_f = (E_{D,q} - E_{perf}) + \sum n_i \mu_i + q(E_V + E_F) \]

Thermal ionization energies

positively charged (donor)
neutral
negatively charged (acceptor)
Properties of Interest

- Defect Formation Energies
- Thermal Ionization Energies
- Optical Ionization Energies
### Geometries of MgO F-Centers

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<tr>
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<th>F</th>
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<th>F⁺²</th>
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<td>Mg-Mg distance (Å)</td>
<td>2.98</td>
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<td>O-O distance (Å)</td>
<td>5.96</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Relaxation Energy (eV)</td>
<td>--</td>
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**Diagram:**
- **Mg**
- **O**

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Elif Ertekin | Mechanical Science and Engineering
Geometries of MgO F-Centers

F - Center

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Exp: 5.00 eV

3.09 eV

4.83 eV
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<td>5.89</td>
<td></td>
</tr>
<tr>
<td>Relaxation Energy (eV)</td>
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<td>0.545</td>
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Exp: 4.95 eV

- 3.71 eV
- 4.83 eV
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<tbody>
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<td>Mg-Mg distance (Å)</td>
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<td>2.97</td>
<td>3.09</td>
<td>3.18</td>
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<tr>
<td>O-O distance (Å)</td>
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<td>5.97</td>
<td>5.89</td>
<td>5.82</td>
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<tr>
<td>Relaxation Energy (eV)</td>
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<td>0.003</td>
<td>0.545</td>
<td>1.182</td>
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**Experimental (Exp):** 2.3 eV

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[Diagram showing F⁻, F⁺, and F⁺² centers with distances and energy values.]
Approach for QMC: Use the DFT-optimized geometries for F, F⁺, F⁺², and then find the corresponding energies in FN-DMC.
Calculating a gap requires many calculations for cells of different sizes in QMC, coupled with an extrapolation to infinite size.

- Extrapolated value is 7.96(0.06) eV
- NB: I use a similar extrapolation scheme to obtain IP, EA

Optical Gap: 7.81 eV (experimental)
Starting many-body wave functions for QMC calculations are constructed via Slater determinants, using single-particle Kohn-Sham orbitals from DFT.

- In this case, both descriptions put the transition levels in the middle of the gap.
- Note large difference in the range for the Fermi energy.
- Charged image interaction problems.
site-resolved charge fluctuations $\langle \psi \big| \left( n_i - \langle n_i \rangle \right)^2 \big| \psi \rangle$
Optical Transitions

\[ \text{Def. Form. Energy } \Delta E_{D,q} \text{ (eV)} \]

\begin{align*}
\text{Mg atom disp. (A)} & \quad 0 & 0.1 & 0.2 & 0.3 \\
F^0 & & & & \\
F^+ & & & & \\
F^{+1} & & & & \\
F^{+2} & & & & \\
\end{align*}

* Rinke, Schleife, et al., PRL 2012
Nitrogen: candidate for p-type ZnO
Lots of experimental scatter in the literature
Conventional DFT: N is a shallow acceptor in ZnO
Hybrid functionals and GW results put the level deep in the gap
• d-orbitals from Zn atoms, p-orbitals from O atoms
• d-p hybridization – similar to what we heard before
• results in over-metallic description, and a DFT-PBE gap of 0.74 eV (vs. 3.4 in exp)
• compare to the QMC gap of 3.4(1) eV.

• **Approach:** Use the DFT-optimized geometries, and compute the corresponding energies for the N and N⁻ defects via QMC
• **For now,** we use DFT-based estimates of charged image interactions (obtained via finite size extrapolation)
• According to QMC, N is deep
  • defect level occurs at 1.62(0.14) eV above the VBM
• Unlike MgO, in this case QMC changes the nature of the defect
• QMC results compare favorably to recent experiments and to other high-accuracy approaches:
  • 1.3 eV (Hybrid, van de Walle 2009), 1.6 eV (GW, Lany and Zunger 2010)
• Some caveats: 48 atom supercells (finite size effects < 0.3 eV)
Metal-Insulator Transition in Chalcogen-Hyperdoped Silicon

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in Magnesium Oxide

in Zinc Oxide

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Laser Hyperdoping of Silicon

Start with c-Si wafer

Micro-structured with femtosecond or nanosecond laser pulses

In the presence of a source of S, Se, or Te atoms

Experimental: Tonio Buonassisi Group, MIT, Mike Aziz (Harvard)

experimentally measured properties ...

- Non-zero conductivity down to temperatures around $T = 2K$.

- Enhanced optical absorption down to photon energies $\sim 0.5$ eV.

\begin{itemize}
  \item High dose: 1 Se per 250 atoms
  \item Low dose: 1 Se per 750 atoms
\end{itemize}


\textit{Courtesy: Mark Winkler, Tonio Buonassisi}
Band Structure/Density of States

Si$_{1023}$Se$_1$

Si$_{249}$Se$_1$

Si$_{127}$Se$_1$
With increasing defect density:
- defect states begin to overlap
- electrons begin to "see" each other

High defect density:
- electron-electron interaction screens the binding fields of the ion cores
- delocalization of electronic wavefunction
- metallic character

Low defect density:
- isolated, localized defect states.
- insulating character, electrons bound to impurity sites

Detailed mechanism for the observed behavior?

well-characterized for shallow defects in Si: P, Al, B, etc.
On the transition to metallic conduction in semiconductors
Impurity State Charge Density

- $\text{Si}_{1023}\text{Se}_1$
- $\text{Si}_{686}\text{Se}_1$
- $\text{Si}_{432}\text{Se}_1$
- $\text{Si}_{250}\text{Se}_1$
- $\text{Si}_{128}\text{Se}_1$
- $\text{Si}_{54}\text{Se}_1$

0 defect state charge density
Defect Formation Energies

Clues to the role of electron correlation at different defect densities

Defect Formation Energy $\Delta E_f$ (eV)

Selenium Content (Atomic)

Insulator $\leftrightarrow$ Metal

QMC

DFT
Our preliminary efforts to apply this technique to point-defects in solids MgO, ZnO, and Si give promising results that compare favorably to experiment and/or other high-accuracy methods. They also reveal some challenges.

Future Work: (lots … !)
- QMC estimate of image-charge interactions
- Application to other materials of interest
- Physics-based studies of the DFT single vs. QMC many–particle descriptions

...THANK YOU FOR YOUR ATTENTION!

Computational resources: NERSC, XSEDE, NCSA

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