"Faster G0W0 implementation for more accurate photovoltaic material design"

Laflamme Janssen, Jonathan ; Rousseau, Bruno ; Bérubé, Nicolas ; Geadah-Antonius, Gabriel ; Côté, Michel

ABSTRACT

Density-functional theory (DFT) is currently the ab initio method most widely used to predict electronic energy levels of new molecules. However, approximations intrinsic to the theory limit the accuracy of calculated energy levels to about ±0.5 eV. More efficient theoretical design of molecules and polymers of interest to photovoltaic applications could be achieved if more precise ab initio methods were available. The G0W0 approach is an ab initio method that provides such an enhanced precision, with predicted energy levels precise to about ±0.05 eV. However, such calculations are currently prohibitive for systems with more than a few hundreds of electrons, thus limiting their use in the photovoltaic community. What limits calculations to this system size is the need in current implementations to invert the dielectric matrix and the need to carry out summations over conduction bands. This poster presents a strategy to avoid both of these bottlenecks. Preliminary results will be presented.

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Faster $G_0W_0$ implementation for more accurate photovoltaic material design

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Abstract
Density-functional theory (DFT) is currently the ab initio method most widely used to predict electronic energy levels of new molecules. However, approximations intrinsic to the theory limit the accuracy of calculated energy levels to about 20.5 eV. More efficient theoretical design of molecules and polymers of interest to photovoltaic applications could be achieved if more precise methods were available. The $G_0W_0$ approach is an ab initio method that provides such an enhanced precision, with predicted energy levels accurate to about ±0.05 eV. However, such calculations are currently prohibitive for systems with more than a few tens of electrons, thus limiting their use in the photovoltaic community. What limits calculations to this system size is the need in current implementations to invert the dielectric matrix and the need to carry out summations over conduction bands. This poster presents a strategy to avoid both of these bottlenecks.

Solution to bottleneck 1
Sternheimer equation

\[ P(\omega) = \sum \left[ \frac{1}{\omega - (E_i - E_f)} - \frac{1}{\omega + (E_i - E_f)} \right] |\varphi_i\rangle \langle \varphi_f| \]

Eliminating $\sum_f$

\[ \langle r^*_i | E_{GW0} | r_f \rangle = \sum_{\omega, \pm} \left[ \frac{|\varphi_i\rangle \langle \varphi_f|}{\omega - \epsilon_i + \pm \omega} \right] \]

\[ \langle \tilde{H} - \epsilon_i + \pm \omega | r_f \rangle = \langle r^*_i | E_{GW0} | r_f \rangle \] (Sternheimer’s equation)

Implementation of solution
1) $H$ is sparse $\Rightarrow$ iterative method
2) $H - \epsilon_i \pm \omega$ can be singular $\Rightarrow$ SQMR instead of CG

Solution to bottleneck 2
Lanczos algorithm

Ideally, $\tilde{\epsilon}(\omega)$ is expressed in a planewave basis. Here, we decrease the size of the matrix by constructing a basis that automatically focuses on the relevant subspace:

\[ \{ |\phi_i\rangle, \tilde{\epsilon}(\omega)|\phi_i\rangle, \tilde{\epsilon}^2(\omega)|\phi_i\rangle, ...., \tilde{\epsilon}^N(\omega)|\phi_i\rangle \} \]

and then orthonormalize it to obtain the Lanczos basis:

\[ \{ |\xi_i(\omega)\rangle, |\xi_i(\omega)\rangle, |\xi_i(\omega)\rangle, ...., |\xi_N(\omega)\rangle \} \]

which is substantially smaller than a planewave basis of equivalent accuracy.

Example : silane

<table>
<thead>
<tr>
<th></th>
<th>Conventional implementation</th>
<th>Present implementation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{\epsilon}(\omega)$</td>
<td>6000 x 6000</td>
<td>200 x 200</td>
</tr>
<tr>
<td>N</td>
<td>3000</td>
<td>-</td>
</tr>
<tr>
<td>CPU time</td>
<td>~48h</td>
<td>~8h</td>
</tr>
</tbody>
</table>

Conclusion
- DFT calculations are useful for sorting a large group of candidate polymers.
- Further refinement of calculations using $G_0W_0$ would be desirable, but unwieldy with current implementations due to 2 bottlenecks:
  1. The sum over conduction states
  2. The inversion of the dielectric matrix
- We assess these bottlenecks using:
  3. Sternheimer’s equation
  4. Lanczos algorithm
- and obtain a 6-fold increase in speed