"Faster G0W0 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 ±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 pr...
Faster \( G_0W_0 \) implementation for more accurate photovoltaic material design

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Abstract
Density-functional theory (DFT) is currently the \textit{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 20.3 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 \textit{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.

Introduction
Using \textit{ab initio} calculations to guide synthesis:
\[
PCE = \frac{V_{oc} J_{sc} FF}{1000W/m^2}
\]
polymer ~0.15 eV 
\[
V_{oc}
\]
PCBM

Assessing the efficiency of a polymer before synthesis requires precise calculations of the \( V_{oc} \) which requires precise calculation of the HOMO and LUMO energies of the polymer.

\textit{Ab initio} methods can do this:
- DFT: fastest, but accurate enough?
- \( G_0W_0 \): more accurate, but unwieldy.

DFT accuracy
Is it accurate enough for polymer design?

Methodology:
- B3LYP functional
- Gaussian 03/09 code
- 6-311g(d)/6-311g(d) basis set
- 29 polymers (mostly push-pull type)

Comparison between DFT and experimental energy levels

The \( G_0W_0 \) method
DFT levels offer quick sorting of candidate polymers.
Further refinement is still desirable given the resources and time required to synthesise a new polymer.
\( G_0W_0 \) can provide such results

In \( G_0W_0 \), DFT eigenstates and eigenvalues are used as a starting point:
\[
\langle t + \hat{V}_{oc} + \hat{V}_{oc} \rangle |\psi\rangle = e^{i\alpha} |\psi\rangle
\]
They are then corrected to first order in perturbation theory using the GW exchange-correlation operator \( \Sigma(\omega) \):
\[
\hat{e}_G = e^{i\alpha} + \langle \hat{\Sigma}(\epsilon_{\omega}) \rangle \hat{V}_{oc} |\psi\rangle
\]
The expectation value of \( \Sigma(\omega) \) being:
\[
\langle \hat{\Sigma}(\epsilon_{\omega}) \rangle |\psi\rangle = \frac{i}{\pi} \sum_{\omega} \int d\omega \left\{ \frac{1}{\omega - (\epsilon_{\omega} - \epsilon_{\omega})} \frac{1}{\omega + (\epsilon_{\omega} - \epsilon_{\omega})} \right\} |\psi\rangle
\]
where \( \epsilon \) is the coulomb operator and where:
\[
\hat{\epsilon}(\omega) = \hat{\epsilon} + \hat{\rho}(\omega)
\]
\[
\hat{\rho}(\omega) = \sum_{\omega'} |\phi\rangle \left\{ \frac{1}{\omega - (\epsilon_{\omega} - \epsilon_{\omega})} \frac{1}{\omega + (\epsilon_{\omega} - \epsilon_{\omega})} \right\} |\phi\rangle
\]

Problematic example: \( C_60 \)
\( N_e = 10^{14} \) is 1200 & 300 000 planes waves
\( (\phi_0, \epsilon_0) = 9 \text{ Gb RAM} \) & days of CPU time
\( \hat{\epsilon}(\omega) = 10000 x 10000 \text{ in planewave basis} \)
\( \hat{\epsilon}^{-1}(\omega) = 1.5 \text{ Gb RAM} \) & days CPU time

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
- \( G_0W_0 \) instead of CG
- SQMR instead of CG

Solution to bottleneck 1
Sternheimer equation

\begin{align*}
\rho(\omega) &= \sum_{\omega} \{|\phi\rangle \langle \phi|\omega\rangle \sum_{\omega} \langle \omega|\rho|\omega\rangle \}
\end{align*}
Eliminating \( \rho \)

Implementation of solution
1) \( H - \epsilon \), \( H - \omega \) can be singular \( \Rightarrow \) SQMR instead of CG

Solution to bottleneck 2
Lanczos algorithm

Usually, \( \hat{\epsilon}(\omega) \) 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:
\[
\{ |\phi_0\rangle, \epsilon(\omega)|\phi_0\rangle, \epsilon(\omega)|\phi_0\rangle, \ldots, \epsilon(\omega)|\phi_0\rangle \}
\]
and then orthonormalize it to obtain the Lanczos basis:
\[
\{ |t_1(\omega)\rangle, |t_2(\omega)\rangle, |t_3(\omega)\rangle, \ldots, |t_n(\omega)\rangle \}
\]
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>
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<tbody>
<tr>
<td>( \hat{\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>

\[\text{References}\]
[1] Py Umariu Gy Stenuitu Sy Baroniu Physy Revy B
[2] Py Umariu Gy Stenuitu Sy Baroniu Physy Revy B