High-throughput GW Calculations

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Abstract

In our work we implement an automated scheme for calculating well converged band gaps on GW-level for a large material dataset. The conventional approach to performing this kind of calculations requires a significant amount of computational resources and user interaction, inhibiting the efficient analysis of larger datasets.

The use of a basis set extrapolation method, proposed by Klimeš et al. [1] makes it possible to significantly reduce the time and workload necessary for retrieving a converged GW-level band gap energy, and can be implemented in a straight-forward protocol. Through this approach it is possible to derive a reliable, automated method for conveniently performing a whole series of GW calculations, while requiring only a minimum of input files and user interference. This could speed up the production rate of GW-level band gap data to a scale, where large data repositories for these calculations can be created and quickly expanded.

Using such a procedure, we have analized a large set of materials, ranging from binary to quaternary compounds, and constructed a preliminary database which, among other properties, collects GW-level band gaps. When the data set is reasonably extensive, data driven methods could be applied to find new ways of calculating accurate band gaps without the explicit use of GW methods. The vision would be to find a way of estimating the quasi-particle shift, and thus the band gap at GW level, only with knowledge of DFT data, similar as some approaches that can already be found in the literature. [3]

Introduction

GW calculations are the next step towards higher standards in materials simulations methods. While pure DFT or hybrid procedures are nowadays rather easy to use and broadly acknowledged as the go-to *ab initio* methods in materials science, their success also depends heavily on an appropriate choice of the exchange-correlation potential used, as well as artificial corrections.

Perturbative approaches like GW methods, although being computationally demanding, show in many cases much better agreement with experimental data. Especially the band gap, as a very important property for modern technology and materials design, is systematically underestimated in DFT simulations, showing the necessity of new standards.

The usage of basis-set extrapolation, as proposed by Klimeš *et al.* [1], might be a step towards less expensive and easier to calculate band gaps on G_0W_0 level. This procedure provides a way to implement an automated protocol to effectively produce a large amount of data. In the presented protocol, only a hand full of G_0W_0 calculations, so-called "single-shot" GW calculations which correct the energy levels produced by DFT only once, are needed to arrive at a converged band gap energy.

In modern computational science a large and accessible data set is a necessity for the implementation of novel computational methods, such as machine learning algorithms or data driven approaches in general. There are already many efforts to find techniques that fit the tasks at hand, although mostly using experimental or DFT level data. [3]

This is mostly due to the lack of comparably large data sets on GW level, again underlining that easier accessible GW calculations for the creation of such a resource is a crucial step towards new standards in computational material science.

Methodology

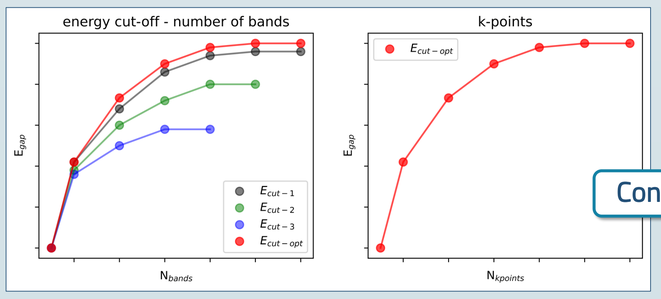
Single shot G_0W_0 calculations as implemented in VASP

VASP updates the Kohn-Sham energies $\epsilon_{n\mathbf{k}}$ only once to get the quasi-particle energies $E^{(1)}_{n\mathbf{k}}$,while leaving the orbitals unchanged. [4] This can be boiled down to the evaluation of following equation, where $\Sigma^{(0)}$ is the self-energy, V_{ext} and V_h the external and Hartree potential respectively, and $Z^{(0)}_{n\mathbf{k}}$ a renormalization factor:

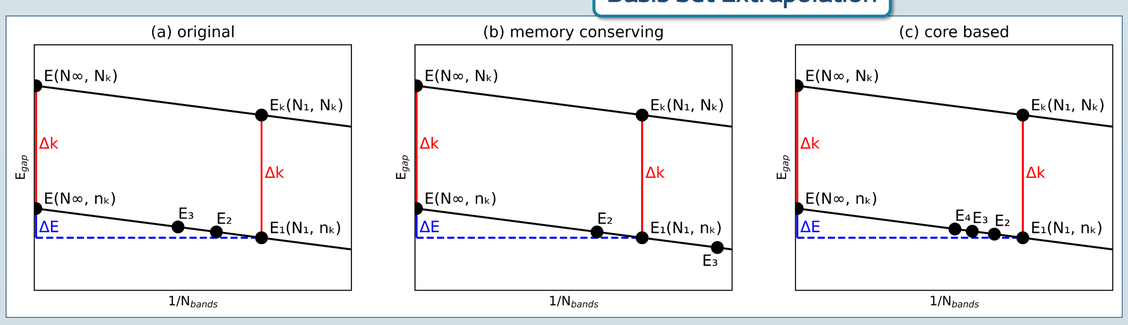
$$E^{(1)}_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} + Z^{(0)}_{n\mathbf{k}} \,\mathrm{Re}\left[\langle\phi^{(0)}_{nq}| -\frac{\Delta}{2} + V_{ext} + V_h + \Sigma^{(0)}(\omega = \epsilon_{n\mathbf{k}}) - \epsilon_{n\mathbf{k}}|\phi^{(0)}_{nq}\rangle\right]$$

Converging G_0W_0 calculations conventionally

In the conventional approach of performing G_0W_0 calculations one has to do several single shots and increase values of various parameters (energy cutoff E_{cut}, number of bands N_{bands}, number of k-points) successively, while monitoring properties like the band gap, to guarantee arriving at converged values.



Conventional Method vs. Basis Set Extrapolation



Basis Set Extrapolation

This method reduces the workload significantly, since only a fixed number of G_0W_0 calculations have to be performed:

$$E_\infty(N_k, N_\infty) \approx E_\infty(n_k, N_\infty) - E\,(n_k, N_1) + E\,(N_k, N_1)$$

1) Several G_0W_0 calculations, each including a different number of energy bands (N_1, N_2, N_3) and using a coarse k-point grid (n_k), are done for the extrapolation. This is possible, since the extrapolation shows to be very insensitive for the number of k-points used. [1]
2) An additional G_0W_0 calculation is then performed with a dense grid (N_k) and a low number of empty bands (N_1). The result is used to correct the extrapolated gap to the dense k-point solution.

Several approaches can be made when choosing the different energy cut-offs and respective basis sets (number of bands) for the extrapolation:

- (a) original: Increase energy cut-off successively and work with the full number of bands compatible. Keep the number of plane waves in the auxiliary basis set at a fixed ratio to the standard basis set.
- (b) memory conserving: Same as original, but the highest energy cut-off calculation is replaced by a low-accuracy one to reduce computational demands
- (c) core based: Choose number of bands compatible to both, the first energy cut-off and the parallelization, and increase in steps compatible to parallelization. This guarantees that both basis sets are increased at the same rate, which is a key point to arrive at the right correction. [1]

E_∞ ... gap energy at infinite band limit
Δ_N ... basis set correction to infinite number of bands ($N \rightarrow N_\infty$)
Δ_k ... k-point correction from low (n_k) to high (N_k) density grid

High-throughput GW

Input
- structure files for each material to be investigated (POSCAR)
- GW PAW-PBE pseudo potentials are used
- high-symmetry paths through 1. BZ of each crystal structure for band structure

Setup Calculation
- use general set of input parameters for all calculations
- set first energy cut-off depending on potentials
- find compatible maximum number of bands for the G_0W_0 calculations (depends on energy cut-off and parallelization)

Low Density K-point Calculations
- multiple calculations using a low density k-point grid for extrapolation at different band numbers
- include maximum number of plane waves (bands) compatible with given energy cut-off (full basis set)
- fix number of bands in auxiliary basis set to $N_{bands}/2$
- 2 DFT calculations and one G_0W_0 calculation per distinct energy cut-off

High Density K-point Calculation
- one calculation using a high density grid for k-point correction
- low energy cut-off to keep computational demands low
- use full basis set and set number of bands in auxiliary basis set to $N_{bands}/2$

DFT Band Structure
- helpful for analyzing G_0W_0 results

Band Gap Calculation
- use band gaps of low density k-point calculations for extrapolation to an infinitely large basis set (corresponds to including an infinite number of empty bands)
- this corrects the error arising due to using a finite basis set and omits the slow convergence of G_0W_0 calculations with respect to number of empty bands
- the extrapolated gap is corrected to a high density k-point grid (k-point correction)
- move to next input structure, no assessment of convergence necessary

The automatic procedure for performing the basis set extrapolation scheme consists only of static, one-shot calculations and can be implemented in a straight-forward way without the use of complicated convergence criteria.

There are two inputs specific to each material: (1) The structure file and (2) the pseudo-potentials for each atom species contained in the material. While the former provides the overall crystal structure and atom species, the latter contains information on how to choose the energy cut-offs for the respective extrapolation scheme. Other input parameters, as well as k-point grids, are kept fixed for all materials investigated.

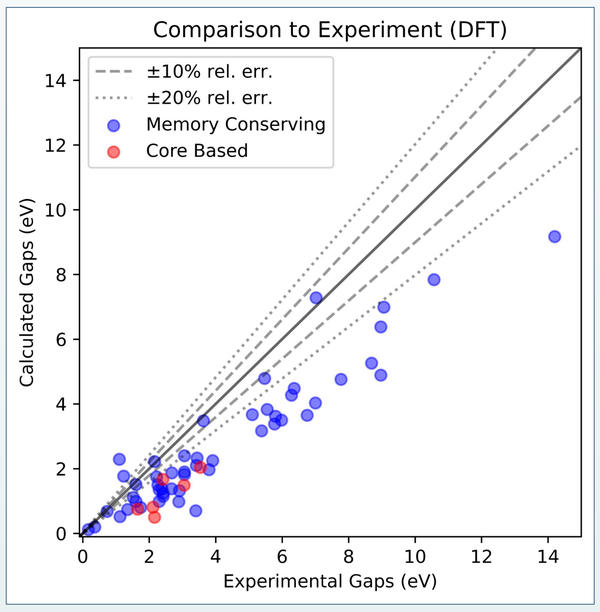
Since the G_0W_0 calculations are done with a full basis set, i.e. as many energy bands are included as are compatible with the given energy cut-offs, this value also governs the exact number of (empty) bands. While in the original and the memory conserving extrapolation approach the energy cut-off is successively increased and the band numbers are chosen accordingly, for the core based approach the band numbers are fixed and a fitting energy cut-off is used.

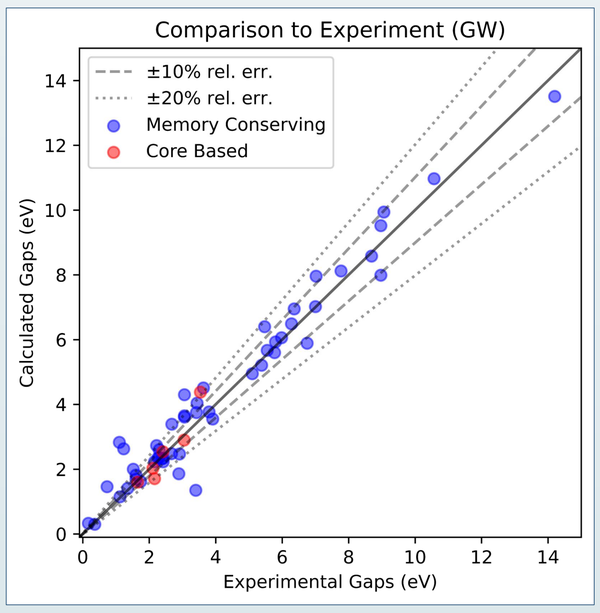
Results and Expectations

Investigating almost 60 different semi-conducting and insulating materials has proven the viability of this automated basis set extrapolation approach. It is immediately clear that the band gap is no longer systematically underestimated like in the corresponding DFT calculations and for many materials the experimental gap is already very accurately predicted.

Some deviations still have to be expected, since the procedure does not use norm conserving pseudo potentials, which can lead to problems when including very high-energy empty bands. [1] Additionally, due to the spirit of the full automatization, most input parameters are kept fixed for all calculations. This leads to less optimized settings for some materials and introduces minor errors. However our results show clearly that the scheme can be used to efficiently calculate the GW-level band gaps for many materials in succession with minimal user interference required.

A recent work investigated the viability of basis set extrapolarion on 2D materials and predicts the possibility of a procedure as implemented here [2], underlining that the basis set extrapolation proves to be a robust and accurate procedure that can be automatized in a straight forward way. This kind of simplicity might be the key for generating large sets of GW-level data for the use in modern computational materials physics and help shift the paradigm more towards more accurate post-DFT methods.





Pros
- straight forward protocol, can be implemented in high-throughput suites (AiiDA, FireWorks) rather easily
- less user interference necessary
- automatic analysis of large data sets
- no subjective assessment of convergence
- strictly derived mathematical background

Cons
- wrong occupations or band inversions from DFT are not corrected by applying only one G_0W_0 iteration
- working with a full basis set can get very memory intensive, especially for higher energy cut-offs
- systems with finite magnetic moments not as straight forward to investigate

Acknowledgements

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References:
[1] Klimeš *et al.*, Phys. Rev. B 90, 075125
[2] Rasmussen *et al.*, npj Computational Materials 7, 22 (2021)
[3] Ramprasad *et al.*, npj Computational Materials (2017) 3:54
[4] VASP-Wiki/GW calculations
[5] VASP reference:
[a] G. Kresse and J. Hafner, Phys. Rev. B 47 558 (1993)
[b] G. Kresse and J. Hafner, Phys. Rev. B 54 11169 (1996)

Data Set

[1] [2] [3] [4]

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