Band gaps in pseudopotential self-consistent $GW$ calculations

V.A. Popa, G. Brocks, and P.J. Kelly
Faculty of Science and Technology and MESA$^+$ Research Institute,
University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
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For materials which are incorrectly predicted by density functional theory to be metallic, an iterative procedure must be adopted in order to perform $GW$ calculations. In this paper we test two iterative schemes based on the quasi-particle and pseudopotential approximations for a number of inorganic semiconductors whose electronic structures are well known from experiment. Iterating just the quasi-particle energies yields a systematic, but modest overestimate of the band gaps, confirming conclusions drawn earlier for CaB$_6$ and YH$_3$. Iterating the quasi-particle wave functions as well gives rise to an imbalance between the Hartree and Fock potentials and results in bandgaps in far poorer agreement with experiment.

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Materials whose metallic or semiconducting nature has not been established experimentally pose a particular problem for first-principles electronic structure calculations. Density functional theory (DFT) calculations which describe them as being metallic are not conclusive because such calculations are known to systematically underestimate band gaps. Conventional many-body perturbation theory (MBPT), in which the dynamically screened Coulomb interaction is treated perturbatively, is problematic because the size of the perturbation depends critically on whether metallic or semiconducting screening is used. For YH$_3$ and CaB$_6$, this problem was solved by iteration to self-consistency. Though these particular theoretical predictions were confirmed by subsequent experiments, recent work casts doubt on the predictive capability of parameter-free MBPT. For this reason, it is important to benchmark the iterative procedure by applying it to a series of semiconducting materials whose band gaps are well documented experimentally.

Of various many-body techniques developed in recent years to provide corrections to DFT descriptions of the electronic structures of real materials, the so-called $GW$ approximation, in which the self-energy $\Sigma$ is approximated by the product of the one-particle Green function $G$ and the dynamically screened electron-electron interaction $W$, has been particularly successful. Because $GW$ calculations are computationally very demanding, it is common to make a number of additional approximations. The Green function is usually approximated by a quasi-particle (QP) expression, where the QP energies are interpreted as a band structure. A further approximation involves using an independent particle expression for $G$ in the computational steps required to evaluate $W$ and $\Sigma$. Generally the energy levels and orbitals obtained in a DFT calculation are used in this expression, most often at the local density approximation (LDA) level. If additionally the QP wave functions are approximated by the LDA orbitals, then the QP energies simply become first-order perturbation corrections to the LDA energy levels. A $GW$ calculation that involves all these approximations is referred to as “single shot”. The single shot $GW$ approach yields good QP band structures and reasonable band gaps for a wide range of semiconductors and insulators provided the reference independent particle spectrum, i.e., the LDA spectrum, has a band gap. For materials which are incorrectly predicted by density functional theory to be metallic, an iterative $GW$ procedure is no longer appropriate. Iteration was suggested as a solution to this problem but in practice the computational expense was prohibitive and instead use was made of the experimentally known dielectric screening to study such materials thereby introducing an element of empiricism. For materials whose experimental character is unclear but which are described by the LDA as being metallic, there is no other option than to iterate the $GW$ solution. Though this iterative $GW$ technique has been applied successfully to YH$_3$ with 24 atoms in its primitive unit cell and to CaB$_6$, its general validity has yet to be demonstrated. We will apply it to a set of materials with band gaps that range from 0.4 to 5.5 eV: InAs, Ge, Si, GaAs, AlP, GaN and C. Note, in particular, that the small band gap semiconductor InAs has a metallic LDA spectrum and that Ge has a vanishingly small LDA band gap.

Computational details. Our main interest lies in developing a practical scheme to handle complex materials, such as YH$_3$, with large unit cells, and we have not attempted to go beyond the QP approximation. For the same reason we use pseudopotentials (PP) to represent the ion cores, since for complex materials all-electron $GW$ calculations are computationally even more demanding. We use the real-space imaginary-time $GW$ technique as implemented by van Gelderen et al. Our starting point is an LDA calculation with a standard exchange-correlation functional, normconserving pseudopotentials and an expansion of the orbitals in a plane wave basis set. The LDA eigenvalues and orbitals are used to set up an initial Green function $G$. The dynamically screened electron-electron interaction $W$ is then calculated using the random phase approximation (RPA) and from $G$ and $W$ the self-energy $\Sigma$.
is constructed. Within the QP approximation the fundamental equation is

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r})\right] \psi_{nk}(\mathbf{r}) + \int d\mathbf{r}' \Sigma^e(\mathbf{r}, \mathbf{r}'; \varepsilon_{nk}) \psi_{nk}(\mathbf{r}') = \varepsilon_{nk} \psi_{nk}(\mathbf{r}),$$  

(1)

where $v_{\text{ext}}$ stands for the sum of all ionic pseudopotentials, $V_H$ is the Hartree potential and $\Sigma^e$ is the exchange or Fock potential. $\Sigma^e$ is the correlation part of the self-energy, which includes the dynamic screening and is energy dependent. $\varepsilon_{nk}$ and $\psi_{nk}(\mathbf{r})$ are, respectively, the QP energy and wave function. The $\varepsilon_{nk}$ are complex; the real parts comprise the band structure and the imaginary parts give the inverse QP lifetimes.

In practice (1) is solved by expanding the QP wave functions in the orthonormal basis formed by the LDA orbitals $\psi_{nk}(\mathbf{r}) = \sum_{n'} c_{n',nk} \psi_{n'k}(\mathbf{r})$. Representing the potentials and self-energy on the same basis, (1) is transformed into a matrix eigenvalue equation,

$$[\mathbf{h}_k + \Sigma^c_k(\varepsilon_{nk})] c_{nk} = \varepsilon_{nk} c_{nk},$$  

(2)

where $\langle \psi_{n'k}^{\text{LDA}} | \mathbf{h}_k | \psi_{nk}^{\text{LDA}} \rangle - \frac{1}{2} \nabla^2 + v_{\text{ext}} + V_H + \Sigma^e | \psi_{nk}^{\text{LDA}} \rangle$ and $\langle \psi_{n'k}^{\text{LDA}} | \Sigma^c | \psi_{nk}^{\text{LDA}} \rangle$. This equation is nonlinear in $\varepsilon_{nk}$ because of the energy dependence of $\Sigma^c$. It is solved by standard diagonalization and root-searching techniques. If the QP and LDA wave functions do not differ significantly, so that $\psi_{nk}(\mathbf{r}) \cong \psi_{n'k}^{\text{LDA}}(\mathbf{r})$ or $c_{n',nk} = \delta_{n',n}$, then (2) breaks up into a set of decoupled equations that involve the diagonal matrix elements only:

$$\langle \mathbf{h}_k \rangle_{nn} + \langle \Sigma^c_k(\varepsilon_{nk}) \rangle_{nn} = \varepsilon_{nk}.$$  

(3)

In our iterative procedures the QP energies and, optionally, the QP wave functions are used to construct a new Green function $G$. We approximate $G$ by an independent particle Green function, using only the real part of the QP energies and setting the QP weights to unity in order to obey the sum rule for the spectral density. The QP wave functions are then explicitly orthogonalized. After constructing a new $W$ and $\Sigma$, the QP equation is solved again. This procedure is iterated until there are negligible changes in the QP energies. Since the first iteration starts from the LDA spectrum, it can sometimes be convenient to open a band gap artificially in this spectrum. We checked that the converged band gap in the QP spectrum does not depend on the size of the initial band gap.

For the materials treated in this paper, all iteration schemes to be discussed below converge to 1 meV or better within 9 iterations. Spin-orbit coupling is not taken into account explicitly in the solids, but the end results are corrected a posteriori when necessary. Typical values for the parameters used in our $GW$ calculations are a real space mesh of $(6 \times 6 \times 6)$ points in the unit cell, $(8 \times 8 \times 8)$ unit cells in the interaction cell and 200 (occupied plus unoccupied) bands. The results are extrapolated to absolute convergence in the individual parameters, and the absolute values of these corrections are summed to define a computational error bar.

**Iteration on QP energies.** The simplest iteration scheme involves QP energies only. The QP wave functions are assumed to be identical to the LDA orbitals and (3) is solved to obtain $\varepsilon_{nk}$. These are used to update $G$, $W$, and $\Sigma$ before (1) is solved again and the procedure repeated until the $\varepsilon_{nk}$ are converged. Note that between iterations only the correlation part of the self-energy needs to be updated.

In the case of InAs care must be taken, since in the LDA band structure the valence and conduction bands overlap. In particular, the “light hole” valence band mixes with the lowest conduction band leading to an avoided crossing around $\Gamma$. In our $GW$ calculations we allow these two bands to “de-mix” by calculating the off-diagonal matrix element of the self-energy in (2) and solving a $2 \times 2$ version of (2) instead of (1).

The band gaps calculated in this way (“eigenvalues only”) are compared with experiment in Fig. 1 and the numerical values are given in the third column of Table I. They are seen to overestimate the experimental values by 5 to 25%. Assuming such overestimates also hold for YH$_3$ and CaB$_6$, whose band gaps were calculated using the same approximations we arrive at an uncertainty in the predicted band gaps of $\lesssim 0.2$ eV, which does not change the prediction that these compounds are semiconductors. The advantage of the iteration procedure is that the final, self-consistent gap does not depend upon

![Fig. 1: Comparison of calculated and experimental band gaps for 7 representative inorganic semiconductors using two different iterative GW schemes discussed in the text.](image-url)
whether the initial LDA band structure corresponds to a metal or a semiconductor.

Table I: Band gaps of 7 representative inorganic semiconductors. The experimental values are taken from Ref. \[22\], except when stated otherwise. The theoretical band gaps were calculated using the two different iterative GW schemes described in the text and have had a spin-orbit splitting correction added to facilitate comparison with experiment. The theoretical “error-bars” are our best estimate of the uncertainties which result from using a finite cutoff, k-point sampling etc. All values are in eV.

| Material   | Exp.  | QP energies | QP energies + functions |
|------------|-------|-------------|-------------------------|
| InAs       | 0.41  | 0.41 ± 0.03 | 1.06 ± 0.10             |
| Ge         | 0.74  | 0.80 ± 0.03 | 1.72 ± 0.11             |
| Si         | 1.17  | 1.44 ± 0.04 | 2.23 ± 0.09             |
| GaAs       | 1.52  | 1.62 ± 0.05 | 2.66 ± 0.15             |
| AlP        | 2.50  | 2.95 ± 0.03 | 3.43 ± 0.12             |
| GaN        | 3.30a | 4.10 ± 0.05 | 4.77 ± 0.31             |
| C          | 5.49  | 6.22 ± 0.04 | 6.94 ± 0.17             |

\[a\]Reference \[22\].

It turns out that the Hartree and the Fock potentials,

\[
V_H(r) = e^2 \sum_{\text{occ}} \int d\mathbf{r}' |\langle \psi_{n\mathbf{k}}(\mathbf{r}') | \psi_{n\mathbf{k}}(\mathbf{r}) \rangle|^2 / |\mathbf{r} - \mathbf{r}'| \tag{4}
\]

respectively,

\[
\Sigma^x(r, r') = -e^2 \sum_{\text{occ}} \langle \psi_{n\mathbf{k}}(\mathbf{r}) | \psi_{n\mathbf{k}}(\mathbf{r}') \rangle / |\mathbf{r} - \mathbf{r}'| \tag{5}
\]

are especially sensitive to the wave functions. Both potentials are large, so small changes in the wave functions can have a large absolute effect. This is confirmed by fixing \(V_H\) at the LDA level while iterating \(\Sigma^x\) and \(\Sigma^c\) using the QP energies and (orthogonalized) wave functions. This leads to a band gap of 4.35 eV for silicon! The Fock potential \(\Sigma^x\) is attractive and during iteration its effect on the occupied states increases, whereas the effect on the unoccupied states decreases, which enlarges the band gap. This effect is partially cancelled by iterating the repulsive Hartree potential \(V_H\), which behaves similarly to \(\Sigma^x\) upon iteration, but with an opposite effect on the band gap due to its sign. The cancellation however is incomplete resulting in band gaps that are considerably too large as seen in Table II and Fig. II.

It is very tempting to speculate that this cancellation would be more efficient in an all-electron (AE) calculation. A number of single-shot AE calculations yield values for the band gap of silicon which are too small compared to experiment.\[4,5,6\] see the third column of Table II. In an even more recent paper reporting on the iteration of an all-electron GW scheme to self-consistency, a value for the bandgap of Si of 1.14 eV was found.\[28\]
TABLE II: Comparison of the results of a number of pseudopotential (PP) and all-electron (AE) GW calculations for the fundamental band gap of Si, based upon the Dyson equation (DE), or the quasi-particle approximation (QP). All values are in eV.

| Reference Method       | $\Sigma_{GW}(GLDA)$ | $\Sigma_{GW}(GW)$ |
|------------------------|----------------------|-------------------|
| [18] PP/DE 26 lowest states | 1.34                 | 1.91              |
| [4] AE/DE, $\Sigma$ diagonal | 0.85                 | 1.03              |
| [5] AE/QP              | 0.90                 |                   |
| [29] AE/QP             | 0.84                 | 1.14              |
| [6] AE/QP              | 0.92                 |                   |
| Present PP/QP          | 1.17                 | 2.23              |
| Present PP/QP; 26 lowest states | 1.04                 | 1.94              |
| [26] Experiment        |                      | 1.17              |

Because AE GW calculations are much more expensive than PP calculations, it is important to understand the source of the discrepancy between the two in order to develop computationally less demanding approximate schemes. If we accept that an all-electron, iterative GW scheme yields results in agreement with experiment then we must conclude that the good agreement with experiment found by single-shot plane-wave pseudopotential (PP) calculations is accidental and comes about from a cancellation of two errors. Since the single-shot AE calculations\textsuperscript{15,16,25} for Si find band gaps ranging from 0.84 to 0.92 eV, the PP scheme would appear to introduce an error of 0.25-0.33 eV\textsuperscript{30}. Because the first-principles pseudopotentials are constructed so as to yield the same Kohn-Sham eigenvalues spectrum as the AE calculation, the error must be introduced by the pseudowavefunctions in the polarization function where it enters via the dipole matrix elements; this could be confirmed by explicit comparison of AE and PP calculations. The error in the single-shot AE schemes are apparently almost exactly compensated on iteration.\textsuperscript{26} In the PP schemes, the combination of iteration and pseudo-wavefunctions leads to an amplification of the error.\textsuperscript{14}

Conclusions. We have tested two iterative, self-consistent GW schemes within the quasi-particle approximation, treating only the valence electrons and using pseudopotentials, on a range of semiconductors and insulators. Iterating the QP energies to self-consistency leads to an overestimation of the band gaps by 5 to 25\%, which is sufficiently accurate for this scheme to have predictive power and leaves unchanged the conclusions drawn in Refs. \textsuperscript{16}. If the QP wave functions are allowed to change in the iterations, the results get worse and the band gaps are overestimated by up to 1.3 eV. More work needs to be done to understand in detail the origin of this error.

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\textsuperscript{28} To reduce the computational effort somewhat we observe that the contribution of the off-diagonal matrix elements decreases with their separation in energy from the matrix diagonal. We therefore approximate the full \textbf{h}_\mathbf{k} and \textbf{\Sigma}_\mathbf{k} matrices by band diagonal form. In our case the dimension of the matrices is 200. Using only 40 off-diagonal elements on each side of the diagonal gives converged QP energies that are within 4 meV of the values obtained if full matrices are used.
This would appear to be confirmed by PP calculations in which the highest atomic (semi)core states were included as valence states in a GW calculation. At least in single shot calculations, inclusion of these semicore states leads to a decrease in the calculated band gaps. However because they have not iterated their calculation, Tiago et al. draw different conclusions from this result.

We can reconcile the value of 1.91 found by Schöne and Eguiluz with our own value of 2.23 eV by iterating a PP GW calculation including only 26 states; we then find agreement with these authors within the error bar of the calculation. We have no explanation for their finding a single-shot Si band gap of 1.34 eV. Our own value of 1.17 (1.04 with 26 states) eV is compatible with other single-shot PP-GW studies.