A finite electric-field approach to evaluate the vertex correction for the screened Coulomb interaction in the quasiparticle self-consistent GW method

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We apply the quasiparticle self-consistent GW method (QSGW) to slab models of ionic materials, LiF, KF, NaCl, MgO, and CaO, under electric field. Calculated optical dielectric constants $\varepsilon_\infty$ show very good agreements with experiments. For example, we have $\varepsilon_\infty$(Slab)=2.91 for MgO, in agreement with the experimental value $\varepsilon_\infty$(Experiment)=2.96, whereas we have $\varepsilon_\infty$(RPA)=2.37 in the random-phase approximation for the bulk MgO. The large discrepancy 2.91 – 2.37 is due to the vertex correction. Our result gives a rationale for methods such as QSGW80 [Deguchi et al., doi:10.7567/JJAP.55.051201].

Introduction – The quasiparticle self-consistent GW (QSGW) is one of the most reliable method to give an independent-particle picture for treating electric excitations of materials [1, 2]. Other methods such as HSE06 [3] and Tran-Blaha-09 functional [4] may work well in many systems, although they contain free parameters to be determined empirically. In contrast, QSGW is parameter free and give reasonable results for a wide range of materials, not only metals and semiconductors, but also transition-metal oxides, and 4f systems [5, 6].

However, QSGW gives a systematic overestimation for band gaps. In fact, Faleev, van Schilfgaarge, and Kotani [1] gave a suggestion that the overestimation is removed if we take into account an enhancement factor of the screening effect due to the electron-hole correlation in the evaluation of the screened Coulomb interaction $W$. The enhancement factor is represented by the vertex correction in the proper polarization function determining $W$. Note that this vertex correction is different from the vertex correction of the self-energy, $\Gamma$ in the expression $\Sigma = igWT$ [8].

Along the suggestion mentioned above, an improvement of QSGW was presented by Shishkin, Marsman and Kresse, where they made an approximation which employs the vertex correction into account [9]. It seems that their approximation includes the vertex of the first-order of $W$: see Eq.(15) around in Ref.10. The method is theoretically quite satisfactory in the sense that both band gaps and optical dielectric constant $\varepsilon_\infty$ are determined self-consistently in agreement with experiments. For example, the calculated $\varepsilon_\infty$ for MgO with including the vertex correction is 2.96, in good agreement with the experiment 2.95. This is followed by the evaluation of the ionization potential in Ref.11. The enhancement of screening can be also due to the lattice polarization [12, 13]. Both the lattice polarization and the electron-hole correlation can contribute to the enhancement of screening. Thus, it is preferable to evaluate the proper polarization in QSGW without lattice polarization without their approximation.

In this paper, we evaluate the size of the vertex correction, not in bulk calculations with such approximations, but by calculating $\varepsilon_\infty$ for slab models with finite electric bias voltage. We obtain $\varepsilon_\infty$ from the ratio of slopes of the electrostatic fields at slab region and at vacuum region. Since we explicitly treat the response to the bias, our method includes higher-order effects in a self-consistent manner. We treat five ionic materials, LiF, KF, NaCl, MgO and CaO.

To clarify the meaning of our method, let us consider such slab calculations in the case of GGA at first. Then we can automatically take into account changes of the exchange-correlation (xc) potential due to the finite perturbation of the bias voltage. In other words, calculated $\varepsilon_\infty$ should contain the effect of the vertex correction, the kernel $f_{xc}$ which is the derivative of the xc potential with respect to the density. Corresponding to this case in GGA, calculated $\varepsilon_\infty$ in QSGW should contain the effect of the vertex correction as a derivative of the self-energy. In the sense that we evaluate $\varepsilon_\infty$ without resorting to RPA, our method is on the same spirit of solving the Bethe-Salpeter equation in Ref.14.

Our findings are that the calculated $\varepsilon_\infty$ in QSGW for the slab models are very close to experimental values. This is in contrast to the fact that $\varepsilon_\infty$ in RPA of QSGW are generally $\sim$ 20 percent smaller than experimental values [2, 15]. This indicates that the vertex correction at the level of derivative of the QSGW self-energy should make $W$ be in agreements with experiments. Our results is consistent with Table II in Ref.9, Thus our results justify their approximation used in in Ref.9.

Instead of the method used in Ref.8, we can use QSGW80 (hybridization of 80% QSGW + 20% GGA) to describe experimental band gaps [16] as a quick remedy including the enhancement factor. The performance of QSGW80 is systematically examined in Ref.17, where we see both the calculated band gaps and effective masses are in good agreements with experiments. In contrast...
to the other GW methods which requires the Wannier-interpolation technique to make band plots in the whole Brillouin zone, we can make band plots easily without resorting to the technique \cite{2}. The QSGW80 is successfully used for practical applications, for example, to the type-II superlattice of InAs/GaSb \cite{17,18}. Our present results support the method of QSGW80, which takes only the 80 percent of QSGW self-energy. We can identify QSGW80 as a simplification of the method in Ref.\cite{9}. Ref.\cite{19} also presents another approximation at the level of QSGW80 for the vertex correction in QSGW, resulting in similar good agreement with experiments.

To obtain \( \epsilon_\infty \), we perform calculations for a slab model in the supercell, where the electric field is applied by the effective screening medium (ESM) method given by Otani and Sugino \cite{20}. We have developed a method QSGW+ESM, that is, combining QSGW with the ESM method.

Our QSGW+ESM is implemented in a first-principles package eca\text{l}j \cite{7,21}, which is based on a mixed-basis method, the augmented plane wave (APW) and Muffin-tin (MT) orbital method (the PMT method) \cite{22,23}. The PMT method is an all-electron full potential method which uses not only the APW basis in the LAPW method, but also the MT orbitals in the LMTO method simultaneously in the expansion of eigenfunctions. It also use the local orbital basis \cite{20}. On top of the PMT method, we had implemented the QSGW method \cite{7,24}. In PMT, we use very localized untuned MTOs which contains damping factor \( \exp(-\kappa r) \), where \( \kappa \) are fixed to be 1/bohr and/or 2/bohr, together with low-cutoff APWs (\( \leq 3 \) Ry). We do not need empty spheres since the APWs can handle vacuum regions of slab models. The charge density is represented in the three component representation, “smooth part”, “true part within MT”, and “counter part within MT” as in the case of PAW method \cite{27}. In the following, we show how to implement ESM in the PMT method, after an explanation of general theory of ESM.

**General theory of the Effective screening medium method** – We apply the ESM method \cite{20} to slab models under an external electric field. We treat a supercell with periodic boundary condition where we have a slab with periodicity in the \( xy \) plane. The slab is at the middle of supercell. Position in the cell is specified by \( r = (r_{//}, z) \). Planes at \( z = -z_0 \) and at \( z = z_0 \) are the left and right ends of the supercells. The electrostatic potential is calculated from the charge density in the supercell assuming two electrodes at \( z = \pm z_0 \) (we set \( z_1 = z_0 \) in Fig.1 of Ref.\cite{20} for applying voltage to the supercell.

Let us start from the energy functional of DFT in the ESM. It is written as

\[
E[n] = E^{\text{kin}}[n] + E^{xc}[n] + E^{\text{es}}[n] + E^{\text{app}}[n].
\]

Here, we have kinetic energy \( E^{\text{kin}}[n] \), xc energy \( E^{xc}[n] \), and the electrostatic energy \( E^{\text{es}}[n] \) terms. In addition, the last term is the applied electrostatic term \( E^{\text{app}}[n] = \int d^3r V^{\text{app}}(r)(n(r) + n_N(r)) \), where \( n(r) \) and \( n_N(r) \) are the electron density and the the charge density of nuclei, respectively; \( V^{\text{app}}(r) \) is a linear function of \( z \), representing the external field.

In ESM, we enforce the periodicity in the supercell for the electrostatic potential. Thus we use \( V^{\text{app}}(r) s(r) \) instead of \( V^{\text{app}}(r) \), where we introduce a support function \( s(r) \) which is unity for most of all regions, but is going to be zero at \( z = -z_0 \) and \( z = z_0 \). It is different from unity only near the boundaries, \( z \approx -z_0 \) or \( z \approx z_0 \). Thus the potential \( V^{\text{app}}(r) s(r) \) recover the periodicity of the supercell. A constant can be added to \( V^{\text{app}}(r) \) so that it keep smooth periodicity over \( z = \pm z_0 \). As long as we use large enough vacuum region, we have little electrons near the boundaries. Thus the choice of \( s(r) \) is irrelevant.

A key in ESM is that we use the Green function \( \bar{v}(r,r') \) for the electrostatic energy \( E^{\text{es}}[n] \) instead of the Coulomb interaction \( v(r-r') \) in usual the GGA calculations. As in Ref.\cite{20}, \( \bar{v}(r,r') \) contains not only the Coulomb interaction \( v(r-r') \) but also the effects due to the polarization of virtual electrodes, which are at \( z = \pm z_1 \) (we use \( z_0 = z_1 \) in our calculations here). Polarization occurs so as to keep the electrostatic potential is constants at electrodes. Corresponding to \( V^{\text{app}}(r) s(r) \), we use \( s(r) \bar{v}(r,r') s(r') \) instead of \( \bar{v}(r,r') \) in practice. Then we have well-defined Kohn-Sham total energy with keeping the periodic boundary condition for given \( V^{\text{app}}(r) \).

The minimization of \( E[n] \) with respect to \( n(r) \) gives the Kohn-Sham potential \( V(r) \) as

\[
V(r) = \int d^3r' \bar{v}(r,r')(n(r') + n_N(r')) + V^{\text{app}}(r) + V^{xc}(r).
\]

Hereafter, we skip \( s(r) \) for simplicity.

Even in the case of QSGW \cite{24} where we cannot derive its fundamental equation from the energy minimization, we can use the one-particle potential of Eq.\cite{2} in the self-consistent cycle, where \( V^{xc}(r) \) is replaced by a static version of the self-energy \cite{1}. Thus, in principle, it is straightforward to perform QSGW+ESM.

**ESM in the PMT method** – In the PMT method, electron density (and also the charge density) is represented by the three component formalism described in Ref.\cite{25}, originally introduced by Soler and Williams in Ref.\cite{26,27,28}. At first, space is divided into MT regions and interstitial regions. Then electron density is represented by three components as \( n = \{n_0(r), \{n_{1,a}(r)\}, \{n_{2,a}(r)\}\} \); following Ref.\cite{29}, this is simply expressed as \( n = n_0 \oplus n_1 \oplus n_2 \). The 0th component \( n_0(r) \) is the spatially smooth functions, expanded in analytic functions, that is, planewaves, Gaussians, and smooth Hankel functions \cite{24}. The 1st components \( n_{1,a}(r) \) is the true electron density within MT at \( \mathbf{R}_a \). The 2nd components \( n_{2,a}(r) \) is the counter part, that is, the projection of \( n_0(r) \) into the MT
at \( \mathbf{R}_a \). \( n_0(\mathbf{r}) \) and \( n_{2,a}(\mathbf{r}) \) are identical within MT at \( \mathbf{R}_a \) up to given angular momentum cutoff in their spherical harmonics expansion.

We can get all charge density \( n^{Z\text{ev}} = n_0^{Z\text{ev}} \oplus n_1^{Z\text{ev}} \oplus n_2^{Z\text{ev}} \) by adding the ion-core contribution to \( n \). Then we apply the multipole transformation clearly defined in Ref. [22], resulting \( n_0^{Z\text{ev}} \oplus n_1^{Z\text{ev}} \oplus n_2^{Z\text{ev}} \) as shown in Eq. (28-30) in Ref. [25]. The transformation makes \( \tilde{n}_0^{Z\text{ev}}(\mathbf{r}), \tilde{n}_1^{Z\text{ev}}(\mathbf{r}), \) and \( \tilde{n}_2^{Z\text{ev}}(\mathbf{r}) \) have the same multipole in each MT site at \( \mathbf{R}_a \), although physically observable density unchanged. The 1st components \( \tilde{n}_1^{Z\text{ev}}(\mathbf{r}) \), unchanged by the transformation, are the sum of ion-core charge density and \( n_{1,a}(\mathbf{r}) \).

From the smooth density \( \tilde{n}_0^{Z\text{ev}}(\mathbf{r}) \), we can calculate electrostatic potential as \( V_0^{\text{es}}(\mathbf{r}) = \int d^3r/\tilde{v}(\mathbf{r}, \mathbf{r}')\tilde{n}_0^{Z\text{ev}}(\mathbf{r}') + V^{\text{supp}}(\mathbf{r}) \). This gives correct interstitial part of the potential \( V_0^{\text{es}}(\mathbf{r}) \) calculated from all charge density. The values of \( V_0^{\text{es}}(\mathbf{r}) \) at MT boundaries are used to determine the electrostatic potential within MTs.

We can use usual procedure to determine the electrostatic potential within MTs. In each MT, we have 1st and 2nd components \( \tilde{n}_1^{Z\text{ev}}(\mathbf{r}) \) and \( \tilde{n}_2^{Z\text{ev}}(\mathbf{r}) \), which have the same multipole. With the condition that the electrostatic potential is zero at the MT boundary, we can calculate the potential generated by the difference of the 1st and 2nd components.

Thus we finally have the electro-static potential \( V_\infty^{\text{es}}(\mathbf{r}) \) represented in the three component formalism. With this potential, we can perform self-consistent calculations for slab models.

Results – In Fig. 1 we illustrate our treatments in the slab models for NaCl-structure ionic materials, LiF, KF, NaCl, MgO, and CaO, where we use \( z_0 = \pm 30 \) a.u.. We use the slabs of nine layers, 18 atoms in the supercell. We use experimental lattice constants of bulk materials, without relaxation of atomic positions. The electrostatic potential \( V_\infty^{\text{es}}(z, E) \) are the average of \( V_0^{\text{es}}(\mathbf{r}) \) in the \( xy \) plane under the bias voltage \( E \). We plot the cases of \( E = 0.2 \) Ry and of \( E = 0.0 \) Ry. \( V_\infty^{\text{es}}(z, E) \) changes linearly as a function of \( z \) in the vacuum regions and in the slab regions. We show \( \Delta V_\infty^{\text{es}}(z) = V_\infty^{\text{es}}(z, 0.2 \text{Ry}) - V_\infty^{\text{es}}(z, 0.0 \text{Ry}) \) in the bottom panel in Fig. 1. From the ratio of two slopes of \( \Delta V_\infty^{\text{es}} \) in the slab region and in the vacuum region, we obtain \( \epsilon_\infty(\text{Slab}) \).

Our main results are \( \epsilon_\infty \) calculated from slab models in QSGW, \( \epsilon_\infty(\text{QSGW, Slab}), \) in Table I. Note that \( \epsilon_\infty(\text{Slab}) \) contains the effect of vertex corrections, because changes of the self-energy caused by the bias \( E \) are self-consistently taken into account. Numerical reliability of our calculations are estimated to be \( \lesssim 1 \) percent. See supplemental materials for computational details [34]. In Table I we also show bulk values \( \epsilon_\infty(\text{RPA}) \).

To obtain them, we first perform self-consistent calculations in QSGW for bulk materials. Then we calculate \( \epsilon_\infty \) in the random-phase approximation (RPA) with/without local field correction (LFC). We also show \( \epsilon_\infty \) in GGA together.

The QSGW values are in good agreements with experiments. For example, \( \epsilon_\infty(\text{QSGW, Slab}) = 1.94 \) for LiF gives surprisingly good agreement with \( \epsilon_\infty(\text{Experiment}) = 1.96 \). In contrast, \( \epsilon_\infty(\text{QSGW, RPA}) = 1.67 \) is very smaller than \( \epsilon_\infty(\text{QSGW, Slab}) = 1.94 \). These are generally true in all other materials. We see that ratios \( \eta = \epsilon_\infty(\text{QSGW, RPA})/\epsilon_\infty(\text{QSGW, Slab}) \) in Table I are \( \sim 0.8 \). This is consistent with Ref. [2] where \( \epsilon_\infty \) for ZnO, Cu_{2}O, MnO, and NiO are presented. From a point of view to estimate the enhancement factors (\( \approx \text{vertex} \) ) of the proper polarization, we may consider ratios \( \gamma = \epsilon_\infty(\text{Slab})^{-1}/\epsilon_\infty(\text{RPA})^{-1} \). As shown in Table I \( \gamma \sim 1.4 \). Since \( \epsilon_\infty(\text{QSGW, Slab}) \) gives very good agreements with \( \epsilon_\infty(\text{experiment}) \), we can say that the vertex correction for bulk should give the difference between \( \epsilon_\infty(\text{RPA}) \) and \( \epsilon_\infty(\text{experiment}) \) very well, where the vertex correction is...
TABLE I. Calculated optical dielectric constant $\varepsilon_\infty$. “RPA” are in bulk calculations with local field correction (LFC). “RPA(noLFC)“ are without LFC. “Slab” are calculated from the slab models in the setting of Fig.1. Ratios $\eta = \frac{\varepsilon_\infty(\text{Slab})}{\varepsilon_\infty(\text{RPA})}$ and $\gamma = \frac{\varepsilon_\infty(\text{Slab})-1}{\varepsilon_\infty(\text{RPA})-1}$ are calculated just simply from the values of $\varepsilon(\text{QSGW, RRA})$ and $\varepsilon(\text{QSGW, Slab})$.

| Material | RPA (noLFC) | RPA Slab | $\eta$ | $\gamma$ | Experiments |
|----------|-------------|----------|-------|--------|-------------|
| LiF | GGA | 2.04 | 1.95 | 2.01 | 0.86 | 1.40 | 1.96 |
| | QSGW | 1.73 | 1.67 | 1.94 | 0.80 | 1.26 | 1.85 |
| KF | GGA | 2.16 | 1.96 | 1.94 | 0.80 | 1.26 | 1.85 |
| | QSGW | 1.79 | 1.68 | 1.86 | 0.90 | 1.26 | 1.85 |
| NaCl | GGA | 2.70 | 2.33 | 2.42 | 0.80 | 1.30 | 2.34 |
| | QSGW | 2.13 | 1.92 | 2.31 | 0.83 | 1.32 | 2.34 |
| MgO | GGA | 3.17 | 2.96 | 3.09 | 0.80 | 1.37 | 2.96 |
| | QSGW | 2.50 | 2.37 | 2.91 | 0.81 | 1.39 | 2.96 |
| CaO | GGA | 3.94 | 3.39 | 3.08 | 0.80 | 1.38 | 3.33 |
| | QSGW | 2.88 | 2.68 | 3.31 | 0.81 | 1.38 | 3.33 |

calculated at the level of the functional derivative of the self-energy in QSGW.

This is in contrast to the case of GGA. For example, look into the case of LiF. The difference $\varepsilon_\infty(\text{GGA, Slab}) - \varepsilon_\infty(\text{GGA, RPA}) = 2.01 - 1.95 = 0.06$ is very small. The difference is originated from the xc kernel $f_{xc}$ in the density functional perturbation theory. This is consistent with results in Ref.[33] where they explicitly evaluate $f_{xc}$ in GGA for bulk materials. Note that $\varepsilon_\infty(\text{GGA, Slab}) = 2.01$ is a little larger than $\varepsilon_\infty(\text{experiment}) = 1.96$; this is true for all other materials. We see that the contributions of vertex corrections $f_{xc}$ do not necessarily improve agreements: $\varepsilon_\infty(\text{GGA, Slab})$ give poorer agreement with $\varepsilon_\infty(\text{experiment})$ than $\varepsilon_\infty(\text{GGA, RPA})$.

TABLE II. Calculated band gaps (eV) of bulk materials. In QSGW80, we show self-consistent results with the hybrid xc potential, 80 % QSGW + 20 % GGA. QSGW80nosc specifies one-shot calculations with the hybrid potentials after QSGW 100% self-consistent calculations. QSGW80nosc is slightly larger because it is not fully self-consistent under such xc potential. See Ref.[7].

| Material | Experiments | QSGW | QSGW80 | QSGW80nosc | GGA |
|----------|-------------|-------|--------|------------|-----|
| LiF | 13.6 | 16.04 | 14.53 | 14.85 | 9.52 |
| KF | 10.9 | 11.78 | 10.53 | 10.82 | 6.43 |
| NaCl | 8.6 | 9.51 | 8.55 | 8.76 | 5.37 |
| MgO | 7.77 | 8.86 | 7.91 | 8.10 | 4.86 |
| CaO | 7.1 | 7.45 | 6.57 | 6.74 | 3.69 |

Let us examine possible methods to take into account such vertex corrections in bulk calculations. A possibility is to develop methods along the line of Ref.[3] by Shishkin et al. In fact, our results is a support to justify their treatment. However, it is computationally very demanding, thus QSGW80 can be a possible simplification. In fact, $\eta = \frac{\varepsilon_\infty(\text{QSGW, RPA})}{\varepsilon_\infty(\text{QSGW, Slab})}$ in Table II are approximately 80 %, and show little material-dependency. Thus we expect that QSGW80 can mimic QSGW with the vertex corrections; too large screened-exchange effect is reduced by the factor 0.8, with adding 0.2 GGA term so as to keep the total size of the xc term. In Table II we show band gaps in QSGW and QSGW80 for materials treated here. The band gaps are systematically too large in QSGW in comparison with experimental values [7], while QSGW80 gives rather better agreements with experimental values. In Ref.[7], we checked the performance of the QSGW80 for ranges of materials. As in the case of Ref.[8], QSGW80 is theoretically reasonable in the sense that the band gaps are improved by using the corrected $W$. To go beyond QSGW80, we have to develop methods to take the vertex correction into $W$ as was done in Ref.[9] in a simple manner. Considering the fact that QSGW80 works well as shown in Ref.[7], we may expect simple methods to represent the vertex correction by a scalar factor or by limited number of parameters. As long as we know, the vertex correction can be relatively insensitive to materials, thus we expect some simple method might be available.

Summary – We have performed QSGW calculations for the slab model under electric field by means of the ESM method. The obtained $\varepsilon_\infty$ are in good agreements with experimental values. Compared with $\varepsilon_\infty$ in bulk calculation in RPA, we evaluated the size of vertex corrections at the level of the functional derivative of the self-energy in QSGW. Our results on $\varepsilon_\infty$ give a justification to the methods such as QSGW80 [7] and method by Shishkin, Marsman and Kresse [9]. The method QSGW+ESM developed for the calculations should be useful even for other purposes such as bias-dependent spin susceptibility in material theory, as well as practical device applications and materials designs.

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