

Accurate *GW* self-energies in a plane-wave basis using only a few empty states: Towards large systems

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The *GW* approximation to the electronic self-energy yields band structures in excellent agreement with experimental data. Unfortunately, this type of calculation is extremely cumbersome even for present-day computers. The huge number of empty states required both in the calculation of the polarizability and of the self-energy is a major bottleneck in *GW* calculations. We propose an almost costless scheme, which allows us to divide the number of empty states by about a factor of 5 to reach the same accuracy. The computational cost and the memory requirements are decreased by the same amount, accelerating all calculations from small primitive cells to large supercells.

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I. INTRODUCTION

Calculating the correct electronic band structure of a solid, especially in the band-gap region, is not a trivial task for *ab initio* methods. The commonly used density-functional theory (DFT)^{1,2} is notoriously insufficient in that respect. To get realistic band structure from the computer, one has to resort to more accurate but also more cumbersome methods. In this context, Hedin's *GW* approximation³⁻⁵ to the electronic self-energy has encountered a wide success for systems where correlation effects are not strong. Unfortunately, the cost of such calculations is generally two orders of magnitude higher than their DFT counterpart. Furthermore, the need to study nanowires, interfaces, or defects drives the interest of the scientific community towards larger and larger systems. It is urgent to find reliable techniques to speed up the *GW* approach and make it tractable for a wider range of applications.

The *GW* self-energy is a convolution of the Green's function G and the screened Coulomb potential $v\varepsilon^{-1}$

$$\Sigma(\omega) = \int d\omega' G(\omega + \omega') v \varepsilon^{-1}(\omega'), \quad (1)$$

where v is the Coulomb interaction and ε^{-1} is the inverse dielectric matrix. The dielectric matrix in turn is obtained from the random-phase approximation (RPA)

$$\varepsilon(\omega) = 1 - v \chi_0(\omega), \quad (2)$$

with $\chi_0(\omega)$ being the Kohn-Sham polarizability. A practical *GW* calculation consists of evaluating the polarizability $\chi_0(\omega)$ and then of performing the convolution in Eq. (1).

The main bottleneck in the efficiency of a *GW* calculation is the dependence with respect to the empty states. In contrast with Kohn-Sham DFT, the two ingredients in a *GW* run, i.e., the polarizability and the *GW* self-energy itself, both involve explicitly the unoccupied states. The evaluation of the *GW* band structure requires, first, calculating a huge quantity of empty Kohn-Sham eigenvectors and eigenvalues and, second, using them in sums running over all the states

of the system. The poor convergence of the *GW* approximation with respect to the empty states has been recognized long ago.⁵⁻⁷ In order to be exact, the number of states should be the same as the dimension of the Hilbert space that is equal to the number of basis functions. In a plane-wave basis or in a real-space representation, the dimension of the space is huge (typically from thousand to millions). As a consequence, a speedup of the *GW* approach should address the elimination or the reduction in the number of empty states in the calculations. This direction has already been identified by several other groups.^{8,9} However, the previously proposed techniques are not widely used nowadays because of either low efficiency or because the cost exceeds the benefits for the available system sizes.

In the context of the optimized effective potentials, the same problem arises—one needs to invert the empty state-dependent Kohn-Sham polarizability in order to obtain the local Kohn-Sham potential that represents best a nonlocal exchange-correlation operator.¹⁰ For this framework, several schemes have been developed to get rid of the empty states dependence. In the 50's, Sharp and Horton¹¹ have already proposed a rough approximation, which was then reused in the celebrated Krieger-Li-Iafrate approximation of the exchange-only potential.¹² More recently, Gritsenko and Baerends¹³ improved much on this approach with their common energy denominator approximation (CEDA).

In this paper, we propose a technique that allows us to reduce the number of unoccupied states required in the two steps of a *GW* calculation (for the polarizability and the self-energy) in a plane-wave implementation. In order to achieve this goal, we transpose the CEDA trick of Gritsenko and Baerends¹³ into the framework of the *GW* approximation. For the polarizability step, this corresponds to a simple extension of the extrapolation method of Anglade and Gonze.¹⁴ By replacing the eigenenergies of the states that are not treated explicitly by a common energy, determined with respect to the highest computed eigenstate through a single adjustable parameter, we will be able to take into account all the states, which are not explicitly included in the calculation through the closure relation

$$\sum_{i>N_b} |i\rangle\langle i| = 1 - \sum_{i\leq N_b} |i\rangle\langle i|, \quad (3)$$

where N_b is the number of states explicitly included in the calculation. The principle can be extended to other formulations which have a large Hilbert-space dimension such as real-space approach. This permits us to provide a correction to the polarizability and to the self-energy that approximates the effect of the states not explicitly taken into account. The only drawback of the extrapolar approximation is the introduction of a parameter that can be thought as *ad hoc*. In this paper, we also present a formula that gives an *ab initio* evaluation of this parameter.

In Sec. II, we focus on the computation of the polarizability with a limited number of empty states. After developing the corresponding equations, we examine the effect of the number of empty states treated in the polarizability on the *GW* corrections for the band gap of SiC. In Sec. III, we propose to use the sum rule for the first moment of the dielectric function to analyze the effect of the eigenenergy approximation as a function of the transferred momentum. Thanks to a proper weight factor; the best value for the adjustable parameter might be determined. In Sec. IV, we perform the same approximation in the self-energy expression assuming the dynamically screened Coulomb interaction to be well represented by a generalized plasmon-pole model for the large-energy transfers. The adequacy of this approximation increases with the number of states explicitly computed. Unlike for the polarizability, no sum rule exists for the self-energy. However, we argue that the value of the adjustable parameter, optimized for the polarizability, is likely close to the optimal value for the self-energy. We apply the methodology to the case of bulk SiC, to a 64-atom supercell of SiC, to the insulator of argon, and also to an isolated benzene molecule.

II. POLARIZABILITY WITH A LIMITED NUMBER OF EMPTY STATES

In this section, we recapitulate the extrapolar approximation of Ref. 14 for the empty states that are not included explicitly in the calculation and derive the corresponding correction to the independent-particle polarizability χ_0 .

The formulas are written here for spin-unpolarized and nonmetallic systems, but they can be straightforwardly extended to spin-polarized systems and to metals by introducing fractional occupations. Using the time-reversal symmetry, the independent-particle polarizability in reciprocal space and frequency reads

$$\chi_{0GG'}(\mathbf{q}, \omega) = \frac{2}{N_{\mathbf{k}}\Omega} \sum_{\substack{N_v < i \leq N_b \\ j \leq N_v}} M_{kij}(\mathbf{q} + \mathbf{G}) M_{kij}^*(\mathbf{q} + \mathbf{G}') \times \left[\frac{1}{\omega - (\epsilon_{\mathbf{k}j} - \epsilon_{\mathbf{k}-\mathbf{q}i}) - i\eta} - \frac{1}{\omega - (\epsilon_{\mathbf{k}-\mathbf{q}i} - \epsilon_{\mathbf{k}j}) + i\eta} \right], \quad (4)$$

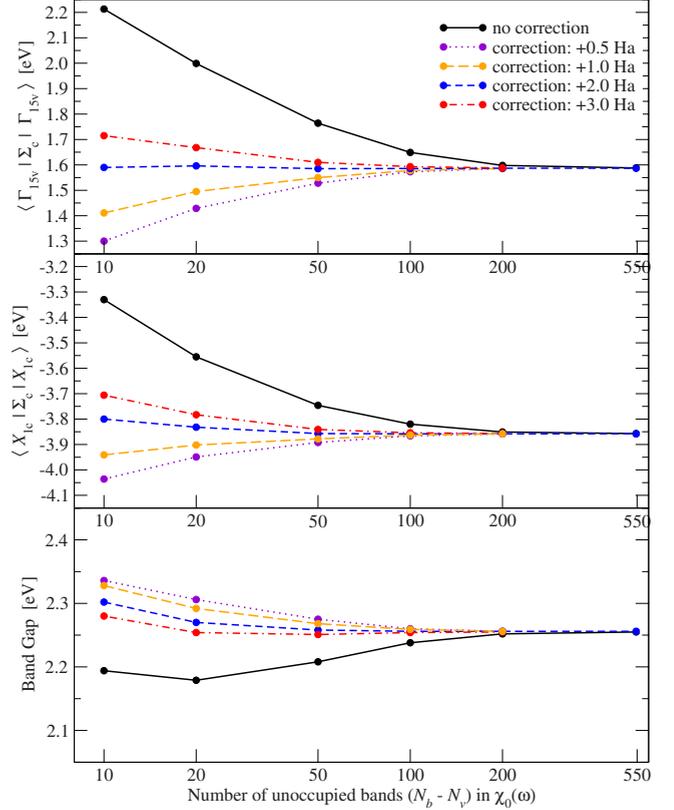


FIG. 1. (Color online) Convergence study of the correlation part of the self-energy at top valence (upper panel) and at bottom conduction (middle panel) and of the band gap (lower panel) of β -SiC as a function of the number of unoccupied states explicitly included in the calculation of the polarizability. The solid curve shows the usual *GW* result with no correction. The other curves include the correction of Eq. (8) with different values for the energy parameter $\bar{\epsilon}_{\chi_0}$: 0.5 Ha, 1.0 Ha, 2.0 Ha, and 3.0 Ha above the last explicitly calculated band.

where Ω is the volume of the unit cell, N_v is the number of valence states, $N_{\mathbf{k}}$ is the number of \mathbf{k} points in the Brillouin zone (the index \mathbf{k} runs over the \mathbf{k} points of the Brillouin zone), and where the matrix elements

$$M_{kij}(\mathbf{q} + \mathbf{G}) = \langle \mathbf{k} - \mathbf{q} | e^{-i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}} | \mathbf{k} j \rangle \quad (5)$$

are the so-called oscillator strengths.

In practice, the number of unoccupied states needed in Eq. (4) can be very large in order to converge the value of the self-energy calculated using this polarizability. In this paper, the numerical applications are performed first on bulk β -SiC, which is slightly more sensitive than the prototypical bulk silicon to the number of states. The solid curve in Fig. 1 illustrates the convergence of the correlation part of the self-energy at the top of the valence band and at the bottom of the conduction band (and the resulting band gap) as a function of the number of unoccupied bands considered in the calculation of χ_0 . More than 100 empty states are required to obtain the self-energy at the top valence Γ_{15v} with the typical accuracy of *GW* calculations, i.e., 50 meV. Furthermore, Fig. 1 shows that the convergence rate of the bottom conduction

band X_{1c} is not the same as of Γ_{15v} . Therefore, it would be interesting to accelerate this poor convergence; thanks to a properly defined correction.

The extrapolar approximation proposes to attribute to all the states above N_b the same ‘‘average’’ high energy $\bar{\epsilon}_{\chi_0}$. Obviously, this energy should lie higher than the energy of the last actually calculated band. But so far, this energy is considered as a parameter.

Let us define the correction $\Delta_{GG'}(\mathbf{q}, \omega)$, which is the quantity neglected in Eq. (4) due to the truncation of the unoccupied state sum. Introducing this average energy in this correction allows one to change the order of the sums as follows:

$$\begin{aligned} \Delta_{GG'}(\mathbf{q}, \omega) = & \frac{2}{N_{\mathbf{k}}\Omega} \sum_{\mathbf{k}} \left[\frac{1}{\omega - (\epsilon_{\mathbf{k}j} - \bar{\epsilon}_{\chi_0}) - i\eta} \right. \\ & \left. - \frac{1}{\omega - (\bar{\epsilon}_{\chi_0} - \epsilon_{\mathbf{k}j}) + i\eta} \right] \\ & \times \sum_{i>N_b} M_{\mathbf{k}ij}(\mathbf{q} + \mathbf{G}) M_{\mathbf{k}ij}^*(\mathbf{q} + \mathbf{G}'), \end{aligned} \quad (6)$$

in which the only quantity depending on the empty states i are the oscillator strengths $M_{\mathbf{k}ij}(\mathbf{q} + \mathbf{G})$.

The closure relation can be straightforwardly applied to

$$\begin{aligned} & \sum_{i>N_b} M_{\mathbf{k}ij}(\mathbf{q} + \mathbf{G}) M_{\mathbf{k}ij}^*(\mathbf{q} + \mathbf{G}') \\ & = \langle \mathbf{k}j | e^{i(\mathbf{G}' - \mathbf{G}) \cdot \mathbf{r}} | \mathbf{k}j \rangle - \sum_{i \leq N_b} M_{\mathbf{k}ij}(\mathbf{q} + \mathbf{G}) M_{\mathbf{k}ij}^*(\mathbf{q} + \mathbf{G}'), \end{aligned} \quad (7)$$

in order to get rid of the states above N_b . The final expression for the correction to the independent-particle polarizability within the extrapolar approximation is

$$\begin{aligned} \Delta_{GG'}(\mathbf{q}, \omega) = & \frac{2}{N_{\mathbf{k}}\Omega} \sum_{\mathbf{k}} \langle \mathbf{k}j | e^{i(\mathbf{G}' - \mathbf{G}) \cdot \mathbf{r}} | \mathbf{k}j \rangle \left[\frac{1}{\omega - (\epsilon_j - \bar{\epsilon}_{\chi_0}) - i\eta} \right. \\ & \left. - \frac{1}{\omega - (\bar{\epsilon}_{\chi_0} - \epsilon_{\mathbf{k}j}) + i\eta} \right] \\ & - \frac{2}{N_{\mathbf{k}}\Omega} \sum_{\substack{i \leq N_b \\ j \leq N_b}} M_{\mathbf{k}ij}(\mathbf{q} + \mathbf{G}) M_{\mathbf{k}ij}^*(\mathbf{q} + \mathbf{G}') \\ & \times \left[\frac{1}{\omega - (\epsilon_{\mathbf{k}j} - \bar{\epsilon}_{\chi_0}) - i\eta} - \frac{1}{\omega - (\bar{\epsilon}_{\chi_0} - \epsilon_{\mathbf{k}j}) + i\eta} \right]. \end{aligned} \quad (8)$$

The calculation of this correction does not require much coding when the polarizability is already available. Furthermore, it produces very little overhead in the calculation time. Indeed, the first term in Eq. (8) does not have any sum over empty states and basically requires one fast Fourier transform per \mathbf{k} point and per occupied state. The second term can

be merged with the corresponding part in the calculation of χ_0 for each triplet index $(\mathbf{k}ij)$. So it does not add any complex operation. The calculation of the correction is really for free.

The extrapolar approximation is not designed to yield the right frequency-dependent polarizability. As this approximation replaces the many neglected high-energy transitions by a single transition with a large weight, the imaginary part of the polarizability would look like a single δ peak at high energy instead of a continuous spectrum. Nevertheless, one can reasonably hope that this approximated polarizability, when integrated, retains some physics. The *GW* self-energy is precisely an integrated quantity as seen in Eq. (1). Let us check before this assumption on the static dielectric matrix. The static dielectric matrix can be considered as an integration of the frequency-dependent dielectric function through the Kramers-Kronig relation

$$\text{Re}\{\epsilon(\omega=0)\} = 1 + \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{+\infty} d\omega' \frac{\text{Im}\{\epsilon(\omega')\}}{\omega'}. \quad (9)$$

Table I shows the convergence with or without correction of the static inverse dielectric matrix. The value of the average extrapolar energy $\bar{\epsilon}_{\chi_0}$ is referenced with respect to the highest calculated energy ϵ_{N_b} . It can be observed from the data that whatever the choice of the extrapolar energy (in a reasonable range), the convergence of diagonal and off-diagonal elements of the dielectric matrix is accelerated.

Now let us describe the quality of the extrapolar correction for the polarizability when it is used to evaluate the *GW* self-energy. The performance for β -SiC is shown in Fig. 1. Whatever the value of $\bar{\epsilon}_{\chi_0}$, the convergence of the self-energy and of the band gap is improved significantly; thanks to the correction. When $\bar{\epsilon}_{\chi_0}$ is chosen too high with respect to the last calculated band, the correction vanishes and the results tend to the uncorrected one. When $\bar{\epsilon}_{\chi_0}$ is chosen too close to the last calculated band, the correction is then slightly overestimated. The best fit is obtained for an average energy of around 2.0 Ha above ϵ_{N_b} . If a reasonable value for $\bar{\epsilon}_{\chi_0}$ is used, the number of empty states can be lowered to around 20 to achieve the 50-meV accuracy. This corresponds to five times fewer states as without correction. As a conclusion, the numerical application strongly supports the use of the correction to the polarizability.

III. USING A SUM RULE TO DETERMINE THE ENERGY PARAMETER

In Sec. II, we have shown that the precise determination of the average energy $\bar{\epsilon}_{\chi_0}$ is not crucial as it provides an accurate correction for a wide range of $\bar{\epsilon}_{\chi_0}$. However, it would be desirable to have a tool, which measures the quality of a choice of an average energy $\bar{\epsilon}_{\chi_0}$ without knowing before the exact target result.

A common procedure to assign the value of parameters is to enforce the fulfillment of exact relations. For response functions, there exists a class of integrals, of which the value is known exactly. For instance, the first moment of the in-

TABLE I. Convergence study of some selected elements of the inverse dielectric matrix of β -SiC as a function of the number of empty bands explicitly included in the calculation of the polarizability. The first element is the macroscopic static dielectric constant. The second element is a diagonal element and the last one is off diagonal.

	Extrapolar energy (Ha)	Number of empty states				$(N_b - N_v)$
		4	10	20	50	200
$1/\varepsilon_{(000),(000)}^{-1}(\mathbf{q} \rightarrow 0, \omega=0)$	No correction	6.617	6.722	6.737	6.748	6.755
	0.5	6.728	6.790	6.762	6.753	6.754
	1.0	6.700	6.776	6.758	6.753	6.754
	2.0	6.673	6.761	6.753	6.752	6.754
	3.0	6.659	6.752	6.750	6.751	6.754
$\varepsilon_{(100),(100)}^{-1}(\mathbf{q} \rightarrow 0, \omega=0)$	No correction	0.792	0.708	0.662	0.645	0.645
	0.5	0.637	0.645	0.646	0.644	0.645
	1.0	0.676	0.658	0.648	0.644	0.645
	2.0	0.715	0.673	0.652	0.645	0.645
	3.0	0.735	0.681	0.654	0.645	0.645
$\varepsilon_{(100),(0\bar{1}0)}^{-1}(\mathbf{q} \rightarrow 0, \omega=0)$	No correction	0.037	0.030	0.027	0.026	0.026
	0.5	0.026	0.026	0.026	0.026	0.026
	1.0	0.029	0.027	0.026	0.026	0.026
	2.0	0.031	0.028	0.027	0.026	0.026
	3.0	0.032	0.028	0.027	0.026	0.026

verse dielectric matrix $\int d\omega \text{Im} \varepsilon^{-1}[\mathbf{q}, \omega]$ is fixed by the so-called *f-sum rule*. This relation allowed Hybertsen and Louie¹⁵ to calculate the free parameters of their model to represent the inverse dielectric matrix.

In the present case, the evaluation of the *f-sum rule* would not be adequate because it would require either modeling the inverse dielectric function or performing a numerical frequency integration subjected to discretization error. Instead, another sum rule exists for the first moment of the dielectric function itself,^{16,17}

$$\int_0^{+\infty} d\omega \text{Im}[\varepsilon_{\mathbf{G}\mathbf{G}}(\mathbf{q}, \omega)] = \frac{\pi}{2} \omega_p^2, \quad (10)$$

where $\omega_p = \sqrt{4\pi n}$ is the classical plasma frequency (n being the average electronic density). The sum rule in Eq. (10), although not valid in general, has been shown to be true for the RPA dielectric matrix.¹⁷ The RPA is precisely the approximation used for the *GW* self-energy. In the present discussion, we will concentrate only on the diagonal elements of the dielectric matrix since these elements yield by far the largest contribution to the *GW* self-energy.

In the RPA approximation, the dielectric matrix is related to the independent-particle polarizability through $\varepsilon(\omega) = 1 - v\chi_0(\omega)$, where v is the Coulomb potential. Hence, the sum rule of Eq. (10) reads

$$\int_0^{+\infty} d\omega \frac{4\pi}{|\mathbf{q} + \mathbf{G}|^2} \text{Im}[\chi_{0\mathbf{G}\mathbf{G}}(\mathbf{q}, \omega)] = -\frac{\pi}{2} \omega_p^2, \quad (11)$$

in which $4\pi/|\mathbf{q} + \mathbf{G}|^2$ is the Fourier transform of the Coulomb potential v .

The check of the validity of Eq. (11) provides a stringent test on the completeness in the calculation of χ_0 . If the sum over states in Eq. (4) has been truncated, the integral in the left-hand side of Eq. (11) will be too small. The advantage of Eq. (11) with respect to the *f-sum rule* is that the evaluation of the integral can be performed analytically, as the frequency dependence of $\text{Im}[\chi_0(\omega)]$ consists only of a series of δ peaks; thanks to the classical identity

$$\lim_{\eta \rightarrow 0} \frac{1}{\omega + i\eta} = \mathcal{P} \frac{1}{\omega} - i\pi \delta(\omega). \quad (12)$$

Practically, introducing the expression of $\text{Im}[\chi_0]$ in Eq. (11), it reduces to

$$\frac{4\pi^2}{N_{\mathbf{k}} \Omega |\mathbf{q} + \mathbf{G}|^2} \sum_{\substack{\mathbf{k} \\ N_v < i \leq N_b \\ j \leq N_v}} |M_{\mathbf{k}ij}(\mathbf{q} + \mathbf{G})|^2 (\epsilon_{\mathbf{k}-\mathbf{q}i} - \epsilon_{\mathbf{k}j}) = \frac{\pi}{2} \omega_p^2. \quad (13)$$

In the upper panel of Fig. 2, we report for β -SiC the evaluation of the left-hand side of Eq. (13) as a function of the transferred momentum $|\mathbf{q} + \mathbf{G}|$ of different number of unoccupied bands included in the calculation. When almost all the states available are included in the calculation (550 unoccupied bands), the sum rule is verified for any value of $|\mathbf{q} + \mathbf{G}|$. Contrastingly, when only a few empty states are taken into account (e.g., ten unoccupied bands), the sum rule is only approximately satisfied for low transferred momenta. This expresses the fact that well-separated occupied and unoccupied states can couple through electronic transition with

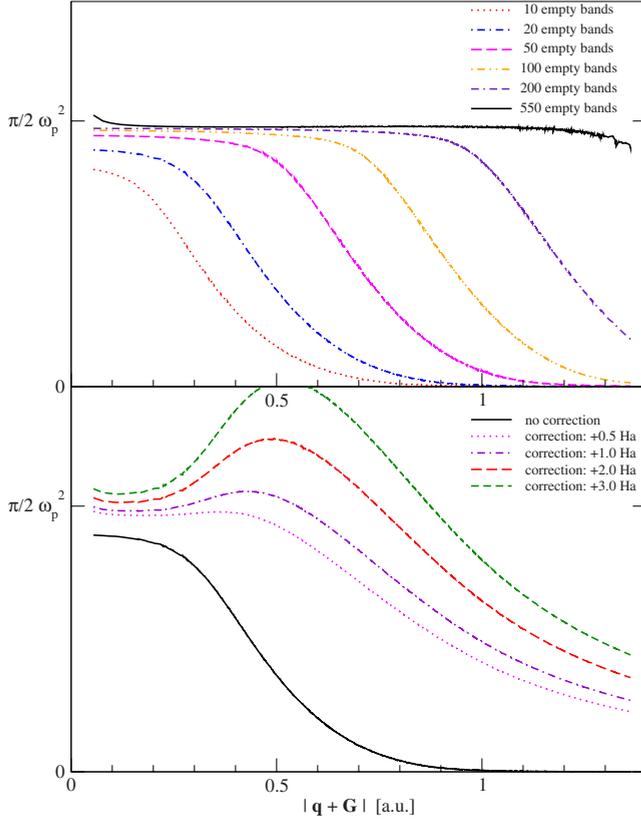


FIG. 2. (Color online) Upper panel: Value of the integral in Eq. (10) as a function of the transferred momentum $|\mathbf{q}+\mathbf{G}|$ without any correction using 10, 20, 50, 100, 200, and 550 empty bands in β -SiC. Lower panel: Value of the integral in Eq. (10) as a function of the transferred momentum $|\mathbf{q}+\mathbf{G}|$ with 20 empty bands using no correction or a correction with an average energy $\bar{\epsilon}_{\chi_0}$ of 0.5, 1.0, 2.0, and 3.0 Ha above the last explicitly calculated band in β -SiC.

a large momentum. For large transferred momenta, the coupling between far apart states cannot be neglected without damaging the polarizability.

The bottom panel of Fig. 2 shows how the extrapolation correction to χ_0 proposed in Eq. (8) affects the sum rule for a fixed number of 20 unoccupied bands with different values of the extrapolation energy parameter. All calculations that include the correction fulfill the sum rule with a much higher accuracy than the reference curve without correction. The completeness correction is a large step towards a fulfillment of the sum rule, especially for large transferred momenta. By using the present correction, it is possible that for some values of $|\mathbf{q}+\mathbf{G}|$, the sum rule gets overestimated. This can allow one to compensate for the underestimation of the highest values of $|\mathbf{q}+\mathbf{G}|$.

As a consequence, a sensible approach is to seek for the value of the extrapolation energy $\bar{\epsilon}_{\chi_0}$, which in average allows for the best compliance to the sum rule. The significance of each transferred momentum has to be weighted by its importance in the subsequent GW self-energy calculation since the ultimate goal is merely to evaluate GW band structures. The contribution of the polarizability χ_0 in the GW correlation is proportional to $(\epsilon^{-1}-1)v$. In order to have a rough estimate of this weight, we can assume that all the matrices χ_0 , ϵ , and

ϵ^{-1} are diagonal and are considered in the static limit $\omega \rightarrow 0$ since this is the dominating contribution. Under these assumptions, the weight w assigned to the sum rule for the momentum $|\mathbf{q}+\mathbf{G}|$ is

$$w(\mathbf{q}+\mathbf{G}) \propto \frac{1}{|\mathbf{q}+\mathbf{G}|^2} [\epsilon_{GG}^{-1}(\mathbf{q}, \omega=0) - 1]. \quad (14)$$

When applying this procedure to β -SiC with 20 unoccupied states (the same conditions as the bottom panel of Fig. 2), the best choice of the average energy appears to be ~ 1.6 Ha above the last explicitly calculated band. This is in good agreement with the quality of the curve with the average energy $\bar{\epsilon}_{\chi_0}$ chosen at 2.0 Ha above the last band in Fig. 1.

IV. SELF-ENERGY WITH A LIMITED NUMBER OF EMPTY STATES

In the expression of the GW self-energy as in the formula of the polarizability, a sum over all the states is present. In the present section, using the same procedure as the one shown previously for the polarizability, we propose a correction to the self-energy that allows us to reduce drastically the number of empty states required.

For the sake of simplicity, we show the derivation of diagonal matrix elements, but the extension to the off-diagonal terms needed in self-consistent GW (Refs. 18 and 19) is straightforward. The exchange part of the GW self-energy is the Fock exchange operator and therefore does not involve empty states. The diagonal matrix element of the correlation part of the GW self-energy expressed in a plane-wave basis reads¹⁵

$$\begin{aligned} \langle \mathbf{k}j | \Sigma_c(\epsilon_{\mathbf{k}j}) | \mathbf{k}j \rangle &= \frac{i}{2\pi N_{\mathbf{k}} \Omega} \int d\omega' \sum_{i \leq N_b} \sum_{\mathbf{q} \mathbf{G} \mathbf{G}'} [W_{\mathbf{G} \mathbf{G}'}(\mathbf{q}, \omega') \\ &\quad - \delta_{\mathbf{G} \mathbf{G}'} v(\mathbf{q}+\mathbf{G})] \\ &\quad \times \frac{M_{ji}(\mathbf{q}+\mathbf{G}) M_{ji}^*(\mathbf{q}+\mathbf{G}')}{\omega' - \epsilon_{\mathbf{k}-\mathbf{q}i} + \epsilon_{\mathbf{k}j} \pm i\eta}, \end{aligned} \quad (15)$$

where η is a vanishing positive real. The sign in front of η is plus when the state i is empty and minus otherwise.

The correction we propose is again to account for the states $i > N_b$ through an extrapolation energy $\bar{\epsilon}_\Sigma$. This permits us to interexchange the order of the sum over bands and all the rest except the oscillator strengths in Eq. (15). Then, we can apply the closure relation written in Eq. (7). Hence, the extrapolation correction $\Delta_{\mathbf{k}j}$ to the self-energy reads

$$\begin{aligned} \Delta_{\mathbf{k}j} &= \frac{i}{2\pi N_{\mathbf{k}} \Omega} \int d\omega' \sum_{\mathbf{q} \mathbf{G} \mathbf{G}'} \frac{W_{\mathbf{G} \mathbf{G}'}(\mathbf{q}, \omega') - \delta_{\mathbf{G} \mathbf{G}'} v(\mathbf{q}+\mathbf{G})}{\omega' - \bar{\epsilon}_\Sigma + \epsilon_{\mathbf{k}j} + i\eta} \\ &\quad \times \left[\langle \mathbf{k}j | e^{i(\mathbf{G}'-\mathbf{G})\cdot\mathbf{r}} | \mathbf{k}j \rangle - \sum_{i \leq N_b} M_{ji}(\mathbf{q}+\mathbf{G}) M_{ji}^*(\mathbf{q}+\mathbf{G}') \right]. \end{aligned} \quad (16)$$

We now have to evaluate the frequency integral in the expression of the correction $\Delta_{\mathbf{k}j}$. According to the polar structure of $W(\omega)$, which is a time-ordered quantity in the Green's

function theory, only the pole located in $\omega' = \bar{\epsilon}_\Sigma - \epsilon_{\mathbf{k}j}$ contributes to the integral by virtue of the residue theorem. The corresponding residue invokes just the antiresonant part of $W(\bar{\epsilon}_\Sigma - \epsilon_{\mathbf{k}j})$, i.e., the part of W having poles in the upper part of the complex plane. The energy difference $\bar{\epsilon}_\Sigma - \epsilon_{\mathbf{k}j}$ is large in practice because $\epsilon_{\mathbf{k}j}$ is typically located in the vicinity of the Fermi level and $\bar{\epsilon}_\Sigma$ will be a “high” energy (above the last one explicitly treated in the calculation). As a consequence, the function $W(\omega)$ in the residue is evaluated only for large values of ω . It is a general result¹⁶ that the dielectric function of an electron gas tends to a single plasmon pole in the limit $\omega \rightarrow \infty$.

Hence, in the calculation of the correction $\Delta_{\mathbf{k}j}$, we will assume that the dynamically screened Coulomb interaction is well represented by a generalized plasmon-pole model¹⁵ even though the plasmon-pole model is not used to calculate the self-energy itself. In other words, the plasmon-pole model is much better justified for the correction $\Delta_{\mathbf{k}j}$ to the self-energy than for the self-energy itself. The plasmon-pole approximation models the dynamically screened Coulomb interaction as

$$W_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega') = \delta_{\mathbf{G}\mathbf{G}'} v(\mathbf{q} + \mathbf{G}) + \frac{\Omega_{\mathbf{G}\mathbf{G}'}^2(\mathbf{q})}{2\tilde{\omega}_{\mathbf{G}\mathbf{G}'}(\mathbf{q})} \left[\frac{1}{\omega - \tilde{\omega}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) + i\eta} - \frac{1}{\omega + \tilde{\omega}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) - i\eta} \right] v(\mathbf{q} + \mathbf{G}'), \quad (17)$$

where $\tilde{\omega}_{\mathbf{G}\mathbf{G}'}(\mathbf{q})$ and $\Omega_{\mathbf{G}\mathbf{G}'}^2(\mathbf{q})$ are parameters determined by simple fits on the *ab initio* calculated dielectric matrices. With this model for $W(\omega)$, the frequency integration in Eq. (16) is performed analytically and yields the final expression for the correction

$$\Delta_{\mathbf{k}j} = \frac{1}{N_{\mathbf{k}}\Omega} \sum_{\mathbf{q}\mathbf{G}\mathbf{G}'} \frac{\Omega_{\mathbf{G}\mathbf{G}'}^2(\mathbf{q}) v(\mathbf{q} + \mathbf{G})}{2\tilde{\omega}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) [\tilde{\omega}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) + \bar{\epsilon}_\Sigma - \epsilon_{\mathbf{k}j} - i\eta]} \times \left[\langle \mathbf{k}j | e^{i(\mathbf{G}' - \mathbf{G}) \cdot \mathbf{r}} | \mathbf{k}j \rangle - \sum_{i=1}^{N_b} M_{ji}(\mathbf{q} + \mathbf{G}) M_{ji}^*(\mathbf{q} + \mathbf{G}') \right]. \quad (18)$$

The first term of the correction $\Delta_{\mathbf{k}j}$ is almost costless since it does not involve the sum over states. The second term can be grouped with the usual evaluation of the *GW* self-energy where all the ingredients to build it are freely available. Note that usually the *GW* self-energy is calculated for several frequencies since the self-energy is a dynamical operator. Yet the correction can safely be assumed static because the energy $\epsilon_{\mathbf{k}j}$ is merely present inside the differences $\bar{\epsilon}_\Sigma - \epsilon_{\mathbf{k}j}$, which are large in all cases.

Here, we can compare our extrapolar-approximation-based correction to the coulomb hole plus screened exchange (COHSEX)-based correction of Tiago and Chelikowsky.⁹ The basic idea is similar—make the denominator independent of the unoccupied state energy with index i —as in Eq. (18) so that one can factorize the denominator out of the sum and apply the closure relation. In Ref. 9, the authors chose to

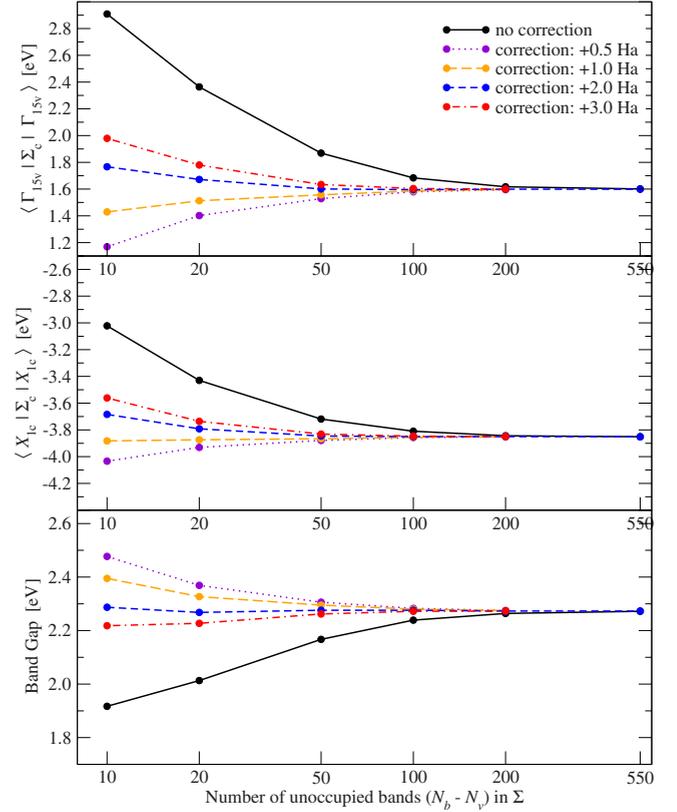


FIG. 3. (Color online) Convergence study of the correlation self-energy at top valence (upper panel) and at bottom conduction (middle panel) and of the band gap (lower panel) of β -SiC as a function of the number of unoccupied states explicitly included in the calculation of the self-energy.

neglect energy differences $\epsilon_{\mathbf{k}-\mathbf{q}i} - \epsilon_{\mathbf{k}j}$ with respect to the plasmon frequencies $\tilde{\omega}_{\mathbf{G}\mathbf{G}'}(\mathbf{q})$. In doing so, the static screening appears in the expression as in the COHSEX approximation to the self-energy. This choice may not be optimal since, when one wants to account for the high-energy bands, the energy differences are typically large compared to the plasma frequency of the system. Instead, the approximation proposed here is to disregard the energy dispersion of the high-energy bands and keep it fixed to an average value $\bar{\epsilon}_\Sigma$. In other words, our approximation assumes that the energy dispersion of the empty states $\epsilon_{\mathbf{k}-\mathbf{q}i} - \bar{\epsilon}_\Sigma$ is small compared to the difference $\tilde{\omega}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) + \bar{\epsilon}_\Sigma - \epsilon_{\mathbf{k}j}$. This is much more realistic in the typical applications and becomes even better when the number of empty bands is increased.

In Fig. 3, we test the performance of the proposed correction in a convergence study of the matrix elements of the *GW* correlation self-energy and of the band gap of β -SiC with respect to the number of unoccupied states explicitly included in the calculation. Consistently with the convergence study on the number of empty states used in χ_0 , the convergence of the results without correction is very slow. In order to achieve the typical accuracy of a *GW*-band structure (~ 50 meV), 100 to 200 unoccupied bands are required. Note that, as usual, the band gap converges faster than the absolute positions of the *GW* energies. When the correction is turned on, the convergence becomes much smoother and

the value of the correction does not depend strongly on the chosen average energy $\bar{\epsilon}_{\Sigma}$. Only 20 bands are necessary to converge the band gap within 50-meV, whereas 50 bands are needed to converge the absolute position of the top valence band named Γ_{15v} .

The evaluation of the optimum average energy $\bar{\epsilon}_{\Sigma}$ for the extrapolar approximation cannot be based on an exact scheme since no sum rule exists for the self-energy. Fortunately, a direct analogy between χ_0 and Σ can be underlined—they both contain a truncated sum over empty states and the summand is for both the squared modulus of the oscillator strengths divided by an energy difference. Yet, the denominator in Σ differs from the one of χ_0 by the presence of the plasmon-pole frequencies $\tilde{\omega}_{GG'}(\mathbf{q})$. In average, these frequencies $\tilde{\omega}_{GG'}(\mathbf{q})$ lie closely to the classical plasma frequency of the system. Considering that in the practical case the plasma frequency is small compared to the energy differences, we can expand the denominator as a function of the small quantity $\tilde{\omega}_{GG'}(\mathbf{q})/(\epsilon_{\mathbf{k}-\mathbf{q}i} - \epsilon_{\mathbf{k}j})$. The leading term in this expansion of the denominator does not involve the quantity $\tilde{\omega}_{GG'}(\mathbf{q})$:

$$\frac{1}{\epsilon_{\mathbf{k}-\mathbf{q}i} - \epsilon_{\mathbf{k}j} + \tilde{\omega}_{GG'}(\mathbf{q})} \approx \frac{1}{\epsilon_{\mathbf{k}-\mathbf{q}i} - \epsilon_{\mathbf{k}j}} \left[1 - \frac{\tilde{\omega}_{GG'}(\mathbf{q})}{\epsilon_{\mathbf{k}-\mathbf{q}i} - \epsilon_{\mathbf{k}j}} \right]. \quad (19)$$

This shows that the determination of the extrapolar energy for the self-energy $\bar{\epsilon}_{\Sigma}$ is to the zeroth order—the same as the determination of the extrapolar energy for the polarizability

$$\bar{\epsilon}_{\Sigma} \approx \bar{\epsilon}_{\chi_0}. \quad (20)$$

In the case of β -SiC with 20 unoccupied states, the evaluation of $\bar{\epsilon}_{\chi_0}$ gave 1.6 Ha above the last band energy. This value would be also suitable for $\bar{\epsilon}_{\Sigma}$ as can be judged from Fig. 3.

V. APPLICABILITY

In order to show that the present scheme possesses a wide range of applications, we further carried out calculations for a supercell of bulk β -SiC and for two other very different systems: a wide band-gap insulator, solid argon and a benzene (C_6H_6) molecule in gas phase.

In Fig. 4, we examine the convergence with the number of unoccupied states explicitly included in the calculation for a 64-atom β -SiC supercell. The tendencies observed for the small unit cell here are even more pronounced. We could not achieve convergence within 50 meV of the uncorrected GW band gap even using almost 1400 empty states. In contrast, applying the proposed correction with the optimal extrapolar energy as evaluated according to the sum rule Eq. (10) allows us to have an accurate evaluation of the GW band gap with as few as 320 unoccupied states. By extrapolation, we can evaluate that the uncorrected GW would require about 3000 empty bands to achieve the same convergence.

As previously noticed,¹⁹ the GW band gap of argon is much smaller than the experimental value (14.2 eV). However, this is not the point here. Figure 5 shows the conver-

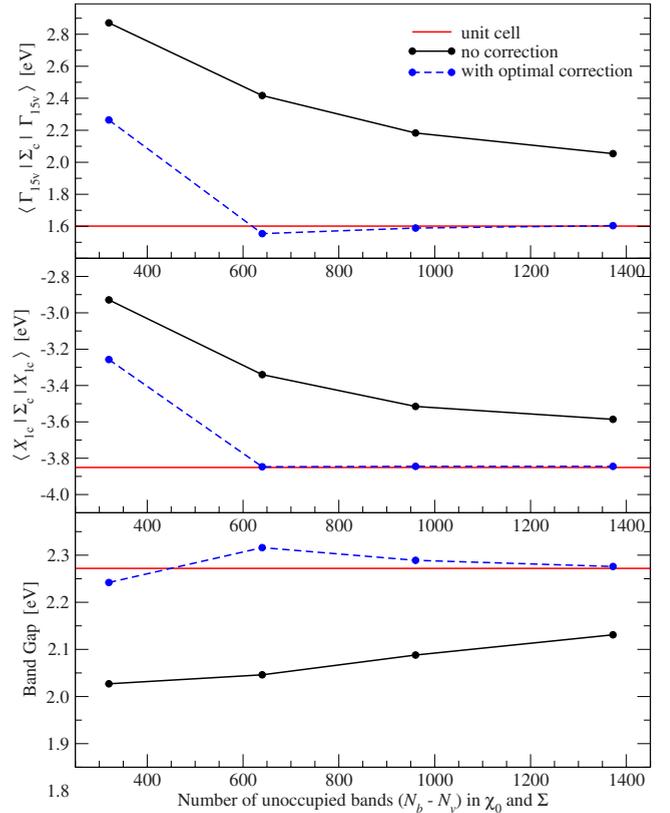


FIG. 4. (Color online) Convergence study of the correlation self-energy at top valence (upper panel) and at bottom conduction (middle panel) and of the band gap (lower panel) of β -SiC in a 64-atom supercell as a function of the number of unoccupied states explicitly included in the calculation of the polarizability and in the self-energy.

gence of the top valence, bottom conduction correlation self-energy, and band gap of this insulator. Once again, the extrapolar approximation performs extremely well even better than in the case of silicon carbide; the number of empty states can be reduced from 200 to 20.

The calculation of finite systems with periodic boundary-condition code should be considered with care, especially for the GW framework, which has long-range interactions. To mimic an isolated benzene molecule, we use a 40-bohr-long box in face-centered cubic geometry. In addition, the Coulomb interaction has been suppressed beyond 20 bohr.^{20,21} As the stress is placed on the convergence behavior and not on the system properties, we applied the usual perturbative procedure for the GW evaluation. But we know that this is not sufficient as shown by Tiago and Cheliskowsky.⁹ The convergence is displayed in Fig. 6. Without the extrapolar approximation, it would not have been possible to produce a reliable result even considering 1000 empty states. By contrast, we are able to obtain an evaluation of the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap with only 200 bands and an absolute energy position of the HOMO and the LUMO with 500 bands.

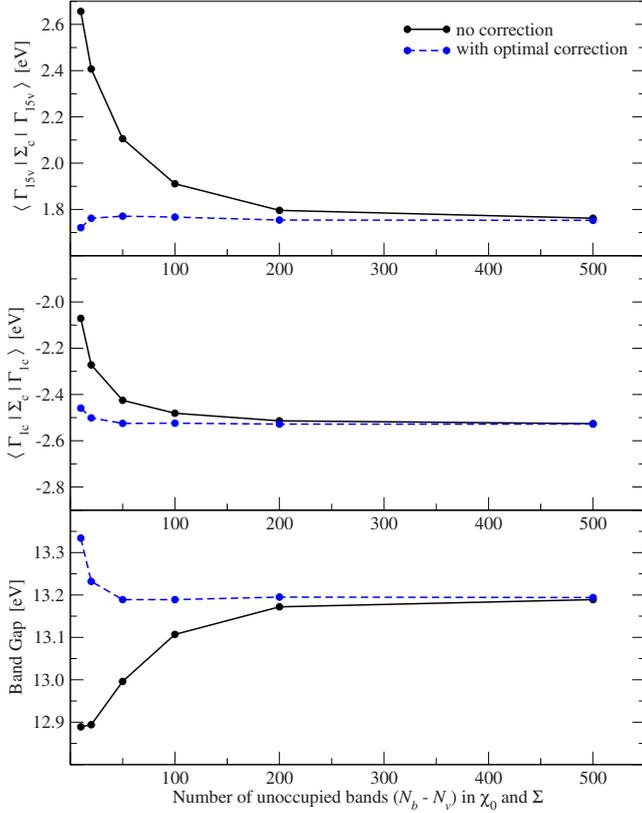


FIG. 5. (Color online) Convergence study of the correlation self-energy at top valence (upper panel) and bottom conduction (middle panel) and of the band gap (lower panel) of solid argon as a function of the number of unoccupied states explicitly included in the calculation of the polarizability and in the self-energy.

VI. CONCLUSION

The number of empty states to be used in present implementations of the *GW* approximation with a plane-wave basis hinders the use of the method for large-scale applications. We have provided here a technique based on the closure relation and the adequate approximation for the eigenenergies of states not treated explicitly largely reduces the prefactor in CPU time and in memory needs. This technique is a generalization of the extrapolar approximation of Ref. 14 and is similar to CEDA developed in the framework of optimized effective potential method by Gritsenko and Baerends.¹³ The gain is already large for bulk cells and it will allow one to consider applications to systems that were previously out of reach of the *GW* method.

We have emphasized that the completeness in the Hilbert space is critical in order to have full convergence of the *GW* band structure. A critical tool to measure this completeness is the fulfillment of the sum rule in Eq. (10). Using this rela-

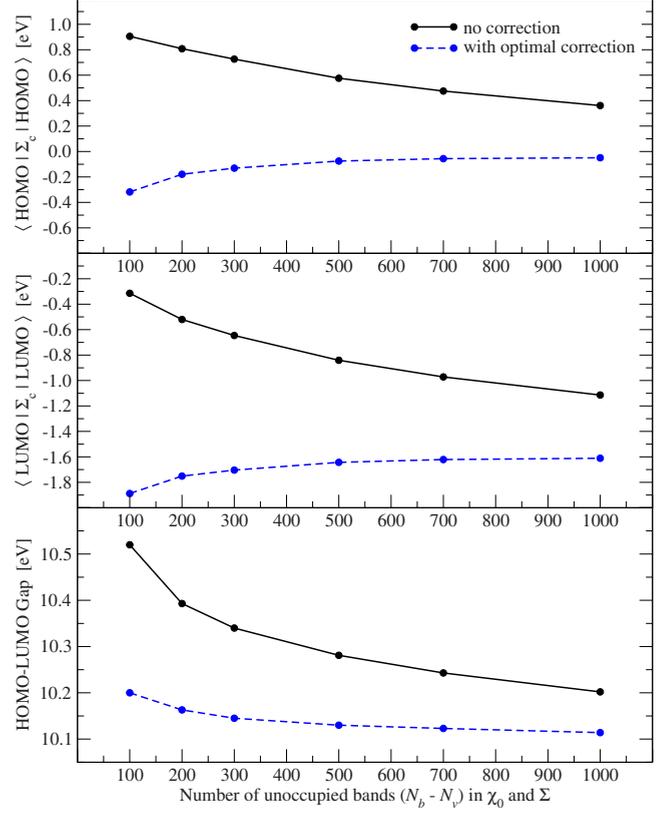


FIG. 6. (Color online) Convergence study of the correlation self-energy at HOMO (upper panel) and at LUMO (middle panel) and of the band gap (lower panel) of the benzene molecule (C_6H_6) as a function of the number of unoccupied states explicitly included in the calculation of the polarizability and in the self-energy.

tion, we have been able to estimate the correct range for the energy parameter to be introduced in the extrapolar approximation. With this determination, the proposed scheme can be considered as *ab initio*.

One immediate application of the presented acceleration technique is the *GW* evaluation of band alignment in junctions, which requires the *absolute* positions of the *GW* energy levels.²²

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- ¹P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- ²W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- ³L. Hedin, Phys. Rev. **139**, A796 (1965).
- ⁴G. Strinati, Riv. Nuovo Cimento **11**, 1 (1988).
- ⁵W. G. Aulbur, L. Jönsson, and J. W. Wilkins, Solid State Commun. **54**, 1 (2000).
- ⁶M. L. Tiago, S. Ismail-Beigi, and S. G. Louie, Phys. Rev. B **69**, 125212 (2004).
- ⁷M. van Schilfgaarde, T. Kotani, and S. V. Faleev, Phys. Rev. B **74**, 245125 (2006).
- ⁸L. Reining, G. Onida, and R. W. Godby, Phys. Rev. B **56**, R4301 (1997).
- ⁹M. L. Tiago and J. R. Chelikowsky, Phys. Rev. B **73**, 205334 (2006).
- ¹⁰S. Kümmel and L. Kronik, Rev. Mod. Phys. **80**, 3 (2008).
- ¹¹R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953).
- ¹²J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Lett. A **146**, 256 (1990).
- ¹³O. V. Gritsenko and E. J. Baerends, Phys. Rev. A **64**, 042506 (2001).
- ¹⁴P.-M. Anglade and X. Gonze, Phys. Rev. B **78**, 045126 (2008).
- ¹⁵M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).
- ¹⁶G. D. Mahan, *Many-Particle Physics*, 3rd ed. (Kluwer, Dordrecht/Plenum, New York, 2000).
- ¹⁷M. Taut, J. Phys. C **18**, 2677 (1985).
- ¹⁸M. van Schilfgaarde, T. Kotani, and S. Faleev, Phys. Rev. Lett. **96**, 226402 (2006).
- ¹⁹F. Bruneval, N. Vast, and L. Reining, Phys. Rev. B **74**, 045102 (2006).
- ²⁰G. Onida, L. Reining, R. W. Godby, R. Del Sole, and W. Andreoni, Phys. Rev. Lett. **75**, 818 (1995).
- ²¹S. Ismail-Beigi, Phys. Rev. B **73**, 233103 (2006).
- ²²R. Shaltaf, G.-M. Rignanese, X. Gonze, F. Giustino, and A. Pasquarello, Phys. Rev. Lett. **100**, 186401 (2008).
- ²³<http://www.abinit.org>
- ²⁴X. Gonze *et al.*, Z. Kristallogr. **220**, 558 (2005).