

**Ab initio calculations of electronic excitations: Collapsing spectral sums**J. A. Berger,<sup>1,2,\*</sup> Lucia Reining,<sup>1,2</sup> and Francesco Sottile<sup>1,2</sup><sup>1</sup>Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-DSM, 91128 Palaiseau, France<sup>2</sup>European Theoretical Spectroscopy Facility (ETSF)

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We present a method for the evaluation of electronic excitations of advanced materials by reformulating spectral sum-over-states expressions such that only occupied states appear. All empty states are accounted for by one effective energy. Thus we keep the simplicity and precision of the sum-over-states approach while speeding up calculations by more than an order of magnitude. We demonstrate its power by applying it to the *GW* method, where a huge summation over empty states appears twice (screening and self-energy). The precision is shown for bulk Si and solid and atomic Ar. We then use it to determine the band gap of the technologically important oxide SnO<sub>2</sub>.

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Many crucial physical quantities, e.g., electron spectral functions, optical response, or total energies, can be expressed in terms of one- or two-particle Green's functions that contain information about the propagation of an electron and/or hole in the system. This physics is directly reflected in their spectral representations in terms of amplitudes and energies. In practice, calculations are often performed using this relatively simple sum-over-states (SOS) formulation in an independent-particle or quasiparticle (QP) approximation. However, the SOS approach suffers from two main drawbacks. First, it does not scale well with the size of the system. Second, one has to sum over an, in principle, infinite, and, in practice, (at convergence) huge number of empty states. This is especially true for large unit cells (dense bands) or for materials with localized states (high-energy cutoff). Prototype examples are, e.g., the transparent conducting oxides (TCOs) based on SnO<sub>2</sub> and ZnO, for which calculations of many-body Green's functions are close to prohibitive. However, for these technologically important materials it is particularly desirable to predict electronic properties and first of all a reliable QP band structure. QP energies can be obtained from many-body perturbation theory; the state-of-the-art approach is the *GW* approximation.<sup>1</sup> However, in a standard *GW* calculation two SOS expressions appear since the self-energy  $\Sigma$ , which accounts for all the many-body effects beyond the Hartree potential, is given by the following convolution:

$$\Sigma(\mathbf{r}, \mathbf{r}', \omega) = i \int \frac{d\omega'}{2\pi} e^{i\delta\omega'} G(\mathbf{r}, \mathbf{r}', \omega + \omega') W(\mathbf{r}, \mathbf{r}', \omega'), \quad (1)$$

where  $G$  is the single-particle Green's function and  $W = \epsilon^{-1} v_c$  is the screened Coulomb potential in which  $\epsilon$  is the dielectric function in the random-phase approximation (RPA):  $\epsilon = 1 - v_c \chi^0$ , where  $\chi^0$  is the time-ordered independent-particle polarizability.<sup>2</sup> Most often both  $\chi^0$  and  $\Sigma$  are evaluated using a slowly converging<sup>3-5</sup> SOS expression. Several methods have been proposed to decrease or avoid completely the summation over empty states,<sup>1,6-10</sup> ranging from a static Coulomb-hole plus screened exchange (COHSEX) approximation<sup>1</sup> which eliminates empty states in  $\Sigma$  only and at the price of a crude description of QP energies,

to methods using a Sternheimer type of approach<sup>7,11</sup> that are, in principle, exact. When applied in a straightforward manner the latter approach does not speed up with respect to the standard SOS formulation<sup>7</sup> but it can be improved by using efficient algorithms<sup>8,9</sup> and by introducing an optimal polarizability basis.<sup>8</sup> The latter methods are promising but require a profound restructuring of the *GW* method and detailed comparisons, in particular, concerning the prefactor and hence the crossover, with the SOS approach are still missing.<sup>12</sup>

In this work, we present a very efficient method which retains all advantages of the SOS approach, namely, simplicity, a good prefactor, and systematic and controlled accuracy but *completely* eliminates empty states from the entire calculation, leading to an *immediate* speedup for *all* system sizes, as well as an improved scaling. Here we calculate *GW* QP energies to demonstrate the power of our approach but the method is general and can be applied to other spectral quantities.

In the calculation of the *GW* self-energy, the main numerical effort lies in the calculation of the matrix elements of  $\Sigma_c$ , the correlation part of the self-energy. For simplicity, we will focus here on the diagonal matrix elements. The extension to off-diagonal elements is straightforward. In its spectral representation, the diagonal matrix elements  $\Sigma_c^n$  are given by

$$\Sigma_c^n(\omega) = \sum_i \sum_{j \neq 0} \frac{|\langle n | V^j | i \rangle|^2}{\omega + \omega_j \operatorname{sgn}(\mu - \varepsilon_i) - \varepsilon_i}. \quad (2)$$

Here  $|i\rangle$  and  $\varepsilon_i$  are the QP states and energies, respectively,  $\omega_j = E(N, j) - E(N, 0) - i\eta$  are the excitation energies of the  $N$ -electron system minus an infinitesimal  $\eta$  which ensures the correct time ordering,  $\mu$  is the chemical potential, and  $V^j(\mathbf{r})$  are fluctuation potentials<sup>13</sup> which, together with  $\omega_j$  represent  $W$ . Although the method that we will describe in this work is valid for both finite and extended systems we will focus here on the latter. Therefore,  $i$  and  $n$  should be considered multi-indices composed of the band index and the Bloch vector. The summation over  $i$  in Eq. (2) can be split into a summation over  $v$  with  $\varepsilon_v < \mu$  and a summation over  $c$  with  $\varepsilon_c > \mu$ . In the following, we will focus on the latter since it is the bottleneck in the calculation of  $\Sigma_c^n$  as it sums over the, in principle, infinite, empty states of the system. Introducing the

Fourier transforms of the fluctuation potentials, we can re-write this part as

$$\Sigma_c^{n,emp}(\omega) = \sum_{j \neq 0} \sum_{\mathbf{q}, \mathbf{G}, \mathbf{G}'} V_{\mathbf{G}}^j(\mathbf{q}) V_{\mathbf{G}'}^{j*}(\mathbf{q}) S_j^n(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega), \quad (3)$$

where we defined

$$S_j^n(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega) = \sum_c \frac{\tilde{\rho}_{cn}^*(\mathbf{q} + \mathbf{G}) \tilde{\rho}_{cn}(\mathbf{q} + \mathbf{G}')}{\omega - \omega_j - \varepsilon_c} \quad (4)$$

in which  $\tilde{\rho}_{cn}(\mathbf{q} + \mathbf{G}) = \langle c | e^{-i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}} | n \rangle$ . It is the above summation over empty states that we want to eliminate. One can always find a function  $\delta_{nj}(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega)$  such that the following equality holds:

$$S_j^n(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega) = \frac{\sum_c \tilde{\rho}_{cn}^*(\mathbf{q} + \mathbf{G}) \tilde{\rho}_{cn}(\mathbf{q} + \mathbf{G}')}{\omega - \omega_j - \varepsilon_n - \delta_{nj}(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega)} \quad (5)$$

since  $\delta_{nj}(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega)$  has sufficient degrees of freedom. Using the closure relation  $\sum_c |c\rangle \langle c| = 1 - \sum_v |v\rangle \langle v|$ , we obtain an expression for  $S_j^n$  which contains a sum over occupied states only. At variance with related ideas,<sup>6,10</sup> the relation in Eq. (5) is exact; the effective energy  $\varepsilon_n + \delta_{nj}(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega)$  takes into account the contributions of all the empty states to  $S_j^n(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega)$ . For this reason we will refer to this approach as the effective-energy technique (EET). It now remains to transform the expression for  $\delta_{nj}(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega)$  such that no empty states appear. Subtracting Eq. (5) from Eq. (4) and making use of the fact that the  $\varepsilon_i$  are eigenvalues of the Hamiltonian  $\hat{H}(\mathbf{r})$  with eigenstates  $|i\rangle$  (Ref. 6), we obtain

$$\begin{aligned} \delta_{nj}(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega) S_j^n(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega) \\ = \sum_c \frac{\tilde{\rho}_{cn}^*(\mathbf{q} + \mathbf{G}) \langle c | [\hat{H}(\mathbf{r}'), e^{-i(\mathbf{q} + \mathbf{G}') \cdot \mathbf{r}'}] | n \rangle}{[\omega - \omega_j - \varepsilon_c]}. \end{aligned} \quad (6)$$

For notational convenience, we consider a Hamiltonian that contains only a local potential. The derivation can be easily generalized to include Hamiltonians with nonlocal potentials. Working out the commutator and dividing both sides by  $S_j^n$ , we obtain

$$\delta_{nj}(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega) = \frac{|\mathbf{q} + \mathbf{G}'|^2}{2} + \frac{\tilde{S}_j^n(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega)}{S_j^n(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega)}, \quad (7)$$

where we defined

$$\tilde{S}_j^n(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega) = \sum_c \frac{\tilde{\rho}_{cn}^*(\mathbf{q} + \mathbf{G}) \tilde{J}_{cn}(\mathbf{q} + \mathbf{G}')}{[\omega - \omega_j - \varepsilon_c]} \quad (8)$$

in which

$$\tilde{J}_{cn}(\mathbf{q} + \mathbf{G}) = \langle c | e^{-i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}} [i \nabla_{\mathbf{r}}] | n \rangle \cdot (\mathbf{q} + \mathbf{G}). \quad (9)$$

In Eq. (7),  $\delta_{nj}$  is expressed in terms of itself through  $S_j^n$ . Since  $\tilde{S}_j^n$  depends on a summation over the empty states solving for  $\delta_{nj}$  will not lead to the desired result. However, in view of the similarity of Eqs. (4) and (8), we can also rewrite Eq. (8) in terms of only occupied states in an equivalent manner as Eq. (5) using a modified  $\delta_{nj}$ . In principle, this

procedure could be continued *ad infinitum*. However, one wishes to truncate the expression for  $\delta_{nj}$  since, in practice, one would like to use simple expressions. In the following, we will show that these simple expressions already lead to excellent results. Here we give explicitly the first three approximations for  $\delta_{nj}$  that we obtain

$$\delta^{(0)}(\mathbf{q}, \mathbf{G}') = \frac{|\mathbf{q} + \mathbf{G}'|^2}{2}, \quad (10)$$

$$\delta_n^{(1)}(\mathbf{q}, \mathbf{G}, \mathbf{G}') = \frac{|\mathbf{q} + \mathbf{G}'|^2}{2} + \frac{f_n^{pj}(\mathbf{q}, \mathbf{G}, \mathbf{G}')}{f_n^{pp}(\mathbf{q}, \mathbf{G}, \mathbf{G}')}, \quad (11)$$

$$\begin{aligned} \delta_{nj}^{(2)}(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega) = \frac{|\mathbf{q} + \mathbf{G}'|^2}{2} + \frac{f_n^{pj}(\mathbf{q}, \mathbf{G}, \mathbf{G}')}{f_n^{pp}(\mathbf{q}, \mathbf{G}, \mathbf{G}')} \\ \times \left[ \frac{\omega_{nj} - \frac{|\mathbf{q} + \mathbf{G}'|^2}{2} - \frac{f_n^{pj}(\mathbf{q}, \mathbf{G}, \mathbf{G}')}{f_n^{pp}(\mathbf{q}, \mathbf{G}, \mathbf{G}')}}{\omega_{nj} - \frac{|\mathbf{q} + \mathbf{G}'|^2}{2} - \frac{f_n^{jj}(\mathbf{q}, \mathbf{G}, \mathbf{G}')}{f_n^{pj}(\mathbf{q}, \mathbf{G}, \mathbf{G}')}} \right], \end{aligned} \quad (12)$$

where  $\omega_{nj} = \omega - \omega_j - \varepsilon_n$  and

$$f_n^{ab}(\mathbf{q}, \mathbf{G}, \mathbf{G}') = \sum_c \tilde{a}_{cn}^*(\mathbf{q} + \mathbf{G}) \tilde{b}_{cn}(\mathbf{q} + \mathbf{G}'), \quad (13)$$

where  $a$  and  $b$  can be either  $\rho$  or  $j$ .<sup>14</sup> We use the closure relation to get rid of the sum over empty states in  $f_n^{ab}$ . Note that, in particular, the expression for  $\delta_{nj}^{(2)}$  is simple but highly nontrivial due to its frequency dependence. Higher-order expressions for  $\delta_{nj}$  will contain terms with higher-order derivatives of the valence wave functions as well as derivatives of the potential. Our results show that these terms can be safely neglected. We note that the EET is exact in the limit of a homogeneous electron gas starting at order  $\delta_n^{(1)}$ .<sup>15</sup> The approximations for  $\delta_{nj}$  in Eqs. (10)–(12) are asymmetric with respect to  $\mathbf{G}$  and  $\mathbf{G}'$ . This is due to the freedom in choosing whether the Hamiltonian in Eq. (6) is applied inside the left or right matrix element. Since the exact  $\delta_{nj}$  is Hermitian, we symmetrize the above results such that this exact constraint is met at each level of approximation.

In practice, the excitation energies  $\omega_j$  that enter  $\Sigma_c^n$  are not known and as a first step  $\epsilon$  has to be calculated. This  $\epsilon$  relies on the calculation of  $\chi^0$  which in its spectral representation is given by

$$\chi_{\mathbf{G}\mathbf{G}'}^0(\mathbf{q}, \omega) = \sum_{s=\pm 1} \sum_{v,c} \frac{\tilde{\rho}_{cv}^*(\mathbf{q} + \mathbf{G}) \tilde{\rho}_{cv}(\mathbf{q} + \mathbf{G}')}{s\omega - (\varepsilon_c - \varepsilon_v) + i\eta}. \quad (14)$$

Since  $\chi^0$  has a similar structure as  $\Sigma_c^n$ , we can also apply the EET here to obtain an expression that does not contain any empty states. The result is given by

$$\chi_{\mathbf{G}\mathbf{G}'}^0(\mathbf{q}, \omega) = \sum_{s=\pm 1} \sum_v \frac{f_v^{pp}(\mathbf{q}, \mathbf{G}, \mathbf{G}')}{s\omega - \delta'_v(\mathbf{q}, \mathbf{G}, \mathbf{G}', s\omega) + i\eta}. \quad (15)$$

The approximations for  $\delta'$  equal those for  $\delta$  given in Eqs. (10)–(12) with the difference that  $\omega_{nj}$  has to be replaced by

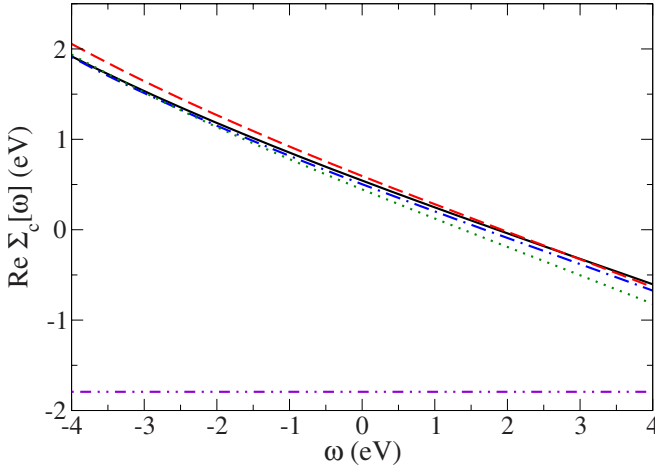


FIG. 1. (Color online) The real part of  $\Sigma_c(\omega)$  for the highest occupied band at  $\Gamma$  for Si around the LDA orbital energy (set to 0 eV). Solid line (black):  $G^0W^0$  (SOS); dotted line (green):  $G^0W^0$  (EET:  $\delta^{(2)}$  and  $\delta^{(0)}$ ); dashed line (red):  $G^0W^0$  (EET:  $\delta^{(2)}$  and  $\delta^{(2)}$ ); dotted-dashed line (blue):  $G^0W^0$  (EET:  $\delta^{(4)}$  and  $\delta^{(4)}$ ); double-dotted-dashed line (violet): COHSEX.

$\omega$ . We have thus arrived at a simple  $GW$  method without summations over empty states. Moreover, once the  $f_n^{ab}$  are determined the calculation of  $\Sigma_c^{emp}(\chi^0)$  scales as  $N_n N_G^2 (N_v N_G^2)$  versus  $N_c N_n N_G^2 (N_c N_v N_G^2)$  for the SOS approach, where  $N_n$  is the number of diagonal matrix elements of  $\Sigma_c$ ,  $N_v$  and  $N_c$  are the number of occupied and empty states, respectively, and  $N_G$  is the number of plane waves. The calculation of the  $f_n^{ab}$  can be done straightforwardly from  $\bar{\rho}$  and  $\tilde{j}$  for an immediate overall speedup for any system on the order of  $N_c/N_v$  with respect to the SOS approach or one can improve the scaling using fast-Fourier transforms.<sup>16</sup> We note that since Eqs. (4) and (5) are similar and also Eqs. (14) and (15), if desired, the EET can be combined with the ideas of Refs. 8 and 9, e.g., basis design, to get further speedups.

To illustrate the EET, we have implemented it in the ABINIT software package<sup>17</sup> and performed  $G^0W^0$  calculations for some materials with zero-order energies and wave functions obtained from Kohn-Sham density-functional theory within the local-density approximation (LDA).<sup>18</sup> We used a generalized plasmon-pole model fitting  $\epsilon^{-1}$  at imaginary frequencies.<sup>19</sup> In Fig. 1, we plot the real part of  $\Sigma_c$  for the highest occupied band of bulk silicon at the  $\Gamma$  point as a function of the frequency around the LDA orbital energy. We compare our EET results using various approximations for  $\delta$  and  $\delta'$  with the converged SOS results (200 empty bands) and those obtained with the static COHSEX approximation. Using  $\delta^{(2)}$  in  $\chi^0$  and  $\delta^{(0)}$  in  $\Sigma$ , we already obtain results that are in excellent agreement with the SOS result over the whole frequency range of interest, thereby largely improving on the COHSEX self-energy (using  $\delta^{(0)}$  in  $\chi^0$  we obtain self-energies which are, in general, not sufficiently accurate). With higher-order approximations, we can improve the results further. Since, in general,  $\delta^{(2)}$  and  $\delta^{(2)}$  lead to  $G^0W^0$  results that are in good agreement with the exact SOS results and since the difference with results obtained using higher-order approximations is small, we will use  $\delta^{(2)}$  and  $\delta^{(2)}$  in the remainder unless stated otherwise.

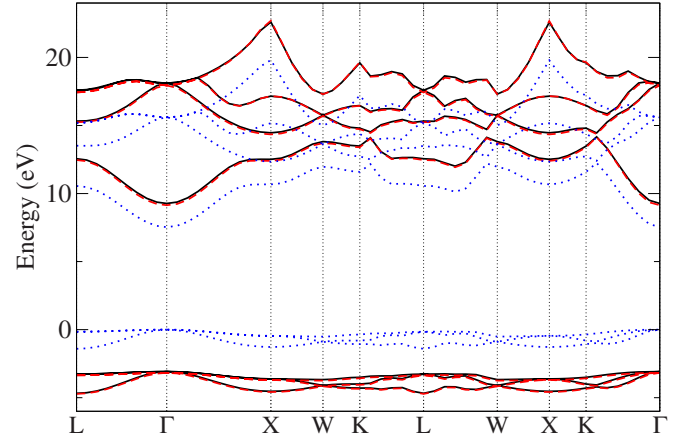


FIG. 2. (Color online) Band structure of solid argon. Solid line (black):  $G^0W^0$  (SOS); dashed line (red):  $G^0W^0$  (EET); dotted line (blue): LDA.

We also applied the EET to solid and atomic argon because they provide good test cases for two reasons: first, they are very inhomogeneous systems and therefore very different from the homogeneous systems for which our expressions become exact and, second, the  $G^0W^0$  QP energies lie far from the LDA energies. In Fig. 2, we plot the  $G^0W^0$  band structure of solid argon for the three highest occupied bands and four lowest empty bands using the standard SOS approach and the EET. The two band structures are almost indistinguishable. We also reported the LDA band structure to show the large difference between LDA and  $G^0W^0$  energies. In Table I, we summarize our EET results for the fundamental gaps of silicon and solid argon, the direct band gap at  $\Gamma$  of silicon and the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap of atomic argon. We obtain a large improvement with respect to the COHSEX results which largely overestimate the  $G^0W^0$  band gaps and a very good agreement with the SOS approach. Moreover, the accuracy of the *absolute* COHSEX energies is in the order of 1 eV while the accuracy of the *absolute* EET energies is in the order of 0.1 eV. This means that accurate calculations of, for example, band off-sets with the EET can be performed since, contrary to COHSEX, it does not rely on error cancellation.

In Table I, we also report the  $G^0W^0$  band gap of  $\text{SnO}_2$  obtained using the SOS approach and the EET which again agree well. We note that the  $\chi^0$  and  $\Sigma$  SOS calculations for  $\text{SnO}_2$  required 1000 and 1600 bands, respectively, while the

TABLE I. Fundamental gaps ( $E_g$ ) of silicon, solid argon, and  $\text{SnO}_2$ , the direct band gap at  $\Gamma$  ( $\Gamma^v - \Gamma^c$ ) of silicon and the HOMO-LUMO gap of atomic argon ( $H-L$ ).

	LDA	$G^0W^0$ (SOS)	$G^0W^0$ (EET)	COHSEX
Silicon ( $E_g$ )	0.52	1.20	1.19	1.75
Silicon ( $\Gamma^v - \Gamma^c$ )	2.56	3.23	3.22	3.76
Solid argon ( $E_g$ )	7.53	12.4	12.3	14.6
Atomic argon ( $H-L$ )	9.81	14.6	14.5	15.8
$\text{SnO}_2$ ( $E_g$ )	0.91	2.88	2.94	4.61

TABLE II. Fundamental gap ( $E_g$ ) of SnO<sub>2</sub> obtained with self-consistent COHSEX+ $G^0W^0$  ( $GW$ ) using the EET.

	LDA	$GW$	Experiment (Ref. 20)
SnO <sub>2</sub> ( $E_g$ ) <sup>a</sup>	0.9	3.8	3.6

<sup>a</sup>Reference 22.

EET calculations just required 34 occupied bands. The  $G^0W^0$  band gap of SnO<sub>2</sub> is not in good agreement with the experimental band gap of 3.6 eV.<sup>20</sup> This is due to the fact that the LDA energies and wave functions do not provide a good starting point for the  $G^0W^0$  calculation. However, within the  $GW$  method, we can recalculate the screening and self-energy using updated energies and wave functions by including some form of self-consistency. Using the SOS approach, even the simplest  $GW$  method involving self-consistency, the self-consistent COHSEX+ $G^0W^0$  approach<sup>21</sup> is computationally quite demanding because  $\chi^0$  has to be recalculated. This means that the energies and wave functions have to be updated during self-consistency. This bottleneck can now be reduced by applying the EET to the calculation of both the static  $\chi^0$  in the self-consistent COHSEX calculation and the subsequent  $G^0W^0$  self-energy. We can thus include self-consistency effects using occupied states only. Using the EET, we were now able to determine the  $GW$  band gap of SnO<sub>2</sub> to be 3.8 eV which is in good agreement with experi-

ment. This result, which is summarized in Table II, confirms that the EET could indeed be the method of choice for the study of, e.g., TCOs.

In conclusion, we have introduced the effective-energy technique which permits a simple and efficient evaluation of spectral representations without summing over the infinite number of empty states. Moreover, the EET speeds up calculations by more than an order of magnitude for systems of any size. We have illustrated our approach by applying it to the  $G^0W^0$  method and shown that the results perfectly reproduce the SOS results. Furthermore, by combining the EET with the self-consistent COHSEX+ $G^0W^0$  approach, we demonstrated its power by calculating the band gap of SnO<sub>2</sub>. The band gap thus obtained is in good agreement with that found in experiment. Large speedups of more advanced self-consistent  $GW$  approaches<sup>23</sup> are also expected when combined with the EET since only QP wave functions and energies of occupied states need to be updated. Other potential applications of the EET include the calculation of RPA total energies,<sup>24</sup> optimized effective potentials<sup>25</sup> and kernels,<sup>26</sup> and the modeling of self-energies.

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<sup>14</sup>Note that Eq. (5) has poles and that an approximate  $\delta$  could lead to spurious poles. In practice, we avoid this by constraining our

approximations using integral mean-value theorems.

<sup>15</sup>Instead, simply replacing  $\delta_{nj}$  with its homogeneous electron-gas expression does, in general, not lead to sufficiently accurate results.

<sup>16</sup>The part of  $\Sigma_c^n(\omega)$  in Eq. (2) for which  $\epsilon_i < \mu$  scales as  $N_n N_v N_G^2$  but the total number of operations is small.

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