

## Exploring the accuracy of the equation-of-motion coupled-cluster band gap of solids

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(Received 22 January 2025; accepted 27 February 2025; published 26 March 2025)

While the periodic equation-of-motion coupled-cluster (EOM-CC) method promises systematic improvement of electronic band gap calculations in solids, its practical application at the singles and doubles level (EOM-CCSD) is hindered by severe finite-size errors in feasible simulation cells. We present a hybrid approach combining EOM-CCSD with the computationally less demanding  $GW$  approximation to estimate thermodynamic limit band gaps for several insulators and semiconductors. Our method substantially reduces required cell sizes while maintaining accuracy. Comparisons with experimental gaps and self-consistent  $GW$  calculations reveal that deviations in EOM-CCSD predictions correlate with reduced single excitation character of the excited many-electron states. Our work not only provides a computationally tractable approach to EOM-CC calculations in solids but also reveals fundamental insights into the role of single excitations in electronic-structure theory.

DOI: [10.1103/PhysRevB.111.L121202](https://doi.org/10.1103/PhysRevB.111.L121202)

**Introduction.** The electronic band gap is an important quantity in semiconductor physics and materials science. It is a fundamental measure of a material's optical and electronic properties. While density functional theory (DFT) is the state-of-the-art computational method for the electronic structure of materials, its predictive power for band gaps is limited. Local and semilocal exchange-correlation density functional approximations (DFAs) significantly underestimate band gaps [1]. Nonlocal functionals that include a fraction of exact exchange can improve accuracy but often require the tuning of parameters. The  $GW$  approximation [2,3], particularly in its noniterative  $G_0W_0$  form, has emerged as the state-of-the-art method for band structure calculations. However,  $G_0W_0$  results are sensitive to the choice of the underlying DFA, known as the starting-point dependence [4,5].

To obtain accurate electronic band gaps, more advanced methods that systematically incorporate higher orders of electronic correlation effects are needed. Currently, one is left with a choice between three methods. The first one consists in the self-consistent solution of Hedin's equations ( $GW$ ) in combination with an additional vertex correction in the screened interaction that is neglected in  $GW$ . The resulting method, known as  $GW^{\text{TC-TC}}$ , has been shown to yield good agreement with experimental band gaps [6]. One must emphasize that in the  $GW^{\text{TC-TC}}$  method only the quasiparticle energies are treated self-consistently while for the orbitals

the single-particle states of the initial mean-field method, in this work the HSE06 DFA [7], are not updated. The high accuracy of  $GW^{\text{TC-TC}}$  can only be inferred by comparing to experimental gaps properly corrected for zero-point renormalization (ZPR) [8–10]. Quantum Monte Carlo (QMC) methods offer an alternative avenue to obtain a highly accurate description of electronic correlation. While QMC ground state energies often serve as benchmark results, their application to the electronic band gap of materials has been explored only very recently [11,12]. Similarly new to the field of materials science, is the equation-of-motion coupled-cluster (EOM-CC) method [13], which has been used to study both neutral [14–16] and charged excitations [17,18] in solids. In both, the QMC and EOM-CC studies the most challenging obstacle to obtain well converged band gaps was identified to be the finite-size error. This error decays relatively slowly with respect to the employed super cell size or  $k$ -point mesh used to sample the Brillouin zone of the primitive unit cell. To better understand the corresponding scaling law, we previously derived the leading order contributions to the finite-size error of the EOM-CC band gap [19]. On top of that, we verified numerically that the finite-size error of both the  $G_0W_0$  and the EOM-CCSD band gap converge with the same rate, which motivates a hybrid approach, in which the convergence behavior can firstly be determined using the substantially cheaper  $G_0W_0$  method and subsequently be employed for the extrapolation of the EOM-CCSD band gap. Here, we apply this new technique to estimate the fundamental EOM-CCSD band gap of a number of insulators and semiconductors.

**Method.** To calculate the electronic band gap in the CC theoretical framework, we employ the ionization potential (IP) and electron affinity (EA)-EOM-CC method. In the case of periodic solids, the IP and EA correspond to the quasiparticle energies of valence and conduction bands, respectively. Here, we provide a succinct summary of the EOM-CC theory. For a

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detailed account of the electronic structure factor in EOM-CC theory, which is crucial for the derivation of the scaling law of the band gap with respect to system size, see Ref. [19] and references therein.

The EOM-CC methodology is based on the similarity-transformed Hamiltonian  $\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$ , where  $\hat{T}$  is the cluster operator of ground-state CC theory and  $\hat{H}$  is the electronic Hamiltonian. The wave function of the  $n$ th excited state of the charged system  $|\Psi_n^{N\mp 1}\rangle$  is obtained by applying an excitation operator  $\hat{R}_n^{\text{IP/EA}}$  to  $|\Psi_0\rangle$ , which is the ground-state wave function of CC theory [13]:

$$|\Psi_n^{N\mp 1}\rangle = \hat{R}_n^{\text{IP/EA}} |\Psi_0\rangle. \quad (1)$$

The ground-state CC many-electron wave function  $|\Psi_0\rangle$  is defined by an exponential ansatz  $|\Psi_0\rangle = e^{\hat{T}} |\Phi_0\rangle$ .  $|\Phi_0\rangle$  is a Slater determinant corresponding to the ground-state wave function of a preceding mean-field calculation, usually Hartree-Fock (HF). The  $\hat{R}_n^{\text{IP}}$  and  $\hat{R}_n^{\text{EA}}$  operators in the EOM-CC method with single and double excitations (EOM-CCSD) are  $\hat{R}_n^{\text{IP}} = \sum_i r_{i,n} \hat{a}_i + \sum_{ij,a} r_{ij,n}^a \hat{a}_i^\dagger \hat{a}_j$  and  $\hat{R}_n^{\text{EA}} = \sum_a r_n^a \hat{a}_a^\dagger + \sum_{iab} r_{i,n}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i$ , respectively. The indices  $i, j$  and  $a, b$  denote occupied and virtual orbitals, respectively. In the case of Bloch orbitals, the orbital index serves as compound index for the  $k$  vector of the primitive unit cell and the band index.

IP/EA-EOM-CCSD excitation energies are the eigenvalues of  $\bar{H}$ :

$$\bar{H}(\hat{R}_n^{\text{IP/EA}} |\Phi_0\rangle) = E_n^{\text{IP/EA}} (\hat{R}_n^{\text{IP/EA}} |\Phi_0\rangle), \quad (2)$$

where  $r_{i,n}$ ,  $r_{ij,n}^a$  and  $r_n^a$ ,  $r_{i,n}^{ab}$  are the amplitudes of excited many-electron states. The fundamental electronic band gap is given by the sum between the first IP and EA excitation energies,

$$E_{\text{gap}}^{\text{EOM}} = E^{\text{IP}} + E^{\text{EA}}. \quad (3)$$

Note that we have dropped the state index  $n$  for brevity. One useful metric to classify EOM-CC excitations is the single excitation character, defined as

$$n_1^{\text{IP}} = \sum_i |r_i|^2 \quad n_1^{\text{EA}} = \sum_a |r_a|^2. \quad (4)$$

Especially for low-order truncations of EOM-CC theory like the EOM-CCSD method values of  $n_1^{\text{IP/EA}}$  close to 1 are associated with an increased accuracy [20].

In this work we employ an efficient extrapolation approach that relates the scaling of EOM-CC and  $G_0W_0$  gaps with respect to super cell size. We first perform a series of  $G_0W_0$  band gap calculations sampling the first Brillouin zone employing a  $k$  mesh with a total of  $N_k$  points. These  $G_0W_0$  band gaps are fitted to

$$E_{\text{gap}, N_k}^{G_0W_0} = E_{\text{gap}, \text{TDL}}^{G_0W_0} + AN_k^{-\frac{1}{3}} + BN_k^{-\frac{2}{3}} + CN_k^{-1}. \quad (5)$$

Although the above equation was derived for EOM-CCSD band gaps ( $E_{\text{gap}}^{\text{EOM}}$ ), we find that it works well for  $G_0W_0$  [19]. This can partly be attributed to the fact that the  $G_0W_0$  and EOM-CCSD methods are closely related, which was elucidated in Refs. [21,22]. We emphasize that there exist well established corrections to the finite-size error in the  $G_0W_0$  band gap, which are referred to as head and wing corrections [23]. Here, however, we take advantage of the similar finite-size scaling in  $G_0W_0$  and EOM-CCSD theory by proceeding

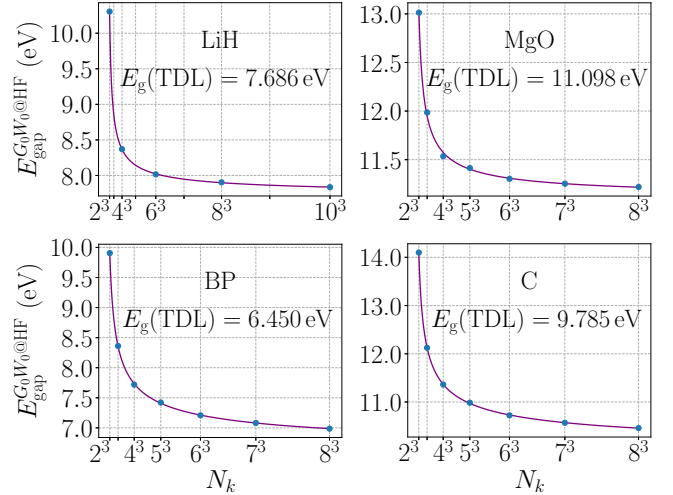


FIG. 1. Scaling of the  $G_0W_0$ @HF band gaps of LiH, MgO, BP, and C with respect to the  $k$  mesh using FHI aims (NAOs). The data points were fitted and extrapolated using the expression  $E_{\text{gap}, N_k}^{G_0W_0@HF} = E_{\text{gap}, \text{TDL}}^{G_0W_0@HF} + AN_k^{-1/3} + BN_k^{-2/3} + CN_k^{-1}$  [see Eq. (5)].  $E_g(\text{TDL})$  is a shorthand notation for  $E_{\text{gap}, \text{TDL}}^{G_0W_0@HF}$ , i.e., the result of a converged  $k$  summation.

without these corrections. Based on Eq. (5), the  $G_0W_0$  and EOM-CCSD band gaps are related by [19]

$$\frac{E_{\text{gap}, N_k}^{\text{EOM}} - E_{\text{gap}, \text{TDL}}^{\text{EOM}}}{E_{\text{gap}, N_k}^{G_0W_0} - E_{\text{gap}, \text{TDL}}^{G_0W_0}} = \frac{A'N_k^{-\frac{1}{3}} + B'N_k^{-\frac{2}{3}} + C'N_k^{-1}}{AN_k^{-\frac{1}{3}} + BN_k^{-\frac{2}{3}} + CN_k^{-1}}, \quad (6)$$

where  $A', B', C'$  correspond to expansion coefficients of  $E_{\text{gap}, N_k}^{\text{EOM}}$ . In the thermodynamic limit (TDL), that is for  $N_k \rightarrow \infty$ , the above equation becomes  $\frac{A'}{A} = b$ . Equation (6) can also be written as

$$E_{\text{gap}, N_k}^{\text{EOM}} = a + b \cdot (E_{\text{gap}, N_k}^{G_0W_0} - E_{\text{gap}, \text{TDL}}^{G_0W_0}), \quad (7)$$

where  $a$  stands for  $E_{\text{gap}, \text{TDL}}^{\text{EOM}}$ . The assumption of the present work is that the EOM-CCSD and  $G_0W_0$  expansion coefficients are proportional, such that  $\frac{A'}{A} \approx \frac{B'}{B} \approx \frac{C'}{C}$ . In this case Eq. (7) holds approximately already for smaller system sizes, which is corroborated by the findings summarized in the next section. Furthermore,  $a$  and  $b$  can be interpreted as system specific parameters determined from fitting Eq. (7) to a set of band gaps computed on the level of  $G_0W_0$  and EOM-CCSD theory for a number of relatively small  $N_k$ 's. We note that for  $G_0W_0$  calculations,  $k$  summations are performed using  $k$  meshes that correspond to the super cells used for the EOM-CCSD calculations. Furthermore the  $G_0W_0$  calculations in the above procedure employ the same HF single-particle energies and wave functions ( $G_0W_0$ @HF).

**Results.** We now assess the system size convergence of the  $G_0W_0$  band gaps and their extrapolation to the TDL based on Eq. (5). Figure 1 shows that the computed  $G_0W_0$  band gaps are well approximated by Eq. (5) previously derived for IP/EA-EOM-CCSD energies, indicating that both methods yield band gaps that converge to the TDL with the same asymptotic behavior. This is supported by Lange and Berkelbach [21], who showed that the  $G_0W_0$ @HF and IP- and EA-EOM-CCSD

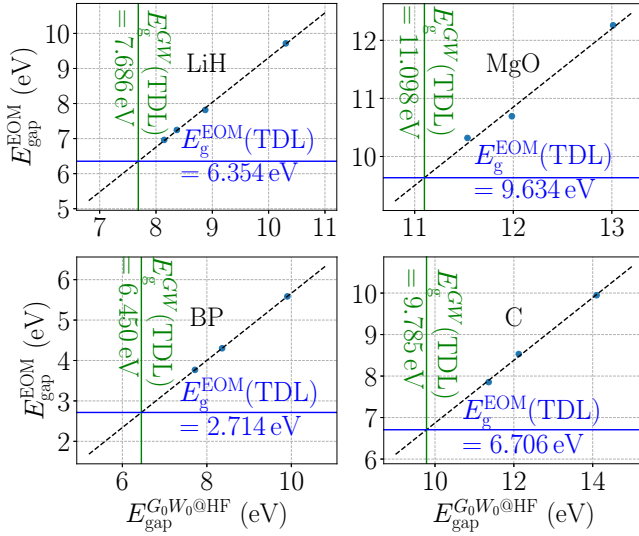


FIG. 2. Correlation of the EOM-CCSD and  $G_0W_0@HF$  band gap convergence of LiH, MgO, BP, and C with increasing super cell size (EOM-CCSD) and  $k$ -mesh density ( $G_0W_0@HF$ ) using FHI aims. The extrapolated TDL value of the  $G_0W_0@HF$  and of the EOM-CCSD band gap is denoted by  $E_g^{GW}(TDL)$  and  $E_g^{EOM}(TDL)$  and marked by green and blue lines, respectively. The number of  $k$  points increases from  $2 \times 2 \times 2$ , over  $3 \times 3 \times 3$  to  $4 \times 4 \times 4$ . For LiH, results for  $5 \times 5 \times 5$  are also shown.

approximations feature identical low-order ring terms that also play an important role for long-range correlation effects in the ground state [24]. In contrast to the ground-state CC correlation energy, which is known to converge to the TDL with a  $1/N_k$  rate for insulators [25,26], our analysis suggests in general a  $1/N_k^{1/3}$  leading-order behavior of the band gap in the large  $N_k$  limit [19]. Moreover, additional next-to-leading-order contributions need to be included to model the band gap convergence for relatively small  $k$  meshes. The results above have been obtained using FHI-aims (see the Supplemental Material for computational details [27] and Refs. [28–32] therein).

The next step in the procedure outlined above lies in determining how the scaling behavior of the  $G_0W_0@HF$  band gap and the EOM-CCSD band gap are correlated with each other. Figure 2 shows the band gaps of the two methods plotted against each other and fitted according to Eq. (7). Note that these band gaps have been obtained using finite basis sets described in the Supplemental Material [27]. Indeed, we find that the data points of the four materials consistently lie on a straight line. The validity of the herein established relation between the two methods is most clear in the case of LiH, where a fourth data point ( $5 \times 5 \times 5$ ) is accessible due to the small number of electrons per unit cell. For LiH, all four points align on a straight line. This enables a direct estimation of the EOM-CCSD band gap in the TDL depicted in the plots of Fig. 2 at the intersection point between the linear fit and the green vertical line, which shows  $E_{gap,TDL}^{G_0W_0@HF}$  determined previously in Fig. 1. Let us emphasize that our approach only depends on the scaling behavior of the  $G_0W_0@HF$  gap, its absolute value is irrelevant. For C, BP, and MgO we find that the extrapolated EOM-CCSD band gap value changes at most by 0.3 eV if the extrapolation is performed using the

$2 \times 2 \times 2$  and  $3 \times 3 \times 3$  data points only, omitting the biggest super cell size of  $4 \times 4 \times 4$ . To confirm the correctness of the IP and EA-EOM-CCSD implementation in combination with FHI aims, a small molecular benchmark was conducted and compared to published results (see Tables S4 and S5 in Ref. [27] and also Refs. [33,34] therein). We note that for the EOM-CCSD band gap calculation of the  $4 \times 4 \times 4$  BP simulation cell, about 1.5 million hours CPU time were used. The CCSD, EA-EOM-CCSD, and IP-EOM-CCSD part of these calculations took 62%, 33%, and 5% of the total time, respectively. We emphasize that our EOM-CCSD calculations were performed for supercells. Taking advantage of momentum conservation would drastically reduce the computational effort, but has not yet been implemented in CC4S.

We now turn to the discussion comparing EOM-CCSD band gaps obtained with different implementations. Specifically, we have carried out EOM-CCSD calculations employing electronic Hamiltonians computed by FHI aims and VASP. These are interfaced implementations [30,32,43] using super cells, equivalent to corresponding  $k$  meshes of the primitive unit cell. Additionally, we compare our findings against EOM-CCSD results from a previous PySCF study by Vo, Wang, and Berkelbach [18]. PySCF calculations used pseudopotentials optimized for Hartree-Fock and Gaussian-type orbitals (GTOs). VASP employs the frozen core approximation with DFT-PBE core states, but including core-valence exact exchange [44]. The present FHI-aims calculations employ the frozen core approximation only on the level of post-HF theories. Therefore core-valence correlation is neglected in all summarized results, whereas the treatment of core-valence exchange differs among the compared methods. In the complete basis set and thermodynamic limit, the band gaps for the same systems should agree to within remaining uncertainties that derive from, e.g., differences in the frozen core approximation. Indeed, we find that VASP and FHI-aims agree well with each other. Table I shows that for LiH and BP our EOM-CCSD band gaps computed with FHI aims and VASP yield excellent agreement to within 0.1 eV. Only for MgO and C, VASP and FHI aims exhibit discrepancies of about 0.3–0.4 eV. This can be partly attributed to the fact that VASP calculations only employed  $2 \times 2 \times 2$  and  $3 \times 3 \times 3$  super cells due to computational constraints. Note that in contrast to the band gaps depicted in Fig. 2, Table I summarizes band gaps that have also been corrected for the basis set incompleteness error as described in Sec. S3 of the Supplemental Material [27].

Table I reveals that the differences between the FHI aims and VASP gaps compared to the PySCF results are significant. For LiH, C, MgO, and BP the average absolute difference of the EOM-CCSD gaps between VASP/FHI aims and PySCF is 0.8 eV, whereas VASP and FHI aims agree to within 0.2 eV on average. What is the reason for these significant discrepancies? Both works have tried to converge the computed band gaps with respect to accessible basis set and system size. For example, Fig. 2 of Ref. [18] depicts TDL extrapolations of EOM-CCSD band gaps for different basis sets. In agreement with our findings, the basis set convergence of EOM-CCSD band gaps is relatively fast, indicating that the most likely source of the discrepancy are finite-size errors. Both TDL extrapolations shown in our Fig. 2 and Fig. 2 from Ref. [18] look reliable at first sight for the system sizes studied ( $2 \times 2 \times 2$

TABLE I. Comparison of EOM-CCSD band gaps calculated using different computer codes: NAO-based FHI-aims and PAW-based VASP results obtained from the linear fit against  $G_0W_0$  gaps as shown in Figs. 2 and S2 and corrected for basis set incompleteness (see discussion in Sec. S3) [27]. PySCF results were taken from Ref. [18].  $GW^{TC-TC}$  results and experimental values are shown for reference. The zero-point renormalized value (w/o ZPR) is shown next to the experimentally observed (obs.) one. All values in eV.

| Material | EOM-CCSD          |                       |       | $GW^{TC-TC}$ |                           | Exp. |
|----------|-------------------|-----------------------|-------|--------------|---------------------------|------|
|          | VASP <sup>a</sup> | FHI aims <sup>b</sup> | PySCF | VASP         | w/o ZPR (obs.)            |      |
| LiH      | 6.25              | 6.32                  | 5.85  | 5.52         | 5.43 (4.99) <sup>g</sup>  |      |
| C        | 5.75              | 6.15                  | 4.88  | 5.88         | 5.80 (5.48) <sup>c</sup>  |      |
| BP       | 2.27              | 2.38                  | 1.65  | 2.19         | 2.26 (2.16) <sup>f</sup>  |      |
| MgO      | 9.52              | 9.19                  | 8.34  | 8.10         | 8.36 (7.83) <sup>i</sup>  |      |
| Si       | 1.29              |                       | 0.93  | 1.24         | 1.23 (1.17) <sup>d</sup>  |      |
| BN       | 6.62              |                       | 6.45  | 6.58         | 6.5 (6.1) <sup>e</sup>    |      |
| LiF      | 16.19             |                       | 15.43 | 14.73        | 15.43 (14.2) <sup>h</sup> |      |
| LiCl     | 9.90              |                       | 9.43  | 9.53         | 9.94 (9.40) <sup>j</sup>  |      |

<sup>a</sup>Extrapolating from  $n \times n \times n$  super cells with  $n = 2$  and 3.

<sup>b</sup>Extrapolating from  $n \times n \times n$  super cells with  $n = 2, 3$ , and 4.

<sup>c</sup>[35]; <sup>d</sup>[36]; <sup>e</sup>[37]; <sup>f</sup>[38]; <sup>g</sup>[39]; <sup>h</sup>[40]; <sup>i</sup>[41]; and <sup>j</sup>[42].

to  $4 \times 4 \times 4$ ). However, we stress that the  $N_k^{-1/3}$  TDL extrapolations in Ref. [18] assume that the studied systems are already large enough such that the band gap convergence is dominated by the corresponding leading-order finite-size error. Yet, based on numerical findings for low-dimensional systems, we expect that system sizes of about  $8 \times 8 \times 8$  would be needed to observe a convergence that follows the single exponent  $N_k^{-1/3}$  behavior [19]. In fact, employing an  $N_k^{-1/3}$  TDL extrapolation of the EOM-CCSD gaps for LiH with VASP and FHI aims would also exhibit a large discrepancy on the scale of more than 1 eV (see the Supplemental Material [27]). We also note that the approach of Ref. [18] yields band gaps that converge from below with increasing  $k$ -mesh densities, whereas our band gaps converge from above. The reason for this different behavior in Refs. [17,18] is that the underlying HF calculations neglect the integrable singularity contribution of the Coulomb potential in the exchange operator, leading to underestimated HF band gaps. We argue that the finite-size errors in the EOM-CCSD band gap of Ref. [18] are still dominated by the underlying HF finite-size errors, which only partly cancel with EOM-CCSD finite-size errors. In contrast, our finite-size errors originate from post-HF EOM-CCSD terms, which decrease the HF band gap for increasing super-cell sizes. The treatment of the singularity of the Coulomb potential strongly affects the finite-size convergence behavior of HF [45] and CC [17,26] theories. To summarize, we conclude that our  $GW$ -scaling EOM-CCSD extrapolation technique efficiently compensates finite-size errors and that the obtained band gaps are better converged than those obtained in a previous study by Vo *et al.* [18].

Before discussing the accuracy of EOM-CCSD band gaps, we briefly focus on  $GW^{TC-TC}$  and the experimental band gaps summarized in Table I.  $GW^{TC-TC}$  calculations were performed using the projector augmented wave (PAW) method

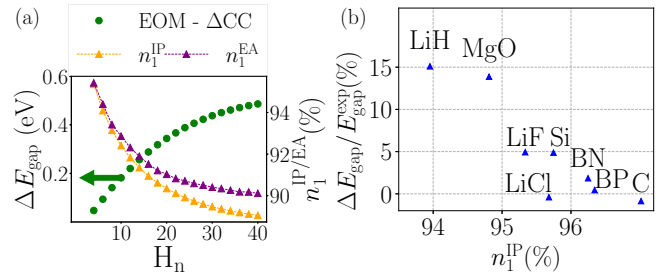


FIG. 3. (a) Single excitation character and gap deviation of EOM-CCSD relative to  $\Delta CCSD(T)$  gap for the molecular hydrogen chain with respect to the chain length. (b) Relation between relative error of EOM-CCSD gap compared to the experiment and single excitation character.

as implemented in VASP (see the Supplemental Material for computational details [27] and Refs. [6,46] therein) and are in excellent agreement with ZPR corrected experimental band gaps for all studied systems, confirming the claims of Refs. [8,9]. The employed ZPR correction is explained in Ref. [9] and computational details can be found in the Supplemental Material [27]. In agreement with recent findings, the ZPR corrections are significant for C and MgO [8]. Here, we show that the ZPR corrections for LiH are also on the scale of about 0.4 eV, substantially larger than previously reported in Ref. [47] and in agreement with experiment [48]. The good agreement between  $GW^{TC-TC}$  and the (ZPR corrected) experiment supports our confidence in the correctness of the experimental gaps.

We now turn to the discussion of the accuracy of EOM-CCSD gaps compared to experiment. Note that FHI-aims EOM-CCSD gaps were obtained using larger super-cell sizes to verify the reliability of the computationally cheaper VASP EOM-CCSD calculations using smaller super cell sizes. The latter approach could also be applied to a larger number of systems. It is noteworthy that our EOM-CCSD gaps are in excellent agreement with ZPR corrected experimental gaps for C, Si, LiCl, BN, and BP. However, the large errors of EOM-CCSD band gaps for LiH, LiF, and MgO are unexpected given the accuracy achieved by IP-EOM-CCSD for small molecules compared to the experiment, where mean absolute deviations of about 0.15 eV have been observed [20]. Is the EOM-CCSD approximation less accurate for periodic systems than for molecular systems? To address this question, we investigate the single excitation character of the EOM-CCSD states,  $n_1^{IP/EA}$ , which has been used in previous studies to explain the performance of a variety of CC methods for molecular IPs [20,49–51] and neutral double excitations [52]. Before discussing our findings for periodic systems, we demonstrate the significance of  $n_1^{IP/EA}$  using the hypothetical example of dimerized hydrogen chains ( $H_4$  to  $H_{40}$ ). We compare band gaps calculated via EOM-CCSD against  $\Delta CCSD(T)$ —a reference method [21,53] that explicitly computes the ground-state energy of the charged  $n + 1$  and  $n - 1$ -electron systems thus capturing orbital relaxation effects upon addition/removal of an electron. Using a 20% bond length alternation to ensure insulating behavior, Fig. 3(a) clearly demonstrates that the agreement of EOM-CCSD with  $\Delta CCSD(T)$  deteriorates

from 50 meV for  $H_4$  to 0.5 eV for  $H_{40}$ . This deviation correlates with a decrease in  $n_1^{\text{IP/EA}}$  from 95% to about 90%, highlighting the limitations of EOM-CCSD for extended systems.

Finally, we investigate the relationship between the single excitation character and the deviation of the EOM-CCSD band gap from the experimental value. Figure 3(b) depicts that we find small relative errors with respect to experiment for  $n_1^{\text{IP}}$  values above  $\approx 95.5\%$ , while all materials with a smaller single excitation character (LiH, LiF, and MgO) exhibit a sizable disagreement compared to the experiment. Figure S7 shows that the single excitation character monotonically decreases with increasing simulation cell size for the IP. The same trend, even though with a smaller magnitude, can be observed for the EA (see Fig. S6 in Ref. [27]). In the case of LiH, whose band gap we find to deviate by 0.82 eV from the experiment, this decrease of  $n_1^{\text{IP}}$  is most prominent, dropping by 2%. For MgO, the single excitation character of the IP is also relatively low (94.2%) and comparable to that of LiH (93.6%). In the case of IP-EOM-CCSD one can clearly see that the magnitude of the single excitation character differs visibly between the materials which are in good agreement with the experiment and those which exhibit sizable disagreement in the band gap value. This is strong evidence that the single excitation character is a useful quantitative marker to determine whether the EOM-CCSD method yields accurate results for a given system.

**Conclusion.** We presented an efficient approach to extrapolate EOM-CCSD band gaps to the TDL using the scaling of  $G_0W_0$  gaps with respect to system size. The precision of this approach was verified through agreement between FHI aims and VASP calculations, while the accuracy was assessed against experimental data and  $GW^{\text{TC-TC}}$  results. We found that the EOM-CCSD band gap quality correlates with the single excitation character of the quasiparticle excitation, with accuracy decreasing significantly for single excitation characters below 95%—a trend confirmed in the alternating hydrogen chain. This paves the way for predictions of band gaps with controllable accuracy. Future work should also explore systems with low single excitation character to better understand its physical origin. Possible approaches include higher-order excitation operators in the  $\hat{T}$  and  $\hat{R}$  operators and the utilization of non-HF-based single particle states.

**Acknowledgments.** This project was supported by TEC1p [the European Research Council (ERC) Horizon 2020 research and innovation program, Grant Agreement No. 740233] and Grant Agreement No. 101087184. T.S. acknowledges support from the Austrian Science Fund (FWF) (DOI:10.55776/ESP335). The computational results presented have partly been achieved using the Vienna Scientific Cluster (VSC) and the Max Planck Computing and Data Facility (MPCDF).

**Data availability.** The data supporting this study's findings are available within the article.

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- [1] J. P. Perdew, W. Yang, K. Burke, Z. Yang, E. K. Gross, M. Scheffler, G. E. Scuseria, T. M. Henderson, I. Y. Zhang, A. Ruzsinszky *et al.*, Understanding band gaps of solids in generalized Kohn–Sham theory, *Proc. Natl. Acad. Sci. USA* **114**, 2801 (2017).
  - [2] L. Hedin, New method for calculating the one-particle Green's function with application to the electron-gas problem, *Phys. Rev.* **139**, A796 (1965).
  - [3] D. Golze, M. Dvorak, and P. Rinke, The *GW* compendium: A practical guide to theoretical photoemission spectroscopy, *Front. Chem.* **7**, 377 (2019).
  - [4] P. Rinke, A. Qteish, J. Neugebauer, C. Freysoldt, and M. Scheffler, Combining *GW* calculations with exact-exchange density-functional theory: an analysis of valence-band photoemission for compound semiconductors, *New J. Phys.* **7**, 126 (2005).
  - [5] F. Fuchs, J. Furthmüller, F. Bechstedt, M. Shishkin, and G. Kresse, Quasiparticle band structure based on a generalized Kohn-Sham scheme, *Phys. Rev. B* **76**, 115109 (2007).
  - [6] M. Shishkin, M. Marsman, and G. Kresse, Accurate quasiparticle spectra from self-consistent *GW* calculations with vertex corrections, *Phys. Rev. Lett.* **99**, 246403 (2007).
  - [7] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, Influence of the exchange screening parameter on the performance of screened hybrid functionals, *J. Chem. Phys.* **125**, 224106 (2006).
  - [8] A. Miglio, V. Brousseau-Couture, E. Godbout, G. Antonius, Y.-H. Chan, S. G. Louie, M. Côté, M. Giantomassi, and X. Gonze, Predominance of non-adiabatic effects in zero-point renormalization of the electronic band gap, *npj Comput. Mater.* **6**, 167 (2020).
  - [9] M. Engel, H. Miranda, L. Chaput, A. Togo, C. Verdi, M. Marsman, and G. Kresse, Zero-point renormalization of the band gap of semiconductors and insulators using the projector augmented wave method, *Phys. Rev. B* **106**, 094316 (2022).
  - [10] M. Zacharias, M. Scheffler, and C. Carbogno, Fully anharmonic nonperturbative theory of vibronically renormalized electronic band structures, *Phys. Rev. B* **102**, 045126 (2020).
  - [11] R. J. Hunt, M. Szyniszewski, G. I. Prayogo, R. Maezono, and N. D. Drummond, Quantum Monte Carlo calculations of energy gaps from first principles, *Phys. Rev. B* **98**, 075122 (2018).
  - [12] R. J. Hunt, B. Monserrat, V. Zólyomi, and N. D. Drummond, Diffusion quantum Monte Carlo and *GW* study of the electronic properties of monolayer and bulk hexagonal boron nitride, *Phys. Rev. B* **101**, 205115 (2020).
  - [13] J. F. Stanton and R. J. Bartlett, The equation of motion coupled-cluster method. a systematic biorthogonal approach to molecular excitation energies, transition probabilities, and excited state properties, *J. Chem. Phys.* **98**, 7029 (1993).
  - [14] X. Wang and T. C. Berkelbach, Excitons in solids from periodic equation-of-motion coupled-cluster theory, *J. Chem. Theory Comput.* **16**, 3095 (2020).
  - [15] A. M. Lewis and T. C. Berkelbach, *Ab initio* linear and pump-probe spectroscopy of excitons in molecular crystals, *J. Phys. Chem. Lett.* **11**, 2241 (2020).
  - [16] A. Gallo, F. Hummel, A. Irmeler, and A. Grüneis, A periodic equation-of-motion coupled-cluster implementation applied to

- F*-centers in alkaline earth oxides, *J. Chem. Phys.* **154**, 064106 (2021).
- [17] J. McClain, Q. Sun, G. K.-L. Chan, and T. C. Berkelbach, Gaussian-based coupled-cluster theory for the ground-state and band structure of solids, *J. Chem. Theory Comput.* **13**, 1209 (2017).
  - [18] E. A. Vo, X. Wang, and T. C. Berkelbach, Performance of periodic EOM-CCSD for bandgaps of inorganic semiconductors and insulators, *J. Chem. Phys.* **160**, 044106 (2024).
  - [19] E. Moerman, A. Gallo, A. Irmeler, T. Schäfer, F. Hummel, A. Grüneis, and M. Scheffler, Finite-size effects in periodic EOM-CCSD for ionization energies and electron affinities: Convergence rate and extrapolation to the thermodynamic limit, *J. Chem. Theory Comput.* **21**, 1865 (2025).
  - [20] D. S. Ranasinghe, J. T. Margraf, A. Perera, and R. J. Bartlett, Vertical valence ionization potential benchmarks from equation-of-motion coupled cluster theory and QTP functionals, *J. Chem. Phys.* **150**, 074108 (2019).
  - [21] M. F. Lange and T. C. Berkelbach, On the relation between equation-of-motion coupled-cluster theory and the *GW* approximation, *J. Chem. Theory Comput.* **14**, 4224 (2018).
  - [22] J. Tölle and G. K.-L. Chan, Exact relationships between the *GW* approximation and equation-of-motion coupled-cluster theories through the quasi-boson formalism, *J. Chem. Phys.* **158**, 124123 (2023).
  - [23] M. S. Hybertsen and S. G. Louie, *Ab initio* static dielectric matrices from the density-functional approach. I. Formulation and application to semiconductors and insulators, *Phys. Rev. B* **35**, 5585 (1987).
  - [24] R. D. Mattuck, *A Guide to Feynman Diagrams in the Many-Body Problem*, 2nd ed., Dover Books on Physics and Chemistry (Dover Publications, New York, 1992).
  - [25] T. Gruber, K. Liao, T. Tsatsoulis, F. Hummel, and A. Grüneis, Applying the coupled-cluster Ansatz to solids and surfaces in the thermodynamic limit, *Phys. Rev. X* **8**, 021043 (2018).
  - [26] X. Xing and L. Lin, Inverse volume scaling of finite-size error in periodic coupled cluster theory, *Phys. Rev. X* **14**, 011059 (2024).
  - [27] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.111.L121202> for computational details including structural parameters of the studied materials, positions of the band edges, calculation settings chosen for the electronic structure calculations of quasiparticle energies and the ZPR, details on the evaluation of the basis set incompleteness error, the  $G_0W_0$  convergence and EOM-CC vs  $G_0W_0$  parity plots for the VASP calculations, additional EOM-CC convergence results, the system size-dependent change of the single-excitation character, and a benchmark of the implemented EOM-CCSD method for a set of small molecules.
  - [28] A. Grüneis, M. Marsman, and G. Kresse, Second-order Møller-Plesset perturbation theory applied to extended systems. II. Structural and energetic properties, *J. Chem. Phys.* **133**, 074107 (2010).
  - [29] I. Y. Zhang, A. J. Logsdail, X. Ren, S. V. Levchenko, L. Ghiringhelli, and M. Scheffler, Main-group test set for materials science and engineering with user-friendly graphical tools for error analysis: Systematic benchmark of the numerical and intrinsic errors in state-of-the-art electronic-structure approximations, *New J. Phys.* **21**, 013025 (2019).
  - [30] E. Moerman, F. Hummel, A. Grüneis, A. Irmeler, and M. Scheffler, Interface to high-performance periodic coupled-cluster theory calculations with atom-centered, localized basis functions, *J. Open Source Softw.* **7**, 4040 (2022).
  - [31] S. V. Levchenko, X. Ren, J. Wieferink, R. Johanni, P. Rinke, V. Blum, and M. Scheffler, Hybrid functionals for large periodic systems in an all-electron, numeric atom-centered basis framework, *Comput. Phys. Commun.* **192**, 60 (2015).
  - [32] cc4s; available from <https://manuals.cc4s.org>. Accessed on 01.05.2025.
  - [33] M. Musiał, S. A. Kucharski, and R. J. Bartlett, Equation-of-motion coupled cluster method with full inclusion of the connected triple excitations for ionized states: IP-EOM-CCSDT, *J. Chem. Phys.* **118**, 1128 (2003).
  - [34] M. Musiał and R. J. Bartlett, Equation-of-motion coupled cluster method with full inclusion of connected triple excitations for electron-attached states: EA-EOM-CCSDT, *J. Chem. Phys.* **119**, 1901 (2003).
  - [35] T. Chiang, *Electronic Structure of Solids: Photoemission Spectra and Related Data* (Springer, Berlin, 1989).
  - [36] O. Madelung, *Semiconductors: Data Handbook* (Springer Science & Business Media, Springer, Berlin, 2004).
  - [37] M. E. Levinshtein, S. L. Rumyantsev, and M. S. Shur, *Properties of Advanced Semiconductor Materials: GaN, AlN, InN, BN, SiC, SiGe* (John Wiley & Sons, New York, 2001).
  - [38] K. Woo, K. Lee, and K. Kovnir, BP: Synthesis and properties of boron phosphide, *Mater. Res. Express* **3**, 074003 (2016).
  - [39] S. Baroni, G. P. Parravicini, and G. Pezzica, Quasiparticle band structure of lithium hydride, *Phys. Rev. B* **32**, 4077 (1985).
  - [40] M. Piacentini, D. W. Lynch, and C. G. Olson, Thermoreflectance of LiF between 12 and 30 eV, *Phys. Rev. B* **13**, 5530 (1976).
  - [41] G. Baldini and B. Bosacchi, Optical properties of Na and Li halide crystals at 55 °K, *physica status solidi (b)* **38**, 325 (1970).
  - [42] R. Whited, C. J. Flaten, and W. Walker, Exciton thermoreflectance of MgO and CaO, *Solid State Commun.* **13**, 1903 (1973).
  - [43] F. Hummel, T. Tsatsoulis, and A. Grüneis, Low rank factorization of the Coulomb integrals for periodic coupled cluster theory, *J. Chem. Phys.* **146**, 124105 (2017).
  - [44] J. Paier, R. Hirschl, M. Marsman, and G. Kresse, The Perdew–Burke–Ernzerhof exchange–correlation functional applied to the G2-1 test set using a plane-wave basis set, *J. Chem. Phys.* **122**, 234102 (2005).
  - [45] R. Sundararaman and T. A. Arias, Regularization of the Coulomb singularity in exact exchange by Wigner-Seitz truncated interactions: Towards chemical accuracy in nontrivial systems, *Phys. Rev. B* **87**, 165122 (2013).
  - [46] S. Massidda, M. Posternak, and A. Baldereschi, Hartree-Fock LAPW approach to the electronic properties of periodic systems, *Phys. Rev. B* **48**, 5058 (1993).
  - [47] B. Monserrat, N. Drummond, and R. J. Needs, Anharmonic vibrational properties in periodic systems: energy, electron-phonon coupling, and stress, *Phys. Rev. B* **87**, 144302 (2013).
  - [48] V. G. Plekhanov, Isotopic and disorder effects in large exciton spectroscopy, *Phys. Usp.* **40**, 553 (1997).
  - [49] A. S. Alag, D. P. Jelenfi, A. Tajti, and P. G. Szalay, Accurate prediction of vertical ionization potentials and electron affinities from spin-component scaled CC2 and ADC(2) models, *J. Chem. Theory Comput.* **18**, 6794 (2022).

- [50] A. Marie and P.-F. Loos, Reference energies for valence ionizations and satellite transitions, *J. Chem. Theory Comput.* **20**, 4751 (2024).
- [51] J. F. Stanton and J. Gauss, A simple scheme for the direct calculation of ionization potentials with coupled-cluster theory that exploits established excitation energy methods, *J. Chem. Phys.* **111**, 8785 (1999).
- [52] F. Kossoski, M. Boggio-Pasqua, P.-F. Loos, and D. Jacquemin, Reference energies for double excitations: Improvement and extension, *J. Chem. Theory Comput.* **20**, 5655 (2024).
- [53] K. Krause, M. E. Harding, and W. Klopper, Coupled-cluster reference values for the *GW*27 and *GW*100 test sets for the assessment of *GW* methods, *Mol. Phys.* **113**, 1952 (2015).