PHYSICAL REVIEW B **94**, 075123 (2016)

Band gaps, ionization potentials, and electron affinities of periodic electron systems via the adiabatic-connection fluctuation-dissipation theorem

Egor Trushin,[1] Markus Betzinger,[2] Stefan Blügel,[2] and Andreas Görling[1,*]
[1]*Lehrstuhl für Theoretische Chemie, Universität Erlangen-Nürnberg, Egerlandstrasse 3, D-91058 Erlangen, Germany*
[2]*Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, D-52425 Jülich, Germany*

(Received 17 July 2015; revised manuscript received 9 June 2016; published 11 August 2016)

An approach to calculate fundamental band gaps, ionization energies, and electron affinities of periodic electron systems is explored. Starting from total energies obtained with the help of the adiabatic-connection fluctuation-dissipation (ACFD) theorem, these physical observables are calculated according to their basic definition by differences of the total energies of the N-, $(N-1)$-, and $(N+1)$-electron system. The response functions entering the ACFD theorem are approximated here by the direct random phase approximation (dRPA). For a set of prototypical semiconductors and insulators it is shown that even with this quite drastic approximation the resulting band gaps are very close to experiment and of a similar quality to those from the computationally more involved GW approximation. By going beyond the dRPA in the future the accuracy of the calculated band gaps may be significantly improved further.

DOI: 10.1103/PhysRevB.94.075123

I. INTRODUCTION

The most important quantity to characterize the electronic properties of a semiconductor or insulator is the fundamental band gap. The calculation of band gaps, more precisely of fundamental quasiparticle band gaps, therefore is a key task in solid state physics and materials science. The standard approach to determine band gaps as well as ionization potentials and electron affinities starts from Kohn-Sham (KS) band structures [1] and then uses the GW method [2,3], i.e., applies many-body perturbation theory. This approach has conceptual as well as computational shortcomings. The common procedure is to carry out the GW calculations completely or partly non-self-consistently, that is, to perform G_0W_0 or GW_0 calculations. In this case the obtained results depend significantly on the choice of the underlying KS method, i.e., the choice of the exchange-correlation functional made in the calculation of the KS band structure [3–5]. Self-consistent GW calculations, on the other hand, are not only computationally expensive but typically yield worse results than G_0W_0 or GW_0 calculations. Finally, the step to supplement self-consistent GW calculations by vertex corrections [6] to increase the accuracy is computationally prohibitively expensive.

We here investigate an alternative strategy to determine fundamental band gaps, ionization potentials, and electron affinities that avoids many-body perturbation theory. Band gaps Δ, ionization potentials IP, and electron affinities EA of periodic systems, in contrast to common wisdom, can be calculated starting from differences of the total energies $E[N]$, $E[N-1]$, $E[N+1]$ of the N-, $(N-1)$-, and $(N+1)$-electron system, respectively, according to their basic definitions $\Delta = E[N-1] + E[N+1] - 2E[N]$, $IP = E[N-1] - E[N]$, $EA = E[N] - E[N+1]$. The required total energies are accessible by density-functional theory more precisely via KS calculations. To that end, however, standard KS methods [7,8] relying on the local density approximation (LDA) or on the generalized gradient approximation (GGA) are not suitable [9]. KS methods that treat the exchange energy exactly and take into account the correlation energy via the adiabatic-connection fluctuation-dissipation (ACFD) theorem [10–19] in conjunction with the direct random phase approximation (dRPA), on the other hand, can be used to that purpose. An approach along these lines was suggested in Ref. [20] and yielded band gaps in good agreement with experiment for carbon and silicon.

In Ref. [20], however, the band gaps were not directly calculated from the total energies $E[N]$, $E[N-1]$, and $E[N+1]$. Instead, starting from differences of the correlation energies $E_c^{dRPA}[N]$, $E_c^{dRPA}[N-1]$, and $E_c^{dRPA}[N+1]$ within the direct random phase approximation (dRPA) of the N-, $(N-1)$-, and $(N+1)$-electron system, expressions for the ionization energy and the electron affinity were derived that resemble those of the GW method. In order to do that, terms vanishing in the limit of infinite periodic systems were neglected. The calculations of Ref. [20] used pseudopotentials and in order to converge the results approximations typically applied in GW methods like the plasmon-pole approximation were used. Moreover, the required KS orbitals and eigenvalues were obtained exclusively from LDA calculations.

In this work we calculate band gaps directly according to their definition from the total energies $E[N]$, $E[N-1]$, and $E[N+1]$ obtained within the dRPA with a plane-wave pseudopotential program, the program MCEXX [21], and with the all-electron full-potential linearized augmented plane-wave (FLAPW) package FLEUR [22,23]. Besides silicon and carbon, we consider band gaps of a prototypical set of semiconductors. The calculations invoke no approximations like the plasmon-pole approximation. Moreover, we investigate the influence of the exchange-correlation potential used to obtain the KS orbitals and eigenvalues, by considering an GGA exchange-correlation potential and the exact-exchange-only potential.

In a second step we then rederive the GW-like expression of Ref. [20] in a slightly different way and investigate how fast the terms neglected in the GW-like expression vanish with the system size by recalculating the band gaps for increasing numbers of $\mathbf{k}$ points. Furthermore we test a perturbative

---

[*] andreas.goerling@fau.de

treatment of the required eigenvalues of the response matrices of the $(N-1)$- and $(N+1)$-electron system.

II. FORMALISM

A. Adiabatic-connection fluctuation-dissipation theorem and the direct random phase approximation

The ACFD theorem [10,11] provides an exact expression for the KS correlation energy E_c in terms of the density-density (potential-density) response functions χ_0 and χ_α of the KS model system and of systems with an electron-electron interaction scaled by a coupling constant $0 \leqslant \alpha \leqslant 1$, respectively:

$$E_c = \frac{-1}{2\pi}\int_0^\infty d\omega \int_0^1 d\alpha \int d\mathbf{r}d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \times [\chi_\alpha(i\omega,\mathbf{r},\mathbf{r}') - \chi_0(i\omega,\mathbf{r},\mathbf{r}')]. \tag{1}$$

The ACFD theorem contains the dynamic, i.e., frequency-dependent, Kohn-Sham response function χ_0 for imaginary frequencies $i\omega$, which reads as

$$\chi_0(i\omega,\mathbf{r},\mathbf{r}') = \sum_i \sum_s \frac{4(\varepsilon_i - \varepsilon_s)}{(\varepsilon_i-\varepsilon_s)^2+\omega^2} \times \varphi_i(\mathbf{r})\varphi_s(\mathbf{r})\varphi_s(\mathbf{r}')\varphi_i(\mathbf{r}') \tag{2}$$

for real-valued orbitals. The summations run over all occupied orbitals φ_i and all orbitals φ_s, respectively. The corresponding orbital eigenvalues are given by ε_i and ε_s. Bloch orbitals are complex-valued. In the presence of time-reversal (complex-conjugation) symmetry, however, Bloch orbitals can formally be converted into real-valued orbitals by a unitary transformation and then the above expression for the KS response function applies; see below for further details.

Besides the dynamic KS response function, the ACFD theorem (1) contains the dynamic response function χ_α, which, in contrast to the KS response function χ_0, is the response function of a system of interacting electrons with an electron-electron interaction scaled by the coupling constant $0 \leqslant \alpha \leqslant 1$. For $\alpha = 0$, χ_α turns into the KS response function χ_0 of the KS model system of hypothetical noninteracting electrons. For $\alpha = 1$, χ_α is the dynamic response function of the real electron system with the physical electron-electron interaction. The electronic systems with a scaled electron-electron interaction are defined by the requirement that they exhibit the same electron density as the real physical electron system.

By the coupling-constant integration in the ACFD theorem (1) the kinetic contribution to the correlation energy is taken into account. This is crucial because the kinetic contribution is substantial; see, e.g., Ref. [14].

The response function χ_α is given by the basic equation

$$\int d\mathbf{r}''\left[\delta(\mathbf{r}-\mathbf{r}'') - \int d\mathbf{r}'\chi_0(\nu,\mathbf{r},\mathbf{r}')f^\alpha_{\mathrm{Hxc}}(\nu,\mathbf{r}',\mathbf{r}'')\right] \times\chi_\alpha(\nu,\mathbf{r}'',\mathbf{r}''') = \chi_0(\nu,\mathbf{r},\mathbf{r}''') \tag{3}$$

of time-dependent density functional theory (TDDFT) in the linear response regime [24–26]. In Eq. (3) the frequency is denoted by ν. Here pure imaginary frequencies $\nu = i\omega$ with ω being real-valued are considered. By f^α_{Hxc} the sum of the Coulomb kernel $f_{\mathrm{H}}(\mathbf{r}',\mathbf{r}'') = 1/|\mathbf{r}'-\mathbf{r}''|$ scaled by α plus the xc kernel f^α_{xc} is denoted. The xc kernel f^α_{xc} is the frequency-dependent functional derivative of the exchange-correlation potential with respect to the electron density. The kernel f^α_{xc} is not known exactly. This is the only point in correlation methods based on the ACFD theorem where approximations are necessary. The approximation to neglect the kernel f^α_{xc} and to only take into account the Coulomb kernel f_{H} is the direct random phase approximation [12–15,18].

Next an orthonormal auxiliary basis set to represent the response functions and the Coulomb kernel is introduced; for details see below. This turns the ACFD theorem into

$$E_c = \frac{-1}{2\pi}\sum_{\mathbf{q}}\int_0^\infty d\omega \int_0^1 d\alpha \times \mathrm{Tr}\{\mathbf{F}_H(\mathbf{q})[\mathbf{X}_\alpha(i\omega,\mathbf{q}) - \mathbf{X}_0(i\omega,\mathbf{q})]\} \tag{4}$$

with the matrices $\mathbf{F}_H(\mathbf{q})$, $\mathbf{X}_0(i\omega,\mathbf{q})$, $\mathbf{X}_\alpha(i\omega,\mathbf{q})$ representing the Hartree kernel f_{H}, the KS response function χ_0, and the response function χ_α. At this point it was used that in a periodic system the linear response functions for perturbations of different Bloch vectors $\mathbf{q}$ do not couple. In case of the plane-wave implementation with pseudopotentials, the auxiliary basis functions are simply plane waves and the matrix $\mathbf{F}_H(\mathbf{q})$ is a diagonal matrix with matrix elements equal to $4\pi/(\mathbf{G}+\mathbf{q})^2$. In the case of the FLAPW implementation an initial auxiliary basis, the mixed product basis [27–29] constructed from products of LAPW basis functions, is introduced and the Coulomb matrix $\mathbf{F}_H(\mathbf{q})$ is calculated according to Ref. [28]. The eigenvectors of this Coulomb matrix then define the final orthonormal auxiliary basis. The matrix elements of the matrix $\mathbf{X}_0(i\omega,\mathbf{q})$ are given in Eqs. (27) and (28) below and in the Supplemental Material [30].

The response matrix $\mathbf{X}_\alpha(i\omega,\mathbf{q})$ is determined by the matrix representation of Eq. (3) after applying the dRPA, i.e., by

$$[\mathbf{1} - \mathbf{X}_0(\nu,\mathbf{q})\alpha\mathbf{F}_H(\mathbf{q})]\mathbf{X}_\alpha(\nu,\mathbf{q}) = \mathbf{X}_0(\nu,\mathbf{q}). \tag{5}$$

Substitution of Eq. (5) into Eq. (4) after setting $\nu = i\omega$ leads to

$$\begin{aligned} E_c &= \frac{-1}{2\pi}\sum_{\mathbf{q}}\int_0^\infty d\omega \int_0^1 d\alpha \mathrm{Tr}\{\mathbf{F}_H(\mathbf{q})[[\mathbf{1} - \alpha\mathbf{X}_0(i\omega,\mathbf{q}) \\ &\quad\times \mathbf{F}_H(\mathbf{q})]^{-1}\mathbf{X}_0(i\omega,\mathbf{q}) - \mathbf{X}_0(i\omega,\mathbf{q})]\} \\ &= \frac{-1}{2\pi}\sum_{\mathbf{q}}\int_0^\infty d\omega \int_0^1 d\alpha \\ &\quad\times \mathrm{Tr}\{[[\mathbf{1} - \alpha\tilde{\mathbf{X}}_0(i\omega,\mathbf{q})]^{-1}\tilde{\mathbf{X}}_0(i\omega,\mathbf{q}) - \tilde{\mathbf{X}}_0(i\omega,\mathbf{q})]\} \end{aligned} \tag{6}$$

with

$$\tilde{\mathbf{X}}_0(i\omega,\mathbf{q}) = \mathbf{F}_H^{1/2}(\mathbf{q})\mathbf{X}_0(i\omega,\mathbf{q})\mathbf{F}_H^{1/2}(\mathbf{q}). \tag{7}$$

The coupling constant integration in Eq. (6) can be carried out analytically with the spectral representation

$$\tilde{\mathbf{X}}_0(i\omega,\mathbf{q}) = \mathbf{U}(i\omega,\mathbf{q})\boldsymbol{\sigma}(i\omega,\mathbf{q})\mathbf{U}^\dagger(i\omega,\mathbf{q}) \tag{8}$$

containing in the columns of the matrix $\mathbf{U}(i\omega,\mathbf{q})$ the eigenvectors of $\tilde{\mathbf{X}}_0(i\omega,\mathbf{q})$ and in the diagonal matrix $\boldsymbol{\sigma}(i\omega,\mathbf{q})$ the corresponding eigenvalues. This leads to the final expression

$$E_c = \frac{1}{2\pi}\sum_{\mathbf{q}}\int_0^\infty d\omega \mathrm{Tr}\{\ln[\mathbf{1}-\boldsymbol{\sigma}(i\omega,\mathbf{q})] + \boldsymbol{\sigma}(i\omega,\mathbf{q})\} \tag{9}$$

for the dRPA correlation energy which is actually evaluated. The response matrix $\tilde{\mathbf{X}}_0(i\omega,\mathbf{q})$ is negative definite and therefore the logarithm in Eq. (9) is always well defined.

In our implementations, the evaluation of the dRPA correlation energy requires (i) the construction of the response matrix $\mathbf{X}_0(i\omega,\mathbf{q})$, (ii) the construction of the scaled response matrix $\tilde{\mathbf{X}}_0(i\omega,\mathbf{q})$ and its diagonalization in order to obtain the eigenvalues, and (iii) the evaluation of expression (9) for the correlation energy. The computationally most expensive step is the construction of the response matrix, step (i). Its computational effort scales with M^4 with the system size M. The linear algebra of step (ii) scales with M^3 and was not an important factor with respect to the computational effort in the actual calculations we performed. The last step (iii) scales linearly with the system size and its computational effort was negligible.

B. Band gaps from total energy differences

We start from the definition of the ionization potential

$$\begin{aligned} IP &= E[N-1] - E[N] \\ &= T_s[N-1] + E_v[N-1] + E_{Hxc}[N-1] \\ &\quad - T_s[N] - E_v[N] - E_{Hxc}[N] \end{aligned} \tag{10}$$

in terms of the total energies $E[N-1]$ and $E[N]$ of the $(N-1)$- and N-electron system, respectively. Then the total energies are decomposed as usual in the KS formalism with T_s denoting the noninteracting kinetic energy, with E_v designating the interaction energy with the external potential v, which usually is the potential of the nuclei, and with E_{Hxc} denoting the sum of Hartree, exchange, and correlation energy.

In order to evaluate Eq. (10), in the most general case, we have to carry out two self-consistent KS ground state calculations, for the N- and $(N-1)$-electron system, namely. In the case of finite systems like atoms and molecules this indeed is necessary. In the case of solids the relaxation of the KS orbitals and eigenvalues upon a change of the particle number by one electron vanishes for large particle numbers N, which in the thermodynamic limit are of the order of Avogadro's number and in a practical calculation equal the number of electrons per unit cell times the number of $\mathbf{k}$ points. We therefore can evaluate the contributions to the energies of both the N- and the $(N-1)$-electron system with the orbitals and eigenvalues determined in a KS calculation of the N-electron system and obtain

$$IP = -\langle\varphi_H| -\tfrac{1}{2}\nabla^2 + \hat{v}|\varphi_H\rangle + E_{Hxc}[N-1] - E_{Hxc}[N]. \tag{11}$$

Here φ_H denotes the energetically highest occupied molecular orbital (HOMO) or the one-electron state representing the top of the valence band. In the following, we use the acronym HOMO as a synonym for both cases.

For exchange-correlation functionals based on the LDA or GGA, the total energy differences of expressions (10) and (11) reduce to the negative of the KS eigenvalue ε_H of the HOMO [9] which is known to be a very poor estimate for the true IP in the LDA or GGA case. This is a shortcoming of the LDA or GGA which must not be interpreted as a fundamental shortcoming of the KS formalism [9].

For the exact exchange-correlation functional and for appropriate orbital-dependent exchange-correlation functionals the total energy differences in expressions (10) and (11) do not reduce to the negative of ε_H. For the difference $E_{Hx}[N-1] - E_{Hx}[N]$ of the Coulomb plus the exact exchange energy of the $(N-1)$- and the N-electron system, respectively, we obtain

$$E_{Hx}[N-1] - E_{Hx}[N] = -\langle\varphi_H|\hat{v}_H|\varphi_H\rangle - \langle\varphi_H|\hat{v}_x^{NL}|\varphi_H\rangle \tag{12}$$

with $\hat{v}_H$ and $\hat{v}_x^{NL}$ denoting, respectively, the Hartree potential and a nonlocal exchange potential of the form of the Hartree-Fock exchange potential but constructed from KS orbitals. This follows from the basic definitions

$$E_H[N] = 2\sum_{i=1}^{N/2}\sum_{j=1}^{N/2}\langle\varphi_i\varphi_j|\varphi_i\varphi_j\rangle \tag{13}$$

and

$$E_x[N] = -\sum_{i=1}^{N/2}\sum_{j=1}^{N/2}\langle\varphi_i\varphi_j|\varphi_j\varphi_i\rangle \tag{14}$$

of the Hartree $E_H[N]$ and the exchange energy $E_x[N]$ of a non-spin-polarized N-electron Slater determinant with

$$\langle\varphi_i\varphi_j|\varphi_i\varphi_j\rangle = \int d\mathbf{r}d\mathbf{r}'\frac{\varphi_i^*(\mathbf{r})\varphi_i(\mathbf{r})\varphi_j^*(\mathbf{r}')\varphi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{15}$$

and

$$\langle\varphi_i\varphi_j|\varphi_j\varphi_i\rangle = \int d\mathbf{r}d\mathbf{r}'\frac{\varphi_i^*(\mathbf{r})\varphi_j(\mathbf{r})\varphi_j^*(\mathbf{r}')\varphi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \tag{16}$$

where φ_i and φ_j denote occupied spatial KS orbitals. Spin is taken into account via the prefactors of the summations.

If we exploit that the KS orbitals do not change upon a removal of an electron in the limit of a large number of electrons, then the sum $E_{Hx}[N-1]$ of the Hartree and the exchange energy of the corresponding $(N-1)$-electron Slater determinant is obtained by simply removing the contributions from an electron in the energetically highest occupied molecular orbital φ_H in Eqs. (13) and (14). The energy difference $E_{Hx}[N-1] - E_{Hx}[N]$ is then given by

$$\begin{aligned} &E_{Hx}[N-1] - E_{Hx}[N] \\ &= \sum_{j=1}^{N/2}[-2\langle\varphi_H\varphi_j|\varphi_H\varphi_j\rangle + \langle\varphi_H\varphi_j|\varphi_j\varphi_H\rangle]. \end{aligned} \tag{17}$$

With the Hartree potential

$$v_H(\mathbf{r}) = 2\sum_{j=1}^{N/2}\int d\mathbf{r}'\frac{\varphi_j^*(\mathbf{r}')\varphi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{18}$$

and the nonlocal exchange potential $\hat{v}_x^{NL}$ with the integral kernel $-\sum_{j=1}^{N/2}\frac{\varphi_j(\mathbf{r})\varphi_j^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$ we obtain Eq. (12).

Inserting Eq. (12) in expression (11) yields

$$\begin{aligned}IP = &-\langle\varphi_H| - \tfrac{1}{2}\nabla^2 + \hat{v} + \hat{v}_H|\varphi_H\rangle - \langle\varphi_H|\hat{v}_x^{NL}|\varphi_H\rangle\\ &+ E_c[N-1] - E_c[N].\end{aligned} \tag{19}$$

The correlation energies $E_c[N-1]$ and $E_c[N]$, need to be approximated. We apply the ACFD theorem and invoke the dRPA. The resulting correlation energies in the dRPA shall be denoted by $E_c^{dRPA}[N-1]$ and $E_c^{dRPA}[N]$.

Next we take into account that the KS orbitals obey the KS equation

$$\left[-\tfrac{1}{2}\nabla^2 + \hat{v} + \hat{v}_H + \hat{\tilde{v}}_x + \hat{\tilde{v}}_c\right]\varphi_i = \varepsilon_i\varphi_i \tag{20}$$

with $\hat{\tilde{v}}_x$ and $\hat{\tilde{v}}_c$ denoting the exchange and correlation potentials needed to generate the KS orbitals and eigenvalues. For $\hat{\tilde{v}}_x$ and $\hat{\tilde{v}}_c$ any of the common LDA or GGA potentials can be chosen; in the case of $\hat{\tilde{v}}_x$ also the exact exchange potential may be employed. If we add and subtract $\langle\varphi_H|\hat{\tilde{v}}_x|\varphi_H\rangle + \langle\varphi_H|\hat{\tilde{v}}_c|\varphi_H\rangle$ to the right-hand side of Eq. (19) we obtain the ionization potential in the form

$$\begin{aligned}IP = &-\varepsilon_H - \langle\varphi_H|\hat{v}_x^{NL} - \hat{\tilde{v}}_x|\varphi_H\rangle\\ &+ E_c^{dRPA}[N-1] - E_c^{dRPA}[N] + \langle\varphi_H|\hat{\tilde{v}}_c|\varphi_H\rangle.\end{aligned} \tag{21}$$

In a completely analogous way we obtain for the electron affinity

$$\begin{aligned}EA = &-\varepsilon_L - \langle\varphi_L|\hat{v}_x^{NL} - \hat{\tilde{v}}_x|\varphi_L\rangle + E_c^{dRPA}[N]\\ &- E_c^{dRPA}[N+1] + \langle\varphi_L|\hat{\tilde{v}}_c|\varphi_L\rangle\end{aligned} \tag{22}$$

with φ_L denoting the energetically lowest unoccupied orbital. The difference between IP and EA yields the band gap

$$\begin{aligned}\Delta &= \varepsilon_L - \varepsilon_H + \langle\varphi_L|\hat{v}_x^{NL} - \hat{\tilde{v}}_x|\varphi_L\rangle - \langle\varphi_H|\hat{v}_x^{NL} - \hat{\tilde{v}}_x|\varphi_H\rangle\\ &\quad + E_c^{dRPA}[N+1] + E_c^{dRPA}[N-1] - 2E_c^{dRPA}[N]\\ &\quad - \langle\varphi_L|\hat{\tilde{v}}_c|\varphi_L\rangle + \langle\varphi_H|\hat{\tilde{v}}_c|\varphi_H\rangle\\ &= \Delta_\varepsilon + \tilde{\Delta}_x + \tilde{\Delta}_c^{dRPA}\end{aligned} \tag{23}$$

with

$$\Delta_\varepsilon = \varepsilon_L - \varepsilon_H, \tag{24}$$

with

$$\tilde{\Delta}_x = \langle\varphi_L|\hat{v}_x^{NL} - \hat{\tilde{v}}_x|\varphi_L\rangle - \langle\varphi_H|\hat{v}_x^{NL} - \hat{\tilde{v}}_x|\varphi_H\rangle, \tag{25}$$

and with

$$\begin{aligned}\tilde{\Delta}_c^{dRPA} = &E_c^{dRPA}[N+1] + E_c^{dRPA}[N-1] - 2E_c^{dRPA}[N]\\ &- \langle\varphi_L|\hat{\tilde{v}}_c|\varphi_L\rangle + \langle\varphi_H|\hat{\tilde{v}}_c|\varphi_H\rangle.\end{aligned} \tag{26}$$

In the following, we consider two choices for $\hat{\tilde{v}}_x$ and $\hat{\tilde{v}}_c$. The first choice is to employ the GGA exchange-correlation potential due to Perdew, Burke, and Ernzerhof (PBE) [31] for the calculation of the KS orbitals and eigenvalues, i.e., $\hat{\tilde{v}}_x = \hat{v}_x^{PBE}$ and $\hat{\tilde{v}}_c = \hat{v}_c^{PBE}$. Using the exact-exchange-only (EXX) method [32–36] to determine the orbitals and eigenvalues represents the second choice. In this case $\hat{\tilde{v}}_x$ equals the exact KS exchange potential $\hat{v}_x$, $\tilde{\Delta}$ equals the exact derivative discontinuity Δ_x of the exchange potential [37–41], and, furthermore, $\tilde{\Delta}_c^{dRPA} = \Delta E_c^{dRPA} = E_c^{dRPA}[N+1] + E_c^{dRPA}[N-1] - 2E_c^{dRPA}[N]$.

A calculation of the required matrix elements containing the operators $\hat{\tilde{v}}_x$, $\hat{\tilde{v}}_c$, and $\hat{v}_x^{NL}$ is straightforward and requires a computational effort less than that of one self-consistency cycle of a Hartree-Fock or a hybrid-DFT calculation. The calculation of the dRPA correlation energy $E_c^{dRPA}[N]$ comprises one somewhat demanding step, the construction of causal density-density (potential-density) KS response matrices for complex frequencies $i\omega$ and perturbing potentials with Bloch vector $\mathbf{q}$. The elements $X_{\mu\nu}^N(i\omega,\mathbf{q})$ of these response matrices are given by

$$\begin{aligned}X_{\mu\nu}^N(i\omega,\mathbf{q}) = &\,4\sum_i\sum_s\sum_{\mathbf{k}}\frac{\varepsilon_{i\mathbf{k}} - \varepsilon_{s\mathbf{k}+\mathbf{q}}}{(\varepsilon_{i\mathbf{k}} - \varepsilon_{s\mathbf{k}+\mathbf{q}})^2 + \omega^2}\\ &\times\langle\varphi_{i\mathbf{k}}|f_{\mu\mathbf{q}}^*|\varphi_{s\mathbf{k}+\mathbf{q}}\rangle\langle\varphi_{s\mathbf{k}+\mathbf{q}}|f_{\nu\mathbf{q}}|\varphi_{i\mathbf{k}}\rangle\end{aligned} \tag{27}$$

with $\varphi_{i\mathbf{k}}$ and $\varphi_{s\mathbf{k}+\mathbf{q}}$ denoting Bloch orbitals with eigenvalues $\varepsilon_{i\mathbf{k}}$ and $\varepsilon_{s\mathbf{k}+\mathbf{q}}$. Note that in Eq. (27) and below we suppress the subscript 0 for the KS response matrices for notational simplicity because only KS response matrices occur in the dRPA correlation energy. By $f_{\mu\mathbf{q}}$ and $f_{\nu\mathbf{q}}$ auxiliary basis functions used to represent the KS response function are denoted. In the simplest case $f_{\mu\mathbf{q}}$ and $f_{\nu\mathbf{q}}$ are plane waves $1/\sqrt{\Omega}\exp[i(\mathbf{G}+\mathbf{q})\mathbf{r}]$ and $1/\sqrt{\Omega}\exp[i(\mathbf{G}'+\mathbf{q})\mathbf{r}]$; i.e., μ and ν correspond to $\mathbf{G}$ and $\mathbf{G}'$. By Ω the crystal volume is denoted. (See Supplemental Material [30] for other choices of $f_{\mu\mathbf{q}}$ and $f_{\nu\mathbf{q}}$.) The summation indices i and s run over all occupied and all orbitals, respectively. We consider non-spin-polarized systems and take into account the spin degree of freedom by appropriate factors.

For the correlation energy $E_c^{dRPA}[N-1]$ we have to construct a corresponding KS response function for the $(N-1)$-electron KS system. This means we remove one electron from the HOMO orbital $\varphi_{H\mathbf{k}_H}$, the energetically highest orbital at the Bloch vector $\mathbf{k}_H$ corresponding to the top of the valence band. In the absence of magnetic fields time-reversal (complex-conjugation) symmetry guarantees that with an occupied orbital $\varphi_{i\mathbf{k}}$ also $\varphi_{i-\mathbf{k}}$ is an occupied orbital contributing to the N-electron KS determinant. Via a unitary transformation we can therefore change from complex-valued Bloch orbitals to real-valued orbitals and then remove an electron from the real-valued orbital $(1/\sqrt{2})(\varphi_{H\mathbf{k}_H} + \varphi_{H-\mathbf{k}_H})$. (In the case $\mathbf{k}_H = \mathbf{0}$ we can directly remove an electron from the orbital $\varphi_{H\mathbf{k}_H}$ which then is real-valued.) In this way not only the N- but also the $(N-1)$-electron KS determinant is real-valued and both response matrices are negative definite. The matrix elements $X_{\mu\nu}^{N-1}(i\omega,\mathbf{q})$ of the $(N-1)$-electron KS response matrix $\mathbf{X}^{N-1}$ are then expressed according to

$$\mathbf{X}^{N-1}(i\omega,\mathbf{q}) = \mathbf{X}^N(i\omega,\mathbf{q}) + \Delta\mathbf{X}^-(i\omega,\mathbf{q}) \tag{28}$$

by the N-electron KS response matrix $\mathbf{X}^N$ plus a difference term $\Delta\mathbf{X}^-$ with matrix elements

$$\begin{aligned}\Delta X^-_{\mu\nu}(i\omega,\mathbf{q}) = &-\sum_s \frac{\varepsilon_{H\mathbf{k}_H}-\varepsilon_{s\mathbf{k}_H+\mathbf{q}}}{(\varepsilon_{H\mathbf{k}_H}-\varepsilon_{s\mathbf{k}_H+\mathbf{q}})^2+\omega^2}\\ &\times\langle\varphi_{H\mathbf{k}_H}|f^*_{\mu\mathbf{q}}|\varphi_{s\mathbf{k}_H+\mathbf{q}}\rangle\langle\varphi_{s\mathbf{k}_H+\mathbf{q}}|f_{\nu\mathbf{q}}|\varphi_{H\mathbf{k}_H}\rangle\\ &-\sum_s \frac{\varepsilon_{H-\mathbf{k}_H}-\varepsilon_{s-\mathbf{k}_H+\mathbf{q}}}{(\varepsilon_{H-\mathbf{k}_H}-\varepsilon_{s-\mathbf{k}_H+\mathbf{q}})^2+\omega^2}\\ &\times\langle\varphi_{H-\mathbf{k}_H}|f^*_{\mu\mathbf{q}}|\varphi_{s-\mathbf{k}_H+\mathbf{q}}\rangle\langle\varphi_{s-\mathbf{k}_H+\mathbf{q}}|f_{\nu\mathbf{q}}|\varphi_{H-\mathbf{k}_H}\rangle.\end{aligned} \tag{29}$$

The evaluation of the matrix elements $X^{N-1}_{\mu\nu}(i\omega,\mathbf{q})$ is carried out with Bloch orbitals, i.e., formally after a unitary transformation of the real-valued orbitals of the $(N-1)$-electron KS determinant back to Bloch orbitals. Moreover, we exploit that the removal of a single electron does not change the KS orbitals in the relevant limit of a large number of $\mathbf{k}$ points. Therefore the matrix elements $X^{N-1}_{\mu\nu}(i\omega,\mathbf{q})$ like the matrix elements $X^{N}_{\mu\nu}(i\omega,\mathbf{q})$ can be evaluated with the orbitals from the N-electron KS determinant. The two summations in Eq. (29) for $\Delta X^-_{\mu\nu}(i\omega,\mathbf{q})$ are computationally much less demanding than those in Eq. (27) for $X^N_{\mu\nu}(i\omega,\mathbf{q})$ because they do not include summations over occupied bands or $\mathbf{k}$ points. The matrix elements $X^{N+1}_{\mu\nu}(i\omega,\mathbf{q})$ of the $(N+1)$-electron response matrices are accessible in an exactly analogous fashion; see Supplemental Material [30].

From the eigenvalues of the N, the $(N-1)$-, and the $(N+1)$-electron response matrices the correlation energies $E_c^{dRPA}[N]$, $E_c^{dRPA}[N-1]$, and $E_c^{dRPA}[N+1]$ can be immediately calculated.

Total energies and their individual components are usually calculated per unit cell. For the energy differences Δ, IP, and EA, however, the energies of the complete system are required. This means the energies per unit cell have to be multiplied by the number of $\mathbf{k}$ points.

C. Alternatives to a calculation of band gaps directly from total energy differences

We again concentrate on the calculation of the ionization energy; the electron affinity can be treated analogously. The difference of the correlation energies of the N- and the $(N-1)$-electron system is given by

$$\begin{aligned}&E_c^{dRPA}[N-1]-E_c^{dRPA}[N]\\ &\quad=\frac{1}{2\pi}\sum_{\mathbf{q}}\int_0^\infty d\omega\mathrm{Tr}\{\ln[\mathbf{1}-\boldsymbol{\sigma}^{N-1}(i\omega,\mathbf{q})]+\boldsymbol{\sigma}^{N-1}(i\omega,\mathbf{q})\}\\ &\qquad-\frac{1}{2\pi}\sum_{\mathbf{q}}\int_0^\infty d\omega\mathrm{Tr}\{\ln[\mathbf{1}-\boldsymbol{\sigma}^{N}(i\omega,\mathbf{q})]+\boldsymbol{\sigma}^{N}(i\omega,\mathbf{q})\}\end{aligned} \tag{30}$$

in the dRPA. The correlation energies $E_c^{dRPA}[N]$ and $E_c^{dRPA}[N-1]$ in the above equation are given by Eq. (9) evaluated for the N- and the $(N-1)$-electron system. The superscripts N and $N-1$ in Eq. (30) and the following equations indicate whether a quantity refers to the N- or the $(N-1)$-electron system. With the difference

$$\Delta\boldsymbol{\sigma}^-(i\omega,\mathbf{q})=\boldsymbol{\sigma}^{N-1}(i\omega,\mathbf{q})-\boldsymbol{\sigma}^{N}(i\omega,\mathbf{q}), \tag{31}$$

Eq. (30) assumes the form

$$\begin{aligned}&E_c^{dRPA}[N-1]-E_c^{dRPA}[N]\\ &\quad=\frac{1}{2\pi}\sum_{\mathbf{q}}\int_0^\infty d\omega\mathrm{Tr}\{\ln[\mathbf{1}-\boldsymbol{\sigma}^{N}(i\omega,\mathbf{q})-\Delta\boldsymbol{\sigma}^-(i\omega,\mathbf{q})]\\ &\qquad-\ln[\mathbf{1}-\boldsymbol{\sigma}^{N}(i\omega,\mathbf{q})]+\Delta\boldsymbol{\sigma}^-(i\omega,\mathbf{q})\}\\ &\quad=\frac{1}{2\pi}\sum_{\mathbf{q}}\int_0^\infty d\omega\mathrm{Tr}\{\ln[\mathbf{1}-[\mathbf{1}-\boldsymbol{\sigma}^{N}(i\omega,\mathbf{q})]^{-1}\Delta\boldsymbol{\sigma}^-(i\omega,\mathbf{q})]\\ &\qquad+\Delta\boldsymbol{\sigma}^-(i\omega,\mathbf{q})\}.\end{aligned} \tag{32}$$

Next we scale the difference $\Delta\mathbf{X}^-$ between the $(N-1)$- and the N-electron response matrix, given in Eqs. (28) and (29) by the Coulomb kernel

$$\Delta\tilde{\mathbf{X}}^-(i\omega,\mathbf{q})=\mathbf{F}_H^{1/2}(\mathbf{q})\Delta\mathbf{X}^-(i\omega,\mathbf{q})\mathbf{F}_H^{1/2}(\mathbf{q}). \tag{33}$$

The elements $\Delta\sigma^-_n$ of the diagonal matrix $\Delta\boldsymbol{\sigma}^-$ then are given in first-order perturbation theory by

$$\Delta\sigma^-_n(i\omega,\mathbf{q})\approx\mathbf{u}_n^\dagger(i\omega,\mathbf{q})\Delta\tilde{\mathbf{X}}^-(i\omega,\mathbf{q})\mathbf{u}_n^\dagger(i\omega,\mathbf{q}) \tag{34}$$

with $\mathbf{u}_n$ denoting the eigenvectors of the N-electron response matrix. That means, the $\mathbf{u}_n$ are the columns of the matrix $\mathbf{U}$ defined in Eq. (8). In the limit of an infinite system, i.e., in the limit of a large number of $\mathbf{k}$ points, Eq. (34) becomes exact. The reason is that the difference $\Delta\mathbf{X}^-$ and subsequently $\Delta\tilde{\mathbf{X}}^-$ scales with the inverse of the crystal volume Ω. This follows immediately from Eq. (29) for the matrix elements of $\Delta\mathbf{X}^-$. It contains two matrix elements, each of which contain two orbitals and one auxiliary basis function with normalization factors of $1/\sqrt{\Omega}$ leading altogether to a factor of $1/\Omega^3$. The integration of each of the matrix elements leads to a factor of Ω. The two integrations together thus provide a factor of Ω^2. Finally a factor of $\Omega^2/\Omega^3=1/\Omega$ remains in the matrix elements of $\Delta\mathbf{X}^-$. This means the difference $\Delta\mathbf{X}^-$ between the $(N-1)$- and the N-electron response matrix is proportional to $1/\Omega$ and therefore vanishes with large numbers of $\mathbf{k}$ points. In this physically relevant limit the perturbative treatment of $\Delta\boldsymbol{\sigma}^-$ according to Eq. (34) becomes exact. Note that in the evaluation of $E_c^{dRPA}[N-1]-E_c^{dRPA}[N]$, Eqs. (30) and (32), a summation over $\mathbf{q}$ occurs. In the limit of an infinite system this integration turns into an integral with a prefactor of $\Omega/8\pi^3$ which cancels the factor of $1/\Omega$ contained in $\Delta\mathbf{X}^-$. Therefore $E_c^{dRPA}[N-1]-E_c^{dRPA}[N]$ converges to a nonzero value in the limit of an infinite system.

If $E_c^{dRPA}[N-1]-E_c^{dRPA}[N]$ is calculated by Eq. (32) in conjunction with the perturbative treatment of $\Delta\mathbf{X}^-$ according to Eq. (34) then only the N-electron but not the $(N-1)$-electron response matrix needs to be diagonalized. The computational savings by avoiding the diagonalization of the $(N-1)$-electron response matrix, however, are not important, because the diagonalizations do not represent the computationally expensive steps. Their computational effort scales with M^3 if M represents the system size, whereas the computational effort for constructing the N-electron response matrix scales with M^4. This latter task represents the computationally most demanding step. In Sec. III B we demonstrate that band gaps calculated according to Eqs. (32) and (34) converge towards those obtained by calculating the required dRPA correlation energies via diagonalization of the N-, the $(N-1)$-, and the $(N+1)$-electron response matrices as described in the previous section.

Next we expand the logarithm in Eq. (32) in a Taylor series

$$\begin{aligned}&\ln\{\mathbf{1}-[\mathbf{1}-\boldsymbol{\sigma}^N(i\omega,\mathbf{q})]^{-1}\Delta\boldsymbol{\sigma}^-(i\omega,\mathbf{q})\}\\&\quad=-[\mathbf{1}-\boldsymbol{\sigma}^N(i\omega,\mathbf{q})]^{-1}\Delta\boldsymbol{\sigma}^-(i\omega,\mathbf{q})+O(1/\Omega^2).\end{aligned}\tag{35}$$

Because $\Delta\boldsymbol{\sigma}^-$ is proportional to $1/\Omega$ the higher order terms in this expansion contain factors of $1/\Omega^n$ with $n\geqslant 2$. If we insert the expansion (35) in Eq. (32) then these higher order terms vanish in the limit of an infinite system, because converting the summation over $\mathbf{q}$ in this limit in an integral only leads to a factor of $\Omega/8\pi^3$ and therefore factors of $1/\Omega^m$ with $m\geqslant 1$ remain in the higher order terms. With the expansion (35), Eq. (32) turns into

$$\begin{aligned}&E_c^{dRPA}[N-1]-E_c^{dRPA}[N]\\&\quad=\frac{-1}{2\pi}\sum_{\mathbf{q}}\int_0^\infty d\omega\mathrm{Tr}\{[\mathbf{1}-\boldsymbol{\sigma}^N(i\omega,\mathbf{q})]^{-1}\Delta\boldsymbol{\sigma}^-(i\omega,\mathbf{q})\\&\qquad-\Delta\boldsymbol{\sigma}^-(i\omega,\mathbf{q})\}.\end{aligned}\tag{36}$$

The first part of the integrand in Eq. (32) can be reformulated according to

$$\begin{aligned}&\mathrm{Tr}\{[\mathbf{1}-\boldsymbol{\sigma}^N(i\omega,\mathbf{q})]^{-1}\Delta\boldsymbol{\sigma}^-(i\omega,\mathbf{q})\}\\&\quad=\mathrm{Tr}\{[\mathbf{1}-\boldsymbol{\sigma}^N(i\omega,\mathbf{q})]^{-1}\mathbf{U}^\dagger(i\omega,\mathbf{q})\\&\qquad\times\mathbf{U}(i\omega,\mathbf{q})\Delta\boldsymbol{\sigma}^-(i\omega,\mathbf{q})\mathbf{U}^\dagger(i\omega,\mathbf{q})\mathbf{U}(i\omega,\mathbf{q})\}\\&\quad=\mathrm{Tr}\{\mathbf{U}(i\omega,\mathbf{q})[\mathbf{1}-\boldsymbol{\sigma}^N(i\omega,\mathbf{q})]^{-1}\mathbf{U}^\dagger(i\omega,\mathbf{q})\\&\qquad\times[\mathbf{U}(i\omega,\mathbf{q})\Delta\boldsymbol{\sigma}^-(i\omega,\mathbf{q})\mathbf{U}^\dagger(i\omega,\mathbf{q})\\&\qquad+\mathbf{U}(i\omega,\mathbf{q})\boldsymbol{\sigma}^N(i\omega,\mathbf{q})\mathbf{U}^{(1)^\dagger}(i\omega,\mathbf{q})\\&\qquad+\mathbf{U}^{(1)}(i\omega,\mathbf{q})\boldsymbol{\sigma}^N(i\omega,\mathbf{q})\mathbf{U}^\dagger(i\omega,\mathbf{q})]\}\\&\quad=\mathrm{Tr}\{[\mathbf{1}-\tilde{\mathbf{X}}^N(i\omega,\mathbf{q})]^{-1}\Delta\tilde{\mathbf{X}}^-(i\omega,\mathbf{q})\}.\end{aligned}\tag{37}$$

In Eq. (37) the matrix $\mathbf{U}^{(1)}$ denotes the difference of the unitary matrix $\mathbf{U}$ containing the eigenvectors of the scaled N-electron response matrix $\tilde{\mathbf{X}}^N$, Eq. (8), and a corresponding matrix containing the eigenvectors of the $(N-1)$-electron response matrix $\tilde{\mathbf{X}}^{N-1}$ in first order in the difference $\Delta\tilde{\mathbf{X}}^-$. The product $\mathbf{U}^{(1)^\dagger}\mathbf{U}$ is a matrix with diagonal elements being zero because the eigenvectors of the response matrices are normalized. As a consequence expressions of the form $\mathrm{Tr}\{[\mathbf{1}-\boldsymbol{\sigma}^N(i\omega,\mathbf{q})]^{-1}\Delta\boldsymbol{\sigma}^-(i\omega,\mathbf{q})\mathbf{U}^{(1)^\dagger}\mathbf{U}\}$ are zero and the terms containing $\mathbf{U}^{(1)}$ can be added. To obtain the last line of Eq. (37) we use that

$$\begin{aligned}\Delta\tilde{\mathbf{X}}^-(i\omega,\mathbf{q})\approx{}&\mathbf{U}(i\omega,\mathbf{q})\Delta\boldsymbol{\sigma}^{(1)}(i\omega,\mathbf{q})\mathbf{U}^\dagger(i\omega,\mathbf{q})\\&+\mathbf{U}(i\omega,\mathbf{q})\boldsymbol{\sigma}^N(i\omega,\mathbf{q})\mathbf{U}^{(1)^\dagger}(i\omega,\mathbf{q})\\&+\mathbf{U}^{(1)}(i\omega,\mathbf{q})\boldsymbol{\sigma}^N(i\omega,\mathbf{q})\mathbf{U}^\dagger(i\omega,\mathbf{q}),\end{aligned}\tag{38}$$

which holds true in first order. In Eq. (38) $\Delta\boldsymbol{\sigma}^{(1)}$ is the first-order approximation to $\Delta\boldsymbol{\sigma}^-$ with matrix elements given in Eq. (34). Similarly also

$$\mathrm{Tr}\{\Delta\boldsymbol{\sigma}^-(i\omega,\mathbf{q})\}\approx\mathrm{Tr}\{\Delta\tilde{\mathbf{X}}^-(i\omega,\mathbf{q})\}\tag{39}$$

holds true in first order.

Inserting Eqs. (37) and (39) in (36) yields

$$\begin{aligned}&E_c^{dRPA}[N-1]-E_c^{dRPA}[N]\\&\quad=\frac{-1}{2\pi}\sum_{\mathbf{q}}\int_0^\infty d\omega\mathrm{Tr}\{[\mathbf{1}-\tilde{\mathbf{X}}^N(i\omega,\mathbf{q})]^{-1}\Delta\tilde{\mathbf{X}}^-(i\omega,\mathbf{q})\\&\qquad-\Delta\tilde{\mathbf{X}}^-(i\omega,\mathbf{q})\}.\end{aligned}\tag{40}$$

In the relevant limit of an infinite system we need to take into account only quantities up to first order in $\Delta\tilde{\mathbf{X}}^-$ and therefore Eq. (40) holds true in this limit.

Finally we define the matrix

$$\mathbf{W}(i\omega,\mathbf{q})=[\mathbf{1}-\tilde{\mathbf{X}}^N(i\omega,\mathbf{q})]^{-1}\tag{41}$$

to turn Eq. (40) into

$$\begin{aligned}&E_c^{dRPA}[N-1]-E_c^{dRPA}[N]\\&\quad=\frac{-1}{2\pi}\sum_{\mathbf{q}}\int_0^\infty d\omega\mathrm{Tr}\{\mathbf{W}(i\omega,\mathbf{q})\Delta\tilde{\mathbf{X}}^-(i\omega,\mathbf{q})\\&\qquad-\Delta\tilde{\mathbf{X}}^-(i\omega,\mathbf{q})\}.\end{aligned}\tag{42}$$

In an analogous fashion we can obtain a corresponding expression for the difference

$$\begin{aligned}&E_c^{dRPA}[N]-E_c^{dRPA}[N+1]\\&\quad=\frac{1}{2\pi}\sum_{\mathbf{q}}\int_0^\infty d\omega\mathrm{Tr}\{\mathbf{W}(i\omega,\mathbf{q})\Delta\tilde{\mathbf{X}}^+(i\omega,\mathbf{q})\\&\qquad-\Delta\tilde{\mathbf{X}}^+(i\omega,\mathbf{q})\}\end{aligned}\tag{43}$$

required in the calculation of the electron affinity. Here $\Delta\tilde{\mathbf{X}}^+$ is obtained by scaling the difference $\Delta\mathbf{X}^+$ of the $(N+1)$- and N-electron response function by the Coulomb kernel according to

$$\Delta\tilde{\mathbf{X}}^+(i\omega,\mathbf{q})=\mathbf{F}_H^{1/2}(\mathbf{q})\Delta\mathbf{X}^+(i\omega,\mathbf{q})\mathbf{F}_H^{1/2}(\mathbf{q}).\tag{44}$$

For the matrix elements of $\Delta\mathbf{X}^+$ see the Supplemental Material [30].

In the limit of an infinite system Eqs. (42) and (43) lead to the same band gaps as does the direct calculation from total energy differences discussed in the previous section. Equations (42) and (43) were used in Ref. [20] to calculate the band gaps of carbon and silicon. In Sec. III B we show how band gaps calculated directly from total energy differences and by using Eqs. (42) and (43) converge to each other with increasing numbers of $\mathbf{k}$ points, i.e., in the limit of infinite systems. For the relation of Eqs. (42) and (43) to the GW method see Refs. [20] and [42].

III. RESULTS

A. Band gaps of prototypical semiconductors

We have calculated fundamental band gaps for a number of prototypical semiconductors and insulators with the plane-wave pseudopotential (PP) program MCEXX [21] and with the all-electron full-potential linearized augmented plane-wave

TABLE I. Comparison of FLAPW and PP dRPA gaps (in eV) with experiment.

	FLAPW	PP		
	PBE	PBE	EXX	Exp.
Si	1.24	1.22	1.34	1.17
BP	2.11	2.14	2.23	2.10
AlAs	2.39	2.40	2.54	2.23
GaP	2.39	2.70	2.82	2.35
SiC	2.56	2.54	2.70	2.42
AlP	2.60	2.77	2.93	2.50
C	5.87	5.91	6.12	5.91[1]
BN	6.65	6.68	6.86	6.40
NaCl	8.65	9.26	9.54	8.50
Ar	13.95	14.31	14.47	14.15
MARE	3.3%	5.9%	10.9%	
MRE	2.9%	5.9%	10.9%	
MARE[2]	3.6%	4.3%	9.4%	
MRE[2]	2.9%	4.3%	9.4%	

[1] Corrected for effects of zero-point vibrations by 0.41 eV according to Ref. [43].

[2] Errors for only Si, SiC, AlP, C, BN, and Ar as in Table III.

TABLE II. Different contributions to the dRPA band gap (in eV) using EXX orbitals and eigenvalues.

	Δ_ε	Δ_x	ΔE_c^{dRPA}
Si	1.10	4.46	-4.18
BP	1.74	5.38	-4.89
AlAs	2.19	4.62	-4.27
GaP	2.32	4.89	-4.35
SiC	2.40	5.59	-5.41
AlP	2.34	5.01	-4.42
C	4.71	7.32	-5.91
BN	5.58	7.78	-6.50
NaCl	6.42	7.09	-3.98
Ar	9.71	8.55	-3.80

(FLAPW) package FLEUR [22,23]. Band gaps as well as their contributions were extrapolated to an infinite number of **k** points. Note that for the correlation contribution ΔE_c^{dRPA} only the occupied valence electrons are taken into account in the all-electron calculations. The core states are considered in the calculation of the KS orbitals and eigenvalues and in the calculation of matrix elements of $\hat{v}_x^{NL}$, $\hat{v}_x$, and $\hat{v}_c$. See Supplemental Material for further technical details [30].

In Table I dRPA band gaps obtained according to Eq. (23) with orbitals and eigenvalues from PBE and EXX calculations are listed. Irrespective of the applied functional in the underlying KS calculation, the dRPA gap lies very close to the experimental result. The band gaps based on EXX orbitals and eigenvalues are systematically larger than those from PBE input data. Hence they are in somewhat less good agreement with the experimental values. The band gaps from the pseudopotential and the all-electron code agree quite well. The larger deviations for NaCl and GaP are due to the inclusion of the Na $2s$ and $2p$ and Ga $3d$ semicore orbitals in the calculation of ΔE_c^{dRPA} with the FLAPW program. We also considered the somewhat critical band gap of wurtzite ZnO [44,45] and obtained a value of 3.27 eV (with PBE orbitals from FLAPW) in reasonable agreement with the experimental value of 3.6 eV which has been corrected for lattice effects [46,47].

The individual contributions Δ_ε, Δ_x, and ΔE_c^{dRPA} to the band gap are shown in Table II for the case of EXX orbitals and eigenvalues as input data (for the PBE case see Supplemental Material [30]). It is evident that Δ_x and ΔE_c^{dRPA} have opposite sign and to some extent cancel each other. (The contributions Δ_ε, Δ_x, and ΔE_c^{dRPA} of Table II do not exactly add up to the band gaps of Table I because they were individually extrapolated to infinite numbers of **k** points; see Supplemental Material [30].)

For comparison Table III lists band gaps obtained with the GW method. Errors with respect to experimental values here range from a mean absolute relative error (MARE) of 2.2% to 9.9% depending on the level of self-consistency in the GW step and on the functionals used to generate the underlying orbitals and eigenvalue. The deviations of 3.6% (all-electron) and 4.3% (pseudopotential) of the dRPA band gaps in case of PBE orbitals and eigenvalues thus are competitive.

B. Equivalence of different ACFD approaches for band gaps

In Fig. 1 deviations of the correlation contributions to the ionization potential, electron affinity, and band gap calculated in different ways are shown as a function of the number of **k** points for GaP. (See Supplemental Material [30] for corresponding data for Si.) On the one hand, Fig. 1 displays deviations between correlation contributions calculated according to the approach of Ref. [20], Eqs. (40) and (43) (without invoking approximations like the plasmon-pole approximation), and those directly calculated from correlation energies obtained from the response matrices of the N-, $(N-1)$-, and $(N+1)$-electron system [(blue) open circles]. On the other hand, deviations due to the perturbative treatment of the eigenvalues of the response matrix of the $(N-1)$- and $(N+1)$-electron system, Eqs. (32) and (34), in comparison to the direct calculation are shown [(red) solid circles]. Figure 1

TABLE III. GW band gaps (in eV) at different levels of self-consistency using PBE or HSE03 orbitals and eigenvalues as input. Data are taken from Refs. [4,5].

	PBE reference			HSE03 reference		
	G_0W_0	GW_0	GW	G_0W_0	GW_0	GW
Si	1.12	1.20	1.28	1.32	1.35	1.37
SiC	2.27	2.43	2.64	2.60	2.68	2.76
AlP	2.44	2.59	2.77	2.69	2.77	2.86
C	5.50	5.68	5.99	5.64	5.92	6.08
BN	6.10	6.35	6.73	6.54	6.66	6.85
Ar	13.28	13.87	14.65	13.70	14.10	14.70
MARE	5.1%	2.2%	6.6%	6.3%	6.9%	9.9%
MRE	-5.1%	-0.01%	6.6%	3.7%	6.8%	9.9%

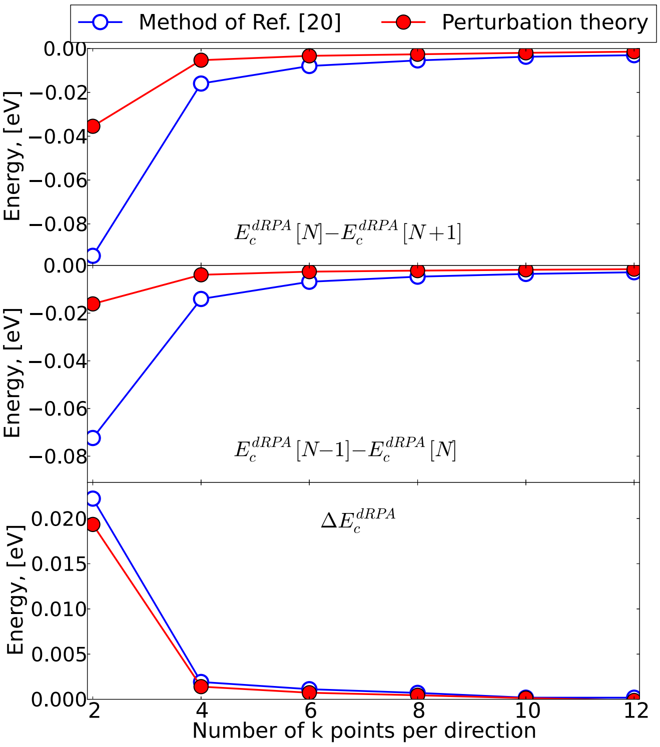

FIG. 1. Deviations of correlation contributions to electron affinity, ionization potential, and band gap calculated by different approaches with the number of **k** points for GaP. Displayed is the difference of the correlation contributions calculated with the approach of Ref. [20] and an approach using perturbation theory for the eigenvalues of the response matrices of the $(N-1)$- and $(N+1)$-electron system to a direct calculation of the correlation contributions from total energies as described in Sec. II B.

clearly shows that the three approaches converge to the same result with increasing number of **k** points.

IV. CONCLUDING REMARKS

It is highly promising that approaches for fundamental bands gaps based on the adiabatic-connection fluctuation-dissipation (ACFD) theorem yield results with an accuracy comparable to corresponding GW results even if they rely on the simplest ansatz, the dRPA. It is known that total electronic energies can be drastically improved by going beyond the dRPA [16–18]. Therefore the strategy of calculating band gaps by total energy differences obtained with the ACFD theorem has the potential to be further improved by going beyond the dRPA, e.g., by including suitable exchange-correlation kernels in the construction of the response functions appearing in the ACFD theorem [48]. If the dRPA correlation potential was taken into account in addition to the exact KS exchange potential then a self-consistent method would result and the energies added in Eqs. (21) and (22) to $-\varepsilon_H$ and $-\varepsilon_L$ to obtain IP and EA, respectively, would equal potential adjustors introduced in Ref. [9] to fix the energetic position of exchange-correlation potentials.

Finally we note that the considered methods can be easily implemented in KS codes for periodic systems that give access to the dRPA correlation energy. Very little additional computational effort is then required to calculate fundamental band gaps in addition to the dRPA correlation energy of the neutral system. Thus band gaps can be obtained almost for free once the KS ground state energy including dRPA correlation has been calculated.

ACKNOWLEDGMENTS

This work was supported by the DFG through Grant No. GO 523/14-1 and the collaborative research center SFB 953. M.B. gratefully acknowledges financial support from the Helmholtz Association through the Helmholtz Postdoc Programme (VH-PD-022).

---

[1] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[2] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002), and references therein .

[3] F. Bechstedt, F. Fuchs, and G. Kresse, Phys. Status Solidi B **246**, 1877 (2009), and references therein .

[4] M. Shishkin and G. Kresse, Phys. Rev. B **75**, 235102 (2007).

[5] F. Fuchs, J. Furthmüller, F. Bechstedt, M. Shishkin, and G. Kresse, Phys. Rev. B **76**, 115109 (2007).

[6] M. Shishkin, M. Marsman, and G. Kresse, Phys. Rev. Lett. **99**, 246403 (2007).

[7] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).

[8] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer, Heidelberg, 1990).

[9] A. Görling, Phys. Rev. B **91**, 245120 (2015).

[10] D. C. Langreth and J. P. Perdew, Solid State Commun. **17**, 1425 (1975).

[11] D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977).

[12] F. Furche, Phys. Rev. B **64**, 195120 (2001).

[13] M. Fuchs and X. Gonze, Phys. Rev. B **65**, 235109 (2002).

[14] A. Heßelmann and A. Görling, Mol. Phys. **109**, 2473 (2011).

[15] H. Eshuis, J. E. Bates, and F. Furche, Theor. Chem. Acc. **131**, 1 (2012).

[16] P. Bleiziffer, A. Heßelmann, and A. Görling, J. Chem. Phys. **136**, 134102 (2012).

[17] J. Paier, X. Ren, P. Rinke, G. E. Scuseria, A. Grüneis, G. Kresse, and M. Scheffler, New J. Phys. **14**, 043002 (2012).

[18] X. Ren, P. Rinke, C. Joas, and M. Scheffler, J. Mater. Sci. **47**, 7447 (2012).

[19] N. Colonna, M. Hellgren, and S. de Gironcoli, Phys. Rev. B **90**, 125150 (2014).

[20] Y. M. Niquet and X. Gonze, Phys. Rev. B **70**, 245115 (2004).

[21] The MCEXX (Magnetization Current Exact-Exchange) code is a pseudopotential plane-wave code developed at the University of Erlangen-Nuremberg .

[22] See http://www.flapw.de.

[23] C. Friedrich, S. Blügel, and A. Schindlmayr, Phys. Rev. B **81**, 125102 (2010).

[24] M. A. L. Marques *et al.*, editors, *Time-Dependent Density Functional Theory*, Lecture Notes in Physics, Vol. 706 (Springer, Heidelberg, 2006).

[25] P. Elliot, F. Furche, and K. Burke, *Excited States from Time-Dependent Density Functional Theory* (Wiley, New York, 2009), p. 91.

[26] C. A. Ullrich, *Time-Dependent Density-Functional Theory* (Oxford University Press, Oxford, 2012).

[27] T. Kotani and M. van Schilfgaarde, Solid State Commun. **121**, 461 (2002).

[28] C. Friedrich, A. Schindlmayr, and S. Blügel, Comput. Phys. Commun. **180**, 347 (2009).

[29] M. Betzinger, C. Friedrich, and S. Blügel, Phys. Rev. B **81**, 195117 (2010).

[30] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.94.075123 for more information on details of the elements of the $(N+1)$-electron KS response matrix and of the contributions to band gaps, on the computational details, on the extrapolation to an infinite number of **k** points, and on the equivalence of different ACFD approaches for band gaps.

[31] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[32] R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953).

[33] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).

[34] M. Städele, J. A. Majewski, P. Vogl, and A. Görling, Phys. Rev. Lett. **79**, 2089 (1997).

[35] M. Städele, M. Moukara, J. A. Majewski, P. Vogl, and A. Görling, Phys. Rev. B **59**, 10031 (1999).

[36] M. Betzinger, C. Friedrich, A. Görling, and S. Blügel, Phys. Rev. B **85**, 245124 (2012).

[37] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).

[38] J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983).

[39] L. J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983).

[40] J. P. Perdew, in *Density Functional Methods in Physics*, edited by R. M. Dreizler and J. da Providencia (Plenum, New York, 1985).

[41] A. Görling and M. Levy, Phys. Rev. A **52**, 4493 (1995).

[42] L.-W. Wang, Phys. Rev. B **82**, 115111 (2010).

[43] B. Monserrat, G. J. Conduit, and R. J. Needs, Phys. Rev. B **90**, 184302 (2014).

[44] B.-C. Shih, Y. Xue, P. Zhang, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **105**, 146401 (2010).

[45] C. Friedrich, M. C. Müller, and S. Blügel, Phys. Rev. B **83**, 081101 (2011); **84**, 039906 (2011).

[46] S. Tsoi, X. Lu, A. K. Ramdas, H. Alawadhi, M. Grimsditch, M. Cardona, and R. Lauck, Phys. Rev. B **74**, 165203 (2006).

[47] H. Alawadhi, S. Tsoi, X. Lu, A. K. Ramdas,, M. Grimsditch, M. Cardona, and R. Lauck, Phys. Rev. B **75**, 205207 (2007).

[48] J. Erhard, P. Bleiziffer, and A. Görling (unpublished).