Band-edge levels of the NaCl(100) surface: Self-consistent hybrid density functional theory compared to many-body perturbation theory

Manuel Hochheim and Thomas Bredow[*]
Mulliken Center for Theoretical Chemistry, Institut für Physikalische und Theoretische Chemie, Universität Bonn,
Beringstraße 4, 53115 Bonn, Germany

(Received 21 December 2017; revised manuscript received 19 April 2018; published 27 June 2018)

The electronic gap of bulk NaCl and the band-edge levels of the NaCl(100) surface are calculated using GW methods and self-consistent dielectric dependent hybrid functionals. Optical spectra are calculated by solving the Bethe-Salpeter equations (GW-BSE). For the calculation of the electronic structure of the surface, a procedure based on dielectric dependent range-separated hybrid (sc-DDRSH) functionals is proposed where the ω parameter is evaluated self-consistently from the surface polarizability tensor. The resulting band-edge energies deviate less than 0.1 eV from the GW results. Both GW and sc-DDRSH results closely match the most recent experimental values of the valence band maximum and the conduction band minimum. The GW-BSE results obtained for the NaCl(100) surface indicate that there are a small number of surface states 0.4–0.5 eV below the first absorption maximum at 7.6–7.7 eV. The calculated optical band gaps of the bulk are 7.7–7.9 eV, close to the range of experimental values.

DOI: 10.1103/PhysRevB.97.235447

I. INTRODUCTION

Sodium chloride is a prototype wide-gap insulator. Therefore, numerous experimental and theoretical investigations of the electronic structure of NaCl have been carried out [1–32]. Due to the large amount of data available for the electronic structure and other properties, sodium chloride is often used as a reference material for benchmarking theoretical methods [33–39]. Particularly, ionization energies IP, electron affinities EA, and fundamental band gaps E_g are of interest for the test of theoretical methods. They are key parameters that define the electronic structure of a material and control processes of charge exchange and transport via interfaces in electronic devices [40,41]. The valence-band maximum (VBM) corresponds to the negative vertical IP and the vertical EA corresponds to the conduction-band minimum (CBM), assuming a reference level of zero and the validity of Koopmans' theorem [42]. Within this approximation, E_g is the difference between CBM and VBM. But Koopmans' theorem refers to the Hartree-Fock (HF) theory and not to density functional theory (DFT). In exact Kohn-Sham DFT, CBM and the CBM-VBM difference have a different physical meaning [43]. In standard DFT based on the generalized gradient approximation (GGA-DFT), the CBM is a poor approximation to EA due to the discontinuity in the exchange-correlation potential [44–46]. Hybrid functionals, particularly long-range corrected hybrid functionals, can overcome the discontinuity problem [47–49].

For the calculation of absolute band energies and fundamental band gaps, it is well known that semilocal density functionals fail mainly due to the self-interaction error (SIE) as a consequence of imbalanced treatment of Coulomb interaction and exact exchange [50,51]. The addition of HF exchange in global hybrid functionals reduces the SIE and improves the results but, still, considerable deviations from experimental values are obtained [50]. A physically more sound alternative is the GW approximation of many-body perturbation theory. The self-energy is described by the one-particle Green's function G and the dynamically screened Coulomb interaction W [52]. It has repeatedly been shown that GW methods provide accurate results for the electronic structure of insulators and semiconductors [53–55]. But as far as the authors are aware, no calculations exceeding the non-self-consistent G_0W_0 level of theory have been performed for the NaCl(100) surface [56]. We therefore performed GW calculations at three different levels of self-consistency for bulk NaCl and the NaCl(100) surface, eigenvalue self-consistent GW ($EVGW_0$) and quasiparticle self-consistent GW ($QPGW_0$ and QPGW). In the $EVGW_0$ procedure, the one-electron eigenvalues are updated in the Green's function G to self-consistency while the screened exchange interaction W_0 is calculated from the GGA wave function and is kept fixed. In the $QPGW_0$ approximation, the wave function is updated in addition to the eigenvalues, whereas W_0 is also kept constant. In QPGW, the eigenvalues and the wave function are updated in G as well as in W. No vertex corrections were included in our GW calculations.

From previous work, QPGW is known to overestimate both band gaps and band widths [57,58]. This error is diminished by including vertex corrections in W [54]. However, vertex corrections are only available in a few GW program packages. It has been shown that $EVGW_0$ and $QPGW_0$ yield similar accuracy as vertex-corrected QPGW [53,54,57–60] due to favorable error cancellation [58].

For the assessment of the quality of theoretical results, reliable experimental reference data are required. Experimental measurements of IP, EA, and E_g of crystalline compounds are affected by a large number of internal and external factors, ranging from the purity of the material

---

[*] bredow@thch.uni-bonn.de

(doping and defect content, charging effects) to the structure (surface crystallographic orientation) and morphology (surface roughness), processing history and surface condition (clean vs contaminated), which is why they are subject to considerable fluctuations for the same material. These fluctuations can be in the range of several tenths of an electronvolt [41]. Furthermore, the results also depend on the spectroscopic method. A common method to measure the ionization potential is ultraviolet photoelectron emission spectroscopy (UPS). Applied to alkali halides, however, this method suffers from charging effects and temperature-dependent phononic broadening of the signals in the spectrum. Thus the valence band width is artificially increased and the measured IP may not be accurate. For these reasons, we performed an extensive literature search and summarized and commented the experimental data.

Measurements of electronic excitations suffer significantly less from the above-mentioned problems because no charging effects occur and the measured optical gap usually corresponds to the first peak maximum. We have calculated the optical spectrum of the NaCl (100) surface solving the Bethe-Salpeter equation (BSE) based on the orbitals and quasiparticle energies obtained by GW methods. These data are compared to experimental spectra.

Even though it is possible to calculate the properties of extended systems using GW methods [61,62], it is computationally very demanding. For this reason, GW methods are still far from being standard for extended systems like adsorbate structures or surface defects. Therefore, it is desirable to have methods at hand that provide comparable results at significantly lower computational cost. Promising parameter-free alternatives are dielectric dependent hybrid (DDH) functionals [34,63] and dielectric dependent range-separated hybrid (DDRSH) functionals [64].

In the next section, details of DDH and DDRSH functionals are given, followed by the computational details. Afterward, we provide a detailed evaluation of literature data on the electronic properties of NaCl. These experimental data are then taken as a reference for the following discussion of our GW and DFT results.

II. METHOD

A. Self-consistent dielectric dependent hybrid and range-separated hybrid functionals

In the Kohn-Sham formalism, the nonlocal potential $v_{KS}(\mathbf{r})$ is given by Eq. (1). It is the sum of the Hartree potential $v_H(\mathbf{r})$, the exchange-correlation potential $v_{xc}(\mathbf{r})$, and the external potential of the nuclei $v_{\text{ext}}(\mathbf{r})$:

$$v_{KS}(\mathbf{r}) = v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}). \tag{1}$$

In the global hybrid formalism, the nonlocal exchange-correlation potential is the sum of a local exchange $v_x(\mathbf{r})$, and correlation $v_c(\mathbf{r})$ potential, and exact exchange $v_x^{ex}(\mathbf{r},\mathbf{r}')$, Eq. (2). Here a is a weighting factor which determines the amount of exact exchange added to the local potential:

$$v_{xc}(\mathbf{r}) = a \cdot v_x^{ex}(\mathbf{r},\mathbf{r}') + (1-a)\cdot v_x(\mathbf{r}) + v_c(\mathbf{r}). \tag{2}$$

In the dielectric dependent self-consistent hybrid (sc-DDH) approach by Skone *et al.*, the appropriate amount of exact exchange is evaluated self-consistently [34,63], corresponding to the inverse of the optical dielectric constant ϵ_∞[65], which is obtained by solving the coupled-perturbed Kohn-Sham equations [66,67]. In this formalism, the elements of the dielectric tensor ϵ_{ij} are calculated from the polarizability tensor elements α_{ij} normalized to the volume of the system V via Eq. (3):

$$\epsilon_{ij} = \delta_{ij} + \frac{4\pi}{V}\alpha_{ij}. \tag{3}$$

For systems that are finite in at least one dimension, such as molecules, polymers, and slabs $\epsilon_\infty \to 1$ since $V \to \infty$, which suggests to include full exact exchange (i.e., $a = 1$) [64]. In global hybrid functionals, this would lead to the neglect of $v_x(\mathbf{r})$, resulting in a HF + $v_c(\mathbf{r})$ approach. But HF is known to provide poor electronic properties due to missing screening effects. To avoid this problem, Brawand *et al.* [68] generalized the DDH functionals to finite systems. Nevertheless, Skone *et al.* have shown for molecular crystals that it is possible to transfer the bulk parameters from sc-DDH to surface calculations [64].

A further possible alternative for finite systems are DDRSH. In range-separated hybrid functionals (RSH) $v_{xc}(\mathbf{r})$ is partitioned into short-range (sr) and long-range (lr) components, Eq. (4). The amount of long-range and short-range exact exchange admixed to the local exchange is given by the coefficients b and c:

$$\begin{aligned} v_{xc}(\mathbf{r}) = b\int v_x^{lr-ex}(\mathbf{r},\mathbf{r}';\omega)d\mathbf{r}' + c\int v_x^{sr-ex}(\mathbf{r},\mathbf{r}';\omega)d\mathbf{r}' \\ + (1-b)\cdot v_x^{lr}(\mathbf{r};\omega) + (1-c)\cdot v_x^{sr}(\mathbf{r};\omega) + v_c(\mathbf{r}). \end{aligned} \tag{4}$$

The long-range exact exchange potential is given by Eq. (5), where $\rho(\mathbf{r},\mathbf{r}')$ is the two-particle density matrix. In our example, we use the error function to partition the Coulomb interaction. But other functions, e.g., the Thomas-Fermi screening function, can be used as well [69]:

$$v_x^{lr-ex}(\mathbf{r},\mathbf{r}';\omega) = -\rho(\mathbf{r},\mathbf{r}')\frac{erf(\omega\cdot|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}. \tag{5}$$

The short-range exact exchange potential is then given via the complementary error function [Eq. (6)]:

$$v_x^{sr-ex}(\mathbf{r},\mathbf{r}';\omega) = -\rho(\mathbf{r},\mathbf{r}')\frac{erfc(\omega\cdot|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}. \tag{6}$$

Hence in RSH functionals, the Coulomb potential is partitioned into short- and long-range parts. This can be interpreted as an approximation to GW where the screening of the exact exchange is calculated numerically depending on the dielectric function. Skone *et al.* have successfully used such DDRSH functionals for molecular systems [64]. They set the parameters c to 0.25 and b to 1.0 and evaluated the screening parameter $\omega_\alpha^{\text{mol.}}$ via Eq. (7), where α is the molecular polarizability:

$$\omega_\alpha^{\text{mol.}} = \left(\frac{1}{\alpha}\right)^{\frac{1}{3}}. \tag{7}$$

In the present study, we used a related procedure to calculate the electronic properties of the NaCl(100) surface since DDH functional calculations give $\epsilon_\infty = 1$ for finite systems. However, we have modified the calculation of the range-separation parameter for surfaces. We use a modified version of Eq. (3) adapted to surfaces where the volume is replaced by the surface area A multiplied by the number of atomic layers n_l. The resulting formula for the surface range-separation parameter $\omega_\alpha^{surf.}$ is given in Eq. (8):

$$\omega_\alpha^{\text{surf.}} = \frac{n_l A}{4\pi\alpha}. \tag{8}$$

The factor n_l normalizes the polarizability tensor with respect to the number of layers since the tensor elements depend linearly on the system size [70] as shown in Fig. S1 in the Supplemental Material [71]. The polarizability α is calculated by averaging over the diagonal elements of the tensor. Skone *et al.* evaluated α from PBE calculations. In the present study, we calculated $\omega_\alpha^{\text{surf.}}$ with a self-consistent procedure. The convergence behavior is shown in Fig. S2 in the Supplemental Material [71]. We did not in all cases increase the long-range HF exchange contribution b to 1. The functionals were designed in a way that the short-range exact exchange coefficient c and the long-range exchange coefficient b sum up to 1.

B. Computational details

The VASP [72–75] program package (version 5.4.4) was used for the GW and GW-BSE calculations. The underlying DFT functional was the Perdew-Burke-Ernzerhof semilocal GGA functional (PBE) [76,77]. Core electrons were represented by the Projector Augmented Waves (PAW) method [78,79]. For the SCF procedure plane-wave cutoffs of 900 eV and 600 eV were selected for the bulk and surface calculations, respectively. The Brillouin zone was divided according to the Monkhorst-Pack scheme [80] using an $8 \times 8 \times 8$ k-point grid for the bulk and a $4 \times 4 \times 1$ k-point grid for the surface. These settings are similar to those used in previous GW studies [51,53].

In all cases, we have chosen 200 eV as the cutoff energy for the GW part. Bulk NaCl was calculated including 256 bands and 32 frequency points in the numerical integration of the dielectric function in the GW part. For the surface models, we used ten-layer models and converged both the vacuum spacing and the number of bands included, N_{bands}. In addition, extrapolation to an infinite number of bands was performed. Similar models were used by Kresse *et al.* [53].

The evaluation of hybrid DFT methods for the calculation of the electronic structure of NaCl was performed using the CRYSTAL17 code [81]. To account for surface relaxation, geometry optimization at PBE level was carried out using the PBE optimized lattice constant for the slab model which consists of ten atomic layers. For the subsequent electronic structure calculation the structure was rescaled to the zero-point energy corrected 0 K lattice constant of NaCl of 5.595 Å [53,82]. The same ten-layer models were used for the GW calculations. In our DFT calculations, we additionally added one layer of ghost atoms on both sides of the slab to reduce the incompleteness error of atom-centered basis sets as used in CRYSTAL and to describe the decay of the wave function to the vacuum properly. The calculations were performed using dielectric-dependent self-consistent global and DDRSH functionals [34,63,64]. A comparison with their non-self-consistent counterparts is given as well. After basis set convergence tests, we decided that a modified *def2*-TZVPP [64,83] basis set is an optimal compromise between accuracy and computational efficiency. The basis set of the ghost atoms is identical to the basis set of the corresponding surface atoms. The employed basis set tests can be found in Table S5 in the Supplemental Material [71,84].

III. ELECTRONIC STRUCTURE

Reliable experimental reference values are essential to evaluate the quality of theoretical calculations. As already mentioned before, there is a large number of experimental investigations of the electronic structure of sodium chloride available in the literature [1–32].

A. Summary of experimental data

The earliest and the most recent works found in the present literature search were carried out by Mott in 1938 [1] and by Heidorn in 2013 [32]. Due to the large number of studies available, it is difficult to summarize the data. To the best of the authors' knowledge, the last major literature review on the electronic structure of NaCl was given by Poole *et al.* in 1975 [19,85]. The reported ionization energies range from 8.1 eV to 8.53 eV, the electron affinities are between −0.1 eV and +0.9 eV and the band gaps range from 8.0 eV to 8.97 eV. By averaging they obtained values of $IP = 8.4$ eV, $EA = 0.5$ eV, and $E_g = 8.5$ eV [19]. These averaged values are still frequently used as experimental references until today. Nordhage *et al.* [22] recommended a band gap value of 9.0 eV and an electron affinity of 0.4 eV. We found no further reviews of literature data since the late 1970s. Therefore, we have prepared an updated summary in this study, see Table I, including more recent studies. For the ionization energy, we found values in the range between 8.1 eV to 9.5 eV. Despite this remarkably wide range of 1.4 eV, about 75% of the IP values reported in the studies are at or above 8.5 eV. In contrast to Poole *et al.*, we have decided not to average the values found due to their diversity and the presence of clear outliers. We rather consider the latest experimental data as most reliable. In case of IP, this corresponds to 9.0 eV obtained by Connor *et al.* [21] from UPS measurements. With 1.2 eV, the range of literature values reported for E_g is similarly wide as for IP. The values range from 7.8 eV to 9.0 eV. More than 80% of the values are larger than or equal to 8.5 eV. Furthermore, the outlier at 7.8 eV was obtained by electron bombardment, which might cause severe surface damage [27]. The latest study by Heidorn *et al.* [32] reports a value of 8.7 ± 0.2 eV.

EA is probably the experimentally most difficult to achieve property. It is usually estimated by subtracting IP and E_g. In some cases, the electron affinity is also determined from a fitting procedure to energy distribution curves obtained from electron scattering experiments [23,24]. For the sign convention of EA we use the IUPAC definition [86]. The reported values range from −0.1 eV to 1.5 eV. All studies except that of Eby *et al.* [4] agree that NaCl exhibits a positive electron affinity. The value of Maruyama *et al.* [23] of 1.5 eV is also questionable, since Wright *et al.* [2] have found that the maximum EA is approximately 1.0 eV. The

TABLE I. Summary of experimental electronic properties of NaCl. Listed are the ionization energy IP, the electron affinity EA, and the band gap E_g. Values obtained by subtraction instead of measurement are displayed in italics and marked with an asterisk. All values are given in eV.

Reference	Method	System	IP	EA	E_g
Mott (1938) [1]	UV absorption/Photoconductivity	Literature data	—	_0.5*_	—
Wright (1948) [2]	UV absorption/Photoconductivity	Literature data	—	_1.0*_	—
Taylor (1959) [3]	UPS	Single crystal on Ni	8.5	—	—
	UPS	film ~ 10 000-20 000 Å on Ni	8.1	—	—
Eby (1959) [4]	UV absorption	~ 0.3 mm film on LiF, 80 ± 2 K	8.5 [3]	_-0.1*_	8.6
Timusk (1961) [5]	Luminescence	Single crystal RT	8.5 [3]	_0.6*_	—
Best (1961) [6]	EELS	Films	8.7 ± 0.1	—	—
Timusk (1962) [7]	Optical absorption/UPS	Single crystal RT	8.8	—	—
Phillips (1964) [8]	Evaluation of Literature spectra[4]	~ 0.3 mm film on LiF, 80 ± 2 K	—	—	8.4
Metzger (1965) [9]	UPS	Film ~ 2500Å on Pt	8.6 [4]	_0.9*_	9.5
Pradal (1966) [10]	EELS	Films	—	—	8.7
Creuzburg (1966) [11]	EELS	Films on carbon coated Ni net	8.1	—	—
Onaka (1967) [12]	Luminescence spectroscopy	0.2 mm NaCl:Ag	—	—	8.6
Roessler (1968) [13]	Reflectance	Single crystal 77 K	—	—	8.97 ± 0.07
Gout (1968) [87]	EELS	Film ~ 1000Å	—	—	8.7
Miyata (1968) [14]	Reflectivity	Single crystal 10 K	8.77	—	—
	Reflectivity	Single crystal 298 K	8.53	—	—
Nakai (1969) [15]	abs. spec.	Films, 1000-3000 Å, 300 K	—	—	8.6
Haensel (1969) [16]	UPS	Films on Au ~ 500Å	≈ 8.5	≈ _0.0*_	8.5 [88]
Hiraoka (1972) [17]	LEERS	Evap. films on stainless steel 77 K/290 K	9.5	_0.8*_	8.65 [4]
Pong (1974) [18]	UPS	Films on stainless steel 500–800 Å 300 K	9.0 ± 0.2	—	—
Poole (1975) [19]	UPS	Single crystal	8.2	—	—
Battye (1976) [20]	EELS	Films ~ 420 K	—	—	8.5(2)
Connor (1977) [21]	UPS	Film <300 Å	9.0	—	—
Nordhage (1977) [22]	examination of literature data	—	—	_0.4*_	9.0
Maruyama (1978) [23]	second. elec. EDC (fit)	films ~ 500-2000Å	—	1.5	8.6
Henke (1979) [24]	second. elec. EDC (fit)	(100) films synchrotron radiation	—	0.58	8.5 [19]
Roy (1985) [25]	EELS	Single crystals and films	—	—	8.8
Rodnyi (1989) [26]	Literature	—	—	—	8.6
Gołek (1996) [27]	Electron bombardment	Evap. films 5-50 ML on W(110)	—	—	7.8 - 8.3
Pearson (1998) [28]	Literature [89]	—	—	—	8.5
Tegenkamp (1999) [29]	EELS	5 ML NaCl(100) on Ge(100) T<100 K	—	—	8.4
Tegenkamp (2002) [30,31]	UPS	2-3 ML NaCl(100) on Al_2O_3 T<180 K	—	—	8.9
Heidorn (2013) [32]	STM	NaCl(100) islands on Ag(111)	—	—	8.7 ± 0.2

other investigations also find values between 0 eV and 1 eV. The latest literature value given by Henke *et al.* [24] is 0.58 eV.

In summary, our literature search results in values of 8.7 ± 0.2 eV for E_g, 9.0 eV for IP, and 0.58 eV for EA. These values are all a few tenths of an eV larger than those given by Poole *et al.* [19]. They do not exactly fulfill the relation $E_g = IP - EA$ due to the different experiments they were obtained from. However, the values are in a reasonable range and, considering the experimental uncertainty, the relation is fulfilled.

In the experiments, electron-phonon coupling affects the measured electron binding energies. Our present calculations do not take electron-phonon coupling into account, we therefore use a theoretically corrected experimental value. Lambrecht *et al.* [39] calculated the effect of the electron-phonon coupling on the band-gap and the band-edge levels of NaCl. For comparison with standard calculations, experimental band-gap values should be increased by 0.166 eV, which originates from a 0.113 eV downshift of the VBM and a 0.053 eV upshift of the CBM. Therefore, our recommended experimental band-structure values for the comparison to 0 K calculations of NaCl are 8.87 ± 0.2 eV [32,39] for E_g, 9.11 eV [21,39] for IP, and 0.53 eV [24,39] for EA.

B. Electronic data from GW calculations

To create a theoretical reference and to investigate differences between bulk and surface on the same theoretical level, GW calculations have been carried out for both model types. Comparable studies have already been performed on bulk NaCl [38]. However, to the authors' best knowledge, only non-self-consistent G_0W_0 calculations have been carried out for the NaCl(100) surface so far [56]. The G_0W_0 variant calculates both Green's function G and screened exact exchange W from the DFT wave function. Due to this strong dependence on the SCF method, usually hybrid methods are required.

1. Fundamental band gaps and band-edge levels by GW

The present GW results are summarized in Table II for the bulk and in Table III for the surface. It is known that the NaCl lattice constant shows a nonnegligible temperature

TABLE II. GW-BSE results for bulk NaCl; 8 × 8 × 8 Monkhorst-Pack grid, $E_{\mathrm{cut}} = 900$ eV (SCF), 200 eV (GW), eight GW cycles, 32 frequencies in the numerical integration; 256 bands in GW and BSE; lattice constant $|\vec{a}|$ (Å), electronic band gap (E_g^{bulk}), first excited state energy S_1^{bulk} (eV).

Method	$\lvert\vec{a}\rvert$	E_g^{bulk}	S_1^{bulk}
EVGW$_0$	5.60	8.69	7.82
	5.64	8.61	7.73
	5.68	8.54	7.64
QPGW$_0$	5.60	8.90	7.99
	5.64	8.82	7.90
QPGW	5.64	9.58	8.34

dependence. The extrapolated 0 K lattice constant is 5.595 Å [82], while the experimental room temperature lattice constant is 5.64 Å [90]. To investigate the impact of this geometrical change, different lattice constants in this range have been used for the calculations of bulk NaCl. In Table II , it is shown that a reduction of the lattice constant from 5.64 to 5.60 Å results in an increase of the electronic band gap by ∼ 0.1 eV. This minor dependence of the band gap on the lattice constant has already been found in other works [57]. Both EVGW$_0$ (8.61 eV) and QPGW$_0$ (8.82 eV) reproduce the corrected experimental band gap of 8.87 eV [32,39] well. There is almost a perfect match with the QPGW$_0$ value and the EVGW$_0$ value deviates by about 0.25 eV. The QPGW calculation, on the other hand, gives a much-too-large band gap, 9.58 eV. We assume that it is reasonable to use EVGW$_0$ and QPGW$_0$ results as reference for DFT.

In a previous study by Freysoldt *et al.* [56], G$_0$W$_0$ calculations were performed on a NaCl(100) slab model with two atomic layers, which resulted in a band gap of ∼ 8.7 eV. In contrast to the bulk, not only E_g but also the absolute band positions relative to the vacuum level are physically meaningful. These values determine the surface reactivity in terms of charge transfer to or from adsorbed molecules. It is therefore of particular importance to correctly predict the band-edge levels. Freysoldt *et al.* only discussed the band gap and not the absolute band-edge positions. In addition, it can be assumed that the two-layer model is too small to calculate the absolute band positions properly. The results of our surface calculations are given in Table III. To check the dependence of the results from model parameters, we converged both the number of bands and the vacuum distance. The convergence tests can be found in Table S2 in the Supplemental Material [71]. We found that a vacuum distance of 20 Å is sufficient to converge the band energies within less than 0.1 eV. The electronic and optical properties are more sensitive to a change in the number of bands than to an increase in the vacuum distance. Therefore, an extrapolation procedure was applied, except for QPGW. EVGW$_0$ and QPGW$_0$ again provide quite similar results. Especially IP is almost identical for both methods, 9.20 eV, and matches the experimental reference value of 9.11 eV [21,39] very well. With a value of 0.46 eV, the EVGW$_0$ EA differs more than 0.1 eV from the QPGW$_0$ value of 0.59 eV. Consequently, the difference in E_g is in the same order of magnitude. Both GW variants match the experimental reference value (0.53 eV [24,39]) within 0.1 eV.

TABLE III. GW and GW-BSE results for the ten-layer NaCl(100) surface model relaxed with PBE; 4 × 4 × 1 Monkhorst-Pack grid, $E_{\mathrm{cut}} = 600$ eV (SCF), 200 eV (GW), six GW cycles, 32 frequencies for numerical integration; vacuum distance (Å), number of bands N_{bands} in GW and BSE; valence band maximum (VBM), conduction band minimum (CBM), electronic band gap ($E_g^{\mathrm{surf.}}$), excited state energies $S_1^{\mathrm{surf.}}$, $S_5^{surf.}$ (eV); extrapolation for N_{bands} with $f(N) = A - Be^{-CN^2}$.

Method	Vacuum	N_{bands}	VBM	CBM	$E_g^{\mathrm{surf.}}$	$S_1^{\mathrm{surf.}}$	$S_5^{\mathrm{surf.}}$
EVGW$_0$	20	extrapol.	−9.20	−0.46	8.74	7.06	7.61
QPGW$_0$	20	extrapol.	−9.18	−0.59	8.59	7.37	7.71
QPGW	20	480	−9.27	−0.40	8.87	7.59	8.03

Our calculations indicate that differences between the electronic structures of the surface and the bulk are quite small, which is expected for an almost perfectly ionic solid. It is difficult to indicate a general trend for the change, as E_g becomes larger from bulk to surface with EVGW$_0$ and smaller with QPGW$_0$.

2. Optical properties and electronic excitation by GW-BSE

A major advantage of optical spectra is that they can be measured very precisely as discussed above. For this reason, we have calculated the optical excitation energies with GW-BSE. The results are also shown in Tables II and III. For comparison, we have listed experimental optical gaps of NaCl in Table IV. The experimental results are quite consistent and give the first excitation peak at 7.9–8.0 eV at low temperatures and at 7.7–7.8 eV at room temperature. In the experimental spectrum, the first excitation signal is a doublet due to spin-orbit coupling. The splitting is given by $\Gamma_{3/2}$ and $\Gamma_{1/2}$ in Table IV. Since we did not include spin-orbit coupling in our calculations, we compare our results to the $\Gamma_{3/2}$ signal. Furthermore, the experimental splitting (0.15 eV) is within the error range of GW-BSE. For bulk NaCl, our EVGW$_0$-BSE and QPGW$_0$-BSE results obtained using the 0 K lattice constant of 5.959 Å [82] are in good agreement with the experiment. EVGW$_0$-BSE (7.82 eV) slightly underestimates the experiment by about 0.1 eV while the QPGW$_0$-BSE value of 7.99 eV is within the experimental range. The temperature dependence of the excitation energy was investigated experimentally by Roessler *et al.* [13] and Miyata *et al.* [14]. In the experiment, a red shift of the optical excitation occurred upon heating the sample. Similar to the calculated band gap, the calculated excitation energy decreases by ∼ 0.09 eV when the lattice constant is increased. The experimental shift is slightly larger, indicating that other influences besides the lattice constant are relevant. As expected, the QPGW-BSE calculation ($a = 5.64$Å) overestimates the experimental optical gap (8.34 eV).

In contrast to the electronic properties, the calculated optical properties of the surface differ more noticeably from those of the bulk. The excited states are denoted as $S_i^{\mathrm{surf.}}$ for the surface and as S_i^{bulk} for the bulk. The index i indicates the number of the excited state in our model calculations. For the surface models, there are four low-lying excitations $S_1^{\mathrm{surf.}} - S_4^{\mathrm{surf.}}$, which were

TABLE IV. Summary of experimental optical gaps of NaCl. The signal in the experimental spectrum is a doublet due to spin-orbit coupling. The two energies resulting from the splitting are given by $\Gamma_{3/2}$ and $\Gamma_{1/2}$. If the spectral resolution was not high enough, no doublet is observed. This is indicated by "*no doublet*" in the $\Gamma_{1/2}$ column. All values are given in eV.

Reference	**Method**	**System**	$\boldsymbol{\Gamma_{3/2}}$	$\boldsymbol{\Gamma_{1/2}}$
Eby (1959) [4]	UV absorption	~ 0.3 mm film on LiF, 80 ± 2 K	7.96	8.09
Timusk (1961) [5]	Luminescence	Single crystal RT	7.9	*no doublet*
Wakita (1964) [91]	Luminescence	NaCl single crystal, 4 K	7.95	*not given*
Sueoka (1965) [92]	EELS	Thin NaCl foil	8.0	*no doublet*
Steinborn (1966) [93,94]	UV absorption		7.85	*no doublet*
Roessler (1968) [13]	Reflectance	Single crystal, 77 K	7.94 ± 0.03	8.09 ± 0.01
	Reflectance	Single crystal, 300 K	7.725 ± 0.025	7.82 ± 0.03
Onaka (1968) [12,95]	Luminescence	0.2 mm NaCl:*Ag*	7.9	*no doublet*
Miyata (1971) [96]	Conductivity spectrum	Single crystal 10 K	7.97	8.12
	Conductivity spectrum	Single crystal 78 K	7.96	8.10
	Conductivity spectrum	Single crystal 195 K	7.89	8.05
	Conductivity spectrum	Single crystal 298 K	7.81	8.00
	Conductivity spectrum	Single crystal 473 K	7.71	7.96
	Conductivity spectrum	Single crystal 573 K	7.65	7.98
Cox (1986) [97]	HREELS	NaCl(100)	7.83	*no doublet*
Matsumoto (1995) [98]	Excitation spectroscopy	Single crystal, 10 K	7.97	8.10
Zielasek (2000) [99,100]	EELS	20 ML NaCl:Ge(001)	7.85	8.10
Tegenkamp (2002) [30,31]	EELS	2-3 ML NaCl(100) on Al_2O_3 T<180 K	7.7	*no doublet*
Kramer (2003) [101]	EELS	Thin films NaCl:Ag(100)	7.8	*no doublet*

identified as surface states. This is the result of an analysis of the orbitals that contribute to these states (for an analysis of the atomic contributions to the surface density of states see Figs. S3–S6 in the Supplemental Material) [71]. The lowest bulklike excited state is $S_5^{\mathrm{surf.}}$, which corresponds to S_1^{bulk}, see Table II. In the experimental studies collected in Table IV, surface states are not visible, most probably due to their low oscillator strength compared to the bulk states.

C. Self-consistent dielectric-dependent hybrid and range-separated hybrid functionals

With CRYSTAL17 [81], it is possible to generate sc-DDH functionals where the amount of exact exchange is evaluated self-consistently [63], determined by the inverse of the optical dielectric constant ϵ_∞[65], which is obtained by solving the coupled-perturbed Kohn-Sham equations [66,67].

1. DFT band gap

The electronic band gap of bulk NaCl was calculated with selected global hybrid functionals, namely PBE0 [102], PBESOL0 [102,103], B1WC [104], B3PW [105–109], B3LYP [105], and WC1LYP [110]. Additionally, to the standard global hybrid calculations, we applied the sc-DDH scheme to the aforementioned functionals.

The resulting gaps can be found in Table V and the corresponding ϵ_∞ are given in Table VI. Since Skone *et al.* already performed sc-DDH calculations on bulk NaCl before [34,64], we provide our bulk data mainly for the sake of completeness, and they will only be discussed briefly. The results from standard hybrid functionals deviate considerably from each other (by up to 0.97 eV), according to their HF

TABLE V. Kohn-Sham energy gaps E_g^{bulk} of bulk NaCl evaluated with sc-DDH functionals and standard global hybrid functionals. $a = a_{\mathrm{std.}}$ refers to the functional with standard amount of Hartree-Fock exchange. $a = 1/\epsilon_\infty^{sc}$ refers to calculations where a is evaluated self-consistently. The corresponding values of a are given in parentheses. All gaps are given in eV.

Functional	Standard	sc-DDH
	$a = a_{\mathrm{std.}}$	$a = 1/\epsilon_\infty^{\mathrm{sc}}$
PBE	5.28 (0.00)	—
PBE0	7.39 (0.25)	8.96 (0.432)
PBESOL0	7.23 (0.25)	8.79 (0.428)
B1WC	6.50 (0.16)	8.81 (0.426)
B3PW	7.06 (0.20)	9.05 (0.432)
B3LYP	6.97 (0.20)	8.94 (0.433)
WC1LYP	6.42 (0.16)	8.71 (0.428)

TABLE VI. Optical dielectric constant ϵ_∞ of bulk NaCl calculated with sc-DDH functionals and standard global hybrid functionals. $a = a_{\mathrm{std.}}$ refers to the functional with standard amount of Hartree-Fock exchange. $a = 1/\epsilon_\infty^{sc}$ refers to calculations where a is evaluated self-consistently.

Functional	Standard	sc-Hybrid
	$a = a_{\mathrm{std.}}$	$a = 1/\epsilon_\infty^{\mathrm{sc}}$
PBE	2.47	—
PBE0	2.38	2.31
PBESOL0	2.41	2.34
B1WC	2.46	2.35
B3PW	2.40	2.31
B3LYP	2.40	2.31
WC1LYP	2.45	2.34

TABLE VII. Electronic structure data of the NaCl(100) surface calculated with sc-DDH functionals. The used amount of Hartree-Fock exchange a is determined from bulk calculations (see Table VI). VBM is the valence band maximum, CBM the conduction band minimum, and $E_g^{\text{surf.}}$ is the electronic band gap of the surface. All values are given in eV.

	sc-PBE0	sc-PBESOL0	sc-B1WC	sc-B3PW	sc-B3LYP	sc-WC1LYP	Exp.
VBM	−9.10	−9.10	−9.06	−9.12	−9.01	−8.92	−9.11 [21,39]
CBM	−0.34	−0.43	−0.38	−0.23	−0.36	−0.52	−0.53 [24,39]
$E_g^{\text{surf.}}$	8.75	8.67	8.67	8.90	8.65	8.40	8.87 ± 0.2[32,39]

exchange coefficients a. From Table V, it can be seen that self-consistent calculation of a significantly improves the results. The calculated band gaps deviate from the experimental reference value (8.87 eV [21,39]) by −0.16 eV to +0.18 eV. This is well within the experimental error range of ±0.2 eV. The remaining scattering of the results obtained with the self-consistent hybrid functionals is due to the different GGA exchange-correlation functionals.

All the standard global hybrid functionals give ϵ_∞ in a narrow range around 2.4 as can be seen from Table VI. The sc-DDH functionals reduce ϵ_∞ to a range between 2.30–2.35, which is closer to the experimental value of 2.33 [111].

2. DFT surface band-edge levels

For molecular crystals, Skone *et al.* have shown that the sc-DDH parameter a obtained for the bulk can be transferred to the calculation of the corresponding surfaces [64]. Therefore, we tested this procedure for the NaCl(100) surface. The results are shown in Table VII. Similar to the bulk, standard global hybrid functionals underestimate E_g of the surface and the band-edge positions considerably deviate from the experiment. The application of sc-DDH functionals leads to a massive improvement of the calculated electronic structure. The VBMs are in the range of −9.1 ± 0.1 eV and therefore are in very good agreement with the experimental and the GW values. Only sc-WC1LYP provides a VBM higher than −9 eV, but with −8.92 eV it is still in good agreement with the experimental value.

The resulting CBM energies range from –0.23 eV for sc-B3PW to −0.52 eV for sc-WC1LYP. Therefore, most sc-DDH functionals are reasonably close to the experimental and GW reference values. Due to the accuracy of the VBM and CBM positions, the resulting $E_g^{\text{surf.}}$ are of good quality as well, with errors of 0.1–0.3 eV. It is therefore evident that sc-DDH functionals provide an accurate description of the electronic structure of both bulk NaCl and the NaCl(100) surface.

For the calculation of finite systems, e.g., molecules in the gas phase, it has been shown that it is advantageous to use DDRSH functionals [64], as an alternative to schemes that adjust the amount of exact exchange in global hybrids [112]. This will become relevant for adsorption studies where charge transfer between molecule and surface is driven by the relative position of VBM, CBM and HOMO, LUMO.

We tested the short- and long-range corrected hybrid functionals LC-BLYP [113,114], RSHXLDA [115,116], and SC-BLYP [113,114]. The results of these calculations are given in Table VIII. It can clearly be seen that the self-consistent variants of the DDRSH (sc-DDRSH) functionals give results comparable to the sc-DDH functionals. sc-LC-BLYP and sc-SC-BLYP give VBM of −8.81 eV and −8.84 eV. These values deviate by 0.2–0.3 eV from the experimental reference. sc-RSHXLDA gives a VBM of −9.20 eV, which deviates by 0.1 eV from the experimental value. The deviations of the calculated CBM from experiment are in the same order of magnitude. sc-RSHXLDA (–0.49 eV) and sc-SC-BLYP (−0.50 eV) provide very similar CBM, which deviate by 0.1 eV from the experimental reference. sc-LC-BLYP gives a CBM of -0.32 eV, which deviates by 0.2 eV from experiment.

Since the fraction of exact exchange from DDH functionals can be transferred from the bulk to the surface we checked if the $\omega_\alpha^{\text{surf.}}$ parameter can be transferred to bulk calculations for NaCl. The results are given in Table IX.

Our results show that sc-DDRSH functionals provide band-edge positions for NaCl with an accuracy that is comparable to sc-DDH. A direct comparison of the best GW, sc-DDH functionals, and sc-DDRSH functionals with the experiment

TABLE VIII. Electronic properties of the NaCl(100) surface calculated with sc-range separated hybrid functionals. VBM is the valence band maximum, CBM the conduction band minimum, and $E_g^{\text{surf.}}$ is the electronic band gap of the surface. All values are given in eV. b is the amount of long-range exact exchange and c the amount of short-range exact exchange [see Eq. (4)]. $\omega_\alpha^{\text{surf.}}$ $[a_0^{-1}]$ is the range-separation parameter obtained self-consistently from the surface polarizability [see Eq. (8)].

	sc-LC-BLYP	sc-RSHXLDA	sc-SC-BLYP	Exp.
VBM	−8.81	−9.20	−8.84	−9.11 [21,39]
CBM	−0.32	−0.49	−0.50	−0.53 [24,39]
$E_g^{\text{surf.}}$	8.49	8.71	8.34	8.87 ± 0.2 [32,39]
b	1.00	1.00	0.80	—
c	0.00	0.00	0.20	—
$\omega_\alpha^{\text{surf.}}$	0.154	0.155	0.194	—

TABLE IX. Electronic band gaps of NaCl obtained using sc-DDRSH functionals. E_g^{bulk} [eV] is the band gap of the bulk. b is the amount of long-range exact exchange and c the amount of short-range exact exchange [see Eq. (4)]. $\omega_\alpha^{\text{surf.}}$ $[a_0^{-1}]$ is the range-separation parameter obtained self-consistently from the surface polarizability [see Eq. (8)] .

	sc-LC-BLYP	sc-RSHXLDA	sc-SC-BLYP	Exp.
E_g^{bulk}	8.57	8.75	8.86	8.87 ± 0.2 [32,39]
b	1.00	1.00	0.80	—
c	0.00	0.00	0.20	—
$\omega_\alpha^{\text{surf.}}$	0.154	0.155	0.194	—

TABLE X. Electronic properties of the NaCl(100) surface. Comparison of the best GW, sc-DDH, and sc-DDRSH methods with the experimental reference. VBM is the valence band maximum, CBM the conduction band minimum, and $E_g^{\text{surf.}}$ is the band gap of the surface. All values are given in eV.

	EVGW$_0$	sc-PBESOL0	sc-RSHXLDA	Exp.
VBM	−9.20	−9.10	−9.20	−9.11 [21,39]
CBM	−0.46	−0.43	−0.49	−0.53 [24,39]
$E_g^{\text{surf.}}$	8.74	8.67	8.71	8.87 ± 0.2 [32,39]

is given in Table X. Even though QPGW$_0$ performs slightly better for the band positions and the energy of the first optical excitation, we have chosen EVGW$_0$ as the best GW method because the optical absorption spectra from both methods differ and the EVGW$_0$ spectrum bears a much closer resemblance to the experiment. The calculated optical absorption spectra can be found in Figs. S7–S10 in the Supplemental Materail [71].

IV. CONCLUSION

In this paper, the performance of self-consistent dielectric dependent global hybrid functionals and self-consistent DDRSH functionals was assessed for the calculation of electronic band gaps and band-edge levels of the prototype insulator NaCl. It was found that all sc-DDH functionals provide similar results, which are substantially different from those obtained with the corresponding standard global hybrid functionals. The agreement with the most recent experimental data and with reference calculations performed with EVGW$_0$ and QPGW$_0$ is quite satisfactory. Results of similar quality were achieved by using sc-DDRSH functionals. These contain the screening parameter ω as an additional degree of freedom, which can be determined individually for surfaces and molecules. In the case of NaCl, the parameters determined from surface calculations can be transferred to bulk calculations. For slab models, which are finite in one direction, the HF contribution in sc-DDH functionals becomes $a = 1$ if it is determined from ϵ_∞^{-1}. The sc-DDH functionals are therefore not self-consistent for slab calculations if a has been obtained for the corresponding bulk system. Global hybrid functionals with $a = 1$ largely overestimate the electronic band gap. It is therefore proposed to apply sc-DDRSH functionals for surface and adsorption studies with parameters b, c, and $\omega_\alpha^{\text{surf.}}$, evaluated for the specific system of interest. Optical gaps determined with EVGW$_0$-BSE and QPGW$_0$-BSE are also very close to experimental values. A small number of surface-specific excited states was observed.

ACKNOWLEDGMENTS

The authors thank the Leibniz University IT Services [formerly Regionales Rechenzentrum für Niedersachsen (RRZN)] for providing computational resources. M.H. thanks the Studienstiftung des deutschen Volkes for support.

---

[1] N. F. Mott, Trans. Faraday Soc. **34**, 500 (1938).
[2] D. A. Wright, Proc. Phys. Soc. **60**, 13 (1948).
[3] J. W. Taylor and P. L. Hartman, Phys. Rev. **113**, 1421 (1959).
[4] J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).
[5] T. Timusk, J. Phys. Chem. Solids **18**, 265 (1961).
[6] P. E. Best, Proc. Phys. Soc. **79**, 133 (1962).
[7] T. Timusk and W. Martienssen, Phys. Rev. **128**, 1656 (1962).
[8] J. C. Phillips, Phys. Rev. **136**, A1705 (1964).
[9] P. H. Metzger, J. Phys. Chem. Solids **26**, 1879 (1965).
[10] F. Pradal, C. Gout, and B. lahaye, Solid State Commun. **4**, 119 (1966).
[11] M. Creuzburg, Z. Phys. **196**, 433 (1966).
[12] R. Onaka, H. Mori, and Y. Shoji, J. Phys. Soc. Japan **23**, 836 (1967).
[13] D. M. Roessler and W. C. Walker, Phys. Rev. **166**, 599 (1968).
[14] T. Miyata and T. Tomiki, J. Phys. Soc. Japan **24**, 1286 (1968).
[15] S. ichi Nakai and T. Sagawa, J. Phys. Soc. Japan **26**, 1427 (1969).
[16] R. Haensel, G. Keitel, P. Schreiber, B. Sonntag, and C. Kunz, Phys. Rev. Lett. **23**, 528 (1969).
[17] K. Hiraoka and W. H. Hamill, J. Chem. Phys. **57**, 3881 (1972).
[18] W. Pong and J. A. Smith, Phys. Rev. B **9**, 2674 (1974).
[19] R. T. Poole, J. G. Jenkin, J. Liesegang, and R. C. G. Leckey, Phys. Rev. B **11**, 5179 (1975).
[20] F. L. Battye, J. Liesegang, R. C. G. Leckey, and J. G. Jenkin, Phys. Rev. B **13**, 2646 (1976).
[21] J. Connor, M. Considine, I. Hillier, and D. Briggs, J. Electron. Spectrosc. and Relat. Phenom. **12**, 143 (1977).
[22] F. Nordhage and G. Bäckström, J. Electrostat. **3**, 371 (1977).
[23] I. Maruyama and R. Onaka, J. Phys. Soc. Japan **44**, 196 (1978).
[24] B. L. Henke, J. Liesegang, and S. D. Smith, Phys. Rev. B **19**, 3004 (1979).
[25] G. Roy, G. Singh, and T. Gallon, Surf. Sci. **152-153**, 1042 (1985).
[26] P. A. Rodnyi, Sov. Phys. J. **32**, 476 (1989).
[27] F. Gołek and E. Bauer, Surf. Sci. **369**, 415 (1996).
[28] R. G. Pearson, Inorg. Chim. Acta **270**, 252 (1998).
[29] C. Tegenkamp, H. Pfnür, W. Ernst, U. Malaske, J. Wollschläger, D. Peterka, K. M. Schröder, V. Zielasek, and M. Henzler, J. Phys.: Condens. Matter **11**, 9943 (1999).
[30] C. Tegenkamp and H. Pfnür, Phys. Chem. Chem. Phys. **4**, 2653 (2002).
[31] U. Malaske, C. Tegenkamp, M. Henzler, and H. Pfnür, Surf. Sci. **408**, 237 (1998).
[32] S. Heidorn, C. Bertram, J. Koch, K. Boom, F. Matthaei, A. Safiei, J. Henzl, and K. Morgenstern, J. Phys. Chem. C **117**, 16095 (2013).
[33] S. Botti and M. A. L. Marques, Phys. Rev. Lett. **110**, 226404 (2013).

[34] J. H. Skone, M. Govoni, and G. Galli, Phys. Rev. B **89**, 195112 (2014).
[35] A. J. Garza and G. E. Scuseria, J. Phys. Chem. Lett. **7**, 4165 (2016).
[36] I.-H. Chu, J. P. Trinastic, Y.-P. Wang, A. G. Eguiluz, A. Kozhevnikov, T. C. Schulthess, and H.-P. Cheng, Phys. Rev. B **93**, 125210 (2016).
[37] E. Trushin, M. Betzinger, S. Blügel, and A. Görling, Phys. Rev. B **94**, 075123 (2016).
[38] A. L. Kutepov, Phys. Rev. B **95**, 195120 (2017).
[39] W. R. L. Lambrecht, C. Bhandari, and M. van Schilfgaarde, Phys. Rev. Materials **1**, 043802 (2017).
[40] J.-L. Bredas, Mater. Horiz. **1**, 17 (2014).
[41] A. Kahn, Mater. Horiz. **3**, 7 (2016).
[42] T. Koopmans, Physica **1**, 104 (1934).
[43] E. J. Baerends, O. V. Gritsenko, and R. Van Meer, Phys. Chem. Chem. Phys. **15**, 16408 (2013).
[44] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).
[45] J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983).
[46] E. Sagvolden and J. P. Perdew, Phys. Rev. A **77**, 012517 (2008).
[47] S. Refaely-Abramson, S. Sharifzadeh, N. Govind, J. Autschbach, J. B. Neaton, R. Baer, and L. Kronik, Phys. Rev. Lett. **109**, 226405 (2012).
[48] T. Tsuneda, J.-W. Song, S. Suzuki, and K. Hirao, J. Chem. Phys. **133**, 174101 (2010).
[49] R. Kar, J. Song, and K. Hirao, J. Computat. Chem. **34**, 958 (2013).
[50] S. Kümmel and L. Kronik, Rev. Mod. Phys. **80**, 3 (2008).
[51] G. Kresse, M. Marsman, L. E. Hintzsche, and E. Flage-Larsen, Phys. Rev. B **85**, 045205 (2012).
[52] L. Hedin, Phys. Rev. **139**, A796 (1965).
[53] A. Grüneis, G. Kresse, Y. Hinuma, and F. Oba, Phys. Rev. Lett. **112**, 096401 (2014).
[54] Y. Hinuma, A. Grüneis, G. Kresse, and F. Oba, Phys. Rev. B **90**, 155405 (2014).
[55] P. S. Schmidt, C. E. Patrick, and K. S. Thygesen, Phys. Rev. B **96**, 205206 (2017).
[56] C. Freysoldt, P. Eggert, P. Rinke, A. Schindlmayr, and M. Scheffler, Phys. Rev. B **77**, 235428 (2008).
[57] M. Shishkin and G. Kresse, Phys. Rev. B **75**, 235102 (2007).
[58] M. Shishkin, M. Marsman, and G. Kresse, Phys. Rev. Lett. **99**, 246403 (2007).
[59] A. Riefer, M. Friedrich, S. Sanna, U. Gerstmann, A. Schindlmayr, and W. G. Schmidt, Phys. Rev. B **93**, 075205 (2016).
[60] B. Kong and Y. Zhang, J. Appl. Phys. **120**, 015101 (2016).
[61] G.-M. Rignanese, X. Blase, and S. G. Louie, Phys. Rev. Lett. **86**, 2110 (2001).
[62] M. Hedström, A. Schindlmayr, G. Schwarz, and M. Scheffler, Phys. Rev. Lett. **97**, 226401 (2006).
[63] A. Erba, J. Phys.: Condens. Matter **29**, 314001 (2017).
[64] J. H. Skone, M. Govoni, and G. Galli, Phys. Rev. B **93**, 235106 (2016).
[65] M. A. L. Marques, J. Vidal, M. J. T. Oliveira, L. Reining, and S. Botti, Phys. Rev. B **83**, 035119 (2011).
[66] M. Ferrero, M. Rérat, R. Orlando, R. Dovesi, and I. J. Bush, J. Phys. Conf. Ser. **117**, 012016 (2008).
[67] B. G. Johnson and M. J. Frisch, Chem. Phys. Lett. **216**, 133 (1993).
[68] N. P. Brawand, M. Vörös, M. Govoni, and G. Galli, Phys. Rev. X **6**, 041002 (2016).
[69] D. M. Bylander and L. Kleinman, Phys. Rev. B **41**, 7868 (1990).
[70] M. Ferrero, M. Rérat, R. Orlando, and R. Dovesi, J. Comput. Chem. **29**, 1450 (2008).
[71] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.97.235447 for convergence tests, density of states calculations, and the calculated optical spectra.
[72] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[73] G. Kresse and J. Hafner, Phys. Rev. B **49**, 14251 (1994).
[74] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
[75] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[76] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[77] J. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **78**, 1396 (1997).
[78] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[79] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[80] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[81] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco, M. Llunell, M. Causá, Y. Noël, L. Maschio, A. Erba, M. Rerat, and S. Casassa, *CRYSTAL17 User's Manual* (University of Torino, Torino, 2017).
[82] V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, Phys. Rev. B **78**, 239907(E) (2008).
[83] F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys. **7**, 3297 (2005).
[84] A. Schäfer, H. Horn, and R. Ahlrichs, J. Chem. Phys. **97**, 2571 (1992).
[85] R. T. Poole, J. Liesegang, R. C. G. Leckey, and J. G. Jenkin, Phys. Rev. B **11**, 5190 (1975).
[86] A. D. McNaught, A. Wilkinson, M. Nic, J. Jirat, B. Kosata, and A. Jenkins, *IUPAC, Compendium of Chemical Terminology (the "Gold Book")*, 2nd ed. (Blackwell Scientific Publications, Oxford, 1997).
[87] C. Gout and F. Pradal, J. Phys. Chem. Solids **29**, 581 (1968).
[88] K. Teegarden and G. Baldini, Phys. Rev. **155**, 896 (1967).
[89] R. G. Pearson, *Chemical Hardness: Applications from Molecules to Solids* (Wiley-VCH, Weinheim, 1977).
[90] R. Leckey, in *Subvolume A*, Landolt-Börnstein—Group III, Condensed Matter, Vol. 23a, edited by A. Goldmann and E.-E. Koch (Springer, Berlin-Heidelberg, 1989), pp. 113–117.
[91] S. Wakita and M. Ueta, J. Phys. Soc. Japan **19**, 924 (1964).
[92] O. Sueoka, J. Phys. Soc. Japan **20**, 2226 (1965).
[93] E. O. Steinborn and G. Gliemann, Theoret. Chim. Acta **4**, 185 (1966).
[94] H. Pick, in *Landolt-Börnstein: Zahlenwerte und Funktionen*, edited by K. H. Hellwege (Springer, Berlin, Göttingen, Heidelberg, 1955), 6th ed., Vol. I, p. 869.
[95] R. Onaka and H. Ogawa, J. Phys. Soc. Japan **24**, 811 (1968).
[96] T. Miyata, J. Phys. Soc. Jpn. **31**, 529 (1971).
[97] P. Cox and A. Williams, Surf. Sci. **175**, L782 (1986).
[98] T. Matsumoto, M. Shirai, and Ken-ichi Kan'no, J. Phys. Soc. Japan **64**, 987 (1995).
[99] V. Zielasek, T. Hildebrandt, and M. Henzler, Phys. Rev. B **62**, 2912 (2000).
[100] V. Zielasek, T. Hildebrandt, and M. Henzler, Phys. Rev. B **69**, 205313 (2004).

[101] J. Kramer, C. Tegenkamp, and H. Pfnür, J. Phys.: Condens. Matter **15**, 6473 (2003).

[102] C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999).

[103] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. **100**, 136406 (2008).

[104] D. I. Bilc, R. Orlando, R. Shaltaf, G.-M. Rignanese, J. Íñiguez, and P. Ghosez, Phys. Rev. B **77**, 165107 (2008).

[105] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[106] J. P. Perdew, in *Unified Theory of Exchange and Correlation Beyond the Local Density Approximation*, in Electronic Structure of Solids 1991, Vol. 11, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991), pp. 11–20.

[107] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).

[108] J. P. Perdew and W. Yue, Phys. Rev. B **40**, 3399 (1989).

[109] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[110] R. Demichelis, B. Civalleri, M. Ferrabone, and R. Dovesi, Int. J. Quantum Chem. **110**, 406 (2010).

[111] J. R. Hardy and A. M. Karo, Phys. Rev. B **26**, 3327 (1982).

[112] V. Atalla, M. Yoon, F. Caruso, P. Rinke, and M. Scheffler, Phys. Rev. B **88**, 165122 (2013).

[113] H. Iikura, T. Tsuneda, T. Yanai, and K. Hirao, J. Chem. Phys. **115**, 3540 (2001).

[114] Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, and K. Hirao, J. Chem. Phys. **120**, 8425 (2004).

[115] J. Toulouse, A. Savin, and H.-J. Flad, Int. J. Quantum Chem. **100**, 1047 (2004).

[116] I. C. Gerber and J. G. Ángyán, J. Chem. Phys. **126**, 044103 (2007).