X-ray absorption using the projector augmented-wave method and the Bethe-Salpeter equation

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We present an implementation of the Bethe-Salpeter equation (BSE) for core-conduction band pairs within the framework of the projector augmented-wave method. For validation, the method is applied to the K edges of diamond, graphite and hexagonal boron-nitride, as well as four lithium-halides (LiF, LiCl, LiI, LiBr). We compare our results with experiment, previous theoretical BSE results, and the density functional theory-based supercell core-hole method. In all considered cases, the agreement with experiment is excellent, in particular, for the relative position of the peaks as well as the fine structure. Comparing BSE to supercell core-hole spectra, we find that the latter often qualitatively reproduces the experimental spectrum, however, it sometimes lacks important details. This is shown for the K edges of diamond and nitrogen in hexagonal boron nitride, where we can resolve within the BSE experimental features that are lacking in the supercell core-hole method. Additionally, we show that in certain systems the supercell core-hole method performs better if the excited electron is added to the background charge rather than to the lowest conduction band. We attribute this improved performance to a reduced self-interaction.

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I. INTRODUCTION

X-ray absorption spectroscopy (XAS) experiments probe the transition probability of exciting an electron from a core state to a conduction-band state. XAS spectra furnish information about the local chemical environment of the probed atom, e.g., coordination number or oxidation state [1]. However, experimental XAS spectra are difficult to interpret without theoretical input.

To simulate XAS spectra, two fairly simple *ab initio* approaches exist. In the initial-state approximation, the XAS spectrum is calculated via Fermi's golden rule, where the initial state is a core state and the final state a conduction-band state. In the final-state approximation [2–6], the final-state wave function is calculated self-consistently using Kohn-Sham density functional theory (DFT) [7] by removing one core electron and placing it in the conduction bands.

These methods have a couple drawbacks. In the initial-state approach, electrons and holes are independent particles and any interactions between them are neglected. In the final-state approach, supercells are required to avoid spurious interactions between core holes located in different unit cells. For this reason, this approach is here called the supercell core-hole (SCH) method. Further, it is assumed that the approximate density functionals remain valid for excited states. Finally, the excited electron is usually placed into the conduction band edge, and it is implied that the resulting renormalized one-electron energies for all conduction bands will be a good approximation for the XAS fine structure.

By looking at these restrictions, an approach is desirable which addresses some of the shortcomings of the SCH method. In particular, an accurate description of the electronic structure is needed, ideally including many-body correlations for the interaction of electrons and holes.

The state-of-the-art approach that resolves both issues is the GW+BSE method. It combines *ab initio* groundstate electronic structure calculations with techniques of many-body perturbation theory [8]. By calculating the oneparticle Green's function *G*, various one-body properties can be obtained, e.g., quasiparticle band gaps and quasiparticle energies [9].

For a description of the mutual interaction of electrons and holes, one needs to go beyond one-particle theory and solve the equation of motion for the two-particle Green's function— the Bethe-Salpeter equation (BSE) [10,11]. The BSE is an integral equation that can be recast into an eigenvalue equation, where the exchange and the screened attraction of electrons and holes are incorporated in the resulting BSE matrix. The BSE approach was applied to optical spectra of semiconductors in the late '70s [12]. *Ab initio* based approaches to the BSE followed in the late '90s [13–16].

In these approaches, the orbitals are usually obtained from a standard ground-state DFT calculation. In the second step, the Green's function is calculated using the DFT orbitals and one-electron energies. Many-body correlation effects are included by replacing the Kohn-Sham exchange-correlation potential with the self-energy in the *GW* approximation and by solving the Dyson equation for the interacting Green's function. The one-electron energies are then updated by equating them to the poles of the resulting interacting Green's

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function. In most cases, a single iteration is performed. Finally, the two-particle BSE is set up and solved. Often one refers to this approach as GW+BSE.

The GW+BSE approach has been extended from the optical to the x-ray regime by covering excitations from core levels to the conduction band. The earliest implementation was presented by Shirley and coworkers [17,18] within a pseudopotential scheme. This work culminated in the OCEAN package [19–21]. Further adaptions within allelectron full-potential methods were established by Olovsson *et al.* in exciting [22] and subsequently by Laskowski *et al.* in WIEN2K [23]. To the best of our knowledge, most available electronic structure codes that implement the projector augmented-wave (PAW) methodology calculate XAS spectra via the SCH method [24–28]. We note that in a recent version of the OCEAN code [29], an augmentation technique reminiscent of the PAW methodology is used for the calculation of transition matrix elements.

In this paper, we present an implementation of the GW+BSE scheme in the PAW method for x-ray absorption spectra. We derive the BSE in the PAW scheme and show what modifications must be made for core states. Our implementation is tested by calculating XAS spectra for the *K* edges of one prototypical covalent system (diamond), two 2D van der Waals layered materials (graphite and hexagonal boronnitride), and four ionic materials with shallow core states (the lithium-halides LiF, LiCl, LiBr, and LiI). We benchmark our results against spectra obtained either by a pseudopotential or an AE implementation of the BSE and point out where the GW+BSE implementation within PAW shows improvements. We furthermore compare our results with experiment and a previously presented implementation of the SCH method [30].

Finally, we show that previously obtained SCH spectra of lithium halides can be improved by adding the electron to the background charge instead of the lowest conduction band. We argue that the improvement comes from a reduction of self-interaction errors. We then connect this explanation to the GW+BSE approach by investigating how the spectra change if the exchange term of the BSE is omitted.

The necessary theory is presented in Sec. II. In Sec. II A, we shortly summarize the BSE as well as the basics of the PAW formalism. In that subsection, we will also point out the approximations made in the current implementation. In Sec. II C, we present details concerning the implementation of the BSE in the PAW formalism. The expressions for the transition probabilities and the dielectric function are then found in Sec. II D. In Sec. III, we summarize the computational methods, followed by a presentation of the results in Sec. IV. In Sec. V, we present the improved SCH spectra for lithium halides and the discussion of the suggested self-interaction effect. Finally, we summarize and conclude the paper in Sec. VI.

II. THEORY

A. Bethe-Salpeter equation

We use notations consistent with a previous publication [31] in which further details on the implementation of the BSE in the PAW can be found. We use the commonly used notation

for space and time variables: $1 = \{r_1, t_1\}$, etc. The systems investigated in this work are nonmagnetic and treated on a scalar relativistic level, however, the equations can be easily generalized to include spin indices. Furthermore, spin-orbit coupling is neglected, as no heavy elements are present in the considered systems.

The BSE is the Dyson equation for the two-particle correlation function *L*:

$$L(1, 2, 3, 4) = L_0(1, 2, 3, 4) + L_0(1, 5, 8, 4)$$

× I(5, 6, 7, 8)L(6, 2, 3, 7). (1)

The independent propagation of a particle from point 1 to point 2 and a hole from point 4 to point 3 is described by L_0 ,

$$L_0(1, 2, 3, 4) = G(2, 1)G(4, 3),$$
(2)

and the irreducible interaction kernel I is given in the GW approximation [12,32,33]:

$$V(1, 2, 3, 4) = \delta(1, 4)\delta(2, 3)v(1, 2) - \delta(1, 2)\delta(4, 3)W(1, 4).$$
(3)

The interaction kernel consists of the repulsive bare Coulomb interaction v(1, 2) and the frequency-dependent attractive screened interaction W(1, 2). In Eq. (1), integration over repeated indices is implied. The first and second terms of the irreducible interaction are obtained by varying the Hartree potential or the exchange and correlation part of the self-energy, respectively, with respect to the Green's function.

At this point, we make the static approximation to the screened interaction W(1, 2) [34]. In this approximation, the full frequency-dependent screened interaction is approximated by its static value: $W(1, 2) \approx W(\mathbf{r}_1, \mathbf{r}_2, \omega = 0)$. Using this approximation, the irreducible interaction I is frequency independent and Eq. (1) can be solved in frequency space for $L(\omega)$:

$$L(\omega)^{-1} = L_0(\omega)^{-1} - I.$$
 (4)

Until now, all equations involved quantities which are continuous functions of space. A basis is needed to cast Eq. (4) into a matrix form. Since we consider neutral electron-hole excitations, a suitable basis are the products of occupied and unoccupied orbitals, called resonant and antiresonant twoorbital states,

$$\Phi_{K}^{a}(\boldsymbol{r},\boldsymbol{r}') = \varphi_{i}(\boldsymbol{r})\varphi_{a}^{*}(\boldsymbol{r}'),$$

$$\Phi_{K}^{a}(\boldsymbol{r},\boldsymbol{r}') = \varphi_{a}(\boldsymbol{r})\varphi_{i}^{*}(\boldsymbol{r}'),$$
 (5)

where the indices i, j, ... and a, b, ... enumerate occupied and unoccupied states, respectively. Here and in the following, we use the notations $K = \{i, a\}$ and $J = \{j, b\}$. In general, one also needs to include a *k*-point index, $K = \{ik, ak\}, J = \{jk', bk'\}$, but for brevity we will suppress it in the following. It can be easily restored by adding *k* to *i* and *a*, and *k'* to *j* and *b*.

Using this basis, resonant-resonant and resonantantiresonant matrix elements of L_0 and I in Eqs. (5) need to be computed. However, in the present paper, we use the well-known *Tamm-Dancoff* approximation [35,36] and thus neglect the resonant-antiresonant matrix elements. We further use the analytical property that response functions derived from $L(\omega)$ are even functions of ω . A method to include the resonant-antiresonant coupling and to go beyond the Tamm-Dancoff approximation is discussed in a previous publication [31].

The resonant-resonant matrix elements of L_0 then take the form

$$(L_0(\omega)^{-1})_{KJ}^{(\mathrm{r},\mathrm{r})} = (\omega - (\epsilon_a - \epsilon_i))\delta_{ij}\delta_{ab}.$$
 (6)

The resonant-resonant matrix elements of the irreducible interaction can be written as

$$\mathcal{H}_{KJ}^{(\mathbf{r},\mathbf{r})} = \int d\mathbf{r}_1 \dots d\mathbf{r}_4 \Phi_K^{\mathbf{r} *}(\mathbf{r}_2, \mathbf{r}_4) \\ \times I(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \Phi_J^{\mathbf{r}}(\mathbf{r}_3, \mathbf{r}_1).$$
(7)

Using the more compact Dirac notation, the resonant-resonant antisymmetrized two-electron integrals corresponding to the interaction *I* are written as

$$\mathcal{H}_{KJ}^{(\mathbf{r},\mathbf{r})} = \langle bi|V|ja\rangle - \langle bi|W|aj\rangle. \tag{8}$$

We have now arrived at a matrix representation of Eq. (4) in the Tamm-Dancoff approximation:

$$(L(\omega)^{-1})_{KJ} = (\omega - (\epsilon_a - \epsilon_i))\delta_{ij}\delta_{ab} - \mathcal{H}_{KJ}^{(r,r)}.$$
 (9)

Elementary excitations are determined by the poles of $L(\omega)$, in other words, those frequencies Ω for which the right-hand side of Eq. (9) is not invertible. This, in turn, means that the kernel of the matrix on the right-hand side of Eq. (9) is nontrivial. Using the shorthand notation

$$A = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \mathcal{H}_{KI}^{(\mathbf{r},\mathbf{r})},\tag{10}$$

this argument leads us to the simplified eigenvalue problem:

$$AX = \Omega X. \tag{11}$$

We have now summarized the BSE formalism and its main ingredients, the matrix elements of the resonant-resonant matrix A, Eq. (7), and the eigenvalue Eq. (11). In the next section, we summarize the pertinent parts of the PAW method, specifically, the basic principles and how core states are treated.

B. Basics of the PAW formalism

The PAW method is an all-electron (AE) method in which the exact orbital $|\psi\rangle$ is obtained from the pseudo (PS) orbital $|\tilde{\psi}\rangle$ via a linear transformation [37]

$$|\psi\rangle = |\tilde{\psi}\rangle + \sum_{n} \left(c_n \left| \phi_n^1 \right\rangle - c_n \left| \tilde{\phi}_n^1 \right\rangle \right), \tag{12}$$

where $|\tilde{\psi}\rangle$ are the PS orbitals represented on a plane-wave grid—these are the variational quantities, and $|\phi^1\rangle$ and $|\tilde{\phi}^1\rangle$ are all-electron partial waves and PS partial waves, respectively, both defined on a radial grid. We use a superscript 1 to denote one-center quantities located inside PAW spheres and evaluated on a radial grid. The coefficients c_n are projections of the PS orbitals on projectors defined inside the PAW spheres:

$$c_n = \langle \tilde{p}_n | \tilde{\psi} \rangle. \tag{13}$$

The index *n* is a shorthand for an atomic site index τ_n , angular l_n , and magnetic quantum numbers m_n , as well as an

additional index for the reference energy ϵ_n . Here and in the following, compound indices *n* and *m* are used to index the projectors, partial waves, and coefficients c_n . The on-site expansion $\sum_n c_n |\tilde{\phi}_n^1\rangle$ must be equal to $|\tilde{\psi}\rangle$ inside the PAW spheres, which implies that

$$\sum_{n} |\tilde{\phi}_{n}^{1}\rangle \langle \tilde{p}_{n}| = 1.$$
(14)

For core states, the coefficients in the transformation Eq. (12) are unity [37]:

$$|\psi_c\rangle = |\tilde{\psi}_c\rangle + \left|\phi_c^1\right\rangle - \left|\tilde{\phi}_c^1\right\rangle. \tag{15}$$

In practice, one can safely assume that all quantities in the above equation are entirely localized inside the PAW spheres, hence $|\tilde{\psi}_c\rangle = |\tilde{\phi}_c^1\rangle$ and $|\psi_c\rangle = |\phi_c^1\rangle$. Furthermore, we will make the assumption that $|\tilde{\psi}_c\rangle = |\phi_c^1\rangle = 0$ (these approximations are used to the best of our knowledge in all PAW implementations). This is justified, since the core orbitals do not contribute outside of the PAW spheres, and in the PAW method one is free to make any choice for the PS partial waves $|\tilde{\phi}_c^1\rangle$, as long as they are identical to the AE partial waves $|\phi_c^1\rangle$ outside the PAW spheres. Since $|\phi_c^1\rangle$ is zero outside the PAW spheres, one can also assume that $\tilde{\phi}_c^1(\mathbf{r}) = 0$ and thus $\tilde{\psi}_c(\mathbf{r}) = 0$ everywhere in space. We will give further support to this argument toward the end of the next subsection.

Inside the PAW spheres, the AE partial waves are solutions of the radial Schrödinger equation for a specific energy ε_n and angular momentum quantum numbers l_n, m_n ,

$$\phi_n^1(\mathbf{r}) = \frac{1}{r} u_{\epsilon_n, l_n}(r) Y_{l_n, m_n}(\theta, \phi), \qquad (16)$$

with radial functions u(r) and spherical harmonics $Y_{l,m}(\theta, \phi)$. These are calculated for isolated atoms when the PAW potentials are generated. The AE core orbitals are also calculated for the Kohn-Sham potential of the isolated atom, imposing the boundary condition that core orbitals become zero at the radius of the PAW sphere [37,38]. This is done in a preprocessing step within the VASP code. Note that except for a Bloch phase-factor $e^{ik \cdot r}$, the core orbitals are identical at all k points.

The PS partial waves $\tilde{\phi}_n^1(\mathbf{r}) = \langle \mathbf{r} | \tilde{\phi}_n^1 \rangle$ are analogously given as

$$\tilde{\phi}_n^1(\mathbf{r}) = \frac{1}{r} \tilde{u}_{\epsilon_n, l_n}(r) Y_{l_n, m_n}(\theta, \phi), \qquad (17)$$

and determined by pseudizing the AE partial waves inside a suitably chosen core radius.

In the next section, we describe in detail how to evaluate the matrix elements in the PAW method, and how the expressions need to be modified when core states are included in the transitions.

C. BSE matrix elements within PAW

We now evaluate the two-electron integrals in Eq. (7). Defining charge densities

$$n_{ab}(\mathbf{r}) = \varphi_a^*(\mathbf{r})\varphi_b(\mathbf{r}), \qquad (18)$$

the two terms of the resonant-resonant matrix elements, Eq. (8), can be written as

$$\langle bi|V|ja\rangle = \int d\mathbf{r} d\mathbf{r}' n_{ia}(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') n_{jb}^*(\mathbf{r}'), \qquad (19)$$

$$\langle bi|W|aj\rangle = \int d\mathbf{r} d\mathbf{r}' n_{ij}(\mathbf{r}) W(\mathbf{r}, \mathbf{r}') n_{ab}^*(\mathbf{r}').$$
(20)

Following convention, we refer to the terms involving v and W as exchange and direct terms, respectively [8].

To calculate the matrix elements of Eqs. (19) and (20), we need to treat the long-range electrostatic interaction accurately within the PAW. This is achieved by introducing augmentation charges, as discussed extensively for valence electrons in the PAW papers of Blöchl [37] and Kresse and Joubert [38]. Augmentation charges are constructed such that inside the PAW spheres, the sum of PS charge density and the augmentation charge \hat{n} has the same moments as the exact charge density,

$$\int_{\Omega_r} [n^1(\boldsymbol{r}) - \tilde{n}^1(\boldsymbol{r}) - \hat{n}(\boldsymbol{r})] |\boldsymbol{r}|^l Y^*_{lm}(\theta, \phi) d\boldsymbol{r} = 0, \qquad (21)$$

where the coordinate system is centered on a particular PAW sphere. Details on the explicit construction of the augmentation charges can be found in Ref. [38]. With this definition of the augmentation charge, we write the exact charge density as a sum of three terms, cf. Eq. (17) of Ref. [39]:

$$n_{ab}(\mathbf{r}) = [\tilde{n}_{ab}(\mathbf{r}) + \hat{n}_{ab}(\mathbf{r})] + n_{ab}^{1}(\mathbf{r}) - [\tilde{n}_{ab}^{1}(\mathbf{r}) + \hat{n}_{ab}^{1}(\mathbf{r})].$$
(22)

The first term is the plane-wave charge density plus the augmentation charge on the regular grid, the second term is the AE charge density, and the last term is the PS charge density plus PS augmentation charge on the radial grid.

By constructing the augmentation charges as in Eq. (21), the correct moments of the AE charge density are taken into account and restored. This leads to moment-restoration. Additionally, the exact AE charge density inside the PAW spheres can be reconstructed by adding so-called shape-restoring functions to the augmentation charges [40]. This process is, accordingly, called shape restoration. Using moment as well as shape restoration makes the PS charge density very similar to the AE charge density for low Fourier components. Typically, both match up to a kinetic energy cutoff of 150–200 eV. With this in mind, we make an important simplification and neglect the second and third terms of Eq. (22):

$$n_{ab}(\mathbf{r}) \approx [\tilde{n}_{ab}(\mathbf{r}) + \hat{n}_{ab}(\mathbf{r})].$$
(23)

This approximation is made consistently in the VASP code for the GW, RPA, and BSE implementations [40]. The construction of the augmentation charges, including moment as well as shape restoration, is outlined in the Appendix.

Using this approximation, we can write an explicit expression for the exchange and direct terms, respectively,

$$\langle bi|V|ja\rangle = \int d\mathbf{r} d\mathbf{r}' [\tilde{n}_{ia}(\mathbf{r}) + \hat{n}_{ia}(\mathbf{r})]$$
$$\times v(\mathbf{r} - \mathbf{r}') [\tilde{n}_{jb}(\mathbf{r}') + \hat{n}_{jb}(\mathbf{r}')]^*, \qquad (24)$$

$$\langle bi|W|aj\rangle = \int d\mathbf{r} d\mathbf{r}' [\tilde{n}_{ij}(\mathbf{r}) + \hat{n}_{ij}(\mathbf{r})] \\ \times W(\mathbf{r}, \mathbf{r}') [\tilde{n}_{ab}(\mathbf{r}') + \hat{n}_{ab}(\mathbf{r}')]^*.$$
(25)

These expressions have already been implemented previously for the case of transitions from valence to conduction band states [31].

We now discuss the case of core states in more detail. If one of the occupied states *i* is a core state *c*, then there are three combinations of orbitals possible: $n_{cc'}$ (two core states), n_{ci} (a core state and a valence band state), or n_{ca} (a core state and a conduction band state). For a core state *c* inside a particular PAW sphere, this core state is confined entirely to the sphere and vanishes beyond this PAW sphere. It is then evident that each of the three charge densities mentioned above contributes only inside the PAW sphere in which the core state *c* is located.

We show here how this implies that the plane-wave contributions \tilde{n} in Eqs. (24) and (25) vanish. We first use the formula for the expectation value of a local operator in the PAW scheme for the real-space projection operator $|\mathbf{r}\rangle\langle\mathbf{r}|$, see Eq. (11) of Ref. [37]:

$$\langle \varphi_{i} | \boldsymbol{r} \rangle \langle \boldsymbol{r} | \varphi_{b} \rangle = \langle \tilde{\varphi}_{i} | \boldsymbol{r} \rangle \langle \boldsymbol{r} | \tilde{\varphi}_{b} \rangle + \sum_{nm} \langle \tilde{\varphi}_{i} | \tilde{p}_{n} \rangle \langle \tilde{p}_{m} | \tilde{\varphi}_{b} \rangle \langle \phi_{n}^{1} | \boldsymbol{r} \rangle \langle \boldsymbol{r} | \phi_{m}^{1} \rangle$$
$$- \sum_{nm} \langle \tilde{\varphi}_{i} | \tilde{p}_{n} \rangle \langle \tilde{p}_{m} | \tilde{\varphi}_{b} \rangle \langle \tilde{\phi}_{n}^{1} | \boldsymbol{r} \rangle \langle \boldsymbol{r} | \tilde{\phi}_{m}^{1} \rangle.$$
(26)

We now restrict state *i* to a core state *c*, while state *b* is a conduction-band state. As argued above, the charge density $\langle \varphi_c | \mathbf{r} \rangle \langle \mathbf{r} | \varphi_b \rangle$ has contributions inside the PAW spheres only. Hence, we can use the completeness relation in Eq. (14), so the first and third terms of Eq. (26) cancel. This finally implies that the plane-wave charge densities \tilde{n} in Eqs. (24) and (25) can be neglected, so the exchange and direct terms can be written as

$$\langle bc|V|ca\rangle = \int d\mathbf{r} d\mathbf{r}' \hat{n}_{ca}(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') \hat{n}^*_{cb}(\mathbf{r}') \qquad (27)$$

and

$$\langle bc|W|aj\rangle = \int d\mathbf{r} d\mathbf{r}' \hat{n}_{cj}(\mathbf{r}) W(\mathbf{r},\mathbf{r}') [\tilde{n}_{ab}(\mathbf{r}') + \hat{n}_{ab}(\mathbf{r}')]^*,$$
(28)

respectively. As shown in Eq. (21), the augmentation charges are constructed in such a way that they restore the exact multipoles of the AE charge density. This implies that even though we use only augmentation charge densities, the longrange electrostatic effects are exactly accounted for. The argument laid out here also confirms that the assumption $\tilde{\phi}_c^{\rm I}(\mathbf{r}) = \tilde{\psi}_c(\mathbf{r}) = 0$ everywhere in space is a valid choice. The expressions above have been implemented in the VASP code for core-conduction as well as core-valence transitions.

D. Transition probabilities and dielectric function

The dielectric function is finally calculated as

$$\varepsilon_{\mathrm{M}}(\boldsymbol{q},\omega) = 1 + \lim_{\boldsymbol{q}\to 0} v(\boldsymbol{q}) \sum_{\Lambda} \left(\frac{1}{\Omega_{\Lambda} - \omega} + \frac{1}{\Omega_{\Lambda} + \omega} \right) \\ \times \frac{1}{N_{k}} \left\{ \sum_{\boldsymbol{k}} \sum_{a,c} \langle a\boldsymbol{k} + \boldsymbol{q} | e^{i\boldsymbol{q}\cdot\boldsymbol{r}} | c\boldsymbol{k} \rangle X_{\Lambda}^{(c\boldsymbol{k},a\boldsymbol{k})} \right\} \{\mathrm{c.c.}\};$$
(29)

compare Eqs. (50) and (51) of Ref. [31]. Here, index Λ labels the eigenvalues Ω_{Λ} and eigenvectors X_{Λ} of the eigenvalue problem in Eq. (11). The total number of k points is denoted as N_k , and v(q) is the Coulomb kernel, in CGS units $v(q) = (1/V)4\pi e^2/|q|^2$, where V is the volume of the unit cell. For clarity, the k-point index was added back. The limit $q \rightarrow 0$ is justified for the systems investigated in this paper. The energy range considered here is from 60 eV to 420 eV, so if we assume that variations of the system are of the order 1Å, then corrections to the long-wavelength limit (i.e., quadrupole transitions) are at most of order $(1 \text{ Å}/30 \text{ Å})^2 \approx 10^{-3}$.

Although the present implementation allows for simultaneous treatment of core-conduction and valence-conduction pairs, we did not consider the valence states in our present BSE calculations. Then, the key ingredient here is the transition probability between core and valence-band states,

$$\lim_{\boldsymbol{q}\to 0} \sqrt{v(\boldsymbol{q})} \langle a\boldsymbol{k} + \boldsymbol{q} | e^{i\boldsymbol{q}\cdot\boldsymbol{r}} | c\boldsymbol{k} \rangle, \tag{30}$$

which in $\mathbf{k} \cdot \mathbf{p}$ perturbation theory is approximated as

$$\sqrt{4\pi e^2/V \langle a \boldsymbol{k} | \boldsymbol{\nabla} | c \boldsymbol{k} \rangle}/(\epsilon_c - \epsilon_{a \boldsymbol{k}}).$$
 (31)

The ∇ term is evaluated inside the PAW sphere between the exact AE partial waves of the core orbitals and the AE partial waves corresponding to the considered conduction band state ck. Note that the present implementation [Eq. (31)] involves the momentum operator and not the velocity operator, as is in principle required for nonlocal potentials [41,42]. However, it was shown that the momentum operator can give very accurate results within the PAW method if the PAW potentials include projectors for large angular quantum numbers L [43].

The required core eigenvalues ϵ_c are assumed to be identical to the DFT core eigenvalues and identical for all kpoints. The conduction band energies ϵ_{ak} are the approximate quasiparticle energies in the GW calculations. VASP routinely calculates the DFT core eigenvalues by evaluating the expectation value of the frozen core orbitals in the self-consistent Kohn-Sham potential. Alternatively, one can specify the core eigenvalue as input. However, results are largely independent of ϵ_c . Changing ϵ_c changes the onset of absorption and scales all intensities by roughly a constant value.

Absolute core energies and hence the onsets of absorption are not yet accurately predicted by standard DFT [44,45]. Absolute core energies are commonly calculated using the Δ -self-consistent field (Δ SCF) and related methods [46,47] or, recently, the *GW* approximation [48,49]. However, these are not yet available within the frozen core PAW VASP implementation. Hence, in this paper, only the conduction band energies are *GW* corrected, and we adjust the onset of the absorption spectrum to the experimental value.

III. COMPUTATIONAL METHODS

A. Numerical details

All *ab initio* electronic structure calculations were performed with the AE plane-wave code VASP [50], which uses the PAW-implementation of Kresse and Joubert [38]. The workflow is the following.

We start with a standard DFT calculation, yielding the Kohn-Sham energies and Kohn-Sham orbitals. In all DFT

System	$E_{\rm cut}~({\rm eV})$
Diamond, graphite	434.9
<i>h</i> -BN	400.0
LiF	487.7
LiCl	262.4
LiBr	216.3
LiI	175.6

TABLE I. Plane-wave energy cutoffs used in the present work for the plane-wave expansion of the orbitals.

calculations, we used the exchange-correlation functional by Perdew *et al.* [51]. The energy cutoffs are listed in Table I. We perform a single-shot *GW* calculation (G_0W_0) to calculate the quasiparticle energies and the dynamic screened interaction in momentum space $W_{G,G'}(\omega)$. The static approximation for *W* is made at the beginning of the BSE calculation. Note that the orbitals are kept fixed at the DFT level. After a convergence study for LiF, the energy cutoff of the response function is set to 150 eV in all systems. Then, the BSE eigenvalue equation is set up using the *GW* quasiparticle energies and the PBE orbitals. Finally, the BSE equation is solved and the BSE dielectric function is calculated.

We reiterate that in this paper we only investigate K edges. Furthermore, transitions from valence states to conduction states are excluded from the calculations. The number of conduction bands included in the transitions is 8 in diamond, 12 in graphite, 12 in *h*-BN, and 15 in all four lithium-halides. These values are chosen so the modeled spectra first reproduce all relevant peaks and, second, cover the same energy range as the experimental spectrum.

We employ the shifted grid technique in all GW+BSE calculations [31] to reduce the computational demand and still obtain highly accurate spectra. First, we generate all irreducible *k*-points $k_{1,...,L}$ and corresponding weights $w_{1,...,L}$ of an $n \times n \times n$ *k*-mesh. Then, we perform *L* independent calculations with an $m \times m \times m$ *k*-mesh, where the *k*-point grid is shifted by one of the *L* irreducible *k* points. This procedure generates all *k* points of a regular $(m \cdot n) \times (m \cdot n) \times (m \cdot n)$ *k*-mesh. Finally, we average the *L* so-obtained dielectric functions, $\varepsilon = \sum_{i}^{L} w_i \varepsilon_i / \sum_{i}^{L} w_i$.

For diamond, graphite, and *h*-BN, we compare the GW+BSE spectra to those of the SCH calculations implemented previously [30]. In all SCH calculations, the supercells contain 128 atoms. Previous publications observed converged results for these supercells [30,52]. In Table II, we list the *k* meshes used in the GW+BSE and SCH calculations.

In the available experimental absorption spectra of graphite [53] and of boron in *h*-BN [54], the incoming radiation was incident at an angle α of 40° and 45° to the surface normal, respectively. In these cases, we have averaged the imaginary parts of the perpendicular and parallel components of the dielectric function according to absorption $\propto \cos(\alpha)^2 \varepsilon_{xx}^{(2)} + \sin(\alpha)^2 \varepsilon_{zz}^{(2)}$, where ε_{xx} , ε_{yy} are the in-plane and ε_{zz} the out-of-plane components of the dielectric function. Details on the polarization are missing for the *K* edge of nitrogen in *h*-BN [55]. For this system, we have weighted each component by a factor of 1/3.

TABLE II. Table of k meshes used for the shifted grid technique and for the supercell core-hole calculations (SCHs). Shifted grid technique: An $n \times n \times n$ mesh results in L irreducible k points. Meshes of size $m \times m \times m$ are then shifted by these L different k points, creating an $(m \cdot n) \times (m \cdot n) \times (m \cdot n) k$ -mesh. All meshes are centered at the Γ point. For the SCH calculations, we specify both the supercell size (number of atoms) and the k-point grids.

Method System	BSE n	BSE L	$BSE m \times m \times m$	SCH atoms	SCH k points
Diamond	3	4	10×10×10	128	9×9×9
Graphite	4	12	16×16×4	128	$4 \times 4 \times 2$
h-BN	3	4	$12 \times 12 \times 4$	128	$5 \times 5 \times 3$
Lithium-halides	3	4	$10 \times 10 \times 10$	128	8×8×8

In all the presented spectra for C, B, and N, an energyindependent Lorentzian broadening of 0.3 eV is applied. To facilitate comparison of our spectra with the results of other authors, a reduced broadening of 0.1 eV is used for the lithium-halides.

Finally, we note that neither the GW+BSE nor the SCH method can quantitatively determine the onset of absorption, hence the energy axes of the modeled spectra are always shifted to obtain best agreement with the experimental spectra.

B. Model dielectric function approach

In the GW+BSE approach, the screened interaction W is the output of the G_0W_0 step. Since we perform single-shot GW calculations, W is calculated in the RPA approximation from the PBE orbitals and eigenvalues. GW calculations are computationally demanding, scaling with the fourth power of the system size and quadratic with the number of k points [56]. We investigate whether W can be obtained more cheaply and still sufficiently accurately by using the model dielectric function approach [57]. In this approach, a standard DFT calculation is done as a preparatory step. Then, the G_0W_0 step is skipped and the screened interaction is instead calculated via $W = \varepsilon^{-1}v$, where ε^{-1} is approximated by a diagonal model dielectric function. In this paper, we use the model dielectric function

$$\varepsilon_{GG}^{-1}(\varepsilon_{\infty}^{-1},\mu) = 1 - (1 - \varepsilon_{\infty}^{-1})e^{-G^2/4\mu^2},$$
 (32)

with $G = |\mathbf{G}|$. It was shown that this model dielectric function yields reasonable results for the diagonal of the dielectric function [57–59] as well as for optical spectra [57,59]. Additionally, it has only two parameters. In the preceding equation, the macroscopic dielectric function ε_{∞} is obtained by averaging the diagonal elements of the macroscopic dielectric tensor corresponding to W in the GW calculations. The screening parameter μ (in Å⁻¹) results from a fit of the model-dielectric function to $\varepsilon_{GG}^{-1}(\mathbf{q} \to 0, \omega = 0)$, where the long-range and short-range limits are set to $1/\varepsilon_{\infty}$ and 1, respectively.

This approach is tested for diamond and B in *h*-BN and compared to the parameter-free GW+BSE spectra. Furthermore, we need to assess how well this approach approximates the diagonal elements of W. To do this, we also show for these two systems GW+BSE spectra where the off-diagonal elements of W have been set to zero in the BSE step.



FIG. 1. XAS spectra of the *K* edge of C in diamond. *Blue filled curve:* Experiment [60]. *Black curve:* GW+BSE spectrum, this paper. *Green dash-dotted curve:* SCH calculation. *Red dashed line:* BSE-spectrum from [18]. *Arrow:* Location of the excitonic shoulder in the GW+BSE spectrum. *Inset:* GW+BSE result using an 18×18×18 *k*-mesh and a reduced Lorentzian broadening. All modeled XAS spectra are centered and adjusted in scale on the peak at 305.5 eV (dotted line).

In summary, we compare for diamond and B in *h*-BN three spectra: a GW+BSE spectrum using the full screened interaction including off-diagonal elements, a GW+BSE spectrum using only the diagonal elements of W, and, finally, a BSE spectrum using the model dielectric function.

IV. RESULTS

A. Diamond

In Fig. 1, we compare the K edge of diamond using the present PAW-GW+BSE implementation with experiment [60], a pseudopotential BSE implementation [18], and an SCH spectrum. Comparing the modeled spectrum to experiment, we see that the positions of the peaks agree very well, but the spectrum lacks intensity toward higher energies. Interestingly, the differences between the theoretical and experimental spectra seem to be mostly a background present in the experimental spectrum: For instance, the intensity modulations around the individual peaks follow the experimental intensity modulations exceedingly well. This is most obvious around the minimum at 302 eV: both on the left- and righthand sides, the experimental and theoretical spectrum change by roughly the same amount. The background consistently increases from the leftmost first peak toward the right, and can be roughly modeled by a parabolic curve with the onset of the parabola located around the onset of absorption. The same discrepancy will be noticeable for all spectra that we show in the present paper. We are not certain about the origin of the



FIG. 2. Inverse dielectric function ε_{GG}^{-1} of diamond. *Crosses:* Inverse dielectric function $\varepsilon_{GG}^{-1}(\boldsymbol{q} \to 0, \omega = 0)$ at the RPA level. *Orange line:* Model dielectric function $\varepsilon_{GG}^{-1}(0.18, 1.7)$, see Eq. (32), where μ is given in 1/Å. *Blue broken line:* $\varepsilon_{GG}^{-1}(0.18, 3.2)$. All lines intercept the y axis at $\varepsilon_{\omega}^{-1} = 0.18$.

discrepancy, but speculate that it is related to multiple scattering events involving core-conduction band pairs at other sites or, alternatively, high energy valence-conduction band pairs. Both are not accounted for by the present level of theory.

Returning to the diamond spectrum, we note that in the experimental spectrum at around 290 eV, a slight, most likely excitonic peak is visible. Compared to the other spectra, our result shows a slight shoulder located at around the same energy (see arrow in Fig. 1). To show that this feature is not an artifact of the shifted grid technique, we plot in an inset up to the first maximum at 291 eV the result of a calculation using a standard nonshifted $18 \times 18 \times 18 k$ -point mesh. Clearly, this spectrum also shows a peak. To make it more visible, we have reduced the Lorenzian broadening in this calculation to 0.2 eV.

In summary, for the case of diamond the present spectrum agrees very well with the experimental spectrum for all peak positions. Even small features in the experimental spectrum are resolved. However, deviations are observed for the absolute intensities of the peaks. We attribute this to the lack of background in the theoretical modeling caused by multiple scattering events in the experiment.

In Fig. 3, we compare the experiment to four GW+BSE spectra. In each panel, we use a different approximation for the screened interaction, as outlined in the computational methods section. All spectra are centered on and adjusted in scale to the peak of the experimental spectrum at 305.5 eV, marked by a vertical dotted line. Comparing the results obtained by including [Fig. 3(a)] or excluding [Fig. 3(b)] off-diagonal elements of W, we see that the magnitude of the first peak is vastly overestimated when only the diagonal elements are included. In Fig. 3(c), we use a model-dielectric function $\varepsilon_{GG}^{-1}(0.18, 1.7)$. As in Fig. 3(b), the first feature is overestimated. In Fig. 3(d), we use a model-dielectric function with unchanged $\varepsilon_{\infty}^{-1}$ and the screening parameter adjusted to



FIG. 3. *K*-edge spectrum of C in diamond, comparing experiment [60] (*blue filled curves*) to *GW*+BSE spectra, using different approximations for the screened interaction W: (a) *W* from G_0W_0 step, (b) same as (a) excluding off-diagonal elements, (c) model dielectric function $\varepsilon_{GG}^{-1}(0.18, 1.7)$, see Eq. (32), where μ is given in 1/Å. (d) model dielectric function $\varepsilon_{GG}^{-1}(0.18, 3.2)$, μ adjusted to fit experiment.

 $\mu = 3.2 \text{ Å}^{-1}$. Increasing μ restores the amplitude of the first peak to that of Fig. 3(a).

Neglecting the off-diagonal elements of the screened interaction from Figs. 3(a) to 3(b) or only using the diagonal model-dielectric function in Fig. 3(c) overestimates the first peak and redshifts the peak at 297 eV slightly to the left. In Fig. 2, we plot the diagonal elements of the RPA dielectric matrix as well as the model dielectric functions $\varepsilon_{GG}^{-1}(0.18, 1.7)$ and $\varepsilon_{GG}^{-1}(0.18, 3.2)$. From this plot, we see that for a given wave vector *G* increasing μ decreases ε_{GG}^{-1} and hence decreases $W = \varepsilon^{-1}v$.

From all these observations, we conclude that the offdiagonal elements of the screened interaction are indispensable for an accurate description of excitonic peaks of localized core states. Neglecting off-diagonal elements of $\varepsilon_{GG'}^{-1}$ amounts to the neglect of local-field effects [9,16]. Local-field effects describe the microscopic variation of the screening field induced by a homogeneous electric charge. Although adjusting the screening length in the model dielectric function can mimic the effect of local-field effects on the spectra, this remains a rather ad hoc approach. Also, the model dielectric function after adjustment of μ clearly does not follow the ab initio results; compare Fig. 2. As to why the off-diagonal components are relevant, we note that one makes similar observations for small molecules and in general for strongly localized states. The diagonal approximation in momentum space is not adequate when dealing with a mixture of localized and itinerant states, whereas it accounts well for transitions



FIG. 4. XAS spectra of the *K* edge of C in graphite. *Blue filled curve:* Experiment [53]. *Black curve: GW*+BSE spectrum, this paper. *Green dashed curve:* BSE-spectrum from Ref. [61]. *Red dash-dotted curve:* SCH calculation. All modeled spectra are centered at 285 eV and adjusted in height to match the integral over the first peak.

involving only bandlike itinerant states. This is an important observation that most likely exposes and underlines the limits of a simple diagonal screening approach.

B. Graphite

In Fig. 4, we present a comparison of our PAW–GW+BSE result of the *K* edge of graphite to experiment [53], to an AE full-potential BSE spectrum [62], and an SCH spectrum. In Ref. [62], perpendicular and parallel components are shown separately, so we have averaged them in the same way as our result. The GW+BSE and SCH peaks have been adjusted in height to the first peak in experiment. Since the spectrum of Olovsson *et al.* [62] has been calculated using less broadening, we have adjusted its height to approximately match the integral over the first peak. Comparing the PAW–GW+BSE spectrum of this paper and the AE result of Ref. [62], we see that both results can match the energy difference of the experimental peak positions at 285 eV and 292 eV.

Graphite is a 2D van der Waals material and we show the in-plane and out-of-plane components of the imaginary parts of the dielectric function in Fig. 5: The peak at 285 eV can be fully attributed to the out-of-plane component $\varepsilon_{\tau\tau}^{(2)}$.

While our result as well as the spectrum from Ref. [62] can reproduce the intensity ratio of the peaks at 287 eV and 292 eV reasonably well, the SCH spectrum overestimates the second peak. We also note the difference in amplitude of our result and experiment in the ranges 285–292 eV and from 292 eV upward. Furthermore, above 305 eV, we find no intensity, whereas the experimental signal remains quite substantial. As before, the experimental data show a substantial



FIG. 5. Imaginary parts of in-plane and out-of-plane components of the dielectric function for the *K* edge of C in graphite. *Black curve:* Averaged components, absorption $\propto \cos(40^\circ)^2 \varepsilon_{xx}^{(2)} + \sin(40^\circ)^2 \varepsilon_{zz}^{(2)}$. *Red dashed curve:* In-plane component, $\varepsilon_{xx}^{(2)}$. *Green dash-dotted curve:* Out-of-plane component, $\varepsilon_{xz}^{(2)}$.

background at higher energies that is lacking in our theoretical calculations. We note that as for diamond, the fine structure of the experimental XAS spectrum is very well-resolved in our theoretical calculations: the peaks at 292, 293, 295, 296, and 303 eV are also visible in the experimental spectrum at least as slight humps.

In Ref. [62], it was suggested that the double-peak structure at 292 eV and 293 eV is due to a breaking of degeneracy induced by the electron-phonon interaction. While we cannot exclude that electron-phonon coupling will enhance the splitting, we clearly observe two peaks even in the absence of any lattice distortions. In the previous BSE calculations of Ref. [62], this feature was not discernible. Reference [62] also discusses the controversy concerning the σ_2^* peak. It is mentioned that some studies interpret this peak as a delocalized bandlike contribution [63]. If we interpret the shoulder in our spectrum tentatively as the σ_2^* peak, then an explanation might be given why we can see the shoulder in our spectrum and not in the work of Ref. [62]: delocalized states are necessarily localized in reciprocal space. The shifted grid technique can sample the reciprocal space sufficiently accurately to capture this feature. Olovsson et al. on the other hand, used a $11 \times 11 \times 3$ k-mesh. While this grid is sufficiently dense to reproduce the main features, it might not be sufficient to resolve the fine structure.

C. Hexagonal boron-nitride

1. Boron

In Fig. 6, we compare an experimental K-edge spectrum of boron in h-BN [54] to the XAS spectrum obtained with



FIG. 6. XAS spectra of the *K* edge of B in *h*-BN. *Blue filled curve:* Experiment [54]. *Black curve: GW*+BSE spectrum, this paper. *Green dashed curve:* SCH-spectrum from Ref. [64]. *Violet dotted curve:* BSE-spectrum from Ref. [62]. *Green dash-dotted curve:* SCH spectrum. All modeled spectra are centered at 192 eV and adjusted in height to match the integral over the first peak.

the present PAW-GW+BSE implementation and to an AE full-potential BSE spectrum [62]. We also show two SCH spectra, one obtained with an AE APW implementation [64] and an SCH spectrum calculated using the implementation presented previously [30]. All spectra have been adjusted in height such that the integrals over the first peak match. All methods reproduce the distance between the exciton peak at 192 eV and the center of the double peak structure, located at 199 eV, while no spectrum can reproduce the double-peak structure or the smaller peak at 194 eV. The latter peak may be caused by double-electron excitations [65,66]. In this case, neither the SCH nor the GW + BSE implementation presented in this paper can capture that feature. As for graphite, the double peak structure has been attributed to a breaking of the degeneracy induced by the electron-phonon interaction [30,62]. Here our results are unambiguous: without the inclusion of electron-phonon couplings, one cannot reproduce the double-peak structure. We note that the experimental double peak is also much more pronounced and distinct than in graphite.

As for graphite, we also show the in-plane and out-of-plane components of the imaginary parts of the dielectric function in Fig. 7. Here we see that the strong peak at 192 eV corresponds to the out-of-plane component, while the features around 199 eV are attributable to the in-plane components.

In Fig. 8, we compare the experiment to BSE spectra. As for diamond, we use different approximations for the screened interaction, as outlined in the section on computational methods and as explored for diamond before. We



FIG. 7. Imaginary parts of in-plane and out-of-plane components of the dielectric function for the *K* edge of B in *h*-BN. *Black curve*: Averaged components, absorption $\propto \cos(45^\circ)^2 \varepsilon_{xx}^{(2)} + \sin(45^\circ)^2 \varepsilon_{zz}^{(2)}$. *Red dashed curve*: In-plane component, $\varepsilon_{xx}^{(2)}$. *Green dash-dotted curve*: Out-of-plane component, $\varepsilon_{zz}^{(2)}$.



FIG. 8. *K* edge of B in *h*-BN, comparing different approaches to the screened interaction *W*. (a) *W* from G_0W_0 step. (b) Same as (a), excluding off-diagonal elements. (c) Model dielectric function $\varepsilon_{GG}^{-1}(0.27, 1.38)$, see Eq. (32), where μ is given in 1/Å. *Blue filled curve:* Experiment [54].



FIG. 9. XAS spectra of the K edge of N in h-BN. Blue filled curve: Experiment [55]. Black curve: GW+BSE spectrum, this paper. Red dashed curve: OCEAN BSE-spectrum, extracted from [29]. Green dash-dotted curve: SCH-spectrum. Violet dotted curve: GW+RPA spectrum. All simulated spectra, except for GW+RPA, are centered on the maximum at 408 eV.

use either (a) *W* including off-diagonal elements, (b) excluding off-diagonal elements, or (c) a model dielectric function $\varepsilon_{GG}^{-1}(0.27, 1.38)$. Here, only the *GW*+BSE spectrum including the off-diagonal elements [Fig. 8(a)] can reproduce the energy difference between the first peak at 192 eV and the middle of the double peak structure located at 199 eV. The model dielectric function or using the diagonal elements of *W* only cannot reproduce the position of the center of the double peak structure. However, the model-dielectric function approach performs slightly better, since in that case the second peak is shifted by approximately 0.1 eV toward the center of the double peak at 199 eV.

2. Nitrogen

In Fig. 9, we show an experimental K-edge spectrum of nitrogen in h-BN [54], a modeled spectrum using the current PAW-GW+BSE implementation, a spectrum obtained via the OCEAN package [29], and an SCH spectrum. Compared to the SCH spectrum, we are able to better reproduce the energy separation between the π^* resonance at 401 eV and the σ^* peak at 408 eV. Furthermore, the GW+BSE spectrum shows a shoulder at 403 eV and a pronounced side peak at 406 eV. These experimental features are missing in the SCH spectrum. We also see that the shape of the first peak of the GW+BSE spectrum agrees better with experiment. Comparing our results with the results obtained by OCEAN, we see that both spectra agree overall. Slight improvements can be seen in our spectrum regarding the peak at 401 eV and the side peak at 406 eV: In the OCEAN spectrum, these are blueshifted with respect to experiment by ≈ 0.1 eV.



FIG. 10. Imaginary parts of in-plane and out-of-plane components of the dielectric function for the *K* edge of N in *h*-BN. *Black curve:* Average of all components, $\frac{1}{3}(\varepsilon_{xx}^{(2)} + \varepsilon_{yy}^{(2)} + \varepsilon_{zz}^{(2)})$. *Red dashed curve:* In-plane component, $\varepsilon_{xx}^{(2)}$. *Green dash-dotted curve:* Out-ofplane component, $\varepsilon_{zz}^{(2)}$.

Again, we show the in-plane and out-of-plane components in Fig. 10. Analogously to graphite, we see that the first peak at 401 eV can be attributed to the out-of-plane component and is identified with the π^* resonance.

We want to briefly discuss the influence of the direct terms on XAS spectra and plot to this end in Fig. 9 a GW+RPA spectrum. The latter is obtained by omitting the direct terms in the GW+BSE Hamiltonian. Note that we employ in this paper the Tamm-Dancoff approximation, and that in principle a treatment beyond Tamm-Dancoff is needed to obtain a full RPA spectrum. However, as was shown in a previous publication [31], omitting the direct terms restores the symmetry of resonant-resonant and antiresonant-resonant matrix elements. This means that we, strictly speaking, do not use the Tamm-Dancoff approximation in the calculation of the GW+RPA spectrum. Overall, including the direct term shifts the peaks downward by about 4 eV (420 \rightarrow 415 eV, 411 \rightarrow 408 eV, and 405 \rightarrow 401 eV). GW+RPA is not able to reproduce the spectrum. In particular, the excitonic peak at 401 eV is missing from the GW+RPA spectrum. This is analogous to results for optical transitions [8,67-69]. GW+RPA results for the K edges of diamond, graphite, hBN, and LiF can be found elsewhere [18,70].

D. Lithium-halides

In Fig. 11, we show the results for the XAS spectra of four lithium-halides with shallow core-states: LiF, LiCl, LiI, and LiBr. In each panel, we compare our PAW–GW+BSE results to experiment [71] and to an AE full-potential BSE spectrum [22]. The XAS spectra of this paper as well as those



FIG. 11. XAS spectra for the *K* edge of lithium in four lithiumhalides. *Blue filled curves:* Experiment [71]. *Black curves: GW*+BSE spectra, this work. *Red dashed lines:* BSE spectra from Ref. [22]. All modeled spectra are centered on the vertical dashed line in each panel.

of Olovsson *et al.* can reproduce the edge positions and the fine structure found in the experimental spectrum, however, our result better matches the peak positions of some features. This can likely be attributed to the fact that in the *GW* step we calculate quasiparticle energies of each conduction band individually, while in the spectra of Olovsson *et al.* the bands were rigidly shifted via a scissor operator. We note that we also used a much finer k-point sampling. Using a finer grid can also change the shape and slightly the position of some peaks.

V. SELF-INTERACTION EFFECTS IN SCH CALCULATIONS

The main issue that we will discuss in this paragraph is the dependence of the SCH method on where one places the excited electrons. To this end, we collect calculated SCH spectra for diamond, N in h-BN, and lithium-halides in Fig. 12. The technical details for the supercell calculations are collected in Table II.

We start with a brief discussion of the SCH method as it is commonly used in quantum chemistry and solid-state physics. The most refined approach is to create a potentially fractional core hole, and at the same time add a fractional charge to a conduction band state and perform a self-consistent DFT calculation. Ideally, self-consistent calculations should be performed for any of the many possible conduction band states. Then the transition probability from the ground state into the excited state is calculated and the spectrum is obtained by combining all these calculations, where the excitation energy is given by the energy difference between the ground state and the excited state and the amplitude by the transition prob-



FIG. 12. XAS spectra for the *K* edges of various systems. We show experimental spectra [55,60,71] (*blue filled curves*), spectra using the current GW+BSE implementation (*black curves*), XCH spectra where the electron was added to the lowest conduction band (*red dashed curve*), and FCH spectra where the electron was added to the background charge (*green dash-dotted curves*). In (a) and (e), we also show with a dotted line GW+BSE spectra without exchange term.

ability. This requires many DFT calculations and is highly impractical for solids since it is impossible to place the electron in a selected conduction band if many k points are used. So, in practice, in solids, the excited electrons are only placed into the conduction band edge or, even simpler, treated as negative background charge [72,73].

All yet reported SCH spectra of this paper have been obtained by adding the core electron back to the conduction band edge, performing a single self-consistent DFT calculation and then calculating the transition probabilities into all available conduction band states. In quantum chemistry, this approach is sometimes more specifically referred to as excited electron and core-hole method (XCH) [73]. Placing the electron into the background charge, hence essentially omitting the excited electron density distribution in the self-consistent calculations, is sometimes referred to as the full core-hole (FCH) method, since a full electron is removed from the core [72].

At this point, it is expedient to study these two approximations, XCH method, and the FCH method for the materials scrutinized here. In the case of diamond and *h*-BN, Figs. 12(a) and 12(b) show that the XCH and FCH spectra are almost identical—compare red and green dashed lines. This implies that the electron that we place into the conduction band is well approximated by a homogeneous background charge. This in turn suggests that the localization of the excited electron is not very sizable in the XCH method for diamond and *h*-BN.

However, this is not the case for the lithium-halides, Figs. 12(c)-12(f). Here we observe significant differences between placing the electron into the conduction band edge or into the background; again compare red and green lines. Compared to the experimental spectrum and GW+BSE, the homogeneous background method (FCH, green line) yields clearly improved results for the peak positions compared to the more often used XCH method (red line). The peak positions for LiCl, LiBr, and LiI are in almost perfect agreement with the GW+BSE results, whereas for the XCH method the higher energy excitations are far too close to the main peak. Obviously, placing the excited electron into the lowest conduction band (LCB) and then calculating the entire spectrum is not a good approximation for lithium-halides, but works reasonably well for diamond and h-BN. To rule out finitesize effects, we repeated the same procedure for LiBr using a supercell containing 250 atoms. The differences persisted even with this larger supercell.

We will now try to explain why the SCH method often works well and when it tends to fail. The first crucial point is that the SCH method yields a reasonable approximation to the BSE, in particular, to the crucial term that describes the electrostatic interaction between the core-hole and the excited conduction band electrons. This is related to the W term (direct term) in the BSE method. In the SCH method, a core hole is created and all the other valence electrons will screen this local core -hole. The screening of the valence electrons is described by the static DFT dielectric function, so effectively the conduction band electrons see an effective screened core hole $\int \varepsilon^{-1}(r', r)/|r - r_c|d^3r$ if the core hole is positioned at r_c . This implies that the SCH method mimics the effects of the direct term in the BSE very well. The successes and failures of the SCH method are then mainly related to the self-interaction of the conduction band electron.

This will be discussed by inspecting the scheme shown in Fig. 13. The FCH spectrum of the *K* edge of Li in Lihalides is schematically shown vertically in the left part of the figure. The LCB level is indicated by the line labeled LCB. For the FCH method, this level is unoccupied, since the excited electron is moved to the homogeneous background. To represent the orbital of the excited conduction band electron, we show schematically a *p*-like orbital. In the XCH method, this orbital LCB becomes occupied with a single electron that essentially experiences the screened Coulomb potential (see above). The resulting localized charge density is added to the total charge density and, in turn, this further modifies the Hartree and DFT exchange-correlation potentials. Unless the



FIG. 13. Sketch describing how the self-interaction error of the additional electron in XCH method can change the spectra. See text for description.

DFT functional is canceling the self-interaction error, this will lead to a sizable self-interaction of the electron. In particular, this self-interaction error is more substantial if the conduction band electron is strongly localized, as it is for the Li-halides.

The self-interaction error in turn causes two effects: First, it shifts the energy level of the conduction band electron up from the initial energy to the new energy LCB'. Second, it delocalizes the electron, which we have visualized by spreading out the p orbital. These effects negatively impact the spectrum of the XCH method, as shown schematically in the left part of the figure. The delocalization reduces the oscillator strength, in turn reducing the amplitude of the first peak. The upshift of the eigenvalue, on the other hand, shifts the position of the peak to higher energies. Furthermore, this conduction band electron somewhat screens the core hole. The energies of higher lying unoccupied conduction band states are then determined in the presence of the screened core-hole potential and the potential of the added electron. This also shifts their energies upward from a, b to a', b'. However, since these states are necessarily orthogonal to the LCB state and since these states are also not as well localized as the LCB state, the energy shift $a \rightarrow a'$ is much smaller than from $LCB \rightarrow LCB'$. This negatively impacts the calculated spectrum and results in a too-small energy separation between the main peak (LCB') and the other peaks (a' and b').

To summarize, the main issue with the conventional XCH method is that the conduction band edge is shifted upward due to self-interaction errors present in most semilocal DFT functionals. If the additional electron is placed into the background, this problem is not observed. Note that selfinteraction is unphysical and would not be present for the exact DFT functional. One might well argue that the conventional XCH methods in combination with DFT functionals that are not self-interaction free is bound to be fairly inaccurate for localized excitons.

At this point, we want to quantify the mechanism outlined above. We do this by calculating the energy differences of the bands corresponding to the DFT conduction band minimum and DFT valence band maximum at the Γ point. We have obtained these values for the DFT, FCH, and XCH calculations for LiBr of Fig. 12(e). These values are 4.94 eV (DFT), 3.37 eV (FCH), and 4.41 eV (XCH). The additional electron in the XCH method shifts the energy of the LCB upward by approximately 1 eV relative to the valence band edge. This orbital shift to higher energies in the XCH method will shift the onset of absorption by the same amount, as outlined in the previous paragraphs.

To make a connection to the GW+BSE approach and to further substantiate our claims, we have also investigated how the exchange terms contribute to the GW+BSE spectra. We first discuss the effect of the exchange term in general. The exchange term has a positive sign and is related to the change of the Hartree potential. It accounts for the repulsive electrostatic interaction of the individual electron-hole pairs, see Eq. (19). If the electron-hole pairs are strongly localized, then including the exchange term will shift oscillator strengths to higher energies. Conversely, omitting the exchange term for strongly localized electron-hole pairs shifts the spectrum to lower energies. We now discuss the effect of the exchange term on excitons, in particular. Above we have argued that self-interaction Hartree effects come into play for strongly localized excitons. Hence, for excitons involving conduction band states where the Hartree self-interaction is large, we should also see a noticeable energy shift of the excitonic peaks when the exchange term is omitted.

In Figs. 12(a) and 12(b), we show the GW+BSE results for diamond and Li in LiBr where the exchange terms were omitted (black dashed line). For diamond, this hardly changes the spectrum, in agreement with the observation that the XCH and FCH methods are very similar. For LiBr though, the first peak, and the first peak only, is shifted toward the left by almost 1 eV. This is also very close to the difference between the XCH and FCH methods. It confirms that the excitation into the first conduction band state in LiBr creates a strongly localized exciton, whereas all the other excitations in LiBr as well as in diamond are fairly delocalized, in line with our previous arguments.

A final note is in place: In the BSE method, changes of the Hartree potential are considered for all excitations individually. On the other hand, in the XCH method, one places the electron into the LCB and assumes that changes of the Hartree potential for this case mimic the changes of the Hartree potential if one would place the electrons into other conduction band states. This is obviously a crude approximation if the LCB state is strongly localized, whereas the other states are delocalized. It seems wiser to leave changes of the potential related to the occupation of the LCB entirely out, as done for the FCH method.

VI. SUMMARY AND CONCLUSION

In the present paper, we have discussed how to implement the BSE within the PAW methodology for the calculation of x-ray absorption spectra. After reviewing the basic theory, we have detailed how to evaluate the matrix elements of the BSE Hamiltonian and explained how the expressions need to be modified when core states are included. In particular, we have discussed that we approximate the overlap charge densities involving core states using augmentation charges only. This suffices, since the augmentation charges are designed to describe long-range electrostatic interactions essentially exactly. However, for the transition probabilities, we use the exact AE core orbitals and the AE partial waves corresponding to the conduction band electrons. We have tested our implementation on four materials classes: a covalent system (diamond), two 2D van der Waals layered materials (graphite and *h*-BN) and four ionic systems with shallow core states (Li-halides).

For diamond, we found that our result could reproduce all relevant peak positions very well. Compared to other theoretical spectra, our spectrum features an additional shoulder at around 290 eV, which we assign to the excitonic peak of the experimental spectrum. As was the case for the SCH method and previous BSE calculations, our spectrum lacks intensity at higher energies. This seems to be mostly related to a background that is present in the experimental data but missing at the level of theory that is commonly used. The origin of the lack of background in the present theories is not entirely clear to us, but could be related to interactions with core-conduction band pairs at other sites or the admixture of core-valence pairs.

For diamond, we have also investigated the influence of different approximations to the screened interaction W on the spectrum. We found that the off-diagonal elements of the screened interaction play an important role for accurate predictions of the individual peaks in the x-ray absorption spectrum. Neglecting the off-diagonal components leads to a quite significant deterioration of the results compared to experiment. This also means that simplified approaches that attempt to model the screening using a diagonal model lead to inaccurate results.

In graphite, the peak positions and intensity ratios also match the experiments well. In our results, we found a shoulder in the σ^* peak that can be tentatively assigned to the σ_2^* peak, suggested by some authors to be related to a delocalized bandlike contribution [63]. So, strictly speaking, electron-phonon coupling may not be required to explain the splitting of the σ^* peak. However, we also do not doubt that the splitting will be enhanced by electron-phonon coupling, as suggested by other authors [62].

For the boron K edge in h-BN, we found again good agreement with experiment and previous BSE and supercell calculations. The results for the nitrogen K edge are somewhat more notable. The GW+BSE approach is able to describe all relevant peaks observed experimentally, while the SCH calculation lacks important features in the spectrum. Specifically, the distance between the π^* and σ^* peaks is in excellent agreement with experiment as well as state-of-the-art results of other authors.

For the Li-halides, we again found excellent agreement between the BSE results and experiment. Compared to previous BSE spectra employing a scissor shift, a slight but noticeable improvement of the peak positions is observed. We have tentatively related this to improved quasiparticle energies, as our calculations rely on the G_0W_0 band structures, whereas previous calculations only employed a scissor-corrected DFT band structure. We also note that our vastly improved *k*-point sampling may have positively impacted our predicted spectra. Finally, we have carefully scrutinized the SCH method for diamond, *h*-BN, as well as the Li-halides. As discussed, the SCH method comes in two variants, one where the excited electron is placed in the conduction band edge and the other where the electron is treated as a homogeneous background charge. For diamond and *h*-BN, both approaches yield almost identical results. For the halides, treating the excited electron as a background charge gives much-improved peak positions almost on par with the BSE. We have tried to argue that the self-interaction errors of present density functionals are the most likely explanation for the failure of the SCH method with the excited electron in the LCB. Self-interaction erroneously pushes the first excitonic peak to too high energies.

In summary, the present paper shows that excellent predictions for x-ray absorption spectra are possible using the PAW method and the BSE approach.

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APPENDIX: CONSTRUCTION OF AUGMENTATION CHARGES

The construction of the augmentation charges proceeds in two steps: first moment restoration and then shape restoration.

We start with moment restoration and write the defining equation for the augmentation charges. This is the requirement that the augmentation charges have the same moments as the difference of the AE and PS charge densities inside the PAW sphere,

$$\int_{\Omega_r} [n^1(\boldsymbol{r}) - \tilde{n}^1(\boldsymbol{r}) - \hat{n}(\boldsymbol{r})] |\boldsymbol{r}|^L Y^*_{LM}(\Omega) d^3 \boldsymbol{r} = 0, \qquad (A1)$$

where $Y_{LM}^*(\Omega)$ are the spherical harmonics, *L* and *M* the total orbital and magnetic quantum numbers, and $\Omega = \{\theta, \phi\}$ the angular variables. In the PAW method, the charge density difference $n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r})$ is written as [38]

$$n^{1}(\boldsymbol{r}) - \tilde{n}^{1}(\boldsymbol{r}) = \sum_{nm} \rho_{nm} Q_{nm}(\boldsymbol{r}), \qquad (A2)$$

with the functions

$$Q_{nm}(\mathbf{r}) = \phi_n^*(\mathbf{r})\phi_m(\mathbf{r}) - \tilde{\phi}_n^*(\mathbf{r})\tilde{\phi}_m(\mathbf{r})$$
(A3)

and occupancies (or one-center density matrix)

$$\rho_{nm} = \langle \tilde{\psi} | \tilde{p}_n \rangle \langle \tilde{p}_m | \tilde{\psi} \rangle. \tag{A4}$$

Furthermore, the indices n, m are compound indices: $n = \{\epsilon_n, l_n, m_n\}$.

We now calculate the moments of the charge difference:

$$q_{nm}^{LM} = \int_{\Omega_r} Q_{nm}(\boldsymbol{r}) |\boldsymbol{r}|^L Y_{LM}^*(\Omega) r^2 dr d\Omega.$$
 (A5)

In the PAW formalism, AE and PS partial waves, Eqs. (16) and (17), respectively, are products of radial waves and spherical harmonics. Inserting these into the preceding equation, the

integral separates into radial and angular parts:

$$q_{nm}^{LM} = \int_0^{r_c} (u_{k_n, l_n} u_{k_m, l_m} - \tilde{u}_{k_n, l_n} \tilde{u}_{k_m, l_m}) |\mathbf{r}|^L dr$$
$$\times \int Y_{l_n, m_n}(\Omega) Y_{l_m, m_m}(\Omega) Y_{LM}^*(\Omega) d\Omega.$$
(A6)

The radial integral of three spherical harmonics (also called Gaunt coefficients) imposes conditions on the angular momenta l_n , l_m , and L. In particular, all the usual rules of the addition of angular momentum apply: $m_n + m_m = M$ and

$$L = |l_n - l_m|, |l_n - l_m| + 2, \dots, |l_n + l_m|.$$
 (A7)

After having calculated the moments, Eq. (A6), the augmentation charge is

$$\hat{n} = \sum_{\substack{LM\\l_n, m_n, l_m, m_m\\n, m}} \rho_{nm} q_{nm}^{LM} Y_{LM}(\Omega).$$
(A8)

The one-center density matrix ρ_{nm} is indexed by the angular momenta l_n, m_n, l_m, m_m . On the other hand, the augmentation charge that will be added to the plane-wave grid is indexed by the total orbital and magnetic quantum numbers L, M. Therefore, we need a change of basis to a ρ_{LM} density matrix. To achieve this, we sum over the l, m indices in the preceding equation. This results in the required L, M-dependent density matrix ρ_{LM} and the L, M-dependent moments q_{nm}^{LM} :

$$\sum_{l_n,m_n,l_m,m_m} q_{nm}^{LM} \rho_{l_n,m_n,l_m,m_m} = q_{nm}^{LM} \rho_{LM}.$$
 (A9)

We then obtain our final result for the moment-restoring augmentation charges:

$$\hat{n} = \sum_{\substack{LM\\n,m}} \rho_{LM} \hat{Q}_{nm}^{LM}, \qquad (A10)$$

$$\hat{Q}_{nm}^{LM} = q_{nm}^{LM} Y_{LM}. \tag{A11}$$

These augmentation charges are added to the PS charge density on the plane-wave grid, as in Eq. (23). We note that the augmentation charges are directly added in real space.

Up to this point, we neglected one-center terms and reconstructed the augmentation charges from the moments of the exact charge density inside the PAW sphere. For post-DFT methods, it can be beneficial to approximate the contributions of the one-center terms and to add these contributions to the augmentation charges. This process is called shape restoration. We add to the right-hand side of Eq. (A9) for each total angular momentum L shape-restoring radial functions $\Delta g_L(r)$, with coefficients c_{nm}^L to be determined:

$$\hat{n} = \sum_{\substack{LM\\n,m}} \rho_{LM} \big[q_{nm}^{LM} Y_{LM}(\Omega) + c_{nm}^L \Delta g_L(r) Y_{LM}(\Omega) \big], \quad (A12)$$

where the shape-restoring functions are written as a sum of two spherical Bessel-functions:

$$\Delta g_L(r) = \sum_{\beta=1}^2 \alpha_\beta^L j_L(q_\beta^L r).$$
 (A13)

The coefficients α_{β}^{L} and q_{β}^{L} are chosen such that the l, m multipole of the shape restoring charge contribution vanishes and that the Hankel transforms of $\Delta g_{L}(r)$ and $Q_{nm}(r)$,

$$Q_{nm}(q) = \int_0^{R_c} Q_{nm}(r) j_L(qr) r^L dr, \qquad (A14)$$

$$\Delta g_L(q) = \int_0^{R_c} \Delta g_L(r) j_L(qr) r^L dr, \qquad (A15)$$

are identical at chosen values of q.

To calculate the coefficients c_{nm}^L , we subtract from the radial part of the charge density difference, Eq. (A3), the radial part of the moment-restoring contribution to the augmentation charge:

$$\delta Q_{nm}(r) = Q_{nm}(r) - \hat{Q}_{nm}(r). \tag{A16}$$

In the next step, we write the quantity $\delta Q(r)$ as a superposition of shape restoring functions:

$$\delta Q_{nm}(r) = \sum_{L} c_{nm}^{L} \Delta g_{L}(r).$$
 (A17)

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We then multiply the preceding equation by $j_L(q_{\beta}^L r)$ and integrate over r^L :

$$\int j_L(q^L_\beta r) \delta Q_{nm}(r) r^L dr$$
$$= \sum_L c^L_{nm} \int j_l(q^L_\beta r) \Delta g_L(r) r^L dr.$$
(A18)

Introducing coefficients

$$b_{\beta} = \int j_L (q_{\beta}^L r) \delta Q_{nm}(r) r^L dr, \qquad (A19)$$

$$A_{\beta,L} = \int j_L (q_{\beta}^L r) \Delta g_L(r) r^L dr, \qquad (A20)$$

Eq. (A18) can be recast as a system of linear equations:

$$\sum_{L} A_{\beta,L} c_{nm}^{L} = b_{\beta}, \qquad (A21)$$

which can be solved by standard methods to determine the coefficients c_{nm}^L .

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