

Efficient G_0W_0 and Bethe-Salpeter equation calculations of heterostructures within an all-electron framework

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The combination of two-dimensional materials into heterostructures offers new opportunities for the design of optoelectronic devices with tunable properties. However, computing electronic and optical properties of such systems using state-of-the-art methodology is challenging due to their large unit cells. This is particularly so for highly precise all-electron calculations within the framework of many-body perturbation theory, which come with high computational costs. Here, we extend an approach that allows for the efficient calculation of the noninteracting polarizability, previously developed for plane wave basis sets, to the (linearized) augmented plane wave method. This approach is based on an additive ansatz, which computes and superposes the polarizabilities of the individual components in their respective unit cells. We implement this formalism in the G_0W_0 module of the `exciting` code and implement an analogous approach for BSE calculations. This allows the calculation of highly precise optical spectra at low cost. So-obtained results of the quasiparticle band structure and optical spectra are demonstrated for bilayer WSe_2 and pyridine@ MoS_2 in comparison with exact reference calculations.

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I. INTRODUCTION

The combination of two-dimensional (2D) materials into weakly bound van der Waals (vdW) heterostructures has received increasing attention in the last decade due to the possibility of tailoring their electronic and optical properties towards desired features and functions [1]. A class of materials with promising optoelectronic properties is transition metal dichalcogenides (TMDCs) [2–5], which can be combined into multilayered structures. Particularly interesting with a high potential for new optoelectronic and photonic devices is the combination of TMDCs with organic molecules [6]. Such hybrid inorganic organic systems (HIOSs) allow us to enhance the specific strengths of the individual materials while compensating for their weaknesses [7–11].

For an efficient exploration of possible combinations of materials, accurate theoretical and computational methods are essential [7–10]. In particular, a reliable description of the band structure and the resulting energy-level alignment [12–15] of such an interface is a must, as it is the basis for understanding the material's excitation spectra [16–19], which in turn determines whether it is suitable for a given

application. Approaches based solely on density-functional theory (DFT) are not useful for vdW heterostructures and HIOSs since many-body effects govern not only their response to light but also their electronic structure. For example, the wrong type of energy-level alignment of HIOSs has been predicted not only by semilocal DFT but also by hybrid functionals [9]. For these reasons, many-body perturbation theory, in particular the G_0W_0 approximation and the Bethe-Salpeter equation (BSE), is the state of the art for studying the electronic and optical properties of such materials.

Unfortunately, both G_0W_0 and BSE calculations are computationally very demanding and therefore often are not feasible for large unit cells. This is the case for interface systems, which typically require combining supercells of the pristine constituents. One of the major bottlenecks in both methods is the calculation of the polarizability, which scales as $O(N^4)$ with the number of atoms N in the unit cell [20,21]. Therefore, recent efforts have focused on reducing the computational cost of polarizability calculations, either by developing algorithms with a more favorable scaling [22–24] or by employing efficient approximations. A particularly efficient approximation for weakly bound systems consists of an additive ansatz, in which the polarizability of the heterostructure is obtained by summing the contributions of the individual components [12,13]. This comes with the additional advantage that the polarizability of the supercell of a constituent does not need to be computed for that supercell and instead can be obtained from the respective unit cell by a folding (expansion) procedure. The combination of these two approaches, called *expansion and addition screening* (EAS) here, has been successfully applied to the calculation of the

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energy-level alignment at molecule-metal interfaces [12,13]. However, in these works, a plane wave representation of the polarizability was used, and thus, it is not directly applicable to other basis sets, in particular those used in all-electron codes [25–27]. However, all-electron calculations are very important for reference calculations, e.g., for benchmarking new implementations or for assessing the impact of pseudopotentials [28,29].

In this work, we extend the EAS approach to the so-called mixed-product basis used in excited-state calculations based on the (linearized) augmented plane wave (L)APW method [30]. We derive the formalism and implement it within the `G0W0` module of the `exciting` code [26,31]. Furthermore, we implement an analogous method for the BSE framework [32]. These developments allow for the calculation of the electronic structure as well as of the optical absorption spectra of large interfaces with high accuracy at significantly reduced computational cost compared to standard approaches. We demonstrate this by computing the quasiparticle (QP) band structures and optical spectra of two prototypical systems, namely, the WSe₂ bilayer and the HIOS pyridine@MoS₂.

This paper is structured as follows. The theoretical background covering the plane-wave-based EAS method is revisited in Sec. II A. The mixed-product basis is summarized in Sec. II B. In Secs. III A and III B, we describe the expansion and addition steps within our basis. In Sec. IV, we present the so-obtained QP band structure and optical spectra of the selected systems and compare them with the exact calculations.

II. BACKGROUND

A. Polarizability in the EAS method with a plane wave basis

The screened Coulomb potential W is central to both GW and BSE calculations since screening is essential for both the electron-electron and the electron-hole interactions, respectively [21,33]. It is defined as

$$W(\mathbf{r}, \mathbf{r}'; \omega) = \int d\mathbf{r}_1 \epsilon^{-1}(\mathbf{r}, \mathbf{r}_1; \omega) v(\mathbf{r}_1, \mathbf{r}'), \quad (1)$$

where $v(\mathbf{r}, \mathbf{r}') = |\mathbf{r} - \mathbf{r}'|^{-1}$ is the bare Coulomb interaction. ϵ denotes the dielectric function, which, in a symbolic notation, can be obtained from the noninteracting random-phase approximation polarizability P as $\epsilon = 1 - vP$. P is typically expanded into a set of basis functions $\{\chi_i^{\mathbf{q}}(\mathbf{r})\}$ according to

$$P(\mathbf{r}, \mathbf{r}', \omega) = \sum_{\mathbf{q}}^{\text{BZ}} \sum_{ij} P_{ij}(\mathbf{q}, \omega) \chi_i^{\mathbf{q}}(\mathbf{r}) [\chi_j^{\mathbf{q}}(\mathbf{r}')]^*, \quad (2)$$

where the first sum runs over all $\mathbf{q}$ -points in the Brillouin zone (BZ). The matrix elements can be obtained as

$$P_{ij}(\mathbf{q}, \omega) = \iint d\mathbf{r} d\mathbf{r}' [\chi_i^{\mathbf{q}}(\mathbf{r})]^* P(\mathbf{r}, \mathbf{r}', \omega) \chi_j^{\mathbf{q}}(\mathbf{r}'). \quad (3)$$

In this work, we consider two different basis sets for the expansion of the polarizability in Eq. (2), namely, a mixed-product basis for GW calculations and plane waves for the BSE. From this point on, we omit the frequency dependence of the polarizability for simplicity since what follows applies to all frequencies.

The key idea of the additive ansatz for the polarizability [12,13] is to compute the total polarizability as the sum of the individual contributions, i.e., $P = \sum_{\mu=1}^2 P^{\mu}$, thus neglecting effects coming from the interface. This additive approach is applicable to systems with negligible covalent interactions, e.g., heterostructures that can easily be separated into two distinct components. Using a plane wave expansion of the polarizability in terms of the reciprocal lattice vectors $\mathbf{G}$, i.e., $\chi_i^{\mathbf{q}}(\mathbf{r}) \rightarrow \chi_{\mathbf{G}}^{\mathbf{q}}(\mathbf{r}) \propto e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}$, this approach can be implemented by computing the coefficients $P_{\mathbf{G}\mathbf{G}'}^{\mu}(\mathbf{q})$ for layer μ and the subsequent addition according to

$$P_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = P_{\mathbf{G}\mathbf{G}'}^1(\mathbf{q}) + P_{\mathbf{G}\mathbf{G}'}^2(\mathbf{q}). \quad (4)$$

Due to the quartic scaling of the polarizability, the additive approach itself already offers significant computational savings. Further savings can be achieved when expanding the individual polarizabilities. In the expansion step, the smallest possible unit cell is identified for each individual component for computing the polarizability. Then the polarizability of the respective component in the supercell of the heterostructure is obtained by an expansion (folding) procedure. This expansion requires mapping all $(\mathbf{q}_{\text{uc}} + \mathbf{G}_{\text{uc}})$ vectors of the unit cell to the corresponding $(\mathbf{q} + \mathbf{G})$ vectors of the supercell:

$$P_{\mathbf{G}_{\text{uc}}\mathbf{G}'_{\text{uc}}}^{\mu}(\mathbf{q}_{\text{uc}}) \rightarrow P_{\mathbf{G}\mathbf{G}'}^{\mu}(\mathbf{q}), \quad (5)$$

with $\mathbf{q}_{\text{uc}} + \mathbf{G}_{\text{uc}} = \mathbf{q} + \mathbf{G}$ and $\mathbf{q}_{\text{uc}} + \mathbf{G}'_{\text{uc}} = \mathbf{q} + \mathbf{G}'$. The expansion is therefore possible only for commensurate grids $\{\mathbf{q} + \mathbf{G}\} \subseteq \{\mathbf{q}_{\text{uc}} + \mathbf{G}_{\text{uc}}\}$.

B. The mixed-product basis

We extend the EAS approach within the (L)APW + local orbital framework. It partitions the unit cell parallelepiped, $\mathcal{A} \subset \mathbb{R}^3$, into two distinct regions consisting of so-called muffin-tin (MT) spheres centered around the atoms, $\mathcal{A}_{\text{MT}} \subset \mathcal{A}$, and the interstitial region, $I \subset \mathcal{A}$, with $\mathcal{A} = \mathcal{A}_{\text{MT}} \cup I$. Note that $\mathcal{A}_{\text{MT}}$ does not refer to one specific muffin-tin sphere but instead includes all muffin-tin spheres of the system. The LAPW method employs augmented plane waves as basis functions, using atomlike functions within the MT spheres and plane waves in the interstitial region. Additional local orbitals that live only in the MT spheres make the basis more flexible. More details on the LAPW basis are presented in Appendix A, where the basis is defined in Eqs. (A1) and (A2).

The G_0W_0 implementation in the all-electron full-potential code `exciting` employs an auxiliary basis, which allows for an optimal representation of the product of two Kohn-Sham states and therefore for a flexible representation of the polarizability [25,26,34]. Similar to the LAPW basis, this so-called mixed-product basis has a different functional form in the MT

and interstitial regions. The basis functions are defined as

$$\chi_j^{\mathbf{q}}(\mathbf{r}) = \begin{cases} \gamma_{\alpha NL}^{\mathbf{q}}(\mathbf{r}^\alpha) = e^{i\mathbf{q} \cdot \boldsymbol{\tau}_\alpha} v_{\alpha NL}(r^\alpha) Y_{LM}(\hat{\mathbf{r}}^\alpha) & r^\alpha < R_{\text{MT}}^\alpha, \\ \Lambda_i^{\mathbf{q}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} \tilde{S}_{\mathbf{G}i}^* e^{i(\mathbf{G}+\mathbf{q}) \cdot \mathbf{r}} \theta_I(\mathbf{r}) & \mathbf{r} \in I, \end{cases} \quad (6)$$

where R_{MT}^α is the radius of the sphere of atom α , centered at position $\boldsymbol{\tau}_\alpha$, and the difference vector from this center is labeled as $\mathbf{r}^\alpha = \mathbf{r} - \boldsymbol{\tau}_\alpha$. The unit cell volume is denoted by Ω . Inside the MT region of atom α , the basis is constructed in terms of radial functions $v_{\alpha NL}(r^\alpha)$ and spherical harmonics $Y_{LM}(\hat{\mathbf{r}}^\alpha)$ with quantum numbers L and M . In the interstitial region, a linear combination of plane waves is used, where $\tilde{S}_{\mathbf{G}i}$ are the renormalized plane wave eigenvectors ensuring orthogonality. $\theta_I(\mathbf{r})$ is the step function, which is 0 within the MTs and 1 outside. For more details on the G_0W_0 module, the reader is referred to Ref. [26] and Appendix A.

III. THE EAS APPROACH IN THE MIXED-PRODUCT BASIS

A. The expansion step

In the expansion step, the polarizability of the supercell is obtained by expanding the polarizability of the smallest unit cell of each component through a folding procedure (orange box in Fig. 1). Owing to the partitioning of the basis following Eqs. (6) and (7), the polarizability is composed of four different blocks according to

$$P = \begin{pmatrix} P_{\text{MT,MT}} & P_{\text{MT},I} \\ P_{I,\text{MT}} & P_{I,I} \end{pmatrix}. \quad (8)$$

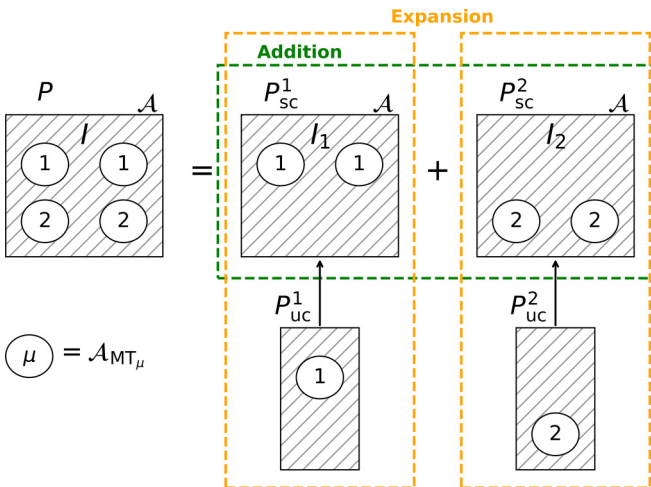


FIG. 1. Scheme of the *expansion and addition* method. The polarizability of the heterostructure P is approximated as the sum of the individual polarizabilities, P_{sc}^1 and P_{sc}^2 , which are obtained as the expansions of the polarizabilities computed in their respective unit cells, P_{uc}^1 and P_{uc}^2 . Circles and hatched areas represent the muffin-tin and interstitial regions, respectively, where the polarizability is expanded in different basis functions. I_μ denotes the interstitial region of layer μ in the heterostructure's unit cell $\mathcal{A}$, while the MT region is denoted as $\mathcal{A}_{\text{MT},\mu}$.

In this notation, block P_{XY} includes all matrix elements P_{ij} [see Eq. (3)], with $\chi_i(\mathbf{r})$ [$\chi_j(\mathbf{r}')$] being defined in region X [Y]. Due to the nature of the mixed-product basis, the MT spheres and the interstitial region require very different approaches for performing the expansion.

We first detail the procedure for the case in which both coordinates are in atomic spheres. The matrix elements of the supercell $P_{\text{MT,MT}}^{\text{sc}}$ can be obtained in terms of the matrix elements of the unit cell $P_{\text{MT,MT}}^{\text{uc}}$ via a transformation from real to reciprocal space as follows:

$$P_{\alpha_{\text{sc}}\beta_{\text{sc}}}^{\text{sc}}(\mathbf{q}^{\text{sc}}) = \sum_{\mathbf{R}^{\text{sc}}} e^{-i\mathbf{q}^{\text{sc}} \cdot \mathbf{R}^{\text{sc}}} P_{\alpha_{\text{sc}}\beta_{\text{sc}}}^{\text{sc}}(\mathbf{R}^{\text{sc}}) \\ = \frac{N_{\mathbf{q}}^{\text{sc}}}{N_{\mathbf{q}}^{\text{uc}}} \sum_{\mathbf{q}^{\text{uc}}} e^{i\mathbf{q}^{\text{uc}} \cdot (\mathbf{R}_{\beta}^{\text{uc}} - \mathbf{R}_{\alpha}^{\text{uc}})} P_{\alpha_{\text{uc}}\beta_{\text{uc}}}^{\text{uc}}(\mathbf{q}^{\text{uc}}), \quad (9)$$

where $\mathbf{R}$ are the real-space lattice vectors, $N_{\mathbf{q}}$ is the number of $\mathbf{q}$ points, and the subscript uc (sc) refers to unit cell (supercell) quantities. The difference in real-space lattice vectors is rewritten in terms of the atomic positions $\boldsymbol{\tau}$,

$$\boldsymbol{\tau}_{\alpha_{\text{sc}}} = \boldsymbol{\tau}_{\alpha_{\text{uc}}} + \mathbf{R}_{\alpha}^{\text{uc}}, \quad (10)$$

as

$$\mathbf{R}_{\beta}^{\text{uc}} - \mathbf{R}_{\alpha}^{\text{uc}} = (\boldsymbol{\tau}_{\beta_{\text{sc}}} - \boldsymbol{\tau}_{\beta_{\text{uc}}}) - (\boldsymbol{\tau}_{\alpha_{\text{sc}}} - \boldsymbol{\tau}_{\alpha_{\text{uc}}}). \quad (11)$$

Once the equivalent atoms in the supercell have been identified using Eq. (10), the implementation of Eq. (9) is straightforward.

For the block involving only the interstitial region $P_{I,I}$, where a linear combination of plane waves is employed [see Eq. (7)], we apply the mapping defined in Eq. (5). This is achieved by first transforming the matrix elements of the unit cell polarizability in the mixed-product basis to the original set of interstitial plane waves using

$$P_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = \sum_{ij} P_{ij}(\mathbf{q}) \langle \chi_i^{\mathbf{q}} | \chi_{\mathbf{G}}^{\mathbf{q}} \rangle^* \langle \chi_j^{\mathbf{q}} | \chi_{\mathbf{G}'}^{\mathbf{q}} \rangle, \quad (12)$$

where the overlap between these two bases is given by

$$\langle \chi_i^{\mathbf{q}} | \chi_{\mathbf{G}}^{\mathbf{q}} \rangle = \frac{1}{\Omega} \int d\mathbf{r} \sum_{\mathbf{G}'} \tilde{S}_{\mathbf{G}'i} e^{-i(\mathbf{q}+\mathbf{G}') \cdot \mathbf{r}} e^{i(\mathbf{q}+\mathbf{G}) \cdot \mathbf{r}} \\ = \sqrt{\lambda_i} S_{\mathbf{G}i}. \quad (13)$$

Here, λ are the eigenvalues of the plane wave overlap matrix [see Eq. (A5)], and we have used Eq. (A6). Second, the polarizability is expanded according to Eq. (5) to obtain it for the supercell in the plane wave basis. Finally, we transform this matrix back to the mixed-product basis of the supercell using the inverse transformation of Eq. (12).

The polarizability matrix further has two off-diagonal blocks, i.e., $P_{\text{MT},I}$ and $P_{I,\text{MT}}$. In these cases, the procedure described above for $P_{\text{MT,MT}}$ ($P_{I,I}$) is applied only to the rows

(columns) and columns (rows) of $P_{\text{MT},I}$ and $P_{I,\text{MT}}$, respectively. Once the expansion is performed, the polarizability of the supercell is added to its counterpart coming from the other component of the heterostructure as described in the next section.

B. The addition step

In the addition step, we construct the polarizability of the heterostructure by calculating the sum of the individual contributions according to $P^{\text{HS}}(\mathbf{q}) = P^1(\mathbf{q}) + P^2(\mathbf{q})$ (green box in Fig. 1). For this part, we assume that the polarizabilities of the individual components are available, either by a direct calculation for the supercell or by applying the expansion procedure presented in the preceding section. This addition procedure is again not trivial due to the dual representation of the basis, as it requires us to transform the polarizability from the bases of the individual components to the basis of the heterostructure.

For weakly bound systems, we approximate the coefficients of the individual polarizability of component μ in the basis of the full heterostructure as

$$P_{AB}^{\mu}(\mathbf{q}) = \sum_{ab} C_{aA}^{\mu*}(\mathbf{q}) P_{ab}^{\mu}(\mathbf{q}) C_{bB}^{\mu}(\mathbf{q}), \quad (14)$$

where $C_{jJ}^{\mu}(\mathbf{q}) = \langle \chi_j^{\mu,\mathbf{q}} | \chi_J^{\mathbf{q}} \rangle$ is the overlap matrix element between a basis function of one individual layer $\chi_j^{\mu,\mathbf{q}}$ and a basis function of the heterostructure $\chi_J^{\mathbf{q}}$, with lowercase and uppercase indices used to distinguish between them. Like for Eq. (8), it is convenient to partition the polarizability of the heterostructure into different blocks:

$$P_{\text{HS}} = \begin{pmatrix} P_{\text{MT}_1,\text{MT}_1} & P_{\text{MT}_1,\text{MT}_2} & P_{\text{MT}_1,I} \\ P_{\text{MT}_2,\text{MT}_1} & P_{\text{MT}_2,\text{MT}_2} & P_{\text{MT}_2,I} \\ P_{I,\text{MT}_1} & P_{I,\text{MT}_2} & P_{I,I} \end{pmatrix}, \quad (15)$$

where each term represents a block of the polarizability with the basis functions coming from the different regions. Here, we took advantage of the fact that the MT region of the heterostructure can be further divided into the two MT regions of the individual components, i.e., $\mathcal{A}_{\text{MT}} = \mathcal{A}_{\text{MT}_1} \cup \mathcal{A}_{\text{MT}_2}$, with $\mathcal{A}_{\text{MT}_1} \cap \mathcal{A}_{\text{MT}_2} = 0$ (see Fig. 1). To compute C , it is convenient to introduce the interstitial region of one individual layer as $I_{\mu} = \mathcal{A}/\mathcal{A}_{\text{MT}_{\mu}}$ such that $\mathcal{A} = \mathcal{A}_{\text{MT}_1} \cup I_1 = \mathcal{A}_{\text{MT}_2} \cup I_2$, with $I_1 \cap I_2 \neq 0$ and $I_{\mu} \cap I \neq 0$. The matrix C^{μ} for component μ can therefore be partitioned according to

$$C^{\mu} = \begin{pmatrix} C_{\text{MT}_{\mu}/\text{MT}_1} & C_{\text{MT}_{\mu}/\text{MT}_2} & C_{\text{MT}_{\mu}/I} \\ C_{I_{\mu}/\text{MT}_1} & C_{I_{\mu}/\text{MT}_2} & C_{I_{\mu}/I} \end{pmatrix}. \quad (16)$$

For convenience, we have omitted the dependence on the $\mathbf{q}$ -vector.

The first term, $C_{\text{MT}_{\mu}/\text{MT}_{\nu}}$, corresponds to the overlap between basis functions in the MT region of layer μ and basis functions in the MT region of layer ν in the heterostructure. Here, we assume that the radial functions in the spheres of the individual component and the heterostructure are identical, owing to the weak interaction between the two layers. Furthermore, since the two regions are disjunct, we can conclude that $C_{\text{MT}_{\mu}/\text{MT}_{\nu}} = \delta_{\mu\nu}$.

The next term that we consider is $C_{\text{MT}_{\mu}/I}$. We note that the MT region of any individual component does not overlap with

the interstitial region of the heterostructure, so $C_{\text{MT}_{\mu}/I} = 0$. Similarly, for the terms C_{I_{μ}/MT_1} and C_{I_{μ}/MT_2} , there is no overlap between the functions of the MT and interstitial regions of the same layer; hence, $C_{I_{\mu}/\text{MT}_{\mu}} = 0$.

The only nontrivial blocks are $C_{I_{\mu}/\text{MT}_{\nu}}$ and $C_{I_{\mu}/I}$, where an element of these matrices is given by

$$C_{aA}^{\mu} = \sum_{\mathbf{G}} \tilde{S}_{\mathbf{G}a}^{\mu} w_{\mathbf{A}\mathbf{G}}^*, \quad (17)$$

with the distinction that for $C_{I_{\mu}/\text{MT}_{\nu}}$ the index a (A) corresponds to the functions of the interstitial (MT) region of layer μ (ν). For $C_{I_{\mu}/I}$ the index a corresponds to the interstitial region of layer μ , while A corresponds to the interstitial region of the heterostructure. In Eq. (17), we have introduced w as the overlap matrix elements between a mixed-basis function and a plane wave [see Eq. (A7) in Appendix A]. In Appendix B, we further show the derivations of the expressions for the different blocks of C^{μ} .

We now show the general expressions to calculate the components of Eq. (15) according to Eq. (14). Concretely, we obtain

$$\begin{aligned} P_{\text{MT}_{\mu},\text{MT}_{\mu}} &= P_{\text{MT}_{\mu},\text{MT}_{\mu}}^{\mu} + (C_{I_{\nu},\text{MT}_{\mu}}^{\nu})^* P_{I_{\nu},I_{\nu}}^{\nu} C_{I_{\nu},\text{MT}_{\mu}}^{\nu}, \\ P_{\text{MT}_{\mu},\text{MT}_{\nu}} &= P_{\text{MT}_{\mu},I_{\mu}}^{\mu} C_{I_{\nu},\text{MT}_{\nu}}^{\nu} + (C_{I_{\nu},\text{MT}_{\mu}}^{\nu})^* P_{I_{\nu},\text{MT}_{\nu}}^{\nu}, \\ P_{\text{MT}_{\mu},I} &= P_{\text{MT}_{\mu},I_{\mu}}^{\mu} C_{I,I}^{\mu} + (C_{I_{\nu},\text{MT}_{\mu}}^{\nu})^* P_{I_{\nu},I_{\nu}}^{\nu} C_{I,I}^{\nu}, \\ P_{I,I} &= \sum_{\mu} (C_{I_{\mu},I}^{\mu})^* P_{I_{\mu},I_{\mu}}^{\mu} C_{I_{\mu},I}^{\mu}. \end{aligned} \quad (18)$$

C. The EAS approach in the Bethe-Salpeter equation

While the polarizability is a key component in GW in the screening of the electron-electron interaction, it plays an analogous role in the screening of the electron-hole interaction in optical excitations. We therefore make use of the same concept and extend the EAS approach to the calculations of optical properties by means of the Bethe-Salpeter equation.

In contrast to the use of a mixed basis in the G_0W_0 implementation, in the BSE implementation of exciting the polarizability is represented in terms of plane waves covering the whole unit cell. This makes the EAS formalism in the BSE code basically identical to the one underlying the original EAS approach in Refs. [12,13] (see Sec. II A). For additional details on the BSE module, we refer the reader to Ref. [32].

IV. RESULTS

We have selected two systems to demonstrate our approach: the WSe₂ bilayer and the HIOS pyridine@MoS₂. Both are weakly bound systems, dominated by vdW interactions. To evaluate the accuracy of our approach, we compare the results of the exact calculations for both G_0W_0 and BSE calculations with the results obtained using EAS. We note that an additional example of the EAS method for the BSE was shown in Ref. [9] for pyrene@MoS₂.

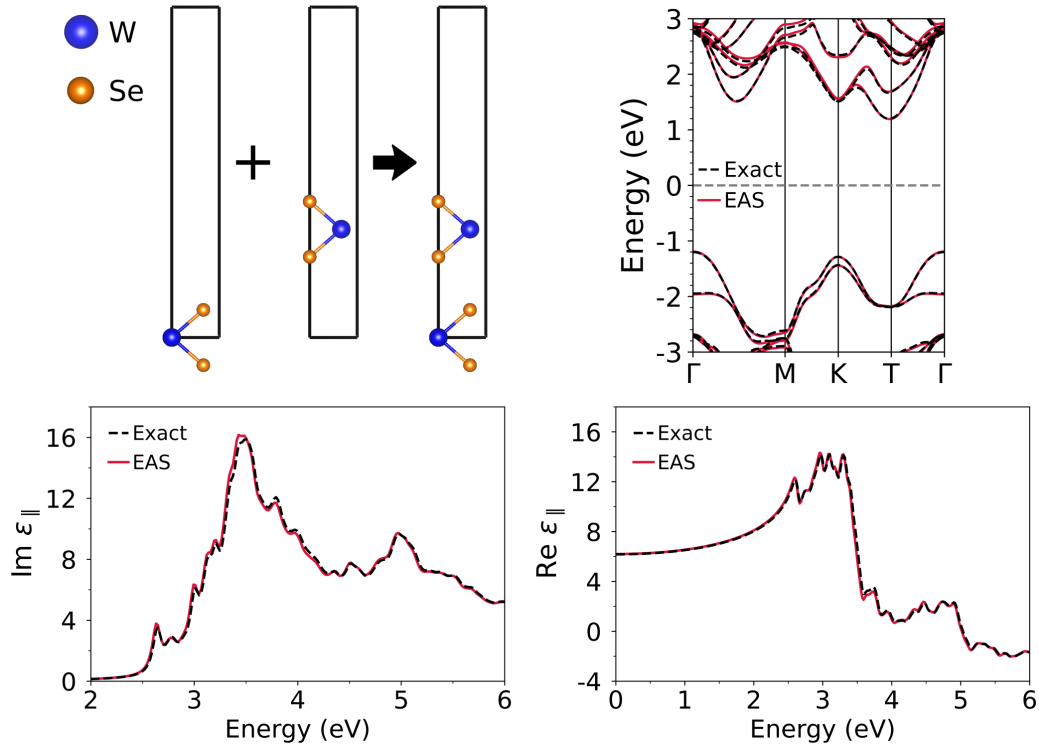


FIG. 2. Top left: schematic representation of how to compute the additive screening for the example of the WSe_2 bilayer. Top right: QP band structure calculated with the EAS method (red) compared to the exact calculation (black). Bottom: Imaginary part (left) and real part (right) of the in-plane component of the dielectric function obtained with the EAS approach (red) and the exact calculation (black).

A. WSe_2 bilayer

The top left panel of Fig. 2 shows the schematic representation of how to compute the additive screening for the example of the WSe_2 bilayer. Since both layers and thus the double layer contain one unit cell, we probe only the additive step in this case. We consider AB stacking [35] and an interlayer distance of 3.21 Å, as obtained by optimizing the geometry using the Perdew-Burke-Ernzerhof functional and the Tkatchenko-Scheffler (TS) vdW correction [36,37]. The sampling of the Brillouin zone (BZ) is performed with a homogeneous $12 \times 12 \times 1$ Monkhorst-Pack $\mathbf{k}$ -point grid, and we use 200 empty states for both the individual components and the heterostructure, which ensures that the band edges are overall sufficiently converged. We further employ a Coulomb truncation along the out-of-plane direction, as used in Ref. [38]. Spin-orbit coupling is not considered. For the solution of the BSE on top of the QP band structure, the screened Coulomb potential is computed using 100 empty bands. In the construction and diagonalization of the BSE Hamiltonian, five occupied and seven unoccupied bands are included, and a $\mathbf{k}$ -mesh of $18 \times 18 \times 1$ is employed.

The top right panel of Fig. 2 shows the QP band structure of the bilayer computed by the EAS and compared to the exact calculation. We observe very good overall agreement in the entire energy range. The indirect fundamental gap, found between Γ and T , has a value of 2.39 eV (2.41 eV) in the EAS (exact) calculation. The values of the direct gap at K are 2.84 and 2.79 eV, respectively. The bottom panels show the imaginary and real parts of the macroscopic dielectric function obtained by computing the polarizability in both GW

and BSE using the EAS approach. Again, we find very good agreement with the exact BSE calculation, finding optical gaps of 2.63 and 2.64 eV with the EAS and the exact calculation, respectively.

We note that the obtained results show some discrepancies from other reported QP band gaps and optical gaps [35]. We attribute them to the strong dependence of these calculations on structural parameters, such as the lattice constant, the interlayer distance, and the stacking, as well as on computational parameters, such as the exchange-correlation functional, spin-orbit coupling, Coulomb truncation schemes, and the $\mathbf{q} = 0$ singularity treatment [38–40]. However, the goal of this work is to show the applicability of the EAS method within one computational setup.

B. Pyridine@ MoS_2

The top left panel of Fig. 3 shows the schematic representation of the EAS calculation for pyridine@ MoS_2 , a prototypical hybrid material. In this example, we are putting our full implementation to the test by performing an expansion of the polarizability calculated for the unit cell of the MoS_2 monolayer to a $3 \times 3 \times 1$ supercell. We note that the expansion step is exact only if the supercell is an exact replica of the unit cell, i.e., no geometry optimization of the heterostructure is performed. In the example shown here, the supercell is commensurate with the MoS_2 unit cell, with the atomic positions kept fixed at ideal lattice sites. The pyridine monolayer is directly placed inside the $3 \times 3 \times 1$ supercell of MoS_2 , and thus, no further expansion is required for this component. The

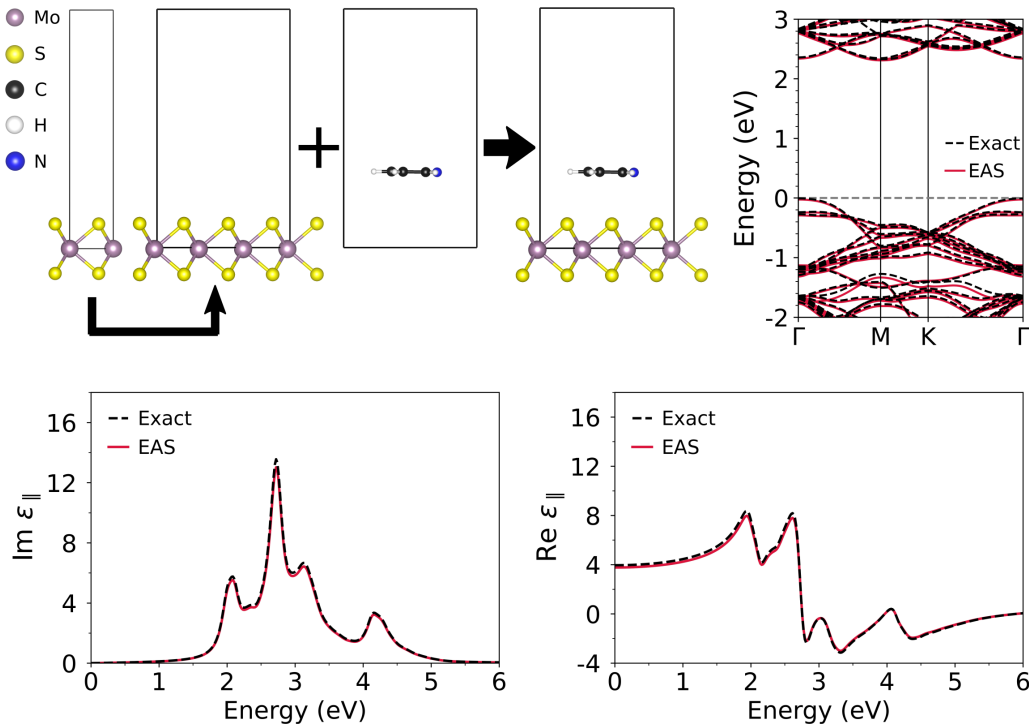


FIG. 3. Top left: schematic representation of how to compute the EAS for the example of pyridine@MoS₂. Top right: QP band structure calculated with the EAS method (red) compared to the exact calculation (black). Bottom: Imaginary part (left) and real part (right) of the in-plane component of the dielectric function obtained with the EAS approach for both *GW* and BSE (red) and the exact calculation (black).

molecular monolayer is placed at an interlayer distance of 3.19 Å, as obtained in Ref. [19] using the TS vdW correction. The BZ of the supercell is sampled with a $3 \times 3 \times 1$ $\mathbf{k}$ grid. As in the previous example, the calculation of the polarizability of the heterostructure is performed by using 200 empty bands, while the polarizability of the unit cell is computed using a $9 \times 9 \times 1$ $\mathbf{k}$ grid and 100 empty bands. Spin-orbit coupling is not considered. For the solution of the BSE on top of the QP band structure, the polarizability of the heterostructure is computed using 200 empty bands and a $\mathbf{k}$ mesh of $9 \times 9 \times 1$. In the construction and diagonalization of the BSE Hamiltonian, 16 occupied and 14 unoccupied bands are included. In the EAS method, the calculation of the polarizability of the MoS₂ unit cell is performed using 100 empty bands and a $\mathbf{k}$ mesh of $27 \times 27 \times 1$. The polarizability of the organic layer is calculated using the same $\mathbf{k}$ mesh used for the heterostructure, as no expansion is required.

In the top right panel of Fig. 3 the QP band structure calculated with the EAS method (red) is compared with the exact calculation (black). As in the case of the WSe₂ bilayer, we find very good agreement. The fundamental gap appears at the Γ point due to the folding of the BZ (K point in the primitive cell). Its value of 2.32 eV comes very close to the result of the exact calculation of 2.36 eV. The optical properties, calculated on top of the QP band structures, indicate optical gaps of 2.00 eV (EAS) and 2.02 eV (exact). Figure 3 depicts the imaginary and real parts of the macroscopic dielectric function of the corresponding spectra, for which we find excellent agreement between the two approaches.

To demonstrate the computational efficiency of our approach, we provide the CPU hours [41] required for the two

methods in Table I. We note that, as described in Ref. [13], the actual performance and timing depend on the architecture of the computer cluster used. Our calculations are performed using the computer clusters Lise and Emmy of NHR@ZIB and NHR@Göttingen, both with Intel(R) Xeon(R) Silver 4210 CPU processors and 2.20 GHz frequency. The calculation of the exact polarizability in the G_0W_0 method for pyridine@MoS₂ requires 3511 CPU hours, while the calculations for the unit cells of MoS₂ and pyridine require 260 CPU hours and 1120 CPU hours, respectively. Including the addition step of 165 CPU hours brings the total run-time to 1545 CPU hours, representing a savings of more than 50% in computing resources. In the BSE case, the exact method requires 9462 CPU hours for the calculation of the polarizability, while the individual components require 1122 and 1840 CPU hours for MoS₂ and pyridine, respectively. This results in a total runtime of 2962 CPU hours, corresponding to a reduction of almost 70% of the computational time. This even larger reduction in the BSE case compared to the G_0W_0 case can be explained by the expensive basis transformations required for treating the mixed-product basis.

We note that EAS reduces only the computational cost associated with the calculation of the polarizability. However, the calculation of the self-energy and the construction and diagonalization of the BSE Hamiltonian remain computationally demanding. Therefore, the total time is reduced by only 25% and 46% for G_0W_0 and BSE, respectively. In the context of BSE, the combination of the EAS method with the interpolative separable density fitting method [42] represents an exceptionally compelling framework for the efficient

TABLE I. Comparison of computing resources for pyridine@MoS₂ for both the exact method and the EAS screening method in the G_0W_0 /BSE framework. Steps that are shared between both methods are listed only once. For G_0W_0 , $\mathbf{k}$ grids of $9 \times 9 \times 1$ ($3 \times 3 \times 1$) were used for the unit cell (supercell); for BSE, $\mathbf{k}$ grids of $27 \times 27 \times 1$ ($9 \times 9 \times 1$) were used.

Framework	Task name	CPU hours, EAS	CPU hours, exact
G_0W_0	Initialization	101	101
	Polarizability		3511
	Polarizability MoS ₂ ^a	260	
	Polarizability pyridine unit cell	1120	
	Addition individual polarizabilities	165	
	Self-energy	4055	4055
	Total	5701	7667
BSE	Initialization ^b	557	557
	Polarizability		9462
	Polarizability MoS ₂ ^a	1122	
	Polarizability pyridine unit cell	1840	
	Addition individual polarizabilities	0 ^c	
	Construction interaction Hamiltonian	3824	3824
	Diagonalization Hamiltonian	318	318
	Total	7661	14161

^aThis task includes the calculation of the unit cell polarizability and the expansion to the supercell.

^bThis task includes the calculation of eigenvalues/eigenvectors and the momentum matrix on the BSE $\mathbf{k}$ grid.

^cRounded.

calculation of optical properties of large weakly bound hybrid systems.

V. SUMMARY AND CONCLUSIONS

In this work, we extended a recently developed method for calculating the polarizability of weakly bound systems using a plane wave basis [12,13] to the case of the (L)APW basis. This method consists of expressing the polarizability of the heterostructure as the sum of the polarizabilities of the individual components. Moreover, we introduced a corresponding approach to compute the optical spectra of such heterostructures within the framework of the Bethe-Salpeter equation. We developed all the necessary transformations in both the expansion and addition steps that are required to account for the atom-dependent nature of the mixed-product basis used in the context of the (L)APW method. While the expansion step requires the basis transformation between the unit cell and the supercell of the individual components, the addition step requires the transformation between the bases of the (expanded) individual components and the basis of the heterostructure.

Our implementation obtains the QP band structure of weakly bound heterostructures with high accuracy, as illustrated by the examples of the vdW heterostructure WSe₂ bilayer and the hybrid material pyridine@MoS₂. Going beyond previous work, we successfully applied the EAS method also within the BSE formalism, which we demonstrated by computing the optical spectra of the two systems. Due to its reduced computational cost, our method will be useful

for providing highly accurate all-electron results of electronic and optical properties of heterostructures much larger than those considered so far. This opens the possibility to extend all-electron benchmarking efforts to more complex systems.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [43,44].

APPENDIX A: THE (L)APW AND MIXED-PRODUCT BASES

In the (L)APW method, the unit cell is partitioned into the MT and interstitial regions, and the basis is defined as

$$\phi_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r}) = \begin{cases} \sum_{\zeta lm} \mathbf{A}_{\zeta lm}(\mathbf{k} + \mathbf{G}) u_{\alpha \zeta l}(r^{\alpha}, \epsilon_{\alpha l}) Y_{lm}(\hat{\mathbf{r}}^{\alpha}) & r^{\alpha} < R_{\text{MT}}^{\alpha}, \\ \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}} & \mathbf{r} \in I. \end{cases} \quad (\text{A1})$$

$$\mathbf{r} \in I. \quad (\text{A2})$$

The MT part of $\phi_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r})$ is expanded in terms of spherical harmonics $Y_{lm}(\hat{\mathbf{r}}^{\alpha})$ and radial functions $u_{\alpha\zeta l}(r^{\alpha}, \epsilon_{\alpha l})$. The latter are solutions of the radial scalar-relativistic Schrödinger equation at fixed reference energies $l\alpha$ (linearization energies) inside each MT for the respective spherically averaged Kohn-Sham potential. The index ζ has been introduced to account for different types of radial functions, which are either $u_{\alpha l}(r^{\alpha}, \epsilon_{\alpha l})$ or $\dot{u}_{\alpha l}(r^{\alpha}, \epsilon_{\alpha l}) \equiv \frac{\partial u_{\alpha l}(r^{\alpha}, E)}{\partial E}|_{\epsilon_{\alpha l}}$ in the LAPW method. The augmentation coefficients $\mathbf{A}_{\alpha\zeta lm}(\mathbf{k} + \mathbf{G})$ are chosen to ensure that the basis functions are continuous at the boundaries of the MT spheres.

To represent products of two Kohn-Sham wave functions, for example, in the G_0W_0 method, a basis with features similar to those of the (L)APW basis should be used [25]. In particular, one can make use of the fact that in the MT spheres, the product of two spherical harmonics can again be expanded in spherical harmonics using Clebsch-Gordan coefficients, while in the interstitial region the product of two plane waves is a plane wave. Therefore, within the MT region, an optimal set of radial functions $v_{\alpha NL}(r_{\alpha})$ is constructed from the products of the radial wave functions $u_{\alpha l}(r^{\alpha}, \epsilon_{\alpha l})$. We calculate the overlap matrix between these products functions,

$$\mathbb{O}_{ll',l_1l'_1} = \int_0^{R_{\text{MT}}} dr^{\alpha} u_{\alpha l}(r^{\alpha}) u_{\alpha l'}(r^{\alpha}) u_{\alpha l_1}(r^{\alpha}) u_{\alpha l'_1}(r^{\alpha}) (r^{\alpha})^2, \quad (\text{A3})$$

which is then diagonalized to give the corresponding set of eigenvalues λ_N^{MB} and eigenvectors $c_{ll',N}$. The eigenvectors are normalized and form the radial basis set according to

$$v_{\alpha NL}(r^{\alpha}) = \sum_{ll'} c_{ll',N} u_l(r^{\alpha}) u_{l'}(r^{\alpha}). \quad (\text{A4})$$

In the interstitial region, the overlap of two plane waves is given by

$$\mathbb{O}_{\mathbf{G}\mathbf{G}'} = \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} \theta_l(\mathbf{r}) e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}, \quad (\text{A5})$$

where $\theta_l(\mathbf{r})$ is the Heaviside function, which has a value of 1 in the interstitial region and is 0 otherwise. To obtain a set of orthonormal basis functions, the overlap matrix is then diagonalized, and the basis is defined in terms of the eigenvalues λ_i^l and eigenvectors S_{Gi} according to Eq. (7) using the normalized eigenvectors defined as

$$\tilde{S}_{Gi} \equiv \frac{S_{Gi}}{\sqrt{\lambda_i^l}}. \quad (\text{A6})$$

Finally, we note that to construct the transformation shown in the addition steps, the exciting code takes advantage of the plane wave representation using the overlap integrals defined as

$$w_{i\mathbf{G}}(\mathbf{q}) \equiv \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} [\chi_i^{\mathbf{q}}(\mathbf{r})]^* e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}. \quad (\text{A7})$$

Since we have already defined $\chi_i^{\mathbf{q}}(\mathbf{r})$ in both the MT region, $\chi_i^{\mathbf{q}}(\mathbf{r}) \rightarrow \gamma_{\alpha NL\mathbf{M}}^{\mathbf{q}}(\mathbf{r})$, and the interstitial region, $\chi_i^{\mathbf{q}}(\mathbf{r}) \rightarrow \Lambda_i^{\mathbf{q}}(\mathbf{r})$, Eq. (A7) allows us to transform between the two. For a detailed overview of the mixed-product basis based on the (L)APW method, the reader is referred to Refs. [25,26].

APPENDIX B: CALCULATION OF THE TRANSFORMATION MATRICES

As part of the addition step (Sec. III B) we define the matrices $C_{jj}^{\mu}(\mathbf{q}) = \langle \chi_j^{\mu,\mathbf{q}} | \chi_j^{\mathbf{q}} \rangle$ to transform the coefficients of the polarizability of a component to the basis of the full heterostructure. Using Eq. (16), we construct the overlap matrix for the case of a two-layered system,

$$C^1 = \begin{pmatrix} C_{\text{MT}_1/\text{MT}_1} & C_{\text{MT}_1/\text{MT}_2} & C_{\text{MT}_1/I} \\ C_{I/\text{MT}_1} & C_{I/\text{MT}_2} & C_{I/I} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & C_{I_1/\text{MT}_2} & C_{I_1/I} \end{pmatrix} \quad (\text{B1})$$

and

$$C^2 = \begin{pmatrix} C_{\text{MT}_2/\text{MT}_1} & C_{\text{MT}_2/\text{MT}_2} & C_{\text{MT}_2/I} \\ C_{I_2/\text{MT}_1} & C_{I_2/\text{MT}_2} & C_{I_2/I} \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ C_{I_2/\text{MT}_1} & 0 & C_{I_2/I} \end{pmatrix}, \quad (\text{B2})$$

where the zero terms have been obtained by using the conditions in Sec. III B. In component 1, Eq. (B1), the only nontrivial contributions to compute are C_{I_1/MT_2} and $C_{I_1/I}$. In the following, we show how to compute them in terms of the plane wave eigenvectors [Eq. (A6)] and the overlap matrices [Eq. (A7)]. We begin with C_{I_1/MT_2} , where one element of this matrix is given by

$$C_{i\alpha}(\mathbf{q}) = \frac{1}{\sqrt{\Omega}} \int_{\text{MT}} d\mathbf{r} \left[\sum_{\mathbf{G}} \tilde{S}_{Gi}^* e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \right]^* \times \left[\sum_{\mathbf{R}} e^{-i\mathbf{q}(\mathbf{R}+\tau_{\alpha})} v_{\alpha NL}(r^{\alpha}) Y_{LM}^*(\hat{\mathbf{r}}^{\alpha}) \right]^* = \sum_{\mathbf{G}} \tilde{S}_{Gi} w_{\alpha\mathbf{G}}^*(\mathbf{q}), \quad (\text{B3})$$

where $w_{\alpha\mathbf{G}}(\mathbf{q})$ is the overlap element of a plane wave with the basis functions in the MT region of the heterostructure.

The other nonzero component of Eq. (B1), $C_{I_1/I}$, is constructed by considering the basis representation of the interstitial region of the individual component and the heterostructure. Therefore, one element of this matrix is given by

$$C_{iI} = \frac{1}{\Omega} \int_{I_{\text{HS}}} d\mathbf{r} \sum_{\mathbf{G}'\mathbf{G}} \tilde{S}_{G'i} e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} \tilde{S}_{GI}^* e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} = \frac{1}{\Omega} \sum_{\mathbf{G}'\mathbf{G}} \tilde{S}_{G'i} \tilde{S}_{GI}^* \int_{I_{\text{HS}}} d\mathbf{r} e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} = \sum_{\mathbf{G}'} \tilde{S}_{G'i} \frac{1}{\Omega} \sum_{\mathbf{G}} \tilde{S}_{GI}^* \int_{I_{\text{HS}}} d\mathbf{r} e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}. \quad (\text{B4})$$

We define $\mathcal{I}_{\mathbf{G}}$ as the integral over a plane wave evaluated for the interstitial region of the heterostructure as

$$\mathcal{I}_{\mathbf{G}} = \int_{I_{\Omega}} d\mathbf{r} e^{i\mathbf{G}\mathbf{r}}, \quad (\text{B5})$$

such that we can express the matrix elements as

$$\begin{aligned} C_{il} &= \sum_{\mathbf{G}'} \tilde{S}_{\mathbf{G}'i} \frac{1}{\Omega} \sum_{\mathbf{G}} \tilde{S}_{\mathbf{G}l}^* \mathcal{I}_{\mathbf{G}-\mathbf{G}'} \\ &= \sum_{\mathbf{G}'} \tilde{S}_{\mathbf{G}'i} \left[\frac{1}{\Omega} \sum_{\mathbf{G}} \tilde{S}_{\mathbf{G}l} \mathcal{I}_{\mathbf{G}'-\mathbf{G}} \right]^* \end{aligned}$$

$$\begin{aligned} &= \sum_{\mathbf{G}'} \tilde{S}_{\mathbf{G}'i} \left[\frac{1}{\Omega} \sum_{\mathbf{G}} \tilde{S}_{\mathbf{G}l} \mathcal{I}_{\mathbf{G}-\mathbf{G}'}^* \right]^* \\ &= \sum_{\mathbf{G}'} \tilde{S}_{\mathbf{G}'i} w_{l\mathbf{G}'}, \end{aligned} \quad (\text{B6})$$

where $w_{l\mathbf{G}}$ is the overlap element of a plane wave with the basis functions in the interstitial region of the heterostructure. For convenience, we have omitted the dependence on the $\mathbf{q}$ -vector.

We conclude this Appendix by noting that the transformation of component 2 can be achieved using Eq. (B3) for C_{l_2/MT_1} and Eq. (B6) for $C_{l_2/l}$.

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